REMOVAL OF LEAD USING PAPER SLUDGE AS BIOSORBENT

Samira MAANE[a], Mohamed FODIL[b]Meriem MERAH[c], Antonio Avalos RAMIREZ[d], Mohamed Fahim HAROUN[e]

[a,b,c,e]Chemistry Department, Sciences Faculty, Farhet ABBAS Setif IUniversity, Setif, Algeria
[b,d] Centre National en Électrochimie et en Technologies Environnementales, 2263 Av. du Collège Shawinigan, Canada
[e] Laboratoire de physique quantique et systèmes dynamiques (LPQSD), Sciences Faculty, Farhet ABBAS Setif IUniversity, Setif, Algeria
Email: [a]samira.messai@univ-setif.dz, [b]mohamed.fodil@univ-setif.dz, [c]meriemmerah.univ.setif@gmail.com, [d]aaramirez@cnete.qc.ca, [e]mohamed.haroun@univ-setif.dz

Abstract
The physio-chemical properties of paper sludge (PS) were examined using various analytical techniques, such as X-ray fluorescence, X-ray, Fourier transform infrared spectroscopy, thermogravimetric analysis, and pH of zero-point charge. PS was utilized as an adsorbent to remove lead ions from wastewater. After analyzing multiple factors, the optimal operating conditions for adsorption were determined, including a pH of 10, a contact duration of 20 minutes, a temperature of 20°C, and an adsorbent concentration of 1 $g.L^{-1}$. The Langmuir isotherm model was found to be the best fit for the experimental results, with an adsorption capacity of qe = 238.09$mg.g^{-1}$. The research also revealed that the lead adsorption on PS is exothermic and spontaneous, and the adsorption process follows a pseudo-second order kinetics reaction system. The study also looked at the thermodynamic characteristics of the adsorption process.
Keywords:Heavy Metals, Lead, Paper Sludge, Adsorption, Wastewater Treatment

1. Introduction

Natural contamination is an incredible concern these days. The creation and request of paper and related items is raising significantly all over the world. Squander created in the paper business relies upon the natural matter utilized for creation and the kind of paper produced. The removal of this waste is a major issue because of its enormous sum. Hence the utilization of this loss to produce a few valuable assets is a major step towards efficient power energy and ecological manageability. The waste delivered from mash and paper industry is classified inrejects, for example, pulping, blanching, washing, and essential slop[1]. These waste materials are possible contaminations of air, soil, and water. Lignocellulosic squander is made out of various inorganic and natural toxin edifices which are discarded as a subordinate of mash blanching method and wood assimilation process[2]. Paper derivatives found in most sectors of activity and consumption. In fact, the paper industry, it is one of most world economic .The paper industry rejects a large quantity of diluted substances with the effluents which are containing chemical compounds, formed during the papermaking and transformation process, as well as natural substances such as particles of wood fiber and other components and a lot of paper sludge[3]. The pulp and paper industry is facing a big problem with the increasing quantities of paper being produced day by day. In fact, the paper industry, by recycling some of its waste and reintegrating it into the manufacturing process, conserves wood and water resources well. Significant progress has been recorded in this area over the past decade. However, several sectors have been used for the recovery of PS as use in the building demand [4, 5]. Energy production and [6] Bioethanol production[7], Industry produces a lot of effluents, the contaminants that must be removed, there are heavy metals, which seriously affect the environment and will have a harmful impact on the health of the ecosystem [8]. During the Industrial Revolution, the production and use of Pb were considerably accentuated by its notable release and accumulation in the environment. Indeed, its density is high and its melting point is low. It is ductile and can be worked with inexpensive techniques. [9]. Lead has been and still is used by innovative technologies for several decades. The dispersion of Pb resulting from industrial activities (manufacture of paint, Pb accumulators, batteries[10]. Infront of the high costs of treating these pollutants, the treatment process water develops, among of the effective treatment methods available, adsorption using a low-cost natural and wastes of natural products industry is the most economical and adequate method, thanks to its simplicity and efficiency for the removal of metal ions comparing with others methods such as coagulation, flotation or precipitation, ultrafiltration [11] even at low concentrations appears to be a promising option that will meet the economic and environmental requirements [12]. The paper is delivered from mostly unrefined components like wood pulps, agro-squander deposits like rice straw[13]. As it is rich in active sites that help adsorption, especially heavy metals with positive charges The original paper makes it a rich material with cellulose, these materials have been used in a wide range of fields, there are also many studies on the relationship of adsorption to cellulose[14], as it is rich in active sites that improve the adsorption, especially positive charges like heavy metals[15]. In order to recover paper sludge, this work focused on characterization and valorization of west sludge piper to adsorb lead ions in aquae solution.

2. Materials and methods

Samples preparation

The PS were dried 24 hours in an oven at 105 °C, then it was ground into a powder which passed through a sieve with a size of 100µm in order to obtain very fine particles.

Characterizations

The pH of zero-point charge

The determination of pHpzc involved preparing ten 100 ml Erlenmeyer flasks, each containing 25ml of distilled water, and adjusting the initial pH to a range of 2 to 14. Next, 0.05g of PS powder was weighed and added to each Erlenmeyer flask. The PS powder was allowed to contact the solutions while stirring for 24 hours, followed by the cessation of stirring and measurement of the final pH of each solution. A graph was plotted with ΔpH = f (pHi), where ΔpH = (pHf-pHi), and the intersection of the curve with the axis passing through zero was used to determine the isoelectric point.

Infrared spectroscopy

Infrared spectroscopy is mainly used to determine the structures of molecules as well as to evaluate their reactivities. the sample of the PS studied at a range between 4000 $cm^{-1}$and 400 cm^{-1}.using (Thermo Fisher, USA).

Thermogravimetric analysis

From the TGA and DTG thermograms giving respectively, the variations in mass loss and from the derivative of the loss of mass as a function of temperature, many temperatures ware determined, the start of decomposition, and the temperatures at which the rate of degradation was changed for each step of the PS decomposition. A sample weighing 10 mg were tested under an atmosphere (N_2), the measurements were conducted with a heating rate of 10°C.min^{-1}, spanning a temperature range of 20°C to 700°C.

X-Ray Fluorescence (XRF)

X-ray fluorescence was employed to determine the chemical composition of SP, the SP sample was pressed into a small disc to form a pellet. The analysis was performed using Rigaku-ZSX Primus IV.

Adsorption study

The adsorption of lead ions from wastewater samples onto PS samples was conducted for each experiment, 50mg of SP sample was added to 50 mL of distilled water containing lead ions, which were dissolved by adding a known amount of lead nitrate ($Pb(NO_3)_2$) at a stirring speed of 200rpm. The experiments were conducted under new optimal conditions for pH, contact time, adsorbent dose, temperature, and initial concentration of lead ions, as determined from previous batch adsorption studies. The concentration of lead ions at both the initial and equilibrium stages was ascertained through the use of inductively coupled plasma (ICP) atomic absorption spectroscopy, with a Perkin Elmer Optima 4300 DV (USA) instrument, while the initial pH values were adjusted using 0.1N HCl and 0.1N NaOH.

Kinetics study

In order to examine the kinetics of Pb (II) adsorption onto SP, the experimental data was compared to the predictions of the pseudo-first order model and the pseudo-second order model. The accuracy of these models was assessed by determining their correlation coefficients (R2) with the experimental data. The kinetics were calculated by fitting the pseudo-first order and pseudo-second order models to the lines obtained from the equations:

Pseudo-first order model

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \cdot t \quad (1)$$

q_e et q_t : represent, the adsorption capacity in (mg/g) at equilibrium and at time t, respectively

k1 : adsorption rate constant (mn^{-1})

Pseudo-second order model

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \quad (2)$$

q_e et qt: represent, the adsorption capacity (mg/g) at equilibrium and at time t, respectively

k_2: adsorption rate constant (g/mg.mn)

Adsorption models

The adsorption results are modeled here based on Freundlich and Langmuir. The equations which are used for the models are given in what follows.

Langmuir

$$\frac{Ce}{qe} = \frac{1}{qmax \cdot b} + \frac{1}{qmax} \cdot Ce \quad (3)$$

Freundlich

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \qquad (4)$$

Thermodynamic study

The thermodynamic quantities ΔG°, ΔS° and ΔH° of the adsorption of Pb^{2+} on SP were also determined by studying the effect of temperature using the Following equations:

$$\ln K_d = \left(\frac{\Delta S^{\circ}}{R}\right) - \left(\frac{\Delta H^{\circ}}{R}\right)\frac{1}{T} \qquad (5)$$

$$K_d = \frac{q_e}{c_e} \qquad (6)$$

$$\Delta G^{\circ} = -RT.\ln K_d \qquad (7)$$

3. Resultants and discussion

CharacterizationFTIR Spectroscopy

(

Fig **1**) shows Infrared spectra were performed using a Fourrier transform IR spectrophotometer. Paper sludge mainly consisting lignocellulosic materials and some other materials as kaolinite, calcite, talc, quartz and muscovite [16]**,** calcium carbonate is used as a whitening agent [17], the band between 3500-3350 cm^{-1}, it is due to the vibration of elongation of the hydroxyl group (OH) which is practically present in the structure of cellulose, hemicelluloses and lignin[18]. The spectra also show an absorption band at 2909cm^{-1} attributed mainly to the C–H elongation of aliphatic molecules[19]. The small band around 1647cm^{-1} is

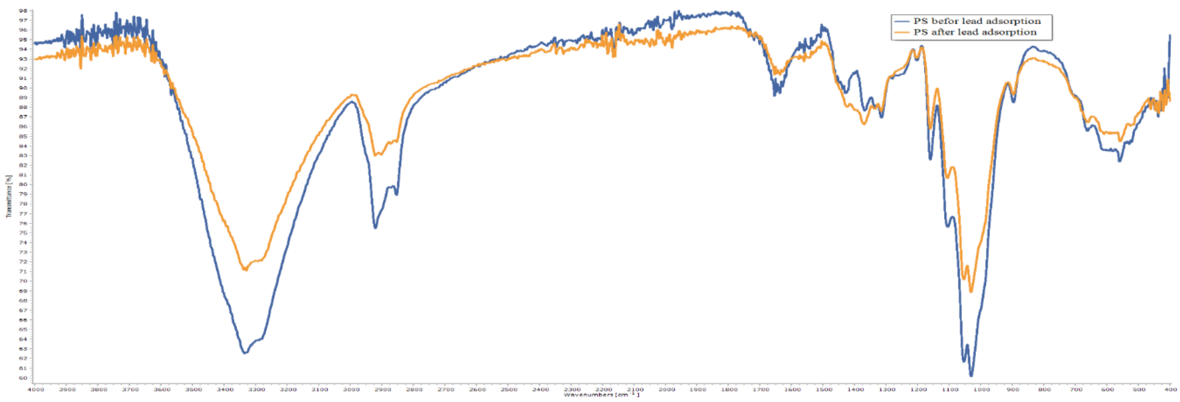


Fig 1. Fourier transform Infrared of PS before and after adsorption

characteristic band is for the vibrations of the C=O groups (carboxylic groups) and that found at 1686 cm^{-1} is due to the vibration of $CaCO_3$ (calcite) [16]. The spectra also show bands at 1430 cm^{-1} and 1310cm^{-1} due to the elongation of the C=C bonds (in the lignin structure)[20] and the presence of $CaCO_3$ at 1399 cm^{-1}[21]. The band between 1050cm^{-1} and 1114cm^{-1} is assigned to the C-O-C binding vibration presentin the structure of cellulose and hemicelluloses[18].

Regarding the band between 750-500cm^{-1} is attributed due to Si-O bonds, while the band noticed has 980cm^{-1} due to Al-OH vibrations [16]**.** Little differences were noticed between spectra FTIR before and after adsorption, the form of band or intensity this indicates that these functions have participated in the adsorption process as O-H, C-O and C=O.

pHof zero-point charge(pH$_{zpc}$).

pHpze of PS greatly influences the adsorption process. To monitor the surface charge of SP. The pH of the value point 0 (pHzpc) is about 7 (**Error! Reference source not found.**). Moreover, it can be concluded that once the pH is less than 7, the surface charge SP is positive, which means it is more attractive to negative charges, and above this pH value, The surface charge SP is negative, which means more than it is attracted to the positive charge, this explains the value of the adsorption capacity when it was at pH = 10 which is a value higher than pHzpc

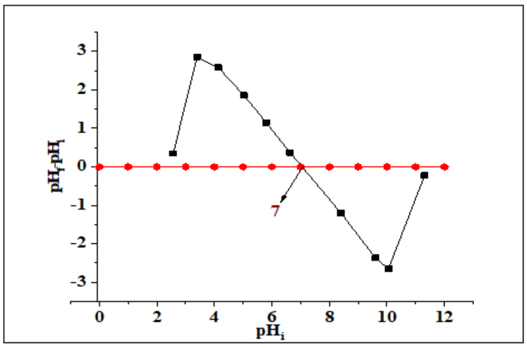


Fig. 2 pH of zero-point charge of PS

X-Ray Fluorescence (XRF)

The main elements present in this sludge are expressed as oxides (Table I), which are mainly silica, alumina and calcium oxide. The loss in ignition is high and ranges from 44 to 49%, which is a sign of an important presence of organic matter and some oxides originating from materials used in the production and processing of paper processes such as kaolin, calcite, talc, quartz and muscovite as mentioned at FTIR characterization.

Table I most content of metallic *oxides rate in SP* determined by X-ray fluorescence

Oxides	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5
%	8.77	2.76	0.1	11.5	11
Oxides	P_2O_5	SO_3	K_2O	CaO	FeO_3
%	11	24	5.08	17.4	9.9

Thermal stability

The TG and DSC analysis were shown in (Fig.3-a). two main sections present by the curve of loss of mass. The first a slight drop (< 220°C) attributed to water evaporation, the second between 220°C and 600°C which corresponds to decomposition of cellulose manly because the lignin and hemicellulose are mostly watched at transformation processes of wood to papier. the one peak appeared in DTG signal (Fig.3-b) obtained during the pyrolysis of PS at 350°C is corresponding to the conversion of cellulose.

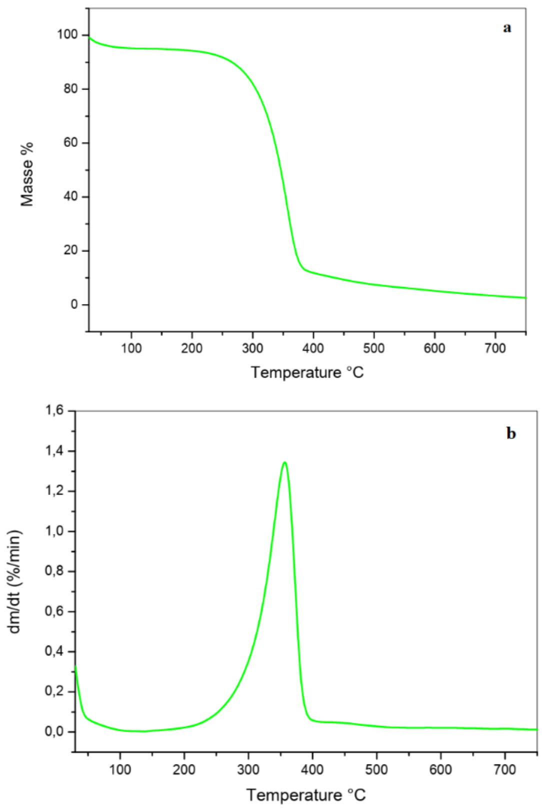


Fig.**3** (a):TG of PS, (b):DTG of PS

Adsorption study

Effect of pH

Fig. **4**showsthe adsorption capacity values incise with incising of pH slowly when pH < 7, in that rage of pH the surface of SP is charged positively as mentioned at pH_{PZC} study, and H^+ charged positive compilate the lead ions to occupied the actives sites. The second stage between pH=7 and pH= 10, there are a fast increasing of adsorption capacity intel the maximum of adsorption capacity at pH=10, in this stage the surface oh SP has a negative charge than the adsorption of positives charges like lead ions became easier. The last stage pH >10, the next round the adsorption capacity decrease faster because the most of lead ions transforms to precipitate of $Pb(OH)_2$

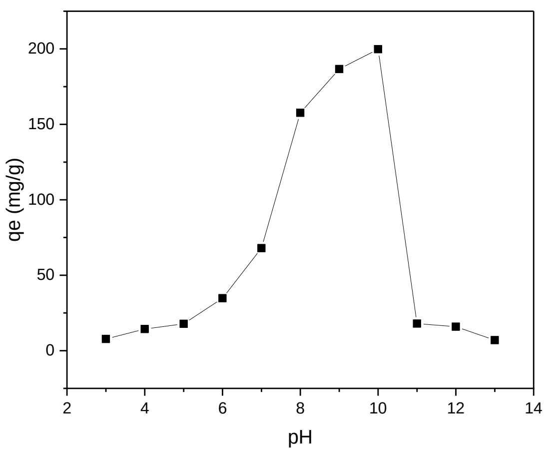


Fig. 4 Effect of pH on adsorption of Pb(II)

Contact time effect

The change in the amount adsorbed as a function of time. It can be seen that the adsorption of lead ions on the PS exhibit the equilibrium of adsorption is on the first 20 minutes of contact. The results obtained at the end of these experiments, represented on the Fig*ure5*, shows that: The evolution of the elimination lead ions by the PS in two phases: a first fast, corresponding of a large existence of easily accessible adsorption sites, after, the adsorption equilibrium where all the sites become occupied.

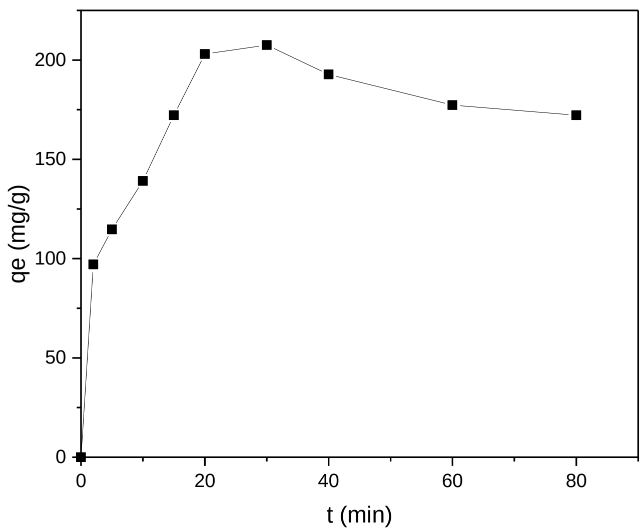


Fig. 5 : Effect of contact time at different initial concentrations.

Adsorbent dose effect

Figure 6 shows that for a dose small dose (25mg) the rate of lead ions removal is 56.25%. at this point, the surface of PS was fully saturated by lead ions. At this point, the adsorption process stops, despite the presence of an abundance of lead ions. With the addition of SP, the maximum rate value of lead ions removal is 68% at 50mg, with adsorption capacity the qe=209.34 mg.g^{-1}.After this, the increase in the amount of PS is useless, as the adsorption rate is constant, and this is due to the aggregation of PS, thus the effective area of the added paper is almost constant, no matter how much PS was added.

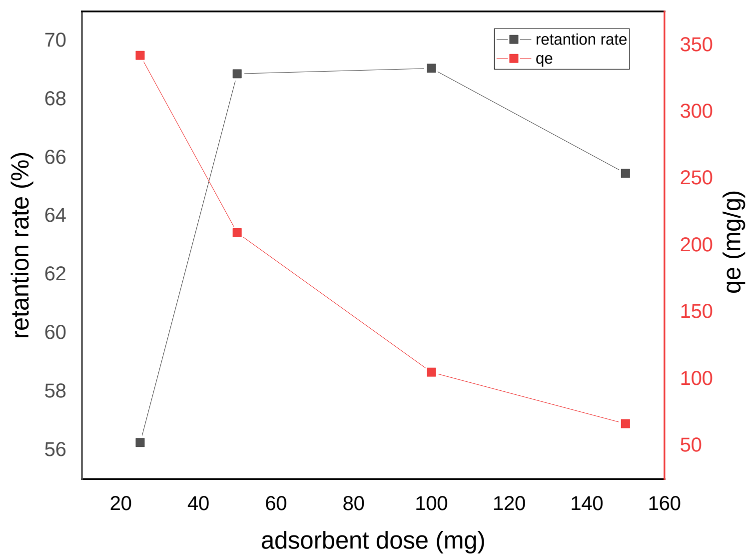


Fig. 6 Effect of adsorbent dose on adsorption of Pb onto PS

Initial Concentration effect

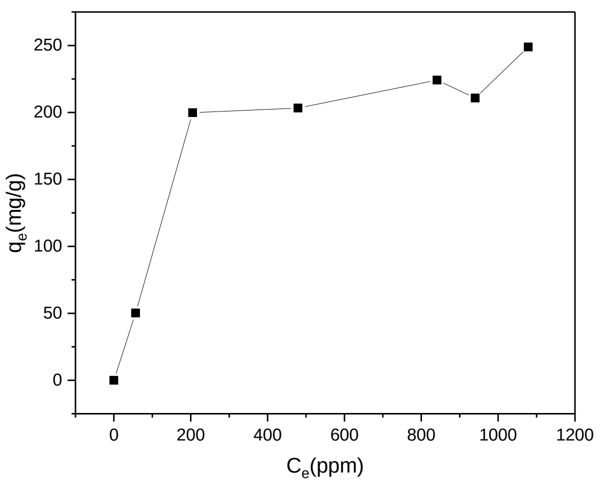
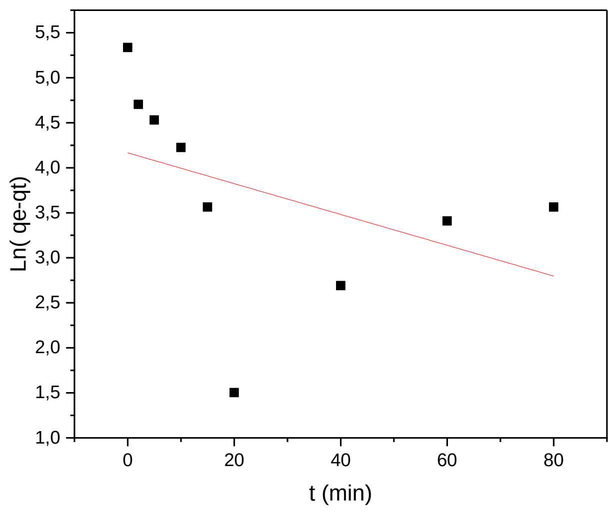


Fig. 7 Influence of the initial concentration on the lead adsorption.

From Figure 7 the adsorption capacity it continues to increase with increasing the lead concentration in solution until a plateau appears at initial concentration = 200ppm with a adsorption capacity qe=199.30mg.g^{-1} indicating dynamic equilibrium which means that the active sites at the surface of adsorbent is fully charged.

Kinetics study



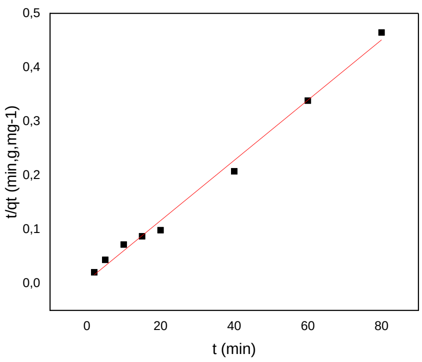


Fig 8. the plot of pseudo first order model and pseudo second order model

The results show in Table II provides a summary of the kinetic parameters attained to application of the kinetic models obtained from theFigure 8. The results displayed in the table indicate that the pseudo second order model is a better fit for the experimental data than the pseudo first order model, as evidenced by the R^2 values exceeding 0.99 for the former and only 0.17 for the latter. Additionally, the calculated value of qmax obtained using the pseudo second order model closely approximates the experimentally determined value.

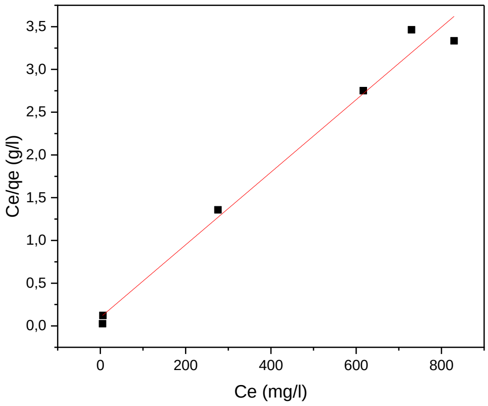
Table II Kinetic constants for Pseudo-first and pseudo-second order

Pseudo-first order			pseudo-second order		
R^2	K_1	qe	R^2	K_2	qe

0,17	-0,04	14672,3	0,993	0,056	178,57

Isotherms

The linear relationship between Ce/se and Ce for the Langmuir isotherm was revealed at (Figure 9), same for Freundlich with the linear curve between Ln(qe) and Ln(Ce). the Regression values R^2 and constants of isotherms were shown inTable III. The figure of Langmuir isotherm shows a strong linearity confirmed by correlation coefficient value R^2= 0.985. when the correlation coefficient value R^2= 0.44 for Freundlich isotherm.



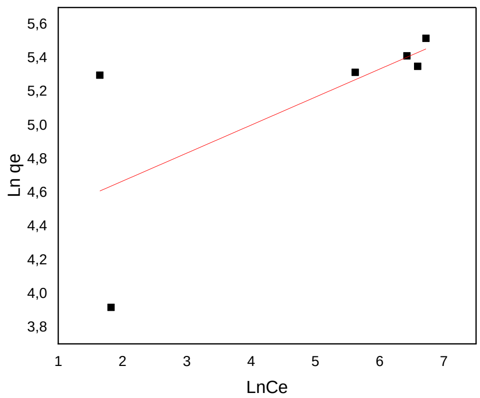


Fig 9. Langmuir isotherm and Freundlich isotherm

Table III. isotherms constants

Langmuir isotherm			Freundlich isotherm		
q_{max}	b	R^2	n	k	R^2
238,09	0,042	0.985	6,01	76,30	0.44

Thermodynamic study

The results obtained (Figure 10-a**)** show that the amount of metal ions adsorbed decreases with increasing temperature from qe=203.6 $mg.g^{-1}$ at 20°C to 137.35 $mg.g^{-1}$ at 60°C, suggesting that there is an exothermic adsorption phenomenon. The Ln(Kd) against 1/T are shown in (Figure 10-b**)**. The value of correlation coefficient R^2= 0.990, that allow to This allows inferring the values of the thermodynamic parameters values (Table IV**)**. The value of the free enthalpy ΔG for the different temperatures is less than zero, which proves that the process of binding of Pb (II) is spontaneous, also the calculated values of the enthalpy (ΔH) at different temperatures are also less than zero, which shows that this process is exothermic

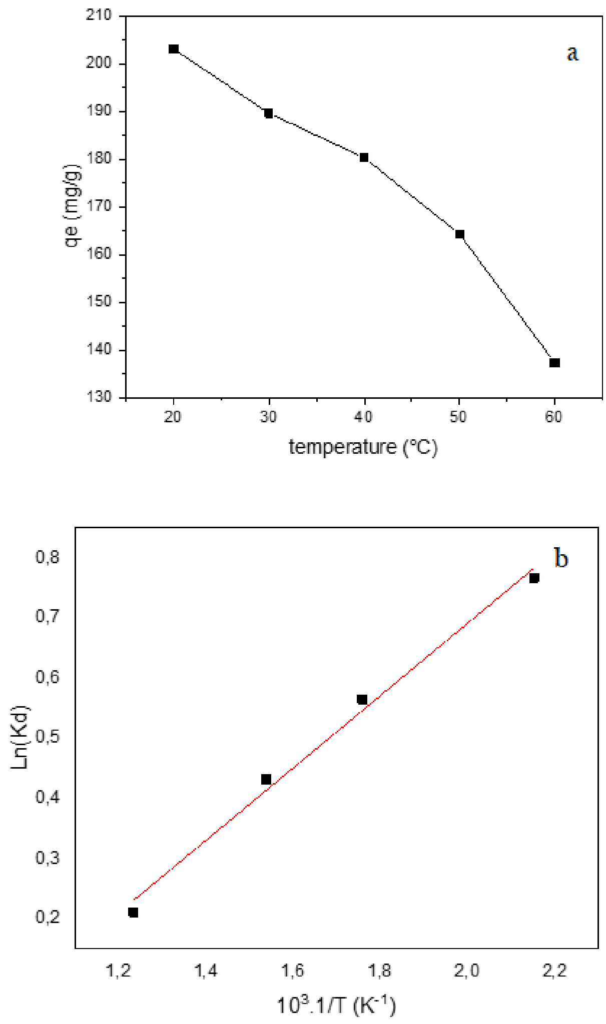


Fig. 10 a: temperature effect b: thermodynamic parameters

Table IV. thermodynamic parameters

T (°C)	ΔG(KJ/mo l)	ΔH(KJ/mo l)	ΔS(J/mo l)	R^2
20	-1,86	-23.62	-41.85	0.990
30	-1,42			
40	-1,12			
50	-0,56			

4. Conclusion

In conclusion, the findings of this study contribute to the understanding of the adsorption behavior of Pb^{2+} onto PS, particularly in terms of the effects of pH, initial concentration, adsorbent dose, contact time, and temperature.

the analysis of PS demonstrates the existence of various functional groups including carboxylic, O–H, C–H, and C=O groups, which participate in the adsorption process. The optimal conditions for maximum adsorption occur at pH=10 and an adsorbent dose of $1g.L^{-1}$

of PS. the adsorption mechanism of Pb^{2+} onto PS was well described by the pseudo-second-order kinetic model, reaching equilibrium within 20 minutes. The Langmuir model showed a high degree of fitting with an adsorption capacity (qmax) of 238.09 $mg.g^{-1}$. Moreover, the thermodynamic study revealed the spontaneous and exothermic nature of the adsorption process. These results not only expand our understanding of the adsorption of Pb^{2+} onto PS but also offer a promising approach to the treatment of wastewater containing heavy metals.

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