Amelioration of nano-Kaolinite deportation for heavy Pb(II)'s, Cd(II)'s, and Cu(II)'s ions from aquatic environments

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Abstract

This study presents a novel solution for the chemical modification of Jerash natural kaolin clay (NC) after HCl leaching to obtain nano-Kaolinite (NK), for the investigations of the adsorption uptake of heavy Pb(II), Cd(II), and Cu(II)-ions onto modified NK from aqueous discharges, under the variation of pertinent constraints such as medium pH, adsorbent dosage, initial metal concentration, contact time, and temperature. Additionally, the BET analysis reveals an increase in the surface area and volume of the mesoporous structure after acid leaching of the natural KC. Thermodynamic analysis reveals negative values for (ΔG^o) and positive figures for (ΔH^o) and (ΔS^o), which accentuates that the adsorption process is spontaneous, random, and endothermic. The Langmuir and Freundlich Isotherms are the best-fit models to predict the adsorption data, the ultimate removal capacities were obtained as 250, 232.6, and 222.2 mg/g$_{adsorbent}$ for heavy Pb(II), Cd(II), and Cu(II)-ions, respectively, at initial metal concentration of 40 mg/L$_{solution}$, medium temperature of 303.15 K, and initial pH 5.5. By considering these merits of synthesizing a porous structure with intensive nucleation sites on the modified NK surface, a competent and low-prized adsorbent could be used for HM-ions remediation from an aqueous environment and the protection of public health.

1. Introduction

Heavy metals (HM) ions are common contaminants in the eco-system, thus, their sources and pathways are diverse from an-/ organic and chemicals, food and drug manufacturing, metal infrastructure, as well as anthropogenic activities in residential areas (Al-Rousan et al., 2012; Al Tarawneh, 2014; Tarawneh et al., 2021; Al-Mubaidin et al., 2022). HM accumulation with harmful levels in the aquatic streams and environments is a vital issue to be globally considered, which is subject to restrictions of their emissions by inter-/national authorities due to slow degradation and high toxicity that leads to a massive impact on soil, water, and air. In developing countries like Jordan, which is suffering from poor aquatic resources, wastewater from industry and residential vicinities is recycled for other applications in agricultural activities like irrigation, animal farms, and bio-facilities. Intake of contaminated water and food products with HM-ions has essential health impacts, which leads to the disruption of numerous biological and biochemical processes inside the human body. Major HM-ions of potential hazards on the human health and environment are namely Lead [Pb(II)], Cadmium [Cd(II)], and Copper [Cu(II)], due to their physico-chemical characteristics, uses, and toxicity. In the middle east regime and specifically in Jordan, HM-ions remediation from aquatic streams is a vital challenge, which requires the implementation of feasible solutions to reduce the HM's concentrations and to maintain with safe and acceptable limitations in the environment.

One of the promising techniques that have been disclosed in literature are applying the natural KC deposits for the adsorption of HM-ions. This clay is naturally distributed with significant quantities in the district of Jerash – northern side of Jordan. Natural KC was investigated for adsorption of HM-ions in aqueous solutions in prior studies of (Wang et al., 2006; Sari et al., 2007; Aragão et al., 2014; El-Maghrabi and Mikhail, 2014, Jiang et al., 2010; Shahmohammadi-Kalalagh et al., 2011; Mustapha et al., 2019). Those techniques have shown crisp uptake of HM-ions from liquid discharges, since there is a relative low cation–exchange capacity and a small surface area of natural KC, (Al-Essa and Khalili, 2018). Else more, desorption of spent natural KC deposits were not feasible, consequently, further treatment processes of clays were foreseen to avoid the accumulation of HM-ions in environment. Consequently, a modification of the physio-chemical characteristics of KCs to ameliorate HM-ions uptake was a demand. In the study of Amer et al. 2010, KC was activated to Sodium polyphosphate-Kaolinite (NaPPK) clay powder, on the other hand, this technique is restricted to pH reading within acidic domain to perform effectively. In previous study by Awwad et al., 2021, KC was modified to Fe(OH)$_3$/kaolinite nanoplatelets. The reported adsorption capacity of Pb(II) ions from aqueous discharges was attributed to a specific surface area and main functional groups in the adsorbent surface, with few investigations of the applicability of this modified adsorbent to other harmful HM-ions.

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Whereas Alasadi et al., 2019 presented a novel technique applying NK as a natural adsorbent for the remediation of several toxic HM-ions like Cu(II), Ni(II) and Zn(II) from aquatic effluents. In this context, the uptake efficiency of the NK is restricted to the ratio of HM ions concentration in the wastewater stream. This finding has been highlighted in Abdallah, 2019. A thermal transformation and acid activation methods were applied to enhance kaolinite clay for the removal of Cu(II) and Zn(II) ions from wastewater discharges. The reported findings indicated that the ion exchange is the driving mechanism of HM-ions uptake with the constraint of identical molar concentrations, hence, a possibility that the HM-ions are being entrapped into the pores of modified kaolinite clays cannot be ruled out. In this context, Unuabonah et al. (2008) have revealed the application of Polyvinyl alcohol-modified (PVA) Kaolinite clay to move Pb(II) and Cd(II) ions from aqueous effluents. However, when the spent adsorbents were recycled with acidic solutions to be subsequently used for the re-adsorption of the concerned HM-ions, less adsorption capacity was obtained, this is attributed to the acid treatment employed for re-generation desorption that may dispute the active sites available for the adsorption of these HM-ions. An analog finding was obtained by Adebowale et al. (2005), Adewuyi et al. (2019), and Chukwuemeka-Okorie et al. (2018) for the re-generation of Phosphate, Amine, and calcined Corncob-modified Kaolinite, respectively, and adsorption of HM-ions form aqueous effluents of wastewater. These techniques have implied physical pre-treatment to improve the physio-chemical characteristics of natural KC. Meanwhile, Gougazeh (2018) has applied a pre-treatment of chemical leaching by Sodium dithionite ($Na_2S_2O_4$) to increase the active sites on the surface of natural KC for the adsorption of Iron and Titanium contaminants from wastewater. Whereas David et al. (2020) implemented thermal and hydrothermal alkaline modification of Enugu KC for the Pb(II) removal from wastewater, their findings showed that the uptake efficiency of the modified KC was improved in comparison to the raw KC due to the increasing the specific pore volume of adsorbent particles. However, this modification approach led to a weak alteration to the KC matrix, since residual ions remain on the active sites of the modified adsorbent, therefore menial re-generation is foreseen. In this context, combined approaches of physical and chemical treatment were apparently applied for the modification of natural kaolinite for enhancing the uptake efficiency of HM-ions from wastewater, as a coincidence Nigeria kaolinite clay was modified by natural Ammonium oxalate and sodium hydroxide (Lawal et al., 2020), calcined sawdust-kaolinite composite (Ogbu et al., 2019), and three kinds of attapulgite clays (Huang et al., 2020) for the remediation of HM-ions from wastewater. From one side, the activation stage was approached by hydrothermal reactions, which contributed to the alternation of the adsorbent surface into needle-like and granular structures, to ensure a better re-generation process and a prolonged cycle-life of the adsorbent. On the other side, it has been indicated that menial adsorption capacity was obtained due to limited nucleation sites of the adsorbent surface. In a recent study by Al Rabadi and Awwad (2021), a

novel approach was presented for the modification of nano-Kaolinite/ Silica oxides composites (nKSOC), for potential immobilization of HM-ions from aqueous solutions, where physical pretreatment and chemical methodologies were combined prior to the implementation of the adsorption stage. In this context, their methodology was effective and further adopted in the current investigations. Up to the authors' knowledge, few studies were conducted on the modification of Jerash KC and its application as an adsorbent for the treatment of contaminated wastewater streams with HM-ions. The potential of the modified NK as an effective adsorbent, for removing the three hazardous HM-ions; Pb(II), Cd(II), and Cu(II), from aqueous ecosystems, is accentuated thoroughly in these experimental investigations.

2. Methods

As a result of the modification strategy, the natural KC underwent physical pre-treatment through size reduction and adsorbent washing. After that, chemical stripping was done to remove contaminants from the adsorbent surface. Finally, washing, gradient drying, and size reduction were used to create a fine powder made of high-purity NK.

2.1 Materials

Sources for the anticipated HM-ion pollutants were provided by the Taufkirchen, Germany-based Sigma-Aldrich company as highly concentrated salt solutions of lead nitrate [$Pb(NO_3)_2$], cadmium nitrate [$Cd(NO_3)_2$], and copper nitrate [$Cu(NO_3)_2$]. The necessary chemicals, including sodium hydroxide (NaOH) and hydrochloric acid (HCl), were purchased from Merck in Darmstadt, Germany. From the Jerash district, KC samples were gathered. Whereas liquid nitrogen (LIN) was delivered locally by a special firm for technical gases. In the experimental study, de-ionized and distilled wastewater were used for washing and solution preparation.

2.2 Treatment methodology of raw KC

The collected and natural samples of Jerash KC were firstly subject to size reduction by being mechanically crushed and sieved with mesh No. 350, the corresponding fine powder has an average pellet size in the macro-range of less than 5μm. The specific surface area and pore volume were determined using the Brunauer-Emmett-Teller (BET) methodology. The sample's adsorption isotherm was measured using Micrometric 2020 and LIN adsorption at 77 K. Before characterization, a 0.3±0.001 g clay sample had been ground up, dried at 423.15 K, and then degassed for 6 h underneath a vacuum. For the HM-ions' adsorption experimentation, a sample of 500±0.01 g of the fine powder was washed with de-ionized water several times to remove any soluble substances, then it was mixed with an HCl solution of concentration 35 % (w/w), the suspended-pellet clay mixture was subject to mechanical stirring for a foreseen time interval of 6 hours. After that, the suspension was incubated overnight at the foreseen surrounding temperature. Following the incubation stage, a red-yellow emulsion was obtained, which was decanted and filtered to separate the emulsified solids, as filter cake to be washed again for few times to remove any traces of acid. The wet filter cake was treated with NaOH solution of a concentration of 20 %

(w/w) under continuous mechanical stirring for a period of 4 hours. Proceeding with the upstream steps of decantation, filtration, and washing the white filter cake with de-ionized water, the wet and kaolinite cake was placed in the dry oven, with gradient warming of 1 K/ 1 minute for the first hour, then baked under steady drying with 353.15 K hot air for additional 4 hours, then gradual cooling of oven content for further one hour. Finally, the dry solids obtained were subject to XRF chemical analysis and optical imaging by Scanning electron microscope (SEM) for the investigation of the appropriateness of the treated nano-Kaolinite pellets for the HM-ions uptake experimentation. SEM is a microscopic technique, which is capable of imaging at significantly higher resolutions than optical microscopes. A portable pH meter from Mettler Toledo was used during the experiment, and the anticipated pH measurement was monitored by adding a buffer solution of either HNO_3 or NaOH with 0.01 M for each. Different temperatures were foreseen for the current investigations: 293.15, 303.15, and 313.15 K. The concentration of the HM-ions supernatants was analyzed with Spectrometer (ICPS-7510).

2.3 Adsorption of HM-ions

The experimentation proceeded in the following manner for the investigation of HM-ions adsorption onto the treated NK: in glass flasks of 250 ml containing 0.5±0.001 g of adsorbent mass and 20 ml of prepared HM-ions solutions with diverse concentrations ranging between 5 to 120 mg/L were mixed, the balance was filled with distilled water, the foreseen HM-ions concentrations were consistent with prior investigations (Aragão et al., 2014; Alasadi et al., 2019; Awwad el al., 2021; Al Rabadi and Awwad, 2021), to simulate a contamination scenario of aqueous solution with HM-ions. The mixtures were shaken with a rotational speed of about 200 rpm until an equilibrium is established by monitoring the temperature at 303.15 K in a water shaker bath, this procedure was repeated for different contact time intervals. Then, the solid phase was separated from the liquid phase by centrifugation at a speed of 2000 rpm for 10 min intervals, then dried according to the procedure described in the above section. The structure and the composition of the separated nano pellets were analyzed by XRD and SEM approaches. For forecasting the size of nano-pellets smaller than 60 nm, the Debye-Scherr equation was used to determine the domain size of the purified nano-pellets based on the width of the XRD peaks (Kurapati and Srivastava, 2018). After equilibrium is being established, the remaining concentrations of HM-ions were analyzed by a Spectrometer (ICPS-7510) and further approved by back titration methods

for HM- salts precipitation. The assessment criteria for the absorption of HM-ions, Pb(II), Cd(II), and Cu(II) onto NK were evaluated by the removal efficiency - equation (1), and uptake capacity – equation (2):

$$R\% = \frac{c_o - c_e}{c_o} \times 100\% \tag{1}$$

$$q_e = \frac{c_0 - c_e}{m/V} \tag{2}$$

Where, C_o (mg/L) is the initial concentration of HM-ions, C_e (mg/L) is the equilibrium concentration in aqueous solution. m is the NK mass, V is the solution volume in liter, q_e is the uptake of the adsorbed HM-ion per gram of adsorbent ($mg/g_{adsorbent}$) and R% represents the removal percentage of HM-ions.

3. Results and discussion

The results for the characteristic modification of NK adsorbent and the assessment criteria under the alteration of the pertinent limitations for the absorption capability of HM-ions, Pb(II), Cd(II), and Cu(II) onto NK will be highlighted.

3.1 Characteristics of modified NK adsorbent

Figure (1) displays the results of the XRD examination for both the untreated NK and natural KC. The major peaks for SiO_2 and Al_2O_3 were found at 2Theta of 20.7° and the second at 26.7°, respectively. Subsequent peaks were found for various oxides. It is demonstrated that the raw clay deposits are mostly constituted of KC and traces of other metal oxides. It was discovered that the clay's peak intensity slightly decreased after HCl treatment. This is because the acid treatment caused a structural disturbance that alters the clay's matrix structure. While a few peaks were apparently obtained for the modified NK at 2Theta of 12.26°, 20.82, 24.91, and 26.46, primarily referring to SiO_3/Al_2O_3 and traces of other oxides. Both XRDs accentuate that different analyses were obtained for both adsorbent's samples before and after modification, highlighting the necessity of the pre-treatment process for the alternation of the characteristics of the adsorbent, this virtue was also confirmed in previous studies (Al Rabadi and Awwad, 2021; Awwad et al., 2021 and Mustapha et al., 2019). Following the observations by Ogbu et al., 2019; Lawal et al., 2020 and Huang et al., 2020, the presence of soluble metal oxides in the raw KC would have an adverse effect on the modification process of the adsorbent, since these soluble metal oxides offer additional nucleation sites for the precipitation of the HM's pollutants, their presence in the raw sample would have an amplified impact on the sorbent's modification process. As a result, the microporosity increases, and the reforming structure of NK adsorbent would ameliorate the uptake capacity towards HM-ion.
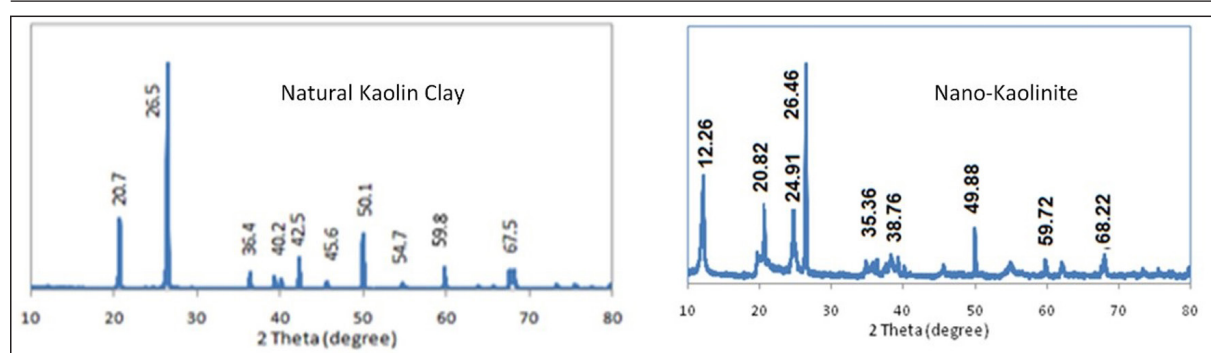

Figure 1. XRD of KC clay and the modified NK adsorbent.

Mineralogical characterization studies of the obtained Jerash KC, have shown that the main constituents are Kaolin (Wang et al., 2006; Sari et al., 2007; Aragão et al., 2014; El-Maghrabi and Mikhail, 2014; Jiang et al., 2010; Shahmohammadi-Kalalagh et al., 2011; Al-Essa and Khalili, 2018). The composition of SiO_2 and Al_2O_3 in raw and modified samples is the primary accomplishment. Table (1) summarizes the chemical composition of the modified NK as well as the Jerash KC. After chemical processing, the treated NK's composition was altered to include more than 88% metal oxides and 10% Kaolin, which is different from the composition of the raw KC deposits. According to El-Maghrabi and Mikhail (2014), the relevant composition with the altered oxide ratio warrants a moderate to high SiO_2/Al_2O_3 ratio with a factor of 3. The BET analysis reveals that the obtained surface area are 1.289 and 3.142 $m^2/g_{adsorbent}$ for KC and NK adsorbent, respectively, while pore volume was altered from the figure of 0.0064 to 0.155 $cm^3/ g_{adsorbent}$ for KC and NK adsorbent, respectively. These BET findings emphasize that HCl leaching of KC led to two advantages. Firstly, the surface structure of NK adsorbent has been converted into modified NK without the treatment of any of the other mineral's oxides like TiO_2, as was reported by Mahandrimanana (2020). On the other hand, the porous structure volume was developed, hence, creating more numbers and pore volumes on the surface of NK adsorbent, which in turn could be more adequate for the deportation of HM-ions out of the aquatic environments, this finding was highlighted in the investigations of Bkour et al. (2016) and Panda et al. (2010).

Table 1. Textural characteristics for natural KC and modified NK adsorbent according to XRD and BET analyses.

Metal ions	Natural KC [% w/w]	Modified NK [% w/w]
SiO_2	59.67	67.45
Al_2O_3	19.13	22.12
Fe_2O_3	4.65	4.89
TiO_2	1.09	NIL
K_2O	1.32	NIL
MgO	1.53	NIL
CaO	1.64	NIL
Miscell.	10.97	5.54
BET		
Surface area [$m^2/g_{adsorbent}$]	1.289	3.142
Pore volume [$cm^3/ g_{adsorbent}$]	0.0064	0.155

Additional evidence of the NK adsorbent's deformation was provided by the SEM imaging of the modified NK, Figure (2). As a result of impurities such as precipitated oxides, which constitute nearly the whole surface of the KC, being leached with HCl treatment, the surface of the NK adsorbent became purified. The mesoporous structure infers plate-like and thin slit-shaped holes from the NK adsorbent surface. According to the Debye-Scherr equation, the modified NK has a target diameter of 24 nm, which is less than the normal nano-pellet size of 60 nm, as can be observed from the SEM. The key considerations influencing the absorption process are the well-developed porous structure, microporosity,

and textural characteristics of the NK adsorbent, implying intense nucleation sites for the migration of HM-ions onto the adsorbents out of an aquatic environment (Hameed et al., 2007; Mojoudi et al., 2019; Somyanonthanakun et al., 2023).
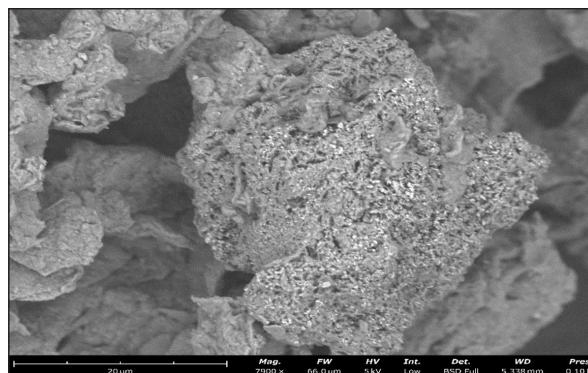

Figure 2. SEM imaging of modified NK adsorbent.

3.2 pH Influence

The alternation of uptake capacity of HM-ions into NK adsorbent with initial pH variation is shown in Figure (3), the investigations of varying the initial pH were performed under a constant temperature of 303 K and an initial HM-ions concentration of 40 $mg/L_{solution}$. The initial pH reading was studied within the range of highly acidic medium (pH = 2) to neutral (pH = 7). The removal percentage of HM-ions from the aqueous solutions increases exponentially with increasing pH in the range from 2.0 to 5.5 to establish a maximum and then decreases under neutral conditions for all the investigated HM-ions. Maximum removal was obtained of 91.9%, 86.3%, and 78.4% for Pb(II), Cd(II), and Cu(II) ions, respectively, within a slightly acidic medium in the pH range of 5.5 – 6. This finding is consistent with prior studies (Wang et al., 2006; Sari et al., 2007; Unuabonah et al., 2008; Al-Essa and Khalili, 2018; David et al., 2020), where the maximum uptake capacity of HM-ions was obtained at initial pH in the range of 5.5 – 6. This finding could be attributed to excess (H^+) concentration in the acidic solution being investigated. Due to the soluble metal oxides, there is an electrostatic competition between the positively charged (H^+) and HM-ions, towards the negatively charged sites of the adsorbent surface. Eventually increasing the initial pH will stimulate (H^+) concentration in an aqueous solution, and the competition between the positively charged HM-ions to be attracted on the negatively charges sites on NK adsorbent surface will increase, hence then HM-ions are the dominating species due to the higher electro-charges, which will attract to the surface of NK due to the driving mechanism of Coulomb interactions (Al-Zboon et al., 2011; Khaleque et al., 2020). Following this finding, an initial pH reading of 5.5 was set as a default value for the proceeding investigations.
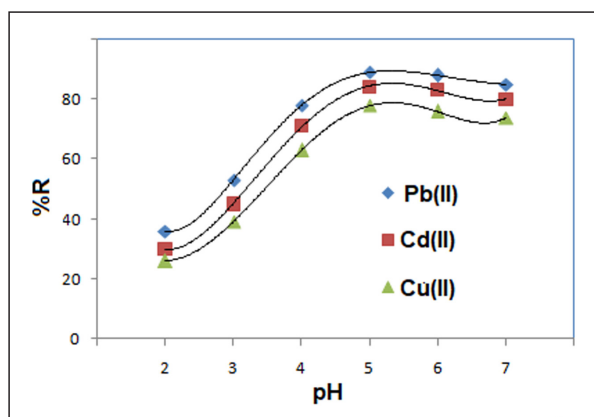
Figure 3. Adsorption removal efficiency of HM-ions onto NK vs. initial pH variation with C_o = 40 mg/$L_{solution}$, 303.15 K.

3.3 Adsorbent dosage Influence

Figure (4) shows the NK dosing for determining the impact on the percentage of HM-ions that are removed from aqueous solutions when the adsorbent dosage is varied from 0.1 to 1.0 $g_{adsorbent}$/$L_{solution}$, pH is 5.5, and medium temperature of 303.15 K. Adsorbent dosage was changed from 0.1 to 0.5 $g_{adsorbent}$/$L_{solution}$ to increase the uptake capacity. This established a maximum removal capacity of HM-ions from the aqueous medium at about 0.5 $g_{adsorbent}$/$L_{solution}$, and for adsorbent dosages higher than this value, there was almost no change in the uptake capacity towards HM-ions. Increased adsorbent dosage may have the effect of increasing the number of nucleation sites available on the adsorbent surface for interaction with free HM-ions in solution. Consequently, the more nucleation sites mean a higher driving force for HM-ions adsorption, a further competition is established adversely between the negatively charged sites towards fewer HM-ions concentration in the aqueous media, thus less removal percentage is accomplished for the HM-ions from the aqueous streams.
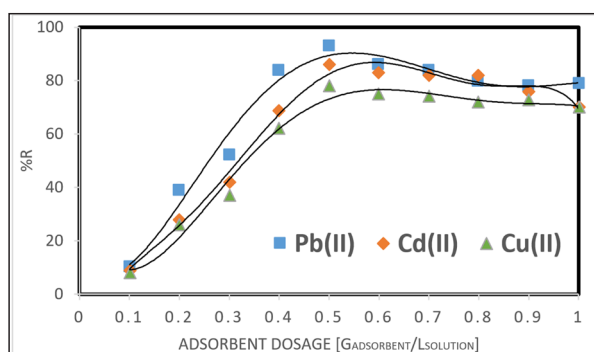

Figure 4. Adsorption removal efficiency of HM-ions onto NK vs. adsorbent dosage variation in the range from 0.1 to 1.0 $g_{adsorbent}$/$L_{solution}$ with C_o = 40 mg/$L_{solution}$, 303.15 K, and initial pH = 5.5.

3.4 Contact time influence

Figure (5) depicts the behavior of the HM-ion adsorption onto NK with a modification in contact time, at a constant temperature of 303.15 K, an initial HM-ion concentration of 40 mg/$L_{solution}$, and a pH value of 5.5. For all the investigation HM-ions anticipated, it was found that the immobilization of HM-ions rises with increasing contact duration, reaching a maximum after 60 minutes of contact time. When a final contact time of 120 minutes was established, the removal percentage remained unchangeable until the experiment was

terminated. The conclusion is that Within the contact time of 60 minutes prior to reaching the adsorption equilibrium, HM-ions are successfully taken up from aqueous solutions. By default, this contact duration was noted as being long enough for HM-ions to adsorb onto NK and was considered in the studies that followed.
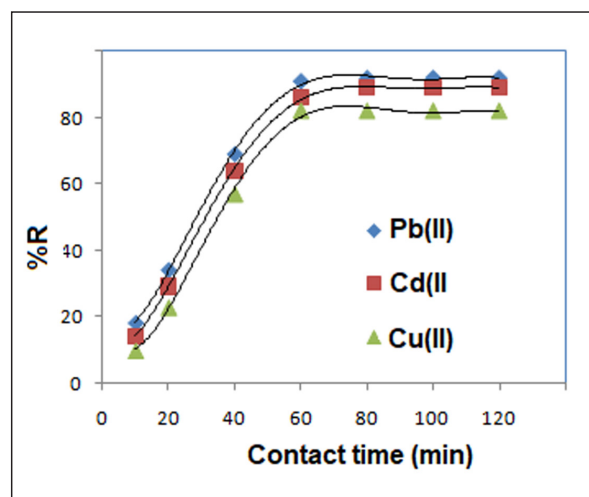

Figure 5. Adsorption removal efficiency of HM-ions onto NK adsorbent vs. contact time variation with C_o = 40 mg/$L_{solution}$, 303.15 K, and initial pH = 5.5.

3.5 HM solubility and temperature Influence

The trend of the HM solubility as a function of temperature for all the investigated HM nitrates salts is presented in Figure (6), the data were outlined from Sigma-Aldrich Chemie (2022). Obviously, the solubility of the nitrate salts indicates an increase within the foreseen range of the investigated temperature. Accordingly, the reported values for HM solubility imply that at a predefined temperature, a higher concentration of free Cu(II) ions are available in the aqueous media compared to Cd(II) and Pb(II) ions, respectively. This means that HM solubility is recorded in the following order Cu(II) > Cd(II) > Pb(II).
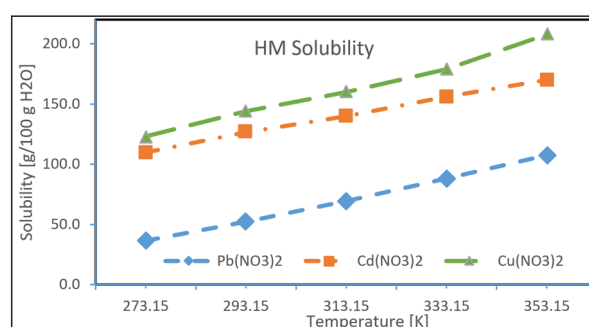

Figure 6. HM solubility vs. temperature (Sigma-Aldrich Chemie, 2022).

The temperature influence on the adsorption process of HM-ions is illustrated in Figure (7), where the uptake capacity of HM-ions from aqueous media (q_e) was plotted as a function of temperature. It can be deduced that the immobilization of HM-ions onto modified NK from aqueous solution is enhanced upon increasing temperature, for an initial metal ion concentration of 40 mg/$L_{solution}$ and pH reading of 5.5. The removal efficiency has been promoted from 135 to 184.4 mg/$g_{adsorbent}$, 128 to 168.7.4 mg/$g_{adsorbent}$, and 113.7 to 158.2mg/$g_{adsorbent}$ for HM-ions of Pb(II), Cd(II), and

Cu(II), respectively, within the investigated temperature range of 293 to 313 K. This finding is consistent with previous studies (Jiang et al., 2010; Shahmohammadi-Kalalagh et al., 2011; Ogbu et al., 2019), where it was stated that the HM-ions removal achieves better effectiveness with higher temperatures. The variation of the uptake capacity of HM-ions on modified NK was found in the order Pb(II) > Cd(II) > Cu(II), this fact is explained by the higher solubility of Cu(II) ions with respect to Cd(II) and Pb(II) ions, hence Cu(II) ions have a higher affinity towards aqueous media than that of Cd(II) and Pb(II) ions, respectively. Consequently, the lower uptake capacity was obtained of Cu(II) ions onto modified NK compared to that of Cd(II) and Pb(II) ions, respectively.
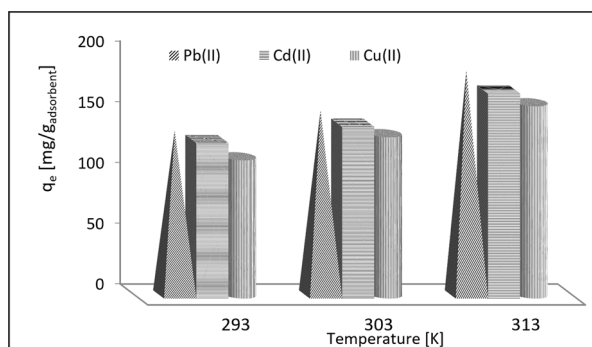

Figure 7. Temperature effect on adsorption capacity of HM-ions onto modified NK adsorbent.

As may be inferred from Figures 6 and 7, elevated temperatures are associated with high solubility figures of the HM, which results in the incorporation of increased concentrations of soluble HM-ions into the aqueous medium. The randomization is then encouraged by the warming of the aqueous medium, increasing the probability that HM-ions will come into closer contact with the nucleation sites on the NK's surface and so increasing the NK adsorbent's capacity for uptake.

3.6 Modelling of Adsorption Isotherms

Adsorption isotherms are the most practical way to describe data for HM-ions removal onto modified NK (Amer et al., 2010; Adewuyi et al., 2019; Alasadi et al., 2019; Al-Essa and Khalili, 2018; Chukwuemeka-Okorie et al., 2018; David et al., 2020; Lawal et al., 2020. To process the experimental data for the removal of Pb(II), Cd(II), and Cu(II) ions onto modified NK, Freundlich and Langmuir adsorption isotherm models were used. Mono-layer adsorption on a homogeneous surface with a finite number of adsorption sites is the basis of the Langmuir model (Langmuir, 1918). As a result, the Langmuir isotherm's linearized form is changed:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L \cdot q_{max}} \tag{3}$$

Where q_{max} is the maximum adsorption capacity (in mg/$g_{adsorbent}$) and K_L is a constant relating to the Langmuir energy of adsorption. A linearized plot is obtained by plotting the right side of equation (3) as a function of (C_e) for the HM-ions of Pb(II), Cd(II), and Cu(II). The slope and intercept of the linear plot of (C_e/q_e) vs. (C_e) in Figure (8) were used to analytically calculate the values of the Langmuir parameters, q_{max} and K_L. The Langmuir isotherm model adequately fits the experimental results of the adsorption of HM-ions onto modified NK from aqueous environments.
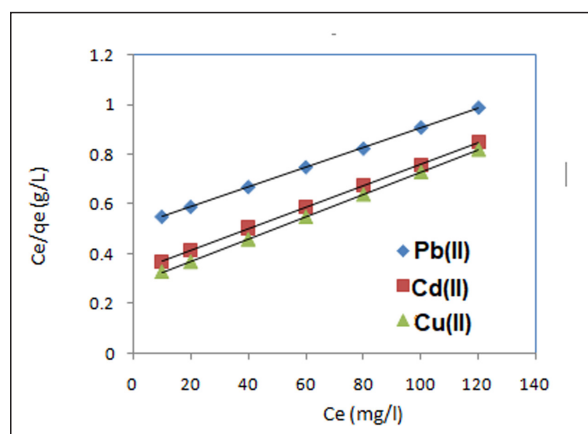

Figure 8. Experimental and model data of C_e/q_e vs. C_e according to Langmuir Isotherm.

The nonlinear function that frequently appears in the adsorption process, according to Freundlich Isotherm (Freundlich and Hellen, 1939), follows the exponential function. The following equation is rearranged for linearization fitting of the experimental adsorption data using the natural logarithm of the exponential form:

$$lnq_e = lnK_F + \frac{1}{n} \cdot lnC_e \tag{4}$$

where K_F is the Freundlich constant and (n) is a function of the strength of adsorption; higher n figures indicate even higher adsorption capacity. The adsorption is linear when (n) equals unity. For (n) figures smaller than unity, adsorption is a chemical process; as a result, enough energy must be provided to force HM-ion exchange with other metal ions onto the adsorbent surface. If (n) figure is higher than 1, then the adsorption process is governed by spontaneous Coulomb interactions acting as the main driving forces behind the electrostatic attractions of positively charged HM-ions to the negative nucleation surface sites. The Freundlich Isotherm prediction of the experimental adsorption data is shown in Figure (9). The intercept of the linearized Freundlich Isotherm's data with the ordinate line is an inherent way to determine (K_F) by charting the term (ln q_e) as a function of the (ln C_e). As opposed to this, the (n) parameter is obtained from the inverse slope of the linearized data fitting. Evidently, the Freundlich Isotherm accurately reproduces the experimental adsorption data for the phenomenon of HM-ions deporting onto modified NK from aqueous environments.
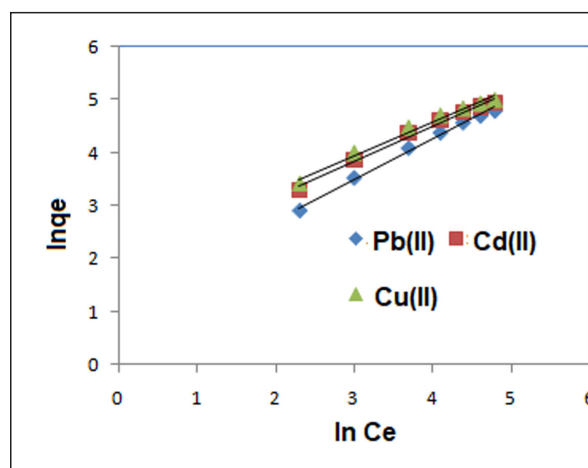

Figure 9. Experimental and model data of (ln q_e) vs. (ln C_e) according to Freundlich Isotherm.

The thermodynamic parameters for the Langmuir and Freundlich isotherms are listed in Table (2). The HM ions of Pb(II), Cd(II), and Cu(II) have an affinity to attract onto modified NK because the magnitude (n) is greater than unity. For HM-ions of Pb(II), Cd(II), and Cu(II), the variation of the maximum absorption capacity of HM-ions on modified NK was determined to be 250.0, 232.6, and 222.2 mg/g$_{adsorbent}$, respectively. This anticipated result is

explained by the metal's solubility in aqueous media. Under unchanging adsorption conditions of a medium temperature of 303.15 K, a pH reading of 5.5, and an initial HM-ion concentration of 40 mg/L$_{solution}$, the adsorption experimental data are accurately reproduced to a large extent, according to obtained regression coefficient (R^2) figures by both models of Langmuir and Freundlich Isotherms.

Table 2. Adsorption isotherms' parameters by Langmuir and Freundlich.

HM-ion	Langmuir			Freundlich		
	q$_{max}$	K$_L$	R^2	n	K$_F$	R^2
	[mg/g]	[L/mg]	[-]	[-]	[(mg/g).(L/mg)^n]	[-]
Pb(II)	250.0	4.3	0.999	1.20	0.7655	0.994
Cd(II)	232.6	4.3	0.999	1.84	0.6610	0.989
Cu(II)	222.2	4.5	0.999	2.05	0.6310	0.985

3.7 Thermodynamic Analysis

The following analysis is done on the thermodynamic behavior of HM-ions of Pb(II), Cd(II), and Cu(II) adsorption onto modified NK adsorbent. Following Tran (2022), the relationship, which combines between the equilibrium constant and change in the Gibbs-Helmholtz energy (ΔG^o) of the adsorption process, can be described as:

$$\Delta G^o = \Delta H^o - T \cdot \Delta S^o = R \cdot T \cdot ln\,K_a, \text{ with } K_a = \frac{q_e}{C_e} \quad (5)$$

where C$_e$ is the equilibrium concentration of remaining HM-ions (mg/L$_{solution}$) in solution, and K$_a$ is the thermodynamic equilibrium constant (L$_{solution}$/g). The Van't Hoff equation was used to calculate the specific enthalpy change, ΔH^o[kJ/mol], and specific entropy change, ΔS^o[J/mol/K] (Amer et al., 2010; Jiang et al., 2010, El-Maghrabi and Mikhail, 2014). After being rearranged, equation (5) is then solved for K$_a$:

$$logK_a = \frac{1}{2.303 \cdot R} \cdot \left(\Delta S^o - \frac{\Delta H^o}{T}\right) \quad (6)$$

where R is the gas constant [8.314 J/(mol.K)] and T is the absolute temperature (K). The adsorption energies (ΔS^o and ΔH^o) were analytically assessed from the slope and intercept of a linearized data plot of (log K$_a$) as a function (1/T), following the methodology by Alasadi et al. (2019), Al-Essa and Khalili (2018), David et al. (2020), Awwad et al. (2021), and Al Rabadi and Awwad (2021). At three anticipated temperatures, 293, 303, and 313 K, under analog conditions with an initial HM-ions concentration of 40 mg/L$_{solution}$ and pH of 5.5 reading, the adsorption energies and the pertinent thermodynamic parameters were measured. Table (3) lists the findings for K$_a$, ΔG^o, ΔH^o and ΔS^o. According to Wang et al. (2006), Sari et al. (2007), and Shahmohammadi-Kalalagh et al. (2011), the adsorption process is endothermic and is generally favored at higher temperatures. This is indicated by the positive figures of (ΔH^o), (ΔS^o), and the decrease in (ΔG^o) with rising temperature. Negative figures of (ΔG^o) indicate the HM-ions adsorption onto modified NK adsorbent is instinctive. This could be attributed to the activation of more nucleation sites on the surface of the modified NK adsorbent. Because the HM-ions are readily soluble in aqueous environments, endothermic adsorption may be explained (Alasadi et al., 2019; Khaleque et al., 2020). While the HM-ions require energy to be absorbed on

the modified NK absorbent surface, the necessary energy must balance the dehydration energy provided by the (H$^+$) ions in the aqueous medium so that the HM-ions can attract to the adsorbent surface. According to Aguado et al. (2009), and Tran (2022) the range of (ΔG^o) for physical adsorption is between -20 and 0 (kJ/mol). The resulting (ΔG^o) was within the range of -3.79 to -5.48 (kJ/mol), -3.52 to -4.95 (kJ/mol), and -3.30 to -3.88 (kJ/mol) for the adsorption of HM-ions of Pb(II), Cd(II), and Cu(II), respectively, onto modified NK adsorbent. In this domain, The primary adsorption of the examined HM-ions was verified to be a physically motivated process. Additionally, the physical adsorption of Pb(II), Cd(II), and Cu(II) ions onto modified NK was successfully achieved with (ΔS^o) values of 84.83, 71.64, and 28.81 (J/mol), respectively. This indicates that the nucleation sites at the adsorbent surface are appropriately random and that there are sufficient driving forces at the aqueous medium interface. When deportation of investigated HM-ions occurs on a modified NK surface, the hydrated water molecules undergo re-substitution before adhering to the surface or penetrating its structure. This reduces heterogeneity, hence increasing the relevant entropy. The adsorption process is endothermic as was highlighted by the positive numbers of (ΔH^o).

3.8 NK reusability and comparison with pertinent adsorbents

The life cycle of NK adsorbent is an important criterion to comprehend its practicality in HM-ions uptake from an aqueous medium, and how feasible its reusability is for repeated cycles from an economic point of view. Figure 10 depicts the percentage removal of heavy HM-ions from modified NK adsorbent versus cycles of reusability, for an initial HM-ions concentration of 40 mg/L$_{solution}$, pH reading of 5.5, and medium temperature of 303.15 K. There is a devaluation in the performance of the modified NK towards the deportation of HM-ions out of the aquatic environment in reverence of implementing re-cycled adsorbent. This finding is attributed to the protonation of the adsorbent surface since some of the positively charged HM-ions are kept attracted to the surface of the regenerated adsorbent due to the electrostatic forces, hence causing a blockage of few nucleation sites. Particularly, the modified NK adsorbent can be regenerated up to four cycles with tolerable performance,

due to the robust textural characteristics that promote the migration of HM-ions from aqueous solutions and ensure

high structural stability of the modified NK adsorbent during the desorption stage.

Table 3. Thermodynamic parameters of HM-ions adsorption onto modified NK adsorbent.

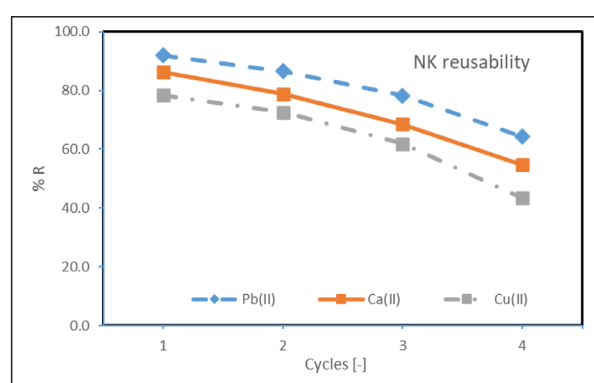| HM-ion	T	K_a	ΔG^o	ΔH^o	ΔS^o
	[K]	[$L_{solution}$/g]	[kJ/mol]	[kJ/mol]	[J/(mol.K)]
Pb(II)	293	4.67	3.79-		
	303	6.42	4.63-	21.07	84.83
	313	8.11	5.48-		
Cd(II)	293	4.22	3.52-		
	303	5.44	4.24-	17.47	71.64
	313	6.67	4.95-		
Cu(II)	293	3.88	3.30-		
	303	4.15	3.59-	5.14	28.81
	313	4.44	3.88-		

Figure 10. Removal efficiency of HM-ions onto modified NK adsorbent vs. cycles of reusability with C_o = 40 mg/$L_{solution}$, 303.15 K, and initial pH figure of 5.5.

For comparison with pertinent adsorbents, Table (4) summarizes the maximal absorption capacity of the modified NK adsorbent to that reported in the pertinent literature. By employing sulfate-modified KC rather than natural Kaolinite, Adebowale et al. (2005) appear to have improved the removal of HM-ions from aqueous media. The chemical modification increased the absorption capacity of the examined HM-ions. On the other hand, Wang et al. (2006) found modest outcomes from chemical treatment when utilizing natural Kaolinite. Regarding the outcomes of Unuabonah et al. (2008) using polyvinyl alcohol modified

Kaolin, Amer et al. (2010) using phosphate modified KC, and Adewuyi et al., 2019 using amine modified KC, respectively, significant accomplishments were noted, which are attributed to the combination of physical and chemical treatment approaches. Whereas poor results were attained when using solely natural Kaolinite (Jiang et al., 2010; Shahmohammadi-Kalalagh et al., 2011; David et al., 2020). On the other hand, promising results were obtained in the investigations of Amer et al, 2010; Ogbu et al., 2019; and Al Rabadi and Awwad, 2021, where Silica oxides contributed to advanced uptake capacity for HM-ions onto modified adsorbent from aqueous media. In general, the observed differences in adsorption uptake can be attributed due to the physico-chemical characteristics of each adsorbent such as surface area and pore volume, modification technique, and the main functional groups in the matrix structure of the adsorbent. By comparing current findings with relevant investigations, a remarkable HM-ions uptake of modified NK adsorbent has been achieved. Consequently, the removal of HM-ions from aqueous solution using modified NK could be effective, eco-friendly, and budgeted-feasible adsorbent for the uptake of HM-ions such as Pb(II), Cd(II), and Cu(II) from aquatic streams even by elevated concentrations, and hence prompting the remediation of environment and protection of public health.

Table 4. Comparison of maximum uptake of HM-ions onto modified NK with relevant studies.

Adsorbent	q_{max} [mg/$g_{adsorbent}$]			Reference
	Pb(II)	Cd(II)	Cu(II)	
Modified NK	250.0	232.6	222.2	Current investigations
Kaolinite	87.26	35.92	71.95	Adebowale et al., 2005
Sulfate modified KC	89.09	42.57	77.09	Adebowale et al., 2005
Natural Kaolinite	-	-	16.79	Wang et al., 2006
Polyvinyl alcohol modified Kaolin	56.18	41.67	-	Unuabonah et al., 2008
Phosphate modified KC	93.89	41.66	80.94	Amer et al., 2010
Kaolinite clay	2.35	0.88	1.22	Jiang et al., 2010
Kaolinite	7.75	-	4.42	Shahmohammadi-Kalalagh et al., 2011
Saw-dust Kaolinite	125	125	-	Ogbu et al., 2019
Amine modified KC	36.41	24.41	-	Adewuyi et al., 2019
Raw Kaolinite	5.42	-	-	David et al., 2020
Alkaline modification of Kaolinite	25.64	-	-	David et al., 2020
nKSOC	172.41	158.73	-	Al Rabadi and Awwad, 2021

4. Conclusion

Based on the addressed findings, a novel solution was introduced for the deportation of HM-ions of Pb (II), Cd (II), and Cu (II) from an aqueous environment. To synthesize an eco- and budgeted-friendly NK adsorbent, the natural KC was structurally modified by integration of physical and chemical methodologies. Under a variety of different constraints, including medium pH and temperature, adsorbent dose, initial HM-ions concentration, and contact time, the modified NK demonstrated efficient behavior for the uptake of HM-ions from aqueous solutions. According to the positive values of (ΔS^o) and (ΔH^o), the thermodynamic scrutiny has shown that the adsorption of HM-ions results is a spontaneous process that is associated with an enhanced randomness at the solid-medium interface. Whilst negative (ΔG^o) figures confirm the endothermic elimination of HM-ions from modified NK. The Langmuir and Freundlich isotherms performed adequately by reproducing experimental adsorption data. This innovative approach could potentially be used for wastewater pollutants remediation in comparison to the deportation by pertinent adsorbents, described in the literature, and with the effective recovery performance.

Conflicts of Interest

The authors declare that this study is their own original work. It was not copied (in whole or in-part) from any other work. Also, to declare that no similar work has been submitted or published in somewhere else, either in English or in any other language, without the written consent of the Publisher.

Authors Contributions

A. Awaad contributed to basic idea for the current study, acquisition of experimental data, M. Mahasneh interpreted the experimental results, and S. Al Rabadi drafted the manuscript. All authors have seen and approved the final manuscript and agreed to its submission for publication by JJEES.

Competing Interests

The authors have no competing interests to declare that are relevant to the content of this study.

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