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Enhancement of Copper Sorption through Acid Blue 29 Treated Oil Palm Pressed Fibres

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ABSTRAK

Pengerapan ion kuprum daripada larutan akueous oleh serabut kelapa sawit semulajadi dan tersalut dengan pewarna, Asid Biru 29, telah dikaji. Proses pengerapan bergantung kepada kepekatan dan pH larutan. Data eksperimen mematuhi model isoterma Langmuir dengan muatan maksimum 2.41 dan 7.71 mg/g untuk serabut kelapa sawit semulajadi dan yang tersalut dengan pewarna berturut-turutan. Kehadiran ion logam lain merencat pengambilan kuprum mengikut tertib Pb > Zn > Ni. Kesan penghalangan agen kelat bersepadan dengan nilai log K. Kajian turus menunjukkan bahawa faktor 'bed-depth' adalah lebih berkesan daripada kadar aliran dalam pengerapan kuprum.

ABSTRACT

The removal of cupric ions from aqueous solution by natural and dye-coated palm pressed fibres was studied. Sorption was both pH and concentration dependent. The equilibrium data followed the Langmuir isotherm model with maximum copper sorption capacities of 2.41 and 7.71 mg/g for natural and dye-treated fibres respectively. The presence of other metal ions inhibited copper uptake in the following order Pb > Zn > Ni. The suppressing effects of chelators correspond to their log K values. Column studies showed that bed-depth had a more pronounced effect on copper sorption than flow rate.

Keywords: sorption, copper, dye-treated oil palm fibre, batch and column studies

INTRODUCTION

Chemical modifications of the surface of biological materials with the objective of increasing metal sorption from aqueous solutions have received considerable attention recently. EDTA modified cellulosic materials showed greater sorption for Cd, Cu and Pb than untreated materials (Okieimen *et al.* 1985). Apple waste treated with phosphorus oxychloride was reported to have greater efficiency in removing heavy metals (Maranon and Sastre

1991). Rice hulls coated with monochlorotriazine-type reactive dyes led to more efficient removal of heavy metals from aqueous solutions (Suemitsu *et al.* 1986). Similarly, Shukla and Sakhardande (1991) demonstrated that the sorption of several metal ions by jute was enhanced significantly upon dyeing the sorbent. The metal sorption capacity of moss was greatly improved upon treatment with reactive dyes (Low *et al.* 1993). This paper reports on the investigation of the potential of dye-treated (Acid Blue 29) oil palm fibres in removing metal under batch and column conditions. The results were compared to those of untreated oil palm fibres.

METHODS AND MATERIALS

Physical and Chemical Methods

Oil palm fibres were obtained from a nearby palm oil mill. The sample was dried at 80°C, ground and sieved. Only fraction in the 250-500 mm range was used throughout this study. Part of the material was boiled with water until the filtrate was clear before it was treated with 1.5 M NaOH solution. The mixture was boiled until the filtrate was colourless. The basicity of the sample was then neutralized with 2 M HCl until the pH of the filtrate was near neutral. This sample was labelled as 'natural oil palm fibre' (NF). The remainder of the original sample was coated with Acid Blue 29 (C.I.20460) according to the method described by Suemitsu *et al.* (1986) and labelled as 'dye-coated oil palm fibre' (DF).

Sorption of Copper on Fibres under Various Conditions

All batch experiments were performed at room temperature on a gyratory shaker (250 rpm). The fibre-solution mixture was equilibrated for 2 h and the copper content in the solution was measured using an inductively-coupled plasma-atomic emission spectrometer (Labtest 710-2000). All experiments were conducted in duplicate and averaged results were presented. The effect of pH on copper uptake by the fibres was tested by equilibrating the sorption mixture (0.1 g fibre in 25 ml solution) at various initial pH values achieved by the addition of 0.1 M HCl or NaOH. The effect of other cations and chelators on the sorption of copper on fibre was tested in solutions containing copper and other cations/chelators in various mole ratios. The cations studied were Pb, Ni and Zn. Sodium salts of ethylenediamine tetraacetic acid (EDTA), nitrilotriacetic acid (NTA) and salicylic acid (SA) were chosen as chelators commonly found in the aqueous environment.

Column Studies

In the column studies, a glass column of internal diameter 1.4 cm was used. The fibre was packed to a height of 5, 10 and 15 cm corresponding to 1.5, 3.0 and 4.5 g of fibre respectively. Columns were preconditioned with

several volumes of distilled water. Copper solution (10 mg/l) was passed through the column at various flow rates, Eluent was collected in 50-ml fractions and analysed for copper.

RESULTS AND DISCUSSION

Batch Experiment

Percentage uptake of copper by fibre is defined as $100 \times (C_t - C_o)/C_o$ where C_t is the concentration of the solution at time t and C_o the initial concentration of the solution. The reproducibility of the sorption capacity of the fibre was shown by treating 7 samples of 0.1 g DF/NF in 100 ml of 12.5 mg/l Cu solution. At equilibrium, the percentage uptakes and relative standard deviations were 3.08 and 0.81 mg/g and 1.1 and 3.5% respectively. This shows the high reproducibility of the copper-fibre system.

Effect of pH

The effect of pH on the removal of Cu by the fibres is shown in *Fig. 1.* Solution pH influences both aqueous Cu chemistry and the surface sorption sites of the fibres. At low pH values the surface of the fibres is closely associated with the hydronium ions (H_3O^+), rendering sorption of Cu^{2+} on the fibre's surface unfavourable. This condition is reflected by the non-sorption of Cu at pH 2. At higher pH, more functional groups on the surface are made available for binding with Cu. Sorption increased with increasing pH to the point where the Cu ions precipitated; this occurred when the pH

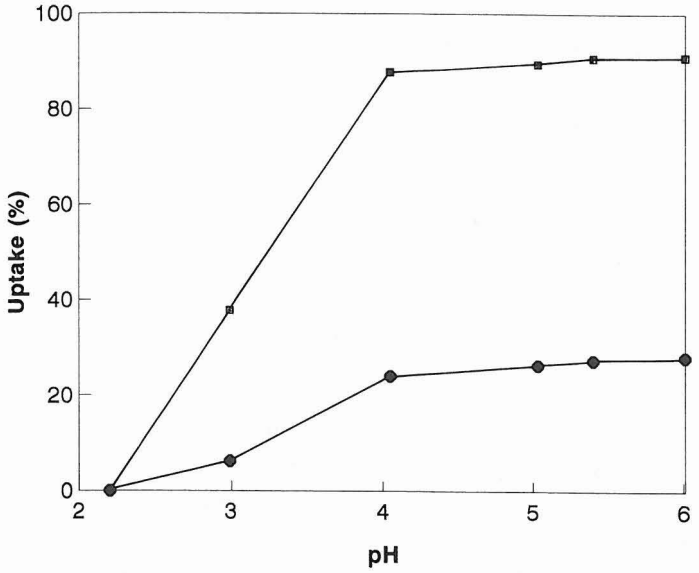

Fig. 1. The effect of pH on the uptake of copper by natural palm pressed fibre (■) and dye-coated fibre (●). Conditions: 0.1 g of fibre in 25 ml of 25 mg/l Cu solution; 2 h equilibrating time

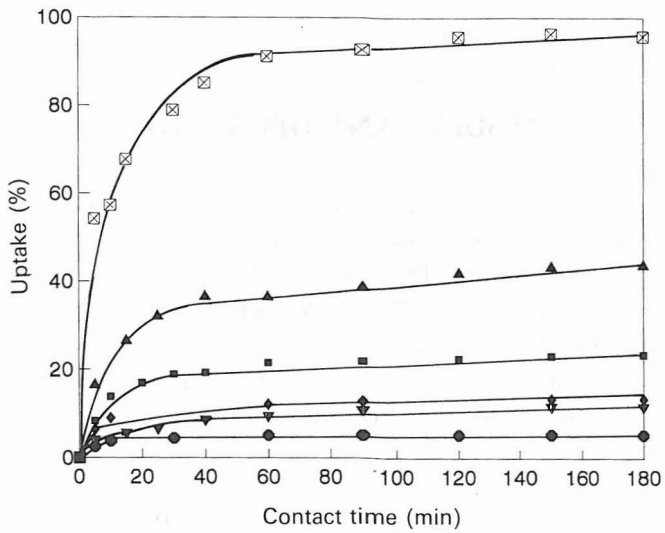

Fig. 2. The uptake of copper at various initial copper concentrations. Conditions: 0.4 g of fibre in 400 ml of Cu solution at various initial concentrations. NF: ■ - 5, ▼ - 15 and ● -50 mg/l Cu. DF: □ - 5, ▲ - 15 and ◆ - 50 mg/l Cu

of fibre-Cu solution reached a value of 6. Optimum pH for the sorption of metals by biological materials in the range of 4-6 has been reported using peanut shells, paddy husks and acacia bark (Randall *et al.* 1974; Kumar and Dara 1982). The dye-coated fibre had a greater sorption capacity than the natural fibre, reflecting the greater number and/or stronger binding groups on its surface. The SO_3^- groups on the dye molecules act as strong binding sites, in comparison to the weaker functional groups of OH^- and CO_2H on the surface of the natural oil palm fibre. The percentage of Cu sorption by the fibres at various initial concentrations is shown in *Fig. 2.* For any particular type of fibre the percentage sorption decreases with increasing concentration of solution. The sorption is characterized by a very rapid initial uptake, followed by a more gradual increase until equilibrium is established. It is clear from the figure that dye-coating on the surface of the fibre led to sorption enhancement.

Effect of Dosage

The effect of sorbent dosage on Cu by the NF is shown in *Fig. 3.* As expected, increasing the fibre/copper ratio leads to increasing sorption efficiency. Furthermore, the time to reach equilibrium remains relatively unchanged. This is attributed to the increase in binding sites as the amount of fibre increases. The same phenomenon is also observed for dye-coated fibre. The only difference is its higher percentage of sorption.

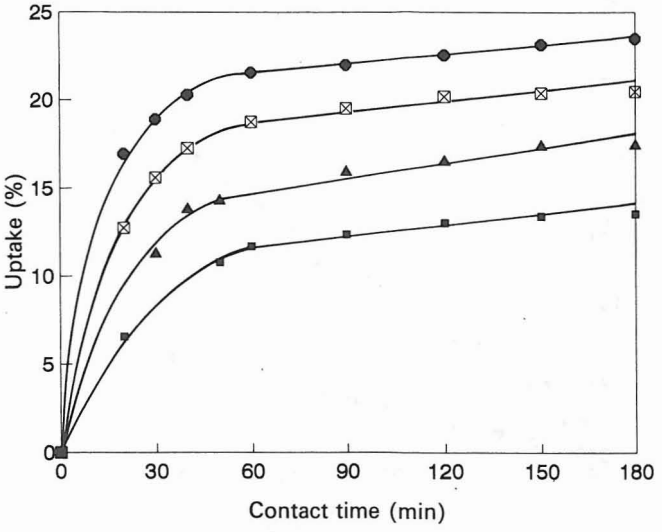

Fig. 3. The effect of dosage on the uptake of copper by natural palm pressed fibre. Conditions: different amounts of fibre in 400 ml of 5 mg/l Cu solution. NF: ■ - 0.1, ▲- 0.2, □ - 0.3 and ● - 0.4 g of fibre

Langmuir Isotherm

Various sorption isotherms can be used to describe the sorption phenomenon of Cu on the fibres. They include Langmuir, Freundlich and BET (Brunauer-Emmet-Teller) types. The Langmuir model was applied to the present Cu-fibre system. The isotherm can be represented by

$$C_e/q_e = 1/q_o b + C_e/q_o$$

where C_e is the equilibrium concentration (mg/l), q_e the amount of Cu sorbed at equilibrium (mg/g), q_o the maximum sorption of the fibre-Cu system and b the Langmuir constant related to the energy of sorption (l/mg). *Fig. 4* shows that the experimental data for Cu sorption on NF and DF fit the Langmuir isotherm. The agreement of the experimental data with the model implied that both monolayer sorption and constant sorption energy existed for the experimental conditions used. From the graphs, the maximum sorption capacities were estimated to be 2.41 and 7.71 mg/g for NF and DF respectively. Dye-coating led to a threefold sorption enhancement.

Effect of Chelators

One problem associated with conventional treatment methods for metal ion removal is the presence of complexing reagent, which may mask the presence of metals rendering sorption incomplete or impossible. Three

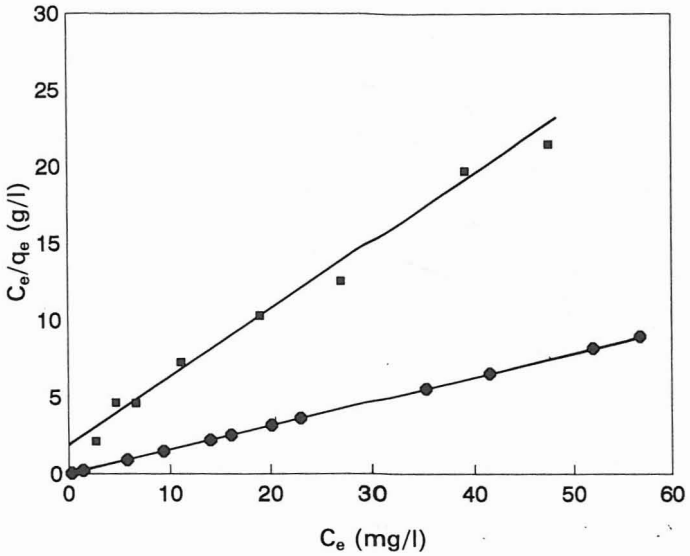

Fig. 4. Langmuir isotherms of copper sorption on natural palm pressed fibre (■) and dye-coated fibre (●)

chelators commonly found in the aqueous environment were used in this study. The copper sorption by the fibres in the presence of various molar ratios is shown in Table 1. The equilibrium is influenced by the nature of the chelator and also by free and complexed copper in solution. From the table it can be seen that the suppressing effect of the chelators corresponds to the log K_1 values. EDTA (log K_1 = 16.28) competes most effectively with the binding sites for copper for both types of fibres. Results show that where the concentration of EDTA was lower than the stoichiometric ratio of EDTA to copper, the uncomplexed part was sorbed. Salicylic acid (log K_1 = 5.55) exerts the least effect on the sorption of copper. NTA (log K_1 = 9.80) has an intermediate effect. Its log K_1 value is intermediate to those of EDTA and SA. This shows that the effectiveness of the fibres in removing

TABLE 1
Sorption of copper in the presence of chelators

Metal/ligand mole ratio	EDTA DF	EDTA NF	NTA DF	NTA NF	SA DF	SA NF
1:0	48.66*	12.84	48.66	12.84	48.66	12.84
1:0.5	20.72	6.12	24.95	8.77	35.16	11.09
1:1.0	2.08	0.35	8.65	5.43	22.59	6.48
1:10	0.47	0.02	0.86	0.29	7.02	2.07

* Percentage removal at equilibrium. Conditions: 0.1 g fibre in 100 ml of 12.5 mg/l Cu solution. Equilibrating time: 2 h.

copper from aqueous solution must be critically assessed if chelators of this nature are suspected to be present.

Effect of Competing Metallic Ions

The maximum sorption capacities of the fibres for copper as derived from the Langmuir model are only applicable if no other competing ions are present. This situation is normally not realized in real samples. Hence the effect of competing ions on the Cu sorption by the fibres was investigated. Table 2 shows the results of such a study. The greater metal affinity of DF is apparent. The number of binding sites on the surface of the fibres is finite and when more than one metal is present in the same solution, they compete for the binding sites. The amount sorbed depends on the equilibrium between sorption competition from the ions present. At low concentration (5 mg/l), a higher percentage of the metals was sorbed as there were sufficient binding sites. However, the competitive effect of other metals became apparent when the concentration of the metals in the solution was increased (50 mg/l). The order of sorption affinity is Pb > Cu > Zn > Ni. This is very similar to the sorption of metals on banana pith (Low *et al.* 1994). The order of affinity is determined by a number of factors, including ionic potential q/r (q is the ionic charge; r, the ionic radius), chemical properties, ionic radius, and hydrolysis (Tobin *et al.* 1984).

TABLE 2
Sorption of copper in the presence of other ions

Initial metal concentration (mg/l)	Cu	Cu/Pb	Cu/Zn	Cu/Ni
5.00 (single)	92.2*	–	–	–
5.00 (mixed)	–	56.9/71.5	69.3/38.4	78.2/26.0
50.00 (single)	14.3	–	–	–
50.00(mixed)	–	5.6/11.2	10.8/2.9	18.8/1.3

* Percentage uptake at equilibrium.
Conditions: 0.1 g fibre in 100 ml of solution at an equilibrating time of 2 h.

The ability of the fibres to remove metal ions was demonstrated using a sample of electroplating wastewater. The results (Table 3) show that the fibres could be used to reduce the metal content prior to secondary treatment of the wastewater.

Column Studies

The various parameters obtained under batch processes are useful in providing basic information on the effectiveness of the fibre-metal system. However, the data obtained are generally not applicable to a continuous flow system where the contact time is normally too short for equilibrium to

TABLE 3
Removal of metals from electroplating waste by fibres

Metal	Concentration (mg/l) Initial	Final	Cation sorbed (mg/l)	Removal (%)
Cu	62.37	46.43* (48.70)**	1.59* (1.37)**	25.56* (21.92)**
Pb	0.59	0.33 (0.41)	0.03 (0.02)	44.07 (30.51)
Cr	4.58	3.62 (4.07)	0.08 (0.05)	20.96 (11.13)
Ni	94.62	93.16 (94.08)	0.15 (0.05)	1.54 (0.57)

* related to DF and ** NF. Conditions: 0.1 g of fibre in 100 ml of electroplating solution at pH 4.35 at an equilibrating time of 2 h.

be established. Hence it is essential to conduct column studies in order to ascertain the usefulness of such a system. The copper loading phase was carried out with a continuous flow of 10 mg/l copper solution. Some typical eluent concentration profiles for copper at various bed-depths and flow rates for the dye-coated fibres are shown in *Figs. 5 and 6* respectively. Increasing the column height leads to higher sorption and a larger breakthrough volume as seen in *Fig. 5*. The increase in biomass allows more sorption sites for copper ions in the aqueous phase. Natural fibre shows similar trends though the sorption capacity was lower. The copper removal efficiency in relation to the flow rate/residence time of the influent in the column for DF is shown in *Fig. 6*. There is a significant increase in uptake with decreasing

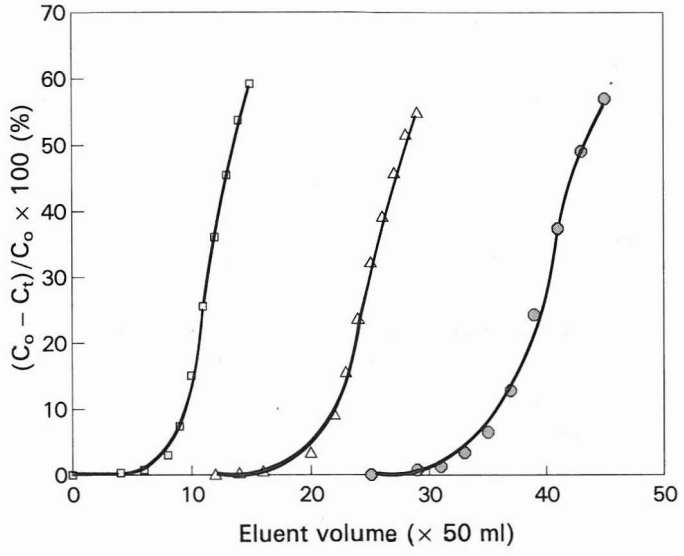

Fig. 5. The effect of bed-depth on the sorption of copper at a constant flow rate of 10 ml/min. DF: □ - 5, △ - 10 and ○ - 15 cm of dye-coated palm pressed fibre. Conditions: concentration of influent Cu solution - 10 mg/l

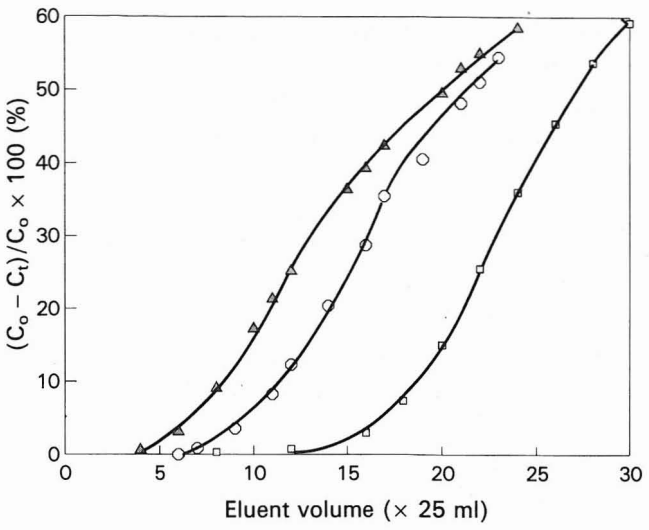

Fig. 6. The effect of flow rate on the sorption of copper at a fixed bed-depth of 5 cm. Conditions: concentration of influent Cu solution - 10 mg/l Cu. DF: □ - 10, ○- 25 and △ - 50 ml/min

flow rate or increasing residence time. The sorption process is essentially a phase equilibrium involving sorption and desorption. There is a time lag for the copper ions to reach and interact with the binding sites on the fibre surface, a process controlled by the overall mass transfer coefficient. Hence, decreasing the flow rate will enable the copper ions to be in better contact with the surface of the fibre. However, too slow a flow rate will also allow desorption to occur. In our study, the flow rate was not low enough to allow desorption to take place.

CONCLUSION

Batch and column experiments of natural and dye-treated oil palm fibres have been shown to be effective in removing copper from aqueous solutions. The enhancement effect of dye coating on the fibres is demonstrated in both processes. Uptake is influenced by pH, initial concentration and the presence of other metal ions and chelators in the batch process whereas flow rate and column height control the percentage removal in the continuous flow study. As no apparent leaching of dye occurred throughout the experiments, the dye-treated oil palm fibre is a potentially useful material for removing or reducing metal in aqueous solution.

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