



## Comparison of Some Soil Mineral's Ability to Adsorb and Release Lead and Rates of its Removal From its Aqueous Solutions

Kadhim Makki Naser <sup>1\*</sup> , Awatif Hameed Dadoosh <sup>2</sup> , Shireen Mudhafar Ali Alkhalil <sup>3</sup> 

<sup>1\*</sup> Department of Soil Sciences and Water Resources, College of Agricultural Engineering Sciences, University of Baghdad, Baghdad, Iraq. E-mail: kadhim.n@coagri.uobaghdad.edu.iq

<sup>2</sup> Department of Soil Sciences and Water Resources, College of Agricultural Engineering Sciences, University of Baghdad, Baghdad, Iraq. E-mail: awatif.h@coagri.uobaghdad.edu.iq

<sup>3</sup> Department of Desertification Combat, College of Agricultural Engineering Sciences, University of Baghdad, Baghdad, Iraq. E-mail: shiren.modhufer@coagri.uobaghdad.edu.iq

### Abstract

To study the comparative use of some soil minerals (zeolite, bentonite, phosphate rock, and limestone) in the adsorption and release of lead and its removal rates from its aqueous solutions using adsorption equations. Two laboratory experiments were carried out for the adsorption and release of lead. The adsorption experiment took 0.5 g of some of the above soil minerals. Lead was added as Pb (NO<sub>3</sub>)<sub>2</sub> at levels of 3.0, 2.0, 1.5, 1.0, 0.5, and 0.0 mmol L<sup>-1</sup> containing a concentration of 0.01M of calcium chloride. The experimental unit's number was 72, the concentration of dissolved lead in the equilibrium solution was estimated and the amount of lead adsorbed was calculated. As for the lead release experiment, samples for the adsorption experiment were treated after separating filtrates from them with a calcium chloride solution with a concentration of 0.01 M. The amount of lead released was estimated. The percentage of lead removal was calculated. Results showed an increased concentration of dissolved lead in the equilibrium solution directly with increased levels of lead added to all materials. Materials were graded in concentrations of dissolved, adsorbed lead and values of maximum adsorption capacity of lead on different soil minerals surfaces as follows: zeolite > bentonite > phosphate rock > limestone, which reached 5000, 384.61, 769.23, and 2500 mg Pb kg<sup>-1</sup>, respectively. Binding energy was 0.0062, 0.0056, 0.0019, and 0.0049 L g<sup>-1</sup>, respectively. The amount of lead released from different adsorption materials varied, with the largest amount released in zeolite amounting to 322.10, 528.20, 696.90, 777.20, and 967.40 mg Pb kg<sup>-1</sup> zeolite then bentonite, quantity reached 187.2, 272.8, 314.2, 324.0, and 375.6 mg Pb kg<sup>-1</sup> bentonite, then phosphate rock, concentrations reached 65.80, 69.80, 77.60, 91.00, and 123.00 mg Pb kg<sup>-1</sup> phosphate rock. Limestone came in fourth and last place in terms of the amount of lead released, concentrations were 25.10, 29.30, 35.00, 38.70, and 40.90 mg Pb L<sup>-1</sup> for lead addition treatments of 0.5, 1.0, 1.5, 2.0 and 3.0 mmol L<sup>-1</sup>, respectively. Soil minerals used varied in their efficiency in removing lead from its aqueous solutions. Zeolite came in first place. Removal rate of lead reached 180.69%, then bentonite 95.47%, phosphate rock 18.48%, and finally limestone 58%.

**Keywords:**

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**Introduction**

The rapid development of various industries, including mining operations, the oil industry, energy production, fertilizer and pesticide industries, electrical industries, etc., has led to the release of waste into the environment and the release of toxic elements directly or indirectly, which led to pollution of various environmental components. The huge increase in the use of heavy metals over the past few decades has ultimately led to an increase in the flow of metal materials into the environment and its pollution (Lu et al., 2004). Heavy metals are defined as those elements whose density is more than five times the water's density, and they have negative effects on the environment when used excessively. Heavy metal pollution is one of the most dangerous forms of environmental pollution and one of the most important problems threatening human health. It can therefore be generally classified as toxic. These toxic elements are extremely harmful even at low concentrations when exposed for a long period because of their ability to accumulate in human and animal bodies (Balaid et al., 2019; Hamil et al., 2016) explained that heavy metals become toxic when their concentration exceeds the maximum permissible limit. Bioaccumulation of heavy metals varies between species, ages, sexes, and organs of organisms (Al-Jatlawi & Hadid 2017). The accumulation of heavy metals in the agricultural soil is a growing concern due to its relationship to food safety, or its consternation through leaching to groundwater and surface water, which may cause potential health consequences (Tunguz, et al., 2019 ; Hassoon & Najem 2017) indicated that pollution of the aquatic environment with heavy metals is one of the main environmental problems, as they are released into the environment without treatment, which causes them to remain and remain stable and are not biodegradable.

Lead is one of the types of hazardous heavy metals that pollute the environment, and it can accumulate through the food chain (Manahan, 2002). It is also very harmful to humans, animals, and plants and can cause harmful effects on human health and the environment, which may cause severe damage to the kidneys, nervous and reproductive systems, and liver (Anzeze et al., 2014). As a result of its wide uses, through human activities, the concentration of lead has increased, especially in aquatic ecosystems, as a result of the cumulative toxic effect of lead on the environment and humans, detailed global studies have been conducted about removing this element from polluted water by many methods, such as chemical precipitation, ion exchange, electrochemical treatment, membrane techniques, adsorption on activated carbon, and others. Results of these studies showed the futility of chemical precipitation and electrochemical treatment in case of low concentrations, in addition to the production of large quantities of waste, which are more difficult to treat. Ion exchange, thin film, and adsorption on activated carbon methods are very expensive, especially when large quantities of water are to be treated. Therefore, researchers have sought to find practical methods such as the adsorption of heavy metal ions on biomasses, which are effectively characterized by the property of retaining ions from complex solutions, and large sizes, in addition to using natural materials such as soil minerals, zeolite, and others, in removing heavy metals, and achieved good results (Etuk et al., 2024). Raw phosphate was also used in removing lead from the aqueous phases in which it is found and achieved high results in removal such as lead, copper, cadmium, and arsenic in a wide range of pH levels (Mahdiraji & Ramezani, 2019). Many studies have been conducted on this, in which raw phosphate from different parts of the world was used with success and high efficiency. The process of removing lead from aqueous solutions using raw

phosphate reflects two phenomena: precipitation and adsorption. The adsorption process using clay minerals has recently gained a lot of attention due to its advantages in the removal process as it has high adsorption properties. The abundance of natural minerals, their non-toxicity, and their chemical stability make them good adsorbents for various pollutants (Maleki & Karimi, 2017; Ibrahim & Naser, 2020) pointed out that soil components differ in their ability to adsorb heavy metals depending on the amount of heavy metals, proportion, and type of soil component, and carbonate minerals play an important role in this (Vij & Prashant, 2024). The word zeolite comes from two Greek words *zeiu* and *lithos*, which means boiling stone. Zeolite belongs to hydrated aluminosilicates of alkaline earth minerals (Salkić et al., 2020; Nasser & Kudher, 2020). Zeolite crystal consists of four oxygen atoms forming a tetrahedron centered on a silicon atom, which can be replaced by aluminum. The crystal structure is open and has spaces occupied by cations such as sodium, calcium, and potassium. Ions can be exchanged with ions of the aqueous medium, which achieves ionic balance.

The ion exchange process in zeolite is affected by several factors, including the concentration and nature of anions and cations, pH value, and crystalline structure of zeolite. The attractive force of cations increases with an increase in their valence, and in the event of equal valence, the attractive force of ions determines their aqueous radius.

Natural zeolite is characterized by its high ion exchange capacity, high porosity and hydraulic capacity, and increased surface area (Trgo & Vukojević-medvidović, 2005). It also has great importance at present time in ion exchange processes due to its availability in nature, low cost, and high performance. It is used in many countries of the world to remove ions and pollutants from aqueous solutions (Nezamzadeh-Ejhi & Amiri, 2013). Shamsham & Al-Sabai (2017) showed a high ability of zeolite to adsorb heavy metals such as copper and zinc (Lu et al., 2004).

Bentonite is a silicate mineral of 1:2. It consists of two layers of tetrahedra and a layer of octahedra linked by weak van Drauwals forces. Therefore, the structural composition is unbalanced (Harbuzaru, 2003), which allows water molecules and cations to enter between layers to balance charges. The mineral has a high exchange capacity and the ability to adsorb ions (Mitchell & Soga, 2005). AL-Rubaie et al., (2022) showed that bentonite has a high capacity to adsorb ions such as phosphorus and zinc due to its high surface area. Naser et al., (2020) demonstrated the efficiency of bentonite and phosphate rock in removing heavy metals such as copper from soil contaminated with it.

Limestone is a sedimentary stone that originates from the original material, which is limestone rocks, or from the sediments of calcified aquatic organisms such as coral, foraminifera, and mollusks, as well as from ink and sea snails. It is composed mainly of mineral calcite (calcium carbonate) and is sometimes known as chemical limestone to distinguish it from organic limestone. Pure limestone is used to remove cations by precipitation, while low-purity limestone can undergo other processes such as chemical and physical adsorption. Al-Abdullah & Al-Qudour (2013) concluded that the adsorption of heavy metals on limestone rocks was low compared to the rest of the materials used in treatment (phosphate rock, silicate rocks, and bentonite), and attributed this to the fact that they are ineffective rocks and have few adsorption sites.

The research aims to study the comparative use of some soil minerals (zeolite, bentonite, phosphate rock, and limestone) in the adsorption and release of lead and its removal rates from its aqueous solutions using adsorption equations.

## Materials and Methods

Lead (Pb) adsorption experiment was carried out by taking 0.5 g aliquots of the soil minerals zeolite bentonite, phosphate rock, and limestone dried, ground, and passed through a 2 mm sieve. Then 0.5 g aliquots of the minerals were weighed into 100 mL polypropylene flasks and equilibrated with 50 mL of 3.0, 2.0, 1.5, 1.0, 0.5, 0.0 mmol L<sup>-1</sup> Pb(NO<sub>3</sub>)<sub>2</sub> solutions prepared in 0.01 M CaCl<sub>2</sub> background to maintain constant ionic strength (Aldaini & Naser, 2020). The samples were shaken for 2 hours at laboratory temperature (25°C ± 1), left for equilibrium for 24 hours, and then shaken for half an hour. The supernatants were then separated by a centrifuge at a speed of 3000 rpm<sup>-1</sup> for 10 minutes. The Pb concentration of the supernatants was determined using an Atomic Absorption Spectrophotometer (AAS) (trade and model required). Adsorption materials (4)\*Lead levels (6)\*Replicates (3)=72

The adsorbed amount of lead is calculated from the following equation:

$$X = (A - C) / S$$

X = amount of lead adsorbed on the surface (μmoles g<sup>-1</sup>-adsorbent)

A = initial P concentration (μmoles mL<sup>-1</sup>)

C = equilibrium Pb concentration (μmoles mL<sup>-1</sup>)

S = weight of the adsorbent (g)

The following linear Langmuir equation is applied for thermally isotropic adsorption (Linear Langmuir equation):

$$C / X = 1 / k_m + C / X_m$$

Where:

Constant representing the binding energy to the surface of the adsorption material (mL μg<sup>-1</sup>):

Draw the relationship between C/ X and C to obtain the values of the equation constants:

The percentage of lead removal is calculated from the following equation

$$\text{Percent removal (\%R)} = 100 * [(C_o - C_e) / C_o]$$

Where, C<sub>o</sub> = initial Pb<sup>+2</sup> concentration (mg L<sup>-1</sup>), C<sub>e</sub> = equilibrium Pb concentration in the supernatants (mg L<sup>-1</sup>).

To study the release of lead, samples for the adsorption experiment were treated with 50 mL of the background solution for 24 h. Then, they were separated by a centrifuge, and the amount of lead released was estimated using an atomic absorption device (Nezamzadeh –Ejehieh & Amiri, 2013).

### *Effect of Different Adsorption Materials on the Concentration of Dissolved and Adsorbed Lead*

Results of Table 1 show an increase in the concentration of dissolved lead in equilibrium solution directly with an increase in added lead levels to zeolite, as they reached 26.09, 64.88, 115.68, 195.12, and 299.76 mg L<sup>-1</sup> for added lead levels of 103.50, 207.00, 310.50, 414.00, and 621.00 mg L<sup>-1</sup>, respectively. An increase in

concentration of dissolved lead in an equilibrium solution is directly proportional to an increase in levels of added lead, which is consistent with what was stated by Taleb (2023), who showed that adding lead at different levels to soil increases concentrations of dissolved lead in equilibrium solution, these results are also consistent with what was stated by (Awda, 2018), who indicated an increase in concentration of dissolved and available lead in soil with an increase in levels of lead added to soil (Talib, 2023).

Table 1. Effect of added lead on the concentration of dissolved and adsorbed lead on surfaces of different adsorption materials

No.	Adsorption materials	Lead ions	Concentration of initial lead (mgL <sup>-1</sup> )				
			103.50	207.00	310.50	414.00	621.00
1	Zeolite	(C)equilibrium lead concentration (μ g mL <sup>-1</sup> )	26.09	64.88	115.68	195.12	299.76
		(X)Adsorbed lead concentration (μ g g <sup>-1</sup> )	774.10	1421.20	1948.20	2188.80	3212.40
2	Bentonite	(C)soluble lead concentration (μ g mL <sup>-1</sup> )	51.68	108.52	168.78	259.20	435.24
		(X)Adsorbed lead concentration (μ g g <sup>-1</sup> )	518.20	948.80	1417.2	1548.00	1857.60
3	Rock Phosphate	(C)soluble lead concentration (μ g mL <sup>-1</sup> )	77.81	167.24	274.74	370.94	559.30
		(X)Adsorbed lead concentration (μ g g <sup>-1</sup> )	256.90	397.60	357.60	430.60	617.00
4	Limestone	(C)soluble lead concentration (μ g mL <sup>-1</sup> )	96.52	196.97	296.8	397.92	599.51
		(X)Adsorbed lead concentration (μ g g <sup>-1</sup> )	66.40	100.30	137.00	160.77	214.90

An increase in the concentration of adsorbed lead was found with an increase in the concentration of added and dissolved lead, as concentrations reached 774.1, 1421.2, 1948.2, 2188.8, and 3212.4 μg g<sup>-1</sup> for addition levels of 103.50, 207.00, 310.50, 414.00, and 621.00 mg L<sup>-1</sup>, respectively. An increase in the amount of adsorbed lead with an increase in amount of lead added to mineral may be attributed to high value of cation exchange capacity of zeolite mineral, which is 100-200 centimoles kg<sup>-1</sup> mineral (Stylioou et al., 2015), in addition to its possession of internal cavities because it is a three-dimensional crystalline porous material (Cabanilla et al., 2016) and has a high surface area that enables it to carry out ion exchange and increase amount of adsorption (Jarosz et al., 2022).

Bentonite behaved in the same manner as zeolite but to a lesser degree. Results of Table 1 and Fig. 2 showed an increase in the concentration of dissolved lead directly with an increase in levels of lead addition, reaching 51.68, 108.52, 168.78, 168.78, 259.20, and 435.24 mg L<sup>-1</sup> for lead addition levels of 103.50, 207.00, 310.50, 414.00, and 621.00 mg L<sup>-1</sup>, respectively, these results are consistent with what was indicated by (Lei et al., 2022), who showed that adding bentonite to soil leads to an increase in availability of nutrients and other elements in equilibrium solution by increasing availability of water and increasing concentrations of dissolved elements in solution (Wei et al, 2022). The amount of adsorbed lead increased with increase in the amount of adsorbed lead with an increase in levels of lead addition and an increased amount dissolved in equilibrium solution, concentrations reached 518.20, 948.80, 1417.20, 1548.00, and 1857.60 μg g<sup>-1</sup> metal for addition levels of 103.50, 207.00, 310.50, 414.00, and 621.00 mg L<sup>-1</sup>, respectively.

An increase in the amount of adsorbed lead directly with an increase in added amount of lead may be attributed to the high exchange capacity value of bentonite, which is 83-53 and may reach 150 centimos  $\text{kg}^{-1}$  mineral (Minhal et al., 2020), therefore, it is efficient in process of ion exchange and adsorption of elements (Tahir and Marschner, 2017). These results are consistent with what (Balidakis et al., 2023; Asrari & Rezaee, 2023) reached, who demonstrated a high ability of bentonite to remove pollutants such as heavy metals from their aqueous solutions.

It is noted that the amount of lead adsorbed on surfaces of bentonite is less than the amount of lead adsorbed on surfaces of zeolite (Table 1). This is due to the difference in the value of the exchange capacity of cations between two minerals. These results are consistent with the findings of (Maleki & Karimi, 2017), who showed that clay minerals have high adsorption properties and are good adsorbents for heavy metals and various pollutants.

Phosphate rock was increasing concentration of added lead led to an increase in the concentration of dissolved lead in the equilibrium solution (Table 1 and Fig.3) dissolved concentrations of lead were 77.81, 167.24, 274.74, 370.94, and 559.30  $\text{mg Pb L}^{-1}$  for addition levels of 103.50, 207.00, 310.50, 414.00, and 621.00  $\text{mg L}^{-1}$ , respectively.

An increase in adsorbed lead concentration was found with increasing lead addition levels, adsorbed concentrations reached 256.90, 397.60, 357.60, 430.60, and 617.00  $\text{mg Pb g}^{-1}$  metal for lead addition levels of 103.50, 207.00, 310.50, 414.00, and 621.00  $\text{mg L}^{-1}$ , respectively.

The increase in the amount of lead absorbed with an increase in the amount of lead added to surfaces of phosphate rock may be because phosphate is a natural substance consisting mainly of tricalcium phosphate and has a sedimentary origin and removes many heavy metals such as lead in a wide range of soil reaction degrees (Ibrahim & Naser, 2020). These results are consistent with what was mentioned by (Mignardi et al., 2012; Zhao et al., 2014; Malaki & Karimi-Jashnig 2017) who indicated the ability of phosphate rock to remove heavy metals such as lead in soil and limit their movement and reduce their transfer to plant.

It is noted that the amount of lead adsorbed on phosphate rock surfaces is less than the amount of lead adsorbed on bentonite and zeolite, and this may be attributed to the low value of cation exchange capacity and a small number of active sites for adsorption (Al-Dayni & Al-Azzawi, 2019).

Results of Table 1 showed the amount of lead dissolved in the equilibrium solution when adding levels of lead to limestone. Concentrations of dissolved lead reached 96.52, 196.97, 296.80, 397.92, and 599.51  $\text{mg Pb L}^{-1}$  for addition levels of 103.50, 207.00, 310.50, 414.00, and 621.00  $\text{mg L}^{-1}$ , respectively. The amount of absorbed lead increased directly with an increase in levels of added lead and concentrations of dissolved lead in the equilibrium solution, reaching 66.40, 100.30, 137.00, 160.77, and 214.90  $\text{mg Pb g}^{-1}$  limestone. These results are consistent with what was indicated by (Al-Awsi & Al-Aliwi, 2015), who showed that the amount of absorbed lead increases with levels of lead added to soil.

It is noted that the amount of lead absorbed on surfaces of limestone is the least compared to other adsorption materials above. This may be attributed to the fact that limestone is a sedimentary stone arising from its original material, which is limestone rocks, or from sediments of calcified aquatic organisms such as coral and sea snails, It is mainly composed of calcite (calcium carbonate) and is usually used to remove metal ions through precipitation. Abdullah Al-Qudour (2013) concluded that the adsorption of heavy metals on

limestone rocks is low compared to other materials used in treatment, they attributed this to the fact that they are ineffective rocks and have few adsorption sites.

### ***Adsorption of Lead on Different Adsorption Materials***

Lead adsorbed represents the difference between the amount of lead added and the amount of lead remaining in the equilibrium solution. Single-plane Langmuir equation was applied to describe the lead adsorption process by calculating equation parameters represented by the maximum lead adsorption amount ( $X_m$ ) and binding energy of lead to adsorbent (Figures 1-4). Table 2 shows values of Langmuir adsorption equation constants, which are maximum adsorption capacity ( $X_m$ ) and binding energy ( $k$ ). Values of maximum adsorption capacity gave a good idea of the maximum amount of lead adsorbed on surfaces of different soil minerals (Khan et al., 2022), it reached 5000 mg pb kg<sup>-1</sup> zeolite, which is the highest value for maximum adsorption capacity compared to the rest of the soil minerals used. This is attributed to the high value of the cation exchange capacity (CEC) of zeolite mineral (200-100 centimos charge kg<sup>-1</sup> mineral), because of its high surface area and presence of internal cavities that enable it to carry out ion exchange process and increase lead adsorption, these results are consistent with what was reached by (Trgo & Vukojević-medvidović, 2005; Nezamzadeh-Ejhih & Amiri 2013). they showed that zeolite has a high surface area and high cation exchange capacity, therefore it is used in many countries to remove ions from pollutants from aqueous solutions. Binding energy reached 0.0062 L<sup>-1</sup> g, which is the highest among binding values of other used soil minerals (Table 2) this may be attributed to the increased ability of a mineral to absorb lead due to its large surface area, which was indicated by Shammam and Al-Sabai (2017), who demonstrated the ability of zeolite to absorb heavy metals with good binding energy.

Table 2. Effect of different adsorption materials on the maximum adsorption values ( $X_m$ ) and binding energy ( $k$ ) of lead

No.	Adsorption materials	Maximum adsorption ( $X_m$ ) (mg Pb kg <sup>-1</sup> metal)	Binding energy ( $k$ ) (mL mg <sup>-1</sup> metal)
1	Zeolite	5000.00	0.0062
2	Bentonite	2500.00	0.0056
3	Rock Phosphate	769.23	0.0049
4	Limestone	384.61	0.0019

Bentonite came in second place in value of maximum adsorption capacity ( $X_m$ ) for lead, as it reached 2500 mg Pb kg<sup>-1</sup>-bentonite, which may be attributed to high value of CEC of mineral (83-53) centimole charge kg<sup>-1</sup>-bentonite), but it is less than zeolite, and these results are consistent with what was indicated by (Dhar et al., 2023) who demonstrated high efficiency of bentonite mineral in removing heavy metals such as lead from their aqueous solutions as a result of their adsorption. Binding energy reached 0.0056 L g<sup>-1</sup>, and it came in second place. This is attributed to the mineral's high ability to adsorb lead ions and good binding energy.

Phosphate rock came in third place in terms of the value of maximum adsorption capacity, which reached 769.23 mg Pb kg<sup>-1</sup> of phosphate rock. This may be attributed to the low ability of phosphate rock compared to zeolite and bentonite minerals to adsorb lead, as they are of sedimentary origin with fewer effective adsorption sites, meaning that their surface area is less. However, they can adsorb and remove many heavy metals ions such as lead and in a wide range of soil reaction degrees. These results are consistent with what Al-Daini and Naser (2020) reached, who showed that phosphate rock can be used as an adsorbent for heavy metals in soil such as lead to limit its movement in soil and reduce harmful effects resulting from its presence. Binding energy reached 0.0049 liters g<sup>-1</sup> of phosphate rock, and it came in third place after zeolite and bentonite, due to its low ability to adsorb lead due to its low CEC and few adsorption sites in it (Al-Dayni

& Al-Azzawi, 2019). The maximum adsorption capacity of limestone was  $384.61 \text{ mg Pb kg}^{-1}$ , and it came in last place. This may be attributed to the fact that limestone is a sedimentary rock that consists mainly of calcite (calcium carbonate) and adsorption sites in it are few compared to the rest of the soil minerals used. These results are consistent with what Abdullah Al-Qudour (2013) reached which showed that the adsorption of heavy metals on limestone rocks was low compared to bentonite and phosphate rock and attributed this to the fact that they are inactive rocks and contain few adsorption sites. However, they are used to remove heavy metal ions through precipitation (Al-Dayni & Al-Azzawi, 2019).

Binding energy was the lowest value, reaching  $0.0019 \text{ L g}^{-1}$  of limestone. This may be attributed to the low ability of limestone to adsorb heavy metal ions due to its ineffectiveness in ion exchange and adsorption processes. Thus, soil minerals used in the lead ion adsorption process can be arranged in terms of values of maximum adsorption capacity and binding energy as follows (Table 2):

Zeolite > Bentonite > Phosphate Rock > Limestone.

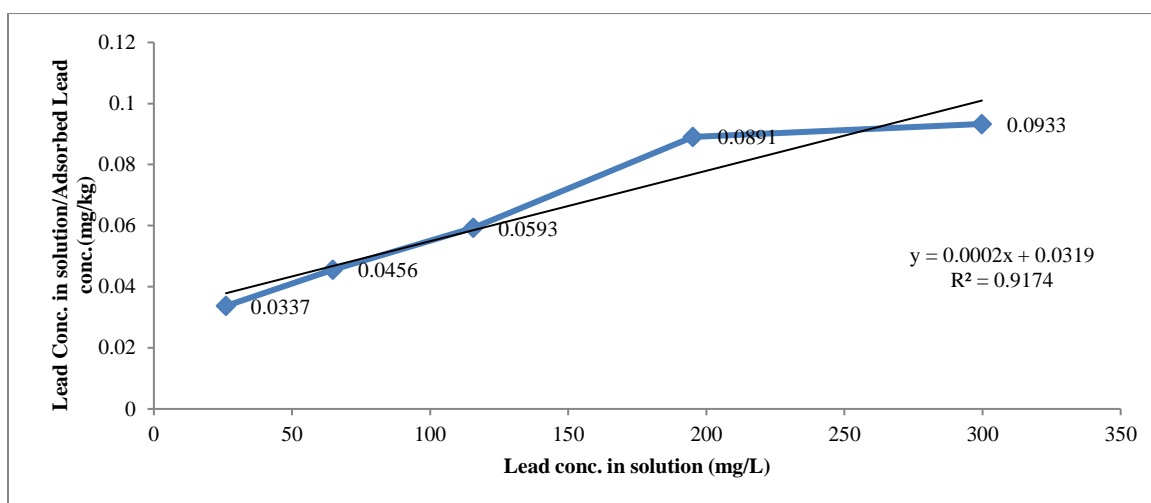


Figure 1. Langmuir curve for the isothermal adsorption of lead on zeolite

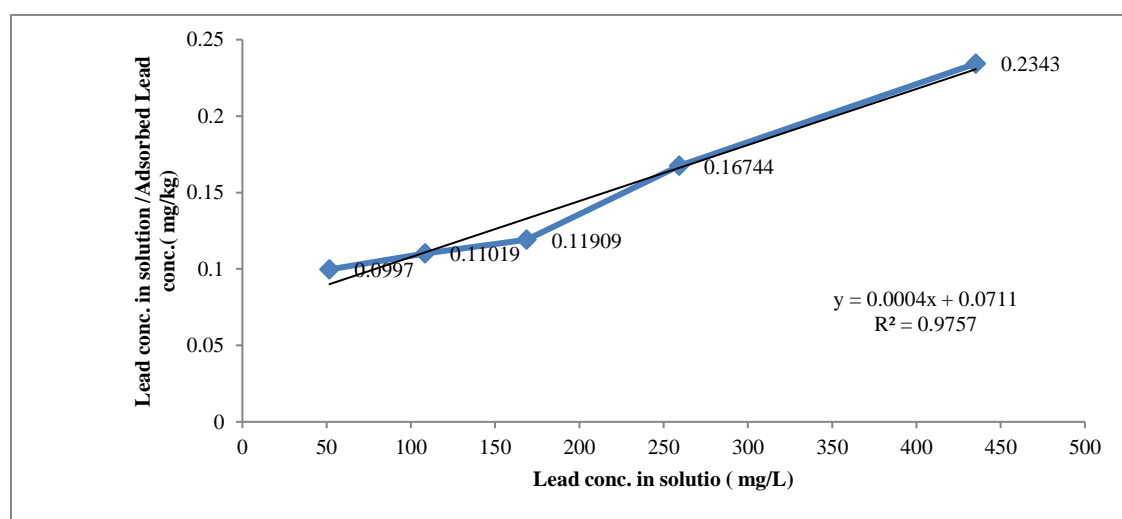


Figure 2. Langmuir curve for the isothermal adsorption of lead on Bentonite



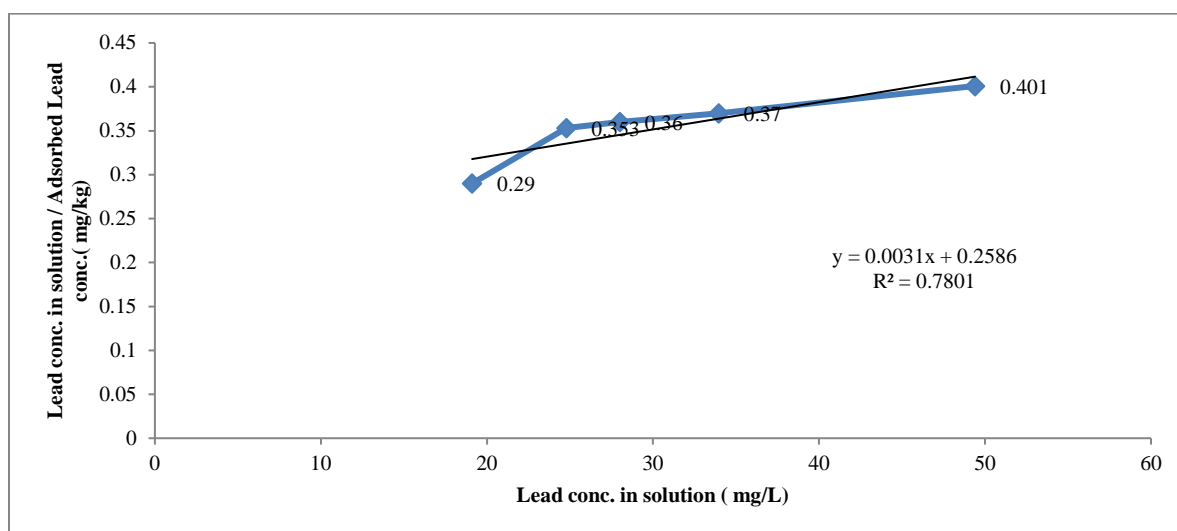


Figure 3. Langmuir curve for the isothermal adsorption of lead on rock phosphate

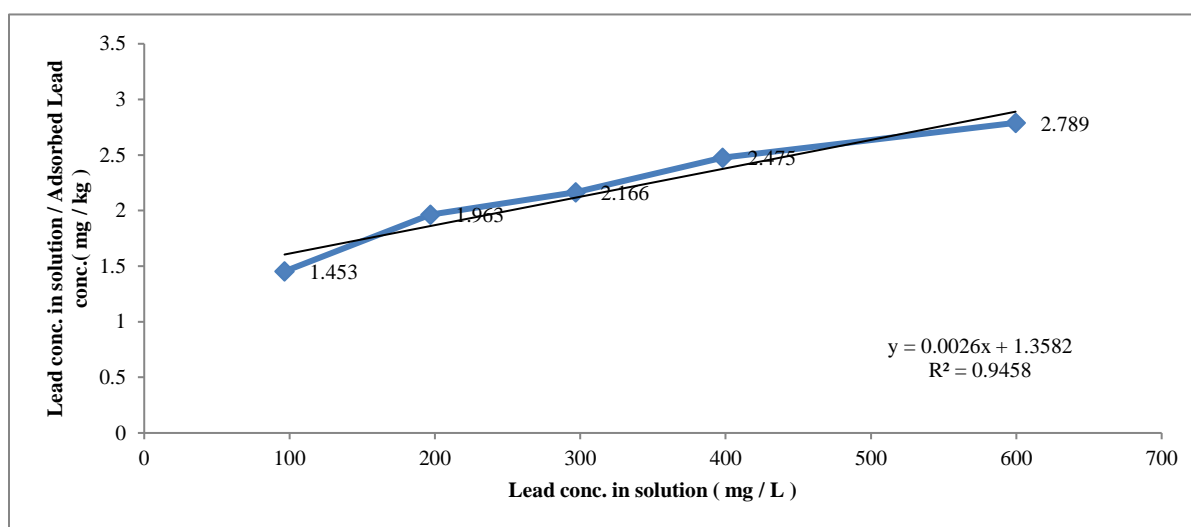


Figure 4. Langmuir curve for the isothermal adsorption of lead on rock limestone

#### ***Effect of Different Adsorption Materials on the Amount of Lead Released***

Figures 5-8 show the difference in the amount of lead released from different adsorption materials. The largest amount released in zeolite was 322.10, 528.20, 696.90, 777.20, and 967.40 mg Pb kg<sup>-1</sup> zeolite (Fig.5) for lead addition treatments of 0.5, 1.0, 1.5, 2.0, and 3.0 mmol L<sup>-1</sup>, respectively, this amount was consistent with amount of lead adsorbed on zeolite mineral, which amounted to 774.1, 1421.2, 1948.2, 2188.8, and 3212.4 mg Pb kg<sup>-1</sup> zeolite for above addition levels. This may be attributed to the high ion exchange power of zeolite, which has a high CEC and an increased surface area (Nezamzadeh-Ejehieh & Amiri, 2013), these results are consistent with those of (Ofiera et al., 2024; Bogdan 2023), who demonstrated the high ability of zeolites to remove pollutants, including heavy metals such as lead, from their aqueous solutions.

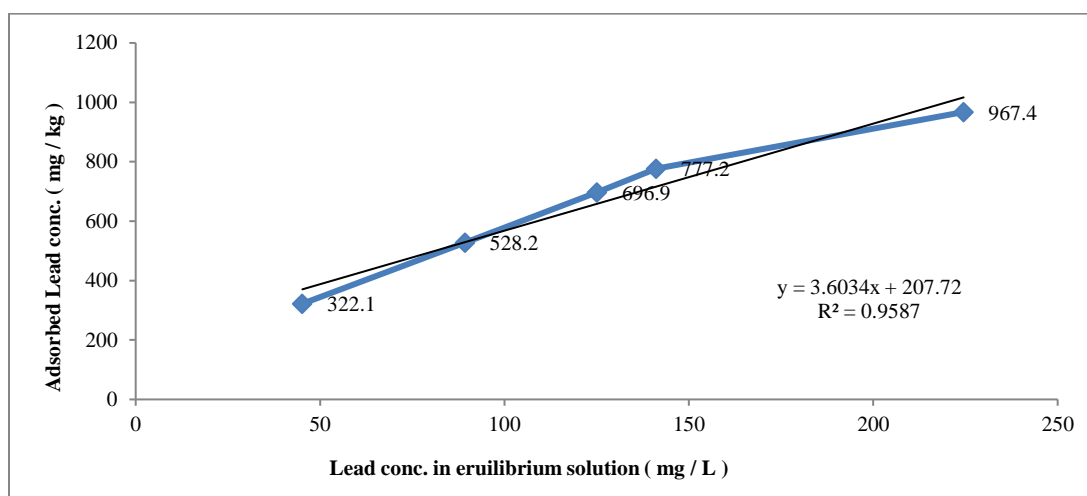


Figure 5. Desorption of lead from zeolite

Bentonite came in second place in terms of the amount of lead released, amounts reached 187.2, 272.8, 314.2, 324.0, and 375.6 mg Pb kg<sup>-1</sup> bentonite (Fig.7) for lead addition levels of 0.5, 1.0, 1.5, 2.0, and 3.0 mmol L<sup>-1</sup>, respectively. These results were consistent with the amount of lead adsorbed on bentonite, which reached 518.20, 948.80, 1417.20, 1548.00, and 1857.60 mg Pb kg<sup>-1</sup>-bentonite for the above addition levels, respectively. The increase in the amount of lead released from bentonite minerals may be attributed to its high adsorption capacity due to its increased CEC (less than zeolite). These results are consistent with what was shown by AL-Rubaie et al. (2022), who showed that bentonite has a high ability to adsorb ions due to its high surface area, and these results are consistent with what was indicated by Naser et al. (2020), who demonstrated the efficiency of bentonite in removing heavy metals from contaminated soil, and (Supriyadi, 2023; Shubber & Kebria 2023; Dhar et al., 2023) who demonstrated efficiency of bentonite in removing heavy metals from aqueous solutions.

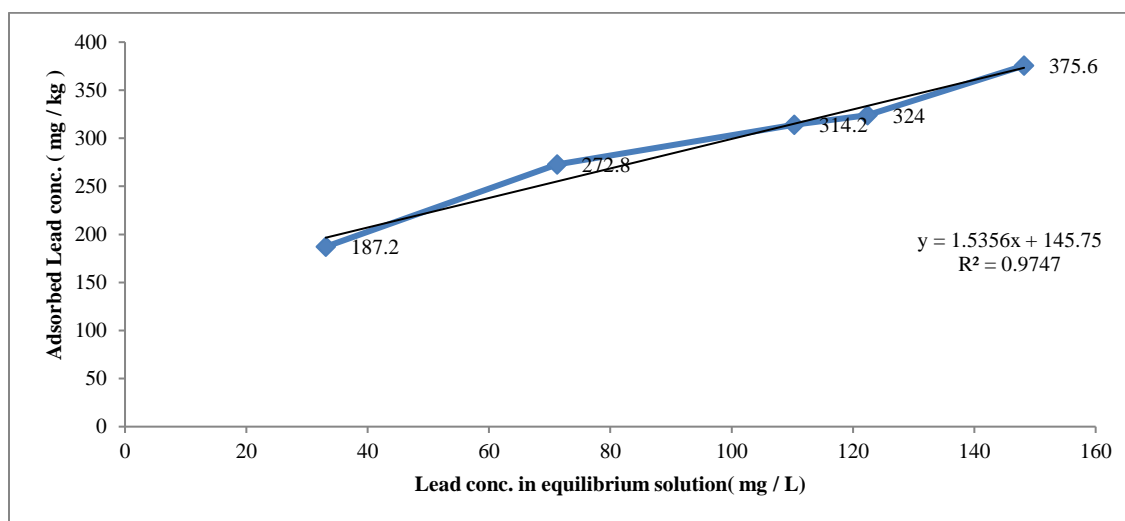


Figure 6. Release of lead from bentonite

Phosphate rock, came in third place in terms of the amount of lead released, with concentrations reaching 65.80, 69.80, 77.60, 91.00, and 123.00 mg Pb kg<sup>-1</sup> of phosphate rock (Fig.7). These concentrations are consistent with the concentration of lead adsorbed on surfaces of phosphate rock which amounted to

256.90, 397.60, 357.60, 430.60, and 617.00 mg Pb kg<sup>-1</sup> phosphate rock for lead addition levels of 0.5, 1.0, 1.5, 2.0, and 3.0 mmol L<sup>-1</sup>, respectively.

The low amount of lead adsorbed and released from phosphate rock may be attributed to the low value of CEC compared to other minerals used, however, phosphate rock is used to remove many heavy metals such as lead from their aqueous solutions due to its abundance in nature and non-toxicity (Maleki & Karimi, 2017), these results were consistent with what was preached by Al-dating and Naser (2020), who showed that phosphate rock can be used as an adsorbent for heavy metals in soil, such as lead, to limit their movement in soil and reduce damage resulting from them.

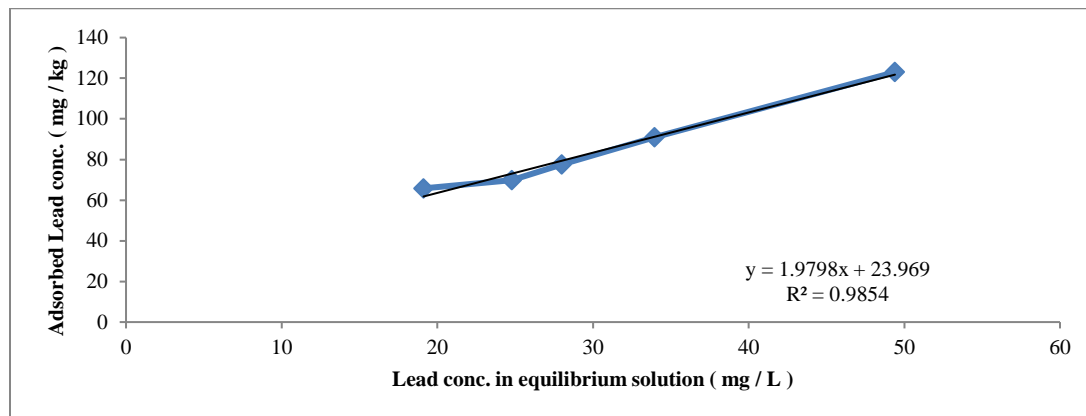


Figure 7. Desorption isotherm of lead from rock phosphate

Limestone, came in fourth and last place in terms of the amount of released lead, as concentrations reached 25.10, 29.30, 35.00, 38.70, and 40.90 mg Pb L<sup>-1</sup> (Fig.8). These results were consistent with the amount of lead absorbed on limestone, which reached 66.40, 100.30, 137.00, 160.77, and 214.90 mg Pb kg<sup>-1</sup> limestone for lead addition levels of 0.5, 1.0, 1.5, 2.0 and 3.0 mmol Pb kg<sup>-1</sup> limestone respectively. The low amount of lead released from limestone was due to a small amount of lead adsorbed compared to other adsorption materials used. These results are consistent with what was stated by Al-Abd and Al-Qudour (2013), who showed that the adsorption of heavy metals by limestone rocks is low because they are inactive rocks consisting of calcite and have a low content of adsorption sites.

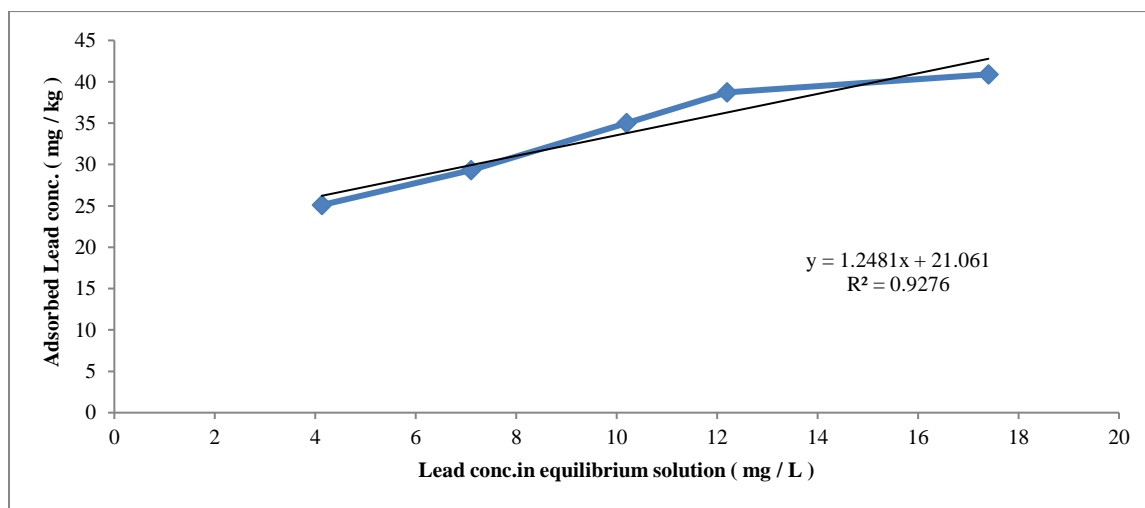


Figure 8. Desorption isotherm of lead from rock limestone

### **Lead Removal Rates**

To calculate the removal rates of lead from its aqueous solutions using some soil minerals, the average removal rates were taken for the initial concentrations of lead added and the final concentrations in the equilibrium solution after the adsorption process for each metal. The soil minerals used varied in their efficiency in removing lead from its aqueous solutions. This depended on the values of the cation exchange capacity (CEC) for each mineral and the maximum adsorption capacity, CEC value for zeolite is 100-200 and 83-53 cool kg-1 for bentonite. Zeolite mineral came in first place, with the removal rate of lead reaching 180.69%, then bentonite at 95.47%, phosphate rock at 18.48%, and finally limestone at 58%. These results are consistent with the values of the maximum adsorption capacity of lead on the used minerals, which were 384.61, 769.23, 2500, and 5000 mg Pb kg-1 for zeolite, bentonite, phosphate rock, and limestone, respectively (Table 2).

### **Conclusions**

Use of some soil minerals (zeolite, bentonite, phosphate rock, and limestone) in adsorption and release of lead and rates of its removal from its aqueous solutions using adsorption equations. The percentage of lead removal was calculated. Results showed an increased concentration of dissolved lead in the equilibrium solution directly with increased levels of lead added to all materials. Materials were graded in concentrations of dissolved, adsorbed lead and values of maximum adsorption capacity of lead on different soil minerals surfaces as follows: zeolite > bentonite > phosphate rock > limestone,

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### **Author Contributions**

All Authors contributed equally.

### **Conflict of Interest**

The authors declared that no conflict of interest.

### **References**

- Al-Abdullah, O., & Al-Qudour, M. B. (2013). Removal of cadmium from solution using soft phosphate rock under dynamic system conditions. *Jordanian Journal of Agricultural Sciences*. 9(3).
- Al-Awsi, W. S. A., & Aliwi, I. A. (2015). Adsorption and release of lead and cadmium in calcareous soils treated with used engine oils. *Al-Qadisiyah Journal of Agricultural Sciences*. 1(5).
- Aldaini, L. J. K., & Naser, K. M. (2020). Evaluation Of the Efficiency of Some Mineralogical and Organic Materials to Remove Some Heavy Metals from Contaminated Soil. *Plant Archives*, 20(1), 915-921.
- Al-Dayni, L. J. K., & Al-Azzawi K. M. N. (2019). Evaluation of the efficiency of some organic and mineral materials in reducing the accumulation of some heavy metals in the soil and growth of corn (*Zea mays* L). *Iraqi Journal of Soil Sciences*. 19(1).

- Al-Jatlawi, Al-B. A., & Hadid, H. A. (2017). The effect of some heavy metals on biological properties of some fish species on shore of Misurata city, Libya, Academy of Graduate Studies - Misurata Branch. 72-1
- AL-Rubaie, I. M. R., Dadoosh, A. H., & Nasser, K. M. (2022). Adsorption of Phosphorous and Zinc, and their interaction and processing power on Bentonite. *Iranian Journal of Ichthyology*, 9, 250-257.
- Anzeze, D. A., Onyari, J. M., Shiundu, P. M., & Gichuki, J. W. (2014). Adsorption of Pb (II) ions from aqueous solutions by water hyacinth (*Eichhornia crassipes*): equilibrium and kinetic studies. *International Journal of Environmental Pollution and Remediation (IJEPR)*, 2(1), 89-95.
- Asrari, E., & Rezaee, A. R. (2023). Cadmium removal from industrial sewage by using Bentonite and Kaolinite absorbent gravels. *EQA-International Journal of Environmental Quality*, 54, 36-40.
- Awda, M. M. (2018). Use of white radish and carrot plants in bioremediation of soil contaminated with some heavy metals. Master's thesis, College of Agriculture, University of Baghdad.
- Balaid, W. N., Al-Ahar, R. A., Saleh, H. M. B., & Nabil, M. (2019). Estimation of level of lead, cadmium and iron in shawarma in some areas of Tripoli city. *Journal of Applied Sciences*, 1, 107-120.
- Dhar, A. K., Himu, H. A., Bhattacharjee, M., Mostufa, M. G., & Parvin, F. (2023). Insights on applications of bentonite clays for the removal of dyes and heavy metals from wastewater: a review. *Environmental Science and Pollution Research*, 30(3), 5440-5474.
- Etuk, H. S., Ebong, G. A., Ekot, A. E., Ekpo, B. O., & Ayi, A. A. (2024). Mineral and elemental compositions of suspended particulate matter (SPM) and sediments from major rivers in the Southeastern Nigeria. *International Journal of Aquatic Research and Environmental Studies*, 4(1), 71-89. <http://doi.org/10.70102/IJARES/V4I1/7>
- Hamil, G., Abdel S. K., Al-Orfali, H. (2016). Study of concentration of heavy metals in gourd fruit, Faculty of Science, Sabha University, 8.
- Harbuzaru, B. (2003). Preparation de Structurants Organiques Et Leur Engagement En Synthese Hydrothermale De Zeolithes (Doctoral dissertation, Université de Haute Alsace-Mulhouse). France. 15-28.
- Hassoon, H. A., & Najem, A. M. (2017). Removal of some trace's heavy metals from aqueous solutions by water Hyacinth leaves powder. *Iraqi Journal of Science*, 611-618.
- Ibrahim, H. S., & Naser, K. M. (2020). Sequential extraction of zinc and nickel elements in contaminated soils. *Plant Archives (09725210)*, 20(1), 320-324.
- Khan, W. U. D., Wei, X., Ali, H. H., Zulfiqar, F., Chen, J., Iqbal, R., ... & El Sabagh, A. (2022). Investigating the role of bentonite clay with different soil amendments to minimize the bioaccumulation of heavy metals in *Solanum melongena* L. under the irrigation of tannery wastewater. *Frontiers in Plant Science*, 13, 958978. <https://doi.org/10.3389/fpls.2022.958978>
- Lei, Z., Xu, S. T., Monreal, C. M., McLaughlin, N. B., Zhao, B. P., Liu, J. H., & Hao, G. C. (2022). Bentonite-humic acid improves soil organic carbon, microbial biomass, enzyme activities and grain quality in a

- sandy soil cropped to maize (*Zea mays* L.) in a semi-arid region. *Journal of Integrative Agriculture*, 21(1), 208-221.
- Lu, X., Kruatrachue, M., Pokethitiyook, P., & Homyok, K. (2004). Removal of cadmium and zinc by water hyacinth, *Eichhornia crassipes*. *Science asia*, 30(93), 103.
- Mahdiraji, E. A., & Ramezani, N. (2019). The Influences of Soil Ionization in the Grounding System and Corona Phenomena on the Injection Lightning Current of 1000 KV UHV Transmission Line. *International Academic Journal of Science and Engineering*, 6(1), 39–50. <https://doi.org/10.9756/IAJSE/V6I1/1910004>
- Maleki, S., & Karimi-Jashni, A. (2017). Effect of ball milling process on the structure of local clay and its adsorption performance for Ni (II) removal. *Applied clay science*, 137, 213-224.
- Manahan, S. E. (2002). *Toxicological chemistry and biochemistry*. CRC Press.
- Mignardi, S., Corami, A., & Ferrini, V. (2012). Evaluation of the effectiveness of phosphate treatment for the remediation of mine waste soils contaminated with Cd, Cu, Pb, and Zn. *Chemosphere*, 86(4), 354-360.
- Mitchell, J. K., & Soga, K. (2005). *Fundamentals of soil behavior* (Vol. 3, p. 558). New York: John Wiley & Sons.
- Naser, K. M., Shref, A. M., & Kudher, M. F. (2020). The effect of adding some organic and mineral substances to calcareous soil on adsorption and desorption of copper and its removal efficiency from soil. *Plant Archives*, 20(1), 549-555.
- Nezamzadeh-Ejhieh, A., & Amiri, M. (2013). CuO supported Clinoptilolite towards solar photocatalytic degradation of p-aminophenol. *Powder Technology*, 235, 279-288.
- Ofiera, L. M., Bose, P., & Kazner, C. (2024). Removal of heavy metals and bulk organics towards application in modified constructed wetlands using activated carbon and zeolites. *Water*, 16(3), 511.
- Salkić, Z., Lugović, B., & Babajić, E. (2020). Petrography and mineral chemistry of oligocene shoshonitic dacites from the central Bosnia. *Archives for Technical Sciences*, 1(22), 1–10.
- Shamsham, S., & Al-Sabai, A. (2017). Study of the possibility of applying Freundlich and Langmuir equations to adsorption of zinc and copper elements on zeolite. *Al-Baath University Journal*. 39(21)
- Shubber, M. D., & Kebria, D. Y. (2023). Thermal recycling of bentonite waste as a novel and a low-cost adsorbent for heavy metals removal. *Journal of ecological engineering*, 24(5).
- Supriyadi, S., Rahman, F. A., Yuhardi, E., & Umam, C. (2023). Serapan N, P, dan K pada jagung Madura-3 di tanah lempung liat berpasir diameliorasi biochar dan bentonit-teraktivasi asam. *Jurnal Tanah dan Sumberdaya Lahan*, 10(2), 185-190.
- Talib, N. N. (2023). Comparison of some ornamental plants in technology of bioreclamation of soils contaminated with some heavy metals (Pb, Cd and Ni). Master's thesis. College of Agricultural Engineering Sciences. University of Baghdad.

- Trgo, M., & Vukojević-medvidović, N. (2005). The effect of concentration and pH on selectivity of ion exchange in system natural zeolite—Na<sup>+</sup>/Zn<sup>2+</sup> aqueous solutions. In *Studies in Surface Science and Catalysis* (Vol. 158, pp. 1051-1056). Elsevier.
- Tunguz, V., Petrović, B., Malešević, Z., & Petronić, S. (2019). Soil and radionuclides of Eastern Herzegovina. *Archives for Technical Sciences*, 1(20), 87–92.
- Vij, P., & Prashant, P. M. (2024). Analyzing Soil Pollution by Image Processing and Machine Learning at Contaminated Agricultural Field. *Natural and Engineering Sciences*, 9(2), 335-346. <https://doi.org/10.28978/nesciences.1575484>
- Zhao, Z., Jiang, G., & Mao, R. (2014). Effects of particle sizes of rock phosphate on immobilizing heavy metals in lead zinc mine soils. *Journal of soil science and plant nutrition*, 14(2), 258-266.