



BATCH NICKEL REMOVAL FROM AQUEOUS SOLUTION BY SPHAGNUM MOSS PEAT

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Abstract—The batch adsorption of Ni(II) onto sphagnum moss peat has been studied. The reaction was pH dependent, the optimum range being 4.0–7.0. Langmuir and Freundlich isotherms, established for various initial nickel concentrations and for a range of pH values, were used to obtain a single relationship between initial metal concentration, metal removal, and initial pH. The latter was found to control efficiency of nickel removal. Kinetic data suggested involvement of a chemical rate-limiting step, and a predictive relationship was derived relating nickel removal to peat dose. In comparison with other metals, nickel removal is poor, and possible reasons are discussed.

Key words—peat, nickel, adsorption, Langmuir and Freundlich

INTRODUCTION

During the last three decades, the value of peat has been recognised as an agent for water pollution control. Indeed, during this period, peat-based systems have been advocated as potential solutions to a wide range of problems. Typical studies have included its use in cleaning-up oil spills (Hennezel *et al.*, 1972), applying peat as an agent for removing heavy metals from wastewaters (Eger *et al.*, 1980; Zhipei *et al.*, 1984), treating slaughterhouse wastewaters, and dairy and animal wastes (Viraraghavan and Kikkeri, 1988), and septic tank effluent treatment (Viraraghavan and Ayyaswami, 1989). These studies have suggested that peat is uniquely valuable as an inexpensive adsorbent, and one would therefore expect it to remove metals from aqueous solution.

This has indeed been found to be so and there are several reports in the literature that peat will bind a variety of metal ions. For instance, Zhipei *et al.* (1984), have shown that Pb^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} and Cr(VI) are all bound to peat, while Eger *et al.* (1980) demonstrated that white cedar bog will adsorb a variety of trace metals. In addition, Coupal and Lalancette (1976) have shown that a peat moss pilot filter could remove nickel from a variety of wastewaters. The efficiency of removing nickel ions from wastewater with several differing Chinese peats has been studied by batch processes (Zhipei *et al.*, 1984). Gosset *et al.* (1984) have investigated nickel removal reactions in batch and determined their kinetics and

thermodynamics. In spite of this considerable amount of recent activity, there has been no systematic study over the whole field. The present work, aimed at rectifying this situation, comprises a study of the removal of Ni(II) by moss peat at various initial pH values and concentrations of nickel solution, and this paper covers the kinetics of adsorption.

MATERIALS AND METHODS

Materials

A standard pack (50 l) of sphagnum moss peat, commercially available in Britain and Ireland, was used for this work. The raw peat was dried in an oven for 24 h at 105°C, and then screened through a 14 mesh sieve (B.S. 410/43) to remove any large non-peat solids. This produced a uniform material for the complete set of adsorption tests.

Analytical grade reagents were used in all cases. A stock nickel(II) solution (1000 mg l^{-1}) was prepared in distilled water using nickel sulphate. All working solutions were prepared by diluting the stock solution with distilled water. The pH adjustments were made with sulphuric acid or sodium hydroxide solutions.

Analysis and procedures

The concentrations of nickel(II) were determined by acetylene-air flame atomic adsorption spectrophotometry (Instrumentation Laboratory aa/ae spectrophotometer 751) with single element hollow cathode lamps.

Batch sorption tests were done in a 25°C constant temperature room on a rotary shaker at 100 rpm using capped 500 ml conical flasks. In the adsorption isotherm tests, 1 g peat was thoroughly mixed into 250 ml nickel(II) solution. The initial pH adjustments were carried out either by sulphuric acid or sodium hydroxide solution and the initial adjusted pH was then recorded as pH_{in} . The six different

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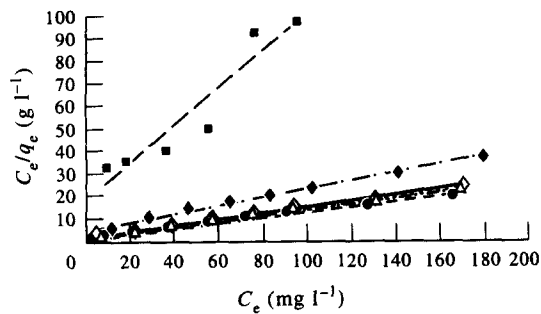


Fig. 1. Linearised Langmuir isotherms for various initial pH values: pH2, ---■---; pH3, - - -◆- - -; pH4, -◇-; pH5, ····△····; pH6, ········; pH7, ---●---

tests at pH_{in} 2.00, 3.00, 4.00, 5.00, 6.00 and 7.00 each used a range of initial nickel(II) concentrations (C_0) from 10 to 200 $mg\ l^{-1}$. After the flasks had been shaken for 4 h, the reaction mixtures were filtered through Whatman filter papers (No. 1), final pH (pH_{fn}) was recorded, and the concentration of nickel(II) was determined in the filtrate.

For each of the sorption kinetic tests, 5 g peat was thoroughly mixed with 250 ml nickel(II) solution in the range 50–400 $mg\ l^{-1}$. Peat suspensions were shaken as before for 2 h at a constant temperature of 25°C, and 2 ml samples were collected and filtered through a 0.45 μm membrane filter every 3 min for the first 15 min, every 5 min for the next 15 min, every 10 min for the next half hour and, finally, every 30 min for the last hour. The filtrates were analysed by atomic absorptions spectrophotometry.

For tests involving variations in the amounts of sorbent, the initial nickel(II) concentration (C_0) was 200 $mg\ l^{-1}$, and the pH_{in} was 5.00. The dose of peat sorbent (W_p) was varied over the range 4.00–40.0 $g\ l^{-1}$. The conical flasks were shaken at 25°C as before for 4 h, after which pH was measured and recorded as pH_{fn} , and nickel(II) content was determined as described above.

RESULTS AND DISCUSSION

Sorption equilibria and adsorption isotherms

The adsorption data were analysed in terms of both the Langmuir and the Freundlich equations. Figure 1 shows the data linearised to fit the Langmuir equation and Table 1 presents the constants, derived by regression analysis, for both equations. The statistics show a high degree of correlation, indicating that either of the equations could be used to describe the adsorption of nickel by peat. The results also show that at initial pH values of 2 and 3, the adsorption was worse than at pH values of 4 and above. Indeed, at initial pH values of 4, 5, 6 and 7 there were only slight differences in the adsorption. The Langmuir coefficient, X_m , is a measure of the maximum adsorption capacity, and, as such, can be thought of as the best criterion for comparing adsorptions. Peat has been used previously to effect the removal of both hexavalent chromium and copper from aqueous solutions. As in this present study, the adsorptions were pH-dependent. Table 2 compares the X_m values for these adsorptions at their optimum pH values. This shows that, of the three, nickel has the lowest value. There is no obvious reason why nickel should bind to peat less readily than copper, which is an ion of similar size and weight. However, it has been noted previously that, in the activated sludge process, nickel is removed less readily than other heavy metals, although no reason for this was suggested (Brown and Lester, 1979).

Earlier work by Ho *et al.* (1994) has reported a technique for obtaining a single relationship between the metal removal, the initial metal concentration and the initial pH. This was achieved by combining a

Table 1. Adsorption isotherm constants for the nickel-peat system

pH_{in}	Langmuir constants			Freundlich constants		
	Correlation coefficient r^2	X_m ($mg\ g^{-1}$)	k ($l\ mg^{-1}$)	Correlation coefficient r^2	K_F ($mg\ g^{-1}$)	$1/n$
2.00	0.895	1.23	0.067	0.827	0.104	0.530
3.00	0.989	4.31	1.28	0.996	0.869	0.347
4.00	0.991	7.84	4.21	0.985	1.72	0.296
5.00	0.991	8.13	4.68	0.982	1.79	0.297
6.00	0.990	8.52	4.90	0.986	1.80	0.305
7.00	0.984	9.18	4.85	0.992	1.76	0.319

Table 2. A comparison of the maximum capacities of peat (Langmuir X_m) for chromium (VI), copper and nickel

Metal	Optimum pH	X_m ($mg\ g^{-1}$)	Source
Cr(VI)	1.5	119	Sharma and Forster (1993)
Cu*	5.0	16.4	Ho <i>et al.</i> (1994)
Ni	7.0	9.18	This study

*From Ho *et al.* (1994)

Table 3. Metal removed (R) by peat at initial pH values of 5 and various initial metal concentrations (C_0)

C_0 ($mg\ l^{-1}$)	Cu			Ni		
	20	50	200	20	50	200
R (%)	97.4	56.5	20.9	61.6	40.9	15.2

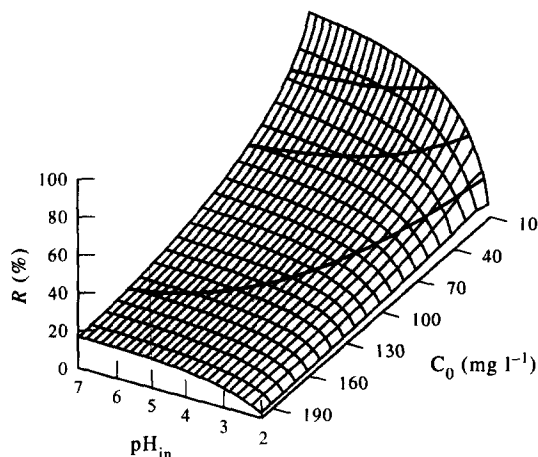


Fig. 2. Effect of nickel concentration and various values of pH_{in} on nickel removal.

series of statistical relationships. When this approach was applied to the current data, a comparable relationship was obtained. The results are shown in Fig. 2 and are based on:

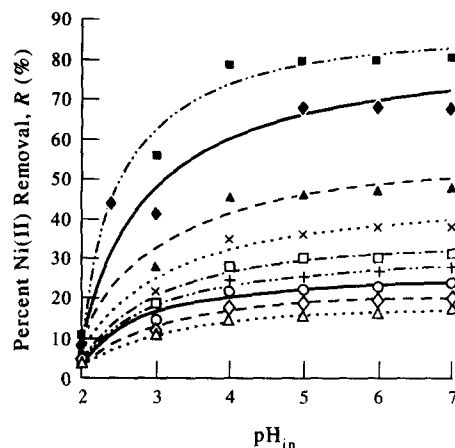


Fig. 3. Effect of pH_{in} on nickel removal: 10 $mg\ l^{-1}$, ■; 20 $mg\ l^{-1}$, ◆; 40 $mg\ l^{-1}$, ▲; 60 $mg\ l^{-1}$, x; 80 $mg\ l^{-1}$, □; 100 $mg\ l^{-1}$, +; 120 $mg\ l^{-1}$, ○; 160 $mg\ l^{-1}$, ◇; 200 $mg\ l^{-1}$, △.

initially. This can be represented as a functional relationship of these two parameters, given by:

$$pH_{fin} = f(pH_{in}, C_0^{-1})$$

where C_0 = initial nickel concentration.

$$R = \frac{1.85C_0 - (pH_{in})C_0 + 8.05 \times 10^{-1}}{1.70 \times 10^{-4}C_0^2 + 9.79 \times 10^{-3}C_0 - 2.07 \times 10^{-4}(pH_{in})C_0^2 - 8.67 \times 10^{-3}(pH_{in})C_0 + 6.98 \times 10^{-3}}$$

Effect of nickel on equilibrium pH

Table 4 shows that as the initial nickel concentration (C_0) increases the resultant equilibrium pH_{fin} decreases for all concentrations of nickel and values of pH_{in} . The more nickel that is added, the greater the effect, whatever the initial pH. It is therefore concluded that as more nickel ions are adsorbed onto the peat, more hydrogen ions are released from the peat into the solution, consequently decreasing the pH of the reaction mixture. The data suggest that complexation and ion-exchange are both playing a part in adsorption, and are consistent with the findings of Gossett *et al.* (1986).

Overall, it is therefore clear that the resulting equilibrium pH is governed by two major factors: the initial pH and the nickel present in the solution

Influence of pH on nickel removal

The efficiency of nickel removal by peat is controlled by the initial pH of the reaction mixture. Figure 3 demonstrates this effect and shows that the removal is favoured both by high pH values and lower nickel concentrations. The sharpest increase in removal efficiency with pH_{in} was noticed as pH_{in} was raised from 2.00 to 4.00. However, when the pH_{in} of the reaction mixture was raised between 4.00 and 7.00, the efficiency of removal increased only marginally. It is revealing that 80.6% Ni(II) removal is achieved when a nickel concentration as low as 10 $mg\ l^{-1}$ is treated at pH 7.00. Above this concentration at pH 7.00, the percent removal was always lower than 80.6%. Thus the maximum removal for 200 $mg\ l^{-1}$ at pH 7.00, was found to be only 17.4%.

Table 4. Equilibrium pH (pH_{fin}) at various initial nickel concentrations

Initial nickel concentration ($mg\ l^{-1}$)	Final pH (pH_{fin})					
	2.00*	3.00*	4.00*	5.00*	6.00*	7.00*
10.0	1.90	2.97	3.63	3.70	3.70	3.78
20.0	1.89	2.94	3.52	3.59	3.59	3.62
40.0	1.90	2.91	3.41	3.48	3.48	3.50
60.0	1.90	2.91	3.38	3.40	3.40	3.43
80.0	1.90	2.91	3.33	3.38	3.37	3.39
100	1.89	2.91	3.30	3.36	3.33	3.37
120	1.90	2.91	3.30	3.34	3.31	3.34
160	1.89	2.90	3.28	3.30	3.30	3.31
200	1.89	2.90	3.24	3.29	3.29	3.30

* = pH of the reaction mixture before peat addition

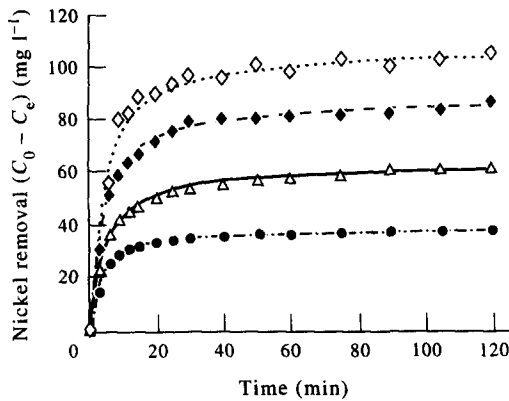


Fig. 4. Adsorption kinetics at various nickel concentrations: 50 mg l⁻¹, ●; 100 mg l⁻¹, △; 200 mg l⁻¹, ◆; 400 mg l⁻¹, ◇.

In contrast, approximately 11.0% removal was achieved when 10 mg l⁻¹ of nickel was treated at pH 2.00.

Kinetics of nickel removal

The effect of contact time on Ni(II) removal was investigated using an initial nickel concentration of 100 mg l⁻¹ and a pH_{in} of 5.00. The results are presented in Fig. 4, and show that removal of nickel reached equilibrium in approx. 25, 40, 60 and 90 min for initial nickel concentrations of 50, 100, 200 and 400 mg l⁻¹ respectively. This indicates that the equilibrium time is not independent of the initial concentration, probably because the adsorption sites adsorbed the available nickel more quickly at low solute concentrations. However, for higher concentrations, interparticle diffusion or creation of new sites were predominant adsorption mechanisms. This decreasing removal rate, particularly towards the end, suggests formation of a monolayer of Ni(II) ions on the outer surface of the peat and pore (interparticle) diffusion onto the inner surface of the adsorbent particles through the film due to continuous agitation maintained during the experiments.

Several hypotheses have been advanced to explain the variations in pH_{in} which arise when peat is added to a metal cation solution. These include: the acidic properties of carboxylic and phenolic functional groups present in humic substances (Bloom and McBride, 1979; Boyd *et al.*, 1981); some ion exchange reactions, e.g. proton release when metal cations bind to peat (Bunzl *et al.*, 1976; Bloom and McBride, 1979; Meisel *et al.*, 1979; Aho and Tummavuori, 1984); or the pH buffering capacity of weak acid groups in the

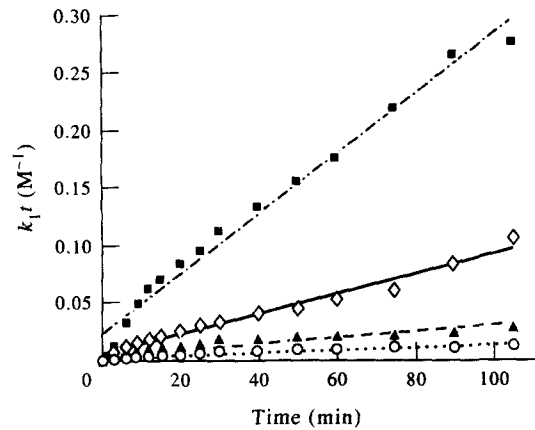


Fig. 5. Kinetic plots showing $k_1 t$ against time: 50 mg l⁻¹, ■; 100 mg l⁻¹, ◇; 200 mg l⁻¹, ▲; 400 mg l⁻¹, ○.

peat which limit possible pH variations related to proton release (Attal *et al.*, 1986).

Gosset *et al.* (1986) have developed an expression for the kinetic constant, k_1 , for the binding of metal ions to peat

$$k_1 t = \frac{1}{(PM)_{lim} - (M)_{in}} \cdot \ln \frac{(M)_{in}}{(PM)_{lim}} \cdot \frac{(PM)_{lim} - (PM)}{(M)_{in} - (PM)}$$

where (PM) and $(PM)_{lim}$ are the variable and equilibrium bound metal concentration, M , and $(M)_{in}$ is the initial free metal concentration, M .

In deriving this expression, it was assumed that:

- The reverse desorption reaction is negligible.
- Peat metal anion stoichiometry is constant for all experimental conditions and equal to one metal ion per binding site.
- Overall kinetics are limited by the binding reaction itself and not the diffusion of species.

Kinetic plots of the data for nickel removal are presented in Fig. 5. The relationship is linear, and the correlation coefficients (Table 5), suggest a strong relationship between the parameters. The kinetic constant, k_1 increased with decreasing nickel concentration (Fig. 6). The linearised k_1 and C_0 values on a double logarithmic plot showed a correlation coefficient (r^2) of 0.996, the relationship between k_1 and C_0 being of the type:

$$k_1 = aC_0^b$$

The values of a and b were found to be 1.98 and -0.497 respectively; and so the equation can be written as:

$$k_1 = 1.98C_0^{-0.497}$$

Table 5. Kinetic constants of adsorption

C_0 (M)	Correlation coefficient r^2	k_1 (M ⁻¹ min ⁻¹)	Saturation time (min)	Removal (%)
0.787	0.982	2.19	25	67.1
1.57	0.974	1.59	40	55.0
3.15	0.843	1.16	60	40.3
6.30	0.785	0.773	75	25.6

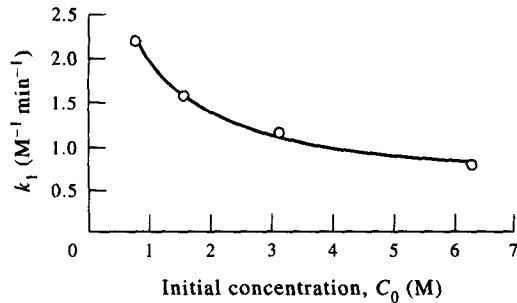


Fig. 6. Variation of k_1 against C_0 .

The quality of this correlation supports the assumptions concerning the kinetics; particularly the assumption of a chemical rate-limiting step. However, flow-through experiments in columns should be used to confirm such kinetic behaviour.

Effect of peat dose on adsorption

The effect of variation in peat dose for an initial nickel concentration of 200 mg l^{-1} is shown in Fig. 7. It is apparent that the equilibrium concentration decreases with increasing adsorbent doses for a given initial nickel concentration. This is to be expected, because for a fixed initial solute concentration, increasing adsorbent doses provides greater surface area (or adsorption sites). The data can also be used to derive a mathematical relationship to relate the nickel removal to the peat dose (using the boundary $m_s = 4.0$ to 40 g l^{-1}). This relationship, for which the correlation coefficient was 0.996, is:

$$R = \frac{m_s}{2.11 \times 10^{-1} + 9.83 \times 10^{-3} m_s}$$

This equation can be used to predict the percent nickel removal for any peat dose within the test limits at pH 5.00 and initial nickel concentration C_0 of 200 mg l^{-1} .

This relationship is similar to that derived for the removal of copper. It is, therefore, useful to compare the removals predicted by these relationships. Table 6

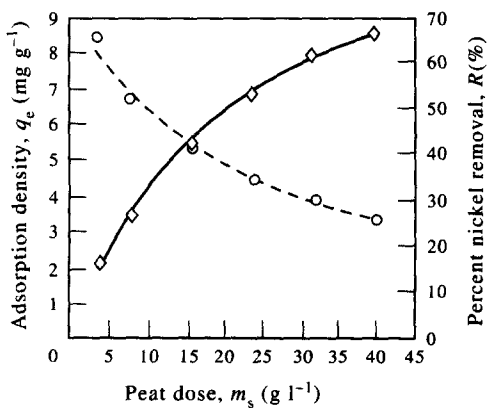


Fig. 7. Variation of adsorption density q_e (\circ), and percent nickel removal, R (\diamond), against peat dose m_s .

Table 6. A comparison of the removal of copper and nickel by varying the dose of the adsorbent, peat

Peat dose (g l^{-1})	Percent removal (%)	
	Cu*	Ni
4	32.53	16.00
10	57.05	32.33
40	91.55	66.20

*From Ho *et al.* (1994)

shows that, at any dose of peat, copper is adsorbed more effectively than nickel. This substantiates the data in Tables 2 and 3. This binding of nickel to bio-surfaces is atypical. Indeed, Gould and Genetelli (1978) have suggested that, with anaerobic sludges, there are some sites which, although suitable for other metals, are not available to nickel. Rudd *et al.* (1984) have noted that extracellular polymer (ECP) from *Klebsiella aerogenes*, continued to bind copper, cadmium and cobalt even after the complexation capacity had been reached, whereas with nickel it did not. The behaviour of nickel in relation to peat is, therefore, understandable if not explainable.

CONCLUSIONS

1. Irish sphagnum moss peat is a suitable adsorbent for the removal of nickel(II) from aqueous solution. However, its removal is poor compared with other metals.
2. Sorption of nickel is pH dependent and the best results are obtained in the pH range 4.0–7.0.
3. Regression analysis showed that the experimental data fitted closely the Langmuir and Freundlich isotherms.
4. Percent nickel removal at equilibrium increased with increasing adsorption dose.
5. A series of mathematical expressions can be derived to describe the adsorption of nickel by peat, and its kinetics.

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