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Original Article

Removal and Reusability of Lead (II) from Aqueous Samples Using the Adsorption Method onto Commercial Activated Carbon: Kinetics and Thermodynamics Studies

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ABSTRACT

Background and Aim: The study focused on the sorption of lead Pb^{2+} from water samples using Commercial Activated Carbon (CAC) sorbent. **Materials and Methods:** The factors affecting the absorbance between Pb^{2+} and CAC were examined the mass of the CAC, ionic strength, pH solution and effect of temperature on the solution. Isotherm models (Langmuir, Freundlich and Temkin) were examined for Pb^{2+} adsorption on CAC. **Results and Discussion:** Freundlich isotherm model was determined as the best lead adsorption model on CAC. Freundlich model parameters R^2, *n*, and kf were found 0.9889, 1.48, 0.53 $mg.g^{-1}$ respectively. The adsorption capacity (qe) was 12.81 $mg.g^{-1}$. Thermodynamic parameters ΔH, and ΔS were found -1422.8 and 5.2389 $KJ.mol^{-1}$ respectively. The adsorption process was exothermic. A Pseudo-Second-Order (PSO) model was followed for the adsorption process. Finally, the method was proved to be highly effective method for the extraction of the Pb^{2+} using CAC three times. The percentage extractions (%ER) found ranged from 107.0-91.9 % for stimulation marketing drink water and tap water. **Conclusion:** CAC is distinguished as an adsorbent that excels other adsorbents in removing the Pb^{2+} from aqueous solutions due to its chemical and physical properties.

Keywords: Lead (II), Commercial activated carbon (CAC), Thermodynamics, Adsorption isotherm models, Kinetics models.

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INTRODUCTION

Toxic heavy metals in aqueous solutions pose a serious threat to the environment, such as lead, (Pb^{2+}).[1] The high concentration of lead element in aqueous solution above the permissible limits endangers the life of the consumer.[2] This metal can be discharged into abrasive solution from various industries, including metal plating, storage batteries, alloying industries, fertilizer and other chemical industries.[3,4] The researchers were interested in removing heavy metals from the aqueous solution by various methods, including adsorption, chemical precipitation, and ion exchange, due to the importance of preserving the aquatic environment with the increase of industrial activities.[5-7] Adsorption is one of the most common processes applied in the purification of aqueous solutions of heavy metals.[8] Lead is a major concern to children due to its environmental source in developing countries.[8] The toxicity of lead metal comes from various human related activities such as smoking, leaded car fuel, contaminated food, ground water, houses painting and drinking water.[9,10] Excessive exposure of children to lead affects the functions of the body causing headache, vomiting, neurons diseases, heart diseases, blood diseases In case children exposed to a high percentage of lead, they suffer an encephalopathy as a result of failure in the performance of the Central Nervous System (CNS).[11-13] Adsorption is one of the most suitable processes for treatment aqueous solutions of metal ions. When a solute liquid accumulates on the surface of the absorbent material, forming an adsorbent, the process is called adsorption.[14] Adsorption is one of the most suitable processes for treatment aqueous solutions of metal ions. The adsorption technology is characterized by ease of use, efficiency and low cost.[15,16] Activated Carbon (AC) is a carbon containing substance produced from organic materials. CAC is classified on the basis of their shape and size and is in the form of pellets or powder.[17,18] CAC's composition containing on different functional groups and medium pores.[19] The surface area of CAC ranges from 500 to 3000 $m^2.g^{-1}$.[19,20] It is used in the treatment of aqueous solutions, recovery of solvents and pharmaceutical industry.[19] CAC has functional groups like carbonyl, phenols,

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quinones, carboxyl, and lactones that play a role in the adsorption of heavy metals from polluted aqueous solutions.[21,22]

MATERIALS AND METHODS

Chemicals and Apparatus

This project used only analytical-grade chemicals. The lead nitrate, Pb $(NO_3)_2$ was obtained from sigma Aldrich and CAC 300-500 µm, from Nen. Tech Ltd., (UK), with a surface area of 500-3000 $m^2.g^{-1}$ and the overall capacity of the pores of 1.4 $cm^3.g^{-1}$. UV-vis spectrophotometer was used to obtain the absorption spectra (SP-3000 nano, Optima, Japan) and pH measurements were performed using an Ezdo pH-pp-201 (Taiwan). In this work, a water bath shaker (Daihan Scientific, Korea) was used.

Procedure

The quantity of Pb^{2+} that was adsorbed by the CAC was determined through calculation. The impacts of the CAC on the adsorption parameters like concentrations of Pb^{2+}, pH solution, mass, ionic strength, and temperature was investigated. A set of various concentrations ranging from 0.1-1.0 $µg.L^{-1}$, a linear calibration curve was obtained at 340 nm to calculate the final Pb^{2+} concentrations in the solution using a spectrophotometer. The R^2=0.9907 was obtained.

Effect of contact time, mass, pH of solution and ionic strength

The effect of time was studied by calculating the final Pb^{2+} concentration in the solution. 100 mg CAC was added to 50 mL solutions containing a primary concentration of 0.55 $µg.L^{-1}$ Pb^{2+} and stirred for 5 to 30 min at 25ºC. The effect of CAC mass on aqueous solutions under agitation time conditions was studied using a series of CAC mass (50 to 1000 mg). The effect of pH on aqueous solutions under agitation time conditions was studied using a series of pH (1.0 to 12.0). The ionic strength effect on aqueous solutions under agitation time conditions was examined via several concentrations of NaCl (0.5-2.0 M). The final of Pb^{2+} concentration was determined.

Adsorption isotherms

The isothermal adsorption impacts of CAC adsorbent were examined at varying concentrations (0.15-0.95 $µg.L^{-1}$) of Pb^{2+} in water solutions., by adding 100 mg of AC, at pH 7 and at different concentrations of Pb^{2+} (0.15 to 0.95 $µg.L^{-1}$). The solutions were stirred at different concentrations at various temperatures (298, 303, 313 and 323K). The Pb^{2+} adsorbent concentration and distribution coefficient were calculated according to Equation formula 1.

$$qe = \frac{(Ci - Cf)}{m} X\ V \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where the qe quantity of adsorbed ($mg.g^{-1}$), initial (C_i, $µg.L^{-1}$), the equilibrium (C_f, $µg.L^{-1}$) Pb^{2+} concentration, m is adsorbent mass (mg).

RESULTS AND DISCUSSION

Effect of contact time, mass of CAC, pH, ionic strength, Pb^{2+} concentration, and Temperature

According to Figure 1a, the % removal of Pb^{2+} was based on the quantity of CAC present in the solution. When the quantity of CAC increased, the % removal of the Pb^{2+} increased; the figure shows that the % removal changes little for masses greater than 100 mg. As Figure 1b shows, in the neutral solution, the % removal of Pb^{2+} increased, but the % removal decreased from 41% in acidic medium (at pH 1) to 30% in basic medium (at pH 12). Figure 1c shows that the percentage removal (% removal) of Pb^{2+} increased with time. The contact time was adjusted at 15 min, it is better to keep the contact time short for economic reasons.[23] As Figure 1d shows, the % removal of Pb^{2+} in the solution decreased with increasing concentrations, reaching 47% at 0.95 $µg.L^{-1}$ and 79% at 0.15$µg.L^{-1}$. The % removal values were slightly decreased at a concentration of 0.55$µg.L^{-1}$. The decrease in the adsorption process of Pb^{2+} is due to the decrease in the active sites for CAC. Figure 1d shows that the distribution coefficient of Pb^{2+} decreased with increasing temperature, which indicates that the process is exothermic. The effect of temperature on the surface of the CAC indicates the destruction of active sites, which led to an increase in the adsorption of Pb^{2+}.

Adsorption isotherm

To determine the ability of CAC to absorb Pb^{2+} from aqueous solutions the Langmuir, Temkin and Freundlich models were used. Table 1 shows that Freundlich's model is the best for adsorption of Pb^{2+} and CAC, indicating that the adsorption is heterogeneous. Table 1 also shows the R^2 values for both the Langmuir and Temkin models. The values indicate that the two models are less suitable. Table 1 shows the n values in the Freundlich Pb^{2+} absorption model (1.4806 to 1.9689 $µg.L^{-1}$). Both values of A and B in Temkin's model showed that the reaction resulting from adsorption of Pb^{2+} and CAC is a physical adsorption.

Adsorption thermodynamic parameters and kinetic models

Enthalpy and entropy were used to determine the adsorption of Pb^{2+} from CAC through equation formula 2.

$$\ln kd = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \ldots\ldots\ldots\ldots\ldots (2)$$

Where the ΔH enthalpy ($KJ.mol^{-1}$), R gas constant is (8.3145 $J.mol^{-1}.K^{-1}$), ΔS entropy ($J.K^{-1}.mol^{-1}$), and kd distribution coefficient. The values of ΔHº and ΔSº were found to be -1422.8 and 5.2389, respectively, as represented in Table 2. The adsorption process of the Pb^{2+} onto CAC was not spontaneous,

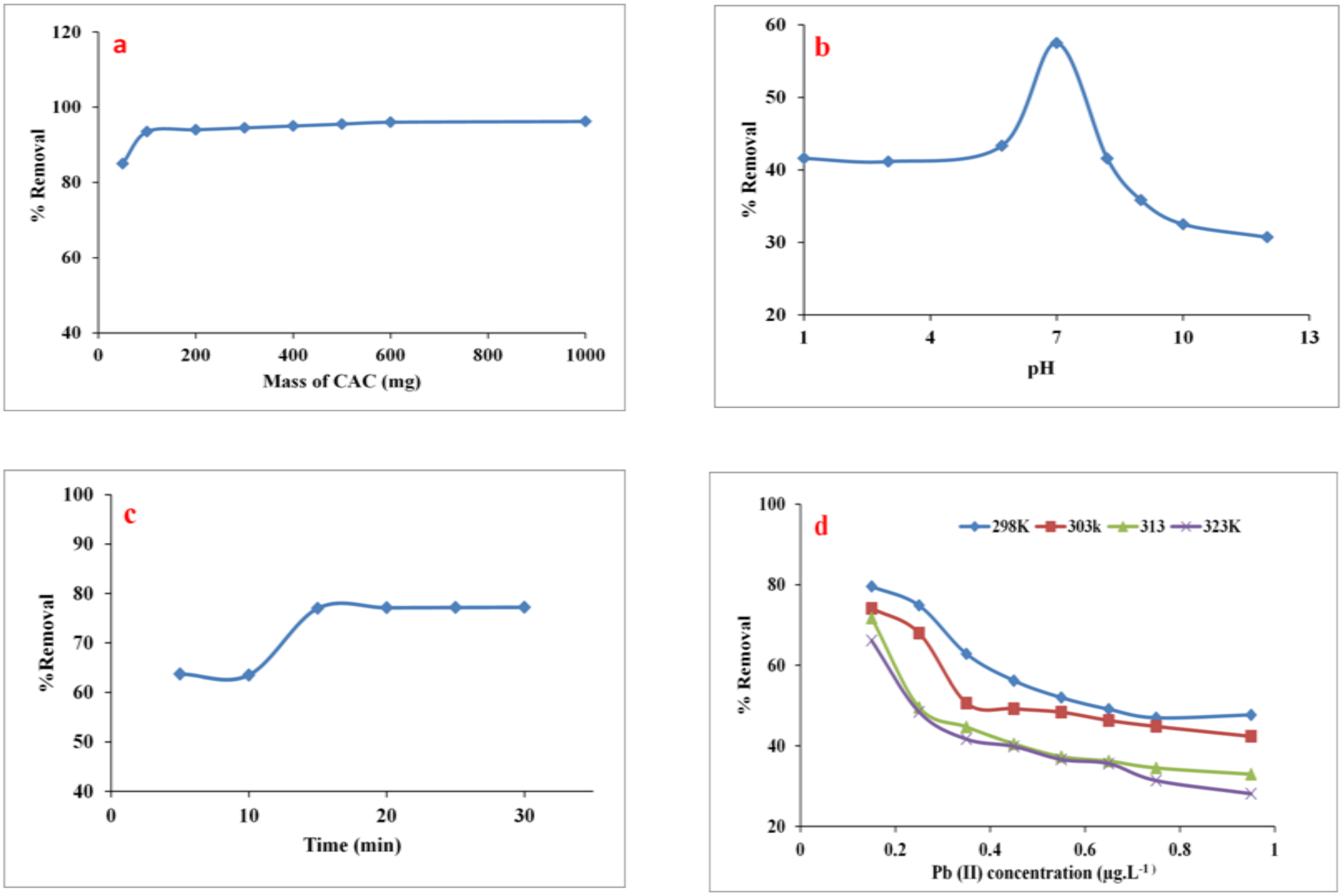

Figure 1: Impact of contact time (a), mass of CAC (b), pH (c), ionic strength (d), concentration, and temperature on the % removal of Pb^{2+} onto CAC.

and exothermic due to the positive value of ΔG, and the negative value of ΔH°. The adsorption of Pb^{2+} onto CAC was highly random during the solid-liquid interface due to the positive value of the ΔS°. The values of (ΔG) increase with increasing the temperature, which indicates that the adsorption of Pb^{2+} with CAC was exothermic.

First Pseudo Order (FPO) and Second Pseudo Order (SPO) were used to examine kinetic models to assess Pb^{2+} adsorption in AC. Table 3 shows that the qe exp. value (mg.g^{-1}) is not close to the qe cal.value (mg,g^{-1}), the R^2=0.9673 indicates that the FPO does not correspond to the sorption of Pb^{2+} in the CAC. The experimental value of qe is consistent with the calculated "qe " and R^2=0.9954 indicates that SPO corresponds to Pb^{2+} adsorption in the CAC.

Reusability of CAC to remove Pb^{2+}

The reuse of the CAC to extract Pb^{2+} was examined in an aqueous solution. Figure 2 shows the values of reuse of the CAC (97.21%, 81.19%, and 73.36%), respectively, showing that the CAC can extract the Pb^{2+} after three cycles.

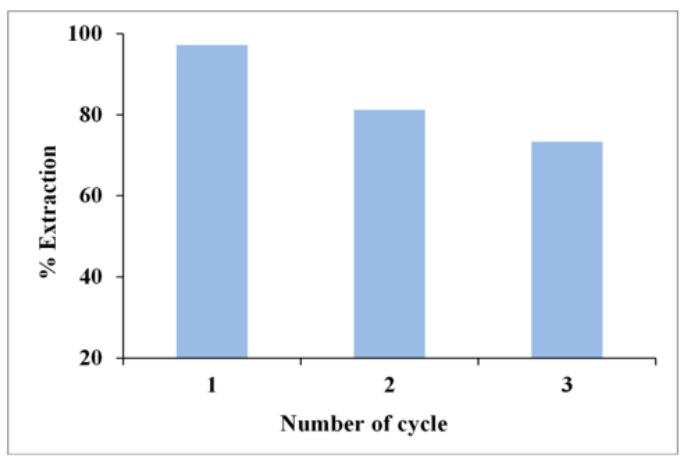

Figure 2: Reuse to extraction of Pb^{2+} using CAC.

Water sample applications

The percentage of extraction recovery (%ER) of Pb^{2+} was determined in tap water samples and marketing drink water samples. The % ER ranged from 107.0- 92.4% and 102.7-91.9% in marketing drink water and tap water samples, respectively, as represented in Table 4.

Table 1: Isotherm parameters of Langmuir, Freundlich, and Temkin models.

Langmuir				Freundlich			Temkin		
T.(K)	R^2	*qmax*	*kl*	R^2	*kf*	*n*	R^2	*A*	*B*
298	0.8041	12.814	1.1077	0.9889	0.3586	1.4806	0.9306	12.2803	0.1598
303	0.7308	6.9909	0.1094	0.9500	0.5847	1.6823	0.9261	14.7052	1.3247
313	0.7030	6.3557	0.1102	0.9880	0.6541	1.5288	0.9192	17.8410	1.3626
323	0.8406	4.5735	0.1552	0.9551	0.5079	1.9689	0.9606	18.5524	1.0324

Table 2: Thermodynamic parameters for the adsorption of Pb^{2+} onto CAC.

ΔH	ΔS	ΔG ($kJ.mol^{-1}$)			
		298 K	303 K	313 K	323K
-1422.8	5.2389	138.4	191.9	216.9	298.4

Table 3: Kinetic parameters for PFO and PSO models.

Pb^{2+} conc. ($\mu g.L^{-1}$)	Pseudo-First-order (PFO)			Pseudo-Second-order (PSO)		
0.55	k_1 (min^{-1})	qe cal. ($mg.g^{-1}$)	R^2	k_2 ($g.mg^{-1}.min^{-1}$)	qe cal. ($mg.g^{-1}$)	R^2
	0.004	3.1485	0.9673	31.6	0.013	0.9954

Table 4: Percentage extraction recovery of Pb^{2+} from marketing drinks water and tap water samples.

Sample	Added ($\mu g.L^{-1}$) ($\mu g.mL^{-1}$) (μM)	Found ($\mu g.mL^{-1}$)	% ER ± SD
Marketing drink water samples	1	0.96	96.0±1.15
	2	2.14	107.0±0.92
	3	2.94	98.2±1.36
	4	4.052	101.3±0.86
	5	4.705	94.1±0.55
Tap water samples	1	0.924	92.4±1.33
	2	1.948	97.4±1.05
	3	3.081	102.7±0.91
	4	3.944	98.6±0.75
	5	4.595	91.9±0.82

CONCLUSION

This study focuses on the environmental aspect of removing toxic Pb^{2+} from solution by using CAC as adsorbent. The adsorption capacity (qe) of the Pb^{2+} on CAC was 12.81 at pH 7, 100 mg of CAC, and 25ºC. The equilibrium adsorption data were better suited to the Freundlich isotherm model using an adsorption isotherm for Pb^{2+} on CAC. Positive ΔG, negative ΔH, and positive ΔS were found to indicate the adsorption process is non-spontaneous, exothermic, and random, respectively. The PSO kinetic model was obeyed for the adsorption of Pb^{2+} with CAC. The CAC can extract Pb^{2+} from an aqueous solution after three times.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

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