

Batch and Kinetic Studies of Ni Adsorption on Highly Humified Newfoundland Peat

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Abstract This study employed batch tests with a saprist peat soil from Newfoundland for adsorbing Ni. The pseudo second order kinetic model with regression coefficients near one was used to determine the kinetic parameters at solution pH of 5.5 for peat doses of 4, 10, 21 and 40 g/L and solution concentrations of 25, 50, 125 and 200 mg/L. Equilibrium sorption parameters were determined for the Langmuir and Freundlich isotherms. The Langmuir isotherm provided the better fit. Over 90% of Ni removal was obtained. Adsorption was strongly influenced by the peat dose and initial metal concentration.

Key Words adsorption isotherm, capacity, intensity, peat dose

Introduction

The metals industry relies heavily on metal precipitation and neutralization processes for effluent treatment but these methods may not be economical or efficient (Zamlow et al., 1990, Brown et al., 2000, Abu Qdais and Moussa, 2004). Concentrations of Ni in the environment depend on soil geology and industrial activities. Ni mining (with Co recovery) in Newfoundland and Labrador (NL) could become a source of pollution if lime precipitation only is used for effluent treatment and the accumulation of the metal in aquatic organisms and plants could pose a serious health risk to humans, animals, and the environment soon if better metal recovery is not in place and enforced. This is because Ni and some of its compounds have been reported to be carcinogen.

Peat lands occupy $\approx 13.4\%$ of the total land area of NL (Daigle and Gautreau-Daigle, 2001) and peat has emerged as a low cost adsorbent. Studies (Coupal and Lalancette, 1976; Gosset et al., 1982; Zhipei et al., 1984; Ho et al., 1995; Crist et al., 1996; Ho and McKay, 1999; Brown et al., 2000) using fibrist peat with varying pre-treatments, have shown it is effective for adsorbing metals but the uptake mechanisms are not fully understood. This study is aimed at establishing the kinetic and sorption equilibria parameters for the uptake of Ni with a saprist NL peat to determine how the peat can be used alone or integrated into a treatment train for metals removal from effluents.

Experimental

Materials

Saprist peat, obtained from a natural bog owned by Traverse Nurseries, Torbay, NL was air dried and sieved and fractions $\leq 850 \mu\text{m}$ constituting about 90% of the peat were separated and used. Analytical grade Nickel (II) nitrate hexahydrate (Anachemia Chemicals) were diluted in distilled water. Solution pH was measured with an ATI Orion 3000 pH/mV/temperature meter supplied by VWR Scientific and adjusted as necessary with 0.25M H_2SO_4 from Fischer Scientific. Equilibrium sorption tests were performed in 50 mL plastic serum bottles containing 40 mL of 25, 50, 125, and 200 mg/L of Ni combined with 0.16, 0.4, 0.84, and 1.6g air dried saprist peat. Kinetic tests were performed in 500 mL plastic serum bottles containing 500 mL of 25, 50, 125 and 200 mg/L of Ni with 2, 5, 10.5 and 20g of air dried saprist peat. The bottles were agitated at high speed on an Eberbach 5900 reciprocal shaker for 0.5, 1 and 2 h intervals for kinetic tests and 24h for sorption tests.

Analysis of Samples

Samples were filtered through 45 μm pore size quantitative filter paper (Anachemia Chemicals) and solutions were acidified with a drop of 0.5 M H_2SO_4 and analysed on a Varian SpectraAA-55 atomic absorption spectrometer (Chemistry Department, Memorial University of NL) in air-acetylene flame at a wavelength of 238nm in absorbance mode.

Peat-Metal Adsorption Kinetics

The pseudo-second order model developed by Gosset et al., (1984) and simplified by Ho and McKay (2000) was used and is shown as equation 1.

$$\frac{t}{q_t} = \frac{1}{K_{1,ad} q_e^2} + \frac{1}{q_e} t \tag{1}$$

In this equation q_t the adsorbed quantity at any time is defined by $q_t = (C_i - C_t)V / M$ in which C_i and C_t are the initial and time t measured metal concentrations (mg/L), V is the volume (L) of contaminant and M is the mass (g) of adsorbent.

A plot of t/q_t versus t is linear and the slope is the reciprocal of the quantity of metal adsorbed at equilibrium q_e (mg/g), while the intercept is the reciprocal of the product of the square of the quantity of metal adsorbed at equilibrium and the pseudo-second order rate constant $K_{1,ad}$ (g/mg.h).

Peat-Metal Uptake Equilibrium

Metal sorption with single solute systems has been mostly represented by the Langmuir and Freundlich isotherm equations (Cooney, 1999). The Langmuir-Freundlich and Redlich-Peterson (modified Radke and Prausnitz) equations have been employed occasionally.

The Langmuir isotherm (equation 2) is a linearized form for monolayer adsorption and is based on the assumption that all active sites possess equal adsorption energy (Ng et al., 2002).

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b q_m C_e} \tag{2}$$

A plot of $1/q_e$ vs $1/C_e$ gives a straight line of slope $1/bq_m$ and intercept of $1/q_m$, where q_m is the monolayer maximum (saturation) capacity that q approaches as the equilibrium concentration, C_e , becomes large (Conney, 1999). It (q_m) is a strong parameter for comparing adsorption capacity (Ho et al., 1995) for potential adsorbents. The constant, b represents the ratio of the rates of adsorption to desorption (Conney, 1999).

Adsorption data with a liquid phase are well represented by the Freundlich isotherm (Cooney, 1999) and equation 3 is its linearized form.

$$\log q = \log K + \frac{1}{n} \log C_e \tag{3}$$

A plot of $\log q$ vs $\log C_e$ gives a straight line with a slope of $\log 1/n$ (Freundlich exponent) and an intercept of $\log K$ (Freundlich constant). Both $1/n$ and K are a measure of the adsorption capacity (Dobbs and Cohen, 1980) and are dependent on factors such as temperature and pH (Cooney, 1999).

Table 1 Variations of Peat dose, Initial Metal Conc., Contact Time and Adsorbed Ni for Kinetic Study at pH 5.5

Peat dose (g/L)	4				10				21				40			
Conc. (mg/L)	25	50	125	200	25	50	125	200	25	50	125	200	25	50	125	200
q_t (mg/g)																
Time (h)																
0.5	4.3	6.4	10.5	9.7	2.2	3.8	7.2	8.9	1.1	2.2	2.5	7.9	0.6	1.2	2.7	4.1
1.0	4.6	6.8	9.9	4.7	2.2	4.2	7.4	9.1	0.9	2.3	4.6	6.3	0.6	1.2	2.7	4.0
1.5	4.8	7.6	10.7	3.9	2.3	4.0	7.4	9.3	1.1	2.1	4.5	6.4	0.6	1.2	2.7	4.0
2.0	4.9	6.7	10.4	7.9	2.3	4.0	7.6	9.8	1.1	2.1	4.5	6.5	0.6	1.2	2.7	4.1
3.0	4.9	6.9	9.5	6.0	1.6	4.8	7.4	9.5	1.1	2.2	4.5	6.3	0.6	1.2	2.7	4.0
4.0	4.8	6.4	10.3	7.9	1.5	4.8	7.4	9.4	1.1	2.2	4.6	6.3	0.6	1.2	2.8	4.0
5.0	4.9	6.9	9.5	6.8	2.3	4.0	7.5	9.4	1.1	2.2	4.6	6.6	0.6	1.2	2.7	4.0
6.0	5.0	6.7	9.8	6.8	2.3	4.0	7.9	10.4	1.1	2.2	4.7	6.7	0.6	1.2	2.8	4.0
8.0	4.7	7.1	9.1	6.2	2.3	4.0	7.5	9.8	1.1	2.2	4.6	6.7	0.6	1.2	2.8	4.1
10.0	4.5	6.1	8.9	8.5	2.2	4.0	7.3	11.2	1.1	2.2	4.6	6.7	0.6	1.2	2.7	4.1

Table 2 Summary of Pseudo-Second Order Kinetic Parameters at pH 5.5

Peat dose (g/L)	4			10			21			40		
Conc. (mg/L)	q_e (mg/g)	$K_{1,ad}$ (g/mg.h)	R^2	q_e (mg/g)	$K_{1,ad}$ (g/mg.h)	R^2	q_e (mg/g)	$K_{1,ad}$ (g/mg.h)	R^2	q_e (mg/g)	$K_{1,ad}$ (g/mg.h)	R^2
25	4.56	-151.57	0.996	2.26	1.21	0.954	1.13	35.19	0.999	0.6	14.57	0.998
50	6.41	-1.01	0.990	25.38	-0.13	0.985	54.64	-0.06	0.985	64.93	-0.04	0.982
125	9.13	-0.59	0.996	69.44	-0.09	0.991	322.58	-44.29	0.984	909.09	-55	0.985
200	7.91	0.19	0.929	10.81	0.3	0.988	6.74	1.79	0.999	4.1	5.55	1

Results and Discussion

Kinetic Parameters for Ni Adsorption

The kinetic data for Ni uptake at constant pH and varying peat doses and metal concentrations are summarized in Table 1. The data fits the pseudo-second order model as the regression coefficients for Ni uptake were near unity for t vs t/q plots as shown in Table 2. The kinetic equilibrium time was ≈ 8 – 10 h and was metal concentration dependent. The kinetic constants from the plots showed that over the range of studied times, the equilibrium concentration of metal in solution was higher at a lower peat dose and the cation removal was higher at a higher peat dose. This might be due to the mode of metal binding between the readily available active sites when the peat dose is small compared to when the peat dose is large. With a large peat quantity, packing could lead to the overlapping of the pores containing the active sites making them inaccessible to the mobile cations at the initial reaction time. This could however be eliminated by consistent agitation during the kinetic study. At a low peat dose, this observation may be negligible.

From Table 2, it is evident that initial metal concentration of 125 mg/L gave the highest Ni equilibrium adsorption for all peat doses used. Equilibrium adsorption could have been attained in a short time due to the predominant reaction or the combination of two or more reactions. The equilibrium trend could be important in column experiments as packing of the peat soil could result in different orientation of the active sites and may affect the metal active mass transfer zone of the peat bed directly dictating replacement and maintenance of the adsorption column.

Equilibrium adsorption isotherms

At a constant pH, the constants for the Langmuir and Freundlich adsorption isotherms were determined as presented in Table 3. The two models described the sorption data, with the Langmuir model giving a better prediction as regression coefficients were closer to unity.

As the peat dose increased the Freundlich constant decreased while the exponent increased. Since the Freundlich equation is characterized by heterogeneous adsorption sites, increased peat dose could be reducing the heterogeneity of the active sites. On the other hand as the peat dose increased, no clear trend was observed for the Langmuir monolayer capacity though a maximum value was obtained at 10 g/L.

Table 3 Summary of Equilibrium Adsorption Parameters of Ni at pH 5.5

Peat dose (g/l)	Langmuir Parameters			Freundlich Parameters		
	$b \cdot 10^{-3}$	q_m	R^2	$1/n$	K	R^2
4	8.42	24.03	0.928	0.56	0.72	0.971
10	3.76	25.37	0.998	0.81	0.16	0.993
21	2.29	20.58	0.995	0.93	0.05	0.995
40	1.04	23.85	0.999	0.96	0.03	0.999

Table 4 % Nickel removed for 100 mg/L initial metal concentration at pH 5.5

As the peat dose increased, the active sites became more equally available to metal cations

Peat dose (g/L)	4	10	21	40
% Ni removed	45	83	91	94

reducing competition for ions. Also as the peat dose increased the Langmuir constant decreased showing that the rate of desorption of adsorbed metal rapidly decreased and approached zero. At a large peat dose metals desorption might be completely neglected in design. The percent of metal removed is summarized in Table 4.

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