Adsorption of Cadmium onto Orange Peels: Isotherms, Kinetics, and Thermodynamics

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Abstract
Batch adsorption of Cd (II) onto orange peel, a residue of the fruits processing industry, has been studied. Equilibrium isotherms, kinetic data, and thermodynamic parameters have been evaluated. Equilibrium data fit well with Langmuir isotherm model. The kinetic data were found to follow the pseudo-second-order model. The negative ΔHº value indicates the exothermic nature of the adsorption process. Orange peel was shown to be a promising adsorbent for Cd (II) removal from aqueous solutions.

Keywords: Adsorption; Isotherms; Kinetic models; Thermodynamics; Orange peel

Nomenclature
- A: Constant describing the energy of interaction between solute and adsorbent surface;
- β: Desorption constant (g/mg) during any experiment;
- C0: Initial concentration (mg/l);
- Ce: Equilibrium concentration (mg/l);
- Kf: Freundlich constant;
- k1: Intraparticle diffusion rate constant (min⁻¹);
- k: Pseudo first-order adsorption rate constant (l/min);
- k2: Pseudo second-order adsorption rate constant (g/mg.min);
- KD: Distribution coefficient (cm³.g⁻¹);
- K: Langmuir constants (L mg⁻¹);
- M: Weight of adsorbent (mg);
- q: Adsorption capacity (mg of Cd (II)/g adsorbate);
- qe: Adsorption capacity at equilibrium, (mg of Cd (II)/g adsorbate);
- qm: Maximum adsorption (mg of Cd (II)/g adsorbate);
- R: Gas constant (8.314 J/mol/K);
- Rc: Percent of Cd (II) adsorbed (mg/g);
- Re: The removal efficiency of Cd (II) (mg/g);
- r²: Correlation coefficient;
- T: Temperature (K);
- t: Contact time (min);
- v: Volume of the solution;
- α: Initial adsorption rate (mg of Cd (II)/g adsorbate. min⁻¹);

Introduction
Cadmium is one of the toxic heavy metals released to environment from a number of industries such as, electroplating process, metallurgy, pigments, plastic, fertilizers and batteries production. The maximum concentration of cadmium ions in drinking water is 0.003 mg/L according to the World Health Organization [1]. Conventional heavy metal clean-up technologies cover precipitation, ion exchange, chemical oxidation/reduction, reverse osmosis, electrodialysis, ultra filtration, solvent extraction, etc.[2]. However some disadvantages of the technologies, such as high cost, sensitive operating conditions and production of secondary sludge [3,4]. Adsorption process has received much interest and become an alternative to conventional precipitation and other techniques, especially for wastewaters that contain low concentrations of metals and its effectiveness [5]. Activated carbon is considered to be a highly effective adsorbent for heavy metal removal from wastewater, but it is readily solubilized under extreme pH conditions [6], and is also very high cost [7]. Low-cost agricultural waste byproducts, such as sugarcane bagasse [8], rice husks [9], sawdust [10], coconut husks [11], and oil palm shell [12], have been investigated to eliminate heavy metals from wastewater. Agricultural residues are usually composed of lignin and cellulose as the major constituents with other polar functional groups such as alcohols, aldehydes, ketones, carboxylic acids and ethers that facilitate metal complexation resulting biosorption of heavy metal ions[13], from wastewaters. The objective of this research was to investigate the removal of Cd(II) from aqueous solutions by orange peel. The effect of adsorbent dosage, initial metal concentration, contact time, temperature and pH were examined. Equilibrium isotherms, kinetic data, and thermodynamic parameters have been studied.

Materials and Methods

Preparation of adsorbent
Orange fruits were purchased from a local market and peeled...
manually. The peels was washed thoroughly with distilled water to remove the dirt, and dried at 80°C for 24 h, finally crushed and sieved to obtain a particle size of 0.355 mm and used as such.

Preparation of adsorbate solutions

1000 mg/L of Cd (II) was prepared as stock solution by dissolving the desired quantity of CdCl2·2H2O (Aldrich, USA) in distilled water. The required solutions were prepared by diluting the stock solution to the desired Cd (II) concentrations. The Cd (II) concentrations were determined by atomic adsorption spectrophotometer.

Adsorption experiments

Batch experiments were carried out to investigate the parametric effects of adsorbent dose, contact time, pH, temperature, and initial Cd(II) concentration for adsorption onto orange peel. 50mL of different concentrations (50-150 mg/L) of Cd (II) solutions (C0) with a range of pH values from 2 to 10 was transferred in a conical flask with a required amount of adsorbent. The solution was agitated at 150 rpm in a thermostatic shaker water bath at different temperature (30, 40, 50 and 60°C). The samples were withdrawn and centrifuged at 5000 rpm for 5 min and the supernatant solutions were analyzed. The pH of the solutions was adjusted with 0.1 N NaOH or 0.1 N HCl.

The removal efficiency of Cd (II) was defined as:
\[ R_e (%) = \frac{C_0 - C_i}{C_0} \times 100 \]  
(1)

In addition, the adsorption capacity (q) is calculated according to the following equation:
\[ q = \frac{C_0 - C_i}{M} \times V \]  
(2)

Adsorption Isotherms Study

Equilibrium studies that give the capacity of the adsorbent and adsorbate are described by adsorption isotherms, which is usually the ratio between the quantity adsorbed and that remained in solution at equilibrium at fixed temperature [14,15]. Freundlich and Langmuir isotherms are the earliest and simplest known relationships describing the adsorption equation.

Langmuir isotherm

The Langmuir equation is used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface and is expressed by [16]:
\[ q_e = \frac{q_{max}K_cC_e}{1 + K_cC_e} \]  
(3)

The linear form of the above equation after rearrangement is given by:
\[ \frac{C_e}{q_e} = \frac{1}{q_{max}K_c} + \frac{C_e}{q_{max}} \]  
(4)

The experimental data is fitted into the above equation for linearization by plotting Ce/qe against Ce. The constants qmax and Ke can be determined from the slope and intercept, respectively.

Freundlich isotherm

The Freundlich model [17], is an empirical equation used to estimate the adsorption intensity of the sorbent towards the adsorbate and is given by:
\[ q_e = K_cC_e^{1/n} \]  
(5)

Also, the value of n indicates the affinity of the adsorbate towards the adsorbent. The above equation is conveniently used in linear form as:
\[ \log q_e = \log K_c + \frac{1}{n} \log C_e \]  
(6)

A plot of ln Ce against lnq yielding a straight line indicates the conformation of the Freundlich adsorption isotherm. The constants 1/n and ln Ke can be determined from the slope and intercept, respectively.

Adsorption Dynamics Study

The study of adsorption dynamics describes the adsorbate uptake rate and evidently, this rate controls the residence time of adsorbate uptake at the solid-solution interface. Kinetics of Cd (II) adsorption on the orange peel was analyzed using pseudo first-order, pseudo second-order, Elovich and intra particle diffusion kinetic models [18,19].

Pseudo-first-order model

The pseudo first order kinetic model [20], was given by equation:
\[ \log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \]  
(7)

Values of k1 and qe were calculated from the slope and intercept values of the straight line of plotting log (qe−qt) versus t.

Pseudo-second-order model

The sorption data were also analyzed in terms of pseudo-second order model [20,21],given by the equation:
\[ \frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} t \]  
(8)

If the initial adsorption rate, h (mg/g. min) is:
\[ h = K_2q_e^2 \]  
(9)

then Equations (11) and (12) become:
\[ \frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \]  
(10)

The plot of t/qt versus t should give a straight line and the pseudo second order rate constant, K2, and equilibrium adsorption capacity, qe, were calculated from the values of intercept and slope, respectively.

The Elovich model

The Elovich model equation is generally expressed as [19]:
\[ \frac{dq_e}{dt} = \alpha \exp(-\beta q_e) \]  
(11)

To simplify the Elovich equation, assumed a bt >> t and by applying the boundary conditions t=0 to t=t and q=0 to q=q, Equation (9) becomes:
\[ q_e = \frac{1}{\beta} \ln (a\beta) + \frac{1}{\beta} \ln (t) \]  
(12)

A plot of q vs. ln(t) should yield a linear relationship with a slope of (1/β) and an intercept of (1/β) ln(aβ).

The intraparticle diffusion model

The intraparticle diffusion model is expressed as [16]:
\[ R_e = K_0 t^{n} \]  
(13)

A linearized form of the equation is obtained as:
\[ \log R_e = \log K_0 + n \log (t) \]  
(14)

If Cd (II) adsorption fits the intraparticle model, a plot of log R vs. log t should yield a linear relationship with a slope of n and an intercept of log k0.
Results and Discussion

Characterization of adsorbent

Figure 1a and 1b represent the SEM photographs of adsorbent before and after adsorption with 1000x magnification. It became apparent from the surface texture or topology of adsorbent before adsorption that the adsorbent surface is rough, porous and irregular shapes. After adsorption, Figure 1b shows that the metal ion being adsorbed on the adsorbent site. In addition, adsorbent surface was stuffed with Cd (II) ion resulting in loss of surface porosity and roughness.

Adsorption dynamics

Effect of pH: The effect of pH has been studied by varying it in the range of 2-10 at 30°C, 2 hrs, 0.5 g adsorbent and particle size of 0.335 mm (Table 1). It was observed that the removal of Cd (II) increases with the increase of pH from 2 to 8. After that, the capacity of adsorption decreases slightly in the pH range of 8-10. The highest adsorption efficiency is observed at pH 5. These observations can be explained by the fact that at lower pH values, the competing of H+ with Cd(II) for the adsorption site. In addition, adsorbent surface was stuffed with Cd (II) ion resulting in loss of surface porosity and roughness.

| Parameter                  | pH:          | 30°C 97.76 4.889 |
|----------------------------|--------------|------------------|
| pH                        | 2            | 25.53 1.277      |
| (Condition: 50 mg L⁻¹, mass = 0.5 g, 3 h, 30 °C) | 3             | 84.45 4.252      |
|                           | 4             | 92.33 4.616      |
|                           | 5             | 97.33 4.889      |
|                           | 6             | 97.58 4.875      |
|                           | 7             | 97.73 4.886      |
|                           | 8             | 97.70 4.888      |
|                           | 9             | 89.34 4.457      |
|                           | 10            | 68.54 3.427      |
| Time (min):               |              |                  |
| (Condition: 50 mg L⁻¹, mass = 0.5 g, pH=5, 30 °C) | 10            | 49.92 2.460      |
|                           | 20            | 56.21 2.811      |
|                           | 30            | 77.33 3.867      |
|                           | 40            | 89.50 4.475      |
|                           | 50            | 93.19 4.659      |
|                           | 60            | 97.76 4.889      |
|                           | 80            | 97.71 4.886      |
|                           | 100           | 97.65 4.882      |
|                           | 120           | 97.75 4.887      |
| Initial concentration (mg/l): | 50             | 97.76 4.889      |
| Condition: pH=5, mass = 0.5 g, 60 min, 30 °C | 75             | 94.29 7.12       |
|                           | 100           | 90.68 9.36       |
|                           | 125           | 76.36 9.35       |
|                           | 150           | 62.28 9.34       |
| Adsorbent dose (g) :      | 0.3           | 78.12 4.075      |
| Condition: 50 mg L⁻¹, 60 min, pH=5, 30 °C | 0.4             | 91.34 4.567      |
|                           | 0.5           | 97.76 4.889      |
|                           | 0.6           | 97.69 4.073      |
|                           | 0.7           | 97.71 4.389      |
| Temperature (°C) :        | 30            | 97.76 4.889      |
| Condition: 50 mg L⁻¹, 60 min, mass = 0.5 g, pH=5 | 40             | 96.50 4.825      |
|                           | 50            | 95.38 4.769      |
|                           | 60            | 92.24 4.612      |

Table 1: Adsorption data of adsorption process.

Adsorption isotherms

The results of this study show that orange peel was effective, in the adsorption of Cd (II) as its removal reached 97.33% at 30°C, pH 5, 60 minutes contact time, 0.5 g of adsorbent and Cd (II) initial concentration of 50 mg/l. The Experimental data were applied in the two isotherms (Figures 2 and 3), which results indicate that the adsorption of Cd (II) onto orange peel fits the Langmuir isotherm model because it gives a higher correlation coefficient (r² = 0.983) value than Freundlich isotherm model (r² = 0.883), verifying the assumption that the adsorbate molecules could be adsorbed in monolayer coverage on the surface of orange peel giving a higher correlation coefficient (r² = 0.983) value than Freundlich isotherm model (r² = 0.883), verifying the assumption that the adsorbate molecules could be adsorbed in monolayer coverage on the surface of orange peel.

Effect of adsorbent dosage: The adsorption percent at various doses of orange peel from 0.3 to 0.7 g is shown in Table 1. Increasing the adsorbent dose to 0.5 g increases the adsorption percent of metal ions, which is due to the increasing in adsorption sites of adsorbent material resulting from increasing of surface area of adsorbent. However, further increase of adsorbent dosage does not afford exhaustive adsorption of Cd (II). This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles.
the adsorbent. The adsorption constants evaluated from the isotherms with the correlation coefficients are given in Table 2.

Adsorption kinetics

From Table 3 and Figures 4-7, show that the pseudo second order model is the best fitting model because it gives a higher correlation coefficient ($r^2=0.988$) than the other kinetic models (pseudo-first-order ($r^2=0.925$), Elovich ($r^2=0.901$) and intraparticle diffusion ($r^2=0.805$) models.

Thermodynamic Studies

The effect of the temperature on the adsorption of Cd (II) ions was studied in the range of 30-60°C. The result shows that temperature has an effect on the adsorption of Cd (II) onto orange peels. Thermodynamic parameters, such as enthalpy variation ($\Delta H^o$), entropy variation ($\Delta S^o$), and change in Gibbs free energy ($\Delta G^o$), were calculated from the curve relating the distribution coefficient ($K_d$) as a function of temperature (Figure 8), using the equations [16]:

$$\ln K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}$$

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

From Figure 8, the values of $\Delta H^o$, $\Delta S^o$ were determined from the slope and intercept values of the straight line of plotting $\ln K_d$ versus $1/T(K)$, respectively (Table 4). Negative value of $\Delta G^o$ indicates the feasibility of the process and indicates the spontaneous nature of the adsorption. Decreasing $\Delta G^o$ values with decreasing temperature suggests that lower temperature makes the adsorption easier. The negative $\Delta H^o$ value indicates the exothermic nature of the adsorption process. The magnitude of $\Delta H^o$ may give an indication about the type of sorption. Two main types of adsorption are physical and chemical.

![Figure 2: Langmuir isotherm of adsorption process.](image)

![Figure 3: Freundlich isotherm of adsorption process.](image)

| Langmuir constant | Freundlich constant |
|-------------------|--------------------|
| $K_L$ (mg/g)      | $q_{max}$ (mg/g)   |
| $r^2$             | $K_r$ (g/mg.min)   |
|                   | $n$                |
|                   | $r^2$              |
| 0.516             | 4.90               |
| 0.983             | 6.150              |
| 0.883             |                    |

Table 2: Langmuir and Freundlich constants of adsorption system.

| Experimental $q_e$ (mg/g) | Pseudo-first-order model | Pseudo-second-order model | Elovich model | Intraparticle diffusion model |
|---------------------------|--------------------------|---------------------------|---------------|-------------------------------|
|                           | $K_1$ (1/min) | $q_e$ (mg/g) | $r^2$ | $q_e$ (mg/g) | $K_2$ (g/mg.min) | $r^2$ | $\beta$ (mg/g) | $\alpha$ (g/mg.min) | $r^2$ | $K_d$ (g/mg.min) | $a$ | $r^2$ |
| 15.91                     | 0.0759           | 6.999         | 0.925 | 4.950         | 0.0971           | 0.988 | 0.759           | 1.231           | 0.901 | 14.79           | 1.366 | 0.805 |

Table 3: Adsorption kinetic model rate constants.
Basically, the heat evolved during physical adsorption is of the same order of magnitude as the heats of condensation, i.e., 2.1-20.9 kJ/mol, while the heats of chemisorption generally falls into a range of 80-200 kJ/mol [23]. From Table 4, the absolute value of $\Delta H^o$ are 34.935, which therefore indicate that Cd (II) adsorption by orange peel could be attributed to a physic-chemical adsorption process rather than a pure physical or chemical adsorption process. Negative value of $\Delta S^o$ indicate a decrease in randomness at the solid/solution interface during the adsorption process while low value of $\Delta S^o$ indicates that no remarkable change on entropy occurs [24].

Conclusion

Orange peel was effective, as a Cd (II) adsorbent, for which the removal reached 97.33% at 30°C. The highest adsorption efficiency is observed at pH 5. Increasing temperature and initial concentration of Cd (II) lead to decreasing the removal of Cd (II). The Langmuir isotherm model appears to be the best fitting model for adsorption process. The kinetics of Cd (II) adsorption on the orange peel was found to follow a pseudo second-order rate equation. Thermodynamic parameters ($\Delta G^o$, $\Delta H^o$ and $\Delta S^o$) showed that the adsorption process is spontaneous and exothermic in nature.

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