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PAGES	PAPERS
1 - 13	Geology and Petrography of the Ash-Sharqi Granitoid Pluton, Southwestern Yemen <i>Abdul-Hamid Malek and Mukhtar A. Nasher</i>
14 - 19	Improvement in Oxygen Demand Capacities of Palm Oil Mill Effluent from Ujiogba Edo State Using Some Selected Bacterial and Fungal Isolates <i>Kingsley Erhons Enerijiofi, Faith Odegwa Igbinovial, and Beckley Ikhajiagbe</i>
20 - 27	Geochemical Characteristics of Rare Earth Elements in Argillic Alteration Zone: An Example from the Kharvana area, NW Iran <i>Ali Abedini and Maryam Khosravi</i>
28 - 36	Preliminary Assessment of Trace Metals in Sediments of the Ebonyi River, Abakaliki Metallogenic Province, Nigeria <i>Olufemi Victor Omonona and Somtochukwu Goodness Azombe</i>
37 - 52	Demarcation of Groundwater Quality Using Drinking Water Quality Index (DWQI), Nitrate Pollution Index (NPI), and Irrigation Indices: A Case Study from Jerash Region <i>Eman Bani Khaled, Mutawakil Obeidat, Ahmad Al-Ajlouni, Muheeb Awawdeh, Muna Abu Dalo</i>
53 - 62	Updated Seismic Hazard Assessment Evaluation for the City of Aqaba, Jordan <i>Qadan, Hani, Al Tarazi, Eid, Jaradat, Rasheed, Abu-Hamatteh, Ziad, Amjad, Yasin</i>
63 - 69	Effect of different Olive Mill Wastewater Treatments on Seed Germination <i>Al-Jedaih Ma'amoun S., Bashaar Y. Ammary, Omar A. Rimawi, and Jalal A. Al-Tabbal</i>
70 - 76	Simulation of Breakthrough Curves of Pb Ions Adsorption by Natural Zeolitic Tuff Using Axial Dispersion and External Mass Transfer Modelsy <i>Ahmad M. Al-Haj-Ali and Ali K. Al-Matar</i>

Geology and Petrography of the Ash-Sharqi Granitoid Pluton, Southwestern Yemen

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Abstract

A reconnaissance study of the Ash-Sharqi area displays that this area is covered by Tertiary rift-related volcanic rocks and their associated plutonic rocks with some exposures of Mesozoic sandstones. These volcanic rocks belong to the Yemen Trap Series (YTS) that form the lower part of the Yemen Volcanic Group (YVG), which consists of a part of the Afro-Arabian continental flood basalt province. The plutonic rocks are represented by intrusion composed of granitoid rocks located in the center of the study area, which is the subject of this paper. These granitoid rocks range in composition from granite (G) to quartz-monzonite - quartz-monzodiorite – quartz diorite (QM-QMD-QD) and are composed of plagioclase (An₃₂₋₄₆: Andesine), K-feldspars, quartz, hornblende with minor, biotite, opaques, allanite and zircon. Secondary minerals are represented by chlorite, sericite calcite sphe, hematite epidote, and kaolinite. These rocks show variations in their colors (color index 6 to 47 vol. %) and grain sizes, which reflect changes in mineral composition and textures. They have equigranular, porphyritic, rapakivi, and anti-rapakivi textures and contain enclaves of various sizes of basalt and diorite blocks. Xenocrysts of pyroxene and plagioclase are found and detritated during the magma-mingling processes. Finally, these granitoid rocks are subjected to various degrees of hydrothermal alterations, including silicification, argillization, hematization, chloritization, epidotization, sericitization, carbonation and spheronization.

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Keywords: *Ash-Sharqi, Granitoid, Monzogranite, Granodiorite, Quartz-monzonite, Enclaves, Alteration, Rapakivi.*

1. Introduction

The Cenozoic igneous activity in Yemen is a part of the widespread Afro-Arabian continental flood basalt province, which is related to the continental rifting and formation of the Gulf of Aden and the Red Sea basins (Mohr and Zanettin 1988; Baker, et al. 1996; Ukstins et al. 2002; Nasher, et al. 2020). They are due to Afar-field stress generated by slab-pull in a subduction zone (Menzies et al. 1990; Robertson Group. PLC 1991) and the arrival of Afar plume beneath this region. This continental flood province covers an area of about 600,000 km² (Baker, et al. 1996) extending from southwest Ethiopia, through Djibouti, Eritrea, southwest Yemen, northwest of Saudi Arabia, Jordan, and Syria up to Turkey (Al-Malabeh, 1994; Al-Malabeh et al. 2004; El-Hasan and Al-Malabeh 2008; Al Smadi et al. 2018; Sharadqah et al. 2020).

In Yemen, all Cenozoic volcanic rocks and their allied intrusion are termed as Yemen Volcanic Group (YVG) (Menzies et al. 1990; Robertson Group. PLC 1991; Davison et al. 1994; Mattash 1994; Beydone et al. 1998) and are dated from the Late Oligocene to recent times (Mattash 1994; J. A. Baker et al. 1997; Volker et al. 1997; Bosworth, et al. 2005).

The YVG covers an area of about 50,000 km² of the western part of Yemen (Mattash 1994; Beydone et al. 1998) and is divided into older Yemen Trap Series (YTS) (late Oligocene-early Miocene) and younger Yemen Volcanic Series (YVS) (late Miocene-Recent) (Mattash 1994).

Yemen Trap Series (YTS) covers an area of about

42000 km² from which is subtracted about 2000 km² for the granitoid intrusions leaving about 40000 km² of volcanic materials (Beydone et al. 1998).

The granitoid intrusions are exposed essentially in the west border of the Yemen Plateau as Jabal Hufash, Jabal Bura, Jabal Dubes, Jabal Hirsh, Jabal Sabir, Jabal Kabba, and Ash-Sharqi (Figures 1a and b). Some information on the geology, mineralogy, geochemistry, petrogenesis, and tectonic position of the Tertiary granitoid plutons are available in the literature (Al-Kadasi 1988; Youssef, et al. 1992; M. H. Youssef 1993; Kruck and Schaffer 1996; Khanbari 2008; El-Gharbawy 2011; Malek, et al. 2014; Al-Qadhi, A. et al. 2016). Detailed field observations, petrographic inspections and chemical compositions of some Tertiary granitic rocks in Taiz area are given in (Al-Kadasi 1988; Youssef, et al. 1992; Khanbari 2008; El-Gharbawy 2011 a, b). Among these granite intrusions are the Sabir, Ash-Sharqi, and Kabba, which are prominent geomorphological landmarks in the Taiz district (southern Yemeni highlands), at an elevation of 3000 m, 2650 m, and 2350 m above sea level respectively (Figures 1c, d and e).

The previous studies on the Ash-Sharqi area are limited and have focused on the regional geological mapping features (Al-Kadasi 1988; Robertson Group. PLC 1991; Kruck and Schaffer 1996) but this study aims to carry out a detailed investigation of the lithological diversity, geological mapping and later alterations for the granitoid rocks of the study area (Figures 1d and e).

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2. Geologic Setting

The study area lies in southwestern Yemen at latitude $13^{\circ} 27' 39'' - 13^{\circ} 32' 54''$ N and longitude $43^{\circ} 48' 49'' - 43^{\circ} 56' 04''$ E (Figures 1a,b). The field survey indicates that the area consists of sandstone overlain by a thick succession of volcanic rocks (commonly basalt) (Figures 1c,d). The volcanic succession was intruded by Ash-Sharqi pluton and was followed by mafic and felsic dykes. The Ash-Sharqi pluton is one of several Tertiary plutons distributed in the south and west Yemeni highlands. The Jabal Sabir and Jabal Kabba mountains are the most important neighbouring plutons located in the southern Yemeni highlands at an elevation up to 3000 m above sea level. They are the youngest granitoid

plutons that intruded into late Tertiary volcanic rocks which may have originated from material derived from the same magma (Al-Kadasi 1988; El-Gharbawy 2011; Youssef, et al. 1992; Malek, et al. 2014; Al-Qadhi, et al. 2016). Sabir pluton shows diverse topographic features with a peak rising 2980 m above sea level, which stretches in a W-E direction in 9.5 km long and 7 km wide with a total area of around (65 km²). The rocks intrude the volcanic rocks with sharp intrusive contacts and are locally capped by them (Al-Kadasi 1988; Malek, et al. 2014). Kabba pluton forms an oval-shaped body of 4.8 km diameter, which elongated in a NE-SW direction (11.5 km²). It is injected in volcanic sequence and is invaded by basalt and rhyolite dykes (Al-Kadasi, 1988).

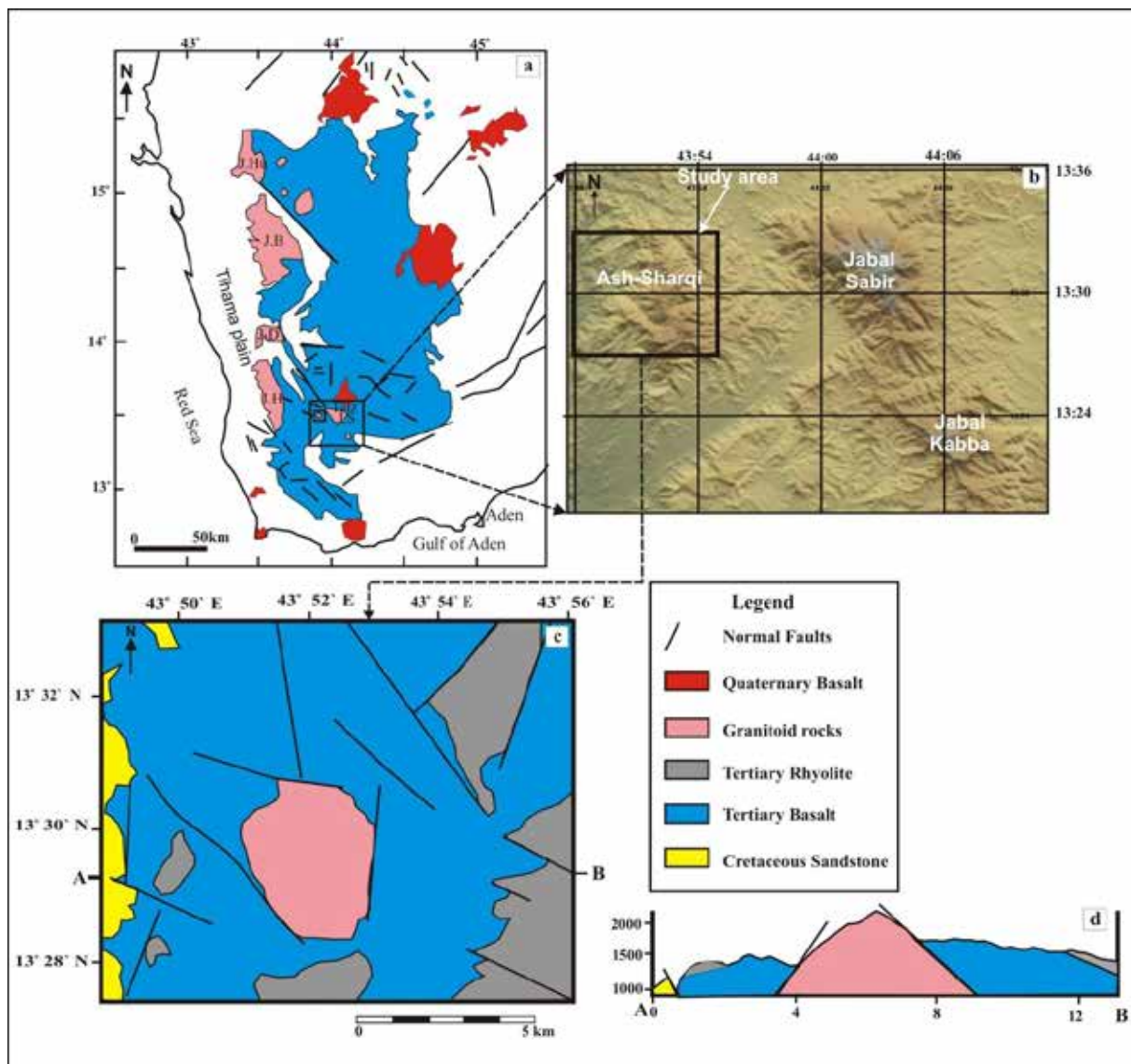


Figure 1. The regional and local position of Tertiary granitic plutons (a) Geological map of western Yemen (modified after (Coleman et al. 1992) displaying the distribution of Cenozoic volcanic and intrusive rocks, (J.Hu) = Jabal Hufash, (J. B.) = Jabal Bura, (J. D) = Jabal Dubes, (J.H) = Jabal Hirsh and (J.S) = Jabal Sabir. (b) DEM of Taiz area showing the location of the study area. (c) Geological map of the Ash-Sharqi area (d) A-B cross section through the mapped area, showing a relationship between rock units and faults.

3. Methods and Scope

This work investigates geological features, which are required for the understanding of a geological map of the Ash-Sharqi area. It includes the description of different rock units with emphasis on granitoid pluton. Besides, studying

field features, geological boundaries, alterations, structures, and sampling of diverse rock types (51 samples) gives reconnaissance geological and mineralogical information of the study area. Field works were carried out along roads, footpaths, and valley channels using the Global Positioning System (GPS) to take accurate positioning and coordinates,

Brunton Compass for measuring data orientation, tap for measuring dimensions, and hammer for sampling. Fresh and altered rock samples were carefully selected for the thin sectioning. The 28 thin sections were studied by using a polarizer microscope. The 16 thin sections were selected for modal analysis by using point counting under a polarizing microscope with an average of 550 counts for each thin section.

4. Results and Discussion

4.1 Field Description

4.1.1 Cretaceous Sandstone

The oldest recognized rocks in the area are clastic sediments that consist of predominantly sandstone, which are correlated with the Tawilah sandstone group, which is exposed in the extreme western part of the mapped area. It is buff to white, fine to medium-grained intercalated with thin beds of shales and conglomerates. The sandstone beds were gently dipping in varying directions causing rupturing by normal faults (Figure 2a).

4.1.2 Volcanic Rock Succession

The volcanic rock succession occurring on most sides of the mapped area, which are mostly basalt in the form of sub-horizontal lava flows, erupted through fissures and intercalated with sporadic cycles of eruption of felsic magma (rhyolite) and pyroclastic rocks. The thickness of this succession is very variable, up to 1500 m in east and south regions (Figure 2b). The basalt flows are generally thick and in some places are thin, grading upward to vesicular and amygdaloidal. The boundaries between basalt flows and felsic or pyroclastic layers are generally sharp, but locally they are gentle with no evidence of erosion traces (Figure 2c). No sediment intercalations have been observed in the volcanic succession. Basaltic flows are commonly aphanitic with subordinate porphyritic containing plagioclase phenocrysts (Figure 2d). Several columnar and entablature columnar jointing and a low amount of vesicles are found in basalt flows (Figure 2e). Some fractures and vesicles are filled with secondary minerals.

The rhyolites are light-colored rocks, aphanitic to porphyritic as phenocrysts of feldspars, impeded in a fine-grained groundmass of feldspar, quartz, and biotite. Pyroclastic rocks, mainly tuff, with subordinate lapilli-tuffs and intercalated tuff-breccia. The tuff units vary in thickness from some centimeters' to a few meters.

The pyroclastic rocks differ in their welding from densely to poorly. The densely welded tuffs are massive and they commonly show highly fractured. The tuff contained either crystal or fragment-rich. The volcanic breccias commonly consist of medium to coarse volcanogenic clasts (usually basaltic clasts) ranging in size from 1 centimeter to nearly 1/2 m diameter with various matrix colors from dark to light grey (Figure 2f). This means that the breccias are spatially and temporally related to the basaltic and rhyolitic eruptions.

4.1.3 Granitoid Rocks

The Ash-Sharqi pluton forms high relief mountains in an oval shape slightly elongated in N-S direction 4 km long and up to 3.4 km wide (11.7 km²) and surrounded from all sides by Tertiary volcanic rocks. The geological boundaries between pluton and volcanic rocks are sharp with cross-cutting relationships characterized by intense post-emplacement alterations and show some deformation features (Figure 3a). The Ash-Sharqi pluton mainly diversifies in colors from light grey rocks to darker types (Figure 3b). The lighter grey rocks are massive, medium to fine-grained with locally coarse-grained. The darker grey rocks occur in the west portion of the granitic pluton medium-grained and equigranular, while finer grained ones occur mainly along the boundaries of the pluton. The alteration zone was produced from hydrothermal alteration and hydration processes that led to the formation of fine-grained quartz and clay minerals. The brecciated contacts and deformation contacts were created from extensive injections of granitic material into a fractured basalt country rock (Figure 3c). The granitoid blocks were locally weathered into spheroidal large blocks (Figure 3d).

4.1.4 Enclaves

Several enclaves of mafic and felsic rocks are seen within the granitoid rocks (Figures 4a and b), which are considered typical features of bimodal magmatism (Tarelow Neto et al 2017). The mafic enclaves are more abundant, dark, rounded to oval-shaped, and range in size from small to large enclaves (a few meters long). Some mafic enclaves have coarser grain sizes, which reflect their deep sources, while the others display finer grain sizes, which may be derived from the surrounding basaltic rocks. Contacts between mafic enclaves and the surrounding granitoid rocks are generally sharp and rarely gradational, with chilling margins characterized by very thin zones (Figure 4a). Mafic enclaves are commonly distributed in the upper part of the granitic pluton and are less common and smaller in the deeper parts that are exposed by erosion. The abundant occurrence of the mafic enclaves in the outer parts of the pluton indicates that this pluton is situated at a relatively shallow depth (El-Gharbawy 2011 a) with incomplete mixing, interaction, and mingling between two types of magmas (Baxter and Feely 2002; Arslan and Aslan 2006; Renna, et al. 2006; Jerram et al. 2011; Perugini and Poli 2012; Ashok et al. 2022; Clemens 2022). In some places, the mafic enclaves have been weathered into reddish-brown rocks. The felsic enclaves are rare, lighter, and coarser in grained equigranular as evidenced by the deeper sources.

4.1.5 Dykes

Several late-stage mafic and felsic dikes crosscut the granitoid pluton. The dykes of mafic composition (basalt) are more abundant, while the felsic dykes (rhyolite) are less common (Figures 5a and b). The dykes are vertical to sub-vertical and differ in thickness from 0.1 to 4 m, with extensions up to several kilometres long. The mafic dykes trend NW-SE, while the felsic dykes take different trends. They are displaying high alteration margins and slight alteration towards their centers.

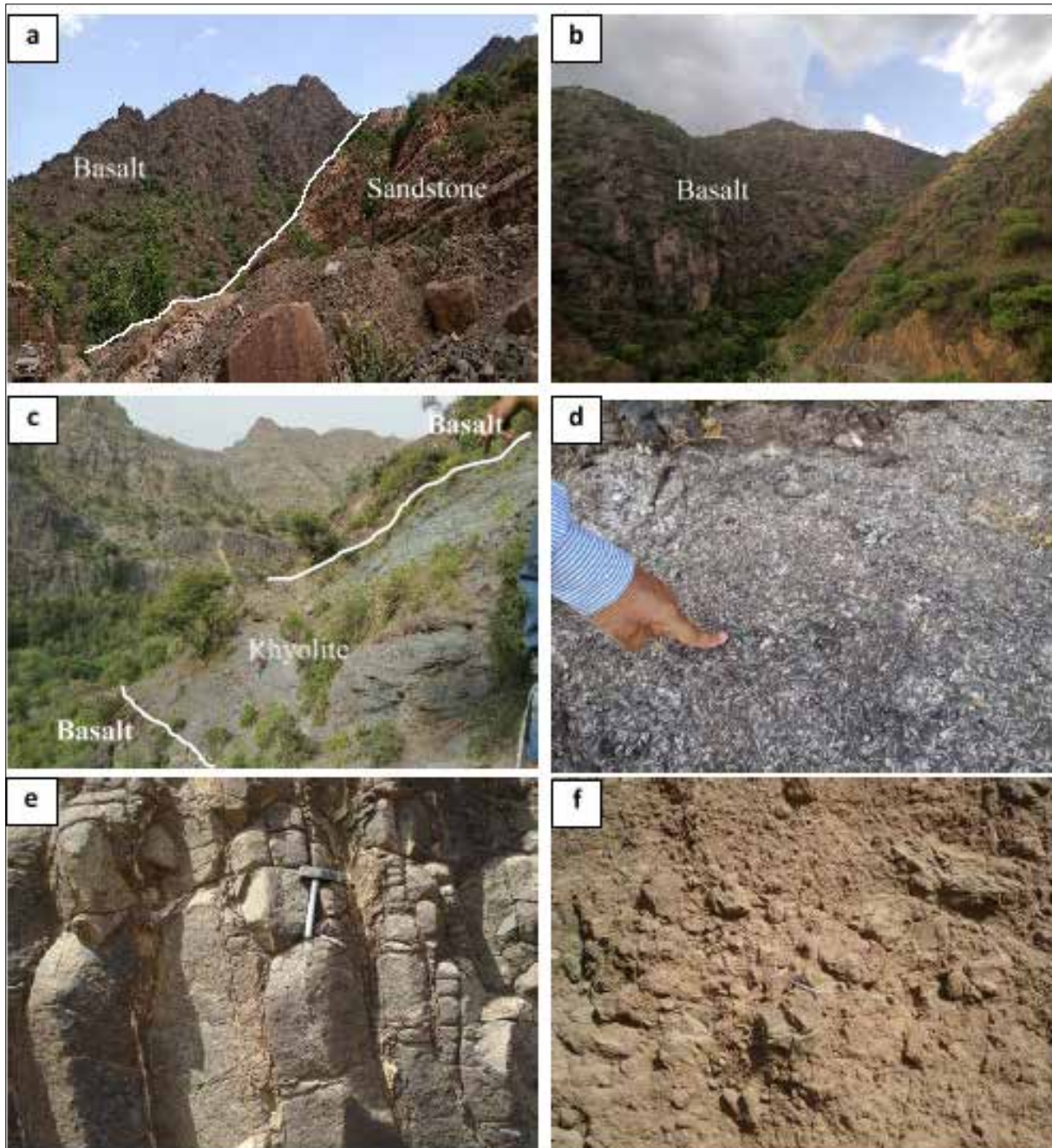


Figure 2. (a). A General view photograph showing the unconformity surface between Tawilah sandstone and Tertiary basalt in the western border of the mapped area. (b) A view showing a huge accumulation of Tertiary basalt at the southern border of granitoid pluton. (c) A view showing light-color rhyolite alternating with dark-colored basalts. (d) Plagioclase phenocrysts display flow structures in basalt. (e) Columnar jointing in basalt (f) Volcani-clastic breccia with basalt fragments in fine-grained tuff matrix

4.1.6 Recent Sediments

Quaternary unconsolidated sediments cover small parts of the study area in the form of poorly sorted clay, silt, sand, gravel, and boulders deposited as alluvial fans at the mouths

of canyons and valleys and as alluvial flood plains bordering ephemeral streams, as landslide deposits and braided-stream sediments filling the drainage channels

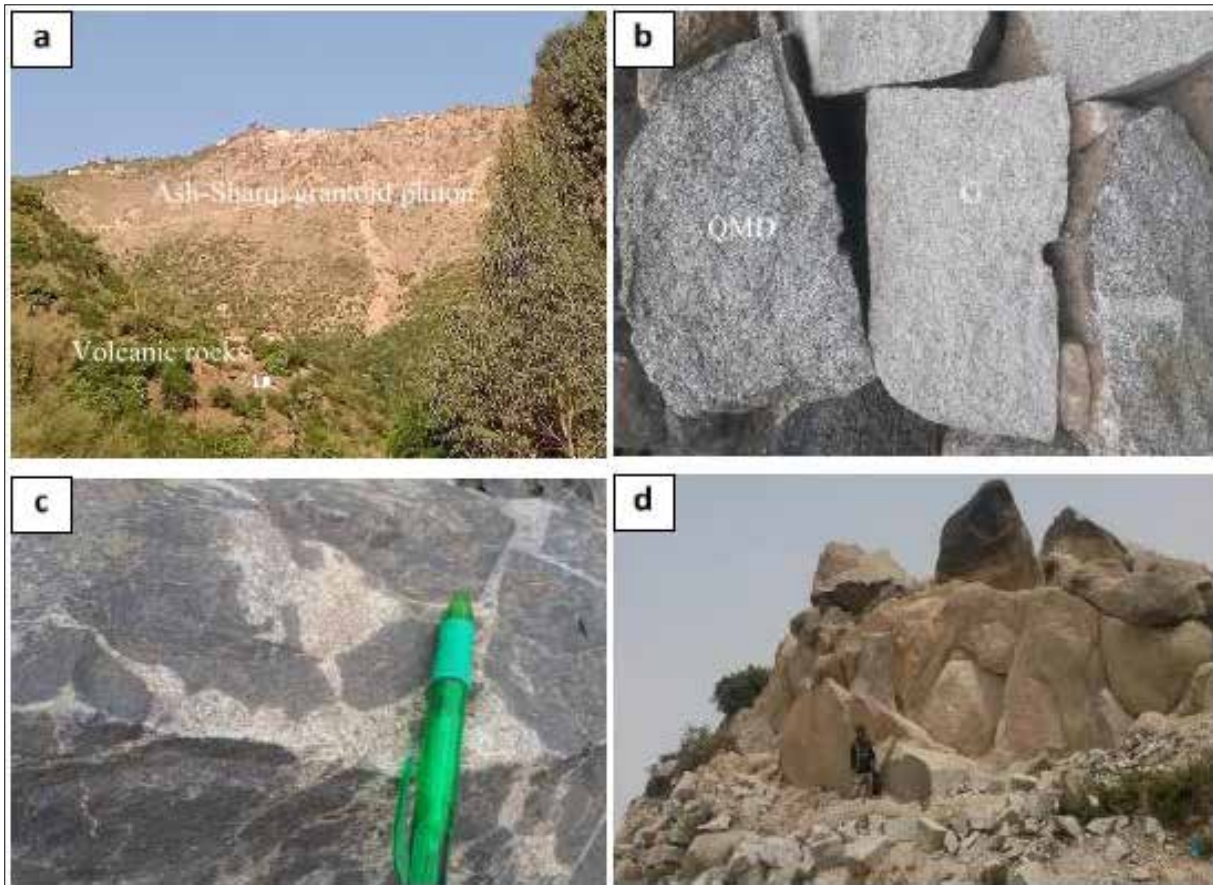


Figure 3. The Field photographs show (a) A general view of the eastern border of granitoid pluton surrounded by volcanic succession. (b) Building stone in the length of 40 cm of granite (GD) (lighter color) and quartz monzodiorite (darker color) (QMD). (c) Injections of granitic melt into fractures at the contact between granitoid pluton and surrounding basalt. (d) Blocky weathering of granitoid rocks with three sets of joints.

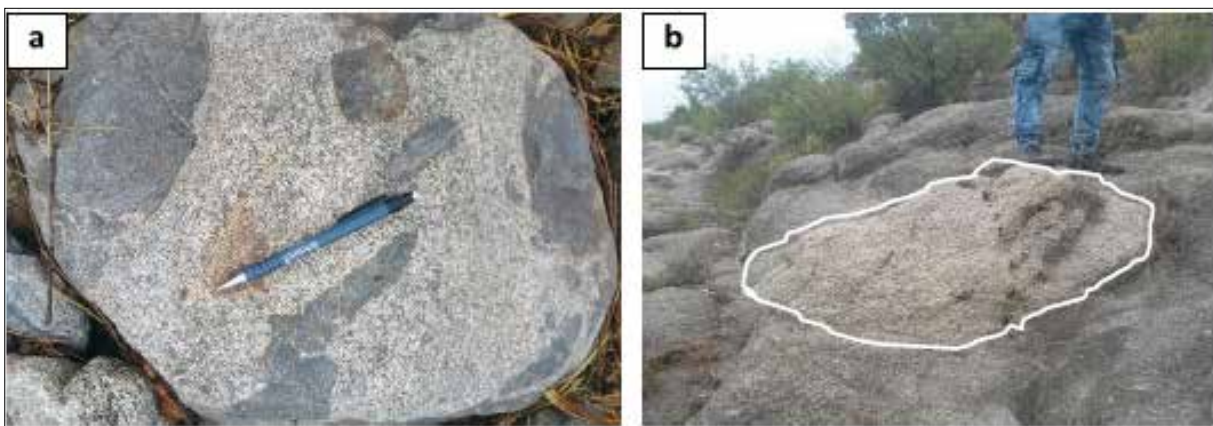


Figure 4. The photographs show (a) mafic enclaves within granitoid pluton, some show chilling margins. (b) Coarse grained felsic enclave within granitoid pluton.



Figure 5. The photographs show (a) The highly altered basalt dyke cutting the granitoid pluton. (c) Rhyolite veins dissecting the granitoid rocks.

4.2 Petrography

Twenty-eight representative samples have been selected from the Ash-Sharqi pluton and its volcanic rocks, dykes, and enclaves' associations for the petrographical studies. The different rock types in the Ash-Sharqi area show analogous and overlapping compositional differences.

The Ash-Sharqi granitoids have been classified based on petrography and the classification scheme of (Streckeisen 1976) into three main groups: 1- Richer in quartz content (>20%) (Granite group G), 2- Moderate content of quartz (5-20%) (quartz monzonite-quartz monzodiorite-quartz diorite (QM-QMD group), and 3- Lower content of quartz (<5%) (Monzodiorite group MD) (Table-1) (Figure 6).

Table 1. Modal composition of selected samples from Ash-Sharqi granitoid rocks (Mineral abbreviations after (Kretz 1983; Siivola and Schmid 2007). The color index (C.I) is calculated as the percentage of dark mafic minerals (M\) (Streckeisen, 1976).

Sample	(G)				(QM-QMD)											MD
	As6	As13	As15	As21	As1	As7	As9	As12	As17	As2	As4	As8	As10	As11	As20	As16
Pl%	25.96	11.21	26.87	23.21	35.63	36.73	32.26	26.32	24.32	48.15	40.95	35.83	40.96	65.52	53.97	69.15
Kfs%	39.42	53.27	35.82	35.71	20.69	26.53	29.03	46.32	42.34	11.11	9.52	10.83	21.69	10.34	9.52	14.89
Qtz%	20.19	25.23	23.88	34.82	13.79	13.27	14.52	11.58	14.41	9.26	6.67	6.67	9.64	4.60	9.52	3.19
Hbl%	6.73	3.74	0.00	0.00	6.90	11.22	8.06	1.05	6.31	3.70	19.05	17.50	9.64	4.60	7.94	0.00
Bt%	2.88	1.87	4.48	2.68	9.20	4.08	1.61	6.32	5.41	0.00	2.86	3.33	6.02	4.60	1.59	9.57
Oq%	4.81	2.80	7.46	1.79	4.60	5.10	3.23	5.26	5.41	20.37	12.38	9.17	6.02	5.75	6.35	2.13
Chl%	-	-	1.49	1.79	2.30	-	6.45	1.05	0.00	-	2.86	5.83	1.20	2.30	-	1.06
Cal%	-	-	-	0.00	0.00	1.02	0.00	1.05	0.00	-	0.00	0.00	0.00	1.15	-	0.00
Ep%	-	1.87	-	0.00	5.75	2.04	4.84	1.05	1.80	7.41	5.71	10.83	4.82	1.15	11.11	0.00
Ttn%					1.15											
Total%	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
C. I	14	10	13	6	30	22	24	15	19	31	43	47	28	18	27	13

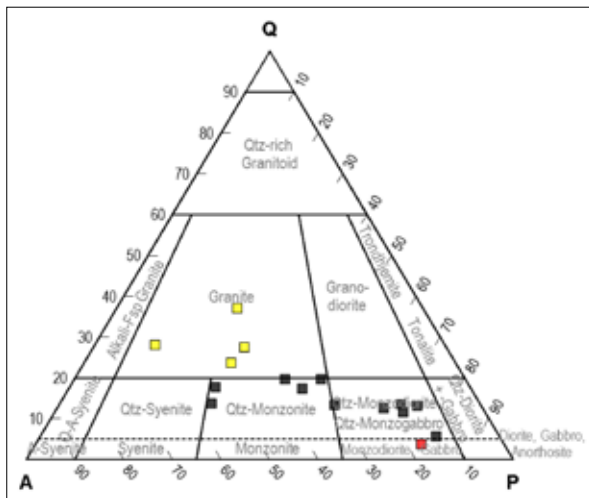


Figure 6. QAPF ternary diagram of IUGS classification (Streckeisen 1976) showing modal composition of Ash-Sharqi granitoid rocks. (■) = G, (■) = QM-QMD, (■) = MD.

4.2.1 Granite (G) Group

The G group predominantly crops out in the northern and eastern parts of the study area, varies with its mineral proportions, and shows remarkably hydrothermal alterations. Rocks are generally light (color index (C.I) = 6-14), medium-grained that have a hypidiomorphic granular texture and rare display, porphyritic texture with phenocryst of plagioclase and K-feldspar. The G rocks consist of mainly K-feldspar (36-53%), plagioclase (11-27%), quartz (20-35%),

hornblende (0-7%), biotite (2-4.5%), and magnetite (2-7.5%) as main minerals. Apatite and zircon are common accessory minerals, while sphene, muscovite, sericite, and epidote are secondary minerals (Table-1). K-Feldspars (up to 0.9 mm) are present as anhedral cloudy grains resulted from incipient alteration with some crystals showing myrmekitic texture due to symplectitic intergrowth with the plagioclase. Some K-feldspar grains are corroded by quartz and the others show quartz-feldspar intergrowths on the form graphic or granophyric textures (Figure 7a). Plagioclase (An_{32-38}) exists as subhedral to euhedral plates (up to 0.8 mm), commonly showing albite twinning. The plagioclase crystals have frequently suffered different degrees of sericitization, especially in their inner parts. Quartz (up to 0.4 mm) is present as colorless, anhedral grains, and sometimes exhibits undulatory extinction and found as aggregate pods or form veinlets. Biotite is present as subhedral flakes. It is yellow-brown to brown-green and strongly pleochroic, filling the interspaces between the feldspar grains. Hornblende occurs as anhedral prismatic crystals (up to 0.5 mm), dark green, and strongly pleochroic with Z= dark green, Y= yellow-green, and X= greenish-yellow. It is occasionally replaced by biotite epidote and magnetite as alteration products. Zircon occurs as short prismatic crystals enclosed within plagioclase, quartz, and biotite to form the poikilitic texture (Figure 7b).

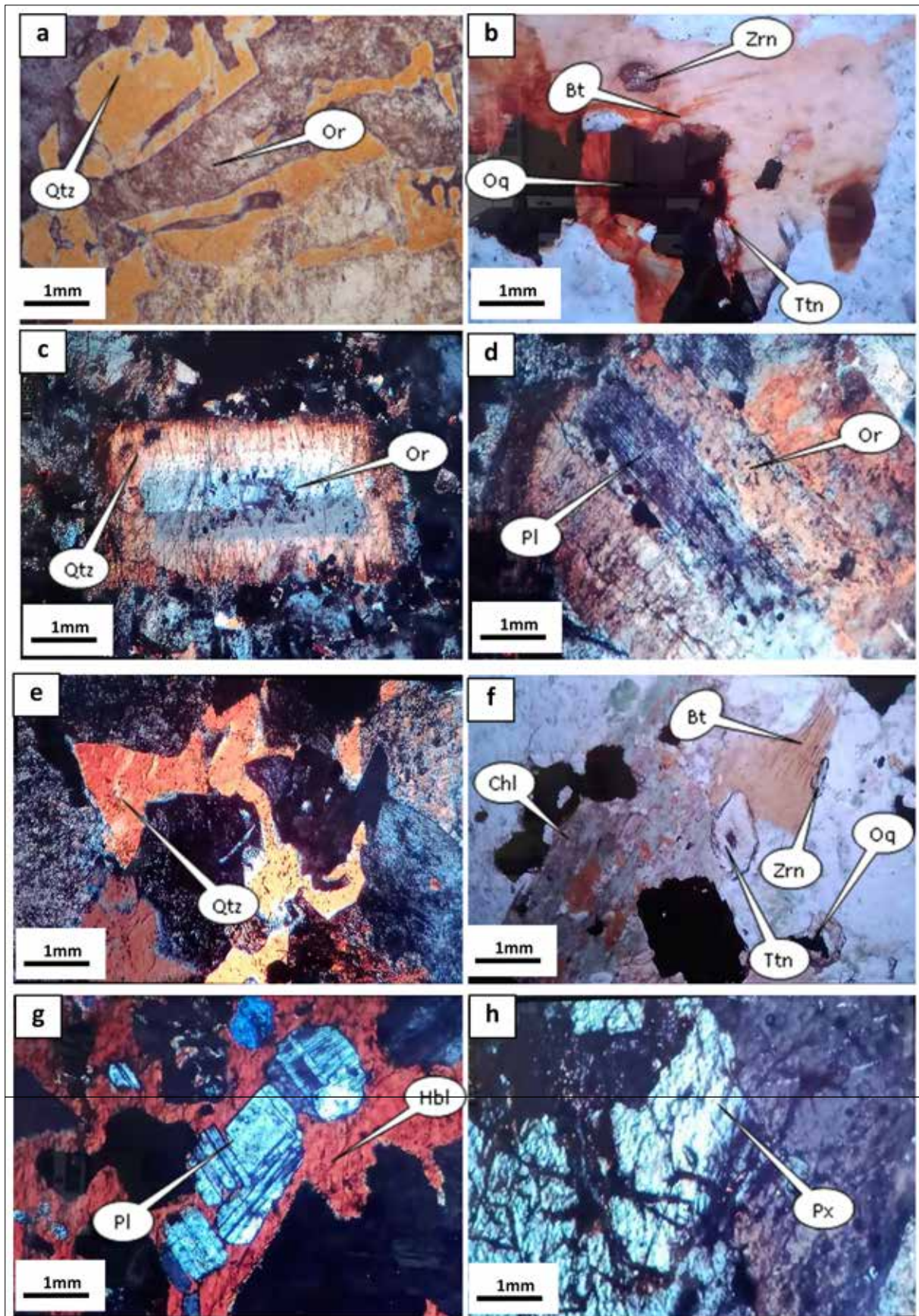


Figure 7. Photomicrographs show (a) Graphic texture produced from intergrowths between K- feldspar (Kfs) and quartz (Qtz). (b) Tiny crystal of zircon (Zrn) enclosed within biotite (Bt) and opaque mineral (Oq) replaced at its margins by titanite (Ttn) (P.L) (c) Phenocrysts of orthoclase (Or) crystal ringed by plagioclase (Pl) forming rapakivi texture. (d) Plagioclase crystal ringed by orthoclase forming anti-rapakivi texture. (e) Quarts surrounding and filling the interstices between the feldspar crystals. (f) Biotite flake replaced by chlorite (Chl), (g) large poikilitic crystal of hornblende (Hbl) enclosing small grains of plagioclase and iron oxide. (h) Part of irregularly resorbed pyroxene (Px) xenocryst display optically continuous with pyroxene in the groundmass.

4.2.2 Quartz Monzonite-Quartz Monzodiorite (QM-QMD) Group

In hand specimens, the QM-QMD are grey to dark grey color (C.I= 15-47), medium to coarse-grained and characterized by an inconspicuous alteration in compared with G.

Microscopically, QM-QMD has allotriomorphic granular texture, composed essentially of plagioclase (37-66%), K-feldspar (10-46%), iron oxides (3-20%), hornblende (1-19%), quartz (5-15%), and biotite (0-9%). Apatite and zircon are accessories. Sphene, epidote, chlorite, sericite, and calcite are present as secondary constituents. In the porphyritic types, plagioclase phenocrysts are surrounded by other varieties. In some samples, K-feldspars are mantled by plagioclase, constituting a rapakivi texture, while in the other samples; the anti-rapakivi is also noted (Figures 7c and d) which indicates the mixing between felsic and mafic magmas (Arslan and Aslan 2006).

Plagioclase (An_{34-46}) occurs as anhedral to subhedral, twinned and untwinned plates (up to 0.7 mm), and is sometimes traversed by irregular fractures filled with minute quartz and biotite. Plagioclase both as phenocrysts and in the groundmass are partially altered into sericite and kaolinite, especially at their outer margins and along fractures. It is normally zoned and usually displays albite twinning. K-feldspar (up to 0.5 mm) occurs as anhedral to subhedral plates, showing cross-hatching (microcline) and simple twinning (orthoclase). It is replaced by myrmekite at the contact with adjoining plagioclase. Quartz is present as water-clear anhedral crystals, usually showing wavy extinction. It is found surrounding or filling the interstices between the plagioclase and K-feldspar (Figure 7e). The Biotite mineral occurs as subhedral to anhedral flakes and forms aggregates of small crystals, which are partly replaced by chlorite (Figure 7f). The hornblende is found as irregular crystals, dark green in color, strongly pleochroic with Z= dark green, Y= yellow-green, and X= greenish-yellow, and a maximum extinction angle of 32°. Some hornblende crystals show dark brown color, irregular shape commonly

contain plagioclase and opaque inclusions (Figure 7g). They contain minute iron oxide granules and are partially altered into green chlorite and iron oxide. Iron oxide occurs as euhedral to anhedral grains, usually associated with titanite. Xenocrystic accessory minerals are less common and are represented by pyroxene and plagioclase, which can be inherited from the country rocks during the ascent of granitic magma (Figure 7h).

Chlorite is present as a secondary mineral and is formed at the expense of biotite and hornblende. It displays a wide variation in shapes and colors vary from green to brown color. Allanite occurs as euhedral prismatic zoned crystals of honey brown colour. Zircon is found as short euhedral prismatic crystals enclosed within plagioclase and K-feldspar.

4.2.3 Felsic enclaves (Monzodiorite MD).

In hand specimen, the felsic enclaves are coarse-grained and of light gray color (Figure 8a). Microscopically, the color index (C.I) of felsic enclaves is 13 and has hypidiomorphic granular and intergranular textures. They are composed mainly of plagioclase (69%), K-feldspar (15%), biotite (10%), and quartz (3%). Iron oxides, apatite, and zircon are accessories, while muscovite and sericite are secondary minerals. The modal compositions of felsic enclaves are given in Table 1. Plagioclase (An_{36-40}) exists as subhedral to euhedral plates, up to 10 mm, commonly showing albite twinning and oscillatory zoning (Figure 8b). The plagioclase crystals have frequently suffered different degrees of sericitization, especially in their inner parts. K-feldspar is present mostly as large subhedral to anhedral crystals with irregular boundaries, up to 8mm. It is commonly replaced by myrmekite overgrowths on adjoining plagioclase crystals. Biotite is present as large-sized to medium flakes, up to 9 mm, of greenish-brown color. It is partly altered to green chlorite. Quartz is present as colorless, anhedral grains, up to 2 mm, and sometimes exhibits wavy extinction. Opaque minerals occur as shapeless grains, up to 1 mm across, associated with biotite and sometimes are mantled by sphene.

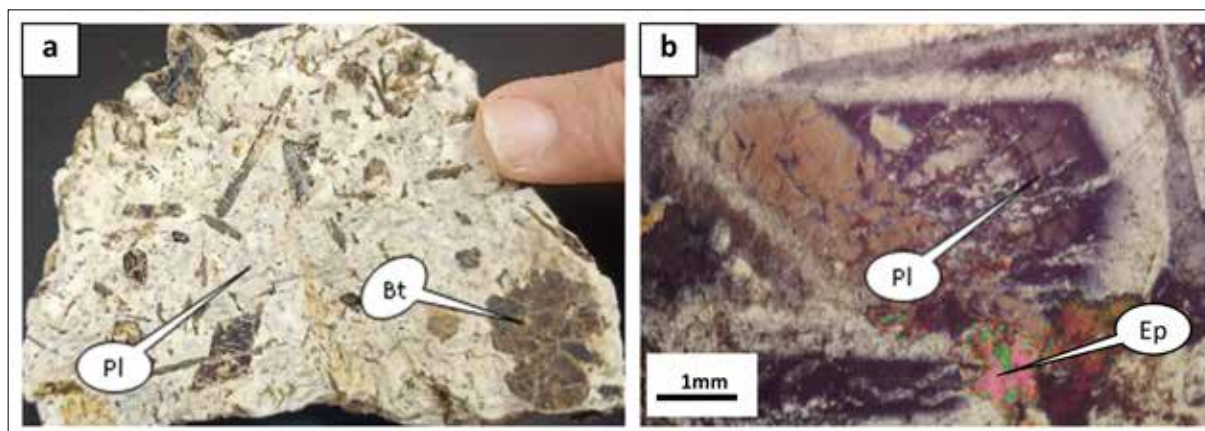


Figure 8. a. A hand-specimen of felsic enclave showing coarse-grained texture consists of plagioclase laths (Pl) and biotite flakes (Bt). (b) A photomicrograph showing euhedrally zoned plagioclase (Pl) partially altered into epidote (Ep).

5. Hydrothermal Alteration

Hydrothermal alteration involves any replacement in the primary mineralogical composition of rock by secondary minerals due to the action of hydrothermal solutions, which take place at temperatures above 50 °C (Galán and Ferrell 2013). Hydrothermal alterations' influence on granitic rocks was studied by several authors. (Ferry 1979; Lee and Parsons 1997; Şener and Gevrek 2000; Boyce et al. 2003; Nishimoto and Yoshida 2010; Jerram et al. 2011; René 2012; Vilalva and Vlach 2014).

The Ash-Sharqi pluton was subjected to hydrothermal alteration owing to the post-magmatic hydrous fluids, which played a major role in the late-stage evolution of the granitic rocks. The hydrothermal alteration is indicated by the extensive silicification, argillization, sericitization, carbonation, chloritization, epidotization, and sphenization processes, which produce several secondary minerals in various manners as replacement products of primary minerals or as patches and as small irregular veinlets cutting the rocks. The degree of alteration varies from very slight to intense, where in very slight alteration; the granitic blocks remain hard to keep their primary minerals and colors, whereas in intense alteration the granitic rocks lose most of their original features and become less coherent and decrease order of strength especially along fractures.

The effect of the alteration on rocks exhibiting cavities and spheroidal features which are commonly noted in the western side of pluton (Figure 9a).

Silicification is produced from reactions with subsequent high-temperature silica-rich solutions ($T = 300\text{--}550^\circ\text{C}$) (Julia et al. 2014; Ren et al. 2022) or from silica removal associated with chloritization and argillization processes (René 2012). The common silicification processes found as small cavities and Jigsaw veins are filled with chalcedony and quartz. The same filling occurs in the small veinlets traversing the granitic rocks.

Argillization alteration occurs as white to pale yellow zones produced from the influence of hydrothermal solutions on feldspars at low temperatures ($50\text{--}150^\circ\text{C}$) (Julia et al. 2014; Ren et al. 2022), where the feldspars transformed into a mixture of weak and easily deformable rocks consists of clay minerals (Figure 9b). This type of alteration has affected nearly most parts of granitic pluton but in various degrees, where the intense alteration takes place in the south and east sides.

Carbonation alteration is linked with the formation of secondary calcite as a replacement product after Plagioclase and hornblende and as pods and veinlets traversing the other minerals (Figure 9c).

Chloritization alteration occurs under thermal conditions ranging between 150°C and 300°C (Julia et al. 2014; Ren et al. 2022). Two types of chlorite are formed in Ash-Sharqi pluton. Chlorite₁ begins with the creation of very small chlorite spots along the cleavage planes of biotite and hornblende (Figure 9d), which may be associated with the

leaching of iron and the formation of yellow to brown iron staining. Chlorite₂ occurs as veinlets transected plagioclase and K-feldspar.

Sericitization alteration is formed after plagioclase and K-feldspar, where plagioclase shows variable degrees of alteration into sericite especially in their inner parts, while K-feldspar commonly along the outer rim (Figure 9e). This process has almost affected the whole granite body, especially the ones with fissures.

Hematization alteration process is concentrated in the outer boundaries of the granitic pluton, which gives red to brown color granite, which has been recognized as hematite. In hand samples and under the microscope, hematite is found as veinlets, with a staining effect, which may be attributed to the later stages of oxidation conditions of ferruginous minerals and mafic xenoliths (Figure 9f).

Epidotization found along cleavages and grain boundaries of plagioclase and amphibole (epidote₁) (Figure 9g). The epidote is also filled with fissures and intergranular spaces between minerals (epidote₂). Some veins preferentially follow boundaries between plagioclase grains.

Sphenization is a sphene that occurs as single grains or as reaction rim around opaque minerals of Fe-Ti oxides (Figure 9h). That sphenization alteration may be due to the reaction of Fe-Ti oxides with remaining hydrothermal fluids (Imaoka and Nakashima 1982).

6. Structures

The normal faults are the major structures in the area. They separate the granitic pluton and the volcanic succession. In some places, the faults are marked by crushed zones consisting of angular fragments of granite and volcanic rocks (Figure 10a). Extensive alteration of the granite takes place along the faults. The granitic pluton itself was crossed by normal faults and joints, which occur either as open and closed joints (Figure 10b). Sometimes the joints show favored in three directions (two vertical and one horizontal) creating wall parallelepiped joint blocks. The joint spacing decreases for the top of the pluton, and the block size increases towards the base of the pluton. Some fractures are closed and the others are filled by the final stages of solutions. The surfaces of joints are affected by alteration as indicated by the development of clay minerals and are stained on the important spaces within the joint blocks.

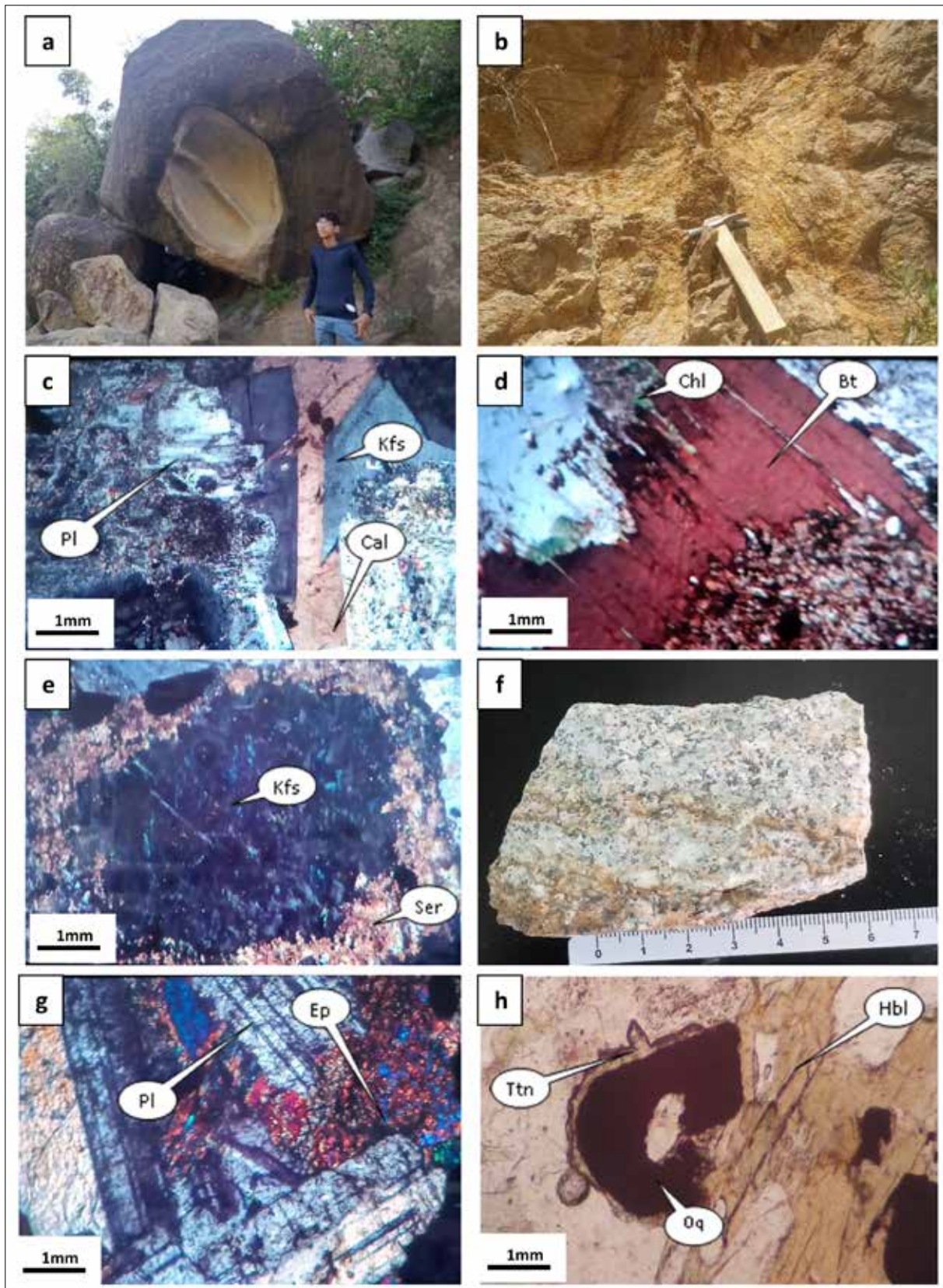


Figure 9. A photograph shows a large cavity within a granite block due to the weathering process. (b) A photograph showing the Argillization alteration zone of the granitoid rocks. (c) A photomicrograph displaying calcite (Cal) vein traversing both plagioclase (Pl) and K-feldspar (Kfs). (d) A photomicrograph showing chlorite (Chl) replacing biotite (Bt). (e) A photomicrograph showing marginally altered K-feldspar (Kfs) into sericite (Ser). (f) A granite hand specimen affected by iron staining along fractures. (g) A photomicrograph showing epidote (Ep) aggregates formed expense plagioclase (Pl). (h) A photomicrograph shows sphene (Titanite) (Ttn) formed expense Fe-Ti oxides (Oq).

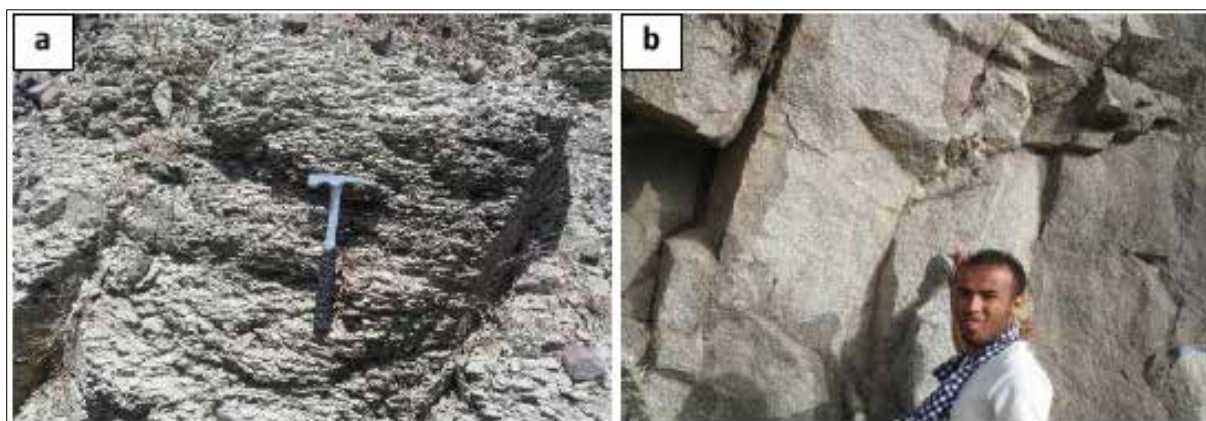


Figure 10. a. A photograph shows crushed zone between granite and basalt. (b) Three sets of joints in granitoid rocks.

7. Conclusions

1- The high magmatic activity of the Western Yemen occurred during the Cenozoic Era and had the following historical evolution:

- (a) Extrusion of huge amounts of basalt flows with minor pyroclastic materials over cretaceous sandstone, followed by extrusion of significant amounts of felsic flows and tuffs with minor pyroclastic.
- (b) Intrusion of a granitoid pluton into earlier volcanic succession.
- (c) Extrusion of basic and felsic flows associated with basic and felsic dykes.
- (d) Faulting and tilting the volcanic succession to their present conditions, where normal faulting took place repeatedly during volcanism, and some movements occurred along the normal faults that occurred after plutonism.

2- Field observations and petrographic investigations of the Ash-Sharqi area recognize five major rock units ordered from bottom to top a- Cretaceous sandstone, b- Tertiary volcanism, c- granitoid pluton, d- mafic and felsic dykes, and e- recent sediments. The present work focuses on granitoid pluton located within the volcanic rock succession.

3- Lithological characteristics and alteration style throughout the Granitoid pluton of Ash-Sharqi area indicate that it is similar to other Tertiary plutons in western Yemen.

4- The Ash-Sharqi pluton is most closely compared to the mainly Sabir pluton. This plutonic suite forms a roughly oval-shaped shape that shows a wider mineralogical variability range in composition from granite to quartz monzonite-quartz monzodiorite-quartz diorite.

5- No clear metasomatic contacts have originated in the area between volcanic succession and granitic pluton.

6- The pre-plutonic mafic, felsic volcanism, post-plutonic mafic, felsic dikes, and magmatic mafic enclaves within the granitic pluton indicate the character of bimodal magmatism.

7- The pluton contained structures such as enclaves and textures such as rapakivi, anti- rapakivi, and resorbed xenocryst indicating the occurrence of magma mixing, interaction, and mingling processes.

8- Hydrothermal alteration and subsequent solutions affecting the granitoid pluton are produced diverse types of alteration processes, including silicification, argillization,

hematization, chloritization, epidotization, sericitization, carbonation, and spheneization.

9- The study area was affected by various trends of structures on the form: (a) normal faults separate granitoid pluton on surrounding volcanic succession (b) faults and joints crossing granitoid pluton.

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Improvement in Oxygen Demand Capacities of Palm Oil Mill Effluent from Ujiogba Edo State Using Some Selected Bacterial and Fungal Isolates

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Abstract

Raw palm oil mill effluent contains a high quantity of organic matter that confers a high amount of biological oxygen demand (BOD) and chemical oxygen demand (COD) on it. Untreated palm oil mill effluent (POME) causes pollution of the environment affecting microorganisms, plants, and humans. The study investigated the bio-treatment capabilities of *Pseudomonas* sp., *Bacillus*, *Penicillium*, and *Aspergillus* species on POME from three oil palm milling sites. These sites have been receiving POME for over a decade at Ujiogba, Edo State, Nigeria. *Bacillus* sp. and *Pseudomonas* sp. were inoculated into the bio-treatment and reduced BOD by 60.79 % and 58.65 %, respectively, whereas the consortium of both isolates reduced BOD by 72.37 %. *Aspergillus* sp. had a percentage reduction value of 65.75%. *Penicillium* sp. had 70.19% while the consortium of *Aspergillus* sp. and *Penicillium* sp. had a percentage reduction of 72.89%. For COD, *Bacillus* sp. and *Pseudomonas* sp. had a reduction of 70.67% and 72.80% respectively, while their consortium had a reduction of 75.31%. *Aspergillus* sp. recorded 50.26%, while *Penicillium* sp. gave a 73.79% reduction. The results showed that the selected isolates, particularly the consortium, showed improved oxygen capabilities of POME thereby increasing its biodegradation and, subsequently, leading to reduced pollution and enhanced environmental sustainability.

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Keywords: Bio-treatment, Environmental sustainability, Oxygen demand, *Pseudomonas* sp., *Penicillium* sp.

1. Introduction

Untreated Palm oil mill effluent (POME) contaminants are more than 100 times compared to household sewage (Lee *et al.*, 2018). The oil palm business remains a main component of the agro-allied industries in Nigeria, and POME is a waste produced in the course of palm oil production. The release of fresh POME directly into soils influences the nearby bodies of water during runoff, which leads to increased acidity and eutrophication of the aquatic environment (Elmi *et al.*, 2015; Ebana *et al.*, 2017; Nehme *et al.*, 2021). The soil can also be influenced by the discharge of heavy metals and other physicochemical assets resulting from machine processing. Normally, POME comprises nutrients such as sodium, phosphorus, and potassium that enhance plant growth, but high contents do not allow them to function properly, particularly at abnormal pH (Nwachukwu *et al.*, 2018). In spite of soil improvement by POME, the soil finds it difficult to support plant growth and becomes moist with organic remains leading to clogging and water logging of the soil pores and eventually resulting in death of the vegetation (Dahnoun and Djadouni, 2020). Such findings are reported in studies on POME by Ogunsina and Akintan, (2020) and Okitipupa, Nigeria and Elmi *et al.* (2015) from Malaysia. They point to the obvious fact that contamination of the environment with POME is worldwide.

Palm oil mill effluent is identified to possess high

values of biological oxygen demand (BOD) and chemical oxygen demand (COD) (Ibrahim *et al.*, 2015). Biological oxidation of organic matter has led to the innovation of a low-cost secondary treatment of wastewater and industrial air emissions (Zainal *et al.*, 2017; Bhowmik *et al.*, 2023). Studies have been documented on the use of POME at final release in composting by vermicomposting and combined composting with empty fruit bunch (EFB) (Adam *et al.*, 2016; Nahrul *et al.*, 2017). In the technologies involved in composting, the biomass, formed from palm oil, possesses a high nutrient value. It is important to invest on additional treatment systems for challenges like content of heavy metals in POME, selection of effective microorganisms, and management of leachate still persist even though the composting technology can be useful. This composting technology can generate more money for the trade, which can sometimes assist in reducing the biogenic component of POME (Nahrul *et al.*, 2017).

Microorganisms are known to gain energy and carbon through the oxidation of organic compounds that are bioavailable in the environment. However, this process is dependent on a number of environmental and climatic factors (Ikhajiagbe *et al.*, 2021). *Pseudomonas aeruginosa*, *Bacillus subtilis*, *Acinetobacter iwoffi*, *Flavobacterium* sp., *Alcaligenes* sp., *Aspergillus* sp., and *Rhizopus* sp. are effective in degrading environmental contaminants

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(Enerijiofi *et al.*, 2017; Enerijiofi, et al., 2022; Enerijiofi and Ikhajagbe, 2021). The utilization of microorganisms in the natural treatment of POME in this current research offers a good alternative to decrease the oxygen demand and the natural burden content of the effluent as reported earlier (Ejeagba and Ihejirika, 2021). Ujiogba community is located in Esan land, Edo State of Nigeria. The community has been involved in the processing of oil palm for decades though at a subsistent level with the POME being emptied into the soil and underground water bodies. However, the reduction in biological and chemical oxygen demand capabilities of POME is very important as it improves the carbon-to-nitrogen ratio thereby utilizing it for improving soil fertilization and boosting agricultural production. This research aimed to utilize selected bacterial and fungal isolates to improve the oxygen demand capabilities of palm oil mill effluent.

2. Materials and Methods

2.1 Description of study area

Ujiogba is one of the agrarian communities in Esan West Local Government Area of Edo State. It lies on latitude 6.5198°N and longitude 6.1315°E. Palm oil mill effluent (POME) samples were collected at three different processing sites at Ujiogba, Esan West local government area of Edo State, Nigeria. These palm oil mill sites have existed for more than ten years with POME from the mill being discharged regularly on the receiving soil.

2.2 Collection of samples

Palm oil mill effluents were collected from three different palm oil processing mill sites at Ujiogba Edo state. Sterile plastic four-litre containers were used to collect the palm oil mill effluent sample in triplicate. POME contaminated soils were collected in polythene bags. Soil samples that were not polluted with POME served as control. The POME samples were instantly transferred to the laboratory for physiochemical and microbiological analyses.

2.3 Determination of total heterotrophic bacterial and fungal count

Tenfold serial dilution of palm oil mill effluent (POME) contaminated soils were prepared, thereafter, 0.1 ml of 10^{-3} , 10^{-6} and 10^{-9} diluents were plated into nutrient agar and potato dextrose agar plates respectively (Enerijiofi *et al.*, 2022). The nutrient agar plates were supplemented with 50 µl of nystatin to inhibit fungal growth while the potato dextrose agar plates were supplemented with 100 µl of streptomycin to inhibit bacterial growth. Bacterial isolation was conducted using nutrient agar plates, which were subsequently incubated at 37°C for 24 hours. In contrast, fungal isolates were cultivated on potato dextrose agar plates at 28°C for 72 hours. The discrete bacterial isolates were characterized and identified at the species level through cultural, morphological, and biochemical tests. The tests included shape, colour, margin, opacity, elevation, gram stain, arrangement, catalase, oxidase, indole, urease, citrate, lactose, sucrose, maltose, sorbitol, glucose, mannitol, and Voges Proskauer (Holt *et al.*, 1994). In addition, the fungal isolates characterized and identified the species level through the microscopic and macroscopic methods like colour, shape, and arrangement of hyphae (Barnett and Hunter, 1972).

2.4 Characterization of POME

This characterization was done before and after the treatment to determine the efficiency of the treatment with the bacterial and fungal isolates. The samples were collected and analyzed using standard methods in order to monitor the treatment process. The Biochemical Oxygen Demand (BOD) of the raw POME was determined using the HACH model 2173 BOD measurement apparatus while Chemical Oxygen Demand (COD) was determined by the titrimetric method as described in the standard method for the examination of water and wastewater (APHA, 2005; Ibegbulam-Njoku *et al.*, 2014b).

2.5 Bio-treatment of POME

Each bacterial and fungal isolate of inoculum size 0.1ml (10^6 spores/ml) was introduced into 500 ml Erlenmeyer flasks containing 100 ml each of raw POME. They were incubated at 30°C on a rotary shaker (200 rpm). The bio-treatment study was done for 15 days with samples drawn at 3-day intervals to determine the changes in biological oxygen demand (BOD) and chemical oxygen demand (COD) (Elmi *et al.*, 2015). The POME samples without the identified bacterial and fungal isolates served as controls for the bio-treatment studies.

2.6 Determination of bio-treatment efficiency

The efficiency of organic load (BOD or COD) reduction was calculated following the method of Elmi *et al.* (2015).

$$\text{Percentage efficiency} = (X - Y) / X$$

Where X = initial (BOD or COD) of the raw POME; Y = final (BOD or COD) after treatment of POME

3. Results

The total heterotrophic bacterial count was 5.2 ± 0.12 cfu/g while the heterotrophic fungal count was 3.24 ± 0.20 cfu/g as documented in Table 1. The bacterial isolates identified were *Acetobacter* sp., *Pseudomonas* sp., *Micrococcus* sp., *Corynebacterium* sp. and *Bacillus* sp. (Table 2) while the fungal included *Aspergillus* sp., *Rhizopus* sp., *Saccharomyces* sp., and *Penicillium* sp. (Table 3). *Pseudomonas* sp. was the most prevalent bacterial isolate (24.35%), followed by *Bacillus* sp. with 23.08% and the least in *Acetobacter* sp. (15.38%). *Penicillium* sp. was the most prevalent fungal isolate (33.60%), followed by *Aspergillus* sp. with 28.00% and the least in *Saccharomyces* sp. 17.60% (Table 4). The bio-treatment potentials of the bacterial and fungal isolates to treat palm oil mill effluent by measuring biological oxygen demand (BOD) are recorded in Table 5. *Bacillus* sp. and *Pseudomonas* sp. had percentage reduction values of 60.79% and 58.65% while a consortium of *Bacillus* sp. and *Pseudomonas* sp. had a percentage reduction value of 72.37%. *Aspergillus* sp. had a percentage reduction value of 65.75%, *Penicillium* sp. had 70.19% while the consortium of *Aspergillus* sp. and *Penicillium* sp. had a percentage reduction of 72.89%. The bio-treatment potentials of the bacterial and fungal isolates of palm oil mill effluent by measuring chemical oxygen demand (COD) are recorded in Table 6. *Bacillus* sp. and *Pseudomonas* sp. had percentage reduction values of 70.67% and 72.80% while a consortium of *Bacillus* sp. and *Pseudomonas* sp. had a percentage

reduction value of 75.31%. *Aspergillus* sp. had a percentage reduction value of 50.26%, *Penicillium* sp. had 73.79% while the consortium of *Aspergillus* sp. and *Penicillium* sp. had a percentage reduction value of 63.05%.

Table 1. Enumeration of bacterial and fungal count from palm oil mill effluent contaminated soil (x10⁶ cfu/g).

Count	Mean ± standard error	Control
THBC	5.20 ± 0.12	0.5 ± 0.01
THFC	3.24 ± 0.20	0.4 ± 0.11

Legend: THBC – Total Heterotrophic Bacterial Count; THFC – Total Heterotrophic Fungal Count.
Values represent mean ± standard error of the triplicate sample

Table 2. Cultural, Morphological, and Biochemical Characteristics of Bacterial Isolates.

Characteristics	A	B	C	D	E
Shape	Circular	Circular	Circular	Irregular	Circular
Colour	Milky	Pale green	Milky	Pink	Milky
Margin	Entire	Entire	Lobate	Crenate	Lobate
Opacity	Opaque	Translucent	Opaque	Translucent	Opaque
Elevation	Flat	Flat	Flat	Flat	Flat
Wet/dry	Wet	Wet	Dry	Dry	Dry
Gram stain	+	-	+	+	+
Shape	Ova	Rod	Cocci	Rod	Rod
Arrangement	Chains	Pair	Single	Single	Pair
Catalase	-	-	+	+	+
Oxidase	+	+	+	+	+
Indole	-	+	+	+	+
Urease	+	-	-	+	-
Citrate	-	+	-	-	-
Lactose	-	+	+	+	+
Sucrose	+	+	-	-	+
Maltose	-	+	+	+	-
Sorbitol	+	-	-	-	+
Glucose	+	+	+	+	+
Mannitol	-	-	-	-	+
Fluorescent	-	+	-	-	-
Amylase	-	+	-	+	+
Voges Proskauer	+	-	+	+	-
H ₂ S Production	-	-	-	+	-
Spore	-	-	-	-	+
Probable Identity	<i>Acetobacter</i> sp.	<i>Pseudomonas</i> sp.	<i>Micrococcus</i> sp.	<i>Corynebacterium</i> sp.	<i>Bacillus</i> sp.

Table 3. Microscopic and Macroscopic Characteristics of Fungal Isolates.

S/N	Cultural Morphology	Microscopic examination	Probable Identity
1	Black fluffy colonies with reverse side yellow	Simple septate and branched conidia in chains.	<i>Aspergillus</i> sp.
2	White and cottony hyphae with reverse side white	Non septate hyphae with sporangiospore and rhizoid	<i>Rhizopus</i> sp.
3	Milky whitish colonies, and white on reverse	Spherical to ova shape fungi Stained positive on gram reaction	<i>Saccharomyces</i> sp.
4	Green flat colony with reverse side dirty white	Brush-like conidia, septate branching conidiophore was smooth/rough walled.	<i>Penicillium</i> sp.

Table 4. Percentage Prevalence of Bacterial and Fungi Isolates from Palm Oil Mill Effluent Contaminated Soil (%).

Bacterial species	Palm oil mill effluent n (%)	Control n (%)
<i>Acetobacter sp.</i>	24 (15.38)	2 (15.38)
<i>Pseudomonas aeruginosa</i>	38 (24.35)	4 (30.77)
<i>Micrococcus sp.</i>	30 (19.23)	3 (23.07)
<i>Bacillus sp.</i>	36 (23.08)	3 (23.07)
<i>Corynebacterium sp.</i>	28 (17.95) 156	1 (7.69) 13
Fungal species		
<i>Aspergillus sp.</i>	35 (28.00)	4 (30.76)
<i>Rhizopus sp.</i>	26 (20.80)	3 (23.10)
<i>Saccharomyces sp.</i>	22 (17.60)	2 (15.38)
<i>Penicillium sp.</i>	42 (33.60) 125	4 (30.76) 13

Table 5. Biological Oxygen demand (BOD5) values of Palm oil mill effluent with bacterial and fungal isolates over 15 days at 3- day intervals (mg/l).

	Day 0	Day 3	Day 6	Day 9	Day 12	Day 15	(%) BOD reduction
Bacterial isolates.							
<i>Pseudomonas sp.</i>	301.17±0.42	293.11±0.10	262.15±0.56	211.22±0.18	142.14±0.31	118.45±0.12	60.79
<i>Bacillus sp.</i>	339.33±0.89	283.24±0.31	251.05±0.59	215.28±0.47	162.10±0.52	140.31±0.67	58.65
<i>Pseudomonas and Bacillus</i>	398.28±0.02	311.12±0.44	242.70±0.18	194.13±0.76	152.05±0.38	110.04±0.41	26.92
Control	158.86±0.19	136.73±0.23	115.07±0.17	106.89±0.62	101.17±0.43	99.74±0.17	37.22
Fungal isolates.							
<i>Aspergillus sp.</i>	132.12±0.10	118.23±0.32	101.60±0.34	96.52±0.52	75.32±0.67	45.25±1.15	65.75
<i>Penicillium sp.</i>	128.23±0.54	114.31±0.25	98.74±0.62	65.19±0.21	55.32±0.49	38.22±2.01	70.19
<i>Aspergillus and Penicillium</i>	162.80±0.23	143.82±0.51	115.45±0.83	86.23±0.17	67.36±1.31	44.12±1.03	72.89
Control	105.76±0.19	88.11±1.11	71.26±0.16	49.37±0.42	32.37±2.13	60.73±0.45	42.58

Legend: Values represent mean ± standard error of triplicate samples

Table 6. Chemical oxygen demand (COD) values of palm oil mill effluent with bacterial and fungal isolates over 15 days at 3- day intervals (mg/l).

	Day 0	Day 3	Day 6	Day 9	Day 12	Day 15	% COD reduction
Bacterial isolates.							
<i>Pseudomonas sp.</i>	206.12±0.41	187.23±0.32	146.11±0.89	123.99±1.23	96.06±1.22	56.06±2.10	72.80
<i>Bacillus sp.</i>	198.21±1.11	164.30±0.54	120.05±0.22	98.55±0.45	77.58±0.34	58.14±0.39	70.67
<i>Pseudomonas and Bacillus</i>	245.51±0.45	202.91±0.58	185.80±0.59	137.74±0.67	102.62±0.81	60.62±0.81	75.31
Control	110.12 ±0.66	96.12 ±0.54	78.06±0.33	66.53±0.86	54.13±0.94	70.29±0.94	36.17
Fungal isolates.							
<i>Aspergillus sp.</i>	191.97±0.85	182.53±2.11	162.63±1.25	125.48±0.56	111.48±0.77	95.48±0.32	50.26
<i>Penicillium sp.</i>	198.01±0.30	178.91±3.01	159.33 ±0.52	123. 66±0.46	99.67±0.15	51.88±0.15	73.79
<i>Aspergillus and Penicillium</i>	232.48±49	206.89±.58	185.82±1.83	144.67±2.08	111.59. ±1.70	85.91. ±2.70	63.05
Control	121.66±2.12	105.64±1.11	92.33±2.10	73.86±0.16	56.94±1.20	80.94±0.32	33.47

Legend: Values represent mean ± standard error of triplicate samples

4. Discussion

The total heterotrophic count revealed that the palm oil mill effluent (POME) contaminated soils had more heterotrophic bacterial and fungal loads than the control. This output indicated that POME contained more nutrients for bacterial and fungal growth and multiplication hence higher counts more than the control. The results of this study concurred with those of earlier authors, Orji *et al.* (2006), Ibegbulam-Njoku, and Achi, (2014b) who reported that palm

oil mill effluent enhanced microbial growth. Palm oil mill effluent (POME) is of great interest to many researchers because of high levels of biogenic matter, which indicates high BOD and COD values as well as oil and grease, which serve as substrates for microorganisms. Oil in palm oil mill effluent is an excellent source of carbon with about twice the energy value of glucose during microbial growth (Ibegbulam-Njoku and Achi, 2014b). The organic nature of palm oil mill effluent (POME) indicates that the effluent

is biologically degradable, and laboratory experimental findings have confirmed it (Orji *et al.*, 2006). The findings also showed that soils with older POME deposits tend to have more numbers and varied microorganisms than nearby soils without POME deposits. This difference is because palm oil mill effluents are rich in biodegradable organic matter and as the micro-organisms biodegrade the organic content of the POME, the receiving soil is inevitably influenced.

This study documented different bacteria and fungi isolates from palm mill effluent-contaminated soil. These include *Pseudomonas*, *Acetobacter*, *Micrococcus*, *Bacillus*, *Corynebacterium*, *Aspergillus*, *Rhizopus*, *Saccharomyces* and *Penicillium* species. The percentage of prevalence had *Pseudomonas* sp. as the highest (24.35%), followed by *Bacillus* sp. with 23.08% and least in *Acetobacter* sp. (15.38%). *Penicillium* sp. was reported to as the most prevalent fungal isolate (33.60%), followed by *Aspergillus* sp. with 28.00% and least in *Saccharomyces* sp. with 17.60%. The different bacterial and fungi isolate could be because the palm oil mill effluent is disposed to degradation by microorganisms resulting from its organic nature as reported earlier (Loretta *et al.*, 2016). The variation in the microorganisms isolated in this study and those of earlier researchers could be attributed to the nature of the environment, whether the microorganisms were mesophilic or thermophilic, and the population changes along the disposal channel. This is in line with the observations of Ewelike *et al.* (2021) who noted that the nature and behavior of the microbial population in the POME environment are influenced by many physiochemical parameters of ecological importance.

The bio-treatment abilities of the selected bacterial and fungal isolates to treat palm oil mill effluent were measured using two parameters: biological oxygen demand (BOD) and chemical oxygen demand (COD). Biological oxygen demand and Chemical oxygen demand indicate organic pollutants in wastewater. Bacteria utilize the organic compounds in the wastewater for growth and metabolism. In the BOD, *Bacillus* sp. and *Pseudomonas* sp. had percentage reduction values of 60.79% and 58.65% respectively while the consortium of *Bacillus* and *Pseudomonas* species gave 72.37% reduction. *Aspergillus* sp. had a percentage reduction value of 65.75%. *Penicillium* sp. gave 70.19% while the consortium of *Aspergillus* and *Penicillium* species had a percentage reduction of 72.89%. However, for the COD, *Bacillus* sp. and *Pseudomonas* sp. had percentage reductions of 70.67% and 72.80% respectively while their consortium gave a percentage reduction of 75.31%. *Aspergillus* sp. had a percentage reduction value of 50.26%, *Penicillium* sp. had 73.79% while the consortium of *Aspergillus* and *Penicillium* species had a percentage reduction of 63.05%. This study revealed that the consortium of the microbial isolates; bacterial-bacterial and fungal-fungal had a higher percentage reduction in both monitored parameters; biological oxygen demand and chemical oxygen demand than the individual isolates. The findings in this study concurred with the earlier submission of Karim *et al.* (2019) who reported that *Bacillus cereus* through the batch fermentation system substantially reduced contamination burden precisely COD and BOD for 50% (v/v) palm oil mill effluent within 6 days.

However, since POME is said to be non-toxic as it does not involve the addition of chemicals during the oil extraction process, it uses up the bioavailable oxygen in the aquatic environment for the degradation process, thereby providing a noble nutrients source for microbial growth and subsequently leading to a reduction in the COD and BOD. It also increases the organic nitrogen available, which supports plant growth and development (Razak *et al.*, 2022; Elmi *et al.*, 2015). Therefore, the results revealed that treatment of POME before discharge would reduce the risk of pollution as corroborated by the submission of Karim *et al.* (2019) that bio-treatment of palm oil sludge using selected microorganisms on continuous fermentation has been shown to improve the quality of the effluent.

5. Conclusion and Recommendation

The study revealed that the POME-contaminated soils contained *Pseudomonas*, *Acetobacter*, *Micrococcus*, *Bacillus*, *Corynebacterium*, *Aspergillus*, *Rhizopus*, *Saccharomyces*, and *Penicillium* species. It also reports treatment of the final discharge palm oil mill effluent focusing on COD and BOD reduction using *Pseudomonas*, *Bacillus*, *Aspergillus*, and *Penicillium* species as revealed by the substantial reduction in their concentrations. Based on these findings, bio-treatment of POME is recommended to prevent environmental contamination and to improve the carbon-to-nitrogen ratio of the effluent making it good for improving soil fertility.

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Geochemical Characteristics of Rare Earth Elements in Argillic Alteration Zone: An Example from the Kharvana area, NW Iran

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Abstract

The emplacement of Oligocene tonalitic, granodiorite, and quartz diorite suites into Cretaceous andesitic rocks causes the generation of an argillic alteration zone in the northeast of the Kharvana area. No detailed geochemical consideration of the argillic alteration zone has been carried out. In this research, factors controlling the mobility and concentration of rare earth elements (REE) in this alteration zone are determined by different geochemical techniques. The mineralogical and geochemical characteristics of the argillic alteration zone were examined by X-ray diffractometer and Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), respectively. Based on mineralogical analyses, quartz, kaolinite, alunite, pyrophyllite, muscovite-illite, rutile, chlorite, jarosite, hematite, goethite, and pyrite are the dominant mineral phases in the Kharvan argillic alteration zone. Chondrite-normalized REE spider diagrams indicate fractionation and enrichment of LREE from HREE, along with Eu and Ce negative anomalies during the development of the argillic alteration zone. Taking into account Al as an immobile monitor element, argillization of andesite rocks was accompanied by leaching and fixation of REE. Whereas, among the lanthanides, Ce displays a decrease in the content of all the argillic samples. Combining the results obtained from mass change calculations and geochemical parameters, such as $(\Sigma\text{LREE}/\Sigma\text{HREE})_N$ and $(\text{La}/\text{Yb})_N$ ratios, shows that the distribution of lanthanides during the development of the argillic alteration zone is controlled by a number of factors, including changes in pH and redox potential of environment, the difference in the degree of destabilization of lanthanide complexes, adsorption, scavenging by metallic oxides and hydroxides, and isomorphic substitution.

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Keywords: Argillic alteration; Mobility; Rare earth elements; Kharvana; Northwestern Iran.

1. Introduction

The mobility, distribution, and fractionation of rare earth elements (REE) during alteration processes in different environments have been documented by several researchers and have been used to determine the chemistry of solutions responsible for alteration and mineralization (Dill et al., 1997; Galan et al., 1998; El-Hasan et al., 2008; El-Hasan and Al-Malabeh, 2008; Parsapoor et al., 2009; Karakaya, 2009; Cravero et al., 2010; Karakaya et al., 2012; Grecco et al., 2012; Siahcheshm et al., 2014; Ercan et al., 2016; Al Smadi et al., 2018; Abedini et al., 2020; Kadir et al., 2022; Abd El-Moghny et al., 2022; Garofalo et al., 2023). The REE mobility is significantly controlled by the availability of complexing ions, such as F^- , Cl^- , CO_3^{2-} , PO_4^{3-} , and SO_4^{2-} , low pH, and high rock/fluid ratios as well (Wood, 1990; Haas et al., 1995; Fulignati et al., 1999; Seewald et al., 2019). In addition, many studies that focused on pertaining the significance of REE for exploration have been used (Qi-Cong and Cong-Qiang, 2002; Weimin et al., 2003; Abedini and Calagari, 2012; Tassongwa et al., 2017; Apollaro et al., 2023). Based on these researches, the ore bodies prospective for metal mineralization might have a distinctive REE signature and, therefore, they may have some applications for exploration (Dill et al., 2015). It

suggests that REE behavior in a hydrothermal environment is complex and no simple rules can address the mobility and fractionation of REE during hydrothermal processes (Parsapoor et al., 2009; Rezaei Azizi et al., 2018a, b).

It is believed that the Alborz–Azarbaijan Mountains and magmatic events in the northwestern part of Iran are a result of the collision of the Gondwana and Arabian Plate with the Eurasian Plate during the late Cretaceous–early Paleogene. This phenomenon causes the development of an extensional basin in the northwestern part of Iran (Mollai et al., 2014; Simmonds et al., 2015; Abedini et al., 2018; Ghasemi Siani and Lentz, 2022). The Cenozoic Ahar–Arasbaran volcanic belt (hereafter AHAVB) in northwestern Iran includes numerous ore deposits and different mineralization types, such as porphyry, Cu–Fe skarn, and epithermal deposits (e.g. Mollai et al., 2014; Jamali and Mehrabi, 2015). The AHAVB, about 100 km wide, extends from NW Iran to Armenia and the eastern Pontide arc in NE Turkey (Jamali et al., 2010). In the last two decades, a lot of research has been carried out on these deposits and their related alteration zones (among others: Simmons et al., 2015; Abedini, 2017; Abedini et al., 2020). However, geochemical characteristics of hydrothermal alterations, especially argillic alteration,

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have not been much studied. In the northeast of the Kharvana city of the AHAVB, the emplacement of Oligocene intrusive rocks into Cretaceous volcanic rocks causes the generation and development of large-scale hydrothermal alterations (Jamali et al., 2010). The main hydrothermal alteration is the argillic alteration zone. The main goals of this study are to provide comprehensive information on factors controlling the mobility and concentration of REE and Eu and Ce anomalies during the development of the argillic alteration zone in the northeast of the Kharvana.

2. Geological Setting of the Study Area

According to the geological zones of Iran of Nabavi (1976), the study area is within the Alborz–Azarbaijan structural zone (Figure 1). The oldest rock units are Cretaceous in age, from the oldest to the youngest, including andesite, limestone, and crystalline tuff interlayered with thin-bedded limestone. The Cenozoic lithological sequence includes Paleocene marl, shale, and limestone, Oligocene diorite, gabbro diorite, tonalite, granodiorite, and quartz diorite (Figure 2). Quaternary alluvial sediments are the youngest rock units in the Kharvana area.

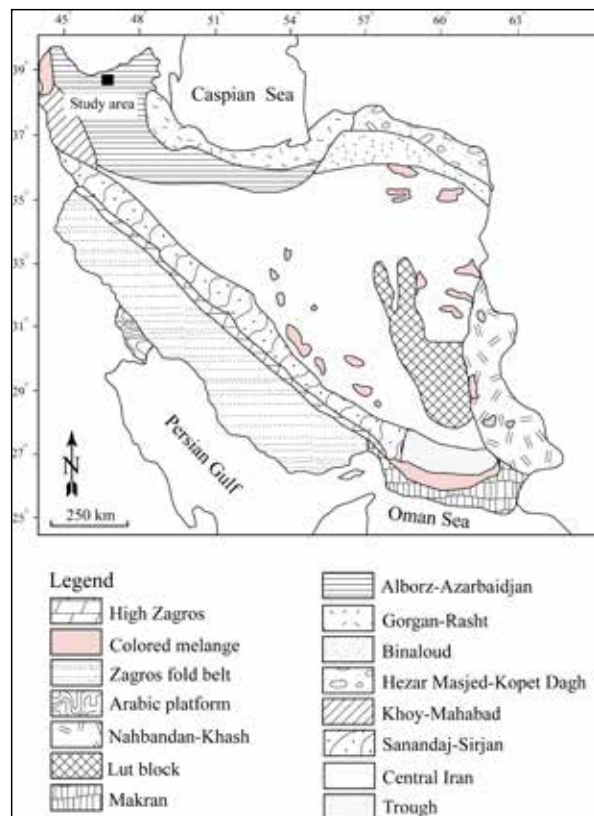


Figure 1. Zonal subdivisions of Iran (Nabavi, 1976); inset shows the location of the Kharvana area within the Alborz–Azarbaijan zone.

The emplacement of Oligocene tonalite, granodiorite, and quartz diorite plutons into Cretaceous andesitic rocks is associated with the development of large-scale argillic alteration zone (Jamali et al., 2010) (Figure 3a, b). Moreover, Cu–Fe skarn deposits are interpreted to have formed in the contact of the aforementioned intrusive suites and Cretaceous carbonate rocks. Coarse crystals of garnet, along with magnetite and chalcopyrite are observed in hand specimens of skarn samples.

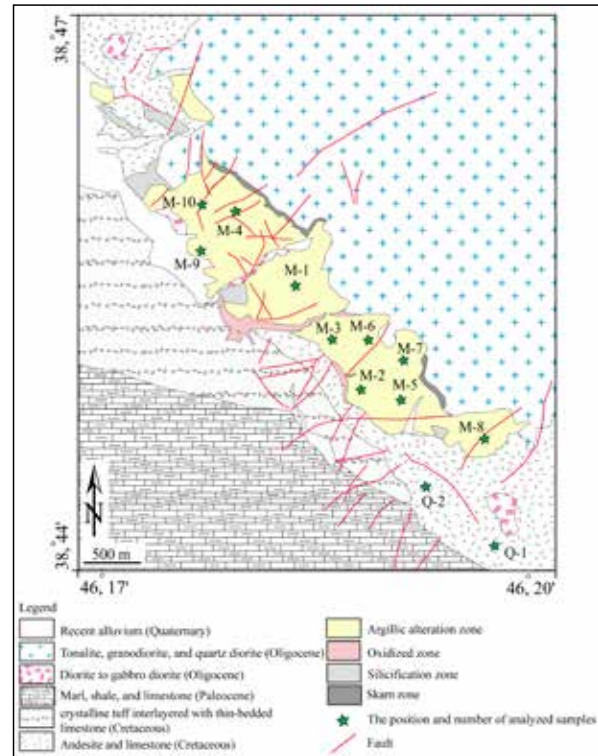


Figure 2. Simplified geological map showing lithological units and the distribution of argillic alteration zone for the northeast of the Kharvana area.

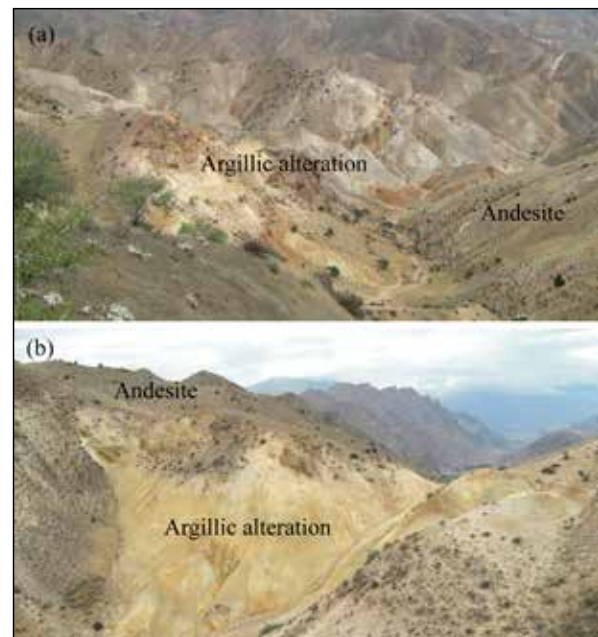


Figure 3. (a, b) The development of argillic alteration zone related to the andesitic rocks in the northeast of the Kharvana area (looking to the south).

Field surveys show that siliceous masses are developed on the argillic alteration zone. The occurrence of faults in the place where siliceous masses outcropped is indicative of Si leaching from the argillic alteration zone by hydrothermal fluids. Fe-bearing minerals, such as hematite, limonite, and jarosite, are also observed in the argillic alteration zone. The existence of chalcopyrite, pyrite, malachite, azurite, gypsum, anhydrite, and barite mineralizations as veins, veinlets, and breccia is other obvious geological characteristics of the argillic alteration zone in the northeast of the Kharvana area.

3. Sampling and Analytical Method

In this study, 12 representative samples were collected from different rock units. Microscopic studies of andesitic rocks were studied using an Olympus BX60F5 optical microscope at the Department of Geology of Urmia University, Iran. Mineralogical compositions of 10 argillic samples were obtained at the Geological Survey of Iran, Tehran by X-ray diffraction (XRD) with a Siemens D5000 X-ray diffractometer with the following operating conditions: Cu-K α radiation at an accelerating voltage of 40 kV and a beam current of 40 mA, scanning speed of 2° per minute, and scan range of 2°–70°. Whole-rock geochemical analysis of all 12 samples (10 samples from the argillic

alteration zone and 2 samples from the least-altered andesitic rocks) was carried out at the Activation Laboratories Ltd. (ALS Chemex, Vancouver, Canada). Major oxides and trace elements were analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP–AES) and Inductively Coupled Plasma-Mass Spectrometry (ICP–MS) respectively. The loss-on-ignition (LOI) was obtained by weight difference after ignition at 950 °C in a muffle furnace for 90 minutes. Results of geochemical analysis and LOI contents of samples from the argillic alteration zone and the least-altered volcanic rocks of the northeast of the Kharvana area are given in Table 1.

Table 1. Chemical analysis of major oxides and REE from the argillic alteration and the least-altered andesitic samples of the northeast of the Kharvana area, northwestern Iran.

	DL	Andesite		Argillic alteration zone									
		Q-1	Q-2	M-1	M-2	M-3	M-4	M-5	M-6	M-7	M-8	M-9	M-10
SiO ₂ (wt%)	0.01	54.65	57.38	60.45	54.25	60.35	63.81	58.78	60.85	57.58	57.09	57.77	65.42
Al ₂ O ₃	0.01	15.82	16.32	16.59	17.03	16.85	16.54	16.56	16.98	16.85	16.98	17.21	16.35
Fe ₂ O ₃	0.04	8.51	7.06	5.06	8.85	6.21	4.02	6.88	3.35	8.84	7.26	7.09	3.16
MgO	0.01	6.58	4.65	0.22	0.51	0.45	0.19	0.54	0.61	0.56	0.61	0.61	0.74
CaO	0.01	7.91	7.55	0.12	0.15	0.13	0.11	0.12	0.16	0.12	0.13	0.14	0.08
Na ₂ O	0.01	3.55	3.69	0.24	0.29	0.26	0.22	0.23	0.32	0.23	0.27	0.29	0.16
K ₂ O	0.01	1.21	1.35	1.21	1.45	1.32	1.09	1.18	1.65	1.17	1.26	1.35	0.79
TiO ₂	0.01	0.66	0.68	0.55	0.78	0.58	0.56	0.54	0.78	0.65	0.69	0.67	0.55
P ₂ O ₅	0.01	0.28	0.29	0.06	0.23	0.19	0.14	0.18	0.18	0.19	0.16	0.12	0.09
MnO	0.01	0.07	0.09	0.23	0.11	0.12	0.07	0.16	0.17	0.08	0.08	0.07	0.03
LOI	–	0.75	0.91	15.2	16.3	13.3	13.1	14.7	14.9	13.7	15.3	14.6	12.6
Sum	–	99.99	99.97	99.93	99.95	99.76	99.85	99.87	99.95	99.97	99.83	99.92	99.97
La (ppm)	0.1	23.8	27.0	22.7	33.5	31.9	25.1	27.6	26.8	34.3	33.3	35.5	14.6
Ce	0.1	49.8	57.7	33.8	50.4	44.7	33.3	40.5	46.6	47.2	51.1	50.9	21.6
Pr	0.02	5.17	6.18	4.83	7.77	6.71	4.62	6.09	7.18	8.01	7.92	9.06	3.36
Nd	0.3	21.4	24.2	15.4	29.3	24.5	16.1	23.3	27.3	30.3	29.7	32.7	11.9
Sm	0.05	3.89	3.59	2.59	5.20	4.40	2.35	4.28	5.23	5.28	5.45	6.08	2.44
Eu	0.02	1.03	1.03	0.70	1.32	1.12	0.65	1.16	1.10	1.31	1.28	1.56	0.68
Gd	0.05	3.47	3.36	2.15	4.57	3.98	1.94	4.02	4.70	4.88	5.06	5.58	2.24
Tb	0.01	0.55	0.53	0.35	0.75	0.65	0.32	0.72	0.79	0.79	0.81	0.91	0.43
Dy	0.05	3.85	3.96	2.08	4.18	3.73	1.78	4.16	4.69	4.27	4.77	5.32	2.61
Ho	0.02	0.75	0.63	0.44	0.86	0.72	0.40	0.85	0.99	0.94	0.97	1.07	0.49
Er	0.03	1.94	2.15	1.36	2.50	2.27	1.24	2.51	2.97	2.67	2.70	2.90	1.63
Tm	0.1	0.32	0.29	0.22	0.39	0.35	0.22	0.39	0.47	0.41	0.44	0.46	0.29
Yb	0.05	1.87	1.95	1.51	2.49	2.30	1.45	2.57	3.18	2.64	2.87	2.86	1.81
Lu	0.01	0.33	0.29	0.25	0.41	0.39	0.24	0.43	0.50	0.42	0.45	0.46	0.29
Σ LREE (La–Eu) (ppm)	–	105.16	119.62	80.00	127.39	113.32	82.09	102.97	114.20	126.30	128.66	135.82	54.47
Σ HREE (Gd–Lu) (ppm)	–	13.08	13.16	8.36	16.13	14.38	7.59	15.63	18.28	17.02	18.07	19.57	9.79
Σ REE (La–Lu) (ppm)	–	118.24	132.78	88.36	143.51	127.70	89.68	118.60	132.48	143.32	146.73	155.39	64.26
Eu/Eu*	–	0.83	0.88	0.89	0.80	0.82	0.90	0.83	0.66	0.77	0.72	0.80	0.87
Ce/Ce*	–	0.98	0.99	0.71	0.69	0.67	0.66	0.69	0.75	0.63	0.70	0.63	0.68
(La/Yb) _N	–	8.62	9.34	10.16	9.10	9.37	11.70	7.25	5.70	8.77	7.83	8.40	5.43
(Σ LREE/ Σ HREE) _N	–	3.53	3.99	4.20	3.46	3.46	4.74	2.89	2.74	3.26	3.12	3.04	2.44

Abbreviations: DL = detection limit, LOI = loss-on-ignition.

Eu/Eu* = $\text{Eu}_N / (\text{Sm}_N \times \text{Gd}_N)^{1/2}$; Ce/Ce* = $2\text{Ce}_N / (\text{La}_N + \text{Pr}_N)$; (La/Yb)_N = $(\text{La}/\text{Yb})_{\text{samples}} / (\text{La}/\text{Yb})_{\text{chondrite}}$; (Σ LREE/ Σ HREE)_N = $(\Sigma \text{LREE} / \Sigma \text{HREE})_{\text{samples}} / (\Sigma \text{LREE} / \Sigma \text{HREE})_{\text{chondrite}}$, where the subscript “N” refers to normalized values to chondrite (Taylor and McLennan, 1985).

Geochemical parameters, such as (Σ LREE/ Σ HREE)_N and (La/Yb)_N ratios, are representative of the fractionation of REE during argillization of the andesitic rocks in the study area, where LREE and HREE are of La–Eu and Gd–Lu respectively. The Eu and Ce anomalies are calculated by the following equations of Taylor and McLennan (1985), where the subscript “N” indicates values normalized to chondrite.

$$\text{Eu}/\text{Eu}^* = \text{Eu}_N / (\text{Sm}_N \times \text{Gd}_N)^{1/2}$$

$$\text{Ce}/\text{Ce}^* = 2\text{Ce}_N / (\text{La}_N + \text{Pr}_N)$$

4. Results and Discussion

Microscopic observations show that the andesite rocks related to the argillic alteration zone have a porphyritic texture, in which phenocrysts are present in a fine-grained matrix. Plagioclase, pyroxene, and hornblende with up to 5 mm in the longest dimension are the most frequent

phenocrysts of these rocks. Sometimes, these phenocrysts are altered into a series of clay minerals, chlorite, epidote, and sericite. Pyrite is the most important metal mineral present in these rocks. This mineral is observed as euhedral to subhedral crystals in the matrix.

According to PXRD analysis, quartz, kaolinite, and pyrophyllite are the main mineral assemblage of all the studied samples from the argillic alteration zone (Figure 4a, b). However, alunite, hematite, jarosite, goethite, muscovite–illite, rutile, pyrite, and chlorite are present at minor contents in the studied samples (Figure 4, b). The existence of pyrophyllite, alunite, jarosite, and rutile minerals shows that Cretaceous andesitic and andesitic–basaltic rocks have experienced an advanced argillic alteration, and the activity of sulfate ions in solutions responsible for alteration was high.

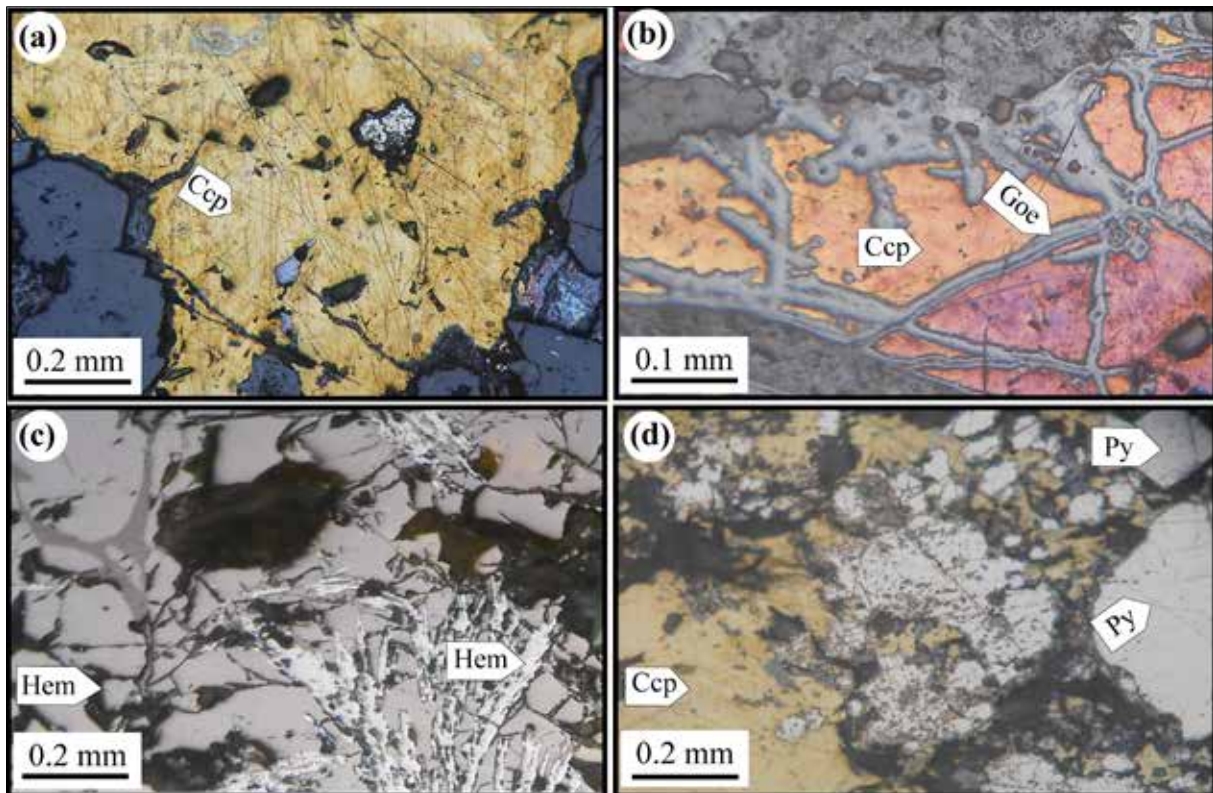


Figure 4. Photomicrographs of mineral phases in mineralized veins/veinlets from the Kharvana area. (a) Subhedral chalcopyrite crystal; (b) goethite in the rim of chalcopyrite; (c) elongated crystals of hematite; and (d) euhedral to subhedral pyrite. All photos are in reflected light. Abbreviations: Ccp = chalcopyrite; Goe= goethite, Hem = hematite, Py = pyrite.

Mineralogical studies show that the major minerals present in veins and veinlets of the argillic alteration zone are chalcopyrite, pyrite, malachite, azurite, and iron oxides and hydroxides, such as goethite, hematite, and limonite (Figure 5a–d). In microscopic sections, chalcopyrite shows no regular geometric shape (Figure 5a), but pyrite occurs as

euhedral to subhedral crystals (Figure 5d) that are strongly tectonized. Hematite is observed as elongated crystals (Figure 5c). Sometimes, chalcopyrite is replaced by goethite during supergene processes (Figure 5b). Malachite and azurite accompanied with goethite are green and bluerespectively.

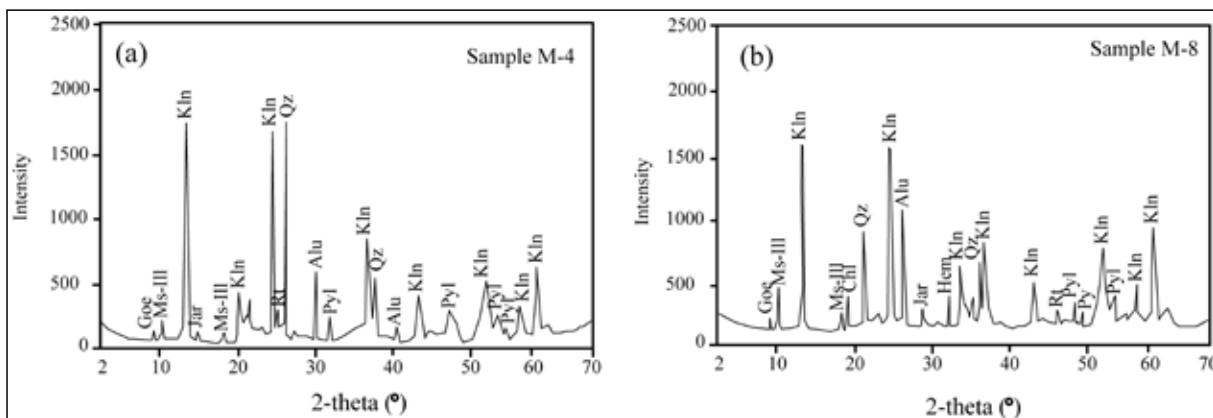


Figure 5. Powder-XRD patterns of the two-argillic samples from the Kharvana area. Abbreviations: Alu = alunite, Chl = chlorite, Goe = goethite, Hem = hematite, Jar = jarosite, Kln = kaolinite, Ms-Ill = muscovite-illite, Py = pyrite, Pyl = pyrophyllite, Qz = quartz, Rt = rutile.

So far, many methods have been presented for the calculation of mass changes of elements during alteration and/or weathering processes by different researchers. The most important methods are volume factor (Gresens, 1967), absolute weathering index (Nesbitt, 1979), isocon analysis (Grant, 1986), immobile elements (Brimhall and Dietrich, 1987; MacLean and Kranidiotis, 1987), percentage of changes in elemental ratios (Nesbitt, 1979; Nesbitt and Markovics, 1997), mobility index (Ng et al., 2001), chemical depletion

fraction, and immobile plateau (Gong et al., 2011). In general, the calculation of mass change in these methods is similar to each other. However, the determination of immobile element(s) for the calculation of mass change is regarded as a key factor. Trace elements, such as Al (Duzgoren-Aydin et al., 2002) and Ti (Siahcheshm et al., 2014), are considered immobile elements during hydrothermal alteration processes. These trace elements have relatively high field strengths with restricted dissolution degrees in water (Little

and Aeolus, 2006). In this study, taking into account Al as a less-mobile element during the argillization of the andesitic rocks, the degree of mobility of REE was calculated by the following equation of Nesbitt (1979):

$$\text{Change} = [(X/Al)_{\text{argillic sample}} / (X/Al)_{\text{andesite}}] - 1 \times 100\%$$

where X is the concentration of the selected element.

Accordingly, negative and positive values indicate a loss and gain in the mass of REE during argillization of the andesite rocks respectively. The resultant results are given in Table 2 and shown in Figure 6. Among the lanthanides, only Ce shows a mass loss, and the rest of the lanthanides show both depletion and enrichment during the formation and evolution of the argillic alteration zone.

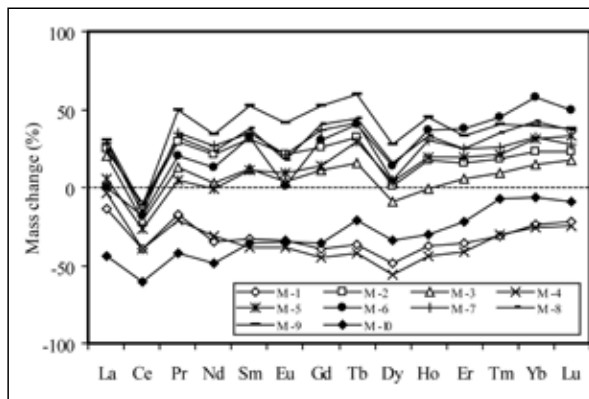


Figure 6. Mass changes of REE for the argillic alteration samples of the northeast of the Kharvana area.

Generally, low and high pH of the environment causes the leaching and precipitation of REE in alteration systems respectively (Patino et al., 2003). Based on mass changes of REE for the argillic alteration samples in Figure 6, except for Ce, which is depleted in all the samples, the behavior of lanthanides depends on the change of pH of solutions during argillization processes. Mass changes of REE show that REE in the argillic alteration samples developed near faults are leached, due to the low pH of alteration fluids. They are subsequently concentrated and enriched far away from faults, due to the decrease of temperature and high pH of alteration fluids.

Several minerals, such as kaolinite, Fe and Mn oxides and hydroxides, and secondary phosphates, are introduced as the main hosts of REE in alteration products (Höhn et al., 2014). Among the lanthanides, there are strong positive correlations among HREE ($r = 0.94-0.99$) compared to LREE ($r = 0.63-0.99$). The positive correlation between Al_2O_3 and REE ($r = 0.93$) (Figure 7a) probably represents the remarkable role of clays, especially kaolinite, in the distribution of REE. In addition, moderate positive correlations between REE and Fe_2O_3 ($r = 0.73$) (Figure 7b), TiO_2 ($r = 0.69$) (Figure 7c), and K_2O ($r = 0.71$) (Figure 7d) indicate that hematite and goethite, along with rutile, muscovite-illite, and jarosite possibly are other minerals controlling the distribution of lanthanides in the Kharvana alteration system. In the end, it can be concluded that factors, such as adsorption, scavenging, and isomorphic substitution, have important roles in the distribution and fractionation of REE in the Kharvana argillic alteration zone.

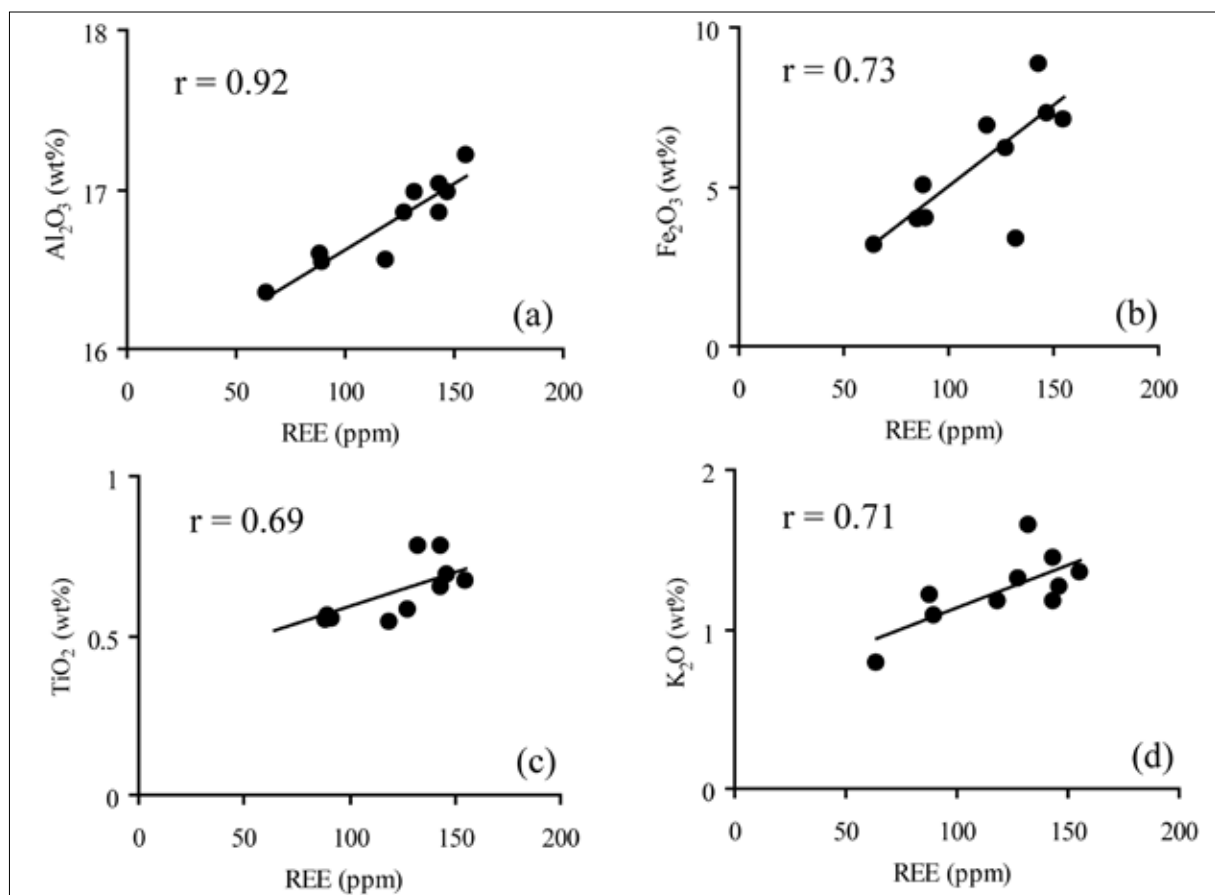


Figure 7. Bivariate diagrams of (a) Al_2O_3 -REE, (b) Fe_2O_3 -REE, (c) TiO_2 -REE, and (d) K_2O -REE for the studied samples from the argillic alteration zone.

Chondrite-normalized REE spider diagrams in Figure 8 indicate fractionation and weak enrichment of LREE relative to HREE during the development of the argillic alteration zone. REE patterns for the andesitic rocks are almost similar to the argillic alteration samples, except for Ce anomaly that shows a significant negative anomaly in most of the argillic alteration samples. The ratios of $(\Sigma\text{LREE}/\Sigma\text{HREE})_N$ and $(\text{La}/\text{Yb})_N$ in the argillic alteration samples are within the range of 2.44–4.74 and 5.43–11.70 respectively. These ratios in the andesitic samples are from 3.53 to 3.99 for $(\Sigma\text{LREE}/\Sigma\text{HREE})_N$ and 8.62 to 9.34 for $(\text{La}/\text{Yb})_N$. These ratios show both an increase and decrease in content for the argillic alteration samples compared to the andesitic rocks, representing fractionation of LREE from HREE during the development of the argillic alteration zone in the study area. It is thought that fractionation of LREE from HREE during alteration processes depends on environmental pH. As a whole, LREE and HREE tend to be mobilized during acidic and alkalic pH respectively (Patino et al., 2003). The $(\Sigma\text{LREE}/\Sigma\text{HREE})_N$ and $(\text{La}/\text{Yb})_N$ decreasing trend in the argillic alteration samples at the contact of faults can be attributed to the low pH of hydrothermal fluids, as stated previously by Patino et al. (2003). The $(\Sigma\text{LREE}/\Sigma\text{HREE})_N$ and $(\text{La}/\text{Yb})_N$ increasing trend in the argillic alteration samples occurs far away from faults, due to the high pH of hydrothermal fluids. As a result, it seems that decreasing temperature and increasing pH of hydrothermal fluids, along with the destabilization of lanthanide complexes played important roles in an increase of $(\Sigma\text{LREE}/\Sigma\text{HREE})_N$ and $(\text{La}/\text{Yb})_N$ ratios in the Kharvana argillic alteration zone. In the end, it can be deduced that changes in the chemistry of solutions responsible for the alteration, such as a change in Eh and pH, and the difference in the degree of destabilization of lanthanide complexes are efficient parameters in REE distribution patterns during the development of the Kharvana argillic system.

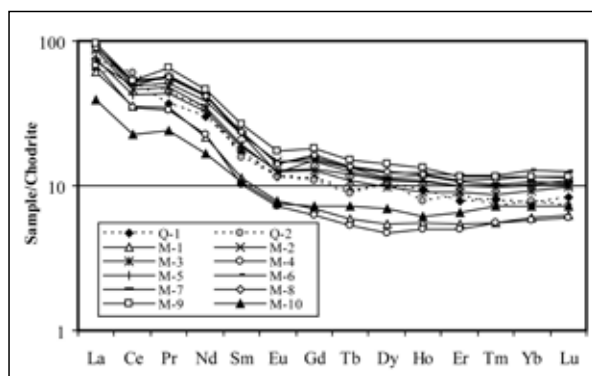


Figure 8. Chondrite-normalized REE spider patterns for the least-altered andesitic and argillic alteration samples.

The Eu and Ce anomalies in the argillic alteration samples are within the range of 0.59–0.86 and 0.63–0.78 respectively. These ratios in the andesitic samples are from 0.83 to 0.88 for Eu/Eu^* and 1.02 to 1.03 for Ce/Ce^* . The comparison of Eu and Ce anomalies between the argillic alteration samples and the least-altered andesitic samples from the northeast of the Kharvana area reveals that the argillization process of the andesites is accompanied by Eu and Ce negative anomalies. Negative Eu anomaly is attributed to the decomposition of plagioclase and hornblende of the andesitic rock at relatively

high temperatures (e.g. Erkoyun and Kadir, 2011; Kadir et al., 2014), and negative Ce anomaly is indicative of a decrease in oxygen fugacity during the generation of argillic alteration zone in the Kharvana area (Burnham and Berry, 2014; Mondillo et al., 2016).

5. Conclusions

The most important conclusions of this study are as follows:

- 1- The presence of pyrophyllite, alunite, jarosite, and rutile minerals shows that the Cretaceous volcanic rocks have undergone advanced argillic alteration, and the activity of sulfate ion in solutions responsible for alteration was high.
- 2- Changes in pH and Eh of solutions responsible for alteration, along with the difference in the degree of destabilization of lanthanide complexes, adsorption, scavenging, and isomorphic substitution are the main factors controlling the distribution of REE in the argillic alteration system.
- 3- Accessory mineral phases, such as muscovite–illite, jarosite, hematite, goethite, and rutile, along with kaolinite played an important role in the distribution of lanthanides.
- 4- Negative Eu anomalies in the argillic samples are attributed to the decomposition of plagioclase and hornblende of the andesitic rocks by hydrothermal fluids.
- 5- Negative Ce anomalies in the argillic samples are indicative of a decrease in oxygen fugacity during alteration of the andesites.

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Preliminary Assessment of Trace Metals in Sediments of the Ebonyi River, Abakaliki Metallogenic Province, Nigeria

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Abstract

Ebonyi River, Nigeria, acts as a sink for the trace metal-laden wastewater discharged from the mining zone into the river. This study evaluated the enrichment characteristics and ecological risks of trace metals in the fluvial sediments of the Ebonyi River. Fifteen sediment samples were collected: five samples were collected at the upstream (US) and midstream (MS), and four samples were collected from the downstream (DS). The MS coincides with the mining zone. A control sample was collected from a lake that was not connected to the river. Different pollution indices, including the geoaccumulation index (Igeo), enrichment factor (EF), and pollution load index (PLI), were used to assess the degree of contamination of these trace metals in the sediments. The associated ecological risk was assessed using the potential ecological hazard index (EI). The results showed that the average values of the concentrations of the trace metals varied spatially (US, MS, and DS). The Igeo results revealed that the sediment samples were practically unpolluted by Cu, Ni, V, and Ba (Igeo < 0) across the three zones but were strongly polluted by Pb and Zn in the midstream. The calculated EI showed the upstream and downstream samples have low ecological risks, while the midstream samples have ecological risks that range from low to considerable.

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Keywords: Contamination, Geochemical pollution indices, Pb-Zn mining, Sediments, Nigeria.

1. Introduction

River sediment contamination by trace metals usually poses a serious threat to ecological and human health because of its persistence and accumulation in the food chain. Trace metal contamination of sediment is a great global concern because of its wide range of sources, high toxicological effects, non-biodegradable properties, mobility, and accumulative behaviors. Trace metals in sediment come from lithogenic and anthropogenic sources. Anthropogenic contributions from industrialization, mining, and agricultural activities produce large amounts of trace metals. Mining of lead (Pb) and zinc (Zn) ores in the Enyigba metallogenic provinces, Nigeria, dates back to 1925 but was halted during the Nigerian Civil War of 1966–1970 (Obiora et al., 2016). However, local mining continued intermittently after the civil war until about 2009, when massive mining activities resumed fully in the area (Omonona et al., 2022). Galena (PbS), Sphalerite (ZnS), and Chalcopyrite (CuFeS₂) are the major ore minerals that are exploited in the area. Acid mine drainage and untreated ore mineral processing wastewater are usually discharged into the nearby streams that follow the Ebonyi River. The Ebonyi River is the only perennial river in the area, and it serves as a source of irrigation water for dry-season farming when food crops are grown. Contamination of river sediments by trace metals from mining activities can have lethal effects on the ecosystem and the environment in general. Potential toxic trace metals (PTMs) associated with the mining of galena, sphalerite, and chalcopyrite include Pb, Zn, As, Cd, Cu, Mn, Sb, Bi, and Se. The accumulation of PTMs in river sediment, when absorbed above stipulated

guideline concentration values by plants and animals, can decimate an extensive population of species.

2. Materials and Methods

2.1. Physiography and Geology of the Study Area

The area of the present study is located in the Upper Cross River basin, bounded by 6° 0' and 6° 40' N, 8° 0' and 8° 20' E (Figure 1). The River Ebonyi takes its origin from the Benue hills and flows through the Ebonyi lowlands into the Cross River in the southeast coastal region. The study area belongs to the Guinea Savannah Belt, which is characterized by two seasons: the wet season, which lasts from April to October, and the dry season, which spans from November to March. A vast portion of the northern section of the study area is cultivated for growing rice because of the swampy nature of the soil. Several government-owned rice farms are located in this region. At the beginning of each year's farming season, herbicides are usually employed to clear the grasses, and pesticides are used for pest control. Agricultural activities dominate the human anthropogenic activities of the northern portion of the area, while the major human anthropogenic activities of the central area are mining activities. Geomorphological features in the area include the Abakaliki anticlinorium, lush plain lands, and a few scattered hills. Geologically, the area is underlain by the shale rock of the Albian Abakaliki formation and the siltstone of the Eze-Aku formation. The shale is impervious, and this encourages surface runoff after precipitation. Several Pb and Zn ore mining companies are located within the study area; however, they are all concentrated around the lower reaches of the Ebonyi River.

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2.2 Sample Collection and Laboratory Analysis

A total of fifteen sediments were collected across the entire length of the Ebonyi River (Figure 1) using the Grab Burrow device and preserved in distilled water and nitric acid-pre-washed polythene bags. The sediment samples were then sent in cool boxes to the Bureau Veritas Laboratory, Canada, for heating, digestion, and analysis processes. Using repeated dilutions, mono-element standard solutions were used to produce a set of composite calibration standard solutions for all metals. All multi-element standards were created in matrix solutions, which comprised alkaline fusion and microwave digestion solutions. Diluting a 100 mg L1 multi-element commercial standard with the suitable matrix solution yielded a 1 mg L1 multi-element quality control standard. A linear calibration was created using up to seven multi-element standards. The first reference material was an external reference material, OxC109, provided by Rock Labs,

Auckland, New Zealand, and the second reference material was an internal reference material, DS 10, provided by Bureau Veritas Commodities, Canada, which was used to verify the repeatability and accuracy of the entire analytical procedure. Inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 8000; Perkin Elmer) was used to analyze the samples. Soil and sediment samples were oven-dried to a constant weight at 60 °C, and fractions larger than 2 mm were collected using nylon sieves. The 2 mm fraction was then pulverized and sieved to ensure a particle size of no more than 100 m; this was done to reduce variability caused by grain size composition. Finally, samples were kept in the refrigerator at 4 °C until they were analyzed. To determine heavy metal contents, sediment samples were digested using microwave-assisted aqua regia digestion (AD). This was chosen so that the microwave apparatus could be utilized with the least quantity of acids.

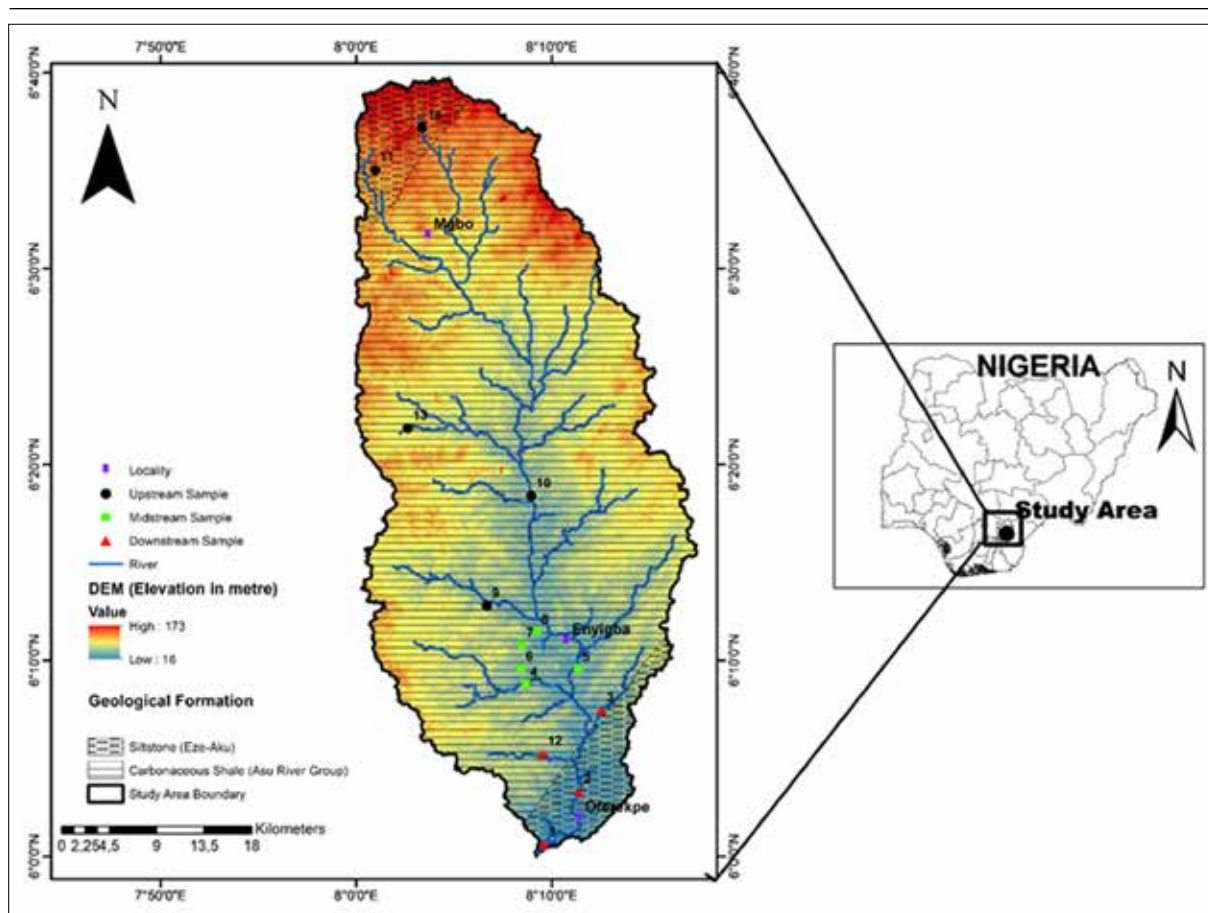


Figure 1. Geological map of the study area with the drainage and topographical (relief) elements.

2.3 Pollution Evaluation Methods

The evaluation of pollution was carried out using the geoaccumulation index (Igeo), enrichment factor (EF), pollution load index (PLI), and potential ecological risk index (RI). In this study, the upper continental crust concentration of trace metals as given by Taylor and McLennan (1985, 1995) was used as the trace metal background concentration for the estimation of the various pollution indices. Al and Fe were used as the reference metals and hence were excluded from the calculation of the pollution indices. In addition, Mn was not used in the estimation of the pollution indices because there was no background concentration set for Mn in

the trace metal background concentration estimates provided by Taylor and McLennan (1998, 1995). For the estimation of RI, only Pb, Cd, Ni, As, Zn, Cr, and Cu were used in the calculation because they were the only trace metals with a toxicity response factor.

The Igeo is a single metal method that gives the degree of metal accumulation above background concentration values; enrichment factor (EF) is often used to evaluate anthropogenic contributions of trace metals to soil and sediments. Pollution load index (PLI) is a multiple element pollution index that provides a cumulative pollution status

resulting from the synergistic effects of different elements on the environment. Finally, potential ecological risk index (RI), a multi-metal index that gives the synergistic ecological risks associated with trace metals pollutions are used. Igeo, EF, PLI and RI were determined using the mathematical equations expressed in equations 1, 2, 3, and 4 respectively (Müller, 1969):

$$I_{geo} = \log_2\left(\frac{C}{1.5Bn}\right) \quad (1)$$

where C is the measured concentration of each trace metal, and Bn is the geochemical background concentration value of each trace metal. (Loska et al., 2003):

$$EF = \frac{\left(\frac{C_i}{C_{ref}}\right)_{sample}}{\left(\frac{S_i}{S_{ref}}\right)_{background}} \quad (2)$$

where C_i is the concentration of the measured trace metal, C_{ref} is the concentration of the reference trace metal used for the normalization process, S_i and S_{ref} are the background concentration value of the measured metal and the background concentration value of the reference metal respectively. EF classification is given as: lithogenic or geogenic origin ($EF < 1.5$) and anthropogenic origin (EF) (Adeyemi et al., 2019). Al was used as the reference element because it best fits the required criteria for a reference metal. Every metal that has low variation in occurrence and is in trace concentration in the environment is suitable to be used as a reference metal.

$$PLI = [Cf_1 \times Cf_2 \times Cf_3 \times \dots \times Cf_n]^{1/n} \quad (3)$$

where Cf_1 represents the contamination factor $\left(\frac{C_i}{S_i}\right)$ of each individual trace metal and n indicates the number of trace metal used in the process (Tomlinson et al., 1980).

When PLI value is less than one, the sediment pollution is at baseline and when PLI is greater than one, it indicates sediment pollution from anthropogenic and lithogenic sources (Hakanson, 1980):

$$RI = \sum_{i=1}^n E_f^i \quad (4)$$

$$\text{where } E_f^i = C_f^i \times T_f^i$$

where E_f^i represents the potential ecological risk factor of each trace metal, C_f^i is the contamination factor for each trace metal, T_f^i indicates the toxicity response coefficient of each trace metal (Pb=5, Cd=30, Ni=5, As=10, Zn =1, Cr=2, Cu=5) (Tian et al., 2020). The degree of ecological risk of sediment pollution is given as: low ecological risk ($ERI < 110$); moderate risk (110 < $ERI < 200$); considerable risk (200 < $ERI < 400$); severe risk ($ERI > 400$) (Tian et al., 2020).

3. Results and Discussion

3.1 Trace Metal Concentrations Characteristics

The results of the laboratory analysis are presented in Table 1 as summary statistics. It was found that the average concentrations of As, Co, Fe, Al, and Mn are highest upstream (Mgbo). The mean concentrations of Cd, Ba, Sr, Al, Cu, Pb, and Zn are highest at the midstream (Enyigba), and the average concentrations of Cr, Ni, and V are highest at the downstream (Oferekpe); see Table 1. The concentrations of Bi and Sb in all the sediment samples analyzed were below the instrument detection limit of 3.0mg/kg (Table 1). The results

(Table 1) also revealed that the average concentrations of Sr, Cr, Ni, Co, Mn, Pb, and Zn in sediment from the upstream zone are higher than the concentrations in the control sample. For the midstream zone, the average concentrations of Ba, Sr, Mn, Cu, Pb, and Zn are higher than the concentrations of the control sample, and for the downstream zone, the mean concentrations of Sr, Cr, Ni, V, and Zn are higher than the concentrations of the control sample, indicating some degree of contamination. It was also observed that there is a wide range of Pb and Zn concentrations in the midstream area. The wide range can be attributed to the size and number of mining pits within a given cluster and thereby the amount of wastewater discharged. Stream flow rate could have contributed to this observed range value of Pb and Zn; a fast-moving stream could lower the number of adsorbed metals. The two localities with very high Pb and Zn concentrations are located close to the mining area, where wastewater is discharged into slow-moving streams.

The sources of As, Co, and Mn concentrations in the sediment of the area may be attributed to agricultural activities, mainly the application of chemical fertilizers and the use of pesticides and herbicides. Mechanized agriculture is predominant in the upstream section, where crops such as rice, cassava, and vegetables are grown. The high concentrations of Pb and Zn around the Midstream area could be attributed to the mining of galena and sphalerite around the zone.

3.2 Trace Metal Pollution Characterization

The results of the geoaccumulation indices of Cd, Sr, V, Cr, Ba, Cu, Pb, Zn, Ni, Co, and As are presented in Figure 2. From Figure 2, it was observed that at the upstream area, the Igeo values of Sr, V, Cr, Ba, Cu, and Ni are below zero, indicating that there is practically no pollution of the sediment by these six trace metals. At the same upstream area, Cd, Pb, Zn, Co, and As have Igeo values that range from -1.0 to 4.7. Based on the classification scheme (Table 2), the pollution by these five metals varied between “unpolluted” and “strongly to extremely polluted.” The Igeo values lower than zero indicate “unpolluted.” For these four trace metals, Cd, Ba, Cu, and As, their Igeo values range from 0.2 to 7.8 (Figure 2). The pollution status of these four trace metals falls within the “moderately polluted” to extremely polluted” class (Table 2).

Finally, in the downstream area, a different scenario was observed. Only three metals, namely Sr, V, and Ba, have Igeo values less than zero, indicating there is no pollution by these three trace metals. The Igeo values of Cd, Cr, Cu, Pb, Zn, Ni, Co, and As, on the other hand, varied between -1.2 (“unpolluted”) and 1.2 (“moderately polluted”). Figure 2 revealed that only Cd, Pb, Zn, Co, and As of the all trace metals used for the estimation of Igeo have values greater than zero at the three zones (upstream, midstream, and downstream), thus, indicating that these trace metals have concentrations above the natural background concentrations in the entire study area. The Igeo values for Pb and Zn at the upstream and midstream are higher than one but lower than one at the downstream (Figure 2). This result indicates that only the upstream and midstream sediments are strongly

contaminated by these metals. The highest Igeo values for Pb (5.1) and Zn (2.7) are found in the midstream sediments, indicating extreme and moderate contamination by these two metals, thus, reflecting the impact of mining activities in the zone. The Igeo value of Cd downstream is lower than one, indicating no contamination by the trace metal, but greater than 4.0 for the upstream and midstream sediments, which indicate strong contamination by Cd.

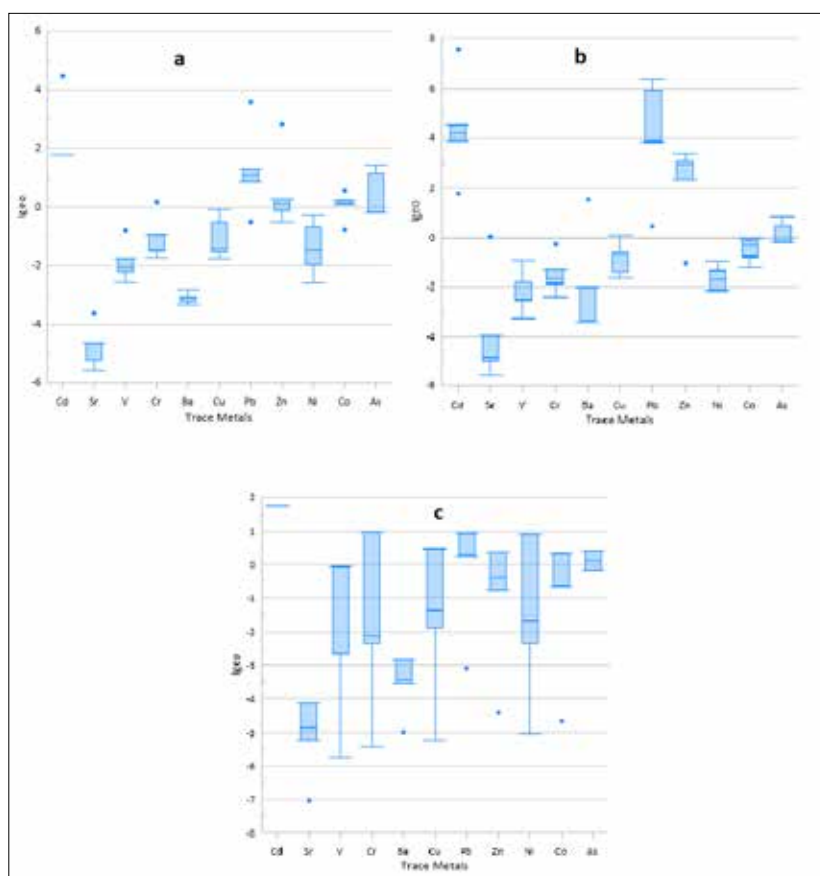
Table 1. Univariate statistics of the trace metals concentrations.

	Cd (mg/kg)	Sr (mg/kg)	V (mg/kg)	Cr (mg/kg)	Ba (mg/kg)	Al (%)	Fe (%)	Cu (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Co (mg/kg)	Mn (mg/kg)	As (mg/kg)	Bi (mg/kg)	Sb (mg/kg)
IDL UPS (n=5)	0.5	2.0	1.0	1.0	1.0	0.01	0.01	1.0	3.0	1.0	1.0	1.0	2.0	2.0	3.0	3.0
Min	0.5	11	27	38	83	0.9	4.5	11	18	75	11	15	945	2	bdl	bdl
Max	3.3	43	93	144	118	2.9	14.5	36	308	757	55	38	1795	6	bdl	bdl
Mean	1.1	22	47.8	67.8	97.2	1.8	7	20	97.6	235	29.6	27.6	1404	3.4	bdl	bdl
Median	0.5	21	38	46	96	1.8	5.5	14	53	117	24	28	1527	2	bdl	bdl
SD		11.2	23.5	39.2	11.9	0.7	3.8	9.6	106.2	261.3	16.1	7.3	313	1.7	bdl	bdl
MDS (n=5)															bdl	bdl
Min	0.5	11	17	24	78	0.8	2.6	12	34	52	15	11	346	2	bdl	bdl
Max	27.6	543	85	107	2380	2.3	14.1	40	2197	1114	34	25	1378	4	bdl	bdl
Mean	7.2	124	40.4	51.2	565	1.6	6.6	22.8	904	689	22	19.2	951	2.6	bdl	bdl
Median	2.7	18	28	40	82	1.5	4.9	23	370	822	20	21	1080	2	bdl	bdl
SD	10.21	209	24.0	29.2	908	0.4	4.1	9.9	831.6	366	7.2	5.3	352	0.8	bdl	bdl
DNS (n=4)															bdl	bdl
Min	0.5	4	3	3	26	0.1	0.2	1	3	5	2	1	28	2	bdl	bdl
Max	0.5	30	154	252	117	4.0	14.4	52	49	138	124	32	908	3	bdl	bdl
Mean	0.5	18	52	78.5	73.7	1.8	5.9	21	28.7	78	43	16.5	603	2.5	bdl	bdl
Median	0.5	19	25.5	29.5	76	1.5	4.6	15.5	31.5	84.5	23	16.5	738	2.5	bdl	bdl
SD	0	9.8	59.6	100.8	32.4	1.4	5.2	19.2	16.5	50.1	48.1	10.9	339	0.5	bdl	bdl
Control (n=1)	0.5	7	47	66	175	1.3	8.1	20	41	63	27	26	829	4	bdl	bdl

IDL: instrument detection limit; bdl: below detection limit; UPS: Upstream; MDS: Midstream; DNS: Downstream; Min: Minimum; Max: Maximum; SD: Standard deviation; trace metal concentrations above control values are written in bold.

Table 2. Range of values for soil classification using pollution indices.

Index value	Class	References
Geoaccumulation index		
$I_{geo} < 0$	Unpolluted	Men et al., 2018
$0 < I_{geo} < 1$	Unpolluted to moderately polluted	Khademi et al., 2019
$1 < I_{geo} < 2$	Moderately polluted	Monged et al., 2020
$2 < I_{geo} < 3$	Moderately to strongly polluted	Adimalla et al., 2020
$3 < I_{geo} < 4$	Strongly polluted	Egbueri et al., 2020
$4 < I_{geo} < 5$	Strongly to extremely polluted	Egbueri et al., 2020
$I_{geo} > 5$	Extremely polluted	Egbueri et al., 2020
Enrichment factor		
$EF < 2$	Deficiency to minimal enrichment	Relic et al., 2019
$2 < EF < 5$	Moderate enrichment	Jiang et al., 2020
$5 < EF < 20$	Significant enrichment	Monged et al., 2020
$20 < EF < 40$	Very high enrichment	Adimalla et al., 2020
$EF > 40$	Extremely high enrichment	Radomirovic et al., 2020
Pollution load index		
$PLI < 1$	Unpolluted	Relic et al., 2019
$1 < PLI < 2$	Moderately polluted	Jiang et al., 2020
$2 < PLI < 10$	Strongly polluted	Egbueri et al., 2020
$PLI > 10$	Extremely polluted	Monged et al., 2020
Risk index		
$RI < 150$	Low ecological risk	Men et al., 2018
$150 < RI < 300$	Moderate ecological risk	Gan et al., 2019
$300 < RI < 600$	Significant ecological risk	Hakanson, 1980
$600 < RI < 5000$	Very high ecological risk	Men et al., 2018
$RI > 5000$	Extremely high ecological risk	

**Figure 2.** Geoaccumulation index across the three zones (a-upstream; b-midstream; c-downstream).

The mean values of EF for the different trace metals are presented in Table 3. From the table, it was revealed that only Cd, Pb, Zn, and As have EF values greater than 1.5. Trace metals with EF values greater than 1.5 indicate the effect of human influences on their sources (anthropogenic contributions), while trace metals with EF values lower than 1.5 indicate geogenic sources (Hu et al., 2013; Islam et al., 2020; Ezewudo et al., 2021). The order of sediment enrichment by trace metals across the zones is midstream>downstream>upstream (Table 3). Most of the trace metals are thought to be released mainly by mining activities at midstream and transported downstream. The results of the pollution load index (Figure 3) revealed that the PLI ranged from 0.09 to 2.08. Figure 3 shows that the least measured PLIs are around the Mgbo area in the north and close to the Oferekpe area in the south. PLI is highest around the mining zone in the Enyigba area. Normally, areas around the downstream (Oferekpe) in the south should

exhibit the highest degree of pollution, but in this case, it is not so. The low PLI occurrence in the downstream zone may be attributed to the very rich clay materials that underlie the entire region. The Abakaliki formation, which underlies a very large percentage of the study area (Figure 1), is very rich in shale, a porous but impermeable rock that has a high adsorption capacity, thereby reducing the amounts of trace metals transported from the source to the sink. Another factor is the size of the Cross River downstream, into which all the other streams drain or empty their water. The volume of water and the size of the Cross River are incomparable to the tributaries that supply the water to the main Cross River. For the midstream zone, the high PLI of the area is largely contributed by Pb and Zn contaminants that result from the galena and sphalerite ore mining in the zone, and for the upstream zone, the sediment contamination is thought to emanate mainly from Cd and As concentrations resulting from agricultural activities.

Table 3. Results of enrichment factor (EF).

Sample ID	Cd	Sr	V	Cr	Ba	Cu	Pb	Zn	Ni	Co	As
UPS											
9	2.6	0.03	0.2	0.2	0.09	0.2	1.6	0.5	0.2	0.9	0.6
10	13.6	0.02	0.1	0.1	0.06	0.5	7.3	4.3	0.3	0.6	0.5
11	4.2	0.03	0.2	0.4	0.12	0.3	2.2	1.1	0.3	1.3	1.1
13	1.7	0.04	0.2	0.5	0.07	0.3	1.2	0.5	0.4	0.7	1.3
14	5.2	0.03	0.5	0.8	0.18	0.5	1.0	1.8	0.2	0.9	3.4
MDS											
4	201	0.06	0.2	0.2	0.10	0.6	14.8	11.2	0.3	0.8	0.9
5	3.1	0.03	0.3	0.3	0.09	0.2	1.2	0.4	0.2	0.9	1.2
6	17.3	0.02	0.4	0.6	0.18	0.8	46.1	3.8	0.2	0.7	1.3
7	11.5	0.6	0.1	0.1	1.82	0.2	9.1	5.3	0.3	0.3	0.5
8	23.8	0.03	0.2	0.3	0.16	1.1	143	12.8	0.3	0.7	1.4
DNS											
1	26.3	0.05	0.1	0.1	0.24	0.2	0.9	0.3	0.2	0.3	6.8
2	4.5	0.03	0.2	0.2	0.13	0.3	1.7	0.7	0.3	0.8	1.1
3	2.5	0.04	0.1	0.2	0.10	0.4	0.8	0.7	0.3	0.5	1.0
12	1.2	0.01	0.3	0.7	0.03	0.5	0.7	0.4	0.6	0.4	0.4
CONTROL	3.7	0.01	0.3	0.5	0.23	0.6	1.7	0.6	0.4	1.1	1.9

* EF values greater than 1.5 are written in bold; UPS-upstream; MDS-midstream; DNS-downstream

Potential ecological risk indices (ERI) of the study area ranged from 167 to 8589, with a mean value of 1094. The RI classification showed that all the sediments in the study area show moderate to very high ecological risk (Table 2). The highest ecological risk at the present time was found around the Enyigba area (midstream), where mining activities are ongoing (Figure 4). The mean contribution of each of the trace metals to the overall RI follows the following order:

Cd (86.98%)>Pb (9.79%)>As (1.89%)>Zn (0.45%)>Cu (0.41%)>Ni (0.33%)>Cr (0.15%). This study reveals that Cd is the trace metal that poses the highest ecological risk out of the trace metals examined. Similar results have been reported for studies carried out in Nigeria (Egbueri et al., 2020; Attah et al., 2022) and other parts of the world (Khudhur et al., 2018; Gan et al., 2019; Yaseen and Al-Hawari 2019; Radmanovic et al., 2020; Tarawneh et al., 2021).

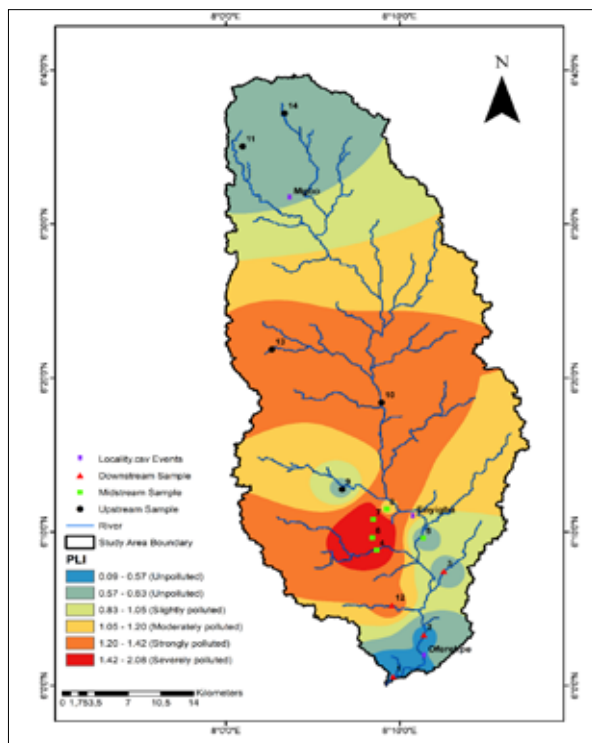


Figure 3. A map of pollution load index (PLI) depicting the spatial variation across the study area.

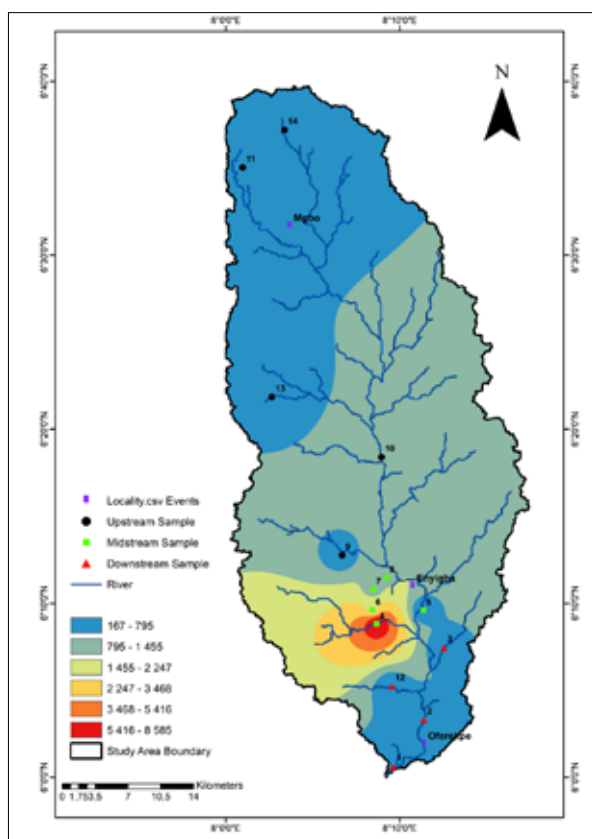


Figure 4. Spatial distribution map of ecological risk index (ERI) for the study area.

3.3 Comparison of the Pollution Indices

The pollution indices used in this study can be grouped into two categories: pollution indices (Igeo and EF) that deal with the individual trace metal accumulation in the earth material (sediment) and enrichment in the environment and pollution indices that deal with the pollution status of the individual sediment samples. Table 4 shows the percentage of pollution classes for the individual trace metals. The table shows that both Igeo and EF distinctively classify the trace metals into different degrees of accumulation and enrichment. It is revealed in Table 4 that there is no conflicting or antagonizing description between the two indices. For example, 7% of Cd classified as “extremely polluted” were also classified as “extremely high ecological risk” by Igeo and EF, respectively. Likewise, Pb has been classified as “extremely polluted” and “extremely high ecological risk” by Igeo and EF, respectively. In addition, all the V concentrations are classified as unpolluted and 100% as “deficiency to minimal enrichment” by Igeo and EF, respectively.

PLI and RI were also perfectly related. All the samples described by PLI as unpolluted are also described by RI as having low to moderate ecological risks. Samples described as moderately polluted by PLI are described as having a moderately high ecological risk. As shown in Table 5, 7% of the samples described as strongly polluted by Igeo were also described by RI as having an extreme ecological risk.

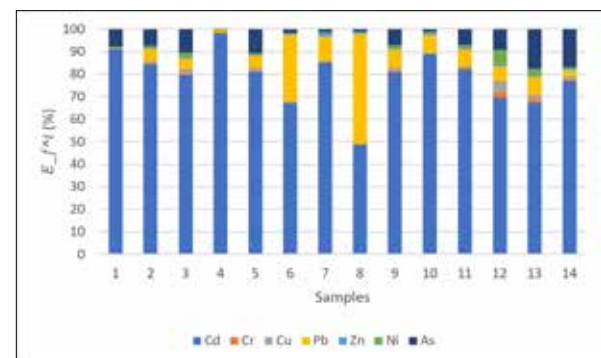


Figure 5. A graphical plot of values showing the contributions of individual trace metals to ecological risk indices.

Table 4. Pollution category distribution of individual trace metals expressed in percentages.

Class	Cd	Sr	V	Cr	Ba	Cu	Pb	Zn	Ni	Co	As
Igeo											
<0	0	93	100	86	93	86	14	36	93	64	57
0-1	0	7	0	14	7	14	37	29	7	36	29
1-2	65	0	0	0	0	0	14	0	0	0	14
2-3	0	0	0	0	0	0	0	21	0	0	0
3-4	7	0	0	0	0	0	21	14	0	0	0
4-5	21	0	0	0	0	0	0	0	0	0	0
>5	7	0	0	0	0	0	14	0	0	0	0
EF											
<2	14	100	100	100	100	100	58	65	100	100	86
2-5	36	0	0	0	0	0	7	14	0	0	7
5-20	29	0	0	0	0	0	21	21	0	0	7
20-40	14	0	0	0	0	0	0	0	0	0	0
>40	7	0	0	0	0	0	14	0	0	0	0

Table 5. Pollution category distribution of sediment samples expressed in percentages.

Class	Unpolluted	Moderately polluted	Strongly polluted
PLI	50	43	7
Class	Moderate ecological risk	Very high ecological risk	Extreme ecological risk
RI	64	29	7

4. Conclusion

The study is centered on the assessment of trace metals in river and stream sediments using pollution indices. The concentrations of the different trace metals examined in sediments around the Enyigba-Abakaliki area varied from one locality to another. The sediment trace metal enrichment factors were in the order of: Fe>Al>Mn>Pb>Zn>Ba>Cr>Sr>V>Ni>Cu>Co>Cd>As.

The results of the Igeo from the study area showed that the soil sample contamination level varied from unpolluted to extremely polluted, with soil samples from the midstream showing the highest trace metal contamination. From the results of the enrichment factor, it can be seen that Cd, Pb, Zn, and As, among the trace metals studied, have their sources mainly from anthropogenic activities. Trace metals that show the predominance of lithogenic sources over anthropogenic activities include Sr, Cu, Ni, Co, V, Cr, and Ba.

The pollution load index revealed that the soil samples are characterized by an unpolluted to severely polluted status. Severely polluted soil samples were those influenced by the effects of human activities. Risks to the environment arising from trace metal contamination evaluated through the ecological risk index showed that no soil sample fell below low ecological risk. The soil samples all varied from moderate ecological risk to extremely high ecological risk.

In general, this study has revealed that the soils around the mining sites have been seriously polluted by heavy metals. Over time, if nothing is done to ameliorate the effects of mine wastewater discharge into the nearby streams, the entire surface water drainage system, groundwater resources, and river sediments will be unfit for use by anyone. The findings of this work will be useful for land management boards and all environmental agencies.

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Demarcation of Groundwater Quality Using Drinking Water Quality Index (DWQI), Nitrate Pollution Index (NPI), and Irrigation Indices: A Case Study from Jerash Region

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Abstract

Groundwater storage represents the ultimate source of drinking water in dry regions. Over-pumping, climate change, and diverse types of pollutants have all contributed to the deterioration of this precious resource. In order to protect human health and efficiently manage resources, it is crucial to conduct groundwater quality assessments for agricultural and domestic uses, especially drinking. In this study, two indices, the DWQI and NPI, are utilized to assess the fitness of the groundwater quality for drinking and to assess the magnitude of contamination by nitrate in Jerash region. Moreover, the fitness of the groundwater for irrigational purposes was assessed using the most commonly used indices, such as Kelly's index (KI), magnesium hazard index (MHI), sodium adsorption ratio (SAR), electrical conductivity (EC), and the sodium percentage (%Na). Hierarchical cluster analysis (HCA) and conventional hydrochemical methods were applied to evaluate the groundwater chemistry. Results showed that the groundwater in the studied area is basically of a Ca-Mg-HCO₃ facies, hardvery hard water. Although 38% of the samples (dry season) and 35% of the samples (rainy season) possess NO₃⁻ concentration above the maximum permissible limit (50 mg/L), the vast majority of the samples (96%) showed good to excellent water quality based on DWQI, authenticating suitability for drinking. On the other hand, the results of the NPI indicated that about 30% of the samples in both seasons present significant to very significant levels of nitrate pollution with nitrate concentration surpassing 50 mg/L. In general, the NPI might be a better expression of water quality than the DWQI, which at low values, obscures or extremely masks important parameters such as nitrate, despite exceeding WHO guidelines. Thus, the DWQI should be used with high precaution, especially at low levels of the used hydrochemical parameters. Based on irrigational water quality indices, the groundwater in the studied area authenticates appropriateness for irrigation.

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Keywords: NPI, DWQI, Jordan, Nitrate Pollution, Groundwater

1. Introduction

Water is the "elixir of life" and the foundation of sustainable socioeconomic advancement (Cosgrove and Loucks 2015). In fact, the majority of freshwater is frozen, and the remainder is primarily stored in groundwater. Only 0.3% of freshwater is available for humans, animals, and plants' requirements (Hotloś, 2008). Groundwater represents the major supply of water for all purposes in dry regions due to limited surface water supplies (Gutiérrez et al., 2018). However, human interventions have degraded groundwater quality to levels that exacerbate water scarcity, especially in water-stressed countries (Elbeltagi et al., 2022). Therefore, protection and sustainable management of groundwater is essential (Liu et al., 2019). Evaluating natural factors/processes as well as human interventions governing groundwater quality is a cornerstone in any sustainable management program of groundwater (Wang et al., 2020). Assessment of groundwater pollution could aid in the identification of potentially harmful sources of pollutants and areas at risk of groundwater pollution for proper water

resources management (Ibrahim, 2019). Nitrate (NO₃⁻) is a big problem in many aquifers around the world, and it poses a big threat to groundwater resources, especially in areas where water is utilized for drinking and irrigation (Troudi et al., 2020; Soleimani et al., 2022). Hence, protecting water sources from NO₃⁻ contamination is vital, especially in water-stressed countries (Zhang et al., 2018; Yang et al., 2020). Numerous researches have shown that overexploitation and the usage of nitrogen fertilizers contaminate groundwater and cause human health problems (Qiu et al., 2023). High nitrate exposure can result in several health problems such as "blue baby syndrome" (primarily in infants less than 6 months), an increased risk of cancer, miscarriages, heart disease, and thyroid enlargement (Gangolli et al., 1994). Additionally, the quality of irrigational water affects soil conditions, and consequently, the growth of crops (Ayers and Westcot 1985). Typically, nitrate contamination is detected in groundwater due to its high solubility (Richa et al., 2022). Many studies have used different models and tools to assess groundwater fitness for irrigation and domestic purposes and its potential

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risk to human health (Adimalla and Wu 2019; Li et al., 2019; Adimalla et al., 2020). The drinking water quality index (DWQI) is a widely used tool to assess water quality and has recently been extensively used to demarcate water quality for domestic purposes (Xiao et al., 2021). The first water quality index was developed by Horton (1965), to convert the hydrochemical parameters into a single number describing the overall water quality. Horton's index classifies the overall water quality into the following categories: excellent, good, poor, very poor, and unsuitable, based on the hydrochemical parameters, and the WHO guidelines of drinking water quality (Rahman et al., 2022). The nitrate pollution index (NPI) was initially developed by Obeidat et al., (2012) to evaluate groundwater contamination by nitrate. The index is a single parameter index that incorporates the measured nitrate concentration in groundwater, and the threshold value of human origin (20 mg/L). It categorizes water quality into the following classification: clean (unpolluted), light pollution, moderate pollution, significant pollution, and very significant pollution (Obeidat et al., 2012). The index has been widely and successfully used to assess groundwater contamination by nitrate (Xiao et al., 2021; El Mountassir et al., 2022). Various criteria are utilized to assess the quality of irrigation water: electrical conductivity (EC), sodium adsorption ratio (SAR), sodium percentage (Na%), Kelley's index (KI), and magnesium hazard (MH) (Subramani et al., 2005). By analyzing similarities/differences between sampling sites, multivariate statistical techniques have been widely utilized to characterize water quality (de Andrade et al., 2008; Obeidat et al., 2013). It provides a dependable technique for water resources management and rapid responses to water pollution (Bodrud-Doza et al., 2016). Among these techniques, cluster and principal component analyses are the most prevalent ones.

Jordan is a country in the arid Middle East region with an area of about 89,210 km². Most of the country is an expanse of desert, where water resources are limited and scarce (Al-Kharabsheh, 2020). The current Jordanian share of freshwater is estimated at 90 m³/per capita/year, making it rank as the second most water-stressed country (Odeh, 2019). Jordan gets about 67% of its water from groundwater extraction, with 27% of that coming from nonrenewable groundwater (Salameh et al., 2014). The crisis is worsening over time because of the high population growth, associated with sudden refugee influxes, agricultural expansion, increasing drought events, climate change, and inefficient water use, placing extraordinary demands on water resources (Al-Kharabsheh, 2020). Within the Jordanian context, several studies have utilized the DWQI to assess the appropriateness of water quality for drinking and irrigation purposes (Ibrahim 2018; Obeidat and Awawdeh 2021; Hyarat et al., 2022). Several studies have shown that the studied area is vulnerable to contamination, particularly nitrate (Hammouri and El-Naqa, 2008). Accordingly, this study was initiated to map the groundwater quality in the studied area. Groundwater contamination by nitrate is a common problem and has gained great concern worldwide. This is attributed to its detrimental effects on human health and the environment. Additionally, the DWQI has been extensively used to assess

water quality fitness for drinking purposes because it helps understand water quality aspects by integrating complex data and producing a score that describes water quality status. Therefore, the present study was initiated with the following specific goals: (1) assessment of the groundwater quality for drinking using DWQI, (2) assessment of the groundwater contamination using the NPI, (3) assessment of the groundwater quality for irrigation, and (4) shedding light on the efficacy of the DWQI, especially at high levels of nitrate, and low levels of other hydrochemical parameters. The above-mentioned goals lie within the milestones of the Sixth Sustainable Development Goal of the United Nations.

2. Studied Area

The studied area is located in the northwestern highlands of the Amman-Zarqa basin (Figure 1a). It encompasses an area of approximately 188.3 km², and is located between the coordinates at 3568545 m - 3582908 m N and 750269 m - 777068m E (UTM system). It is just a few kilometers west of Jerash city, which is home to some of the best-preserved Roman ruins in the world. Jerash city is located 48 kilometers north of Amman, the capital of Jordan. The climate of the area under study is both arid and Mediterranean. Winter temperatures are a few degrees Celsius below zero, while summer temperatures average around 40 degrees Celsius (Al-Fugara et al., 2022). Average monthly temperature ranges from 7.9 °C in January to 25.7 °C in August. Minimum average temperature ranges from 3.6 °C to 19.3 °C, and maximum average temperature ranges from 12.7 °C in January to 33.1 °C in August. The area experiences a wide range of precipitation, which varies from 319 mm to 560 mm (Figure 1b). As shown in Figure 1c, the agricultural land occupies about (33.4%) of the study area, followed by urban (29.5%), bare (28%), and forestlands (9%).

Geologically, the sedimentary rocks of the Upper Cretaceous Ajloun (A) and Belqa (B) groups dominate the studied area. These rocks overlie the sandstones of Kurnub group of the Lower Cretaceous (Figure 2a). The lithological and geological characteristics were thoroughly discussed in several studies (Bender 1974; Al Mahamid 2005; Hammouri and El-Naqa 2008; Al Kuisi et al., 2014; Al-Fugara et al., 2022). The main lithological characteristics of the rock formations in the studied area are presented in Table 1. In the studied area, there are three aquifer complexes: The Kurnub sandstone aquifer, the Lower Ajloun aquifer (Na'ur and Hummar aquifers), and the Amman/Wadi As-Seir aquifer (Figure 2b). Kurnub aquifer is a potentially good aquifer in Jordan; however, in the studied area, it shows poor water quality and produces an uneconomical groundwater supply (Hammouri and El-Naqa 2007). Na'ur aquifer (A1/2) overlies the Kurnub, and it has a specific capacity in the range of 0.01-12 m³/hr. Transmissivity is in the range of 0.3-100 m²/d corresponding to a hydraulic conductivity of 0.0083 to 2.7 m/d (Salameh and Bannayan 1993). Hummar aquifer has a transmissivity of 32 to 300 m²/d, corresponding to a hydraulic conductivity of 8.1 *10⁻⁷ to 7.6 *10⁻⁴ m/d (Rimawi, 1985). The groundwater level contour maps of Na'ur and Hummar aquifers are presented in Figure 3. Groundwater flow in both aquifers is directed towards the southwest and southeast of the study area.

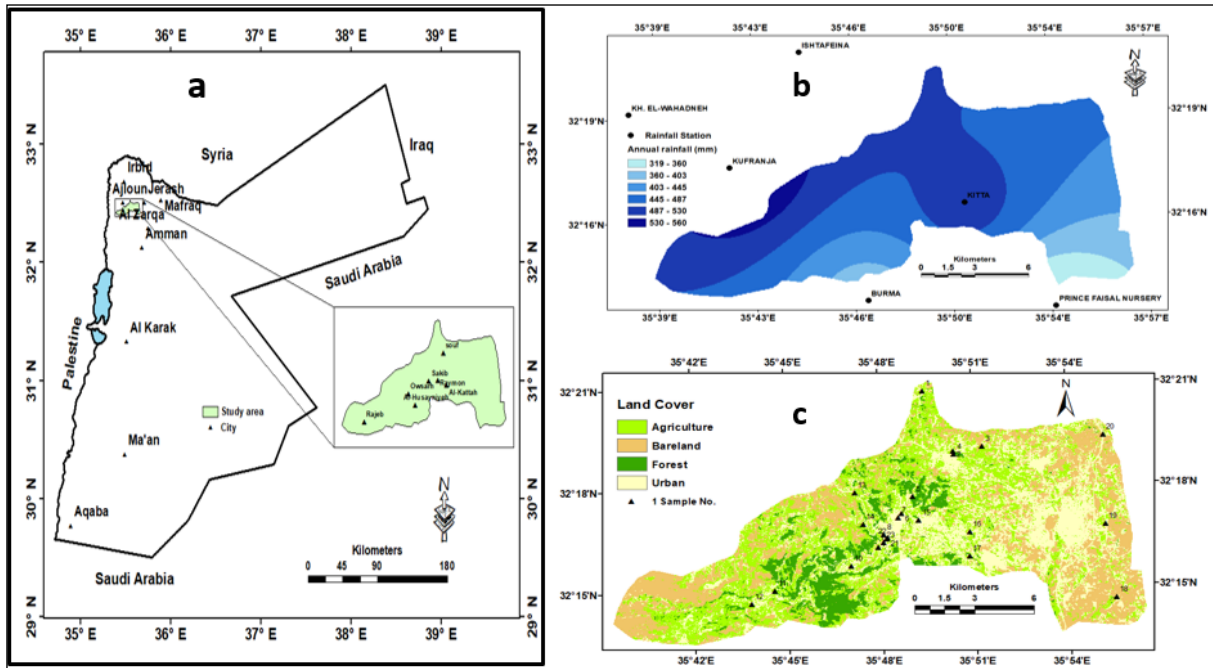


Figure 1. Location map of the studied area a), a rainfall map b), land use/land cover with sampled localities c).

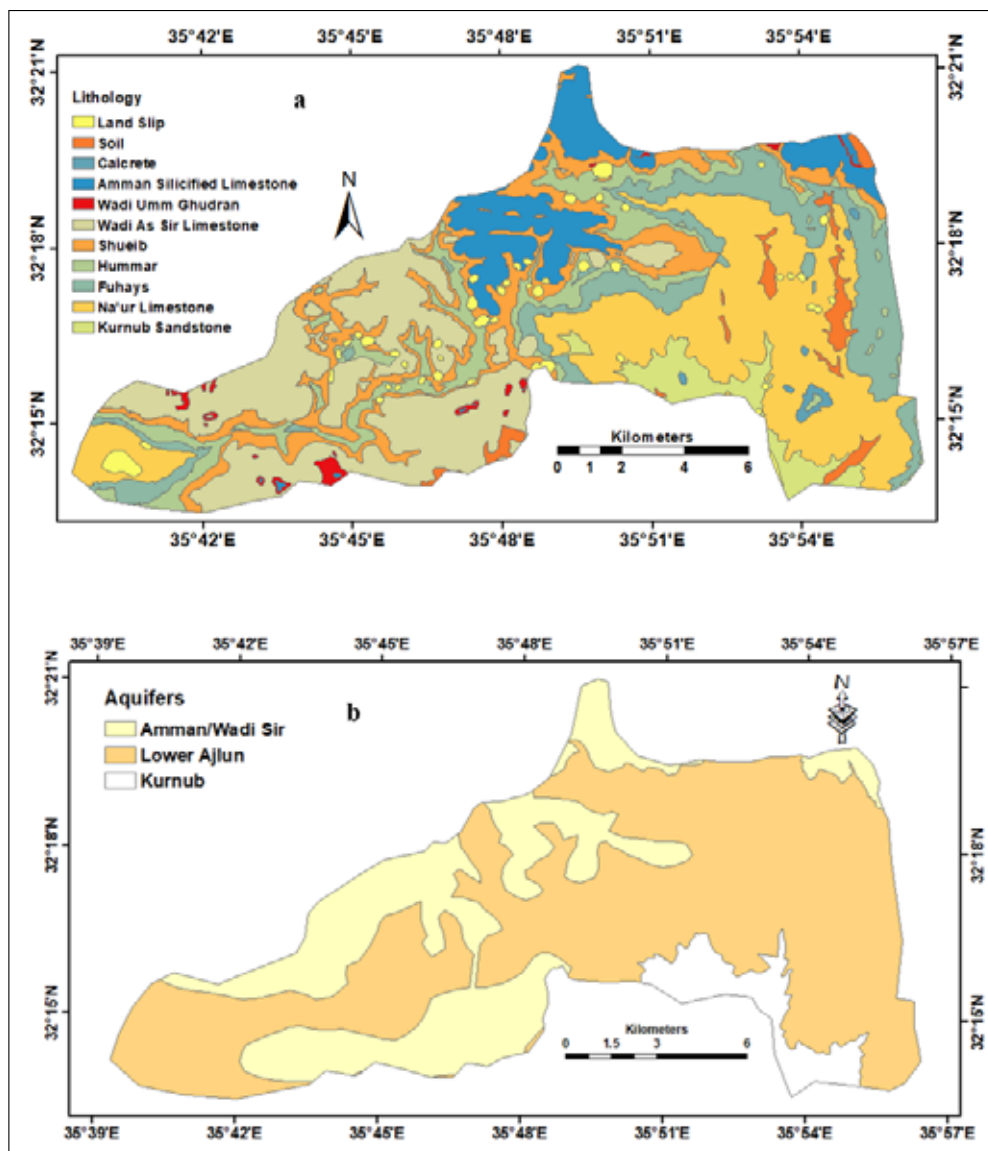
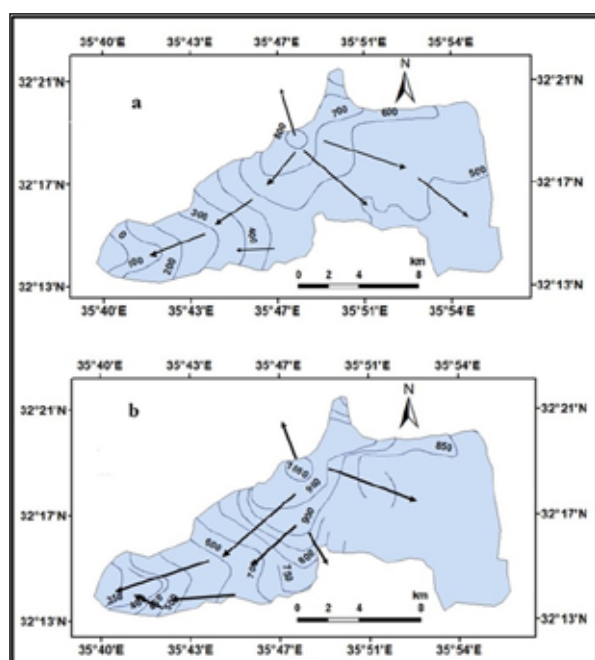


Figure 2. Geological map of the study area a), and hydrogeological units b).

Table 1. Geological and Hydrogeological Classification of the Rock Units in the Studied Area.

Age	Group	Formation name	Symbol	Lithology	Thickness (m)	Aquifer potentiality
Maestrichtain	Belqa	Muwaqqar	B3	Chalk, marl, chalky limestone	60-70	Poor
Campanian		Amman	B2	Chert and limestone with phosphate	80-120	Poor
Santonian		Ghudran	B1	Chalk, marl, marly limestone	15-20	Poor
Turonian	Ajloun	Wadi As Sir	A7	Hard limestone, dolomitic limestone, with some chert	90-110	Excellent
Cenomanian		Shueib	A5/6	Light gray limestone, inter-bedded with marl and marly limestone	75-100	Poor
Cenomanian		Hummar	A4	Hard, high density limestone, dolomitic limestone	40-60	Good
Cenomanian		Fuheis	A3	Gray, olive, soft marl, marly limestone	60-80	Poor
Cenomanian		Na'ur	A1/2	Limestone interbedded with marl and marly limestone	150-200	Good
Lower Cretaceous	Kurnub	Kurnub	K	Massive, white, multicolored sandstone	300	Good (poor water quality)

**Figure 3.** Groundwater level contour map and groundwater flow direction of a) Na'ur aquifer, and b) Hummar aquifer.

3. Material and Method

3.1. Sampling and Fieldwork

Forty-four groundwater representative samples were gathered from 25 wells and springs distributed in the studied area (Figure 1c). All samples belong to the Lower Ajloun aquifer (Na'ur and Hummar aquifers). Two sampling campaigns were conducted: The first one, which represents the rainy season in Jordan, was conducted in March 2021, and the second campaign, which represents the dry season, was conducted in September 2021. The first campaign included samples no. (1-23), which represent one well (sample no. 19) and twenty-two springs. The second campaign included samples no. (1-9, 11-14, 16-21, 24, and 25), which represent one well (sample no. 25) and twenty springs. The pH value, temperature, dissolved oxygen (DO), total dissolved solids (TDS), and electrical conductivity (EC) were all measured in using portable meters by Thermo Scientific (Elite PCTS pH/

Conductivity/TDS/Salinity Pocket Testers) and Lovibond (SensoDirect 150 (Set 3) pH/Oxi/Temp). The accuracy of the devices is as follows: Electrical conductivity ($\pm 1\%$ full scale), pH (± 0.02), TDS ($\pm 1\%$ full scale), and dissolved oxygen (0.4 mg/L). The samples were taken at the mouths of springs. Prior to sampling, the sampled wells were purged by removing a minimum of three well volumes or until T, EC, temperature, and pH became constant. The goal is to assure that the taken water samples accurately demonstrate the subsurface environment's features and circumstances. The samples were filtered using a 0.45 μm acetate cellulose membrane and, then, moved to a pre-washed low-density polyethylene (LDPE) bottle gathered in 1000 mL and 60 mL with proper storage and preservation techniques for the laboratory examination. The procedures given by American Public Health Association (APHA) (Apha, 1998) were utilized during fieldwork and laboratory work analyses. The coordinates of the sampled places were determined using GPS (GARMIN, GPS map 60CSx).

3.2. Laboratory Chemical Analyses

Thermo Scientific Ion Chromatograph (Dionix ICS-1600) was used to determine the concentrations of Cl^- , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} . The concentrations of SO_4^{2-} and NO_3^- were determined using a spectrophotometer (Lovibond 712005 SpectroDirect Spectrophotometer). Bicarbonate (HCO_3^-) concentration was determined by the titration method.

Determination of the total hardness (TH) was carried out using the formula given by Todd (1980):

$$\text{TH (as mg/l CaCO}_3\text{)} = 2.497 (\text{Ca}^{2+}) + 4.11 (\text{Mg}^{2+}) \quad (1)$$

The analytical uncertainty is less than 4%, where samples were analyzed in triplicate. The ionic charge balance was utilized to evaluate the analysis's correctness, where it was reproducible within $\pm 10\%$ error limits (Appelo, 2005). According to Freeze and Cherry (1979), it can be calculated as follows:

$$\text{Error (\%)} = \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \times 100 \quad (2)$$

The concentrations are expressed in meq/L.

The results were compared against the established Jordanian Standards (JS, 2015) and WHO (2011) guidelines for drinking water quality.

3.4. Statistical Analysis

Using univariate and multivariate statistical methods, large data sets are streamlined and arranged to provide substantial insight into the relationships between variables (Dixon and Massey Jr 1951). ANOVA test was utilized to determine whether dry and rainy water chemistry differed significantly. The P-value 0.05 was utilized as the statistical significance threshold. Hierarchical cluster analysis (HCA) was applied to the experimental groundwater data from Jarash studied area. The goal is to deduce the primary natural and anthropogenic processes/factors influencing groundwater quality. Ten parameters, including the major cations and anions, EC, and TDS are the input data for the analysis. Hierarchical clustering is the most prevalent technique, which gives conjectural similarity relationships between a single sample and the complete data set and is often represented as a dendrogram (McKenna Jr, 2003). To reduce the impact of the difference in the data dimensions, the data were normalized by z-scale transformation (Liu et al., 2003). The statistical analyses and tests were performed using SPSS 13 (version 21, SPSS Inc., Chicago, Illinois, United States) and MS Excel.

3.5. Drinking Water Quality Index (DWQI)

To evaluate groundwater quality for drinking purposes, eight parameters (TDS, Mg^{2+} , Ca^{2+} , Na^+ , Cl^- , SO_4^{2-} , K^+ , and NO_3^-) were utilized. Four steps were followed to calculate the DWQI (Swamee and Tyagi 2007):

1- Determination of the selected parameters' levels in the samples.

2- Assigning a weight (AW_i) to the parameters. The weight was estimated based on the parameter's degree of significance for drinking (Table 2). The weight falls in the range of 1 to 5. NO_3^- , SO_4^{2-} , Cl^- , and TDS have been assigned the highest weight (5) because of their importance in assessing water quality (Srinivasamoorthy, et al., 2008). Na^+ was assigned a weight of 4, and Ca^{2+} , Mg^{2+} and K^+ were assigned a weight of 3 (Obeidat and Awawdeh, 2021). The following formula was utilized to estimate the relative weight (RW_i) of each parameter (Njuguna et al., 2020):

$$RW_i = \frac{AW_i}{\sum_{i=1}^n AW_i} \quad (3)$$

, where

RW_i : the relative weight, AW_i : the parameter's assigned weight, n: the number of parameters

3- Calculating the parameter's quality rating (q_i) using the following formula:

$$q_i = \frac{C_i}{S_i} \times 100 \quad (4)$$

, where

q_i : the quality rating, C_i : the parameter's measured concentration (mg/L), S_i : WHO (2011) drinking water guideline (mg/L) for each parameter.

4- Calculating the water quality index using the following formula (Rabeiy, 2018):

$$DWQI = \sum_{i=1}^n W_i \times q_i \quad (5)$$

The DWQI values obtained are classified as follows (Ismail et al., 2020): excellent, good, poor, very poor, and unsuitable with the DWQI values: <50, 50-100, 100-200, 200-300, and >300, respectively.

Table 2. WHO Guidelines, Assigned Weight (w_i) and Calculated Relative Weight (W_i) for each Parameter.

Parameter	WHO (2011)	Assigned weight (AW_i)	Relative weight (RW_i)
TDS (mg/L)	1000	5	0.15
Cl^- (mg/L)	250	5	0.15
SO_4^{2-} (mg/L)	250	5	0.15
NO_3^- (mg/L)	50	5	0.15
Na^+ (mg/L)	200	4	0.13
Ca^{2+} (mg/L)	75	3	0.09
Mg^{2+} (mg/L)	100	3	0.09
K^+ (mg/L)	10	3	0.09
Sum of weights		33	1

3.6. The Nitrate Pollution Index (NPI)

The NPI was initially developed by Obeidat et al., (2012) for the purpose of assessing the level of nitrate pollution in groundwater. It is a single-parameter water quality index and can be calculated using the following formula (Obeidat et al., 2012):

$$NPI = \frac{Cs - HAV}{HAV}, \text{ where} \quad (6)$$

, where

NPI refers to the nitrate pollution index.

Cs refers to the measured nitrate concentration of each

sample.

HAV refers to the human-affected value (20 mg/L) (Spalding and Exner 1993).

The level of groundwater nitrate pollution was classified into five groups as shown in Table 3.

Table 3. NPI Classes (Obeidat et al., 2012).

NPI value	Classification
< 0	Clean water
0-1	Light pollution
1-2	Moderate pollution
2-3	Significant pollution
>3	Very significant pollution

3.7. Assessment of Water Quality for Irrigation

Water appropriateness for irrigation can be evaluated based on the presence of undesirable dissolved chemicals. Since a considerable portion (33.4%) of the land-use in the studied area is agricultural, the groundwater quality was assessed for its suitability for irrigation purposes. The main parameters used in this study to assess groundwater for irrigation purposes are EC, sodium adsorption ratio (SAR), sodium percentage (Na%), Kelley's index (KI), and magnesium hazard (MHI) (Table 4). These parameters were

calculated based on the following formulae:

$$\text{Na\%} = \frac{(\text{Na}+\text{K})}{(\text{Ca}+\text{Mg}+\text{Na}+\text{K})} \times 100 \quad (\text{Wilcox, 1955})$$

$$\text{SAR} = \frac{\text{Na}}{\sqrt{(\text{Ca}+\text{Mg})/2}} \quad (\text{Spandana et al., 2013}) \quad (7)$$

$$\text{KI} = \frac{\text{Na}}{(\text{Ca}+\text{Mg})} \quad (\text{Kelley, 1940})$$

$$\text{MHI} = \frac{\text{Mg}}{(\text{Mg}+\text{Ca})} \times 100 \quad (\text{Spandana et al., 2013})$$

Concentrations are expressed in meq/l.

Table 4. Water Quality Classification Based on the SAR (Spandana, Suresh et al. 2013), Na% (Wilcox 1955), KI (Kelley 1940), MHI (Spandana, Suresh et al. 2013) and EC (Rajankar, Tambekar et al. 2011).

Parameter	Range	Water Class	Sample no.	
			Rainy season	Dry season
Sodium adsorption ratio (SAR)	<10	Excellent (S1)	All samples	All samples
	10-18	Good (S2)	---	---
	18-26	Doubtful (S3)	---	---
	>26	Unsuitable (S4)	---	---
Sodium ratio (Na%)	<20	Excellent	1, 2, 5, 9, 11, 13, 14, 15, 16, 21, 22, 23	2, 3, 5, 6, 11, 14, 16, 17, 24, 25
	20-40	Good	3, 6, 7, 10, 12, 17, 19, 20	1, 7, 8, 12, 13, 18, 19, 20, 21
	40-60	Permissible	4, 8, 18	4, 9
	60-80	Doubtful	---	---
	>80	Unsuitable	---	---
Kelley's index (KI)	<1	Good	All samples	All samples
	>1	Unsuitable	---	---
Magnesium hazard index (MHI)	<50	Good	All samples except sample no. 19	All samples except sample no. 20
	>50	Bad	19	20
EC $\mu\text{S}/\text{cm}$	<250	Excellent	---	---
	250-750	Good	2, 3, 5, 9, 10, 11, 13, 14, 15, 19, 20, 21, 22, 23	2, 3, 5, 6, 9, 11, 12, 13, 14, 16, 17, 19, 20, 21, 24
	750-2,000	Permissible	1, 4, 6, 7, 8, 12, 16, 18	1, 4, 7, 8, 16, 25
	2,000-3,000	Doubtful	---	---
	>3,000	Unsuitable	---	---

4. Results and Discussion

4.1 Hydrochemical Characterization

The descriptive statistics of the hydrochemical parameters alongside with WHO (WHO, 2011) guidelines for drinking water quality and the Jordanian standards (JS, 2015) are shown in Table 5, and the detailed analytical results of nitrate, which are the main focus of this study, are presented in Table 6. The pH value ranges from 7.3 to 8.6 with an average of 7.7 in the rainy season, and from 7.2 to 8.3 with an average of 7.5 in the dry season. The groundwater is of slightly alkaline type, with a limit pH value considered safe between 6.5 to 9.0, based on WHO and Jordanian standards (JS, 2015). The DO concentration ranges from 4.6 mg/L (sample no. 7) to 11.6 mg/L (sample no. 4) with an average of 7.5 mg/L in the rainy season and from 5.0 mg/L (sample no. 14) to 9.2 mg/L (sample no. 11) with an average of 6.9 mg/L in the dry season. About 9% and 29% of the samples during the rainy and dry seasons, respectively, showed DO levels of less than 6.5 mg/L, which could indicate a polluted or overgrown watershed system. The TDS content falls in the range of 324 mg/L (sample no. 3) to 1030 mg/L (sample no. 4) in the rainy season, with an average of 539 mg/L, and from 172 mg/L (sample no. 12) to 690 mg/L (sample no. 4),

with an average of 351 mg/L in the dry season. According to WHO and JS, all of the water samples in the studied area have TDS levels of less than 1000 mg/L and are considered safe, with the exception of sample no.4 in the northeast of the studied area with a TDS value of 1030 mg/L in the rainy season. The EC value lies in the range of 457 $\mu\text{S}/\text{cm}$ (sample no. 2) to 1423 $\mu\text{S}/\text{cm}$ (sample no. 4) with an average of 759 $\mu\text{S}/\text{cm}$ in the rainy season (Figure 3a), and from 354 $\mu\text{S}/\text{cm}$ (sample no. 12) to 1368 $\mu\text{S}/\text{cm}$ (sample no. 4) with an average of 705 $\mu\text{S}/\text{cm}$ in the dry season (Figure 3b). The high spatial variation in EC value can be attributed to differences in geology, agricultural activity, soil conditions, and leaching of surface contaminants (Daghara et al., 2019). For health purposes, the recommended value of EC is no more than (1,500 $\mu\text{S}/\text{cm}$) (WHO, 2011). All measured values of EC fall within the acceptable limits of the WHO and JS. ANOVA test revealed that there is no significant difference between the EC values of collected groundwater samples in the dry and rainy seasons. This was because the calculated F-value (1.6) was less than the critical F-value (4.1), and the calculated P-value (0.3) was greater than 0.05. This means that there are no seasonal variations in the EC. The TH ranges from 152.4 mg/L (sample no. 3) to 426.4 mg/L (sample no. 4), with an

average of 262.2 mg/L, and from 15.8 mg/L (sample no. 6) to 459.9 mg/L (sample no. 4), with an average of 293.4 mg/L in the rainy and dry seasons, respectively. Consequently, the groundwater in the studied area falls in the categories hard

or very hard water, with the exception of sample no.6 in the middle part of the studied area in the rainy season, which can be classified as soft water.

Table 5. Descriptive Statistics of Hydrochemical Parameters during the Rainy and Dry Seasons in the Studied Area, Jordanian Standards (JS 2015), and WHO Guidelines (WHO 2011).

Season	Parameter	Min.	Max.	Mean	Standard deviation	Coefficient of variation (CV) (%)	WHO (2011)	Jordanian standard (2015)
Rainy season	pH	7.3	8.6	7.7	0.4	5.2	6.5–8.5	6.5–9.0
	Temp	13.6	21.6	17.9	1.5	8.4	-	-
	TDS (mg/L)	324	1030	539.3	163.8	30.4	500–1000	500–1500
	EC ($\mu\text{S}/\text{cm}$)	457	1423	758.9	228.2	30.1	1000–1500	750–2300
	TH (mg/L CaCO_3)	152.4	426.4	57.4	13.0	22.6	500	500
	DO (mg/L)	4.6	11.6	7.5	1.27	16.9	-	-
	Na^+ (mg/L)	10.3	80.5	26.8	18.6	69.4	200	200–400
	K^+ (mg/L)	0.10	26.0	2.6	5.4	200.1	10–12	10–50
	Mg^{2+} (mg/L)	5.9	32.3	14.0	7.7	55	50	50–150
	Ca^{2+} (mg/L)	44.3	156.0	81.9	23.7	28.9	75	75–200
	SO_4^{2-} (mg/L)	13.0	117.7	33.4	22.4	67.1	250	200–500
	Cl^- (mg/L)	14.2	139.1	47.2	36.0	76.3	250	200–500
	HCO_3^- (mg/L)	64.0	128.0	96.9	19.0	19.6	250–500	100–500
	NO_3^- (mg/L)	3.5	230.8	50.9	56.4	100.1	50	70
Dry season	pH	7.2	8.3	7.5	0.3	4.0		
	Temp	17.8	27.5	21.0	2.3	11		
	TDS (mg/L)	172.1	690	351.2	129.8	37		
	EC ($\mu\text{S}/\text{cm}$)	354	1368	704.6	254.9	36.2		
	TH (mg/L CaCO_3)	15.8	459.9	293.4	92.0	31.4		
	DO (mg/L)	5	9.2	6.9	1.0	14.5		
	Na^+ (mg/L)	0.6	93.8	31.5	24.9	79		
	K^+ (mg/L)	0.1	32.8	3.4	7.0	200.1		
	Mg^{2+} (mg/L)	1.0	37.4	18.0	9.9	55		
	Ca^{2+} (mg/L)	4.7	164.0	87.8	32.5	37		
	SO_4^{2-} (mg/L)	12.2	127.6	33.5	24.7	73.7		
	Cl^- (mg/L)	13.0	154.4	57.5	46.0	80		
	HCO_3^- (mg/L)	76.0	136.0	107.4	16.6	15.5		
	NO_3^- (mg/L)	2.5	262.6	60.2	70.1	100.2		

4.2 Major Cations and anions

Minerals are usually more easily absorbed in the intestines from water than from food (Rosborg and Kozisek, 2016). Their origin is largely rooted in the bedrock and some anthropogenic activity, and they can all be present in high or low quantities in the groundwater as well as surface water (Rosborg and Kozisek 2016). In the studied area, the order of dominance of major cations is as follows: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$, whereas that of anions is $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-}$. The major source of calcium in water comes from limestone weathering (Meybeck, 1987) and agricultural fertilizers (Weyhenmeyer et al., 2019). Calcium concentration lies in the range of 44.3 mg/L (sample no. 19) to 155.9 mg/L (sample no. 4) with an average of 81.8 mg/L in the rainy season and 4.7 mg/L (sample no. 6) to 164 mg/L (sample no. 4) with an average of 87.7 mg/L in the dry season. About 71%, and 57% of the samples in the dry and rainy seasons, respectively, exceeded the maximum calcium levels set by the WHO guidelines. However, according to the Jordanian

standards (JS, 2015), all groundwater samples are considered safe in both seasons. Sodium and magnesium in groundwater originate from natural sources such as mineral dissolution (silicate weathering and magnesium-containing rocks) (Lakshmanan et al., 2003). Agricultural operations, sewage, and industrial effluents may be additional sources of sodium and magnesium in the groundwater (Hem, 1985). None of the samples exceeded the maximum magnesium and sodium levels set by the WHO guidelines and JS. In the rainy season, potassium concentration ranges from 0.10 mg/L (sample no. 21) to 26.04 mg/L (sample no. 4), with an average of 2.59 mg/L and ranges from 0.12 mg/L (sample no. 6) to 32.76 mg/L (sample no. 4), with an average of 3.39 mg/L in the dry season. None of the samples exceeded the maximum potassium levels set by the WHO and JS, except sample no.4 during both the rainy and dry seasons. Throughout the rainy season, bicarbonate concentration ranges from 64.0 mg/L (sample no. 6) to 128.0 mg/L (sample no. 16), with an average of 96.9 mg/L, and in the dry season It ranges from 76.0 mg/L

(sample no. 3) to 136.0 mg/L (sample no. 9), with an average of 107.4 mg/L. The aquifer's calcite and dolomite weathering would contribute 50% of the bicarbonate ions. This process adds calcium, magnesium, and bicarbonate ions to the groundwater (Jeevanandam et al., 2007). Typically, chloride level in groundwater does not exceed 30 mg/L, but in arid areas, concentrations of 1000 mg/L or higher are typical (Saha et al., 2019). A high chloride concentration is detrimental to metal pipelines, structures, and agricultural crops (Khashoggi and El Maghraby 2013). In the rainy season, chloride concentration ranges from 14.2 mg/L (sample no. 14) to 139.1 mg/L (sample no. 4) with an average of 47.23 mg/L, while in the dry season, its concentration ranges from 12.0 mg/L (sample no. 3) to 154.4 mg/L (sample no. 4) with an average of 57.5 mg/L. In the rainy season, sulfate concentration ranges from 13.0 mg/L (sample no. 9) to 117.7 mg/L (sample no. 4), with an average concentration of 33.4 mg/L, and in the dry season, its concentration ranges from 12.2 mg/L (sample no. 3) to 127.6 mg/L (sample no. 4), with an average concentration of 33.5 mg/L. Dry fallout and industrial runoff are among the primary human activities that raise sulfate concentration (Venkatesan et al., 2021). Oxidation of marcasite and pyrite may play a significant role in this link (Rahman et al., 2013). The levels of bicarbonate, chloride, and sulfate in all groundwater samples are below the WHO guidelines and JS. Nitrate ion has a high solubility in water and readily reaches the groundwater. Its concentration ranges from 3.5 mg/L (sample no. 19) to 230.8 mg/L (sample no. 4) with an average of 50.9 mg/L in the rainy season, and from 2.5 mg/L (sample no. 19) to 262.6 mg/L (sample no. 4) with an average of 60.1 mg/L in the dry season. About 81%, and 91% of the samples from both dry and rainy seasons, respectively, showed NO_3^- concentrations exceeding the concentration of natural origin (5-10 mg/L (Panno et

al., 2006), indicating human-induced nitrogen pollution. About 38%, and 35% of the samples from both dry and rainy seasons, respectively, showed NO_3^- concentration higher than the WHO guidelines and JS of 50 mg/L. The favorable factor for the high level of nitrate in the studied region is primarily anthropogenic, consisting of agricultural practices, livestock farming, and home sewage (Al-Ajlouni et al., 2019; Al Kuisi et al., 2009). As a result of contamination, eight groundwater wells and springs (sample no. 1, 4, 7, 8, 12, 17, 18, and 25) are not recommended for drinking purposes. ANOVA test revealed no significant difference between the NO_3^- values of the collected groundwater samples in the rainy and dry seasons because the calculated F-value (0.005) was less than the critical F-value (4.1), and the calculated P-value (1.0) was greater than 0.05. This means that there are no seasonal variations in nitrate concentration. Analyzing the groundwater samples, using a Piper diagram (diamond shape), revealed that the predominant water type is Ca-Mg-HCO_3 , followed by a Ca-Mg-Cl and a Ca-Mg-SO_4 types during both the rainy and dry seasons (Figures 4a and b). The Ca-Mg-HCO_3 type reflects the weathering of limestone and dolomite that comprise the region's primary rock formations. This type of freshwater indicated that it has been recently introduced and has not been contaminated by human activity (El Yaouti et al., 2009). Ca-Mg-Cl water type originates as a result of invasion of highly saline, polluted water into unpolluted freshwater, followed by ion exchange reactions (Selvam et al., 2016). The majority of samples falls within the Ca-dominant zone of the cation facies, followed by the zone where no cation-anion pair exceeded 50%. Furthermore, the majority of samples was found within the anion zone's no-dominating zone, with only a few samples falling within the HCO_3^- and Cl^- zones.

Table 6. Detailed Analytical Results of Nitrate (the Focus of This Study), EC, DO, and pH.

Samples no	Rainy season					Dry season				
	pH	DO (mg/L)	TDS (mg/L)	EC ($\mu\text{S/cm}$)	NO_3^- (mg/L)	Ph	DO (mg/L)	TDS (mg/L)	EC ($\mu\text{S/cm}$)	NO_3^- (mg/L)
1	7.7	6.2	602	851	54.3	7.76	5.4	375	758	39.5
2	7.4	7.1	471	659	24.1	7.64	6.7	309	627	33.5
3	8.0	7.5	324	457	13.8	7.94	6.6	220	449	13.1
4	7.4	11.6	1030	1423	230.8	7.44	7.5	690	1368	262.6
5	7.3	7.7	456	643	10.3	7.36	6.4	316	638	6.8
6	7.4	7.1	590	832	73.4	7.35	8.2	346	698	42.8
7	7.9	4.6	573	804	63.2	7.4	7	382	767	62.6
8	7.4	9.4	787	1114	120.3	7.46	5.9	614	1220	172.2
9	7.3	7.3	489	684	12.1	7.19	8.4	331	679	7.3
10	7.6	7.7	475	667	31.1	—	—	—	—	—
11	8.1	7.8	511	716	20.2	7.93	9.2	289	586	17.8
12	7.6	7.5	762	1080	164.4	7.41	6.3	172.1	354	190.3
13	7.5	6.8	434	609	16.2	7.94	5.7	233	497	17.2
14	7.3	7.8	420	592	14.7	7.22	5	276	555	8.4
15	7.9	8.2	442	618	18.1	—	—	—	—	—
16	7.3	7.5	550	796	43.5	7.27	7.6	314	629	40.1
17	7.3	7.5	623	876	72.5	7.19	7.9	337	674	52.5
18	7.3	7.3	750	1055	97.4	7.22	7.5	510	1015	97.4
19	7.7	8.1	511	723	3.5	7.5	6.5	313	632	2.5
20	8.5	8.4	409	576	46.7	8.25	6.9	285	519	37.2
21	7.8	6.6	418	587	14.8	7.55	7.7	271	547	19.9
22	8.1	7.2	406	572	14.1	—	—	—	—	—
23	8.6	6.2	370	520	12.4	—	—	—	—	—
24	—	—	—	—	—	7.41	6.3	269	542	21.7
25	—	—	—	—	—	7.38	6.9	523	1042	118.5

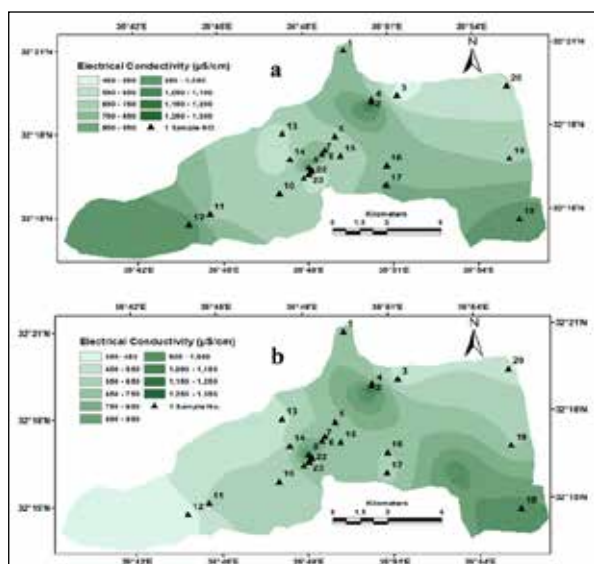


Figure 4. Spatial distribution of EC ($\mu\text{S}/\text{cm}$) in the rainy season a), and in the dry season b).

4.3 Hierarchical Cluster Analysis (HCA)

Hierarchical cluster analysis (HCA) has been recently adopted for the purpose of groundwater quality evaluation (Lee et al., 2001; Kumar et al., 2009). It was applied to obtain common clusters of the sampled locations that have similar characteristics in the studied area. The dendrogram plot, which is useful in tracing HCA, was used, and two main clusters were extracted (Figure 5). The variables used in generating the clusters cover the major cations and anions, EC, and TDS of the groundwater for both the rainy and dry seasons. Table 7 presents the two major clusters with their average composition in the rainy and dry seasons. The distance between clusters 1 and 2 is 25, which shows that the geochemical properties of the water samples in cluster 1 are different from those in cluster 2. In the rainy season, cluster 1 encompasses the samples (no. 1, 2, 3, 5, 6, 7, 9, 10, 11, 13, 14, 15, 16, 17, 19, 20, 21, 22, and 23), whereas Cluster 2 encompasses the samples (no. 4, 8, 12, and 18). Cluster 1 represents 83% of the samples, and the water of this cluster can be classified as Ca-Mg-HCO_3 with the lowest TDS content (477.6 mg/L) and lowest mean concentrations for all major parameters. The water of ten samples of this cluster (samples no. 3, 5, 9, 13, 14, 15, 19, 21, 22, and 23) was found to be affected by human activities and by water-rock interaction processes (dissolution and ion exchange reactions) as it is indicated in the slightly higher nitrate concentration (5-10 mg/L). Five samples (no. 2, 10, 11, 16, and 20) were found to be contaminated due to human activities since nitrate concentration exceeds the threshold value of (5-10 mg/L) but still less than WHO guidelines and JS (50 mg/L). The four remaining samples (no. 1, 6, 7, and 17) have NO_3^- concentrations higher than the WHO guidelines and JS, demonstrating the impact of nitrogen pollution resulting from human activities. Due to contamination, these samples are not recommended for drinking. Cluster 2 represents 17% of the samples, showing higher ionic concentrations than

cluster 1 does, and its water can be classified as Ca-Na-Cl . The nitrate concentration in this group is much higher than the WHO permissible limit (average NO_3^- concentration of these samples = 153.2 mg/L), indicating that the origin of nitrate pollution is mainly due to human activities. The water of this cluster is unfit for drinking. In the dry season, Cluster 1 includes the samples (no. 1, 2, 3, 5, 6, 7, 9, 11, 12, 13, 14, 15, 16, 17, 19, and 21), whereas Cluster 2 includes the samples (no. 4, 8, and 18). Cluster 1 represents 84% of the samples, with the lowest concentration of dissolved ions and the water can be classified as Ca-Mg-HCO_3 indicating the water is affected by water-rock interaction processes with slightly higher nitrate concentration than when it is in the natural background. Cluster 2 represents 16% of the samples, showing higher ionic concentrations than cluster 1 does, with nitrate concentration exceeding the WHO permissible limit (average NO_3^- concentration = 177.4 mg/L), indicating that the origin of pollution is from human activities. The water of this group can be classified as Ca-Na-Cl . When plotted using Schoeller diagram (Figure 6a and b), it can be concluded that the two clusters stem from a common origin, but due to water rock interaction and human impacts, the two clusters have been generated. Potential anthropogenic sources of groundwater contamination in the study area include cesspits, sewer overflows, illegal dumping of fluid wastes, olive tree cultivation (Hammouri and El-Naqa 2008). This can be confirmed by the land use/land cover map of the study area (Figure 2c). Accurate and specific identification of these sources requires more advanced techniques such as the stable isotope composition of the dissolved nitrate, which is the focus of another research being currently developed by the authors. In both seasons, the average values of all parameters are higher for cluster 2, and most of the samples belong to cluster 1. Additionally, the values of Cl^- , NO_3^- , Ca^{2+} , K^+ , and EC are higher in the dry season. No significant changes in the values of SO_4^{2-} , HCO_3^- , and Na^+ . Ca-Mg-HCO_3 facies are considered the baseline groundwater in the study area. It is worth mentioning that some of the springs sampled in the wet season were not sampled in the dry season, since they became dry. Moreover, there are two additional points sampled in the dry season.

Table 7. The Average of the Main Hydrochemical Parameters of Cluster 1 and Cluster 2 during the Rainy and Dry Seasons.

parameters	Rainy seasons		Dry seasons	
	cluster 1	cluster 2	cluster 1	cluster 2
Cl^-	33.0	114.7	38.6	142.1
NO_3^-	29.4	153.2	37.0	177.4
SO_4^{2-}	26.2	67.3	25.3	76.2
HCO_3^-	95.4	104.0	107.3	101.3
Na^+	19.6	61.1	29.1	55.0
K^+	1.4	8.3	1.8	13.3
Mg^{2+}	13.0	19.1	18.8	15.3
Ca^{2+}	76.1	109.5	83.9	115.8
EC	672.7	1168.0	600.6	1201.0
TDS	477.6	832.3	298.1	604.7

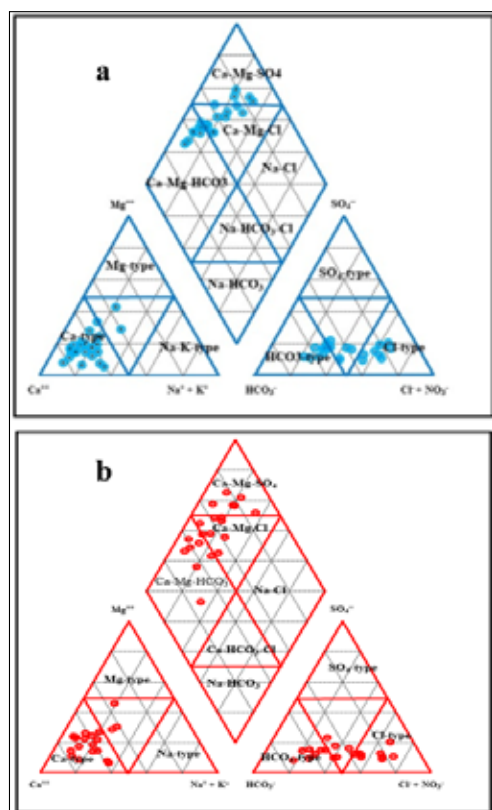


Figure 5. Piper's trilinear diagram showing different facies of the groundwater in the studied area during the rainy season a), and in the dry season b).

4.4 Drinking Water Quality Index (DWQI)

The Drinking Water Quality Index (DWQI) is a rating technique that offers the combined effect of individual water performance indicators of overall water quality based on several chemical parameters (Eslami et al., 2017). The WHO (2011) guidelines for drinking water quality have been used to calculate the DWQI, where water quality was divided into five groups based on the DWQI results (Table 8). The values of the DWQI fall in the range of 19.3 and 148.3 with an average of 43.4 in the rainy season and between 19.5 and 162.4 with an average of 46.0 in the dry season. The highest values of DWQI were found in the northeastern parts of the studied area (sample no. 4) in both the rainy and dry seasons (Figure 7a and b). During the rainy season, the lowest values of DWQI were found in the northeastern, southwestern, southeastern, northwestern, western, and middle parts of the studied area (samples no. 1, 2, 3, 5, 7, 9, 10, 11, 13, 14, 15, 16, 19, and 23), whereas in the dry season, the lowest values of DWQI were found in the northeastern, southwestern, southeastern, northwestern, western, and middle parts of the studied area (samples no. 1, 2, 3, 5, 6, 7, 9, 11, 13, 14, 16, 17, 19, 20, 21, and 24). Accordingly, about 95% of the groundwater samples possess good and excellent water quality, although more than one third of the samples possesses nitrate levels higher than 50 mg/L. The wide variation in the DWQI reflects the variability of the levels of the used parameters, mainly TDS, Cl⁻, and NO₃⁻, which in turn reflects the influence of human activities on the water quality.

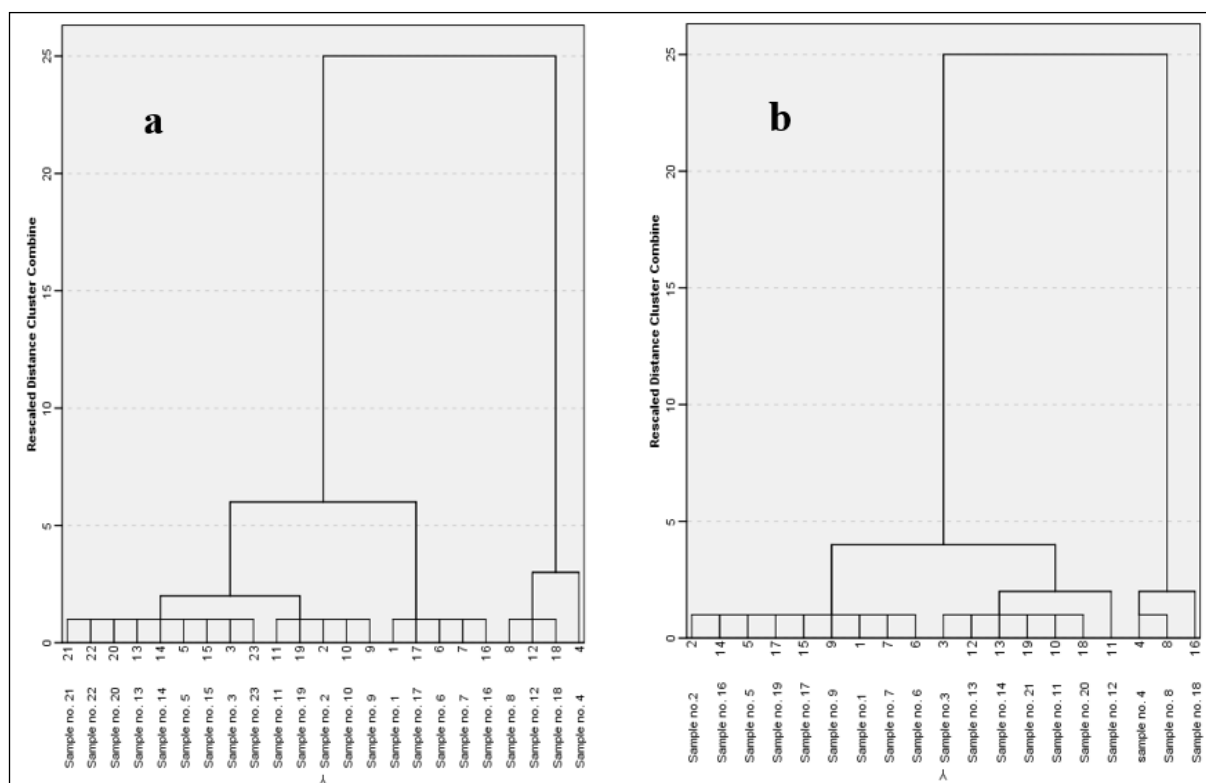
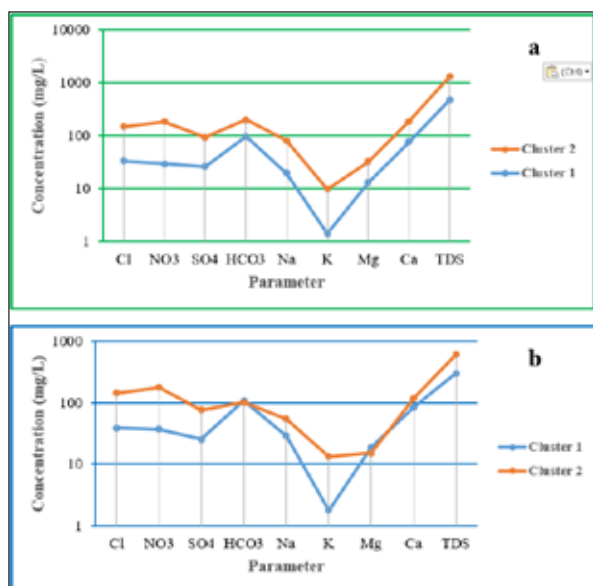


Figure 6. Dendrogram of clusters of the hydrochemical parameters in the rainy season a), and in the dry season b).

Table 8. Water Quality Classification Based on the Water Quality Index (DWQI).

DWQI Range	Type of water	WHO (2011) guidelines	Rainy Samples no.	Dry samples no.
<50	Excellent water	NO ₃ ⁻ below 50 mg/L, except for samples no. 1 and 7 in rainy season, and samples no. 7, and 17 in the dry season	1,2,3,5,7,9,10,11,13,14,15,16,19,20,21,22,23	1,2,3,5,6,7,9,11,13,14,16,17,19,20,21,24
50–100	Good water	NO ₃ ⁻ exceeding 50 mg/L	6,8,12,17,18	8,12,18,25
100–200	Poor water	NO ₃ ⁻ exceeding 50 mg/L	4	4
200–300	Very poor water	NO ₃ ⁻ exceeding 50 mg/L	---	---
>300	Water unsuitable	NO ₃ ⁻ exceeding 50 mg/L	---	---

**Figure 7.** Schoeller's diagram of the two clusters for the rainy a) and dry seasons b).

4.5 Nitrate Pollution Index (NPI)

The nitrate pollution index (NPI) has been utilized as an indicator for nitrate pollution of the groundwater in the studied area. As shown in Table 9, the NPI values fall in the range of -0.82 to 10.5 with an average of 1.5 in the rainy

season, and -0.87 to 12.1 with an average of 2.0 in the dry season. In the rainy seasons, 44% of the overall groundwater samples are classified as clean water, 13% light pollution, 13% moderate pollution, 13% significant pollution, and 17% very significant pollution. While 38% of the total groundwater samples in the dry season are considered as clean water, 19% light pollution, 14% moderate pollution, 5% significant pollution, and 24% very significant pollution. In the rainy season, the highest values of the NPI are found in the northeastern, southeastern, southwestern, and middle parts of the studied area (samples no. 4, 8, 12, and 18). The lowest values of the NPI are found in the northeastern, southwestern, northwestern, western, eastern, and middle parts of the studied area (samples no. 3, 5, 9, 13, 14, 15, 19, 21, 22, and 23) (Figure 7c). In the dry season, the highest values of the NPI are found in the northeastern, southeastern, southwestern, and middle parts of the studied area (samples no. 4, 8, 12, 18, and 25). The lowest values of NPI are found in the northeastern, southwestern, northwestern, western, eastern, and middle parts of the studied area (samples no. 3, 5, 9, 11, 13, 14, 19, and 21) (Figure 7d). According to NPI values, light nitrate pollution dominates most of the area. Medium, high, and very significant levels of human-caused nitrate pollution are most common in the central region, which is dominated by agriculture and urbanization. Thus, these regions have significant nitrate concentrations.

Table 9. Water Quality Classification Based on the Nitrate Pollution Index (NPI).

NPI value	NPI class	WHO (2011) guidelines	Rainy Samples no.	Dry samples no.
< 0	Clean (unpolluted)	NO ₃ ⁻ below 50 mg/L	3,5,9,13,14,15,19,21,22,23	3,5,9,11,13,14,19,21
0–1	Light pollution	NO ₃ ⁻ below 50 mg/L	2,10,11	1,2,20,24
1–2	Moderate pollution	NO ₃ ⁻ below 50 mg/L, except for samples no. 1 (rainy season) and no.17 (dry season)	1,16,20	6,16,17
2–3	Significant pollution	NO ₃ ⁻ exceeding 50 mg/L	6,7,17	7
> 3	Very significant pollution	NO ₃ ⁻ exceeding 50 mg/L	4,8,12,18	4,8,12,18,25

4.6 Comparison between DWQI and NPI

Except for sample no. 4, which has poor water quality, all samples' DWQI values correspond to good-excellent water quality classes, thus authenticating their appropriateness for drinking. On the other hand, NPI values show a wide range of nitrate pollution levels in groundwater in the studied area. Table 10 presents the matchup of the DWQI and NPI as water quality indicators compared to the WHO guidelines. When compared together, it is found that samples no. 1 (rainy season) and 17 (dry season) fall in the category "excellent water" based on the DWQI, and in the category "moderate pollution" based on the NPI. However,

both samples have NO₃⁻ concentrations above the WHO guidelines of 50 mg/L. Furthermore, samples no. 6, 7, and 17 (rainy season) and no. 7 (dry season) are classified as "good-excellent" by the DWQI and "significant pollution" by the NPI, despite having NO₃⁻ concentrations above 50 mg/L in all of them. Despite having NO₃⁻ concentrations above 50 mg/L, samples no. 8, 12, and 18 (rainy season) and no. 8, 12, 18, and 25 (dry season) fall into the category "good water" based on DWQI and the category "very significant pollution" based on NPI. Sample no. 4, representing the rainy and dry seasons, has a NO₃⁻ concentration greater than 50 mg/L and is classified as "poor water" by DWQI and "very

significant pollution” by NPI. According to Obeidat et al., (2012), the NPI categories “significant pollution” and “very significant pollution” have NO_3^- concentrations above 50 mg/L. By grouping measurements of selected parameters such as pH, EC, major cations, and anions, it also provides a concise summary of the overall water quality status (Abbasi and Abbasi 2012). Because it is easy to introduce bias when selecting parameters and calculating individual weighing

values, it may not be sufficient to comprehend the DWQI of a large body of water as a whole, although the calculations are straightforward. Certain parameters can influence water quality in a way that can be disregarded during calculation. Hence, the NPI may be a better indicator of water quality than the DWQI, which, at low values, obscures or masks very important parameters such as nitrate despite having levels that exceed WHO guidelines.

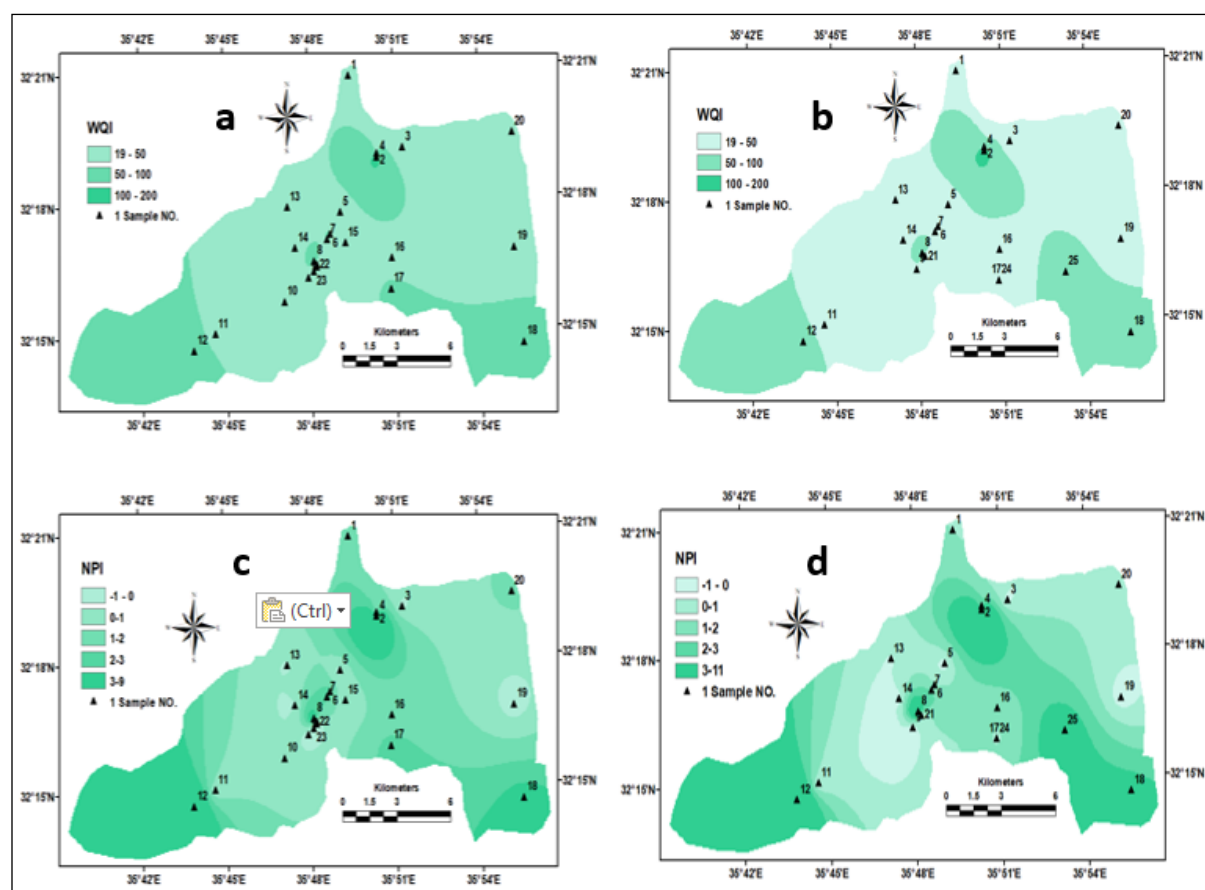


Figure 8. Spatial distribution of DWQI values in the rainy season a), and in the dry season b), and spatial distribution of NPI in the rainy season c), and in the dry season d).

Table 10. Comparison between DWQI and NPI Water Quality Classification.

DWQI Water Type	NPI Water Type	WHO (2011) Guidelines	Rainy Sample no.	Dry Sample no.
Excellent water	Clean (unpolluted)	NO_3^- below 50 mg/L	3,5,9,13,4,15,19,21, 22,23	3,5,9,11,13,14,19,21
Excellent water	Light pollution	NO_3^- below 50 mg/L	2,10,11	1,2,20,24
Excellent water	Moderate pollution	NO_3^- exceeding 50 mg/L except for (samples no. 16 and 20) rainy season, and (samples no. 6 and 16) dry season	1,16,20	6,16,17
Excellent to good water	Significant pollution	NO_3^- exceeding 50 mg/L	6,7,17	7
Good to poor water	Very significant pollution	NO_3^- exceeding 50 mg/L	4,8,12,18	4,8,12,18,25

DWQI has been utilized by several studies to assess water quality for drinking purposes in Jordan. El-Naqa and Al Raei (2021) assessed the DWQI in the Greater Amman, Jordan in the period between 2012-2016. Results indicated that the computed DWQI has values in the range of 29.17-62.32, corresponding excellent to good water quality classes. Additionally, it was found that the water quality in the study area has been deteriorated over time. The highest values of the DWQI were attributed to the high values of TDS, Ca^{2+} ,

K^+ , Cl^- , HCO_3^- , NO_3^- , and SO_4^{2-} . A study was carried out by Hyarat et al., (2022) to assess groundwater quality using water quality index in Amman and Zarqa areas, Jordan. Based on the index values, 12%, 53%, and 35% of the samples can be described as having excellent, good, fair, and poor quality, respectively. The values of the index were in the range of 31-335 with an average of 95. Evaluation of the groundwater quality suitability for drinking purpose using water quality index in the Yarmouk basin, Jordan,

was carried out by Ibrahim (2018). Based on the index scale classification, the groundwater quality of the studied locations falls in the excellent to poor quality, corresponding to the computed index values of 26.3 to 107.93. Ibrahim (2019) investigated the suitability of groundwater in major groundwater basins in Jordan using the water quality index. Groundwater from 16 stations within one year monitoring period (March 2015–February 2016) was used. The findings of the study indicated that the computed index values are in the range of 40–4295, corresponding to the quality classes of excellent, good, poor, and very poor water quality. Three locations were classified as excellent water, nine samples as good, one as poor, and two as very poor water. Assessment of groundwater quality in the area surrounding Al-Zataari camp, Jordan, using cluster analysis and water quality index was conducted by Obeidat and Awawdeh (2021). The index calculation indicated that the groundwater quality falls in three classes: excellent covering 46% of the samples, good covering 50% of the samples, and poor involving two samples. The NPI was firstly applied in the Northern part of Jordan by Obeidat and Awawdeh (2021). Since then, the index has been widely utilized to assess groundwater contamination worldwide (El Mountassir et al., 2022; Egbueri et al., 2023; Paneerselvam et al., 2023). In both seasons, three zones of high DWQI and NPI values can be observed: in the northern part, where groundwater levels are high (700–900 masl; see Figure 3), which can be considered as recharge areas; the other two zones are located in eastern and southeast parts of the study area, where groundwater tables become shallower, and these areas might represent discharge areas.

4.7 Water Quality for Irrigation

Water quality for irrigation is determined by the kind and magnitude of the dissolved solids. In the studied area, the EC, the sodium adsorption ratio (SAR), the sodium percentage (Na%), and the magnesium hazard index (MHI) were used to determine the suitability of water for irrigation purposes. SAR is a characteristic that reveals the relative amounts of Na^+ , Ca^{2+} , and Mg^{2+} in water samples. SAR takes into account the fact that the negative effects of sodium are mitigated by calcium and magnesium ions. When the SAR value is higher than 12–15, the soil becomes much damaged and plants have trouble getting water. The results of SAR range between 0.4 and 2.4 with an average of 1.0 in the rainy season, and between 0.1 and 1.9 with an average of 0.8 in the dry season. As seen in Table 2, water quality for irrigation purposes was graded into four groups according to the sodium adsorption ratio (SAR) (Anandakumar et al., 2009). The results show that all groundwater samples in our study are less than 10 and are classified as excellent (S1). The sodium concentration in groundwater is crucial for determining its appropriateness for irrigation purposes. This is because sodium ions have a tendency to react with soil formations and the soil will become less permeable (Mohamed et al., 2017). The value of Na% ranges between 8.8% and 45.4% with an average of 21.9% in the rainy season, and between 6.6% and 49.1% with an average of 22.3% in the dry season. As seen in Table 2, water quality for irrigation purposes was graded into five groups (Wilcox, 1955). According to the Na% classification, 51% of the total groundwater samples represent excellent

water, 35% good water, and the remaining 19% permissible water during the rainy seasons. While through the dry season, the classification of Na%, 43% of the total groundwater samples represent excellent water, 48% good water, and the remaining 9% permissible water. The lowest value of Na% relative to excellent water was found in samples no.14 and no.11 in the rainy and dry seasons, respectively, which are located in the middle and southwestern parts of the studied area. The highest value of Na% relative to permissible water was found in sample no.4, which is located in the northeastern part of the study region in both seasons. Based on the interpretation, it can be recognized that the majority of the samples exhibit excellent to good characteristics. The ratio of Na^+ to Ca^{2+} and Mg^{2+} is used to calculate Kelley's index (Kelley, 1940). A Kelley's index (KI) greater than one shows an increased level of sodium in the water. Therefore, water with a KI of less than one is suitable for irrigation, whereas those with a ratio greater than one provide alkali dangers and are unsuitable for irrigation (Kelley, 1940). The KI value in the studied area ranges from 0.1 to 0.4 with an average of 0.2 in the rainy season and from 0.1 and 0.5 with an average of 0.2 in the dry season. The Kelley's ratio values show that all the groundwater samples are less than 1, and this indicates suitable water quality for irrigation purposes in both seasons. Ca^{2+} and Mg^{2+} maintain equilibrium in the majority of the water. As the soil gets more alkaline, high quantities of magnesium in the water will negatively impact crop production (Subhash Chandra, 2017). The value of MHI ranges from 8.6 to 54.6 with an average of 22.3 in the rainy season and from 10.7 to 56.8 with an average of 25.5 in the dry season. Water quality was graded into two groups based on the MHI results (Subhash Chandra, 2017). Based on the MHI value, all groundwater samples are suitable for irrigation purposes, which control the majority of the area in the study region. A very small portion (2%) of the higher MHI concentration was recorded as harmful and unsuitable for irrigation purposes, specifically samples no.19 and no.20 in the rainy and dry seasons, respectively, in the eastern and northeastern parts of the studied area. According to Marmontel et al., (2018), electrical conductivity is crucial in determining the appropriateness of water for irrigation purposes. In the studied area, the EC range from 457 to 1423 $\mu\text{S}/\text{cm}$ with an average of 759 $\mu\text{S}/\text{cm}$ in the rainy season, and from 354 to 1368 $\mu\text{S}/\text{cm}$ with an average of 705 $\mu\text{S}/\text{cm}$ in the dry season. Water quality is classified into five groups according to the range of EC (Rajankar et al., 2011). The results indicated that water in the studied area is obviously classified as good or permissible for irrigation purposes.

5. Conclusion and Recommendations

The present study aimed to evaluate the quality of groundwater in the Jerash region using the DWQI and NPI as water quality indicators. The DWQI should be used with extreme caution due to the fact that it gives a false impression of water quality by masking pollutants at levels that exceeded the acceptable limit for a drinking water quality. In contrast, the nitrate pollution index (NPI) revealed that approximately 43% of the samples fall into the categories "moderately polluted," "significantly polluted," and "very significantly polluted," with NO_3^- concentrations exceeding

the WHO and JS-mandated maximum permissible limit of 50 mg/L. The main sources of nitrate pollution in the studied area are synthetic fertilizers and sewage intrusion. On the other hand, water-rock interaction is the primary natural process affecting groundwater quality, as indicated by the predominant carbonate rock composition of the aquifer material. The quality of all tested groundwater samples was suitable for irrigation with no seasonal variation in the groundwater chemistry. The results shed light on the protection and allocation of usable groundwater supplies, particularly for irrigation and drinking and offer decision-makers an important tool for putting into place effective measures to protect groundwater in the studied area. It is highly recommended to apply best management practices and efficient land use planning including improved agriculture and sanitation techniques. In addition, selecting the most suitable environmental parameters is crucial and will provide the user with a particular form of the algorithm and the potential effects of water body pollution. Furthermore, statistical methods can be utilized to reduce uncertainty in processes like parameter selection.

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Updated Seismic Hazard Assessment Evaluation for the City of Aqaba, Jordan

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Abstract

The Gulf of Aqaba area in Jordan is characterized by moderate to high seismic activity over the past 100 years in comparison to other parts of the Jordan-Dead Sea Transform. Nevertheless, some major earthquakes occurred in the area that affected the major cities of the Gulf such as Aqaba city. For the purposes of this study, nineteen active seismic sources were considered to assess the seismic hazard in Aqaba city. The Peak Ground Acceleration (PGA) and Response Spectra curves (RS) for different return periods (475, 975, and 2475 years) and nine selected sites representing different soil profiles in the city are determined. It is noted that 95% of the seismic hazard of the studied area is due to the sources lying within the influencing circle (i.e., ≤ 300 km). The calculated PGA value for a return period of 475 years was 0.3g. Meanwhile, it is considered in the Jordan Building Code as 0.2g. Furthermore, the PGA for return period of 975 years and 2475 years is 0.45g and 0.52g respectively. The results for soil profiles of hard rock and stiff soil for periods 0, 0.2, and 1 second were 0.3g, 0.7g, 0.2g, 0.35g, 0.79g, and 0.2g for a return period of 475 years respectively. It is calculated that the maximum spectral acceleration is 0.87g at Aqaba's southern coast for stiff soil profile, while its minimum value is 0.7g at the northern part of Aqaba for a return period of 475 years.

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Keywords: Seismic Hazard; Response Spectra; Peak Ground Acceleration; Aqaba city; Jordan; Seismic Risk.

1. Introduction and Geologic setting

A seismic hazard refers to the likelihood of an earthquake, happening in a specific location, within a specific timeframe, with the intensity of the ground motion exceeding a specific threshold. This aids in estimating future risks, such that the decisions regarding building codes for typical structures, the design of infrastructure projects, land use planning, and insurance rates can be considered.

The strike-slip motion between the African plate and the Arabian plate is accommodated by the 'Jordan-Dead Sea Transform (JDST). The JDST extends into the Gulf of Aqaba, where the main rupture associated with the strike-slip mechanism is situated. These strike-slip type movements along the JDST occur when a fracture in the crustal rocks of the Earth, causing these rock masses to slide past one another parallel to the strike. It is due to these movements that the stress accumulates over time and gets a release in the form of earthquakes. (Al-Adamat and Diabat 2022). Results revealed that the existence of a strike-slip regime in all stress tensors. Three swarms within the Gulf of Aqaba occurred in 1983, 1990, and 1993 (Klinger *et al.*, 1999). The tectonic evaluation carried out through lineament and fracture analyses indicates that the regional development is tectonically related to the opening of the Red Sea, the development of the Dead Sea transform fault, and other distinct regional tectonic features. However, with a moment magnitude of $M_w=7.1$, the significant earthquake that struck

on November 22, 1995, marked the start of a seismic swarm that occurred in the central region of the Gulf of Aqaba. This seismic activity continued until December 31, 1997. It was thousands of small to moderate earthquakes that took place during this swarm. The Jordan Seismological Observatory recorded and examined 2089 of these earthquakes (Al-Tarazi and Qadan 1997; Al-Tarazi, 2000). The Gulf of Suez's rifting direction corresponds to the major trend of the extension stress pattern, which may be connected to the paleo stress that existed along the Gulf of Suez and Aqaba throughout the Middle to Late Miocene period (Abdel Fattah, *et al.*, 1997; Malkawi *et al.*, 1995; Abdelazim, *et al.*, 2023; Abou Karaki, *et al.*, 2022, Al-Amoush *et al.*, 2017).

Moreover, it is assumed that at 2.3 ka, a catastrophic geological event, caused by down faulting in the northwestern edges of the Gulf of Aqaba, devastated the 'Elat' fringing coral reef. The encircling reefs at the northwest end of the gulf keep deteriorating over time due to damage brought on by down-throwing earthquakes (Shaked, *et al.*, 2004). More than 500 small local earthquakes (ML 4.85) occurred in the Gulf of Aqaba region between January 21 and April 20, 1983. The majority of the activity, including the greatest shocks, was confined to the region caused by strike-slip faults between latitudes $29^{\circ}07'$ and $29^{\circ}15'$ and longitudes $34^{\circ}33'$ and $34^{\circ}42'$. According to this data, the Gulf of Aqaba which is part of the JDST is characterized by seismic activity that falls into the foreshock-aftershock and swarm categories (El-

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Isa, *et al.*, 1984). This seismic activity, resulting from the collision of the Arabian and African plates with the Eurasian plate, has greatly disturbed the tectonic framework of the JDST (ten-Brink and Ben-Avraham, 1989; Alvarado-Corona *et al.*, 2014).

In light of the extent of vigorous seismic activity in past situations. This study aims to determine and analyze the seismic hazard in the Aqaba City located in South Jordan using previously collected data to elaborate on the seismic risks, which may arise in the future.

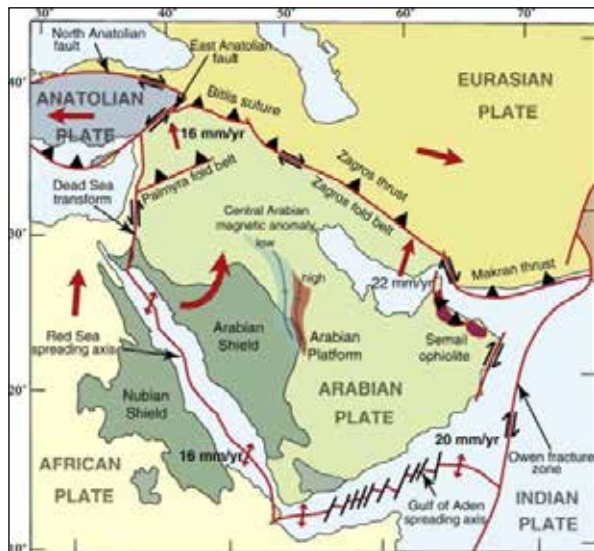


Figure 1. Regional tectonic of the Jordan Dead Sea Transform, indicating the movements and directions of the plate (Pascucci and Lubkowski, 2008).

2. Materials and Methods

2.1 Data Collection

Identification of the seismic sources in this study is dependent on the geology, local and regional tectonics, and historical and instrumental seismic data (Figure 1 and Figure 2). With delineation of these sources that depend on the uniformity of geotectonic features, the homogeneity of earthquake occurrences and consistency of its focal mechanism are shown in Figure 3. Seismic sources can be modeled as point, line, or area sources. In this investigation, the area source was adopted depending on Figures (1, 2, and 3), taking into consideration many previous studies of Al-Tarazi and Gruenthal (2003), Al-Tarazi (2005, 1994), El-Isa and Al Shanti (1989), Arieh and Rabinowitz, (1989), Garfunkel (1981). For the purpose of this study and depending on the above considerations to determine the seismic sources, 19 seismic area sources were identified and delineated as shown in Figure 4 and listed in Table 2. The influence of the seismic events located 300 km away from the study sites was considered negligible.

The seismic data was collected from several studies such as, USGS (2020), Al-Tarazi, (2003) Qadan, (1987), Jaradat *et al.*, (2008), Baaqeel *et al.*, (2016), Araya, and Armen, (1988) and Konstantinos *et al.*, (2019). The seismic events used in this study date back to 4000 years ago. Two types of data were collected, namely historical data from 31 BC until 1899

AD as shown in Figure 5 and data regarding instrumental earthquakes covering period from 1903 to 2019, specified in Figure 6.

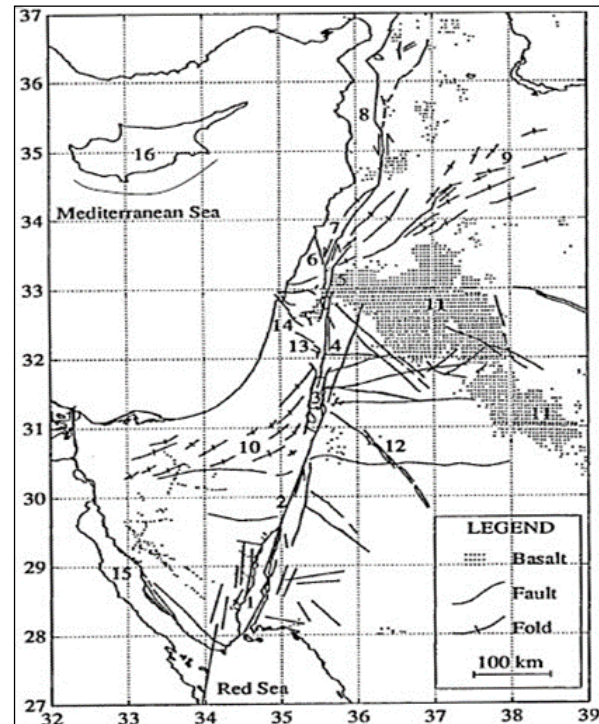


Figure 2. The Tectonic Map of Jordan and Vicinity. (1) Aqaba Gulf fault, (2) Wadi Araba fault, (3) Dead Sea Basin, (4) Jordan River Fault and Tiberias, (5) Rachaya Fault, (6) Ed Damur fault, (7) Yammounh Fault, (8) Ghab Fault, (9) Palmyra Fold Belt, (10) Levantine Fold Belt, (11) Wadi Sirhan Graben, (12) Karak-Fayha Fault, (13) Farah Fault, (14) Al Karmel Fault, (15) Suez fault, (16) Cyprus (after Al-Tarazi, 1992).

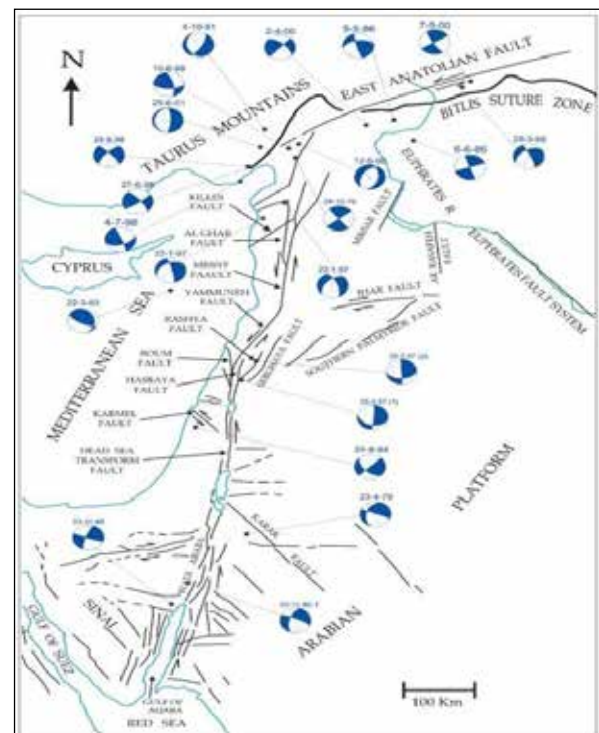


Figure 3. Summary of major fault zones of the northern Arabian plate (after Sbeinati *et al.*, 2005).

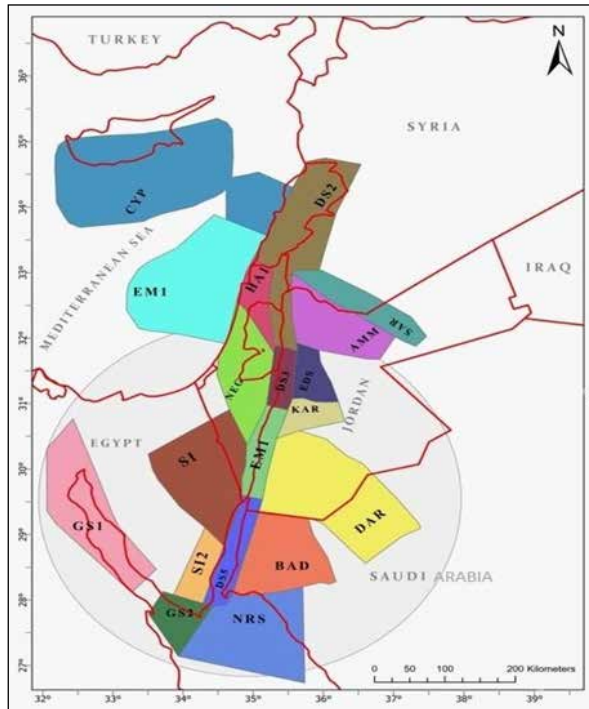


Figure 4. Area source model showing 19 seismic area sources delineated for the purpose of this study (Modified after Al-Tarazi and Gruenthal, 2003).

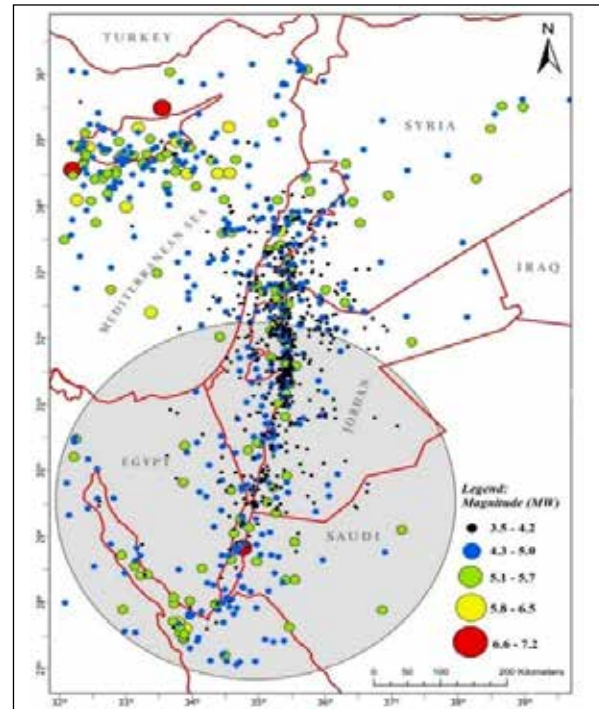


Figure 5. Epicenters of instrumental main earthquakes occurred in the JDST and around, during the period 1903 to 2019 and used in this study.

Table 1. Calculated Seismic Hazard Parameters for the 19 seismic sources.

No.	Source	a	b	β	λ_4	$M_{max} (M_w)$	Max. Focal depth (Km)	Min. Focal depth (Km)
1	Amman (AMM)	2.7787	0.7085	1.6311	0.88044	5.5	40	10
2	Eastern Gulf of Aqaba (BAD)	1.1315	0.4239	0.9760	0.2728	5.5	21	10
3	Cyprus (CYP)	3.7388	0.861	1.9825	2.4819	7	67	20
4	Southeast of Jordan (DAR)	3.1739	0.8183	1.8842	0.0035	5.5	39	10
5	Northern Dead Sea (DS2)	3.9613	0.9569	2.2033	1.3605	7.6	33	10
6	Dead Sea Basin (DS3)	4.5687	1.119	2.576	1.2376	7.6	33	10
7	Gulf of Aqaba (DS5)	2.379	0.6398	1.4732	0.6604	7.0	33	10
8	East Dead Sea (EDS)	1.5625	0.4437	1.0216	0.6133	5.5	10	10
9	Wadi Araba (DS4)	3.6411	0.9853	2.2687	0.5010	7.0	25	10
10	Suez Gulf-1 (GS1)	1.6516	0.5673	1.3062	0.2412	6.5	33	20
11	Suez Gulf-2 (GS2)	2.8141	0.7327	1.6871	0.7644	6.5	39	20
12	Haifa Zone (HA1)	3.4686	0.9331	2.1485	0.5447	5.5	22	10
13	Karak Zone (KAR)	4.9904	1.2041	2.7725	1.4928	5.5	20	10
14	Naqab Zone (NEG)	6.0801	1.5315	3.5264	0.8997	5.5	23	10
15	Sarhan Zone (SAR)	2.2645	0.7404	1.7048	0.2009	6	28	10
16	Central Sinai Zone (SI)	2.4457	0.6604	1.5206	0.6369	5.5	24	10
17	Eastern Mediterranean (EM1)	3.8114	0.9694	2.2321	0.8586	7.7	31	10
18	South Saini (SI2)	0.9833	0.4771	1.0985	0.1188	5.5	14	10
19	Northern Red Sea (NRS)	5.4217	1.269	2.9862	1.7143	6	26	10

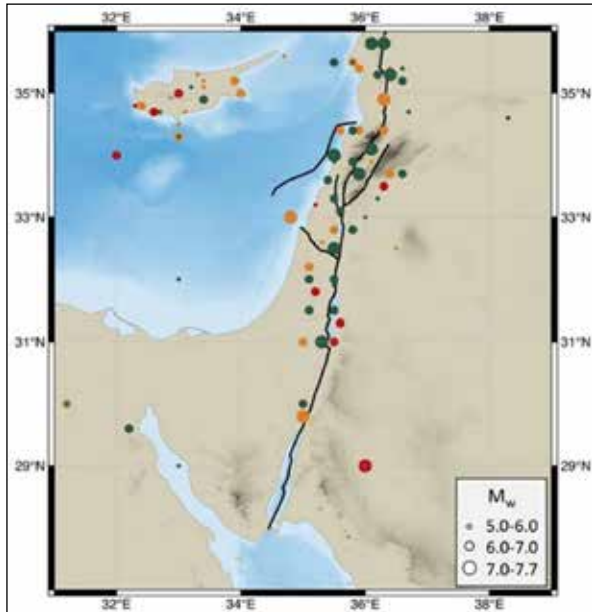


Figure 6. Map with all earthquakes with magnitudes $M_w \geq 5$ between 31 BC and 1900, inside our investigated zone (Gardner and Knopoff, 1974).

Gardner and Knopoff (1974). Clustering was used to remove the foreshocks and aftershocks from the data collected. An approximation of the windows sizes according to Gardner and Knopoff (1974) is shown in the following equations:

$$D_i = 10^{0.1238M + 0.983} \quad (1)$$

For $M \geq 6.5$

$$T_i = 10^{0.038M + 2.7389} \quad (2)$$

Else

$$T_i = 10^{0.5409M - 0.547} \quad (3)$$

Where D_i is a distance in Km and T_i is time in days.

Based on these equations, the size of the window for each magnitude interval is determined and listed in Table 2.

Table 2. Threshold values of distance (D_i) and time (T_i) for the identification of foreshocks and aftershocks following the window method approach (Campbell and Bozorgnia, 2014).

M_w	D_i (Km)	T_i (Days)
4.0-4.4	30	42
4.5-4.9	35	83
5.0-5.4	40	155
5.5-5.9	47	290
6.0-6.4	54	510
6.5-6.9	61	790
7.0-7.4	70	915
7.5-7.9	81	960
8.0-8.4	94	985

Based on this criterion, a software using MatlabTM was prepared to identify the main shocks of the earthquakes catalog used in this study. Additionally, alternative window parameter settings proposed by others of MatlabTM code (CORSSA Website; Al-Taani, 2011) were used (Campbell and Bozorgnia, 2014). The online supplement to this article provides codes written in Java as well as MatlabTM.

2.2 Probabilistic Seismic Hazard Assessment Model

The calculations of the seismic hazard procedures considered by this study are summarized in the following:

2.2.1 Linear Gutenberg -Richter relationship:

The frequency of the occurrence of earthquakes was determined by the linear Gutenberg-Richter relationship:

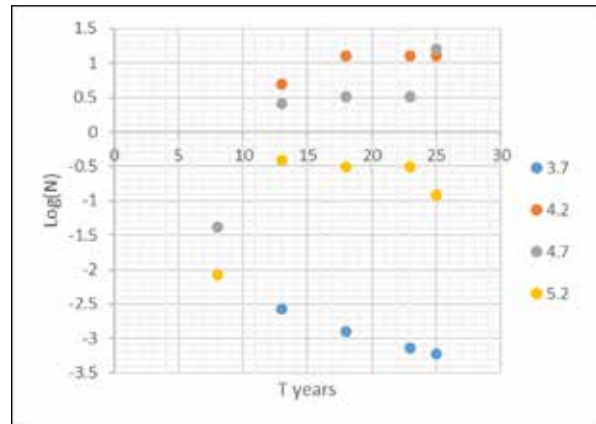
$$\log N(m) = a - bm \quad (4)$$

Where $\log$ is the logarithm, having a base of 10, $N(m)$ is the number of the shocks having magnitude equal to or greater than m . Over a given time interval, a and b are constants to be determined from the available data for the region using standard least squares method. Equation (4) can be rewritten as:

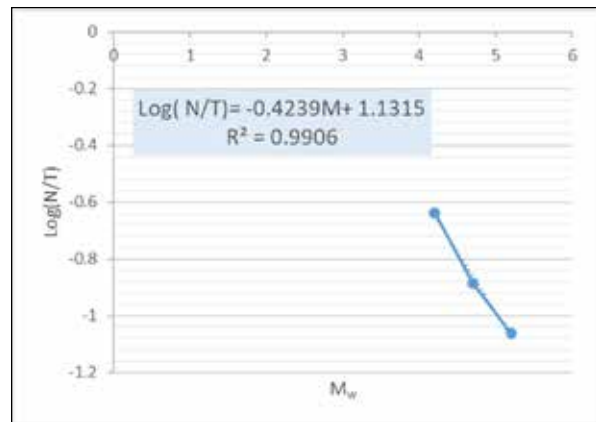
$$N(m) = e^{a - \beta m} \quad (5)$$

Where $a = a \ln 10$ and $\beta = b \ln 10$ (where $\ln$ is natural logarithm). To take into consideration the incompleteness of data in the prepared earthquake catalog, for the assessment of constants a and b and consequently α and β for all seismic sources, Stepp's method was adopted. The calculation sample for the Gulf of Aqaba seismic source is shown in Figure 7.

The same procedure was used to determine the parameter β for the nineteen seismic active sources delineated in this study as listed in Table 2.



(a) Variation of a number of earthquakes in a period.



(b) Gutenberg - Richter relationship

Figure 7. Stepps' Method Applied for Eastern Gulf of Aqaba Seismic Source.

2.2.2 Annual Rate of Seismic Activity:

In this study, the minimum earthquake magnitude considered for engineering interests is $M_w=4$. Thus, the number of main shocks exceeding magnitude 4 is taken as in the following:

$$\lambda 4 = e^{-4\beta} \quad (6)$$

2.2.3 Poisson's Distribution

Qadan (1987) showed that the occurrence of the main shocks of earthquake events is independent. In order to determine this, they used the X2 statistics test for the intendant of earthquake events, so Poisson's distribution is adopted using:

$$P(n, t) = \frac{\lambda t e^{-\lambda t}}{n!} \quad (7)$$

Where:

(n, t) = the probability of occurrence of n earthquakes in a time.

λ = the mean rate of earthquake occurrences per unit of time, which is generally taken as one year.

2.3 The maximum expected magnitude (Mmax):

The value of the maximum expected earthquake for each seismic source (Mmax) can be estimated using different methods. None of these methods is reliable, including the rupture length-magnitude and slip-magnitude relationships. So, in this research, (Mmax) was determined for each source depending on the utilized historical earthquake catalog. The maximum observed magnitude for each source was taken as the maximum expected magnitude. The minimum bound earthquake magnitude (Mmin) was selected in such a way that any earthquake below that magnitude is not of engineering interest or that the statistical data is not reliable and complete²³, which is equal to 4 for all seismic sources. Furthermore, the minimum and the maximum focal depth for each seismic source were determined and considered in the calculations of the hazard in this study as listed in Table 2. Depending on the above considerations, the seismic hazard parameters were calculated for each seismic source based on the data collected. The data was then checked, using the related equations mentioned above.

2.4 Attenuation Equation Models

Campbell and Bozorgnia (2014) investigated and developed a new ground motion prediction equation for the average horizontal components of PGA, PGV, and linear pseudo-absolute acceleration response spectra at 21 periods ranging from 0.01 s to 10 s corresponding to 5% damped. Furthermore, Darvasi and Agnon (2019) calibrated a new attenuation curve for the Dead Sea region using surface wave dispersion surveys in sites damaged by the 1927 Jericho earthquake.

To select a suitable attenuation equation for the seismic hazard analysis, the researchers referred to the collection of ground motion prediction equations by Douglas *et al.*, (2006). The most suitable attenuation equations in this region are already utilized in the studies of Abrahamson and Silva (2008; 2009), Boore, and Atkinson (2008), in terms of Peak Ground Acceleration (PGA). The choice of these two

equations is due to the following reasons:

- They took into consideration the engineering soil profile by considering the shear wave velocity Vs30 which is adopted in the international building codes.
- The equations are applicable for the Mw range of 5 to 8.5 strike-slip faults, including the maximum earthquakes considered in this study (Table 2).
- The actual peak ground acceleration $Y_a=N1Y$, where Log N1 is a random variable normal distribution with a mean value of zero and standard deviation ranging from 0.5 to 1.05 (Araya, and Armen, 1988).

The final step in the seismic hazard analysis is to calculate the seismic hazard for the area under consideration using the area source model (Paz and Leigh 2004).

$$P(Y > y) = \sum_{i=1}^n \frac{v_i}{v} \iint_{MR} P(Y > y|m, r) f_{R|M} dr f_M(m) dm \quad (8)$$

$$T_y = \frac{1}{vP(Y>y)} \quad (9)$$

Where $P[Y>y]$ is the probability that a random site peak ground acceleration (Y) at the site will exceed a certain acceleration (y) and T_y is the return period of a certain acceleration y. Given the location (r) and the closest length of rupture (R), the nearest distance from the rupture to the site is calculated. Integration over m, r, and y gives the total probability that Y will be exceeded due to a single event of random variables M, R, and Y.

3. Results and Discussion

The resulting hazard parameters are listed in Table 2 shown below. The maximum expected magnitude (Mw) values are also given along with the maximum and minimum focal depth (km).

3.1 Peak Ground Acceleration (PGA)

Most districts of Aqaba have soil profiles of hard rock (SA) or stiff soil (SD) as reported by ASEZA (2010) and shown in Fig. 8 and Table 3. This classification is based on Jordan National Building Code for Seismic Resisting Design (JBC). The shear wave velocity for soil profiles of SA and SD ranges between 760 to 1500 m/s and 180 to 360 m/s respectively. Another parameter is the thickness of the sediments covering the bedrock (Z1). Physically, Z1 represents the depth at which the shear wave velocity equals 1000 m/s. Z1 value is zero for the hard rock site profile and 600 m for the stiff soil site profile (Table 3). Site E is selected to represent the rest of the sites due to its important location as it represents the center of the city.

The analysis which is carried out based on the seismicity parameters of seismic sources is shown in Fig. 4 and Table 2. Two attenuation equations were used to evaluate the seismic hazard (Boore and Atkinson, 2008; Yucmen, 1977) for the nine sites representing different areas in Aqaba (Figure 5). Their coordinates and soil profile properties for each site are listed in Table 3. A software EZ FRISK was used for this purpose. The results of the analysis indicate that the average values of the PGA are closer to Abrahamson and Silva's (2009) attenuation equation.

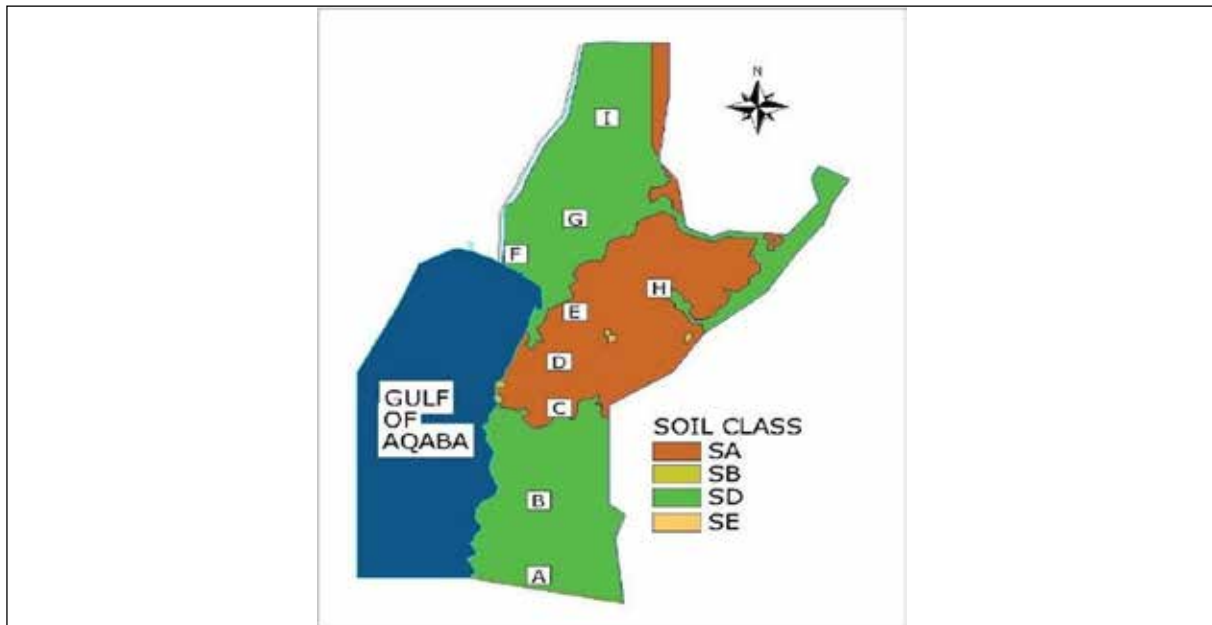


Figure 8. The soil profile classification and distribution in Aqaba city and around (SA: Hard rock, SB: Rock, SD: Stiff soil profile, and SE: Soft soil profile). (A-I) are the locations of the nine sites studied.

Table 3. Coordinates and soil profile properties of the nine studied sites in Aqaba and its vicinity.

Site	Latitude	Longitude	Soil Profile	C_a	C_v	V_{s1}	Z_{11}	V_{s2}	Z_{12}
A	29°21'57.58"N	34°58'27.77"E	SD	0.28	0.4	270	600	760	0
B	29°24'59.39"N	34°58'45.55"E	SD	0.28	0.4	270	600	760	0
C	29°28'50.47"N	34°59'23.72"E	SA	0.16	0.16	760	0	NA	NA
D	29°30'33.69"N	34°59'59.20"E	SA	0.16	0.16	760	0	NA	NA
E	29°32'10.23"N	35° 0'24.67"E	SD	0.28	0.4	270	600	760	0
F	29°32'34.83"N	34°58'58.44"E	SD	0.28	0.4	270	600	760	0
G	29°34'6.94"N	34°58'59.36"E	SD	0.28	0.4	270	600	760	0
H	29°33'3.83"N	35° 1'30.06"E	SA	0.16	0.16	760	0	NA	NA
I	29°36'29.56"N	35° 1'6.53"E	SD	0.28	0.4	270	600	760	0

Where: C_a is the acceleration coefficient according to the UBC-97 code. C_v is the velocity coefficient according to the UBC-97 code. V_{s1} and V_{s2} are the seismic shear wave velocities at different depths in m/s and represent soil profiles of SA and SD respectively. Z_{11} and Z_{12} are the depth at which the shear wave velocity is equal to 1000 m/s corresponding to V_{s1} and V_{s2} respectively.

A sample of the resulting hazard curves is shown in Figures 9 and Figure 10. It was observed that the PGA in Aqaba ranges from 0.3g to 0.4g corresponding to a return period of 475 years. Furthermore, Table 4 lists the results taken from the derived curves showing the return period corresponding to PGA for different soil profiles, where the PGA values for the SD profile are higher than that of the SA profile for site E. Furthermore, the present study covers a wider range of PGA in the comparison done by Qadan (1987). This is due to more refined input data.

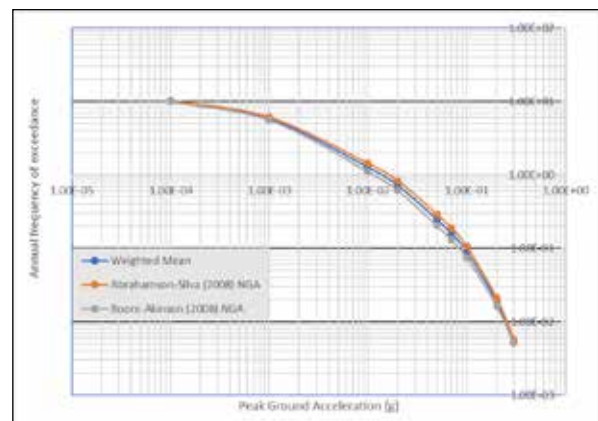


Figure 9. Total mean hazard of average horizontal component of Peak Ground Acceleration (weighted average) for site E in Aqaba, compared to Abrahamson and Silva (2009), and Boore and Atkinson (2008), attenuation equations results.

Table 4. Calculated PGA of site E at the center of Aqaba city.

Probability of Exceedance (return period)	PGA (g), $V_s=270$ m/s, $Z_1=600$ m	PGA (g), $V_s=760$ m/s, $Z_1=0$
10% (475 years)	0.3	0.4
5% (975 years)	0.4	0.45
2% (2475 years)	0.5	0.52

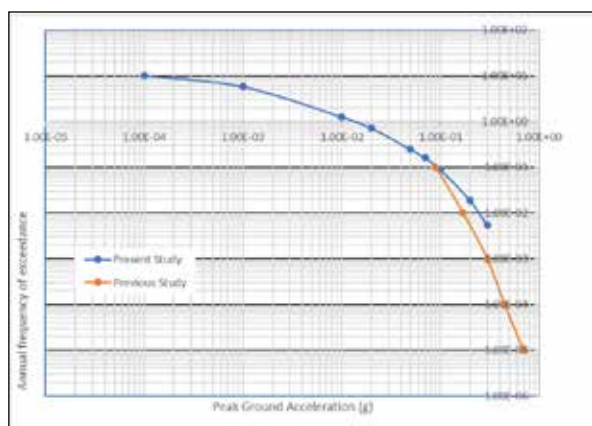


Figure 10. Comparison of this study to Qadan study (1987).

3.2 Response Spectra Curves for Aqaba City

Originally, the derivation of response spectra curves is performed by calculating the response excitation of single degree of freedom system, which depends on the strong motion records of major earthquakes (JBC, 2005). Moreover, the international building codes derive the response spectra by assessment of PGA using the seismic hazard analysis (corresponding to return period of 475 years) in relation to the soil profile type. Usually, seismic response spectra curves are used in the international building codes for seismic design of engineering structures for return period of 475 years (10% of being exceeded in 50 years). Other curves of different return periods are used for more important facilities like dams and nuclear power plants. A further set of results of this study was calculated for response spectra curves for 5% damping, corresponding to different return periods of 475, 975, and 2475 years, for the nine selected sites. A sample of these resulted curves is shown in Figure 11.

The response spectra curves for Aqaba city based on JBC for seismic design are shown in Figure 12. These curves are originally based on $PGA = 0.2g$ (Zone 2B) which correspond

to a return period of 475 years as derived from Jordan zoning map, and soil profiles of SA and SD.

Table 5 compares the Spectral Acceleration of this study (Figure 11) and the corresponding values for Aqaba based on JBC (Figure 12) for spectral periods 0, 0.2, and 1 second. The values are very close except for the spectral acceleration corresponding to 1 second, which is 33% more than JBC (2005) value. This difference may be due to refined and updated input data used in the analysis of this study considering the site effects of the studied area. Figure 13 shows the comparison of response spectra of the present and the JBC (2005) code for Site E.

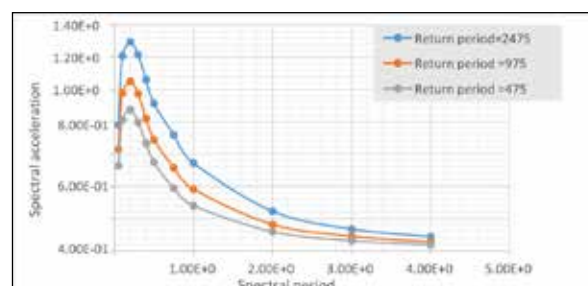


Figure 11. Calculated Response Spectra of average horizontal component acceleration for 5% damping for return periods of (475, 975, and 2475 years) for site E.

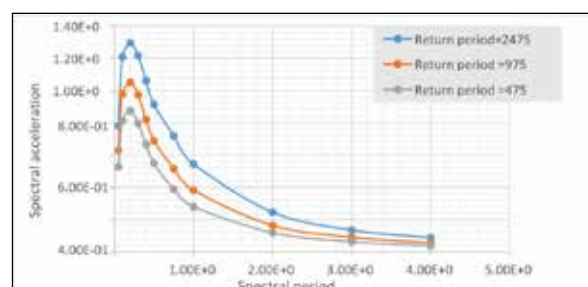


Figure 12. Response Spectra for different soil profiles at Aqaba city (zone 2B) as per JBC (2005).

Table 5. Spectral acceleration results of the values investigated sites within the study area compared to those listed in the national building code (JBC 2005).

Site	Soil Profile	SA @ t=0 s	SA @ t= 0.2s	SA @ t= 1s	PGA (475 years)
A	SD	0.35	0.87	0.21	0.35
B	SD	0.35	0.8	0.20	0.35
C	SA	0.35	0.75	0.20	0.35
D	SA	0.35	0.75	0.20	0.30
E	SD	0.40	0.86	0.30	0.35
F	SD	0.30	0.75	0.20	0.3
G	SD	0.35	0.70	0.14	0.35
H	SA	0.30	0.75	0.15	0.3
I	SD	0.35	0.70	0.15	0.35
JBC for Aqaba	SD	0.30	0.70	0.40	0.20
JBC for Aqaba	SA	0.16	0.40	0.17	0.20

As shown in Figure 13, the higher mode of acceleration for the derived curve is less than the JBC response spectra. On the other hand, the fundamental acceleration in the derived response spectra is more than that of the JBC code. Spectral acceleration range for current study is (0.3-0.86) g, while it is (0.4-0.7) g for JBC code. Moreover, high frequency

resulted from some earthquakes, produces high acceleration. For more study that is refined using logic tree structure will estimate more realistic output and consequently more refined response spectra curves.

In the design of multistory buildings, the design is mostly controlled by dynamic analysis. In this case, for higher

modes, the spectral acceleration is less than the fundamental mode acceleration.

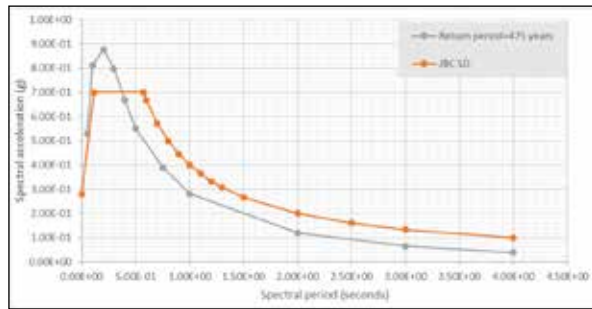


Figure 13. Comparison of response spectra of this study and the JBC (2005) code for Site E

Figure 14 shows a proposed response spectrum for a combination of the results of this study and the JBC curve.

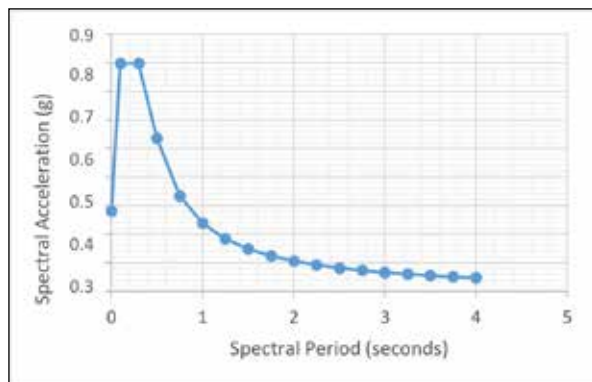


Figure 14. Proposed Response Spectra for Site E.

A set of response spectral curves are prepared for Aqaba city (north coast) using data collected from Nuweiba earthquake 1995 $M_w=7.1$ (Al-Tarazi, 2000) that affected Aqaba city for different soil profiles (results shown in Figure 10). The spectral acceleration values obtained from Figure 10 equaling 0.13 g are generally in agreement with the readings of the shoreline strong motion stations for the 1995 earthquake (0.16 g) (Al-Tarazi, 2000). The slight difference is due to the location accuracy of the strong motion station, which recorded the event. Furthermore, Fig. 15 and Table 6 also show the response spectra of three soil profiles S1 (Rock and stiff soil), S2 (Deep cohesion less or stiff clay soils), and S3 (Soft to medium clays and sands). The period of the peak spectral acceleration S1 is smaller than that of the same value for soil profiles S2 and S3. This phenomenon helps in the structural design of buildings to resist major earthquakes.

Table 6 lists the spectral acceleration values for different spectral periods (0.0, 0.2 and 1.0 second) from Figure 8, for site E. Moreover, these values are compared to the response spectra acceleration values, which are determined for Gulf of Aqaba earthquake (Figure 15).

It is noted that the spectral acceleration values at the critical points (i.e., $t=0.0$, 0.2, 1.0 second) are less than the current study values. This is due to the calculation of spectral acceleration in this study which is based on many seismic sources and wide range of earthquake data. Therefore, the results of this study are expected to be more realistic compared to the calculations of Nuweiba earthquake of 1995.

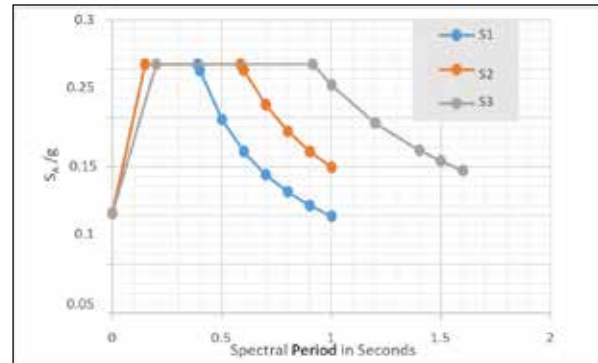


Figure 15. Response Spectra for Nuweiba earthquake 1995 for different soil profiles at the coastline.

Table 6. Comparison between the spectral acceleration of this study for site E with the effects of the Nuweiba earthquake 1995.

Site	Soil Profile	S_A at $t=0$ s	S_A at $t=0.2$ s	S_A at $t=1$ s
E (This Study)	SD	0.40	0.86	0.3
1995 ($M_w=7.1$)	S1	0.1	0.25	0.15
	S2	0.1	0.23	0.1
	S3	0.1	0.25	0.23

4. Conclusion

The results of this study could be summarized as follows:

- 1- The PGA value for 10% of being exceeded in 50 years (475 years return period) is (0.3-0.4) g. Meanwhile, the PGA for JBC for earthquake loads is 0.2g only (i.e., JBC is underestimating the seismic hazard).
- 2- The PGA value of 5% which is being exceeded in 50 years (975 years return period) is in the range from (0.45 to 0.50) g, while for 2% which is being exceeded in 50 years (2475 years return period) is in the range from (0.56 to 0.6) g.
- 3- The results of response spectra for soil profile SA for site E for spectral periods 0, 0.2, and 1 second are 0.3g, 0.7g, and 0.2 g, respectively.
- 4- The results of response spectra for soil profile SD for site E for spectral periods 0, 0.2, and 1 second are 0.35g, 0.79g, and 0.2 g, respectively.
- 5- The response spectra for the rest of the studied sites of the spectral period zero range between (0.3 to 0.4) g, for a spectral period 0.2-second range (0.7 to 0.87) g, and spectral period 1-second range (0.15 to 0.21) g.
- 6- The JBC response spectra for soil profile SA for spectral periods 0, 0.2, and 1 second is 0.17g, 0.4g, and 0.16g respectively, while for soil profile SD for spectral periods 0, 0.2, and 1 second are 0.3g, 0.7g, and 0.4g respectively.

Conflict of Interest

The authors declare no conflict of interest.

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Effect of Different Olive Mill Wastewater Treatments on Seed Germination

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Abstract

Untreated olive mill wastewater (OMW) has generally detrimental effects on seed germination. In the present study, the effect of treated OMW by filtration using some different media types on the germination of barley was investigated. Ten media types with a depth of 0.5 m were used. All media types, except hay and sawdust, increased the low pH value of OMW. The highest pH values and the lowest turbidity values were obtained when (rubber and zeolite) were used as filter media. The best removal efficiencies of COD and phenols were obtained in (rubber and clay loam) and (zeolite) filters, respectively. Untreated OMW has completely prevented the germination and the growth of the seedlings. However, treated OMW, using column filters of clay loam, loamy sand, rubber granules, zeolite, and rubber and zeolite mixtures, improved the germination percentage and seedling growth especially effluent generated from clay loam and loamy sand soil filters.

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Keywords: Wastewater reuse, Land application of OMW, Filtration, Industrial wastewater, Barley germination.

1. Introduction

Olive mill wastewater (OMW) is the main residual product of the olive oil industry, and its disposal may cause many environmental problems, especially in Mediterranean countries, where olive oil production is large and concentrated in a short time. If not managed properly, OMW may cause soil and water contamination, which may affect human health and the environment. About 30 million m³ of OMW is generated worldwide (mainly in the Mediterranean region) every year from olive oil production (Niaounakis and Halvadakis 2006).

OMW effluent is rich in nutrients such as organic matter, N, P, K, and Mg, which are favorable for agriculture (Mechri et al., 2011) in addition to water content (Ammar et al., 2005). In semi-arid areas, soils usually have a deficiency in nutrients and organic matter content (Garcia et al., 1994). OMW contains various phenolic compounds, which have antimicrobial and phytotoxic effects (Hachicha et al., 2009). The Polyphenolic fraction is gradually degraded in soil with time and is partially transformed into humic substances. Thus, polyphenol degradation and incorporation into the soil humic fraction depend on environmental conditions (Sierra et al., 2007).

The direct application of organic fertilizers to cropland is the most common method nowadays (Mekki et al., 2006; Ben-Rouina et al., 1999). Adding OMW to cropland as irrigation water in the Mediterranean countries will balance both water shortages and low soil fertility. Many studies pointed out the beneficial effects of spreading fresh OMW, stored or treated, on the cultivated soil (Ayoub et al., 2014),

emphasizing the positive effects of utilization of OMW in agriculture..

Crop response to OMW application is variable. For example, olive fruit yields and quality were not affected by the OMW application (Chartzoulakis, et al, 2010). Ryegrass and proteic pea yields were increased with untreated OMW application, whereas clover yield was negatively affected (Montemurro et al., 2011). In another study, maize growth was not affected, while plant stress parameters increased following the application of untreated OMW (Belaqziz et al., 2008). Hanifi and El Hadrami (2008) found an increase in maize yield following moderate and progressive OMW application. Al-Tabbal and Al-Zboon (2019), used olive mill cake along with stone-cutting sludge as a soil amendment. They found that the addition of olive cake negatively impacted the growth of maize. However, the addition of stone-cutting sludge to olive mill cake on clayey soil resulted in an improvement in maze growth parameters. Germination problems were also observed due to the phytotoxic effects of the phenolic compounds contained in the OMW (Mekki, et al, 2007; Massoudinejad, et al, 2014).

Several treatment methods have been used to treat OMW. These methods include advanced oxidation processes (Alrousan, 2021; Al-Bsoul et al., 2020), anaerobic and aerobic biological treatment (Shabir et al., 2023; Ammary, 2007), liquid extraction, filtration, flotation, adsorption, flocculation, coagulation, dilution, centrifugation electrohydrolysis, electrocoagulation, photocatalytic membrane reactor, Fenton and Fenton-like processes, combustion, pyrolysis, co-digestion and composting (Al-

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Hmoud et al., 2020; Shabir et al., 2023). Ojodale et al. (2022) used bacteria and fungi for the bioremediation of cassava, cocoa, and palm oil industry effluents. They found that bioremediation represents a promising method for the bioremediation of these effluents.

The present study evaluated the effect of treated OMW on barley germination. OMW was treated using filtration. Different filter media were used and the results were compared.

2. Material and Methods

A germination experiment was conducted to determine the effects of OMW generated from various filters at Al-Huson University College. Twenty seeds of barley were sterilized with sodium hypochlorite solution (Khan et al., 1992) and, after drying, were grown on Petri dishes that contained a double layer of filter paper. Ten ml of OMW taken from the effluent of various filters were placed on each petri dish. The filter paper was changed daily to prevent contamination. The seeds were supported to sprout at $26^{\circ}\text{C} \pm 1^{\circ}\text{C}$ for 10 days. The seeds were considered as germinated seeds when radicle reached 2 mm long.

2.1 Experimental layout

OMW effluent, taken from various filters with different media (zeolite, hay, pomace, rubber, clay loam soil, loamy sand, fruit peel, sawdust, coal, and rubber + zeolite), in addition to control (tap water), were used for the germination experiments. Figure 1 shows the various filters used for

OMW treatment with different media types and depths. Each germination experiment was made in triplicate.

2.2 Germination Parameter Measurements

The number of germinated seeds was recorded daily from the beginning of the experiment until the 10th day when the germination process was assumed to be completed. At the end of this experiment, shoot and root, lengths were measured and, then, the roots and shoots were separated from the seeds, and their weights were taken separately using the digital balance. The ratio of root to shoot was also calculated from the data obtained. The germination percentage at the end of the experiment was calculated by dividing the number of germinated seeds by the total number of used seeds using the formula below (Al-Tabbal and Al-Zboon, 2019):

$$\text{Germination Percentage} = \frac{\text{Number of germinated seeds}}{\text{Total number of seeds}} \times 100\%$$

Germination speed index, relative germination rate, and germination energy were also calculated. (Al-Tabbal and Al-Zboon, 2019):

$$\text{Germination Speed Index} = \frac{Gt}{Dt} \quad (1)$$

$$\text{Relative Germination Rate} = \frac{a}{b} \quad (2)$$

where

Gt: germinated seed in time days

Dt: the number of germination days

a: germinated percentage of treatment

b: germination percentage of control.

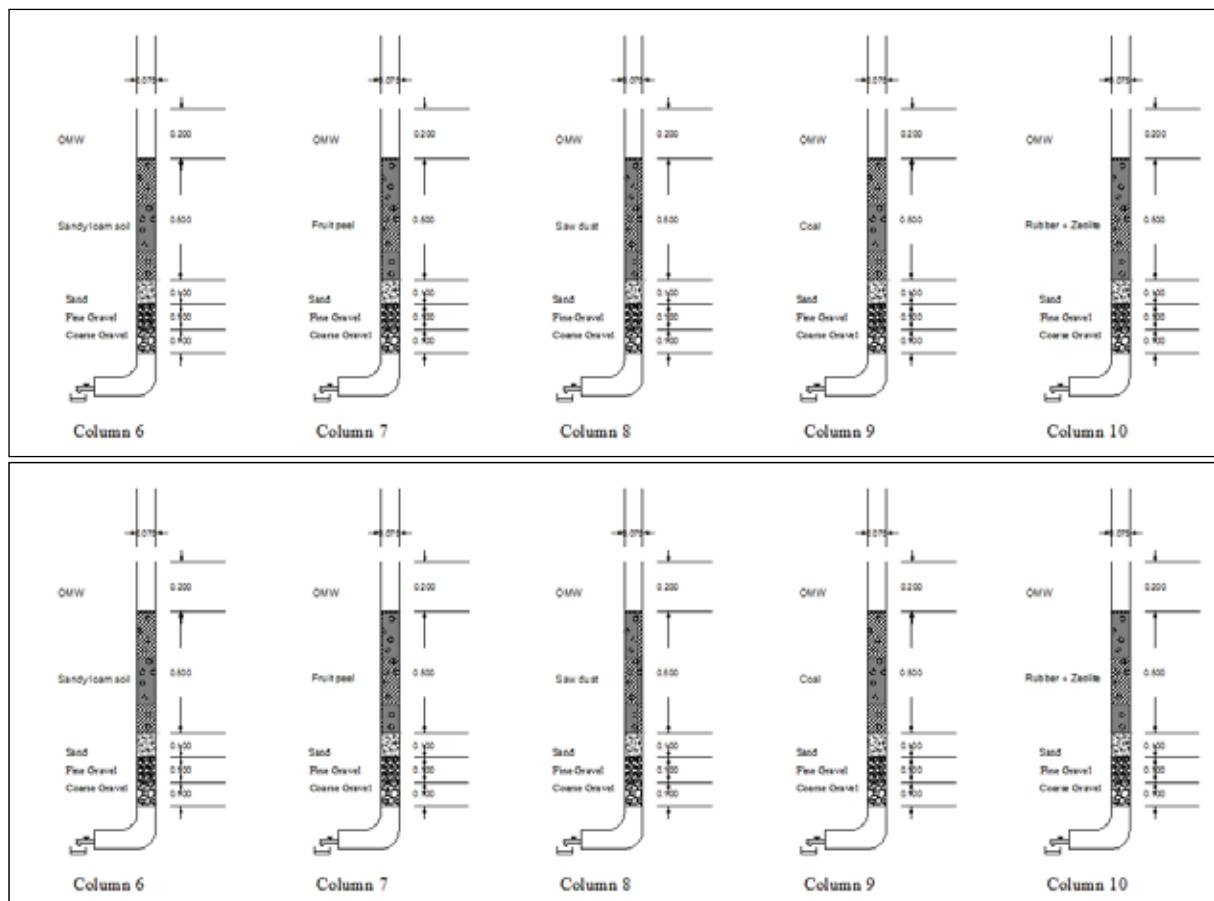


Figure 1. Schematic of experiment layout.

All columns filter from bottom: coarse gravel (10 cm), fine gravel (10 cm), sand (10 cm), filter media (50 cm), and then 20 cm of OMW. Column diameter = 7.5 cm.

Column #1: Zeolite, Column #2: Hay, Column #3: Pomace, Column #4: Rubber, Column #5: Clay loam soil,
Column #6: Loamy sand soil, Column #7: Fruit peel, Column #8: Saw dust, Column #9: Coa, Column #10: Rubber + Zeolite

$$\text{Germination Energy} = \frac{a}{b} \quad (3)$$

where

a: total germinated seed in OMW in fourth days

b: total number of seeds to germinate

The germination rate was measured using mean germination time (Younsheng and Sziklai, 1985).

At the end of the experiment, the promptness index (PI) and various stress tolerance indexes including germination stress tolerance indexes (GSTI), shoot length stress tolerance indexes (SISI) (%), root length stress tolerance indexes (RLSI) (%), shoot dry weight stress tolerance indexes (SDSI) (%), root dry weight (RDSI) (%), and seedling vigor index (SVI) (%) were estimated using the following formulas (Al-Tabbal and Al-Zboon, 2019):

$$\text{Promptness Index (PI)} = \text{nd}2(1) + \text{nd}4(0.75) + \text{nd}6(0.5) + \text{nd}8(0.25) \quad (4)$$

where nd2, nd4, nd6 and nd8 = Number of seeds germinated on the 2nd, 4th, 6th and 8th day, respectively.

$$\text{Germination Stress Tolerance Index (\%)} = \frac{\text{PI of Stressed Seeds}}{\text{PI of Control Seeds}} \times 100\% \quad (5)$$

$$\text{Shoot length Stress Index (\%)} = \frac{\text{shoot length of stressed plant}}{\text{shoot length of control plants}} \times 100\% \quad (6)$$

$$\text{Root length Stress Index (\%)} = \frac{\text{Root length of stressed plant}}{\text{Root length of control plants}} \times 100\% \quad (7)$$

$$\text{Shoot dry weight Stress Index (\%)} = \frac{\text{shoot dry weight of stressed plant}}{\text{shoot dry weight of control plants}} \times 100\% \quad (8)$$

$$\text{Root dry weight Stress Index (\%)} = \frac{\text{root dry weight of stressed plant}}{\text{root dry weight of control plants}} \times 100\% \quad (9)$$

$$\text{Seedling vigour index} = \text{germination percentage} \times \text{seedling length} \quad (10)$$

$$\text{Seedling length} = \text{shoot length} + \text{root length}$$

Measurements were analyzed with SAS program for data analysis using statistical analyses with analysis of variance and the means were compared using LSD ($P < 0.05$) (SAS, 2004).

3. Results

A germination experiment was conducted to determine the effects of OMW generated from various filters at Al-Huson University College. Twenty seeds of barley were sterilized with sodium hypochlorite solution (Khan et al., 1992) and, after drying, were grown on Petri dishes that contained a double layer of filter paper. Ten ml of OMW taken from the effluent of various filters were placed on each petri dish. The filter paper was changed daily to prevent contamination. The seeds were supported to sprout at $26^\circ\text{C} \pm 1^\circ\text{C}$ for 10 days. The seeds were considered as germinated seeds when radicle reached 2 mm long.

The characteristics of treated and untreated OMW are summarized in Table 1.

Table 1. Physicochemical Properties of Treated and Untreated OMW Using Filters Filled with Various Materials.

Parameter	Unit	Untreated OMW	OMW generated from various filters								
			Clay Loam soil	Zeolite + Rubber	Saw dust	Rubber	Hay	Zeolite	Loamy Sand soil	Pomace	Coal
EC	dS/m	10.5	6.08	7.3	6.7	5.5	4.7	5.9	6.5	6.5	6
pH		4.22	5.72	5.2	4.5	5.95	4.34	5.8	5.6	5	4.7
Turbidity	NTU	14420	6380	4120	11300	4270	5300	4215	8120	*	*
TSS	mg/l	23.8	19.3	21.2	23.1	*	*	15.8	*	*	*
COD	g/l	44.8	10	16.8	35	10	25	19.7	12.5	29	31
Phenol	g/l	8.2	4.6	5.6	6.7	5.3	6.2	4.5	4.8	6	6.1

* Not measured

Table 1 shows that untreated OMW is an acidic waste. Utilizing various materials in the filters to filter OMW increased the pH of OMW, compared to untreated water except for hay and sawdust filters. The highest pH values were obtained by rubber and zeolite filters followed by loamy sand and clay loam soil. Untreated OMW has the highest value of EC (10.5), followed by the waste generated from rubber + zeolite while the lowest value was obtained from hay filter. Turbidity was the highest for untreated olive wastewater followed by sawdust while the lowest turbidity was obtained from zeolite + rubber. The COD values were the highest for the untreated OMW, while the lowest COD was obtained from rubber and clay loam filters followed by sandy soil. Phenols were the highest for the untreated OMW while the lowest value was obtained by zeolite followed by clay loam soil then loamy sand soil.

3.1 Effects of Irrigation with Treated OMW with Various Materials on Germination

The present study was conducted to decide the impacts of irrigation with OMW, treated with various low-cost filters on germination and seedling establishments of barley. The results indicated that the investigated traits after irrigation with different treated OMW were significantly ($P < 0.01$) different. The highest germination percentage was recorded

after irrigation with tap water (96.7%) compared to 66.7%, 25%, 23%, 18%, 16%, 8.4%, 6.7%, and 5% after irrigation with OMW that was filtered with clay loam, rubber, loamy sand, rubber+ zeolite, pomace, fruit peel, zeolite, and coal, respectively (Figure 2).

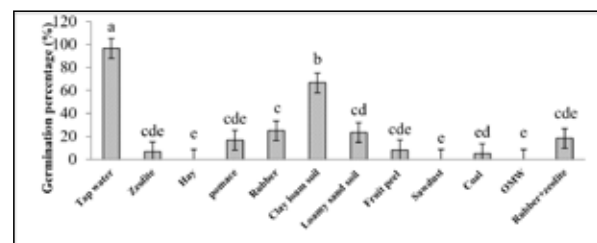


Figure 2. Germination percentage of barley seeds irrigated with treated OMW.

Irrigation with olive oil wastewater filtered with hay and sawdust without filtration led to the failure of the process of germination.

Relative germination rate (Figure 3) was also significantly different within the treatments. The relative germination rate was higher in tap water (1) than it is in the other treatments. The lowest relative germination rate was observed after irrigation with OMW and OMW filtered with either hay or sawdust filter.

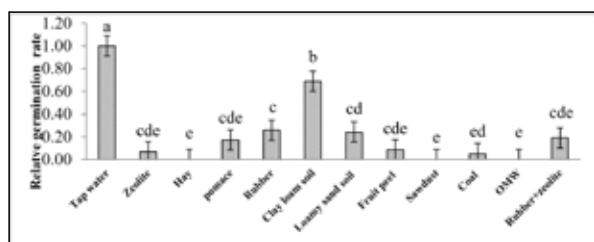


Figure 3. Relative germination rate of barley seeds irrigated with treated OMW.

The germination speed index (Figure 4) was significantly different within the olive oil mill wastewater treatments where the highest speed index was scored by tap water (22.44) compared to 12.46%, 7.65%, 5.25%, 5%, 4.95%, 3.5%, 3%, 2.71% after irrigation with OMW that was filtered with clay loam soil, rubber, loamy sand soil, pomace, rubber + zeolite, fruit peel, zeolite and coal, respectively.

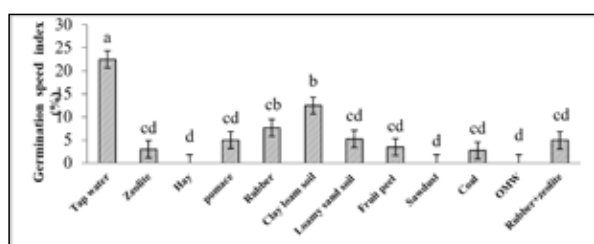


Figure 4. Germination speed index of barley seeds irrigated with treated OMW.

Significant effects of the different types of treated OMW resulted from the filtration process on morphological parameters in the seedling stage. The results indicated that the OMW produced from clay loam filters scored the highest shoot length (Figure 5) as well as root lengths (7.55 and 10.40 cm, respectively) (Figure 6) among the various filtrated OMW. These values were not significantly different from tap water (7.59 and 10.56 cm, respectively). Although they scored lower values than clay loam filters did, there was no significant differences between shoot length of seeds, irrigated with OMW and produced from rubber, loamy sand, rubber + zeolite, fruit peel, and pomace filters. These were, however, significantly higher than shoots irrigated with OMW filtered with coal, hay, sawdust, or without filtration.

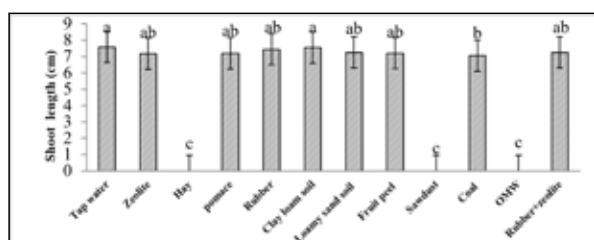


Figure 5. Shoot length of barley seeds irrigated with treated OMW.

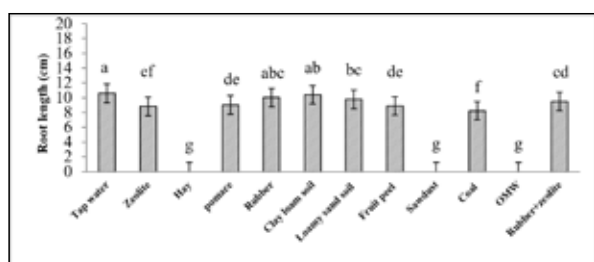


Figure 6. Root length of barley seeds irrigated with treated OMW.

The significant effect of filtered OMW on shoot and root length was reflected on the shoot dry weight (SDW) (Figure 7) and root dry weight (RDW) (Figure 8). The impact of various filtration media was highly significant on the shoot and root dry weight. OMW, discharged from clay loam, rubber, loamy sand, coal, zeolite and mixture of rubber and zeolite filters, scored the highest shoot dry weight that was not significantly different from tap water. The root dry weight was significantly different from the other filter media treatments ($p = 0.05$).

OMW, discharged from clay loam and rubber filters, produced the highest root dry weights, which were not significantly different from tap water.

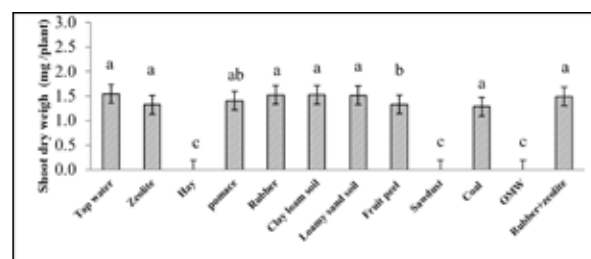


Figure 7. Shoot dry weight of barley seeds irrigated with treated OMW.

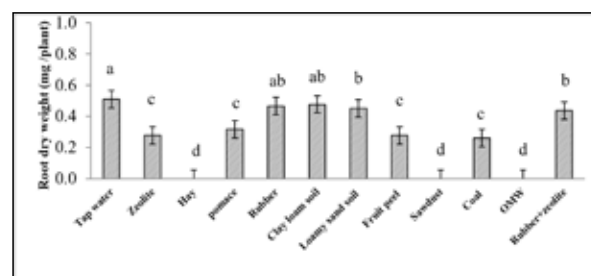


Figure 8. Root dry weight of barley seeds irrigated with treated OMW.

Root to shoot dry weight was variably affected by OMW, discharged from various filters. It was indicated that OMW, discharged from clay loam and rubber, gave the highest root to shoot ratio that has insignificant difference from tap water (Figure 9).

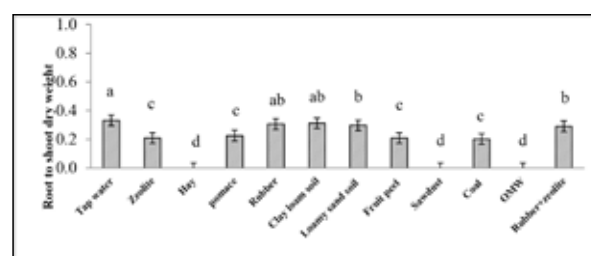


Figure 9. Root to shoot dry weight of barley seeds irrigated with treated OMW.

The percentage of decrease in germination energy is a useful parameter to assess the negative effect of waste containing phenol compound on seed germination. Germination energy was severely damaged for seeds irrigated with untreated OMW as well as for seed irrigated with treated OMW and contained high quantity of phenol compound. OMW, treated with clay loam, gives the highest germination energy after the control while OMW, generated from sawdust and hay filters, gave the lowest germination

energy (figure 10). Promptness Index (Figure 11) was calculated to estimate germination stress tolerance index (identify the negative type of treated OMW on seeds) (Figure 12). Germinated seeds, irrigated with OMW and generated from clay loam soil, produced highest promptness index and germination stress tolerance index after the control (Tap water) while seeds, irrigated with untreated OMW or treated by sawdust and hay filters, gave the lowest values.

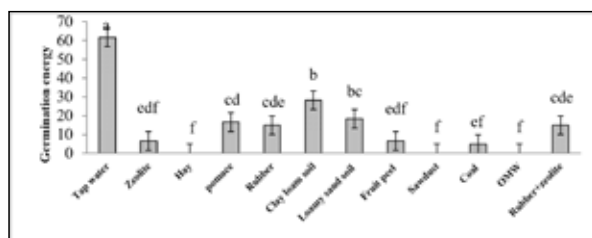


Figure 10. Germination energy of barley seeds irrigated with treated OMW.

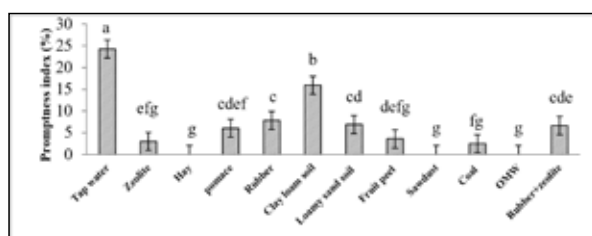


Figure 11. Promptness index of barley seeds irrigated with treated OMW.

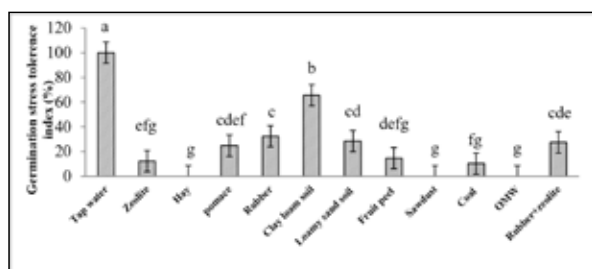


Figure 12. Germination stress tolerance index of barley seeds irrigated with treated OMW.

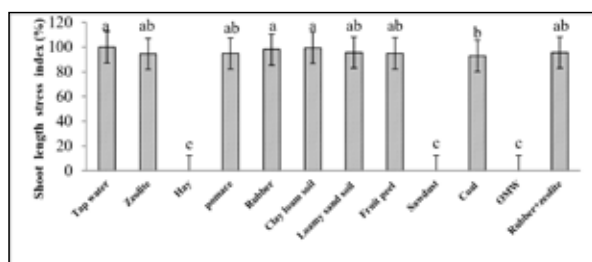


Figure 13. Shoot length stress index of barley seeds irrigated with treated OMW.

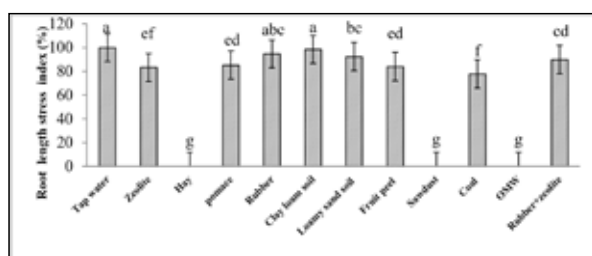


Figure 14. Root length stress index of barley seeds irrigated with treated OMW.

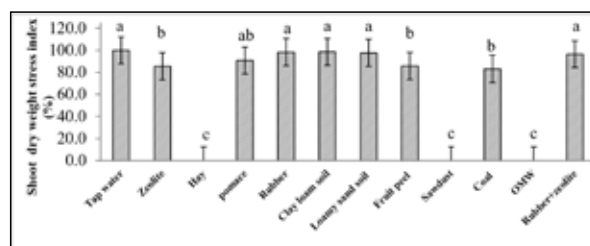


Figure 15. Shoot dry weight stress index of barley seeds irrigated with treated OMW.

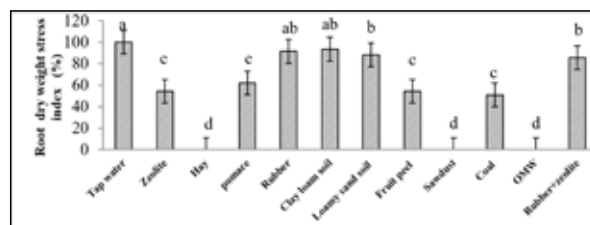


Figure 16. Root dry weight stress index of barley seeds irrigated with treated OMW.

It was found that there were significant ($P < 0.05$) differences between treatments on the shoot and root dry index (Figures 15 and 16). The highest values were observed for seeds irrigated with tap water followed by OMW generated from filters containing clay loam soil, rubber, sandy soil, and rubber + zeolite while the lowest value were obtained for untreated wastewater as well as for OMW generated from sawdust filter and hay filter. Results represented in Figure 17 showed that the seedling vigour index was the highest for the control treatment followed by olive oil mill wastewater generated from clay loam filter. The lowest seedling vigor index value was observed for the untreated OMW treatment as well as for OMW generated from hay and sawdust followed by coal filter and zeolite filter.

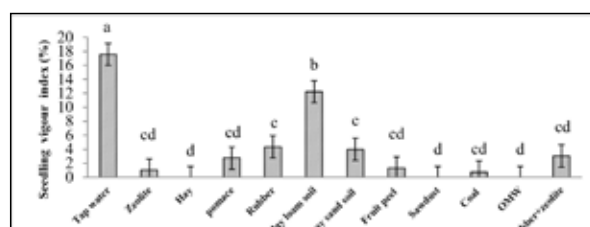


Figure 17. Seedling vigour index of barley seeds irrigated with treated OMW.

4. Discussion

Germination percentage and seedling establishments are considered important parameters during germination, which decide the victories of plant foundation beneath antagonistic environment conditions (Peralta et al., 2001). Untreated OMW leads to complete destruction of germinated seeds. The negative effect of the untreated OMW on seed germination of barley was probably attributed to the high phenolic compounds contained in the OMW (Rusan et al., 2015). The negative impact of phenolic compound in the higher plants is highly severe during germination process (Krogmeievr and Bremmer, 1989). Various works have recommended that phenolic compounds are involved in the OMW germinability suppression or lessening which they can influence the germinability (Muscolo et al., 2001; Muscolo et al., 2002). For this reason, it is necessary to remove

this compound from OMW in order to utilize this waste in agriculture. Filtration of OMW using various materials leads to the reduction of the phenolic compound from OMW (Table 1). The lowest amount of phenolic compounds was found in OMW generated from clay loam filters. In this treatment, the germination percentage was the second after the control (Figure 2). Looking at other results, germination speed index, relative germination rate, shoot length root length shoot and root dry weight, and root to shoot ratio, indicated that OMW generated from clay loam filter has the highest values compared to other filters. Germination rate index can be utilized as a pointer of phytotoxicity with the higher values representing a more rapid rate of germination.

In the present study, decreased germination energy in OMW can be describe due to seed deterioration and degradation of cell membranes (Falleri, 1994). Other investigators stated that the increase in the osmotic concentration decreased the energy of seed germination (Ahmadloo et al, 2011). In previous experiments, the promptness index and germination stress tolerance index were used as indications to identify drought-tolerant genotypes (Partheeban et al., 2017). Higher values indicate the tolerance of those genotypes to drought stress. In this experiment, the promptness index and germination stress tolerance index were used to identify the negative impact of OMW and OMW generated from various filters compared to tap water. Promptness index and germination stress tolerance index (GSTI) decreased with increasing concentration of stress levels. The highest promptness index and germination stress tolerance index were found for seeds irrigated with tap water followed by OMW generated from clay loam filters. This means that OMW generated from clay loam filters has less negative impact on barley seeds compared with other filters especially untreated OMW as well as OMW generated from sawdust and hay filters.

The germination stress tolerance index was used to interpret differences in the rate of germination due to environmental stress (Bouslama and Schapaugh, 1984). A higher value of the germination stress tolerance index indicates a high rate of germination, which was inversely related to environmental stress. Reduction in shoot length stress index, root length stress index, shoot dry weight stress index, and root dry weight stress index reflect the impacts of the phenolic compound effect generated from OMW. The highest reduction was observed for seeds irrigated with untreated OMW as well as seeds irrigated with OMW and generated from sawdust and hay filters. The highest values were observed for seeds irrigated with tap water followed by OMW generated from filters containing clay loam soil, rubber, sandy soil and rubber + zeolite.

OMW treatment with various filters has dissimilar and statistically significant effects on seedling vigor index. Therefore, we concluded that this variation would be attributed to the phenolic stress variation of the treated OMW by different filters (Table 1). A similar assumption was drawn by other reports stating that the vigor index is reduced by environmental stress effects (Motamedi et al.

2013; Khodarahmpour 2011; Mensah et al. 2006).

It has been stated that OMW results in a strong prohibition of seeds and seedling growth (Casa et al. 2003 and Komilis et al. 2005). These researchers have reported a decrease in OMW toxicity and the inhibition effect of seed germination with various processes. In this study, it was concluded that utilization of various naturally made filters can be used to decrease the negative impact of phenolic compounds that prevent seed germination and seedling growth. Investigators have reported that the germination rate index was significantly reduced by OMW application due to the phenolic compounds contained in OMW (Aggelis et al. 2003). They found that reducing phenolic compounds enhanced the germination rate index.

5. Conclusions

This study reveals the following conclusions:

- 1- The low pH value of OMW increased when it passed through the different media, except hay and sawdust. When rubber in combination with zeolite was used as the filter media, the pH of OMW increased to the extreme.
- 2- Rubber and zeolite in combination as filter media produced the lowest turbidity values as compared to the other types of used media.
- 3- The best removal efficiencies of COD and phenols were obtained in (rubber and clay loam) and (zeolite) filters, respectively.
- 4- The use of untreated OMW has completely prevented the germination process of barley seeds.
- 5- It was found that the use of clay loam and loamy sand along with granular rubber, zeolite, and rubber and zeolite mixtures as filter media was efficient in the treatment of OMW.
- 6- The use of treated OMW has a negative effect on the germination process of barley as compared to germination when tap water was used.
- 7- Treated OMW, using most filter media types used in this research, improved the germination percentage and seedling growth, as compared to untreated OMW, especially effluent generated from clay loam and loamy sand soil filters.

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Simulation of Breakthrough Curves of Pb Ions Adsorption by Natural Zeolitic Tuff Using Axial Dispersion and External Mass Transfer Models

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Abstract

The axial dispersion model (ADM) was applied to the breakthrough curves data obtained for lead ions removal from aqueous solutions by a natural zeolitic tuff in a lab-scale packed bed column apparatus. The axial dispersion coefficient and Peclet number were determined from simulations at different superficial solution velocities, bed heights, and particle size cuts of the mineral. The axial dispersion coefficient varied from 6.19×10^{-6} to $8.28 \times 10^{-4} \text{ m}^2 \cdot \text{s}^{-1}$ and was found to increase with solution velocity and particle size while decreasing with bed height. The external film mass transfer coefficient was determined for different solution velocities and particle size cuts and was found to be 4.93×10^{-5} to $7.85 \times 10^{-5} \text{ m} \cdot \text{s}^{-1}$, suggesting a considerable mass transfer resistance.

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Keywords: Adsorption, Zeolitic tuff, Lead ions, Dispersion model, Peclet number, Transfer coefficient.

1. Introduction

Modeling and simulation are important tools in designing, scaling up, and optimizing environmental engineering processes such as adsorption and ion exchange, which are widely used to remove toxic and objectionable pollutants from water and industrial wastewater (Verma, 2014). In practical industrial-scale systems, these processes are conducted in packed bed columns continuously operated at steady state conditions. Mathematical models formulated to describe a particular process are validated by fitting them to data obtained from laboratory scale experiments and comparing them with the computed output. Physically significant process parameters such as fluid dispersion and mass transfer coefficients are the main targets for evaluation.

Several models have been reported in the literature for packed bed adsorbers. Each model may have a merit over others but suffers drawbacks such as weak correlation, a large number of parameters and unsuitability for multi-stage resistance or multi-component systems. Many research publications on the removal of heavy metal ions, dyestuff, and phenol among chemical pollutants of water focused on the use of empirical kinetic models such as Bohart-Adams, Thomas, Clark and Moon-Nelson (Barrows et al., 2013; Xu et al., 2013). Although these models are useful and simple to use, they give less practical information in terms of mass transfer resistance encountered and the non-ideal behavior of the adsorption system. Models that describe the process's dynamics and mechanism, mostly based on external and/or internal mass transfer resistances and fluid dispersion, have been successfully applied (Inglezakis et al., 2020; Patel, 2019; Taamneh and Al Dwairi, 2013).

The axial dispersion model (ADM) has been widely

used in chemical and environmental process engineering to represent the flow of fluid inside packed bed contactors in combination with models correlating dimensionless groups to express the external film mass transfer effects at the solution/ particle boundaries (Hethnawi et al., 2020; Delgado, 2006). Axial dispersion is the result of coupling molecular diffusion and convection. It is affected by mixing due to splitting and merging flows of liquid around the bed particles. Dispersion and mass transfer coefficients obtained from these models are more useful in packed beds design and operation compared with the empirical kinetic models characterized by pseudo or lump-sum rate constants.

In practical plug-flow column-type reactors, flow is usually non-ideal due to inlet and exit flow disturbances as well as axial dispersion, which is an expression of the degree of back-mixing and deviation from ideal plug flow behavior. Axial dispersion is an important parameter affecting the performance of fixed bed columns (Hill and Root, 2014). The axial dispersion model has been employed for tall columns containing packed beds of porous materials such as cylindrical charcoal particles (Popa et al., 2015).

In this work, the theoretical axial dispersion reactor model has been used to analyze the convective and diffusive mass transfer during Pb ions exchange over Na-saturated zeolitic tuff particles at low fluid velocities. This system is important in environmental applications as natural zeolitic minerals have increasingly demonstrated their efficacy as adsorbents or ion exchange materials for water and wastewater treatment, environmental remediation as well as sub-surface barriers to prevent groundwater pollution (Perez-Botella et al., 2022; Morante-Carballo et al., 2021; Misaelides, 2011). Zeolites are hydrated aluminosilicates

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of alkaline and alkaline earth metals that with a unique framework structure associated with remarkable physical and chemical properties. According to Velarde et al., (2023), the properties of natural zeolites include ease of ion exchange, adsorption, dehydration, and rehydration, as well as being eco-friendly, low-cost, regenerative, easily accessible, and available to make them excellent adsorbents.

Zeolitic tuff minerals were generated from the alteration of volcanic tuff located mainly in the northeast and center of Jordan. The Jabal Aritain deposits only contain estimated geological reserves of 170 million tons. Phillipsite, chabazite, and faujasite are the most abundant zeolite minerals found in the Jordanian zeolitic tuff (Nawasreh et al., 2006; Dwairi, 1992). Over the last 25 years, these minerals have been mined, processed, and made commercially available for cement manufacture and agricultural applications.

Environmental applications of Jordanian zeolites, as adsorbents and ion exchangers for pollutant removal, have been the subject of extensive investigation. Published studies from different locations in Jordan over the past three decades have demonstrated that Jordanian zeolite tuffs are efficient adsorbents for the decontamination of industrial effluents containing toxic and radioactive metal ions (Khouri, 2019; Al Dwairi et al., 2013; Taamneh and Al Dwairi, 2013; Al-Shaybe and Khalili, 2009; Ibrahim et al., 2002; Dwairi, 1992).

2. Theory and Mathematical Models

The axial dispersion model is described by Hill and Root (2014) and Fogler (2006) for fixed granular bed contactors receiving one phase fluid flow, dispersed over column length and time. The assumptions of the model are as follows: (1) plug flow at isothermal conditions, (2) homogeneous porosity and size distribution throughout the bed, (3) single component involving no chemical reaction, (4) radial dispersion negligible due to small diameter/ length ratio, and (5) boundary film mass transfer is significant. The model is given by the basic equations below:

$$D_L (\partial^2 C / \partial z^2) - u (\partial C / \partial z) = \partial C / \partial t \quad (1)$$

Initial conditions (at $t = 0$): $C = C_0$ at $z < 0$ and $C = 0$ at $z > 0$ (2)

Boundary condition at $z = 0$: $-D_L (\partial C / \partial z) + u(C) = u(C_0)$ at $t = 0$ and $t > 0$ (3)

Where $z > 0$ designate the position just inside the column at $z = 0$. D_L is the axial dispersion coefficient, which is the coefficient that can characterize the degree of back-mixing and quantify the deviation from ideal plug flow behavior.

$$\text{Exit condition } (z = L, t = 0 \text{ and } t > 0): dC/dz = 0 \quad (4)$$

The solution of this model is simplified by substitution to convert the partial differential equation into an ordinary differential equation:

$$d^2 C^* / d\alpha^2 + 2\alpha dC^* / d\alpha = 0 \text{ and } \alpha = (z - u.t) / (\sqrt{4D_L.t}) \quad (5)$$

where: C^* is the dimensionless concentration C/C_0 . The boundary conditions become:

$$C^* = 1 \text{ for } \alpha = -\infty \text{ and } C^* = 0 \text{ for } \alpha = \infty \quad (6)$$

For ideal reactors, the mean residence time, $\tau = V/Q = L/u$; since the cross-sectional area is constant. For non-ideal reactors, however, the mean residence time is defined as follows:

$$\tau = \int_0^\infty t E(t) dt \quad (7)$$

The solution of the above equations gives C/C_0 for different values of $\alpha = f(z, t)$:

$$C/C_0 = \frac{1}{2} [1 - \text{erf} (1/2 \sqrt{Pe} \cdot (1 - t/\tau) / (\sqrt{t/\tau}))] \quad (8)$$

Where:

$$Pe = u d_p / D_L = (\text{rate of bulk fluid convection} / \text{rate of adsorbate diffusion}) \quad (9)$$

Pe is the Peclet number for particles, which is used as a direct parameter to measure the relative importance of convective transport (bulk movement of fluid due to its velocity) versus molecular diffusion of adsorbate across the liquid-solid boundary film. High Pe indicates an advective transport dominance, while low Pe indicates a mainly diffuse flow. Pe values around 1.0 indicate comparable significance of the two types of mass transport. A plot of C/C_0 versus t/τ gives a breakthrough curve with a shape that is dependent on the values of D_L (or Pe).

The external boundary film mass transfer coefficient, k_p , can be obtained using generalized empirical models or correlations involving the dimensionless groups of Sherwood number (Sh), Reynolds number (Re) and Schmidt number (Sc). The Wilson- Geankoplis (1966) correlation at Reynolds' low number values ($0.0015 < Re < 55$) is commonly used and widely applicable:

$$Sh = (1.09/\epsilon) (Re.Sc)^{1/3} \quad (10)$$

Where:

$$Sh = k_p d_p / D_m; Re = \rho d_p u / \mu; Sc = \mu / \rho D_m \text{ and } k_f = D_m / \delta \quad (11)$$

D_m is the molecular diffusivity (diffusion coefficient) of metal ions from bulk aqueous solution through a stagnant liquid film with a thickness δ to the external surface of zeolite particle at steady state. It is also noteworthy that Peclet number (Pe) is the product of Re and Sc .

2. Materials and Methods

For the validation of the axial dispersion model suggested in this paper, published breakthrough data on Pb ions removal from aqueous solutions as a single metal by natural zeolite tuff were utilized (Al-Haj-Ali and Al-Hunaidi, 2004). A natural phillipsite zeolitic tuff, from the basaltic desert area of Jabal Aritain in northeastern Jordan, was crushed and sieved into several size fractions using ASTM standard sieve set. XRD showed that the tuff is rich in phillipsite, with calcite as a major impurity (Al-Haj-Ali and Marashdeh, 2014). According to published data reviewed by Khouri (2019), the percentage of phillipsite in Jabal Aritain zeolitic tuff ranges between 27- 49%, with an average of 35%.

Three size fractions (355-500, 500-710, and 710-850 μm) were used. This moderate particle size range, which excludes large particles, is associated with high surface area needed to provide a large number of adsorption sites. Very fine

particles ($< 355 \mu\text{m}$) are also excluded to avoid blocking fixed bed voidage responsible for creating high operating pressure drop for the liquid passage. Each size fraction was washed with tap water until the dust and fines are removed. The mineral was immersed in 25 g.dm^{-3} solution of pure NaCl in distilled, deionized water at room temperature for 24 h. The solution is replaced by a fresh one, and the mineral continued to be immersed for another 24 h. The Na-treated zeolite was then filtered, washed gently with distilled, deionized water and oven dried at 35°C . Non-sieved zeolitic tuff has a bulk and particle densities of 1035 and 2380 kg.m^{-3} , respectively, as well as a surface area of $120 \text{ m}^2.\text{g}^{-1}$.

The used apparatus consists of bench-mounted glass column, 90 cm in length and 1.5 cm inside diameter (1.767-cm^2 cross-sectional area). The column is gently packed with a certain amount NaCl-washed zeolitic tuff to give an appropriate bed height. The feed solution is pumped from a glass storage tank to an overhead constant-level tank made of plexiglass and down flow fed to the column through a glass flow meter. Air bubbles are gently expelled before starting the experiment, and flow control is achieved by valves fitted at the top and at the bottom of the column. Samples from effluent solution are withdrawn at predetermined time intervals and analyzed for metal ion concentrations using a Pye-Unicam atomic absorption spectrophotometer. The bed voidage is 0.40 and is estimated from the ratio of particle diameter to bed diameter as reported by Dixon (1988) and Inglezakis (2010).

Table 1. Lists the experimental conditions at which the considered breakthrough curves were obtained. As evident from the sieving size cuts, all the zeolite particles involved are relatively small (less than 0.85 mm). The column dimensional ratio of $90/1.5$ is around 1000 times the mean particle diameter. The adsorption capacity for Pb ions obtained by applying the bed-depth service-time (BDST) analysis was determined to be 24.27 , 28.71 and 35.73 mg.g^{-1}

¹ for $500\text{-}710 \mu\text{m}$ sieve cut at solution velocities of 36.8 , 28.30 , and $14.15 \text{ cm.min}^{-1}$, respectively (Al-Haj-Ali and Al-Hunaidi, 2004).

4. Results and Discussion

4.1. External Film Mass Transfer

This step is often overlooked as a resistance in the literature on packed-bed dynamic models, although it requires more attention to adequately interpret the process kinetics (Inglezakis et al., 2020). Vilardi et al. (2019) have reported the importance of the mass transfer resistance in their adsorption study of Cr(VI) ions by composite nanomaterials. It was recognized as a rate-controlling factor at the early stages of the breakthrough curves in metal ion removal packed bed systems. This was confirmed to be valid by the application of the Wolborska model to the experimental breakthrough curves of Pb^{2+} ions removal by zeolitic tuff process (Al-Haj-Ali and Al-Hunaidi, 2004). Two important differences appeared upon the application of the Wolborska and ADM model to the experimental breakthrough curves of Pb ions/zeolitic tuff system. Firstly, the Wolborska model was applicable only at the low C/Co range, that is, in the initial stage of the adsorption process, while ADM fitted satisfactorily the whole range of the curves. Secondly, the Wolborska model has one lumped kinetic coefficient which reflects both convective and diffusive mass transfer, whereas the ADM distinguishes between the two transport effects by providing two separate coefficients (the axial dispersion coefficient, D_L , and the external film mass transfer coefficient, k_p).

For small particle size range and at low fluid velocities, a focus on external liquid-film mass transfer is justified. In this study, the values of coefficient, k_p , and the liquid-film thickness, δ , were calculated by applying the generalized empirical correlation with appropriate dimensionless groups (equations 10 and 11) to the experimental data. They are presented in Table 2.

Table 1. Summary of Experimental Conditions for Breakthrough Curves.
(Initial Pb ions concentration = 250 mg.dm^{-3} and temperature of 22°C).

Solution velocity, u (cm.min^{-1})	Particle size cut, d_p (μm)	Bed height*, L (cm)
14.15 ($2.358 \times 10^{-3} \text{ m.s}^{-1}$)	500-710	4.4
		8.8
		13.2
28.30 ($4.717 \times 10^{-3} \text{ m.s}^{-1}$)	500-710	8.8
	355-500	13.2
	500-710	
	710-850	
	500-710	17.6
36.80 ($6.133 \times 10^{-3} \text{ m.s}^{-1}$)	500-710	13.2
		17.6
		22.0

*Each 4.4 cm bed height is equivalent to 10 g of zeolite.

Table 2. External Film Mass Transfer Properties for Pb Ions at Different Liquid Velocities and Average Zeolite Particle Diameters.

Superficial velocity, u (m.s ⁻¹)	2.358 x10 ⁻³	4.717 x10 ⁻³	6.133 x10 ⁻³	4.717 x10 ⁻³	4.717 x10 ⁻³
Particle size cut*, d_p (μm)	500-710	500-710	500-710	355-500	710-850
Reynolds number, Re	1.574	3.148	4.094	2.226	4.134
Schmidt number, Sc	941.8				
Sherwood number, Sh	31.07	39.15	42.73	34.88	42.87
Mass transfer coefficient, k_f (m.s ⁻¹)	4.93 x10 ⁻⁵	6.21 x10 ⁻⁵	6.78 x10 ⁻⁵	7.85 x10 ⁻⁵	5.19 x10 ⁻⁵
Stagnant liquid film thickness, δ (μm)	19.2	15.2	14.0	12.0	18.2
Solution properties:	Density, ρ = 1000 kg.m ⁻³ , Dynamic Viscosity, μ = 8.9 x10 ⁻⁴ kg.m ⁻¹ .s ⁻¹ Pb ²⁺ Molecular Diffusivity, D_m = 9.45 x10 ⁻¹⁰ m ² .s ⁻¹				
Bed voidage, ϵ	0.40				

*Average particle diameter is taken as the geometric mean of upper and lower cut sizes.

The coefficient (k_f) can be directly related to process parameters and solution properties for better illustration of their effects. Deriving a specific correlation from equations 10 and 11 as follows:

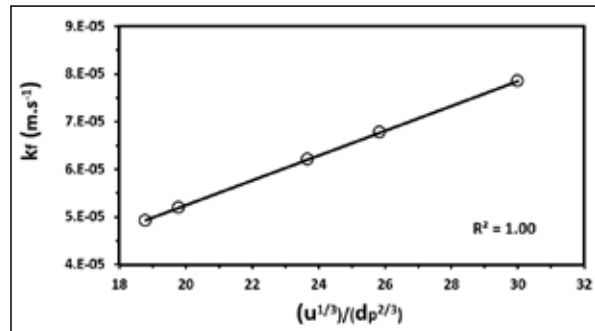
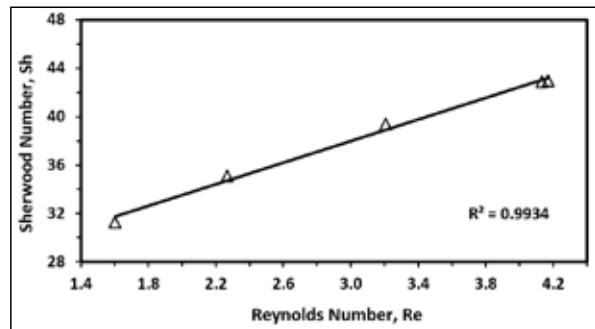
$$k_f d_p / D_m = (1.09/\epsilon) (\rho d_p u / \mu)^{1/3} (\mu / \rho D_m)^{1/3} \quad (12)$$

$$k_f = (1.09/\epsilon) u^{1/3} (D_m / d_p)^{2/3} \quad (13)$$

For Pb ions in particular, and using the molecular diffusivity value in Table 2, the correlation becomes:

$$k_f = 2.63 \times 10^{-6} u^{1/3} / d_p^{2/3} \quad (14)$$

Equations 13 and 14 indicate that k_f increases with superficial solution velocity and decreases with particle size. A perfectly linear plot (correlation coefficient $R^2 = 1.0$) is obtained for k_f versus $u^{1/3} / d_p^{2/3}$ (Figure 1), demonstrating that the Wilson and Geankoplis correlation is appropriate to describe the external mass transfer in this system and process. The calculated increase in k_f with temperature increase is 37.5 %, while the decrease in k_f with increasing the average particle diameter is 51%. Another linear correlation ($R^2 = 0.99$) was obtained by plotting Sherwood number versus Reynolds number as shown in Figure 2. This highlights the importance of external mass transfer resistance in process dynamics under the investigated conditions.

**Figure 1.** Effect of superficial solution velocity and zeolite particle size on the external film mass transfer coefficient for Pb²⁺ ions.**Figure 2.** Dependence of Sherwood number on Reynolds number for external film mass transfer.**Table 3.** Axial Dispersion Coefficients and Peclet Number Values Calculated by Fitting ADM to Breakthrough Data of Pb /Zeolite System.

Size Cut*, d_p (μm)	u (m.s ⁻¹)	Re	L (cm)	D_L (m ² .s ⁻¹)	Pe (-)
500-710	2.358E-03	1.574	4.4	2.935E-05	0.852444
			8.8	1.535E-05	1.704888
			13.2	0.602E-05	2.557333
500-710	4.717E-03	3.148	8.8	4.388E-04	1.704888
			13.2	3.814E-04	2.557333
			17.6	2.385E-04	3.409777
500-710	6.133E-03	4.094	13.2	8.282E-04	2.557333
			17.6	7.057E-04	3.409777
			22.0	6.891E-04	4.262221
355-500	4.717E-03	2.226	13.2	2.1407E-04	3.616614
710-850		4.105		5.529E-04	1.961385

*Average particle diameter is taken as the geometric mean of upper and lower cut sizes.

Moreover, Table 2 reveals that for a given particle size cut (500-710 μm), which is used for most experiments, the stagnant liquid film thickness (δ) decreased from 19.2 to

14.0 μm as solution velocity increased from 14.15 to 36.8 cm.min⁻¹. This decrease reveals that external film mass transfer resistance is important at lower solution velocities.

4.2. Axial Dispersion

The ADM equations were solved using common spreadsheet. The model application to experimental breakthrough data (C/C_0 versus contact time) enabled the determination of the axial dispersion coefficient (D_L), as well as the Peclet number. It was found that D_L (also known as longitudinal diffusion coefficient or effective diffusivity) is a function of operating conditions including liquid velocity, bed height and zeolite particle size (d_p). Initial Pb ions concentration was kept constant at 250 mg.dm^{-3} , and solution temperature at 22°C . Table 3 summarizes the model fitting results.

The predictions of the model are shown along with experimental breakthrough data (C/C_0 vs. contact time) in Figures 3- 5, designated as ADM in the legend. It can be observed from Figure 3 (a, b, c) that the model describes quite well the breakthrough data obtained at different bed heights while keeping liquid velocity constant. Bed height is another expression of the quantity or mass of zeolite available for Pb ions removal which ranged from 4.4 cm (10 g) up to 22 cm (50 g). It is a key parameter in the design of fixed-bed columns. Tall beds allow for longer service time before regeneration is needed. Both the data and the simulation results are consistent with the common trend of sigmoidal shape, where curve flattening is due to the widened mass transfer zone as bed height is increased. This is quite evident at the lower solution velocity (Figure 3, a).

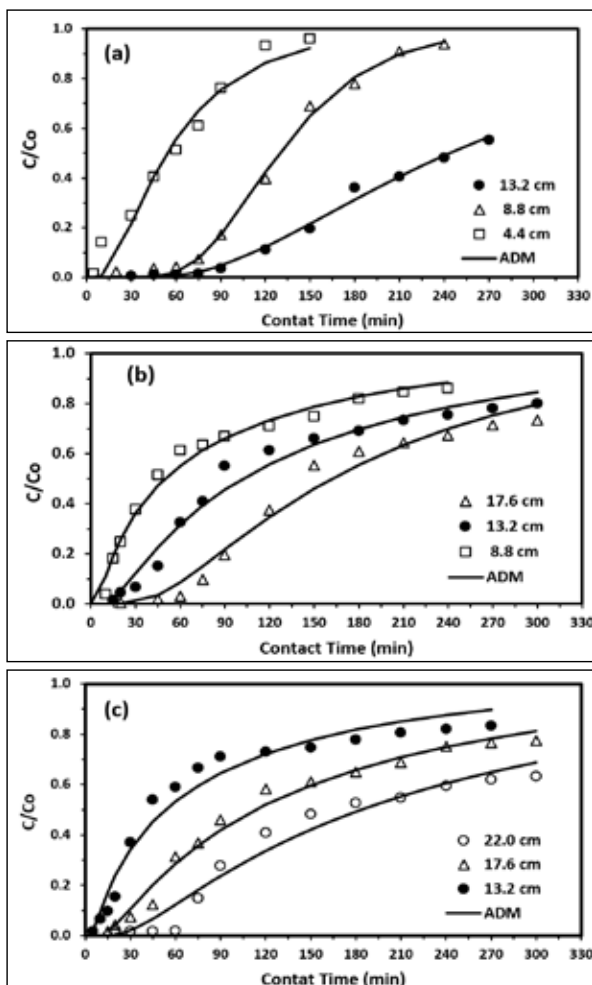


Figure 3. Axial dispersion model (ADM) fitted to breakthrough curves at various bed heights: (a) $u = 14.15 \text{ cm.min}^{-1}$ (b) $u = 28.3 \text{ cm.min}^{-1}$ (c) $u = 36.8 \text{ cm.min}^{-1}$.

The scattering of experimental data around the model representation can be explained in part due to the deviation of actual bed/ column conditions from assumptions on which the model is based, such as the zeolite, which may not be represented accurately in the simulations by the average particle diameter. Taking an average particle diameter instead of full particle size distribution may result in lower values of the axial dispersion coefficients calculated by the model. Also, some of the data scattering and deviation may be attributed to a minor contribution of intraparticle diffusion, which is not usually a part of the mass transfer resistances in the axial dispersion model. Excluding solid diffusion resistance can be justified for using a small particle size range ($355\text{-}850 \mu\text{m}$) and testing a simpler mathematical model.

Figure 4. compares the modeled breakthrough curves plotted at different superficial solution velocities obtained at constant zeolite bed height. Both the experimental data and the fitted ADM are in agreement with expected results of longer breakpoint time, and, thus, higher degree of zeolite bed utilization as the solution velocity is reduced. This result is because more contact time is available for the transfer process of ions from solution to the surface of zeolite particles over a wide mass transfer zone. The effect of solution velocity on axial dispersion coefficient is illustrated quantitatively below.

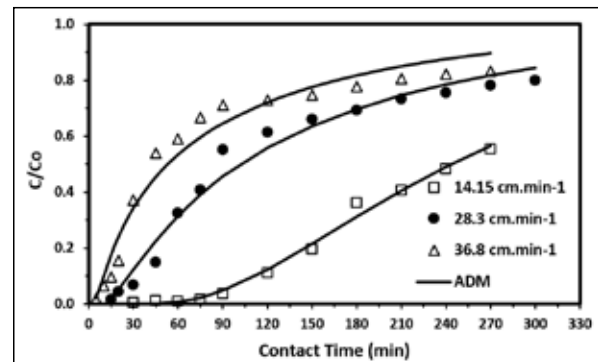


Figure 4. Effect of superficial solution velocity at constant bed height.

The effect of using three zeolite particle size cuts is shown in Figure 5. Compared to the effect of liquid velocity and bed height, the variation in the shape of breakthrough curves or breaktime is not substantial. This variation can be attributed to the relatively narrow size range investigated ($355\text{-}850 \mu\text{m}$ or below 0.85mm). Within this size range, it is evident that the lower size cut provided a longer break time and a shape closer to the typical S-curve due to the larger surface area with more ion exchange sites available for Pb^{2+} uptake. A general conclusion from this minor effect of particle size is that intraparticle diffusion is not the main resistance in the process dynamics compared to the effects of fluid dispersion and molecular diffusion.

Effects of superficial solution velocity (u) and zeolite particle size (d_p) on the axial dispersion coefficient are shown in Figure 6 as D_L versus Reynolds number, which is directly proportional to both " u " and " d_p " (equation 11). D_L is strongly dependent on solution velocity where it increased from 6.0×10^{-6} to $8.2 \times 10^{-4} \text{ m}^2.\text{s}^{-1}$ when the Reynolds number increased from 1.57 to 4.09 by increasing velocity from 14.15

to 36.8 cm.min^{-1} using the same size cut. For small values of the liquid phase velocity, the increase of the axial dispersion coefficient D_L is negligible, which is in agreement with the findings of Popa et al. (2015) who also reported a dependence of D_L on solution velocity for NaCl tracer solution dispersed through charcoal beds. Similarly, D_L increased by 158% when the particle size cut was changed from 355-500 to 710-850 μm at constant solution velocity. This increase is in agreement with the reported results of studies on similar systems reviewed by Delgado (2006), where the axial dispersion coefficient increased by a factor of 1.5 as the ratio of particle diameters went from a value of 2 to 5.

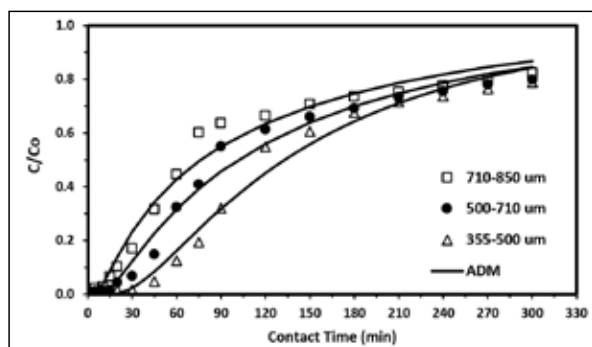


Figure 5. Breakthrough curves using different zeolite particle size cuts.

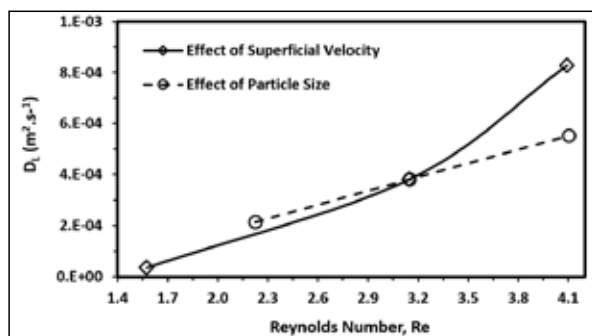


Figure 6. Effects of superficial solution velocity and zeolite particle size on the axial dispersion coefficient.

The effect of bed height on the axial dispersion coefficient is shown in Figure 7 at each of the three studied solution velocities. At $14.15 \text{ cm.min}^{-1}$, D_L is quite low and rather independent of bed height. At a constant bed height of 13.2 cm, D_L is higher with higher velocity. Moreover, at a constant velocity of 28.3 and 36.8 cm.min^{-1} , D_L decreased by 45 and 17 % respectively. Compared with the breakthrough curves shown in Figure 3 (a, b, c), the favorable S-shaped curves are shown to be connected with lower dispersion coefficients (higher Peclet numbers), indicating the dominance of convective (bulk fluid) transport. Similar results were obtained by Yun et al. (2005) who identified a trend of decreasing the axial dispersion (film diffusion) coefficient with increasing bed height, giving more importance to convective transport.

The above observation can be explained on the basis of the Peclet number definition and values (discussed earlier in the theory and model development). Since Pe values are higher than 1.0 for most of the operating conditions (as shown in Table 3), convective (bulk liquid) transport appears to be dominant and thus controls the overall process dynamics.

In this case, the values of the dispersion coefficient, D_L , are correspondingly low, indicating negligible diffusion resistance to adsorbate transfer from solution to adsorbent surface. The above inference agrees with the theory and also with studies reported in the literature (Delgado, 2006) that convective transport becomes dominant over molecular diffusion as the fluid flow rate is increased.

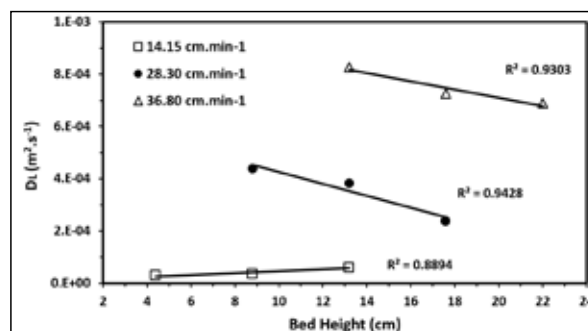


Figure 7. Effect of zeolite bed height on the axial dispersion coefficient of Pb ions.

5. Conclusion

The axial dispersion model is capable of predicting the performance of Pb ions sorption by packed beds of natural zeolite as it was successfully validated with breakthrough curves over variable experimental conditions. The Wilson-Geankoplis correlation describes the external film mass transfer process properly with high correlation coefficient. Both axial dispersion and external film mass transfer coefficients are determined and found to be the functions of the superficial solution velocity and zeolite particle size. D_L is proportional to " $u \cdot d_p$ ", whereas k_f is proportional to " u/d_p ". Furthermore, D_L decreases with bed height at a given solution velocity.

Small values of both k_f (in the 10^{-5} m.s^{-1} range) and D_L (in the 10^{-4} m.s^{-2} range) indicate that the two mechanisms are significantly important in modeling and describing the considered packed bed system. Axial dispersion is more effective with high liquid velocity, whereas film mass transfer resistance is essential at low flow rates. Both transport effects should be included in analyzing, modeling, and design of metal ions/zeolite adsorption systems.

The model was able to well predict the breakthrough curves of metal ions over the whole contact period, and to provide quantitative information on the effect of mass (metal ion) transfer on the adsorption process dynamics. The above conclusions indicate that using ADM is justified and beneficial to extract the dispersion coefficient (which is the most significant parameter in process dynamics) and mass transfer coefficient from experimental breakthrough data. The ADM would be a means of prediction, scale-up, equipment design, and optimization for the adsorption process.

Nomenclature

ADM: Axial dispersion model

C: Pb ion concentration in solution at any time during the process, mg.dm^{-3}

D_m : Molecular diffusivity of metal ion transferring across stagnant liquid film of thickness δ to the external surface of

zeolite particle, $\text{m}^2.\text{s}^{-1}$

D_L : Axial dispersion (longitudinal diffusion) coefficient, $\text{m}^2.\text{s}^{-1}$

d_p : Average diameter of zeolite particle size cut, μm or m

δ : Stagnant liquid-film thickness, μm or m

k_f : External film mass transfer coefficient over liquid-particle interface, $\text{m}.\text{s}^{-1}$

L : Fixed-bed length, cm

μ : Dynamic viscosity of solution, $\text{kg}.\text{m}^{-1}.\text{s}^{-1}$

ρ : Solution density, $\text{kg}.\text{m}^{-3}$

t : Contact time, min or s

u : Superficial velocity of solution through the bed, $\text{cm}.\text{min}^{-1}$ or $\text{m}.\text{s}^{-1}$

τ : Mean residence time, s

Dimensionless groups:

These are four the packed particles in the bed, where the characteristic length is the average particle diameter, d_p . They are defined in equations 9 and 11:

Pe: Peclet number

Re: Reynolds number

Sc: Schmidt number

Sh: Sherwood number

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