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Adsorption of copper(II) and lead(II) ions from aqueous solutions by porcellanite

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Abstract - This work is concerned with one of the applications of adsorption behavior from aqueous solution. It deals with the adsorption of copper (II) and lead (II) ions on the surface of porcellanite, which is locally available in Iraq. The purpose of this study is to search for surfaces that are highly applicable for copper (II) and lead (II) ions adsorption to treat the pollution of aqueous solution in nature. The different variables affecting the adsorption capacity of the porcellanite such as contact time, initial metal ion concentration in the feed solution, pH of the medium and temperature, were investigated on a batch process mode. The optimum contact time to attain equilibrium is 90 min for copper (II) ion, 30 min for lead (II) ion, and the pH values in the range of 2-10. The results showed the optimum pH for Cu(II) is 8 and for Pb(II) is 4. The experimental data of adsorption were fitted to two different isotherms, namely; Langmuir and Freundlich. These isotherms equations were applied at different temperatures. The results obtained showed that, the Langmuir isotherm equation is better fitted to the experimental data than the Freundlich isotherm equation. The thermodynamic parameters indicated that ΔH was endothermic, ΔG was a spontaneous process and ΔS was positive value.

Keywords: Porcellanite, batch adsorption, copper and lead, Langmuir and Frendlich, thermodynamics.

Introduction

Pollution is the addition of undesirable foreign matter to the environment as a result of enormous industrial development and modernization (Zietz *et al.*, 2003). Heavy metal ions existing in aqueous waste streams of various industries such as metal plating, mining operations, battery manufacturing and tannery Fabrication are posing serious risk to the environment. Leaking of the toxic heavy metals to the soil contaminates ground and surface water leading to serious impacts on the health of human and animals. Treatment of high volumes of waste water containing low concentrations of heavy metals pollutants is becoming increasingly important as the discharge regulations become more stringent (Zhu *et al.*, 2008). The harmful heavy metals ions associated with such industrial activities include Ni(II), Cr(II), Cu(II), Cd(II), Pb(II), Fe(III), Mn(II), Zn(II) and Hg(II) (Amdur *et al.*, 1991).

Copper contamination of the environment is primarily due to man made (anthropogenic) activities, making it the most everywhere toxic metal in the environment. Copper is one of the most common toxic metals that find its way to water sources from various industries, includes electroplating, mining, electrical and electronics ion and steal production, printing and photographic industries. Copper concentration in humans have increased to toxic levels causing various diseases and disorders such as liver damage (Zhu *et al.*, 2008).

Lead pollution includes the use of tetra methyl and tetra ethyl lead as gasoline additives, the main facture of storage batteries, the formation of alloys with antimony and tin to be use in power and telephone cables, the manufacture of soldering materials and lead paints (Newland and Dawn, 1982). In addition lead is also generated in the effluents from the production of television picture tubes, pigments, petroleum, fuels, photographic materials, explosives, printing, glass industrial operations and inorganic chemical manufacturing industries are also main sources of lead pollution. The toxicity and deleterious of lead are well documented, as it has been recognized for centuries as accumulative poison (WHO, 1977; ltorrison and laven, 1981). Acute lead poisoning in humans causes sever destruction in kidney, reproductive system, liver, brain and central nervous system. Mild lead poisoning causes anemia, the victim may have headache and sore muscles and may generally feel fatigue and irritable. Lead is also toxic to aquatic organisms. The concentration of lead in water below the world health organization standard (50 mg/l) cannot be considered as a serious of lead intake (Fugas and Saric, 1981). The accumulation of relatively small amounts of lead over along period of time in human body can lead to the malfunctioning of the organs and chronic toxicity (Stoker and Seager, 1976). According to the WHO, the maximum permissible limit (MPL) of lead in drinking water is (0.05 mg/l) (WHO, 1984). For these reasons, copper and lead must be removed as much as possible from industrial effluents. Several methods has been reported such as cementation of Pb(II) on spheres, on affixed bed contractor, adsorption on inert material treated with chelating reagent having selective affinity for Pb(II), non aqueous solvent extraction using organo-phosphorous compounds and chemical treatment followed by removal as precipitated carbonated (Taher *et al.*, 2011), precipitation, ion exchange, electro chemical reduction, exploration, reverse osmosis, etc. Most of these methods are very costly and economically unfavorable. Adsorption is effective, cheap method among the chemical treatments (Hawari *et al.*, 2009). A number of materials have been used to remove heavy toxic metals from water such as sawdust (Bulut and Tez, 2007), magnetic egg shell Fe_3O_4 powder (Jianwe *et al.*, 2011), nation 117 membrane (Nasef and Yahaya, 2009), activated carbon from pesia populnea bark (Prabakaran *et al.*, 2011), *Conocarpus erectus* leaves (Al-tameemi *et al.*, 2012), activated carbon synthesized from water melon shell and walnut shell (Moreno-Barbosa *et al.*, 2013). The present study is to investigate the possible use of locally porcellanite as an adsorbent material for removal of Cu(II) and Pb(II) ions from aqueous solution. The effect of adsorbent dose, contact time, initial metal ion concentration, temperature of solution and pH of the medium were calculated and discussed.

Materials and Methods

Preparation of adsorbent:

Porcellanite rock was obtained from the General Company for Geological

Survey and Mining, Baghdad, Iraq, washed with deionized water to be completely free from dirt, dried in an oven at 120°C for a period of 3h, then ground and sieved in, to different particle sizes ranges between 75 to 300 µm, the powder was preserved in glass bottles for use as adsorbent.

Chemical reagents:

Metal salts used was of analytical reagent grade (Merk). Deionized water was used for the preparation of solution. Stock solutions of different concentrations (0.02-4 mg/l) of Cu(II) and (0.5-12 mg/l) of Pb(II) were prepared by dissolving exactly the amount of metal salt in deionized water.

Adsorption studies:

Batch adsorption method was employed for the study of adsorption of Cu(II) and Pb(II) onto adsorbent. Adsorption of ions was carried out in 50ml stopper conical flask by adding 0.5g of porcellanite of particle size of 75 µm to 50 ml of 50 mg/l of Cu(II) and Pb(II) ions. All experiments were done at room temperature, often gentle shaking for desired time at 120rpm. The contents were filtered through filter paper (Qualitative filter paper). Concentrations of ions in the filtrate were then determined by using flame atomic absorption spectrophotometer (Pg instruments AA500). The amount of ions adsorbed were calculated based on the difference between the ions concentration in aqueous solution before and after adsorption from relation (Chu and Hashim, 2001).

$$Qe = V(C_o - C_e)/m \text{ .... } (1)$$

Where; Q_e is the equilibrium adsorption capacity (mg/g), V is the volume of solution (l), m is the weight of the adsorbent (g), *Co*= Initial concentration of solution, *Ce*= Concentration of the solution after adsorption.

Results and Discussion

Characterization of the adsorbent:

FT-IR apparatus type Shimadzu (400-4000 cm-^{1}) was used in order to identify the functional groups in the powder of porcellanite. The FTIR spectra as show in Fig. (1) indicate the appearance of strong band in the region (3460-3621 cm^{-1}) attributed to stretching vibration of hydroxyl group, the band at 1138 cm^{-1} belong to the stretching vibration of the (Si = O) group, the band at 476.42 cm^{-1} related to the stretching vibration Fe-O group and the band at 792 cm^{-1} related to the stretching vibration Al-O group (Silverstein *et al.*, 2005).

Effect of contact time:

The effect of contact time on the amount of metal ions adsorbed was investigated at different period (5-180 min) at 25°C. Figure (2) shows that the metal ions removal percentages increased with an increase in contact time before attaining equilibrium. The rate of metal removal is higher at the beginning due to the large surface area of the adsorbent being available for the adsorption of the metal (El-Ashtoukhy *et al.*, 2008). Equilibrium time was attained at 90 min for Cu(II) and 30min for Pb(II). The removal percentage of metal ions in porcellanite powder for Cu(II) and Pb(II) were found to be 68.96% and 97.43% respectively.

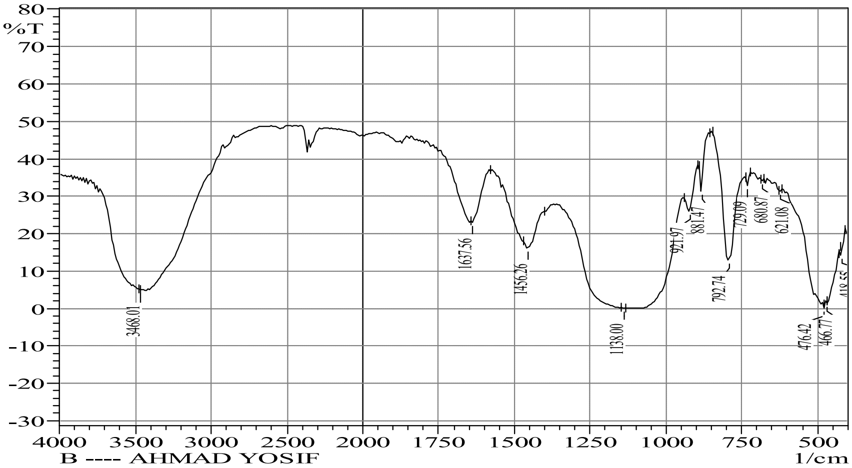

Figure 1. FT-IR of porcellanite powder.

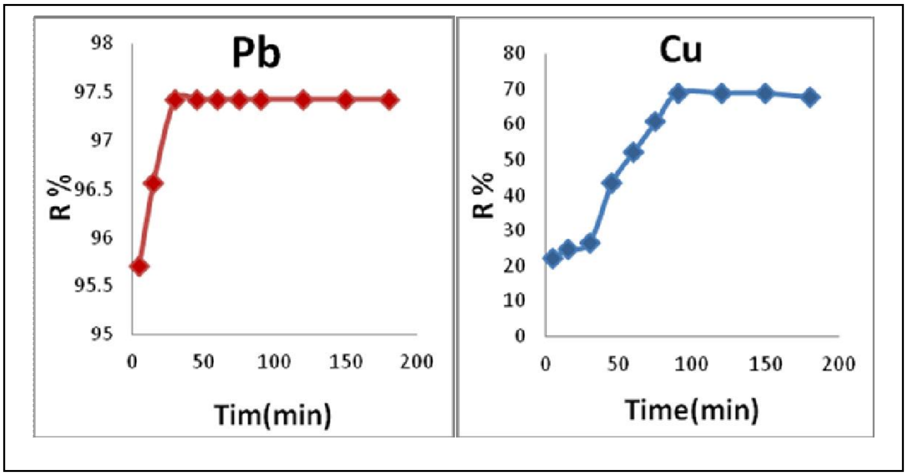

Figure 2. Effect of contact time on adsorption of Cu, Pb ions onto porcelanite.

Effect of pH on the adsorption:

pH is an important parameter for adsorption of metal ions from aqueous solution, because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and degree of ionization of the adsorbate during reaction (Adamson and Gast, 2001).The effect of pH on the adsorption of Cu(II) and Pb(II) ions on the porcellanite in different media (pH=2, 4, 6, 8 and 10) was studied by using a fixed concentration 50 mg/l and time contact of 30, 90min for Cu(II) and Pb(II) at 25°C respectively. Figure (3) demonstrate the influence of pH on the adsorption.

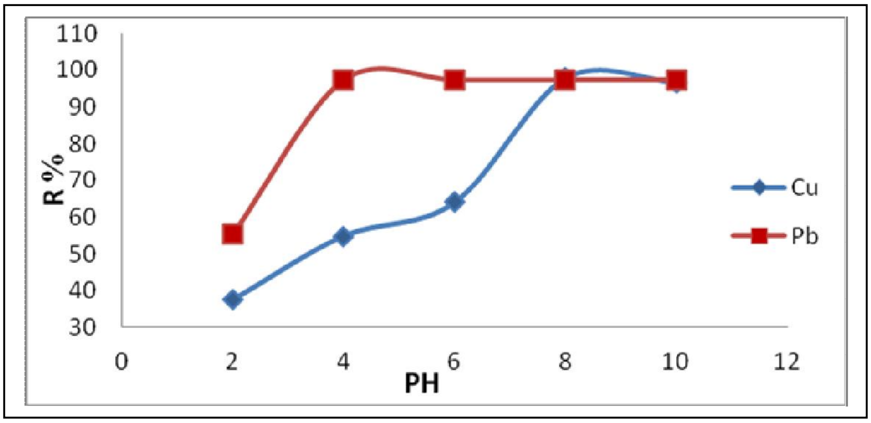

Figure 3. Effect of pH on Cu(II) and Pb(II) adsorption on porcellanite.

The results showed an increase in the removal percentage of Cu(II) and Pb(II) with increasing pH values of the solution. At low pH value, binding sites are generally protanated or positively charged by the hydronium ions, this repulsion occurs between the metal cation and the adsorbent. At a higher pH value, binding sites start deprotonation, and make different functional groups available for metal binding. In general, cation binding increase as pH increases (Esposito *et al.*, 2012). In addition, the solubility of Cu(II) and Pb(II) ions are greatly decreased as the pH increased causing an increase in the adsosption affinity towards the porcellanite surface (Lund, 1994). Accordingly, the subsequent experiments were done at pH 6.5 to avoid uncertainly in results as additional mechanism such as precipitation might play a role in metal removal from solution.

Effect of initial concentration of Cu(II) and Pb(II) ions:

The effect of initial concentration of metal ions on the adsorption was carried out for different initial concentrations of metal ions in the range of (10-100mg/l), (50-400mg/l) to Cu(II) and Pb(II), respectively. The dependence of percent of metal ion removal on initial concentration of metal ions is represented in Fig. (4). Percent removal was found to be maximum at low initial concentrations of metal ions. It is 89.25 %, 97.43 % for 10 mg/l, 50 mg/l of Cu(II) and Pb(II), respectively. At low initial concentrations of metal ions nearly all the metal ions adsorbed due to availability of active adsorption sites. As the metal concentration increases active sites become occupied and hence the less adsorption (Meena *et al.*, 2005).

Adsorption isotherm:

The adsorption of Cu(II), Pb(II) from aqueous solution on porcelanite has been studied at different temperatures (10, 25, 37.5 and 50°C). The general shapes of Cu(II), Pb(II) adsorption isotherm are shown in Fig. (5) where the quantities adsorbed on porcelanite (Qe) are plotted as a function of equilibrium concentration (Ce) at (10, 25, 37.5 and 50°C).

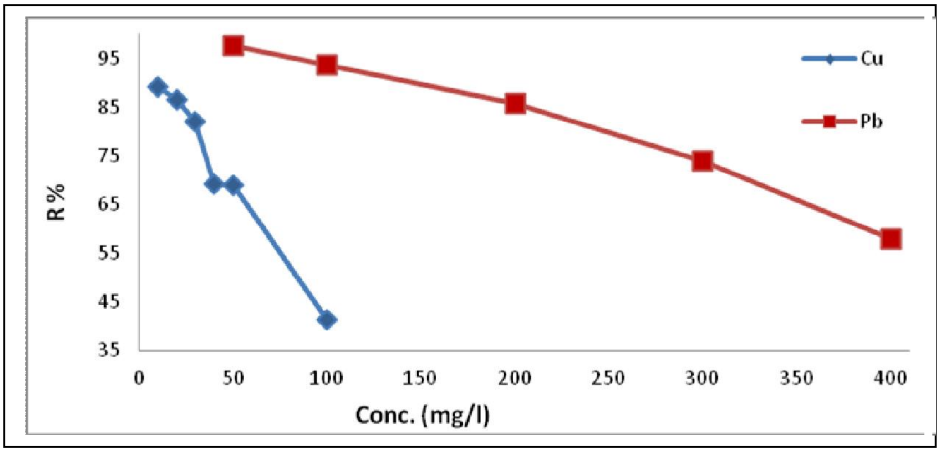

Figure 4. Effect of initial concentration on adsorption of Cu(II), Pb(II).

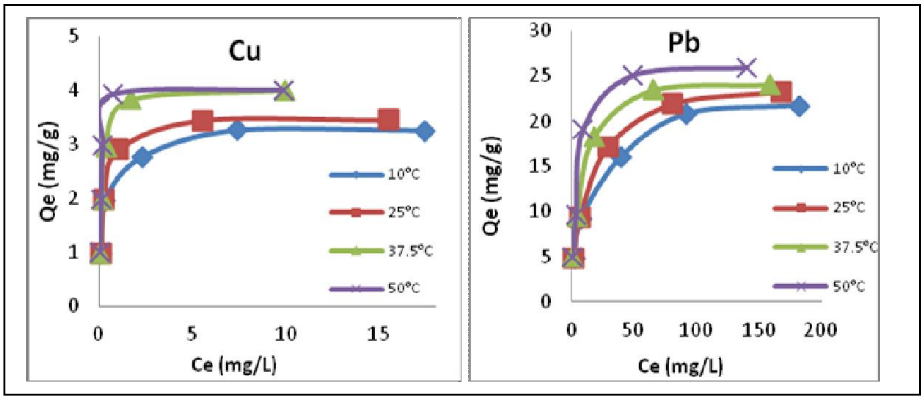

Figure 5. Adsorption isotherm of Cu(II), Pb(II) on porcellanite surface at different temperatures.

The shape of the adsorption isotherm of Cu(II), Pb(II) on porcellanite is consistent with H-type on the Giles classification. H-type adsorption isotherm indicated high affinity between Cu(II), Pb(II) and porcellanite surface in very diluted solution (Giles *et al.*, 1960). The experimental adsorption data were applied to both the theoretical Langmuir isotherm equation and empirical Freundlich equation. The results of applying Freundlich (eq.2) and Langmuir (eq. 3) (Veena and Robert, 2002), isotherm on the adsorption data are listed in Table (1).

$$\log Qe = \log Kf + 1/n \log Ce \text{......... (2)}$$

Where Kf is a fanction of the adsorption capacity and n is the intensity of adsorption.

$$Ce/Qe = 1/Qmb + Ce/Qm \text{ ....(3)}$$

Where Qm is the maximum adsorption capacities (mg/g) and b is related to the adsorption energy.

Table 1. Results of the application of Freundlich and Langmuir isotherms on the system studied.

Ion	Temp. (°C)	n	Kf	R2	Qm (mg/g)	b(L/g)	R2
Cu(II)	10.0	4.43	1.99	0.848	3.31	3.39	0.999
	25.0	4.50	2.25	0.814	3.49	5.55	0.999
	37.5	3.94	2.81	0.747	4.06	6.42	0.999
	50.0	4.44	3.11	0.665	4.05	12.22	0.999
Pb(II)	10.0	2.79	3.89	0.956	23.18	0.08	0.998
	25.0	3.00	4.86	0.971	24.38	0.11	0.998
	37.5	3.13	5.76	0.943	24.97	0.18	0.999
	50.0	3.31	7.17	0.917	26.68	0.27	0.999

The Freundlich and Langmuir isotherms are applied on the experimental data of the adsorption of Cu(II) and Pb(II) ions on porcellanite by plotting log Q_e versus log C_e and C_e/Q_e versus C_e, respectively (Fig. 6 and 7). The results of Table (1) show that the Langmuir isotherms is better fitted on this system than the Freundlich as shown by the linear relationship of (C_e/Q_e) versus (C_e) (Fig. 7).

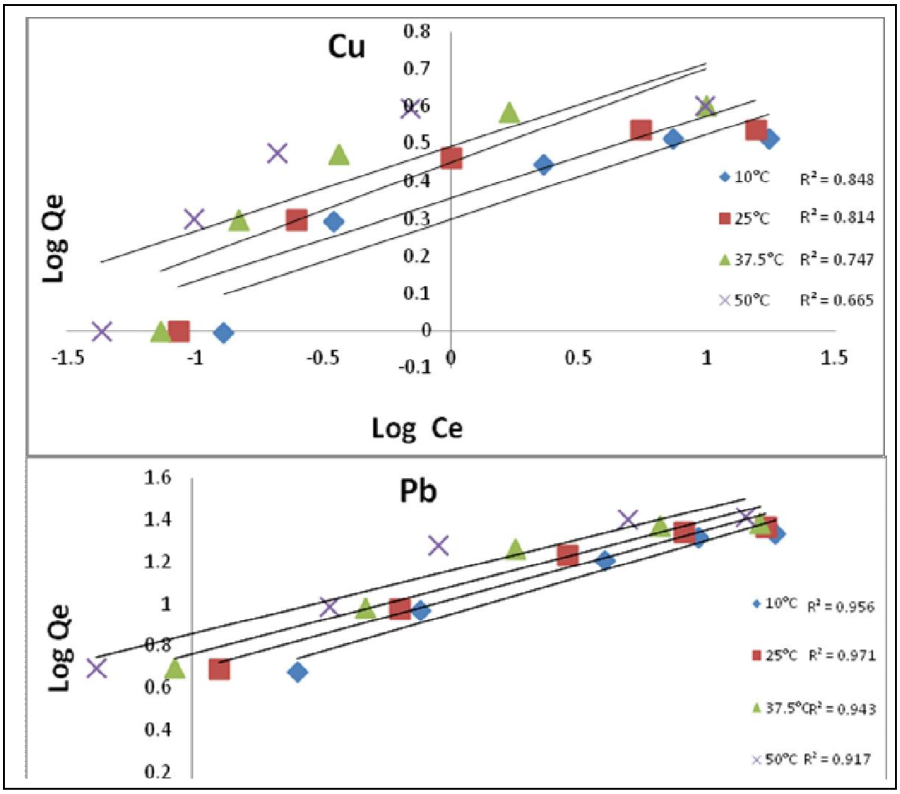

Figure 6. Linear form of Freundlich isotherms of Cu(II), Pb(II) on porcellanite at different temperatures.

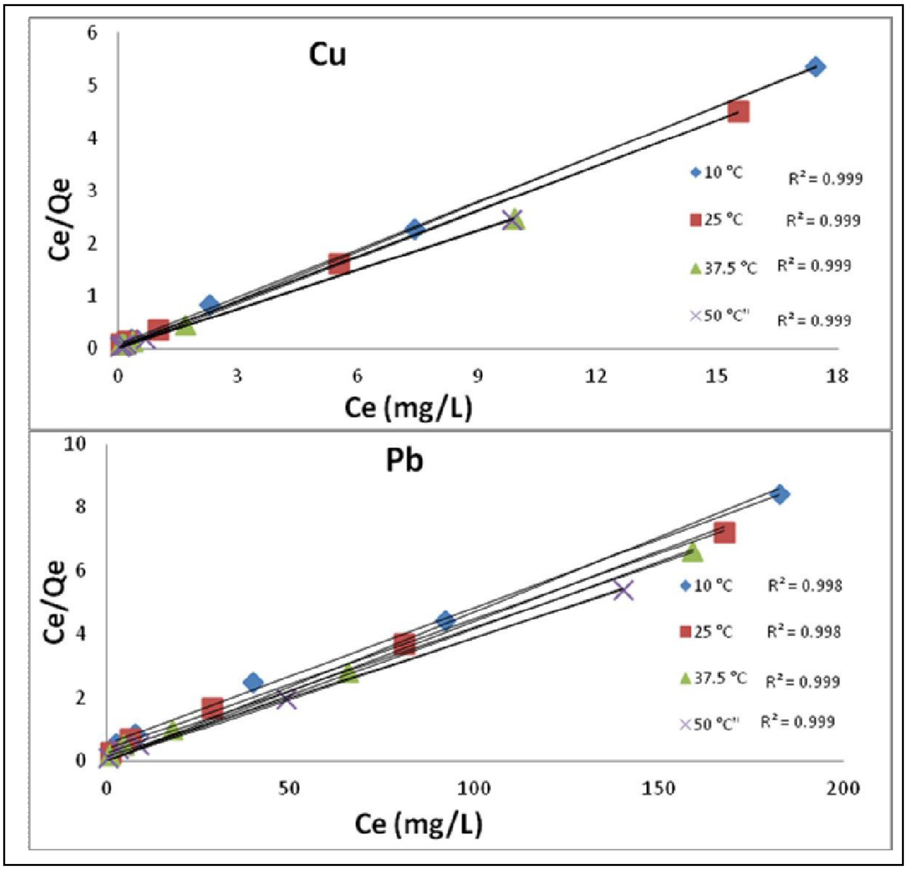

Figure 7. Linear form of Langmuir isotherms of Cu(II), Pb(II) on porcellanite at different temperatures.

Thermodynamic studies:

The effect of temperature on the adsorption of Cu(II) and Pb(II) was studied in the range of 10-50°C using different initial concentrations .The feasibitility of the adsorption process can be estimated by the Thermodynamic parameters of Gibbs energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) by the following equations.

$$\Delta G = -RT \ln k \ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$
$$K = C_{solid} / C_{liquid} \ldots\ldots\ldots\ldots\ldots\ldots (5)$$
$$\ln K = \Delta S / R - \Delta H / RT \ldots\ldots (6)$$

Where ΔG is the Gibbs energy change (KJ.mol^{-1}), K is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/l), C_{liquid} is the liquid phase concentration at equilibrium (mg/l), T is the temperature in Kelvin and R is the gas constant (0.0083 KJ.mol^{-1} K^{-1}).

ΔH (KJ.mol^{-1}) and ΔS (KJ.mol^{-1}.k^{-1}) can be calculated from the slope and intercept of Eq.(6), respectively. The Thermodynamic parameters at the studied temperature ranges are listed in Table (2).

The plots of *lnK* versus. 1/T were found to be linear with a correlation coefficient (R^2 = 0.871-0.977) and (0.948-0.990) for adsorption of Cu(II) and Pb(II), respectively (Fig. 8).

Table 2. Thermodynamic functions for adsorption of Cu(II), Pb(II) ions.

ion	Co (mg/l)	K				- ΔG				ΔH	ΔS
		Temperature									
		283	298	310.5	323	283	298	310.5	323		
Cu(II)	10	76.51	115.27	135.98	231.55	9.87	11.44	12.75	19.84	14.07	0.10
	20	56.80	79.64	134.13	201.02	9.24	11.03	12.52	24.43	14.01	0.12
	30	12.00	29.12	81.19	142.54	5.48	8.33	10.70	48.29	13.08	0.19
	40	4.40	6.22	22.68	56.55	2.77	5.58	7.91	50.14	10.25	0.18
	50	1.86	2.22	4.04	4.07	1.12	2.06	2.85	16.71	3.64	0.06
Pb(II)	50	18.44	37.91	57.34	115.82	6.58	8.73	10.51	33.88	12.30	0.14
	100	11.96	14.55	20.21	28.17	5.44	6.59	7.56	16.34	8.52	0.07
	200	4.01	5.96	10.11	21.22	2.84	4.64	6.14	31.11	7.64	0.12
	300	2.25	2.70	3.57	5.14	1.50	2.40	3.15	15.48	3.90	0.06
	400	1.18	1.38	1.511	1.85	0.40	0.80	1.06	8.07	1.65	0.03

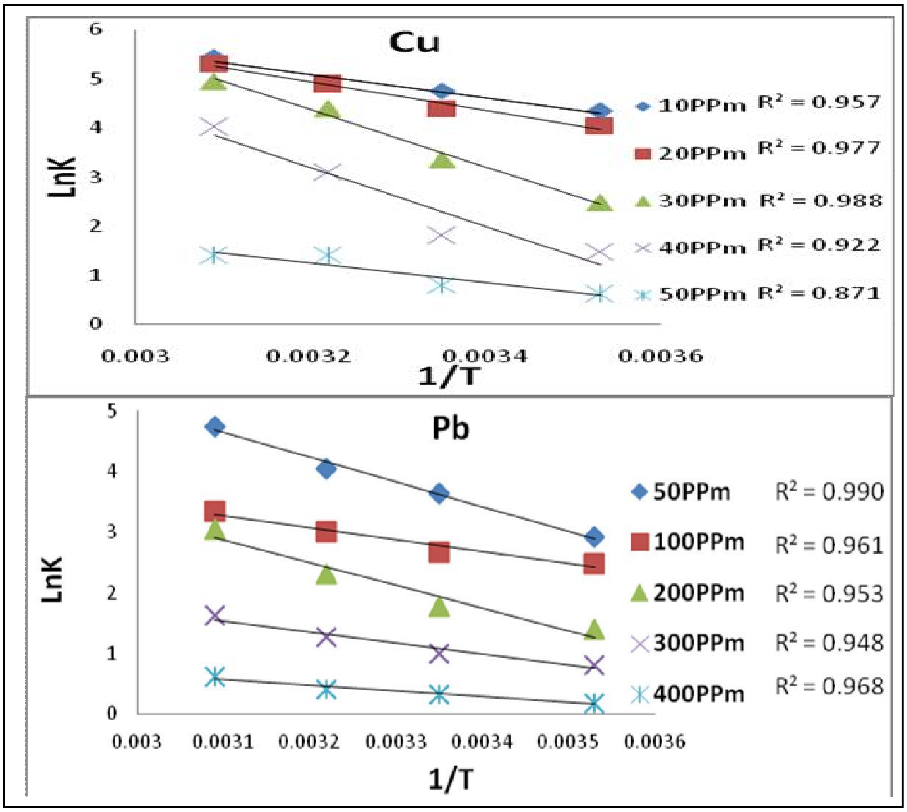

Figure 8. Plot of van, t Hoff relationship between LnK versus 1/T.

Table (2) indicate, ΔG at all temperatures were negative and increrased with an increase in temperature, indicating the spontaneity of the adsorption of Cu(II) and Pb(II) onto porcellanite powder (Hefne *et al.*, 2008). The positive value of ΔH indicates endothermic nature of the adsorption process, while the positive value of ΔS revealed the increase in randomness at the solid/solution interface during the adsorption process (Al-Saadie and Jassim, 2010).

Conclusion

The present study emphasize that porcellanite powder was employed as an adsorbent for the removal of Cu(II) and Pb(II) from aqueous solutions. The material showed enhanced Cu(II) and Pb(II) adsorption capacities compared with most materials reported in literature. the equilibrium data followed Langmuir isotherm model. The maximum percentage removal of 68.96% and 97.43% for Cu(II) and Pb(II) occurred at pH 6.5 and 25°C. It can be concluded that porcellanite powder is a promising low lost and high efficiency adsorbent for Cu(II) and Pb(II) removal from waste water and can be applied in a magnetically assisted water treatment technology.

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دراسة عملية الامتزاز للأيوني النحاس والرصاص من المحاليل المائية باستخدام البورسلينات

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المستخلص – تناول هذا البحث احد تطبيقات ظاهرة الامتزاز من المحاليل المائية. حيث تم دراسة امتزاز ايونات النحاس والرصاص على سطح البورسلينات المتوفرة محلياً في العراق، لغرض البحث عن سطح ذي قابلية عالية لامتزاز ايونات النحاس والرصاص بهدف معالجة تلوث المحاليل المائية في الطبيعة بايونات هذه العناصر، تم دراسة المتغيرات المختلفة التي تؤثر على سعة الامتزاز مثل زمن الاتزان والتركيز الابتدائي للايونات والدالة الحامضية ودرجة الحرارة، كان أعظم زمن للاتزان عند 90 دقيقة لايون النحاس، 30 دقيقة لايون الرصاص. تم دراسة تأثير الدالة الحامضية وبالمدى (2 – 10) وأشارت النتائج إلى أن أعظم دالة حامضية لايون النحاس هي pH=8، لأيون الرصاص pH=4. استخدمت النتائج التي تم الحصول عليها من دراسة تأثير درجة الحرارة في تطبيق المعادلات الرياضية لايزوثيرمات Langmuir و Freundlich على البيانات العملية للامتزاز، قد أعطت معادلة Langmuir علاقة خطية بمعاملات ارتباط جيده أفضل من ايزوثيرم Freundlich. بينت الدراسة الثرموديناميكية إن عملية الامتزاز ماصة للحرارة من قيم لـ ΔH الموجبة، وتلقائية من القيم السالبة لـ ΔG، بينما دلت القيم الموجبة لـ ΔS على زيادة العشوائية لعملية الإزالة.