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Removal of Chromium (III) from Aqueous Solution Using Chrome Sludge

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The toxicity of chromium to aquatic organisms, mammals and humans has been well documented (Gaughafar and Bianchi 1991). At high levels it is reported to be carcinogenic and mutagenic. The main contributing source of chromium to the aquatic environment is from the untreated effluents of tannery, dye, paint, electroplating and textile industries. Various methods for the removal or reduction of chromium from such effluents have been reported. These include reduction followed by precipitation and ion-exchange. These methods are generally expensive. Recently, the use of natural mineral mixtures (Ahmad and Qureshi 1991), hulls and bran (Marshall *et al.* 1993) and natural fibers (Tan *et al.* 1993) for the removal of chromium has been reported. These materials have considerable economical importance because of their low cost and abundant availability. Chrome sludge, a waste material of chrome electroplating processes, has no known commercial value. It is generally stored for indeterminable periods in the vicinity of the plant awaiting treatment or appropriate disposal. In the present study, the sorption of chromium(III) from aqueous solution on chrome sludge was investigated.

MATERIALS AND METHODS

Chrome sludge obtained from an electroplating plant in Senawang Industrial Estate, Negri Sembilan, was used as a sorbent. It was washed throughly with distilled water, dried , ground and sieved to less 500 mμ in size. The weight ratio of Cr, Cu and Ni in the chrome sludge was approximately 24:5:2. $Cr(NO_3)_3.9H_2O$ was used as the source of Cr(III). All experiments were carried out in duplicate. Sorption was measured by equilibrating a known weight of the chrome sludge with various aqueous solutions of Cr(III) for a specific time. At the end of the equilibration, the solution was centrifuged at 3000 rpm for phase separation. The Cr concentration of the supernatant was determined using an inductively coupled plasma-atomic emission spectrometer (Perkin Elmer P1000).

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RESULTS AND DISCUSSION

The effect of pH on the sorption level of Cr(III) is shown in Fig 1. The study of pH is important in establishing the optimum sorption of Cr at the solid/liquid interface and it also regulates the release of the free metals from the chrome sludge into the aqueous system. At pH 2, the sorption of Cr(III) was low. With the increase of pH from 2 to 2.5. the sorption increased rapidly from 25 to almost 100%. The sudden increase in sorption probably indicates that the zero point charge of the chrome sludge lies between these values. At pH 2, sorption becomes unfavorable due to electrostatic repulsion between the positively charged surface and the chromium ions. Release of metals also occurs at this pH value. Subsequent experiments were conducted at pH greater than 5. At pH >7 precipitation of Cr as hydroxide occurs.

The sorption isotherm at 28°C of Cr(III) on chrome sludge is shown in Fig 2. Maximum experimental uptake was 24.4 mg/g.

Optimum contact time between chrome sludge and liquid phase is shown in Fig 3. For Cr solutions of less than 50 mg/L equilibrium is reached after 120 minutes. At higher concentration a longer contact time is necessary. The sorption isotherms are characterized by two waves. The first one occurred in the first thirty minutes and was relatively well-defined; the second one a slowly rising isotherm. Hence, the sorption process is complex and may involve more than one mechanism. Percent uptake ($C_t/C_i x100$) where C_t is the Cr concentration at time t and C_i the initial concentration, follows the usual trend of a greater percentage uptake with decreasing concentration.

Results of the sorption studies were fitted into the following Langmuir isotherm:

$$C_e/N_e = 1/N^*b + C_e/N^*$$

where C_e is the equilibrium concentration (mg/L), N_e, the amount of Cr(III) sorbed (mg/g) at equilibrium, N^*, the maximum sorption capacity of the sorbent (mg/g) and b, a Langmuir constant related to the energy of sorption. The linearity of such a plot is shown in Fig 4, indicating sorption of Cr(III) on chrome sludge follows the Langmuir model. Values of b and N^* 0.294 L/mg and 24.04 mg/g respectively. N^* agrees very well with the experimental value. This value is comparable with those for coconut husk (28.60 mg/g) and rice straw (15.60 mg/g) (Tan *et al.* 1993).

The dependence of the sorption of Cr on the amount of

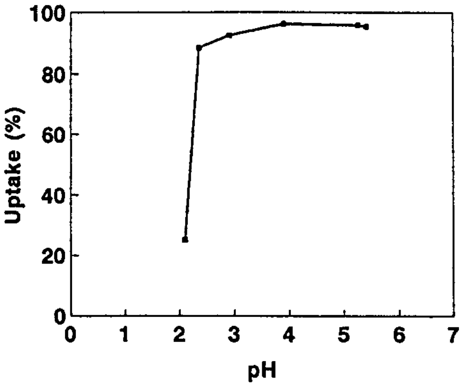

Figure 1. Percent sorption of chromium(III) by chrome sludge as a function of pH. 0.1 g of chrome sludge in 25 mL of 20 mg/L Cr(III) solution.

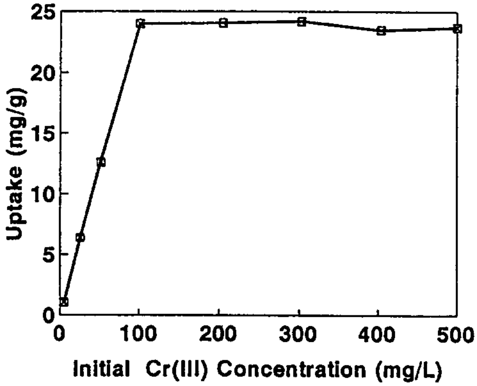

Figure 2. Cr(III) uptake by chrome sludge in relation to concentration. 0.1 g chrome sludge in 25 mL of Cr(III) solution at various concentrations.

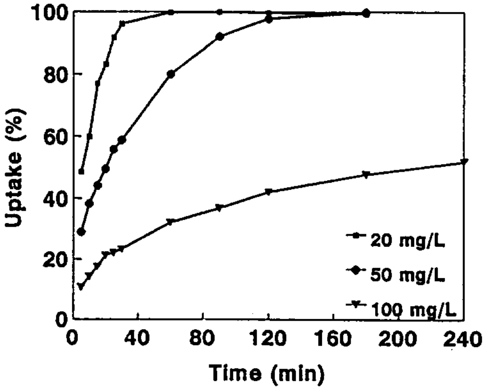

Figure 3. Sorption of chromium (III) by chrome sludge in relation to concentration and duration. 1.0 g of chrome sludge in 500 mL of Cr(III) solution.

chrome sludge was studied in the range of 0.02-0.60 g, using a 100 mg/L Cr(III) solution and the results are shown in Fig5. The percent sorption increased with increasing amount of sorbent. It increases from 15 % to about 100 % from 0.02 to 0.30 g. This increase is evidently related to a larger surface of the chrome sludge with larger quantity of material.

The relationship between the distribution coefficient, Kc, defined as : (mg Cr(III) /g sorbent)/(mg/L Cr(III) solution at equilibrium), and absolute temperature, T (K), of the Cr(III) sorption is shown in Fig 6 by a van't Hoff plot (Glasstone and Lewis 1965). The distribution coefficient increased linearly with increasing reciprocal values of the absolute temperature. From the slope of such a plot, the enthalpy of the sorption was estimated to be -19.1 kJ/mol indicating the sorption involved an exothermic reaction and that the sorption process is likely to be physical (Helfferich 1962).

The sorption of Cr(III) on chrome sludge is generally not representative of the existing conditions in a real aqueous effluent. Hence the effect of the other metal ions on the Cr(III) sorption was investigated and the results are shown in Table 1. The reduction of Cr(III) suggests a competition of the metal-binding sites on the chrome sludge. Metal ions like Cu and Pb present the highest inhibition capacity while Zn and Cd gave an intermediate effect. The effect of Ni ions on Cr(III) sorption was negligible. For various molar ratios of Cr(III):M, the order of increasing effect on the sorption of Cr(III) could be represented as Cu, Pb > Zn

Table 1. Effect of metal ions on the uptake of Cr(III).

M^{2+}	$Cr^{3+}:M^{2+}$	Cr^{3+} sorption(%)	M^{2+} sorption(%)
	1:0	95.0	-
Cu	1:0.5	85.6	73.4
	1:1	79.4	60.1
	1:5	70.8	22.7
Pb	1:0.5	84.3	90.2
	1:1	78.1	74.2
	1:5	68.6	22.0
Zn	1:0.5	93.8	51.3
	1:1	85.4	33.1
	1:5	81.1	14.3
Cd	1:0.5	91.3	43.5
	1:1	89.6	27.2
	1:5	86.2	10.3
Ni	1:0.5	97.8	29.0
	1:1	95.7	19.1
	1:5	92.1	12.3

Initial concentration of Cr(III):0.004 M

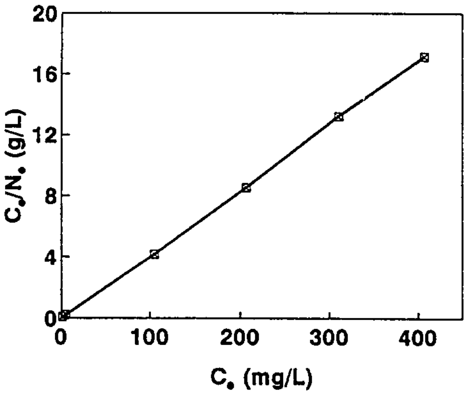

Figure 4. Langmuir isotherm of chromium(III) on chrome sludge.

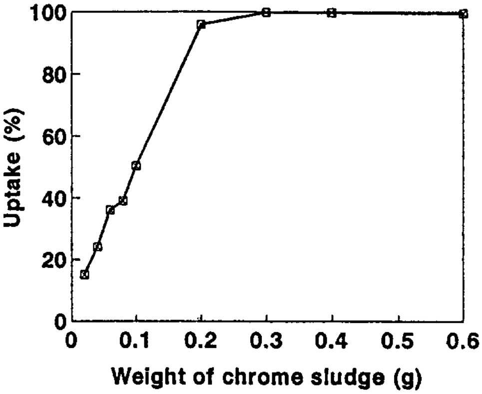

Figure 5. Dependence of chromium(III) sorption of the amount of chrome sludge. Various amounts of chrome sludge in 25 mL of 100 mg/L Cr(III) solution.

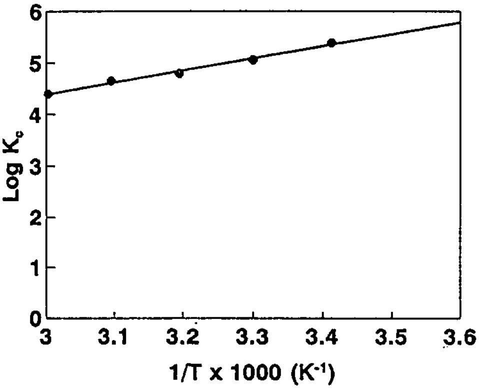

Figure 6. van't Hoff plot of chromium(III) sorption on chrome sludge for a 50 mg/L Cr(III) solution.

>Cd >Ni. The order of sorption is determined by various factors such as ionic potential, radius, charge, chemical properties and hydrolysis. It is likely that the higher charge of Cr(III) contributes to greater sorption in the series of metals studied. The sum of sorbed cations is much higher than in the case of single chromium ions. This is due to the higher total concentration of metal ions in the solution.

These results show that chrome sludge, an electroplating waste, could be used to remove or reduce the level of Cr(III) from aqueous solution. The data obtained are useful in the design of treatment plants for chromium in wastewaters.

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