The use of sago waste for the sorption of lead and copper

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Abstract

Sago processing waste, which is both a waste and a pollutant, was used to adsorb lead and copper ions from solution. The sorption process was examined in terms of its equilibria and its kinetics. The effect of pH, contact time, sorbate concentration, particle size and sorbent mass were also studied. The most effective pH range was found to be 4 to 5.5 for both metals. The equilibrium data for both metals fitted both the Langmuir and the Freundlich models and, based on the Langmuir constants, the sago waste had a greater sorption capacity for lead (46.6 mg/g) than for copper (12.4 mg/g). The kinetic studies showed that the sorption rates could be described better by a second-order expression than by the more commonly applied Lagergren equation.

Introduction

Industrial and mining waste waters are the major source of pollution by heavy metals. Futhermore, in developing countries, many industries are operated at small or medium scale, or even as a family business within the residential premises of the owner. These smaller units can generate a considerable pollution load which, in many cases, is discharged directly into the environment without any facilities for waste-water treatment. This is because the capital investment, turnover and profit for these industries are also small. In Malaysia, such a situation exists, and the discharge of waste water containing chemicals and metallic ions into near-by watercourses is well documented (Sohaili, 1990). Heavy metals can pose health hazards if their concentrations exceed allowable limits. Even when the concentration of metals does not exceed these limits, there is still a potential for long-term contamination, since heavy metals are known to be accumulative within biological systems.

In recent years, increasing awareness of the environmental impact of heavy metals has prompted a demand for the purification of industrial waste waters prior to discharge into natural waters. This has led to the introduction of more strict legislation to control water pollution, such as the Environmental Quality (Scheduled Wastes) Regulation 1989 in Malaysia (Yeoh and Chong, 1991), which will probably affect metal-related industries. This effect is likely to be even more pronounced for small- and medium-scale industries where profit is small and expertise on waste-water treatment is unlikely to be available. Conventional methods, for example, ion-exchange, chemical precipitation, ultrafiltration, or electrochemical deposition do not seem to be economically feasible for such industries because of their relatively high costs. Therefore, there is a need to look into alternatives to investigate a low-cost method which is effective and economic, and can be used by such industries.

Adsorption has advantages over other methods. The design is simple, and it is sludge-free and can involve low investment in terms of both the initial cost and land (Viraraghaven and Dronamraju, 1993). Activated carbon has been recognised as a highly effective adsorbent for the treatment of heavy metals in waste water (Reed and Arunachalam, 1994). However, it is relatively expensive to produce. Therefore, there is increasing research interest in using alternative low-cost adsorbents. Many such materials have been investigated, including microbial biomass, peat, compost, leaf mould, palm press fibre, coal, straw, wool fibre and rice milling by-products (Wase and Forster, 1997; Singh and Rawat, 1997). Not all of these are effective. Therefore, it is still important to identify suitable low cost adsorbents for heavy metal removal.

In this study, a material relevant to the situation in Malaysia, sago processing waste, was chosen. Malaysia exports 25 000 to 30 000 t of sago flour annually and the residues from its production tend to be discharged to rivers (Fig. 1). These residues, which are largely composed of celluloses and lignins (Vikineswary et al., 1994) are, therefore, both a waste and a pollutant. Their chemical composition suggests that they could have some potential as a biosorbent. This paper reports the results of a study which examined the sorption of copper and lead, both of which are pollutants in Malaysian watercourses (Anon., 1993).
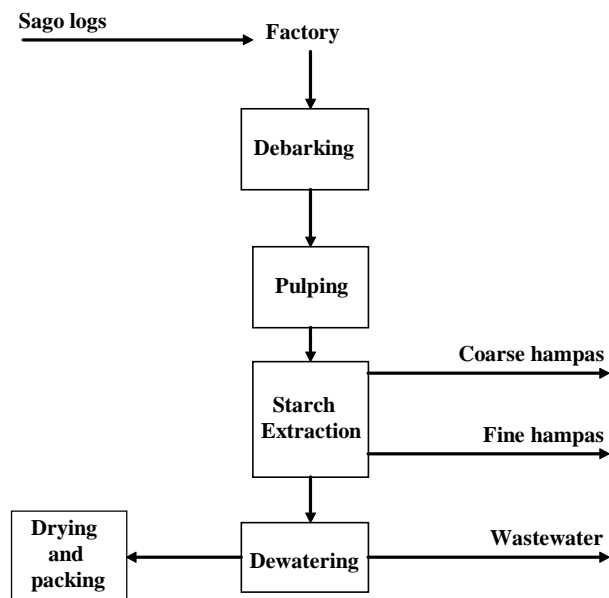

Figure 1
*Schematic flow diagram for sago processing
(adapted from Yean and Lan, 1993)*

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TABLE 1
SUMMARY OF THE CONDITIONS USED IN THE SORPTION TRIALS WITH SAGO WASTE

Test	pH	Concentration of sago waste (g/ℓ)	Metal concentration (mg/ℓ)
Effect of pH - Pb	2 - 5.5	4	50 - 200
- Cu	2 - 5.5	4	25 - 100
Sorption - Pb	4.5	4	20 - 750
- Cu	5.0	4	20 - 500
Time - Pb	4.5	4	100
- Cu	5.0	4	100
Particle size - Pb	4.5	4	100
- Cu	5.0	4	50
Sago dose - Pb	4.5	1 - 12	100
- Cu	5.0	1 - 12	100

Materials and methods

The sago waste was donated by Dr. Vikineswary of the Institute of Advanced Studies at the University of Malaysia and, before use, was ground using a food processor (Magimix Cuisine System 5000), dried in an oven (Gallenkamp, Model OV-160, England) at 105°C for 24 h and then screened through a 14 mesh sieve (B.S. 410/43). This was done to remove any large particles and to obtain adsorbents with a known particle size range. The sieved material was then stored in an airtight plastic container for further experiments. When the effect of particle size was being examined, the sago waste was screened again to give three different sizes: < 500 µm, 500 to 1200 µm and 1 200 to 2 000 µm.

All the chemical reagents used in these studies were of analytical grade. Stock solutions (1 000 mg/ℓ) were prepared from lead nitrate (BDH Ltd., Poole, England) and hydrated copper sulphate (Fisons, Loughborough, England). These were then diluted with distilled water to obtain the solutions used in the adsorption experiments.

All the experiments were carried out on a Cooled Orbital Shaker (Gallenkamp, England) set at 150±5 r·min⁻¹ and maintained at 25±5°C using capped conical flasks (250 mℓ). In all sets of experiments (except for the adsorbent effect experiments), fixed amounts of adsorbent were thoroughly mixed with the metal ion solution (200 mℓ) having the desired initial concentration. After shaking the flasks for 24 h, the reaction mixtures were filtered through Whatman filter paper (No. 1) and the concentration of metal ion in the filtrate was measured.

All experiments were duplicated. The precise conditions used are specified in Table 1. Two different controls were also performed. The control without adsorbent determined if metal ions were adsorbed by the wall of the conical flask. The control without metal ions (distilled water was used instead of metal solution) was to estimate any leaching from adsorbents during the study period.

Metal ion concentrations were measured by atomic absorption spectrophotometry (Model 939, ATI Unicam, Cambridge, England) using an air-acetylene flame and single element hollow cathode lamps. The instrument was calibrated with standard solutions; 1 to 20 mg/ℓ for lead and 1 to 8 mg/ℓ for copper. Lead absorbances were measured at 217.0 nm and those for copper at 324.7 nm. The spectrophotometer was linked to a microprocessor using SOLAAR AA software.
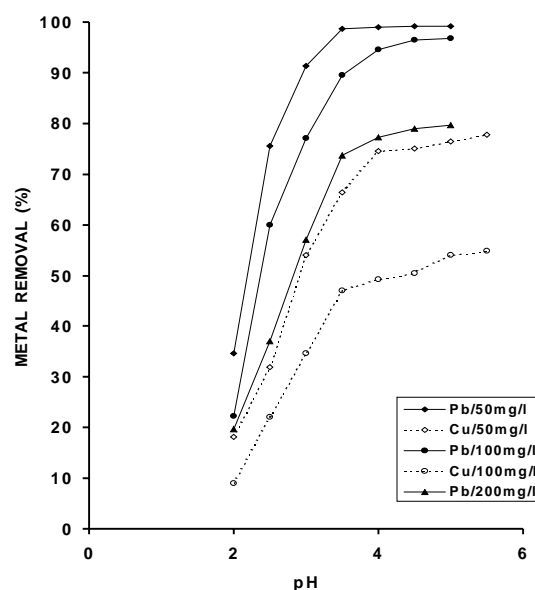

Figure 2
Effect of pH on the sorption of copper and lead by sago waste (4 g/ℓ)

Results and discussion

The removal of metal ions from aqueous solution by adsorption is related to the pH of solution, as the latter affects the surface charge of adsorbents, the degree of ionisation and the species of adsorbate. The first set of tests, therefore, examined the effect of pH on the adsorption equilibrium. A typical set of results (Fig. 2) showed that for both metals, the removal by sago waste decreased as the pH of the solution decreased.

The extent of this decrease in efficiency depended on the concentration of metal being treated, with the efficiency decreasing at the higher concentrations. The metal removal efficiency also depended on the metal being adsorbed. The removal of lead was significantly higher than that of copper. The critical pH values were 4.5 for lead and 5 for copper. The selection of the optimum pH must take into account the fact that, if too high a pH value is chosen, precipitation of lead would occur. This would defeat the purpose of employing adsorption. Tests showed that

TABLE 2
SORPTION ISOTHERM CONSTANTS AND COEFFICIENTS OF DETERMINATION FOR SAGO WASTE

	Langmuir equation			Freundlich equation		
	X_m (mg/g)	k (ℓ/mg)	R^2	K_F (mg/g)	1/n	R^2
Lead	46.64	0.246	0.980	16.84	0.235	0.961
Copper	12.42	0.069	0.991	4.22	0.185	0.915

precipitation of lead nitrate occurred at about pH 5.6. It can also be seen that at low pH values, the adsorption of the metals was not efficient; especially for higher initial lead concentration where the lead removal was less than 20%. Similar results were reported by other researchers using other adsorbents (Salim et al., 1994; Özer et al., 1994). According to Low et al. (1995) at low pH values the surface of the adsorbent would be closely associated with hydronium ions (H_3O^+) which hinder the access of metal ions, by repulsive forces, to the surface functional groups, consequently decreasing the percentage of metal removal.

Measurements of the equilibrium pH showed that the reactions which occurred during the sorption process caused some slight increases in the solution pH. The magnitude of these increases depended on the initial pH and the concentration of the metal but, typically, they ranged from 0.02 to 0.5 pH units.

The sorption data for the two metals were tested against the standard isotherm models, the Langmuir and Freundlich equations. The Freundlich equation was linearised in the form:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where:
  C_e = the equilibrium concentration of the solute (mg/ℓ)
  q_e = the adsorption capacity at equilibrium (mg solute/g adsorbent)
  K_F and n are the Freundlich constants

The coefficients of determination (R^2) and the isotherm constants are given in Table 2. The former show that the Langmuir equation linearised in the form:

$$\frac{C_e}{q_e} = \frac{1}{X_m k} + \frac{C_e}{X_m}$$

where:
  X_m and k are the Langmuir constants,

was the more appropriate model for these systems. A comparison of the Langmuir constants, X_m, shows that the sago waste had a mass capacity for lead which was some 3 times greater than that for copper. Even viewed on a molar basis, the capacity of the sago waste was greater for lead (0.225 µM/g) than for copper (0.195 µM/g). An examination of the Langmuir maximum capacities, X_m, at the different pH values (Fig. 3) confirms that sago waste is a less effective sorbent at lower pH values and that lead is bound more strongly than copper.

The Langmuir capacities can also be used to compare the efficiency of coir with other materials which have been tested as biosorbents for lead and copper. Table 3 makes such a comparison and, although it is not based on a comprehensive survey,
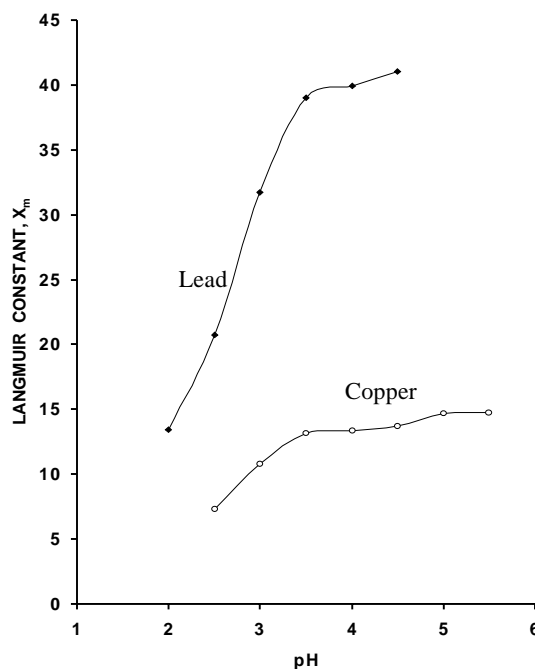
Figure 3
Variation in the Langmuir constant, X_m, with pH

shows that, for lead, the sago waste has a greater capacity than many of the materials tested previously. For copper the effect is not as marked.

Figure 4 examines two aspects of the sorption process, the effect of time and the impact of altering the metal concentration. The data show that the sorption process was rapid, being complete in 30 to 40 min. The results also show that the effect caused by increasing the lead concentration from 50 to 100 mg/ℓ was negligible, whereas for copper, there was a very marked effect. This was most likely due to the differences in the maximum sorption capacities.

The effect of altering the sorbent particle size on the kinetics showed that, over the first 10 to 15 min, there was a more rapid removal of both metals by the smaller particles (Fig. 5). This was most probably due to the increase in the total surface area which provided more sorption sites for the metal ions. However, after this initial period, the rates for lead and the removal efficiency became almost the same. This was not the case with the sorption of copper which showed an intermediate rate, between 15 and 30 min for the larger particle size. The enhanced removal of sorbate by smaller particles has been noted previously during a study into the removal of colour by silica (McKay et al., 1980).

Increasing the mass of sago waste caused the sorptive capacity, q_e, to be reduced (Fig. 6). Once again, the effect was most

TABLE 3
COMPARISON OF THE LANGMUIR CONSTANTS FOR LEAD AND COPPER

| Metal	Sorbent	X_m (mg/g)	Source
Lead	Sphagnum moss peat	30.7	Ho et al. (1996a)
	Groundnut husks	39.3	Okieimen et al. (1991)
	Sago waste	46.64	This study
	Tea leaves	78.7	Tan and Khan, 1988
	Penicillium chrysogenum	116	Niu et al. (1993)
	Cladophora crispata	251	Özer et al. (1994)
Copper	Oil-palm fibres	2.0	Low et al. (1993)
	Aspergillus orysae	6.9	Huang et al. (1991)
	Treated *A. niger*	10.1	Nagendra et al. 1993
	Sago waste	12.42	This study
	Sphagnum moss peat	16.4	Ho et al., 1994
	Anaerobic sludge	49.0	Gould and Genetelli (1978)
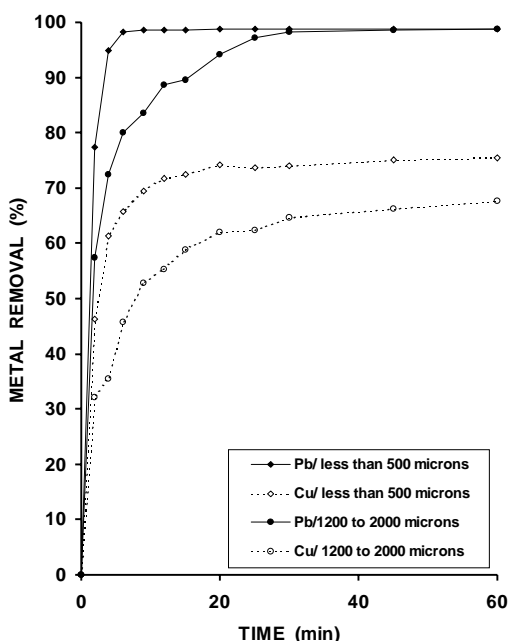
Figure 4
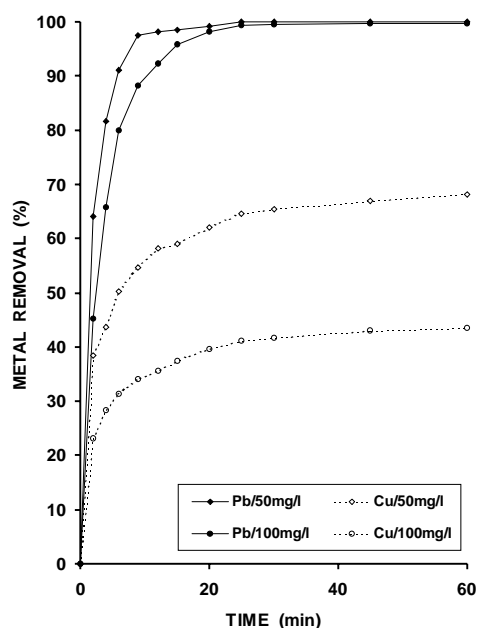*Effect of different initial metal concentration on the sorption of copper and lead*

Figure 5
Effect of different particle size on the sorption of copper and lead by sago waste (4 g/ℓ) with the initial metal concentration being Pb = 100 mg/ℓ, Cu = 50 mg/ℓ

marked with the sorption of lead. In looking at this effect, it is pertinent to examine the data in relation to the theoretical maximum, assuming that all of the metal ions would be sorbed onto the sago waste.

When this is done (Fig. 7), it shows that, in practice, the sago waste does not bind all the metal ions and that there is a very significant difference between the two metals. This means that if sago waste were being considered in a commercial role for the removal of lead, a mass equivalent to, at least 3 g/ℓ would have to be used. It also means that sago waste would probably not be used for the removal of copper.

Quantifying the changes in sorption with time requires that an appropriate kinetic model is used and, traditionally, the first-order Lagergren equation has been applied to sorption kinetics (Gaid et al., 1994):

$$\log(q_e - q_t) = \log(q_e) - Kt$$

where:

q_e = the mass of metal adsorbed at equilibrium (mg/g)
q_t = the mass of metal adsorbed at time t (mg/g)
K = the rate constant

Recently, a pseudo-second-order equation has been suggested as being more appropriate for describing this type of adsorption (Ho, 1996):

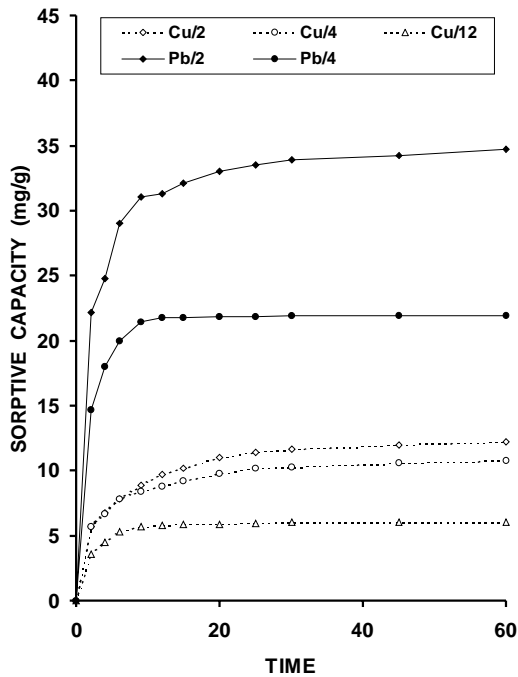$$\frac{t}{q_t} = \frac{1}{2k\,q_e^{\,2}} + \frac{t}{q_e}$$

Figure 6
Effect of varying the sorbent dose with initial concentration of Pb = 2 and 4 mg/ℓ and of Cu = 2, 4 and 12 mg/ℓ

Figure 7
Effect of sorbent dose on the sorptive capacity

TABLE 4
A COMPARISON OF THE APPLICABILITY OF THE FIRST- AND SECOND-ORDER KINETIC MODELS

Sorption system	Coefficient of determination, R^2	
	First order	Second order
Copper (50 mg/ℓ)	0.906	0.998
Lead (50 mg/ℓ)	0.902	0.999
Copper (100 mg/ℓ)	0.900	0.998
Lead (100 mg/ℓ)	0.924	0.998

In this equation, the initial rate of adsorption, h, is given by:

$$h = 2kq_e^2$$

The data for both metals at concentrations of 50 and 100 mg/ℓ were, therefore, tested against both models. The results showed that the second-order equation was the more appropriate (Table 4) and it was, therefore, used to analyse the data for all the sorption/time trials, with attention being focused on the initial rate of adsorption. The results are presented in Table 5 and show that although lead had a higher initial rate than copper, increasing the metal concentration had little effect on its magnitude.

Previous work, using peat as the sorbent, has also shown that lead had a greater initial rate than copper (Ho, 1996). In addition, it reported very similar values for the rates with copper (Ho et al., 1996b). Table 5 also shows the effect of increasing the sorbent dose. Essentially, the data are in agreement with the earlier analysis which examined the sorptive capacity expressed as a
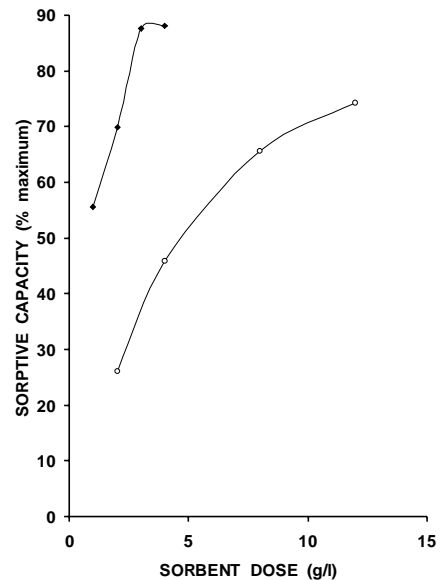
TABLE 5
INITIAL SORPTION RATES (mg/g·min)

Sorption system	Initial rate; h (mg/g·min)	
	Cu	Pb
Metal concentration (mg/ℓ)		
20	3.2	-
45	-	17.3
50	3.5	-
75	3.4	-
90	-	20.3
100	4.1	-
120	-	21.4
170		20.3
Sorbent size (μm)		
<500	10.1	83.9
500 to 1200	3.6	58.5
1200 to 2000	2.8	17.9
Sorbent dose (g/ℓ)		
2	3.9	26.0
4	4.1	32.8
8	6.4	46.3
12	6.6	59.3

percentage of the maximum value (Fig. 7). In other words, to achieve the best results, sorbent doses of >3 g/ℓ are required.

Conclusions

- The results clearly show that the sago waste is a better adsorbent for lead than for copper, having the higher initial sorption rate and the greater sorption capacity.

- To achieve the best results, sorbent doses of >3 g/ℓ were needed for lead removal and >12 g/ℓ for copper.
- The most effective pH range was 4.5 to 5.5 .

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