Adsorption of nickel and copper onto natural iron oxide-coated sand from aqueous solutions: Study in single and binary systems

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ABSTRACT

Natural iron oxide-coated sand (NCS), extracted from the iron ore located in North-West of Tunisia, was employed to investigate its capacity to remove copper and nickel from aqueous solutions. The aim of this work was to characterize the considered sorbent (NCS) and to assess the possibility of removing nickel and copper from aqueous solutions by this sorbent. The effects of agitation time, pH, initial metal ion concentration and temperature on the removal of these metals were studied. In order to study the sorption isotherm, two equilibrium models, the Freundlich and Langmuir isotherms, were analyzed. The effect of solution pH on the adsorption onto NCS was studied in the pH range from 2 to 7 and 2 to 9 for copper and nickel respectively. The adsorption was endothermic and the computation of the parameters, ΔH°, ΔS° and ΔG°, indicated that the interactions were thermodynamically favourable. Experiments with Cu and Ni adsorption measured together showed that Cu severely interfered with Ni adsorption to the NCS and vice versa under the conditions of the two coexisted ions adsorption.

1. Introduction

Heavy metal ions have become an ecotoxicological hazard of prime interest and increasing significance, because of their accumulation in living organisms [1]. Both Ni(II) and Cu(II) are present in effluents of a large number of industries. People often suffer from allergy due to exposure to nickel-containing materials and the carcinogenic effects of nickel have also been well documented [2]. Copper pollution arises from copper mining and smelting, brass manufacture, electroplating industries and excessive use of Cu-based agri-chemicals. Copper along with arsenic and mercury, is recognized as the highest relative mammalian toxic species [3] and continued inhalation of copper containing sprays is linked with an increase in lung cancer among exposed workers [4]. Copper sulphate is used widely as an algicide in ornamental ponds and even in water supply reservoirs, which are affected by blooms of blue-green alge [5]. Nickel is a toxic heavy metal that is widely used in silver refineries, electroplating, zinc base casting and storage battery industries [6]. The chronic toxicity of nickel to humans and the environment has been well documented. For example, high concentration of nickel(II) causes cancer of lungs, nose and bone. It is essential to remove Ni(II) from industrial wastewater before being discharged. Hence, removal of copper and nickel from water and wastewater assumes importance. The conventional methods for heavy metal removal from water and wastewater include oxidation, reduction, precipitation, membrane filtration, ion exchange and adsorption. Among all, adsorption is highly effective and economical. Though the use of commercial activated carbon is a well-known adsorbent for the removal of heavy metals from water and wastewater, the high cost of activated carbon limits its use as an adsorbent in developing countries. Hence, several research workers used different low-cost adsorbents such as coconut coir pith [7], sawdust [8], sludge ash [9], banana pith [10], activated phosphate rock [11], vermiculite [12], and montmorillonite [13]. In spite of several researchers adopted various low-cost adsorbents there is still a need to develop suitable adsorbents for the removal of copper and nickel from aqueous solutions. Adsorption of trace heavy metals onto solid phases and associated surface coatings is considered very important in controlling heavy metal activity. In recent years considerable attention has been paid to the investigation of different types of low-cost sorbents especially using metal-oxide modified adsorbents, such as sand [14–16], zeolite [17,18], diatomite [19]. In addition to the well-established effects of solution chemistry, adsorption of trace heavy metals is expected to be governed by the composition of solid phases, particularly the content of metal oxides (iron oxides and manganese oxides) and organic materials [20]. Iron oxides are abundant components in solid phases that have been studied extensively and are considered important sorbents for trace heavy metals [21,22].

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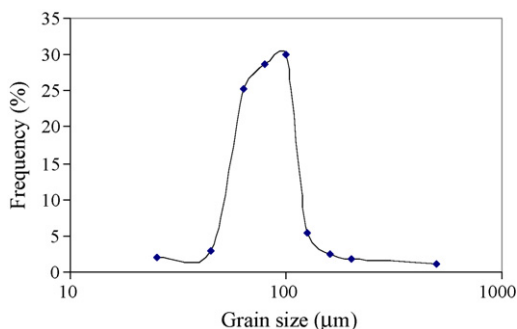
Fig. 1. Grain size frequency distribution.

Fig. 2. Variation of SNC sorbent suspension pH as a function of the initial pH of the solutions.

Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration. However, less research was reported on the natural surfaces coating [23,24], and in particular no investigation was focused on the adsorption mechanisms of heavy metals onto the natural surfaces coating. Previously, the three most important geochemical components have been identified as Fe, Mn oxides and organics materials within the solid phases [25–27].

Natural iron oxide-coated sediment constitutes one of the principal richness in Tunisia. To the authors knowledge this ore was not yet exploited. The main objective of this study is to investigate the feasibility of using natural iron oxide-coated sediment as sorbent for the removal of copper and nickel from aqueous solution. The choice of this material is based on its low cost considering its abundance in Tunisian ores.

In this work the chemical and mineralogical characteristics of new discovered natural coated sand (SNC) were investigated. The purpose of this study was to evaluate the uptake of Cu^{2+} and Ni^{2+} ions by NCS in single and binary system.

2. Experimental

The solid used in this work was natural iron oxide-coated sand (ferruginous sand) extracted from an iron ore located in Nefza (North West of Tunisia). The grain size distribution is presented in Fig. 1. We can observe a majority peak whose diameter is from 0.63 to 100 μm, only this fraction which concentrates NCS grains was used. It was used without any preliminary treatment.

The surface area of the solid was determined by the BET methodology and it was found to be 6.97 m^2/g.

This sorbent was characterized using:

- IR spectral analysis: An IR transmittance spectrum of the considered sample was obtained in the 4000–500 cm^{-1} range using a SHIMATZU IR 470 spectrometer.
- Scanning electron microscope (SEM) (Philips XL30) and energy dispersive X-ray analysis (EDAX) (PhilipsEDAX9100) were used to characterize our sorbent for constituent and morphology.
- X-ray diffraction: using an X-ray diffractometer (Siemens, Germany) with Cu Kα radiation (λ = 0.154 nm). Scans were conducted from 0° to 60° at a rate of 2θ per min.

The pH of zero point of charge (pHzpc) was determined by adding a known amount of adsorbent (0.1 g) to a series of bottles that contained 50 mL of deionised water. Before adding the adsorbent, the pH of the solutions was adjusted to be in the range of 1.0–9.0 by the addition of either 0.1 M HNO$_3$ or 0.1 M NaOH. These bottles were th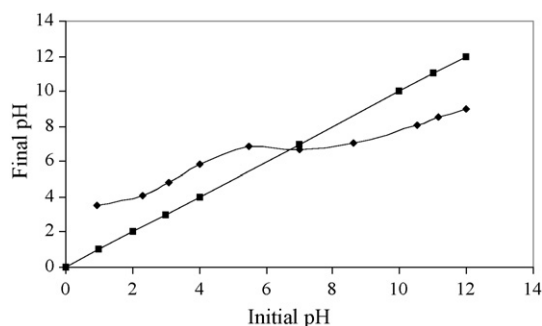en rotated for 1 h in a shaker and pH values were measured at the end of the test. The pH of the suspensions is represented as a function of the initial pH of the solutions. The curve obtained (Fig. 2) theoretically cross the bisector of axes at the point of zero charge [28].

Batch experiments included: the kinetic studies, pH effect and sorption isotherms.

Sorption experiments for the kinetic study were conducted as follows: 1 g of NCS was suspended in 25 mL solution containing 30 mg/L of Ni^{2+} (obtained from Nickel chloride hexahydrate (NiCl$_2$·6H$_2$O) or Cu^{2+} (obtained from copper sulphate pentahydrate CuSO$_4$·5H$_2$O). The solution pH was adjusted to 5 and 7 with 1 M HNO$_3$ and 1 M NaOH for copper and nickel respectively. The suspensions were stirred for different time intervals (1–360 min) .The solutions were filtered through a 0.45 μm membrane filter (MFS) and the concentrations of metal ions were determined by Hitachi Z-6100 model Atomic Absorption Spectrometer (AAS) operating with an air-acetylene flame.

To determine the influence of pH, experiments were performed at various initial pH, ranging between 2–7 for copper and 2–9 for nickel respectively. Initial concentration of 30 mg/L of nickel or copper and 1 g of sorbent per 25 mL of solution were used. The suspensions were stirred for 2 h.

For single metal–NCS systems, initial metal ion concentration was varied from 30 to 110 mg/L. In binary metal ion mixture–NCS systems, for each initial concentration of Cu^{2+} solution, viz., 30, 50, 70, 90 and 110 mg/L, the nickel concentration was varied in the range of 30–90 mg/L (viz., 30, 60 and 90 mg/L). The pH$_0$ of the solutions was maintained at 5 and 7 for copper and nickel respectively.

The sorption equilibrium data of copper and nickel on NCS were analyzed in terms of Freundlich and Langmuir isotherm model [29].

The Freundlich isotherm equation is given as follows:

$$Q = K_F C_e^{1/n} \tag{1}$$

where Q and C_e are the equilibrium concentrations of copper and nickel in the adsorbed and liquid phases in mg/g and mg/L, respectively. K_F and n are the Freundlich constants that are related to the sorption capacity and intensity, respectively.

Eq. (1) can be written in the linear form as given below:

$$\log Q = \log K_F + \frac{1}{n} \log C_e \tag{2}$$

Freundlich constants K_F and n can be calculated from the slope and intercept of the linear plot, with log(Q) versus log C_e.

The Langmuir sorption isotherm equation is given as follows:

$$Q = \frac{Q_m b C_e}{(1 + b C_e)} \tag{3}$$

where Q_m and b are Langmuir constants which are related to sorption capacity and energy of sorption, respectively.

On linearization Eq. (3) becomes:

$$\frac{C_e}{Q} = \frac{C_e}{Q_m} + \frac{1}{Q_m b} \qquad (4)$$

Q_m and b can be calculated from the intercept and slope of the linear plot, with C_e/Q versus C_e.

In order to determine the effect of temperature on sorption phenomenon, isotherms were established at 283, 293 and 313 K.

For the desorption studies: 5 g sorbent were contacted with 250 mL metallic solutions ($110\,mg\,L^{-1}$). After adsorption step, the sample was collected by filtration and washed with distilled water, for three times, to remove residual Cu^{2+} and Ni^{2+} on the surface. Then, it was transferred into 250 mL desorbent solution: 0.1 M HNO_3, 0.1 M HCl, 0.1 M NaOH, 0.1 M CH_3COOH or H_2O. The mixture was shaken for 48 h, then the filtrate was analyzed to determine the concentration of the desorbed metals.

Desorption ratio was calculated according to the following equation:

Desorption ratio (%) = (Amount of metal ions desorbed/

Amount of metal ions adsorbed) $\times 100$ (5)

3. Results and discussion

3.1. Characterizations of the sorbent

SEM photographs of NCS (Fig. 3) showed a rough surface because of the deposited iron oxyhydroxide. Elemental composition of the sorbent was determined from its EDAX spectra (Fig. 4). The EDAX spectrum showed only the presence of silica, iron oxides and other minerals witch can be attribute the clayey nature of this sorbent.

As determined by EDAX, the predominant chemical compositions of NCS are given in Table 1. These results showed that the predominant chemical compositions of this sorbent include silica, iron oxide, aluminium oxide, and other oxides are present in trace amounts.

The infrared absorption spectrum (Fig. 5) of natural coated sand showed that in addition to bands characteristic of silica (1040.06; 795.92 and 688.5 cm^{-1}) and iron oxide (1580 cm^{-1}),
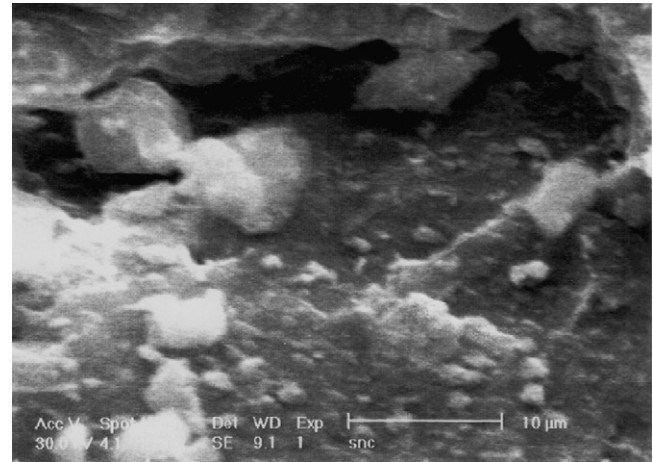
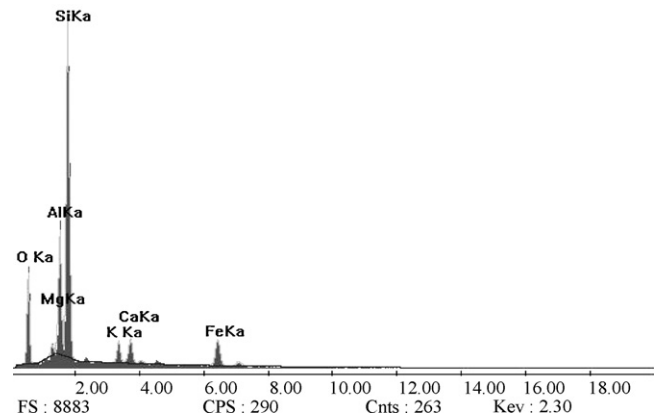**Fig. 3.** SEM micrograph of natural iron oxide-coated sand (NCS).

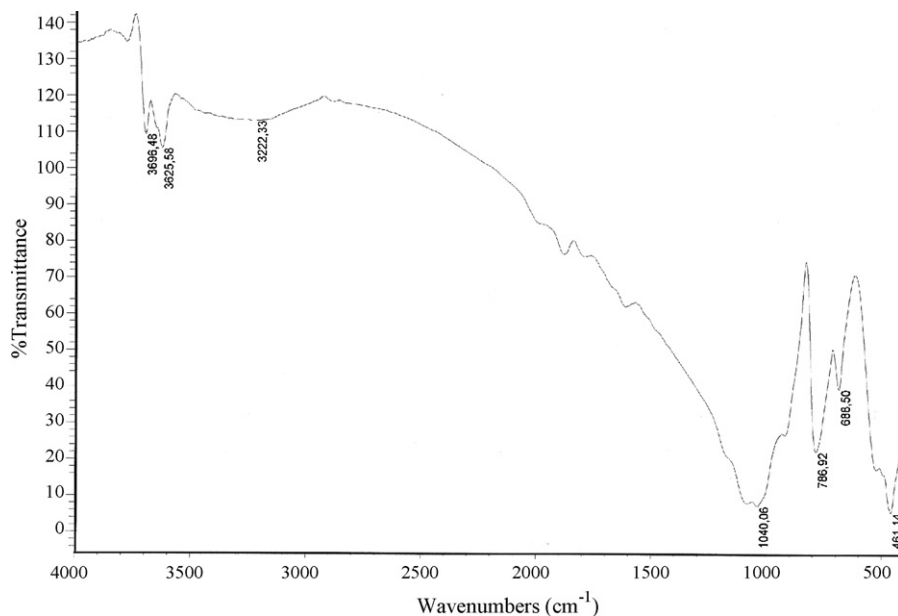**Fig. 4.** EDAX spectrum of natural iron oxide-coated sand (NCS).

Fig. 5. Infrared spectrum of natural iron oxide-coated sand (NCS).

Table 1
Chemical composition of NCS

Chemical composition	Compound amount (%)
SiO₂	61.98
Al₂O₃	10.84
CaO	2.66
MgO	1.41
K₂O	4.6
Fe₂O₃	18.45

bands appeared at 3625 cm^{-1} are assigned to stretching vibration of the surface hydroxyl groups Si-Si-OH or Al-Al-OH [30].

Pure iron oxides, whether they can be identified as having a particular crystal structure or not, typically have pH$_{ZPC}$ in the range 7–9 [31]. The fact that the measured pH$_{ZPC}$ of the NCS is 9.5, one might expect some Si to be incorporated into the coating, but such a process cannot explain the high pH$_{ZPC}$, since Anderson and Benjamin [32] reported that incorporation of Si into Fe oxide precipitates lowers the pH$_{ZPC}$. In any case, regardless of whether the actual pH$_{ZPC}$ of the NCS was greater than 9 strongly suggest that the Fe oxide dominates NCS/solution interactions.

Examination of the XRD patterns of NCS (data not shown) reveals in addition to the peak characteristic of silica and clay the presence of iron oxide as evidenced by its diffraction peak corresponding to a d_{hkl} = 3.022 Å.

3.2. Effect of agitation time on adsorption

The agitation time was evaluated as one of the most important factors affecting the adsorption efficiency. The optimum time for both copper and nickel removal were determined at 120 min (Fig. 6). As a result of the experimental studies, it is seen that high efficiency for copper and nickel adsorption can be obtained at short time periods.

3.3. Effect of sorbent dose

In the copper and nickel removal, it is seen that the adsorption efficiency increases as the NCS amount increases until the dosage reaches 2 g/100 mL. The increase in the efficiency can be explained by the increasing surface area where the adsorption takes place. As seen in Fig. 7, optimum sorbent dosages that can be used in copper and nickel removal are 2 g/100 mL.
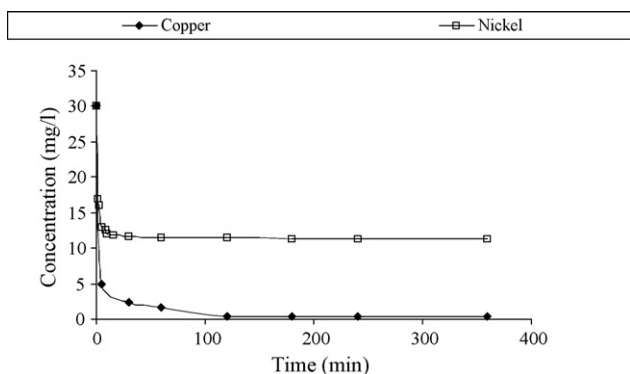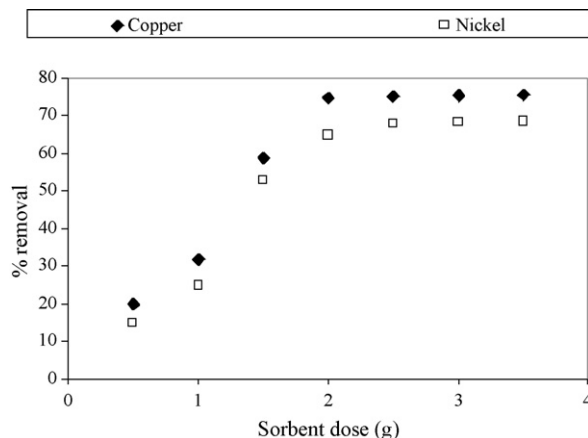

Fig. 7. Effect of sorbent dose (in 100 mL solution) on the removal of Cu²⁺ and Ni²⁺ ions at 20 °C, initial Cu concentration = initial Ni concentration = 30 mg/L, pH 5 for Cu and 7 for Ni, adsorption time 120 min.

3.4. Effect of pH

The results of the pH effect in the adsorption process were shown in Fig. 8. The effect of pH changes due to the adsorbent type, its behaviour in the solution and the type of ions adsorbed [33]. In this study, the optimum pH values for the copper and nickel removal were determined as 5 and 7, respectively. So, further experiments were carried on by using these selected values.

3.5. Sorption isotherms

Sorption isotherms of Cu²⁺ and Ni²⁺ ions are shown in Fig. 9. The sorption data were described using the Langmuir and Freundlich isotherm models. The results of these analyses, using linear regression procedures, are shown in Table 2. The shape of Cu²⁺ isotherm is of "L2"' type, while that of Ni²⁺ is "L1" type according to Giles classification for isotherms [34]. One of the important differences between these isotherms is that the slope of L2 isotherm is steeper than that of L1 isotherm [34]. L-isotherm type (or Langmuir isotherm type) is usually associated with ionic substrates (e.g., metal cations) sorption with weak competition from the solvent molecules [34].

3.5.1. Langmuir isotherm

Table 2 indicates that Langmuir model has perfectly application for copper and nickel sorption with a regression coefficient,

Fig. 6. Effect of contact time on the removal of Cu²⁺ and Ni²⁺ ions on NCS ([Cu²⁺] = [Ni²⁺] = 30 mg/L, 1 g sorbent/25 mL solution, T = 20 °C, pH 5 and 7 for Cu and Ni respectively).
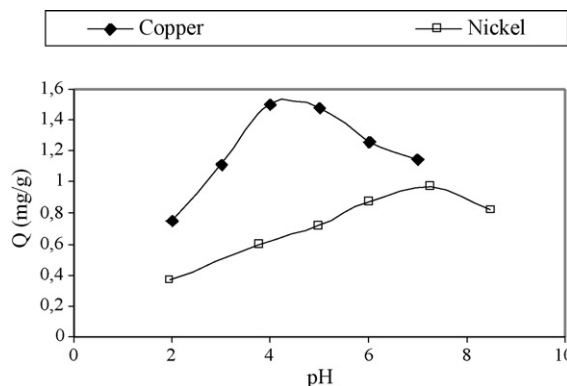

Fig. 8. Effect of initial pH on removal of Cu²⁺ and Ni²⁺ ions on NCS([Cu²⁺] = [Ni²⁺] = 30 mg/L, 1 g sorbent/25 mL solution, T = 20 °C, pH 5 and 7 for Cu and Ni respectively, 120 min).
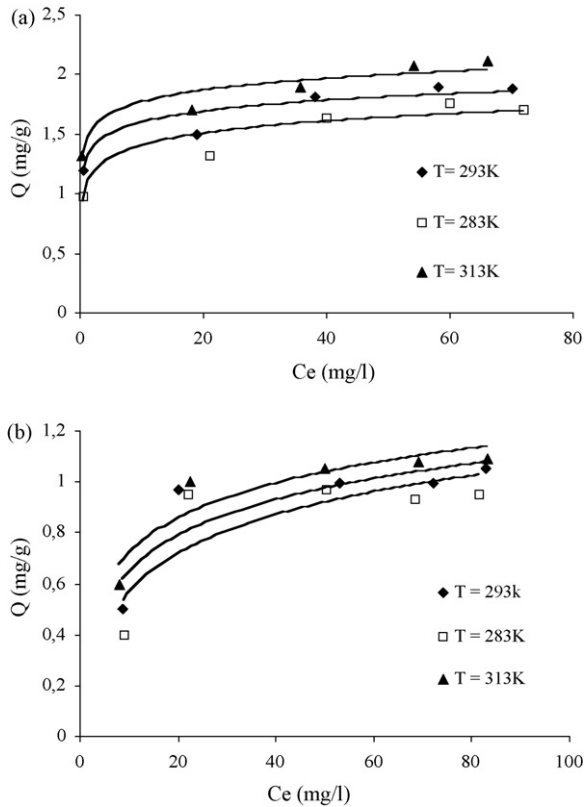
Fig. 9. Equilibrium isotherms for Cu^{2+} and Ni^{2+} ions removal by NCS (5 g sorbent/250 mL solution, T = 10, 20 and 40 °C, pH 5 and 7 for Cu and Ni respectively).

Table 2
Freundlich and Langmuir constants for Cu^{2+} and Ni^{2+} sorption on NCS

Metals	Temperature (K)	Langmuir constants			Freundlich constants		
		b (L/mg)	Q (mg/g)	R^2	K_F	$1/n$	R^2
	283	0.14	1.85	0.99	2.1	0.18	0.95
Cu(II)	293	0.92	2.04	0.99	1.8	0.13	0.97
	313	3.83	2.17	0.99	1.4	0.10	0.92
	283	0.12	0.9	0.99	0.98	0.31	0.81
Ni(II)	293	0.28	1	0.97	0.7 2	0.27	0.73
	313	1.08	1.26	0.93	0.39	0.24	0.83

R^2 equal to 0.97 and 0.99, respectively. Using the Langmuir model, the maximum sorption capacity for the metals can be estimated as: Cu (2.04 mg/g) and Ni (1 mg/g), this result indicates that the used sorbent (NCS) can remove the two metal ions with a higher affinity for Cu^{2+}.

3.5.2. Freundlich isotherm

Table 2 indicates that there is a slight deviation from linearity using the Freundlich isotherm model for describing Cu^{2+} sorption (R^2 equal to 0.97). The model gives a poor presentation for Ni^{2+} sorption behaviour (R^2 equal to 0.73). Freundlich parameters (K_F
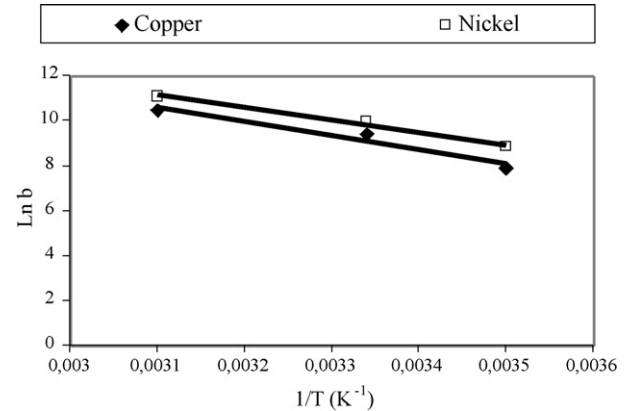

Fig. 10. Van't Hoff plot for the sorption of Cu^{2+} and Ni^{2+} ions on all considered sorbent.

and n) indicate whether the nature of sorption is either favourable or unfavourable [35]. The intercept is an indicator of sorption capacity and the slope is an indicator of sorption intensity. In the two sorption systems, values obtained of $1 < n < 10$ imply favourable sorption. The K_F values, reported in Table 2, can be used to indicate the relative sorption capacity of the system [36]. It was noted that K_F values show the same trend as that of Q_{max} for the metals studied (Table 2).

3.6. Thermodynamic parameters of adsorption

In order to explain the effect of temperature on the adsorption thermodynamic parameters, standard Gibbs free energy ($\Delta G°$), standard enthalpy ($\Delta H°$), and standard entropy ($\Delta S°$) were determined. The adsorption process of metal ions can be summarized by the following reversible process which represents a heterogeneous equilibrium. The equation given below was used to determine the Gibbs free energy of adsorption ($\Delta G°$) [37,38]:

$$\Delta G° = -RT \ln b \tag{6}$$

where R is the gas constant, 8.314×10^{-3} kJ/(mol K), T is absolute temperature, K, and b is equilibrium constant at the temperature T, respectively. The other useful relationships are the change in standard enthalpy, $\Delta H°$, and standard entropy, $\Delta S°$, and they are given by:

$$\ln b = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{7}$$

when $\ln b$ is plotted against $1/T$, a straight line with slope $\Delta H°/R$, and intercept $\Delta S°/R$ is obtained (Fig. 10). The values of $\Delta H°$ and $\Delta S°$ were obtained from the slope and intercept of the Van't Hoff plots of $\ln b$ versus $1/T$ (Fig. 10). The thermodynamic parameters for the adsorption process are given in Table 3.

The Gibbs free energy indicates the degree of spontaneity of the adsorption process and the higher negative value reflects a more energetically favourable adsorption.

Positive values of $\Delta H°$ suggest the endothermic nature of the adsorption of Cu(II) and Ni(II) on NCS. The negative values of $\Delta G°$

Table 3
Thermodynamic parameters for the adsorption of Cu^{2+} and Ni^{2+} at various temperatures on NCS

Temperature (°C)	Copper			Nickel		
	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/(mol k))	$\Delta G°$ (kJ/mol)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (kJ/(mol k))
10	−19.14	52.32	0.25	−22.34	45.75	0.23
20	−19.36	52.32	0.25	−22.88	45.75	0.23
40	−20.91	52.32	0.25	−24.4	45.75	0.23

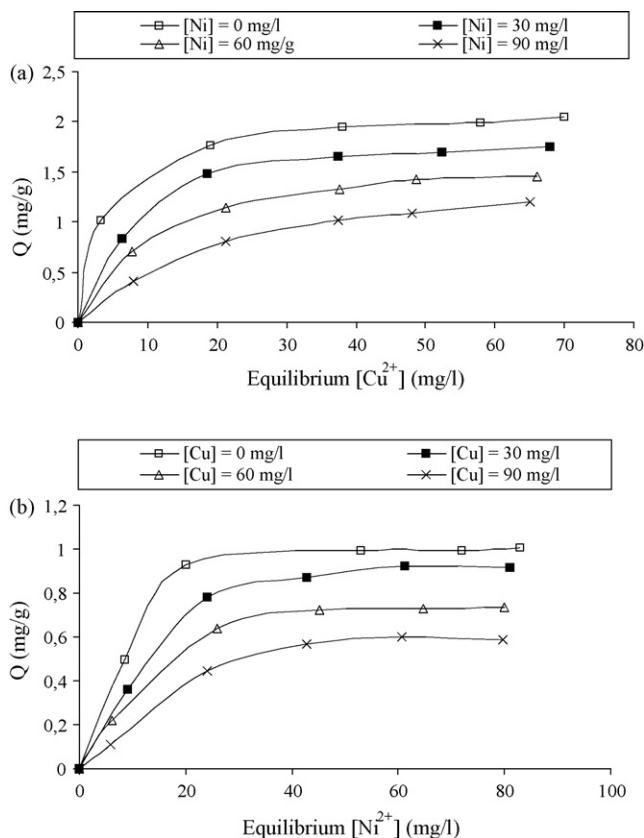**Fig. 12.** Ni^{2+} and Cu^{2+} desorption on NCS.

Fig. 11. Comparison of non-linearized adsorption isotherms of (a) Cu^{2+}ion in the presence of increasing concentration of Ni^{2+} ion and (b) Ni^{2+}ion in the presence of increasing concentration of Cu^{2+} ion (for each initial concentration of Cu^{2+} solution, viz., 30, 50, 70, 90 and 110 mg/L, the nickel concentration was varied in the range of 30–90 mg/L (viz., 30, 60 and 90 mg/L), 120 min, 4 g sorbent/200 mL solution, 20 °C, pH 5 and 7 for Cu and Ni respectively).

at various temperatures indicated the feasibility of the process and spontaneous nature of the adsorption. However, the negative value of ΔG° decreased with an increase in temperature, indicating that the spontaneous nature of adsorption of Cu(II) and Ni(II) were inversely proportional to the temperature. The positive values of ΔS° reflect the affinity of NCS for Cu(II) and Ni(II) and show the increasing randomness at the solid/liquid interface during the sorption of metal ions on NCS.

3.7. Competitive adsorption in binary metal system

In this group of experiments, competitive adsorption of Cu^{2+} and Ni^{2+} ions from their binary solutions was investigated by following a similar procedure as described above. These studies were performed at an initial pH of 5.0 at 293 K. The experiments of competitive adsorption of Cu^{2+} and Ni^{2+} included two parts:

 (i) the competitive adsorption of Cu^{2+} and Ni^{2+} in the total concentration was changeless;
(ii) the effect on adsorption of Cu^{2+} with the presence of Ni^{2+} in the solution, and the effect on adsorption of Ni^{2+} with the presence of Cu^{2+} in the solution.

The objective of this part of work was to study the effect of two metal ions coexistence on the total adsorptive capacity of NCS. The result was shown in Fig. 11(a and b).

As shown in Fig. 11, values of the amount of metal ions adsorbed Q obtained from the experiment results for the binary component
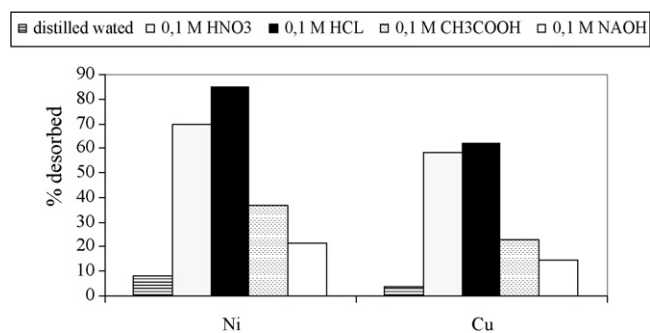
system at described conditions (the pH_0 of the solutions was maintained at 5 and 7 for copper and nickel respectively, 4 g of sorbent per 200 mL of solution at 20 °C) were ranging from 1.2 to 1.75 mg/g and 0.6 to 0.9 mg/g for Cu^{2+} and Ni^{2+}, respectively, which were less than those for the single-component solutions (2.04 mg/g for Cu^{2+} and 1 mg/g for Ni^{2+}). However, the total amount for these two metals in binary system was less than this in single-component systems. One type of the metal ion present interfered with the uptake of another one in the system, and the overall total metal uptake was slightly lower than that in single system. It is indicated that the functional groups on the surface of NCS had a relatively stronger affinity for Cu^{2+} than Ni^{2+}.

3.8. Desorption experiments

Desorption studies were conducted to regenerate metal adsorbed NCS in various HCl, HNO_3, CH_3COOH, NaOH solutions and distilled water. As it can be seen in Fig. 12, for the blank test conducted with distilled water as desorbent, the desorption percentage of each metal is very weak. On the other hand, it can be observed that HCl and HNO_3 were more efficient than the other tested desorbents: acetic acid and sodium hydroxide solutions. It is to note that, besides complex formation, the greater acidity of HCl compared to HNO_3 can also intervene in the explanation of HCl desorption efficiency.

4. Conclusion

Natural iron oxide-coated sand (NCS) used in this work is an effective sorbent on removing Cu^{2+} and Ni^{2+} ions from aqueous solution. The equilibrium sorption capacities of the metals were: 2.04 and 1 mg/g for Cu^{2+} and Ni^{2+} at pH 5 and 7, respectively. Removal of Cu^{2+} ions, for both the single and binary metal solutions under specific experimental conditions, was marginally greater than Ni^{2+}. The adsorption phenomena of Cu^{2+} and Ni^{2+} ions on the NCS can be satisfactorily and adequately represented by the Freundlich and Langmuir models. Sorption on single system is more effectives that this on binary system. Finally, it may be concluded that NCS may be used for the individual and simultaneous removal of Cu^{2+} and Ni^{2+} ions from metal-containing effluents.

Acknowledgments

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