Removal of Chromium(III) Ions by Raw and Activated Carbon Derived from Mandarin Peel

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Removal of chromium(III) ions was investigated using raw mandarin peel and activated carbon derived from it. The percentage removal of Cr³⁺ ions was studied as a function of initial concentration of the heavy metal solution, pH and separation time. The results showed that the maximum percentage removal of chromium(III) of 67 % at 0.1 × 10⁻³ mg/L by raw mandarin peel sample and 80 % at 0.025 × 10⁻³ mg/L by activated carbon sample, 73 % in alkaline media and 60 % in natural media by activated carbon and raw mandarin peel, respectively, and reached to 67 and 81 % after 30 min of separation time by raw mandarin peel and activated carbon, respectively. Further, the observation also showed an acceptable efficiency for the removal of Cr³⁺ ions by the both adsorbents, particularly by activated carbon when compared to raw mandarin peel sample.

Keywords: Mandarin peel, Chromium(III) ions, Activated carbon, Adsorbent.

INTRODUCTION

Chromium exists in nature, ranging from Cr(II) to Cr(VI) [1]. In natural environment, the most stable oxidation forms are hexavalent chromium (Cr⁶⁺) and trivalent chromium (Cr³⁺) [2]. Trivalent chromium (Cr³⁺) is less toxic than chromium(VI) and it could be a nutrient for humans at a low dosage. However, the ion might have harmful effects on human health at high concentrations and allergic skin reaction could be also caused at long-term exposure [3]. It is released into the environment by many industrial applications such as iron and steel manufacturing, tanning and chromium plating [4].

Due to its simplicity, sludge-free operation, low cost and its efficiency in the removal of heavy metals at low concentration levels, adsorption is considered as one of the most efficient methods for the removal of contaminants in wastewater treatment. Agricultural waste materials could be used as a biomass adsorbent as well as good sources for producing activated carbon. Several studies have been published on removal of heavy metal by agricultural waste materials, almost all were achieved via batch experiments and only few studies have been reported on the removal of Cr³⁺ using a column. Some of these works have already been published [5-10]. Therefore, the aim of this work was to study the removal efficiencies of raw mandarin peel (Citrus reticulate) and derived activated carbon towards Cr³⁺ ion by this method, considering the effect of the concentration, pH and separation time on the removal process.

EXPERIMENTAL

Mandarin peels were collected, cleaned, cut and dried by sunlight for a few days and then using an oven at 80 °C for 24 h, grinded and sieved to a particle size of ≤ 0.5 mm. A chemical process was used to prepare the activated carbon by boiling 40 g of mandarin peel powder with 120 mL of conc. H₃PO₄ (1:3 weight ratio) for 6 h in an air condenser system. After cooling, the product was filtrated, washed several times with aqueous solution of NaHCO₃ solution followed by distilled water until neutral pH and dried at 110 °C for 24 h. Finally, it was stored in a desiccator. The activated carbon and mandarin peel samples were labelled as AC and MP, respectively. The yield of the sample was calculated from the following equation [11]:

\[
\text{Yield (\%)} = \frac{W_o - W_e}{W_o} \times 100
\]

where \(W_o\) and \(W_e\) are the mass of material before and after carbonization, respectively.

Characterization of adsorbent: Surface area and bulk density of the adsorbents samples were determined by mercury intrusion porosimeter (Poresizer-9320, Micromeritics). The moisture content of activated carbon was determined by weighing the sample before and after drying at 100 °C for 24 h. The ash content was determined by igniting the moisture free activated carbon in a furnace at 500 °C for 1 h followed by second ignition 700 °C for 4 h and weighing.
Further analysis of samples was carried out by FT-IR spectroscopy; BIO-RAD FTS-40 and scanning electron microscope (SEM); JEOL JEM (2010).

Removal experiments: For all experiments, a glass column of 25 cm length and 1 cm internal diameter was packed with 1.5 g of the adsorbent material. Then, a solution of Cr\(^{3+}\) ions was added, keeping the column closed until complete matrix humidification. All the experiments were performed at room temperature.

To study the effect of initial concentration of metal solution, the column was filled individually with \((0.025, 0.05, 0.1, 0.5, 1) \times 10^{-3}\) mg/L of Cr\(^{3+}\) solutions. After about 25 min, the column effluents were collected, and 2 mL withdrawn for determining the metal ions content by atomic absorption spectrometry (AAS) (model Z-8100 polarized Zeeman, Hitachi Ltd., Japan). This is referred to as 1st cycle. Then, the rest was reloaded into the column, 2 mL was withdrawn for analysis and this step is referred to as 2nd cycle.

To study the effect of pH, the column was filled individually with 0.1 \times 10^{-3} mg/L of Cr\(^{3+}\) solution at different pH (2, 4, 6, 8 and 10). The column effluents were collected and 2 mL was withdrawn for analysis after about 25 min. This was performed in two cycles.

Separation time effect was performed by filling the column individually with Cr\(^{3+}\) solution (0.1 \times 10^{-3} mg/L). The effluents of the column was periodically collected after 10, 15, 20, 30 and 60 min, and 2 mL was withdrawn for analysis each time. Further, the removal efficiency was calculated according to the following equation:

\[
R (\%) = \frac{C_o - C_e}{C_o} \times 100
\]  

where \(R\) is the percentage removal and \(C_o\) and \(C_e\) are the concentrations of Cr\(^{3+}\) ions (mg/L) in the solution before and after adsorption, respectively.

**RESULTS AND DISCUSSION**

Physical characterization: For the adsorption process or removal of the pollutants from the environment, the surface area of adsorbent is a key factor [12]. In Table-1, the physical characteristics of the adsorbents, including the surface area analysis are summarized. Well-developed micro-pores of AC surface were noticeable and it was higher than that of the MP sample, because of the carbonization and activation process. Therefore, the nitrogen adsorption was enhanced.

<table>
<thead>
<tr>
<th>Adsorbents samples</th>
<th>MP</th>
<th>AC</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBET (N(_2) adsorption) (m(^2)/g)</td>
<td>28.23</td>
<td>189.56</td>
</tr>
<tr>
<td>Micro pores area (m(^2)/g)</td>
<td>10.55</td>
<td>133.56</td>
</tr>
<tr>
<td>Average pore diameter (cm(^3)/g)</td>
<td>0.597</td>
<td>0.3677</td>
</tr>
<tr>
<td>Micro pore diameter (cm(^3)/g)</td>
<td>0.0631</td>
<td>0.1816</td>
</tr>
<tr>
<td>Bulk density (g/cm(^3))</td>
<td>2.14</td>
<td>1.39</td>
</tr>
<tr>
<td>Yield (%)</td>
<td>–</td>
<td>47.95</td>
</tr>
<tr>
<td>Point of zero charge (PZC)</td>
<td>–</td>
<td>6.5</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>–</td>
<td>4.9</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>–</td>
<td>8.5</td>
</tr>
</tbody>
</table>

Scanning electron microscopy (SEM) studies: SEM was used to study the surface morphology of MP and AC samples. As seen in Fig. 1, progressive changes with large pores are clearly observed on the AC surface. This indicates the effectiveness of carbonization and activation conditions in creating developed pores on the AC surface, leading to a porous structure and large surface area of the prepared activated carbon.

FTIR analysis: The FTIR spectra of MP and AC samples provide information about the functional groups of the active components based on the absorbance peak positions in IR spectra. Addition, the changes in spectrum of MP after carbonization and activation process indicate the changes in the functional groups. The FTIR spectrum of MP is shown in Fig. 2, which displays many absorption peaks, indicating that the compounds in MP sample included carboxylic acids, alkanes, esters and aromatic compounds. There is a broad and intense absorption peak at 3423.67 cm\(^{-1}\), indicating the presence of OH group carboxylic acids or NH group of amines. The peak located at 2920.58 cm\(^{-1}\) could be assigned to the stretching vibration of CH group of alkanes. The carbonyl band appearing at 1820 cm\(^{-1}\) is assigned to the C=O stretching of carboxylic acid or ester. The peaks observed at 1614, 1457, 1110.43 and 820.20 cm\(^{-1}\) could be attributed to the NH bend of primary amines, C–C stretch in

Fig. 1. SEM images of MP and AC
aromatics, CN stretch and out-of-plane C-H bending of aliphatic amines and aromatics, respectively. However, these bands shift to 3436.16, 2923.16, 2849.74, 2098.42, 1622.30, 1458.91, 1226.30 and 728.49 cm$^{-1}$ in the spectra of AC, as a result of carbonization and activation process.

**Initial concentration:** The removal process of Cr$^{3+}$ ion was investigated at concentrations ranging from $0.025 \times 10^{-3}$ to $1 \times 10^{-3}$ mg/L at room temperature. The effect of initial concentration on the percentage removal of Cr$^{3+}$ ion is illustrated in Figs. 3 and 4. As shown in Fig. 3, the removal efficiency (R, %) from the second cycle was higher than that for first cycle. The maximum value of R ( %) from the second cycle reached 67 % at $0.1 \times 10^{-3}$ mg/L, and 80 % at $0.025 \times 10^{-3}$ mg/L for MP and AC, respectively.

In general, R (%) of Cr$^{3+}$ ions by MP and AC of the first second cycles consists of two stages separated by a critical concentration, which is $0.1 \times 10^{-3}$ mg/L for both the cycles for both samples. The removal of Cr$^{3+}$ ions by MP is both cycles had the same characteristic whereas different characteristics were observed for AC in the two cycles. This could be related to number of active sites of adsorbents.

In case of MP, R (%) increases with an increase in the ion concentration until the critical concentration, after which it decreases because of the availability of the active sites for ions adsorption which were already engaged. Therefore, the R (%) decreased upon increasing initial ion concentration in the second stage.

In case of AC, R (%) increases slightly in the first stage and then significantly in second one of the first cycle because active sites were not completely saturated. In contrast, in the second cycle, R (%) decreases with increasing the initial ion concentration in the first stage owing to the limited active sites numbers on surface and then it increase with the increase of ion concentration in the second stage. This could be an indication of the formation of another adsorption layer, wherein the first layer of adsorption becomes a new surface for the adsorption.

**pH:** One of the important parameters which affects adsorption is the surface charge of the adsorbent. The equivalence of the sums negative and positive charges is called the point of zero charge (PZC) [13,14]. In general, the negative and positive charges of the adsorbent surface depends on the pH of aqueous phase, wherein surface become negatively charged if the solution pH is $> PZC$ and positively charged if the solution pH is $< PZC$ [13,14]. Jo et al. [14] stated that the mass distribution of metal ions can be expressed by the following equations:

$$\text{Total mass of metal ions} = \text{Metal ions remaining in the aqueous phase + Metal ions removed}$$

$$\text{Metal ions removed} = \text{Metal ions adsorbed on adsorbent + metal ions precipitated by pH of solution}$$

In this work, the effect of pH on the removal of Cr$^{3+}$ by MP and AC was investigated by observing the R (%) over a wide pH range of 2-10. The variation in the removal of Cr$^{3+}$ with pH is presented in Figs. 5 and 6.

As shown in Fig. 4, the removal of Cr$^{3+}$ ions by MP and AC in both cycles is almost the same although the R (%) of Cr$^{3+}$ ions from the second cycle is higher than that from first one. As illustrated in Fig. 6, the optimum amount of R (%)
Cr\(^{3+}\) for MP and AC from the second cycle is 60 % (pH = 6) and 66 % (pH = 6), respectively.

For both cycles, R (%) by MP increases with increasing pH until pH = 6 then decreases even though the reduction in ions removal was clearer in the second cycle compared to that of first cycle. This is largely due to the adsorption of Cr\(^{3+}\) ions where the positive ions compete with the hydrogen ion for binding site on the adsorbent surface, whereas at higher pH, the ions started to precipitate in the solution, implying that precipitation is a dominant factor in the alkaline medium over adsorption.

For removal of Cr\(^{3+}\) by AC, R (%) increases with increasing pH because the negative charge density on the adsorbent surface increases in alkaline media, resulting in attraction between the positively charged ion and negatively charged surface of the adsorbent. This explanation is confirmed by PZC of the adsorbent surface, which is equal to 6.5 as shown in Table-1. In the acidic media, pH < PZC, the adsorbent surface is positively charged, resulting in week attraction between the positively charged ion and the adsorbent surface as a result of the repulsive forces. This repulsion is stronger at lower pH. In the alkaline media, pH > PZC, the negative charge density on the adsorbent surface increases, resulting in attraction between the positively charged ion and the surface of adsorbent. This situation appeared obviously in the second cycle, whereas in the first cycle, the precipitation of metallic ions occurs in the solution after pH = 8.

Separation time: To study the effect of separation time for the removal of Cr\(^{3+}\) ion, the experiment was carried out at different contact times with a fixed adsorbent dose. The results are presented in Fig. 5. It is observed that the uptake of Cr\(^{3+}\) ion increases with time for both MP and AC, and the saturation state was not noticeable within the range of studied time. During first 30 min, the adsorption occurred rapidly because of the available adsorption sites, which become poor with the passage of time. Therefore, it is noticed that the removal becomes slower a later time. The maximum removal was observed at 60 min with R (%) of Cr\(^{3+}\) equal to 67 and 81 % by raw mandarin peel and activated carbon, respectively.

Comparison MP with AC: It is obvious from the previous results that the efficiency for removal was better for AC sample compared to MP, over all the studied variables, and this was expected because of the porous nature of the AC surface as shown in SEM images (Fig. 6).

Finally, it is worthy to say that the comparison of the present work with the other reported works seems to be difficult because the experimental methods and conditions are different. Nevertheless, Table-2 summarized the findings of this work compared to other reported biomass.

**Conclusion**

Raw mandarin peel (MP) and activated carbon derived from it (AC) were used as bio-adsorbents and characterized using SEM and FTIR techniques. The results of SEM indicated a porous structure of raw mandarin peel after the carbonization and activation processes. Additionally, several changes were observed in FTIR spectrum of AC compared to raw mandarin peel. Both samples were used for the removal of Cr\(^{3+}\) ions by the column system. The experimental observations revealed that the most of Cr\(^{3+}\) ions were successfully removed by these adsorbents from the solution. Further, the AC sample showed superior removal percentage compared to raw mandarin peel. The results suggest that these materials could be used for adsorption applications.

**REFERENCES**


**TABLE-2**

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Maximum removal (%)</th>
<th>Method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange peel</td>
<td>76.6 % at pH = 4</td>
<td>Batch system</td>
<td></td>
</tr>
<tr>
<td>Kiwi cortex</td>
<td>91 % (particle size = 1 mm) of biomass and ≈ 90 (pH = 6)</td>
<td>Batch system</td>
<td></td>
</tr>
<tr>
<td>Tangerine cortex</td>
<td>88 % (particle size = 1 mm) of biomass and ≈ 90 (pH = 6)</td>
<td>Batch system</td>
<td></td>
</tr>
<tr>
<td>Banana cortex</td>
<td>42 % (particle size = 1 mm) of biomass and ≈ 45 (pH = 6)</td>
<td>Batch system</td>
<td></td>
</tr>
<tr>
<td>Saccharomyces cerevisiae</td>
<td>53.7 %</td>
<td>Column system</td>
<td></td>
</tr>
<tr>
<td>Mandarin peel</td>
<td>67 % (60 min) and 60 % (pH = 6)</td>
<td>Column system</td>
<td>Present work</td>
</tr>
<tr>
<td>AC derived from mandarin peel</td>
<td>81 % (60 min) and 66 % (pH = 6)</td>
<td>Column system</td>
<td>Present work</td>
</tr>
</tbody>
</table>

Fig. 6. Maximum removal of Cr\(^{3+}\) ions by AC in comparison with MP