

Removal of lead(II) by adsorption using treated granular activated carbon: Batch and column studies

Jyotsna Goel^{a,b}, Krishna Kadirvelu^{a,*}, Chitra Rajagopal^a, Vinod Kumar Garg^b

^a Centre for Fire, Explosives and Environment Safety (CFEES), Defence R&D Organisation (DRDO),
Brig. S.K. Majumdar Marg, Timarpur, Delhi 110054, India

^b Department of Environmental Science and Engineering, Guru Jambheshwar University, Hisar, Haryana 125001, India

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Abstract

In the present study, a deeper understanding of adsorption behavior of Pb(II) from aqueous systems onto activated carbon and treated activated carbon has been attempted via static and column mode studies under various conditions. It probes mainly two adsorbents that is, activated carbon (AC) and modified activated carbon (AC–S). Characterization of both the adsorbents was one of the key focal areas of the present study. This has shown a clear change or demarcation in the various physical and chemical properties of the modified adsorbent from its precursor activated carbon. Both the adsorbents are subjected to static mode adsorption studies and then after a comparison based on isotherm analysis; more efficient adsorbent is screened for column mode adsorption studies. The lead removal increased for sample of treated carbon. The extent of Pb(II) removal was found to be higher in the treated activated carbon. The aim of carrying out the continuous-flow studies was to assess the effect of various process variables, viz., of bed height, hydraulic loading rate and initial feed concentration on breakthrough time and adsorption capacity. This has helped in ascertaining the practical applicability of the adsorbent. Breakthrough curves were plotted for the adsorption of lead on the adsorbent using continuous-flow column operation by varying different operating parameters like hydraulic loading rate ($3.0\text{--}10.5\text{ m}^3/(\text{h m}^2)$), bed height (0.3–0.5 m) and feed concentrations (2.0–6.0 mg/l). At the end, an attempt has also been made to model the data generated from column studies using the empirical relationship based on Bohart–Adams model. This model has provided an objective framework to the subjective interpretation of the adsorption system and the model constant obtained here can be used to achieve the ultimate objective of our study that is, up scaling and designing of adsorption process at the pilot plant scale level. AC–S column regeneration using 0.5 and 1.0 M concentration of HNO_3 has been investigated. It has shown a regeneration efficiency of 52.0% with 0.5 M HNO_3 .

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1. Introduction

The importance of heavy metal pollution control has increased significantly in last decades. Environmentalists are primarily concerned with the presence of heavy metals due their high toxicity and impact on human health and environment.

Therefore, there have been tremendous efforts on reducing the concentration of heavy metals in the effluent wastewaters

in view of ethical obligations as well as to meet stringent permissible discharge levels, as set by the various pollution control and regulatory authorities in various countries. One of the toxic metals among the potentially toxic heavy metal list is lead [1].

Lead poisoning in human causes severe damage to the kidney, nervous system, reproductive system, liver and brain. Severe exposure to lead has been associated with sterility, abortion, stillbirths and neo-natal deaths [2,3].

Process industries, such as acid battery manufacturing, metal plating and finishing, ammunition, tetraethyl lead manufacturing, ceramic and glass industries and environmental cleanup services treat and disposal of lead con-

* Corresponding author. Tel.: +91 11 23907278; fax: +91 11 23819547.
E-mail address: kadirvelu@lycos.com (K. Kadirvelu).

taminated water are the major sources of lead pollution [4].

The permissible level for lead in drinking water is 0.05 mg/l. The permissible limit (mg/l) for Pb(II) in wastewater, given by Environmental Protection Agency (EPA), is 0.05 mg/l and that of Bureau of Indian Standards (BIS) is 0.1 mg/l [5].

For lead in wastewater, current abatement and remediation procedures include pH adjustment with lime or alkali hydroxides, coagulation–sedimentation, reverse osmosis and ion exchange. The current study is based on exploring its removal method based on adsorption technique. Adsorption compared with other method appears to be an attractive process in view of its efficiency and ease with which it can be applied in the treatment of wastewater containing heavy metals [6].

In the present batch mode adsorption study, two types of adsorbent are explored one is commercial activated carbon as such and other is alkali sulphide treated activated carbon. More efficient adsorbent out of the two is opted for column studies after assessing the adsorption potential of two adsorbents with respect to the lead removal.

The idea following enriching the sulphur content of the commercial activated carbon is that heavy metals have more affinity for sulphides than other anions as can also be seen from the natural occurrence of most of the metals in their sulphide form [7]. The chemical affinity of the lead towards sulphur groups is higher. This is also consistent with the fact, as reported by Pearson [8] and Gomez-Serrano et al. [9], that molecules where donor atom is F, O or N are all very hard, whereas for the similar molecules where the donor atom is Cl, S or P there is always a large drop in absolute hardness. Since, lead chemical species show a high affinity toward sulphur (also reported by Ochiai, 1985) [10], a tentative method of enhancing the adsorption capacity of activated carbon could be based on the introduction of surface sulphur in the material. Moreover, the chemical treatment was essentially required to introduce suitable functional groups on its surface for the improvement in the adsorption affinity and efficiency of the AC.

Several studies are available which are in covenant with the above statement [9,11,12]. Krishnan and Annirudhan has modified activated carbon prepared from bagasse pith using SO_2 and H_2S gases [12].

The majority of adsorption investigations were conducted in the batch mode. The search for an effective and economical removal of Pb(II) from wastewater resulted in the use of various low-cost adsorbents like bagasse pith sulphurised activated carbon, blast furnace sludge, biogas residual slurry, olive mill products and peanut hull carbon [13–17]. 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. The reason for this is that the high adsorption capacities in equilibrium with the influent concentration rather than the effluent concentration can be achieved [18]. 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, 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 methods

2.1. Adsorbent

Coconut shell based granulated activated carbon (AC) produced from Active Carbon Ltd.; Hyderabad, India was used as precursor carbon in the study. The carbon was washed with distilled water to remove fines and impurities, oven dried at 110 °C for 6 h and stored in plastic containers for further use. This adsorbent is termed as AC.

To enrich the sulphur percentage, 99.5 g of AC is immersed for 24 h in minimum quantity of distilled water containing 0.5 g of Na_2S . The mixture was heated almost to dryness and then dried in an oven for 4 h at 110 °C. The dried sample was washed with distilled water several times till it gave nil concentration of sulphide. The washed sample was again dried at 110 °C for 4 h cooled in the dessicator and stored in airtight plastic container for further use. The physico-chemical properties of both the adsorbents are summarized in the Table 1. The adsorbents were characterized with the aim of assessing its various physical and chemical properties, so that a better interpretation of the mechanism involved during the adsorption process can be provided. Carbon was analyzed for various parameters like pH, conductivity, moisture content, volatile matter and ash content by using standard methods [19,20]. Determination of C, H, N, S and O (by difference) was performed with a GmBH Elemental Analyzer System of from ELEMENTAR Analysensysteme, Germany. The surface area (BET) measurements of the adsorbents were obtained using BET method with nitrogen gas at 77 K using Micrometrics surface area analyser (Model ASP-2010, USA). The surface functional groups on the adsorbent were measured using Boehm Titration Method [21]. The surface morphological changes in the AC after treatment were visualized by using a scanning electron microscopy (SEM) with JSM-840 JEOL microscope of JEOL Techniques LTD, Japan at 2500× magnification.

Table 1
Main characteristics of the adsorbent

Parameters	Value	
	AC	AC-S
Raw material	Coconut shell	Coconut shell
Surface area (m ² g ⁻¹) (based on BET)	1000	900
Bulk density (g ml ⁻¹)	0.5	0.5
Particle density (g ml ⁻¹)	0.85	0.98
Ash content (on dry basis) (%)	3.59	2.00
Moisture content (%)	5.0	7.0
pH _{ZPC}	5.3	4.5
Conductivity (μS cm ⁻¹)	94.0	110.0
Particle size	8–20 mesh	8–20 mesh
Elemental analysis (%)		
C	66.0	63.0
H	3.5	1.75
N	0.331	0.281
O	29.6	27.109
S	0.56	7.86
Acidic surface functional groups (meq g ⁻¹)		
Carboxylic	0.105	0.119
Phenolic	0.006	0.026
Lactonic	0.003	0.03
Carbonyl	Nil	Nil

2.2. Adsorbate

Stock solution of Pb(II) was prepared (1000 mg/l) by dissolving required amount of, Pb(NO₃)₂ in acidified double distilled water. The stock solution was diluted with distilled water to obtain desired concentration ranging from 5 to 70 mg/l. All the chemicals used were of analytical reagent grade and obtained from SD fine chemicals, Mumbai, unless and otherwise mentioned.

2.3. Analytical method

Lead concentration was analyzed using atomic absorption spectrophotometer (AAS; model GBC 935) at 217 nm.

2.4. Batch mode adsorption studies

Stock solution of the adsorbate was diluted as required to obtain standard solutions containing 5–70 mg/l of Pb(II). A 100 mg of adsorbent was added to 50 ml of Pb(II) solution of a desired concentration at pH 5.0 in 125 ml reagent bottles and were agitated at 120 rpm for 20 h at room temperature (37 ± 2 °C) in a mechanical shaker. At the end of agitation, suspensions were separated by filtration and analyzed for their Pb(II) content. From Pb(II) concentration measured before and after adsorption (*C_i* and *C_e*, respectively) dry weight of the adsorbent (*W*) and the volume of aqueous solution (*V* in l), the amount of equilibrium adsorption of metals (*q_e*) was calculated using the Eq. (1a):

$$q_e(\text{mg/g}) = \frac{(C_i - C_e)V}{W} \quad (1a)$$

The removal percentage (*R*%) is defined as the ratio of difference in metal concentration before and after adsorption (*C_i* – *C_e*) to the initial concentration of Pb(II) in the aqueous solution (*C_i*) was calculated using the Eq. (1b):

$$R(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1b)$$

The batch adsorption study was replicated thrice for each of the adsorbents (AC and AC-S).

2.5. Dynamic column study experimental details

Experimental arrangement used for the dynamic column studies was same as used by Rajagopal and Kapoor [22] in their study for adsorptive removal of explosive contaminated wastewater using granulated activated carbon. The experimental arrangement is shown in Fig. 1 and it consists of column of borosilicate glass of 20 mm diameter. Sampling points before and after the column were also provided for drawing the effluent samples at regular intervals. Effluent after passing through the columns was discharged into a sump below the column. Previously wetted and degassed treated activated carbon is packed up to desired bed height (m) in water filled column of 20 mm (internal diameter) and was kept submerged throughout the runs to avoid air entrapment in the bed. Columns are mounted vertically and the AC-S bed is supported on perforated plate. The operation is in down flow plug mode.

A control valve to regulate the flow and a rotameter to monitor hydraulic loading rate is incorporated in the feed line of the column. Effluent and influent samples are collected after a regular interval. All the sorption experiments were carried out at the room temperature of 37 ± 2 °C and initial pH of 5.0. The residual concentration of lead in aqueous sample was determined using atomic adsorption spectrophotometer as before.

3. Result and discussion

3.1. Physical and chemical characterization of the adsorbents

3.1.1. Scanning electron microscopy

The SEM enables the direct observation of the changes in the surface microstructures of the carbons due to the modifications. Studies are available which have reported the utilization of the scanning electron microscopy analysis for showing the surface modification changes in the developed adsorbent [23]. As can be observed from Fig. 2(a) [AC] and Fig. 2(b) [AC-S], there is clear demarcation in the surface morphology of AC after treatment.

3.1.2. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) was used to determine the vibration frequency changes in the functional

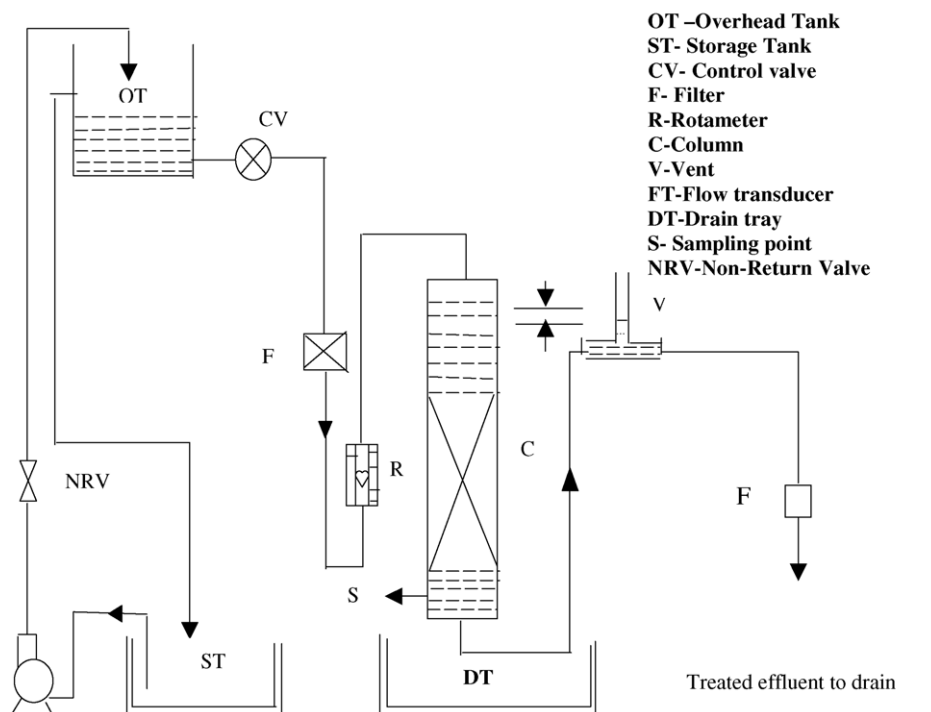


Fig. 1. Experimental setup for dynamic column studies.

Table 2

Some fundamental FTIR frequencies of activated carbon (AC) and the sulphurised activated carbon (AC-S)

Band position (cm ⁻¹)		Possible assignments
AC	AC-S	
3550	3450	O–H stretching (intermolecular dimeric)
1725	1749	C=O stretching (aldehydic)
3040	3010	=C–H stretching (alkenes)
–	1190	–C=S stretching
–	1380	–S=O stretching (sulphonates)
–	460	–S–S stretching

groups in the carbons. The spectra of carbons were measured by an FTIR spectrometer (Buckner, Germany) within the range of 400–4000 cm⁻¹ wave number. Spectra were plotted for both the adsorbents that is, AC and AC-S using the same scale on the transmittance axis. Table 2 presents the fundamental frequencies of AC and AC-S, and their respective possible band frequencies in the FTIR spectrum. As can be inferred from FTIR analysis, there is presence of sulphur functional groups like –C=S, S=O and S–S on the AC-S surface.

3.1.3. Elemental analysis

Elemental analysis provided the complete elemental composition of both the adsorbents as shown in Table 1. Presence of the sulphur functional groups, as interpreted from the FTIR spectrum of AC-S is again substantiated by increases in sulphur composition to 7.86% in AC-S from 0.56% in AC.

3.2. Pb(II) equilibrium adsorption isotherms

Adsorption isotherm data for Pb(II) adsorption were plotted and presented in Fig. 3. Equilibrium data obtained for the two adsorbents were fitted to the Langmuir and Freundlich isotherms. The following expressions of a straight line were used, found by means of mathematical transformation of isotherms:

For Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \quad (2)$$

where C_e is the equilibrium metal ion concentration (mg/l), q_e the amount of lead adsorbed at equilibrium (mg/g) and Q_0 (mg/g) and b (l/mg) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively [24].

For Freundlich isotherm:

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

where C_e is the equilibrium metal ion concentration (mg/l), x the amount of lead removed (mg), m weight of adsorbent used (g) and K_f and n are the Freundlich constants incorporating all the factors effecting adsorption capacity, an indication of favourability of metal adsorption onto adsorbent [25].

Linear plots of C_e/q_e versus C_e and $\ln(q_e)$ versus $\ln C_e$ show that the adsorption follows Langmuir and Freundlich isotherm models. As presented in the Table 3, a high value of coefficient of correlation, R^2 for both the adsorbents indi-

Table 3
Adsorption constants for Langmuir and Freundlich isotherm models

Adsorbents	Langmuir constants			Freundlich constants		
	Q_0 (mg/g)	b (l/mg)	R^2	K_f ($\text{mg}^{1-1/n} \text{l}^{1/n}/\text{g}$)	$1/n$	R^2
AC	21.88	3.51	0.9971	11.4937	0.409	0.858
AC-S	29.44	0.67	0.9313	12.44166	0.373	0.956

icates good agreement between experimental and predicted data using Langmuir equation.

Triplicate runs for batch mode adsorption experiments were made for each adsorbent to determine the relative deviation of the experiments. The adsorption of metal ions on the adsorbent material remained almost constant with the relative deviation of the order of $\pm 2\%$.

Maximum adsorption capacity [Q_0 (mg/g)] was found to be 29.44 mg of Pb(II) per g of AC-S as adsorbent. Values of adsorption capacity Q_0 (mg/g) of the other adsorbents are given in Table 4 for comparison.

Pb(II) adsorption onto AC-S shows about 35% increase over the adsorption onto AC, as can be seen by comparing Q_0 values for both the adsorbents. Hence, justify the validity of the modification process for activated carbon.

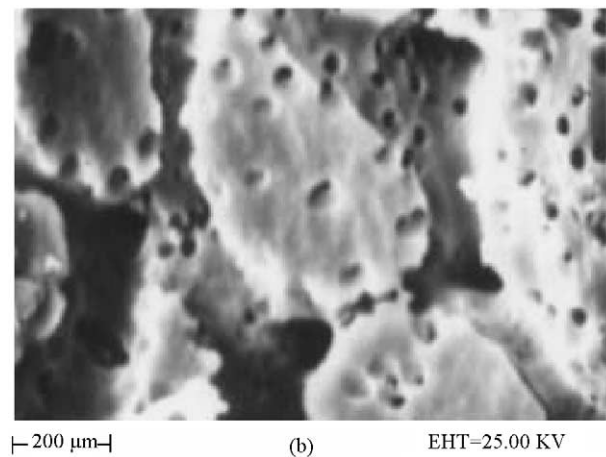
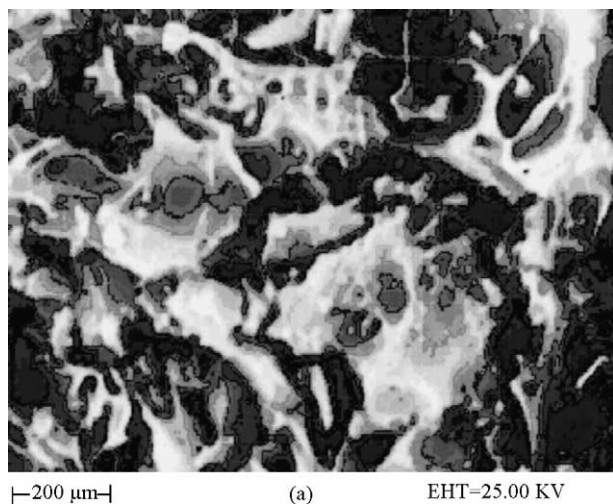


Fig. 2. (a) Scanning electron micrograph (SEM) of AC. (b) Scanning electron micrograph (SEM) of AC-S.

Table 4
Comparison of adsorption capacity of other adsorbents for Pb(II)

Adsorbent	Adsorption capacity (mg/g)	Reference
Olive mill product	21.56	[16]
GAC saturated with bacteria	26.40	[26]
Eicchornia carbon	16.61	[27]
Carbon aerogel	34.72	[28]
Carbon nano tubes	12.41	[29]
Sphagnum moss peat	19.90	[30]
Red mud	64.79	[31]
Bentonite	15.38	[32]
Bituminous coal	8.89	[33]
AC-S	29.44	This work

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 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 feed concentration (C_f). Breakthrough curve were plotted-giving ratio of effluent and feed (influent) concentrations (C_e/C_f) and time (h) for varying operating conditions.

The approach of Treybal [34] has been adopted for calculating the column capacity for the removal of Pb(II). Break-through capacity $Q_{0.5}$ (at 50% or $C_e/C_f = 0.5$) expressed in

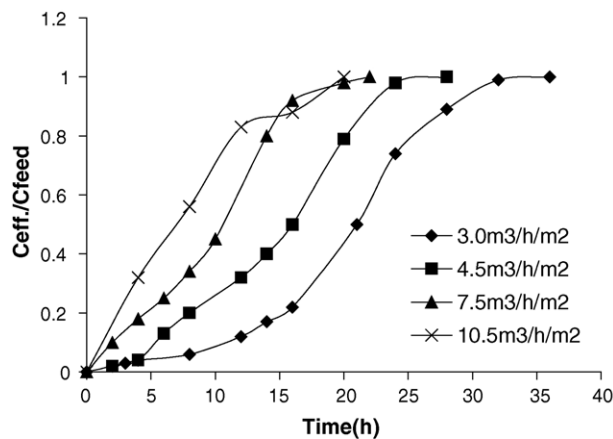


Fig. 3. Break through curve for different hydraulic loading rate at constant bed height of 0.4 m and feed concentration of 6 mg/l.

Table 5
Column adsorption capacity, $Q_{0.5}$ at various operating conditions at 50% break through concentrations

Concentration (mg/l)	Breakthrough time, 50% (h)	Hydraulic loading rate ($\text{m}^3/(\text{h m}^2)$)	Bed height (m)	Adsorption column capacity (mg/g)
2	20	7.5	0.5	1.75
3	17	7.5	0.5	2.23
4	15	7.5	0.5	2.63
6	21	3.0	0.5	2.21
6	16	4.5	0.5	2.52
6	11	7.5	0.5	2.89
6	7	10.5	0.5	2.57
6	6	7.5	0.4	1.91
6	12.5	7.5	0.6	2.79

mg of lead(II) adsorbed per gram of adsorbent was calculated using Eq. (4):

$$\begin{aligned} \text{Breakthrough capacity, } Q_{0.5} &= \frac{\text{metal adsorbed on adsorbent bed(mg)}}{\text{mass of adsorbent in bed(g)}} \\ &= \frac{\text{breakthrough time (at 50\%)} \times \text{flowrate} \times \text{feed concentration}}{\text{mass of adsorbent in bed}} \end{aligned} \quad (4)$$

Table 5 presents the column adsorption capacity for lead onto the adsorbent for varying operating variables that is bed height, flow rate and feed concentration. The column capacity for Pb(II) adsorption for the bed height of 0.4 m, hydraulic loading rate of $7.5 \text{ m}^3/(\text{h m}^2)$ and the feed concentration of 6 mg/l for 50% breakthrough concentration were found to be 2.89 mg/g. From comparison of adsorption capacity from Langmuir isotherm and column experiments, we can see that the less-stirred property in column mode reduced the lead(II) adsorption capacity on AC-S.

3.3.2. Effect of hydraulic loading rate

The experiments were conducted at bed height of 0.4 m, at constant feed concentration of 6 mg/l, with hydraulic loading rate ranging from 3.0 to $10.5 \text{ m}^3/(\text{h m}^2)$. Results of the experiments on effect of hydraulic loading rate (HLR) are plotted in Fig. 4, which shows that breakthrough time decreases from 21 to 7 h, as HLR increases from 3.0 to $10.5 \text{ m}^3/(\text{h m}^2)$. The adsorption capacity, calculated using Eq. (4), accordingly shows a maximum for $7.5 \text{ m}^3/(\text{h m}^2)$ as shown in Table 5. The variation in the slope of the breakthrough curve and adsorption capacity may be explained on the basis of mass transfer fundamentals. Increase in the hydraulic loading rate causes increase in zone speed, resulting in decrease in the time required to achieve breakthrough [35].

3.3.3. Effect of bed height (adsorbent mass)

Break through experiments were conducted at bed heights of 0.3, 0.4 and 0.5 m at constant feed concentration of 6 mg/l and at the hydraulic loading rate of $7.5 \text{ m}^3/(\text{h m}^2)$ optimized

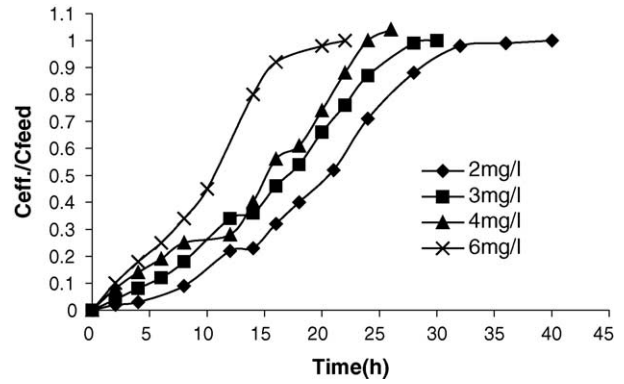


Fig. 4. Break through curve for different feed concentration at constant bed height of 0.4 m and hydraulic loading rate of $7.5 \text{ m}^3/(\text{h m}^2)$.

above (as showing the maximum adsorption capacity). Experiments on effect of bed height showed a decrease in minimum effluent concentration with bed height keeping other parameter constant. Minimum effluent concentration is defined as the average concentration of the metal ion at the column outlet (or effluent) in initial constant phase. As the bed height increases, the length of the bed through which the effluent passes increases. The increase in the total adsorptive capacity of the bed results in a decrease in the solute concentration in the effluent. Beyond a bed height of 0.4 m, the curve shows no appreciable change in minimum effluent concentration with further increase in bed height, hence 0.4 m has been chosen as optimized bed height for rest of the experiments [36].

3.3.4. Effect of feed concentration

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 gradient affects the saturation rate and breakthrough time, or in other words, the diffusion process is concentration

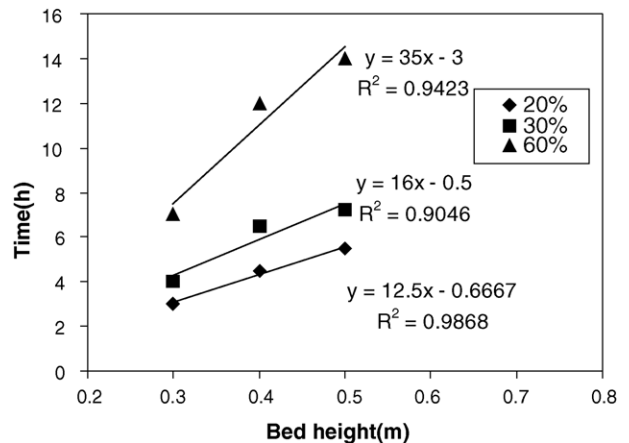


Fig. 5. Iso-removal lines for 20, 30 and 60% breakthrough for different bed height at constant feed concentration of 6 mg/l and hydraulic loading rate of $7.5 \text{ m}^3/(\text{h m}^2)$: Bohart–Adams modeling at mini-column studies.

dependent. As the feed concentration increases, metal loading rate increases, but so does the driving force for mass transfer, which in a decrease in the adsorption zone length. The net effect is an appreciable increase in adsorption capacity [37] as presented in Table 4.

3.4. Modeling of column study results: Bohart–Adams model

Bohart–Adams model based on the surface reaction theory [18] and it assumes that equilibrium is not instantaneous; therefore, the rate of the sorption is proportional to the fraction of sorption capacity still remains on the sorbent [38,39]. According to the Bohart–Adams model, the following equation to predicts the performance of continuous adsorption columns:

$$t = \frac{N_0 X}{C_0 v} - \ln \left[\left(\frac{C_0}{C_b} \right) - 1 \right] \times \frac{1}{[C_0 K]} \quad (5)$$

where, t is the time to break point (h); C_0 the influent concentration (mg/l); C_b the concentration at break through (mg/l); N_0 the adsorptive capacity of the adsorbent (mg adsorbed per litre of solution); X the bed depth of column (m); v the linear flow rate (m/h); K is the rate constant (l/(mg h)).

A simplified form of the Bohart–Adams Model is:

$$t = aX + b \quad (6)$$

where

$$a = \frac{N_0}{C_0 V} \quad (7)$$

and b in Eq. (6) is given by:

$$b = \ln \left[\left(\frac{C_0}{C_b} \right) - 1 \right] \times \frac{1}{[C_0 K]} \quad (8)$$

From iso-removal lines, i.e. the plots of time versus bed height (Fig. 5) regarding column operation under constant experimental conditions (except for bed height), the main parameters of the Bohart–Adams model can be calculated. Iso-removal lines were plotted for linear flow rate of $7.5 \text{ m}^3/(\text{h m}^2)$ for three different bed heights that is, 0.3, 0.4 and 0.5 m with the influent concentration of 6.0 mg/l. The breakthrough time at desired breakthrough concentrations exhibit linearity with bed depth. From the slope (a) and intercept (b) of the respective lines the adsorption capacity (N_0) and the rate of constant of adsorption (K), respectively. The calculated constants for the Bohart–Adams model for the adsorption of Pb(II) on to the AC–S are presented in Table 6 and will be of use in the design of the column.

From the respective linear equation, the necessary bed height for a pre-selected time period can be directly calculated until a defined breakthrough concentration [39].

The slope constant for a different flow rate can be directly calculated by multiplying the original slope (a) by the ratio

Table 6

The calculated constants of Bohart–Adams model for the adsorption of Pb(II) onto AC–S

Iso-removal percentage (%)	a (h/m)	b (h)	N_0 (mg/l)	K (l/(h mg))	R^2
20	12.5	−0.7	187.5	0.346	0.9423
30	16.0	−0.5	240.0	0.282	0.9046
60	35.0	−3.0	525.0	−0.022	0.9868

between the original (V_0) and the new flow rates (V_n). Accordingly,

$$a_{\text{new}} = a_{\text{old}} \left(\frac{V_0}{V_n} \right) \quad (9)$$

Similarly the equation can be developed for one concentration can be modified to be applying for another concentration:

$$a_{\text{new}} = a_{\text{old}} \left(\frac{C_0}{C_n} \right) \quad (10)$$

$$b_{\text{new}} = b_{\text{old}} \left(\frac{C_0}{C_n} \right) \left[\frac{\ln(C_n - 1)}{\ln(C_0 - 1)} \right] \quad (11)$$

where C_0 and C_n are the original and the new feed concentrations.

Based on Eqs. (9)–(11), breakthrough time was predicted for a new feed concentration and flow rate using the calculated Bohart–Adams model constants and obtained results are presented in Tables 7a and 7b, respectively. Good correlation prediction has been found for the case of changed feed concentration and flow rate. This is proved by the low value of standard deviation. Thus, developed model and the constants evaluated can be employed for the design of adsorption columns over a range of feasible flow rates and concentrations.

3.5. Column regeneration studies

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.

In the present study, elution of the lead (adsorbate) from aqueous solution was done using two concentrations of HNO_3 that is, 1.0 and 0.5 M under identical conditions of hydraulic loading rate of $4.5 \text{ m}^3/(\text{h m}^2)$, adsorbent bed height of 0.5 m as used for preloading of adsorbent with 6 mg/l of lead(II) as feed concentration. The results obtained with the two concentrations of HNO_3 are shown in Fig. 6.

From comparison of the elution histograms, the use of 1.0 M HNO_3 appeared to be more effective than 0.5 M HNO_3 . It can be inferred from Fig. 6 that the total eluant

Table 7a

Predicted breakthrough time based on the Bohart–Adams constants for a new feed concentration

Break point (%)	a_{old}	b_{old}	C_0	C_n	C_0/C_n	a_{new}	b_{new}	Bed height (m)	Predicted time (h)	Observed time (h)	E^a
60	35	-3	6	4	1.5	52.5	-3.07	0.4	17.92	18	0.03
30	16	-0.5	6	4	1.5	24.0	-0.51	0.4	9.08	10	
20	12.5	-0.7	6	4	1.5	18.8	-0.68	0.4	6.81	6	

Table 7b

Predicted breakthrough time based on the Bohart–Adams constants for a new flow rate

Break point (%)	a_{old}	b_{old}	V_0	V_n	V_0/V_n	a_{new}	Bed height (m)	Predicted time (h)	Observed time (h)	E^a
60	35	-3	7.5	4.5	1.67	58.3	0.4	20.33	17.5	0.04
30	16	-0.5	7.5	4.5	1.67	26.7	0.4	10.16	11.5	
20	12.5	-0.6	7.5	4.5	1.67	20.8	0.4	7.66	8.00	

$$^a \text{ Standard deviation } (E): E = \sum_{j=1}^N \left[\frac{(q_e)_{\text{experimental}} - (q_e)_{\text{predicted}}}{(q_e)_{\text{experimental}}} \right]^2$$

volume amounted to be 60 ml for 1.0 M HNO₃ and 80 ml for 0.5 M HNO₃, respectively, with corresponding total amounts of lead(II) desorbed being 1.66 and 1.37 mg/g of lead(II), respectively. The reason for this behaviour could be that 1.0 M HNO₃ provided more exchangeable H⁺ ion with metal ion than in case of 0.5 M HNO₃.

However, in terms of the quantity of eluant used (as difference between eluant's volumes used in two cases are not much significant) in the actual elution process as well as serious problems caused by disposal of waste with a higher acid content, it could be that 0.5 M HNO₃ may be more suitable as eluant.

After the metal ion was recovered, column regenerated with 0.5 M HNO₃, was washed with distilled water and again loaded with lead(II) concentration of 6 mg/l under the identical conditions as used for regeneration. Regeneration efficiency was calculated using Eq. (12) was found to be 52.0% for lead(II) [40]:

$$\text{RE\%} = \frac{A_r}{A_0} \times 100 \quad (12)$$

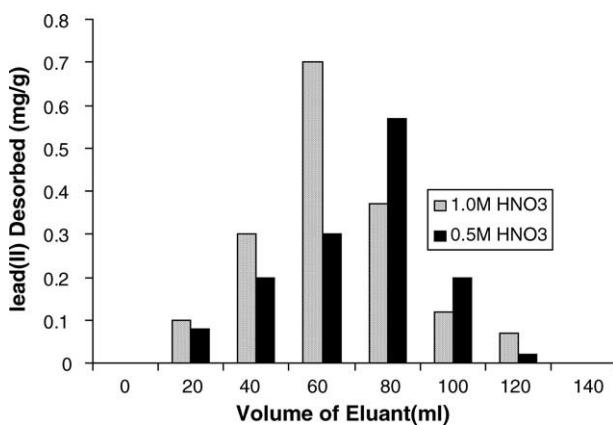


Fig. 6. Regeneration of AC–S adsorbent column with 1.0 and 0.5 M HNO₃ for desorbing lead(II).

In the above equation, A_r is the adsorptive capacity of the regenerated column and A_0 is the original capacity of the virgin adsorbent.

3.6. Approach to the adsorption mechanism: pH profile at pilot scale level

The most important factor influencing the adsorption rate and capacity is the adsorption pH. All the column experiments were carried out at initial pH 5.3 and the pH profile of exit solution for the sorption of Pb(II) onto AC–S is examined at the pilot plant level. At pilot plant operating conditions were maintained at the hydraulic loading rate of 4.93 m³/(h m²), bed height of 80 cm, column diameter of 10 cm, initial pH of 5.3 and initial feed concentration of 6 mg/l.

The pH profile of exit solution for the sorption of Pb(II) onto AC–S in the pilot scale column is shown in the Fig. 7. From pH profiles it has been demonstrated that at the beginning of the experiment the exit pH initially increased from 6.4 to 7.34 for the first 10 h, indicating the release of alkali

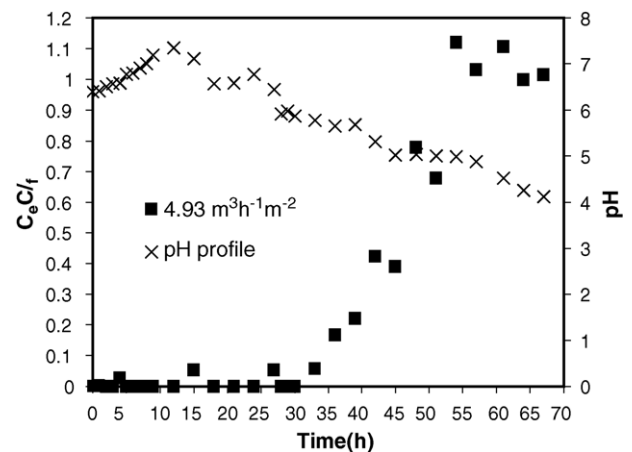


Fig. 7. Break through curve at pilot studies at 4.93 m³/(h m²) and the pH profile at the exit of the column at pilot studies, Conditions: bed height = 80 cm, column diameter = 10 cm, initial pH 5.3 and feed concentration of 6 mg/l.

ions from activated carbon surface. The very low liquid-phase Pb concentration during initial stage of run suggests possibility of some $\text{Pb}(\text{OH})_2$ precipitation on the adsorbent surface in the bed [37]. Zhan and Zhao has also reported increase in the final pH value due to the precipitation of lead(II) in adsorbent synthesized from natural condensed tannin [41]. Subsequently, a drop in pH profile of outlet solution was observed, which indicates release of cationic species like H^+ in the effluent during the adsorption of free Pb(II) ions onto AC-S. This suggests that adsorption of Pb(II) by AC-S is initially by surface precipitation followed by ion exchange and surface complexation of Pb(II) at carbon surface. Above mechanisms are very much in agreement with Fig. 7.

4. Conclusions

The objective of this work was to study the dependence of adsorption on adsorbent and adsorbate (lead) characteristics by means of both batch and column studies. Modeling of results of column mode studies can be used for further up-scaling process. Conclusions from the present study are as follows:

1. Characterization has shown a clear demarcation in the physico-chemical properties of the two adsorbents.
2. Pb(II) adsorption onto treated activated carbon (AC-S) shows about 35.0% increase over the adsorption onto AC, as can be seen by comparing Q_0 values for both the adsorbents. Hence the more efficient adsorbent, AC-S is further investigated by column mode studies.
3. Adsorption of Pb(II) on AC-S followed both Langmuir and Freundlich adsorption isotherm models.
4. Adsorption capacity for 6 mg/l feed concentration of Pb(II) at hydraulic loading rate of $7.5 \text{ m}^3/(\text{h m}^2)$ and 0.4 m bed height is found to be 2.89 mg/g, which indicates that practically adsorption capacity of AC-S 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.
5. Removal of Pb(II) onto adsorbent depends on adsorbent concentration, and hydraulic loading rate, feed concentration and adsorbent bed height.
6. Column studies data has shown a good agreement with the predicted results obtained by application of Bohart-Adams model as can be concluded from low value of standard deviation. The constants evaluated from Bohart-Adams model can be employed for the designing of adsorption columns over a range of feasible flow rates and concentrations.
7. The adsorbed lead(II) ion can be effectively eluted with the use of mineral acid such as HNO_3 of 0.5 M concentrations with the regeneration efficiency of 52%.
8. The investigation of the pH profile studies at the pilot scale level elucidates the adsorption mechanism. The mechanism includes ion exchange/adsorption, surface complexation and surface precipitation.

Similar work is in progress for investigating the efficacy of ACS for other heavy metals. Initial results imply that ACS has good adsorption capacity for other heavy metals and hence ACS can be used for wastewater applications in multi-component system due to its universality and easy preparation method. On the basis of bench scale column studies and an adsorption model developed to predict breakthrough curve, a pilot plant for the treatment of Pb(II) effluent wastewater is now in operations.

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