

Column performance of granular activated carbon packed bed for Pb(II) removal

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Received 14 October 2007; received in revised form 16 December 2007; accepted 17 December 2007

Available online 4 January 2008

Abstract

The excessive release of lead from lead acid batteries, smelting plant into the environment is a major concern worldwide. Adsorption process is among the most effective techniques for lead removal from wastewater and activated carbon has been widely used as an adsorbent. In this paper an attempt has been made to investigate the adsorption behaviour of Pb(II) from aqueous systems onto granular activated carbon using the batch mode and continuous mode in a packed bed column with more successive service and regeneration. The experiments were performed at constant temperature and dimensions of column and packed bed of granular activated carbon with variation of flows through the bed and concentrations of lead solutions. Breakthrough points were found out for the adsorption of lead on the adsorbent using continuous-flow column operation by varying different operating parameters like hydraulic loading rate from 4 to 16 m³/h m² and feed concentrates from 20 to 60 mg/l. Granular activated carbon column regeneration using 0.5 M concentration of HNO₃ has been investigated. Results indicate encouraging performance towards removal of Pb(II).

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Keywords: Pb(II) removal; Granular activated carbon; Adsorption; Wastewater treatment; Packed bed column

1. Introduction

Lead is one of the potentially toxic heavy metals when adsorbed into the body [1]. The pollution of water resources due to indiscriminate disposal of lead metals has been causing worldwide concern for the last few decades. The presence of lead in drinking water even at low concentration may cause diseases such as anemia, encephalopathy, hepatitis and nephritic syndrome [2]. Lead is non-biodegradability and can accumulate in living tissues, thus becoming concentrated throughout the food chain and can be readily absorbed into the human body [3]. Even a very small amount can cause severe physiological or neurological damage to the human body. It is in general metabolic poison and enzyme inhibitor, also cause mental retardation and semipermanent brain damage in young children.

Lead, an element which has been used by man for years, can be regarded as a longstanding environmental contaminant. It released into the environment in a number of ways, like as process industries engaged in lead acid batteries, pulp and paper, petrochemicals, refineries, printing, pigments, photographic materials and explosive manufacturing, ceramic, glass, paint, oil, metal, phosphate fertilizer, electronic, wood production and also combustion of fossil fuel, forest fires, mining activity, automobile emissions, sewage wastewater, sea spray are just few examples [4–6]. The industrial wastewaters are considered to be the main source of lead impurities.

The presence of high levels of lead in the environment may cause long-term health risks to humans and ecosystems. It is therefore mandatory that their levels in drinking water, waste water and water used for agricultural and recreational purposes must be reduced to within the maximum allowable concentrations recommended by national and international health authorities such as world health organisation. Its removal from wastewater prior to discharge into environment is, therefore, necessary. Current EPA drinking water standard for lead are 0.05 mg/l, but a level of 0.02 mg/l has been proposed and is under

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Nomenclature

A_0	original adsorptive capacity of the virgin adsorbent (mg/g)
A_r	adsorptive capacity of the regenerated column (mg/g)
b	Langmuir constant (l/g)
C_e	equilibrium lead concentration (mg/l)
C_i	initial lead concentration (mg/l)
k	measure of adsorbent capacity (l/g)
K_L	Langmuir constant (mg/g)
M	metal adsorbed on adsorbent bed (mg)
m	mass of adsorbent in column (g)
$1/n$	sorption intensity, dimensionless
Q	flow rate of the influent ($(\text{m}^3/(\text{h m}^2))$)
$Q_{0.5}$	adsorption column capacity (mg/g)
q_e	amount of lead adsorbed at equilibrium (mg/g)
T	temperature ($^{\circ}\text{C}$)
t	time (h)
t_b	breakthrough time (h)
V	volume of the solution (l)
W	weight of adsorbent (g)

review [7]. According to Indian Standard Institution, the tolerance limit for discharge of lead into drinking water is 0.05 mg/l and in land surface waters is 0.1 mg/l [8]. Increasingly stringent legislation on the purity of drinking water has created a growing interest in the development of conventional treatment processes. Various chemical and physico-chemical methods for the treatment of wastewaters containing lead wastes are known, such as chemical precipitation, electrochemical reduction, ion exchange, biosorption and adsorption [9–13]. The choice of treatment depends on effluent characteristics such as concentration of lead, pH, temperature, flow volume, biological oxygen demand, the economics involved and the social factor like standard set by government agencies. Various methods of wastewater treatment were examined and adsorption emerged as one of the most promising technique [14] as it is generally preferred for the removal of lead due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness.

The use of activated carbon (AC) is still very popular and different grades are available, but are quite expensive and the regeneration of the carbon is not always possible. Activated carbon has been chosen as an adsorptive media for removal of lead, by many researchers [15–18]. Activated carbon is a black solid substance resembling granular or powder charcoal and are carbonaceous material that have highly developed porosity, internal surface area of more than $400 \text{ m}^2/\text{g}$ and relatively high mechanical strength. They are widely used as adsorbents in wastewater and gas treatments as well as in catalysis. The increasing usage and competitiveness of activated carbon prices, has prompted, a considerable research work has been done in the search of inexpensive adsorbents especially developed from various agricultural waste materials, i.e. the usage of agricultural by-products such as fruit stones [19], coconut shell [20,21],

bagasse [22,23], nutshells [24,25] as raw materials to prepare AC. These solid wastes are not only cheap and easily available but are considered as wastes that contribute to disposal problems. In this study coconut shell has been chosen as an adsorptive media. As it is suitable for preparing microporous activated carbon due to its excellent natural structure and low ash content.

In practice, activated carbon is found in two general forms: granular activated carbon (GAC) and powdered activated carbon (PAC). GAC is composed of particles with sizes greater than 0.1 mm, about the size of coarse sand [26]. PAC, of course, is composed of particles smaller than that value. Exact specifications vary, but GAC is generally said to have a larger internal surface area and smaller internal pores, while PAC is thought to have larger pores and a smaller internal surface area. Because PAC has a faster adsorption rate, it was often used in the past, but disposal and handling concerns have made granular activated carbon (GAC) a more popular alternative for most applications. GAC is used in the filtration process in water treatment, and then regenerated when it becomes less effective due to saturation with chemicals. GAC is also usually much easier to handle and transport than PAC. The special advantages of packed bed are that it has high residence time to and excellent heat and mass transfer characteristics. GAC is bigger in size and it has no elutriation from the bed and loss is minimum than PAC.

In the present batch mode and fixed-bed column adsorption study, GAC coconut shell origin is chosen as an adsorptive media to understand the adsorption behaviour of lead ions from aqueous systems of synthetic waste water of lead contaminated water. Although batch laboratory adsorption studies provide useful information on the application of adsorption to the removal of specific waste constituents, continuous column studies provide the most practical application of this process in wastewater treatment. Batch reactors were easy to use in the laboratory study, but less convenient for industrial applications. On the other hand, fixed-bed columns were widely used in various chemical industries because of their simple operation. Fixed-bed adsorption has been applied to remove organic contaminants for many years with encouraging results. The reason for this is that the high adsorption capacities in equilibrium with the influent concentration rather than the effluent concentration can be achieved. In static mode adsorption studies, the same solution remains in contact with a given quantity of the adsorbent. The adsorption process continues, however, till equilibrium between the solute concentration in solution, and the solute adsorbed per unit weight of the adsorbent is reached. This equilibrium established is static in nature, as it does not change further with time. In dynamic column adsorption, solution continuously enters and leaves the column, so that the complete equilibrium is never established at any stage between the solute in solution and the amount adsorbed. Equilibrium has to be continuously established, as each time, it meets the fresh concentrations, and hence, equilibrium in column mode is termed as dynamic equilibrium. Additional information on the efficiency of the treated adsorbent in the column mode has been gathered in order to ascertain the practical applicability of the adsorbent for real industrial wastewaters.

2. Experimental technique

2.1. Adsorbate

A stock solution of Pb(II) was prepared (1000 mg/l) by dissolving required amount of, $\text{Pb}(\text{NO}_3)_2$ in tap water. The stock solution was diluted with tap water to obtain desired concentration ranging from 20 to 60 mg/l.

2.2. Adsorbent

The commercial grade coconut shell origin granulated activated carbon was used as precursor carbon in this study. The carbon was washed with tap water to remove fines and impurities, oven dried at 110 °C for 6 h and stored in plastic containers for further use. The proximate analysis was carried out using the standard procedure. The BET surface areas of the coconut shell activated carbon were measured in BET-Flowsorb-2300 analyzer on the basic principle of monolayer adsorption. Nitrogen and helium mixture nearly 30–35% was used to form the monolayer. In this method first sample quantity is optimized after several trial runs so that surface area falls within 0.5–2.5 m². The sample is dried in an air oven at 105 °C and free from any gases or vapors for which 200–250 °C for 15 min is adequate. Surface area in Flowsorb-2300 is displayed in terms of quantity of sample contained in sample tube holder and the displayed number is converted to specific surface area by dividing the weight of the sample.

To identify the functional group responsible for the adsorption in the GAC of coconut shell origin, Fourier transform infrared spectroscopy (FTIR) analysis was carried out. The ratio between the sample and potassium bromide (KBr) was at about 1:100 prior to compacting into thin pellet using an 8 tons force hydraulic press for 5 min. Infrared spectrum was obtained in transmission and was set to operate in the range of 400–4000 cm⁻¹.

2.3. Reagents

All the chemicals used in the study were from Merck (India) Ltd. and Qualigens Glaxo (India) Ltd. analytical grade.

2.4. Analytical method

Atomic-absorption spectrophotometry utilizes the phenomenon that atoms absorb radiation of particular wavelength. By atomic-absorption spectrophotometer, the metals in water sample can be analyzed. It consists of four basic structural elements; a light source (hollow cathode lamp), an atomizer section for atomizing the sample (burner for flame, graphite furnace for electrothermal atomization), a monochromator for selecting the analysis wavelength of the target element, and a detector for converting the light into an electrical signal. It detect concentration of Pb(II) in ppm level in the solution and volume of sample required is only 1ml for one analysis.

2.5. Method of experiment

2.5.1. Batch mode adsorption studies

Batch adsorption experiments were performed by contacting 0.1 g of the selected GAC samples with 200 ml of the aqueous solution of different initial concentration (20, 30, 40, 60 mg/l) at natural solution pH. The experiments were performed in a thermal shaker at controlled temperature (30 ± 2 °C) for a period of 24 h at 120 rpm using 250 ml Erlenmeyer flasks containing 200 ml of different lead concentrations at room temperature. Continuous mixing was provided during the experimental period with a constant agitation speed of 120 rpm for better mass transfer with high interfacial area of contact. The remaining concentration of Pb(II) in each sample after adsorption at different time intervals, was determined by atomic-absorption spectroscopy after filtering the adsorbent with Whatmen filter paper to make it carbon free. The batch process was used so that there is no need for volume correction. The lead concentration retained in the adsorbent phase was calculated according to

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

where C_i and C_e are the initial and equilibrium concentrations (mg/l) of lead solution respectively; V is the volume (l); and W is the weight (g) of the adsorbent. Two replicates per sample were done and the average results are presented.

2.5.2. Column adsorption studies

The experimental arrangement for lead removal is shown in Fig. 1. The effective column of borosilicate glass height, internal diameter, area, volume of the column and weight of adsorbent taken are listed in Table 1. The column was packed with adsorbent between two supporting layers of sand. The adsorbent was added from the top of the column and allowed to settle by gravity force. Granular activated carbon is packed up to desire bed height in water filled column of and was kept submerged throughout the runs to avoid air entrapment in the bed. Columns are mounted vertically and the GAC bed is supported on perforated plate. The upper portion of the adsorbent was covered with sand beads of 5 cm height.

Effluent after passing through the columns was discharged into a sump below the column. The operation is in down flow plug mode. Two control valves to regulate the flow and a rotameter of range 0–50 lit/min to monitor hydraulic loading rate is incorporated in the feed line of the column. The synthetic wastewater was pumped by a centrifugal pump from the storage tank of lead contaminated water. All the sorption experi-

Table 1
Specification of packed bed column

Parameters	Values
Column bed height (cm)	60
Internal diameter of the column (cm)	4.0
Volume of the column (cm ³)	1004.8
Bulk density (g/ml)	0.512
Weight of the adsorbent taken (g)	385.84

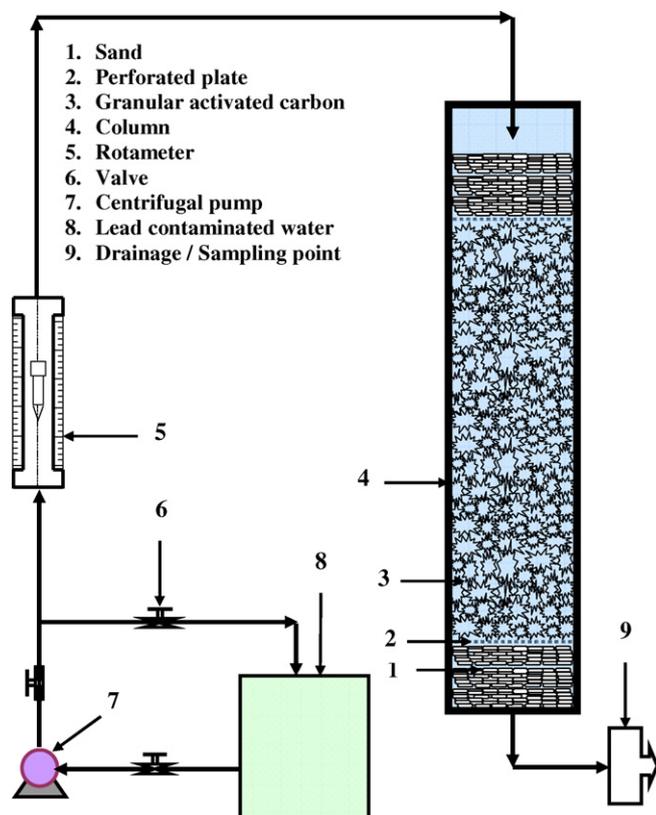


Fig. 1. Schematic diagram of experimental setup for column studies.

ments were carried out at the room temperature of $30 \pm 2^\circ\text{C}$. The samples were collected in regular time intervals and stored for analysis. The residual concentration of lead in aqueous sample was determined using atomic adsorption spectrophotometer.

2.5.3. Regeneration

Regeneration of the adsorbent material is of crucial importance in the economic development. The aim is to remove the loaded metal from the column in the smallest possible volume of an eluting solution. Regeneration must produce small volume of metal concentrates suitable for metal-recovery process, without damaging the capacity of the adsorbent, making it reusable in several adsorptions and desorption cycles. Regeneration should also ensure that eluted solution is not posing any disposal problem waste in terms of high acidity.

3. Result and discussion

3.1. Physical and chemical characterization of the adsorbent

3.1.1. Fourier transform infrared spectroscopy (FTIR) analysis

The spectra of carbons were measured by an FTIR spectrometer within the range of $400\text{--}4000\text{ cm}^{-1}$ wave number. Spectra were plotted for the adsorbent GAC coconut shell origin was shown in Fig. 2. The broad band at 750 cm^{-1} that represents bounded O–H groups. On the other hand, =C–H stretch could

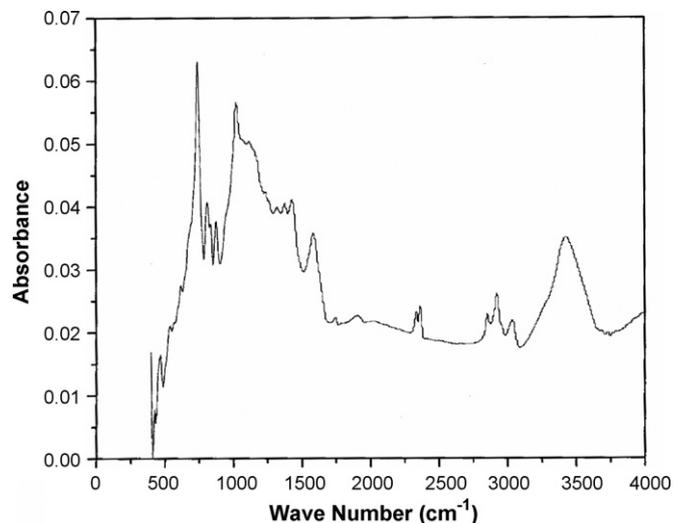


Fig. 2. FTIR analysis of GAC of coconut shell origin.

be ascribed to the band that appeared at 1085 cm^{-1} . The C=O stretch could be ascribed to the bend that appeared at 2830 cm^{-1} .

3.1.2. Chemical properties

Granular activated carbon pH may influence the removal efficiency. Distinctly acidic activated carbon may react with the material to be removed and may hamper the surface properties of the activated carbon. For our experiment the pH of carbon was 6.5. Ash content of the carbon is the residue that remains when the carbonaceous portion is burned off. The ash consists mainly of minerals such as silica, aluminum, iron, magnesium and calcium. Ash in activated carbon is not required and considered to be an impurity. Table 2 shows the proximity analysis of GAC coconut shell origin. As the ash content is 4.3% it resembles good adsorbent.

3.1.3. Physical properties

Particle size distribution analysis was done manually. Initial sample of weight 400 gm was taken for analysis. This sample was passed through different sieves and amount of fine and coarse were measured the mesh size 8–20. The nominal particle size was found 0.11 mm. Density is particularly important in removal. If two carbons differing in bulk density are used at the same weight per liter, the carbon having higher bulk density will be able to remove more efficiently. Average bulk density can be calculated by water displacement method. In this method, volume of water displaced is observed by a particular amount of carbon. The average bulk density was found 0.5125 g/ml. The BET surface area of granular activated carbon of coconut shell

Table 2
Proximate analysis of GAC of coconut shell origin

Parameters	Values
Moisture (%)	4.8
Ash (%)	4.3
Volatile matter (%)	18.2
Fixed carbon (%)	72.7

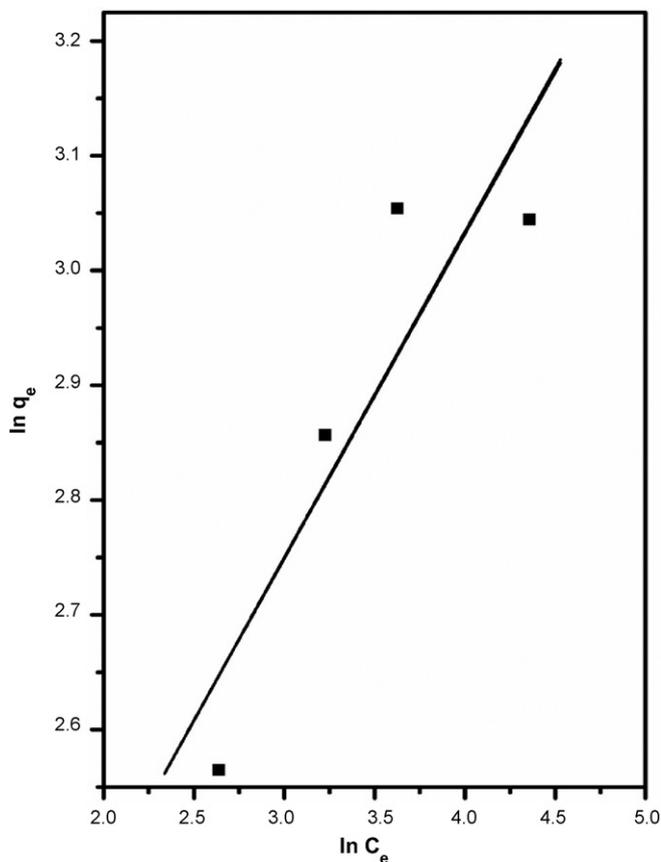


Fig. 3. Freundlich adsorption isotherm for lead at 0.1 g/200 ml of adsorbent concentration.

origin was measured and it was found 1015 m²/g. The average pore diameter was found 26.14 Å. This shows that GAC is reasonably good for adsorption.

3.2. Pb(II) equilibrium adsorption isotherms

Several models have been used in the literature to describe the experimental data of adsorption isotherms. The Freundlich and Langmuir models are the most frequently employed models. In the present work both models were used.

The Freundlich equation is purely empirical based on sorption on heterogeneous surface, which is commonly presented as:

$$q_e = KC_e^{1/n} \quad (2)$$

The lead sorption isotherm followed the linearized Freundlich model as shown in Fig. 3. The relation between the metal uptake capacity ' q_e ' (mg/g) of adsorbent and the residual metal ion concentration ' C_e ' (mg/l) at equilibrium is given by

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e. \quad (3)$$

where the intercept $\ln k$ is a measure of adsorbent capacity, and the slope $1/n$ is the sorption intensity. The isotherm data fit the Freundlich model well ($R^2=0.89$). The values of the constants k and $1/n$ were calculated to be 6.699 and 0.2824.

Since the value of $1/n$ is less than 1, it indicates a favourable adsorption.

The Langmuir isotherms model is valid for monolayer adsorption on to surface containing finite number of identical sorption sites which is described by the following equation:

$$q_e = \left(\frac{K_L b C_e}{1 + b C_e} \right). \quad (4)$$

The Langmuir equation relates solid phase adsorbate concentration (q_e), the uptake, to the equilibrium liquid concentration (C_e). The Langmuir equation can be rearranged to linear form for the convenience of plotting and determining the Langmuir constants as below:

$$\frac{C_e}{q_e} = \frac{1}{b K_L} + \frac{C_e}{K_L} \quad (5)$$

where K_L and b are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively. It can be seen from Fig. 4 that the isotherm data fits the Langmuir equation well ($R^2=0.99$). The values of K_L and b were determined from the figure and were found to be 26.546 mg/g and 1.7138 l/mg, respectively. The outcome values of parameters k , n , K_L , b , R^2 for all the experiments with pH of solution at natural for maximum removal of Pb(II) are presented in Table 3. Maximum adsorption capacity was found to be 26.546 mg of Pb(II) per g of GAC as adsorbent.

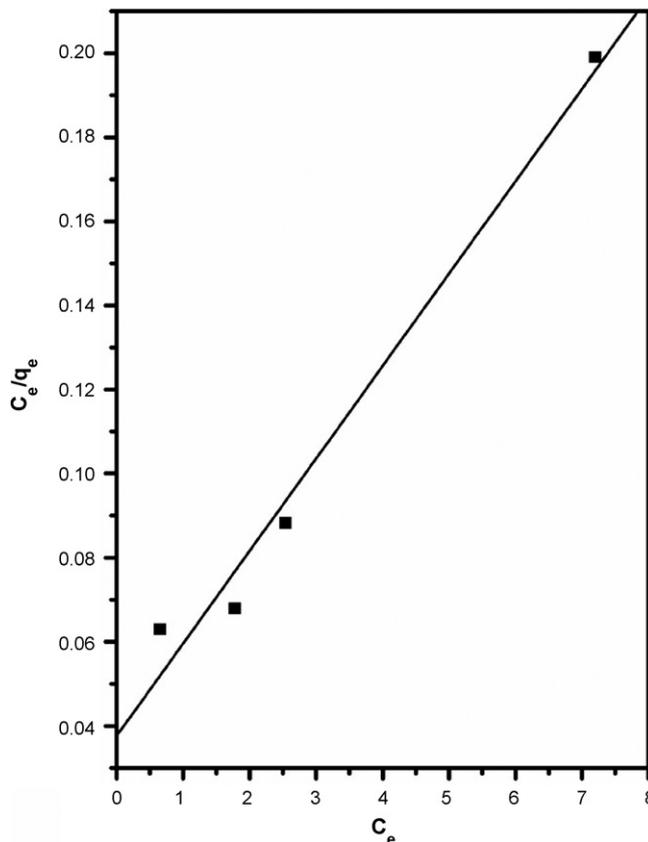


Fig. 4. Langmuir adsorption isotherm for lead at 0.1 g/200 ml of adsorbent concentration.

Table 3
Adsorption isotherms parameter for lead(II) removal

Parameters	K_L (mg/g)	b (l/mg)	R^2	k (l/g)	$1/n$
Values	26.546	1.713	0.990 Langmuir 0.890 Freundlich	6.699	0.282

3.3. Adsorption dynamic column studies

3.3.1. Column adsorption capacity

As the adsorbate solution passes through column, the adsorption zone (where the bulk of adsorption takes place) starts moving out of the column and the effluent concentration start rising with time. This is termed as break point. The time taken for the effluent concentration to reach a specific breakthrough concentration of interest is called the break though time. The results of examinations in the column are represented by breakthrough curves. The breakthrough is the point on the S-shaped curve at which the solute concentration reaches its maximum allowed value (usually 5% of its influent value), and the point of the column exhaustion is the point where the effluent concentration reaches 95% of its influent value [27]. The breakthrough time (t_b) for each of the columns operation was defined as the time when the effluent concentration (C_e) of Pb(II) reached 50% of the initial concentration (C_i). Breakthrough curve were plotted-giving ratio of effluent and feed (influent) concentrations (C_e/C_i) and time (h) for varying operating conditions.

The approach of Treybal [28] has been adopted for calculating the column capacity for the removal of Pb(II). Breakthrough capacity $Q_{0.5}$ (at 50% or $C_e/C_i = 0.5$) expressed in mg of Pb(II) adsorbed per gram of adsorbent was calculated using Eq. (6):

$$Q_{0.5} = \frac{M}{m} = \frac{t_b Q C_i}{m} \quad (6)$$

where M is the metal adsorbed on adsorbent bed (mg), m is mass of adsorbent in bed (g) and Q is flow rate of the influent ($m^3/(h m^2)$).

Table 4 presents the column adsorption capacity for lead onto the adsorbent for varying operating variables that is flow rate and feed concentration. The column capacity for Pb(II) adsorption for the bed height of 0.6 m, hydraulic loading rate of $12 m^3/(h m^2)$ and the feed concentration of 30 mg/l for 50% breakthrough concentration were found to be 2.0132 mg/g. From comparison of adsorption capacity from Langmuir isotherm and column experiments, we can see that the less-stirred prop-

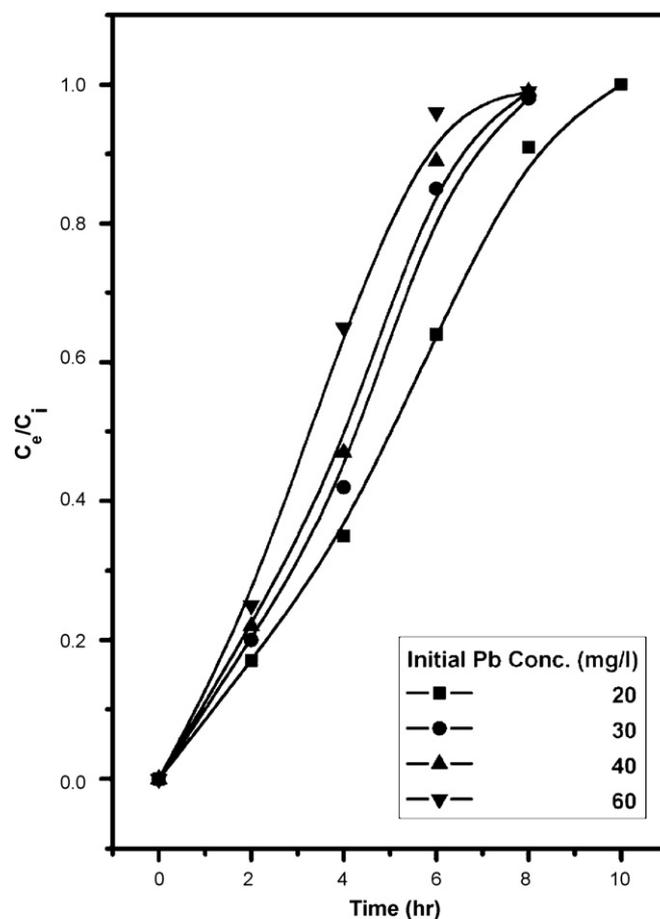


Fig. 5. Break through curve for different feed concentration at constant hydraulic loading rate of $12 m^3/h/m^2$.

erty in column mode reduced the lead(II) adsorption capacity on GAC.

3.3.2. The effect of initial concentration

The effect of the initial lead concentration on the breakthrough curve shape has been examined on the GAC with flow rate $12 m^3/(h m^2)$ and changing initial concentration from 20–60 mg/l. The change in the initial metal ion concentration has a significant effect on breakthrough curve as illustrated in Fig. 5. The larger the initial feed concentration, the steeper is the slope of break through curve and smaller is the breakthrough time. These results demonstrate that the change of concentration gra-

Table 4
Column adsorption capacity, $Q_{0.5}$ at various operating conditions at 50% break through concentrations

Initial concentration (mg/l)	Breakthrough time, 50% (h)	Hydraulic loading rate ($m^3/(h m^2)$)	Adsorption column capacity, $Q_{0.5}$ (mg/g)
20	5	12	0.7540
30	4.4	12	0.9953
40	4.5	12	1.3572
60	3.25	12	1.4703
60	5.4	4	0.8144
60	4.95	8	1.4930
60	4.45	12	2.0132
60	3.10	16	1.8352

In the above equation, A_r is the adsorptive capacity of the regenerated column (mg/g) and A_0 is the original capacity of the virgin adsorbent (mg/g).

4. Conclusions

The column performance characteristics have been investigated for GAC packed bed to remove lead(II) from the wastewater. Adsorption of Pb(II) on GAC followed both Langmuir and Freundlich adsorption isotherm models. Adsorption capacity for 60 mg/l feed concentration of Pb(II) at hydraulic loading rate of $12 \text{ m}^3/(\text{h m}^2)$ and 0.6 m bed height is found to be 2.0132 mg/g, which indicates that practically adsorption capacity of GAC is far less than batch mode results. This may be due to the potential irreversibility of the sorption process and the different approaches to adsorption equilibrium in different systems, i.e. the solution-phase concentration is continuously decreasing in the adsorption isotherm and in the batch systems while that concentration is continuously increasing in the column system. Removal of Pb(II) onto adsorbent depends on adsorbent concentration, and hydraulic loading rate and feed concentration. The adsorbed lead(II) ion can be effectively eluted with the use of mineral acid such as HNO_3 of 0.5 M concentrations.

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