Remediation of heavy metal ions using hierarchically porous carbon monolith synthesized via nanocasting method

Manisha Sharma\textsuperscript{a}, Jasminder Singh\textsuperscript{a}, Satyajit Hazra\textsuperscript{b}, Soumen Basu\textsuperscript{b,}\textsuperscript{\textdagger}

\textsuperscript{a} School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala, Punjab, 147004, India
\textsuperscript{b} Saha Institute of Nuclear Physics, Kolkata, 700064, India

\textbf{ARTICLE INFO}

\textbf{Keywords:}
Carbon monoliths
Micropore
Metal ions
Adsorption
Kinetic study
Thermodynamic study

\textbf{ABSTRACT}

The synthesis of most promising and robust adsorbents to purify water has been fostered as a great interest in the most promising fields. Many adsorbents based on carbon material have been studied worldwide due to the high surface area, high chemical stability, compact structure and appropriate for bulk production. Here, carbon monoliths (CM) with micro/mesopore have been synthesized via nanocasting method, using silica monoliths as a solid template. On the micrometer scale, synthesized CMs are considered as a positive replica of parent silica monoliths. CMs with the high surface area (1103 m\textsuperscript{2}/g) is tested first time as an adsorbent for effective removal of Pb(II) and Cd(II) ions from aqueous solution. Also, through batch experiments various effective and applicable parameters were successfully studied for instance pH, contact time, adsorbate/adsorbent concentration, temperature etc. The maximum monolayer adsorption efficiency for Pb(II) and Cd(II) ions is 1128 mg/g and 989 mg/g, respectively. Kinetic data for the adsorption process shows best fit to pseudo-second order. Due to solid rock-like structure, carbon monoliths can be reusable and be fitted as highly effective and economical adsorbent for heavy metal ion adsorption process as compared to other adsorbents known in literature like SiO\textsubscript{2}, TiO\textsubscript{2}, MnO\textsubscript{2}, ZnO and activated carbon.

\textbf{1. Introduction}

For a healthy life, water is an important resource on the earth for life [1]. With the growth of scopes in science and technology, various after effects have been rising together with environmental disorder due to rapid growth in the generation of hazardous waste from developed industries and population expansion [2,3]. Therefore, industrial world legislation over worldwide has been advanced in concern to industrial discharge. Removal of heavy metal ions (e.g. lead and cadmium) from industrial wastewater can be achieved by physical or chemical treatment processes like ion exchange, adsorption, membrane filtration, precipitation and reverse osmosis etc. [4–7] Among all above mentioned processes, adsorption is considered as adequate and economically feasible and even effective for removal of heavy metal ions at trace levels. Researchers all over the world are carrying out work on the development of cheaper and highly effective adsorbents for removal of heavy metal ions from wastewater. A number of adsorbents for removal of toxic pollutants have been already reported in literature includes zeolites, activated carbon, chitosan, silica, CNT, porous metal oxides, clay materials etc [8–13].

Mesoporous adsorbents due to the high surface area, uniform and ordered pore size distribution have incomparable adsorption efficiency [14]. However, the synthesis cost for these mesoporous adsorbents may get an increase but it can be transformed into cost-effective by development in bulk and by execution of regeneration experiments for removal of heavy metal ions. Monoliths containing bi-/tri-modal porosity are universally known porous materials (like porous silica and metal oxide monoliths formed by the sol-gel method and nanocasting method) are most attractive subject in separation science due to their extraordinary surface properties [15]. Owing to solid rock-like structure, the monolithic system has an advantage over powder porous particles in separation media [16]. Without using any expensive filtration devices, monoliths can be easily extracted from separation media and be capable of reuse for several times. So, in this regard, carbon monoliths with micropores have various benefits and individuality as compare to other known adsorbents from literature. Carbon monoliths have low toxicity, high surface area/porosity, thermal/chemical stability, high adsorption capacity and resistance to acidic and basic medium. At present, nano-casted carbon monolith (having micro- and mesopores) has gained an interest in a wide range of applications like catalysis, double-layer capacitors, and molecular separation. Considering these facts, carbon monoliths can be counted as an incomparable adsorbent for metal ion
removal from wastewater. In our previous studies [17], novel silica monoliths via the sol-gel method and metal-oxides monoliths via nanocasting process were successfully synthesized, aiming to boost the adsorption efficiency of the adsorbent for toxic pollutants. Here, carbon monoliths were prepared by the nanocasting method as a negative replica of previously synthesized silica monoliths. Up to now, no systematic investigation of heavy metal ion adsorption by CM has been reported. Hence, we have anticipated that synthesized carbon monoliths have favorable potential to be used as an adsorbent for Pb(II) and Cd(II) removal.

2. Material and methods

All the chemicals used were purchased from Sigma-Aldrich and Merck and used without further purification. Mesoporous silica monoliths synthesized in previous studies [18] have been used as a mold for the synthesis of carbon monoliths. In a brief, HNO₃ (30% v/v) was added to a mixture of tetraethylorthosilicate and PEG solution and stirred until a translucent solution was obtained. Subsequently, CTAB was added and again stirred until the surfactant got dissolved completely. Silica gel was attained after 72 h of aging at 40 °C and later hardening of synthesized silica monolith was soaked into NaOH solution (1 M) at 90 °C for 9 h. Later, monoliths were washed and dried at 40 °C, followed by the calcination at 550 °C at 1 °C/min heating ramp. The synthesis process for carbon is as follow: furfuryl alcohol (FA) and oxalic acid (OA) in ratio $\eta_{\text{FA}} - \eta_{\text{OA}}$ (200–300) were mixed in 1,3,5-trimethylbenzene (TMB) and the obtained solution was impregnated into the pore of parent silica monoliths. After completion of impregnation, the white monoliths became transparent. Afterward, transparent monoliths were heated at 80 °C for the polymerization of FA and later heated to 300 °C at a heating rate of 1 °C/min. At last, the temperature was increased up to 800 °C for 4 h at a heating ramp of 1 °C/min. Finally, the CM was obtained after silica removal by using 2 M NaOH solution.

2.1. Characterization of adsorbent

X-ray diffraction analysis (XRD) was performed using PANALYTICAL X’Pert PRO X-ray diffractometer having Cu Kα (λ = 1.540 Å) radiation operated at 45 KV with scanning range (2θ) from 10° to 80°. To confirm the morphology and elemental composition, field emission scanning electron microscopy (FESEM), JEOL-7000 FESEM equipped with Energy Dispersive X-ray Spectroscopy (EDX) detector was used. Surface area was analyzed through BET surface area analyzer of Microtrac BEL Corp. Pvt. Ltd, Japan (Microtec Belsorp Mini–II). Prior to analysis, synthesized CM was degassed at 200 °C for 3 h. FTIR spectra were collected using Agilent Resolution Pro-carry 660. For FTIR determination samples were prepared via grinding 1 mg of sorbents with 80 mg of spectral grade KBr in an agate mortar. Atomic absorption spectrophotometer (AAS) of GBC 932AA was used to analyze the metal ion concentrations. The pH was adjusted and measured using a pH meter, model cyber scan pH 1100 (Eutech, Singapore).
3. Adsorption study

Metal ions adsorption on the CM was executed in a batch system using favorable conditions. Dry CM (0.02 g) was added to a 50 mL of a synthetic solution of metal ion (5–50 mg/L for Pb(II) and 5–20 mg/L for Cd (II)) and stirred at a speed of 200 rpm for different time periods. After completion of adsorption period, the solution was centrifuged for 10 min at 8000 rpm and the supernatant solutions were analyzed to determine the residual metal ion concentration left in the solution by AAS. AAS was used to analyze the dissolved concentration of metal ions from a standard solution of lead nitrate and cadmium carbonate respectively, using calibration curve. The adsorption capacity ($Q_e$) was calculated by the uptake amount of metal ions adsorbed per mass unit of monoliths (mg/g) using the formula:

\[
Q_e = \frac{(C_0 - C_e)}{m} \times V
\]

where $C_0$ is the initial and $C_e$ is the equilibrium concentration (mg/L), while $V$ is the volume of the solution (L) and $m$ is the weight of the adsorbent (g). Also, to compare the adsorption efficacy of the synthesized CMs, some commercially available mesoporous materials have also been used as an adsorbent. All kinetic parameter studies were performed for 2.5 h. To control precision, each one of the adsorption experiments was performed in triplicates and the average value was reported.

3.1. Adsorption kinetics

In an attempt to study the adsorption process of Pb(II) and Cd(II) ions on solid CMs, various kinetic models like pseudo-first-order,
pseudo-second-order, Elovich’s model and intraparticle diffusion were used to observe the adsorption mechanism. Based on the literature, the proposed models define the adsorption process and adsorption efficacy of adsorbents. Linear kinetic equations for these models are as follow [10,19]:

\[ \frac{t}{Q_t} = \frac{1}{K_1Q_e} + \frac{1}{Q_e} \times t \]  

(3)

\[ Q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln(t) \]  

(4)

\[ Q_t = k_i t^{0.5} + I \]  

(5)

Where \( Q_e \) (mg/g) is a number of metal-ions adsorbed at equilibrium, \( Q_t \) (mg/g) is the quantity of metal ions adsorbed at time \( t \), \( K_1 \) is the rate constant for the pseudo-first order reaction for adsorption (min\(^{-1}\)), \( K_2 \) is the rate constant for pseudo-second-order reaction (g/mg min), a is the primary adsorption rate (mg/g min), b is the desorption constant (g/mg), \( k_i \) is the diffusion rate constant (mg/(g min\(^{1/2}\))) and I is the intercept. The plot for intra particle diffusion for adsorption of Pb(II) and Cd(II) ions shows multi-linearity and adsorption process occurred in two steps. At first, in instantaneous diffusion stage, adsorption process takes place at the external surface of the adsorbent. After attaining equilibrium at the surface, diffusion resistance increased leading to decrease in diffusion rate.

### 3.2. Equilibrium studies and modeling

The interaction between adsorbate and adsorbent can be described by adsorption isotherm through optimization of the adsorption process. In this study, adsorption data was evaluated by fitting Langmuir and Freundlich isotherm model. The batch experiments were executed at 298 K with 0.02 g/L adsorbent dose to provide a better understanding of single or multilayer adsorption mechanism.

![Fig. 4. a) Plot for effect of pH [adsorbent amount: 0.02 g/L], b) plot showing point of zero charge (PZC) on CM, c) effect of adsorbent dose for carbon monoliths, and d) comparative percentage adsorption of metal ions using different adsorbent [agitation speed: 200 rpm, temperature: 25°C; time: 2.5 h].](image)

![Fig. 5. Plot showing effect of temperature for adsorption studies on carbon monoliths [adsorbent concentration: 0.02 g/L, agitation speed: 200 rpm, pH: 6, temperature: 25°C, time: 2.5 h].](image)
3.2.1. Langmuir isotherm

Langmuir model is utmost well-known isotherm model for monolayer formation of adsorbate layer on the adsorbent surface. This model is based on the concept that binding energy of all active sites is constant and no transmigration is possible on the surface of adsorbate. Formerly, this model was recognized for gas phase adsorption phenomena, then it had been extensively efficient for adsorbate-adsorbent interaction in the liquid phase. The Langmuir isotherm model is given as follows [3]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m}$$  \hspace{1cm} (6)

where $C_e$ (mg/L) is the equilibrium of metal ion concentration, $Q_e$ (mg/g) is the amount of adsorbate adsorbed per gram of adsorbent. $Q_m$ (mg/L) and $b$ are the Langmuir constants correlated to maximum adsorption capacity and energy of adsorption, respectively.

3.2.2. Freundlich isotherm

Freundlich model is used to define the adsorption process based on both homogeneous and heterogeneous surfaces. According to this model, the strong binding site gets occupied first. Meanwhile, an increase of the degree of site occupation results in a decrement of binding strength. It can be described as [20,21]:

$$\log Q_e = \log K_f + \frac{\log C_e}{n}$$  \hspace{1cm} (7)

Freundlich constants, $K_f$ (mg$^{1-1/n}$L$^{1/n}$g$^{-1}$) and $n$ depict the adsorption capacity at unit concentration and intensity, respectively and these constants can be evaluated through the plot of log $Q_e$ vs. log $C_e$. For promising results, ‘$n$’ values should lie between 1 and 10. By comparing the data of Pb(II) and Cd(II) ion adsorption and regression coefficients, indicates better fitting to Freundlich adsorption model at equilibrium.

4. Results and discussion

4.1. Characterization of the adsorbent

The specific surface area of synthesized carbon monoliths was described by N$_2$ sorption measurement and calculated through multipoint BET equation which was found to be 1103 m$^2$/g. Synthesized CM exhibited an uptake of nitrogen between 0.4–0.5 relative pressure (P/P$_0$) (Fig. 1a). The mesopore size and pore volume obtained by Barrett-

![Fig. 6. Linear fit curves for (a) pseudo first order, (b) pseudo second order, (c) elovich’s model, and (d) intra-particle diffusion model for carbon monoliths [adsorbent concentration: 0.02 g/L, agitation speed: 200 rpm, pH: 6, temperature: 25 °C].](image)
obtained micropore size and pore volume is 1.3 nm and 0.56 cm³/g, porous in nature, which is confirmed by micropore analysis and the obtained micropore size and pore volume is 1.3 nm and 0.56 cm³/g, respectively (inset of Fig. 1a). Synthesized CMs are mostly microadsorbent for adsorbate adsorption. Fig. 1c shows difference between BET surface area, along with micropores, CM would become most consistent adsorbent for adsorbate adsorption. Due to the huge surface area and pore size, the relative adsorption performance of CM is mainly dependent on surface area and pore size. With the increase of dosage of adsorbent (3–20 mg/L) for both the metal ions) adsorption was observed. Fig. 4a shows the effect of contact time at a different concentration of adsorbate is shown in Fig. 3(a–b). The agitation time for all the concentration was kept 10–150 min. In this study, moderately fast adsorption of metal ions was observed in the first 30 min (external surface adsorption) followed by the slow adsorption in which adsorption efficiency increases until equilibrium was achieved (60 min). It was observed that the percentage adsorption was increased with increase in the concentration of adsorbate (for Pb, 5–50 mg/L and for Cd, 5–20 mg/L) [2]. The initial concentration offers the desired driving forces to overcome the resistance to mass transfer of Pb(II) and Cd(II) ions between aqueous and solid phase. Accordingly, increase in initial concentration also enhances the interaction between heavy metal ions and CM.

Joyner-Halenda (BJH) analysis were found to be 3.68 nm and 0.67 cm³/g, respectively (inset of Fig. 1a). Synthesized CMs are mostly microporous in nature, which is confirmed by micropore analysis and the obtained micropore size and pore volume is 1.3 nm and 0.56 cm³/g, respectively (Fig. 1b). The result of EDS analysis represents that different elements are present in the synthesized CM. Also, carbon monoliths is shown in Fig. 1d. Peaks in the region of 2θ = 24.5° and 43.04° representing mesoporous carbon through index reflection pattern of 002 and 110 respectively. The successful synthesis of CM was achieved because of the thermally stable precursor of furfuryl alcohol (FA) and trimethylbenzene. FTIR spectrum for synthesized carbon monoliths is shown in Fig. 1d. Peaks in the region of 3615–3856 cm⁻¹ are corresponding to stretching vibrations of O–H. The characteristic C=C vibrations are seen at 1520–1705 cm⁻¹. Also, peaks at 1232 cm⁻¹ and 1040 cm⁻¹ are corresponding to C–O stretching and O–H bending, respectively. As discussed above, FA and OA were used as a precursor which was mixed in TMB for CM synthesis and later impregnated inside the pores of parent silica monoliths. Fig. 2a shows the digital photograph of synthesized solid CM after calcination. Pure CM with a micropore diameter of 1.3 nm has been synthesized after removal of silica content which is being confirmed by EDS analysis (Fig. 2b). The result of EDS analysis represents that diffusion of silica content from micro/mesopores of CM. Also, morphological structure of prepared CM was investigated using FESEM at different magnification scale (Fig. 2c–d). Though we have previously discussed the structure of silica monoliths in detail [18], here we have focused only on the effect of FA and OA on the micro/mesoporous structure of monoliths for adsorption process. Accordingly, we have tried to emphasize on micro/mesoporous structure of synthesized CM, but due to charging effect in FESEM, the proper porous structure of positive carbon replica can’t be shown.

4.2. Adsorption study

4.2.1. Effect of contact time at a different concentration of adsorbate

In the adsorption process, pH parameter plays an important role in leading the Pb(II) and Cd(II) ion adsorption by influencing the surface charge. Here, the impact of pH on adsorption efficiency was investigated over the range from 2.0 to 7.0 because above pH 7, the surface of CM becomes negatively charged. Fig. 4a shows the effect of adsorption efficiency with respect to the increase of pH from 1 to 6. Under acidic conditions (below pH 6), most of the surface of CM get highly protonated and the repulsive forces between metal ions and active sites increases and due to which the bond formation get interrupted among adsorbate and adsorbent. The obtained point of zero charge on the surface of CM has been shown in Fig. 4b. Here, adsorption of metal ions on the surface of CM would be explained on the basis of a number of active/vacant sites present.

4.2.2. Effect of pH

In the adsorption process, pH parameter plays an important role in leading the Pb(II) and Cd(II) ion adsorption by influencing the surface charge. Here, the impact of pH on adsorption efficiency was investigated over the range from 2.0 to 7.0 because above pH 7, the surface of CM becomes negatively charged. Fig. 4a shows the effect of adsorption efficiency with respect to the increase of pH from 1 to 6. Under acidic conditions (below pH 6), most of the surface of CM get highly protonated and the repulsive forces between metal ions and active sites increases and due to which the bond formation get interrupted among adsorbate and adsorbent. The obtained point of zero charge on the surface of CM has been shown in Fig. 4b. Here, adsorption of metal ions on the surface of CM would be explained on the basis of a number of active/vacant sites present.

4.2.3. Effect of adsorbent dosage

Mass of adsorbent also has a major persona in the adsorption process. With the increase of dosage of adsorbent (3–15 mg), an increase in the percentage of adsorbate (20 mg/L for both the metal ions) adsorption was observed. Fig. 4c shows that the removal of almost 100% metal ions and later impregnated inside the pores of parent silica monoliths. Accordingly, we have tried to emphasize on micro/mesoporous structure of synthesized CM, but due to charging effect in FESEM, the proper porous structure of positive carbon replica can’t be shown.
availability of high surface area and more active sites for adsorption.

concentration: 0.02 g/L, agitation speed: 200 rpm, pH: 6, temperature: 25 °C,
a) plot showing the recyclability/reusability of monoliths [adsorbent
Fig. 8.

proportional to the dosage of the CMs.

Freundlich Model

Kf
n
R2
χ2

Langmuir Model

Q0
b
R2
χ2

IOARM
TiO2
CCM 8000
Activated
carbon
GO-TiO2
Mesoporous
silica
Silica
nanotubes
(SNT)
Silica exhibiting
DSDH
CM

1128
1.05
0.990
3.45

989
0.78
0.986
2.76

Table 3
A comparative account of the adsorption efficiency of heavy metal-ions by
different adsorbents.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Surface area (m²/g)</th>
<th>Q0 (mg/g)</th>
<th>Conditions</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>IOARM</td>
<td>–</td>
<td>117.6</td>
<td>pH – 6</td>
<td>[4]</td>
</tr>
<tr>
<td>TiO2</td>
<td>220</td>
<td>857</td>
<td>pH – 6</td>
<td>[17]</td>
</tr>
<tr>
<td>CCM 8000</td>
<td>469.8</td>
<td>71.95</td>
<td>pH – 6</td>
<td>[24]</td>
</tr>
<tr>
<td>Activated</td>
<td>1127</td>
<td>28.90</td>
<td>pH: 6-6.5</td>
<td>[25]</td>
</tr>
<tr>
<td>carbon</td>
<td>GO-TiO2</td>
<td>65.6</td>
<td>pH – 5.6</td>
<td>[26]</td>
</tr>
<tr>
<td>Mesoporous</td>
<td>662</td>
<td>184.32</td>
<td>pH – 7</td>
<td>[27]</td>
</tr>
<tr>
<td>silica</td>
<td>Silica</td>
<td>42.85</td>
<td>pH – 4, 7, 9,</td>
<td>[28]</td>
</tr>
<tr>
<td>nanotubes</td>
<td>(SNT)</td>
<td>–</td>
<td>Temp–30°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Silica exhibiting</td>
<td>616</td>
<td>pH – 5.2</td>
<td>[29]</td>
</tr>
<tr>
<td>DSDH</td>
<td>CM</td>
<td>1103</td>
<td>pH – 6</td>
<td>Present Study</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1128</td>
<td>Temp–30°C</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>989</td>
<td>Time–150 min</td>
<td></td>
</tr>
</tbody>
</table>

Table 4
Isotherm parameters for adsorption of Pb(II) and Cd(II) ions.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>CM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>Q0, b, R², χ²</td>
<td>Pb(II) 989, Cd(II) 200</td>
</tr>
<tr>
<td>Freundlich</td>
<td>Kf, n, R², χ²</td>
<td>Pb(II) 17.86, Cd(II) 3.2</td>
</tr>
</tbody>
</table>

Fig. 8. a) plot showing the recyclability/reusability of monoliths [adsorbent concentration: 0.02 g/L, agitation speed: 200 rpm, pH: 6, temperature: 25 °C, time: 2.5 h].

ions by using 15 mg of CM in 50 mL of metal ion solution, due to the availability of high surface area and more active sites for adsorption. This result confirms that the removal efficacy of metal ions is directly proportional to the dosage of the CMs.

4.2.4. Comparative study of different adsorbent

In this study, we have used six different adsorbent materials e.g. SiO2, MnO2, TiO2, ZnO, AC and CM to adsorb 50 mL of 20 mg/L of both the metal ion solutions. Fig. 4d shows clearly that CM has the highest efficiency for adsorption of metal ions than SiO2, MnO2, TiO2, ZnO and AC adsorbents. This graph suggests that there are different sorption performances depending on the specific metal. Aqueous Pb(II) adsorption percentage clearly is the biggest for all materials here studied. Cd (II) removal is found to be inferior to lead behavior and the percentage.

4.3. Thermodynamic parameters

The influence of thermodynamic parameters like change in entropy, enthalpy and Gibb’s free energy of heavy metal ions adsorption onto the surface of CM was investigated at temperature ranging from 298 to 313 K. The mathematical representation for free energy change and equilibrium distribution of adsorption can be described by Van’t Hoff equation as follow [22]:

\[ \Delta G^\circ = -RT \ln \left( \frac{Q_e}{C_0} \right) \]

(8)

Where R is the universal gas constant (8.314 Jmol⁻¹ K⁻¹) and T is the absolute temperature. In other representation, change in entropy and enthalpy can be calculated by:

\[ \ln \left( \frac{Q_e}{C_0} \right) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \]

(9)

Nature of adsorption process can be defined by evaluation of these thermodynamic parameters (Fig. 5). For instance, the adsorption process is known as spontaneous and endothermic when \( \Delta G^\circ \) has negative values and \( \Delta H^\circ \) has positive values. Thermodynamic parameters of adsorption for Pb(II) and Cd(II) are listed in Table 1. The increase of negative values of \( \Delta G^\circ \) along with the increase of temperature represents better adsorption and favorable adsorption.

4.4. Adsorption kinetics

Adsorption study rate of Pb(II) and Cd(II) ions on solid CMs was carried out at 200 rpm agitation speed for the different time period while keeping the constant initial concentration. These batch experiments were repeated for three times and the average of the kinetic data of pseudo first order, pseudo-second order, elovich’s model and intra-particle diffusion model for CMs on the adsorption of Pb(II) and Cd(II) ions are plotted in Fig. 6, respectively. Linear arrangements of the kinetic data are mostly used in order to check the validity of these models and to calculate their characteristic parameters. From Fig. 6, it is clear that pseudo-second-order is most suitable to describe the kinetic behavior as the model shows better fitting corresponding to other models which suggest that adsorption process in this study characterizedly controlled by chemisorption. The calculated parameters for all kinetic models are summarized in Table 2.

4.5. Equilibrium studies and modeling

Fig. 7(a–b) shows the isotherms for adsorption of Pb(II) and Cd(II) on CM, where both the isotherms show a sharp initial slope accordingly indicating that CM act as high efficacy adsorbents at low concentration of Pb(II) and Cd(II). The fitting constants and regression coefficients evaluated using Langmuir and Freundlich isotherms are given in Table 3. While comparing the regression coefficient of the isotherms, higher adsorption rate was obtained via Freundlich isotherm due to multilayer adsorption process. The value of Q0 is much higher than the reported data due to the presence of both micro and mesopores on the microporous wall structure of CM. As adsorption mechanism is generally based on an ion exchange or formation of bidentate binuclear surface complexes between adsorbate and adsorbent. CMs are more
competent to hold other metal ions. In this case, the bond between heavy metal ions and CMs surface is strong due to which monoliths can adsorb metal ions from very diluted metal ion solutions [23]. A comparative study for maximum monolayer adsorption efficiency of different adsorbents for Pb(II) and Cd(II) ions are listed in Table 4 and here it could be concluded that the as-synthesized carbon monoliths could be employed as an alternative adsorbent for metal ions adsorption at low concentrations.

4.5.1. Error analysis
To estimate the accuracy of performing experiments, non-linear regression values were calculated via IBM SPSS Statistics 20 software. To describe the adsorption occurrence, to evaluate the asset of the models and to correlate the experimental data chi-square test can be used, which is given as:

$$\chi^2 = \sum \frac{(q_{\text{exp}} - q_{\text{cal}})^2}{q_{\text{cal}}}$$

(10)

where $q_{\text{exp}}$ and $q_{\text{cal}}$ are the experimental and calculated equilibrium volume data, respectively. If the data from the model are similar to the experimental data, the value of $\chi^2$ will be small, otherwise, it will be large.

4.6. Reusability of adsorbent
To access the reusability of used CMs as an adsorbent, their regeneration using NaOH (2 M) [23,30] and reusability for adsorption of heavy metal ions (Pb(II) and Cd(II)) were carried out up to 3 cycles which have been shown in Fig. 8. The adsorption efficacy for both Pb (II) and Cd(II) ions decreases steadily with the increased number of cycles because most of the adsorption sites get occupied due to bond formation between adsorbent and adsorbate. The good reusability of CM is due to the micrometer-sized structure with the high surface area, which has a benefit of reducing the overall cost of the adsorption process. Furthermore, desorption conditions are more simple and accessible as no specific filtration technologies are required for adsorbent extraction due to its large size.

5. Conclusions
In this work, porous carbon monoliths synthesized via nanocasting method shows an excellent adsorption ability for the removal of Pb(II) and Cd(II) ions from water. The equilibrium between CM and metal ion solution has been investigated at pH 6 in approximately 60 min. The maximum monolayer adsorption efficiency for Pb(II) and Cd(II) ions is 1128 mg/g and 989 mg/g, respectively. Kinetic data for the adsorption process reveals that the adsorption rate is fast and can be best fitted to pseudo-second-order. CM monoliths can be reusable (because of solid rock like structure) and become highly effective and economical adsorbent for heavy metal ion adsorption process.

Acknowledgments
The authors want to acknowledge DAE/BRNS (34/14/63/2014), India for providing financial support to undertake this work. Authors also want to acknowledge Thapar University for providing instrument/infrastructure facilities.

References

Journal of Environmental Chemical Engineering 6 (2018) 2829–2836