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Research Article

Adsorption of Ferric Ions on to Banana Peel Carbon and Tapioca Peel Carbon Activated by Microwave, Thermal, and Chemical Means

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ABSTRACT

Batch adsorption studies are carried out for removing ferric ions onto thermally (TABPC), chemically (CABPC) and microwave activated (MABPC) carbons. Variables like initial metal in concentration, pH, adsorbent dosage, contact time and temperature are taken into account. The equilibrium isotherms are fitted with Langmuir and Freundlich isotherms following first order kinetics. Thermodynamic parameters such as $\Delta H°$, $\Delta G°$ and $\Delta S°$ are reported. The adsorbent is characterized using IR and SEM. Microwave activated carbon is found to be more efficient in removing methylene blue than chemically and thermally activated Banana peel carbon and Topioca peel carbon.

Keywords: Thermally activated Banana peel carbon (TABPC), Chemically activated Banana peel carbon.

INTRODUCTION

Waste water from sources like pharmacological industries and Iron and steel industries, metal corrosion, metal finishing, etc., increase concentration of iron in aquatic systems. Concentration of iron in excess of 0.2 to 0.3 mg/l may damage the gastro-intestinal tract and liver. Iron accumulation leads to hemochromatosis and siderosis[1]. A normal man absorbs 1 mg of iron per day, but with this disease the absorption will be altered to 3 mg per day. One out of every fifteen people is reportedly suffering from this problem[2]. Fe (II), once getting into water bodies, is easily oxidized by the environment. Hence in water treatment and adsorption studies, sample Fe (III) is preferred over Fe (II).

Among the conventional waste water treatment techniques adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of adsorbents, and cost effectiveness. Activated carbon is usually prepared by treating carbon with acid, alkali[3], zinc chloride[4], and hydrogen peroxide [5]. In the present work Banana peel carbon and Tapioca peel carbon is activated using sulfuric acid. A scan of literature has indicated that no work has been reported on micro wave activation of carbon. So this prompted us to carry out a systematic study to assess the potential feasibility of microwave treated Banana peel carbon and tapioca peel carbon to remove Iron from water bodies.

Microwaves range from 1 cm to 1 mm in wavelength in electromagnetic spectrum and lie between the infrared and radio/radar frequencies. Materials submitted to microwave exposure result in heating of product from material were interaction. Materials when submitted to microwave radiation induce stirring and friction of polar molecules which dissipates internal homogeneous heating. The heat dissipation inside the material is much more homogeneous when compared to classical heating. The profile of gradients in temperature are inverted when going from normal heating to microwave heating (MW)

EXPERIMENTAL

Preparation of banana peel carbon and tapioca peel carbon

Banana peel was collected and dried well. The dried peel was carbonized in the absence of air. It was then washed well with double-distilled water to remove any soluble materials in the carbon and separated into three different portions. First portion was dried well in hot air oven for 6 hrs at 120° C. This was taken as untreated thermally activated carbon (TABPC). Second portion was treated with 1:1 sulfuric acid and kept overnight as such. It was then washed well with double distilled water to remove any H^+ ion present in it and dried well in a hot oven at 120° C. This was taken as chemically activated Banana peel carbon (CABPC). The third portion of the BPC was dried well and activated in a domestic microwave oven for half a second with full power. This is taken as microwave activated Banana peel carbon (MWBPC). Tapioca peel was also collected and carbonized and activated in same fashion as in above said method.

Preparation of stock solution

Ferric alum of AR grade was used for preparing solution. The stock solution was prepared by dissolving accurately weighed ferric alum in distilled water to a concentration of 500 ppm. The experimental solutions were obtained by diluting the stock solution in accurate proportions to different initial concentrations.

The pH of the solution was adjusted to 4 to 5. Adsorption of ferric ions on activated carbon was carried out using a batch experimental method in a rotary shaker at 150 rpm. The effect of contact time, pH of the solution, initial concentration and adsorbent dosage were studied. For the effect of contact-time 20 ml of the ferric solutions were taken in corning bottles and 0.01 g of adsorbent dosage was added and shaken constantly. The sample solutions were withdrawn in pre-determined time intervals. The solutions were filtered, converted into thiocyanate complex and measured for color intensity in a deep vision digital photo colorimeter (312E 8 FILTERS) at 540 nm. The effect of pH was studied in the pH range from 2 to 6 using dil. hydrochloric acid and dil. sodium hydroxide. The solutions were kept in a mechanical shaker with optimum dosage of the adsorbents.

The optimum dosage was found from varying the dosage of the adsorbent from 0.25 g/l to 2.5 g/l for the three different adsorbents. The effect of initial metal ion concentration is also studied from 10 ppm to 50 ppm for optimum dosage of the adsorbent. The isotherm study was carried out by varying the initial concentration of the solution. Percentage adsorption was found using the formula [6–9].

Percentage adsorption

$$= \frac{C_i - C_e}{C_i} \times 100 \qquad \textbf{(1)}$$

where C_i and C_e are initial and equilibrium concentration in mg/l

The adsorptive capacity q_e was computed using the formula

$$q_e = (C_i - C_e)\frac{V}{m} \qquad \textbf{(2)}$$

where v is volume of the solution taken and m is the mass of the adsorbent

The equilibrium constant k be computed using the formula

$$k = \frac{1}{t} \ln \frac{C_e}{C_i} \qquad \textbf{(3)}$$

where t is the contact time

Characterization of adsorbents

The adsorbents were characterized using IR spectral analysis and scanning electron microscopic studies. Infrared spectroscopy was used in order to find out the functional group responsible for metal uptake. Scanning electron microscopy was used to study the external morphology of the adsorbents.

RESULTS AND DISCUSSION

Effect of contact time

Experiments were performed to optimize the adsorption time. The effect of contact time on ferric ion adsorption was presented in Figure 1. The extent of removal is 100% for all the six absorbents (TABPC, CABPC, MWBPC, TATPC, CATPC, MWTPC).

In case of banana peel carbon, as the contact time increased adsorption also increased for all the three adsorbents but for acid treated carbon adsorption is observed at 30 minutes and then the adsorption is increased. Untreated carbon and microwave activated carbon showed 100% adsorption in 20 minutes. Thus optimum contact time is 20 minutes for untreated carbon and microwave activated carbon and it is 40 minutes for acid treated carbon.

In case of Tapioca peel carbon increase in contact time from 10 to 50 minutes increased the percentage of adsorption. Percentage adsorption is increased to 100% at 40 minute for untreated carbon and the equilibrium contact time decreased to 30 and 20 for acid treated and microwave activated carbon.

All the six adsorbents showed 100% adsorptions. But microwave activated carbon of banana peel and tapioca peel showed equilibrium contact time at 20 minutes. This is given in Figure 1.

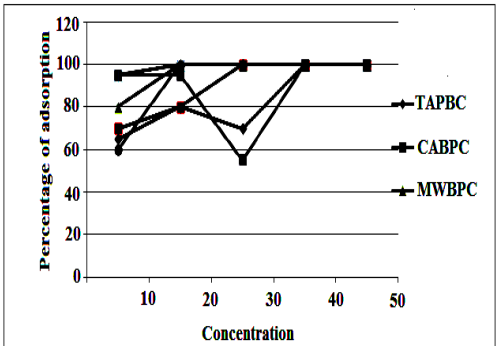


Figure 1. Adsorption on various activated carbons as a function of concentration

Effect of dosage

In the case of Tapioca peel carbon the adsorbent dosage from 0.005g/20ml to 0.01g/ 20ml of Fe solution was tried out for one hour agitation. It is evident from the result that increase in dosage increases the adsorption. This may be due to the increase in the number of adsorbing sites owing to increased surface area. Minimum dosage of 0.015 g/ 20 ml is found sufficient for microwave carbon to remove the metal ion to 100 percent and it is 0.03 g/20 ml for untreated and acid-treated carbon. Similarly in the case of banana peel increase in adsorbent dosage increases the percentage removal of Fe (III). This is shown in Figure 2.

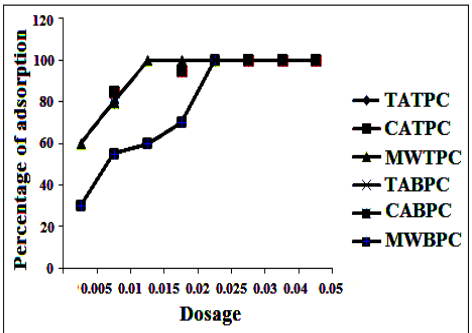


Figure 2. Percentage of adsorption vs. dosage

Effect of concentration

All the six adsorbents showed decrease in adsorption with increase in concentration. This may be due to overloading of adsorbent as the concentration increased. This is shown in Figure 3.

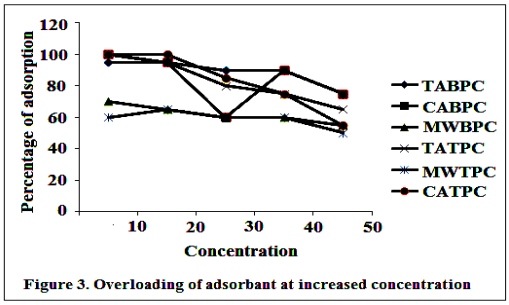


Figure 3. Overloading of adsorbant at increased concentration

Effect of Temperature

In case of banana peel increase in temperature increases the adsorption. In the case of Tapioca peel all the three adsorbent showed no great change with increase in temperature above 40º C. There is a sudden increase in adsorption up to 50º C. Then there is no further increase in adsorption with rise in temperature. G value is negative up to 50º C. Hence the process is spontaneous. S is positive. Thus the disorderliness increases during adsorption process. Above 50º C the temperature has got no effect on adsorption process. This is shown in Figure 4.

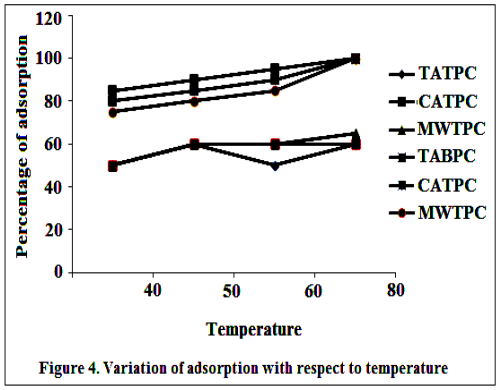


Figure 4. Variation of adsorption with respect to temperature

Effect of pH

With all the six adsorbents, as the pH increases from 2.0 to 6.0 the percentage of adsorption increases. The optimum pH is found to be 4.0 for acid treated and microwave activated carbon. The decrease in adsorption at lower pH may be due to competition for H^+ ions in the metal ions to get attached to the negative sites. Decrease in pH decreases the concentration of H^+ ions and so the metal ions get adsorbed preferably on the active sites. pH greater than 6 is not considered since Fe gets precipitated as hydroxide at increased pH. This is shown in Figure 5.

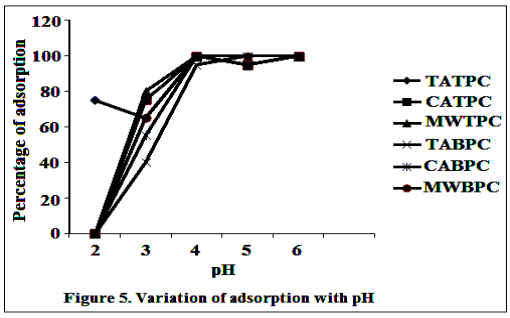


Figure 5. Variation of adsorption with pH

Isotherm studies

The adsorption isotherm indicates how the adsorption molecules are distributed between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state.

The equilibrium data obtained were modeled with Freundlich and Langmuir isotherm[10, 11].

Langmuir adsorption isotherm

The Langmuir adsorption isotherm is given by

$$\frac{C_e}{q_e} = \frac{1}{q_m} + \frac{C_e}{bq_m} \qquad (4)$$

where C is equilibrium concentration of the adsorbate in mg/l, q_e is the amount of the adsorbate adsorbed per unit mass of adsorbate (mg g-1), and Q_m and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. When C_e/q_e was plotted against Ce, straight line with slope $1/Q_m$, was obtained, The Langmuir constants 'b' and 'Q_m' were calculated from this isotherm and their values are given in Table 1.

Table 1: Adsorbents and various parameters of adsorption

Adsorbent	$1/q_m$	b	q_m	R_L
TABPC	0.0007	2E-05	1.395E	0.9996
CABPC	0.00006	2.6E-05	1.5E	0.9995
MWBPC	0.25	0.0003	4	0.994
TATPC	1.5E-05	5.7E-05	0.65 E	0.9994
CATPC	2.5E-05	2.4E-05	0.41 E	0.9995
MWTPC	0.25	0.00036	4	0.9928

Table 2: Adsorbents and the K_f values

Adsorbent	1/n	log K_f	K_f
TABPC	0.35	3.2	1.5 E
CABPC	0.75	3.2	1.5 E
MWBPC	3.9	3.02	1.04 E
TATPC	0.55	3.27	1.86
CATPC	0.33	3.35	2.2E
MWTPC	4.8	1.2	0.15E

Essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless equilibrium parameter R_L

$$R_L = \frac{1}{1+bc} \qquad (5)$$

where b is Langmuir constant and C_o is initial concentration of the solution.

The value of R_L indicates the type of the isotherm to be either unfavorable (R_L >1), linear (R_L =1), favorable (0< R_L <1) or irreversible (R_L =0).

Freundlich adsorption isotherm

The Freundlich isotherm is given by

$$L_n q_e = \ln K_f + \left(\frac{1}{n}\right) \ln C_e \qquad (6)$$

where q_e is the amount adsorbed at equilibrium (mg/g) C_e is equilibrium concentration of the adsorbate K_f and n are Freundlich constants.

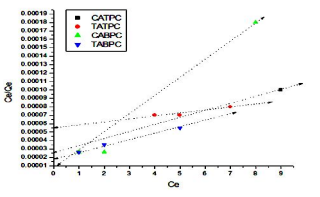


Figure 6. Plot of Ce/Ci vs. k with TATPC, CATPC, and MWTPC

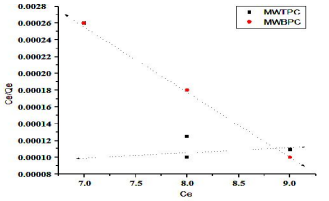


Figure 7. Plot of Ce/Ci vs. k with TABPC, CABPC, and MWBPC

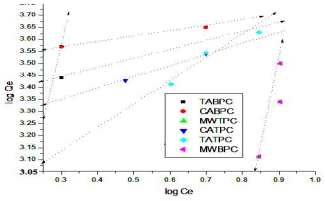


Figure 8. Plot of log Qe vs. log Ce with TABPC, CABPC, MWTPC, CATPC, TATPC, and MWBPC

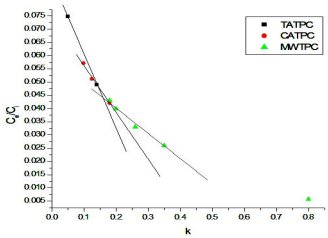


Figure 9. Plot of Ce/Ci with CATPC and MWTPC

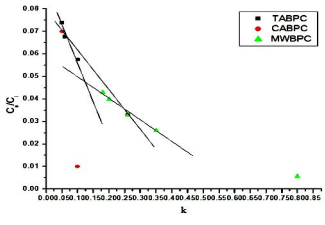


Figure 10. Plot of Ce/Ci vs. k with TABPC, CABPC, and MWBPC

Characterization of the adsorbents

IR adsorption frequencies of TABPC (cm^{-1})

3783: O-H str. (free); 3704.08: O-H str.; 3632.27: O-H str.; 3302.5: Hydrogen-bonded O-H; 2924.52: C-H str. in methyl; 1048.12: C-O-C str.

IR absorption frequencies of CABPC (cm^{-1})

3704.58, 3782.69, 3632.27: free O-H str.; 2923.56: C-H str. in methyl; 1590.99: enolic str.; 1091.51: ether str.

IR absorption frequencies of MWBPC (cm^{-1})

3704.58, 3783.65, 3632.27: free O-H -str.; 3331.27: Hydrogen bonded O-H str.; 2922.59: C-H str.;
1590.02: enolic str.; 1374: C-O str. in phenols

IR absorption frequencies of TATPC (cm^{-1})

3762: free O-H str.; 3400: Hydrogen bonded O-H; 2929.34: C-H str.; 3400: Hydrogen bonded O-H; 2929.34: -C-H str.; 1576.56: N-H bending; 1030.77: ether str.

IR absorption frequencies of CATPC (cm^{-1})

3860.7: free O-H str.; 3401.82: Hydrogen bonded O-H; 1698.98: Carbonyl str.; 1582.31: enolic str.; 1090.55: ether C-O-C str.

IR absorption frequencies of MWTPC (cm^{-1})

3838.61, 3886.07, 3918.54, 3785.05, 3632.27: free O-H str., 3309.25: Hydrogen bonded O-H str.
2923.56: C-H str., 1589.06: N-H bending, 1375: C-O str. in phenols, 1035.55: ether str.

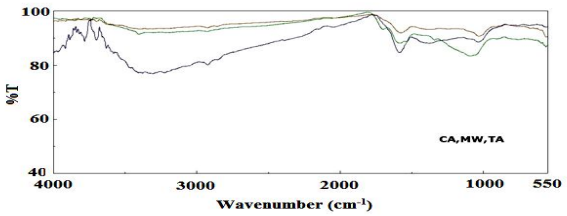


Figure 11. IR spectrum of TABPC

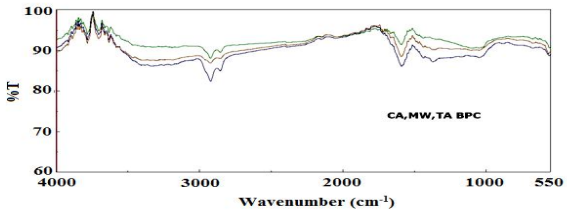
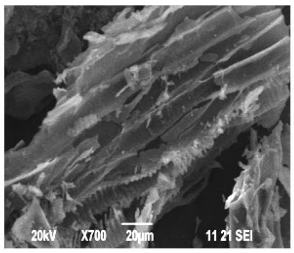
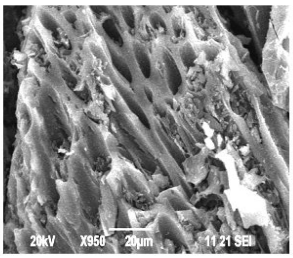


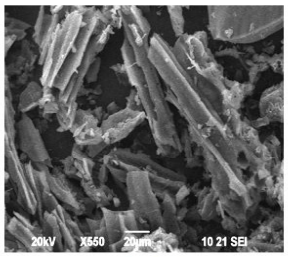
Figure 12. IR spectrum of CABPC



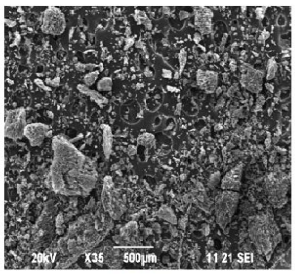
TABPC



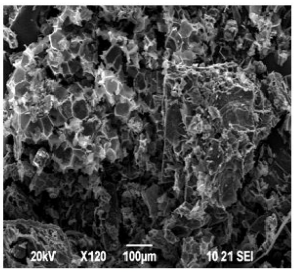
CABPC



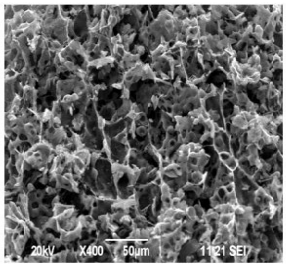
MWTPC



CATPC



TATPC



MWBPC

Figure 13. SEM images of various adsorbates

CONCLUSIONS

In case of Banana peel carbon optimum contact time for TABPC is 40 minutes, the optimum contact time for CABPC and MWBPC is 20 minutes. Optimum dosage is 0.03 g for TABPC and CABPC but it is only 0.025g for MWBPC. Optimum pH is 4 for all the three adsorbent. Increasing temperature increased the adsorption. In case of Tapioca peel carbon optimum contact time for TATPC is 40 minutes, the optimum contact time for CATPC is 30 minutes. For MWTPC it is only 20 minutes. Optimum dosage for TATPC and CATPC is 0.03 g. The temperature above 50° does not affect the adsorption process.

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