

Original Research Article

Removal of lead (II) from waste water by adsorption

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ABSTRACT

Keywords

Adsorption,
Lead;
Activated
Carbon;
Bentonite.

The adsorption properties of natural American bentonite and activated carbon, the removal of Pb⁺⁺ from aqueous solution were studied. The results show that the amount of adsorption of Pb⁺⁺ increases with initial metal ion concentration, contact time and solution PH but decreases with amount of adsorbent and temperatures. The adsorption process has fit pseudo-second order kinetic model. Langmuir and Freundlich adsorption isotherm models were applied to analyze adsorption data and both were found to be applicable to these adsorption process. Thermodynamic parameters e.g. ΔG° , ΔS° and ΔH° of the adsorption process was found to be endothermic. Finally it can be seen that bentonite was found to be more effective for removal of Pb⁺⁺ than activated carbon.

Introduction

As a result of rapid industrialization, toxic metals and metalloid such as cadmium, lead, chromium, mercury, arsenic and copper are released into the environment resulting in damage in ecosystems and human health. Unlike organic pollutants, heavy metals are non-biodegradable in the environment and can accumulate in living tissues particularly in human bodies causing significant physiological disorders such as damage of central nervous system and blood composition, production of energy and irreversible damage of vital organs of body. Hence the presence of heavy metals in natural or industrial wastewaters is a subject of great interest in environmental science which is one of the

most serious worldwide environmental problem (Axtell et al., 2003; Amarasinghe et al., 2007).

Among the different heavy metals, lead is one of the common and most toxic pollutants into the natural waters from various industrial activities such as metal plating, oil refining and battery manufacturing (Yurtsever and Sengil, (2008). Lead ions are taken into body via inhalation, ingestion or skin adsorption. As a result when the body is exposed to lead, it can act as a cumulative poison. Lead accumulates mainly in bones, brain, kidney and muscles and may cause many serious disorders like anaemia, kidney

disease, nervous disorder and sickness even death (Kazi et al., 2008; Afridi et al., 2006). Lead can replace calcium, which is an essential mineral for strong bones and teeth, while play important role in sympathetic actions of nerve and blood vessel for normal functioning of nervous system. The high level of lead damages cognitive development especially in children. It also acts as an enzyme inhibitor in body, e.g. replaces essential element zinc from heme enzymes (Skerfving et al., 1998; Soylac et al., 2002). In drinking water maximum allowable limit of total Pb of $50 \mu\text{gL}^{-1}$ is considered safe by the World Health Organization, whereas less than $15 \mu\text{gL}^{-1}$ is adopted by the United States Environmental Protection Agency (Raungsomboon et al., 2007). Due to toxic effects of lead and other toxic metal ions, the removal of them from water and wastewater is important in terms of protection of public health and environment (Unlu and Ersoz, 2006).

The traditional methods, for the treatment of lead and other toxic heavy metal contaminated wastewaters, include complexation, chemical oxidation or reduction, solvent extraction, chemical precipitation, reverse osmosis, ion exchange, filtration, membrane processes, evaporation and coagulation. Besides the classical wastewater treatment techniques, adsorption of heavy metals is the most promising separation and purification method because this technique has significant advantages including high efficiency in removing very low levels of heavy metals from dilute solutions, easy handling, high selectivity, lower operating cost, minimum production of chemical or biological sludge and regeneration of adsorbent (King et al., 2007).

The objectives of this study was to investigate the adsorption potential of activated carbon and bentonite for the removal of Pb(II) ions from wastewater. The effect of several parameters such as contact time, initial concentration, pH value of the solution, adsorbent dose, volume and temperature were studied. The adsorption mechanisms of Pb(II) ions onto activated carbon and bentonite evaluated in terms of thermodynamic and kinetics. The adsorption isotherm were described by using Langmuir and Freundlich models.

Materials and Methods

Experimental

All chemicals used in this present work were either of analytical reagent or laboratory reagent grade and were used as received. Lead Nitrate supplied by BDH chemicals Ltd. Distilled water was used in all preparations. Lead nitrate and deionised water were used to prepare synthetic chromium containing wastewater. Powder activated carbon (PAC) produced from natural origin by ADWIC was used as adsorbent as well as American Wyoming calcium bentonite used in Saudi Arabia Company for Refractory's.

Powder activated carbon (PAC) and bentonite (clay) were supplied from ADWIC and Saudi arabia Company for Refractory's, respectively. Elemental analysis for bentonite was evaluated using X-ray fluorescence (Philips PW 1390) as shown in (Table-1).

Magnetic hot plate stirrer was used to stir the heavy metal ions solutions with adsorbents (activated carbon or bentonite). A definite volume of heavy metal ions

ELEMENTAL ANALYSIS FOR BENTONITE WAS EVALUATED USING X-RAY FLUORESCENCE (PHILIPS PW 1390)			
Oxides (wt. %)	Bentonite	Oxides (wt. %)	Bentonite
SiO ₂ (%)	55.89	Na ₂ O (%)	0.34
Al ₂ O ₃ (%)	16.03	TiO ₂ (%)	0.15
Fe ₂ O ₃ (%)	4.19	P ₂ O ₅ (%)	0.086
CaO (%)	3.25	SO ₃ (%)	0.23
MgO (%)	2.75	LOI (%)	17.2
K ₂ O (%)	0.49	–	–

Fig.1 Pseudo-first order kinetic plots for the adsorption of different initial concentrations: 50, 100 and 200 ppm Pb²⁺ ions onto different adsorbents doses of activated carbon: a) 0.1 g/250 mL and b) 0.3 g/250 mL, (pH: 5.5; agitation speed: 200 rpm; temperature: 25°C)

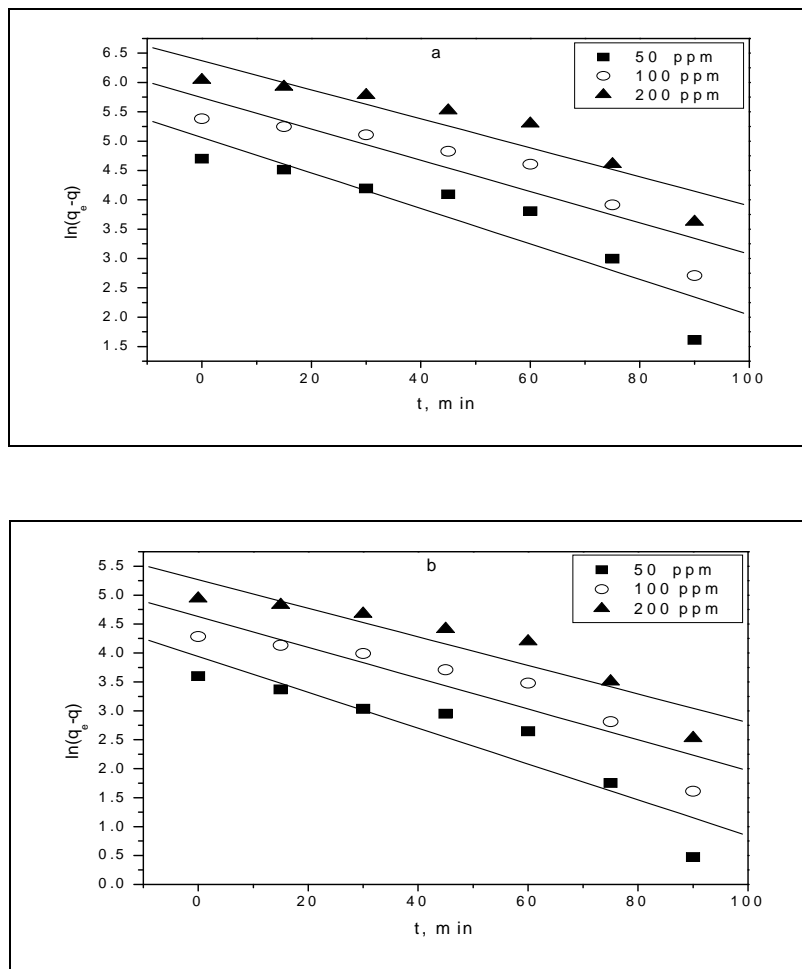


Fig.2 Pseudo-first order kinetic plots for the adsorption of different initial concentrations: 50, 100 and 200 ppm Pb^{2+} ions onto different adsorbents doses of bentonite: a) 0.1 g/250 mL and b) 0.3 g/250 mL , (pH: 5.5; agitation speed: 200 rpm; temperature: 25°C)

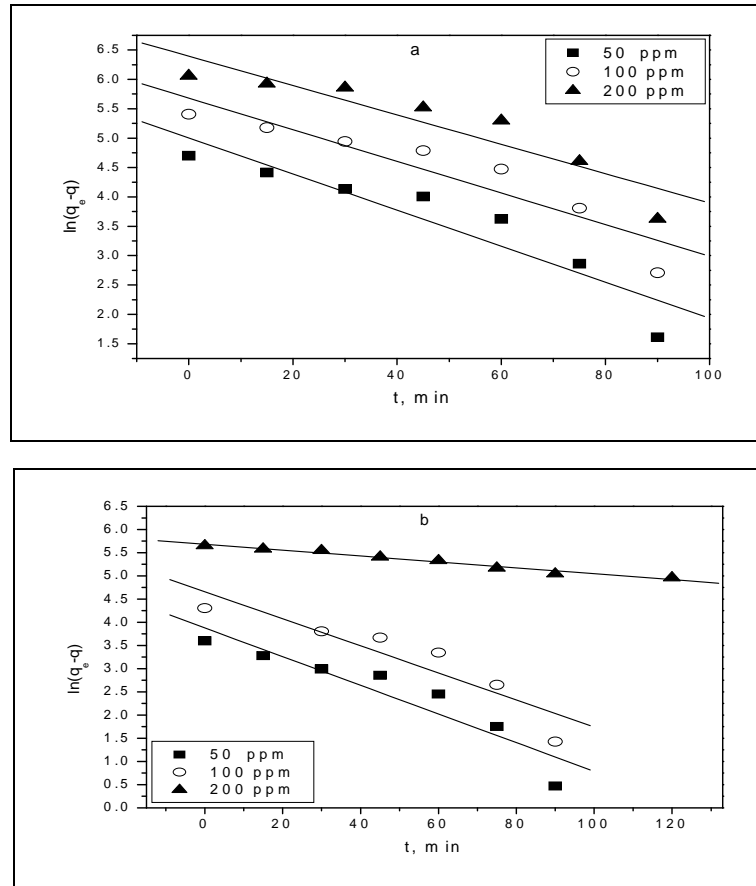
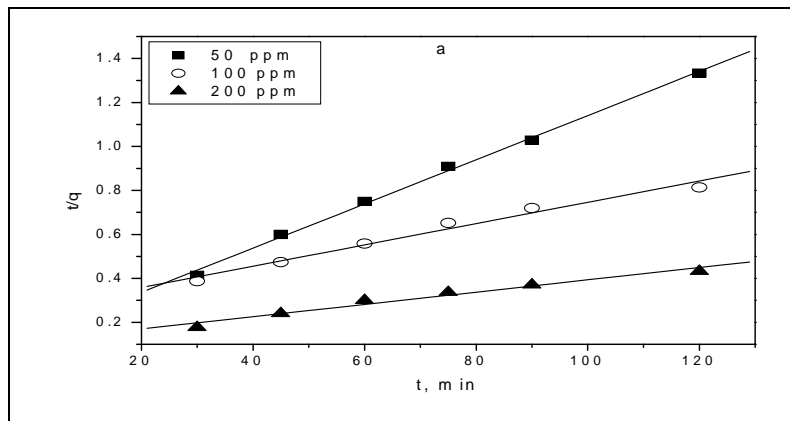


Fig.3 Pseudo-second order kinetic plots for the adsorption of different initial concentrations: 50, 100 and 200 ppm Pb^{2+} ions onto different adsorbents doses of activated carbon: a) 0.1 g/250 mL and b) 0.3 g/250 mL , (pH: 5.5; agitation speed: 200 rpm; temperature: 25°C)



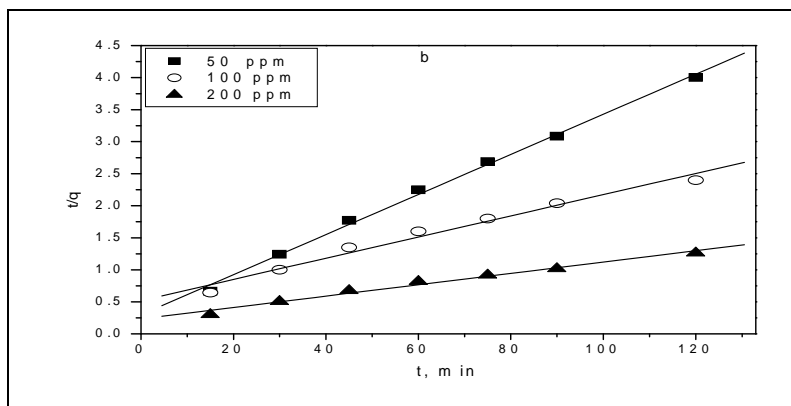


Fig.4 Pseudo-second order kinetic plots for the adsorption of different initial concentrations: 50, 100 and 200 ppm Pb^{2+} ions onto different adsorbents doses of bentonite: a) 0.1 g/250 mL and b) 0.3 g/250 mL, (pH: 5.5; agitation speed: 200 rpm; temperature: 25°C)

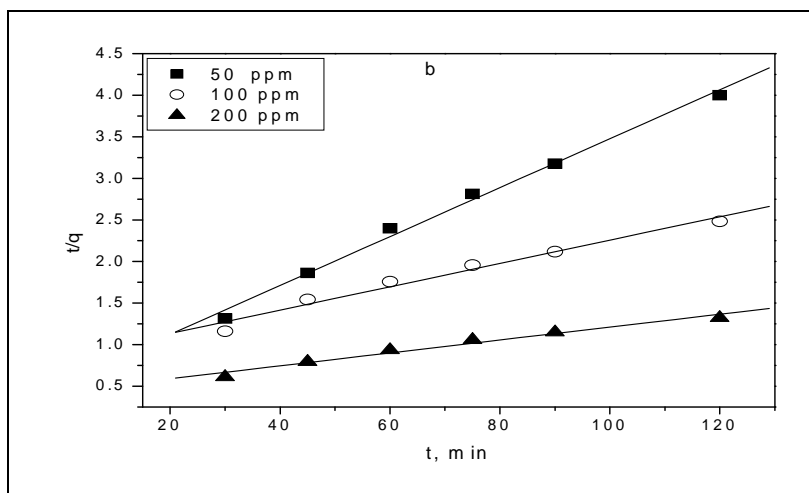
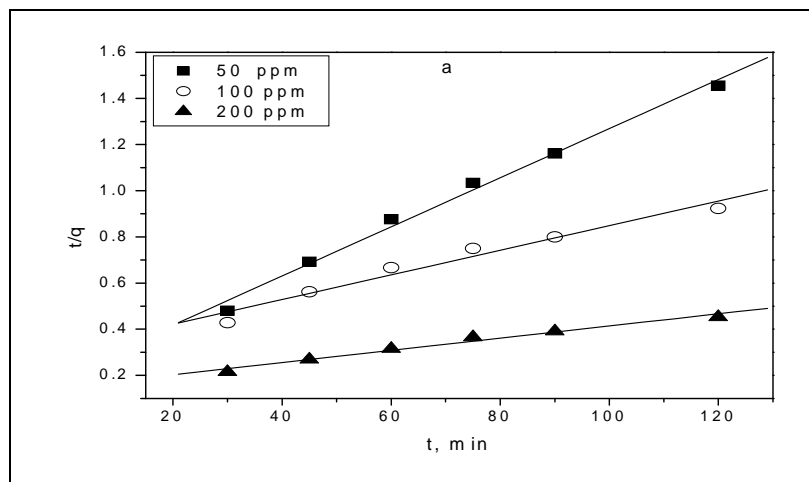


Table.1 The adsorption kinetics model rate constants for adsorption of Pb²⁺ ions onto activated carbon and bentonite at various concentrations and constant temperature 25 °C

Adsorbent (0.1 g)	C _o (mg/L)	q _{e, exp.} (mg/g)	Lagergren first order			Pseudo-second order		
			K ₁ (min ⁻¹)	q _{1, theo.} (mg/g)	R ²	k ₂ (gmg ⁻¹ min ⁻¹)	q _{2, theo.} (mg/g)	R ²
Activated Carbon	50	110	3.0x10 ⁻²	158	0.918	4.5x10 ⁻⁴	108	0.991
	100	217	2.6x10 ⁻²	311	0.913	7.1x10 ⁻⁵	215	0.995
	200	420	2.4x10 ⁻²	584	0.924	3.6x10 ⁻⁵	416	0.996
Bentonite	50	110	3.1x10 ⁻²	148	0.932	1.1x10 ⁻³	108	0.998
	100	222	2.6x10 ⁻²	293	0.933	1.9x10 ⁻⁴	220	0.995
	200	427	2.5x10 ⁻²	559	0.925	1.3x10 ⁻⁴	420	0.996

Adsorbent (0.3 g)	C _o (mg/L)	q _{e exp.} (mg/g)	Lagergren first order			Pseudo-second order		
			K ₁ (min ⁻¹)	q _{1, theo.} (mg/g)	R ²	k ₂ (gmg ⁻¹ min ⁻¹)	q _{2, theo.} (mg/g)	R ²
Activated Carbon	50	37	3.1x10 ⁻²	52	0.921	2.6x10 ⁻³	36	0.995
	100	73	2.7x10 ⁻²	103	0.919	3.2x10 ⁻⁴	74	0.996
	200	140	2.5x10 ⁻²	184	0.925	2.7x10 ⁻⁴	138	0.996
Bentonite	50	36	3.0x10 ⁻²	48	0.936	2.0x10 ⁻³	35	0.998
	100	74	2.9x10 ⁻²	105	0.920	3.7x10 ⁻⁴	72	0.996
	200	285	6.3x10 ⁻²	293	0.987	2.9x10 ⁻⁴	283	0.998

Fig.5 Effect of contact time (min) on % removal of Pb^{2+} ions for: a) 50 ppm and b) 100 ppm, in the presence of different amounts of activated carbon (temp. = 25°C, pH = 5.5 and equilibrium time = 2 h)

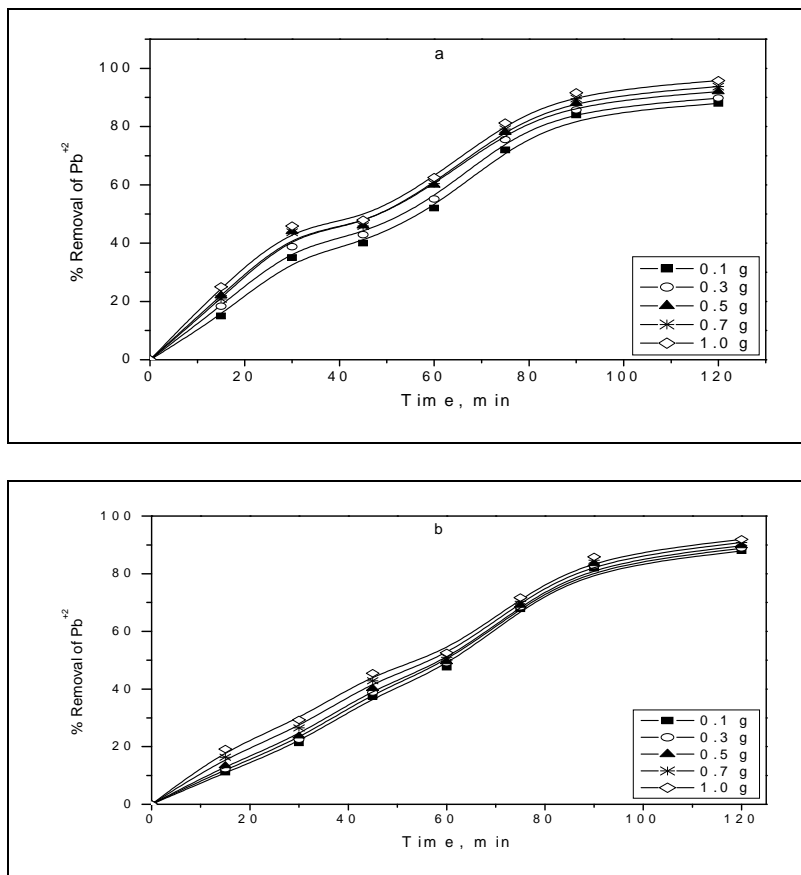
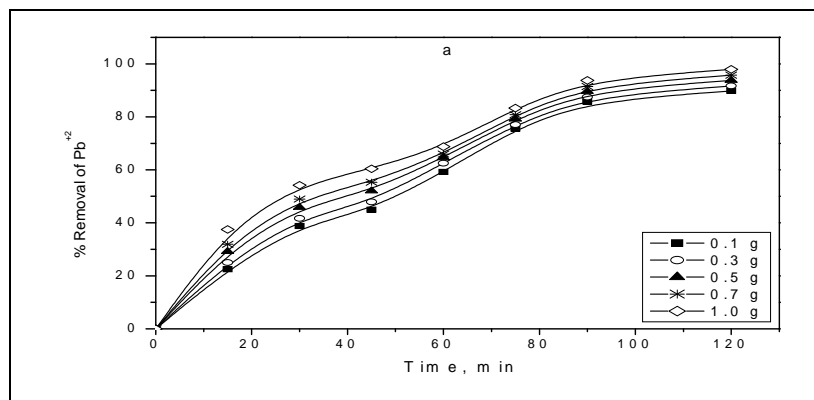


Fig.6 Effect of contact time (min) on % removal of Pb^{2+} ions for: a) 50 ppm and b) 100 ppm, in the presence of different amounts of bentonite (temp. = 25°C, pH = 5.5 and equilibrium time = 2 h)



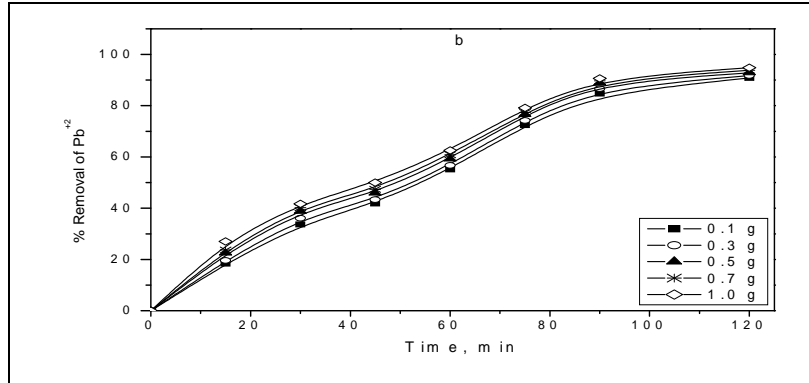


Fig.7 Effect of contact time on adsorbed amount of Pb^{2+} for different concentrations: a) 50 ppm and b) 100 ppm, in the presence of different amounts of activated carbon (temp. = 25°C, pH = 5.5 and equilibrium time = 2 h)

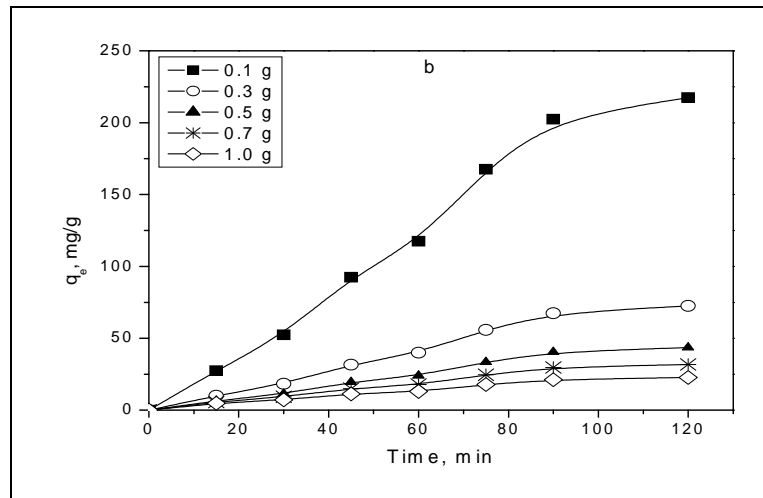
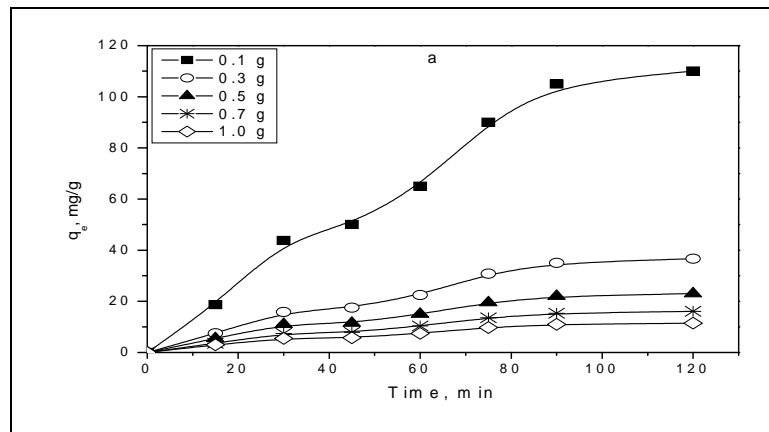


Fig.8 Effect of contact time on adsorbed amount of Pb^{2+} for different concentrations: a) 50 ppm, b) 100 ppm, in the presence of different amounts of bentonite (temp. = 25°C, pH = 5.5 and equilibrium time = 2 h)

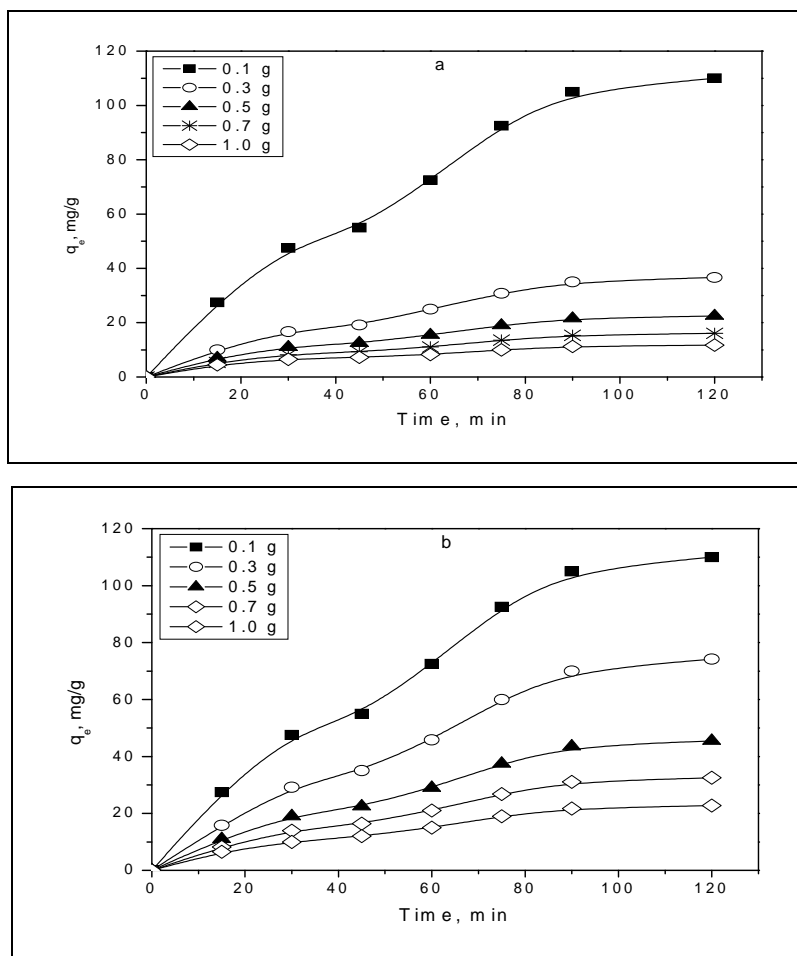


Fig.9 The effect of variant activated carbon adsorbent doses (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 mL) on % removal for different Pb^{2+} ions initial concentrations solution at 25°C

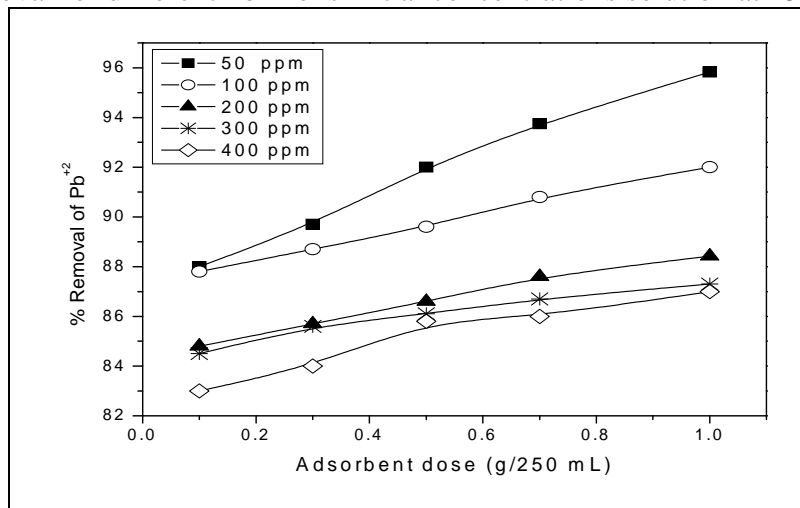


Fig.10 The effect of variant bentonite adsorbent doses (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 mL) on % removal for different Pb^{2+} ions initial concentrations solution at 25°C

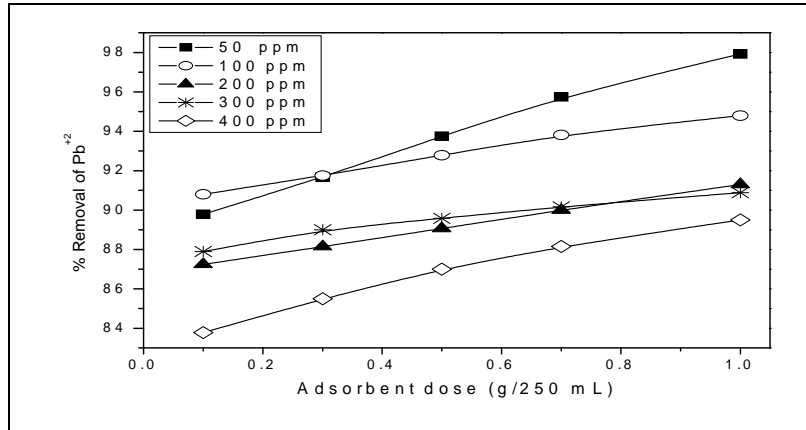


Fig.11 The effect of variant activated carbon adsorbent doses (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 mL) on the quantity adsorbed for different Pb^{2+} ions initial concentrations solutions at 25°C

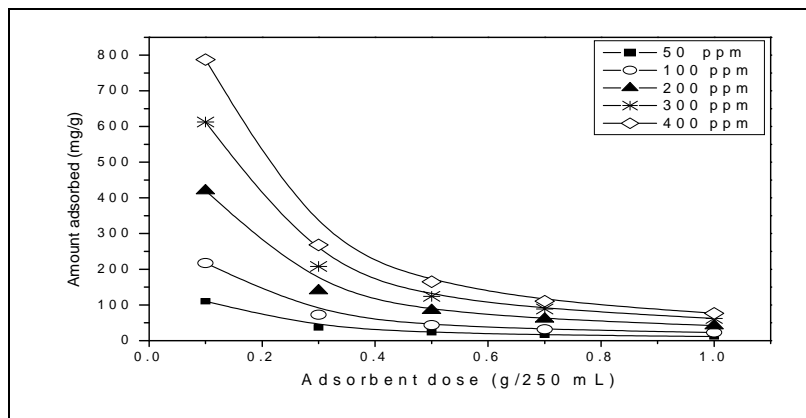


Fig.12 The effect of variant bentonite adsorbent doses (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 mL) on the quantity adsorbed for different Pb^{2+} ions initial concentrations solutions at 25°C

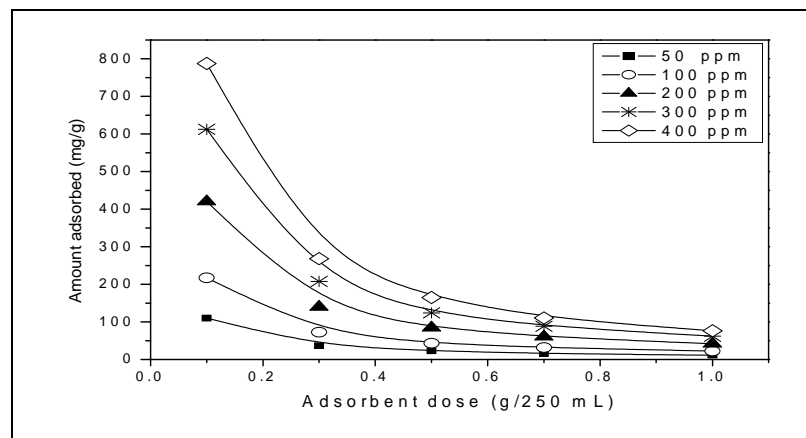


Fig.13 The effect of initial concentrations (namely 50, 100, 200 and 300 mg/L) on % removal of Pb^{2+} ions in the presence of different amounts of activated carbon (temp. = 25°C, pH = 5.5 and equilibrium time = 2 h)

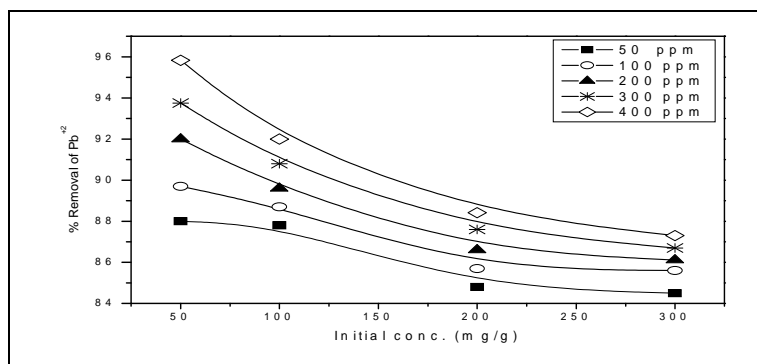


Fig.14 The effect of initial concentrations (namely 50, 100, 200 and 300 mg/L) on % removal of Pb^{2+} ions in the presence of different amounts of bentonite (temp. = 25°C, pH = 5.5 and equilibrium time = 2 h)

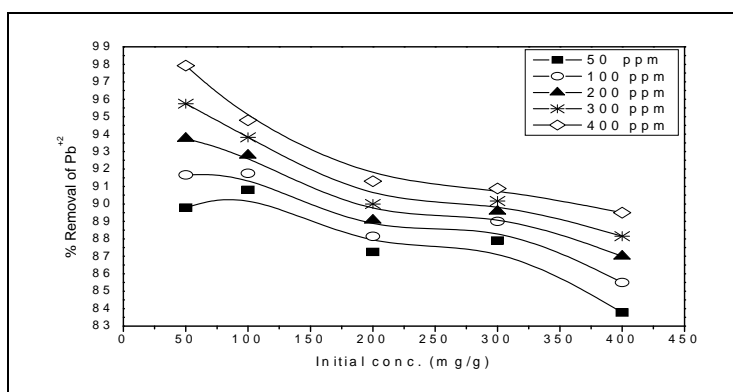


Fig.15 The effect of initial concentrations (namely 50, 100, 200 and 300 mg/L) on quantity adsorbed of Pb^{2+} ions in the presence of different amounts of activated carbon (temp. = 25°C, pH = 5.5 and equilibrium time = 2 h).

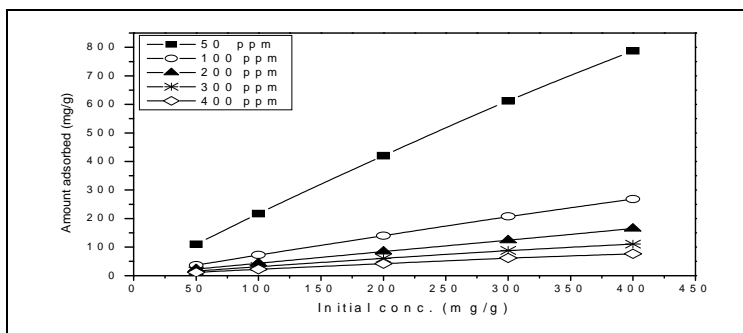


Fig.16 The effect of initial concentrations (namely 50, 100, 200 and 300 mg/L) on quantity adsorbed of Pb^{2+} ions in the presence of different amounts of bentonite (temp. = 25°C, pH = 5.5 and equilibrium time = 2 h)

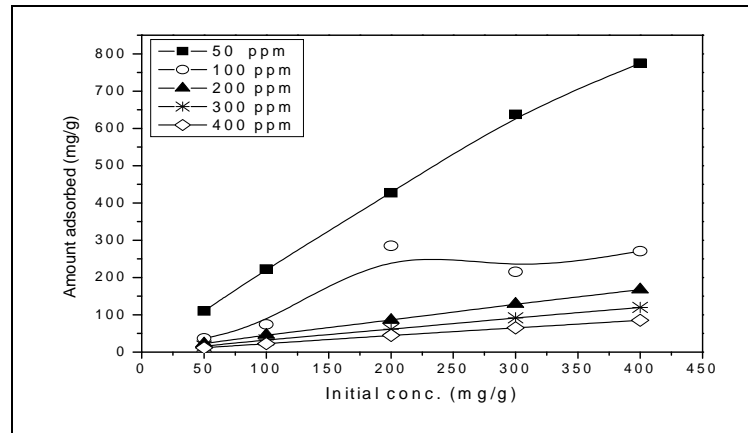


Fig.17 Effect of pH value for the adsorption of Pb^{2+} ions onto activated carbon (conditions; Pb^{2+} ions initial concentration: 100 mg/L; adsorbents dose: 0.5 g/250 mL; agitation speed: 200 rpm; contact time: 2 h) at 25°C

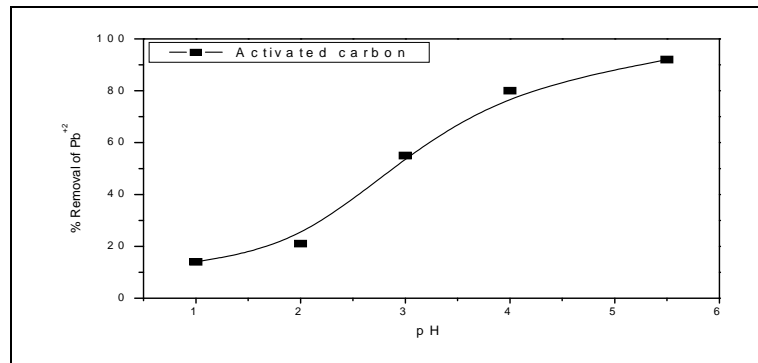


Fig.18 Effect of pH value for the adsorption of Pb^{2+} ions onto bentonite (conditions; Pb^{2+} ions initial concentration: 100 mg/L; adsorbents dose: 0.5 g/250 mL; agitation speed: 200 rpm; contact time: 2 h) at 25°C

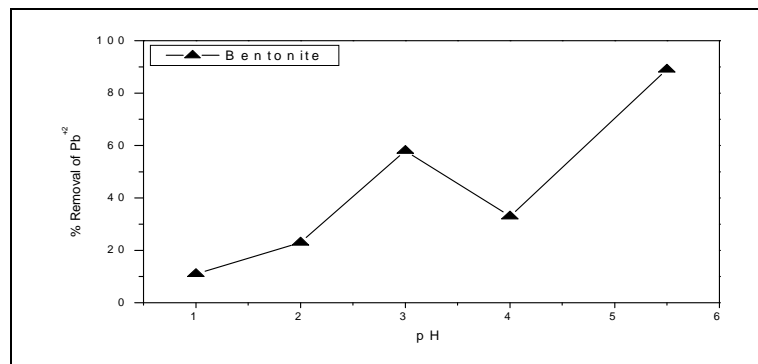


Fig.19 Langmuir adsorption isotherm for Pb^{2+} ions adsorption onto different amounts of activated carbon at constant temperature 25°C and contact time 2 h

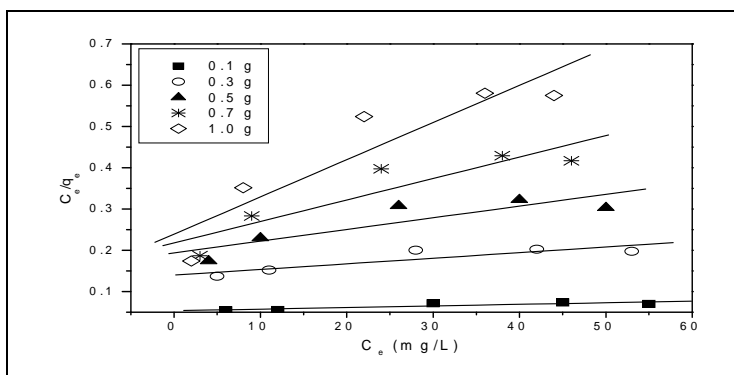


Fig.20 Langmuir adsorption isotherm for Pb^{2+} ions adsorption onto different amounts of bentonite at constant temperature 25°C and contact time 2 h.

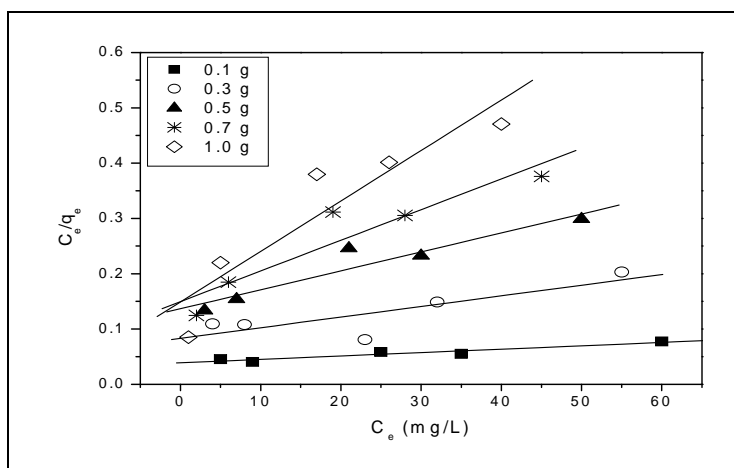


Fig.21 Freundlich adsorption isotherm for Pb^{2+} ions adsorption onto different amounts of activated carbon at constant temperature 25°C and contact time 2 h.

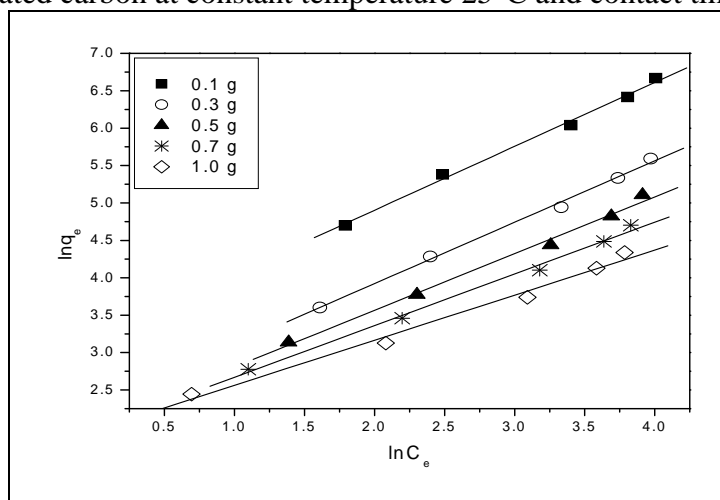


Fig.22 Freundlich adsorption isotherm for Pb^{2+} ions adsorption onto different amounts of bentonite at constant temperature $25^{\circ}C$ and contact time 2 h

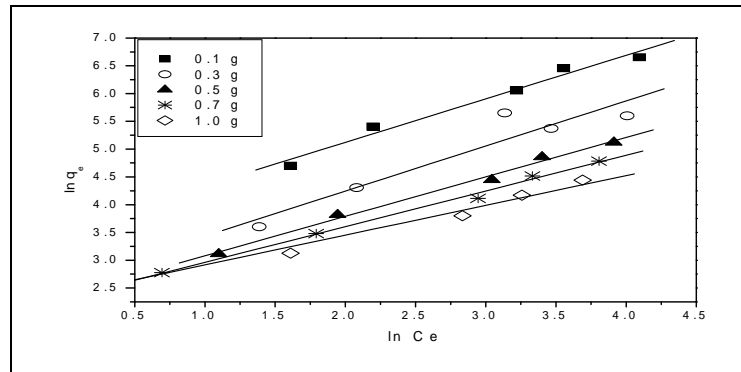


Fig.23 Equilibrium isotherm of Pb^{2+} ions adsorption using different amounts of activated carbon at constant temperature $25^{\circ}C$ and contact time 2 h.

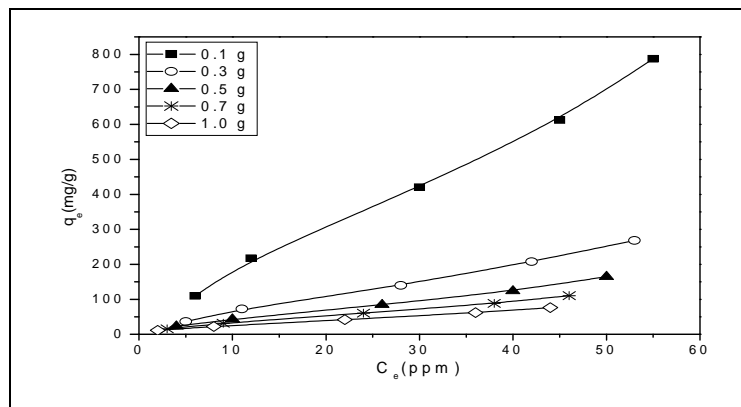


Fig.24 Equilibrium isotherm of Pb^{2+} ions adsorption using different amounts of bentonite at constant temperature $25^{\circ}C$ and contact time 2 h

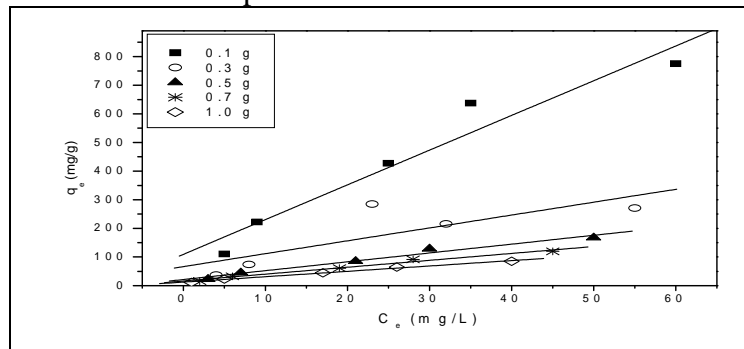


Table.2 Langmuir and Freundlich isotherm for the adsorption of Pb²⁺ ions onto different doses of activated carbon and bentonite at constant temperature (25°C)

Adsorbent (0.1 g/250 mL)	Langmuir Isotherm constants			Freundlich Isotherm constants		
	q _{max} (mg/g)	b (L/mol)	R ²	K _F (mg/g)	n	R ²
Activated Carbon	48	2.9x10 ⁻²	0.968	24.4	1.170	0.995
Bentonite	31	1.7x10 ⁻²	0.965	35	1.231	0.990
Adsorbent (0.3 g/250 mL)	Langmuir Isotherm constants			Freundlich Isotherm constants		
	q _{max} (mg/g)	b (L/mol)	R ²	K _F (mg/g)	n	R ²
Activated Carbon	85	9.7x10 ⁻³	0.889	9.795	1.219	0.996
Bentonite	73	2.3x10 ⁻²	0.785	13.730	1.231	0.991
Adsorbent (0.5 g/250 mL)	Langmuir Isotherm constants			Freundlich Isotherm constants		
	q _{max} (mg/g)	b (L/mol)	R ²	K _F (mg/g)	n	R ²
Activated Carbon	99	1.5x10 ⁻²	0.880	7.74	1.318	0.993
Bentonite	85	2.5x10 ⁻²	0.852	10.68	1.408	0.992
Adsorbent (0.7 g/250 mL)	Langmuir Isotherm constants			Freundlich Isotherm constants		
	q _{max} (mg/g)	b (L/mol)	R ²	K _F (mg/g)	n	R ²
Activated Carbon	191	2.3x10 ⁻²	0.883	7.218	1.446	0.997
Bentonite	243	2.7x10 ⁻²	0.881	10.17	1.556	0.995
Adsorbent (1 g/250 mL)	Langmuir Isotherm constants			Freundlich Isotherm constants		
	q _{max} (mg/g)	b (L/mol)	R ²	K _F (mg/g)	n	R ²
Activated Carbon	111	3.7x10 ⁻²	0.883	7.08	1.424	0.990
Bentonite	110	6.2x10 ⁻²	0.886	10.866	1.516	0.990

Fig.25 A plot of $\ln K_c$ versus $1/T$ for Pb^{2+} ions adsorption onto activated carbon for different initial concentrations at constant adsorbents dose: 0.5 g/250 mL

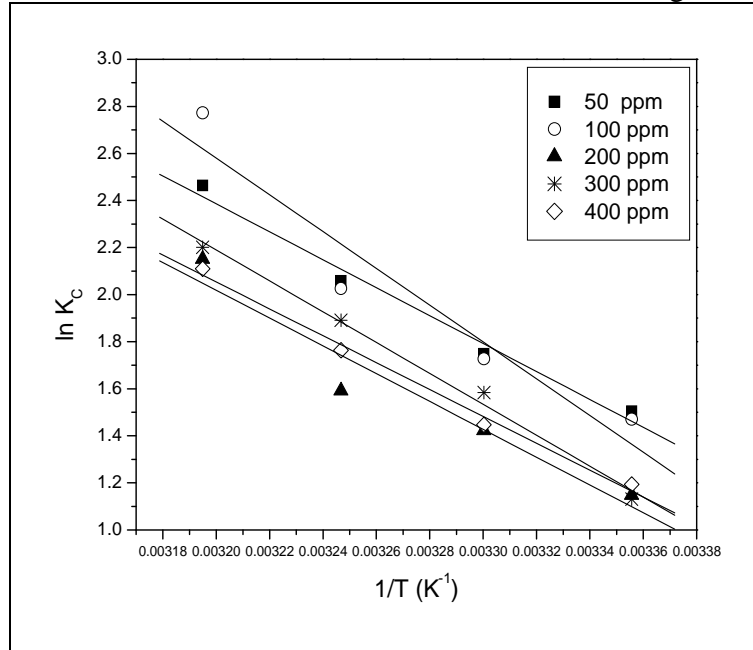


Fig.26 A plot of $\ln K_c$ versus $1/T$ for Pb^{2+} ions adsorption onto bentonite for different initial concentrations at constant adsorbents dose: 0.5 g/250 mL.

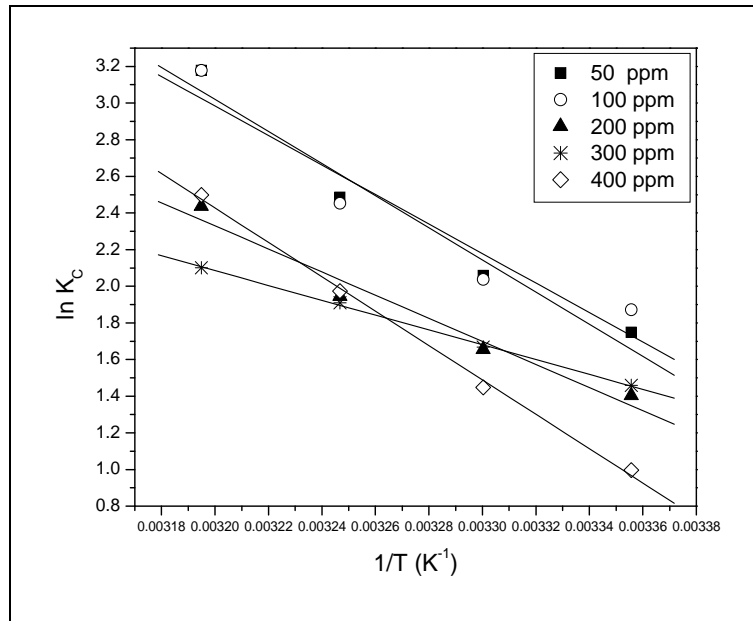


Table.3 Thermodynamic parameters for different concentrations of Pb²⁺ ions onto activated carbon and bentonite

Adsorbent	C _o (mg/L)	ΔH° (kj mol ⁻¹)	ΔS° (j mol ⁻¹ K ⁻¹)	ΔG°(kj mol ⁻¹)			
				25°C	30°C	35°C	40°C
Activated carbon	50	49	177	- 3.6	- 4.3	- 5.1	- 6.1
Bentonite		72	258	- 3.9	- 5.3	- 6.5	- 7.8
Adsorbent	C _o (mg/L)	ΔH° (kj mol ⁻¹)	ΔS° (j mol ⁻¹ K ⁻¹)	ΔG°(kj mol ⁻¹)			
Activated carbon	100	65	229	- 3.3	- 4.4	- 5.6	- 6.7
Bentonite		67	239	- 4.3	- 5.5	- 6.7	- 7.9
Adsorbent	C _o (mg/L)	ΔH° (kj mol ⁻¹)	ΔS° (j mol ⁻¹ K ⁻¹)	ΔG°(kj mol ⁻¹)			
Activated carbon	200	50	174	- 2.7	- 3.6	- 4.5	- 5.5
Bentonite		52	187	- 3.3	- 4.3	- 5.2	- 6.3
Adsorbent	C _o (mg/L)	ΔH° (kj mol ⁻¹)	ΔS° (j mol ⁻¹ K ⁻¹)	ΔG°(kj mol ⁻¹)			
Activated carbon	300	55	192	- 2.9	- 3.6	- 4.5	- 5.3
Bentonite		34	125	- 3.6	- 4.2	- 4.9	- 5.5
Adsorbent	C _o (mg/L)	ΔH° (kj mol ⁻¹)	ΔS° (j mol ⁻¹ K ⁻¹)	ΔG°(kj mol ⁻¹)			
Activated carbon	400	47	169	- 2.9	- 3.7	- 4.6	- 5.4
Bentonite		78	269	- 2.1	- 3.5	- 4.9	- 6.2

solution with a known initial ions concentration was stirred with a definite amount of adsorbent for certain time at fixed temperature and agitation rate. The pH values of the solutions were measured by digital pH meter (Model ì pH system-361, India). The metal ion concentration was measured using atomic-absorption spectrophotometer, AAS, (Model, AA55; Varian Inc., USA).

Experimental procedures: Lead Nitrate and redistilled water were used to prepare

a stock solution with a concentration of 1000 ppm lead which was diluted for preparation of test solutions. Several solutions with different initial concentrations of lead nitrate (50, 100, 200, 300 and 400 ppm) were prepared. The required pH was adjusted by drop wise addition of 0.1 N NaOH depending on the acidity of the sample. All experiments were carried out at 25 °C by adding different amounts of adsorbents (0.1, 0.3, 0.5, 0.7 and 1.0 g) to different concentrations of 250 ml of heavy metal

ions solution. The agitation rate for all experiments was 200 rpm and the residence time was (0, 15, 30, 45, 60, 75, 90 and 120 min)..

1 mL of sample was taken from reaction solution and diluted to 10 ml by redistilled water; adsorbents were then separated from the solution by using filter paper (Whatman No. 40) and the residual Pb^{+2} ions concentration in the solution was then determined by atomic-absorption spectrophotometer. The effects of several parameters, such as contact time, initial concentration, adsorbent dose, pH and temperature on the adsorption of Pd(II) ions onto activated carbon and bentonite were studied.

Adsorption kinetics

The kinetics study for the adsorption of Pb^{2+} was completed in 2 h for the concentrations (50, 100 and 200 mg/L Pb^{2+} ions onto (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 ml) doses of activated carbon and bentonite at 25°C.

Two kinetic models were considered to investigate the mechanism of lead adsorption, as follows:

Lagergren proposed a pseudo-first order kinetic model, the integral form of the model is:

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (1)$$

where q is the amount of lead sorbed (mg/g) at time t (min), q_e is the amount of lead sorbed at equilibrium (mg/g), K_1 is the equilibrium rate constant of pseudo-first order adsorption (min^{-1}). This model was successfully applied to describe the kinetics of many adsorption systems.

The adsorption kinetics may also be

described by a pseudo-second order reaction. The linearized-integral form the model is:

$$t/q = t/q_e + 1/k_2 q_e^2 \quad (2)$$

where K_2 is the pseudo-second order rate constant of adsorption.

The applicability of the above two models can be examined by each linear plot of $\ln(q_e - q)$ vs. t , and (t/q) vs. t , respectively and are represented in Figs. (1,2) and (3,4), respectively. To quantify the applicability of each model, the correlation coefficient, R^2 , was calculated from these plots. The linearity of these plots indicates the applicability of the two models. However, the correlation, R^2 , showed that the pseudo-second order model, fits better the experimental data ($R^2 > 0.990$) than the pseudo-first order model (R^2 in the range of 0.9108 – 0.986), the kinetic parameters calculated are shown in Table 10.

Effect of contact time

The effect of contact time on the adsorption of Pb(II) ions onto activated carbon and bentonite was performed by contacting of (50, 100, 200, 300 and 400 mg/L) of Pb(II) concentration at initial pH 5.5 onto (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 mL) of adsorbent dose. The results are depicted in Figs. (5,6). The Pb(II) adsorption rate is high at the beginning of the adsorption because the adsorption sites are open and Pb(II) interacts easily with these sites. A larger amount of Pb(II) was removed in the first 1 h of contact time, and after that Pb(II) increased slowly till equilibrium time (2 h). The relation between the amount of adsorbed Pb(II) ions per gram of adsorbent and contact time in presence of different amounts of both activated carbon and bentonite is

illustrated in Figs. (1). It can be seen that, q_e increased rapidly with increasing time till the maximum adsorption.

Effect of adsorbent dose

The effect of adsorbent dosage (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 mL) for both activated carbon and bentonite on % removal of (50, 100, 200 and 400 mg/L) of Pb(II) ions concentrations at 25°C is shown in Figs. (9,10). It is apparent that by increasing the dosage, % removal increased till reached maximum at 1.0 g dosage of both activated carbon and bentonite. The increase in percentage of removal as dosage was increased due to the increased in the surface of both adsorbents. A higher adsorbent dosage also reflects a greater number of available adsorption sites, therefore, more lead ions were able to be adsorbed. On the other hand, the adsorption capacity decreased with the increase in adsorbent dosage for both adsorbent Figs. (Vijayaraghavan et al., 2006; Shukla et al., 2002). It is important to note that the concentration of lead was fixed while the adsorbent dosage was increased. Therefore, as the dosage increased, the ratio of number of adsorption sites to the number of heavy metal ions would increase and there would be plenty of unabsorbed adsorption sites. Another possible reason could be due to the particle aggregation, which would lead to a decrease in total surface area of the adsorbent (Shukla et al., 2002).

Effect of initial lead(II) ions concentration

Figs. (13,14) show the effect of varying initial concentration of lead(II) ions from 50 to 400 mg/L on the adsorption under the optimized conditions of pH 5.5 at 25°C

and (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 mL) of both activated carbon and bentonite. It can be seen from the figures that, with increased Pb(II) initial concentration, there was decreases in % removal of lead(II) for both adsorbent. However, amount of metal adsorbed per unit weight of adsorbent, q , is higher at high concentration as shown in Figs. (15,16) for both activated carbon and bentonite. According to (Balasubramaniam et al., 2009), the adsorption capacity and percentage of removal are equally important in adsorption experiments because both factors usually take part in deciding the adsorption performance of given adsorbent.

Effect of pH on the uptake of Pb²⁺

The influence of pH on the adsorption of Pb(II) onto activated carbon and bentonite examined in the pH range 1-5.5, initial concentration of Pb(II) 100 mg/L and adsorbent dose 0.5 g/250 mL for both selected adsorbents at 25°C. Figs.(17,18) shown that for activated carbon, % removal of lead(II) increased with an increase in pH of the solution from 1-5.5. For bentonite, it can be seen that, there is a decrease for pH 4. This decrease in the adsorption of Pb(II) probably reflects a reduction in the quantity of negative surface charges on the clay. At low pH, the silica attracts positively charged adsorbate ions by coulombic forces. This negative charge density on the surface of the adsorbent decrease as the pH increases and this leads to low adsorption of Pb(II) from wastewater at high pH. It is therefore evident, that the presence of a negative charge on the silica surface sites of the adsorbent over the pH range investigated is the main reason for Pb(II) adsorption.

Adsorption isotherm

The equilibrium adsorption isotherms are one of the promising data to understand the mechanism of the adsorption. Various isotherm equation are well known and two different isotherms are selected in this study, which are the Langmuir and Freundlich isotherms.

The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has found successful applications in many adsorption processes of monolayer adsorption. The linearized Langmuir isotherm equation is represented by the following (Balasubramaniam et al., 2009).

$$C_e/q_e = 1/(q_{max}b) + (1/q_{max}) C_e \quad (7)$$

Where q_{max} is the maximum metal ions uptake per unit mass of adsorbent (mg/g), which is related to the adsorption capacity and b is Langmuir constant (L/mol) which is exponentially proportional to the heat of adsorption and related to the adsorption intensity. Therefore, a plot of C_e/q_e versus C_e for the adsorption of lead(II) ions onto activated carbon and bentonite gives a straight line of the slope $1/q_{max}$ and intercept $1/(q_{max} b)$ as shown in Figs. (19,20).

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The linearized form of the Freundlich isotherm equation is:

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (5)$$

where the Freundlich constants K_F and n , which respectively indicating the adsorption capacity and the adsorption

intensity, were calculated from the intercept and slope of the plot of $\ln q_e$ versus $\ln C_e$ for the adsorption of lead(II) ions onto activated carbon and bentonite as shown in Figs. (21,22).

The Langmuir and Freundlich parameters for the adsorption of (50, 100 and 200 mg/L) initial concentrations of lead(II) on (0.1, 0.3, 0.5, 0.7 and 1.0 g/250 mL) for both activated carbon and bentonite at 25°C are listed in Table 11. In other words, the Freundlich isotherm model fits very well than that of Langmuir isotherm model when the R^2 values are compared in Table 11 (R^2 values of Freundlich plot > 0.99 was close to unity, indicating isotherm data fitted well to Freundlich model). The Freundlich constant n is the measure of the deviation from linearity of the adsorption. If a value for n is below to unity, this implies that adsorption process is govern by a chemical mechanism, but a value for n is above to unity, adsorption is favourable a physical process. The values of n at equilibrium are between (1.70-1.87), representing favourable adsorption at studied temperatures and therefore this would seem to suggest that a physical mechanism, which is referred the adsorption bond weak and conducted with Van der Waales forces.

Plots of (q_e) versus (C_e) are represented in Figs. (4.117-4.118), from figures (q_e) increased by increasing (C_e) suggesting a very strong surface interaction between the metal ions Pb^{2+} and both adsorbents (activated carbon and bentonite).

Thermodynamic parameters

The determination of thermodynamic parameters has a great importance to evaluate spontaneity and heat change for the adsorption reactions. Thermodynamic parameters such as free energy (ΔG°),

enthalpy (ΔH°) and entropy (ΔS°) changes of adsorption can be evaluated from the following equations (21,15):

$$K_c = C_{Ae}/C_e \quad (21)$$

$$\Delta G^\circ = -RT \ln K_c \quad (15)$$

Where K_c is the equilibrium constant and C_{Ae} and C_e (both in mg/L) are the equilibrium concentrations for solute on the sorbent and in the solution, respectively. The K_c values are used in Eqs. (21) and (15) to determine the ΔG° , ΔH° and ΔS° , the K_c may be expressed in terms of the ΔH° (kJ mol⁻¹) and ΔS° (kJ mol⁻¹K⁻¹) as a function of temperature, Eq. (17):

$$\ln K_c = -\Delta H^\circ/RT + \Delta S^\circ/R \quad (17)$$

Thermodynamic parameters such as free energy of sorption (ΔG°), the heat of sorption (ΔH°) and standard entropy (ΔS°) changes during the sorption process were calculated using Eqs. (21) and (15) on a temperatures range of 25-40°C at initial concentrations (50, 100, 200, 300 and 400 mg/L) of Pb²⁺ ions and dose 0.5 g/250 mL for activated carbon and bentonite, (ΔH°) and (ΔS°) were obtained from the slope and intercept of a plot of $\ln K_c$ versus $1/T$ Figs. (25,26). The values of these parameters were recorded in Table 3.

The negative values of ΔG° confirm the feasibility of the process and the spontaneous nature of the adsorption of Pb²⁺ onto activated carbon and bentonite. On the other hand, the more negative value with increase of temperature indicates that a better adsorption is actually obtained at higher temperatures.

The positive values of ΔH° confirmed the endothermic nature of adsorption which was also supported by the increase in value of Pb²⁺ uptake of the adsorbent with the rise in temperature. The positive values of ΔS° showed the increased randomness at solid/solution interfaces during the adsorption of metal ions onto both adsorbents and also reflected the affinity of activated carbon and bentonite toward Pb²⁺ ions under consideration.

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