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Batch Removal of Nickel by Eggshell as a Low Cost Sorbent

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Abstract

The Removal of Ni(II) ions from aqueous solutions by adsorption onto eggshell (ES) was investigated. The sorbent is cheap, widespread and may represent an environmental problem. The main parameters (i.e., solution pH, initial concentration of metal ions, sorbent dose, shaking time and temperature) influencing the sorption process, were examined. The Freundlich and Langmuir were applied. Thermodynamic parameters viz. the change in Gibbs free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were also calculated. Under the optimum experimental conditions employed, the removal of ~100% of Ni(II) ions was attained. The procedure was successfully applied to remove Nickel(II) from aqueous and different natural water samples.

Keywords: Adsorption isotherms; Eggshell; Natural water; Nickel(II); Sorption; Thermodynamic parameters.

1. Introduction

The well-established toxicity of metals in solution at sufficiently high concentration affects human, animal and vegetation [1, 2]. The pollution of water and soil with heavy metal cations has increased and spreading dramatically throughout the world in the last years as a consequence of the expansion of industrial activities: a lot of metals considered to be toxic and dangerous heavy metals [2, 3]. They can be readily adsorbed by marine animals and directly enter the human food chains, thus presenting a high health risk to consumers [4]. Metals are among the main environmental concerns because of their unique characteristics: unlike organic pollutants, they non-biodegradable hence are accumulated by living organisms [5]. The

presence of toxic heavy metal ions in the water and wastewater over the permissible limits pose a significant threat to the environment and public health. In view of the toxicity, incremental accumulation in the food chain and persistence in the ecosystem, wastewaters containing heavy metals are required to be properly treated prior to discharge into receiving waters [6]. It is well established that heavy metals interfere with functional groups of essential enzymes even at very lower concentration [7].

Nickel was selected as adsorbate because its compounds have widespread applications in many industrial processes such as non-ferrous metal, mineral processing, paint formulation, electroplating, batteries manufacturing,

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forging, porcelain enameling, copper sulfate manufacture and steam-electric power plants, dye industries [8-10], thus leading to relatively high concentrations in aquatic environment [11, 12]. Nickel is one of the toxic heavy metals which are common pollutants of the environment [5]. In humans, nickel can cause serious problems, such as dermatitis, allergic sensitization, lungs, kidneys, skin and nervous system damages. It is also known as carcinogen [5, 13]. In view of toxic effects of nickel to human and animal life, it is important to treat industrial effluents polluted with Ni(II) ions before their discharge into the receiving water bodies [6].

Adsorption onto solid materials is an easier and cheaper technique, whereby the adsorbate is accumulated on the surface of or inside an adsorbent [13]. Adsorption compared with other methods appears to be an attractive process in view of its efficiency and the ease with which it can be applied in the treatment of heavy metal containing wastewater [14]. It is necessary to have a low-cost material to treat large volumes of waste water. The use of lowcost sorbents has been thoroughly investigated instead of other more expensive materials, for example, natural and waste materials coming from industrial, agriculture and forestry activities have high capacity for removing metal ions [15]. The removal efficiency of new and inexpensive adsorbents can be tested first in model aqueous solutions (distilled water) and then in spiked ground and drinking water. One cheap and easily available material having possibilities as a suitable sorbent for Ni (II) ions is eggshell. Due to their high calcium content, eggshells usually have no commercial importance. Disposal of eggshells is also a serious problem for egg processing industries due to stricter environmental regulations and high landfill costs [16]. Since eggshell is composed mainly of calcium carbonate, it

should behave as known sorbents that contain this compound, i.e. calcite [17], calcareous soil [18]. The hen eggshell mainly consists of two regions: the mammillary matrix (i.e., eggshell membrane) consisting of interwoven protein fibers and spherical masses, and the spongy matrix (i.e., calcified eggshell) made of interstitial calcite or calcium carbonate crystal [19, 20]. The by-product eggshell weighs approximately 10% of the total mass (~ 60 g) of hen egg [21], representing a significant waste from the egg-derived products processor because it was traditionally useless and commonly disposed of in landfills without any pretreatment.

The present work aims to describe the batch adsorption characteristic of Ni(II) on eggshell concentrating on various operational parameters; such as pH, contact time, initial Ni(II) and ES concentrations. Experimental data have been analyzed by adsorption isotherms. kinetics and thermodynamic parameters. Moreover, the powdered eggshell (ES) as a cheap and effective inorganic sorbent, widespread and may represent environmental problem was used for the removal of Ni(II) ions from aqueous solutions.

2. Experimental

2.1. Sorbent samples and solutions

The eggshells samples (poultry eggshells) used in this study were obtained, free of charge, from some private restaurant located in Mansoura City, Egypt. The samples were collected, washed with water and dried for 2 h in large trays in an oven maintained at 125°C, allowed to cool to room temperature, crushed, sieved and those with size (25-63 µm) were used in the experiments. The samples were then packed into stoppered bottles and stored in desiccators for future use. The chemical composition (by weight) of by-product eggshell has been reported as followswicaldiaming

carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%) [20, 21]. Functional groups of eggshells were characterized through infrared analysis. The observable peaks at about 710, 875, 1420, 1807 and 2520 cm⁻¹ coincided with those of pure CaCO₃.

All the solutions were prepared from certified reagent grade chemicals. Aqueous solutions were prepared in doubly distilled water. The nickel stock solution 1000 mg/L was prepared from (BDH Ltd, Poole, England) by dissolving 0.25 g salt in 250 mL doubly distilled water. Further dilutions were prepared daily as required.

2.2. Apparatus

A VWR model 3500 digital shaker was used for shaking solutions. Infrared spectroscopy was undertaken via a Mattson 5000 FT-IR spectrophotometer using the KBr disc method. The measurements were carried out using atomic absorption spectrophotometer AAS240FS (Varian, Australia). Also, the stirring of solutions was performed with a magnetic stirrer, Jenway 1000. The pH was measured using pH meter (symphony, USA) provided with a glass electrode.

2.3. Procedure

Unless stated otherwise, all batch sorption experiments were done at room temperature $(25 \pm 2 \, ^{\circ}\text{C})$. Known volumes of Ni(II) stock solution were pipetted into quick-fit glass bottles containing 0.1g of ES sorbent in 50 mL aqueous solution to give concentrations ranging from 1 mg/L to 60 mg/L. Since the pH of any resulting solution was 7.0, no further controlling of pH was necessary since pH 7 was suitable for most adsorption experiments. The resulting solutions was then shaken at 250 rpm and samples were taken at fixed time periods $(1, 3, 5, 10, 15, 30, 60, 120 \, \text{min})$ in

order to study the kinetics of the adsorption process. Preliminary experiments showed that 30 min was sufficient for adsorption of Ni(II) ions onto ES. The samples were subsequently filtered off and the residual Ni(II) ions concentration in the filtrate was determined by atomic absorption spectrometry (at a wavelength of 232 nm, lamp current 4 mA, slit width 0.2 nm, acetylene as fuel, air as support and flame stoichiometry is oxidizing). The percentage adsorption of Ni(II) ions from the solution was calculated from the relationship:

% Adsorption =
$$(C_i - C_r)/C_i \times 100$$
 (1)

where C_i corresponds to the initial concentration of Ni(II) ions and C_r is the residual concentration in the filtrate after shaking for a definite time period. The metal uptake q (mg/g) was calculated as:

$$q = [(C_i - C_r)/m].V$$
 (2)

where m is the quantity of sorbent (g) and V the volume of the suspension (L). To assess the applicability of the procedure, another series of experiments was conducted on 50 mL of clear and pre-filtered natural water samples with an initial pH adjusted to 7.0. These suspensions contained 10 mg/L of Ni (II) ions, 0.1 g of ES and were shaken for the optimum time (30 min) at 250 rpm.

3. Results and discussion

3.1. Effect of pH value

One of the most important process parameters in adsorption is pH of the medium. Moreover, the sorption of divalent nickel by ES is also influenced by the surface properties of the sorbent and nickel species present in aqueous solution. In order to study the effect of pH on Ni(II) adsorption by ES, pH of solution was varied from 3.0 to 11.0. From Fig. 1, it is observed that the adsorption of nickel varies with pH and is highly pH-dependent. It is well-established that at pH < 8, the predominant

species of nickel is Ni²⁺. At pH > 8, nickel ion in the 2+ state seems to be capable of being hydrolyzed to NiOH+, soluble Ni(OH)2 and Ni(OH)₃ and solid Ni(OH)₂. [22, 23]. The powdered eggshells (ES) consists mainly of CaCO₃. When calcium carbonate (as sparingly soluble salt-type mineral) is suspended with water, HCO₃-, Ca²⁺, CaHCO₃+ and CaHO+ are formed as surface-charged species and their presence is a function of solution pH [24]. Moreover, OH, H and HCO3 are considered as potential determining ions in addition to Ca²⁺ and CaCO₃. The dissociation of OH groups on the surface leads to an acidic or alkaline surface (positive or negative surface charge).

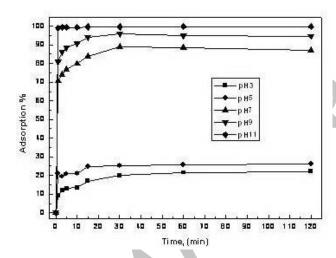


Fig. 1. Adsorption % of Ni (II) ions 10 mg/L by ES 0.1 g vs. shaking time at different pH values.

At low pH values, H⁺ ions compete with Ni(II) ions for the surface of the adsorbent which would hinder the Ni(II) ions from reaching the binding sites of the adsorbent caused by repulsive forces. Also, the lower removal of Ni(II) ions at pH 3 may be attributed to the partial solubility of ES sorbent used (consists mainly of CaCO₃). At pH > 4, the removal efficiency begins to increase, reaching a maximum value, about 100%, at pH 11. When pH is increased, the Ni(II) ions get precipitated due to increase in hydroxide anion

forming a nickel hydroxide precipitates. As a function of time, the equilibration was obtained after shaking time of 30 min for all the investigated pH values. For this reasons, the optimal pH was selected to be 7.0 with 30 min shaking for the further experiments.

3. 2. Effect of Ni(II) ions concentration and sorbent dose

The effect of initial Ni(II) ions concentration on its adsorption at pH 7 by ES (0.1 g) after shaking from 1 to 120 min was shown in fig. 2. It was found that the increase of initial Ni(II) ions concentration, leads to an increase of q [metal uptake (mg/g)]. Increase of q with the increase of C_0 [initial metal ion concentration (mg/L)] was expected due to the increase of the sorbed ion concentrations per unit weight of ES. Moreover, with increasing the Ni(II) concentration in the solution, the diffusion of Ni(II) ions in the boundary layer increases resulting in higher sorption by ES.

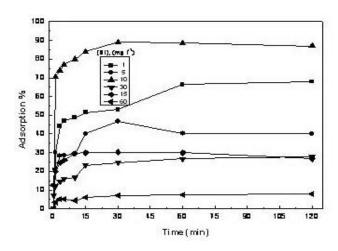


Fig. 2. Adsorption % of different Ni(II) ion concentrations (mg/L) onto 0.1 g ES vs. shaking time at pH 7.

The effect of varying amounts of ES in the range 0.025-1 g, on the adsorption of Ni(II) ions 10 mg/L from aqueous solutions of pH 7 was depicted in Fig. 3. The data show that the adsorption increases as the amount of ES increases which may be attributed to an

increase in the number of binding sites available to adsorb metal ions. This agrees well with the data shown in Fig. 2. Moreover, 0.1 g/L dose of ES was an optimum one for further experiments.

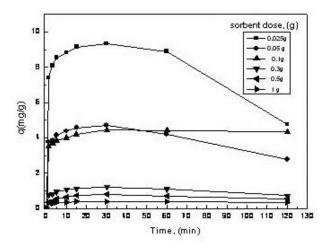


Fig. 3. Effect of ES dose on adsorption % of Ni(II) at different shaking times.

3.3. Kinetics of the adsorption process

Fig. 2 shows the variation of the Ni(II) uptake by ES with shaking time at pH 7 using 0.1 g ES. The data depicted in this figure indicate that the adsorption of Ni(II) ions was quite rapid at the first stage, which may suggest that adsorption occurred mainly at the surface of the solid sorbent and to some extent by the internal macro-pores, transitional pores and The uptake increased with micro-pores. increasing the initial Ni(II) concentration, which may be attributed to higher collision between the Ni(II) ions and sorbent. On the basis of the results, 30 min of shaking was found suitable for maximum adsorption and were used in all subsequent measurements.

When the data in Fig. 2 were re-plotted against the square root of the shaking time, the obtained linear correlation (Fig. 4) may verify the Morris-Weber equation.

$$q = K_d(t)^{1/2}$$
 (3)

where q is the amount of Ni(II) ions adsorbed (mg/g). This indicates that an intrapore diffusion mechanism was involved in

adsorption of Ni(II) ions by ES. Fig. 4 shows that two distinct regions were observed: an initial linear portion which may be due to the boundary layer effect [25] and a second portion which may be due to the intra-particle diffusion effect [26]. However, the fact that the line depicted in (Fig. 4) does not pass through the origin indicating that intra-pore diffusion is not the controlling step in sorption of Ni (II) ions by ES [27, 28]. These data agree with those of Juang et al. [29]. The value of the rate constant K_d was evaluated as 0.084 (min) which give indication about the mobility of the Ni(II) ions toward the ES surface.

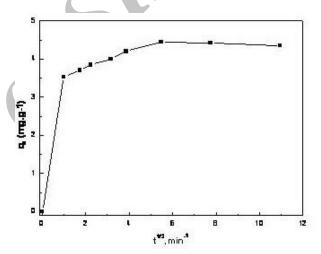


Fig. 4. Plot of the amount of Ni(II) adsorbed onto ES (0.1g) vs. square root of time at pH 7.

The kinetic data in Fig. 2 for the adsorption of Ni(II) ions onto ES was examined by Bangham equation [30]:

$$loglog[C_i/(C_i-qm)] = log(K_om/2.303V) + \alpha logt$$
 (4)

Plot of Loglog[C_i /(C_i -qm)] vs. logt gives a straight line (Fig. 5). The results show that the diffusion of Ni(II) ions into ES pores played a role in the adsorption process and were similar to those described elsewhere [31]. The deduced values of K_o and α constants were 0.765 and 0.04, respectively.

Again the kinetic data obtained in Fig. 2 for Ni(II) ions adsorption by ES were tested by

Lagergren equation, as cited by Gupta and Shukla [32]:

$$log (q_e - q) - log q_e = - K_{ads} t /2.303$$
 (5)

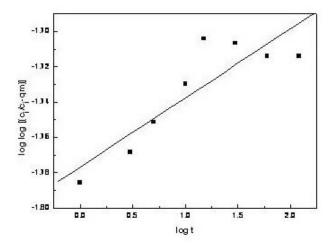


Fig. 5. Plot of log log $[C_i/(C_i - qm)]$ vs. log t for the adsorption of Ni(II) ions onto ES (0.1 g) at pH 7.

The linear plot of log $(q_e - q)$ versus t (Fig. 6) shows the appropriateness of the above equation and consequently the first-order nature of the process involved. The value of K_{ads} was calculated to be 0.09 min⁻¹.

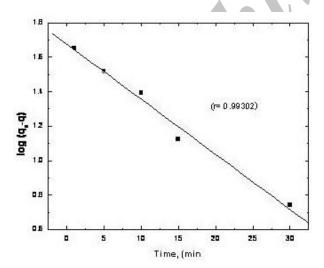


Fig. 6. Plot of log (q_e-q) vs. stirring time (t) for the adsorption of Ni (II) ions by ES (0.1g) at pH 7.

3. 4. Adsorption isotherms

Adsorption isotherms can be generated based on numerous theoretical models where Langmuir and Freundlich models are the most

commonly used. The Langmuir model assumes that the uptake of Ni(II) ions occurs on a homogenous surface by monolayer adsorption without any interaction between the adsorbed ions. The linear form of the Langmuir equation applied to the Ni(II) ions adsorption data in Fig. 2 was:

$$1/q_e = 1/k_L + (1/k_L b) 1/C_e$$
 (6)

where q_e is the amount of Ni(II) ions adsorbed at equilibrium (mg/g), C_e is the final equilibrium concentration (mg/L), b (mL/mg) is the Langmuir constant and k_L (mg/g) is the monolayer adsorption capacity. Fig. 7 shows that the plot of $1/q_e \, vs. \, 1/C_e$ gave a straight line suggesting the applicability of the Langmuir model. The values of k_L , b and the correlation coefficient (r) were 2.36 mg/g, 0.478 mL/mg and 0.9873, respectively.

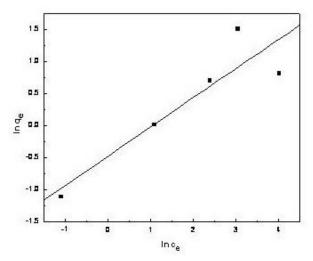


Fig. 7. Langmuir plot for Ni(II) ions adsorption onto ES (0.1 g).

On the other hand, the Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented by:

$$\ln q_e = \ln K_F + 1/n \ln C_e \tag{7}$$

where K_F and 1/n are the Freundlich constants characteristic of the ways fem,

indicating the adsorption capacity and the adsorption intensity, respectively. Fig. 8 shows the applicability of this equation on the adsorption of Ni(II) ions on ES. The parameters K_F and n for Ni(II) ions adsorption onto ES were calculated from intercept and the slope of the figure giving values of 0.620 mg/g and 2.199, respectively with a correlation coefficient r=0.9099. It was known that favorable adsorption occurs when the (n) value is greater than unity [33].

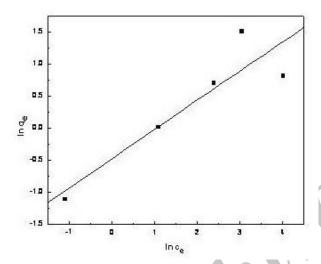


Fig. 8. Freundlich plot for Ni(II) ions adsorption onto 0.1g ES.

The sorption data was modeled by Dubinin-Radushkevich (D–R) isotherm equation (Fig. 9) to determine the adsorption type (physical or chemical). The linear form of this model [30, 34] is expressed by:

$$\ln q_e = \ln q_m - \beta \epsilon^2 \tag{8}$$

where q_e is the amount of the metal adsorbed per unit dosage of ES (mol/L), q_m the monolayer capacity (mol/g), and β is the activity-coefficient related to mean sorption energy (mol²/J²) and ϵ is the Polanyi potential described as:

$$\varepsilon = RT \ln (1 + 1/C_e) \tag{9}$$

The mean sorption energy, E (kJ/mol), can be calculated by equation (10) [27, 34]:

$$E = (-2 \beta)^{-1/2}$$
 (10)

From Fig. 9, the slope of the D–R plot gives β constant and was evaluated as -0.0065. The mean sorption energy (E) was found to be 8.77 kJ/mol. It is generally assumed that if the sorption energy is below 8 kJ/mol, the sorption can be affected by physical forces such as Van Der Walls forces, while if E is between 8 and 16 kJ/mol, the sorption is governed mainly by ion exchange [34]. Sorption may be governed by particle diffusion if E> 16 kJ/mol [35]. Therefore, the E value calculated for the adsorption of Ni(II) ions onto ES showed that the sorption may be chemical in nature and takes place by ion exchange mechanism.

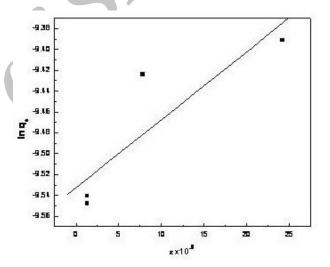


Fig. 9. D-R isotherm for Ni(II) ions adsorption onto 0.1g ES.

3.5. Effect of temperature and thermodynamic parameters

The temperature has two major effects on the sorption process. Increasing the temperature is known to increase the rate of diffusion of the sorbate; changing the temperature will change the equilibrium capacity of the sorbent for a particular sorbate. In this study, a series of experiments were conducted on the adsorption of 10 mg/L Ni(II) ions onto 0.1g of ES at 278, 283, 298, 313 and 333 K to investigate the effect of temperature on the sorption dynamics at different stirring

times. The results depicted in Fig. 10 showed that the sorption increases as the temperature increases confirming that the process is endothermic in nature. Such results may either be attributed to the creation of some new active sites on the sorbent or to the acceleration of originally slow adsorption some Moreover, the enhancement of mobility of Ni(II) ions from the bulk of solution towards the adsorbent surface should also be taken into consideration. This agrees well with the literature data [36, 37]. Moreover, there was a decrease in the equilibration time to reach to a 100% for nickel adsorption. Such results could suggest that the adsorption of Ni(II) ions involves chemical bond formation and ion exchange [36]. Accordingly, chelate formation may occur between Ni(II) ions and oxygen atoms on the ES surface together with ion exchange to form NiCO₃ [38]. Since most industrial effluents are usually hot, the simple adsorption procedure presents here may find application in the industrial wastewater treatment for the removal of Ni(II) ions.

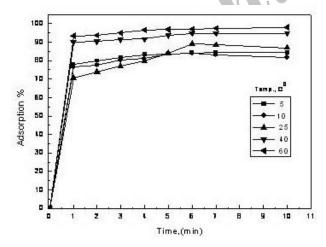


Fig. 10. Effect of temperature on the sorption % of Ni(II) ions onto 0.1g ES at different shaking times.

In order to investigate the thermodynamic parameters for the adsorption of Ni(II) ions by ES, the distribution coefficient K_d (L/g) was calculated at 278, 283, 313, 333 K according to the following equation [34, 39]:

$$K_{d} = q_{e} / C_{e} \tag{11}$$

The K_d values calculated for the sorption of Ni(II) ions by ES are 2.69, 2.59, 9.12, and 24.02 l/g. These results show that the K_d increases with temperature and revealing that the sorption of Ni(II) ions by ES may be endothermic. The enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the slope and intercept of the plot of ln K_d against 1/T, respectively, as depicted in Fig. 11 and according to the following equation [34, 40, 41]:

$$\ln K_{\rm d} = \Delta S^{\circ}/R - \Delta H^{\circ}/RT \tag{12}$$

The Gibbs free energy change (ΔG°) was calculated according to:

$$\Delta G^{\circ} = -RT \ln K_{d} \tag{13}$$

where R is the universal gas constant (8.314 J/molK) and T is the absolute temperature (K).

The calculated enthalpy change ΔH° was found to be 31.29 J/mol for the sorption of Ni(II) ions by ES. The positive value of ΔH° clarified that the sorption process is endothermic. The entropy change (ΔS) was found to be 119.49 J/molK. According to Sari et al. [34], this result showed that Ni(II) in bulk phase (aqueous solution) is in a much chaotic distribution compared with the relatively ordered state of solid phase (sorbent surface). Moreover, the Gibbs free energy change (ΔG°) was -2.29, -2.24, -5.75, and -8.80 kJ/mol for the adsorption of Ni(II) ions at 278, 283, 313 and 333 K, respectively. The negative ΔG° values indicate that the adsorption of Ni (II) ions on ES is feasible and spontaneous thermodynamically.

3. 6. Application

To investigate the applicability of the recommended procedure, a series of experiments were performed to recover 10

mg/L of Ni (II) ions added to aqueous and some natural water samples. The adsorption experiments were carried out using 50 mL clear, filtered, uncontaminated sample solutions with their natural pH values (~7). The results obtained (Table 1) show that the recovery was satisfactory and quantitative. However, the lower recovery values of some samples were enhanced to reach about 100% by increasing the ES dose.

3.7. Comparison of nickel uptake by eggshell with other sorbents

The values of Ni(II) uptake by different adsorbents collected from the literature along with the results of this work are given in Table 2 in the form of monolayer adsorption capacity. The value of Ni(II) uptake found in this work is higher than some of the reported elsewhere. The comparison of adsorption capacities of ES

used in this study with those obtained in the literature shows that the ES is effective for the removal of nickel(II) from aqueous solution. Moreover, the eggshell (ES) sorbent is a cheap and, widespread.

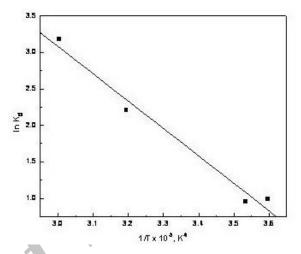


Fig. 11. Thermodynamic distribution coefficient (K_d) calculated for the adsorption of Ni(II) ions onto ES as a function of temperature.

Table 1. Recovery of Ni(II) ions added to some water samples using 0.1g of ES sorbent at pH 7.

Sample (location)	Added (mg/L)	Adsorbed (mg/L)	Re %
Distilled water	10	8.90	89.0
Tap water (our laboratory)	10	8.30	83.0
Nile water (Mansoura City)	10	7.55	75.5
Underground water (Mansoura City)	10	7.77	77.7

Table 2. Comparison of adsorption capacity of Ni(II) onto various adsorbents.

Adsorbent	Adsorption capacity (mg/g)	References
Parthenium hysterophorus	17.2	[42]
Tea factory waste	15.26	[43]
Sphagnum moss peat	9.18	[44]
Sheep manure waste	7.2	[45]
Fly ash	0.03	[46]
Rhizopus nigricans	1.0	[47]
Granular activated carbon	1.49	[48]
Natural clay	12.5	[49]
Eggshell	2.36	Our investigation

4. Conclusions

The powdered eggshell (ES) as a cheap and effective inorganic sorbent was used for the removal of Ni(II) ions from aqueous solutions. The experimental results revealed the following:

- 1. The adsorption occurred mainly at the surface of the solid ES and slightly by the internal pores.
- 2. The adsorption data well described by Freundlich and Langmuir models over the concentration range studied. Moreover, the adsorption is chemical and endothermic in nature. Moreover, the negative ΔG° values indicate that the adsorption of Ni (II) ions on ES is feasible and spontaneous thermodynamiccally.
- 3. The adsorption occurs, depending on the solution pH, through ion exchange, adsorption of hydrolytic species, Ni(OH)⁺ ions, and/or the precipitation of nickel hydroxide onto ES sorbent.
- 4. The procedure was successfully applied for the removal of Ni(II) ions from some natural water amples.
- 5. Moreover, the nickel ions were essentially held by ES sorbent and would not be leached out by acids owing to the solubility of the sorbent. Therefore, the metal-loaded solid waste could be solidified to an environmentally safe form thereby serving the double-fold aim of water treatment and solid waste disposal.

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