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Removal of Lead Ions from Simulated Industrial Wastewater by Using Activated Carbon Produced From Heavy Oil Fly Ash

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Abstract

The disposal of industrial waste has become a significant environmental issue. In this work, industrial waste, heavy oil fly ash (HOFA) produced from burning heavy oil in the power station was investigated to produce activated carbon (AC) as adsorbent from modified HOFA for lead removal. Batch experiments of lead removal were conducted at a different adsorbent dose and time contact. Equilibrium isotherm results with a good match in with Freundlich model with R^2=0.971 which shows the heterogeneous surface of adsorbent and multilayer of adsorbate on the surface of (AC). A maximum adsorption capacity of 10mg/g at equilibrium was achieved. Kinetic study showed rapid adsorption at first 60min, with good matching to second order pseudo model with R^2=0.9998 and this equalized to experimental and theoretical adsorption capacity, which refers to chemisorption process.

Paper type: Research paper

Keywords: Heavy oil fly ash, lead, adsorption isotherm, adsorption kinetics.

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Introduction

One of the globally important issues is nowadays posing danger to human living is environmental pollution. The heavy metals released from solid and liquid materials pollute our environment and pose a risk to public health (Padmavathy *et al.*, 2016). The concentrations of heavy metals in materials are deemed very low (ppb range of less than 10 ppm), therefore they consider trace elements. Heavy metals are considered metallic elements that have a high density that is widespread and non-biodegradable (Atieh *et al.*, 2017). Heavy metals are widely known, including chromium, lead, mercury, cadmium, and arsenic), their usage and concentrations in the environment are increasing (Alguacil *et al.*, 2018). Industrial processes use lead in various ways. Lead may stay in the environment for a long period and it is very dangerous for living systems because it is persistent. A hazardous element is a lead. The existence of Pb as free radicals causes damage to the living system. Lead exposure is also noted to produce reactive nitrogen species which are found to play a significant role in hypertension incidence (Wu *et al.*, 2016). Adsorption technology is considered the best method for removing organic and inorganic contaminants from an aqueous solution (Al-Wahbi, 2018). Adsorption was superior to other techniques for water reuse in terms of simplicity of design, initial cost, ease of operation, and insensitivity to toxic substances (El Qada, 2020). The most important part of the information is the equilibrium information. Adequate explanation and understanding of adsorption isotherms are important for the overall improvement of adsorption mechanism pathways and the beneficial design of the adsorption system (Ayawei *et al.*, 2017). The mechanisms of adsorption can be classified according to adsorption nature physically or chemically. Adsorption with physical behavior results from Wan der Waals forces. The surface of the adsorbent and the properties of the adsorbed material such as (molecular size and mass and boiling) play as factors that can affect the capacity of adsorption.

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In this present study, activated carbon (AC) produced from modified heavy oil fly ash (HOFA) was chosen as the low-cost adsorbent. Finally, efforts must be made to control pollution resulting from waste disposal by converting these unwanted wastes to usable raw material for various beneficial uses. Therefore, the objectives of this work are: studying the effect of adsorbent mass and contact time on the removal of lead from polluted water and investigating the adsorption using equilibrium isotherm models and the rate of adsorption during kinetic conditions.

1 Materials and Methods

1.1 Preparation of activated carbon

Raw heavy oil flies ash as adsorbent had been collected from electro-static precipitator (ESP) power plant south Baghdad for this experiment. This material is processed to remove impurities through washing and leaching. The chemicals used in the washing and leaching process are 28 percent of nitric acid and 15 percent of hydrochloric acid. A 10g of heavy oil fly ash was treated with 50ml of aqueous nitric acid solution at 60°C for 2h. The magnetic bar was placed in the solution and stirred continuously at the speed of 200rpm. The filtrate material was washed to remove NO^{3-} ions many times with distilled water till the pH of the material reach 7. After that, the filtrate material was mixed with 15 percent of hydrochloric acid at 60°C for 1h. Then washing process for filtrate with distilled water several times to remove chloride ions and dried at 100°C for 5h to get unburned carbon. Dry unburned carbon was activated by mixing with phosphoric acid at 80 °C for 30 minutes, and then the material got was placed in an oven for drying at 100 °C for 5h. After this process, the carbonization process applies to the material at 800 with a heat rate 5°C/min with a constant nitrogen flow of 5ml/ min. In the carbonization process, all organic material is converted into carbon at high temperatures and eliminated the volatile materials from the material. Then the calcined material was mixed with 0.5N of hydrochloric acid at 80°C for 30min. The filtrate material which is activated carbon was washed till the pH reached 7 and then dried at 100°C for 5h. The whole method was taken from Mofarrah *et al.*, 2014 when they studied converted fly ash to activated carbon.

1.2 Adsorption studies experiments

Adsorption studies were achieved by batch technique to get removal of lead and the adsorption capacity of activated carbon produced from HOFA. The stock solution of 1000mg/l of lead by dissolving of 0.8g of Pb $(NO3)_2$ in distilled water 500ml in acidic condition. Equilibrium experiments were conducted using 25mg/l lead, which was diluted from the concentrated solution. The percentage removal of lead was calculated from equation (1) and equation calculated the adsorption capacity of adsorbent (2) (Shehata *et al.*, 2003).

$$\% \, Removal = (Ci - Ce) * \frac{100}{Ci} \quad (1)$$

$$\% \, qe = \frac{Ci - Ce}{m} * V \quad (2)$$

Where Ci and Ce are the initial and equilibrium of lead in mg/l before and after adsorption, m, is the amount of the adsorbent in gram. V, is the volume of the sample in ml. The activated HOFA dosages were (0.05, 0.1, 0.3, 0.6, 1g) added to 5 samples contain 50ml of the aqueous solutions of 25ppm of lead. The contact time was 4 hours at temperature 25°C and agitation speed 250rpm. 500ml of aqueous solution of 25ppm of lead was taken in a 1000ml beaker and add 2.5g of adsorbent. The sampling were achieved at interval times (5, 10, 15, 30, 60, 120, 180, 240) min with agitation speed 250rpm using magnetic stirrer.

1.3 Adsorption isotherm

Langmuir and Freundlich are well known for several equilibrium models have been developed to describe adsorption isotherm relationships. Langmuir and Freundlich isotherm formulas were used to analyze the data (Astuti *et al.*, 2021). Langmuir isotherm applies to characterize adsorbent heavy metal sorption. Maximum adsorption potential that corresponds to the monolayer coverage completely on the surface, where the complete saturation of monolayer is given by the linear Langmuir equation (Foo and Hameed 2010).

$$\frac{C_e}{q_e} = \frac{1}{k_l q} + \frac{C_e}{q} \quad (3)$$

Where C_e, is the equilibrium concentration (mg/l), q_e, is the amount of metal ion adsorbed (mg/g). The q, is the amount adsorbed at a complete monolayer (mg/g) and k_l, is the adsorption energy parameter. Freundlich isotherm is an empirical equation that

uses isotherms to characterize adsorption equilibrium. Freundlich isotherm is commonly used to describe the adsorption of adsorbate on a wide range of adsorbents. The expression of the Freundlich equation is shown below (Foo and Hameed 2010).

$$q_e = k_f C_e{}^{1/n} \tag{4}$$

The equation of the linear form can be written as

$$logq_e = logk_f + \frac{1}{n} logC_e \tag{5}$$

Where k, and n are the constants of Freundlich related to the adsorption capacity and the adsorption intensity, respectively. The intercept and the slope of the linear plot of log q_e versus log C_e, at given empirical conditions give the values of k_f and 1/n, respectively.

1.4 Adsorption kinetics

The pseudo-first and second-order equations were applied to modal the kinetics of lead ion adsorption onto Activated HOFA to investigate the mechanism of nature of adsorption processes such as mass transfer and chemical reaction.

1.4.1 Pseudo-first-order model

Lagergren introduces the first pseudo kinetic model (Vani *et al.*, 2012) as in the following equation:

$$\log(q_e - q_t) = logq_{th} - \frac{k_1}{2.303} * t \tag{6}$$

Where q_t (mg/g), and q_e (mg/g) is the amount of adsorbed ions per adsorbent mass at time t (min), and at equilibrium respectively, q_{th} theoretical mass of metal adsorbed ions per mass of adsorbent (mg/g), and k_1 is the rate constant of the pseudo-first-order adsorption (1/min) at equilibrium.

1.4.2 Pseudo-second-order model

The pseudo second order reaction describes the adsorption kinetics (Feddal *et al.*, 2013). The linearized integral form of the model is

$$\frac{t}{q_t} = \frac{1}{k_2 q_{th}{}^2} + \frac{t}{q_{th}} \tag{7}$$

Where $k_2$the pseudo second order is the rate constant of adsorption.

2 Results and Discussion

2.1 Adsorbent mass effect

The adsorbent mass effect on the lead removal was determined using variable quantities of Activated carbon produced from HOFA ranging from (0.05 to 1g) at fixed volume 50 ml with initial dye solution Ci of 100g/ml. Other parameters kept constant at 25°C, agitation speed 250rpm, contact time of 4h. The results are shown in **Figure 1**. The maximum adsorption of lead was obtained for adsorbent mass 1g. The removal of lead ions increases with the increasing mass of adsorbent because of more available adsorption sites which caused by increased surface area (Man *et al.*, 2012). The results illustrated that the optimum adsorbent mass of Activated HOFA at 1g, which represents adsorbent value for effective lead removal. Hence, 1g/0.1 liter was chosen as an optimal Activated HOFA mass for other experiments.

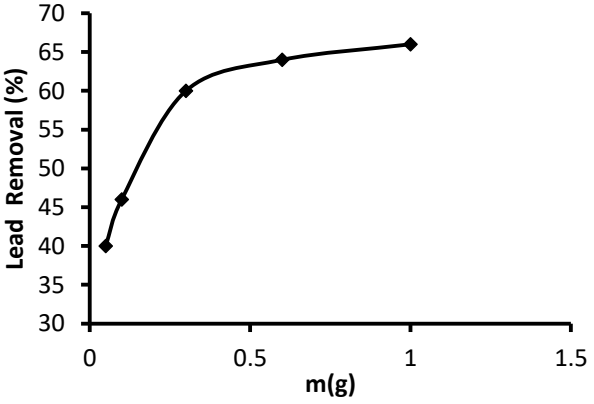

Fig. 1 Adsorbent mass effect on Lead removal.

The effect of equilibrium concentration of Activated carbon produced from HOFA is shown in **Figure 2**. It was observed that the adsorption capacity of Activated HOFA decline at increase adsorbent dosage. The maximum value of adsorption capacity (q_e=10mg/g) was achieved with low an adsorbent mass (0.05g~C_e=15mg/ml). In contrast, lowest adsorption capacity (q_e=0.8 mg/g) decreases as adsorbent mass increase (1g~C_e=8.5mg/ml). Further increment of adsorbent mass resulted in a decline in adsorption capacity. The similar trend was reported by Man *et al.*, (2012).

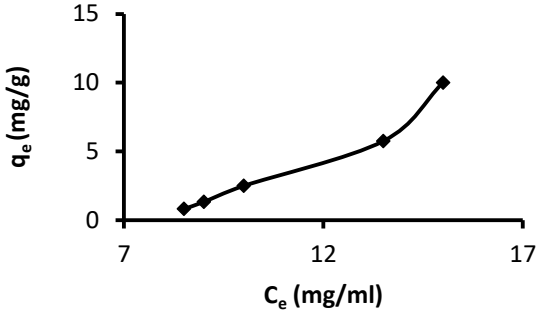

Fig. 2 Empirical equilibrium isotherm at different Activated HOFA mass.

In order to fitting the result of effect of mass by equilibrium, isotherm models (Langmuir and Freundlich) were the line plot of C_e vs $\frac{C_e}{q}$ for Langmuir and log q_e vs log C_e of Freundlich to estimate models' constants as shown in **Table 1,** where experimental results in **Figure 3** show more fitting with Freundlich model while invalid with Langmuir model due to negative slope which give unacceptable value. This refers to multilayer adsorption and heterogeneous surface of adsorbent.

Table 1 Values of Langmuir and Freundlich constant for lead adsorption isotherms.

Model	**Parameters**
Langmiur	k_l=-0.6634
	q_e=0.9156
	R^2=0.7717
Freundlich	k_f =1.9✗ 10^{-4}
	1/n=4
	R^2=0.971

2.2 Resident time effect

A 500ml aqueous solution of 25ppm concentration with 2.5g of Pb was agitated for various interaction times (from 5min to 240min). Best Pb adsorption had occurred at 60min. A higher removal rate was observed in the initial stages, and this can be related to the existence of sufficient surface adsorbent area at the initial stages of adsorb lead. When time increases, more ions of lead get adsorbed onto the surface of the Activated carbon. **Figure 4** shows lead removal with contact time and **Figure 5** shows adsorption capacity at intervals time.

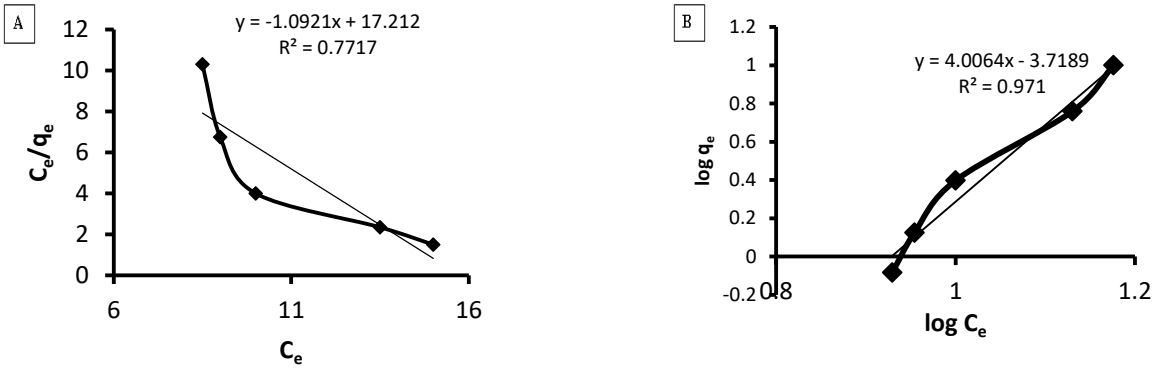

Fig. 3 Linearized isotherm for lead adsorption on Activated HOFA (A) Langmuir isotherm (B) Freundlich isotherm.

From the results of Fig. 5, the kinetic study has been achieved with kinetic models pseudo first and second order models by linear fitting. From log $(q_e - q_t)$ vs time and t/q_t vs time as shown in **Figures 6**, and **7** for pseudo-first and second order models (equations 6, and 7) respectively, the results show a better fit with pseudo second order than pseudo first order with R^2=0.9998 as shown in **Table 2**, and theoretical adsorption capacity q_{th}=3.637mg/g, which is approximately equal to the experimental adsorption capacity q_e=3.6mg/g, which is based on the assumption that the limiting step rate is chemi-sorption with valence forces that sharing or exchanging the electrons between Activated HOFA and lead solution (Ong *et al.*, 2010).While these results in agreement with previous works that corresponding of fitting second-order model of removal of lead by fly ash (Ishwardas, 2017).

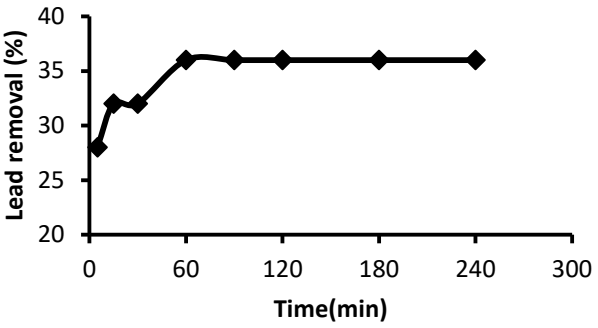

Fig 4. Effect of residence time on lead removal.

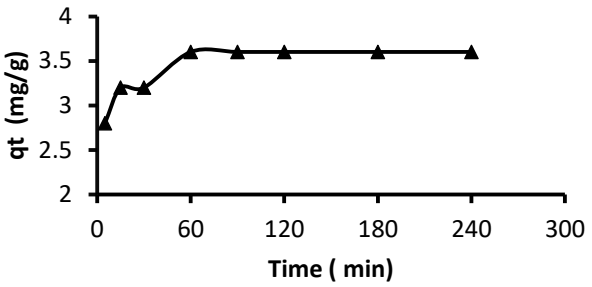

Fig 5 Effect of residence time on lead adsorption capacity.

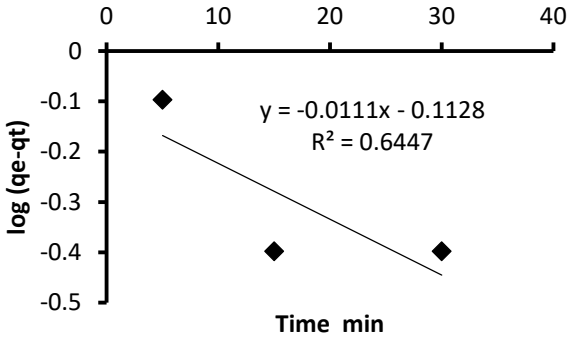

Fig.6 First order pseudo model linear formula

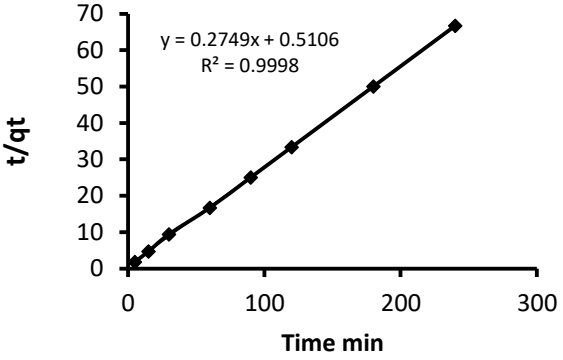

Fig.7 Second order pseudo model linear formula.

Conclusions

Table 2 Adsorption kinetics parameters of lead on AC.

Model	**Parameters**
Pseudo first order kinetic	k_1 = 0.02556 (min^{-1})
	q^{th}= 0.975 (mg/g)
	R^2= 0.6447
Pseudo second order kinetic	k_2= 0.148 (g/(mg min))
	q^{th}= 3.637 (mg/g)
	R^2= 0.9998

Activated carbon produced from heavy oil fly ash was used as adsorbent for lead ions removing from simulated waste water. Studies kinetic on parameters for adsorption of heavy metal Pb ions from an aqueous solution. The removal of lead ions increases with the increasing mass of adsorbent to 1g. One hour is the optimum time for lead ion adsorption. The kinetic study revealed that Pb adsorption obeys the pseudo-second-order kinetics as chemisorptions of Pb^{+2} ions by activated HOFA with square correlation coefficient R^2=0.9998. Theoretical adsorption capacity 3.637mg/g while the experimental obtained was 3.6mg/g and the equilibrium data were in good consistent with Freundlich equilibrium isotherm model as multilayer adsorption on heterogeneous adsorbent's surface.

Nomenclature

Ci	=initial concentration	[mg/l]
Ce	=equilibrium concentration	[mg/l]
q_e	=the amount of metal ion adsorbed per mass of adsorbent	[mg/g]
m	=the amount of the adsorbent	[g]
V	=the volume of the sample	[ml]
q	=the amount adsorbed per mass of adsorbent at a complete monolayer	[mg/g]
k_l	=Langmuir constant	[l/mg]
k_f	=Freundlich constant	[mg/g]
n	=Freundlich intensity constant	[-]
t	=time	[min]
q_t	=the amount of adsorbed ions per adsorbent mass at time	[mg/g]
q_{th}	=theoretical mass of metal adsorbed ions per mass of adsorbent	[mg/g]
k_1	=the rate constant of the pseudo-first-order	[1/min]
k_2	=the rate constant of the pseudo-second-order	[g/(mg min)]

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