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Adsorption study on orange peel: Removal of mercury (II) and chromium (III) from aqueous solution

Zahra Abbasi*, Mohammad Alikarami
Department of Chemistry, Eyvan-e-Gharb Branch, Islamic Azad University, Eyvan (IRAN)
E-mail : Zahra.abbasi886@gmail.com

ABSTRACT

The adsorption of Mercury (II) and Chromium (III) on orange peel has been studied in batch mode using flame atomic absorption spectroscopy for metal estimation. The effects of Mercury (II) and Chromium (III) ions concentration, agitation time and temperature on adsorption of heavy metals onto orange 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 Mercury (II) and Chromium (III) adsorbed (q_m), as evaluated by Freundlich isotherm, were 7.79 mg and 6.43 per gram of powder of orange peel, respectively. All adsorption processes can attain equilibrium within 30 min and kinetics was well fitted by psesudo-second order equation. It is proposed that the adsorption mechanism was complexation. Thermodynamic parameters (ΔG°, ΔS° and ΔH°) for sorption system was determined at five different temperatures.

KEYWORDS

Langmuir isotherm;
Freundlich isotherm;
Heavy metals;
Orange 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]. Heavy metal ions, aromatic compounds (including phenolic derivatives, and polycyclic aromatic compounds) and dyes are often found in the environment as a result of their wide industrial uses. wastes containing soluble toxic heavy metals requires concentration of the metals into a smaller volume followed by recovery and secure disposal. Heavy metals can be removed by adsorption on solid matrices.

Mercury (Hg) emissions from waste incineration are a global problem, indicated by that nearly half of the Hg emissions reaching the Arctic originates from waste incineration[2]. In most countries, the total Hg emissions from waste incineration are largely underestimated because of poor knowledge about Hg content in wastes and due to economic reasons there are no or only limited analyses available on Hg content in flue gases from a majority of the waste incineration plants in operation[3].

Chromium (Cr) compounds are widely used by many modern industries such as leather tanning, electroplating, metal finishing, paint and pigments, resulting in a large quantity of this element being discharged into effluent industrial wastewaters. Waters containing a high concentration of Cr can cause serious environmental problems as well as induce toxic and carcinogenic health effects on humans[4]. Therefore, the removal of Cr from wastewaters arouses great attention.

Orange 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[5-8].

The goal of this study was to investigate the extent of removal of contaminant heavy-metal species (Hg and Cr) from aqueous Solution by orange 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.

EXPERIMENTAL

Experiments were conducted with orange peel, Peels were separated from the fruit gently, washed thoroughly and dried in sun light for 3 days and then in an oven at 70 °C. The dried banana peels were then cut into small pieces, ground to a size of 200-400 μm and used in adsorption test.

Standard solution of Cr (III) was prepared by dissolving 7.6960 g $Cr(NO_3)_3 \cdot 9H_2O$ (reagent grade from Merck, Darmstadt, Germany) in 250 mL deionized water and diluting to 1 L adding HNO_3 to obtain a final concentration of 2% (v/v); this was checked against a titrisol standard solution from Merck (Darmstadt, Germany). The Hg (II) stock solution was prepared by dissolving 1 g of 5 M nitric acid prior to dilution with deionised water to 1 L volume. Standard solutions of the desired concentrations (10–100 μgmL^{-1}) were prepared by successive dilutions of the corresponding stock solutions. The pH was adjusted using 0.1 M HCl and NaOH solutions.

Equipment and apparatus

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}). Mercury and Chromium content in each experiment were determined with flame atomic absorption spectrophotometer (Perkin Elmer, AAnalyst 100).

Adsorption isotherms

The adsorption isotherms were obtained by employing 100 mg of orange peel and 25 mL of Waste solution with different concentrations (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 μg mL^{-1}). These solutions were stirred in a mechanical shaker until they reached adsorption equilibrium. The system was shaken for 100 min and then both phases were separated by filtration. The metal content of the filtrate was determined by atomic spectrometry.

pH optimization

The removal of Hg (II) and Cr (III) at different pH was studied in batch mode. A 25-ml of test solution of fixed concentrations was treated with 0.5 g of orange peel and agitated intermittently for 30 min. The contact time and conditions were selected on the basis of preliminary experiments, which demonstrated that equilibrium was established in 30 min. After this period the solution then both phases were separated by filtration. The metal content of the filtrate was determined by atomic spectrometry. The metal concentration retained in the sorbent phase (q_e, mg/g) was calculated by using Eq. (1)

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

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 orange peel (g).

Kinetic modeling in a batch system

In order to investigate the mechanism of adsorption kinetic models are generally used to test experimental data. Pseudo-first-order and pseudo-second-order equations can be used assuming that the measured concentrations are equal to surface concentrations. The pseudo-first-order rate Lagergren model is:

$$\frac{dq}{dt} = k_{1,\mathrm{ads}}(q_e - q) \quad (2)$$

where q (mg/g) is the amount of adsorbed heavy metals on the adsorbent at time t and $k_{1,ads}$ (min^{-1}) is the rate constant of first-order adsorption. The integrated form of Eq. (2) is:

$$\log(q_e - q) = \log q_e - \frac{k_{1,ads}}{2.303}t \quad (3)$$

q_e the equilibrium sorption uptake, is extrapolated from the experimental data at time t = infinity. A straight line of log (q_e - q) versus t suggests the applicability of this kinetic model. q_e and $k_{1,ads}$ can be determined from the intercept and slope of the plot, respectively. The pseudo-second order kinetic model is expressed as:

$$\frac{dq}{dt} = k_{2,ads}(q_e - q)^2 \quad (4)$$

where $k_{2,ads}$ (g/mg min) is the rate constant of second-order adsorption. The integrated form of Eq. (4) is:

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_{2,ads}t \quad (5)$$

Eq. (5) can be rearranged and linearized to obtain:

$$\frac{t}{q} = \frac{1}{k_{2,ads}q_e^2} + \frac{1}{q_e}t \quad (6)$$

The plot t/ q versus t should give a straight line if second order kinetic model is applicable and q_e and $k_{2,ads}$ can be determined from the slope and intercept of the plot, respectively. It is important to notice that for the application of this model the experimental estimation of q_e is not necessary.

Equilibrium modeling in a batch system

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. 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;

$$q_e = K_f(C_e)^{1/n} \quad (7)$$

This equation is conveniently used in the following linear form:

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \quad (8)$$

where K_f is Freundlich isotherm constant (L/g) and n_F is Freundlich isotherm exponent. Values of K_F and n_F 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. The value of n_F should be greater than one confirming good adsorption of heavy metals onto peels of banana. 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:

$$q_e = \frac{Q^0 b C_e}{1 + bC_e} \quad (9)$$

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:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad (10)$$

By plotting (C_e/q_e) versus C_e, Q^0 and b can be determined if a straight line is obtained. 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:

$$R_L = \frac{1}{1+bC_0} \qquad (11)$$

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[9], R_L values between 0 and 1 indicate favorable adsorption.

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 heavy metals concentration on adsorption

Figure 1 shows equilibrium adsorption isotherm of Hg (II) and Cr (III) on orange peel at 298 ÚÚK. The equilibrium adsorption density q_e is increased with the increase in Hg (II) and Cr (III) concentration.

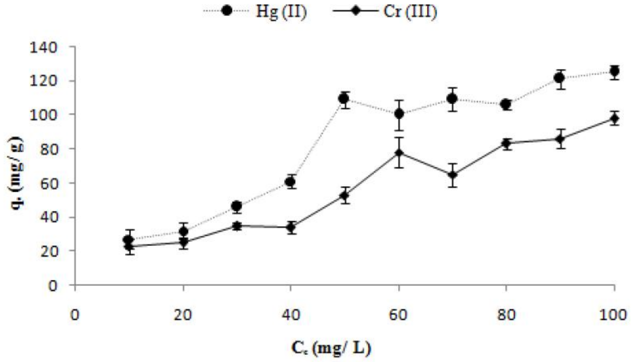

Figure 1 : Equilibrium adsorption isotherm of of Cr (III) and Hg (II) on orange peel.

At low equilibrium heavy metals concentrations C_e, the equilibrium adsorption densities q_e of the orange peel reach almost the same q_e as those at high equilibrium Hg (II) and Cr (III) concentrations. It indicates that orange peel have high adsorption density even at low equilibrium Hg (II) and Cr (III) concentrations. Figure 1 shows the effect of heavy metals concentration on orange peel adsorption. An increase in initial concentration of heavy metals led to an increase in the adsorption capacity of heavy metals on orange peel. This indicates that the initial concentration of heavy metals played an important role in the adsorption capacity of heavy metals on adsorbent. The dotted lines in Figures 2 and 3 represent a linear regression fit to the results for both isotherms. However, since adsorption data are of a nonlinear nature, nonlinear regressions are also performed on each set of data points. These nonlinear regression fits are represented as solid lines in Figures 2 and 3.

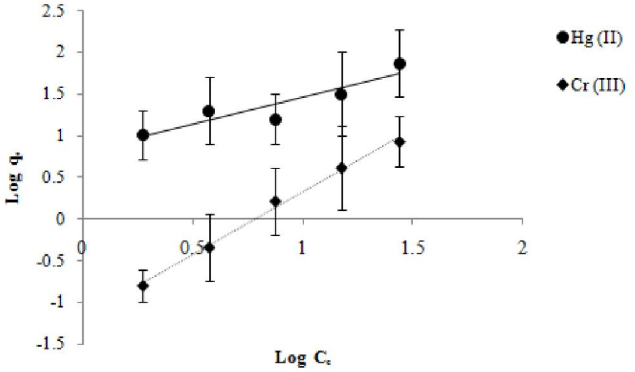

Figure 2 : Freundlich adsorption isotherm at 298 ÚK.

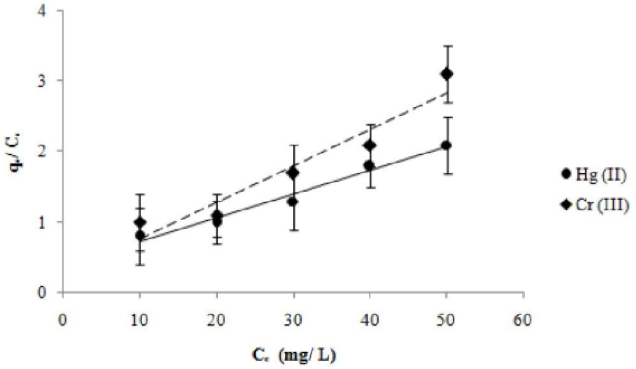

Figure 3 : Langmuir adsorption isotherm at 298 ÚK

The correlation coefficients obtained with both kinds of regression for both adsorption isotherms are summarized in TABLE 1. The correlation coefficient values in TABLE 1 indicate that the data fitthe Langmuir isotherm better than the Freundlich isotherm, both in case of linear and nonlinear regression.

Effect of shaking time

On increasing the contact time between metal wastes and orange peel we found an increase in the retention percentages of both elements studied up to a maximum recovery of 75% for Hg (II) and 68% for Cr (III) at 30 min; the use of a shaking times of 45 or 100 min practically does not improve the metal retention by orange peel (see Figure 4).

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
Cr (III)	6.43	0.322	0.99	3.21	1.59	0.97
Hg (II)	7.79	0.549	0.98	4.43	1.24	0.99

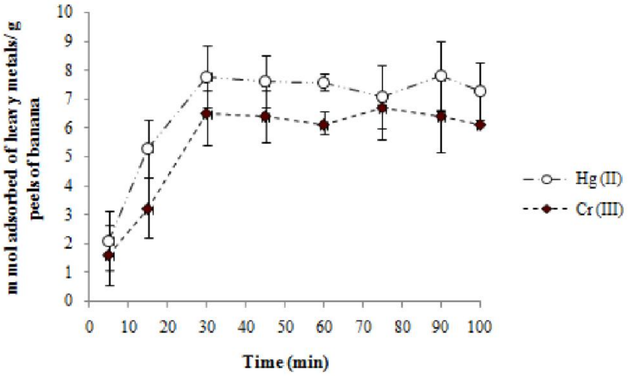

Figure 4 : Adsorption rate of Cr (III) and Hg (II) by orange peel from aqueous solutions. Adsorption conditions; initial concentration of heavy metals: 20 mg/L, amount of chitosan: 0.5 g, volume of adsorption medium: 25 mL, temperature: 298 ÚK.

Effect of pH

To study the effect of pH on adsorption, experiments were carried out in the pH range 1–9 for Hg (II) and Cr (III). Figure 5 shows that the removal of metal ions was increased with increasing initial pH of metal ion solution and maximum value was reached at pH 4 for Cr (III), 5-6 for Hg (II).

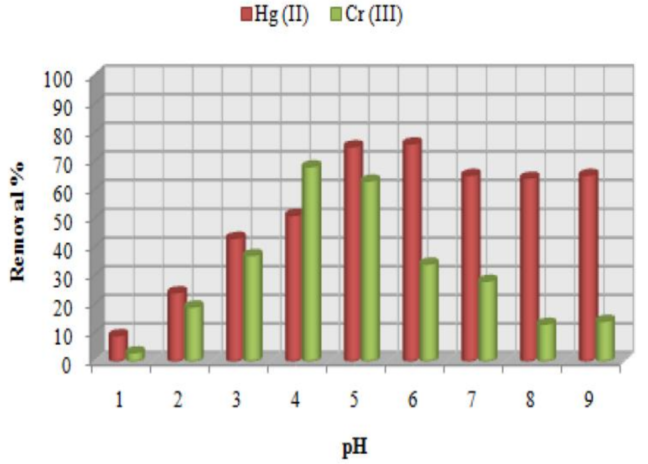

Figure 5 : Effect of pH on adsorption of Cr (III) and Hg (II) on orange peel.

Kinetic modeling

For evaluating the adsorption kinetics the pseudo-first-order and pseudo-second-order kinetic models were used to fit the experimental data. It was observed that the q_e values estimated by first-order kinetic model differ substantially from those measured experimentally, suggesting that the adsorption is not a first-order reaction. The correlation coefficients for the second-order kinetic model are nearly equal to 1 and the theoretical values of q_e also agree very well with the experimental values. This suggests that the adsorption of heavy metals on orange peel follows the second-order kinetic model. Figure 6.

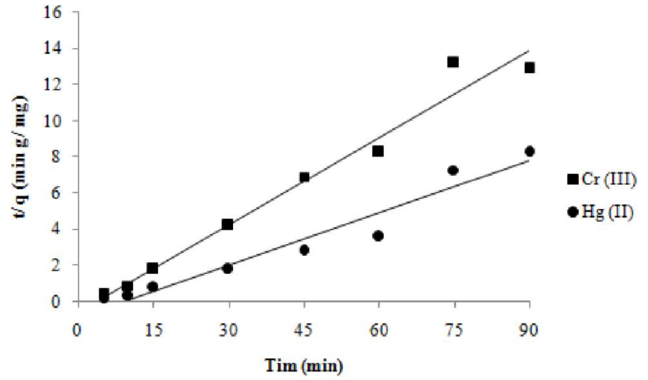

Figure 6 : Pseudo-second-order kinetic model fitting for Cr (III) and Hg (II) adsorption on orange peel.

Changes of free energy

The effect of temperature on the adsorption of heavy metals on orange peel was investigated by conducting experiments for 30 mg/L of initial metals ion concentrations at 298, 303, 308, 313, and 318 °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:

$$\ln\left(\frac{q_e m}{C_e}\right) = \frac{\Delta S^\circ}{R} + \frac{-\Delta H^\circ}{RT} \qquad (12)$$

$$\Delta G^\circ = \Delta H - T\Delta S^\circ \qquad (13)$$

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 $\ln (q_e m/C_e)$ vs. 1/ T, respectively, thereafter ΔG° values were determined from Eq. (12). 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. This result suggested that a high temperature is favoured for the adsorption of heavy metals on orange 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 orange peel was endothermic. A positive ΔS suggested that heavy metals were not stable on the adsorption sites of orange peel probably due to the increase in translational energy of metals ion.

TABLE 2 : Thermodynamic parameters for adsorption of Hg (II) and Cr (III) on orange peel.

Metal ions	ΔH° (kJ/mol)	ΔS° (Jmol/K)	- ΔG° (kJ/mol)				
			298 °K	303 °K	308 °K	313 °K	318 °K
Hg (II)	49.51	202.53	10.843	11.856	12.869	13.881	14.894
Cr (III)	35.43	134.96	4.788	5.462	6.137	6.812	7.487

CONCLUSIONS

The current study emphasizes on the ability of orange peel to adsorb heavy metals from aqueous solutions. In batch mode studies the adsorption was dependent on initial metals ion concentration and agitation time. The adsorption process followed pseudo-second-order kinetics and obeyed Langmuir adsorption isotherm for metals ion studied. Although the adsorptive capacity of orange peel is not excessively. high for heavy metals, low cost of the material together with its adsorptive ability could offer a promising procedure for depollution of industrial wastewaters. 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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