

Fe removal by adsorption using ash from oil palm factory

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ABSTRACT: Heavy metals are often present in water and wastewater as contaminants. From the public health and environmental protection point of view, it is important that their concentrations be limited to permissible levels. Technologies for heavy metals removal include ion exchange, chemical precipitation, reverse osmosis, etc. which are often ineffective or expensive. Adsorption is a commonly used method for the removal of heavy metals from aqueous solutions. However, for the process to be economical, the adsorbent should be easily and cheaply available in abundance and it should require minimal or no pre-treatment; for expensive pre-treatment procedures would add to the overall treatment cost. The present study focuses on iron (Fe) removal by adsorption using oil palm by-products (fibre, shell, ash) without pre-treatment or activation. The results show that among the materials tested, ash was the most effective adsorbent. The optimum agitation time and optimum pH were 90 minutes and 5 respectively. The removal followed the Freundlich isotherm closely with $R^2 = 0.9479$. Desorption of over 98 % was achieved with 0.15 N HCl.

Key words: low cost, adsorption, iron (Fe), oil palm by-products, ash

1 INTRODUCTION

Heavy metals are commonly found in water and wastewater. They are generally present in the wastewaters of electroplating, metal finishing, leather tanning, paint manufacturing, steel fabrication, metal fabrication and pigments, as well as battery manufacturing and other industries. Heavy metals can cause serious water pollution and threaten the environment. It is therefore, essential to control and prevent the unsystematic discharge of heavy metals into the environment. Hence, increased attention is being paid to the development of technical know-how for their removal from metal bearing effluents before their discharge into water bodies and natural streams.

Earlier researchers have reported various methods for the removal of heavy metals from waters and wastewaters, with the aim of preservation and protection of the environment from the damages due to their accumulation. Traditional technologies, such as ion exchange, chemical precipitation or reverse osmosis are often ineffective or expensive, particularly for the removal of heavy metal ions at low concentrations. Efficient and environment-friendly technologies are, therefore, needed to be developed to reduce heavy metal contents in wastewaters to ac-

ceptable levels at inexpensive costs (Saeed and Iqbal, 2003).

In recent years, the discharge of heavy metals into the environment has decreased in many countries due to more stringent legislations, improved cleaning technologies, and altered industrial activities. However, the demand for an economic and environmental friendly method for heavy metals removal still exists.

The present study focuses on the removal of iron (Fe) from water. Fe is one of the most abundant elements found in nature. It is an important element not only due to its widespread industrial applications but also because it is essential for all life forms; animals and plants. However, it can cause lesions when in excess. The presence of iron in excess may also produce a metallic taste to water and clothes may stain a yellow to brownish colour. In the natural environment iron exist in Fe (II) and Fe (III) oxidation states. The WHO allowable concentration in drinking water for Fe is 0.3 mg/l. The Malaysian limit for discharge of Fe into inland water is 1 mg/l (Environmental Quality Act and Regulations, 2002). Hence it is necessary to remove Fe from water/wastewater to acceptable levels.

The main objective of the present study was to determine the feasibility of using easily available low

cost materials as adsorbents in Fe removal from aqueous solutions. Adsorption involves the separation of a substance (adsorbate) from one phase (aqueous, in the present study) accompanied by its accumulation or concentration at the surface of another (adsorbent). For an adsorption procedure to be truly low cost not only should the adsorbent be easily and cheaply available in abundance but it should also require minimal or no pre-treatment; for expensive pre-treatment procedures would add to the overall treatment cost.

Recently researchers have concentrated their work on low cost, unconventional adsorbents for the treatment of wastewater (Sommerfield, 1999). Agricultural wastes or derivatives have generally been used as adsorbents in these studies. Some of the reported low cost adsorbents include saw-dust (Zarra, 1995), bark (Vazquez et al., 1994), leaves (Gardea-Torresday et al., 2002), etc. The abundance and availability of agricultural by-products make them good sources of adsorbents (Bansode et al., 2003).

An adsorbent with no pre-treatment was sought from oil palm due to its abundance in Malaysia. This research was carried out in two main phases, viz., preliminary tests and isotherm generation. The objectives of the preliminary tests were to determine a suitable adsorbent from the oil palm industry, agitation time and optimum pH for the effective removal of Fe from aqueous solution. The objective of isotherm generation was to obtain an adsorbent-adsorbate relationship (model) that would describe the removal of Fe from aqueous solution.

2 MATERIALS AND METHODS

2.1 Materials

The materials (fibre, shell and ash) used as adsorbents were collected from a local oil palm factory and were dried at 105 °C over night before the tests. Ferrous sulphate ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$) solution of approximately 20 mg/l concentration was used for the study. The exact concentration of Fe in the solution was determined before each set of adsorption tests. Different amount of adsorbents were added to the ferrous sulphate solution and subjected to batch adsorption tests with the help of a mechanical shaker.

2.2 Methods

2.2.1 Preliminary test

2.2.1.1 Test for suitable adsorbent

Three conical flasks were each filled with 100 ml of ferrous sulphate solution. 500 mg of palm by-products i.e. fibre, shell and ash were measured and added to the conical flasks (one material per flask). The three conical flasks were then agitated at 350

rpm for 60 minutes using a mechanical shaker. The samples were then filtered and analysed for Fe concentration. The most suitable adsorbent was decided based on the highest Fe adsorption.

2.2.1.2 Test for agitation time

Eight conical flasks with 100 ml of ferrous sulphate solution were prepared. Initial concentrations of samples were measured. 500 mg of chosen adsorbent (most suitable adsorbent among the three materials) was measured and added to each of the conical flasks. The flasks were then agitated at 350 rpm using a mechanical shaker. They were removed from the shaker for Fe analysis one after the other at 10, 20, 30, 40, 60, 80, 100 and 120 minutes. The samples were filtered and the final Fe concentrations were measured.

2.2.1.3 Test for optimum pH

Eight conical flasks with 100 ml of ferrous sulphate solution were used. The samples were adjusted to pH 4-9 by using 0.1 N sodium hydroxide (NaOH) or 0.1 N hydrochloric acid (HCl). 500 mg of adsorbent was measured and added in each flask. The flasks were agitated at 350 rpm for the selected contact time. Then the samples were filtered and the final Fe concentrations were measured.

2.2.2 Isotherm generation

Six conical flasks with 100 ml of ferrous sulphate solution were arranged. All samples were adjusted to the optimum pH. 300, 400, 500, 600, 700 and 800 mg of adsorbent was measured and added to the samples. The conical flasks were agitated at 350 rpm for the selected contact time. The samples were filtered and the final Fe concentrations were measured.

2.3 Analytical techniques

Fe concentrations of the samples were measured using a Direct Reading Spectrophotometer (DR2010) after filtration with GFC micro fibre filters. pH was measured with a pH-meter.

3 RESULTS AND DISCUSSION

3.1 Preliminary tests

3.1.1 Test for suitable adsorbent

Palm by-products were used as adsorbents without pre-treatment or activation for the removal of Fe. The experiment was conducted with 500 mg of palm by-products in 20 mg/l (approximately) of metal solution. The volume of metal solution was 100 ml and the mixture was agitated for 60 minutes at 350 rpm. The results are shown in Table 1.

Table 1 shows that among the palm by-products tested, ash was the most effective adsorbent for Fe removal with the percentage of Fe adsorbed as high

as 97 %. Thus ash was chosen as adsorbent for the subsequent studies.

Table 1. Fe adsorption by oil palm by-products

	Materials		
	Fibre	Shell	Ash
Initial Fe conc. (mg/l)	18.5	18.5	18.5
Final Fe conc. (mg/l)	2.4	6.1	0.55
Fe adsorbed (mg/l)	16.1	12.4	17.95
Fe adsorbed (%)	87	67	97

3.1.2 Test for agitation time

By using the selected adsorbent i.e. ash, preliminary test was carried out to determine a suitable contact, equilibrium or agitation time. Agitation time plays an important role in the efficient removal of heavy metals. Selvi et al. (2001) stated that the equilibrium time was independent of initial metal concentration. Increase in initial concentration decreased the percent of adsorption.

The agitation time was varied from 10-120 minutes in order to observe the amount of Fe adsorbed on 500 mg of ash from 100 ml of aqueous ferrous sulphate solution. Figure 1 shows the results obtained.

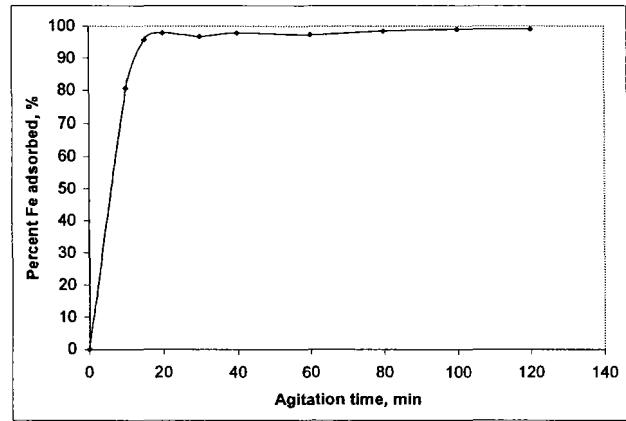


Figure 1. Agitation time

From Figure 1, it is noted that there was a sharp increase in the amount of Fe adsorbed during the first 20 minutes of agitation. Thereafter, the rate and amount of Fe adsorbed decreased. The process was essentially complete after 90 minutes. Hence for the subsequent studies the agitation time was chosen as 90 minutes.

3.1.3 Test for optimum pH

In addition to agitation time, pH is an important parameter that controls the metal ion adsorption process. Hence experiments were conducted to determine the optimum pH.

Different metals require different pH levels for their effective removal. This has been shown by various researchers. Kadirvelu and Namasivayam (2002) stated that the maximum removal of cadmium, Cd (II), using coconut coir pith was attained over the pH range 5-10. Selvaraj et al. (2003) found 93% removal of chromium, Cr (VI) by distillery sludge at pH 2-3 and that, when the pH was increased above 3 there was a reduction in adsorption. In another research, the maximum adsorption occurred at pH below 5 for chromium, Cr (VI), using rice husk activated carbon (Guo et al., 2002).

In this research the pH range of 4-9 was chosen to determine the optimum pH for Fe adsorption. The results are plotted in Figure 2. Over 97 % of Fe was removed at pH 5. The removal decreased to 95.6 % at pH 6 and then again increased to 99.6 % at pH 7. Thus, increasing the pH from 5 to 7 provided only a 2.5 % improvement in Fe removal. Also as metals tend to precipitate at elevated pH levels, the total removal obtained at pH 7 may be the result of both adsorption as well as precipitation. Hence, pH 5 was chosen as the optimum pH for Fe adsorption in this study.

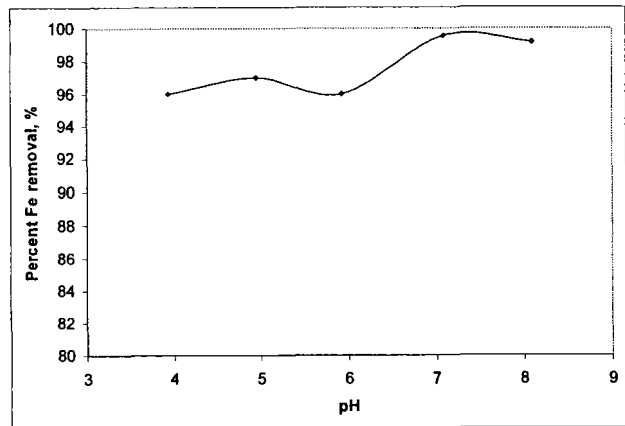


Figure 2. Optimum Ph

3.2 Isotherm generation

Isotherms are mathematical relationships used to describe the adsorption behaviour of a particular adsorbent-adsorbate combination. They help in modelling adsorption behaviour and in calculating the adsorption capacity of materials. Three common adsorption isotherms are the Langmuir, Freundlich, and Brunauer-Emmett-Teller (BET) isotherms. The equations representing these isotherms and their corresponding rearranged forms to obtain linear plots are as follows:

Langmuir equation,

$$\frac{x}{m} = \frac{abC}{1+aC} \tag{1}$$

$$\frac{1}{(x/m)} = \frac{1}{abC} + \frac{1}{b} \quad (2)$$

Freundlich equation,

$$\frac{x}{m} = KC^{1/n} \quad (3)$$

$$\log\left(\frac{x}{m}\right) = \frac{1}{n} \log C + \log K \quad (4)$$

BET equation,

$$\frac{x}{m} = \frac{ACx_m}{(C_s - C) \left[1 + (A-1) \frac{C}{C_s} \right]} \quad (5)$$

$$\frac{C}{(C_s - C)} \frac{x}{m} = \frac{1}{Ax_m} + \frac{A-1}{Ax_m} \left(\frac{C}{C_s} \right) \quad (6)$$

where, x= mass of material adsorbed (mg); m= mass of adsorbent (mg); C = concentration of adsorbate in solution after adsorption is complete (mg/l); C_s = saturation conc. of adsorbate (mg/l); x_m= amount of adsorbate adsorbed in forming a complete monolayer (mg/g); a, b, K, n and A are constants

Figures 3, 4 and 5 show the Langmuir, Freundlich and BET plots respectively for Fe adsorption. It can be seen from the plots that Fe adsorption by ash is best represented by the Freundlich isotherm (highest R²).

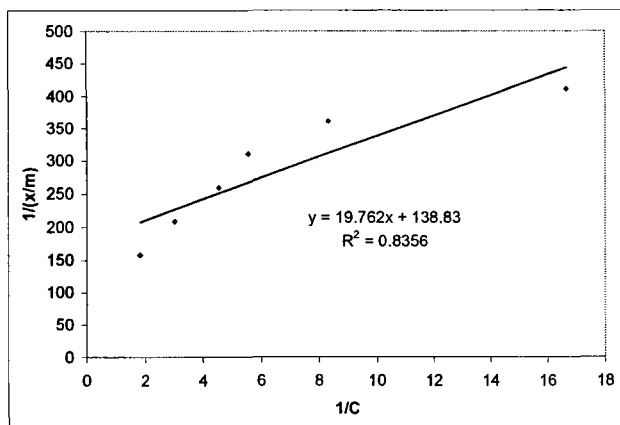


Figure 3. Langmuir isotherm

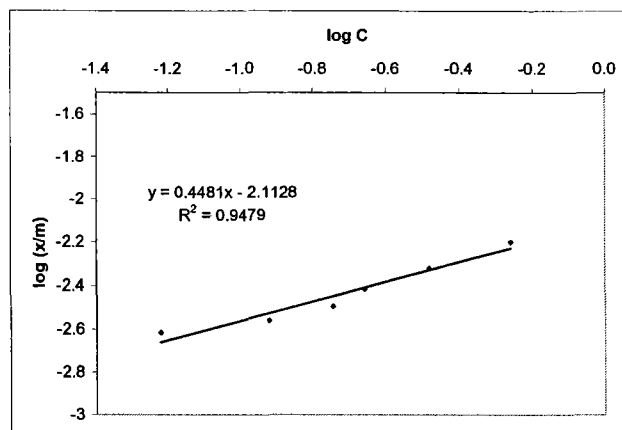


Figure 4. Freundlich isotherm

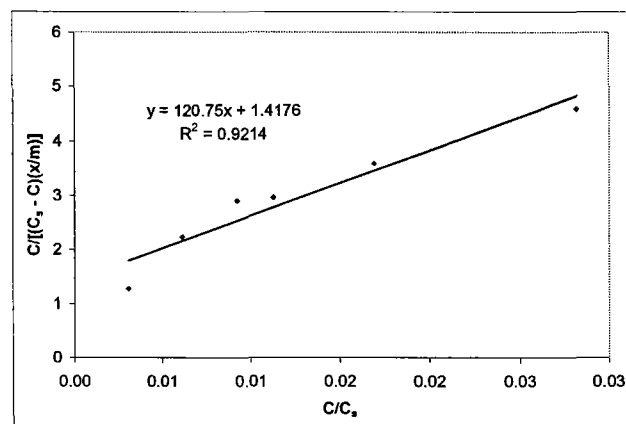


Figure 5. Brunauer-Emmett-Teller (BET) isotherm

From Figure 4,

Slope, $1/n = 0.4481$

$n = 2.2316$

Intercept, $\log K = -2.1128$

$K = 7.713 \times 10^{-3}$

Thus the Freundlich adsorption expression for Fe removal under the present test conditions is given by:-

$$\frac{x}{m} = 7.713 \times 10^{-3} C^{0.4481}$$

3.3 Desorption studies

Subsequent desorption studies showed a high degree of Fe recovery from the adsorbent. Figure 6 shows the effect of hydrochloric acid on the desorption of Fe from ash. It is noted that Fe desorption increased with increase in normality of HCl. The metal desorption was almost complete (over 98 %) at HCl concentration of 0.15 N.

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6 REFERENCES

- Bansode, R.R., Losso, J.N., Marshall, W.E., Rao, R.M. and Portier, R.J. (2003). Adsorption of Metal Ions by Pecan Shell-Based Granular Activated Carbons. *Bioresource Technology*, 89, 115-119.
- Environmental Quality Act and Regulations, MDC Publishers Printers Sdn. Bhd., Kuala Lumpur, 2002.
- Gardea-Torresdey J., Hejazi M., Tiemann K., Parsons J.G., Duarte-Gardea and Henning J. (2002) 'Use of hop (*Humulus lupulus*) agricultural by-products for the reduction of aqueous lead (II) environmental health hazards', *J. of Hazard. Mat.*, 91(1-3), 95-112.
- Guo, Y., Qi, J., Yang, S., Yu, K., Wang, Z. and Xu, H. (2002). Adsorption of Cr (VI) on Micro and mesoporous Rice Husk-Based Activated Carbon. *Material Chemistry and Physics*, 79, 132-137.
- Kadirvelu, K. and Namasivayam, C. (2002). Activated Carbon from Coconut Coirpith as Metal adsorbent: Adsorption of Cd (II) from Aqueous Solution. *Advances in Environment Research*, 7, 471-478.
- Saeed, A. and Iqbal, M. (2003). Bioremoval of cadmium from aqueous solution by black gram husk (*Cicer arietinum*). *Water Research*. 37: 3472-3480.
- Selvaraj, K., Manonmani, S. and Pattabi, S. (2003). Removal of Hexavalent Chromium Using Distillery Sludge. *Bioresource Technology*, 89, 2007-2011.
- Selvi, K., Pattabi, S., and Kadiravelu, K. (2001). Removal of Cr (VI) from Aqueous Solution onto Activated Carbon. *Bioresource Technology*. 80:87-89.
- Sommerfeld, E. O. (1999). Iron Bacteria and Organic Carbons: What They Mean to Iron and Manganese Removal. Presentation to the 1999 AWWOA Operator's Seminar, Banff Park Lodge, Thursday, March 11, 1999.
- Vazquez G., Antorrena G., Gonzalez J. and Doval M.D. (1994) 'Adsorption of heavy metal ions by chemically modified *Pinus pinaster* bark', *Bioresource Technol.*, 48, 251-255.
- Zarra, M.A. (1995) 'A study on the removal of chromium (VI) from waste solutions by adsorption on to sawdust in stirred vessels', *Adsorption Sci. Technol.*, 12(2), 129-138.

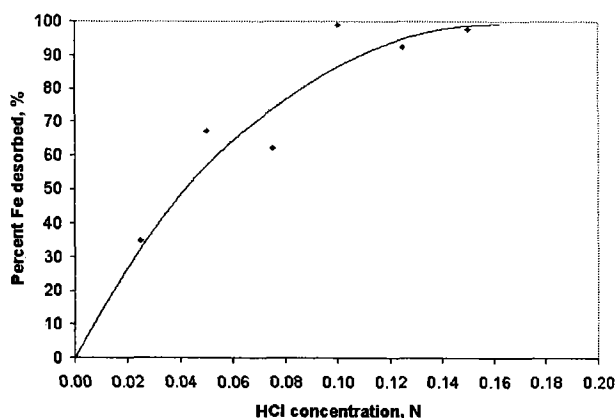


Figure 6. Fe desorption

4 CONCLUSIONS

The following conclusions can be drawn from the present study:

- Ash from oil palm industry, capable of removing over 99 % of Fe from aqueous solution, is an effective adsorbent for Fe.
- A suitable agitation time for Fe adsorption is 90 minutes.
- The optimum pH for Fe adsorption is 5.
- Fe adsorption is well described by the Freundlich isotherm with values of constants K and n as 7.713×10^{-3} and 2.2316 respectively. The resulting Freundlich equation is:

$$\frac{x}{m} = 7.713 \times 10^{-3} C^{0.4481}$$

- Desorption using 0.15 N HCl was almost complete (over 98 %).