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REMOVAL OF CADMIUM AND NICKEL FROM AQUEOUS SOLUTION USING EXPANDED PERLITE

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Abstract - The adsorption characteristics of cadmium and nickel onto expanded perlite from aqueous solution have been investigated with respect to changes in pH of solution, adsorbent dosage, contact time and temperature of the solution. The maximum removal efficiency of Cd (II) is 88.8% at pH 6 and exposure to 10 g/L expanded perlite, while for Ni (II), it is 93.3% at the same pH and exposure to 8 g/L adsorbent. For the adsorption of both metals, the Freundlich isotherm model fitted the equilibrium data better than the Langmuir isotherm model. Experimental data are also evaluated in terms of kinetic characteristics of adsorption and it was found that the adsorption process for both metal ions follows well pseudo-second-order kinetics. Thermodynamic functions, the change of free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) of adsorption are also calculated for each metal ion. The results show that the adsorption of these metal ions on expanded perlite is feasible and exothermic at 20-50°C.
Keywords: Expanded Perlite; Cadmium; Nickel; Adsorption; Kinetics.

INTRODUCTION

The progressive increase of industrial technology results in a continuous increase of pollution, so that a great effort has been devoted to minimizing these hazardous pollutants and, therefore, avoiding their dangerous effects on animals, plants and humans. Metals can pose health hazards if their concentrations exceed allowable limits. Even when the concentrations of metals do not exceed these limits, there is still a potential for long-term contamination, since heavy metals are known to be accumulative within biological systems (Ong et al., 2007; Morais Barros et al., 2006, Silva et al., 2003). Cadmium, zinc, copper, nickel, mercury, and chromium are often detected in industrial wastewaters, which are originated from metal plating, mining activities, smelting, battery manufacture, pesticides, nuclear industry, etc. Several methods have been applied over the years in order to eliminate these metal ions from industrial waste waters and soils. The common traditional methods used for removal of heavy metal ions from aqueous solutions include ion-exchange, solvent extraction, chemical precipitation, phytoextraction, ultra-filtration, reverse osmosis, electrodialysis and adsorption.

Adsorption using low-cost adsorbents has been effectively applied to remove heavy metals from aqueous solutions (Unlü and Ersoz., 2006). Cadmium and nickel are of major concern because of their frequent handling in developing countries and their non-degradable nature. Cadmium is one of the heavy metals with the greatest potential hazard to

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humans and the environment. Chronic exposure to elevated level of cadmium is known to cause renal dysfunction, bone degeneration, liver damage, and blood damage. The chronic toxicity of nickel to humans and the environment is also well-known and high nickel concentrations cause gastrointestinal irritation and lung and bone cancers. In recent years, various adsorbents have been used for removal of Cd (II) and Ni (II) from aqueous solution (Benguella and Benaissa, 2002; Gomez-Salazar et al., 2003; Gupta et al., 2003; Singh et al., 2005; Nwabanne and Ibbokwe, 2008). However, new adsorbents with local availability, high adsorption capacity and composed of economical materials are still needed.

Perlite is a naturally occurring dense, glassy volcanic rhyolitic rock and can be expanded up to 20 times its original volume when heated rapidly at 800-1200°C (Alkan and Dogan, 2002). Expanded perlite (EP) acts as an excellent insulator, both thermal and acoustical, resists fire and is classified as an ultra-light weight material. The expanded perlite is white in color, and has a density of about 32 g/L. Perlite is generally chemically inert and has a pH of approximately 7. Perlite is very cheap and easily available in Iran markets. The cost of expanded perlite is less than US$ 0.2 per kg in Iran. This could make it a viable candidate as an economical adsorbent for removing heavy metals such as lead, copper, cadmium and chromium (Alkan and Dogan, 2001; Chakir et al., 2002; Sarı et al., 2007a).

The objective of the present study is to investigate the adsorption potential of Iranian expanded perlite (EP) in the removal of Cd (II) and Ni (II) ions from aqueous solution. The effects of pH, adsorbent dosage, contact time and temperature on adsorption capacity of EP have been investigated. The Langmuir and Freundlich isotherms models are used to investigate equilibrium data. The adsorption mechanisms of Cd (II) and Ni (II) ions onto EP are also evaluated in terms of kinetics and thermodynamics.

EXPERIMENTAL

Expanded perlite samples were obtained from Kaneh Azar Co. (Tabriz, Iran). The expanded perlite was used without any chemical treatment for the sorption reported here. The chemical composition of the perlite determined by XRF is given in Table 1. The specific surface area of expanded perlite is $1.89 m^2/g$. It was measured by BET N_2 adsorption. The particle size ranged between 10 and 40μm and its porosity was 82%. Cadmium and nickel solutions and standards were prepared by using analytical grade cadmium chloride ($CdCl_2$) and nickel chloride ($NiCl_2.6H_2O$). The solutions of Cd (II) and Ni (II) were prepared from stock solutions containing 1000 mgL^{-1} of Cd (II) and Ni (II), respectively. All the solutions in the study were prepared using double distilled water.

Table 1: Chemical composition of expanded perlite

Constituent	Percentage (wt. %)
SiO_2	79.6
Al_2O_3	11.5
K_2O	4.8
CaO	0.8
Fe_2O_3	0.8
Na_2O	0.5
MgO	0.5
SO_3	0.2
TiO_2	0.1
MnO_2	0.065
Loss on ignition	1.135

Adsorption experiments were carried out at the desired pH value, contact time and adsorbent dosage level using the necessary adsorbent in 250mL conical flasks containing 100mL of the metal ion solutions. The flasks were sealed with Parafilm "M". The initial concentrations of both metals were 5, 10, 20, 30, 40, and $50 mgL^{-1}$. Samples were collected at 5, 10, 20, 30, 45, 60, 90, 120, 150, and 180 min to determine optimal shaking time. The pH values were adjusted to 3, 4, 5, 5.5, 6, 6.5, 7, and 8 using 0.1M NaOH or HNO_3 solution. The effect of adsorbent dosage on Cd (II) and Ni (II) removal was studied by using 10 mgL^{-1} initial Cd (II) and Ni (II) concentrations in conjunction with 1, 2, 4, 6, 8, 10, 12, and 15 gL^{-1} of expanded perlite. The adsorption studies were also carried out at 20, 30, 40, and 50°C to determine the effect of temperature and to evaluate the adsorption thermodynamic parameters. During the adsorption process, the flasks were agitated on a shaker at 170rpm. The contents of the flasks were filtrated through filter paper and the filtrate was analyzed for metal concentration by using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The amount of Cd (II) and Ni (II) absorbed per unit mass of adsorbent (q_e) was calculated from the following equation.

$$q_e = \frac{V(C_i - C_e)}{M} \quad (1)$$

where C_i and C_e represent initial and equilibrium concentrations of metal ions in aqueous phase, respectively. V is the volume of the solution in liters

(L) and M is the mass of the adsorbent in grams. The adsorption percentage of metal ions was calculated as follows:

$$\text{Adsorption}(\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

where C_i and C_f are the initial and final metal ion concentrations, respectively.

The average absolute value of relative error, AARE, is used to compare the predicted results with the experimental data. This is defined as follows:

$$\text{AARE} = \frac{1}{\text{NDP}} \sum_{i=1}^{\text{NDP}} \frac{\left|\text{Predicted value-Experimental value}\right|}{\text{Experimental value}}$$

in which NDP is the number of data points.

RESULTS AND DISCUSSION

Effect of Adsorbent Dosage

Adsorbent dosage is one of the important parameters in adsorption processes because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate under a given set of operating conditions. Figure 1 shows the effect of adsorbent dosage on the adsorption of Cd (II) and Ni (II) ions. As can be seen in this figure, the adsorption percentage increases with increasing adsorbent dosage from 33 to 87% for Cd (II) and from 43 to 90.5% for Ni (II) ions. The increase in the removal efficiency may be attributed to the fact that, with an increase in the adsorbent dosage, more adsorbent surface is available for the solute to be adsorbed (Gence et al., 2003). This figure shows that the adsorption percentage becomes almost constant at 10 g/L for Cd (II) and at 8 g/L for Ni (II). On this basis, these values are used for further experiments.

Effect of pH

The pH of the adsorbate solutions has been identified as the most important parameter governing sorption of metal ions on different adsorbents. This is partly due to the fact that hydrogen ions themselves are a strong competing sorbate and partly to the fact that the solution pH influences the chemical speciation of metal ions. The effect of pH on adsorption of cadmium and nickel ions onto EP is shown in Figure 2. As shown in this figure, at low pH values, the adsorption percentage is low due to the increase in positive charge density(protons) on the surface sites, resulting in electrostatic repulsion between the metal ions (Cd^{2+} or Ni^{2+}) and edge groups with positive charge ($Si\text{-}OH^{2+}$) on the surface. Electrostatic repulsion decreases with increasing pH because of the reduction of positive charge density on the sorption edges, thus resulting in an increase in metal ion adsorption on the surface. In an alkaline medium, the surface of EP becomes negatively charged. According to Figure 2, the maximum adsorption of both metal ions occurred at pH 6.0. At pH values higher than 6, metal precipitation occurred and adsorbent capacity was decreased with accumulation of metal ions. Therefore, an optimum pH 6.0 was selected for further experiments.

Effect of Shaking Time

The effect of shaking time on adsorption of Cd (II) and Ni (II) on EP is illustrated in Figure 3. This figure indicates that the metal concentration in aqueous solution decreases rapidly during first 30 min and remains nearly constant after 120 min for Cd (II) and 105 min for Ni (II), suggesting that the adsorption of both metal ions is fast. Therefore, 120 min and 105 min are selected as optimum shaking times for Cd (II) and Ni (II), respectively.

Adsorption Isotherm Models

The equilibrium adsorption isotherm is of fundamental importance in the design of adsorption systems. The Langmuir model, which is valid for monolayer adsorption onto a surface containing a finite number of identical sites, is the model most frequently used to represent data on adsorption from solution. The exact shape of the adsorption isotherm for a heterogeneous adsorbent will depend on the distribution of the K_L values or, more specifically, on the frequency distribution of the adsorption energies of site on the adsorbent (Langmuir, 1918; Do, 1998). This model can be expressed as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

or $$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

where q_e is the equilibrium metal ion concentration on the adsorbent (mg/g), C_e the equilibrium metal ion concentration in the solution (mg/L), q_m the monolayer adsorption capacity of the adsorbent (mg/g) and K_L represents the Langmuir adsorption constant (L/mg), related to the free energy of adsorption. This type of adsorption is valid when: (i) the adsorbent surface is homogeneous; (ii) both surface and bulk phases exhibit ideal behavior; and (iii) the adsorption film is monomolecular.

The Freundlich model (Weber, 1972; Do, 1998) is an empirical equation and can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. The equation is commonly given by:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F is a constant related to the adsorption capacity and 1/n is a empirical parameter related to the adsorption intensity, which varies with the heterogeneity of the material.

The non-linearized form of the Langmuir isotherm is used to obtain the constants of this model. The Langmuir model constants are given in Table 2. The correlation coefficient (R^2) is found to be 0.93 for the adsorption of Cd (II) ion and 0.953 for the adsorption of Ni (II) ion indicating that the Langmuir model is able to describe adsorption of both metal ions adequately. The value of the maximum capacity (q_m) is found to be 1.79 (mg/g) for Cd (II) ions and 2.24 (mg/g) for Ni (II) ions. The K_L value is 0.919 (L/mg) for Cd (II) ion and 1.922 (L/mg) for Ni (II) ion.

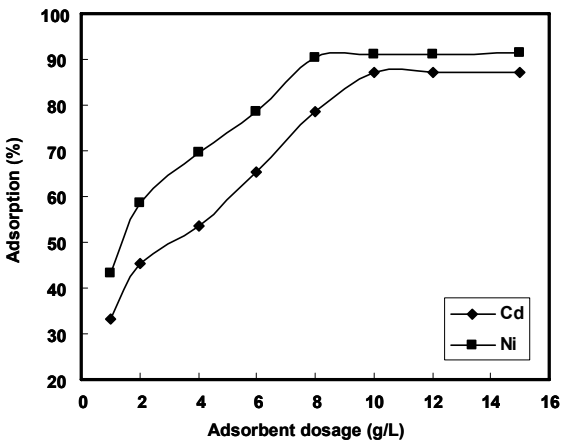

Figure 1: Effect of adsorbent dosage on the adsorption of Cd (II) and Ni (II) onto EP (metal concentration: 10 mg/L; temperature: 20ºC)

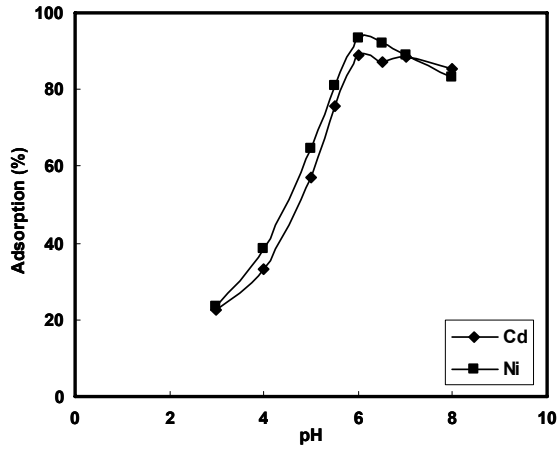

Figure 2: Effect of pH on the adsorption of Cd (II) and Ni (II) on EP (metal concentration: 10 mg/L)

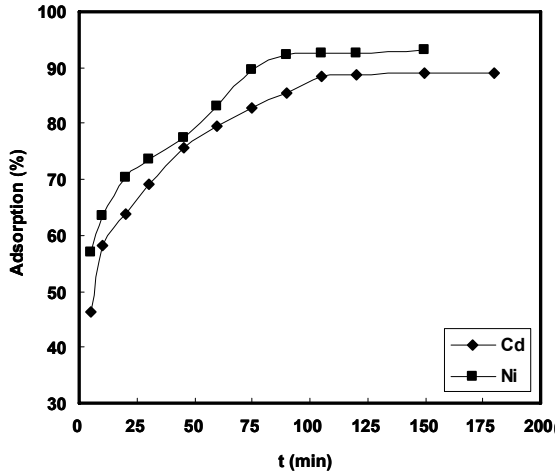

Figure 3: Effect of contact time on the adsorption of Cd (II) and Ni (II) on EP (metal concentration: 10 mg/L; temperature: 20ºC)

Table 2: Langmuir and Freundlich constants for adsorption of Cd (II) and Ni (II) on EP

	Langmuir model				Freundlich model		
Metal ions	**q_m (mg/g)**	**K_L (L/mg)**	**R**	**AARD%**	**1/n**	**K_F**	**AARD%**
Cd (II)	1.791	0.919	0.0352-0.851	14.59	0.263	0.79	4.88
Ni (II)	2.24	1.922	0.0169-0.866	14.72	0.20	1.22	6.42

The shape of the isotherm can also be considered when predicting whether an adsorption system is "favorable" or "unfavorable". The essential characteristic of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor or equilibrium parameter R (Alkan and Dogan, 2001), which is defined by the following equation:

$$R = \frac{1}{1 + K_L C_e} \tag{5}$$

According to the value of R, the isotherm shape may be interpreted as given in Table 3. As shown in Table 2, the adsorption of Cd (II) ion and Ni (II) ion onto perlite is favorable. A plot of ln q_e vs ln C_e enables the empirical constants K_F and 1/n to be determined from the intercept and slope of the linear regression. Fig. 5 shows the Freundlich isotherm obtained by plotting ln q_e versus ln C_e values. Table 2 also presents the results for the Freundlich isotherm model constants and correlation coefficient. The values of K_f and 1/n are found to be 0.79 and 0.263 for Cd (II) ion and 1.22 and 0.20 for Ni (II) ion. The 1/n values are between 0 and 1, indicating that the adsorption of both metal ions onto EP is favorable under the selected operating conditions.

The R^2 values are found to be 0.985 and 0.980 for Cd (II) ion and Ni (II) ion, respectively. The comparison of experimental data with the values of q_e obtained by both models is shown in Figs. 4 and 5. As can be seen in these figures, the adsorption results obtained are best described by the Freundlich isotherm model.

Table 3: Separation factor for shape of isotherm

Value R	Type of adsorption
R>1.0	Unfavorable
R=1.0	Linear
0<R<1.0	Favorable
R=0	Irreversible

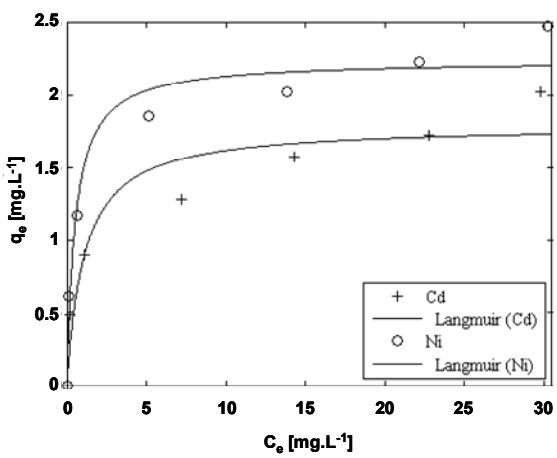

Figure 4: Comparison of the experimental data with the q_e values obtained by Langmuir isotherms

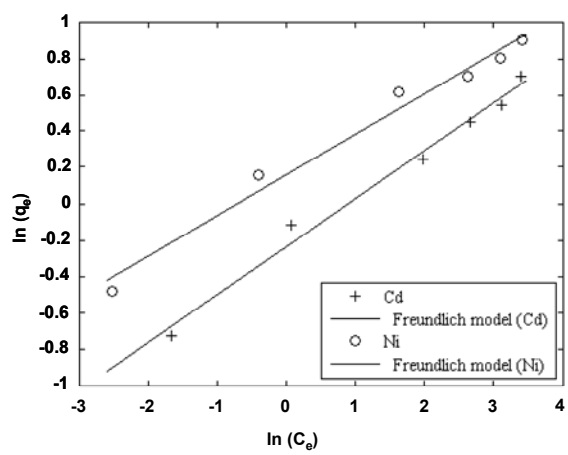

Figure 5: Comparison of the experimental data with the q_e values obtained by Freundlich isotherms

Adsorption Kinetics

In order to clarify the adsorption kinetics of Cd (II) and Ni (II) ions onto EP Lagergren pseudo-first-order and pseudo-second-order kinetic models are applied to the experimental data. The Lagergren pseudo-first-order rate equation (Lagergren, 1989) used by researchers to study the kinetics of heavy metals adsorption is as follows:

$$\ln(q_e - q_t) = \ln q_t - k_1 t \tag{6}$$

where q_t (mg/g) is the amount of the metal ion adsorbed at t (min) and k_1 is the rate constant of the adsorption (min^{-1}). Fig. 6 shows the Lagergren pseudo-first-order model for the kinetics of cadmium and nickel adsorption on EP.

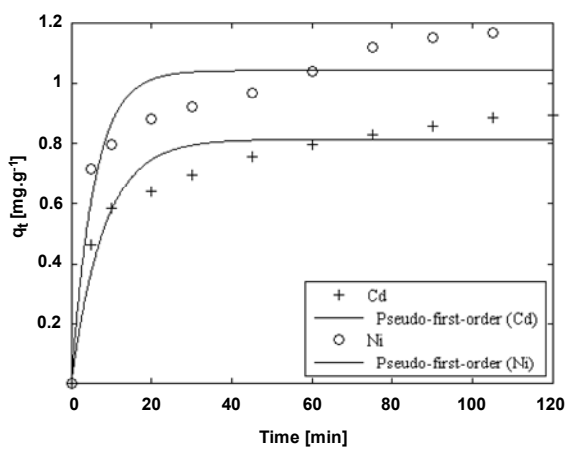

Figure 6: The Lagergren pseudo-first-order model plot for cadmium and nickel adsorption on expanded perlite

Ho and McKay (1999) used a pseudo-second-order reaction rate equation to study the kinetics of adsorption of heavy metals on peat. The pseudo-second-order equation is given by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_t^2} + \left(\frac{1}{q_e}\right) t \tag{7}$$

where k_2(g/mg min) is the rate constant of the pseudo-second-order equation. This model is more likely to predict the kinetic behavior of adsorption with chemical sorption being the rate controlling step (Wen et al., 2006).

The rate constant (k_2) and correlation coefficient of this equation are listed in Table 4. It is clear from the results that the adsorption of Cd (II) and Ni (II) ions onto EP follows well the pseudo-second-order kinetics. Fig. 7 shows Ho's pseudo-second-order model for the kinetics of cadmium and nickel adsorption on EP.

The first-order kinetic rate constants reported by a few other researchers are 1.398 h^{-1} for cadmium on fly ash (Mathialagan and Viraraghavan, 2002), and 0.44 h^{-1} for cadmium adsorption on Aspergillus niger biomass (Kapoor, 1998). A comparison of the first-order rate constants from the present study with other studies shows that the rate of cadmium and nickel adsorption on expanded perlite is quite rapid (Srivastava et al., 2009).

Adsorption Thermodynamics

The temperature range used in the study was from 20 to 50°C. Thermodynamic parameters, including the change in the free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°), were determined using the following equation:

$$\Delta G^\circ = -RT \ln K_D \tag{8}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{9}$$

where R is the universal gas constant (8.314 J/mol.K), T is the temperature (K) and K_D is the equilibrium constant. The enthalpy change (ΔH°) and entropy change (ΔS°) of adsorption are obtained from the following equation

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{10}$$

According to Equation (10), (ΔH°) and (ΔS°) parameters can be calculated from the slope and intercept of a plot of $\ln K_D$ versus 1/T, respectively (Fig. 8).

Table 4: Lagergren rate equation constants and pseudo-second-order rate equation constants for adsorption of Cd (II) and Ni (II) onto EP

	Lagergren rate equation			pseudo-second-order rate equation		
Metal ions	**k_1 (min^{-1})**	**R^2**	**AARD%**	**k_2 (g/mg min)**	**R^2**	**AARD%**
Cd (II)	0.124	0.933	8.44	0.213	0.994	6.05
Ni (II)	0.177	0.92	9.49	0.193	0.991	7.60

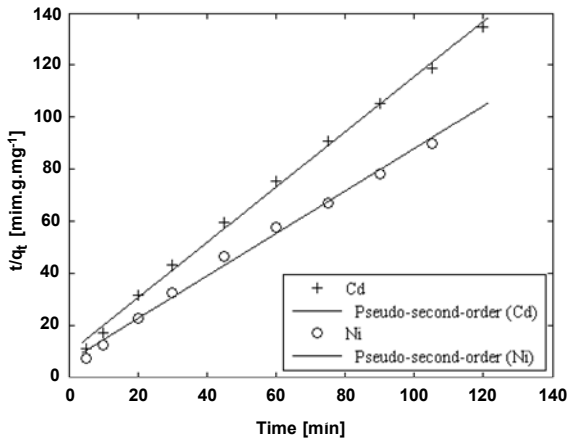

Figure 7: Ho's pseudo-second-order model plot for cadmium and nickel adsorption on expanded perlite

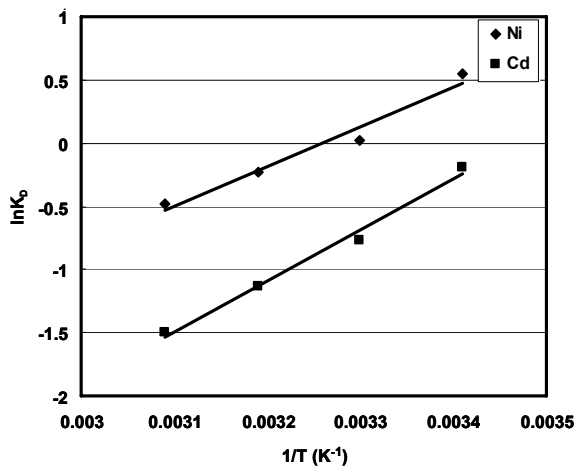

Figure 8: Plot of ln K_D vs. 1/T for estimation of thermodynamic parameters for the adsorption of Cd (II) and Ni (II) on EP (metal concentration: 10 mg/L).

From Equation (8), the Gibbs free energy change of adsorption (ΔG°) is calculated by using $\ln K_D$ values for different temperatures. The values of ΔG° are found to be 0.462, 1.944, 2.94 and 4.03kJ/mol for the adsorption of Cd (II) and -1.34, -0.3, 0.62 and 1.29kJ/mol for the adsorption of Ni (II) at 20, 30, 40 and 50°C, respectively.

The negative ΔG° values indicate that thermodynamically feasible and spontaneous nature of the adsorption of Ni (II) at 20 and 30°C. The positive and small values of ΔG° indicate that the process is feasible but non-spontaneous. The ΔH° parameter has a value of -33.82 and -26.48 kJ/mol for the adsorption of Cd (II) and Ni (II) ions, respectively. These negative values indicate the exothermic nature of the adsorption of both metal ions onto EP in the temperature range of 20-50°C. The values of ΔS° are found to be -117.44 and -6.31 J/mol.K for the adsorption of Cd (II) and Ni (II), respectively. The negative values of ΔS° suggest a decrease in the randomness at the solid/solution interface during the adsorption of Cd (II) and Ni (II) ions onto EP.

The adsorption capacities (q_m) of different adsorbents for adsorption of Cd (II) and Ni (II) ions under different environmental conditions reported in the literature are compared in Table 5. It may be seen that q_m values differ widely for different adsorbents. Comparison of q_m values shows that EP exhibits a reasonable capacity for Cd (II) and Ni (II) adsorption from aqueous solutions. The cost of the adsorbent is also an important issue that must be considered when selecting an adsorbent. The regeneration and reuse of perlite may also play an important role in making this a practical process. The cost of regeneration/disposal of the spent adsorbent would have to be considered in any detailed economic analysis required to determine the most economical adsorbent.

Table 5: Adsorption capacity of various adsorbents for the adsorption of cadmium and nickel

Cadmium			Nickel		
Adsorbent	**q_m (mg/g)**	**Reference**	**Adsorbent**	**q_m (mg/g)**	**Reference**
Red mud	106.064	Apak et al. (1998)	Seyitomer fly ash	1.174	Bayat (2002)
Seyitomer fly ash	0.224	Bayat (2002)	Pine bark	6.28	Villaescusa et al. (2000)
Aspergillus niger	4.0	Kapoor (1998)	Yohimbe bark	8.80	Bayat (2002)
Crushed coconut shell	0.91	Bhattacharya and Venkobachar (1984)	Baker's yeast	11.38	Padmavathy et al. (2003)
Giridh coal	0.83	Bhattacharya and Venkobachar (1984)	Grape stalks wastes	10.68	Villaescusa et al. (2004)
Akaganeite-type nanocrystals	17.02	Deliyanni and Matis (2005)	Afsin-Elbistan fly ash	0.998	Al-Asheh and Duvnjak (1998)
Rice husk ash	3.02	Srivastava et al. (2009)	Rice husk ash	4.87	Srivastava et al. (2009)
Corncob	5.04	Leyva-Ramos et al. (2005)	Bagasse fly ash	6.51	Srivastava et al. (2006)
Activated carbon	3.4	An et al. (2001)	Maple sawdust	0.294	Shukla et al. (2005)
Olive stone	7.33	Calero et al. (2009)	Tea factory waste	15.26	Malkoc and Nuhoglu (2005)
Expanded perlite	1.79	Present work	Expanded perlite	2.24	Present work

CONCLUSIONS

The adsorption behavior of Cd (II) and Ni (II) on expanded perlite was investigated in batch experiments. The adsorption was found to be drastically dependent on pH, adsorbent dosage, and contact time. The optimum pH for adsorption of both metal ions was found to be 6.0. The rate of Cd (II) and Ni (II) adsorption was rapid. The cadmium-perlite and nickel-perlite systems attained equilibrium in 120min and 105min, respectively. Isotherm analysis of the data showed that the adsorption pattern of both metal ions on EP followed the Freundlich model. Using the Langmuir model equation, the maximum capacity of EP was found to be 1.79 (mg/g) for Cd (II) ions and 2.24 (mg/g) for Ni (II) ions. The pseudo-second-order reaction rate model described the kinetic data best for both metal ions. Thermodynamic parameters depicted the exothermic nature of adsorption and the process was favorable.

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