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Hexane-Extracted Spent Bleaching Earth as a Sorbent for Copper in Aqueous Solution

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The removal of toxic metals from an aqueous environment using inorganic materials, especially waste products from industry offers the advantage of recycling waste and overcoming disposal problems. Attempts have been made to utilize spent bleaching earth (SBE) for the removal or reduction of pollutants in water. Pollards *et al.* (1990) reported that SBE was effective in the stabilization/solidification of mixed streams organic matters. The same material could also be converted into a low-cost, heterogeneous, clay-carbon sorbing material through physical and chemical activation (Pollards *et al.* 1991). It was shown to have high phenol sorption capacity. However, much energy is required in the activation process.

A large amount of SBE is generated in the palm oil industry in Malaysia. which is the largest producer of refined palm oil in the world. Expected Malaysian palm oil production for the current year is 7.8 million tons (Chow 1994). Up to 2.5 %(w/w) of bleaching earth is mixed with the crude palm oil in the bleaching process. This spent bleaching earth, approximately 195,000 tons, is generally disposed of in 1andfill. However SBE still contains 25 % of the oil which can be recovered through solvent extraction. Hexane has been shown to be a suitable solvent. In our continued effort to utilize low-cost materials for the removal of heavy metals in the aqueous environment, we investigated the potential of hexane-extracted SBE as a sorbent for copper in aqueous solution under various experimental conditions. In order to be cost effective, no pretreatment was performed on SBE other than extracting the oil with hexane. The hexane -extracted spent bleaching earth is labeled as HSBE.

MATERIALS AND METHODS

Spent bleaching earth obtained from a palm oil processing plant was extracted several times with hexane to remove as much oil as possible and the resulting earth was dried at 80° C , ground and sieved to less than 150 µm in size. The removal of the oil was confirmed by recording the infra-red spectra of SBE

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and HSBE The characteristic bands at 2,928, 2,854 cm^{-1} (C-H stretching) and 1,746 cm^{-1} (C=O) for triglyceride disappeared in HSBE spectrum. All experiments were conducted in duplicate and the relative standard deviation was less than 5 %. Sorption was measured by equilibrating a known weight of HSBE with various aqueous solutions of Cu at an agitation rate of 150 rpm for a specific time. At the end of equilibration time the sorbent-solution mixture was centrifuged at 3,000 rpm for phase separation. The Cu concentration of the supernatant was determined using an inductively coupled plasma-atomic emission spectrometer (Perkin Elmer P1000).

RESULTS AND DISCUSSION

The study on the sorption of Cu by HSBE as a function of pH is shown in Table 1. This study is important because it determines the amount of free metal ions from bound chemical forms in an aqueous environment. Furthermore, it controls sorption of the metal ions at the surface of the sorbent. At pH 3-6 sorption was favorable. Precipitation of Cu occurred at pH 7. At pH lower than 1.5, sorption was totally inhibited. This is probably due to the presence of excess of H^+ competing for binding with Cu^{2+}. Leaching of Al was also noted at pH<2, with high elevation of Al ions. The sorption mechanism is uncertain as HSBE contained a mixture of deformed clay, and, possibly some activated carbon derived from the activation of palm oil during the bleaching process which occurred at 450° C. Subsequent experiments were conducted at a pH range of 4.5-6.

Table 1. Effect of pH on the sorption of Cu by HSBE

PH	1.51	2.20	3.27	4.46	5.84	6.50
% sorption	0	15.87	77.92	83.20	89.59	90.10

Conditions: 0.1 g HSBE in 20 ml of 20 mg/L Cu solution. Agitation time and rate: 3 hr and 100 rpm respectively.

The rates of Cu uptake at various initial concentrations are shown in Fig. 1. The percent uptake ($100(C_i - C_t)/C_i$ where C_i is the initial concentration and C_t the concentration at time t), follows the usual trend of a greater percentage uptake with decreasing concentration. The uptake was rapid in the first phase of the sorption. This was followed by a more gradual sorption process until equilibrium was established in about 60 min. Similar trends of sorption were also reported on Ni-zeolite and clinoptiolite systems (Papachristou *et al.* 1993).

When HSBE was treated with Cu solutions of initial concentration of 5-500 mg/L, the final bulk equilibrium concentration (C,) was reduced to 0.58-429.38 mg/L. The sorption isotherm is shown in Fig. 2. The amount of Cu sorbed increased with increasing initial concentration until all the binding sites were occupied, where upon increase in concentration had no appreciable effect

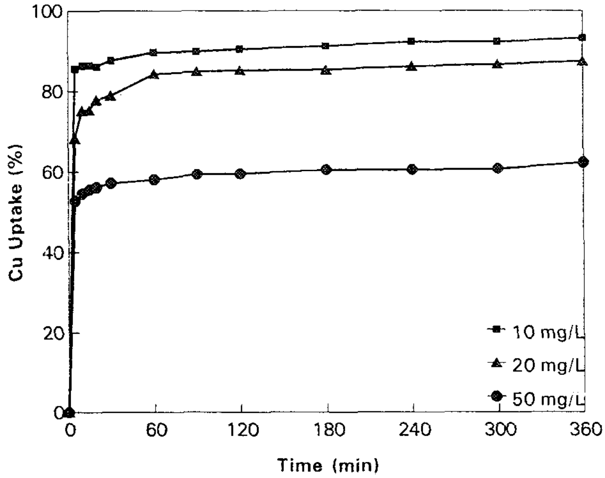

Figure 1. Percentage Cu uptake by HSBE at different initial concentrations. Conditions: 0.1 g HSBE in 20 ml of Cu solution. Agitation rate: 100 rpm.

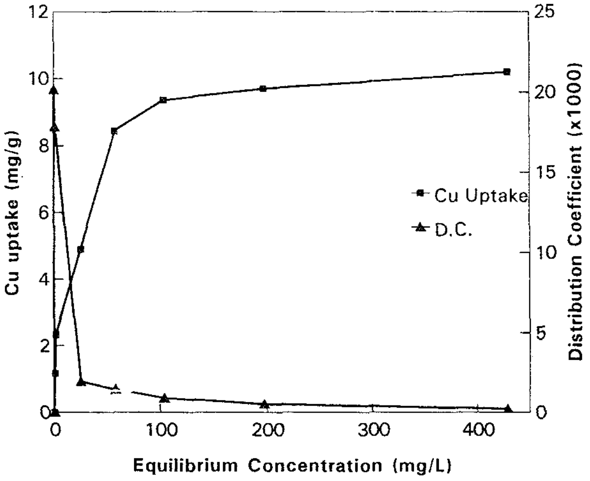

Figure 2. Cu uptake and distribution coefficient, K_c, for the sorption of Cu by HSBE. Conditions: 0.1 g HSBE in 20 ml of Cu solution at different concentrations. Agitation time and rate : 3 hr and 100 rpm respectively.

on uptake. The maximum sorption was estimated to be 10.3 mg/g sorbent. The distribution coefficient, K_c defined as (mg Cu sorbed/g HSBE)/(concentration of Cu solution at equilibrium , mg/L) varied from 20,160 to 226 from the least to the most concentrated of the initial Cu solution. The high value of K_c of the sorbent system means that HSBE possesses useful separation properties for Cu, especially in dilute solutions.

Results from the sorption experiment were fitted into a modified Langmuir model of the form : $C_e/N^e=1/(N^* b) + C_e/N^*$ where N_e is the amount of Cu sorbed at equilibrium (mg/L) and N* the maximum sorption capacity (mg/g) of the sorbent, and b a Langmuir constant related to the energy of sorption. The linearity of such a plot as shown in Fig. 3 shows that the Langmuir isotherm can be successfully applied to the Cu-HSBE system The value of N* was found to be 11 mg/g as compared to the experimental value of 10.3 mg/g.

The variation of Cu uptake with agitation rate is shown in Fig. 4. Increasing agitation rate increased the external film mass transfer coefficient and hence the rate of uptake. This is due to the reduction of the film boundary layer surrounding the HSBE particles. However, beyond 150 rpm the rate of Cu uptake was not affected, indicating that the external mass transfer was not limiting in a well-agitated system. The results are in agreement with Findon *et al.* (1993) in their study of sorption of Cu by chitosan particles.

The dependence of the sorption of Cu on the amount of HSBE is shown in Fig. 5. The amount sorbed increased with increasing dosage of sorbent. The removal of Cu increased from 40 to 96 % when the dosage was increased from 0.05 to 1.00 g. However, the increase was not directly proportional to the amount of sorbent. The would mean that in a batch process, maximum removal of Cu from aqueous solution would be achieved by multiple-step sorption.

In a real situation various other metal ions are co-present with Cu ions as in the case of electroplating waste. Hence, it is imperative to investigate the sorption characteristics in the presence of other common metal ions. The results of such a study is shown in Table 2. On a weight basis, the order of sorption affinity is Pb>Cr>Cd,Cu>Zn>Ni>Mg. The amount of Cu sorption varied with the nature of the other metals present. Ni, Mg and Zn did not appear to have appreciable influence on Cu sorption. The influence of Cr was most pronounced, reducing sorption from 57 (single metal sorption)

Table 2. Competitive sorption of copper in the presence of other metal ions

Cu/Mg	Cu/Pb	Cu/Cd	Cu/Ni	Cu/Zn	Cu/Cr
23.81/51.34*	26.99/3.51	26.92/32.57	22.02/39.21	24.37/34.62	32.67/11.98

*** Concentration of metal ion at equilibrium. Conditions: 0.1 g sorbent in 20 ml of binary solution of 50 mg/L.**

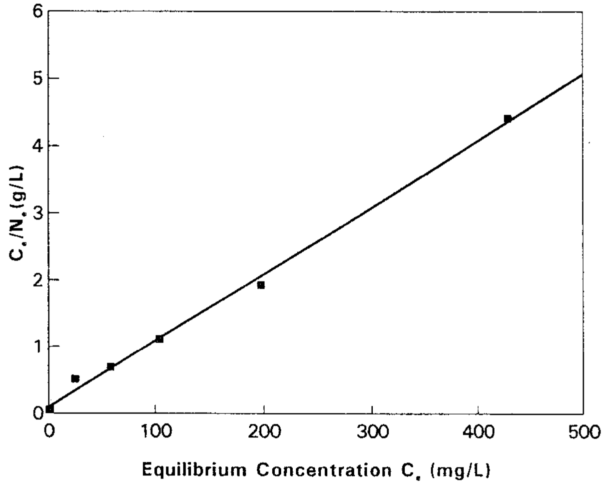

Figure 3. Langmuir isotherm for the sorption of Cu - HSBE system at room temperature.

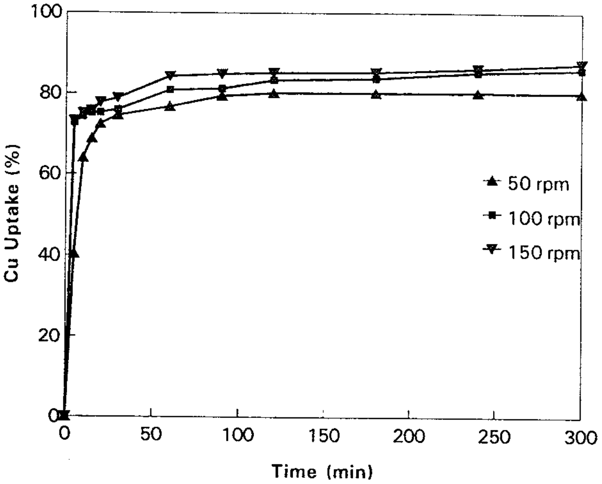

Figure 4. Effect of agitation rate on the sorption of Cu by HSBE. Conditions: 0.1 g HSBE in 20 ml of 20 mg/L Cu solution at various agitation rates.

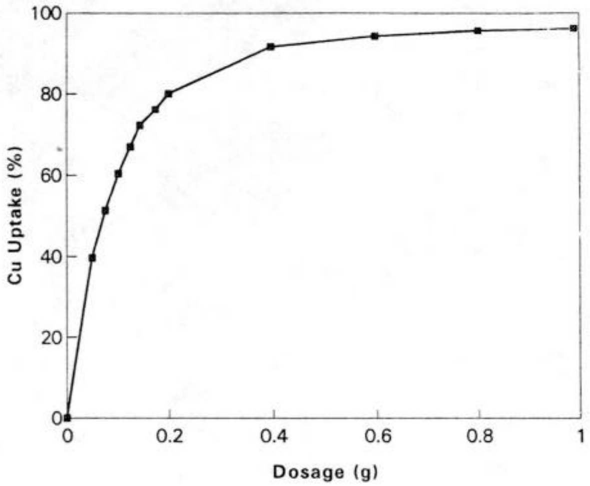

Figure 5. Effect of dosage on the sorption of Cu by HSBE. Conditions: 20 ml of 20 mg/L Cu solution with various amounts of HSBE. Agitation time and rate: 3 h and 100 rpm respectively.

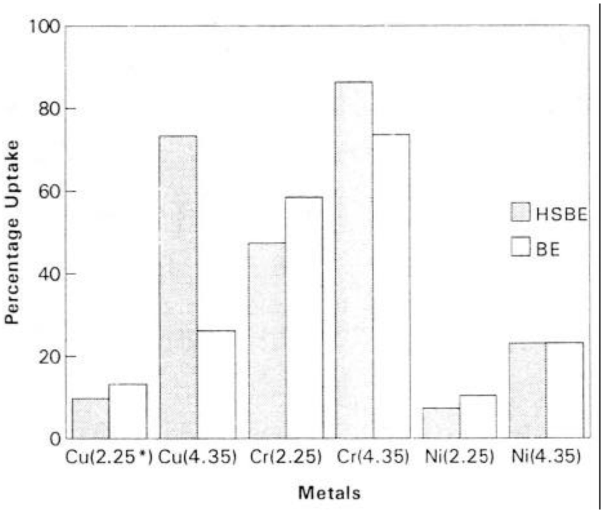

Figure 6. Sorption capacity of HSBE for Cu, Cr and Ni in electroplating wastewater at pH values of 2.25 and 4.35. Initial metal concentrations (mg/L) at pH 2.25 Cu: 19.95, Cr:3.07 and Ni:30.69 and at pH 4.35 - Cu:18.71, Cr:2.15 and Ni:29.30. Conditions: 0.1 g HSBE in 20 ml electroplating wastewater. Agitation time and rate : 3 h and 100 rpm respectively.

to 35%.

Beside the presence of metal cations which will influence the sorption of Cu, organic ligand may also suppress its uptake. The ligands may mask the presence of Cu, rendering its removal from aqueous solution difficult or impossible. Three commonly found ligands in the aqueous environment were investigated to determine their influence on Cu removal by HSBE. They were the sodium salts of salicylic acid (SA), nitriloacetic acid (NTA) and ethylenediamine tetraacetic acid (EDTA), with log K_1 values of 5.55, 9.80 and 16.28, respectively. The effect of ligands on Cu sorption is shown in Table 3. It is clear that salicylic acid had very little effect on the sorption of Cu, regardless of its concentration. At very high concentrations (1: 10), salicylic acid molecules would hinder the approach of Cu ions to the binding sites of the sorbent, rendering sorption slightly less favorable. At high molar ratios of Cu:NTA and EDTA the sorption of Cu was almost completely suppressed. Hence, the use of HSBE in the removal of Cu must take into consideration the nature of the ligands present in the same environment as Cu.

TABLE 3. Effect of organic ligands in the sorption of copper by HSBE

Mole ratio of Cu:ligand	1:0	1:0.5	1:1	1:10
Cu:SA	2.68*	2.58	2.74	3.80
Cu:NA	2.68	3.79	17.44	18.53
Cu:EDTA	2.68	3.81	17.94	18.66

*Concentration of Cu solution at equilibrium. Conditions: 0.1 g HSBE in 20 ml of (20 mg/L Cu + equimolar ligand) solution.

The usefulness of the HSBE in removing Cu and its related metals is shown in the treatment of an electroplating wastes at different pH values (Fig. 6). At a low pH value of 2.25, bleaching earth showed better sorption than HSBE for all metals. However, the trend was reversed when the solution pH was 4.35. This demonstrates that HSBE could be useful in removing or reducing metal content in electroplating wastes under batch processes.

Hexane-extracted spent bleaching earth appears to be a useful sorbent for copper both in synthetic solution and electroplating effluent under batch conditions. This ion-exchange property of HSBE would convert a waste material into a value added product in the treatment of wastewater. However, its commercial applications to metal removal from aqueous solution can only be ascertained after its effectiveness in column applications has been established. Work is currently being carried out to address this issue.

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