



Removal of some metal ions by activated carbon prepared from *Phaseolus aureus* hulls

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ARTICLE INFO

Article history:

Received 19 July 2008

Received in revised form

15 November 2008

Accepted 1 December 2008

Available online 6 December 2008

Keywords:

Lead

Zinc

Copper

Cadmium

Phaseolus aureus hulls

ABSTRACT

Removal of lead [Pb(II)], zinc [Zn(II)], copper [Cu(II)], and cadmium [Cd(II)] from aqueous solutions using activated carbon prepared from *Phaseolus aureus* hulls (ACPAH), an agricultural waste was studied. The influence of various parameters such as effect of pH, contact time, adsorbent dose, and initial concentration of metal ions on the removal was evaluated by batch method. The removal of metal ions by ACPAH was pH dependent and the optimum pH values were 7.0, 8.0, 7.0 and 6.0 for Cu(II), Cd(II), Zn(II), and Pb(II), respectively. The sorption isotherms were studied using Langmuir, Freundlich, Dubinin–Radushkevich (D–R), and Temkin isotherm models. The maximum adsorption capacity values of ACPAH for metal ions were 21.8 mg g⁻¹ for Pb(II), 21.2 mg g⁻¹ for Zn(II), 19.5 mg g⁻¹ for Cu(II), and 15.7 mg g⁻¹ for Cd(II). The experiments demonstrated that the removal of metal ions followed the pseudo-second-order kinetic model. Desorption experiments were carried out using HCl solution with a view to regenerate the spent adsorbent and to recover the adsorbed metal ions.

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1. Introduction

Contamination of various natural resources including water by heavy metals is a great concern nowadays. Large volumes of waste generated by rapid industrialization are one of the main causes for the contamination of water and other environmental resources with heavy metals. Heavy metal ions present in the waste streams from mining operations, tanneries, electronics, electroplating and petrochemical industries, as well as in textile mill products [1]. The release of large quantities of heavy metals into the natural environment, e.g. irrigation of agricultural fields by using sewage, has resulted in a number of environmental problems [2]. Due to the non-biodegradability and long biological half-life, heavy metal ions can be accumulated in the environmental elements such as food chain, and thus may pose a significant danger to human health [3]. Based on the industrial applications and potential pollution impact on the environment, the metals of environmental concern are Pb, Zn, Cu, and Cd. Pb heads the list of environmental threats because even at extremely low concentrations it causes brain damage in children [4]. The increasing demand for alkaline Zn manganese batteries, instead of mercury based ones, brings serious problems when those batteries are not disposed off properly [5]. Cd is a non-essential, non-beneficial, and highly toxic element to plants and

animals [6]. The toxic effects of Cu are well documented by Sobocka [7]. Moreover, in many countries concentrations of heavy metals in water are exceeding the permissible/accepted limits. The permissible concentrations of Pb, Zn, Cu, and Cd in drinking water have been set as 0.1, 5.0, 0.05 and 0.01 mg L⁻¹ in India, 0.005, 5.0, 1.0 and 0.01 mg L⁻¹ in USA, 0.05, 5.0, 3.0 and 0.005 mg L⁻¹ in UK, and 0.01, 5.0, 1.0 and 0.005 mg L⁻¹ in Canada, respectively [8,9].

Therefore, there is a considerable need to treat industrial effluents containing such heavy metals prior to discharge to protect public health. Treatment processes for metal contaminated wastewater include chemical precipitation, membrane filtration, reverse osmosis, ion exchange, and adsorption. These methods have been found to be limited, since they often involve high capital and operational costs and may also be associated with the generation of secondary wastes which present treatment problems. Over the last few years, adsorption has been shown to be an economically feasible method for removal of metal ions from water and wastewater. The biggest barrier in the application of this process by the industries is the high cost of adsorbents presently available for commercial use. The cost of adsorption technology application can be reduced if the adsorbent is inexpensive.

Activated carbon adsorption appears to be a particularly competitive and effective process for the removal of toxic heavy metals [10]. The adsorption capacity of an adsorbent is determined by its pore size, chemical structure that influences its interaction with polar and non-polar adsorbates, and active sites which determine the type of chemical reactions with other molecules [4]. However, commercial activated carbon (CAC) remains an expensive material

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for heavy metal removal. The use of local, natural, and cheap materials that are available in large quantities or certain waste from agricultural operations for treatment of water and wastewater containing heavy metals in developing countries is an area that is gaining interest.

There are many studies in the literature relating to the preparation of activated carbon from agricultural wastes such as peanut husks [11], sugarcane bagasse pith [12], nut shells [4], black gram husk [13], maize cob husk [14], walnut, hazelnut, almond, pistachio shell, and apricot stone [15] and their application for the removal of lead, zinc, copper, and cadmium from water and wastewater. In spite of several researchers adopted various low-cost adsorbents there is still a need to develop suitable adsorbents for the removal of metal ions from aqueous solutions.

Phaseolus aureus is a pulse crop largely grown in India. The hulls generated after collecting seeds are disposed of as a solid waste in rural India. The objective of this study was to investigate whether activated carbon prepared from *Phaseolus aureus* hulls (ACPAH) could be used as an alternative for commercial activated carbon for the removal of heavy metals from water and wastewater. The influence of various parameters such as pH, initial concentration of metal ion, contact time, and adsorbent dose on the removal efficiency of the ACPAH was studied. The kinetics of metal ions adsorption onto the ACPAH was analyzed by kinetic models. The experimental equilibrium adsorption data were analyzed by Freundlich, Langmuir, Dubinin–Radushkevich (D–R), and Temkin isotherm models to determine the best fit isotherm equation.

2. Materials and methods

2.1. Procedure of adsorbent preparation and activation

Phaseolus aureus hulls were collected from local fields of Rudrakota village in the Nellore district in the state of Andhra Pradesh, India, in the months between April and June. The preparation and activation of the carbon prepared from *Phaseolus aureus* hulls was performed by the following procedure. The collected hulls were cut into small pieces, washed with tap water several times to remove dust and dirt, rinsed with deionized distilled water several times until the pH and electrical conductivity (EC) of rinsings were constants, and then air-dried. The carbonization was performed in a muffle furnace which was initially purged with a flow of nitrogen for 10 min. The dried *Phaseolus aureus* hulls were placed in the muffle furnace and carbonization was carried out at 200 °C for 2 h. Thereafter, about 50 g of the prepared carbon was placed in a graphite tube and positioned at the center of the furnace. Steam produced by a steam generator was purged to enter into the graphite tube at a rate of approximately 5 mL min⁻¹. The sample was heated at a rate 10 °C min⁻¹ to 400 °C and held at this temperature for 1 h. After allowing the furnace to cool to room temperature, the steam activated carbon was ground in a mill followed by washing with deionized distilled water until the pH and EC of the washings were constant and then air-dried. The dried sample was sieved to pass through a 100-mesh sieve and stored in a desiccator for further use.

2.2. Characterization of adsorbent

The most important property of an adsorbent is its adsorption capacity, which is related to its surface area. Generally, the higher the surface area, the larger is its adsorptive capacity [16]. It has been reported that the activated carbons contain highly developed pore structures characterized by large surface area [17,18]. Steam activation showed best potential for producing activated carbons with high surface area and good pore ratio [19]. Surface area of the ACPAH was determined according to the method proposed by Shoemaker

and Garland [20]. The point of zero charge (pH_{pzc}) of the ACPAH was determined by the method described by Kinniburgh et al. [21]. Ash content, pH, and electrical conductivity (EC) of the ACPAH were determined by the methods proposed by Ng et al. [22]. Moisture content of the ACPAH was determined by the method described by Boynton [23]. After the ACPAH was digested with 0.01 M HCl, its organic C, H, and total N contents were determined by an elemental analyzer (Vario EL, Elementar, Germany) and then expressed on ash-free basis.

2.3. Batch mode adsorption studies

All the chemicals used were of analytical reagent grade. Deionized double distilled (DDD) water was used throughout the experimental studies. Copper (1 mg mL⁻¹): 1.000 g of copper metal was dissolved in 20 mL of concentrated HNO₃ and diluted to 1000 mL with deionized double distilled water. Cadmium (1 mg mL⁻¹): 1.000 g of cadmium metal was dissolved in 40 mL of concentrated HNO₃ and diluted to 1000 mL with deionized double distilled water. Lead (1 mg mL⁻¹): 5.324 g of lead nitrate Pb(NO₃)₂ was dissolved in about 200 mL water, and 1.5 mL concentrated HNO₃ was added and diluted to 1000 mL with deionized double distilled water. Zinc (1 mg mL⁻¹): 1.000 g of zinc metal was dissolved in 200 mL HCl (1 + 1) and diluted to 1000 mL with deionized double distilled water. Working standards were prepared by progressive dilution of stock solution of each metal. ACS reagent grade HCl, NaOH and buffer solutions (E. Merck) were used to adjust the solution pH.

Removal of Pb(II), Zn(II), Cu(II), and Cd(II) ions onto the ACPAH was carried out by batch method and the influence of various parameters such as effect of pH, contact time, activated carbon dose, and initial metal ion concentration were studied. For each experimental run, 50 mL of metal solution of known concentration was taken in a 100 mL stoppered reagent bottle, pH was adjusted to the desired value, and a known amount of the activated carbon was added. This mixture was agitated at room temperature (30 ± 1 °C) using a mechanical shaker (Macro scientific works, Delhi, India) at a constant rate of 150 rpm for a prescribed time to attain equilibrium. At the end of the predetermined time intervals, the sample was taken out and the supernatant solution was separated from the ACPAH by centrifugation at 20,000 × g for 20 min and analyzed the concentration of each metal ion (Pb(II), Zn(II), Cu(II), or Cd(II)) remaining in solution using atomic absorption spectrophotometer (AAS, Varian spectra AA, 55 Australia). Blank solutions were treated similarly (without adsorbent) and the recorded metal ion concentration by the end of each operation was taken as initial one.

Effect of pH was studied over the range of 2.0–9.0 and pH adjustments were made by the addition of dilute aqueous solutions of HCl, NaOH or buffer solutions. Effect of adsorbent dose was studied in the range of 100–900 mg of adsorbent in 50 mL of metal solution. Kinetics and effect of contact time on adsorption were determined at different time intervals over a range of 5–120 min. Adsorption isotherms were studied by varying the initial metal ion concentration from 20 to 250 mg L⁻¹. The effect of initial metal ion concentration studied over a range of 20–200 mg L⁻¹. All the batch experiments were carried out in duplicate and the values were reported average of two readings.

The atomic absorption spectrophotometer described above with single element hollow cathode lamps of respective elements operating with an air-acetylene flame, was used to analyze the concentrations of Pb, Zn, Cu, and Cd. An Elico (LI-129) pH meter was used for pH measurements. The mechanical shaker described above was used for agitating the samples. Fourier transform infrared spectrophotometer (Thermo-Nicolet FT-IR, Nicolet IR-200, USA) was used to analyze the organic functional groups of adsorbent. Vario EL, Elementar, Germany was used for elemental analysis of the ACPAH.

Muffle furnace (Tempo, Bombay, India) was used for carbonization and activation of the adsorbent.

2.4. Desorption studies

The reversibility of adsorption was investigated by carrying out desorption experiments. Once equilibrium was reached, activated carbon saturated with Pb(II), Zn(II), Cu(II), or Cd(II) was removed from solution and transferred into stoppered reagent bottles (250 mL capacity), containing 100 mL of (0.05–0.25 M) HCl solution and the bottles were shaken at 150 rpm for 4 h at room temperature ($30 \pm 1^\circ\text{C}$) using a mechanical shaker. The sorbent was then removed by centrifugation at $20,000 \times g$. The concentrations of metal ions in the aqueous solutions were determined by AAS.

2.5. Sorption isotherm models

The sorption equilibrium data of metal ions onto the ACPAH were analyzed in terms of Langmuir and Freundlich isotherm models [24] and also in terms of Dubinin–Radushkevich (D–R) and Temkin isotherm models [25] for the purpose of interpolation and limited extrapolation of the data. The relative coefficients of these models were calculated using least-squares fitting.

The Langmuir sorption isotherm equation $q_e = Q_m b C_e / (1 + b C_e)$ on linearization becomes

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

where q_e and C_e are the equilibrium concentrations of metal ions in the adsorbed and liquid phases in mmol g^{-1} and mmol L^{-1} , respectively. Q_m and b are Langmuir constants which are related to sorption capacity and energy of sorption, respectively, and can be calculated from the slope and intercept of the linear plot, C_e/q_e versus C_e .

The essential characteristics of the Langmuir isotherm can also be expressed in terms of a dimensionless constant of separation factor or equilibrium parameter, R_L , which is defined as

$$R_L = \frac{1}{1 + b C_0} \quad (2)$$

where b is the Langmuir constant and C_0 is the initial concentration of metal ions. The R_L value indicates the shape of isotherm [26]. R_L values between 0 and 1 indicate favorable adsorption, while $R_L > 1$, $R_L = 1$, and $R_L = 0$ indicate unfavorable, linear, and irreversible adsorption isotherms.

The Freundlich isotherm equation $q_e = k_f C_e^{1/n}$ can be written in the linear form as given below.

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (3)$$

where q_e and C_e are the equilibrium concentrations of metal ions in the adsorbed and liquid phases in mmol g^{-1} and mmol L^{-1} , respectively. k_f and n are the Freundlich constants which are related to the sorption capacity and intensity, respectively. The Freundlich constants k_f and n can be calculated from the intercept and slope of the linear plot with $\log q_e$ versus $\log C_e$.

The Dubinin–Radushkevich (D–R) isotherm approach assumes that there is a surface area where the adsorption energy is homogeneous. The D–R isotherm has the form:

$$q_e = Q_m \exp \left(-K \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \right) = Q_m \exp(-K\varepsilon^2) \quad (4)$$

where ε (Polanyi potential) = $RT \ln(1 + 1/C_e)$, Q_m is the D–R constant, K is related to the mean free energy of sorption per mole of the sorbate when it is transferred to the surface of the solid from infinity

in the solution and this energy can be computed using the following relationship:

$$E = \frac{1}{\sqrt{2K}} \quad (5)$$

The Temkin isotherm was derived assuming that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. It is expressed as:

$$q_e = \frac{RT}{b} \ln(K_T C_e) = B_1 \ln(K_T C_e) \quad (6)$$

where constant $B_1 = RT/b$ is related to the heat of adsorption, R the universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), T the temperature (K), b the variation of adsorption energy (J mol^{-1}) and K_T is the equilibrium binding constant (L mg^{-1}) corresponding to the maximum binding energy.

2.6. Kinetic models

The sorption kinetic data of metal ions measured using the ACPAH was analyzed in terms of pseudo-first-order and pseudo-second-order sorption equations [24]. The pseudo-first-order equation can be written as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

where k_1 (min^{-1}) is the rate constants of the pseudo-first-order sorption, q_t (mg g^{-1}) denotes the amount of sorption at time t (min), and q_e (mg g^{-1}) is the amount of sorption at equilibrium. The sorption rate constant k_1 , can be calculated by plotting $\log(q_e - q_t)$ versus t . The pseudo-second-order equation can be written as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

where k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of the pseudo-second-order sorption.

k_2 and q_e can be obtained from the intercept and slope of plotting t/q_t versus t .

3. Results and discussion

3.1. Characteristics of the adsorbent

The specific surface area of the ACPAH was $325 \text{ m}^2 \text{ g}^{-1}$. The pH (7.50) of aqueous suspension of the ACPAH (1%, w/v) was much higher than its pH_{PZC} (6.20) indicating that ACPAH in aqueous suspension showed the characteristics of negatively charged surface. Appreciable amount of ash (9.1%) and moisture (5.0%) indicate the presence of metals and hygroscopic water in the ACPAH. Compared to hydrogen content (3.4 g kg^{-1}), organic C and especially N and O contents (206, 489, and 301 g kg^{-1} , respectively) of the ACPAH were extremely high and these N and O may be in heterocyclic structure and/or in N- and O-containing functional groups. X-ray diffractogram of the ACPAH (Fig. 1) showed pore spacing mainly at around 0.699 nm and very weak appearance of pore spacing at around 0.298 nm, showing regular pore size spacing for adsorption in the structure. All these characteristics indicate that the ACPAH possessed the advantageous properties for well-defined adsorbent.

The FTIR absorption spectrum of the ACPAH is shown in Fig. 2, which is similar to the FTIR absorption spectrum of different batch of the ACPAH reported by Rao et al. [27]. The qualitative and semi quantitative information of the functional groups of the ACPAH were mainly elucidated by assigning the peaks, bands, and/or shoulders of FTIR spectrum as proposed by Stevenson [28] and Silverstein and Webster [29]. In addition, specific functional groups emphasized and discussed by the authors were cited. A

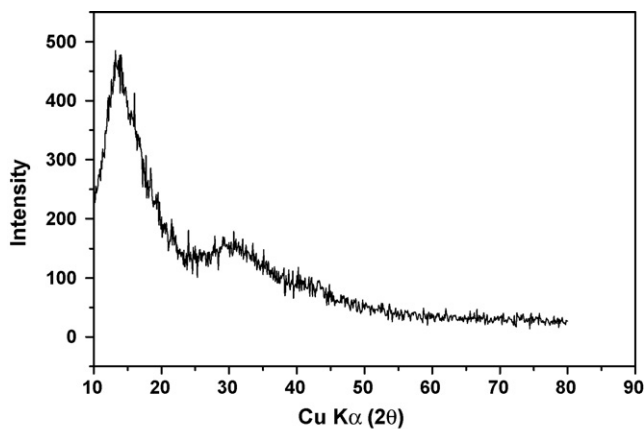


Fig. 1. X-ray diffractogram of the ACPAH.

weak but sharp absorption bands at 3797 and 3736 cm^{-1} appeared in the spectrum of the ACPAH may be ascribed to isolated OH groups [30]. The absorption spectrum showed a broad band in the 3500–3300 cm^{-1} region which is due to stretching vibrations of OH or N–H groups with varying degrees of H bonding and is probably attributed to adsorbed water [31,32]. The absorption band at 2920 cm^{-1} is assigned to the stretching vibrations of aliphatic CH, CH₂, and CH₃ side chain groups of the aromatic nuclei. The absorption peaks at 2355 and 2323 cm^{-1} appeared for the ACPAH is possibly attributed to C≡N stretching [33]. The FTIR spectrum of the ACPAH contains absorbance peak at 1567 cm^{-1} which is the characteristics of C=O in quinone [34] structure. The medium absorption band at 1423 cm^{-1} shows an aromatic ring of the ACPAH. The broad bands at 1300–1000 cm^{-1} have been assigned to C–O stretching vibrations in alcohols and phenols confirming the OH group in the ACPAH. Absorption peaks at 876 and 775 cm^{-1} are ascribed to out-of-plane deformation mode of C–H in variously substituted benzene rings [30]. The ACPAH contains –OH and C=O functional groups which could be involved in chemical bonding and may be responsible for the adsorption [35]. The oxygen of each carbonyl and hydroxyl group is considered a strong Lewis base because of the presence of nonbonding electron pairs. The oxygen base makes coordination bonds with the metal ions (which are Lewis acids).

3.2. Effect of solution pH

The interaction between the metal ions and the functional groups of the ACPAH depends on nature of the adsorbent as well

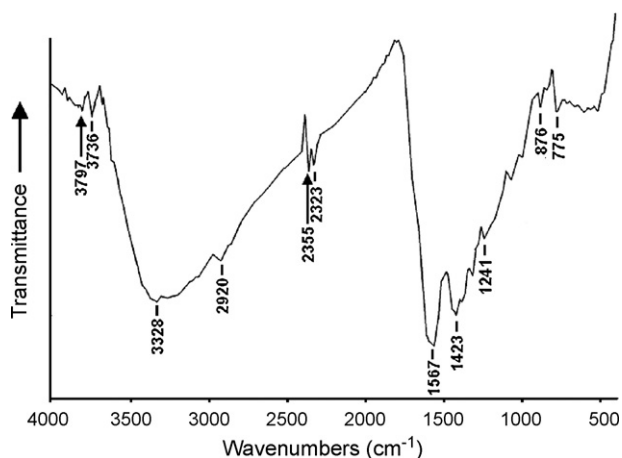


Fig. 2. FTIR spectrum of the ACPAH.

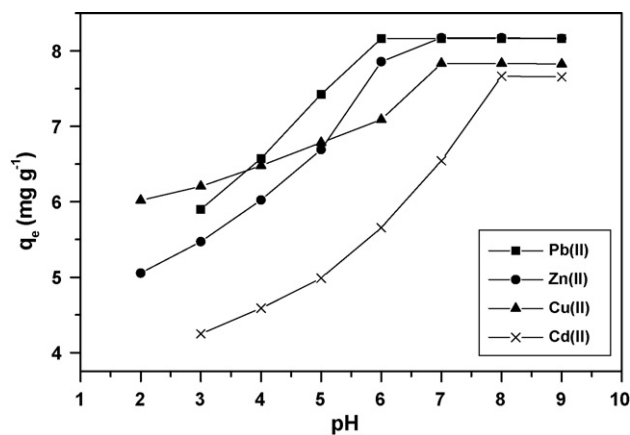
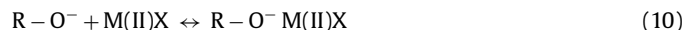
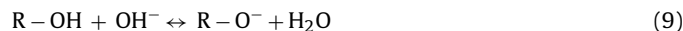


Fig. 3. Effect of pH on the removal of metal ions by the ACPAH.

as on solution chemistry of the adsorbate, which in turn depends on pH of the solution [36] considerably influencing metal speciation, sequestration, and/or mobility [37–39]. Therefore, the effect of hydrogen ion concentration was examined using solutions in the pH range of 2.0–9.0. Fig. 3 summarizes the removal of lead(II), zinc(II), copper(II), and cadmium(II) by the ACPAH as a function of pH. It is observed that the removal of metal ions increased with increasing solution pH, reaching an optimum value at pH 6.0 for Pb(II), pH 7.0 for Zn(II) and Cu(II), and pH 8.0 for Cd(II). The lower removal of the studied metal ions at below optimum pH values can be attributed to effective competition between higher concentration of H⁺ or H₃O⁺ and metal ions present in the forms of M²⁺ and M(OH)⁺ according to their (Pb, Zn, Cu and Cd) speciation diagrams [40–42]. The increase in metal removal as pH increased can be explained on the basis of a decrease in competition between proton (H⁺ or H₃O⁺) and positively charged metal ions [M²⁺ and M(OH)⁺] at the surface sites. Also as pH increased surface positive charge of the ACPAH decreased which resulted in lower repulsion of the adsorbing metal ions. The pHPZC of the ACPAH was 6.20, indicating negatively charged surface sites of the ACPAH at pH higher than 6.20. Except for Pb(II), the optimum pH values for Zn(II), Cu(II), and Cd(II) were much higher than pHPZC of the ACPAH (Fig. 3). At optimum pH values surface functional groups of the ACPAH may dissociate, by deprotonation resulting in negatively charged functional groups. Consequently, such negatively charged groups were showing affinity towards the positively charged or neutral metal species due to electrostatic interaction which may be responsible for the significant removal of metal ions by the following possible reactions [43].



[M(II)X = Metal species of Pb, Zn, Cu, or Cd].

Below pH 8.0 the predominant species of Pb in solution were only Pb²⁺ and Pb(OH)⁺ [44,45]. Therefore, the main species of Pb adsorbed by the ACPAH at pH lower than 6.0 was Pb²⁺ (Fig. 3). The predominant Zn species in solution was Zn²⁺ when pH was below 7.7, whereas Zn(OH)⁺ was more prevalent above this pH [45]. As seen from Fig. 3, Zn²⁺ was thus the main species adsorbed by the ACPAH at pH below 7.0. The predominant Cu species in the reaction system was Cu²⁺ when the pH was below pH 6.9 while Cu(OH)₂⁰ was the major solution species above this pH [44,45]. Therefore, Cu²⁺ and trace amount of Cu(OH)₂⁰ were the main species adsorbed by the ACPAH at pH lower than 7.0 (Fig. 3). None of the hydrolyzed species were contributing significantly to total Cd in solution except Cd(OH)⁺ and Cd(OH)₂⁰ at pH above 7.5 [45]. Therefore, as seen from Fig. 3, the main species adsorbed by the ACPAH at pH below 8.0 were

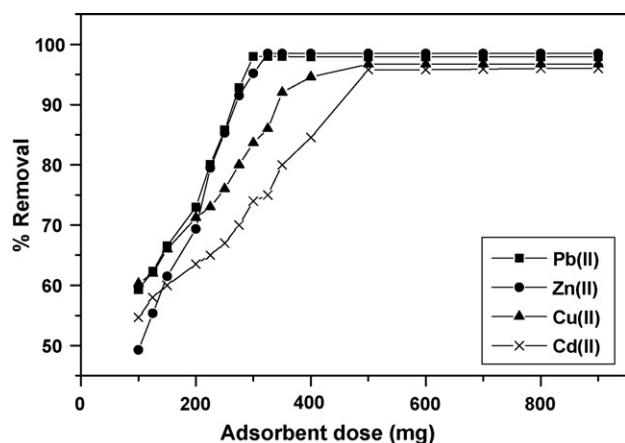


Fig. 4. Effect of adsorbent dose on the removal of metal ions by the ACPAH.

predominantly Cd^{2+} and less amounts of $\text{Cd}(\text{OH})^+$ and $\text{Cd}(\text{OH})_2^0$. Consequently, at the depicted pH values where each corresponding q_e of the four metals Pb, Zn, Cu, and Cd started becoming constants with increasing pH (Fig. 3), all the species of the four metals were thus predominantly in ionic forms and/or trace amount of water soluble neutral molecules of metal hydroxides below each depicted pH. When the pH was higher than the optimum pH (beyond the pH values of 6.0 for Pb, 7.0 for Zn and Cu, and 8.0 for Cd (Fig. 3)) the metal ions may get converted to their hydroxides, and this resulted in a decrease in the removal of metals by the active sites of the ACPAH [42,46–48]. Further, the sorption process of metals by the ACPAH is kinetically faster than the precipitation of metal hydroxides under higher pH. The precipitation of metal hydroxide into the pores or spaces around the particles is hardly possible. Moreover, the percentage removal of metal ion was much greater by adsorption than by precipitation [48].

3.3. Effect of adsorbent dose

Dosage study is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of metal ion solution. The effect of adsorbent dose on the percent removal of Pb(II), Zn(II), Cu(II), and Cd(II) at initial concentration of 100 mg L^{-1} is shown in Fig. 4. From the figure it can be observed that increasing of adsorbent dose increased the percent removal of Cu(II) and Cd(II) up to 96.7 and 95.8%, respectively, with the required optimum dosage of 500 mg. The percent removal of Pb(II) and Zn(II) reached up to 98.5 and 99.2%, respectively, with the required optimum dosage of 325 mg (Fig. 4). Beyond the optimum dosage the removal efficiency did not change with the adsorbent dose. As expected, the removal efficiency increased with increasing the adsorbent dose for a given initial metal concentration, because for a fixed initial adsorbate concentration increasing adsorbent dose provides greater surface area or more adsorption sites. Further, it can be attributed to the binding of metal ions onto the surface functional groups present on the ACPAH. On the other hand, when the ACPAH dose increased the adsorption capacity (the amount adsorbed per unit mass of adsorbent) decreased from 24.1 to 4.29 mg g^{-1} for Cu(II), 21.9 – 4.76 mg g^{-1} for Cd(II), 14.8 – 6.14 mg g^{-1} for Pb(II), and 12.3 – 6.15 mg g^{-1} for Zn(II). The decrease in adsorption capacity with increase in the adsorbent dose is mainly due to the increase of unsaturation of adsorption sites through the adsorption reaction. Another reason may be due to the particle interactions, such as aggregation, resulting from high sorbent concentration. Such aggregation would lead to decrease in total active surface area of the sorbent.

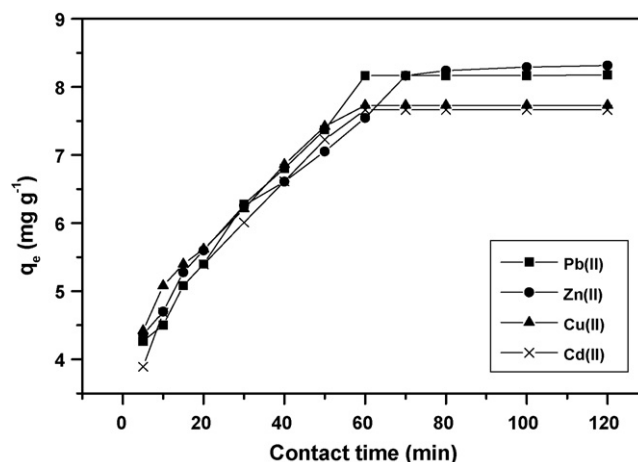


Fig. 5. Effect of contact time on the removal of metal ions by the ACPAH.

3.4. Effect of contact time

Equilibrium time is one of the important parameters for an economical wastewater treatment system [49]. The experimental results relating to the effect of contact time on removal of Pb(II), Zn(II), Cu(II), and Cd(II) are shown in Fig. 5. It can be clear from the figure that the removal of metal ions increased with increase in agitation time and attained equilibrium by 60 min for Cu(II) and Cd(II) with concentration of 80 mg L^{-1} , 60 min for Pb(II) with concentration of 50 mg L^{-1} , and 70 min for Zn(II) with concentration of 50 mg L^{-1} onto the ACPAH. The majority of metal ions removal was attained within the first 30 min. The behavior suggests that at the initial stage, sorption takes place rapidly on the external surface of the adsorbent.

3.5. Effect of initial concentrations of metal ions

The effect of initial concentrations of Pb(II), Zn(II), Cu(II), and Cd(II) on their removal by the ACPAH is shown in Fig. 6. From this figure, it can be observed that removal of metal ion increased per unit weight of the ACPAH from 3.30 to 23.4 mg g^{-1} for Pb(II), from 3.30 to 23.1 mg g^{-1} for Zn(II), from 2.00 to 17.2 mg g^{-1} for Cu(II), and from 2.00 to 14.7 mg g^{-1} for Cd(II), as the initial concentrations of metal ions increased from 20 to 200 mg L^{-1} . At lower initial concentration of metal ion, the ratio of the initial number of metal ions to the available sorption sites of the ACPAH is low and subsequently the fractional adsorption of metal ion by the

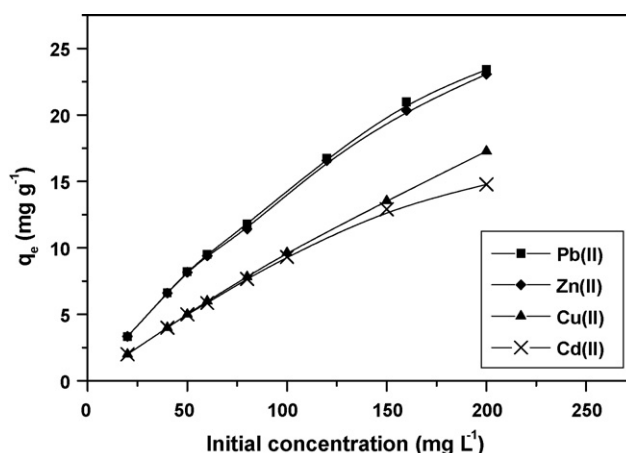


Fig. 6. Effect of initial concentrations of metal ions on their removal by the ACPAH.

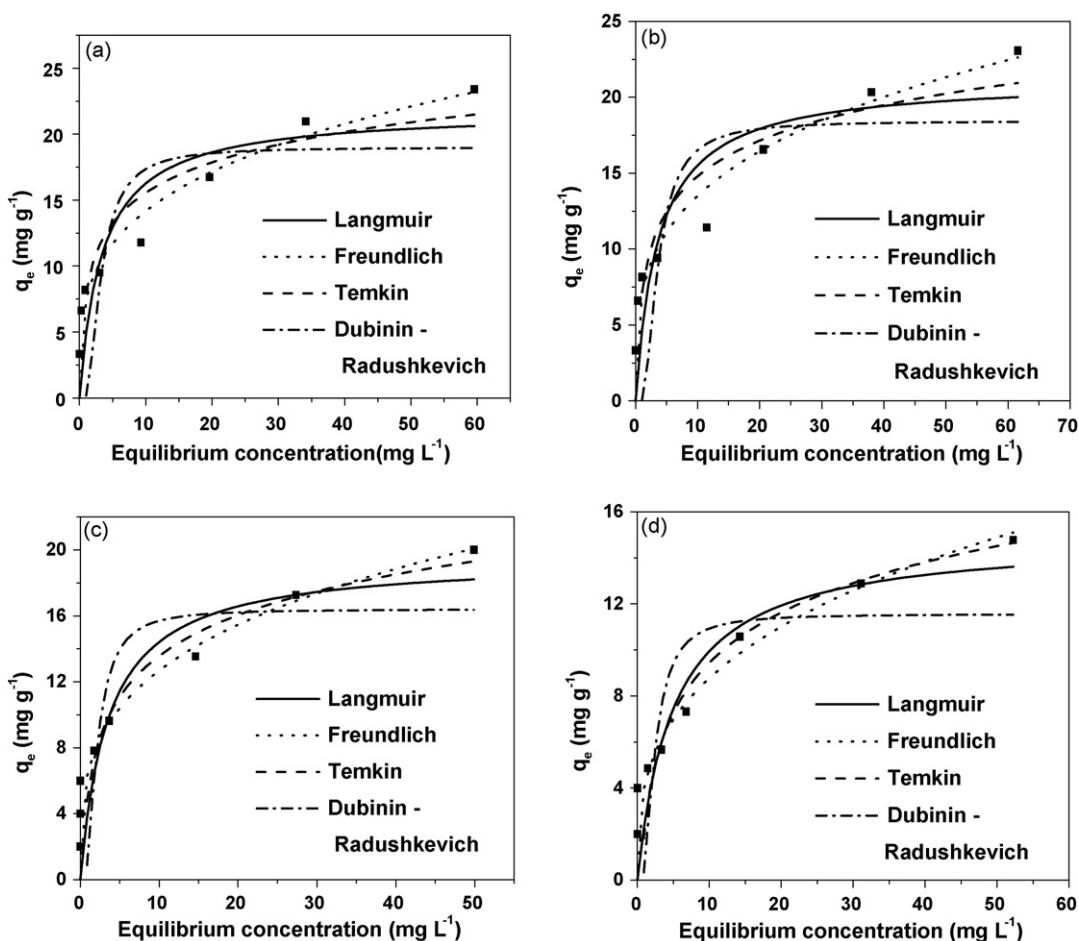


Fig. 7. Adsorption isotherms of (a) Pb(II), (b) Zn(II), (c) Cu(II), and (d) Cd(II) onto the ACPAH.

ACPAH becomes independent of its initial concentration. However, at higher initial concentration of metal ion the available adsorption sites of the ACPAH becomes fewer and hence the percent removal of metal ion is dependent upon its initial concentration.

3.6. Adsorption isotherms

The relationship between the amount of a substance adsorbed per unit mass of adsorbent at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. The equilibrium adsorption isotherms are important in determining the adsorption capacity of metal ions [Pb(II), Zn(II), Cu(II), and Cd(II)] and diagnose the nature of adsorption onto the ACPAH. The sorption data were fitted to Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin adsorption isotherm models described in Section 2.5. As can be seen from the isotherms in Fig. 7 and regression coefficients in Table 1, the Freundlich and Temkin models show the best fit compared to Langmuir and Dubinin–Radushkevich models.

The adsorption capacities of Pb(II), Zn(II), Cu(II), and Cd(II) by the ACPAH expressed by Langmuir coefficient Q_m demonstrate that adsorption capacity increased in the sequence, Cd(II) < Cu(II) < Zn(II) < Pb(II), which is in the same order of increasing ionic radius of metal ions studied [11]. The removal order of preference for the four metals were also the same as those revealed by Brown et al. [50] and Rao et al. [51]. The dimensionless parameter (R_L) value, which is defined in Eq. (2) described above can be computed by substituting the values of b and C_0 to the equation. The R_L values were 0.066 for Pb(II), 0.071 for Zn(II), 0.044 for Cu(II),

and 0.061 for Cd(II). For the four metal ions the values of R_L were between 0 and 1, pointing out the favorable adsorption onto the ACPAH [26].

Freundlich coefficient K_f , which represents the adsorption capacity was found to be increased in the sequence, Cd(II) < Cu(II) < Zn(II) < Pb(II), which is the same as that revealed by Langmuir coefficient Q_m (Table 1). The other Freundlich coefficient

Table 1

Constants of Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin isotherm models for Pb(II), Zn(II), Cu(II), and Cd(II) adsorbed by the ACPAH.

Model	Metal ion			
	Pb(II)	Zn(II)	Cu(II)	Cd(II)
Langmuir				
Q_m	21.8	21.2	19.5	15.7
b	0.28	0.26	0.27	0.19
R^2	0.8999	0.8997	0.8975	0.9162
Freundlich				
K_f	7.50	6.93	6.57	4.11
n	3.62	3.40	3.50	3.04
R^2	0.9987	0.9787	0.9811	0.9811
Dubinin–Radushkevich				
Q_m	19.0	18.44	16.24	11.55
E	0.141	0.141	0.099	0.098
R^2	0.5964	0.5609	0.8361	0.7692
Temkin				
b	9.50	9.32	8.82	10.0
K_T	10.85	8.00	4.51	2.00
R^2	0.9346	0.9325	0.9643	0.9174

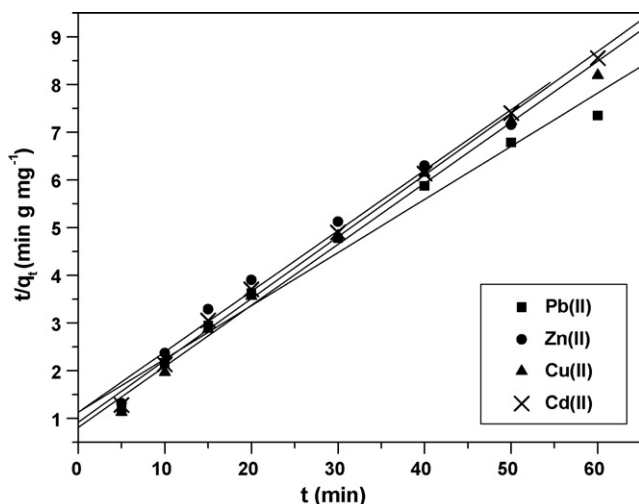


Fig. 8. Pseudo-second-order kinetics plots for the removal of Pb(II), Zn(II), Cu(II), and Cd(II) by the ACPAH.

"*n*" values fulfilled the condition of $0 < n < 10$ for favorable adsorption. The Freundlich type adsorption isotherm is an indication of surface heterogeneity of the adsorbent. This leads to the conclusion that the surface of ACPAH is made of small heterogeneous patches which is favorable for adsorption phenomenon.

The Temkin isotherm assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies, up to maximum binding energy.

3.7. Adsorption kinetics

The prediction of kinetics is necessary for the design of sorption systems. Measurement of sorption rate constants and order of the reaction are important physico-chemical parameters to evaluate the basic qualities of a good sorbent. In this study it was found that removal of metal ions from aqueous solution is a linear phase within a time period of about 60 min for Pb(II), Cu(II), and Cd(II), and 70 min for Zn(II) (Fig. 5). This behavior can be attributed to the utilization of available adsorbing sites on the surface of ACPAH adsorbent. After this phase, sorption of metal ions was almost ignorable (Fig. 5). In order to observe the sorption process of Pb(II), Zn(II), Cu(II), and Cd(II) ions onto the ACPAH, pseudo-first-order and pseudo-second-order kinetic models which are described in earlier Section 2.6 were implemented. The pseudo-second-order plots for the removal of Pb(II), Zn(II), Cu(II), and Cd(II) by the ACPAH are shown in Fig. 8, which were used to calculate the four rate constants k_2 and adsorption capacities q_e . In the same manner, the pseudo-first-order plots (figure not shown) for the removal of Pb(II), Zn(II), Cu(II), and Cd(II) by the ACPAH were used to calculate the four rate constants k_1 . The adsorption rate constants (k_1 and k_2) and adsorption capacity (q_e) for the removal of metal ions by the ACPAH are thus reported in Table 2. Since the correlation coeffi-

Table 2
Adsorption kinetics for removal of Pb(II), Zn(II), Cu(II), and Cd(II) by the ACPAH.

Metal ion	Pseudo-first-order		Pseudo-second-order		
	k_1 (min^{-1})	R^2	q_e (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2
Pb(II)	3.47×10^{-2}	0.9607	8.69	1.16×10^{-2}	0.9877
Zn(II)	4.67×10^{-2}	0.9734	7.88	1.42×10^{-2}	0.9911
Cu(II)	4.11×10^{-2}	0.9408	7.80	2.02×10^{-2}	0.9962
Cd(II)	5.52×10^{-2}	0.9545	7.71	1.82×10^{-2}	0.9979

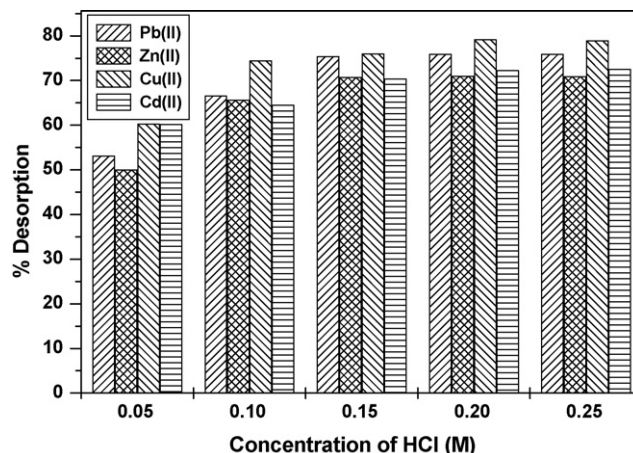


Fig. 9. Effect of HCl concentration on the desorption of Pb(II), Zn(II), Cu(II), and Cd(II) from the ACPAH.

icients are consistent and closer to unity for pseudo-second-order kinetic model than for pseudo-first-order kinetic model (Table 2), the adsorption kinetics can be well explained by pseudo-second-order kinetic model for the removal of Pb(II), Zn(II), Cu(II), and Cd(II) by the ACPAH.

3.8. Desorption studies

Desorption studies help the recovery of the metal from waste and the recycling of the adsorbent. The use of thermal activation to regenerate the adsorbent could require high energy and adsorbent loss in each cycle. Hence, studies were carried out to use chemical regeneration for adsorbate desorption. Desorption studies were carried out using different concentrations of HCl solution, which has been reported to be an efficient metal desorbent [13]. Desorption of Pb(II), Zn(II), Cu(II), and Cd(II) using HCl solution by disruption of coordination of these metal ions with the surface of ACPAH and subsequent release into desorption medium was studied. The results relating to desorption of metal ions by HCl solution are shown in Fig. 9. The results showed that with increase in concentration of HCl solution the desorption also increased but attained constant at 0.20 M HCl for Cu(II) and Cd(II) and 0.15 M HCl for Pb(II) and Zn(II). The desorbed percentages were 79.2% for Cu(II), 72.3% for Cd(II), 75.5% for Pb(II), and 70.8% for Zn(II) from the ACPAH.

4. Conclusions

The functional groups on the surface of ACPAH such as phenolic hydroxyls and carbonyl groups that were formed during the activation process played effective role in the removal of heavy metal ions. Sorption process was affected by experimental parameters such as pH, initial metal ion concentration, contact time, and adsorbent dosage. Sorption isotherms were better described by Freundlich and Temkin models in comparison to Langmuir and Dubinin–Radushkevich models. Thus these studies revealed that activated carbon prepared from *Phaseolus aureus* hulls generated after collecting seeds, which is being disposed of as a solid waste in rural India, can be effectively used as an alternative for commercial activated carbons for the removal of heavy metals from water and wastewater.

Acknowledgements

The authors are highly thankful to M/S Amara Raja Batteries Limited, Karakambadi, Tirupati, for providing AAS facilities and IICT, Hyderabad for providing elemental analysis of adsorbent.

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