Role of Activated Carbon Modified by H_3PO_4 and K_2CO_3 From Natural Adsorbent for Removal of Pb (II) From Aqueous Solutions

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Abstract

Most heavy metals are well-known toxic and carcinogenic agents and when discharged into wastewater represent a serious threat to the human population and the fauna and flora of the receiving water bodies. The present study aims to develop a procedure for Pb (II) removal. This procedure is based on using powdered activated carbon, which was prepared from walnut shells that were generated as plant wastes and modified with potassium carbonate and phosphoric acid as chemical agents. The main parameters, such as effect of pH, effect of sorbent dosage, Pb (II) concentrations, and various contact times influence the sorption process. The experimental results were analyzed by using Langmuir, Freundlich, Tempkin, and Dubinin-Radushkevich adsorption models. The kinetic study of Pb (II) on activated carbon from walnut shells was performed based on pseudo- first order and pseudo- second order equations. The data indicate that the adsorption kinetics follow the pseudo- second order rate. The procedure was successfully applied for Pb (II) removal from aqueous solutions.

Key words: Pb (II), walnut shells, phosphoric acid, potassium carbonate, isotherms

1. Introduction

Environmental pollution by heavy metals is a serious and complex problem that at all times occupies worldwide attention. Heavy metals are classified as the chief surface and groundwater pollutants. Industrial and municipal wastewaters frequently contain metal ions that can be harmful to aquatic life and human health. Heavy metals are usually found in industrial wastewater, for example, that from the production of textiles, from paint manufacturing, from leather tanning, etc. [1]. In general, heavy metals are not biodegradable and they tend to accumulate in living organisms, causing cause various diseases and disorders. In adults, Pb (II) can increase blood pressure and cause fertility problems, nerve disorders, muscle and joint pain, irritability, and memory or concentration problems [2]. The treatment methods for metal-bearing effluents commonly include chemical precipitation, membrane filtration, electrolytic reduction, solvent extraction, ion exchange, and adsorption [3]. Among these treatments, adsorption is considered to be an effective and economical method and has attracted considerable interest. Activated carbons are adsorbents that are suitable for industrial use in multiple processes for product separation and purification, and for the treatment of liquid and gaseous effluents. Considering the high cost of activated carbon and the tedious procedures for the preparation and regeneration of activated carbons, there is a continuing search for low-cost potential adsorbents. Lignocellulosic materials and wastes such as peanut skins, cotton, onion skins, rice hulls, maize stalks, bark, jute fibers, bagasse, rice straw, corncoobs, and palm kernel husks have received much attention in the field of heavy metal ion removal [4]. Various functional groups such as carboxylates, phenolic and aliphatic hydroxyls, and carbonyl groups in these materials have the ability to adsorb

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some metal ions. In order to increase the metal ion adsorption in cellulose, it was chemically modified by introducing different groups such as phosphoric acid (H_3PO_4) and potassium carbonate (K_2CO_3) [5].

2. Materials and Methods

2.1. Adsorbent

2.1.1. Physical activation

Walnut shells were obtained from local natural resources. After they were obtained, the fresh walnut shells were washed several times with distilled water to remove surface impurities; shells were then dried at room temperature for one day. The samples were heated and burned and the charcoal was crushed with a grinder and then ground fine enough for the powder to pass through a 100-mesh sieve for further experiments. Powder was activated to a final temperature of 500°C by heating it in a muffle furnace for six hours.

2.1.2. Chemical activation

Chemical activation methods using H_3PO_4 and K_2CO_3 were used to activate the raw material. One gram of each raw material was weighed and then the weighed raw sample was impregnated in 5 mL of 50% (v/v) concentration of phosphoric acid and 5 mL of 20% (w/v) concentration of potassium carbonate for 1 h at room temperature. After that, the blend was transferred to a muffle furnace, where carbonization was carried out under an air atmosphere. The plant material was chemically modified with H_3PO_4 and K_2CO_3 in three steps of temperatures and times. The furnace was heated to 200°C and maintained at this temperature for 30 min in order to allow the free evolution of water; a black sticky solid was obtained. Then, the furnace was heated to 500°C , and maintained at this temperature for 60 min. finally the furnace was heated to 700°C and maintained at this temperature for 15 min. After cooling to room temperature, the solid was washed with ultra pure water at 25°C to remove excess H_3PO_4 and K_2CO_3 . The carbon samples were dried at 50°C < t < 80°C .

2.2. Batch equilibrium studies

Activated carbon (0.05 g) was added to the solutions of $\text{Pb}(\text{NO}_3)_2$ with different initial concentrations. The mixture was stirred for 15 min at room temperature (25°C). The amount of remaining metal ions was determined using an atomic absorption spectrophotometer (Shimadzu-Japan). The amount of Pb (II) adsorbed on the adsorbent at adsorption equilibrium was calculated according to the following Eq. (1)

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e (mg/L) are the initial and equilibrium Pb (II) concentrations, respectively. V is the volume of the solution (L) and W is the mass of adsorbent used (g).

In the order to study the effect of contact time between adsorbent and adsorbate, at first, we put 20 ppm of Pb (II) and 0.05 g of activated carbon in contact for 240 min; with this contact of 0.05 g of activated carbon, a maximum of adsorption took place

in the first 15 min of contact.

To analyze the effect of initial Pb (II) concentration, at first we changed the concentration of Pb (II), in a range from 5 to 23 ppm. Then, we put the samples in contact with the adsorbent for 15 min; at this stage, maximum adsorption in 20 ppm concentration of Pb (II) had taken place.

The effect of the pH on the metal adsorption for modified activated carbon was studied for pH 3, 4, 5, 6, 7, 8, 9, and 11, at which the material exhibits chemical stability.

The effect of activated carbon from walnut shells (ACW) dosage on the adsorption process was investigated by varying the sorbent dosage from 0.01 g-1 g of Pb (II) solution. The experiment was conducted by measuring 20 ppm of Pb (II) solution. Appropriate dosage of the ACW was measured into the sample and sample was agitated for 15-240 min.

2.3. Isotherm modeling

According to the Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent, and once an adsorbate occupies a site, no further adsorption can take place at this site. Thus, the Langmuir model is given by equation [6].

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{bq_{\max}} \quad (2)$$

where $q_{\max}$ and b , the Langmuir constants, are the saturated monolayer adsorption capacity and the adsorption equilibrium constant, respectively. A plot of C_e/q_e versus C_e would result in a straight line with a slope of $(1/q_{\max})$ and intercept of $1/bq_{\max}$. The Langmuir parameters can be used to predict the affinity between the sorbate and the adsorbent using the dimensionless separation factor R_L :

$$R_L = \frac{1}{(1 + bC_0)} \quad (3)$$

The R_L value indicates the shape of the isotherm, as follows [7]:

$R_L > 1$ Unfavorable

$R_L = 1$ Linear

$0 < R_L < 1$ Favorable

$R_L = 0$ Irreversible

The Freundlich model stipulates that the ratio of solute adsorbed to the solute concentration is a function of the solution. The empirical model was shown to be consistent with an exponential distribution of active centers, characteristic of heterogeneous surfaces. The amount of Pb (II) adsorbed onto the modified ACW at equilibrium, q_e , is related to the concentration of Pb (II) in the solution, C_e , following [8]:

$$q_e = K_f C_e^{1/n} \quad (4)$$

This expression can be linearized to give

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

where K_f and n are the Freundlich constants, which represent adsorption capacity and adsorption intensity, respectively. A plot of $\ln q_e$ versus $\ln C_e$ would result in a straight line with a slope of $(1/n)$ and intercept of $\ln K_f$.

The Dubinin-Radushkevich (D-R) isotherm was employed in the following linear form [9]:

$$\ln q_e = \ln Q_m - K \varepsilon^2 \quad (6)$$

The Polanyi potential ε , can be expressed as

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (7)$$

The Temkin equation suggests a linear decrease of sorption energy as the degree of completion of the sorptional centers of an adsorbent is increased. The Temkin isotherm has been generally applied in the following form [10,11]:

$$q_e = B \ln A + B \ln C_e \quad (8)$$

where $B=RT/b$, R is the gas constant, b is the Temkin isotherm constant, T is the absolute temperature (K), and A is the Temkin isotherm constant (L/mg). Therefore, by plotting q_e versus $\ln C_e$, one can determine the constants A and B .

3. Results and Discussion

3.1. Adsorption isotherms

A list of the parameters obtained, together with the R^2 values, is given in Table 1. The experimental results were analyzed by using Langmuir, Freundlich, Tempkin, and D-R isotherm models. The correlation coefficients for the Langmuir and Tempkin equations fitted better than those of the Freundlich and D-R equations for activated carbon modified by H₃PO₄; the correlation coefficients for the Langmuir and D-R equations fitted better than those of the Freundlich and Tempkin equations for activated carbon modified by K₂CO₃. The experimental data indicate that the adsorption isotherms are well described by the

Table 1. Comparison of the coefficients isotherm parameters for adsorption of Pb (II) onto activated carbon modified by H₃PO₄ and K₂CO₃

Isotherm	Constant parameters	H ₃ PO ₄	K ₂ CO ₃
Langmuir	$q_{max} \text{ (mg/g)}$	14.43	58.82
	$K_L \text{ (Lit/mg)}$	0.121	1.062
	R_L	0.282	0.039
	R^2	0.982	0.936
Freundlich	K_F	2.112	7.87
	n	1.763	1.424
	R^2	0.948	0.891
Temkin	$A \text{ (Lit/mg)}$	1.271	2.267
	$b \text{ (J/mg)}$	822.21	269.1
	R^2	0.981	0.873
Dubinin-Radushkevich	$K \text{ (J}^2\text{)}$	1×10^{-6}	1.9×10^{-4}
	$q_m \text{ (mg/g)}$	7.760	28.022
	R^2	0.946	0.932

Langmuir isotherm equation and that the calculated adsorption capacity of activated carbon was 14.43 (mg/g) at 25°C for activated carbon modified by H₃PO₄ and 58.82 (mg/g) for activated carbon modified by K₂CO₃. Based on the data in Table 1, it is clear that the correlation coefficient R_L is comparatively higher than R_F , R_T , and $R_{(D-R)}$. The value of R_L for the adsorption of Pb (II) with activated carbon modified by H₃PO₄ was 0.282 and the value of R_L for the adsorption of Pb (II) with activated carbon modified by K₂CO₃ was 0.039. These values indicate that the adsorption behavior of activated carbon was favorable.

3.2. Adsorption kinetics

In order to elucidate the mechanisms and the possible rates of solute adsorption of solutions, different kinetic models have been applied.

The pseudo first-order equation was presented by Lagergren [9] for the sorption of oxalic acid and malonic acid onto charcoal. Afterwards, many researchers reported first order Lagergren kinetics for adsorption of different pollutants on different sorbents [13]. The linearized form of the pseudo first-order equation of Lagergren is generally expressed as follows [14]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (9)$$

where q_t is the amount of Pb (II) adsorbed (mg/g) at time t , k_1 is the equilibrium rate constant of the pseudo-first order kinetics (min^{-1}), and t is the constant time (min). According to Eq. (9), the plots of $\ln(q_e - q_t)$ vs. t for the adsorption of Pb (II) onto ACW were also tested in order to obtain the rate parameters.

The linearized form of the pseudo- second order chemisorptions kinetic rate equation is presented below [15-18]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

where k_2 (g/mg min) is the rate constant for the pseudo- second order adsorption. The intercept and slope of $\frac{t}{q_t}$ vs. t (Figs. 1 and 2) were used to calculate the pseudo- second order rate constants k_2 and q_e , respectively.

Fig. 1. Fitting of pseudo- second order model for Pb (II) on activated carbon modified by K₂CO₃.

Fig. 2. Fitting of pseudo- second order model for Pb (II) on activated carbon modified by H_3PO_4 .

Fig. 3. Effect of pH on the adsorption of Pb (II) on activated carbon modified by K_2CO_3 .

The results obtained from these studies were analyzed by using pseudo- first order and pseudo- second order kinetic models. The calculated q_e values agree very well with the experimental data; also, the correlation coefficients for the second-order kinetic model are higher than 0.99 in all cases for activated carbon modified by K_2CO_3 and H_3PO_4 . These results indicate that the adsorption of acid dyes from wastewater onto activated carbon obeys the pseudo- second order kinetic model.

3.3. Effect of pH

The pH level of the aqueous solution is an important variable for the adsorption of metals onto the adsorbent. The effect of the pH on Pb (II) adsorption by activated carbon modified was studied for pH 3, 4, 5, 6, 7, 8, 9, and 11, at which the material exhibits chemical stability. The efficiency of Pb (II) sorption depends on the pH level of the aqueous solutions. The various influences of pH on the adsorption of Pb (II) onto modified activated carbon are shown in Figs. 3 and 4. It is apparent that using the solution at $\text{pH} > 1$ gives the highest removal of Pb (II) on activated carbon modified by K_2CO_3 . We can see that the adsorption capacity is low at $\text{pH} < 1$ and that Pb (II) adsorption decreases with the pH decrease from 4 to 8

Fig. 4. Effect of pH on the adsorption of Pb (II) on activated carbon modified by H_3PO_4 .

Fig. 5. The effect of the initial Pb (II) concentration.

Pb (II) on activated carbon modified by K_2CO_3 . The amount of adsorbed Pb (II) is at its minimum rate at $\text{pH} > 6$ on activated carbon modified by H_3PO_4 ; the maximum adsorption capacities were calculated at $\text{pH} = 5$.

3.4. Effect of contact time

The effect of contact time on the amount of Pb (II) adsorbed per gram of ACW by H_3PO_4 and K_2CO_3 was investigated. Equilibrium is reached after 15 min of immersion; the adsorption process is a relatively fast one.

The maximum adsorption, mentioned above, is due to the following factors:

- 1) Reduction of the weight of activated carbon
- 2) Reduction in the speed of pore development
- 3) Filling of pores during the activation time

3.5. Effect of initial Pb (II) concentration

The effect of initial dye concentration has been studied and results are presented in Fig. 5. These results show the effect of the Pb (II) concentration on the adsorption of the different levels of Pb (II) at pH 5. The figure shows that the amount of Pb

Fig. 6. Effect of adsorption dosage on adsorption Pb (II).

(II) adsorbed increases with increasing concentration and then tends to level off. The maximum milligrams per gram of Pb (II) adsorption is 8.23.

3.6. Effect of sorbent dosage

Fig. 6 shows the effect of ACW according to H_3PO_4 and K_2CO_3 dose on the removal percentage of Pb (II). The effect of ACW dosage on the adsorption process was investigated by varying the sorbent dosage from 0.01-1 g of Pb (II) solution. The experiment was conducted by measuring 20 ppm of Pb (II) solution. The appropriate dosage of ACW was measured in and sample was agitated for 15-240 min. Samples were withdrawn at fixed intervals and analyzed for residual Pb (II); the amount of sorbate sorbed per unit mass of the ACW was calculated by using the mass balance procedure.

4. Conclusions

Activated carbon adsorption of metallic ions (mainly Pb (II)), at levels similar to or even better than those obtained using commercial products, was performed by chemical activation of walnut shells.

The results show that as the amount of the adsorbent increased, the percentage of Pb (II) removal increased accordingly.

The optimum pH value for lead adsorption was determined to be 5. The maximum removal of Pb (II) was obtained at pH 5, at a level of 98.84% for activated carbon modified by H_3PO_4 and 99.03% for activated carbon modified by K_2CO_3 ; the adsorbent dose was 0.05 g and the initial Pb (II) concentration at room temperature was 20 mg/L.

The experimental results were analyzed using Langmuir, Freundlich, Tempkin and D-R isotherm models. The correlation coefficients for the Langmuir and Tempkin equations fitted better than those of the Freundlich and D-R equations for the activated carbon modified by H_3PO_4 and the correlation coefficients for Langmuir and D-R equations fitted better than Freundlich and Tempkin equations for the activated carbon modified by K_2CO_3 .

The results of this investigation show that activated carbon modified by H_3PO_4 and K_2CO_3 has a suitable adsorption capacity for the removal of Pb (II) from aqueous solutions.

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