Chapter 5
Comparative adsorption of Pb (II) and Cd (II) onto Furnace H$_2$SO$_4$ activated carbon

5.1 Introduction

The phenomenon of water pollution through the contamination by toxic heavy metals has acquired serious dimensions all over the world. Among heavy metals, mercury, cadmium and lead are the ‘‘big three’’ toxic metals. These metals are concentrated throughout the food chain to the extent of posing serious threat to health. The removal, recovery and reuse of heavy metals from the wastewaters and industrial wastes have become a very important environmental concern [1]. Amongst the heavy metal pollutants, lead and cadmium are considered as priority environmental pollutants. The heavy metal lead is commonly used in wide industrial processes such as textile dyeing, ceramic, glass, petroleum refining, battery manufacture and mining industries [2]. As per the guidelines of the WHO, the maximum permissible level of lead in drinking water is 0.05 mg L$^{-1}$ [3]. At higher concentration, lead contamination may cause permanent damage to the human nervous system, blood vascular system, skeletal system and cardiovascular system [4].

Another important heavy metal considered being toxic to both humans and aquatic life is cadmium. The major sources of cadmium metal is surface water, urban and agricultural wastewaters or storm water runoffs, as cadmium is used in a number of industries, such as welding and soldering, photography, production of iron, steel and cement, use of superphosphate fertilizers and pesticides and production of nickel-cadmium batteries [5]. Prolonged exposure to cadmium can affect the liver, cardiovascular and nervous system and may lead to renal failure and can cause death in mammals and humans [6a, 6b]. It has been classified as a human carcinogen and teratogen impacting kidneys, liver, reproductive organs and lungs [7]. As per the guideline of World Health Organization (WHO) the maximum permissible concentration of cadmium in drinking water is 0.003 mg L$^{-1}$ [3].

Heavy metal pollution is a serious environmental problem. Major efforts to clean up waste discharge have been set up in order to implement and device various treatment technologies [8, 9]. The removal of toxic heavy metal ions from aqueous solutions have been reported by several treatment techniques, such as, electrochemical reduction, chemical
precipitation, solvent extraction, ion exchange, evaporation, reverse osmosis, and adsorption [10-12]. Amongst these methods, adsorption is an attractive process, used for its efficiency and easiness [13]. Activated carbon is a widely selected adsorbent due to its large surface area and high adsorption capacity as well as surface reactivity [14]. The adsorptive removal of heavy metal ions from aqueous solution plays an important role in water pollution control.

In present study, the prepared activated carbon by chemical activation followed by heat treatment (WASAC) from the agricultural waste wood apple shell (Limonia acidissima) was used as an adsorbent. In the literature for the removal of Cd (II) and Pb (II) metal ions by the adsorbent, the activated carbon were prepared from Coirpith [15], apricot stone [16], fertilizer waste [17], bagasse [18], coconut coirpith [19], Cassava peel [20], and used for the removal of metal ions from wastewater aqueous solution.

In the present research work, the effects of contact time, pH, and temperature on adsorption of metal ions were studied for the optimization of parameters and further, the adsorption isotherms and kinetics were investigated.

5.2 Experimental

5.2.1 Adsorbent preparation and characterization

The prepared activated carbon (Chapter 4) by H₂SO₄ impregnation and activated in muffle furnace was used as an adsorbent for the removal of Cd (II) and Pb (II) metals and was labeled as WASAC. The characterization of same activated carbon was reported in the previous chapter 4 in terms of point of zero charge (pHpzc), X-ray diffraction, SEM and FTIR analysis.

5.2.2 Preparation of solutions

Stock solution of 1000 mg L⁻¹ of Cd (II) and Pb (II) ions were prepared by dissolving 2.744 g and 1.598 g of A. R. grade cadmium nitrate tetrahydrate, [Cd(NO₃)₂.4H₂O] and lead nitrate [Pb(NO₃)₂] in double distilled water, respectively. The sample solutions of concentrations ranging from 10 to 100 mg L⁻¹ were prepared by diluting the stock solution to the desired concentrations.

5.2.3 Adsorption experiments

The effect of pH of initial aqueous solution on the adsorption of Pb (II) and Cd (II) on WASAC was analyzed by adjusting the pH of 50 mg/L aqueous solution between 2 and 8 with 0.05 N HCl or 0.05 N NaOH.
Investigation of adsorption kinetic experiments, a batch adsorption were conducted by shaking 0.05 g of WASAC and 50 ml of Cd (II) and Pb (II) ions solutions (50 and 100 mg L\(^{-1}\)) were transferred in a conical flask with pH 5 maintained using 0.05 N HCl or 0.05 N NaOH, and shaken on a thermostated magnetic stirrer at 298 K for preset time interval of 10 min up to 80 min. All the mixtures after adsorption operation were centrifuged and the Cd (II) and Pb (II) ions concentration in the supernatant solution was estimated by Atomic Absorption Spectroscopy (Model: SPECTR AA 220) at Department of Geology, University of Pune [21].

The amount of Cd (II) and Pb (II) ions adsorbed, \(q_t\) (mg g\(^{-1}\)) at time, \(t\) (min) was calculated from following equation:

\[
q_t = \frac{C_o - C_f}{M} \times V
\]  

(5.1)

Where \(V\) is the volume of Cd (II) and Pb (II) ions solution (L), \(M\) is the mass of WASAC (g), the adsorption equilibrium isotherm were obtained in batch studies, by shaking 0.05 g of WASAC and 50 ml of Cd (II) and Pb (II) ions solutions at six different concentrations ranging from 10 - 80 mg L\(^{-1}\) with pH 5 maintained using pH-meter (systronic), were transferred in a conical flask, and shaken on a thermostated magnetic stirrer at three different temperature up to 100 min (the time required for equilibrium to be reached). All the mixtures after adsorption operation were centrifuged and the Cd (II) and Pb (II) ions concentration in the supernatant was estimated by Atomic Absorption Spectroscopy. All the adsorption experiments were repeated twice to substantiate the results.

Removal efficiency of Cd (II) and Pb (II) ions and the amount of Cd (II) and Pb (II) ions adsorbed at equilibrium, \(q_e\) (mg g\(^{-1}\)), was calculated by the equation 5.2 and 5.3, respectively:

\[
\% \text{ removal of metal ions} = \frac{C_o - C_e}{C_o} \times 100
\]

(5.2)

Where \(C_o\) (mg L\(^{-1}\)) and \(C_e\) (mg L\(^{-1}\)) are initial and equilibrium concentrations of Cd (II) and Pb (II) ions in aqueous solutions, respectively.

\[
q_e = \frac{C_o - C_e}{M} \times V
\]

(5.3)
Where \( V \) is the volume of Cd (II) and Pb (II) ions solution (L), \( M \) is the mass of WASAC used (g). The data was analyzed to study equilibrium adsorption isotherms which include Langmuir and Freundlich isotherms at 299, 309 and 319 K.

5.3 Result and Discussions

5.3.1. Effect of pH on Pb (II) and Cd (II) ion adsorption

The effect of pH on adsorption of Cd (II) and Pb (II) on WASAC was investigated by adsorption measurements in the pH range from 2 to 8. WASAC dosage was 50 mg per 50 ml of aqueous solution and initial heavy metal concentration was 50 mg/L for both Cd (II) and Pb (II) ions. The amount of metal ions adsorbed against initial pH was plotted for both the metal ions. The effect of initial pH on heavy metal adsorption onto WASAC is shown for Cd (II) and Pb (II) ions in Figure 5.1. At low pH, Cd (II) and Pb (II) ions removal by WASAC was very low (<5 mg/g), because high concentration of H\(^+\) ions in the solution prevent the exchange or adsorption of metal ions Cd (II) and Pb (II) with protonated surface of WASAC [22]. In addition, net surface charge on activated carbon was positive at lower pH and hence, there was repulsive electrostatic interaction between positively charged activated carbon surface and cationic metal ions [23]. These effects were reduced with increasing pH and maximum adsorption capacities were noticed at pH 5. The adsorption capacity of both metal ions were remained essentially constant between pH 5 and 7 and then sharply decreased at pH 8, where the hydrolysis of metal ions is predominant [24]. Similar trends were observed by other researchers for the removal of Pb (II) metal ions at low pH, as the positively charged surface reduces adsorption capacity of activated carbons to adsorb Pb(II) [25]. The adsorption capacities of metal ions on WASAC were almost less than 5% at pH 2.
5.3.2 Effect of contact time

The effect of contact time on the adsorption of Cd(II) and Pb(II) is shown in Fig. 5.2. From the figure, it is evident that the adsorption rate of both the metal ions increases rapidly with the increase of contact time and then becomes slower until equilibriums were reached. The higher initial adsorption rate of metal ions were due to the large amount of surface area onto activated carbon available at the initial stage of the adsorption [26], which is then reduced with increasing coverage of the adsorbent surface [27]. The equilibrium time was observed around 100 min, and beyond this time no further change in adsorption was occurred. For developing the adsorbent-based water technology, the rate of adsorption is of great significance [28]. Thus, the ability of WASAC to adsorb the maximum amount of Cd(II) and Pb (II) ions within 100 min. indicates its suitability as an effective adsorbent [29].
5.3.3 Effect of temperature

The effect of temperature on the adsorption of Cd(II) and Pb(II) were studied at three different temperature (299, 309 and 319 K) of initial concentration 10 mg/L at pH 5 and up to contact time 100 min. The plot of amount of heavy metal ions adsorbed onto WASAC versus temperature is shown in Fig. 5.3. From the figure, it is observed that adsorption increases with increase in temperature of Cd (II) and Pb (II) metal ions suggesting that the adsorption was endothermic process.
5.3.4 Adsorption kinetics

Kinetic parameters are important for optimization of operation conditions and in engineering design of adsorption in a continuous removal process [30a]. The kinetics of adsorption of Cd (II) and Pb (II) on WASAC was investigated at 298 K. The relationships between the amount adsorbed and time at 50 and 100 mg/L, initial concentrations of Cd (II) and Pb (II) are shown in Fig. 5.4.

![Fig. 5.4 Adsorption kinetics of Cd (II) and Pb (II) onto WASAC at different concentrations](image)

The figure 5.4 shows that the adsorption process can be divided into two steps; the rapid 60 % uptake of metal ions were observed within first 30 to 35 minutes and slow uptake was observed until equilibrium was reached.

In the present study three different models are employed to investigate the kinetics of the adsorption; namely pseudo-first-order, pseudo-second-order, and Elovich kinetic models are considered to interpret the experimental data. A good correlation of the kinetic data explains the adsorption mechanism of the metal ions on the WASAC.

The pseudo-first order model was the first equation employed to the kinetics data of present system and from the plot of log (q_e – q_t) versus t, the constants, k_1 (min^{-1}) and q_e (mg g^{-1}) were determined from the slope and intercept of linear portion (Fig. 5.5) at two concentrations of Cd (II) and Pb (II) metal ions and are listed in Table 5.1. The experimental data, q_e, exp differ from theoretical values (q_e, cal) (Table 5.1), which suggests that the
adsorption of Cd (II) and Pb (II) metal ions on activated carbon does not entirely follow the pseudo-first order adsorption kinetics.

**Fig. 5.5** Pseudo-first order plot of Cd (II) and Pb (II) onto WASAC at different concentrations

The Pseudo-second order plot of \( t/q_t \) versus \( t \), gives the values of \( q_e \), and \( k_2 \) from intercept and slope, respectively. The initial rate of adsorption, \( h_0 \) were obtained from the values of \( q_e \), and \( k_2 \) by using equation \( (h_0 = 1/k_2 q_e^2) \).

**Fig. 5.6** Pseudo-second order plot of Cd (II) and Pb (II) onto WASAC at different concentrations
The plot of $t/q_e$ versus $t$ gives an excellent straight line relation for adsorption of Cd (II) and Pb (II) on WASAC (Figure 5.6). The kinetic parameters for adsorption of Cd (II) and Pb (II) ions by WASAC are given in Table 5.1. Based on the obtained correlation coefficients ($R^2>0.998$), the pseudo second-order kinetic model shown best fit for the experimental data for studied metal ions [30b]. The calculated $q_{e,cal}$ values from the pseudo-second order kinetic model exhibit excellent agreement with the experimental $q_{e,exp}$ values. Thus, the adsorption process was pseudo-second order, suggesting chemical adsorption as the rate-limiting step of the adsorption mechanism [31-34]. It can also be seen in Table 5.1 that the initial rate of adsorption ($h_o$) increases with an increase in initial metal concentrations, whereas the rate constant of adsorption ($k_2$) is fairly constant. Further, the equilibrium uptake, $q_e$ calculated from pseudo-second order model for the Cd (II) ion is relatively greater than Pb (II) ion at same concentration, indicating that the WASAC can be more effectively utilized for the removal of Cd (II) ions rather than Pb (II) ions.

Table 5.1 Kinetic parameters of Pb (II) and Cd (II) ions adsorption onto WASAC ($R^2$ regression coefficient)

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Initial Conc. of Metal ions ($C_o$) (mg L$^{-1}$)</th>
<th>Exp. $q_{e,exp}$ (mg g$^{-1}$)</th>
<th>Pseudo-first order kinetic</th>
<th>Pseudo-second order kinetic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$q_{e,cal}$ (mg g$^{-1}$)</td>
<td>$k_1$ (min$^{-1}$)</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>50</td>
<td>26.85</td>
<td>24.04</td>
<td>0.0092</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>47.22</td>
<td>33.80</td>
<td>0.0139</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>50</td>
<td>38.78</td>
<td>33.88</td>
<td>0.0115</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>60.2</td>
<td>48.08</td>
<td>0.0138</td>
</tr>
</tbody>
</table>

Elovich equation was initially applied to evaluate the kinetics of chemisorption of gases onto heterogeneous solids [35]. Recently, the Elovich equation has been applied to describe the kinetics of chemisorption of heavy metals and dyes from liquid phase onto the solid adsorbent [36-39].
The metal ions Pb (II) and Cd (II) adsorption on WASAC fits the Elovich model, since the plot of $q_t$ versus $\ln (t)$ yields linear relationship (Fig. 5.7) with regression coefficient ($R^2$>0.990). It further, confirms that the adsorption of metal ions onto WASAC was chemisorptions mechanism [40, 41]. The Elovich constants ($\alpha$ and $\beta$), were evaluated from the intercept and slope from the linear plots, respectively and are listed in Table 5.2. The relatively higher magnitude of Elovich initial rate of adsorption, $\alpha$ indicates that chemisorption of Cd (II) was faster than Pb (II) ion and the smaller fractional values of desorption constant, $\beta$ suggests that the adsorbed metal ions can easily desorbed from the WASAC surface [37,39].

Fig. 5.7 Elovich plot of Cd (II) and Pb (II) onto WASAC at different concentrations

Table 5.2 Adsorption kinetic parameters of Elovich kinetic model

($R^2$ regression coefficient)

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Initial con. of metal ions (mg L$^{-1}$)</th>
<th>Elovich model kinetic parameters</th>
<th>$\alpha$ (mg g$^{-1}$ min$^{-1}$)</th>
<th>$\beta$ (g mg$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb (II)</td>
<td>50</td>
<td></td>
<td>31.76</td>
<td>0.1660</td>
<td>0.990</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td></td>
<td>26.26</td>
<td>0.0933</td>
<td>0.994</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>50</td>
<td></td>
<td>42.96</td>
<td>0.1141</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td></td>
<td>50.15</td>
<td>0.0715</td>
<td>0.995</td>
</tr>
</tbody>
</table>
To realize the exact diffusion mechanism, the adsorption kinetic data were further analyzed by a Weber and Morris intra-particle diffusion model [42]. According to this model, if the plot of $q_t$ versus $t^{1/2}$ gives a straight line, then the adsorption process is controlled by intra-particle diffusion and if the data exhibits multi-linear plots, then two or more steps controls the adsorption process [43, 44]. In the present research, two distinct linear portions of the plot at 50 and 100 mg L$^{-1}$ concentration of both the metal ions (Figure 5.8), indicates that the adsorption was not controlled by only intra-particle diffusion.

The first linear portion was due to the external surface adsorption in which uptake rate of metal ions was high due to the film diffusion of Cd (II) and Pb (II) ions through solution onto the external surface of activated carbon. The later gradual linear portion refers to slow intra-particle pore diffusion. This indicates that both external film and intra-particle pore diffusion mechanism was involved in the Cd (II) and Pb (II) adsorption onto WASAC. Similar results were reported by many other researchers for the adsorption diffusion mechanism of metal ions [45, 46].

![Intra-particle diffusion plot of Cd (II) and Pb (II) onto WASAC at 50 and 100 mg/L concentrations](image)
5.3.5 Adsorption isotherms

The experimental data for heavy metal ions such as Cd (II) and Pb (II) adsorption onto the WASAC were analyzed by using two common linear forms of Langmuir and Freundlich isotherms. The linear plot \( C_e/q_e \) versus \( C_e \) and \( \log q_e \) versus \( \log C_e \) for the Langmuir and Freundlich isotherms are shown in figure 5.9a, 5.9b and 5.10a, 5.10b, respectively at three different temperatures. The slope and the intercept of each linear plot in Fig. 5.9 and 5.10 are used to calculate Langmuir and Freundlich parameters and the calculated Langmuir and Freundlich parameters are listed in Table 5.3. The Langmuir monolayer adsorption capacities were calculated at 299 K for the Pb (II) and Cd (II) ions and are found to be 58.82 and 125.0 mg g\(^{-1}\), respectively. The monolayer adsorption capacity decreases with increase in temperature from 299 to 319 K as 58.82 mg g\(^{-1}\) to 43.47 mg g\(^{-1}\) for the Pb (II) ions and 125.0 mg g\(^{-1}\) to 90.91 mg g\(^{-1}\) for the Cd (II) ions. Further, the energy of adsorption, \( K_L \) evaluated from Langmuir isotherm for both the metal ions increases with increase in temperature, reveals that the adsorption was relatively less feasible at higher temperature.

The Freundlich constant 1/n indicates the adsorption intensity. The 1/n values in the present adsorption systems are smaller than 1, which indicates favorable adsorption of Cd (II) and Pb (II) metal ions onto the WASAC. The lower the value of 1/n (<0.1), the more nonlinear is the adsorption isotherm, and the adsorption approaches the so called rectangular or irreversible isotherm. The higher the value of the exponent 1/n (closer to unity but < 1), the higher will be the affinity and the heterogeneity of the adsorbent sites [47a]. The essential features of the Langmuir isotherm can be expressed in terms of \( R_L \), a dimensionless constant. As the \( R_L \) values lie between 0 and 1, the adsorption process is favorable [47b]. In either case, the \( R_L \) values for the present experimental data fall between zero and one, which is an indication of the favorable adsorption of the two metals on the adsorbent WASAC (table 5.4). These results reveal that both Langmuir and Freundlich isotherms agree well with the obtained experimental data of adsorption Cd (II) and Pb (II) ions onto WASAC [48-51].
Table 5.3 Isotherm parameters of metal ions Pb (II) and Cd (II) adsorption onto WASAC at different temperatures (R² regression coefficient)

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Temp. (K)</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>qₘ (mg g⁻¹)</td>
<td>K_L (L mg⁻¹)</td>
</tr>
<tr>
<td>Pb (II)</td>
<td>299</td>
<td>58.82</td>
<td>0.0247</td>
</tr>
<tr>
<td></td>
<td>309</td>
<td>47.61</td>
<td>0.0905</td>
</tr>
<tr>
<td></td>
<td>319</td>
<td>43.47</td>
<td>0.150</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>299</td>
<td>125.0</td>
<td>0.0093</td>
</tr>
<tr>
<td></td>
<td>309</td>
<td>111.11</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>319</td>
<td>90.91</td>
<td>0.032</td>
</tr>
</tbody>
</table>
Fig. 5.9a Langmuir adsorption isotherms of Cd (II) ions at three different temperatures

Fig. 5.9b Langmuir adsorption isotherms of Pb (II) ions at three different temperatures
Fig. 5.10a Freundlich adsorption isotherms of Cd (II) ions at three different temperatures

Fig. 5.10b Freundlich adsorption isotherms of Pb (II) ions at three different temperatures
Table 5.4 Separation factor, $R_L$ at different temperatures and concentrations of metal ions

<table>
<thead>
<tr>
<th>Heavy Metal ions</th>
<th>Temperature (K)</th>
<th>$R_L$ values at different concentrations (mg L$^{-1}$) of metal ions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Pb (II)</td>
<td>299</td>
<td>0.802</td>
</tr>
<tr>
<td></td>
<td>309</td>
<td>0.525</td>
</tr>
<tr>
<td></td>
<td>319</td>
<td>0.400</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>299</td>
<td>0.915</td>
</tr>
<tr>
<td></td>
<td>309</td>
<td>0.833</td>
</tr>
<tr>
<td></td>
<td>319</td>
<td>0.757</td>
</tr>
</tbody>
</table>

5.4 Conclusions

In this study, we investigated the ability of WASAC for the removal of heavy metal ions, Pb (II) and Cd (II) in single component solutions. The following specific conclusions can be drawn:

1. The pH of the solution significantly influenced the adsorption capacity of WASAC towards Cd (II) and Pb (II) metal ions. Low pH was not favorable for Cd (II) and Pb (II) adsorption.
2. The adsorption of Cd (II) and Pb (II) was optimum in the pH range 5-6 in single system.
3. Batch adsorption kinetic studies showed that, the adsorption of cadmium and lead metal ions followed pseudo-second order kinetics and at the two concentrations studied, indicating chemisorptions is the rate-limiting step.
4. Elovich kinetic model data further confirm that adsorption of Cd (II) and Pb (II) ions onto WASAC was chemisorption.
5. Equilibrium data were well described by the Langmuir and Freundlich isotherm, suggesting the monolayer adsorption as well as the heterogeneous nature of WASAC for the adsorptions of Cd (II) and Pb (II) ions.
6. The amount of metal ions adsorption on WASAC increases with increase in temperature indicating that the adsorption was endothermic process.
7. The maximum monolayer adsorption capacities of Cd (II) and Pb (II) were 125.0 and 58.82 mg per gram of prepared WASAC at 299 K.
References:
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