Removal of Copper (II) and Cadmium (II) from Synthetic Effluents Using Low-Cost Adsorbents by Batch Mode Operation

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Abstract: Mixed adsorbent prepared from activated charcoal and bone charcoal was used to remove the copper and cadmium ions from aqueous solution by batch study and these investigations were reported in this paper. The effect of pH, temperature, initial metal ion concentration, agitation rate, adsorbent dosage contact time shown that the highest % removal the optimized conditions. The potential capacity of the mixed adsorbent as a low cost material for the removal of Cu (II) and Cd (II) from the synthetic metal ion solutions has been studied. The Langmuir model has been studied for both the metals at optimized conditions.

Key words: Activated Charcoal • Bone charcoal • Adsorption • Langmuir model

INTRODUCTION

The contamination of surface waters by heavy metal ions has become a serious ecological issue and health problem due to their toxic effect even at very low concentrations. Heavy metals are of special concern because they are non-degradable and thus persistent. Heavy metal ions such as cobalt, copper, chromium, nickel, palladium, lead, zinc are detected in the waste streams from the mining operations, tanneries, electronics, electroplating, batteries and petrochemicals industries has major effects on the human and aquatic life [1].

A number of conventional treatment technologies have been considered for treatment of wastewater contaminated with organic substances. Among them, adsorption is found to be the most effective method. Adsorption as a wastewater treatment process is found to be the most effective method. Commercial activated carbon is regarded as the most effective material for controlling the organic load. However due to its high cost and about 10-15% loss during regeneration it is not considered to be a potentially viable material for adsorption. Therefore, an attempt has been made to physically mix the available activated charcoal and bone charcoal and used as a mixed adsorbent for the removal of heavy metals from industrial effluents.

The present work focus on the adsorption performance and selectivity of copper and cadmium metals by activated charcoal and bone charcoal. The adsorption performance was investigated as a function of pH, temperature, initial concentration of metal ions, Agitation rate, adsorbent dosage and contact time. The adsorption isotherms in the form of Langmuir and Freundlich models have been studied to fit the data.

MATERIALS AND METHODS

All the chemicals including adsorbents used for the studies were purchased from Sigma Aldrich, India and have purity above 99.5 %. All the reagents, buffer solutions used for the study were of Analytical grade. Activated Charcoal and Bone charcoal purchased from Sigma Aldrich with 99.5% purity were used as adsorbent for this study.
Methods: This section gives an overview of methods involved in the preparation of adsorbent, characterization of the prepared adsorbent, procedure carried out for adsorption in batch study. Rotary shaker (Spectra Lab instruments Pvt Ltd & Industrial Research (Delhi) Model HM8T) was used for agitating the solutions containing the AC and BC. Atomic Absorption Spectrophotometer (Thermo Scientific iCE 3000 series) for sample Analysis before and after adsorption.

Preparation of the Mixed Adsorbent: The adsorbent (Activated Charcoal, AC + Bone charcoal, BC) was prepared in 1:1 ratio by adding 0.25 g of AC+BC (50% each) and sieve analysis (SELEC XT 264, AIMIL company ltd) was carried out in a rotary sieve shaker to determine the particle size of the adsorbent. A weight of 17g containing (50-50% each Activated charcoal and Bone charcoal) was sieved and the average particle diameter of the mixed adsorbent is calculated as 33.05 μm.

Characterization of the Adsorbent: Proximate and ultimate analysis (ASTM D3176-09, 2009). FTIR analysis, BET analysis were performed to characterize the adsorbent.

Batch Studies: Batch adsorption experiments were carried out by presterilizing the flask from 90 to 180 rpm for a fixed period of time using Rotary Shaker. Following a systematic process the removal of heavy metal ions by taking 50-50% mixture of activated charcoal and bone charcoal (0.25 g each) are studied. The data obtained in the present studies were used to calculate the equilibrium metal adsorptive quantity by using the mass balance relationship and the percentage removal of heavy metal ion were calculated. According to pre experiment a series of flasks (100 ml) containing 50 ml metal solution were prepared for all the adsorption study. The pH is adjusted by adding 0.1M NaOH or 0.1M HCl. The adsorption studies were carried out in a shaker incubator and Atomic Adsorption Spectrophotometer (AAS) (Mishra, 2011) is used to measure the metal ion concentration after the adsorption from the filtered sample. Experiments were conducted in triplicate and the average values were taken as result as shown in Fig. 1.

The Equilibrium metal adsorptive capacity of the metal ions (q_e) and % removal were calculated by using mass balance relationship given by;

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

(1)

\[ \% \text{removal} = \left( \frac{C_o - C_e}{C_o} \right) \times 100 \]  

(2)

where \( q_e \) is the amount of heavy metal ion adsorbed onto per unit weight of adsorbent in mg/g, \( V \) is the volume of the solution treated in liter. \( C_o, C_e \) is the initial and equilibrium concentration of metal ions in mg/L. \( M \) is the mass of the adsorbent in grams.

RESULTS AND DISCUSSION

Characterization of the Mixed Adsorbent

Proximate & Ultimate Analysis: Proximate analysis is a type of assay used in the determination of different constituents present in the coal sample. The standard specific procedures are followed to determine the bulk density, Average diameter, moisture content, volatile matter, Ash content, fixed carbon and surface area as shown in Table 1 [2]. Ultimate analysis gives about the composition of the biomass in terms of wt % of Carbon, Nitrogen, Hydrogen and Oxygen as well as Sulfur and Nitrogen. The carbon determination includes that present
Fig. 2: FTIR spectrum of the adsorbent (50-50% each) before adsorption

Table 1: Characterization of the mixed adsorbent

<table>
<thead>
<tr>
<th>Property</th>
<th>Composition of mixed adsorbent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (g/cc)</td>
<td>0.74</td>
</tr>
<tr>
<td>Average diameter (um)</td>
<td>33</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>3.43%</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>23.61%</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>4.39%</td>
</tr>
<tr>
<td>Fixed carbon (%)</td>
<td>68.57%</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>951</td>
</tr>
</tbody>
</table>

BET Analysis: BET theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for the measurement of the specific surface area of the mixed adsorbent. [3, 4]. The BET surface area of the adsorbent was found to be 951 m²/g.

Effect of pH: pH is one of the most important environmental factor influencing not only site dissociation but also the solution chemistry of the heavy metals, hydrolysis, complexation by organic and/or inorganic ligands. Redox reactions, precipitation are strongly influenced by pH and, on the other site, strongly influence the speciation and the adsorption availability of the heavy metals. Accordingly adsorption was principally dependent on the type and ion state of the functional groups (ligands) present in the adsorbent. At low pH values, the surface of adsorbent would also be surrounded by hydronium ions which decrease the metal ion interaction with binding sites of Activated charcoal and bone charcoal by greater repulsive forces and therefore lower adsorption takes place. In contrast as the pH increased, the competing effect of hydrogen ions decreased and more ligands were available. Therefore at high pH values the overall surface on the Activated charcoal and bone charcoal became more negative and adsorption increased. The study at pH higher than 6 were not conducted, because insoluble copper and cadmium hydroxides get precipitated and restricted the true adsorption studies as shown in Fig. 5 [5]. The experiment was conducted with the adsorbent conditions at a temperature of 30°C, 50 mg/L of initial metal ion concentration for 60 minutes with an adsorbent dose of 0.25 grams of the mixed adsorbent.
Fig. 3: FTIR spectrum of the mixed adsorbent after adsorption for Cu (II)

Fig. 4: FTIR spectrum of the mixed adsorbent after adsorption for Cd (II)

Fig. 5: Effect of contact time for Cu (II) and Cd (II)
Effect of Contact Time: Results indicated that the rate of adsorption increases with increase in the time of contact between adsorbent and metal ion solution. After certain amount of time all the active sites of the adsorbent were either filled with metal ions or the solution itself is saturated. So increase in rate of adsorption ceases and percentage removal becomes constant as shown in Fig. 6 [6]. The experiment was conducted with the adsorbent conditions mentioned as 50 mg/L of metal ion concentration and 0.25 g each (Activated and bone charcoal) at the pH of 6 for copper and cadmium respectively. The temperature of the reaction is kept constant at 30°C, Agitation rate of 180 rpm.

Effect of Temperature: The experiment was conducted with the adsorbent conditions mentioned as 50 mg/L concentration and 0.25 g of mixed adsorbent for 60 minutes at a pH of 6 for both copper and cadmium and the results show that increase in temperature decreases the adsorption rate as shown in Fig. 7 [7]. At higher temperatures particles will try to move away from the active surface and resulted the decrease in adsorption to the sites.

Effect of Adsorbent Dosage: Adsorbent dose is considered significant for effective metal removal as it determines sorbent- sorbate equilibrium of the system. It was observed that the amount of copper adsorbed varied with varying mixed adsorbent concentration. The amount of copper adsorbed per unit mass of adsorbent was decreased with an increase in adsorbent dosage from 0.25 to 1.5 g is added into the solution determine the number of binding sites available for adsorption. The number of adsorption sites or surface area increases with the weight of adsorbent and hence results in a higher percent of metal removal at a high dose as shown in Fig. 8. [8]. The experiment was conducted at a temperature of 30°C, 50 mg/L concentration for 60 minutes at a pH of 6 for copper and cadmium.
Effect of Agitation Rate: Agitation was an important in adsorption because it helps in overcoming the external mass transfer resistance. At higher agitation rate the mass transfer resistance related to ion diffusion through the liquid film surrounding the Activated and bone charcoal (mixed adsorbent) is reduced as the film thickness reduces due to agitation resulting in greater metal uptake. Agitation of the mixture not only results in a decrease in film transfer resistance but also results in the abrasion of Activated and bone charcoal, producing freshly broken and highly reactive locations on the surface. So this mechanical effect increases the number of possible adsorption locations/sites, resulting in an increase in the rate of adsorption as shown in Fig. 10. However, the production of fine particles due to abrasion, has its disadvantages, mainly that it becomes increasingly difficult to separate the solids from the liquid [10]. The experiment was conducted with the adsorbent conditions 50 mg/L of metal ion concentration and 0.25 g of Activated and bone charcoal (mixed adsorbent) for 60 minutes at the pH of 6 for both copper and cadmium and the temperature were kept constant at 30°C.

Isotherm Mode Results of Adsorption for Batch Mode Operation of Copper and Cadmium

Langmuir Isotherm: Langmuir adsorption isotherm, originally developed to describe gas solid phase adsorption onto activated carbon, has traditionally been used to quantify and contrast the performance of different bio-sorbents. In its formulation, this empirical model assumes monolayer adsorption (the adsorbed layer is one molecule in thickness), with adsorption can only occur at a finite (fixed) number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites. In its derivation, Langmuir isotherm refers to homogeneous adsorption, which each molecule possess constant enthalpies and sorption activation energy (all sites possess equal affinity for the adsorbate), with no transmigration of the adsorbate in the plane of the surface is low. The Langmuir equation is given as below. The present work follows Langmuir model with higher R² values [11].

\[
\frac{1}{q_e} = \frac{1}{q_{\text{max}}} \frac{1}{kC_e} + \frac{1}{q_{\text{max}}}
\]

(3)

An essential factor for Langmuir isotherm to be satisfied is the value of R, dimensionless constant separation factor or equilibrium parameter which ranges from 0 to 1 and is given by;
Fig. 11: (i) Langmuir Isotherm for copper

Fig. 11: (ii) Langmuir Isotherm for cadmium

Table 2: Langmuir Isotherm model parameters

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Copper</th>
<th>Cadmium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>0.4692</td>
<td>0.794</td>
</tr>
<tr>
<td>Intercept (1/Qₘ₀)</td>
<td>0.072</td>
<td>0.1023</td>
</tr>
<tr>
<td>Rₛ (Separation factor)</td>
<td>0.1152</td>
<td>0.1344</td>
</tr>
<tr>
<td>k (Langmuir Constant)</td>
<td>0.1535</td>
<td>0.12884</td>
</tr>
<tr>
<td>R² (Regression coefficient)</td>
<td>0.9468</td>
<td>0.8187</td>
</tr>
</tbody>
</table>

\[ Rₐ = 1/(1 + kC) \]  \hspace{1cm} (4)

If \( Rₐ > 1 \) it is unfavourable

= 1, linear

0 < \( Rₐ < 1 \), Favourable,

= 0, irreversible

Fig. 11 Study of Langmuir model for Cu (II) & Cd (II).

Analysis of Langmuir Model for Cu (II) and Cd (II) in Batch Study: From the above graph of Fig. 11 (i) and (ii) it was calculated that \( Rₐ = 1/(1 + bCₗ) = 0.1152, 0.1344 \) for Cu (II) and Cd (II) respectively which is in the range of 0 to 1 and indicates that the adsorption is favourable at the operating conditions. The data of the Langmuir model for both the metals are given in Table 2.

CONCLUSIONS

Experiments were conducted to investigate copper and cadmium removal of an aqueous solution by mixed adsorbent prepared from activated charcoal and bone charcoal. Approximately 90% of the copper and cadmium ions originally present in the solution were adsorbed onto the adsorbent within about 60 minutes after the start of the adsorption and equilibrium was reached within 2 hours. The maximum adsorption capacities were 9 mg/g and 8.5 mg/g for copper and cadmium ions respectively. The order of affinity was follows: Cu (II) > Cd (II). Therefore the potential capacity of the mixed adsorbent (Activated Charcoal and bone Charcoal) as a low cost material for the removal of copper and cadmium from synthetic metal solutions can be used.

- Effect of pH on % removal of Cu (II) & Cd (II) shows that the highest % removal is obtained at a pH of 6 for both copper and cadmium and the % removal is 87.67% and 84 % respectively.
- Effect of Initial metal ion concentration on % removal of Cu (II) & Cd (II) shows that the highest % removal is obtained at a pH of 6 for both copper and cadmium and the % removal is 93.75 and 86.5 respectively.
- Effect of Adsorbent dosage on % removal of Cu (II) & Cd (II) shows that the highest % removal is 98, 90 for 1.5 g of adsorbent at pH 6.
- Effect of Temperature on % removal of Cu (II) & Cd (II) shows that the highest % removal is obtained at a pH of 6 for both copper and cadmium and the % removal is 86 and 79% respectively at 30°C.
- Effect of Agitation rate on % removal of Cu (II) & Cd (II) shows that the highest % removal is obtained at a pH of 6 for both copper and cadmium and the % removal is 87 and 85.5 respectively at 180 rpm speed (Agitation rate).
- Effect of Contact time on % removal of Cu (II) & Cd (II) shows that the highest % removal is obtained at a pH of 6 for both copper and cadmium and the % removal is 92 and 80 respectively.

The Langmuir Isotherm model fits for both Cu (II) and Cd (II) with higher R² values and the adsorption is favorable.

REFERENCES