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Biosorption of Nickel(II) ions from aqueous solutions by using Chicken eggshells as low-cost biosorbent

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ABSTRACT/RESUME

Abstract: *The aim of this present study was to evaluate the feasibility of using chicken eggshells as low-cost biosorbent for nickel(II) ions adsorption from aqueous solutions. In order to clarify the adsorption process, batch experiments were performed to study the effect of operating parameters such as biosorbent dose (1-10 g/L), initial concentration of nickel ions (10-50 mg/L), contact time (5-120 min) and temperature (20-50 °C). To describe the adsorption equilibrium, the experimental data were analyzed by the Langmuir, Freundlich and Temkin isotherm models. The Freundlich model showed better representation of data (R^2> 0.999).The maximum adsorption capacity of chicken eggshells for nickel ions was approximately 2.3 mg g^{-1} at 20 °C. The results of the present study suggest that chicken eggshells can be used beneficially as low-cost biosorbent for nickel(II) ions adsorption from aqueous solution.*

I. Introduction

Heavy metal pollution is an environmental problem of worldwide concern. The heavy metals are among the most common pollutants found in industrial effluents [1]. Nickel is one of toxic heavy metals and it can be present in wastewater from electroplating, refining and welding industries [2]. The chronic toxicity of nickel to humans and the environment has been well documented and high concentration of nickel causes cancer of lungs, nose and bone [3]. Several processes have been employed for the removal of nickel ions from water and wastewater including chemical precipitation, ion-exchange, membrane filtration, electrochemical treatment and adsorption [4]. However, most of these methods have several disadvantages such as high operating costs, low selectivity, incomplete removal, and production of large quantities of wastes. Therefore, physicochemical approach by using adsorption method has been proposed to solve this problem [5]. Generally activated carbon, silica gel, activated alumina and ion exchange resin have higher capacity in the removal of toxic heavy metals. So, their utilization is not common and confined to special treatment due to high installation and operating cost. Thus, many researchers have applied regenerated natural wastes as low-cost biosorbent to treat heavy metals from aqueous solutions [6]. Various biomaterials produced or harvested from natural resources or agricultural products, mostly in metabolically inactive states, have been used in disposal of heavy metal effluents by biosorption. These include lignocelluloses biomaterials, such as rices hulls [7], cocoa shells [8], Turkish fly ash [9], banana peel [10], bagasse fly ash [11], rice husk [12], chicken eggshells [6] and sugarcane bagasse [13].

Meanwhile, chicken eggshells are used in enormous quantities by food manufacturers, restaurants and household and the shells are disposed of as solid waste. Chicken eggshells have a little developed porosity and pure $CaCO_3$ as an important constituent [6]. Investigations have been conducted to explore the possibility of useful applications of chicken eggshells, especially for wastewater treatment [14]. Research has shown that chicken eggshells may be used as a biosorbent for iron [15], cadmium [16], chromium [6], lead [17], reactive dye [18], cationic dye [19] and lignosulfonate [20]. However, there has so far been no study reported in academic literature related to the use of powdered chicken eggshells as an biosorbent for removing of nickel(II) ions from aqueous solution. Therefore, the aim of the present study was the use of powdered chicken eggshells as low-cost biosorbent for adsorption of nickel ions from aqueous solutions. The effects of several operating parameters, such as biosorbent dose, initial nickel ions concentration, contact time and temperature have been investigated. Thereafter, the adsorption equilibrium study were carried out and analyzed to describe the retention process.

II. Materials and methods

II.1. Sorbent Preparation

Chicken eggshells were collected and were washed with tap water for several times and afterwards with distilled water for three times. Then, they were dried at 105 °C for 24 h to achieve constant weight, and then were crushed and milled. Thereafter, they were sieved into a uniform size.

II.2. Batch Adsorption Experiments

The effects of experimental parameters: biosorbent dose (2–10 g L^{-1}), initial nickel ions concentration (10–50 mg L^{-1}), contact time (5−120 min) and temperature (20–50 °C) on the adsorptive removal of Ni(II) ions were studied in a batch mode using 50 mL of each Ni(II) solutions. After adsorption process, the biosorbent was separated by filtration. Nickel solutions were analyzed using a flame atomic absorption spectrometer (Perkin Elmer AAnalyst 400) at a wavelength of 232.0 nm.
The removal rate *R* (%) and the equilibrium amount of nickel(II) ions adsorbed per unit mass of biosorbent q_e (mg g^{-1}) were, respectively, calculated from the following equations:

$$R\ (\%) = \frac{(C_i - C_e)}{C_i} * 100 \qquad \textbf{(1)}$$

$$q_e = \frac{(C_i - C_e)}{m} * V \qquad \textbf{(2)}$$

Where C_i (mg L^{-1}) is the initial Ni(II) ions concentration; C_e (mg L^{-1}) is the equilibrium Ni(II) ions concentration; *V* (L) is the volume of the solution; and *m* (g) is the mass of the biosorbent.

III. Results and discussion

III.1. Effect of biosorbent dose

The effect of biosorbent dose in the range of 2 to 10 g L^{-1} was used for the adsorption experiments and the results are given in Figure 1. We note that, the removal rate of Ni(II) ions increases gradually with increasing biosorbent dose. It increases from 5.06 to 35.46 %. This raise in removal rate of Ni(II) ions could be due to availability of more surface area and functional groups. The biosorbent dose of 10 g L^{-1} is considered as equilibrium value and was taken as the optimal biosorbent dose for the subsequent experiments.

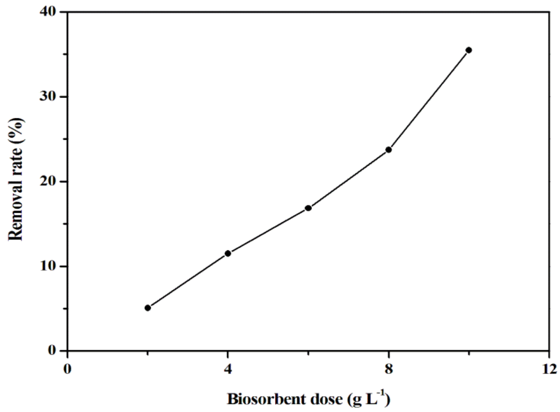

Figure 1. *Effect of chicken eggshells dose on the removal rate of Ni(II)ions.*

III.2. Effect of initial Ni(II) ions concentration

The effect of initial Ni(II) ions concentration (10–50 mg L^{-1}) was studied at pH of 5.6 and the results were illustrated in Figure 2. The plot revealed that an increase in the Ni(II) concentration from 10 to 50 mg L^{-1} lead to a decrease in removal rate of nickel(II) from 63.4 % to 35.46. This latter could be attributed to the saturation of available active sites on the biosorbent above a certain concentration of Ni(II) ions.

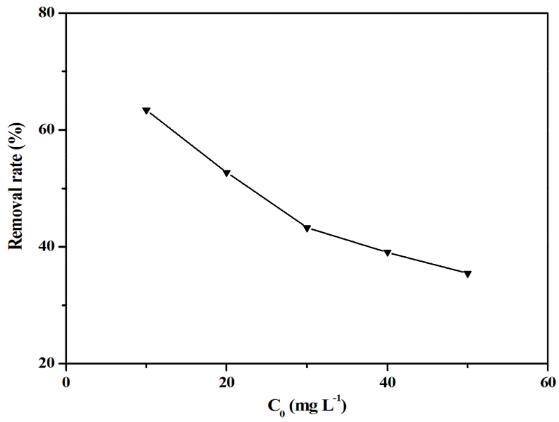

Figure 2. *Effect of initial Ni(II) concentration on the removal rate of Ni(II) ions*

III.3. Effect of contact time

The effect of contact time on the Ni(II) ions adsorption was determined and the corresponding variation of removal rate is shown in Figure 3. The obtained results indicate that the removal of Ni(II) ions increased with time up to 90 min and thereafter increased slowly. The removal rate of Ni(II) ions was 35.4 % at 90 min and 35.46 % at 120 min by chicken eggshells, respectively. According to the results, the equilibrium reached at 120 min was

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taken as the optimal contact time for the subsequent experiments.

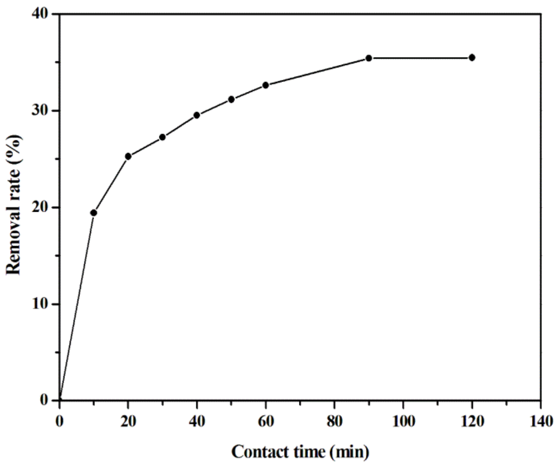

Figure 3. *Effect of contact time on the removal rate of Ni(II) ions*

III.4. Effect of temperature

Figure 4 shows that the removal rate of Ni(II) ions on chicken eggshells increases with the increase of temperature. It increases from 35.46 to 52.3 % in the temperature range 20−50 °C. The increase in removal rate of Ni(II) ions could be due to the intraparticle diffusion rate of Ni(II) ions into the pores of chicken eggshells which is accelerated at higher temperatures. The results indicate that the biosorption of Ni(II) ions onto chicken eggshells is an endothermic process.

III.5. Adsorption Equilibrium Study

For adsorption equilibrium study: Langmuir, Freundlich and Temkin adsorption isotherms have been tested and were applied to describe the adsorption process of the experimental results. Linear form of Langmuir isotherm equation can be expressed as follows [21]:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{K_L\,Q_{max}} \qquad (3)$$

Where K_L (L mg^{-1}) is the Langmuir constant, Q_{max} (mg g^{-1}) represents the maximum adsorption capacity under the experimental conditions. Q_{max} and K_L are determined from the slope and intercept of plotting C_e/q_e versus C_e, respectively.

The linearized Freundlich isotherm equation is represented by the following equation [22]:

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (4)$$

Where K_F (mg g^{-1}) (L g^{-1})$^{1/n}$ is the Freundlich constant related to the bonding energy. n is the heterogeneity factor and wich is a measure of the deviation from linearity of adsorption. K_F and n are, respectively, determined from the intercept and slope of plotting ln q_e versus ln C_e.

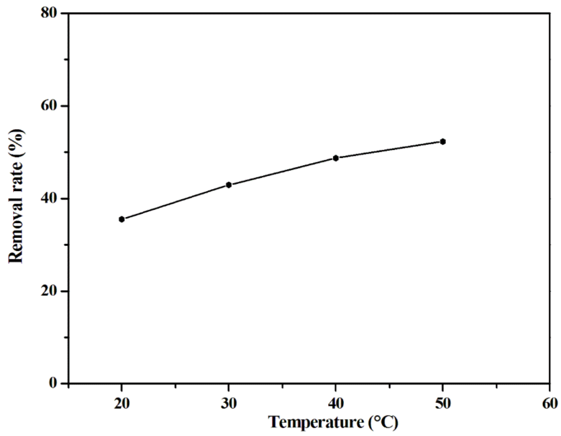

Figure 4. *Effect of temperature on the adsorption of Ni(II) by eggshells*

The Temkin isotherm equation assumes that the fall in the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies up to some maximum binding energy [23]. The Temkin isotherm has been applied in the following form:

$$q_e = \frac{RT}{B}\ln A + \frac{RT}{B}\ln C_e \qquad (5)$$

Where A (L g^{-1}) and B (J mol^{-1}) are the Temkin constants. T is the absolute temperature and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). A and B are determined from the intercept and slope of plotting q_e versus ln C_e, respectively.

The values of isotherms constants are presented in Table 1. From this table one can point out that the adsorption of Ni(II) ions onto chicken eggshells was well correlated with the Freundlich and Langmuir isotherms for the studied concentration range, which may be due to the distribution of active sites onto chicken eggshells surface. It could be seen from these data, that the linear correlation coefficients (R^2) for the Freundlich isotherm model has the highest value of regression coefficient compared to the Langmuir and Temkin isotherms, which indicate that this model describe very well the adsorption process and suggests that the adsorption on the surface of chicken eggshells was a multilayer adsorption. The maximum adsorption capacitiy (Q_{max}) of Ni(II) ions found in the present study was compared with those of other biosorbent reported in the literature and are presented in Table 2.

Table 1. *Isotherms parameters for Ni(II) ions adsorption by eggshells*

Langmuir model		**Freundlich model**		**Temkin model**	
Q_{max} (mg g^{-1})	2.2980	K_F (mg g^{-1}) (L g^{-1})$^{1/n}$	0.0923	A (L g^{-1})	0.4187
K_L (L mg^{-1})	0.0295	$1/n$	0.7280	B (kJ mol^{-1})	6.0840
R^2	0.9929	R^2	0.9997	R^2	0.9787

Table 2. *Maximum adsorption capacities for Ni(II) ions removal by various biosorbents.*

Biosorbents	**Q_{max} (mg g^{-1})**	**References**
Rices hulls	1.82	[7]
Cocoa shell	2.60	[8]
Turkish fly ash	1.16	[9]
Banana peel	6.60	[10]
Bagasse fly ash	6.50	[11]
Rice husk	5.52	[12]
Sugarcane bagasse	2.23	[13]
Fly ash	0.03	[24]
Sawdust-phosphate treated	0.70	[25]
Aspergillus niger	1.10	[26]
Chicken eggshell	2.30	Present study

The maximum adsorption capacity of chicken eggshells to bind nickel(II) ions was compared with other biosorbents. From Table 2, one can see that adsorption capacity value of eggshells is lower than that of banana peel [10], bagasse fly ash [11] and rice husk [12]. On the other hand, this value is higher or considerably greater than other reported biosorbents [7, 13, 24-26]. The comparison shows that the chicken eggshells used in this research shows a favorable adsorption capacity for Ni(II) ions if compared to the other biosorbents. The different performances of nickel uptake could be explained in term of the following factors: (i) the heterogeneous nature and composition of biosorbents; (ii) the textural and surface properties of each biosorbent such as structure, functional groups and their surface area.

IV. Conclusion

Batch adsorption studies for the removal of Ni(II) ions from aqueous solutions have been carried out using eggshells as low-cost biosorbent. Batch studies demonstrated that under laboratory conditions, a 10 g L^{-1} biosorbent dose was found to be optimum at a pH of 5.6, contact time of 120 min and temperature of 50 °C for achieving a removal rate greater than 52 % of Ni(II) ions from synthetic solution containing 50 mg L^{-1} of Ni(II) ions concentration. Equilibrium isotherm data were in good agreement with Freundlich than Langmuir and Temkin isotherms models. The maximum monolayer adsorption capacity, Q_{max}, of nickel(II) calculated from Langmuir model was found to be 2.3 mg g^{-1} at 20 °C. Based on the obtained results, it can be concluded that since the eggshells is an easily, locally available and low-cost biosorbent; it may be treated as a cost effective and a potential biosorbent for the removal of Ni(II) ions from aqueous solutions and treatment of wastewater.

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