

Original Article

Adsorption Efficiency of Iron Modified Carbons for Removal of Pb(II) Ions from Aqueous Solution

Mohammad Hossein Salmani¹, Mohammad Abedi^{*1}, Seyed Ahmad Mozaffari¹

¹. Department of Chemical Technologies, Iranian Research Organization for Science and Technology (IROST), Tehran, Iran

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Abstract

Introduction: The Lead causes severe damage to several systems of the body, especially to bony tissues. Until now, several low-cost biosorbents have been studied for removal of heavy metal ions from aqueous solutions. In the present study, carbonized pomegranate peels were modified with Fe²⁺ and Fe³⁺ ions and then removal of Pb(II) ions from aqueous solution was investigated.

Materials & Methods: the washed granola of pomegranate peel was separately soaked with FeCl₃ and FeCl₂ solutions for 24 h. Then, the granules were carbonized at 400 °C for 3 h in a programmable furnace in the atmosphere of nitrogen. The adsorption experiments were carried out for two types of iron-modified carbons by batch adsorption procedures using one variable at a time.

Results: The optimum conditions included contact time 90 min, initial concentration 50 mg/l, and adsorbent dose, 1.0 g/100 ml solution. Maximum removal efficiency was calculated as 80% and 90% for Fe³⁺ and Fe²⁺ impregnated pomegranate peel carbons, respectively. The maximum adsorption capacity estimated by means of the Langmuir model was 34.5 and 17.8 mg.g⁻¹ for two adsorbents.

Conclusion: The surfaces of iron treatment pomegranate peel carbons were well modified for adsorption of heavy metals. The results showed that chemical modification of the low-cost adsorbents originating from agricultural waste has stood out for lead removal capabilities.

Keywords: Adsorption, Iron modified carbon, Pomegranate peel, Pb removal, Equilibrium Isotherm

* Corresponding author; Tel: 02156276631 email:mabedi50@yahoo.com;

Introduction

Lead is one of the major pollutants, highly toxic to humans, plants, and animals. The presence of lead in drinking water causes severe damage to the kidney, nervous system, reproductive system, liver, brain, and bony tissues [1-3]. The maximum threshold limit of 0.015 mg/l for Pb^{2+} in drinking water was approved by the Environmental Protection Agency (EPA). It is important to remove it from contaminated water before its discharge into the environment. Many traditional methods such as coagulation, electrolytic deposition, reverse osmosis, and ion exchange were applied to remove heavy metals from solutions. One of the most efficient and economical methods for removal of ionic pollutants from wastewaters is adsorption. However, the cost of used adsorbents and their separation from water phase after adsorption are the most important restricting factors in applicability of adsorption process. In recent years, considerable attention has been paid to the development of alternatives from cheaper and readily available materials and agricultural wastes for preparation of activated carbon to remove pollutants to approach the standard levels [4, 5]. Until now, several low-cost agricultural biosorbents, including pineapple fiber [6], ocoa pod husk [7], potato peel [8], modified onion skins [9], the carbon of walnut, hazelnut, almond, pistachio shell, and apricot stone [10] have been explored for removal of $Pb(II)$ ions from aqueous solutions.

Pomegranate peels as an industrial waste is produced in large scales in Iran. Pomegranate fruits are widely processed into juice, jams,

syrup, and sauce. The non edible portion (peel) of fruit is about 40–45% of its total weight. Therefore, the idea to change the wastes of pomegranate manufacturing products to activated carbon for cleaning the environment is valuable. Previous study conducted by El-Ashtouky et al., used the raw pomegranate peel, activated carbon prepared from pomegranate peel (AC1), and chemically-treated pomegranate peel (AC2) for removal of lead(II) and copper(II) from aqueous solution [11]. Abedi et al., presented a new chemical method for preparation of activated carbon from pomegranate peel by impregnation of Fe^{2+} and Fe^{3+} ions and applied them for removal of $Cd(II)$ ions from aqueous solutions [12].

The main objective of this research was to use iron modified pomegranate peel carbons for removal of $Pb(II)$ ions from aqueous solution after optimization of adsorption process by one factor at a time methodology.

Materials and Methods

This descriptive study was performed in the laboratory scale. The stock solution of 1000 mg/l $Pb(II)$ ions was prepared from lead nitrate in distilled water. The treatment of pomegranate peels was performed by $FeCl_3$ and $FeCl_2$ solutions. Standard and working solutions for adsorption experiments were prepared from the stock solution of 1000 mg/l through dilution with 1% (v/v) HNO_3 . The concentrations of Pb^{2+} in all solution were determined by atomic absorption spectrometer.

Pomegranate peels were prepared from Nodoushan farm in Yazd province, Iran. They were dried at 27° C in the absence of sunlight and sieved in the size range of 0.6–2.0 mm. To modify it, 20 g of dried granules were separately soaked with 20 ml of 0.1 M FeCl₃ or FeCl₂ solutions at 25 °C for 24 h. Then, the granules were carbonized at a temperature of 400 °C for 3 h in the atmosphere of nitrogen. The mixture was washed several times with distilled water to remove any excess ions from the produced activated carbons. Finally, the iron modified pomegranate peel activated carbons were dried at 100 °C and kept for further uses.

Batch adsorption experiments were conducted by closed containers using orbital shaker. To obtain the optimize conditions the effect of initial Pb(II) concentration, adsorbent dose, and volume of Pb(II) solution were determined at temperature (25 °C) based on the following experiments. The effect of initial Pb(II) concentration was studied using 0.5 g of activated carbon and 100 ml of different concentrations of Pb(II) solution in the range of 10 to 100 mg/l in the screw-capped containers. The influence of adsorbent dose on Pb(II) adsorption was determined by taking 50 ml of 50 mg/l of Pb(II) solutions and shaking with varying amounts of adsorbents ranging from 0.1 to 1.5 g. The effect of volume of Pb(II) solution was carried out by taking different volumes of 50 mg/l Pb(II) solution using 0.10 g of adsorbents in the range of 50 to 200 ml. In each step, the solids were separated using filters and the absorbance of the clear liquid was analyzed by flame atomic

absorption spectrometer at a maximum wavelength of 283.3 nm. Then, the plot of adsorption chose the optimum amount of each factor efficiency via parameter changes.

All of the experiments were carried out at an initial solution pH of 6.5 and fixed in 150 RPM shaking rate. At the end of the experiments, removal efficiency (RE) was determined as follows:

$$RE = (C_0 - C_t) \times \frac{100}{C_0} \quad (3)$$

Where C₀ and C_t are ion concentrations (mg/l) at initial and time t, respectively.

In order to evaluate the equilibrium adsorptive behavior, a satisfactory selection of isothermal model was examined. Several important two-variable isotherms were available to design the adsorption systems [13]. The most common isotherm models are the Langmuir and Freundlich isotherm that were considered in this study. The linear form of the Langmuir isotherm models is described as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (1)$$

Where K_L is the Langmuir constant related to the energy of adsorption and q_m is the maximum adsorption capacity (mg/g).

The linear form of Freundlich equation is expressed as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

Where K_F and n are Freundlich isotherm constants related to adsorption capacity and adsorption intensity, respectively, and C_e is the equilibrium concentration (mg/l).

Results

SEM of adsorbents

The SEM photograph of impregnation of Fe^{2+} ions pomegranate peel carbon is shown in Fig 1. The morphology of adsorbent was

homogenous with small porous based on the SEM photograph.

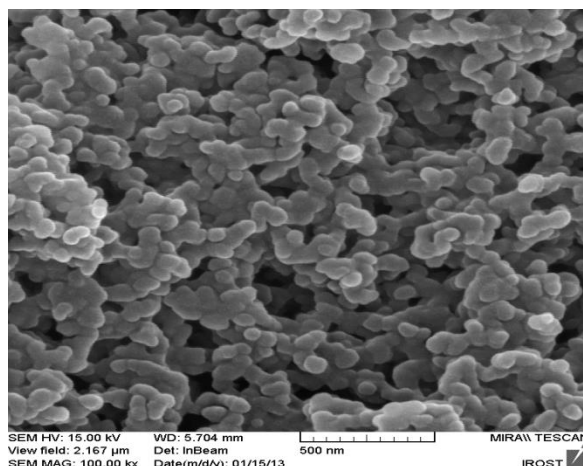


Figure 1. SEM images of iron modified pomegranate peel carbon (Fe-PPC)

Effect of contact time

The time required for the adsorbate concentration to reach a constant value during the adsorption process was defined as the adsorption equilibrium time. Fig. 2

demonstrates the results of experiments conducted to determine the equilibrium time required for the uptake of Pb(II) ions by the two adsorbents.

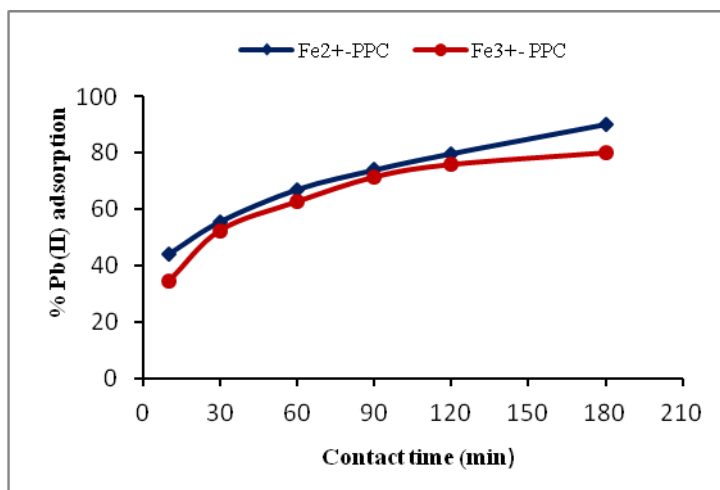


Figure 2. The effect of contact time on Pb(II) adsorption by iron modified pomegranate peel carbons (Fe^{2+} PPC and Fe^{3+} PPC)

For Fe^{2+} -PPC and Fe^{3+} -PPC, 53% and 56 % of lead were adsorbed in the first 30 min, respectively. The maximum uptake of metal ions for Fe^{2+} -PPC and Fe^{3+} -PPC increased to 80% and 90% after 180 min of contact time.

Effect of initial Pb(II) concentration

Fig. 3 represents the effect of initial Pb(II) concentrations of 10 to 100 mg/l in aqueous solution on adsorption efficiency at pH of 6.5.

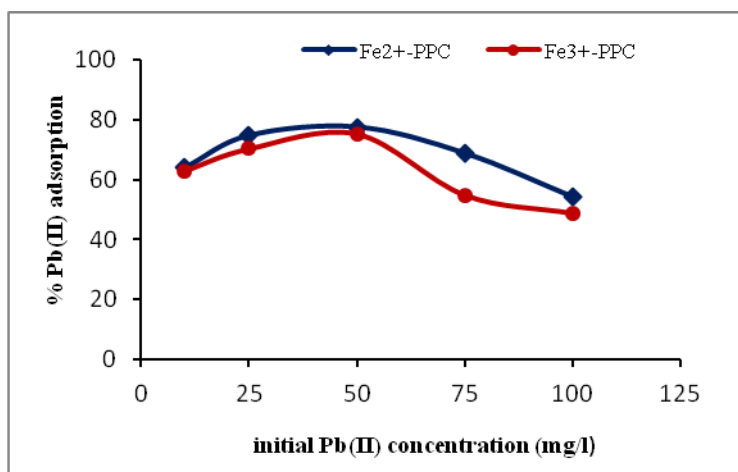


Figure 3. The effect of initial Pb(II) concentration on Pb(II) adsorption by iron modified pomegranate peel carbons (Fe²⁺PPC and Fe³⁺PPC)

As it can be seen, the adsorption efficiency of Pb(II) increased from 64% to 78% for Fe²⁺-PPC and 63% to 75% for Fe³⁺-PPC until 50 mg/l, but it decreased to 49% and 55% by increasing in initial Pb(II) concentration from 50 to 100 mg/l.

Effect of adsorbent dose

The influence of adsorbent dose on the adsorption process at constant initial Pb(II) concentration was studied to obtain the right adsorbent mass. Fig. 4 represents the plot of Pb (II) adsorption versus adsorbent doses.

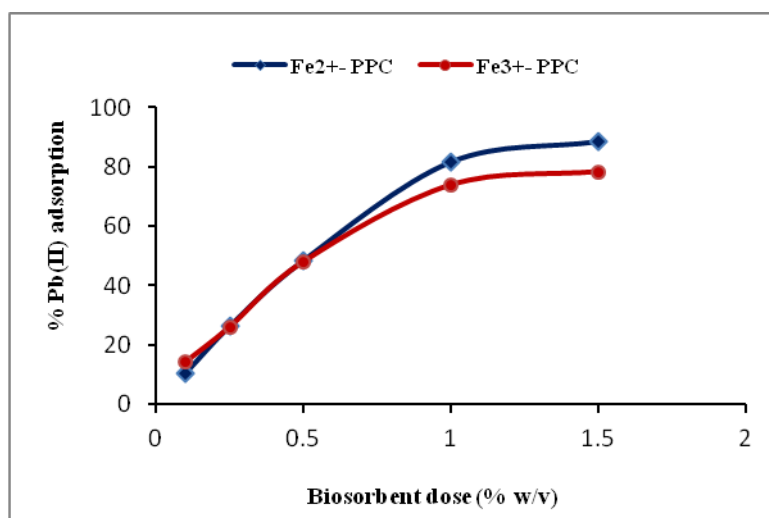


Figure 4. The effect of biosorbent dose on Pb(II) adsorption by iron modified pomegranate peel carbons (Fe²⁺PPC and Fe³⁺PPC)

The adsorption of Pb(II) increased from 10% and 14% to 88% and 78% with an increase in biosorbent dose from 0.10 to 1.50 w/v% for Fe²⁺-PPC and Fe³⁺-PPC, respectively.

Effect of solution volume

From Fig. 5, it is evident that Pb(II) adsorption decreased with increasing solution volume for both adsorbents. As it is observed, the adsorption efficiency of Pb(II) ions decreased from 82.1% to 46% for Fe²⁺-PPC, and 72% to

45% for Fe³⁺-PPC with an increase in volume from 50 to 200 ml.

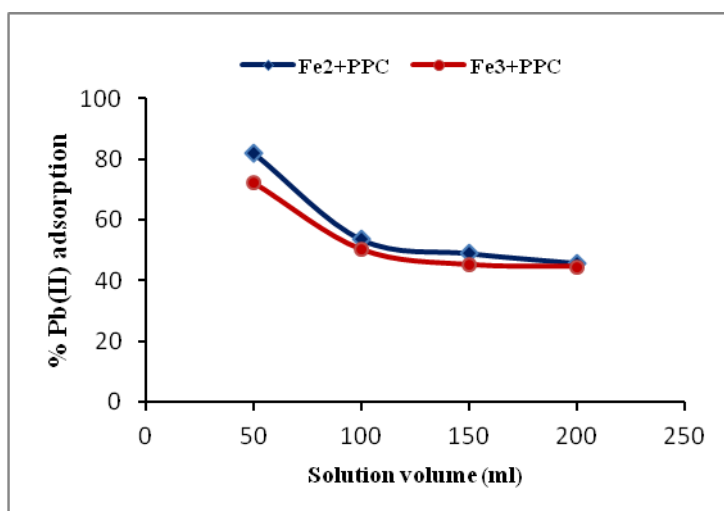


Figure 5. The effect of solution volume on Pb(II) adsorption by iron modified pomegranate peel carbons (Fe²⁺PPC and Fe³⁺PPC)

Actually, by increasing solution volume, the adsorption efficiency decreased for both adsorbents. When solution volume increased up to 100 ml, the removal percentage of Pb(II) reached to nearly 50% for Fe³⁺-PPC and Fe²⁺-PPC, hence, the volume of 100 ml was chosen as the optimum solution volume.

Adsorption isotherm

Various isotherm models are used for evaluation of the equilibrium adsorption process. The equilibrium data of the two models were calculated from equations (1) and (2) and are then summarized in Table 1.

Table 1. The equilibrium adsorption data for Pb(II) ions on iron modified pomegranate peel activated carbons

Adsorbent	Langmuir			Freundlich		
	q _m	b	R ²	n	K _F	R ²
Fe ²⁺ PPC	34.5	0.58	0.958	3.14	2.46	0.922
Fe ³⁺ PPC	17.8	0.10	0.960	1.14	1.54	0.947

Discussion

The SEM image (Fig. 1) illustrated that the treated PPC has regular surfaces with some nano pores. It is also indicated that iron modified PPC causes an increasing number of particles on the surface and develops their porosity of modified adsorbent, consequently, the active surfaces of carbon particles is enhanced.

The adsorption process depends on various factors such as pH, temperature, adsorbent dose, concentration of pollutant, adsorbent type, contact time, and agitation time. In this study, the factors of initial lead concentration, adsorbent dose, and solution volume were screened for removal of Pb(II) ions by Fe²⁺ and Fe³⁺ impregnated PPC adsorbents.

According to Fig. 2, the rate of Pb(II) adsorption was fast in the beginning times (first 30 min) due to the enough available surface area on the adsorbent. As the time increased (> 30 min), more amount of Pb(II) adsorbed onto the active sites on the adsorbent surface by attraction forces and caused a decrease in available surface areas on adsorbent [14]. In general, about 70% of the total Pb(II) adsorption was achieved within 90 min. Therefore, in subsequent experiments, 90 min was selected as the contact time.

The two states of Pb(II) adsorption (Fig 3) indicated that from 0-50 mg/l the adsorption capacity increased due to the existence of unoccupied adsorption sites on both adsorbents, but from 50-100 mg/l the adsorption sites gradually saturated and the additional concentration of Pb(II) remained in solution. Therefore, the efficiency of adsorption decreased.

The effect of adsorbent mass on removal efficiency at constant Pb(II) concentration is shown in Fig. 4. It indicates that the adsorption efficiency of Pb²⁺ ions increased with increasing mass of the adsorbents. This is due to the existence of more available sites on the surface of biosorbents at higher doses and the fact that some adsorption sites remained unsaturated during the adsorption process [15]. The adsorption efficiency of Pb²⁺ ions was marginal to 81% and 74% for Fe²⁺-PPC and Fe³⁺-PPC, respectively, when adsorbent dose increased from 1.0 to 1.5 % w/v. This drop in the adsorbed amount per unit mass of adsorbent is a normal behavior which has also been reported by Acharya et al. [16]. Hence, all other experiments were conducted at optimum value of 1% w/v of adsorbent dose.

Comparing the maximum adsorption capacities of Fe-PPCs for Pb(II) ions with other adsorbents is presented in Table 2.

Table 2 Comparison of adsorption capacities of Fe-PPC with those of various adsorbents for removal of Pb(II) ions from aqueous solutions

Adsorbent	q _m (mg/g)	Ref.
Commercial activated carbon	5.9	[17]
Kaolinite	7.7	[18]
Coffee residue	63.0	[19]
Tea leaves	78.7	[20]
Palm shell carbon	86.0	[21]
Orange peel modified with NaOH	20.8	[22]
Activated carbon	9.4	[16]
Fe ³⁺ -PPC	17.8	This work
Fe ²⁺ -PPC	34.5	This work

The direct comparison of adsorption efficiency of adsorbents is difficult due to the difference in the experimental conditions. The adsorption

capacity of Fe-PPCs was compared to the other low-cost adsorbents to suggest their ability of Pb(II) ions removal from

contaminated wastewater. Among these adsorbents, the pomegranate peel carbon modified with Fe^{2+} had an acceptable adsorption capacity (34.5 mg/g) for Pb(II) ions. This can be attributed to the presence of chelating functional groups such as carboxyl, phenol, and hydroxyl on the surface of Fe^{2+} -PPC, which possess high affinity for removal of Pb(II) ions.

Obtaining of the equilibrium data is essential to develop an equation for designing the system and for understanding the mechanism of process by fitting the experimental data to adsorption isotherm models. The most common isotherm models are Langmuir and Freundlich models. The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place on that site. As such, the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The Freundlich isotherm is applicable to both monolayer and multilayer

adsorption and is based on the assumption that the adsorbates adsorb onto the heterogeneous surface of comparison between the correlation coefficients of two models, concluded that the Langmuir equation provides better results for the adsorption system. The maximum adsorption capacity estimated by means of the Langmuir model was 34.5 and 17.8 mg.g^{-1} for Fe^{2+} PPC and Fe^{3+} PPC, respectively.

Conclusion

The treatment of pomegranate peels with Fe^{2+} and Fe^{3+} solutions and the carbonization at 400°C modified their surfaces for adsorption of heavy metals. The batch experiments of Pb(II) ions adsorption on iron modified pomegranate carbons operated in the pH of 6.0 – 6.5. The maximum removal efficiency of Pb(II) ions under optimum conditions was 84% and 89% for Fe^{3+} -PPC and Fe^{2+} -PPC, respectively. It is evident that after conversion into activated carbon and chemical modification of the low-cost adsorbents originating from agricultural waste has stood out for metal removal capabilities.

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