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Biochar for Lead Removal from Aqueous Solution

Maamoun Al Jedaih, Zaydoun Abu Salem*, Kamel Alzboon

Al-Balqa Applied University, Department of Environmental Engineering, Al-Huson University College, Al-Huson, Irbid, Jordan

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Abstract

Biochar as an eco-friendly and low-cost material generally produced from organic wastes such as agricultural wastes, forestry residues, and municipal wastes has attracted increasing attention shown by its increasing use in different environmental applications. This work has been conducted to determine the effectiveness of biochar in immobilizing and removing Pb^{+2} from aqueous solution. This work includes the production of biochar from the branches of lemon and olive trees and utilizing it for Pb^{+2} removal from an aqueous solution. The effects of pH, biochar doses, and contact time were investigated. The results showed that Pb^{+2} can be removed successfully using a low dose of biochar within a short time. A removal efficiency of 99.4% of 50ppm of Pb^{+2} can be achieved by a dose of 0.5g of biochar. A high concentration of Pb^{+2} needs higher doses up to 3g and a lengthy time up to 180 minutes. The pseudo-second order model provided the best fitting for isotherm data and is the best in describing kinetic behavior.

Keywords: *Biochar, Lead, Heavy Metal Ions, Pollutants, Removal Efficiency.*

1. Introduction

The world's water resources are deteriorating due to the continuous discharge of many organic and inorganic contaminants such as dyes, heavy metals, surfactants, pharmaceuticals, pesticides, and personal care products from industries and municipalities into water bodies. Most of these pollutants are highly persistent in nature and are otherwise converted into recalcitrant form. The uncontrolled discharge of these pollutants is a concern because of their suspected negative effects on ecosystems (Zulfiqar et al., 2019).

Several conventional technologies are applied worldwide for the removal of wastewater pollutants including coagulation-flocculation, adsorption, membrane filtration, reverse osmosis, chemical precipitation, ion exchange, electrochemical treatment, solvent extraction, and flotation for the removal of inorganic pollutants (Razzak et al., 2022). However, these technologies suffer from a range of disadvantages stretching from inefficiency in removing pollutants at low concentrations to completely converting pollutants into biodegradable materials, less toxic byproducts, high energy and chemicals consumption, process complexity, high maintenance, and operation costs, etc. An efficient and workable treatment process should meet both economic and environmental requirements to be marketed and applied on a large scale. The incorporation of low-cost and available materials in different treatment processes could decrease the global treatment cost and increase the process efficiency (Al-Zboon et al., 2011; Hamad, 2013).

Biochar is a carbon-rich material produced by pyrolysis of organic matter, such as wood, crop residues, and animal manure. When used as a soil amendment, biochar has proven various mechanisms for removing pollutants (Tomczyk et al., 2020; Ahmad et al., 2014; Tang et al., 2013).

Biochar, as an eco-friendly and low-cost material generally produced from organic wastes such as agricultural wastes, forestry residues, and municipal wastes, has attracted increasing attention due to its increasing use in different environmental applications. As a stable carbon-rich material, it shows incredible potential to handle water/wastewater contaminants. Its application is gaining increasing interest due to the availability of feedstock, the simplicity of the preparation methods, and their enhanced physic-chemical properties. In addition to biochar, compost is also produced by converting organic wastes through biological fermentation. (Al-Zawahreh et al., 2022)

Biochar application improves soil fertility via two mechanisms: supplying nutrients to the soil, such as potassium and, to a lesser degree, micronutrients, or keeping nutrients from other sources, including the soil itself. Adding biochar into the soil increased the pH of acidic soils by 0.5-1, such as yellow-brown soil and fluvial-aquic soil. However, the charcoal and fertilizer treatments had a different effect. Biochar, rather than being a key source of nutrients for microorganisms, is thought to enhance the physical and chemical soil environment, making bacteria more comfortable (Lehmann et al., 2006; Qadan, 2022). Biochar, applied to soil, improves plant growth and crop yields, enhancing food production and sustainability in areas of depleted soils, low organic resources, insufficient water, and/or limited access to agrochemical fertilizers (Chen et al., 2011). It is a carbonaceous residue created by the pyrolysis of biomass that has been shown to improve moisture retention, air permeability, and soil structure. Biochar contains both organic C and inorganic C (ash). It also increases the overall porosity of clayey soil. Similarly, a rise in porosity has been

* Corresponding author e-mail: zaydoun@bau.edu.jo

recorded in coarser soils(Cimo et al., 2014; De Ridder et al., 2012).

During biochar production, bio-oil and gases, such as hydrogen, are produced and can be used as energy sources supplying power to homes or automobiles. Biochar has the capacity for remediation of contaminated soil and provides additional benefits to the environment.

Biochar is formed by the pyrolysis (thermal decomposition) of organic biomass or agricultural residues (Xiao et al., 2014). It is mainly used to improve soil nutrient content and to sequester carbon from the environment (Lehmann, 2006). Its highly porous structure makes it an attractive choice for soil amendment as it improves the water-holding capacity of the soil by increasing its total surface area. After adding biochar, improvements in the physicochemical characteristics of the soil and crop productivity are anticipated since it may retain moisture and nutrients. Biochar raises soil pH and organic carbon content, increases soil water-holding capacity, lowers pollutant levels, and increases crop yields. Meta-analyses show average crop yield increases 10%–42% after adding biochar, with the greatest increases in low-nutrient P-sorbing acidic soils (common in the tropics) and in sandy soils in drylands due to an increase in nutrient retention and water-holding capacity (Srinivasarao et al., 2013).

Biochar is considered a cost-effective alternative to the activated carbon in water and soil treatment due to its practical production and low cost. It has been used to remove various pollutants, including volatile organic compounds, heavy metal ions, pesticides, drugs, dyes, and polycyclic aromatic hydrocarbons (El-Naggar et al., 2021; Zhao et al., 2021). Biochar's efficiency in removing pollution is due to its high surface area, porous structure, and chemical properties (Liang et al., 2021).

A clean biochar has limited potential for absorbing and removing pollutants, as its surface area is relatively modest. The characteristics of pollutants can be influenced by abiotic and/or biotic processes. Various modification approaches, such as coating, enhancing additives, base treatment, acid treatment, magnetic modification, and composites with other materials, have been increasingly highlighted to improve biochar's surface and mechanical characteristics (Arif et al., 2021).

Biochar properties are influenced by various parameters, such as heating speed, pyrolysis temperature, biomass type, and residence time. The interaction between heavy metals and biomass involves reduction, electrostatic attraction, complexation, precipitation, and cation exchanges. which are influenced by factors such as pH levels, dissolved organic carbon, and biomass content. Organic pollutants interact with biochar through hydrophobic interactions, Pi-interactions, and hydrogen bond interactions (Khalid et al., 2020).

These properties enable biochar to efficiently immobilize inorganic pollutants in soil, thereby reducing their bioavailability and potential environmental and human health risks. However, the effectiveness of biochar for pollution removal can vary depending on factors such as the type and concentration of pollutants, soil characteristics, and biochar properties (Mohanty et al., 2018; Qambrani et al., 2017; Xiang et al., 2022).

According to the most recent study, biochar can be used in various wastewater treatment applications, including catalysis, adsorption, redox, and biocidal processes. all of these applications involve different reaction mechanisms (Zhao et al., 2021; Zhou et al., 2014). Biochar-based materials offer several advantages, such as high porosity, large surface area, improved ion exchange capacity, and abundant functional groups. Numerous publications have supplied detailed discussions on the physicochemical properties of biochar and its potential environmental applications (Yuan et al., 2019).

Liang et al., (2021) investigated preparation techniques and physicochemical features of biochar composites and their performance in removing sewage contaminants. They discussed the use of biochar and biochar-based materials for breaking down and changing organic pollutants, as well as sorbing heavy metals and radionuclides. Biochar is typically produced from low-cost biomass, such as forest wastes, agricultural residues, food waste, fertilizers, and sludge, which are widely available and abundant worldwide. However, these different types of byproducts pose disposal challenges, making the conversion of waste to biochar a workable and sustainable solution.

In a batch study, Karishma et al., (2021) investigated the efficiency of Ulva lactuca carbon for removing lead from aqueous solutions. The study considered the effects of various parameters, including pH, adsorbent dosage, effective contact time, and initial concentration. The optimal conditions were found to be a pH of 3, an adsorbent dose of 0.8 g, and a contact time of 30 minutes. The results indicated that Ulva lactuca carbon is a cost-effective and efficient material for removing lead from aqueous solutions. The carbon can be reused by removing lead after being treated with 0.1M HNO_3, and the study concluded that seaweed carbon is more efficient when activated than when untreated.

Lei et al., (2019) prepared biochar from bio-physical dry sludge and found that increasing the pyrolysis temperature has improved the adsorption effect of biochar on Pb^{+2}, and the adsorption capacity of lead has also increased with increasing of the pH solutionvalue. Mireles et al., (2018) conducted a study on lead removal from aqueous solutions using biochars derived from corn stover, orange peels, and pistachio shells in the Lower Rio Grande Valley in South Texas, USA. The study found that the efficiency of lead ion (Pb^{+2}) removal through batch adsorption experiments has increased with increasing pH from 2 to 6, reaching a maximum adsorption of Pb^{+2} at a pH of 6. The results also indicated that biochar is a cost-effective adsorbent material for heavy metals in water.

Mahdi et al., (2018) conducted a study on the removal of lead (II) from aqueous solutions using biochars produced from date seed biomass in Riyadh, Saudi Arabia. The study found that the amount of Pb^{+2} adsorbed varied significantly with initial Pb^{+2} concentration, solution pH, and contact time. The study found that the maximum adsorption capacity of DSB550-3 was obtained at a pH of 6. Yonggang et al., (2020) investigated the influence of pyrolysis temperature on the characteristics and lead(II) adsorption capacity of phosphorus-engineered poplar sawdust biochar.

Inorganic pollution has several adverse effects on the environment, including soil degradation, decreased soil fertility, and contamination of groundwater and surface water. Moreover, inorganic pollutants can accumulate in plants and animals, leading to bioaccumulation and biomagnification in food chains, which can ultimately impact human health (Kristanti et al., 2021; Khan et al., 2018; Khudhur et al., 2018; Rashmi et al., 2020).

Researchers have extensively studied the negative impacts of inorganic pollution in soil on the environment and human health. Overall, inorganic pollution in soil poses a significant threat to the environment and human health, highlighting the need for effective pollution remediation strategies such as the use of biochar as a soil amendment. Inorganic pollutants have the potential to change the physical and chemical properties of soil, resulting in soil degradation and reduced fertility, which can have significant impacts on agricultural productivity and food security (Gautam et al., 2023; Qin et al., 2021; Cui et al., 2023). Exposure to heavy metals, such as lead, cadmium, and mercury, can result in neurological and developmental disorders, kidney damage, and cancer. (Sevim et al., 2020; Jyothi et al., 2020; Fu et al., 2020; Engwa et al., 2019).

Bolan et al. (2022) emphasized the necessity of implementing effective management and remediation strategies to decrease the negative impacts of inorganic pollution in soil on the environment and human health. The use of biochar as a soil amendment is one potential strategy that has shown promise in reducing the bioavailability of inorganic pollutants in soil.

Biochar has mechanisms for pollution removal through various methods, such as adsorption, precipitation, and ion exchange. Adsorption occurs when pollutants bind to the surface of biochar through physical and chemical interactions, helped by the high surface area and porous structure of biochar. Biochar can also ease the precipitation of inorganic pollutants by changing soil pH or providing a surface for the formation of mineral phases. Precipitation occurs when pollutants react with biochar or other soil components to form insoluble compounds that can be immobilized in the soil. Additionally, biochar can remove inorganic pollutants through ion exchange, where the positively charged biochar surface attracts and binds with negatively charged ions of pollutants, such as heavy metals (Barquilha and Braga, 2021; Zeghioud et al., 2022).

Pyrolysis is a thermochemical conversion process of biomass that occurs under a low or no-oxygen environment. It can be categorized into three broad types: fast pyrolysis, intermediate pyrolysis, and slow pyrolysis. The first type occurs within a few seconds and is influenced by phase transition phenomena, heat and mass transfer processes, and chemical reaction kinetics. Depending on the process parameters such as temperature, residence time, heating rate, and flow rate of sweeping gas, slow pyrolysis can retain up to 50% of the feedstock carbon,yielding more biochar than any other type of pyrolysis. Temperature increases also result in a decrease in the amount of final solid product, with a concurrent rise in ash content due to naturally existing inorganic components in all biomasses (Shaaban et al., 2014).

The biochar structure is made up of aligned honeycomb-like groups of pores, generated by the carbonaceous skeleton, and is formed during the thermal decomposition of the raw material. This structure is the outcome of the raw material's biological capillary structure. Volume is reduced due to the loss of volatile organic molecules during thermal decomposition (Lehmann et al., 2006).

Lead is a bluish-white metal with a glossy finish that is extremely soft, pliable, ductile, and a poor electrical conductor. Although it is highly corrosion-resistant, it tarnishes when exposed to air. Most lead found in the environment originates from human activity. Lead is among the metals that have the most significant negative effects on human health, including increased blood pressure, kidney damage, and fever. Due to the presence of oxygen-containing functional groups such as phenolic, lactones, and carboxyl in their structure, lead can bond with heavy metals. (Mohan and Pittman, 2007; Liu and Zhang, 2009).

The pH of an aqueous solution has been proven in studies to impact the sorption of pollutants onto biochar. This impact is due to the fact that the oxygen-containing functional groups in biochar are pH-dependent, resulting in variations in surface charge and ionization at the biochar surface. As a result, biochar's adsorption ability for eliminating pollutants varies with pH (Barquilha and Braga, 2021).

Lead has been removed from water using a variety of techniques, including filtration, sedimentation, coagulation/flocculation, precipitation, ion exchange, chemical reduction, phytoremediation, bioremediation, immobilization, electrocoagulation, and electrokinetic remediation (Lei et al., 2019; Liang et al., 2021; Liu and Zhang 2009). Adsorption is preferred over other removal methods because it is less expensive, natural adsorbents are available, the process is safe, and it is simple to separate the adsorbate from the solution (Hosseini et al., 2022). Hosseini et al. found that a novel ligand-based conjugate material (CMA) corresponded well with the Langmuir isotherm model, had a maximum adsorption capacity of 196.35 mg/g, and could remove 99 percent of Pb^{+2} from water under ideal conditions. Researchers discovered that lead could be effectively removed from water-based solutions, using biochar generated from solid and liquid waste from olive mills. The maximum lead removal percentages were obtained when a high dose of biochar was combined with slightly acidic pH values (Kypritidou et al., 2022). With an estimated maximum adsorption capacity of 40.8 mg/g, this biochar fared better than others derived from other biomass sources.

As mentioned earlier, biochar is anticipated to be an effective product in reducing lead contamination because of its intense porous structure and high adsorption affinity for pollutants. Biochar was selected due to its ease of use, low cost, and flexible preparation methods that can be employed in various ways. Additionally, agricultural waste, such as fruit and vegetable scraps, dried branches, and fallen leaves, can be used to produce biochar, which can enhance soil health and provide agricultural benefits. In the current research, biochar was derived from accumulated lemon and olive tree branches under controlled heating conditions. The produced biochar is tested by removing Pb ions under different operational conditions including pH, adsorbent dosage, and contact time. Under optimized conditions, kinetic tests, and equilibrium isotherms are measured. Both kinetic profiles and isotherms are presented by different models to elucidate the Pb interaction mechanism with biochar.

2. Methodology

2.1 Production of Biochar

The experiments were prepared at Al-Huson College, Al-Balqa University campus, Jordan. A thorough cone-shaped hole has been dug into the ground, and a fire has been ignited from the base of the hole to keep the lemon and olive tree branches from drying out by exposing them to light. The fire spread, and more branches and twigs were placed on top of the layer that had previously prevented the stick surfaces from being coated in ash. The expert continued to add boards to the fire until the material was completely burned, and he reached the top of the cone. The next step is to submerge the object in water and maintain a suitable temperature. Regular application of biochar to the floor of the shed increased its surface area, which accelerated the drying process and reduced biochar particle size (passing sieve #50). The final product is shown in Figure 1 which illustrates the steps used for the preparation process.

Figure 1. Biochar preparation

2.2 Adsorption Experiments

The Pb^{+2} stock solution (1000 mg/L) was prepared by mixing 1.599 g of lead nitrate ($Pb(NO_3)_2$) with 1000 mL of deionized water. The base solution included $NaNO_3$ (0.01 mol/L). Before the adsorption trials, the stock solution was diluted to 200 and 20 mg/L. All adsorption studies were carried out in 100-ml glass bottles containing 50 ml of Pb^{+2} stock solution. Three different tests with parallel results and a blank experiment were carried out for each measurement.

After making the lead solution, 50 ml of 200 mg/l Pb^{+2} stock solution was added to four flasks for the initial studies on the influence of pH on lead adsorption. Each flask received 0.5g of biochar smaller in size than 2 mm, which was stirred for one minute. Using NaOH and H_2SO_4, the pH was changed to different levels (5, 6, 7, and 8). The samples were then filtered in a Büchner funnel using filtering paper, and the pH values of each sample were recorded.

In the second experiment, 50ml of 20 mg/l Pb^{+2} stock solution was introduced to three flasks to investigate the effect of biochar dosage on lead adsorption. The pH of all flasks was adjusted to the optimal level when mixing with NaOH and H_2SO_4. Biochar dosages of less than 2 mm were applied to each flask of 1, 2, and 3 grams before mixing for one minute. Filtration paper was used to filter the samples in a Büchner funnel.

In the third experiment, the impact of contact time on lead adsorption was investigated by adding 50ml of 1000 mg/l Pb^{+2} stock solution to five flasks. The pH of all flasks was adjusted to the optimal level when mixing with NaOH and H_2SO_4. At varying rater durations of 5, 30, 60, 90, and 180 minutes, fast mixing at 200 RPM was applied to the samples. Filtration paper was used to filter the samples in a Büchner funnel.

The lead concentrations in the treated samples were determined by atomic absorption spectrometry (SHIMADZU AA-7000). To adjust the pH of the solution, a digital pH meter (pH Meter, Zonedeal) was used for this purpose.

2.3 Adsorption Parameters:

Adsorption tests Removal efficiency and Equilibrium capacity were used to determine the efficiency of the biochar adsorption. The percentage removal efficiency (E) was calculated using the following equation (Al-Zboon, 2016):

$$E=(Co-Ce)/C0\times 100\% \quad (1)$$

where: Co is the initial concentration of Pb^{+2} (ppm), and Ce is the residual concentration of Pb^{+2} ion in solution after equilibrium (ppm). The amount of Pb^{+2} uptake by biochar was calculated as the following [AlHarahshah et al., 2015]:

$$q=(Co-Ce)\times V/m \quad (2)$$

where q is the amount of Pb^{+2} uptake by biochar (mg (metal)/g (Biochar), V is the volume of sample (l), and m is the mass of Biochar (g).

2.4 Isotherm Study

Three isotherm models were used in this research: Langmuir, Freundlich, and Temkin models, as shown in Equations (3-5), respectively (Alzboon, 2023):

$$1/qe=(1/kaqm)*(1/Ce)+(1/qm) \quad (3)$$

$$\log(qe)=\log(kf)+(1/n)\log(ce) \quad (4)$$

$$qe=B\ln(At)-B\ln Ce \quad (5)$$

where qe is the equilibrium adsorption capacity at a certain concentration, Co, qm refer to the optimum equilibrium uptake capacity, Ka is a constant related to the heat of adsorption, and Ce is the remaining concentration. The linear trend of plotting of 1/qe vs. 1/Ce results in 1/qm (the constant), and the slope is 1/(ka*qm) where Kf, n, and k are the Freundlich model's coefficients.

The term A in Equation (5) is the constant of equilibrium binding (l/g), and B is a constant of heat adsorption (J/mol) which can be calculated by Equation (6):

$$B=RT/bt \quad (6)$$

where R is the universal gas constant (8.314 J/ mol.K), T is the temperature (K), bt is the isotherm constant.

2.5 Kinetic Study

Three kinetic models were used: second-order pseudo-kinetic, first-order pseudo-kinetic, and intraparticle models. While second-order and first-order pseudo-kinetic models are functions of time, the intraparticle model is a function of t^0.5. The linear forms of the mentioned models are shown in Equations (7–9), respectively (Al-Zboon et al., 2011):

$$t/qt=1/k_1q_e^2+t/qe \quad (7)$$

$$\ln(qe-qt)=\ln(qe)-k_2t \quad (8)$$

$$qt=k_3t^{1/2}+k_4 \quad (9)$$

where qe is the equilibrium adsorption capacity, qt is the adsorption capacity at time t, k_1, k_2, $k_{3,}$ and k_4 are constants of the models, respectively, while t is the time in minutes. K_1, $k_{2,}$ and k_3 values can be obtained by plotting a graph of t/q against t, ln (q e − q t) against t and qt against t 0.5, respectively.

3. Results and Discussion

3.1 Effect of pH on Adsorption

Figure (2) shows how different pH values (5, 6, 7, and 8) affect adsorption efficiency. Equation (1) was used to determine the lead removal efficiency (E%), while Equation (2) was used to estimate the equilibrium capacity (qe). The results indicate that when pH rises, lead removal effectiveness (E%) increases until it reaches about 99.4% at a pH of 8. Similarly, qe increased in tandem with increasing pH. The phenomenon could be caused by the minerals in biochar having a higher concentration of positively charged sites. Static energy effectively attracts and attaches lead ions to these sites in this environment (Al-Zboon et al., 2016). Low pH causes a significant rivalry between H^+ and Pb^{+2}, which explains why there is less H^+ in the solution. This low pH decreases the competition between H^+ and Pb^{+2} and increases the likelihood that Pb^{+2} will be adsorbed on the accessible pores (Al-Zboon, 2023). pH impacts biochar's sorption of pollutants due to surface charge variations. The surface charge of biochar is dependent on the pH of the surrounding environment. On the other hand, the biochar surface may produce a greater negative charge at higher pH values, which would enable it to draw positively charged contaminants. The pore structure of biochar is also important because it provides a surface area on which pollutants may be adsorbed. Compared to materials with a less developed porous structure, biochar with a high porosity and well-formed pore network may be more able to extract contaminants from water or soil.

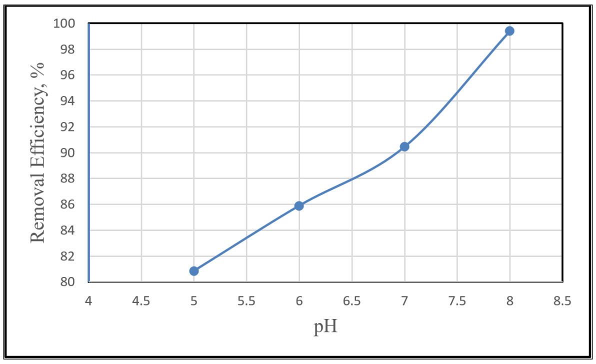

Figure 2. Effect of pH on the removal of Pb^{+2} from aqueous solution.

3.2 Effect of Biochar Dose on Adsorption

The effect of biochar dose on the removal efficiency is shown in Figure 3. As the dose increases from 1-3 g/L, the removal of Pb^{+2} increases from 83.25% to almost 99.8%. It becomes anticipated that the removal process depends on the availability of unoccupied pores surfaces. Because of that, the high biochar dose offers additional active sites for Pb^{+2} adsorption, hence increasing Pb uptake from the solution. No significant increase in Pb uptake was observed at dose ≥ 2.0 g/L. The usefulness of using low dosages of low-cost biochar for the removal of heavy metals is demonstrated by 80% Pb removal at only 1.0 g/L does, hence the earlier dose was used in the coming tests. Consequently, biochar offers an effective material for Pb^{+2} removal through a simple safe procedure. The high removal efficiency that was attained within the first 5.0 min as shown in Fig 4 suggests that biochar has a high porosity and is effective at removing low concentrations of Pb^{+2} quickly.

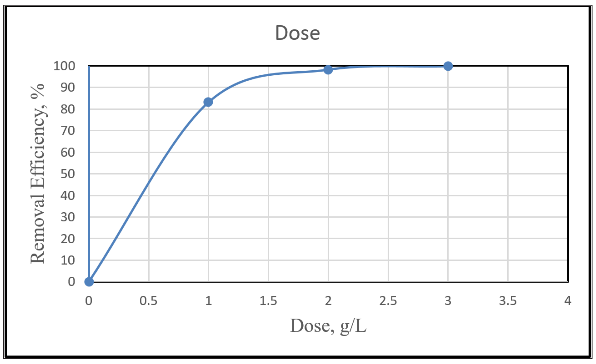

Figure 3. Effects of biochar dose on the removal of Pb^{+2}

3.3 Effects of Contact Time on Adsorption

Figure (4) shows the effects of contact time between a 1.0 g/L dose of (biochar) and a 1000 mg/l lead solution. Equation (1) was used to determine the lead removal efficiency (E%), while Equation (2) was used to estimate the equilibrium capacity (qe). The removal efficiency rises with longer contact times and reaches about 100% after 180 minutes. In a similar trend, qe increased with increasing contact duration, rising from 35.3 mg/g after 30 minutes to 50 mg/g after 180 minutes. The fast Pb adsorption at the beginning of the process was attributed to the availability of excess active sites on biochar. Over time, the active sites filled with Pb until the equilibrium of the process which was achieved around 100 min. (Al-Hamaiedah et al., 2023). The experiment's findings suggest that, with a lengthy contact time, biochar can be utilized to remove high concentrations of lead (1000 ppm) from aqueous solutions. After 90 minutes, an adequate removal efficiency of 94.4% can be attained, suggesting that more time is not practical.

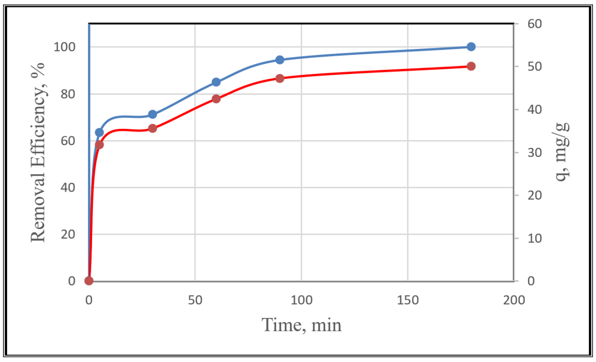

Figure 4. Effect of the contact time on the removal of Pb^{+2}

3.4 Adsorption Kinetics

Adsorption kinetics models are used to determine the required time for the adsorption process to reach the equilibrium status.

Based on the correlation coefficient, the model's validity can be ranked as pseudo-second order (R^2=0.99)> pseudo-first order (R^2= 0.86)> intraparticle model (R^2=0.76) as shown in figure 5. The obtained values of variables in Equations 7,8, and 9 are 0.02 for k1 in Equation 7, 0.043 for k2 in Equation 8, 3.25 for k3 in Equation, and 13.67 for k4 in Equation 9.

The second order pseudo-kinetic model assumes that the adsorption rates are a function of the absorption capacity and independent of the absorbate concentration. The second order models also anticipate behavior across the whole adsorption range and indicate that chemical sorption, or chemisorption, is the rate-limiting step.

This model assumed the following assumptions:

A non-reversible adsorption reaction between Pb and active sites of biochar:

$2Pb^{2+} + -S \rightarrow -S(Pb)_2$

where –S is the active site of biochar.

b) There is no interaction between adsorbed Pb^{2+} and the adsorption process at discrete active sites.

c) Adsorption energy is independent of surface coverage.

d) A saturated monolayer of adsorbates on the adsorbent surface equates to maximum adsorption.

e) Chemisorption, which is the rate-limiting phase, works by exchanging or sharing electrons between Pb2+ and the biochar.

The first-order model assumes that the adsorption is directly proportional to the difference in the concentration of ions with time and the amount of solid absorbed. According to the first-order concentration model, there are three stages in the adsorption process: the external diffusion stage, which lasts from 0 to 5 minutes and has a sharp increase in Pb^{+2}'s removal and adsorption capacity. The intra-diffusion stage, which lasts from 5 to 90 minutes, is represented by a linear line with a medium slope. The third stage, which lasts from 90 to 180 minutes, represents the near-equilibrium low-diffusion process because of limited metal concentrations, which is explained by Al Jarrah et al., (2018).

Intraparticle models assume that the diffusion process depends mainly on the particle porosity and tortuosity. Since the second-order model provides the best fitting, it means that adsorption process might be the rate-limiting step, and the adsorption capacity is the key parameter that determines the adsorption rate while the concentration of Pb^{+2} is not an important factor (Sahoo and Prelot, 2020). Many researchers reported the effectiveness of 2nd order model in describing the kinetic adsorption process (Al-Zboon, 2023; Al-Zboon et al., 2016; Al-Hamaiedh et al., 2024). In general, the limited application of intraparticle diffusion model ($R^2 = 0.76$) would indicate that intraparticle diffusion of Pb ions inside biochar was not dominating the entire process.

3.5 Adsorption Isotherms

Langmuir, Freundlich, and Temkin were used in this paper to determine the isotherm behavior of Pb^{+2} adsorption on biochar. While Temkin model provided the highest correlation (R^2=1), Langmuir model provided the lowest one (R^2= 0.93). Temkin model suggests that there is an indirect interaction between the adsorbent and the adsorbate, and the adsorption heat (enthalpy) decreases linearly (not logarithmically) with the increase in the surface coverage (Ayawei et al., 2017). It was reported that the Temkin model is valid for intermediate concentration of ions which explains the high R^{+2} of the model in comparison with other models. Langmuir model assumes that the adsorption occurs on a single layer and stops when all the sites on the adsorbent's surface are equal, however, the Freundlich model states that adsorption occurs on many levels (multilayers) and that the adsorbent's surface is heterogeneous (Ayawei et al., 2017). This demonstrates that the adsorption process takes place in a heterogeneous manner over multilayers of the used biochar and Pb^{+2} with a reduction in the adsorption heat with surface coverage. The Freundlich model showed n values of 6.1 as shown in Table 1, indicating a favorable sorption process (Dada et al., 2012).

The Temkin model was used successfully to describe the adsorption of methylene blue by miswak leaves and the adsorption of cadmium by Fe nanoparticles (Ayawei et al., 2017). Others reported that the adsorption of Pb^{+2} on fly ash-based geopolymer followed the Langmuir model (Al-Zboon et al., 2011), or Dubinin-Radeshkovich model in the case of using the Dead Sea mud as an adsorbent (Al-Hamaiedh et al., 2024).

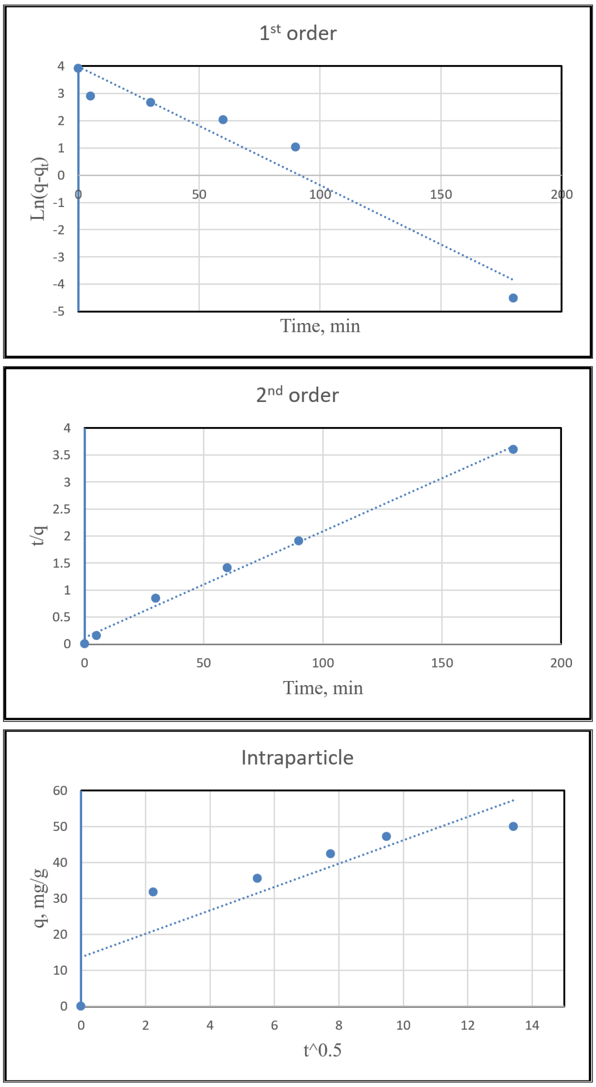

Figure 5. Modeling of adsorption rate of Pb^{+2} by biochar using different equations.

Table 1. Results of Langmuir, Freundlich, and Temkin Models Parameters

Model	Langmuir model	Frendluich Model	Temkin Model
Equation	1/qe = (1/kaqm)*(1/Ce)+(1/qm) (g mol^{-1})	log(qe)=log(kf)+ (1/n) log(ce)	qe = B ln(At) - B lnCe (mol g-^{1})
R^2	0.93	0.99	1
Variable 1	qm = 12.02 mol g-^{1}	n= 6.1	B = -1.59 J g mol-^{2}
Variable 2	ka = 12.24 L mol^{-1}	Kf = 9.89 L mol^{-1}	At = 0.20 L mol^{-1}

4. Conclusion

Biosorption of lead, using biochar produced from the branches of olive and lemon trees, has been studied in this research. The results of these experiments strongly suggested that this biochar is cost-effective and capable of removing lead from aqueous solutions. The findings show that biochar is an effective natural adsorbent for eliminating lead ions (Pb^{+2}) from water.

Because of its low cost, abundance of raw materials, and ease of preparation, the use of biochar to remove lead from polluted water is a viable option. Biochar has a high adsorption capacity for lead ions in water and may be made more efficient by adjusting variables such as pH, temperature, and contact duration time.

The results show that the increasing in pH of the solutions helps to improve the adsorption process by which at value of pH=8 reaching 99.4% efficiency. At a dose of 1g of (Biochar) per batch (200 ml), a starting concentration of 1000 mg/l of lead ion in the solution, a temperature of 25 ◦C, a mixing speed of 15 rpm, and a contact period of 3 hours, 100% lead ion removal efficiency was attained, and a more contact time leads to more increase of the adsorption of Pb^{+2}. The study includes both kinetic and isothermal models to determine the optimal parameters for achieving the highest adsorption capacity.

Second-order pseudo-kinetic model was found to be more suitable since it had a higher R^{+2} than the first-order model. The most effective model for illustrating the adsorption process was Temkin isothermal model. Physically, the exothermic, spontaneous adsorption process took place. To further understand how well (Biochar) absorbs other heavy metals, further research is necessary. Despite this, the data demonstrate that the zero-order- model well describes the concentration-pH relationship. Finally, more studies are needed to examine biochar's long-term stability and environmental impact on soil microbial communities and ecosystems.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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