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Adsorption study on pomegranate peel: Removal of Ni^{2+} and Co^{2+} from aqueous solution

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ABSTRACT

The aims of the study were to investigate the effect of Pomegranate peel on adsorption of Co^{2+} and Ni^{2+} by using flame atomic absorption spectroscopy for metal estimation. The effects of Co^{2+} and Ni^{2+} ions concentration, agitation time and temperature on adsorption of heavy metals onto Pomegranate Peel was investigated. The experimental isotherm results were fitted using Langmuir and Freundlich equations. The Langmuir and Freundlich model agrees very well with experimental data. The maximum amounts of Co^{2+} and Ni^{2+} adsorbed (q_m), as evaluated by Freundlich isotherm, were 8.98 mg and 7.54 per gram of powder of Pomegranate peel, respectively. Study concluded that Pomegranate peels, a waste material, have good potential as an adsorbent to remove toxic metals like Co^{2+} and Ni^{2+} from water.

KEYWORDS

Langmuir isotherm;
Freundlich isotherm;
Heavy metals;
Pomegranate peel;
Pontaneous.

INTRODUCTION

Heavy metal pollution has become an environmental problem throughout the world because heavy metals can be accumulated into the food chain and cause serious problems, not only for ecosystems but also for human health. The selective removal of industrial heavy metals from liquid waste is consequently the subject of considerable ecological and economic interest[1,2]. Wastes containing soluble toxic heavy metals require concentration of the metals into a smaller volume followed by recovery and secure disposal. Heavy metals can be removed by adsorption on solid matrices[3-5].

Pomegranate peel is abundant in soft drink industries and usually treated as wastes. It is mostly composed of cellulose, pectin, hemi-cellulose, lignin, chlorophyll pigments and other low relative-molecular-mass hydrocarbons[6-8].

It is therefore, essential to search agricultural by-products and to transform such materials to adsorbents. Nowadays, agricultural materials are receiving more and more attention as adsorbents for the removal of pollution from water[9]. A recent study by Memon et al[6]. showed that banana waste material removed about 95% chromium ions from industrial effluent. Abbasi and Alikarami[10] showed that Removal of acetic acid from Aqueous Solutions Using Banana. Najim and Yassin[11] showed that Removal of Cr (VI) from Aqueous Solutions Using Pogmeranate.

The goal of this study was to investigate the extent of removal of contaminant heavy-metal species (Ni^{+2} and Co^{+2}) from aqueous Solution by Pomegranate peel.

Maximum adsorption capacity of adsorbent, adsorption intensity of the adsorbate on adsorbent surface and adsorption potentials of adsorbent were estimated by Langmuir and Freundlich isotherms, respectively.

MATERIALS AND METHODS

Experiments were conducted with Pomegranate peel, Peels were separated from the fruit gently, washed thoroughly and dried in sun light for 3 days and then in an oven at 90 °C. The dried Pomegranate peels were then cut into small pieces, ground to a size of 200-400 ìm and used in adsorption test.

pH adjustments were made with digital pH-meter (Sartorius, Model PP-20) using HCl (0.1 mol L^{-1}) and NaOH (0.1 mol L^{-1}). Ni^{+2} and Co^{+2} content in each experiment were determined with flame atomic absorption spectrophotometer (Perkin Elmer, Analyst 100).

Adsorption experiments

Standard solution (1000 mg/ L) of each metal ion was prepared by dissolving required amount of nitrate salt of metal ion ($Co(NO_3)_2·6H_2O$ and $Ni(NO_3)_2·6H_2O$ obtained from Merck) into deionized water. The experimental solution of desired concentration was prepared by successive dilution of stock solution. In order to determine the effect of physicochemical parameters such as pH, Adsorbent dose, contact time, initial metal ion concentration of solution and temperature. The adsorption experiments were performed by batch equilibrium method. The experiments were carried out in 150 ml of conical flasks by mixing a preweighed amount of adsorbent with 50 ml of metal ion solution. Initial pH of solutions was adjusted by 0.1 M NaOH or 0.1 M HNO_3. All experiments were performed at room temperature and kept for stirring for given period of time.

There after the mixture was centrifuged and the initial and final metal ion concentrations were determined by Atomic Absorption Spectrophotometer. the removal percentage of metal ion and amount of metal ion adsorbed on Pomegranate peel (q_e) was calculated by Eqs. (1) and (2), respectively:

$$\text{removal}(\%) = 100\frac{C_0 - C_e}{C_0} \quad (1)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 and C_e are the initial and final (equilibrium) concentrations of the metal ion in solution (M), V the solution volume (l) and m is the mass of Pomegranate peel (g). All adsorption experiments were performed in triplicate and the mean values were used in data analysis.

RESULTS AND DISCUSSION

The adsorption kinetics is influenced by various factors, which include initial heavy metals concentration, amount of adsorbent and time. The initial heavy metals concentration is one of the most important factors that determines the equilibrium concentration, but also determines the uptake rate of heavy metals and the kinetic character.

Effect of pH

To study the effect of pH on adsorption, experiments were carried out in the pH range 1–6 for Ni^{+2} and Co^{+2}. Figure 1 shows that the removal of metal ions was increased with increasing initial pH of metal ion solution and maximum value was reached at pH 6 for Ni^{+2} and Co^{+2}.

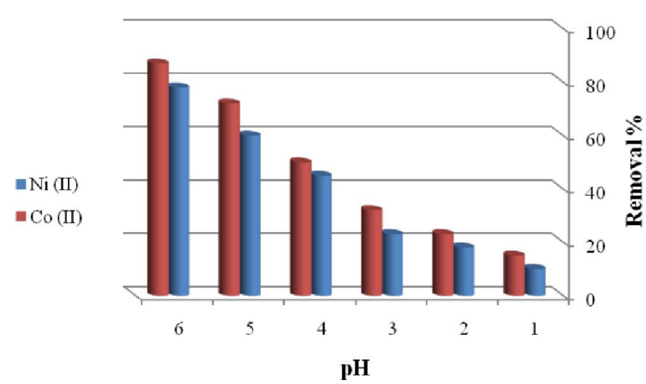

Figure 1 : Effect of pH on adsorption of Ni^{+2} and Co^{+2} on pomegranate peel

Effect of adsorbent dose

Figure 2 shows that the adsorbent of metal ions increased from 46 to 87% and 38 to 78% for Co^{2+} and Ni^{2+}, respectively, as Pomegranate peel dose increased from 1 to 3 g/L. This is because at higher dose of adsorbent, due to increased surface area, more adsorption sites are available causing higher removal of Co^{2+}

and Ni^{2+}[10,11] Further increase in adsorbent dose, did not cause any significant increase in the removal percentage of metal ion. This was due to the concentration of metal ions reached at equilibrium status between solid and solution phase.

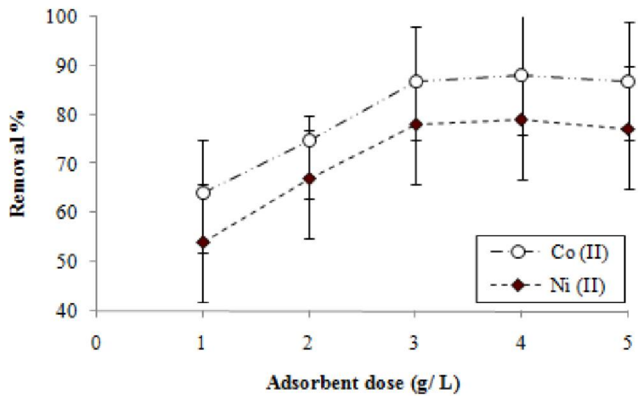

Figure 2 : Effect of adsorbent dose on adsorption of Ni $^{+2}$ and Co $^{+2}$ on pomegranate peel

Effect of contact time

Influence of contact time on adsorption of Co^{2+} and Ni^{2+} on Pomegranate peel was investigated in the range of 5–60 min for the initial concentration of 10 mg/L for each metal ion (Figure 3). Maximum rate of removal occurred within 5 min of contact time there after removal rate became slow and after 35 min of contact time no change was observed for Co^{2+} (87.2%) and Ni^{2+} (78%), which established that the system has reached the equilibrium point.

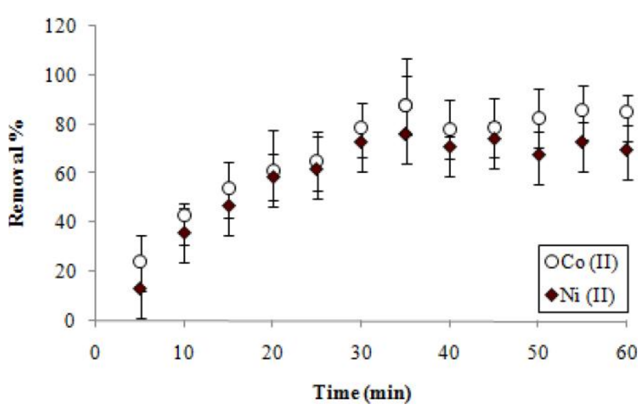

Figure 3 : Effect of contact time on adsorption of Ni $^{+2}$ and Co $^{+2}$ on pomegranate peel

Effect of equilibrium metal ion concentration

The effect of different concentration of Co^{2+} and Ni^{2+} on the adsorption has been investigated at 303 K, Co^{2+} and Ni^{2+} adsorption capacities of Pomegranate peel were given as a function of equilibrium concentration in Figure 4. It was clear that Co^{2+} and Ni^{2+} adsorption capacities of Pomegranate peel increased with increase of equilibrium concentration. The Increase in adsorption capacity with increase in equilibrium metal ion concentration for different metal ions was in the order $Co^{2+} > Ni^{2+}$.

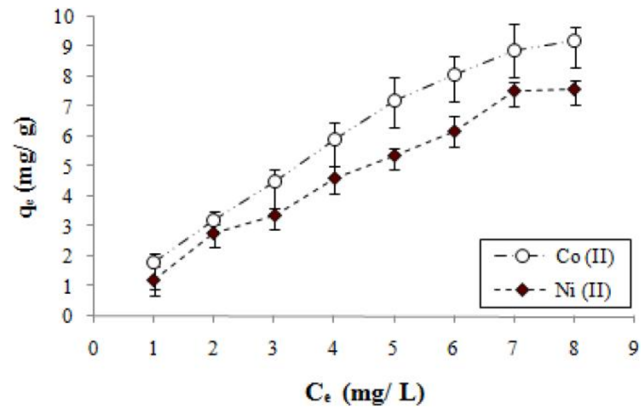

Figure 4 : Effect of equilibrium metal ion concentration on adsorption of Ni $^{+2}$ and Co $^{+2}$ on pomegranate peel

Adsorption isotherm

Analysis of equilibrium data is important for developing an equation that can be used to compare different biomaterials under different operational conditions and to design and optimize an operating procedure[3-5]. The Langmuir and Freundlich equations are commonly used for describing adsorption equilibrium for water and wastewater treatment applications.

Two important physicochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibrium of the adsorption and the kinetics. Equilibrium studies give the capacity of the adsorbent. The equilibrium relationships between the adsorbent and the adsorbate are described by the adsorption isotherms. The adsorption curves were applied to both the Langmuir and Freundlich equations. The Freundlich isotherm model, which assumes that the adsorption occurs on heterogeneous surfaces, is often expressed as;

$$q_e = K_f (C_e)^{1/n} \quad (3)$$

This equation is conveniently used in the following linear form:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (4)$$

where K_f is Freundlich isotherm constant (L/g) and n is Freundlich isotherm exponent. Values of K_f and n were calculated from the intercept and slope of plots ln q_e vs ln C_e and a straight line indicates the confirmation of the Freundlich isotherm for adsorption (Figure 5). The value of n should be greater than one confirming good adsorption of heavy metals onto peels of Pomegranate. Langmuir isotherm, which assume that a monolayer of heavy metals is formed on a relatively regular adsorbent surface, using the partially protonated groups of the adsorbent. The Langmuir isotherm has been successfully applied to many real sorption processes and is expressed as follows:

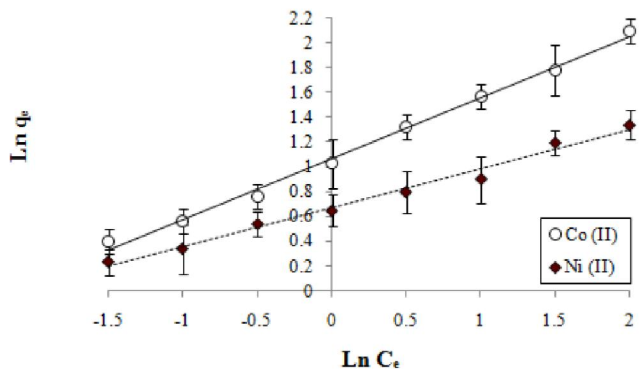

Figure 5 : Freundlich adsorption isotherm at 298 °K

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \quad (5)$$

where q_e is the amount adsorbed at equilibrium (mg/ g), C_e the equilibrium concentration (mg/ L), b a constant related to the energy or net enthalpy of adsorption (L/ mg), and Q_0 the mass of adsorbed solute required to saturate a unit mass of adsorbent (mg/ g). Q_0 represents a practical limiting adsorption capacity when the surface is fully covered with heavy metals and allows the comparison of adsorption performance, particularly in the cases where the adsorbent did not reach its full saturation in experiments. The Langmuir equation can be described by the linearized form as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad (6)$$

By plotting (C_e/q_e) versus C_e, Q^0 and b can be determined if a straight line is obtained (Figure 6). The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor or equilibrium parameter, R_L, which is defined by:

$$R_L = \frac{1}{1 + b C_0} \quad (7)$$

where b is the Langmuir constant and C_0 the initial heavy metals concentration (mg/L). R_L value indicates the type of isotherm. According to[12] R_L values between 0 and 1 indicate favorable adsorption (TABLE 1).

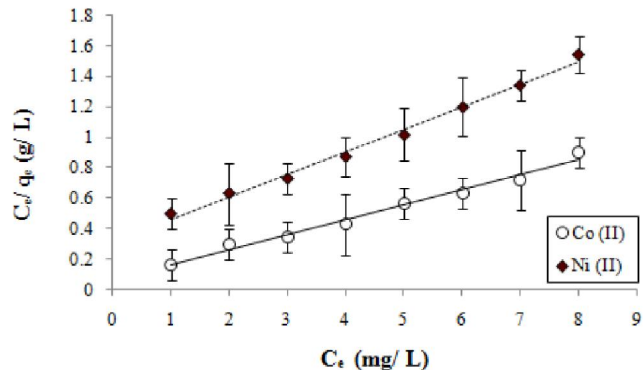

Figure 6 : Langmuir adsorption isotherm at 298 °K

TABLE 1 : Freundlich and langmuir adsorption isotherm constants

Metal ions	Langmuir constants			Freundlich constants		
	Q° (mg/g)	b (L/ mg)	R^2	K_F (L/mg)	n	R^2
Ni (II)	7.54	0.198	0.996	1.029	1.63	0.997
Co (II)	8.98	0.328	0.997	2.017	1.47	0.993

Effect of temperature and thermodynamic parsmeters

The effect of temperature on the adsorption of heavy metals on Pomegranate peel was investigated by conducting experiments for 30 mg/L of initial metals ion concentrations at 303, 313 and 323 °K. It was observed that on increasing the temperature percentage removal of heavy metals increased. This showed that the adsorption process was endothermic in nature.

The thermodynamic parameters Gibb's free energy (ΔG°), enthalpy (ΔH) and entropy (ΔS°) were calculated using the following equations:

$$\ln\left(\frac{q_e m}{C_e}\right) = \frac{\Delta S^0}{R} + \frac{-\Delta H^0}{RT} \quad (8)$$

$$\Delta G^\circ = \Delta H - T\Delta S^\circ \quad (9)$$

where m is the adsorbent dose (g/ L), C_e is concentration of metals ion (mg/ L), q_e is the amount of metals ion at equilibrium in unit mass of adsorbent (mg/ g), q_e/C_e is called the adsorption affinity. ΔH, ΔS° and ΔG° are change in enthalpy (kJ/ mol), entropy (J/ (mol K)) and free energy (kJ/ mol), respectively. R is the gas constant (8.314 J/mol K) and T is the temperature (K).

The values of ΔH and ΔS° were obtained from the slopes and intercepts of the Van't Hoff plots of ln (q_em/ C_e) vs. 1/ T, respectively, thereafter ΔG° values were determined from Eq. (9). The values of thermodynamic parameters are presented in TABLE 2. The results showed that the ΔG° values are negative and increased in their absolute values with temperature[13] This result suggested that a high temperature is favoured for the adsorption of heavy metals on Pomegranate peel, indicated a spontaneous adsorption process. The values of heat of adsorption, ΔH is positive for metals ion, indicated that the adsorption process of heavy metals on Pomegranate peel was endothermic. A positive ΔS suggested that heavy metals were not stable on the adsorption sites of Pomegranate peel probably due to the increase in translational energy of metalsion.

TABLE 2 : Thermodynamic parameters for adsorption of Ni^{+2} and Co^{+2} on pomegranate peel

Metal ions	ΔH° (kJ/mol)	ΔS° (Jmol/K)	- ΔG° (kJ/mol)		
			303 °K	313 °K	323 °K
Ni (II)	31.224	115.148	3.665	4.817	5.968
Co (II)	38.548	148.541	6.459	7.945	9.431

CONCLUSIONS

The current study emphasizes on the ability of Pomegranate peel to adsorb heavy metals from aqueous solutions. The negative values of ΔG° suggested that the adsorption was spontaneous in nature. The positive value of ΔH and ΔS indicated endothermic adsorption process and increased randomness at surface–solution interface, respectively.

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