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HIGH AQUEOUS Pb(II)-REMOVAL STRENGTH USING NATURAL POZZOLAN AS A NOVEL ADSORBENT MATERIAL: KINETICS AND ADSORPTION ISOTHERMS STUDIES

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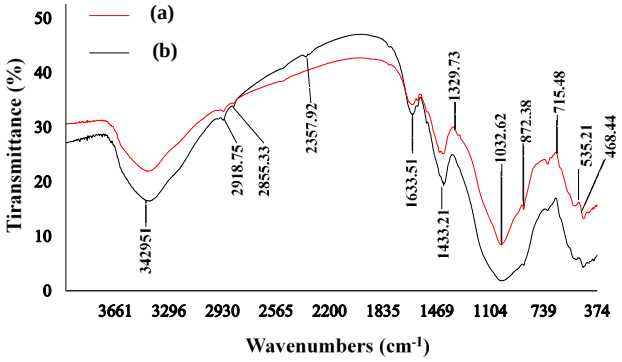
The aim of this work was to investigate the removal of a heavy metal from aqueous solutions using a natural adsorbent, with the prospect of its future application in wastewater treatment. Batch adsorption experiments were carried out in a closed reactor at room temperature (23 ± 2 °C) under continuous stirring at 160 rpm using raw pozzolan as an adsorbent for Pb(II) removal. The influence of experimental parameters, including contact time, solution pH, adsorbent dosage, and initial Pb(II) concentration, on the adsorption performance was systematically considered. The obtained results showed that the maximum Pb(II) removal efficiency reached 99% under the optimum conditions of 70 min equilibrium time, pH 4, adsorbent dosage of 0.1 g, and an initial Pb(II) concentration of 1 mg·L^{-1}. The equilibrium data were analyzed using several adsorption isotherms models, namely Freundlich, Langmuir, Dubinin–Radushkevich, and Temkin. The results indicated that the adsorption process was best described by the Freundlich and Langmuir models, with a maximum monolayer adsorption capacity of 137 mg·g^{-1}. Furthermore, the kinetic study revealed that the adsorption process followed the pseudo-second-order kinetic model, with correlation coefficients close to unity. Overall, the findings demonstrate that natural pozzolan is an economical and eco-friendly adsorbent with high potential for the effective removal of lead from wastewater.



INTRODUCTION

Among the hazardous pollutants, heavy metals present a serious environmental contaminant, due to their presence in various environmental compartments, including groundwater and surface water, where they may pose severe risks to ecosystem and public health.[1] So, lead is considered

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as one of the most toxic metal due to its widespread release from anthropogenic activities.[2,3] This metal is extensively used in numerous industrial applications, including battery manufacturing, paint pigments, fuels, photographic materials, explosives, coatings, automobile, aeronautical and steel industries.[4]

According to the United States Environmental Protection Agency (EPA), the permissible limit of lead in drinking water is 0.05 $mg \cdot L^{-1}$; therefore, even low concentrations of lead can be highly toxic, it may cause severe health disorders, including neurological damage, organ dysfunction, and in extreme cases death.[5,6] Unlike organic pollutants, which can undergo biological degradation, heavy metal ions are non-biodegradable and tend to accumulate in living organisms and in the environment.[7]

Currently, several physical and chemical methods are available for the removal of heavy metals from wastewater, including chemical precipitation, reverse osmosis, electrolytic treatment, ion exchange, and adsorption.[8–12] However, many of these techniques have significant limitations, such as high operational costs, process complexity and generation of secondary pollutants.[2] Among these methods, adsorption has emerged as one of the most effective and widely applied techniques, due to its simplicity, low cost, high efficiency and non-toxic/regenerable adsorbent materials.[13,14] In addition, adsorption processes offer considerable flexibility in both design and operation, making them suitable for large-scale industrial applications. Activated carbon is one of the most commonly used adsorbents because of its excellent adsorption properties. [15] Nevertheless, its relatively high cost, particularly in large-scale wastewater treatment applications.[4] Consequently, increasing attention has been directed toward the development of low-cost and locally available alternative adsorbents, such as eggshells, orange peels, oil palm shells, shrimp shells, and other agricultural or natural materials that exhibiting high adsorption capacities.[16–19]

Pozzolans are materials that can be obtained from various sources, including sedimentary deposits, fly ash, blast furnace slag, silica fume, metakaolin, ceramic waste, demolition and construction waste, rice husk ash, biomass ash, paper sludge, and volcanic rocks. Among these, volcanic rocks have been widely used as raw materials for the removal of various pollutants from wastewater due to their porous and homogeneous structure, as well as their eco-friendly properties.[20,21] Furthermore, these materials are extensively utilized in cement production and are also commonly fabricated into membranes for wastewater microfiltration and desalination processes.[21,22]

In the environmental field, pozzolan has been widely used for the removal of cationic and anionic dyes from industrial textile wastewater, achieving removal efficiencies of up to 96% and a maximum adsorption capacity (Qmax) of 0.881 $mg \cdot g^{-1}$ for methylene blue at 25°C.[21,23,24] Pozzolan has also been applied for the removal of heavy metals such as arsenic.[25] In some cases, pozzolan has been incorporated into composites with other materials to enhance its adsorption capacity and increase the number of active sites.[24,26]

The objective of this study was to investigate the adsorption capacity of pozzolan as an economical, eco-friendly, and alternative adsorbent for the removal of Pb(II) from aqueous solution. The physicochemical characteristics and sorption properties of pozzolan were analyzed using XRF, XRD, FTIR, BET and SEM techniques. The effects of operational parameters, including contact time, pH, adsorbent dosage and initial lead concentration, were evaluated to optimize the effective removal process. In addition, various equilibrium isotherm and kinetic models were applied to determine the nature, rate, and mechanisms of the adsorption process, as well as the pozzolan efficiency.

RESULTS AND DISCUSSION

Adsorbent characteristics

The characterization of the adsorbent materials was effectuated by different analysis, including XRF, XRD, FTIR, SEM and BET analysis methods, in order to define the chemical compositions and the surface morphology, notably the adsorption sites.

So, XRF analysis results indicated that SiO_2, CaO, Al_2O_3, Fe_2O_3 and MgO were the major constituents of the tested pozzolan, reflecting high amounts of silica together with low contents of Ca, Fe, Al, and Mg ions (Table 1). These findings suggest that the used pozzolan is a siliceous material.

Table 1

Chemical composition of pozzolan

Chemical composition	Percentage [%]
SiO_2	43.59
Al_2O_3	16.86
Fe_2O_3	6.83
CaO	21.45
MgO	6.34
Mn_2O_3	0.94
Na_2O	2.20
K_2O	1.58
SO_3	0.54
P_2O_5	0.40

Moreover, XRD patterns of pozzolan before and after Pb (II) adsorption are given in Fig. 1. According the figure, several peaks were appeared at different positions, so those appeared at 26.65° (3.342 Å), 20.85° (4.257Å) and 50.14° (1.818 Å) represent the quartz peak, whereas the peaks matched at 29.86° (2.990 Å), 56.78° (1.620 Å) and 65.18° (1.430 Å) represent the Augite peak. Moreover, the XRD pattern of pozzolan after adsorption is similar to that of before adsorption with a weak decreasing in their intensities.

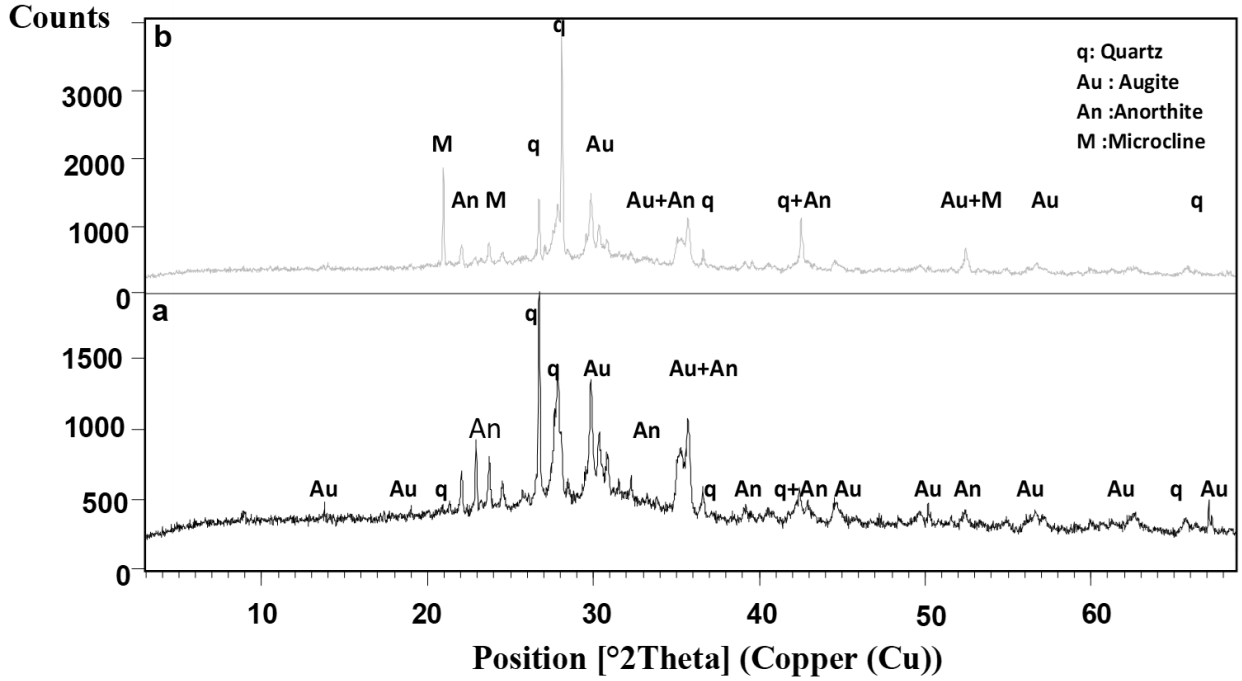

Fig. 1 – The XRD pattern of the pozzolan: a) before adsorption; b) after adsorption.

In the other hand, Fourier Transform Infrared spectroscopy (FTIR) technique was utilized to identify functional groups capable to adsorb metal ions.[27] The FTIR spectra of our adsorbent before and after the process were presented in Fig. 2. In the first spectrum (curve 'a' in Fig. 2), the major absorption bands were observed at 3624, 3429.51 cm^{-1}, 2918.75 cm^{-1}, 2855.33 cm^{-1}, 1633.51 cm^{-1}, 1433.21 cm^{-1}, 1329.73 cm^{-1}, 1032.62 cm^{-1}, 872.38 cm^{-1}, 715.48 cm^{-1}, 535.21 cm^{-1} and 468.44 cm^{-1}. So, the broad bands of 3624 cm^{-1} and 3429 cm^{-1} are due to O–H stretching vibration of the silanol (Si–OH) groups and H–OH vibration of the water molecules adsorbed on the solid surface.[28] The weak bands of 2918 cm^{-1} and 2995 cm^{-1} correspond to the stretching vibrations of $–CH_2–$ groups,[15] while the characteristic peak at 1636 $cm^{-1}$is assigned to the bending vibration of H–O–H derived from the pore water and surface absorbed water.[29] Moreover, the frequencies range interval of 1410–1450 cm^{-1} corresponds to the carbonate bands.[30] The adsorption band marked at 1329 cm^{-1} can be assigned to Si-O.[31] Additionally, most of the peaks in pozzolan spectra between 1100 and 400 cm^{-1} can be assigned to minerals such as quartz. [32] Furthermore, the broad absorption bands observed at 1040 cm^{-1}, 535.21 cm^{-1} and 468.44 cm^{-1} can be allocated to the characteristic peaks of $(SiO_4)^{-2}$ groups due to the stretching vibration of Si–O–Si.[33,34]

Hence, the major bands in the spectrum 'b' in Fig. 2 are similar to that of 'a', except the appearance of a peak at 2357.92 cm^{-1}, corresponding to Pb links that confirms the adsorption of these ions onto pozzolan surface.

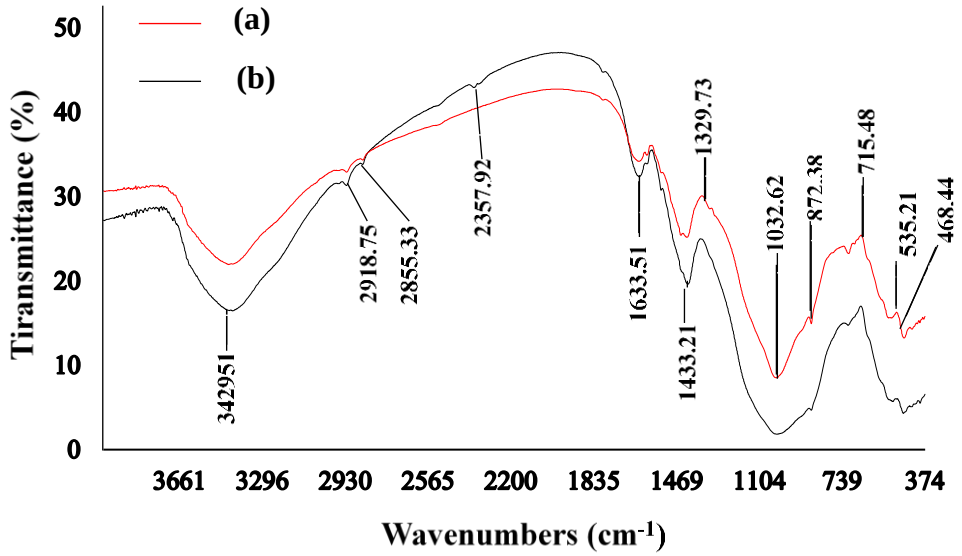

Fig. 2 – The FTIR spectra of the pozzolan: a) before; b) after adsorption.

Regarding SEM method, the analysis was carried out for pozzolan to study the surface morphology and to verify its porosity and the presence of adsorption active sites.[35] According to the Figs. 3a–c, the tested pozzolan present clearly a porous morphology that allowed it to adsorb different metal ions such as Pb(II) ions.

The comparison between SEM images before and after Pb(II) adsorption, notably with magnification of 1000x (Figs. 3c,e), We clearly observed the obstruction of the pozzolan pores, indicating the retention of Pb ions within these cavities.

The results of the BET analysis showed that the average specific surface area of pozzolan was 9.92 $m^2 \cdot g^{-1}$, with total pore volume of 0.0504 $cm^3 \cdot g^{-1}$ and average pore diameter of 3.6094 nm. According to the pores classification of IUPAC, our material exhibited mesopores with an average diameter ranging from 2 to 50 nm, which is the most desirable feature for the adsorptive removal of metal ions from aqueous solution.[35,36]

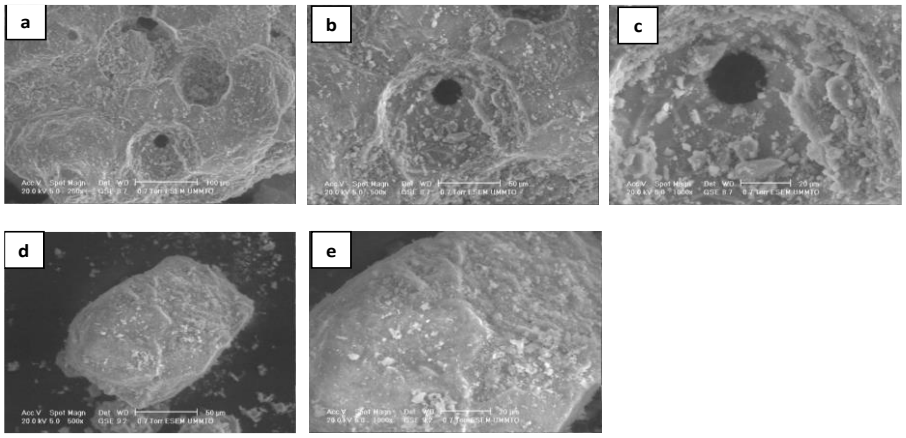

Fig. 3 – SEM micrographs of natural Pozzolan before adsorption process; 250 (a), 500 (b), and 1000 (c) magnifications. And after adsorption process; 500 (d), and 1000 (e) magnifications.

Zero-point charge (pH zpc) of adsorbent

The pH_{zpc} of an adsorbent is a significant characteristic that can determine the pH at net electrical neutrality of the adsorbent surface. So, at this pH value, the acidic or basic functional groups are completely neutralized, consequently the external electric field does not influence the adsorbent and the functional group present on the surface does not contribute to the pH of the solution.[37] Moreover, the pH_{zpc} depends on the surface acidity; low acid concentrations of the group on the surface group increase the pH_{zpc} values.[38]

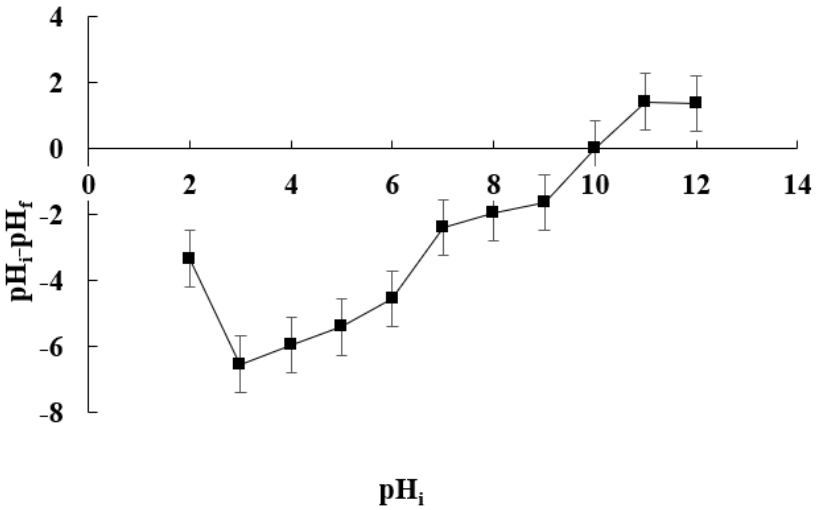

Fig. 4 – Experimental determination of pH_{zpc} from the plot of ΔpH against pH_i.

In this case, the obtained pH_{zpc} values, around 10 (Fig. 4), suggested the basic nature of adsorbent surface, which indicate that the adsorption of cationic ions is more important compared to anionic one.

Furthermore, the obtained results of zeta potential of pozzolan showed a negative electrical charge in water (–13 and –27 mV) at pH range from 2 to 10. These zeta potential values offer the possibility of further application of our material for the adsorption removal of cationic pollutants from aqueous solution.

Adsorption assay study of the Pb(II) removal from aqueous solution

Effect of contact time

Contact time is an essential parameter in assessing the economic viability of wastewater contaminant removal.[37] The required contact time for a complete sorption is important to give insight about the adsorption kinetic process, so, the influence of contact time on Pb(II) adsorption by our natural pozzolan was investigated in batch experiment at various periods times, starting from 10 min until 100 min, while, the other experimental conditions were maintained at; Pb(II) initial concentration of 5 mg·L^{-1}, pH=6, agitation speed 160 rpm, temperature 23°C and adsorbent dosage 0.1 g.

According to the results presented in Fig. 5, Pb(II) adsorption occurred rapidly, reaching a removal percentage of 85% within the first 10 min. So, the equilibrium state was established after 70 min where the adsorption level increased up to 99%. Therefore, the adsorption kinetic pass through two phases; the first one was rapid (within about 10 min), which may be due to the availability of active sites on the adsorbent surface until reaching the equilibrium state at about 70 min. This results indicating a monolayer coverage of Pb(II) on the adsorbent surface.[39,40] Thus, the short equilibrium time indicates a high efficiency and economic feasibility of the adsorbent for further industrial applications.

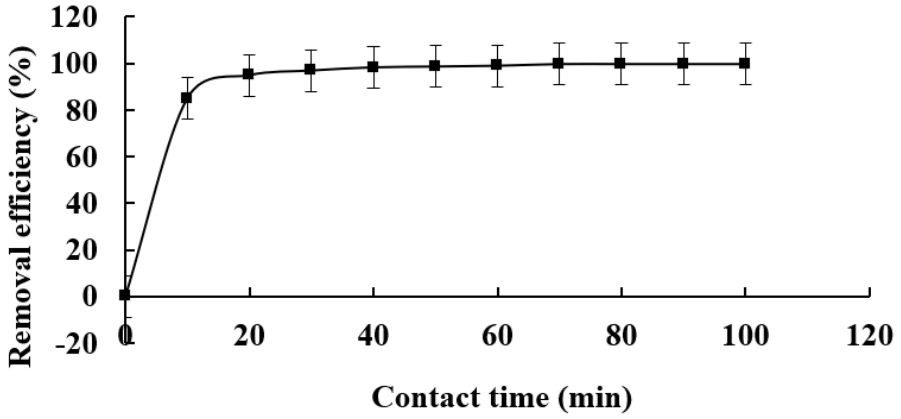

Fig. 5 – Effect of contact time on the adsorption of Pb(II) on pozzolan (temperature = 23°C, pH = 6, adsorbent dosage = 0.1g, Pb (II) initial concentration = 5 mg·L^{-1}, agitation speed = 160 rpm).

Effect of pH

The solution pH value is one of the most important factors influencing the surface binding sites and thus the metal ions adsorption on the sorbents. It can intervene on the degree of ionization and speciation of adsorbate during adsorption process and extent of dissociation of functional groups on the active sites of the adsorbent.[15,41-43] The effect of initial pH on sorption of Pb(II) was studied at different pH values, ranging from 2 to 10, at the following operational conditions; room temperature (23°C), 200 mL of Pb(II) at an initial concentration of 5 mg·L^{-1}, adsorbent dosage of 0.1 *g*, and contact time of 70 min.

As shown in the Fig. 6 that present the pH effect on the Pb(II) adsorption by pozzolan, it can be seen that the percent removal increased from 86% to 99% with increasing of pH values from 2 to 4 until reaching a plateau value at a pH = 4. Indeed, at low pH the removal capacity of our adsorbent was low because of the competition of H^+ ions versus Pb(II) ions for occupy the binding sites of the adsorbent surface. Likewise, at pH = 2 the positive charge of the adsorbent surface produced an electrostatic repulsion with cationic metal charges.[44] While, with increasing pH values the surface charge of adsorbent became negative and thus the adsorption of Pb(II) ions increases.[45] However, with increasing pH, more functional groups became available for Pb(II) ligation due to the reduction in the H^+ concentration; consequently, Pb(II) adsorption was enhanced.[46] Besides, lead ions can be precipitated at pH values higher than 6 in the solution, in presence of hydroxyl ions, which allowed a decrease in percentage adsorption.[45] In order to avoid the effect of chemical precipitation on metal ion adsorption, pH 4 was selected as the optimum value for the following experiments.

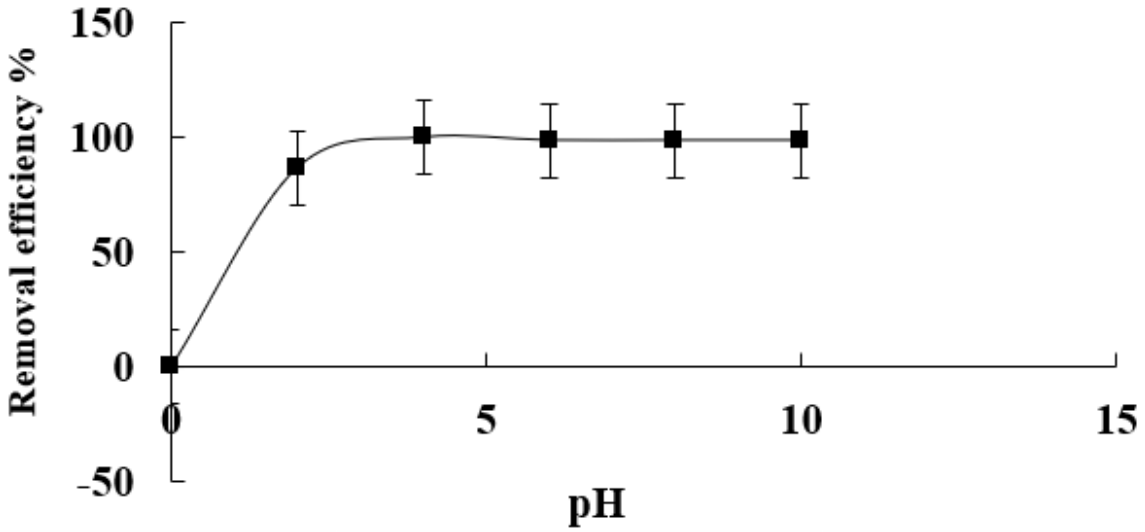

Fig. 6 – Effect of pH on Pb(II) adsorption by pozzolan (temperature = 23°C, adsorbent dosage = 0.1g, contact time = 70 min, Pb (II) initial concentration = 5 mg·L^{-1}, agitation rate = 160 rpm).

Effect of adsorbent dosage

The adsorbent dosage is also an important parameter; it can determine the adsorption capacity of a material for a given adsorbate initial concentration.[47] The effect of pozzolan dosage on the sorption of Pb(II) ions was investigated using the following Pozzolan amounts of 0.01 to 0.3 g in 200 mL of Pb(II) solution, at an in initial concentration of 5 mg·L^{-1}, an equilibrium time of 70 min, pH = 4 and at 23°C. The results of calculate percentage removal as a function of pozzolan dosage is presented in the Fig. 7.

As shown in the curve of the Fig. 7, the percent removal of Pb(II) was increased from 94% to 99% with an increase in pozzolan dose from 0.01 to 0.1 g. The increased adsorption efficiencies with increasing adsorbent amounts indicated the accessibility of a larger number of sorption sites at higher dosage to adsorb lead ions.[34] However, at a pozzolan amount superior to 0.1 g, there was no any change in percentage removal of lead which may be attributed to the overlapping of active sites and the establishment of equilibrium between the sorbent and the metal ions.[48] Thus, a dosage of 0.1 g was selected as the optimum adsorbent amount for Pb(II) adsorption in the subsequent experiments.

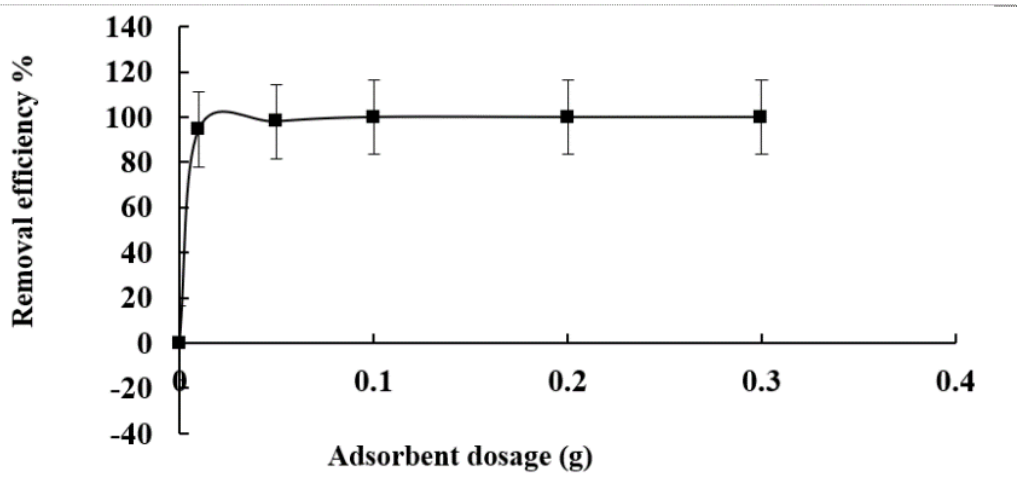

Fig. 7 – Effect of adsorbent dosage on the Pb(II)adsorption by pozzolan (temperature = 23°C, pH = 4, contact time =70 min, Pb(II) initial concentration = 5 mg·L^{-1}, Agitation rate = 160 rpm).

Effect of Pb (II) initial concentration

Metal sorption depends on the initial concentration of the target heavy metal ion, as this concentration provides an important driving force to overcome mass transfer resistance between the aqueous and solid phases.[27,49] Batch adsorption studies were carried out for various Pb(II) concentrations, ranging from 1 to 100 mg·L^{-1} using pozzolan as adsorbent. The results of removal percentage by pozzolan as a function of Pb(II) concentrations were presented in the Fig. 8.

According the curve in the Fig. 8, we have observed that the removal efficiency was important (can archived about 99%) at the first tested concentration of 1 mg/L, when the initial Pb (II) concentrations increased up to this value, the removal efficiency slightly decreased (99–88%). This observation can be explained by a limited number of active sites of the adsorbent, which can be saturated above high lead concentration. Similar observations were reported in the previous researches.[50]

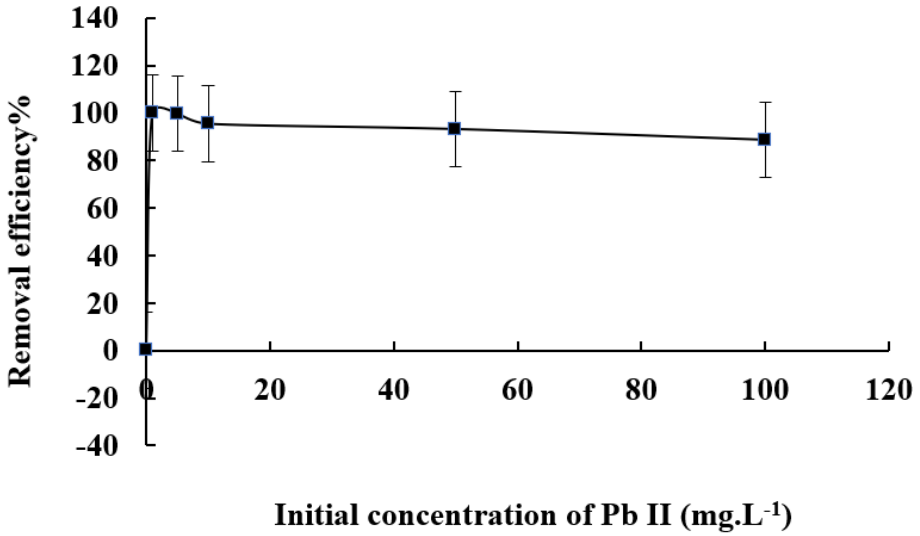

Fig. 8 – Effect of initial concentration on the adsorption of Pb(II) on pozzolan (temperature = 23°C, pH = 4, contact time =70 min, adsorbent dose = 0.1g, agitation rate = 160 rpm).

Adsorption isotherm study

The adsorption isotherm approach is an important parameter for optimizing the conditions of sorption applications such as the sorption capacity, bond energy and affinity properties between adsorbate species and adsorbent.[51] Therefore, the adsorption isotherm describes the relationship between the amount of the adsorbed ions at equilibrium and the equilibrium

concentration of adsorbate in solution.[52] In the present study, the adsorption equilibrium data were modulated using different equations; Langmuir, Freundlich, Temkin and Dubinin–Radushkevich.[53] The plots of linear studied models were shown in Fig. 6, and the parameters of each isotherm models were shown in Table 2 .

Langmuir isotherm model

The Langmuir model assumes that adsorption occurs in a monolayer, where the active sites are identical and energetically equivalent without interactions or transmigration between the adsorbed molecules on the adsorption surface.[40] The linear form of Langmuir isotherm presented in Fig. 9a, was calculated by the following eq. 1.[54]

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m} x \frac{1}{C_e} \quad (1)^{54}$$

where q_e [mg·g^{-1}] is the adsorbed amount at equilibrium and C_e [mg·L^{-1}] is the equilibrium concentration of the adsorbate. Q_m [mg·g^{-1}] and K_L [L·mg^{-1}] are the maximum sorption capacity and energy of sorption respectively. The essential characteristics of the Langmuir model can be expressed by a separation factor (R_L) that can be expressed as eq. 2.[55]

$$R_L = \frac{1}{1+K_L C_0} \quad (2)^{55}$$

where C_0 [mg·L^{-1}] is the solute initial concentration in highest aqueous phase. The separation factor (R_L) indicates the adsorption nature to be unfavourable (R_L> 1), linear (R_L =1), favourable (0 <R_L< 1), or irreversible (R_L= 0).[56]

Freundlich isotherm model

Unlike Langmuir model, the Freundlich isotherm is based on the assumption that the adsorption occurs on heterogeneous sites with non-uniform distribution of energy levels.[57] A linear form of the Freundlich model presented in the Fig. 9b was deduced from the expression of eq. 3.[58]

$$Lnq_e = LnK_F + \frac{1}{n} LnC_e \quad (3)^{58}$$

where K_F [mg·g^{-1}(L·mg^{-1})$^{1/n}$] and n are Freundlich constants, which represent adsorption capacity and adsorption strength respectively. The value of n ranging from 1 to 10 indicated that the adsorption process is favourable.

Temkin isotherm model

Temkin isotherm supposed a linear decrease of adsorption heat of all molecules in the layer with coverage due to adsorbent– adsorbate interactions. It was also characterized by a uniform distribution of binding energies to some maximum energy.[59] The linear form of Temkin isotherm model (Fig. 9c) is described as follow eq. 4.[47]

$$q_e = \frac{RT}{b_T} LnK_T + \frac{RT}{b_T} LnC_e \quad (4)^{47}$$

where b_T is the Temkin constant related to the heat of sorption [kJ·mol^{-1}], K_T is the equilibrium binding constant corresponding to the maximum binding energy [L·g^{-1}], T is the absolute temperature [K] and R is the gas constant [8.314 x 10^{-3} kJ·mol^{-1}·K^{-1}].

Dubinin–Radushkevich model

The Dubinin-Radushkevich model allow to determine the order process adsorption, chemical or physical and thus it allow to calculate the mean free energy of adsorption.[43] The linear form D–R isotherm shown in the Fig. 9d was calculated from eq 5.[60]

$$Lnq_e = LnQ_D - \beta\varepsilon^2 \quad (5)^{60}$$

where, Q_D [mg·g^{-1}] is Dubinin-Radushkevich monolayer adsorption capacity, β [mol^2·kJ^{-2}] is a constant related to free energy of sorption and ε is the Polanyi potential given by the following relationship eq 6.

$$\varepsilon = RT\, Ln\,(1 + \frac{1}{C_e}) \quad (6)^{60}$$

where R is the gas constant [kJ·K^{-1}·mol^{-1}], T is the temperature (K) and E [kJ·mol^{-1}] is the mean free energy of adsorption per molecule of adsorbate, when it is transferred from infinity in the solution to the solid surface.[61]

$$E = \frac{1}{\sqrt{2\beta}} \quad (7)^{61}$$

The value of E [KJ·mol^{-1}] specifies the type of sorption mechanism. So, for physical sorption processes the E value comprises in the range of 1–8 kJ·mol^{-1} and or chemical adsorption, the E value is in the interval of 8 to 16 kJ·mol^{-1}.[54]

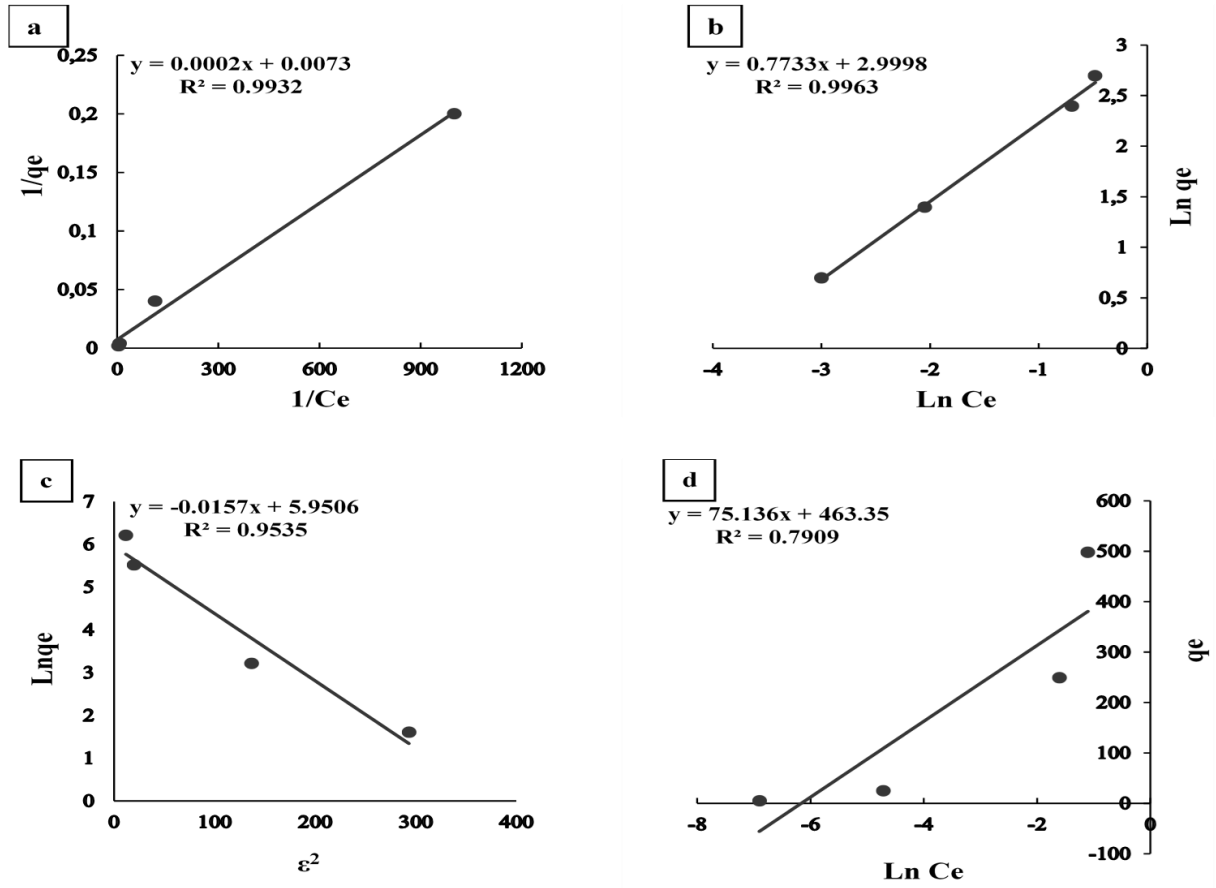

Fig. 9 – Linear plot presentations of adsorption isotherm models of: a) Langmuir; b) Freundlich; c) D-R; d) Temkin of the sorption of Pb (II) onto pozzolan (T= 296 K).

Table 2

Langmuir, Freundlich, Temkin and D-R model parameters for Pb(II) removal by pozzolan at various Pb(II) concentrations (T= 296 K)

Models	Parameters	Values	R^2
Langmuir	q_m [mg·g^{-1}]	137	0.99
	K_L [L·mg^{-1}]	37	
	R_L	2.10^{-4}	
Freundlich	K_F [mg·g^{-1}(L·mg^{-1})$^{1/n}$]	20.9	0.99
	n	1.29	
Temkin	b_T [kJ·mol^{-1}]	0.03	0.79
	K_T [L·g^{-1}]	477	
D-R	B [mol^2·kJ^{-2}]	1.57E^{-02}	0.95
	Q_D [mg·g^{-1}]	384	
	E [kJ·mol^{-1}]	5	

As shown in the Fig. 9 and in the Table 2, the relatively high values of correlation coefficient (R^2= 0.99) was attributed to the Langmuir and Freundlich models indicating that the equilibrium data of Pb (II) adsorption was fitted by both models. Moreover, the monolayer coverage of lead ions on the adsorbent was occurred with a maximum adsorption capacity of 137 mg·g^{-1} with the values of R_L ranging from 0 to 1, so these findings confirm a favourable retention of Pb (II) on pozzolan.

Furthermore, the heterogeneity factor (n) was greater than 1 indicates that the sorption intensity was preferable for all studied concentrations. The Langmuir and Freundlich constants suggested that the pozzolan has a high adsorptive capacity for removing Pb (II) from aqueous solution.

In the other hand, the correlation coefficient of linear D–R isotherm model was 0.95 with E value was 5 kJ· mol^{-1} that was in the range of 1–8 kJ·mol^{-1},

indicating that the adsorption was essentially physical type.

Kinetic study

Adsorption kinetic are typically studied at the solid/solution interface and expressed by the solute removal rate as a function of time.[62] Adsorption kinetic generally depends on the physical and/or chemical characteristics of the adsorbent materials which describe the reaction pathways and the reaction rates.[63] In order to control the adsorption process mechanism, such as; mass transfer, diffusion control and chemical reaction; several models were used to test experimental data.[64] The modelling of the kinetics experimental data was investigated by evaluation and analysis of Pb (II) removal rate by various conventional models, like Lagergren pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models.[65,66.]The results of linear plots models and the kinetic parameters determined from the intercepts and the slopes of respective plots were presented in the Fig. 10 and Table 3 respectively.

Pseudo-first-order model

The Lagergren equation is commonly used to describe the adsorption rate in a liquid-phase system, it considers that the rate of adsorption sites occupation is proportional to the number of unoccupied sites and it assumes that the adsorbate binds only to a single active site on the adsorbent surface. So, it has been widely used to describe the adsorption of pollutants from wastewater in different fields.[3,4,47,57] The integrated linear form of the considered model was shown in the Fig. 10 a, the calculation of the parameters was carried out according to eq. 8.[62]

$$Log\ (q_e - q_t) = Log\ q_e - \frac{K_1}{2.303}t \qquad (8)^{62}$$

where q_e and q_t are the amount of lead adsorbed by pozzolan at equilibrium and at the instant time t (*min*) respectively, K_1 is the model rate constant [min^{-1}]. A plot of $log\ (q_e - q_t)$ *vs t* gives a straight line, from which the values of q_e and K_1 were obtained from the intercept and slope respectively.

Pseudo-second order model

Ho and Mckay developed a pseudo second order equation based on the number of adsorbed ions on the sorbent. The pseudo-second-order model considers that the rate is proportional to the square of the remaining free surface sites number.[47,67] The pseudo-second-order kinetic model of our study was presented in the Fig. 10 b, and the used mathematical expression can be written as follows eq 9.[68]

$$\frac{1}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (9)^{68}$$

where K_2 [$g \cdot mg^{-1} \cdot min^{-1}$] is the pseudo-second-order constant that can be estimated from the plot of t/q_t against *t* with q_e.

Intraparticle diffusion model

The possibility of intraparticle diffusion was examined to describe the adsorption mechanism using the Weber-Morris model, it is usually considered to determine the rate-limiting step. The main assumption of the intra-particle diffusion model is that film diffusion is negligible and intra-particle diffusion is the only rate-controlling step.[34,69] To determine the type of diffusion mechanism occurs during the adsorption process, the model of Weber and Morris (1963) was used. This model is defined by eq 10[70] and presented in the Fig. 10c.

$$q_t = K_i t^{0.5} + C \qquad (10)^{70}$$

where K_i is the constant of intraparticle diffusion [$mg \cdot g^{-1} \cdot h^{-0.5}$]; and *C* is a constant [$g \cdot mg^{-1}$].

Elovich model

Elovich equation is a well-known equation describing the adsorption of different ions in aqueous solutions. It assumes that the actual solid surfaces are energetically heterogeneous and that neither desorption interaction between the adsorbed species could substantially affect the kinetics during low surface coverage. The linear form of Elovich model was presented in the Fig. 10 d and calculated by eq. 11.[57]

$$q_t = \beta Ln(\alpha\beta) + \beta Lnt \qquad (11)^{57}$$

where α and β are the Elovich coefficients, which represent the initial adsorption rate [$g \cdot mol^{-1} \cdot min^{-1}$] and the desorption coefficient [$mol \cdot g^{-1} \cdot min^{-1}$] respectively. The Elovich coefficients can be calculated from the plots of q_t *vs ln t*.

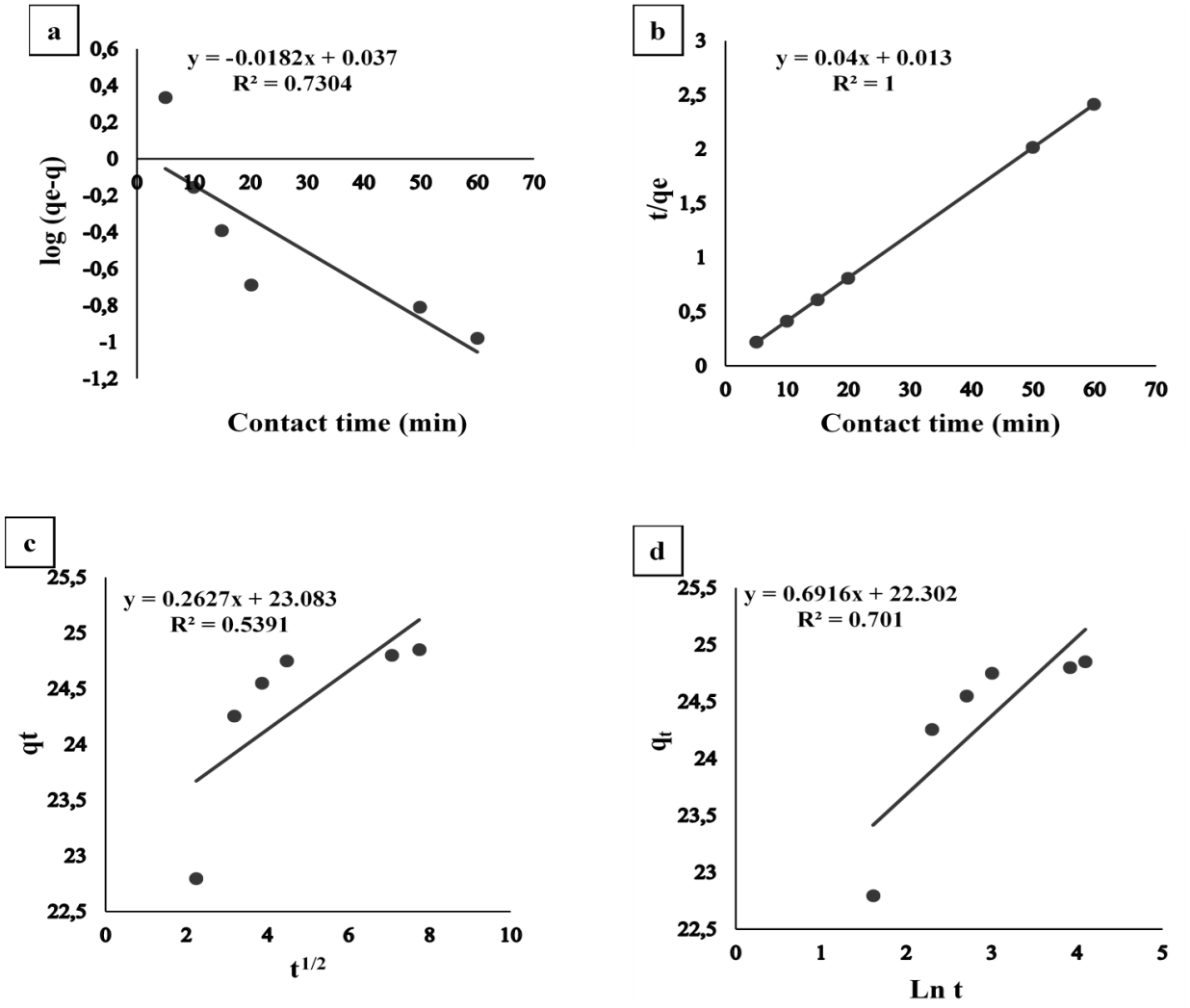

Fig. 10 – Linear regression of Pb(II) sorption experimental data on pozzolan by kinetics models of; a) Pseudo-first-order; b) Pseudo-second-order; c) Intraparticle diffusion; d) Elovich (296 K).

Table 3

Kinetic parameters of studied models; Pseudo -first-order, Pseudo -second order, intraparticle diffusion and Elovich, for Pb (II) removal by pozzolan at 296 K

Models	Parameters	Values	R^2
Pseudo-first-order	q_e [mg·g^{-1}]	0.08	0.73
	K_1[min^{-1}]	0.04	
Pseudo-second order	q_e [mg·g^{-1}]	25	1
	K_2 [g·mg^{-1}·min^{-1}]	0.12	
Intraparticle diffusion	K_i [mg·g^{-1}·h$^{-0.5}$]	0.26	0.53
	C [g·mg^{-1}]	23.08	
Elovich	α [g·mol^{-1}·min^{-1}]	1146	0.70
	β [mol·g^{-1}·min^{-1}]	2.77	

The applicability of these models was quantified from the coefficient of determination (R^2 values). According to the values of Table 3, R^2 was close to unity for the pseudo second-order model. For the pseudo-first-order model, the R^2 was equal to 0.73 that was lower than that noticed for the pseudo-second order model. Moreover, the intraparticle diffusion plot was not linear over the entire time range, indicating that intraparticle diffusion was not the rate-limiting step. The Elovich model did not provide a satisfactory fit to the experimental data, as the R^2 value was lower than that obtained for the other models. Consequently, the pseudo-second-order model showed the best suitable with the

experimental data among the studied kinetic models. it is based on the assumption that the rate-controlling step is chemisorption, which may involve valence forces through the sharing or exchange of electrons between the adsorbate and the adsorbent.[42,71]

Comparison of the present adsorbent with adsorbents reported in previous studies

The results obtained from the present study suggested that pozzolan is an important candidate adsorbent material because of its several advantages at environmental and economic levels, such as; effectiveness, availability, inexpensive, easily regenerated and as an eco-friendly process that does not cause secondary pollution. It also possesses several advantages that make it an excellent material for environmental applications, such as high adsorption capacity and adsorption rate.

The maximum adsorption capacity (q_m) of Pb(II) obtained with pozzolan in the present study was compared with those reported for several adsorbents previously described in the literature in order to evaluate its adsorption performance and practical applicability. The compared materials included ion-imprinted polyvinyl imidazole–silica hybrid copolymer,[4] raw and activated charcoals of *Melocanna baccifera* Roxburgh,[5] *Portulaca* plant biomass,[7] inulin,[13] manganoxide minerals,[34] silica nanopowders/alginate composite,[54] green porous lignin-based spheres,[55] and waste litchi peels.[56] The adsorption capacities reported for these adsorbents were 7.6 $mg \cdot g^{-1}$, 0.66 $mg \cdot g^{-1}$, 53.76 $mg \cdot g^{-1}$, 17.24 $mg \cdot g^{-1}$, 0.74 $mg \cdot g^{-1}$, 98 $mg \cdot g^{-1}$, 83.33 $mg \cdot g^{-1}$, 31.8 $mg \cdot g^{-1}$ and 78.74 $mg \cdot g^{-1}$ respectively.

Compared with ion-imprinted polyvinyl imidazole–silica hybrid copolymer and manganoxide minerals, which exhibited adsorption capacities of only 7.6 and 0.74 $mg \cdot g^{-1}$, respectively, pozzolan showed a remarkably higher adsorption performance, indicating a much greater affinity toward Pb(II) ions. Similarly, the adsorption capacity of pozzolan was considerably superior to that of raw and activated charcoals of *Melocanna baccifera* Roxburgh (0.66 $mg \cdot g^{-1}$), suggesting that the mineralogical composition and porous structure of pozzolan provide a larger number of available active sites for Pb(II) uptake.

Although some biosorbents such as *Portulaca* plant biomass (53.76 $mg \cdot g^{-1}$), inulin (17.24 $mg \cdot g^{-1}$), and waste litchi peels (78.74 $mg \cdot g^{-1}$) demonstrated moderate adsorption capacities, their performances remained significantly lower than that obtained with pozzolan (137 $mg \cdot g^{-1}$). Even advanced composite materials, including silica nanopowders/alginate composite and green porous lignin-based spheres, which exhibited relatively high adsorption capacities of 98 and 83.33 $mg \cdot g^{-1}$, respectively, were less efficient than pozzolan under the investigated experimental conditions.

The superior adsorption capacity of pozzolan may be attributed to its heterogeneous porous structure, high surface reactivity, and the presence of active functional groups and mineral phases capable of interacting with Pb(II) ions through adsorption and ion-exchange mechanisms. Furthermore, pozzolan achieved adsorption equilibrium within only 70 min using a low adsorbent dosage of 0.1 g, which demonstrates not only its high adsorption efficiency but also its economic and operational advantages compared with many previously reported adsorbents. These findings suggest that pozzolan represents a promising, low-cost, and highly effective adsorbent for the removal of Pb(II) ions from aqueous media

EXPERIMENTAL

Chemical reagents

All chemical reagents used in this study were supplied by Sigma–Aldrich. Lead nitrate was used to prepare lead solutions as model toxic pollutants. A stock solution of Pb (II) were prepared from $Pb(NO_3)_2$ (99.0%) in distilled water. The 0.1 $mol \cdot L^{-1}$ NaOH and 0.1 $mol \cdot L^{-1}$ HNO_3 were used for pH adjustments of the test solutions.

Preparation and characterization of the absorbent

The pozzolan used in the experiments is a siliceous material that was obtained from a deposit situated in Beni Saf in western Algeria. Gross pozzolan was ground by a grinder and passed through two sieves of 53 μm and 100 μm respectively. Therefore, the size of pozzolan granulometry used in this study was between 53 - 100μm and without treatment.

The physico-chemical characteristics of pozzolan were determined by the following methods:

– *Crystal structure* that was identified by X-ray diffraction (XRD – X'Pert PRO PANalytical)

operated at 45 *kV* and40 mA. Step sizes of 0.017° for a time per step of 92s were used.
– *X-ray measurements* that were performed using a glancing angle of 2θ in a range of 2–70°, using Cu Ka radiation (l = 1.5418 $\AA$).
– *X-ray fluorescence* by the device of S8 TIGER- BRUKER for the determination of chemical composition.
– *Surface functional groups* that were determined by Fourier transform-infrared (FT-IR;BRUKER), the spectra were recorded from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1} using a pressed KBr pellet.
– *Specific surface area* that was measured by Brunauer– Emmett–Teller (BET) method and determined by nitrogen adsorption at 77 *K*.
– *Surface morphology* that was observed by scanning electron microscopy SEM (Philips-FEI XL30 ESEM).

Determination the point zero charge (pH_{pzc})

Determination of pH_{pzc} of pozzolan has been carried out to investigate the surface charge properties of adsorbent material. To determine the pH_{pzc}, a solution of NaCl 0.01 M has been prepared with various pH values of 2 to12 that was adjusted by addition of HCl or NaOH 0.1 M. After that, 50 mL of each sample were put in reagent bottles with 0.2 *g* of adsorbent for 48 h, after this duration, the pH of each solution was measured.[37] The difference between initial and final pH values ($\Delta pH = pHi - pH_f$) was plotted against pHi. The point of intersection of the resulting curve with abscissa, at which $\Delta pH = 0$, gave the pH_{pzc}.[72]

Batch adsorption experiments

Batch adsorption study allowed determining the optimum conditions for the removal of lead ions from aqueous solution. The adsorption of Pb(II) by pozzolan was studied using batch experiment under different operational conditions, including contact time (from 10 to 100 min), pH (from 2 to 10), pozzolan dosage (0.01 to 0.3 g) and initial Pb (II) concentration (from 1 to 100 $mg{\cdot}L^{-1}$). In experimental studies, a quantity of pozzolan was added into 200 mL of Pb (II) solution. For all adsorption experiments the mixture was shaken at 160 *rpm* for a predetermined contact time at room temperature (296*K*). When equilibrium was reached, the adsorbent was separated by centrifugation at 3000 rpm for 20 min and the supernatant solution was analysed.

The concentration of Pb ions before and after adsorption was determined using an atomic absorption spectrophotometer (ZEEnit 700 P-Analytik Jena). The removed Pb (II) percentage is calculated from the following eq. 12.[66]

$$Removal\ efficiency\ (\%) = \frac{(C_0 - C)}{C} \quad (12)^{66}$$

where C_0 and C are the initial concentration and the equilibrium concentration respectively of the metal ion in solution ($mg{\cdot}L^{-1}$).

Adsorption kinetics

The effect of contact time on the adsorption process was performed in the 200 ml of Pb (II) solution at a concentration of 100 $mg{\cdot}L^{-1}$, under agitating of 160 rpm *via* electromagnetic stirrer at room temperature. Thus, the solution was contained 0.1 g of pozzolan homogenously dispersed in solution during a predetermined time interval from 0 to 60 min. After of each experiment, the mixture was centrifuged for 20 min at 3000 rpm. The actual amount of Pb(II) adsorbed at time t, q_t ($mg.\ g^{-1}$), was calculated according to the following eq. 13.[66]

$$q_t = \frac{(C_i - C_t)V}{m} \quad (13)^{66}$$

where C_i and C_t ($mg{\cdot}L^{-1}$) are the concentrations of Pb (II) at initial and at any time t, respectively. V (L) is the solution volume and m (g) represent the mass of pozzolan adsorbent.[73]

Adsorption isotherms

0.1 g of pozzolan was added into a series of flasks containing 200 mL of Pb (II) solution with different initial concentrations (1, 5, 50, 100, $mg{\cdot}L^{-1}$). The shaking speed was adjusted at 160 rpm, under the optimized conditions of pH, time and temperature. At equilibrium time, the mixtures were centrifuged and the supernatants were analysed in order to determine residual Pb (II) concentrations.

The amount of Pb(II) ions adsorbed onto pozzolan was calculated by the following eq. 14.[66]

$$q_e = \frac{(C_i - C_e)V}{m} \quad (14)^{66}$$

where q_e ($mg{\cdot}g^{-1}$) is the equilibrium amount of Pb (II) adsorbed onto 1 g of pozzolan surface, C_i and C_e ($mg{\cdot}L^{-1}$) are the initial and final equilibrium concentrations of Pb(II) ions respectively, V (L) is the volume of the Pb(II) solution and m (g) is the pozzolan adsorbent mass.[66]

Analysis data

The results are expressed as the mean values obtained from three replicates, with error bars representing the standard deviations. Data analysis was performed using Microsoft Excel software (Version 2019).

CONCLUSIONS

The present study demonstrated the significant potential of natural pozzolan as an efficient and eco-friendly adsorbent for the removal of Pb(II) ions from aqueous solutions. The experimental investigation showed that the adsorption process was influenced by several operating parameters, including pH solution, adsorbent dosage, contact time, and initial metal concentration. So, the optimum adsorption conditions were obtained at pH 4, with an adsorbent dose of 0.1 g, a contact time of 70 min, and an initial Pb(II) concentration of 1 $mg \cdot L^{-1}$, under which a removal efficiency, of approximately 99%, was achieved. These results indicate the high affinity of pozzolan toward lead ions, highlighting its suitability for wastewater treatment applications.

In addition, the physicochemical characterization of the adsorbent by SEM and FTIR analyses confirmed the involvement of surface functional groups in the adsorption process and revealed clear interactions between Pb (II) ions and the pozzolan surface. The pH_{pzc} value, determined to be around 10, indicated the predominantly basic nature of the adsorbent surface, which favors the adsorption of positively charged metal ions under acidic conditions.

Moreover, the equilibrium data were satisfactorily described by both Langmuir and Freundlich isotherm models, suggesting that Pb(II) adsorption occurred through a combination of monolayer and heterogeneous multilayer adsorption mechanisms. The maximum adsorption capacity calculated from the Langmuir model reached 137 $mg \cdot g^{-1}$, demonstrating the high adsorption capability of pozzolan compared with many conventional low-cost adsorbents reported in the literature. Furthermore, the mean free energy of adsorption, estimated at approximately 5 $kJ \cdot mol^{-1}$, indicated that the adsorption process was mainly governed by physical interactions, particularly weak van der Waals forces.

In the other hand, the kinetic study revealed that the adsorption behavior followed the pseudo-second-order kinetic model with correlation coefficients close to unity, indicating that the adsorption rate was dependent on the interaction between Pb(II) ions and the available active sites on the adsorbent surface.

Overall, the findings of this work confirm that natural pozzolan represents a promising, low-cost, abundant, and eco-friendly adsorbent for the effective removal of Pb(II) from contaminated water. Its high adsorption efficiency, combined with its local availability and low environmental impact, makes it a suitable alternative material for sustainable wastewater treatment and heavy metal remediation processes.

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