

KINETIC STUDIES OF COMPETITIVE HEAVY METAL ADSORPTION BY SPHAGNUM MOSS PEAT

Y.S HO¹, D.A.J. WASE², AND C.F. FORSTER*

¹School of Civil Engineering and ²School of Chemical Engineering, Birmingham University, Edgbaston, Birmingham, B15 2TT, UK.

ABSTRACT

Much of the work on the adsorption of metals by low-cost, natural biosorbents has focussed on the uptake of single metals. In practice, wastewaters are polluted with multiple metals. In addition, the kinetics of adsorption, which are important in the design of treatment systems, have largely been neglected. This paper describes the results of an examination into the adsorption by peat of copper and nickel from both mono and bi-solute systems. These showed that, in general, pore diffusion appeared to be the rate-controlling step and that the presence of 'contaminant' copper ions reduced the binding of nickel. In fact, the best interpretation which could be placed on the data was that the behaviour of nickel was unusual. The results also showed that the kinetics of adsorption were best described by a second-order expression rather than a first-order model.

Keywords: Peat, adsorption, heavy metals, kinetics

INTRODUCTION

In recent years there has been an increased awareness of the potential impact of pollutants such as heavy metals. Moreover, the traditional methods for treating aqueous streams containing metal contaminants are expensive and can have inadequate efficiencies (1). This is particularly true in developing countries. This has led to the examination of alternative technologies. The use of biological materials to remove metals is one such technology which has received considerable attention and many materials have been examined. For example, wood-rotting fungi have been used for the removal of rare earths (2), the sorption of uranyl ions by chitosan has been studied by Saucedo et al. (1992), tea leaves have been used for the removal of lead, cadmium and zinc (4) and the uptake of lead and zinc by lignin has been examined by Srivastava et al. (1994). Peat has also been used as a biosorbent (6, 7, 8). Many of the studies into the effectiveness of biosorbents have concentrated on the sorption of single metals whereas, in practice, wastewater streams will contain several metal ions. This means that the possibility of competition for adsorption sites will occur. This paper examines the use of peat for the removal of two metals, copper and nickel, from both mono-solute and bi-solute solutions. In particular, it reports the effect that a competing ion has on the rates of removal and examines the mechanisms which may affect the uptake of metals.

MATERIALS AND METHODS

Sphagnum moss peat, which is available commercially in Britain and Ireland, was used as the sorptive material. The raw peat was dried for 24 hours at 105 °C and then screened

through a 14 mesh sieve (BS 410/43) to remove any large, non-peat solids. This gave a uniform material for the entire series of tests.

Analytical grade reagents were used in all cases. Stock solutions of copper and nickel (1000 mg l⁻¹) were prepared using copper sulphate and nickel sulphate. The working solutions were prepared by dilution with distilled water. Metal concentrations were measured by acetylene-air atomic adsorption spectrophotometry (Instrumentation Laboratory aa/ae 751) with single element hollow cathode lamps.

The sorption experiments were conducted in a constant temperature room (25°C) on a rotary shaker (100 rpm) using capped 500ml conical flasks. For single-solute systems, the peat (1.2 g) was mixed with the aqueous solution (300ml) containing the metal ions (10, 25, 50 and 100 mg l⁻¹). The pH was adjusted to a value of 5.0. The peat suspensions were then shaken for 3 hours. Samples (2 ml) were taken periodically, filtered through a membrane filter (0.45 µm) and their metal concentration measured. Although replicate samples were not taken, replicate measurements (n = 5) of the metal concentrations were made and an average value reported. Typically, the standard deviation of these replicates was 5%. For bi-solute systems, 3.2 g of peat were used together with a larger volume (800 ml) of the solution of metal ions containing equal concentrations (w/v) of the two metals. In these cases, when, for example, copper concentrations were measured, copper was considered as the primary metal and nickel as the secondary metal.

RESULTS AND DISCUSSION

Figure 1 shows how the presence of the secondary metal affects the adsorption of both copper and nickel and,

although this Figure contains only data for initial concentrations of 50 mg l⁻¹, the pattern of behaviour is typical of the other concentrations. It is clear from this that the presence of the second solute has a distinct impact on the sorption of the primary metal. With both bi-solute systems, the equilibrium concentrations of the primary metal in the liquid phase were lower than in their respective mono-solute systems and it can be seen that copper appears to have a greater effect as the 'contaminant' than nickel. This can be quantified by an examination of the specific adsorption values (X/M; mg metal g⁻¹ of peat) calculated at 180 minutes. Table 1 shows these values, together with values for the reduction in the specific adsorption of the primary metal in the bi-solute systems.

Kinetic studies are important in determining the time needed to reach equilibrium and examinations into the rates of adsorption can be used to develop models and an understanding into the processes which influence the uptake of solutes. If diffusion through the bulk liquid is ignored, three such processes can be identified;

Mass transfer (Boundary layer diffusion).

Sorption of ions onto sites.

Intraparticle diffusion.

External mass transfer is characterised by the initial rate of solute sorption (9). This can be calculated from the initial slope of the Ct/Co - time curves (Figure 2). These slopes can be derived either from a derivation of the polynomial approximation of Ct/Co at t = 0 (3) or, more simply, by

Table 1. Values for the specific adsorption (mg.g⁻¹) after 180 minutes showing the reductions caused by the addition of a second metal

Initial concentration (mg l ⁻¹)	Mono-solute	Copper Bi-solute	Δ (%)	Mono-solute	Nickel Bi-solute	Δ (%)
10	2.38	2.15	9.5	2.13	2.06	3.3
25	5.68	5.00	12.0	3.78	2.15	43.0
50	9.03	7.75	14.2	5.99	2.28	61.9
100	12.29	9.37	23.8	7.15	2.46	65.7

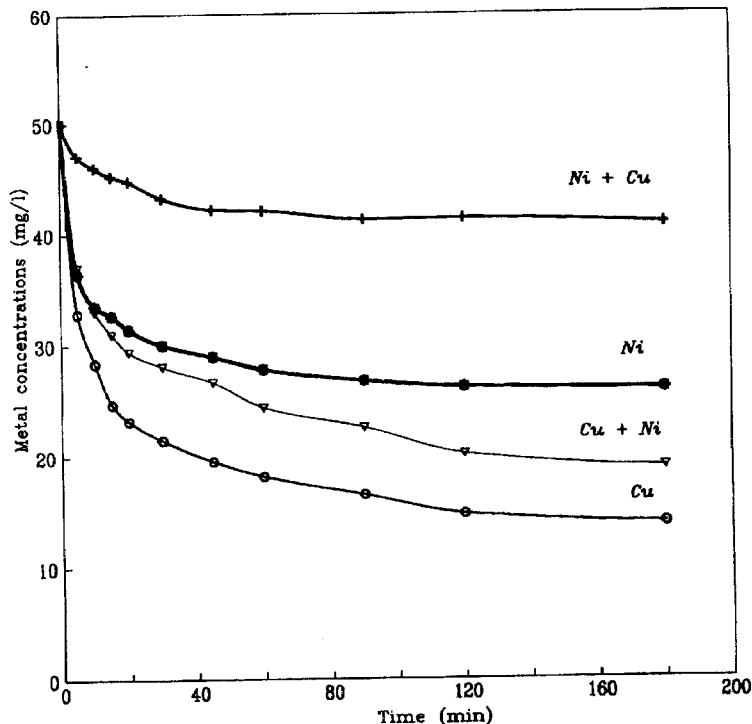


Figure 1. Variations in the metal concentrations with time for both mono and bi-solute systems.

assuming that the relationship is linear over the first 5 - 10 minutes (10). Table 2 presents a comparison of the initial rates calculated on this latter basis. These results show that increasing the initial metal concentration resulted in a decrease in the initial rate. The data also show that the most marked effect occurred when the initial concentration increased from 10 to 25 mg/l and that further increases in the metal ion concentration had less of an effect.

Weber and Morris (1963) have concluded that, for processes which are controlled by site adsorption, the initial rate will be directly proportional to the solute concentration. The non-proportionality shown in Table 2, therefore, indicates that the sorption phase is not the rate controlling step (11, 3). Intraparticle diffusion is characterised by a dependence between the specific adsorption (X/M) and the square root of time with the slope of the relationship being the intraparticle diffusion rate parameter. As can be seen from a typical set of data for the systems investigated (Figure 3), the relationships are not linear. This non-linearity has been reported previously (12, 13, 14) and has been explained in terms of both of the diffusion processes having an effect on the adsorption. The initial part of the curve is attributed to boundary layer effects and the final portion to intraparticle diffusion. It is possible to derive an initial rate parameter (j) by linear regression between $t = 0$ and t_{lim} where t_{lim} is the first breakpoint in the $X/M - \sqrt{t}$ relationship. Values for these parameters are given in Table 3. These are rate parameters with units of $mg\ g^{-1}\ min^{-0.5}$ and, as such, are not a direct quantification of the

rates. Nevertheless, they can be interpreted in relative terms. Examined in this way, the data show that, except for the nickel bi-solute system, the rate of diffusion increases with the initial metal concentration. According to the theoretical equations for diffusion, when intraparticle diffusion is the only rate determining step, the rate parameter is directly related to the square root of the initial concentration (11).

$$j = (C_0)^n$$

where $n = 0.5$

Regression analysis showed that there was little difference between the value obtained for 'n' and that the values ranged from 0.21 to 0.29. This confirms that intraparticle diffusion is not the only operative mechanism.

The results in Table 3 also show that increasing concentrations of copper ions had a significant effect on the uptake of nickel in the bi-solute system causing a decrease in the diffusion rate. Although this is obviously a competitive effect, the mechanism by which it occurs is, at the moment, unclear. However, it is known that the binding of nickel to certain types of biological material is different from other metals (15). This anomalous behaviour has been attributed to there being binding sites which are available to other metals but not to nickel (16).

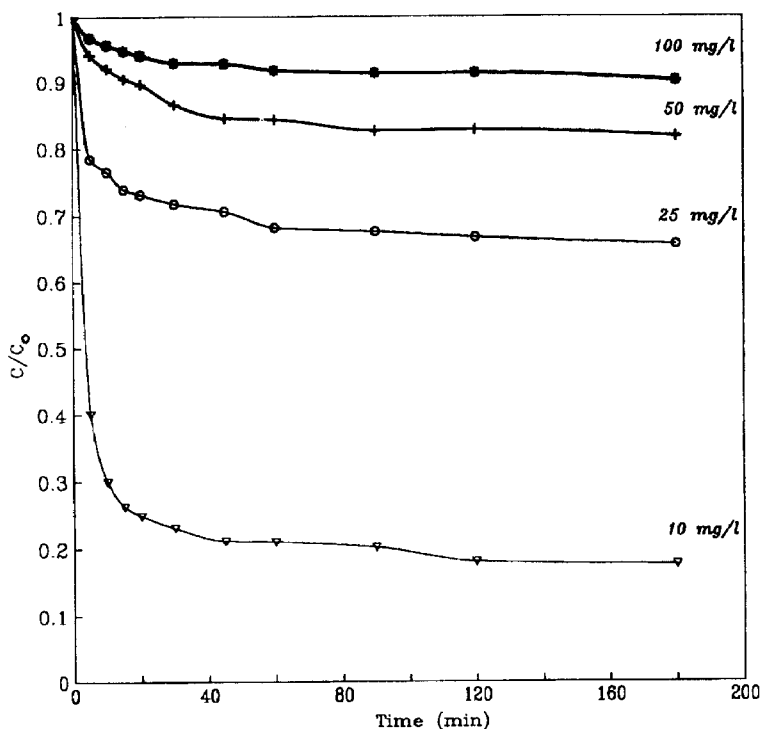


Figure 2. The effect of initial nickel concentration on the changes in C_t/C_0 with time for the Ni/Cu bi-solute system.

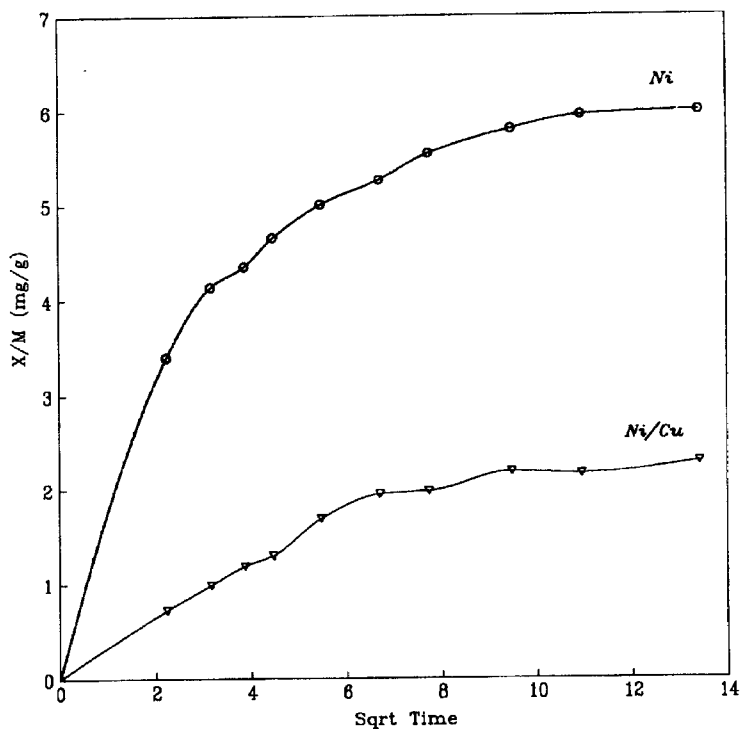


Figure 3. The effect of copper on the pore diffusion model for nickel (50 mg l⁻¹).

Table 2. Initial (5 minute) sorption rates (min⁻¹) based on [(1 - (C₅/C₀))/5]

Initial concentration (mg l ⁻¹)	Copper		Nickel	
	Mono-solute	Bi-solute	Mono-solute	Bi-solute
10	0.182	0.158	0.120	0.120
25	0.127	0.083	0.066	0.043
50	0.069	0.052	0.054	0.012
100	0.042	0.033	0.029	0.006

Table 3. Initial rate parameters (mg.g⁻¹ min^{-0.5})

Initial concentration (mg l ⁻¹)	Copper		Nickel	
	Mono-solute	Bi-solute	Mono-solute	Bi-solute
10	1.02	0.88	0.67	0.58
25	1.58	0.98	0.80	0.38
50	1.53	1.17	1.35	0.30
100	2.15	1.44	1.17	0.32

The kinetics of adsorption by biological materials have been described previously by the first order expression given by Langergren (17);

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

where;

q_e = mass of metal adsorbed at equilibrium (mg g⁻¹)

q_t = mass of metal adsorbed at time, t (mg g⁻¹)

K = rate constant

It was found that, although this equation provided a very good description for some of the current data, it was not applicable to all the results. No further consideration of this model was, therefore, attempted. It has been established

Table 4. Second order constants for copper adsorption ($q_e = \text{mg g}^{-1}$; $k = \text{g mg}^{-1} \text{min}^{-1}$; $h = \text{mg g}^{-1} \text{min}^{-1}$)

Initial concentration (mg l^{-1})	Mono-solute			Bi-solute		
	q_e	k	h	q_e	k	h
10	2.37	0.26	2.94	2.16	0.201	1.88
25	5.74	0.051	3.34	5.12	0.020	1.11
50	9.36	0.006	1.12	8.13	0.005	0.66
100	12.7	0.005	1.55	9.88	0.005	0.94

Table 5. Second order constants for nickel adsorption ($q_e = \text{mg g}^{-1}$; $k = \text{g mg}^{-1} \text{min}^{-1}$; $h = \text{mg g}^{-1} \text{min}^{-1}$)

Initial concentration (mg l^{-1})	Mono-solute			Bi-solute		
	q_e	k	h	q_e	k	h
10	2.16	0.080	0.74	2.08	0.103	0.089
25	3.90	0.021	0.63	2.20	0.031	0.367
50	6.20	0.013	1.01	2.46	0.014	0.171
100	7.49	0.008	0.93	2.57	0.013	0.171

recently (Ho, Wase and Forster, unpublished data) that a pseudo second order reaction can be used to describe a multi-component system;

$$t/q_t = [1/2.k.q_e^2] + t/q_e$$

where;

k = the rate constant for adsorption ($\text{g mg}^{-1} \text{min}^{-1}$)

q_e = the amount of metal adsorbed at equilibrium (mg g^{-1})

q_t = the amount of metal adsorbed at any time, t (mg g^{-1})

The initial adsorption rate (h) is given by;

$$h = 2.k.q_e^2$$

Values for these constants were derived from a regression analysis of (t/q_t) against t and are given in Tables 4 and 5 and comparisons between the data and the predictions made by the equation are shown in Figures 4 and 5. The data in these Figures shows that the second order equation does provide a realistic description of the adsorption process.

Applying the Weber and Morris philosophy to the

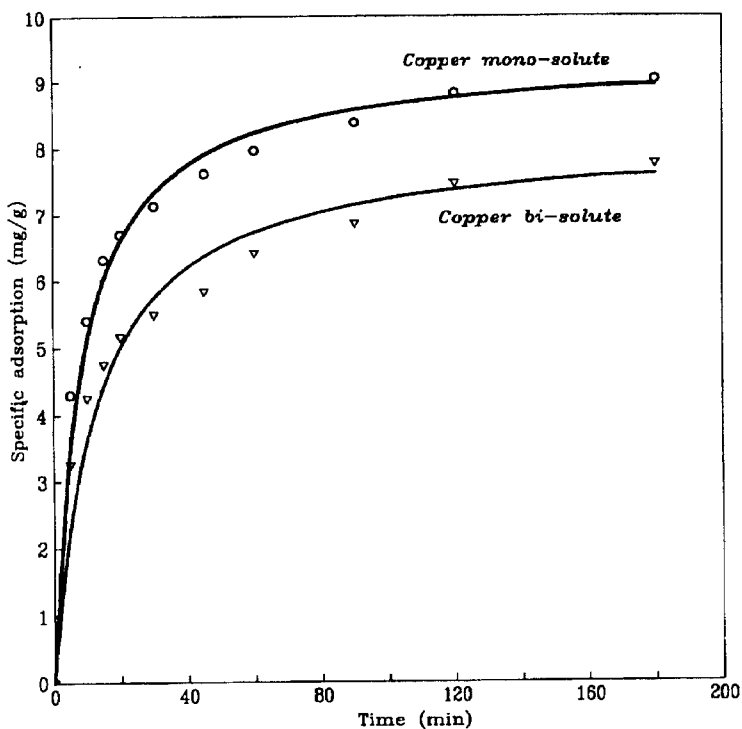


Figure 4. Data (points) and predictions (curves) for the 2nd-order rate model applied to the mono and bi-solute systems for copper (50 mg l^{-1}).

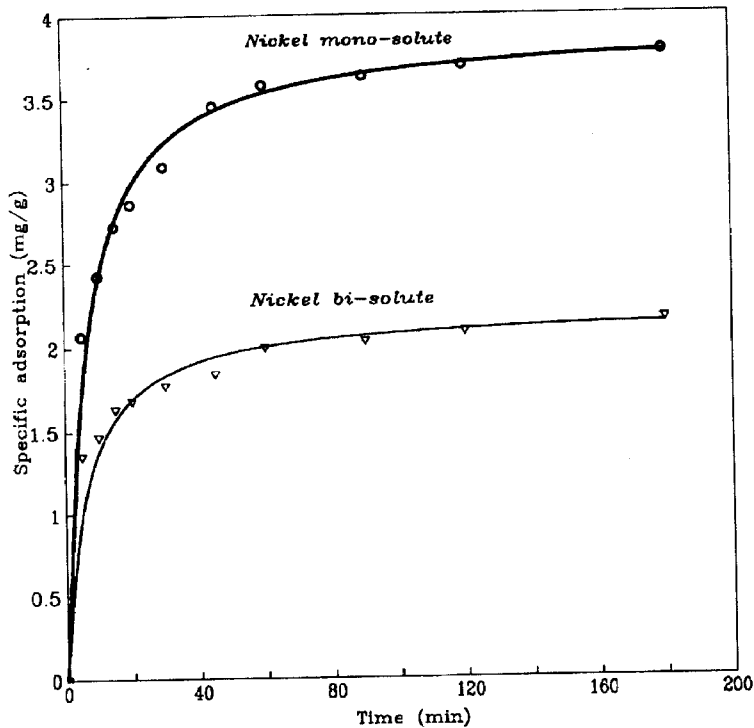


Figure 5. Data (points) and predictions (curves) for the 2nd-order rate model applied to the mono and bi-solute systems for nickel (25 mg l^{-1}).

variations in the initial rate (h) with C_0 shows that in none of the cases is there any consistent relationship;

- the rate is not directly proportional to C_0 which confirms the earlier analyses and indicates that the sorption process was not the rate limiting step.

- the rate is not directly related to the square root of C_0 which again implies that intraparticle diffusion was not the only mechanism involved.

CONCLUSIONS

The results clearly establish that a pseudo second order

model provides a more appropriate description of the mono and bi-solute binding of copper and nickel to peat than a first order equation. The results also imply that nickel behaves differently, particularly when a second metal is present. The precise reason for this, currently, is unclear but it is a behaviour which has been noted previously and is one which has been attributed to the size of the nickel ion and to the chemical nature of the binding sites. The data also confirm that both mass transfer and pore diffusion are important in determining the adsorption rates and that their relative significance depends on the initial metal concentrations.

REFERENCES

1. Davila, J.S. Matos, C.M. and Cavalcanti, M.R. Heavy metals removal from wastewater using activated peat. *Water Sci. Technol.*, **26**, 2309-2312 (1992)
2. Muraleedharan, T.R., Philip, L., Iyengar, L. and Venkobachar, C. Application studies of biosorption for monazite processing industry effluents. *Bioresource Technol.*, **49**, 179-186 (1994)
3. Saucedo, I., Guibal, E., Roulph, Ch. and Le Cloirec, P. Sorption of uranyl ions by a modified chitosan: kinetics and equilibrium studies. *Environ. Technol.*, **13**, 1101-1116 (1992)
4. Tee, T.W. and Khan, A.R.M. Removal of lead, cadmium and zinc by waste tea leaves. *Environ. Technol. Lett.*, **9**, 1223-1232 (1988)
5. Srivastava, S.K., Singh, A.K. and Sharma, A. Studies on the uptake of lead and zinc by lignin obtained from black liquor - a paper industry waste material *Environ. Technol.*, **15**, 353-361 (1994)

6. Allen, S.J., Murray, M., Brown, P. and Flynn, O. Peat as an adsorbent for dyestuffs and metals in wastewaters. *Resources, Conservation and Recycling*, **11**, 25-39 (1994)
7. Viraraghavan, T. and Dronamraju, M.M. Removal of copper, nickel and zinc from wastewater using peat. *J. Env. Sci. Health*, **28**, 1261-1276 (1993)
8. Sharma, D.C. and Forster, C.F. Removal of hexavalent chromium using sphagnum moss peat. *Water Res.*, **27**, 1201-1208 (1993)
9. McKay, G. and Poots, V.J.P. Kinetics and diffusion processes in colour removal from effluent using wood as an adsorbent. *J. Chem. Tech. Biotech.*, **30**, 279-282 (1984)
10. Forster, C.F., Mehrotra, I. and Alibhai, K.R.K. The multiple binding of heavy metals by digested sludge. *J. Chem. Tech. Biotech.*, **35B**, 145-154 (1985)
11. Weber, W.J. and Morris, J.C. Kinetics of adsorption on carbon from solutions. *J. Sanit. Engng. Div. Am. Soc. Civ. Eng.*, **89**, 31-60 (1963)
12. McKay, G., Otterburn, M.S. and Sweenet, A.G. The removal of colour from effluent using various adsorbents - III. Silica rate processes. *Water Res.*, **14**, 15-20 (1980)
13. Gupta, G.S., Prasad, G. and Singh, V.N. Removal of chrome dye from aqueous solutions by mixed adsorbents: fly ash and coal. *Water Res.*, **24**, 45-50 (1990)
14. Gaid, A., Kaoua, F., Mederres, N. and Khodjsa, M. Surface mass transfer processes using activated date pits as adsorbent. *Water SA*, **20**, 273-278 (1994)
15. Forster, C.F. Factors involved in the settlement of activated sludge - II. The binding of heavy metals. *Water Res.*, **10**, 1265-1271 (1985)
16. Gould, M.S. and Genetelli, E.J. Heavy metal complexation behaviour in anaerobically digesting sludge. *Water Res.*, **12**, 505-512 (1978)
17. Namasivayam, C. and Yamuna, R.T. Removal of Congo red from aqueous solution by biogas waste slurry. *J. Chem. Tech. Biotech.*, **53**, 153-157 (1992)