Removal of Nickel ions from aqueous solution using peppermint stem powder

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Abstract

In this work, peppermint stems (PMS) which were collected from Baghdad area, is a wild plant, samples were dried and ground to particle size of about 200-500µm, and washed repeatedly with plenty of deionized water to remove all soluble materials. The PMS samples thus prepared were used for removal of Ni (II) ions from aqueous solution. Adsorption of Ni(II) ions onto PMS was found to be pH dependent and maximum removal of Ni(II) ions were obtained at pH 7. The adsorption kinetic data of Ni (II) onto PMS was best fitted with the Pseudo-second-order kinetic model. The equilibrium data were also fitted well with the Langmuir and Freundlich isotherm models. From R_L values, it was concluded that the adsorption of Ni(II) onto PMS was favored. The activation energy E_a of the adsorption process was determined and found to be 7.7 KJ mol^{-1} for the adsorption of Ni(II) onto PMS reflecting the physisorption process.

Introduction

Pollution of natural water resources by heavy-metal ions is one of the most important problems faces and threats the world. These contaminants are produced from liquid wastes discharged from a number of industries such as electroplating, dyes and dye intermediates, textiles, tanneries, oil refineries, mining, smelters and others [1-3]. The industrial wastes reach water effluent without any treatment making series problem of heavy metal accumulation in the polluted water. Nickel and its compounds are ubiquitous in the environment and are, thus, found frequently in surface water. Ni (II) ion is the most commonly occurring species in the environment and is toxic to living organisms. The toxicity of nickel to living organisms is essentially exerted on enzymes, because nickel, like other heavy metals, has a high affinity for ligands containing oxygen, nitrogen and sulfur donors. Excess Ni(II) may cause cancer of the lungs, nose and bone [4]. Acute nickel poisoning after ingestion may show systemic effects such as headache, nausea, dizziness, chest pain and vomiting [5]. Therefore, nickel-containing wastewater needs to be treated before discharge. There are many treatment processes that can be used for the removal of metal ions from aqueous solution; These include chemical precipitation [6], chemical

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reduction[7], electrolytic recovery, membrane separation [8], nanofiltration[9], liquid-liquid extraction (LLE) and solid phase extraction (SPE) techniques [10-12]. Solid phase extraction technique (SPE) has become known as a powerful tool for separation and enrichment of various inorganic and organic analytes [13,14]. The basic principle of SPE is the transfer of the analyte from the aqueous phase to bind to active sites of the adjacent solid phase. The (SPE) technique has several advantages over other techniques, including stability, reusability of the solid phase, reach of high pre concentration factors, easiness of separation, no need for organic solvents and more important most of the extractors, specially the agricultural wastes, are environment friendly [11].

In the present work Peppermint stem powder was used as solid phase extractor for removal of nickel ions from aqueous solution. Kinetic and isotherm studies were conducted to investigate the efficiency of this technique.

Methods

Preparation of Ni(II) solution

Nickel nitrate obtained from Fluka Chemical Company of purity 99.8% was used for preparation of stock solution. Stock solution 500mg/L of Ni(II) was prepared in deionized water and diluted to get the desired concentrations of Ni(II).

Biosorption studies

Biosorption experiments were carried out by mixing 0.1g adsorbent in a 100 ml flask with 50ml Ni(II) solution of desired concentration. The mixture was agitated at 140 rpm for 150min. The influence of hydrogen ion concentration on the biosorption process was studied over a pH range of 3.0-8.0, with adjustments being made using 0.1M HCL or 0.1M NaOH. The effect of Ni(II) concentration was studied in the range from 10 to 200 mg L^{-1} at pH 7.0. The effect of temperature on the biosorption capacity was investigated at 25 and 35°C. The adsorbent dose effect was also studied in the range 1 to 16 g/L at pH 7.0.

The biosorption capacity, q_e (mg/g), was calculated as follows:

$$q_e = \frac{(C_o - C_e)V}{W} \qquad (1)$$

The removal efficiency (R%) of Ni(II) ions by adsorbent, was calculated using the following equation:

$$R\% = \frac{C_o - C_e}{C_o} \times 100 \qquad (2)$$

Where, C_o and C_e are the initial and final concentrations (mg/L) of Ni(II) ions, respectively, W is the adsorbent dosage (g) and V the volume of solution (L).

All experiments were carried out at least two times and the average values were taken into consideration. The residual nickel ions in the filtrate were analyzed by atomic absorption spectrometer type (Phenoix-696).

Results and Discussion

Characterization of the adsorbents

FT-IR spectra for PMS was obtained by KBr pellets method operated on FT-IR spectrophotometer type Jasco-4200, to investigate the functional groups present in the adsorbents. Fig.1 shows the characteristic peaks of PMS the broad peak located at 3200-3600 may, belong to carboxyl, bonded hydroxyl, N-H of amine or phenol groups, while the absorption peak at 2928 cm^{-1} could be assigned to –CH stretching vibrations of -CH_3 and -CH_2 functional groups. The peak at 1739, 1639 and 1631 cm^{-1} characterizes carbonyl groups stretching from carboxyl, aldehydes or ketones. The adsorption peaks at 1631, 1512 and 1425 cm^{-1} may correspond to the primary and secondary amide bands. The strong band within 1100-1000 cm^{-1} is due to C-O-C group, which are characteristics peaks of polysaccharides.
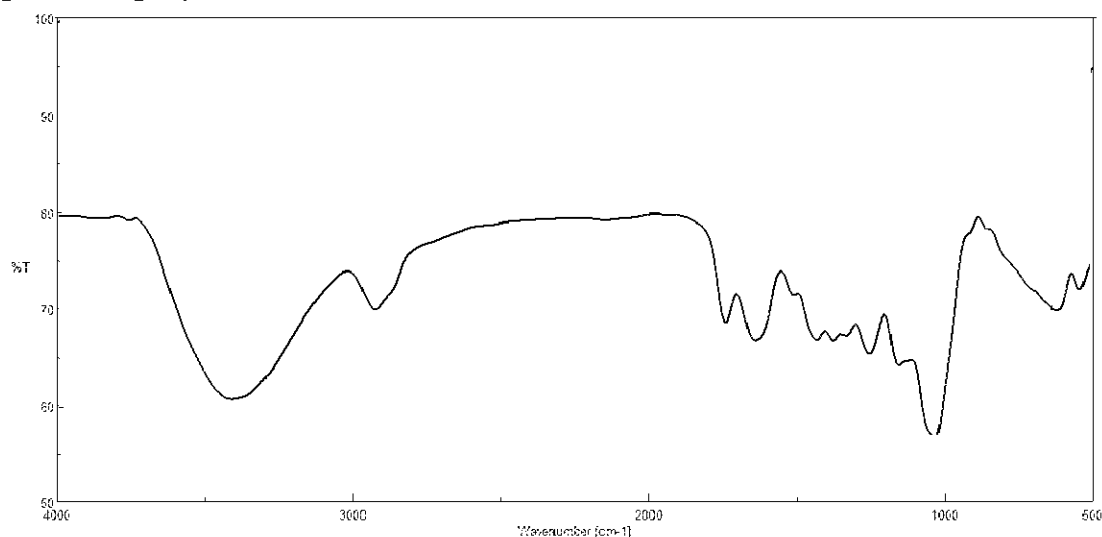

Fig.1 FTIR of Peppermint stem

Effect of pH

pH is an important parameter influencing heavy metal adsorption from aqueous solutions. It affects both the surface charge of adsorbent and the degree of ionization of the heavy metal in solution [12]. Plot of pH versus removal efficiency R% for PMS is shown in Fig.2. The optimum pH was found to be 7. The maximum removal efficiency of Ni(II) by Peppermint stem was 91% at 1g/L of biosorbent and 20 mg/L of Ni(II) concentration. At pH values higher than 7.0, insoluble Nickel hydroxide start precipitating from the solutions.
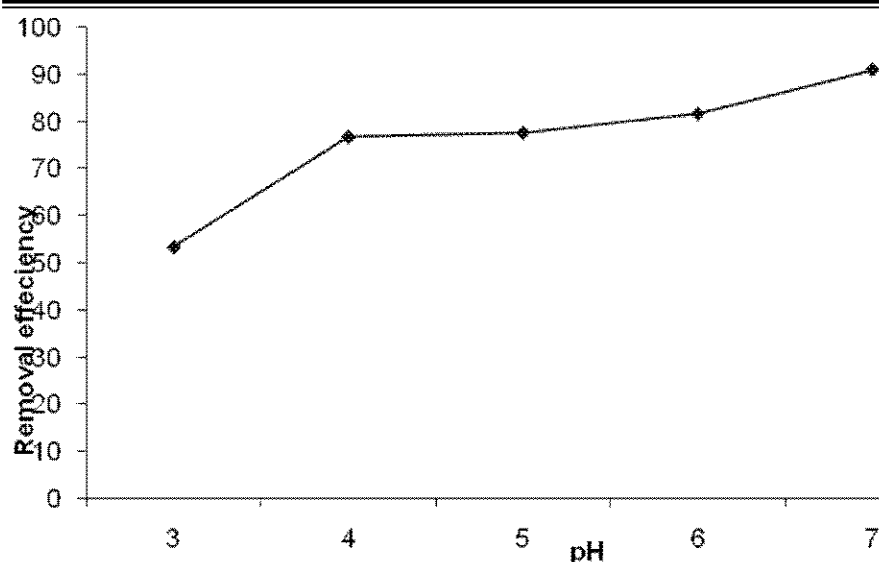
Figure 2. Effect of pH on the adsorption of Ni(II) onto PMS.

Effect of contact time

Contact time is an important factor in the process of evaluation of the PMS. The batch experiments were performed at different contact times with a fixed sorbent concentration 1.0 g/L, Ni(II) concentration 20 mg/L at pH 7.0 and 50 ml of reaction solution, these experiments were done at different temperature 25, 35. The equilibrium is reached at about 100 min.

Adsorption Kinetic Studies

Kinetic models have been used to investigate the mechanism of sorption and potential rate controlling steps, which is helpful for selecting optimum operating conditions for the full-scale batch process [13]. In order to clarify the biosorption kinetics of Ni(II) ions onto PMS, the kinetic models, Lagergren's pseudo-first-order [14], pseudo-second-order [15] models were applied to the experimental data. The linearized form of the pseudo-first-order rate equation by Lagergren is given as:

$$\log (q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \qquad (3)$$

Where q_e and q_t are the amount of metal ion sorbed (mg g^{-1}) at equilibrium and at time t, respectively. K_1 is the Lagergren rate constant (min^{-1}).

The kinetic of adsorption can also be described by pseudo-second-order equation and it is given by the following equation:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad (4)$$

Where K_2 (g mg^{-1} min^{-1}) is the second order rate constant. For calculating these rate constants, Lagergren equation as well as the pseudo-second order equation is plotted at two different temperatures 25 and 35°C with fixed biosorbent dose 1.0 g L^{-1} and 20 mg L^{-1} of Ni(II) solution. The values of the reaction rate

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constants and correlation coefficients obtained are listed in table1. Fig.3 represent the plot of second-order equation for adsorption of Ni(II) onto PMS.

A comparison between the pseudo-first-order and pseudo-second-order kinetics rate constants suggest that the adsorption of Ni(II) onto PMS, followed closely the second-order kinetic rather than first-order kinetic. This is Further confirmed from the capacity q_e, the calculated values from the second-order kinetic equation is very close to the experimental q_e values, whereas, the calculated q_e values from the first-order kinetic equation did not agree with the experimental q_e.
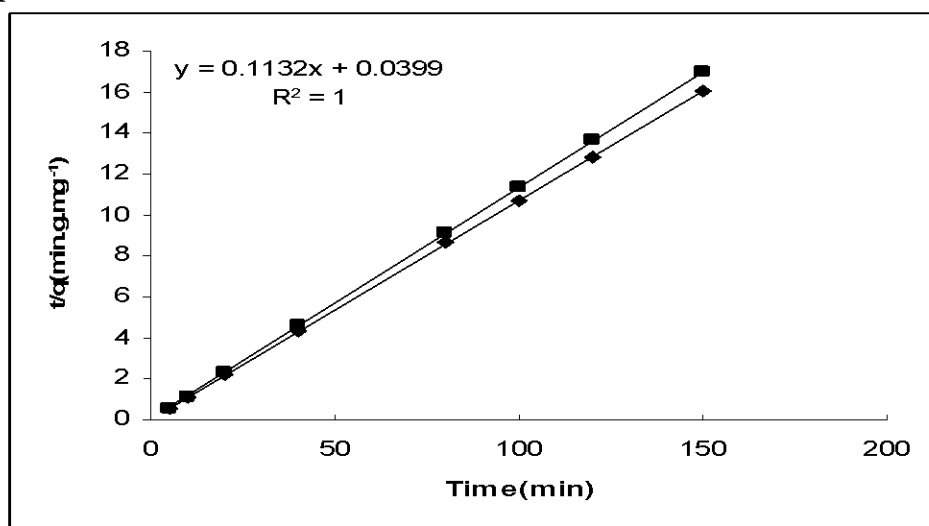

Figure 3. Pseudo-second-order plot for the adsorption of Ni(II) onto PMS at 25 and 35°C.

Table1. Kinetic parameters of adsorption of Ni(II) onto peppermint stem.

1st-order	25°C	35°C
k_1 (min^{-1})	0.014	0.0076
Qe(exp) mg/g	9.38	8.92
Qe(cal) mg/g	0.263	0.269
R^2	0.8898	0.9353
2nd-order		
k_2 (g mg^{-1} min^{-1})	0.290	0.321
Qe(cal) mg/g	9.35	8.834
R^2	1.000	1.000

Adsorption Equilibrium Studies

The adsorption isotherm is the relationship between equilibrium concentration of solute in the solution and equilibrium concentration of solute on the sorbent at constant temperature. The Nickel(II) uptake capacity of PMS was evaluated

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using the **Langmuir** [16] and **Freundlich** equations [17]. The linearized form of **Langmuir** equation is as follows:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{1}{q_{max}}C_e \qquad (5)$$

Where q_{max} is the maximum (theoritical) adsorption capacity of PMS (mg g^{-1}), q_e is the Ni(II) ion concentration on the adsorbent (mg g^{-1}) at equilibrium, C_e is the metal ion concentration at equilibrium in solution, b is the Langmuir constant (L mg^{-1}). Values of b and q_{max} calculated from intercept and slope of the linear plot of C_e/q_e versus C_e for PMS as shown in Fig.4, table 2. The values of q_{max} for PMS were found to be 13.6, 20.0, 22.7 mg g^{-1} at 35, 45 and 50°C respectively, and b found to be 0.591, 0.274, and 0.223 at 35, 45, and 50°C respectively. The essential characteristics of Langmuir isotherm can be expressed in term of dimensionless equilibrium parameter (R_L) [18] which is defined as follows:

$$R_L = \frac{1}{1 + b \times c_o} \, .$$

The value of R_L indicates the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The R_L values for Ni(II) sorption onto PMS were 0.078, 0.154, and 0.183 at 35, 45, and 50°C respectively, which indicate clearly that the adsorption of Ni(II) onto PMS is favorable. moreover the values of q_{max} of PMS increases with temperature increase reflecting the endothermic process.

The linearized form of **Freundlich equation** is as follows:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (6)$$

Where, K_F and 1/n are Freundlich constants indicators of the sorption capacity and intensity, respectively. The K_F and 1/n can be calculated from the intercept and slope of the above equation and shown in Fig.5, the isotherm parameters are presented in table 2. The values of n are higher than one indicating favorable adsorption process for PMS [19]. To investigate type of adsorption whether it is chemical or physical, activation energy of the adsorption was calculated using a linearlized form of Arrhenius equation at 35 and 45°C:

$$\ln\frac{k_1}{k_2} = \frac{Ea}{R}(\frac{1}{T_2} - \frac{1}{T_1}) \qquad (7)$$

Where Ea is the activation energy of the adsorption process (KJ mol^{-1}), k_1 and k_2 are the pseudo-second-order rate constants at 25 and 35°C, R is the gas constant (8.314 J mol^{-1}K^{-1}) and T is the solution temperature in Kelvin (K). The activation energy value gives an information on whether the adsorption is mainly physical or chemical.

Physisorption process normally had activation energy of 5-50 KJ mol^{-1}, while chemisorption had higher activation energy 40-800 KJ mol^{-1} [20]. From the above equation the activation energy of the adsorption process was calculated and found to be 7.68, these results indicate that the adsorption of Ni(II) onto PMS is physical.
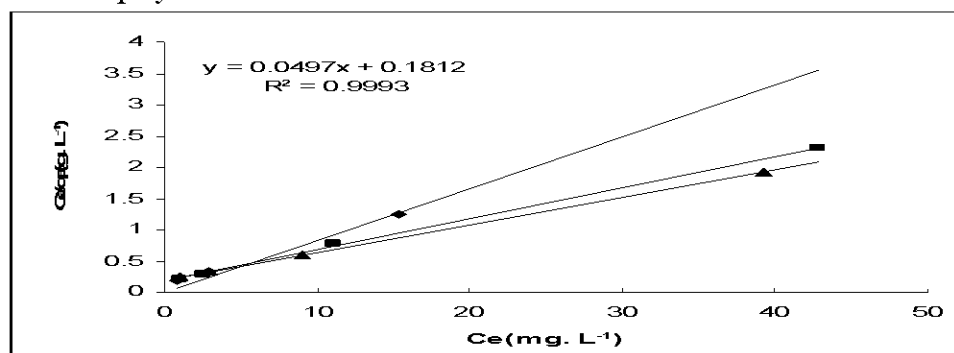

Figure 4. Langmuir plot for the adsorption of Ni(II) onto PMS at different temperatures.

Table 2. Isotherm parameters of the adsorption of Ni(II) onto Peppermint stem.

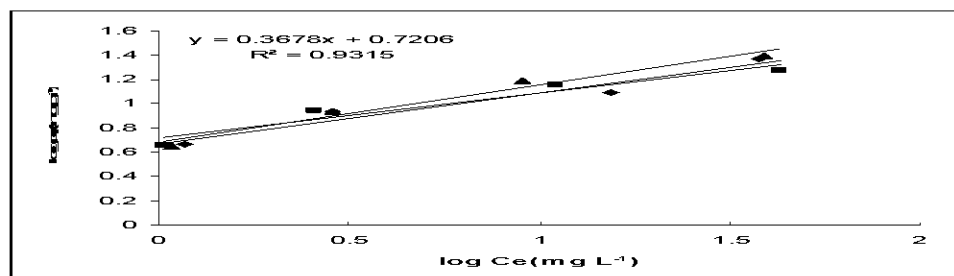| Langmuir	35°C	45°C	50°C
Qmax (mg/g)	13.64	20.12	22.7
b	0.591	0.274	0.223
R^2	1.000	0.9993	0.9999
Freundlich			
K_F	5.02	5.32	4.82
n	2.47	2.75	2.12
R^2	0.9474	0.938	0.9731

Figure 5. Freundlich plot for the adsorption of Ni(II) onto PMS at different Temperatures.

Conclusion

Peppermint stem powder was prepared and characterized by FTIR. The PMS was used as adsorbent for removal of Ni(II) ions. The experimental data were fitted very well with the pseudo-second-order equation with correlation coefficient of 1.00. and also well fitted to the Langmuir and Freundlich isotherms. The adsorption mechanism onto PMS surfaces may be physical On the other hand, the adsorbent is cheap and environment friendly.

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أزاله ايونات النيكل من المحلول المائي باستخدام مطحون سيقان النعناع

الملخص

استخدمت سيقان نبات النعناع PMS بعد طحنها الى(200-500μm) وغسلها بتكرار بالماء اللاايوني لازالة ايونات النيكل الثنائي Ni (II) من المحاليل المائية ، ووجد ان عملية امتزاز Ni (II) على سطح PMS تعتمد على الدالة الحامضية pH وان افضل ازالة عند 7 =pH ، دراسه حركيه الامتزاز تتفق مع مرتبه التفاعل الثانيه الكاذبه, النتائج العملية لقيم الاتزان الحراري تتفق مع معادلات لانكموير و فريندليش ، ووجد من خلال قيم ال RL ان عملية ازالة النيكل الثنائي باستخدام سيقان النعناع هي مفضلة، وأخيرا تم تعيين قيمة طاقة التنشيط وكانت مساوية الى 7.7 KJ/mol والتي تشير الى ان عملية امتزاز Ni (II) على سطح PMS هي عملية فيزيائية .