



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

MASHAEL ALSHABANAT

Department of Chemistry, Science College, Princess Nourah bint Abdulrahman University, Riyadh, Kingdom of Saudi Arabia

Corresponding author: E-mail : ma.naif@hotmail.com

Received: 23 December 2017;

Accepted: 2 February 2018;

Published online: 30 April 2018;

AJC-18876

Removal of chromium(III) ions was investigated using raw mandarin peel and activated carbon derived from it. The percentage removal of Cr^{3+} 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 Cr^{3+} 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 (Cr^{6+}) and trivalent chromium (Cr^{3+}) [2]. Trivalent chromium (Cr^{3+}) 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 Cr^{3+} 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 reticulata*) and derived activated carbon towards Cr^{3+} 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. H_3PO_4 (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 NaHCO_3 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]:

$$\text{Yield (\%)} = \frac{W_o - W_e}{W_o} \times 100 \quad (1)$$

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, 1×10^{-3} mg/L) of Cr^{3+} solutions. After about 25 min, the column effluents was 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 0.1×10^{-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 (0.1×10^{-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:

$$R (\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

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.

Adsorbents samples	MP	AC
SBET (N_2 adsorption) (m^2/g)	28.23	189.56
Micro pores area (m^2/g)	10.55	133.56
Average pore diameter (cm^3/g)	0.597	0.3677
Micro pore diameter (cm^3/g)	0.0631	0.1816
Bulk density (g/cm^3)	2.14	1.39
Yield (%)	–	47.95
Point of zero charge (PZC)	–	6.5
Moisture content (%)	–	4.9
Ash content (%)	–	8.5

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 1614.14 , 1457 , 1110.43 and 820.20 cm^{-1} could be attributed to the NH bend of primary amines, C–C stretch in

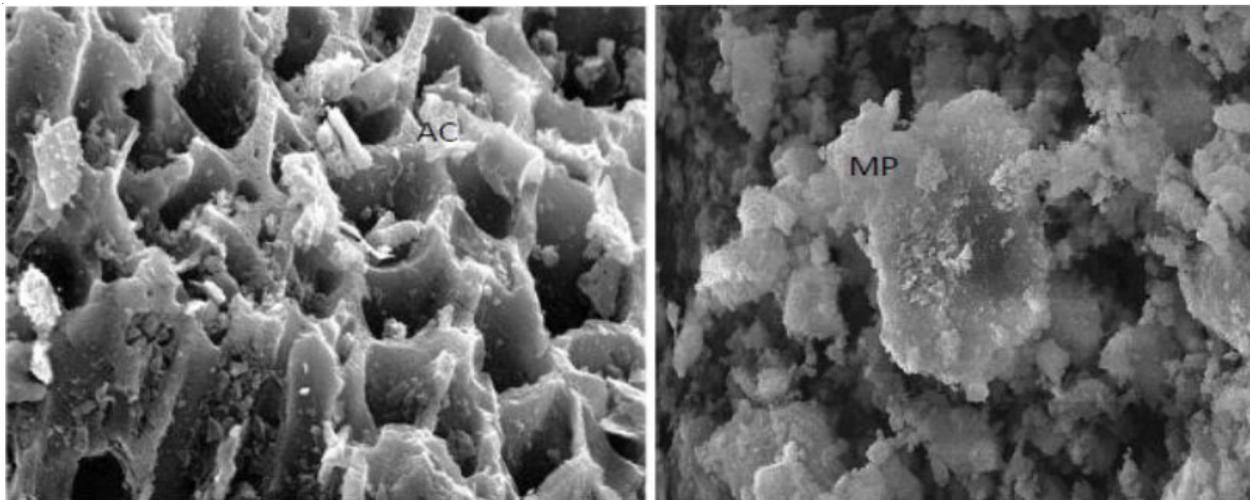


Fig. 1. SEM images of MP and AC

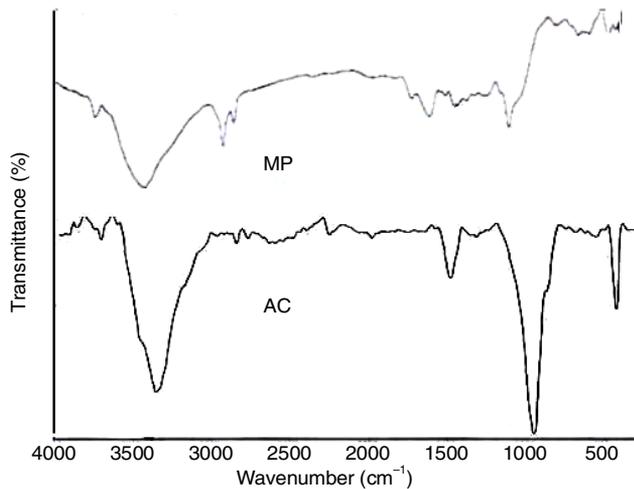
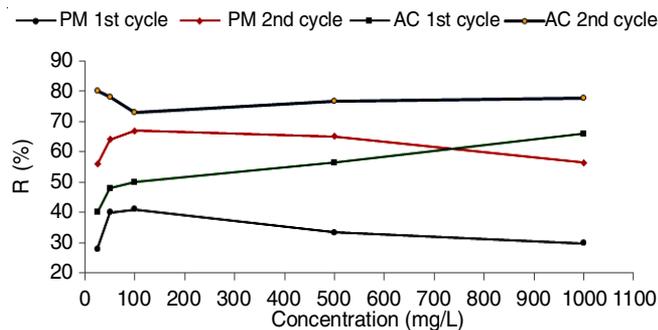
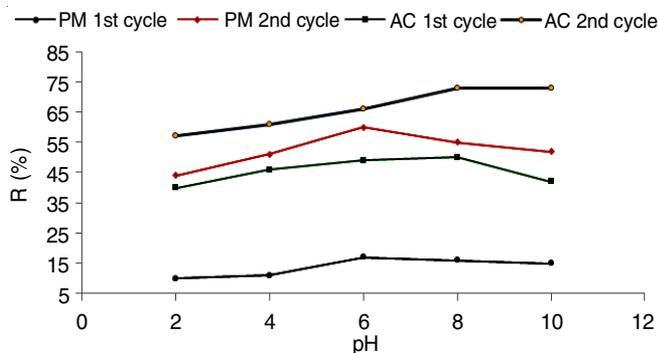


Fig. 2. FTIR spectra of MP and AC

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 0.025×10^{-3} to 1×10^{-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 0.1×10^{-3} mg/L, and 80 % at 0.025×10^{-3} mg/L for MP and AC, respectively.

Fig. 3. Effect of initial concentration of Cr^{3+} ions on its removalFig. 4. Effect of pH of solution on removal of Cr^{3+} ions

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 0.1×10^{-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:

$$\text{Total mass of metal ions} = \text{Metal ions remaining in the aqueous phase} + \text{Metal ions removed} \quad (3)$$

$$\text{Metal ions removed} = \text{Metal ions adsorbed on adsorbent} + \text{metal ions precipitated by pH of solution} \quad (4)$$

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 (%)

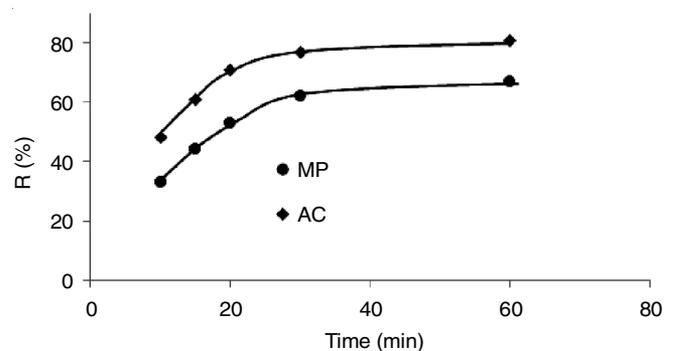
Fig. 5. Effect of separation time on removal of Cr^{3+} ions

TABLE-2
COMPARISON OF VARIOUS ACTIVATED CARBON DERIVED FROM DIFFERENT AGRICULTURAL BIOMASS FOR REMOVAL OF CHROMIUM(III) IONS

Biomass	Maximum removal (%)	Method	Ref.
Orange peel	76.6 % at pH = 4	Batch system	[15]
Kiwi cortex	91 % (particle size = 1 mm) of biomass and ≈ 90 (pH = 6)	Batch system	[16]
Tangerine cortex	88 % (particle size = 1 mm) of biomass and ≈ 90 (pH = 6)	Batch system	
Banana cortex	42 % (particle size = 1 mm) of biomass and ≈ 45 (pH = 6)	Batch system	
<i>Saccharomyces cerevisiae</i>	53.7 %	Column system	[17]
Mandarin peel	67 % (60 min) and 60 % (pH = 6)	Column system	Present work
AC derived from mandarin peel	81 % (60 min) and 66 % (pH = 6)	Column system	Present work

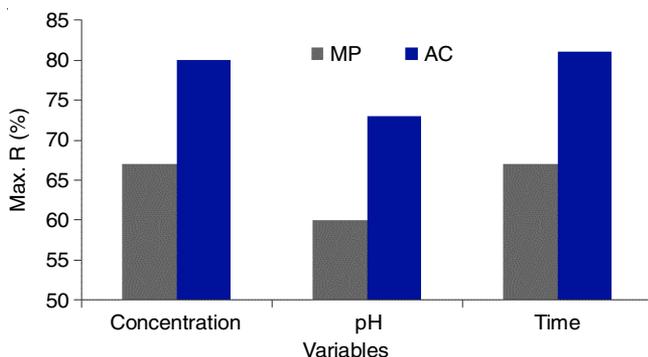


Fig. 6. Maximum removal of Cr³⁺ ions by AC in comparison with MP

Cr³⁺ 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 Cr³⁺ 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 Cr³⁺ 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 weak attraction between the positively charged ion and the positive charge of 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 Cr³⁺ 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 Cr³⁺ 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 Cr³⁺ 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 Cr³⁺ ions by the column system. The experimental observations revealed that the most of Cr³⁺ 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

- J. Emsley, *The Elements*, Oxford University Press, New York (1989).
- F.C. Richard and A.C.M. Bourg, *Water Res.*, **25**, 807 (1991); [https://doi.org/10.1016/0043-1354\(91\)90160-R](https://doi.org/10.1016/0043-1354(91)90160-R).
- V.J.P. Vilar, J.A.B. Valle, A. Bhatnagar, J.C. Santos, S.M.A.G.U. de Souza, A.A.U. de Souza, C.M.S. Botelho and R.A.R. Boaventura, *Chem. Eng. J.*, **200**, 140 (2012); <https://doi.org/10.1016/j.cej.2012.06.023>.
- M.A. Maine, N.L. Suñé and S.C. Lagger, *Water Res.*, **38**, 1494 (2004); <https://doi.org/10.1016/j.watres.2003.12.025>.
- F.A. Pavan, I.S. Lima, E.C. Lima, C. Airoidi and Y. Gushikem, *J. Hazard. Mater.*, **137**, 527 (2006); <https://doi.org/10.1016/j.jhazmat.2006.02.025>.
- K. Kelly-Vargas, M. Cerro-Lopez, S. Reyna-Tellez, E.R. Bandala and J.L. Sanchez-Salas, *Phys. Chem. Earth*, **37-39**, 26 (2012); <https://doi.org/10.1016/j.pce.2011.03.006>.
- D.Z. Husein, *Desal. Water Treat.*, **51**, 6761 (2013); <https://doi.org/10.1080/19443994.2013.801793>.
- G.C. Ribeiro, L.M. Coelho, E. Oliveira and N.M.M. Coelho, *BioResources*, **8**, 3309 (2013); <https://doi.org/10.15376/biores.8.3.3309-3321>.

9. R. Rehman, M. Salman, T. Mahmud, F. Kanwal and W. Uz-Zaman, *J. Chem. Soc. Pak.*, **35**, 611 (2013).
10. I. Acosta-Rodríguez, E. Coronado-Quintero, J.F.C. González, J. Tovar-Oviedo and V.M. Martínez-Juárez, *J. Nat. Sci.*, **1**, 29 (2013).
11. M.A. Ahmad, N.A. Ahmad Puad and O.S. Bello, *Water Resour. Ind.*, **6**, 18 (2014);
<https://doi.org/10.1016/j.wri.2014.06.002>.
12. M.A. Salam, M.S.I. Makki and M.Y.A. Abdelaal, *J. Alloys Compd.*, **509**, 2582 (2011);
<https://doi.org/10.1016/j.jallcom.2010.11.094>.
13. J.P. Reymond and F. Kolenda, *Powder Technol.*, **103**, 30 (1999);
[https://doi.org/10.1016/S0032-5910\(99\)00011-X](https://doi.org/10.1016/S0032-5910(99)00011-X).
14. Y.-H. Jo, S.-H. Do, Y.-S. Jang and S.-H. Kong, The Removal of Metal Ions (Cu²⁺ and Zn²⁺) using Waste-reclaimed Adsorbent for Plating Wastewater Treatment Process; Proceedings of the World Congress on Engineering and Computer Science, vol. 2, pp. 20-22 (2010).
15. V. Lugo-Lugo, C. Barrera-Díaz, F. Ureña-Núñez, B. Bilyeu and I. Linares-Hernández, *J. Environ. Manage.*, **112**, 120 (2012);
<https://doi.org/10.1016/j.jenvman.2012.07.009>.
16. Kh.M. Al-Qahtani, *J. Taibah Univ. Sci.*, **10**, 700 (2016);
<https://doi.org/10.1016/j.jtusci.2015.09.001>.
17. M.E. Ramírez Carmona, M.A. Pereira da Silva, S.G. Ferreira Leite, O.H. Vasco Echeverri and C. Ocampo-López, *J. Taiwan Inst. Chem. Eng.*, **43**, 428 (2012);
<https://doi.org/10.1016/j.jtice.2011.12.002>.