Original Article

Biosorption Study of Ni(II) on Apple Peel Granola from Aqueous Solution

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Abstract

Introduction: Nickel is found in various industrial processes such as electroplating, leather tanning, cement preservations, paints and pigments, textile, steel fabrication and canning industries. It has been proven that Ni(II) has several health hazards and is carcinogenic. The aim of this study is to evaluate Ni(II) adsorption on apple peel granola from aqueous solution.

Material and Methods: This study was done in the laboratory scale and batch condition. In this study, the effects of adsorbent dose, contact time and pH were investigated on the removal of nickel by batch process. The apple peels granola was prepared in lab conditions, and sieved by standard sieves of 60-100 mesh. The nickel concentration in standard and unknown samples was measured by AA spectrophotometer. To understand the adsorption process, the experimental data were analyzed with some isotherm and kinetic models.

Results: The maximum removal was found at pH= 7. The nickel removal efficiency decreased from 50.1 to 25% by increasing adsorbent dosage. By increasing the pH from 3 to 7, the removal efficiency increased from 19.8% to 35.0% at 30 min contact time. The adsorption isotherm and Kinetic analysis of our results showed that the results were compatible with Freundlich isotherm model (R2= 0.909) and pseudo-first-order kinetic model (R2= 0.926).

Conclusion: The results showed that apple peel granola was able to absorb nickel from aqueous solutions and removal efficiency was more in pH=7. Preparing apple peel granola adsorbent is simple, cheap, and superior in application because of its porous structure in comparison with other natural adsorbents.

Keywords: Biosorption, Nickel, Apple peel granola, Isotherm, Kinetic

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Introduction

The environmental and health risks caused by heavy metals are the most important problems. These metals are extremely toxic and even accumulate in the food chain. Water pollution is a major concern worldwide due to the disposal of heavy metals [1]. Heavy metals are not biodegradable, and their presence in rivers and lakes has led to bio-accumulation in living organisms causing health problems for animals, plants and humans. Some heavy metals such as Ni(II) are toxic and pose a serious risk to humans and other biological systems. In recent years, the level of nickel in surface waters is rising due to the discharge of industrial wastewater [2-3].

Nickel is an element that exhibits valances of 0, +1, +2 and +3. Metallic nickel is not commonly found in nature but Ni(II) is found in many minerals. Nickel occurs predominantly as the ion $Ni(H_2O)_6^{2+}$ in natural waters at pH 5–9[3]. Complexes with ligands, such as OH^-, SO_4^{2-}, HCO_3^-, Cl^-, and NH_3, are formed in a minor degree in this pH range. Nickel concentrations in groundwater depend on the soil use, pH, and depth of sampling. The average concentration in groundwater ranges from 7.9 μg/l (urban areas) to 16.6 μg/l (rural areas) [4]. Acid rain increases the mobility of nickel in soil and thus might increase nickel concentrations in groundwater [3].

Nickel is used primarily in the manufacturing of stainless steel and other alloys due to its favorable properties such as hardness, corrosion-resistance, heat-resistance and strength. Examples of alloys include copper-nickel alloys and nickel-chromium alloys. Nickel is also used as a catalyst in plating, coins, batteries, electrodes, electrical contacts, spark plugs and machinery parts. Several treatment technologies have developed to remove of heavy metals from water and wastewater. The conventional methods are chemical precipitation [5], ion flotation [6], membrane separation, ultra-filtration, electro coagulation, reverse osmosis [7-9], adsorption / filtration etc. [10]. Another method is the biosorption process which follows by material accumulation at the interface between the two phases [11].The main advantages of biosorption are its low cost and its high efficiency in the removal of heavy metals [12]. In this study, apple peel granola has been used as a natural adsorbent for Ni[II] removal from aqueous solution. For this purpose, the effect of parameters such as adsorbent dose, contact time and solution pH was investigated by the adsorption process of Ni(II) on apple peel granola.

Materials and Methods

Batch experiments were performed in laboratory scale and temperature (25±2℃). All the used chemical materials were in pure analytical grade. In this study, apple peels were collected from a supermarket in Yazd. At first, the apple peels were washed by water and by distilled water, and were then dried at lab temperature (25±2 ℃) for 72 h. To obtain

the granola of the adsorbent, the apple peels were crushed in an electrical mill and then sieved through standard sifters (mesh no 60-100).

Adsorption studies

The stock (1000 mg/L) solution of Ni(II) was prepared by dissolving of 4.995 g $Ni(NO_3)_2.6H_2O$ salt in double distilled water. The adsorption experiments were done to add the appropriate amount of adsorbent to a series of 250 mL Erlenmeyer. The Erlenmeyer was then sealed and placed on the shaker at 125 rpm to admix and appropriate contact of adsorbent with Ni(II) ions. The effects of the main parameters such as pH (3, 4, 5, 7), adsorbent dose (0.25, 0.5,1 and 2 g/100 ml), and contact time (10, 15, 20, 25, 30, 35 min and 24 hr) were studied.

The Ni(II) concentration in standard and unknown samples was measured by AA spectrophotometer at wavelength of 352.5nm in calibration mode (concentration vs. absorbance). At the end of mixing, the adsorbent particles were separated from the suspensions by filtration through 0.45μ cellulose filter paper. The pH was adjusted using solutions of 0.1N or 1N H_2SO_4 and was measured by pH meter (corning 120) which was previously calibrated with standard buffer solutions.

The percentage of Ni(II) removal (R) and the adsorption capacity (amount of Ni(II) adsorbed per unit of adsorbent mass), q (mg/g), were calculated using the following equations [13-14]:

$$R = \frac{C_0 - Ce}{C_0} \times 100 \qquad (1)$$

$$q = \frac{C_0 - Ce}{m} \times V \qquad (2)$$

Where C0 and Ce are the Ni(II) initial and equilibrium concentrations (mg/L), respectively, V is the volume of solution (L), and m is the mass of adsorbent (g).

The pseudo-first and second order equations are simple kinetic analyses of adsorption that are given in the following equations, respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (5)$$

In equations 4 and 5, k1 and k2 are the pseudo-first-order and the pseudo-second-order adsorption rate constants, respectively and qe and qt are the amount of Ni(II) adsorbed (mg/g) at equilibrium and at time t, respectively [15].

Several sorption isotherm models have been applied to describe the experimental data of sorption isotherms. The Langmuir and Freundlich models are the most frequently employed models. In this study, Langmuir and Freundlich isotherms have been studied. Equation (6) is a linear form of Langmuir equation:

$$\frac{1}{q_e} = \frac{1}{K_L q_m Ce} + \frac{1}{q_m} \qquad (6)$$

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In Equation 6, q_e is the solid phase adsorbate mass to unit of solid adsorbent mass in equilibrium (mg/g), q_{max} is the maximum adsorption capacity (mg/g), C_e the adsorbate concentration in equilibrium (mg/L) and K_L is the Langmuir constant (L/mg).

A linear form of the Freundlich equation can be obtained by Equation (7):

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (7)$$

In Equation 7, q_e and C_e are as explained above and K_F is the Freundlich constant (mg/g) and $1/n$ indicates the intensity of the adsorption [16].

Results

The effect of contact time on removal efficiency

To determine the best contact time, sampling was performed at 10, 15, 20, 25, 30 and 35 min. As shown in Fig. 1, the removal efficiency increased by increasing the contact time so that by increasing the contact time from 10 to 30 min, in 50 mg/L Ni(II) concentration, the removal efficiency increased from 10.8% to 31.2%.
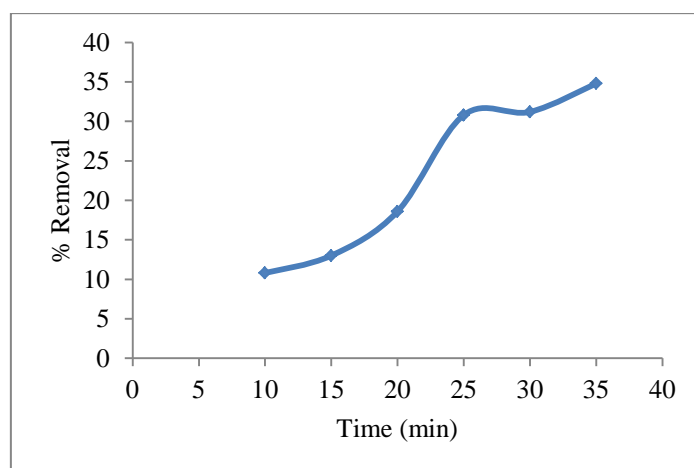

Fig 1. The effect of contact time on Ni (II) removal (m =0.25 g/100 ml, pH=7)

The effect of contact time on the adsorption process showed that nickel adsorption at 30 min reaches equilibrium and then the amount of absorption is negligible.

The effect of adsorbent dose on removal efficiency

According to Fig. 2, by increasing the adsorbent dose, the removal efficiency decreased so that by increasing the adsorbent dose from 0.25 to 2 g/100ml at 50 mg/L of initial nickel concentration, Ni(II) removal

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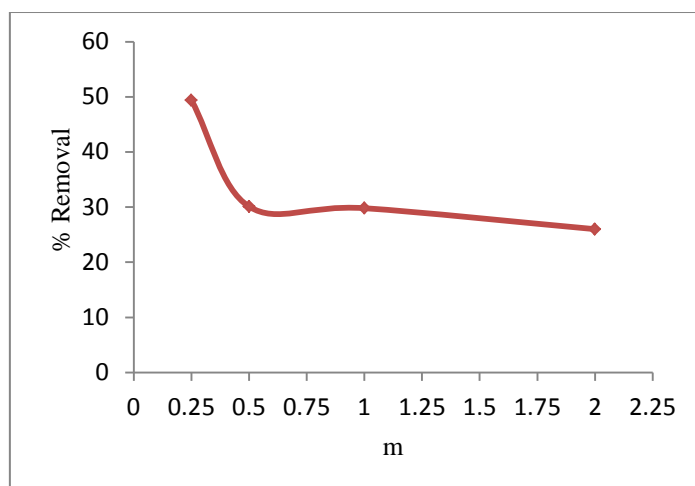efficiency in 30 min contact time decreased   from 51% to 22%.

Fig 2. The effect of adsorbent dose on Ni (II) removal (C_0= 50 mg/l and pH=7)

In order to investigate the adsorption capacity of Ni(II) on the apple peel granola, the data of the experiment were analyzed and the qe values were calculated for different conditions. According to data obtained in this stage, the amounts of qe for apple peel granola at 0.25, 0.5, 1, and 2 g/100ml adsorbent dose after 24 h were 15.06, 2.49, 0.75 and 0.32 mg/g, respectively.

The effect of pH on removal efficiency

The effect of pH on the adsorption of Ni (II) by the apple peel granola is presented in Fig.3. The results showed that adsorption efficiency of Ni(II) increased remarkably with increasing pH values until 7, so that by increasing pH from 3 to 7 after contact time of 30 min, removal efficiency increased from 19.8% to 35.0%.
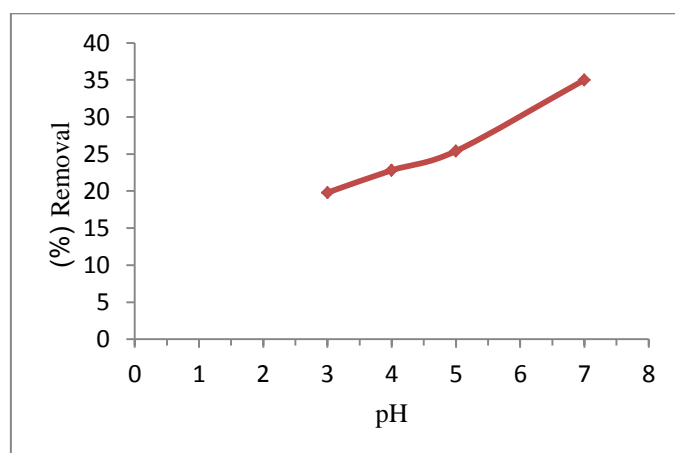

Fig 3. The effect of pH on Ni (II) removal (C_0 = 50 mg/l, m = 0.25 g/100 ml)

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Adsorption kinetics

Fig 4 shows the pseudo-first-order kinetic for the adsorption of Ni(II) by apple peel granola (pH=7, C0= 50 mg/L, and m= 0.25 g/L). The R2 regression coefficient (R2=0.926) showed that nickel adsorption kinetic followed by pseudo-first-order model.
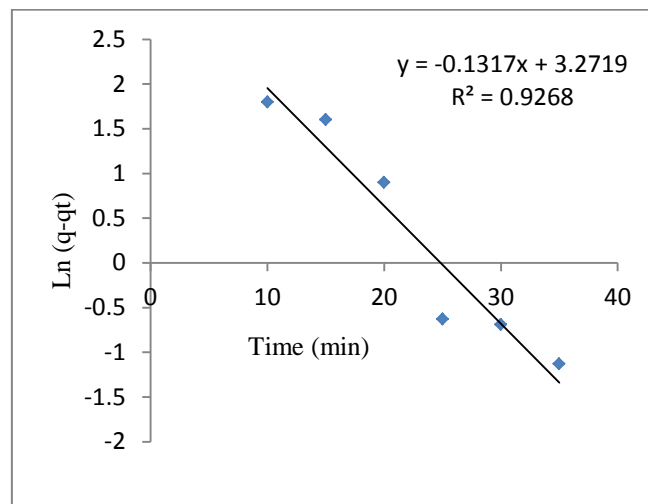

y = -0.1317x + 3.2719
R^2 = 0.9268

Fig 4. The pseudo-first-order kinetic curve for the adsorption of Ni(II) by apple peel granola (pH=7, C_0= 50 mg/L, and m=0.25 g/L)

Adsorption isotherms

According to the data obtained from experiments, Langmuir and Freundlich isotherm models were evaluated and presented in Table 1.

Table 1. Linear and obtained equation of isotherm models

Isotherm	Linear equation	obtained equation	R^2
Langmuir	$\dfrac{1}{q_e} = \dfrac{1}{K_L q_m Ce} + \dfrac{1}{q_m}$	y = -799.1x + 22.45	0.866
Freundlich	$\ln q_e = \ln K_F + \dfrac{1}{n} \ln C_e$	y = -15.79x + 57.58	0.909

The adsorption data were compatible with Freundlich isotherm model (R^2 = 0.909). The Freundlich isotherm constants KF and n are determined from the intercept and slope of a plot of logqe versus logCe. Fig. 5 shows the Freundlich isotherm plot for 50 mg/L nickel concentration in pH=7
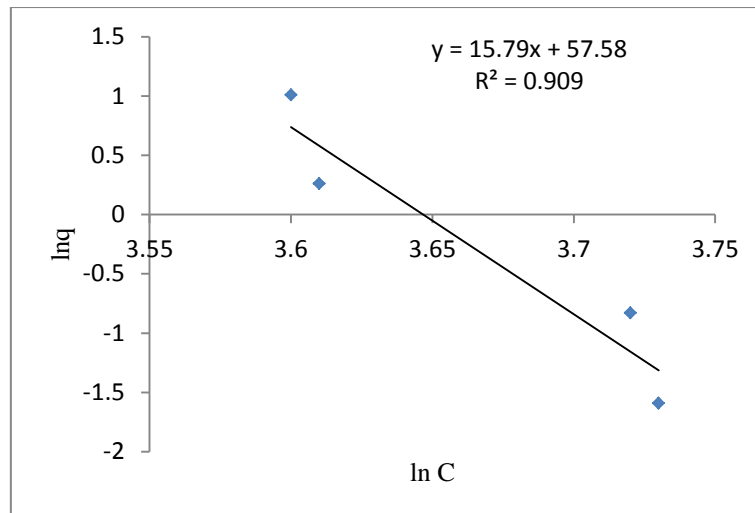
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Fig 5. The Frundlich isotherm for the adsorption of Ni(II) by apple peel granola (C_0=50 mg/L and pH=7)

In this study n value from Freundlich isotherm was obtained 0.06 which is lower than one. Isotherms with n<1 are classified as isotherms reflecting a low affinity between adsorbate and adsorbent which indicates physisorption.
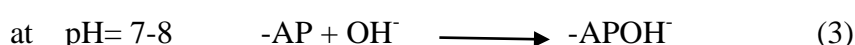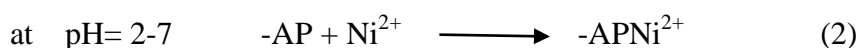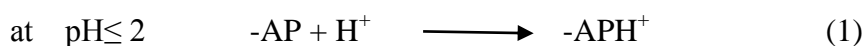
Discussion

Two parameters, namely, contact time and adsorbent dosage have a pronounced effect on the removal of adsorbate species from aqueous solution. The contact time is one of the parameters that affects the design and operation of the absorbance process. It is clear from Fig. 2 that the plot has two portions. It is indicated that the removal is rapid in the initial stages, saturates slowly, and acquires a maximum removal at the time of 30 min. Adsorbent dose is an important parameter in the determination of adsorption capacity.

As the adsorbent dosage increases, adsorbent sites availability for Ni (II) ions are also decreased and consequently lower adsorption takes place. So by increasing the adsorbent dose, adsorption capacity decreased and according to the obtained results (Fig 3), the maximum adsorption efficiency was obtained in 0.25 g/100ml adsorbent dose.

The solution pH affects the surface charge of adsorbent, the degree of ionization and speciation of the surface functional groups. For this reason, it has been pointed out that the solution pH is one of the most important parameters affecting removal percent. By changing of pH, adsorbates can form different types of bonds with the surface of adsorbent. In physical adsorption, the adsorbate is held at the surface only by relatively weak Van der Waals bonds or electrostatic forces between the two charged particles. Electrostatic adsorption occurs due to the attraction of opposite charges as described by Coulomb's law. In chemical adsorption, much stronger ionic or covalent bonds form between the adsorbate and the surface site [17].

It is clear from Fig. 1 that adsorption removal of Ni(II) ions increased by increasing pH of the solution to 7. The removal yield of Ni(II) ions is very low at acidic pH values. This situation may be explained on the basis on electrostatic repulsion forces between positively charges H+ and Ni2+ ions.

The main mechanisms of physisorption include hydrogen-bonding, and ion exchange. Usually, in batch experiments, different pHs are carried out in order to check their effect on the biosorption of metal ions. Reactions 1-4 show the adsorption process.

$$\text{at} \quad pH \leq 2 \qquad \text{-AP} + H^+ \longrightarrow \text{-APH}^+ \qquad (1)$$

$$\text{at} \quad pH = 2\text{-}7 \qquad \text{-AP} + Ni^{2+} \longrightarrow \text{-APNi}^{2+} \qquad (2)$$

$$\text{at} \quad pH = 7\text{-}8 \qquad \text{-AP} + OH^- \longrightarrow \text{-APOH}^- \qquad (3)$$

$$\text{at} \quad pH \geq 8 \qquad Ni^{2+} + OH^- \longrightarrow Ni(OH)_2 \qquad (4)$$

Reaction (1) indicates the protonation reaction of the functional groups of apple peel on the adsorbent at pH lower than 2. Reaction (2) shows the formation of surface complexes of nickel ions with the functional groups at pH=2-7, and reaction (3) describes the adsorption of OH− ions from the solution through hydrogen bond at pH ≥ 7 values [18]. The reaction (1) favored the protonation of the functional groups to form–APH+ at lower pH values.

With the conversion of more –AP groups to – APH+, there were only fewer –AP sites available on the apple peel surface for Ni2+ adsorption through reaction (2). Moreover, the electrostatic repulsion between the Ni2+ and the surfaces of the adsorbent increased with the formation of more –APH + sites on the surface. All these effects would result in the decrease of Ni2+ adsorption on the apple peel with decreasing solution pH values. On the other hand, with the increase of solution pH,

the reaction (1) proceeded to the left, resulting in an increase of the number of –AP sites on the surface of apple peel for nickel ion adsorption through reaction (2) and thus increasing the adsorption capacity.

But at higher solution pH (basic pH), the reaction (3) might proceed. This reaction could on the one hand decrease the adsorption of nickel ions through surface complexation in reaction (2), but on the other hand it might increase the adsorption of nickel ions through the Van der Waals attraction. According to reaction 4, when the pH increases to values of higher than 8, the nickel ions react with hydroxide ions to form a neutral particle and so the adsorption process decreases.

An adsorption isotherm describes the fraction of sorbate molecules that are partitioned between liquid and solid phases at equilibrium. Several mathematical models have been applied for describing equilibrium studies for the removal of pollutant on the

solid surface. In this study, equilibrium modeling of the process of removal of nickel was carried out by using the Langmuir and Freundlich adsorption isotherm. The high R2 value obtained (R2 = 0.909) as shown in Table 1, indicated that experimental data obeyed Freundlich isotherm model.

The Freundlich isotherm is applicable to both monolayer (chemisorption) and multilayer adsorption (physisorption) and is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent [19].

Conclusion

The aim of this paper was to investigate the ability of apple peel to remove Ni ions from aqueous solutions. It was found that the adsorption performance of apple peel is affected by initial metal concentration, biosorbent dose, and solution pH. The removal yield decreased with increasing biosorbent dosage, increased with increasing contact time,

and reached the equilibrium state within 30 min.

The adsorption of Ni (II) ions was dependent on solution pH and maximum removal was found to be 50.5% in pH = 7. The equilibrium data were described satisfactorily by the Langmuir and Freundlich isotherm models. However, the correlation coefficients determined for linear Freundlich isotherm were higher than the others. Adsorption of Ni(II) onto apple peel is an pseudo-first order process.

Acknowledgments

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