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Removal of Lead from Aqueous Solution onto Untreated Coffee Grounds: a Fixed-bed Column Study

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Removal of lead by untreated coffee grounds was investigated in a packed bed up-flow column. The experiments were conducted to study the effect of important design parameter such as flow rate (5, 7 and 10 mL/min). Data confirmed that the breakthrough curves were dependent on flow rate. At a bed height of 7.5 cm and flow rate of 10 mL min−1, the metal-uptake capacity of coffee grounds for lead was found to be 78.95 mg g^{-1}.

The breakthrough time increased and the saturation time decreased with the increase of flow rate. The Adams–Bohart, Thomas and BDST models were applied to the adsorption under varying experimental conditions to predict the breakthrough curves and to evaluate the model parameters of the fixed-bed column that are useful for process design. The Adams–Bohart model was in good agreement with the experimental data. The untreated coffee grounds column study states the value of the excellent adsorption capacity for the removal of Pb (II) from aqueous solution.

1. Introduction

The excessive use of heavy metals for industrial and domestic practices contaminates ground and surface water and is considered as a major challenge to the environment. Industries such as electroplating, lead batteries, paint and dyes, glass operation, mining and smelters discharging large amounts of heavy metals in water bodies (Darvishi et al., 2013). The known toxic pollutant metals include lead, chromium, cadmium, copper, nickel, zinc, arsenic and mercury (Hamza et al., 2013). Lead, the metal considered in this study, is known to be one of the most poisonous environmental contaminants. It can enter human body through inhalation, ingestion or skin contact and may accumulate in bones, brain, kidney and muscles causing severe damage to kidney, nervous and reproductive system. It causes anemia and sometimes even death. Owing to the hazardous effects of Pb(II) it is essential to check waste streams containing Pb(II) before being discharged into the water resources. The maximum permissible limit assigned by World Health Organization (WHO) for Pb(II) in drinking water is 0.05 mg/L (Seolatto et al., 2012; Teoh et al., 2013). Many conventional techniques have been applied to remove heavy metal ions from industrial effluents, including chemical precipitation, adsorption onto activated carbon, electrochemical treatment, membrane processes, solvent extraction, ion exchange and so. Adsorption is considered quite attractive in terms of its efficiency of removal from dilute solutions. Although, the use of commercially available activated carbon and zeolites of different grades is still very popular, but it is very expensive. Thus, there is a growing demand to find relatively efficient, low cost and easily available adsorbents for the adsorption of lead, particularly if the adsorbents are the wastes. The researchers were oriented towards no expensive adsorbents which are the vegetable wastes such as: waste of tea, degreased coffee beans, sawdust, the tree fern, chitosan, the olive oil waste, the orange juice waste, the orange barks, the algae, plants dried and olive stone waste (Azouaou et al., 2010). In fact, coffee is currently known as one of the most widespread types of beverage consumed around the world, as drinking coffee everyday is a habit of many people, whether it is espresso, freshly ground, latte, cappuccino or even instant coffee. As a consequence its residues, the coffee grounds, increasingly need alternatives to be adequately managed. Some possibilities include its use as adsorbent to remove heavy metals (Caetano et al., 2013)

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The present study was carried out to show the potential of adsorption of lead on untreated coffee grounds coming from cafeterias and constitute a waste. The aim of this work was to found an untreated waste with a better maximum capacity of adsorption which can be used in fixed bed and next step in pilot scale.

2. Materials and methods

2.1 Preparation of the adsorbent

The adsorbent used in this study was coffee grounds coming from cafeterias and constitute a waste. It was used with no further treatment just only dried at the ambient air. Chemical composition of material was analyzed by X-ray fluorescence spectrometer (XRF), BET surface area was determined from nitrogen adsorption and some physical and chemical properties have been estimated.

2.2 Preparation of the metal solution

The lead solution is prepared by dissolving lead nitrate ($Pb(NO_3)_2$), from Biochem, in distilled water. The initial concentration was 100 mg/L. The initial pH of the solution is adjusted by using a solution of HNO_3 or NaOH.

2.3 Metal adsorption experiment

A fixed mass of coffee grounds was packed in a glass column of 45 cm height and 3.5 cm diameter. The metal ion solution of Pb (II) having an initial concentration of 100 mg/L at optimum pH value and 25 °C was pumped through column at a desired flow rate by a peristaltic pump (ISMATEC-MCP) in an up-flow mode. The outlets metal ions concentrations were carried out at quite time intervals, filtered through filter paper (Double Boxing rings 102). Lead analysis was realised by atomic absorption spectrophotometer (PERKIN ELMER, A 800) with a wavelength of 217 nm, a slit of 0.5 and one flame of the air-C_2H_2 type.

3. Theory of models for fixed-bed studies

The breakthrough curves showed the performance of fixed-bed column. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and dynamic response of a sorption column. The effluent concentration (C_t) from the column that reaches about 5% of the influent concentration (C_0) is the breakthrough point (t= t_p). The point where the effluent concentration reaches 95% (t= t_s) is usually called the ‘‘point of column exhaustion’’. The breakthrough curve is usually expressed by C_t/C_0 as a function of time or volume of the effluent for a given bed depth (Chen et al., 2012). The effluent volume, V_{eff} (mL), can be calculated from the following equation:

$$V_{eff} = Q \times t_{total} \quad (1)$$

Where Q is the volumetric flow rate (mL/min), t_{total} is the total flow time (min).
The value of the total mass of metal adsorbed, m_{ad} (mg), can be calculated from the area under the breakthrough curve (Eq. (2)) (Han et al., 2009):

$$m_{ad} = \frac{Q}{1000}\int_0^{t_s} C_{ad}\,dt \quad (2)$$

Where C_{ad} is the concentration of metal removal (mg/L), and t_s is the time corresponding to exhaustion point (min).
Equilibrium metal uptake or maximum capacity of the column, q_0 (mg/g), is calculated as the following:

$$q_0 = \frac{m_{ad}}{m} \quad (3)$$

Where m is the dry weight of adsorbent in the column (g). Total amount of metal ion entering column (m_0) is calculated from the following equation (Oguz and Ersoy, 2010):

$$m_0 = (Q \,.\, C_0 \,.\, t_s)/1000 \quad (4)$$

and the removal percentage of Pb(II) ions can be obtained from Eq(5).

$$R(\%) = \frac{m_{ad}}{m_0}.100 \quad (5)$$

In order to facilitate the design of adsorption column with untreated coffee grounds as the fixed-bed material, prediction of breakthrough curve for effluent is desirable. As such, it is necessary to fit the adsorption data using established models and subsequently determine salient parameters associated with these models to determine their influence for optimization of the fixed-bed adsorption process. Modeling of the breakthrough curves was carried out using three established models, namely, Bohart-Adams, Thomas and Bed-Depth-Service-Ttime (BDST) models.

3.1. Bohart-Adams model (1920)

Bohart and Adams in 1920 established the fundamental equation, which describes the relationship between C_t/C_0 and t in a continuous system, and, although it was originally applied to a gas-solid system. This model assumes that the sorption rate is proportional to the residual capacity of the solid and the concentration of the sorbed substance and is used to describe the initial part of the breakthrough curve (Calero et al., 2009). Its equation can be described by the following expression:

$$Ln\left(\frac{C_t}{C_0}\right) = K_{AB}C_O t - K_{AB}N_O\left(\frac{Z}{U_0}\right) \quad (6)$$

With C_0 and C_t are the metal ion concentrations of influent and effluent respectively (mg/L), Z the bed deph (cm), U_0 the linear velocity (cm/min), N_0 the maximum volumetric sorption capacity of bed (mg/L), and K_{AB} is the kinetic constant (L/mg.min).

3.2. The Thomas model (1944)

This kinetic model was developed byThomas (Thomas, 1944). The Thomas solution is one of the most general and widely used methods in column performance theory (Han et al., 2006). The expression by Thomas for an adsorption column is given as follows:

$$Ln\left(\frac{C_0}{C_t} - 1\right) = \left(\frac{MK_{th}q_0}{Q}\right) - \left(\frac{V_{eff}K_{th}C_0}{Q}\right) \quad (7)$$

The value of C_0/C_t is the ratio of the influent and the effluent metal ion concentrations, Q is the flow rate (mL/min), M the adsorbent mass (g) and V_{eff} is the effluent volume. The kinetic constant k_{th} (mL /mg.min) and the adsorption capacity q_0 (mg/g) can be obtained from the plot of C_t/C_o against time t at a given flow rate using linear regression.

3.3. The Bed Depth Service Time model (BDST Model) (1946)

BDST is a simple model, which states that bed height (*Z*) and service time (*t*) of a column bears a linear relationship. The equation can be expressed as (Hutchins, 1973):

$$C_0 t = \left(\frac{N_0 H}{U}\right) - \left(\frac{1}{K}\right) . Ln\left(\left(\frac{C_0}{C_t}\right) - 1\right) \quad (8)$$

With K is a rate constant of the adsorption (L/ mg. min), N_0 the sorption capacity of bed (mg/L), H the bed depth (cm), t time (min) and U is the linear velocity (cm/min). From the plots of time versus $Ln\left(\left(\frac{C_0}{C_t}\right) - 1\right)$ we can determine N_0 and K.

4. Results and discussions

4.1. Characterisation of adsorbent

Some chemical and physical characteristics of untreated coffee grounds are presented in table 1.

Table1: Physical and chemical properties of untreated coffee grounds.

Mean diameter (μm)	389.20
Moisture (%)	1.71
Organic compounds (%)	97.13
Mineral compounds (%)	1.16
Surface area BET (m^2/g)	298.60
pH_{zc} (pH of zero charge)	5.70

4.2. X-ray fluorescence analysis

The chemical composition of untreated coffee grounds was determined using X-ray fluorescence (XRF) spectrometer (Bruker-Axs: SRS 3400) and listed in table 2.

Table 2: Chemical composition of untreated coffee grounds.

Element	K_2O	P_2O_5	MgO	CaO	SO_3	SiO_2	Na_2O	Fe_3O_3	Cl	Al_2O_3	CuO	Sr
%(w)	33.98	23.21	15.32	12.63	3.98	3.54	3.09	1.84	0.98	0.95	0.19	0.016

Element	Mn	Zn	Pb	Ti	Ni	Nb	Rb	Co	Cr	Ba
%(w)	0.06	0.084	0.05	-	0.04	0.01	0.03	-	-	-

The results indicate mainly the presence of potassium, phosphore, magnesium and calcium. The analysis supported the existence of sulphur and suggested the absence of nitrogen, similar results have been reported by Kaikake et al (2007). The presence of Fe, Cl, Cu and the other elements may be due to the cistern water used in cafeteria for the preparation of coffee drinking (Azouaou et al., 2010).

4.2. Effect of flow rate on breakthrough curve

The breakthrough curves at various flow rates of metal ion are shown in figure.1. Figure.1 shows that the breakthrough occurred faster with increasing flow rate. As indicated also in table.3, as the flow rate was increased from 5 to 10 mL/min, the exhaust time was found to be decreased from 10,200 to 7,020 min. At higher flow rate, the external film mass resistance at the surface of the adsorbent tends to decrease and the residence time decreases; hence the saturation time decreases, and in turn gives the lower removal efficiency (Han et al., 2009). With the increase of flow rate from 5 to 7 mL/min, the removal efficiency was decreased from 33.4 % to 27.7 %, similar tendency has been found by other researches (Chaolin et al., 2013). The influent flow rate also strongly influenced the metal uptake capacity, as flow rate increased from 5 to 10 mL/min, the amount of total Pb(II) uptake q_0 increased from 58.86 to 78.95 mg/g, this is due probably to the higher intraparticle diffusion effect, a smaller transfer zone and the sufficient time for the bonding capacity of the Pb(II) ions onto functionnal groups present in the adsorbent.

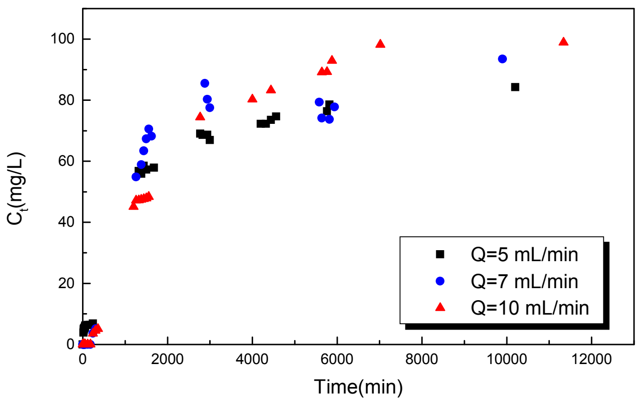

Figure.1: Effect of various flow rates on the breakthrough curve of Pb(II) adsorption onto untreated coffee grounds. $[Pb]_0$=100 mg/l, pH= 5.7, m= 30 g, H= 7.5 cm, T= 25°C.

Table3: Parameters in fixed-bed column for Pb (II) adsorption by untreated coffee grounds.

Q (mL/min)	t_p (min)	t_s (min)	m_{ad} (mg)	R (%)	q_0 (mg/g)
5	35	10,200	1,765.77	33.4	58.86
7	308	9,900	1,958.36	27.7	65.27
10	360	7,020	2,368.62	33.1	78.95

4.3. Modelling of breakthrough curves

Tables 4–6 present the values of respective Thomas, BDST, and Bohart-Adams model parameters obtained from slopes and intercepts of linear plots. Analysis of r^2 values indicates that the Pb^{2+} adsorption data fit very well Bohart-Adams model. This indicates that Bohart-Adams model is valid for the application of adsorption of Pb^{2+} onto untreated coffee grounds. The values of K_{AB} decreased with increase of influent flow rate, it was indicated that the overall system kinetics was dominated by external mass transfer in the initial part of adsorption in the column (Ahmad and Hameed, 2010; Han et al., 2009; Aksu and Gonen,

2004). It is obvious that increases in flow rate result in increases of N_0 values; this trend indicates that the external and internal diffusions were not the limiting step (Chen et al., 2012).
An increase in sorption capacity q_0 was observed when the solution flow rate was increased from 5 to 10 mL/min. This was attributed to the availability of active sites of the adsorbents by the numerous adsorbate molecules present in higher flow of solution.

Table 4: Parameters of different models using linear regression analysis (Q= 5 mL/min).

Thomas Model			BDST Model			Bohart-Adams Model		
K_{th} (mL/mg.min)	q_0 (mg/g)	r^2	K (L/mg.min)	N_0 (mg/L)	r^2	K_{AB} (L/mg.min)	N_0 (mg/L)	r^2
$7.29.10^{-3}$	50.16	0.74	$9.76.10^{-6}$	$2.62.10^{4}$	0.74	$5.79.10^{-4}$	$5.23.10^{2}$	0.95

Table 5: Parameters of different models using linear regression analysis (Q= 7 mL/min).

Thomas Model			BDST Model			Bohart-Adams Model		
K_{th} (mL/mg.min)	q_0 (mg/g)	r^2	K (L/mg. min)	N_0 (mg/L)	r^2	K_{AB} (L/mg. min)	N_0 (mg/L)	r^2
$5.80.10^{-3}$	51.25	0.61	$2.81.10^{-6}$	889.01	0.61	$4.91.10^{-5}$	$1.21.10^{4}$	0.99

Table 6: Parameters of different models using linear regression analysis (Q= 10 mL/min).

Thomas Model			BDST Model			Bohart-Adams Model		
K_{th} (mL/mg. min)	q_0 (mg/g)	r^2	K (L/mg. min)	N_0 (mg/L)	r^2	K_{AB} (L/mg. min)	N_0 (mg/L)	r^2
$6.22.10^{-3}$	69.55	0.85	$7.29.10^{-6}$	$4.21.10^{4}$	0.85	$2.94.10^{-5}$	$2.58.10^{4}$	0.96

5. Conclusion

This study identified untreated coffee grounds as an effective and promising adsorbent to be utilized for the removal of Pb (II) ions from aqueous solution. The coffee grounds were characterized for their moisture content (1.71 %), organic compounds (97.13 %), mineral compounds (1.16 %) and important surface area BET (298.60 m^2/g). Uptake of Pb (II) through a fixed-bed column was dependent on flow rate; the adsorption capacity was increased with flow rate (58.86 to 78.95 mg/g), the exhaust time was found to be decreased with increasing flow rate. Investigation of fitness of dynamic adsorption models, to predict the breakthrough curves, to the experimental data revealed that Bohart–Adams dynamic model best described the process than the Thomas and BDST as exhibited by the higher r^2 values. The results obtained indicate that the overall system kinetics was dominated by external mass transfer in the initial part of adsorption in the column and the external and internal diffusions were not the limiting step.
Furthermore, further studies about the effect of bed depth, initial concentration of Pb (II) ions, desorption and regeneration under different conditions should be investigated and taken into consideration. Finally, high sorption capacity of untreated coffee grounds makes it very attractive material for the treatment of lead from aqueous systems for environmental protection purpose.

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