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Original Article

Adsorption efficiencies of calcium (II) ion and iron (II) ion on activated carbon obtained from pericarp of rubber fruit

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Abstract

Determination of adsorption efficiencies of activated carbon from pericarp of rubber fruit for calcium (II) ion and iron (II) ion has been performed by flowing the solutions of these ions through a column of activated carbon. The weights of activated carbon in 500 mL buret column (diameter 3.2 cm) for flowing calcium (II) ion and iron (II) ion solutions were 15 g and 10 g, respectively. The initial concentration of calcium ion was prepared to be about eight times more diluted than the true concentration found in the groundwater from the lower part of southern Thailand. Calcium (II) ion concentrations were analysed by EDTA titration and its initial concentration was found to be 23.55 ppm. With a flow rate of 26 mL/min, the adsorption efficiency was 11.4 % with passed through volume 4.75 L. Iron (II) ion concentrations were analysed by spectrophotometric method; its initial concentration was found to be 1.5565 ppm. At a flow rate of 22 mL/min, the adsorption efficiency was 0.42 % with passed through volume of 34.0 L.

Key words: activated carbon, calcium (II) ion, iron (II) ion, adsorption efficiency

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1. Introduction

The groundwater from areas of the lower part of southern Thailand that has been analysed by the Central Equipment Division, Faculty of Science, Prince of Songkla University, Hat Yai, mostly contained calcium and iron. Calcium dissolved in water is the most common mineral that makes the water “hard”. The hardness of the water was 203.6 ppm, which was higher than the standard quality of drinking water of 100.0 ppm (Announcement of the Ministry of Public Health, 1991). Therefore, it is necessary to purify the water that is supplied to the households before it is used for drinking or cooking. Activated carbon filters are commonly used to treat the household water. These filters can remove objectionable taste and odor, color, chlorine, and organics, including halogenated organic compounds, and dissolved metals such as iron, lead, and cadmium.

In this work, we study the adsorptive capacity of activated carbon obtained from pericarp of rubber fruit for calcium (II) ion and iron (II) ion. The efficiency of any activated carbon filter depends on a “useful flow rate” of the filter and estimated filter lifetime, which are governed largely by the size of the filter and the amount of activated carbon it contains. The results can be used as a model for estimating how long the activated carbon filters can be fully utilized.

2. Materials and Methods

2.1 Preparation of activated carbon

The raw material, pericarp of rubber fruit, was dried in the sun for 2-3 days and dried again in the oven at 110°C for 3 h. The carbonization was then conducted in a muffle furnace at 400°C for 1 h by placing the raw material into a stainless steel box with cover. After carbonization, the

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residual char was grounded using a laboratory jar mill to pass between a 25-50 mesh sieve. The grounded char was mixed with concentrated $ZnCl_2$ of ratio 1:2 in porcelain. Then the sample was activated at 600 $^{\circ}$C for 3 h in a muffle furnace (Sirichote *et al.,* 2002). The obtained activated carbon was washed with 1 % HCl, soaked in hot water for 5 min and then the water was drained through a Buchner funnel. This step was repeated two more times. The yield relative to the raw material was 17.54 %. The raw material, carbonized char, and activated carbon are shown in Figure 1.

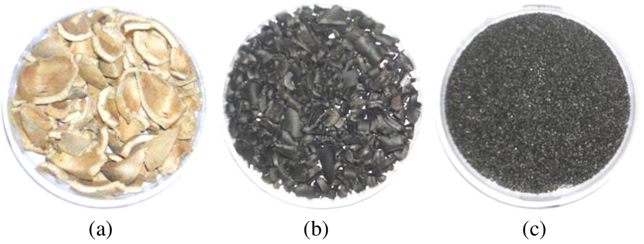

Figure 1. Photographs of raw material (a), carbonized char (b), and activated carbon (c) all from pericarp of rubber fruit.

2.2 Characterization of the activated carbons

1) Surface area and pore size analysis

The surface area and the pore size distribution of activated carbon was determined from nitrogen adsorption isotherms at 77 K by a Coulter apparatus, model SA3100 at the Department of Chemical Engineering, Prince of Songkla University, Hat Yai, Thailand. The apparent surface area was determined according to the BET model. The pore size distribution was calculated by using the Barrett-Joyner-Halenda (BJH) model (Barrett *et al.*, 1951).

2) Iodine number

The iodine number of activated carbons was analyzed using the method from the American Standard of Testing Material (1999) (ASTM D4607-94).

2.3 Determination of adsorption efficiency of activated carbon for calcium (II) ion

The concentrations of calcium were determined by using standard technique of EDTA titration from General Chemistry for Engineering Laboratory Manual, 2006. Department of Chemistry, Faculty of Science, Prince of Songkla University, Songkhla, Thai version. pp 25.

1) Reagents needed

0.001 M EDTA solution, dissolved 0.744 g of ethylenediaminetetra-acetic acid disodium salt into a 2 L volumetric flask and diluted to the mark with distilled water.

0.002 M Ca^{2+} solution (primary standard $CaCO_3$), dissolved 0.050 g of $CaCO_3$ in a 100 mL beaker. Added 15 mL distilled water, then dropped concentrated HCl drop by drop, shaked well to let the solid of $CaCO_3$ to be dissolved completely. Heated the solution to boil, then added 25 mL of distilled water. Cooled the solution to room temperature. Transferred to a 250 mL volumetric flask and diluted to the mark.

0.003 M Mg^{2+} solution, dissolved 0.030 g of $MgCl_2$ $6H_2O$ into a 50 mL volumetric flask and diluted to the mark with distilled water.

0.010 M Eriochrome Black T, dissolved 0.150 g of Eriochrome Black T together with 15 mL of triethanolamine. Added 15 mL of ethanol and kept in a dark bottle.

Buffer pH 10, dissolved 68 g of NH_4Cl in 570 mL of concentrated NH_3 in 1L volumetric flask and diluted to the mark.

1 M HCl, dissolved 82 mL of concentrated HCl in a 1 L volumetric flask and diluted to the mark.

25 ppm Ca^{2+} solution, dissolved 0.250 g of $CaCO_3$ in a 100 mL beaker. Added 15 mL drop by drop of concentrated HCl, shaked well to let the solid to be dissolved completely. Heated to boil and added 25 mL distilled water. Cooled down to room temperature. Due to the low percentage of the yield of activated carbon we could not prepare a column of activated carbon weighted up to 800 g which was the weight of activated carbon filter in the house. Transferred the solution into a 10 L tank, diluted to the mark and mixed well. The exact concentration of Ca^{2+} solution was determined by EDTA titration as follows.

2) Blank titration

Added 10 mL of distilled water, 10 mL of the pH 10 buffer and two drops of Eriochrome Black T indicator into an 125 mL Erlenmeyer flask. The solution then turned blue as shown in the left hand side of Figure 2 (a, b). The blue

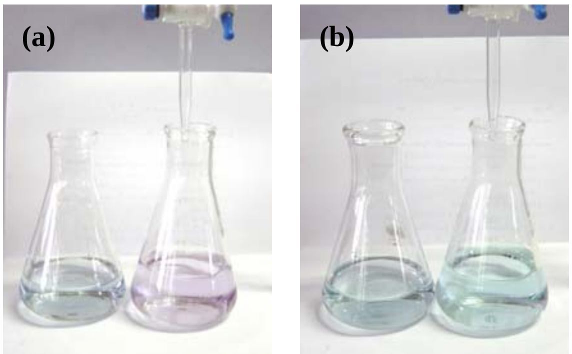

Figure 2. The solution of distilled water mixed with pH 10 buffer and two drops of Eriochrome Black T indicator without three drops of 0.003 M $MgCl_2$ (left hand side of (a) and (b)) and with three drops of 0.003 M $MgCl_2$ before titration with EDTA (right hand side of (a)), and after titration with EDTA (right hand side of (b)).

color was a reference color for the end point of the titration. For blank titration, added 10 mL of distilled water, 10 mL of pH 10 buffer, and two drops of Eriochrome Black T indicator into an 125 mL Erlenmeyer flask. Then added three drops of 0.003 M $MgCl_2$ to turn the solution wine red (Slowinski *et al.*, 1977) as shown in the right hand side of Figure 2 (a). Added EDTA drop by drop from buret to the solution until the last tinge of purple just disappeared. The blue solution in the right hand side of Figure 2 (b) represented the end point of the titration. Read the volume required for the blank. Repeated all steps two more times to determine the average value.

3) Standardization of 0.001 M EDTA

Pipetted 10 mL of 0.002 M Ca^{2+} into an 125 mL Erlenmeyer flask. Added two drops of indicator, 10 mL of pH 10 buffer, and three drops of 0.003 M $MgCl_2$, then shaked well. Titrated the solution with EDTA until its color matched the reference solution. The volume from blank titration must be substracted from the total EDTA volume used. Repeated all steps two more times to determine the average volume.

4) Determination of apparent concentration of calcium (II) ion

Pipetted 50 mL of 25 ppm Ca^{2+} solution into an 125 mL Erlenmeyer flask. As before, added two drops of indicator, three drops of 0.003 M $MgCl_2$, and 10 mL of pH 10 buffer. Titrated the solution with EDTA until it reached the end point. Repeated all steps two more times to determine the average concentration of Ca^{2+} solution.

5) Preparation of the column of activated carbon to adsorb calcium (II) ion

A 500 mL buret (diameter 3.2 cm) was used as a column for packing. Placed a cotton inside the buret at the bottom up to 2 cm above the stopcock. The activated carbon with a weight of 15.0 g was introduced into the column in small quantities. Shaking the column when each quantities was introduced in order to make a good arrangement, with no air inside the column. Covered the top surface with 2 cm thick cotton to prevent the spread out of activated carbon when filling the Ca^{2+} solution. After packing, the column was washed with 25 mL of 1 M HCl by leaving the acid in the column for 10 min, then drained out and repeated two more times. The column was washed with 50 mL distilled water several times until there were no Ca^{2+} or Mg^{2+} left in the column. These could be tested by dropping one drop of Eriochrome Black T into the eluting water. If the color of the solution changed from sky blue to wine red, it meant that those ions were still present. Testing for Cl^- by adding one drop of $AgNO_3$. If the white precipitate of AgCl appeared, it meant the presence of Cl^-.

A 10 mL tank of Ca^{2+} solution was placed on the shelf behind the column and let the faucet in the positon above the top of column. The 50 mL volumetric flasks were used to collect the eluting water as shown in Figure 3. Adjusted the Ca^{2+} solution flow into the column by keeping the level of Ca^{2+} solution 2 cm high above the top of the surface of the activated carbon with a controlled flow rate of 26 mL/min. Determined the concentration of Ca^{2+} from the collected eluting water by EDTA titration.

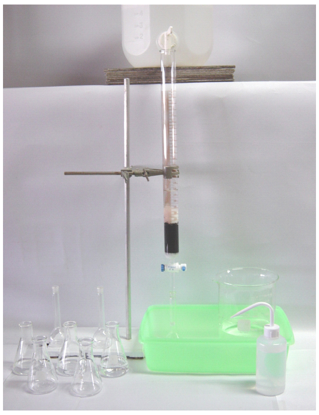

Figure 3. Ca^{2+} solution which has flown through the activated carbon column, was collected in a 50 mL volumetric flask.

2.4 Determination of adsorption efficiency of activated carbon for iron (II) ion

1) Reagents needed

Stock iron solution 200 ppm, weighed 1.404 g of $FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$ into a 1 L volumetric flask. Then dissolved in 50 mL of distilled water containing 20 mL of concentrated H_2SO_4. Diluted to the mark, and mixed well.

Standard iron solution 50 ppm, pipetted 50 mL of 200 ppm stock iron solution into a 1 L volumetric flask and diluted to the mark with distilled water.

Hydroxylamine hydrochloride, dissolved 10 g of $H_2NOH{\cdot}HCl$ into a 100 mL volumetric flask and diluted to the mark with distilled water.

1,10-Phenanthroline monohydrate, dissolved 0.1 g 1,10-phenanthroline monohydrate in 100 mL of water.

Ammonium acetate buffer, dissolved 250 g $NH_4C_2H_3O_2$ in 150 mL of water. Added 700 mL of glacial acetic acid and mixed well.

2) Preparation of calibration curve

A series of standard iron solutions were prepared, pipetted 0.5, 1.0, 1.5 and 2.0 mL of standard iron solution into 50 mL volumetric flasks, respectively. Added 1 mL of the hydroxylamine solution, 10 mL of ammonium acetate buffer, and 2 mL of 1,10-phenanthroline solution to each. Then diluted each to the mark and mixed well. Allowed the mixtures to stand for 15 min. Ferrous ion reacted with 1,10 phenanthroline to form an orange-red complex $[(C_{12}H_8N_2)_3Fe]^{2+}$ (Vogel, 1961; Skoog *et al.*, 1982). Determined the absorbance of each standard iron solution with reference to blank at wavelength 510 nm using UV-Visible recording spectrophotometer UV-160A SHIMADZU. Plotted a calibration curve between absorbance and concentration.

3) Preparation of the column of activated carbon to adsorb ferrous (II) ion

The procedure for packing the column was the same as mentioned before. But the weight of activated carbon used for packing was changed to 10 g. There was no necessity to wash Ca^{2+} or Mg^{2+} ions from the column. The Fe^{2+} ion concentrations before and after flowing into the column were determined by using the calibration curve.

3. Results and Discussion

The iodine number (IA) and BET surface area (S_{BET}) of activated carbon obtained from pericarp of rubber fruit was 868 mg/g and 877 m^2/g, respectively. Determination of Ca^{2+} ion concentration was performed by EDTA titration. The initial concentration of Ca^{2+} ion was analysed to be 23.55 ppm. The Ca^{2+} ion concentration for each 0.1 L Ca^{2+} solution, after passing through the activated carbon column, was analysed. The results are listed in Table 1. The adsorption efficiencies of activated carbon for each quantity of Ca^{2+} solution was calculated as followed:

$$\text{Efficiency} = \frac{\text{initial concentration (ppm) - collected concentration (ppm) x 100}}{\text{initial concentration (ppm)}} \quad (1)$$

The graph of adsorption efficiencies and collected volumes of Ca^{2+} ion solution is plotted in Figure 4. It was found that the lowest adsorption efficiency of 15 g activated carbon for Ca^{2+} ion with a flow rate of 26 mL/min was 11.4 % and the passed through volume of solution was 4.75 L. Therefore, we can use this result to estimate the expiry date of an activated carbon filter in the same way.

The Fe^{2+} concentrations were determined by spectrophotometric method. The adsorption efficiency for each collected quantity calculated from equation (1) is listed in Table 2. The graph of efficiencies and collected volume of Fe^{2+} ion solution is plotted in Figure 5. The lowest adsorption efficiency of 10 g activated carbon for Fe^{2+} ion with a

Table 1. The volumes of collected Ca^{2+} (in L) solution after flowing through the column including their Ca^{2+} ion concentrations (in ppm) and the efficiencies (in %)

Fraction (L)	$[Ca^{2+}]$ (ppm)	Efficiency (%)
0.10	0.00	100.0
0.20	0.00	100.0
0.25	0.00	100.0
0.30	0.52	97.8
0.40	5.37	77.2
0.50	8.26	64.9
0.60	8.57	63.6
0.70	11.57	50.9
0.75	11.98	49.1
0.80	12.60	46.5
0.90	13.22	43.9
1.00	14.46	38.6
1.25	15.70	33.3
1.50	17.35	26.3
1.75	17.77	24.6
2.00	17.77	24.6
2.25	17.87	24.1
2.50	18.80	20.2
2.75	19.21	18.4
3.00	19.63	16.7
3.25	19.83	15.8
3.50	20.04	14.9
3.75	20.04	14.9
4.00	20.04	14.9
4.25	20.04	14.9
4.50	20.56	12.7
4.75	20.87	11.4
5.00	20.87	11.4

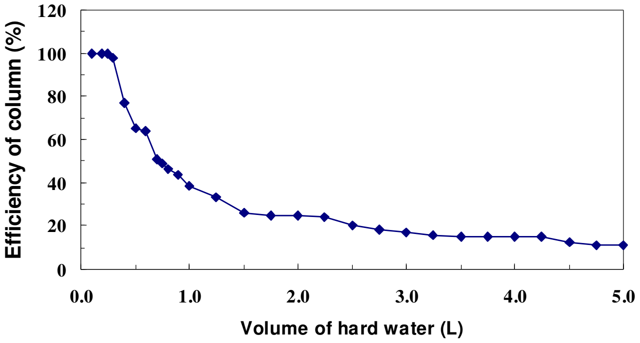

Figure 4. Efficiency of the column (in %) in relation to the volumes of collected solution of Ca^{2+} (in L).

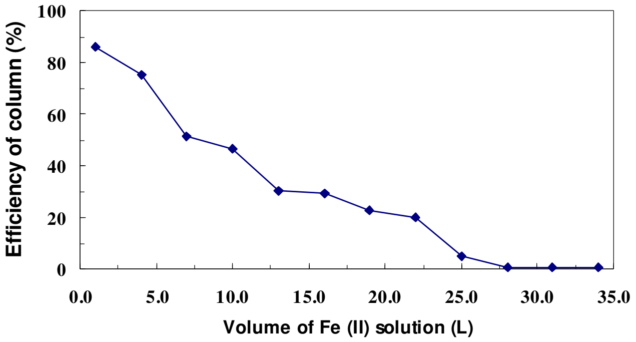

Figure 5. Efficiency for Fe^{2+} adsorption (in %) and the passed through volume of Fe^{2+}solution (in L).

Table 2. The volumes of collected Fe^{2+}solution (in L) including their Fe^{2+} ion concentrations (in ppm) and the efficiencies (in %)

Fraction (L)	$[Fe^{2+}]$(ppm)	Efficiency (%)
1.0	0.2190	85.93
4.0	0.3881	75.07
7.0	0.7580	51.24
10.0	0.8367	46.24
13.0	1.0874	30.14
16.0	1.1042	29.06
19.0	1.2031	22.70
22.0	1.2463	19.93
25.0	1.4836	4.68
28.0	1.5473	0.59
31.0	1.5495	0.45
34.0	1.5500	0.42

flow rate of 22 mL/min was 0.42% and the passed through volume of water was 34.0 L.

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