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Effect of Temperature on Removal of Ni(II) from Aqueous Solutions by Adsorption onto Fire Clay

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The removal of Ni(II) from aqueous solutions by adsorption on fire clay has been studied as a function of temperature. The amount of Ni(II) removed is highly dependent on temperature and favours high temperature, thus showing endothermic nature of the process. Also the initial concentration of adsorbate affects the extent of adsorption significantly. The various rate parameters of the adsorption process have been determined at different temperatures. Activation energy of the process was found to be 34.59 kJ mol^{-1}. The uptake of Ni(II) exhibited Langmuir type adsorption behaviour which was also confirmed by regression analysis. The various thermodynamic parameters have been calculated to reflect the nature of the adsorption process.

INTRODUCTION

Heavy metals are among the most important pollutants in source and treated water and are becoming a severe public health problem. Although heavy metals removal from aqueous solutions has been traditionally carried out by chemical precipitation, electrode deposition, ultrafiltration, solvent extraction, etc., but in the last few years adsorption has proved to be the most significant and economically feasible alternative method for removal of trace metals from waste water and water supplies. Various conventional adsorbents such as activated carbon[1–7], metal oxides[8], hydrous oxide gels[9], goethite have been successfully used for this purpose. Moreover, non-conventional adsorbents like fly-ash[11, 12], bituminous coal dust[13], china clay[14], wood[15], sepiolite[16], etc. have also been attempted and proved to be more useful for poor and developing countries, as the process is more economical with these adsorbents. The present paper deals with the study of the feasibility of Ni(II) removal by fire clay as a function of temperature of the adsorbate solution.

EXPERIMENTAL

Fire clay was obtained from Bagharaji village in Jabalpur district of state Madhya Pradesh, and was fractionated into different fractions of varying particle sizes (100–290 μm) by passing through standard sieves of mesh sizes 52, 100 and 150 having geometrical mean particle diameters 290, 150 and 100 μm respectively. Although the fire clay was fractionated into different particle sizes 290, 150 and 100 μm, the adsorption experiments were, however, carried out with the adsorbent of particle size 150 μm. The surface area of the adsorbent was determined by a "three point" N_2 gas adsorption method. The porosity and density of adsorbent were determined by using a mercury porosimeter and specific gravity bottle, respectively. The adsorbent was analyzed by Indian standard methods of chemical analysis[17] of fire clay and silica refractory materials (Table-1).

TABLE-1
CHARACTERIZATION OF FIRE CLAY

Constituents	Weight (%)
Al_2O_3	23.0
SiO_2	68.0
Fe_2O_3	2.0
TiO_2	2.0
CaO	2.2
MgO	1.2
Other trace elements	1.6
Loss on ignition	7.0
Porosity	0.34
Surface area	12.56 $m^2 g^{-1}$
Specific gravity	1.38 $g cm^{-3}$

Batch adsorption experiments were carried out by shaking 1.0 g of the adsorbent with 25 mL of the aqueous solution of nickel sulphate, prepared in distilled water, of the desired concentration and pH in a temperature controlled shaking water bath. The initial pH of the solution was adjusted with 0.1 M NaOH and HCl, using a pH meter. Continuous mixing was provided during the experimental period with a constant agitation speed of 125 rpm. The remaining concentration of Ni(II) in each sample, after adsorption at different time intervals, was determined spectrophotometrically, using the dimethylglyoxime method and a spectronic-20 spectrophotometer set at a wavelength of 445 nm.

RESULTS AND DISCUSSION

It is clear from Table-1 that the main constituents of fire clay are Al_2O_3 and SiO_2 while other constituents are present in traces. So it is expected that the silica and alumina content of fire clay should play a major role in the removal of nickel.

Adsorption Kinetics

The adsorption of Ni(II) from liquid phase to solid phase can be considered as a reversible reaction[18, 19] of an equilibrium type:

$$S \underset{K_2}{\overset{K_1}{\rightleftharpoons}} A \tag{1}$$

with the reactions in both the directions of the first order. Here S and A represent solution phase and adsorbent phase respectively. Similarly, K_1 and K_2 are the rate constants for adsorption and desorption respectively. The resultant rate equation for the reaction may be expressed as

$$\ln [1 - u(t)] = K't \tag{2}$$

where $\mu(t)$ represents the fractional attainment of equilibrium and is given as

$$u(t) = q/q_e \tag{3}$$

Here q and q_e are the amounts (mg g^{-1}) of Ni(II) adsorbed at time 't' and at equilibrium respectively. Moreover,

$$K' = K_1(1 + 1/K_c) = K_1 + K_2 \tag{4}$$

where K′ is the overall rate constant (min^{-1}) and K_c is the equilibrium rate constant which may be given as

$$K_c = \frac{C_{a(e)}}{C_{s(e)}} = \frac{K_1}{K_2} \tag{5}$$

where $C_{a(e)}$ and $C_{s(e)}$ are the amounts of Ni(II) present at equilibrium on the adsorbent and in the solution phase respectively. The effect of temperature on the kinetics of adsorption of Ni(II) onto fire clay has been depicted in Fig. 1 which clearly shows that higher temperature favours adsorption. The overall rate constant K′ has been determined from the slope of the straight line plots of ln (1 − u(t)) versus t (Fig. 2) and have been summarized in Table-2.

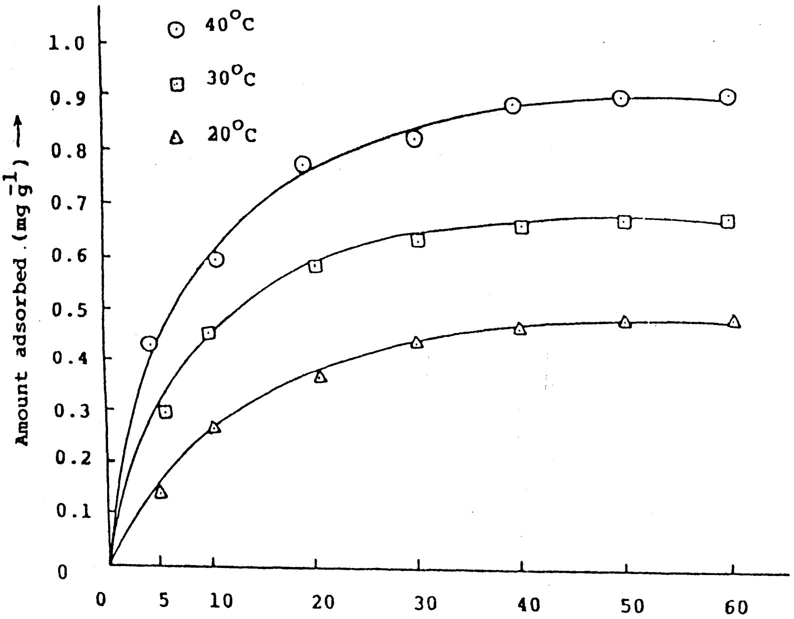

Fig. 1. Effect of temperature on kinetics of removal of Ni(II) from aqueous solutions. [Ni(II)] = 60 ppm; pH = 6.5, particle size = 100 μm.

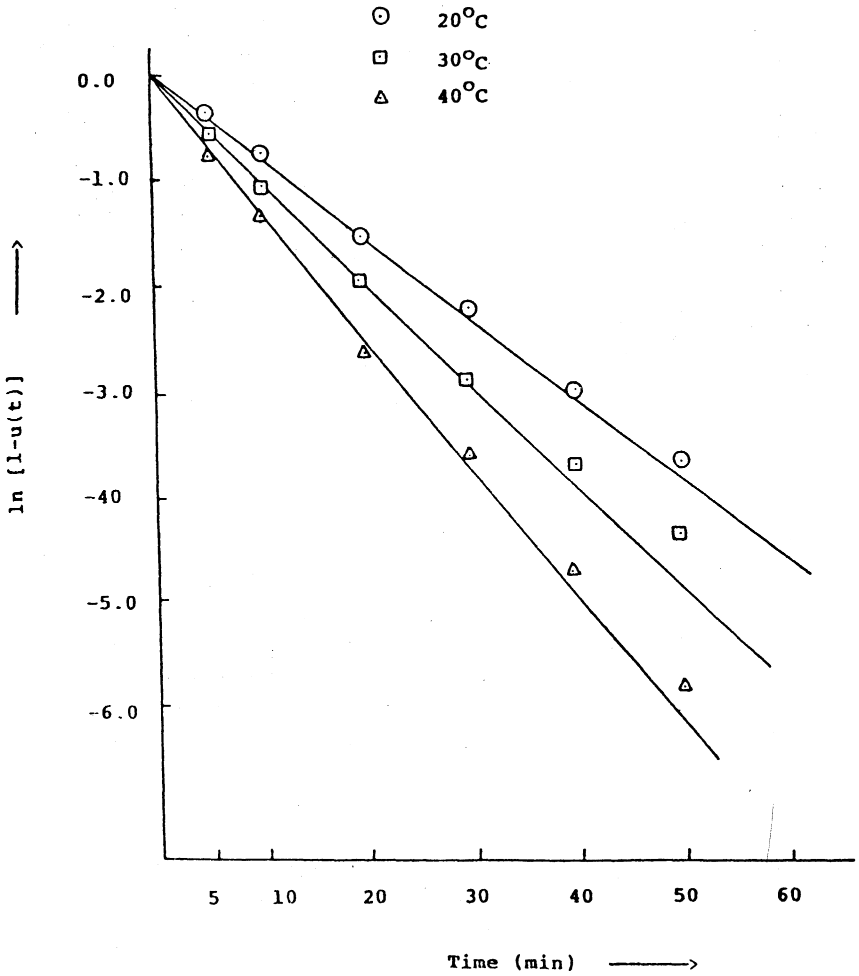

Fig. 2. First order reversible kinetic fit of Ni(II) uptake by fire clay at different temperatures. [Ni(II)] = 60 ppm; pH = 6.5; size = 100 μm.

TABLE-2

DATA SHOWING VALUES OF RATE CONSTANTS, INTRAPARTICLE TRANSPORT RATE CONSTANT (K_{id}) AND PORE DIFFUSION COEFFICIENT (D) AT DIFFERENT TEMPERATURES

[Ni(II)] = 60 ppm; pH = 6.5; size = 100 μm

Temperature (°C)	K′ (min^{-1})	K_1 (min^{-1})	K_2 (min^{-1})	K_{id} ($mg\ g^{-1}\ min^{-0.5}$)	D ($cm^2\ s^{-1}$) × 10^8
20	0.0750	0.0255	0.0495	0.0750	16.8750
30	0.0900	0.0407	0.0492	0.0500	24.0000
40	0.1100	0.0834	0.0465	0.0480	31.4621

The observed increase in the extent of adsorption with the solution temperature is due to increase in number of active surface centres available for sorption.[20] The increase in uptake of Ni(II) may also be due to enhanced rate of intraparticle diffusion of sorbate as the diffusion is an endothermic process.[21]

As the adsorbent fire clay is porous in nature, pore diffusion is also expected in addition to surface adsorption. In order to calculate the rate constant of intraparticle transport (K_{id}), curves were plotted between amount adsorbed (q_e) and square root of time ($t^{0.5}$) at different temperatures in accordance with the equation (6), given by Weber and Morris.[22]

$$q = k_{id}t^{0.5} \tag{6}$$

The values of K_{id} were calculated from the slopes of the linear portion of the respective plots (Fig. 3) with units of mg g^{-1} $min^{0.5}$ and have been summarized in Table 2.

The double nature of these plots (initial curved portions and final linear portions) may be explained by the fact that intial curved portions are due to boundary layer

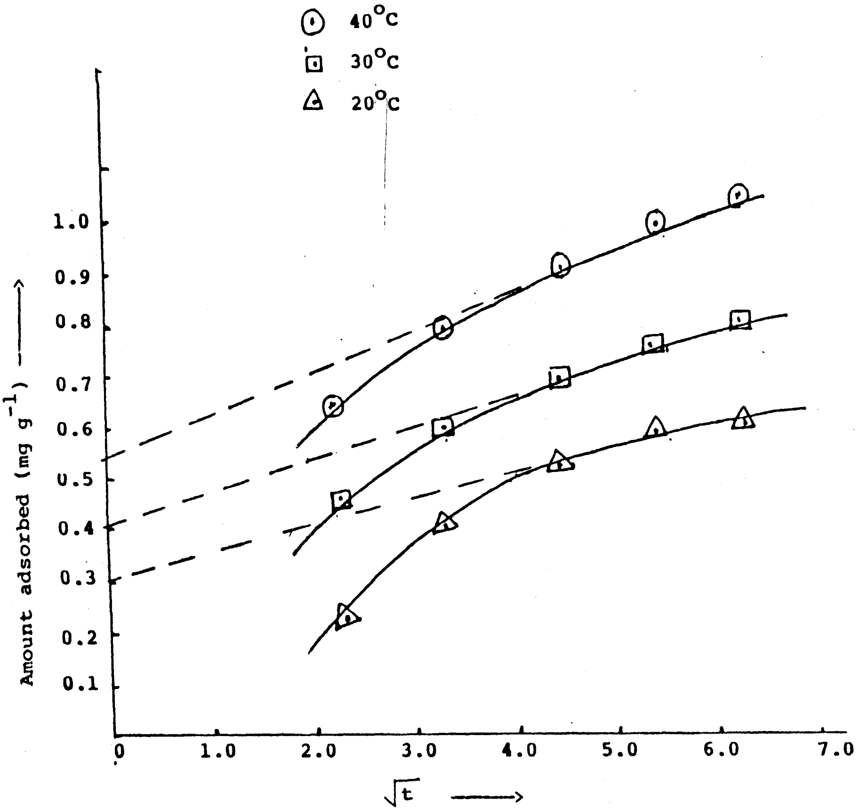

Fig. 3. Plots for the rate constants of pore diffusion at different temperatures [Ni(II)] = 60 ppm, pH = 6.5; size = 100 μm.

diffusion effects[23] while the final linear portions are a result of intraparticle diffusion effects.[24] Therefore the linear portions of the plots were extrapolated and slopes were determined to evaluate K_{id}. Moreover, the intercepts of these extrapolations on the axis are proportional to the extent of boundary layer thickness.

The pore diffusion coefficient D (Table-2) of Ni(II) within the pores of the adsorbent at various temperatures has been determined assuming spherical geometry for the adsorbent, by using the following equation[18]:

$$D = \frac{0.030 r_0^2}{t_{1/2}} \tag{7}$$

where r_0 is the radius of sorbent, D is the pore diffusion coefficient ($cm^2\ s^{-1}$), and $t_{1/2}$ is the time for half sorption.

The energy of activation was determined from the slope of the Arrhenius plot of ln K_{id} *vs.* l/T (Fig. 4) and was found to be 34.59 kJ mol^{-1}. The positive value of activation energy suggests that rise in solution temperature favours the removal of Ni(II) by adsorption on fire clay. Hence the process is endothermic in nature.

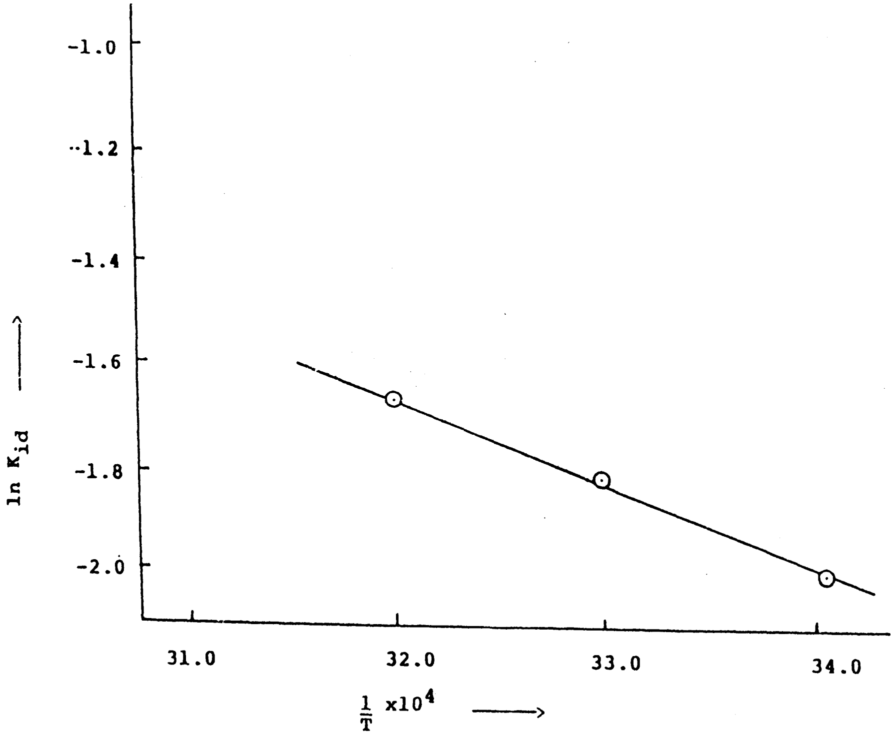

Fig. 4. Arrhenius plot for the determination of activation energy.
[Ni(II)] = 60 ppm, pH = 6.5, size = 100 μm.

Langmuir adsorption isotherm

The rearranged form of Langmuir adsorption isotherm equation is

$$\frac{C_e}{q_e}=\frac{K}{Q_0}+\frac{C_e}{Q_0} \tag{8}$$

where Q_0 is the adsorption capacity (mg g^{-1}) and C_e is concentration of Ni(II) in the solution at equilibrium. The plots of $\frac{C_e}{q_e}$ *vs.* C_e (Fig. 5) were found to be linear,

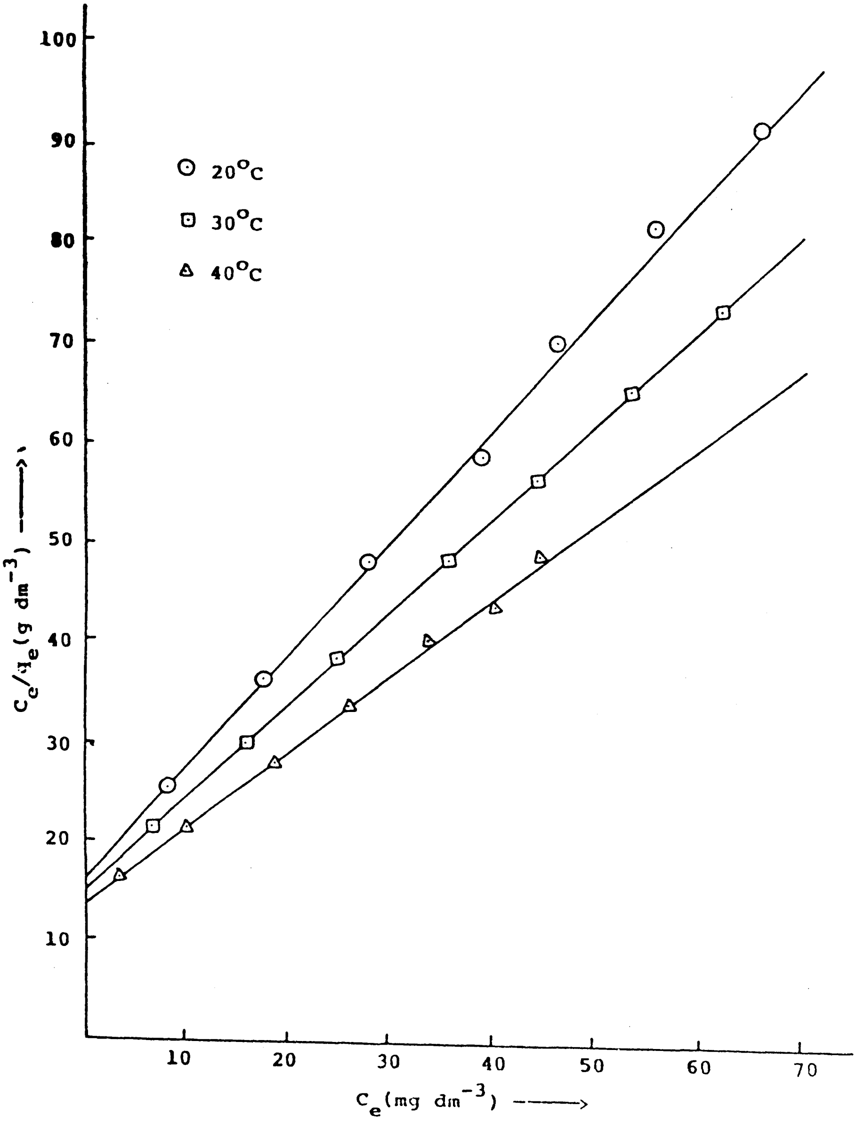

Fig. 5. Langmuir plot at different temperatures pH = 6.5; size = 100 μm.

thus suggesting the suitability of Langmuir type adsorption behaviour for the Ni(II) fire clay system. The values of Q_0 and K were determined from the slopes and intercepts of the straight line plots and have been summarized in Table-3. The increasing values of Langmuir constants with rise in temperature further support the experimental results.

TABLE-3
DATA SHOWING VALUES OF LANGMUIR CONSTANTS AT DIFFERENT TEMPERATURES

Ni(II) = 60 ppm; pH = 6.5; size = 100 μm

Temperature (°C)	Values of Q_0 and K at different temperatures			
	Graphical values		Regression values	
	Q_0 (mg g^{-1})	K (mg dm^{-3})	Q_0 (mg g^{-1})	K (mg dm^{-3})
10	0.833	13.332	0.821	13.021
30	0.952	14.923	0.938	14.236
40	1.200	16.800	1.211	16.532

The validity of the Langmuir isotherm was further confirmed by the regression analysis of the equilibrium data at different temperatures and are presented in the form of simple straight line equations:

$$\frac{C_e}{q_e} = 1.2180C_e + 15.8587 \text{ at } 20°C \qquad (9)$$

$$\frac{C_e}{q_e} = 1.0660C_e + 15.1775 \text{ at } 30°C \qquad (10)$$

$$\frac{C_e}{q_e} = 0.8264C_e + 13.6634 \text{ at } 40°C \qquad (11)$$

By comparing these equations with the Langmuir equations, Q_0 and K were calculated (Table-3) at different temperatures and were found to be in good agreement with graphical values.

Thermodynamic parameters

The thermodynamic parameters (Table-4) calculated for the uptake of Ni(II) are the standard free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°). The following equations were used to calculate the parameters:

$$\Delta G° = -RT \ln K \qquad (12)$$

$$\Delta H° = R\frac{T_1T_2}{(T_2 - T_1)} \ln \frac{k_2}{k_1} \qquad (13)$$

and

$$\Delta S° = \frac{\Delta H° - \Delta G°}{T} \qquad (14)$$

TABLE-4

DATA SHOWING THERMODYNAMIC PARAMETERS AT DIFFERENT TEMPERATURES FOR THE REMOVAL OF Ni(II) FROM AQUEOUS SOLUTIONS

[Ni(II)] = 60 ppm; pH = 6.5; size = 100 μm

Temp. (°C)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1})
20	–6.3025	8.6580	50.2031
30	–6.8131	8.9588	51.2074
40	–7.3332	—	—

The negative values of ΔG° indicate the spontaneous nature of the process and positive values of ΔH° is the indication of the endothermic nature of the uptake process. The positive entropy change (ΔS°) indicates rather slower interaction with the active sites of adsorbent.

Concentration Effect

The dependence of process of removal of Ni(II) from aqueous solutions of different initial concentrations (5–100 ppm) is illustrated in Table-5. At very low concentrations (below 20 ppm) sorption was 90–95%. This suggests that fire clay can be used to remove most of the Ni(II) from the solution at low initial concentrations. The examination of the data also reveals that at a fixed adsorbent dose, the amount adsorbed increases with the concentration of the solution but the percentage of adsorption decreases. In the case of lower concentrations the ratio of initial number of moles of metal to the available surface area is low; however at higher concentrations the available sites of adsorption become fewer and subsequently the percentage removal of metal ion depends upon the initial concentrations.

TABLE-5

EFFECT OF INITIAL CONCENTRATION ON THE ADSORPTION OF Ni(II) ONTO FIRE CLAY

pH = 6.5; temperature = 30°C; size = 100 μm

Initial conc. (ppm)	Amount adsorbed (mg g^{-1})	% Removal
5	0.1183	94.70
10	0.2335	93.40
15	0.3438	91.70
20	0.3417	68.34
40	0.5512	55.12
60	0.6812	45.41
80	0.8648	43.24
100	0.8791	35.16

Conclusions

By adjusting the temperature and dose of the adsorbent (fire clay), the Ni(II) concentration in water and wastewaters can be diminished below the permissible limit. The experimental finding, thus, may be helpful to environmental sanitary engineers for establishing plants for treatment of polluted water enriched in Ni(II). The cost of removal will be quite low as the adsorbent is quite cheap and available in large quantities.

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