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Adsorption of Nickel from aqueous solution by the use of low-cost adsorbents

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Abstract−The removal of Ni(II) from aqueous solution by different adsorbents was investigated. Calcined phosphate, red mud, and clarified sludge (a steel industry waste material) were used for the adsorption studies. The influence of pH, contact time, initial metal concentration, adsorbent nature and concentration on the selectivity and sensitivity of the removal process was investigated. The adsorption process was found to follow a first-order rate mechanism and rate constant was evaluated at 30 °C. Langmuir and Freundlich adsorption isotherms fit well in the experimental data and their constants were evaluated. The thermodynamic equilibrium constant and the Gibbs free energy were calculated for each system. The adsorption capacity (q_{max}) calculated from Langmuir isotherm and the values of Gibbs free energy obtained showed that calcined phosphate has a higher capacity and affinity for the removal of Ni(II) compared to the other adsorbents used in the study.

Key words: Calcined Phosphate, Red Mud, Clarified Sludge, Langmuir Isotherm, Freundlich Isotherm, Gibbs Free Energy, First-order Rate Mechanism

INTRODUCTION

Pollution by heavy metals is currently of great concern, due to the increased awareness of the potentially hazardous effects of elevated levels of these materials in the environment Nickel is commonly used in refining, electroplating and welding industries, and human exposure to nickel is highly probable in such environments. Nickel can cause a variety of pathologic effects like skin allergy, lung fibrosis and cancer [1-5]. The most important health problems due to exposure to nickel and nickel compounds are allergic dermatitis (nickel itch) and increased incidence of cancers. Nickel is genotoxic and mutagenic as well. Though there are very many harmful effects of nickel on human health, production of its compounds is essential and one has to look at the ways of reducing its entry into the environment from the waste streams. The health hazards of nickel in waters have been reported by many researchers [6,7]. The U.S. Environmental Protection Agency (EPA) requires nickel not to exceed 0.015 mg/*l* in drinking water [8]. Therefore, cost-effective treatment technologies are needed to meet these requirements of recovery and/or removal of metal ions. During the past years, increasing attention has been focused on the separation, pre-concentration and/or determination of trace metal ions in the environment. This field of interest is becoming a real challenge due to the specificity, accuracy and sensitivity required by more and more stringent regulations [9,10]. Conventional technologies for the removal of heavy metal such as chemical precipitation, adsorption, electrolysis, ion exchange and reverse osmosis are often neither effective nor economical [8-15]. Among the physico-chemical treatment processes, adsorption is found to be highly effective, cheap and easy to adapt. Activated carbon in most cases has been used as an adsorbent for reclamation of municipal and industrial wastewater for almost the last few decades [16-19]. But the high cost of activated carbon has inspired investigators, especially in developing countries like Tunisia, to search for suitable low-cost adsorbents.

As a result, recent research has focused on the development of cost-effective alternatives using various natural sources and industrial wastes [20-22]. Industrial wastes are potential low-cost adsorbents for metal removal since some of them display high ion exchange capability. Pretreatment of adsorbent is also commonly used to increase the adsorption capacity of these materials. Several researches have made significant contributions in this area, utilizing a number of materials including fly ash [23,24], sugar beet pulp [25], clay [26,27], chitosan [28], coconut coirpitch carbon [29], biomass [30, 31], zeolites [32,33], rice bran, soybeans and cotton seed hulls [34], sunflower stalks [35], low-grade phosphate [15], tea leaves [36], natural zeolite [37], almond shells, olive stones and peach [38], sediments of rivers [39], peanut hull [40], bentonite [41], saw dust [42, 43], baggage fly ash [44], banana and orange peels [45], carrot residue [46], etc. The objective of this study was to investigate comparative adsorption characteristics for removal of Ni(II) from aqueous solution by the use of low-cost abundantly available nonconventional adsorbents like calcined phosphate, red mud and clarified sludge. The effects of pH, contact time, adsorbent dosage level and initial metal concentration on the adsorption capacity were studied. During the work program, adsorption kinetics, isotherm models and thermodynamic parameters were also investigated.

MATERIALS AND METHODS

1. Adsorbents Used

Phosphate rock used here came from an extracted ore in Gafsa, Tunisia. The fraction of 100-400 μm grain size was washed with water, calcined at 900 °C for 2 h, washed again, calcined at 900 °C

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for 0.5 h and ground (63-125 μm). The structure of calcined phosphate (CP) is similar to that of fluorapatite. The chemical composition was determined as follows: Ca (54.12%), P (34.24%), F (3.37%), Si (2.42%), S (2.21%), C (1.13%), Na (0.92%), Mg (0.68%), Al (0.46%), Fe (0.36%), K (0.04%), and others metals in the range under 6 ppm.

The clarified sludge was collected from sludge thickener of Basic Oxygen Furnace of Steel Industry, Steel Authority of Russia Limited, Belgorod.

Red mud (RM) is a fine-textured residue from bauxite refining that is currently dumped in holding ponds, for which large areas of land are required. Its texture and composition (its principal components are oxides of Fe, Al, and Si) confer upon RM a high surface reactivity.

2. Reagents and Instruments

HACH-DR-4000 UV Visible Spectrophotometer was used for determination of Ni(II) content in standard and treated solution. The pH of the solution was measured with a 5500 EUTECH pH Meter using FET solid electrode calibrated with standard buffer solutions. A stock solution containing 1,000 mg/L of Ni(II) was prepared by dissolving pure nickel metal in 1 : 1 hydrochloric acid solution and then diluting the same up to 1,000 ml in a volumetric flask with double distilled water.

3. Batch Adsorption Studies

The necessary adsorbents were used in a 250 ml stopper conical flask that contained 100 ml of test solution. Batch adsorption studies were carried out at the desired pH value, contact time and adsorbent dosage level. Different initial concentration of Ni(II) solutions was prepared by dilution from stock 1,000 mg/L Ni(II) standard. pH of the solution was adjusted by adding 0.1 M HCl and 0.1 M NaOH solution as per required pH value. Necessary amount of adsorbent material was then added and contents in the flask were shaken for the desired contact time in an electrically thermostated reciprocating shaker at 110 strokes/min at temperature, i.e. 30±2 °C. The time required for reaching the equilibrium condition was estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered through filter paper and the filtrate was analyzed for Ni(II) concentration using HACH-DR-4000 UV Visible Spectrophotometer following standard methods for examination of water and wastewater, APHA, AWWA 20th edition [47].

The percent removal of Ni(II) was calculated as follows:

$$\%\text{Removal of Ni(II)} = \frac{C_{initial} - C_{final}}{C_{initial}} \times 100 \qquad (1)$$

where $C_{initial}$ and C_{final} are the initial and final Ni(II) concentrations, respectively.

Adsorption experiments for the effect of pH were conducted by using a solution having 25 mg/L of Ni(II) concentration with adsorbent dosage of 10 g/L and stirring the same for a contact time of 4 h. The effect of adsorbent dosage level on percent removal of Ni(II) was studied for Ni(II) concentration of 25 mg/L, pH adjusted to 5. In this study, the contact time was varied from 15 to 300 min, the pH of the solution from 3 to 11, the initial nickel concentration from 3 to 50 mg/L and the amount of adsorbent from 2.5 to 30 g/L.

4. Adsorption Kinetics

The kinetic parameters for the adsorption process were studied on the batch adsorption of 25 mg/L of Ni(II) at pH 5. The contact time was varied from 15 to 300 min and the percent removal of Ni(II) was monitored during the study. The data was fitted to the Lagergren equation [48].

$$\text{Log}(q_e - q) = \log q_e - \frac{K_{ad}}{2.303} \times t \qquad (2)$$

where q is the amount of Ni(II) (mg/g of adsorbent) removed at time t (min), q_e the amount of Ni(II) removed at equilibrium and K_{ad} is the rate constant of adsorption (min^{-1}).

5. Adsorption Isotherms

The adsorption isotherms for the Ni(II) removed were studied by using an initial concentration of Ni(II) between 10 and 100 mg/L at an adsorbent dosage level of 10 g/L. The data obtained were then fitted to the Langmuir adsorption isotherm [48] applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \times b} + \frac{C_e}{q_{max}} \qquad (3)$$

where C_e is the equilibrium concentration of adsorbate (mg/L), q_e the amount adsorbed at equilibrium (mg/g adsorbent), and q_{max} (mg/g) and b (L/mg) are the Langmuir constant related to the adsorption capacity and energy of adsorption, respectively.

The adsorption data obtained were then fitted to the Freundlich adsorption isotherm [48], which is expressed by the following equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (4)$$

where q_e is the amount of adsorbate adsorbed per unit weight (mg/g of adsorbent), C_e the equilibrium concentration (mg/L) of the adsorbate and K_f is the Freundlich constant.

6. Thermodynamic Parameters

The thermodynamic equilibrium constant (K) for each system was obtained at 30±2 °C by calculating the apparent equilibrium constant K'_C at different initial concentration of Ni(II) and extrapolating the same to zero.

$$K'_c = \frac{C_a}{C_e} \qquad (5)$$

where C_a is the concentration of Ni(II) on the adsorbent at equilibrium in mg/L and C_e is the equilibrium concentration of Ni(II) in solution in mg/L.

The Gibbs free energy (ΔG^0) for the adsorption process was obtained at 30±2 °C using the formula

$$\Delta G^0 = -RT\ln K_c \qquad (6)$$

where R is the ideal gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature in K.

RESULTS AND DISCUSSION

1. Effect of pH

The uptake of Ni(II) as a function of hydrogen ion concentration was examined over a pH range of 3-11. The removal efficiency was found to be highly dependent on hydrogen ion concentration present

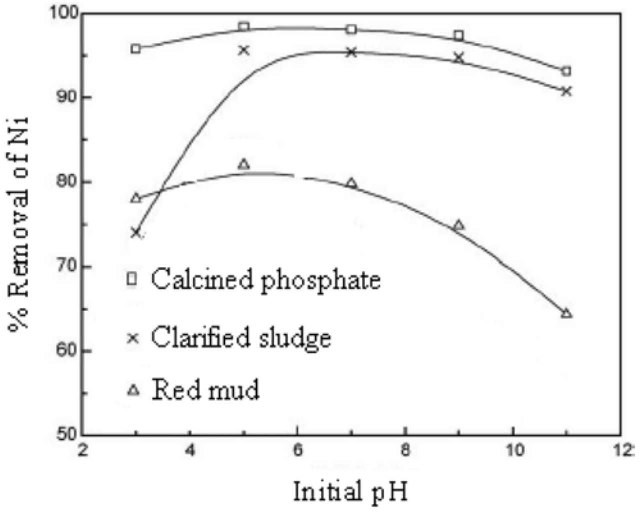

Fig. 1. Effect of pH on the adsorption of Ni(II) by selected adsorbents, initial Ni(II) concentration 25 ppm, adsorbent dosage 10 g/L, contact time 4 h and temperature 30 °C.

in solution. The effect of pH on adsorption efficiency is shown in Fig. 1. Maximum Ni(II) removal was obtained in the pH range of 5-7. For calcined phosphate with an initial concentration of 25 mg/L of Ni(II), maximum 96.8% removal was obtain at a pH value of 5. For clarified sludge, optimum pH for adsorption of Ni(II) as found to be 5. In case of red mud also, maximum sorption of Ni(II) from aqueous solution occurred at a pH value around 5. Hence, pH 5 was considered to be the optimum pH for further studies. The effect of pH can be explained considering the surface charge on the adsorbent material. At low pH, due to high positive charge density due to protons on the surface sites, electrostatic repulsion will be high during uptake of metal ions resulting in lower removal efficiency. With increasing pH, electrostatic repulsion decreases due to reduction of positive charge density on the sorption sites, thus resulting in an enhancement of metal adsorption. The above fact related to the effect of pH on adsorption was also supported by several earlier workers [49,50]. At higher pH values OH ions compete for Ni(II) with the active sites on the surface of the adsorbents [51].

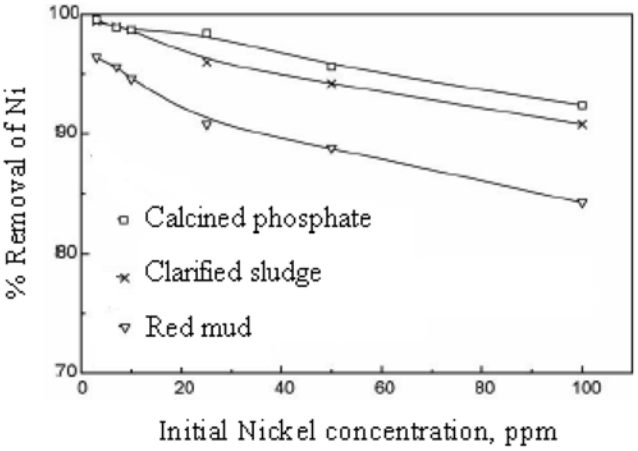

Fig. 2. Effect of initial concentration on the adsorption of Ni(II) by selected adsorbents: pH 5, adsorbent concentration 10 g/L, contact time 4 h and temperature 30 °C.

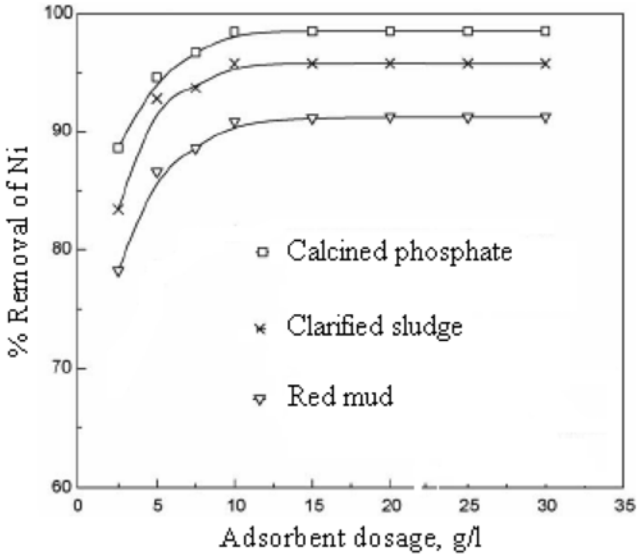

Fig. 3. Effect of adsorbent concentration on adsorption of Ni(II) by selected adsorbents: pH 5, initial Ni(II) concentration 25 ppm, contact time 4 h and temperature 30 °C.

2. Effect of Initial Ni(II) Concentration

The efficiency of Ni(II) removal is affected by the initial metal ion concentration, with decreasing removal percentages as concentration increases from 3 to 50 mg/L at constant pH of 5 (Fig. 2). Adsorbent dosage level was maintained at 10 g/L for all the adsorbents considered for study. This effect can be explained as follows: at low metal ion/adsorbent ratios, metal ion adsorption involves higher energy sites. As the metal ion/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in decreases in the adsorption efficiency [29,52].

3. Effect of Adsorbent Type and Concentration

The effect of adsorbent type and its concentration is depicted in Fig. 3. The selected adsorbents (calcined phosphate, red mud, clarified sludge) were used at concentration ranging from 2.5 to 30 g/L in a batch adsorption. In each case an increase in adsorbent concentration resulted in an increase in percent removal of Ni(II). After a certain adsorbent dosage the removal efficiency is not increased so significantly.

At 5 g/L of adsorbent dosage level the removal of Ni(II) was found to be between 94.6% (calcined phosphate) and 82.3% (red mud). At 10 g/L of calcined phosphate the removal of Ni(II) from solution was found to be 98.7%. In case of clarified sludge, Ni(II) removal efficiency of 95.8% was achieved at an adsorbent dosage level of 1 0 g/L, and for red mud under the same condition the removal efficiency was 89.7%. It is evident that for all the adsorbents maximum removal efficiency was achieved at an adsorbent dosage level of 10 g/L. Therefore, the following experiments were carried out at adsorbent concentration of 10 g/L. The variation in sorption capacities between the various adsorbents could be related to the type and concentration of surface group responsible for adsorption of metal ions from solution [53]. With increasing adsorbent dosage more surface area is available for adsorption due to an increase in active sites on the adsorbent. The adsorption of Ni(II) on the calcined phosphate surface is due to the diffusion of nickel ions into hydroxyapatite and the release of cations originally contained within hydroxyapatite (ion-ion exchange mechanism). Adsorption Ni(II) by clarified sludge may be attributed due to the combined effect of silica, metal oxides and carbon present in it as major constituents. In the case of red mud the removal of nickel ions is attributable to chemisorption reaction at the surface of the oxides components which principally constitute RM.

4. Effect of Contact Time and Adsorption Rate Kinetics Mechanism

The experimental runs measuring the effect of contact time on the batch adsorption of 25 mg/L Ni(II) at 30 °C and at initial pH value 5 are shown in Fig. 4. It is obvious that increase in contact time from 0.5 to 2.0 h enhanced significantly the percent removal of Ni(II). The nature of adsorbent and its available sorption sites affected the time needed to reach the equilibrium. For calcined phosphate this time is 1 h. In case of clarified sludge, time needed to reach the equilibrium is 3 h. For red mud, a contact time of 4 h is needed for equilibrium to be established. All the other experiments on the physical properties of adsorption were conducted after 4 h of contact time.

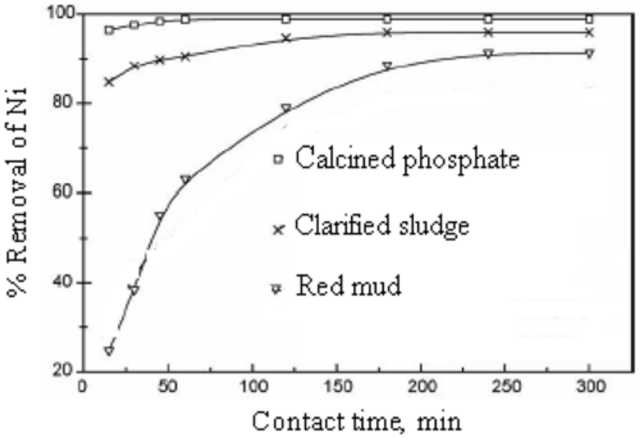

Fig. 4. Effect of contact time on the adsorption of Ni(II) by selected adsorbents: initial Ni(II) concentration 25 ppm, adsorbent dosage 10 g/L, pH 5 and temperature 30 °C.

Table 1. Lagergren rate constants for adsorption of Ni(II) on different adsorbents

Adsorbents	Lagergren rate constants, K_{ad} (min^{-1})	r^2
Calcined phosphate	6.9×10^{-2}	0.9958
Clarified sludge	2.55×10^{-2}	0.9922
Red mud	1.86×10^{-2}	0.9875

The kinetics of Ni(II) adsorption was studied from the time versus %removal curves. The rate kinetics of Ni(II) adsorption on the calcined phosphate as well as on the other adsorbents were observed to follow the first-order rate law derived by Lagergren (Eq. (2)). Fig. 5 shows the Lagergren plot of $\log(q_e-q)$ versus time (min) for all adsorbents. The linearity of these plots indicates that a first-order mechanism is indeed followed in this process. The rate constants (K_{ad}) for each system were calculated from the linear least square method and are given in Table 1 along with the correlation coefficient (R^2). It is pertinent to mention that pH of the solution does not change significantly during the adsorption process.

5. The Adsorption Isotherms

The relation between the initial concentration of Ni(II) and its percentage removal from solution was studied for all adsorbents included in the study. The initial concentrations of Ni(II) studied were 10, 25, 40, 50, 80 and 100 mg/L at an adsorbent concentration of 10 g/L. The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent q_e and the solute concentration for the solution at equilibrium C_e. The equilibrium data for Ni(II) adsorption on different adsorbents were fitted to the Langmuir equation (Eq. (3)): an equilibrium model able to identify chemical mechanism involved. Linear plots of C_e/q_e versus C_e (Fig. 6) were employed to determine the value of q_{max} (mg/g) and b (L/mg). The data obtained with the correlation coefficients (R^2) are listed in Table 2. The Langmuir constants q_{max} and b are related to the adsorption capacity (amount of adsorbate adsorbed

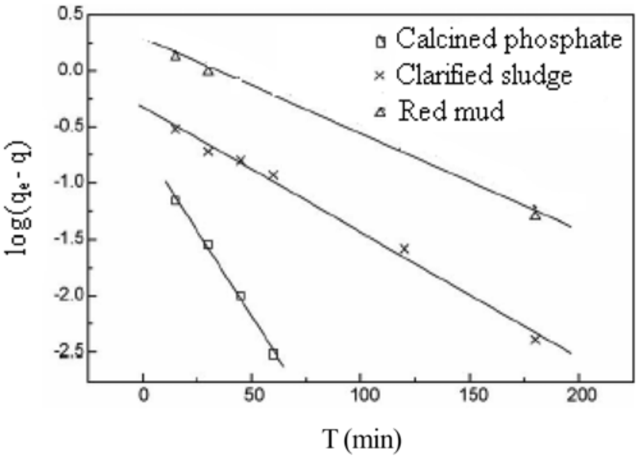

Fig. 5. Lagergren plot for the adsorption of Ni(II) by selected adsorbents: pH 5, initial concentration 25 mg/L, adsorbent dosage 10 g/L and temperature 30 °C.

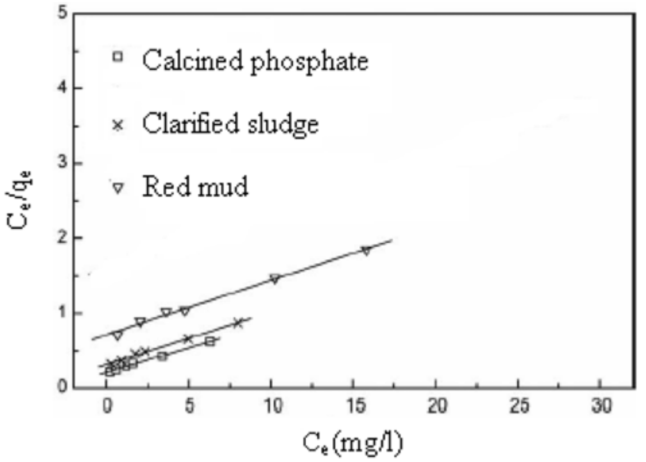

Fig. 6. Langmuir plot for the adsorption of Ni(II) by selected adsorbents: pH 5, adsorbent dosage 10 g/L, contact time 4 h and temperature 30 °C.

Table 2. Langmuir adsorption isotherm constants for Ni(II) on different adsorbents

Adsorbents	Q (mg g^{-1})	b (mg^{-1})	r^2
Calcined phosphate	15.53	0.299	0.9971
Clarified sludge	14.3	0.222	0.9955
Red mud	13.69	0.102	0.9932

per unit mass of the adsorbent to complete monolayer coverage) and energy of adsorption, respectively.

The value of adsorption capacity q_{max} (maximum uptake) is highest (15.53 mg/g) for calcined phosphate because adsorption of ions on the solid surface, followed by their diffusion into hydroxyapatite and the release of cations originally contained within hydroxyapatite (ion-ion exchange mechanism).

Red mud shows the lowest value of adsorption capacity q_{max} (13.69 mg/g). However, the isotherm parameters, together with the correlation coefficients, of the Langmuir equation for the adsorption of Ni(II) on different adsorbents, show that the Langmuir equation gives a good fit to the adsorption isotherm. Weber and Chakraborti [54] expressed the essential characteristics and the feasibility of the Langmuir isotherm in terms of a dimensionless constant separation factor or equilibrium parameter R_L, which is defined as,

$$R_L = \frac{1}{1 + bC_0} \qquad (7)$$

where b is the Langmuir constant and C_0 is the initial concentration of Ni(II). The R_L value indicates the shape of the isotherm as follows:

According to McKay et al. [55] R_L values between 0 and 1 indicate favorable adsorption. The R_L values for the adsorption of Ni(II) on different adsorbents at initial concentration of 3 mg/L (lowest concentration studied) and 100 mg/L (highest concentration studied) are listed in Table 3. The data obtained represent a favorable adsorption for all the adsorbents under study. The equilibrium data also fitted to Freundlich equation (Eq. (4)), a fairly satisfactory empirical isotherm can be used for nonideal adsorption. The Freundlich isotherm constants K_f and n are constants incorporating all factors affecting the adsorption process such as of adsorption capacity and intensity of adsorption. The constants K_f and n were calculated from Eq. (4) and Freundlich plots (Fig. 7). The amount of absorbent required to reduce any initial concentration to predetermined final concentration can be calculated. The values for Freundlich constants and correlation coefficients (R^2) for the different adsorbents used during the study are also presented in Table 4. The values of n between 1 and 10 (i.e., 1/n less than 1) represent a favorable adsorption [29,49,56]. The adsorption capacity K_f was highest for calcined phosphate followed by clarified sludge and red mud. The values of n, which reflect the intensity of adsorption, also presented the same trend. The n values obtained for all the four adsorbents considered for study represent a beneficial adsorption.

Table 3. Separation factor or equilibrium parameter R_L for adsorption of Ni(II) on different adsorbents

Adsorbents	Separation factor or	Equilibrium parameter (R_L)
	Initial Ni(II) concentration, 10 mg/*l*	Initial Ni(II) concentration, 100 mg/*l*
Calcined phosphate	0.256	0.033
Clarified sludge	0.312	0.043
Red mud	0.495	0.089

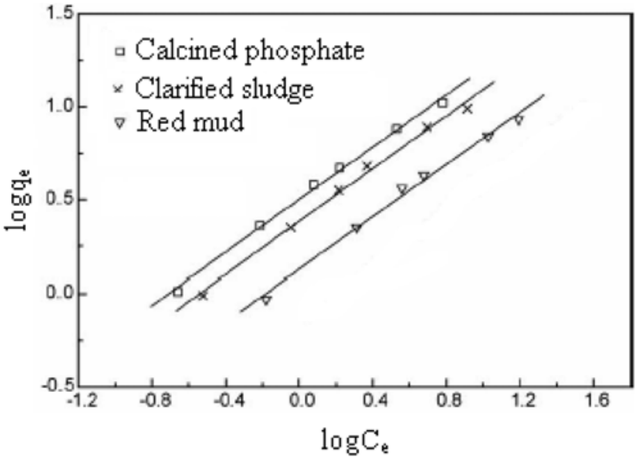

Fig. 7. Freundlich plot for the adsorption of Ni(II) by selected adsorbents: pH 5, adsorbent dosage 10 g/L, contact time 4 h and temperature 30 °C.

Table 4. Freundlich adsorption isotherm constants for Ni(II) on different adsorbents

Adsorbents	K_f	1/n	n	r^2
Calcined phosphate	3.16	0.705	1.418	0.9964
Clarified sludge	2.44	0.709	1.410	0.9945
Red mud	1.34	0.701	1.426	0.9923

6. Thermodynamics for Adsorption

The previous results suggested that adsorption of Ni(II) on the selected adsorbents involves a complex mechanism, and in the adsorption process there are two distinct stages - the initial stages of boundary layer diffusion due to external mass transfer effects, and in the later stages it was due to intraparticle diffusion which contributes to the rate-determining step.

The thermodynamic equilibrium constant (K) was obtained from calculating the apparent equilibrium constant (K_C') at different initial concentrations of Ni(II) and extrapolating to zero. The Gibbs free energy for the adsorption process was obtained at 30 °C by using Eq. (6) (Table 5). The Gibbs free energy indicates the degree of spon-

Table 5. Thermodynamic equilibrium constant (K) and Gibbs free energy (ΔG^0) at 30±2 °C for adsorption of Ni(II) on different adsorbents

Adsorbents	Equilibrium constant, K	Gibbs free energy (−) ΔG^0 (KJmol^{-1})
Calcined phosphate	0.472×10^2	9.713
Clarified sludge	0.351×10^2	8.964
Red mud	0.155×10^2	6.912

taneity of the adsorption process, where more negative values reflect a more energetically favorable adsorption process. The ΔG^0 values obtained in this study for the adsorbents confirm the feasibility of these adsorbents and spontaneity of the adsorption. The ΔG^0 for the calcined phosphate shows that it has the largest capacity and affinity for the selective removal of Ni(II) from aqueous solution over the other adsorbents used in this study.

CONCLUSIONS

Batch adsorption experiments were performed for the removal of Ni(II) from aqueous solutions by using three different adsorbents. The adsorption characteristics have been examined at different pH values, initial metal ion concentrations, contact time and adsorbent dosages. The obtained results can be summarized as follows:

1. The pH experiments showed that the governing factors affecting the adsorption characteristics of all adsorbents are competition of the H^+ ions with Ni(II) ions at low pH values, maximum adsorption at pH 5 and at higher pH precipitation of nickel hydroxyl species onto the adsorbents (pH 6-11).
2. Increase in mass of adsorbent leads to increase in Ni(II) adsorption due to increase in number of adsorption sites. Maximum uptake of Ni(II) obtained at adsorbent dose of 10 g/L for all the adsorbents.
3. Adsorption of Ni(II) for all the adsorbents was found to follow the first-order Lagergren rate kinetics.
4. The Langmuir and Freundlich adsorption isotherm models were used to represent the experimental data. Both the models were fitted well. The highest monolayer adsorption capacity was obtained 15.53 mg/g for calcined phosphate and lowest for red mud 13.69 mg/g at optimum pH 5.0.
5. Thermodynamic calculations showed that the Ni(II) adsorption was spontaneous in nature. The range of Gibbs free energy values ΔG^0 varies from -9.713 kJ/mol for calcined phosphate to -6.912 kJ/mol for red mud.
6. The best adsorbent for the Ni(II) removal is the calcined phosphate. The optimum conditions were pH 5, adsorbent dosage level 10 g/L, equilibrium contact time 1 h.

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