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Adsorption of Pb (II) and Zn (II) ions on Libyan kaolinite from Aqueous Solutions, (Isotherms Study)

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Abstract

This investigation was carried out to follow the ability of Libyan kaolinite as a new local natural adsorbent to adsorb lead Pb (II) and zinc Zn (II) ions from water using the laboratory batch method. The chemical structure of Libyan kaolinite adsorbent was investigated by XRF. The factors influencing the adsorption process, including pH, contact time, initial metal concentration, and the amount of kaolinite were studied, and the XRF results showed that Libyan kaolinite contains SiO_2 (49.0%) and Al_2O_3 (34.2%) as main compounds. The equilibrium adsorption results were analyzed by both Langmuir and Freundlich models to follow the mechanism of the adsorption process, according to the Langmuir equation the optimum adsorption capacity (mg\g) was 13.41 and 9.03 for Pb (II) and Zn (II) respectively at pH 3, 5. The equilibrium time was reached within 40 min for both metals. By increasing the initial metal ions concentration, the adsorption efficiencies were decreased, and the adsorption capacity of was increased with an increase in the initial pH. The results demonstrate the potential of Libyan kaolinite as a cost-effective and sustainable adsorbent for removing heavy metals from aqueous solutions, offering valuable insights for water treatment applications.

Keywords: Adsorption, Heavy metal, Lead, Zinc, Libyan kaolinite.

امتزاز أيونات الرصاص الثنائي والزنك الثنائي على الكاولينيت الليبي من المحاليل المائية (دراسة خطوط تساوي الحرارة)

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الملخص

تم إجراء هذا البحث لدراسة قدرة الكاولينيت الليبي كمادة ماصة طبيعية محلية جديدة على امتصاص أيونات الرصاص (II) والزنك (II) من الماء باستخدام طريقة التكرار المختبرية. تم فحص التركيب الكيميائي لطينة الكاولينيت الليبية بواسطة XRF. تمت دراسة العوامل المؤثرة في عملية الامتزاز بما في ذلك الأس الهيدروجيني ووقت التلامس وتركيز المعدن الأولي وكمية الكاولينيت وأظهرت النتائج XRFأن الكاولينيت الليبي يحتوي على SiO_2 (%49.0) وAl_2O_3 (%34.2) كمركبات رئيسية. تم تحليل نتائج امتصاص التوازن بواسطة منحنيي الادمصاص الايزوترمي لكل من لانجمير (Langmuir) وفرندلش (Freundlich) لمتابعة آلية عملية الامتزاز ،

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وفقا لمعادلة Langmuir كانت قدرة الادمصاص المثلى 13.41 و9.03 (mg\g)للرصاص (II) والزنك (II) على التوالي. تم الوصول إلى زمن الاتزان بعد 40 دقيقة لكلا العنصرين. من خلال زيادة تركيز أيونات المعادن الأولية، انخفضت كفاءة الامتصاص وزادت قدرة امتصاص الكاولينيت الليبي مع زيادة الأس الهيدروجيني. وبهذا توضح النتائج إمكانات الكاولينيت الليبي كمادة ماصة فعالة ومستدامة لإزالة المعادن الثقيلة من المحاليل المائية، مما يوفر رؤى قيمة لتطبيقات معالجة المياه.

الكلمات المفتاحية: الامتزاز، المعادن الثقيلة، الرصاص، الزنك، الكاولينيت الليبي

1. Introduction

The toxicological implications of Pb (II) and Zn (II) ions on ecosystems and human health render them particularly hazardous. The presence of these heavy metals in wastewater can lead to severe environmental and health concerns, including organ damage, neurotoxicity, and bioaccumulation [1]. Lead contamination poses a significant threat to aquatic environments, as even at minimal concentrations, it has been associated with brain damage, particularly in children. Lead is extensively utilized in industrial applications such as alloy manufacturing, electrical components, chemical catalysis, metal surface finishing, and battery production [2]. Zinc, while essential in trace amounts, becomes detrimental to human health when present in excessive concentrations. It is widely used in galvanization, pigment synthesis, stabilizers, thermoplastics, alloys, and battery manufacturing [3]. During metallurgical processes, non-degradable metal residues are often released into the environment, particularly into agricultural fields, where they can accumulate within the food chain and pose substantial health risks [4]. Various treatment techniques, including chemical precipitation, ion exchange [5], photocatalysis, and adsorption [6], have been employed for the removal of toxic heavy metal ions from water and wastewater [5, 6]. Kaolinite, a naturally occurring clay mineral, has demonstrated potential as an effective adsorbent for heavy metals due to its high surface area, cost-effectiveness, and environmental sustainability [7]. Libyan kaolinite, owing to its abundant reserves and high purity, presents a promising opportunity for environmental applications [8]. This study investigates the adsorption efficiency of Libyan kaolinite, sourced from the Sabha quarry, in the removal of Pb (II) and Zn (II) ions from aqueous solutions. The crystal structure, thermal properties, and chemical composition of the mineral have been characterized through various studies [7, 8, 9, 10]. The adsorption mechanisms and capacity of kaolinite for heavy metal removal have been extensively studied, demonstrating its efficacy in wastewater treatment [10]. The current research evaluates the adsorption performance of kaolinite obtained from the Sabha region in southern Libya for the removal of Pb (II) and Zn (II) ions from aqueous solutions.

2. Material and Experimental Procedure

Kaolinite samples were collected from the Sabha region in southern Libya. The chemical composition of the mineral was determined using X-ray fluorescence (XRF) analysis, Zinc nitrate ($Zn(NO_3)_2$ and lead nitrate ($Pb(NO_3)_2$, procured from Sinopharm Chemical Reagent Co. Ltd., were used as the metal ion sources. All reagents were of analytical grade and utilized without further purification. Deionized water was employed for the preparation of all solutions. The pH of the solutions was adjusted using 0.1 mol/L HNO_3 or 0.1 mol/L NaOH.

Stock solutions of Zn(II) and Pb(II) ions (1000 mg/L) were prepared by dissolving $Zn(NO_3)_2$ and $Pb(NO_3)_2$ in deionized water. The adsorption experiments were performed in duplicate to ensure reproducibility. The adsorption studies were conducted at ambient temperature (25°C) over a duration of 240 minutes. Each experiment was carried out in a 250 mL conical flask containing 100 mL of 280 mg/L metal ion solution and 300 mg of kaolinite. Adsorption isotherms for Pb (II) and Zn (II) were analyzed by varying the initial metal ion concentration between 30 and 280 mg/L, while maintaining a constant agitation speed of 160 rpm. The pH was adjusted between 2 and 5, and the experiments were conducted at 25°C for 4 hours. Following the adsorption process, supernatants were filtered, and the residual metal ion concentrations were quantified using atomic absorption spectroscopy (AAS). The adsorption capacities of kaolinite (qe, mg/g) for Zn (II) and Pb (II), were estimated from mass balance calculations according to Equation (1). The adsorption efficiency for each metal ion was subsequently assessed. The results presented in this study represent the mean values of three independent measurements [11, 12]. The amount of Pb (II) and Zn (II) adsorbed by Libyan kaolinite was determined using a mass balance equation expressed in equation (1):

$$q_e = \frac{C_0 - C_e}{m} \times V \qquad (1)$$

where *qe* is metal concentration on the Libyan kaolinite (mg/g) at equilibrium, C_e is metal concentration in solution (mg/L) at equilibrium, C_0 is initial metal concentration in solution (mg/L), *v* is volume of initial metal solution used (L), and *m* is mass of kaolinite used (g).

3. Results and Discussion

3.1 Chemical Analysis of Clay

Chemical and mineralogical composition of Libyan kaolin was determined by X-ray florescent (XRF) (Philips PW 1730): The XRF analysis revealing SiO_2 (49.0%) and Al_2O_3 (34.2%) as the primary constituents (Table 1).

Table (1):XRF of Libyan kaolinite.

Composition of kaolinite	Weight %
SiO_2	49.0
AlO_3	34.2
FeO_3	2.15
CaO	0.98
Na_2O	0.11
K_2O	0.98
TiO_2	1.39
LOI	10.1

3.2 Effect of Initial Concentration

Metals concentration of Pb (II) and Zn (II) ions were determined by adding 0.5 g of kaolin with 50 ml of metal ions of Pb (II) and Zn (II) solutions at concentrations of 40, 80, 120, and 200 mg/L. The pH of the solutions was adjusted to 5.0 with 1.0 N of NaOH and HNO_3 concentrations, and then the obtained suspension was shaken on a rotary shaker for 240 min at a speed of 160 rpm. After reaching equilibrium, suspensions were filtered and then metal ions concentration in filtrate was determined as the amount of removal. The effect of initial metals concentration on the removal of Pb (II) and Zn (II) ions from aqueous solutions by

Libyan kaolin is shown in *Figure* 1. As the results show, increasing the amount of absorbed ions per unit weight of the adsorbent (mg/g) occurred by increasing in initial metal concentration.

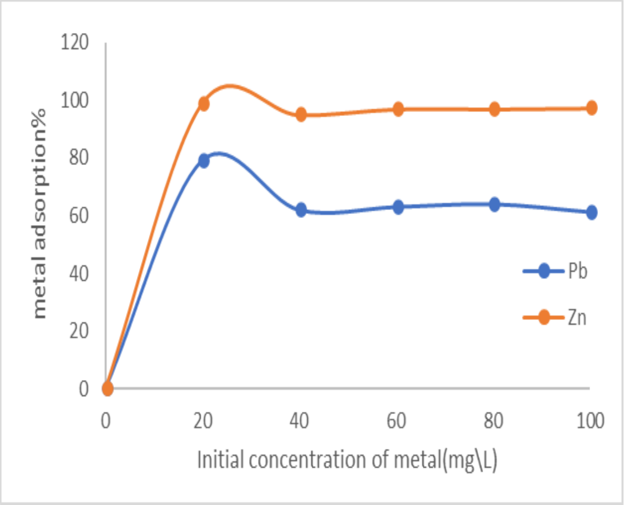

Figure 1: Effect of initial concentration on the sorption of Pb^{2+} and Zn^{2+} ions by kaolin**.**

3.3 Effect of Adsorbent Dosage

The dosage of Libyan kaolin adsorbent was varied between 10 and 30 mg/L while maintaining a constant concentration of Pb (II) and Zn (II) ions at 50 mg/L. A solution volume of 50 mL was placed in 300 mL flat-bottom flasks and agitated using a rotary shaker at a speed of 160 rpm for 240 minutes. Following the adsorption process, the suspensions were filtered, and the concentration of metal ions in the filtrate was analyzed to determine the adsorption capacity of the kaolin. As illustrated in *Figure 2*, an increase in kaolin dosage resulted in enhanced adsorption of Pb (II) and Zn (II) ions. At an adsorbent dose of 30 mg/L, the removal efficiencies for Pb (II) and Zn (II) reached 99.9% and 84%, respectively. This enhanced removal efficiency can be attributed to the increased adsorbent surface area available for ion adsorption, as well as the rise in the final pH of the solution, which likely facilitated the precipitation of heavy metal ions**.**

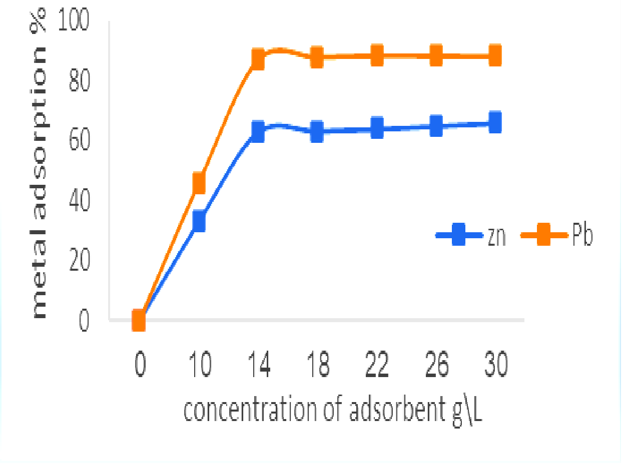

Figure 2: Effect of concentration on the adsorbent of Pb^{+2} and Zn^{+2} ions by kaolin

3.4 Effect of Initial pH

To evaluate the effect of pH on the adsorption capacity of Pb (II) and Zn (II) ions onto Libyan kaolin, a series of experiments were conducted using 50 mL solutions of Pb (II) and Zn (II) (50 ppm) mixed with 0.5 g of kaolin adsorbent. The pH of the solutions was adjusted within the range of 1.5 to 5 while maintaining it below 7.0 to prevent chemical precipitation. This ensured that heavy metal ion removal was primarily attributed to the adsorption process. The influence of initial solution pH is illustrated in *Figure* 3. The results indicate that adsorption at low pH levels is minimal; however, as pH increases, the adsorption efficiency of Pb (II) and Zn (II) ions significantly improves, which is a well-documented behavior for metal ion adsorption by natural clay minerals. In highly acidic conditions, the abundance of H^+ ions compete with metal ions for active adsorption sites on the kaolin surface, thereby reducing Pb (II) and Zn (II) ion removal. As the pH increases, the concentration of H^+ ions decrease, leading to reduced competition for adsorption sites and, consequently, enhanced adsorption of Pb (II) and Zn (II) ions. A sharp increase in adsorption is observed between pH values of 2.5 and 3.5, after which the removal efficiency stabilizes at higher pH levels. Additionally, an increase in the initial pH of the solution results in a corresponding rise in the final pH, facilitating the removal of heavy metal ions through multiple mechanisms, including chemical precipitation, ion exchange, co-precipitation, and complex formation.

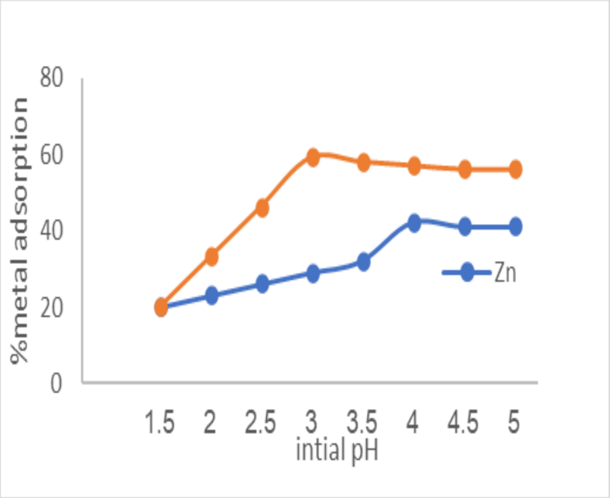

Figure 3: Effect of initial pH on the sorption of Pb^{2+} and Zn^{2+} ions by kaolin**.**

3.5 Effect of Reaction Time

A solution mixture consisting of 50 mL of Pb (II) and Zn (II) solutions (50 ppm) and 0.5 g of Libyan kaolin as the adsorbent was prepared. The pH of the mixture was adjusted to 3.0 ± 0.1. The suspension was then placed on a rotary shaker and agitated for 240 minutes at 160 rpm. Afterwards, the mixture was filtered using Whatman filter paper, and the concentration of the metal ions in the filtrate was measured to determine the adsorption capacity. *Figure* 4 illustrates the effect of contact time on the removal efficiency of Pb (II) and Zn (II) ions from aqueous solutions using Libyan kaolin. The results show that equilibrium was reached relatively quickly, within 40 minutes, indicating that the adsorption sites on the kaolin surface were readily available for metal ion uptake. Furthermore, the adsorption capacity and reaction rate for Pb (II) were found to be higher than for Zn (II), suggesting that Libyan kaolin provides more favorable adsorption sites for Pb (II) ions.

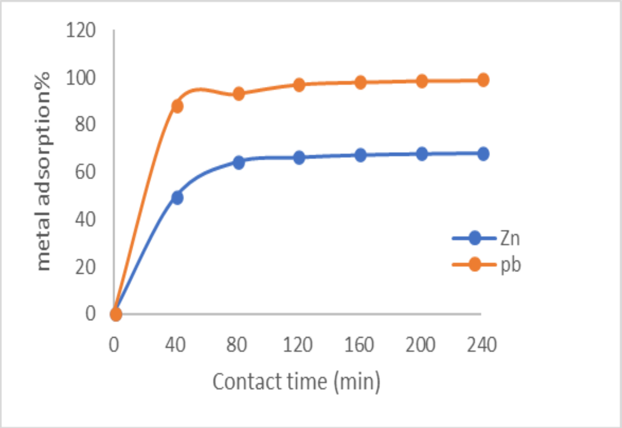

Figure 4: Effect of reaction time on the sorption of Pb^{2+} and Zn^{2+} ions by kaolin.

3.6 Adsorption Isotherms

Adsorption isotherms are mathematical models used to represent how an adsorbate species is distributed between the liquid and solid phases. These models are built on specific assumptions regarding the surface characteristics of the solid—whether it's homogeneous or heterogeneous—the nature of the adsorbate coverage, and potential interactions between adsorbate molecules. In this study, the equilibrium data were evaluated using the Langmuir and Freundlich isotherm models.

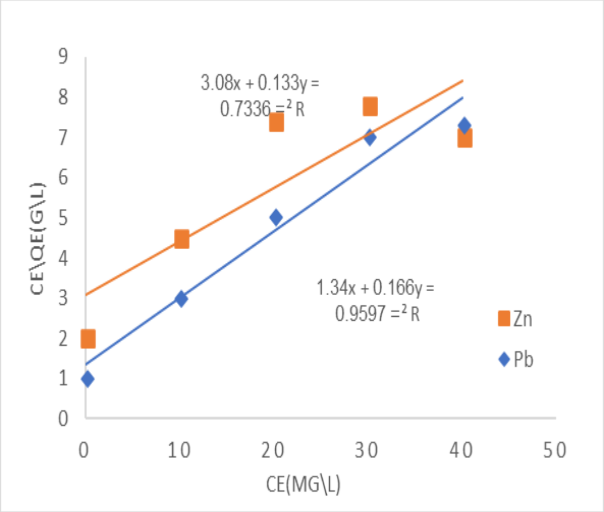

Figure 5: Langmuir adsorption isotherm of Pb^{+2} and Zn^{+2}

The Langmuir model assumes that uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The Langmuir equation may be written as:

$$qe = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (2)$$

The last equation can be expressed in its linear form as Equation (3):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (3)$$

In which, q_e is the amount of metal ions absorbed on kaolin (mg/g); C_e is the equilibrium concentration (mg/L) of Pb (II) and Zn (II) ions [4], q_m (mg/g) is the maximum amount of adsorbed metal ion per unit mass of sorbent corresponding to complete coverage of the adsorptive sites [12]. The Langmuir constants K_L, The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the kaolinite surface. The plots of specific sorption (Ce/qe) against the equilibrium concentration (C_e) for Pb (II) and Zn (II) are shown in *Figure 5* and the linear isotherm parameters, qm, K_L and the coefficient of determinations are presented in *Table 2*. The adsorption capacity, qm, which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage showed that the kaolinite had a mass capacity for Pb^{2+} (13.04 mg/g) than Zn^{2+} (9.39 mg/g). The data in *Table 2* further indicated, the effectiveness of kaolinite in the adsorption of the two metals.

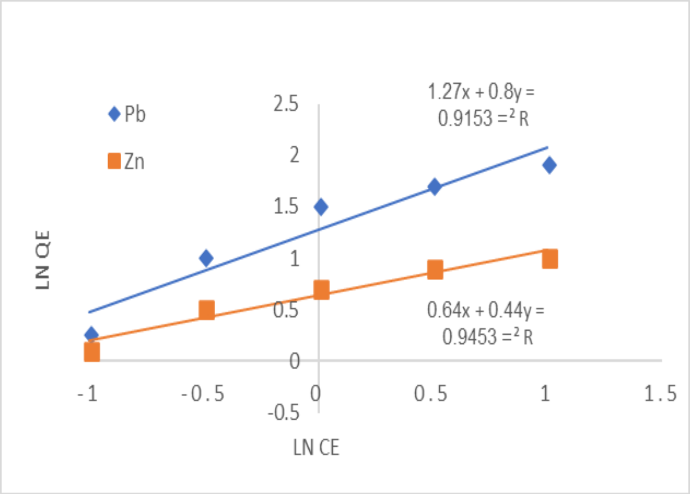

Figure 6: Freundlich adsorption isotherm of Pb^{+2} and Zn^{+2}.

The Freundlich adsorption isotherm. The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented as:

$$q_e = K_f \, C_e \; 1/n \qquad (4)$$

$$\ln qe = lnKf + \frac{1}{n} \, (lnc_e) \qquad (5)$$

Where qe is the amount of metal ion adsorbed at equilibrium time, C_e is the equilibrium concentration of a metal ion in solution. The constant n is the Freundlich equation exponent that represents the parameter characterizing energetic heterogeneity of the adsorption surface K_f is isotherm constants which indicate the capacity of the adsorption [4,13,15,16]. The isotherm constants can be calculated from the intercept and slope of the plot between ln qe and ln Ce. Figure 6 shows fitting the results on the Freundlich isotherm. Freundlich constants i.e. adsorption capacity, K_f and rate of adsorption, n, are calculated from the plot. The value of 'n' is larger than 1 which indicates the favorable nature of adsorption, *Table 2* [12,13]. Thus, it describes a heterogeneous system characterized by physical adsorption. The linear Freundlich isotherm constants for Pb (II), Zn (II) on Libyan kaolinite are presented in *Table 2*. The Freundlich isotherm parameter n

measures the adsorption intensity of metal ions on the kaolinite. The high *n* value of Pb (II) (2.71) and Zn (II) (1.62), first indicate the preferential sorption of both Pb (II) and Zn (II) probably due to physical-chemical properties including electronegativity, ionic radius, hydrated radius, hydrolysis constant among and secondly shows the ability of the kaolinite to remove these metal ions from solution even at high concentrations [16,17].

Table (2): Freundlich and Langmuir adsorption constants

	Freundlich adsorption			Langmuir adsorption		
	K_f	n	R_2	Q_0	K_L	R_2
	5.43	2.71	0.91	13.04	1.33	0.96
	0.63	1.62	0.94	9.39	0.16	0.73

The isotherms results were better fitted by Langmuir models than by Freundlich models. The results showed that the maximum adsorption capacities of kaolinite for Pb (II) and Zn (II) were 13.04, and 9.03 mg/g respectively, which is in agreement with the experimental results.

3.7 Adsorption Mechanism

The adsorption discussed herein is the interaction between the heavy metal surface and free electrons in absorbent molecules (kaolin), the clay materials still exhibited good adsorption capacities for the remediation of heavy metal from impure water. Moreover, the crystal structure of the kaolinite cell was formed based on the parameters obtained from studies that were achieved previously [12,13], they have suggested that the (001) surface of kaolinite is mainly involved in adsorption, which consists of hydrophilic Al–O octahedrons [5,13,15]. The adsorption reaction that occurs between the OH group and ,Pb and Zn metal ions is through the formation of a coordination complex. Because the oxygen atom in the OH group has a lone pair electron, while the metal ions of both pb and Zn have an unpaired d orbital. The calculations results showed that the states of Zn, and Pb, that may be adsorbed by kaolinite in aqueous solution are Zn (II), and Pb (II) respectively, and their respective complex ions, namely, $[Zn\ (OH)]^+$, $[Pb\ (OH)]^+$. The clusters of complex ions are large and are more easily adsorbed, so, in this study, simple complex ions $[Zn\ (OH)]^+$, $[Pb\ (OH)]^+$ were performed. The chemical reaction mechanism of adsorption on kaolinite is shown in *Figure* 7.

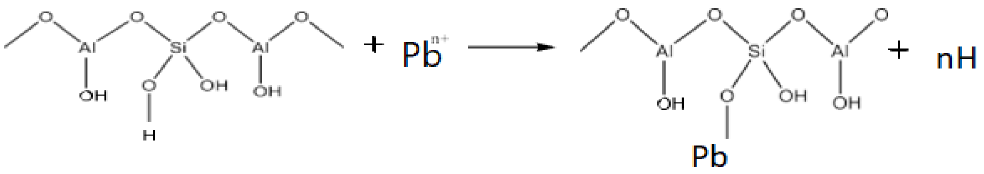

Figure 7: Mechanism of Pb ion adsorption by Libyan kaolin.

The Libyan kaolinite used in this study has a variable chemical composition that may explain the difference in the metal adsorptive capacities. Sdiri et al [18] mentioned that metals with higher electronegativity should adsorb more readily as was the case of the studied metals. The same theory suggested that metals of higher hydrolysis constants have better adsorptive capacity Zarifeh Raji et al [19]. Moreover, differences in kaolinite affinity for the studied metals (i.e, $Pb^{2+}$and Zn^{2+}) are mainly contingent upon those metals' physical-chemical properties including electronegativity, ionic radius, hydrated radius, hydrolysis constant among others Al-Degs et al. [20]. This assumption can give a reasonable explanation for the higher removal of Pb^{2+} and Zn^{2+}. For example, Pauling electronegativity of $Pb^{2+}$and Zn^{2+} are 2.33, and 1.65. also, other studies showed that kaolinite sample's affinity of Pb^{2+} more than Zn^{2+}, which is consistent with the electronegativity values. Furthermore, the hydrated radius showed the sequence Pb^{2+}= 4.01 A° and Zn^{2+} = 4.43 A°, indicating that smaller radius favored metal interaction with the sorbent surface [21]. Numerous studies reported that metals of ionic radius smaller adsorb stronger [17, 18, 19, 20 and 21]. According to those works, pb^{+} should have higher sorption capacity than Zn^{2+} as the case for the present study.

4. Conclusion

In the present work, all tests were achieved to evaluate the capacity of natural local Libyan kaolinite clay powder as adsorbents for lead and zinc from aqueous solution. The Libyan kaolinite clay showed higher specific removal of lead and zinc in different conditions which makes it suitable for use in water purification. The obtained results applied for both heavy metals proved their good efficiency in the adsorption processes, The empirical values are evaluated according to the Langmuir and Freundlich isotherms that are generally used to describe the adsorption processes. It is stated that the isotherm model fits very well. According to the obtained results, the adsorbent proved to be efficient for the elimination of heavy metals from aqueous solutions.

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