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Cadmium Removal from Aqueous Solution by Canola Residues: Adsorption Equilibrium and Kinetics

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Abstract
Cadmium is a hazardous non-biodegradable material that enters the food chain. In this study, the removal of cadmium from aqueous solutions by Canola residues (a natural biosorbent) was investigated. The effect of parameters such as contact time, pH, cadmium concentration and adsorbent dose were evaluated, the results showed that increasing of pH, contact time and adsorbent caused increasing of efficiency of removal cadmium from aqueous solutions. A comparison between non-linear and linear of estimating the isotherm and kinetic parameters was discussed. The results confirmed that the non-linear method was a more efficient method to gain isotherm and kinetic parameters.

Keywords: *Canola residues, Aqueous Two Phase, Biosorption, Biokinetics*

1. Introduction
Heavy metals are highly toxic and considered a serious threat to human health and the environment. The increase of heavy metals in the environment is largely a result of industrialization. As a result of this problem, the need to remove and recover these heavy metals has increased [1]. Cadmium is highly toxic at low concentrations and widely used in various applications. If the metal is used by humans, in addition to osteoporosis, it accumulates in the kidneys, causing them to malfunction. Cadmium is a contaminant that is among the priority pollutants of the American Environmental Protection Agency (USEPA) [2]. The proposed maximum contaminant level (MCL) and maximum contaminant level goals (MCLG) value for cadmium is 0.005mg/l [2]. The maximum permitted concentration by the World health Organization (WHO) is determined 0.001mg/l. The main sources of cadmium to the aquatic environments are via wastewaters of some industrial processes such as plating, pottery, tiles, plastics, metals, mining and smelting, paint, Cd-Ni batteries, and industries which produce chemical fertilizers and pesticides [2]. The surrounding soils of agricultural lands are one of the important areas that has been contaminated with cadmium due to phosphatic fertilizers or sewage sludge used to improve soil.

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Different methods such as chemical precipitation, ion exchange, electro-dialysis and adsorption, etc. have been studied and used for removal of heavy metals where each method has its own disadvantages [3]. Adsorption by organic matters such as algae, bacteria, fungi, leaves, trees and agricultural wastes have been widely studied in recent years as a convenient and inexpensive method for heavy metals removal (to maintain high efficiency at low to medium concentrations). Agricultural residues contain lignin and cellulose, which usually constitute the main structure of it. There are compounds such as hemi-cellulose, lipids, proteins, glucose, starch, water, hydrocarbons and other compounds in their structure. These groups have the ability to link with heavy metals in solution by replacing hydrogen ions or giving a pair of electrons of these groups to form complexes with metal ions. Canola waste can be considered as a low-cost adsorbent for the removal of heavy metals due to fiber characteristics, porosity and low molecular weight. Carboxylic and hydroxyl groups on the surface structure of Canola waste have a great affinity for heavy metal ions [4]. In addition, Canola residue is inexpensive, available and easy to prepare, it can be considered as an effective biosorbent used in water and wastewater treatment [5].

Agriculture biosorbent including grape skin [6], apple peels, apple kernel [6], orange waste [7], olive stone [8], medlar peels [9] coconut shell powder [10], pine sawdust [11] and papaya wood [12] have been used for removal of the heavy metals from aqueous solutions.

The aims of the present work are: (i) to determine maximum removal of Cadmium in different conditions such as pH, contact time, adsorbent dose and initial concentration of Cadmium, (ii) to estimate linear and nonlinear method the isotherms parameters and kinetic model parameters.

1-1. Adsorption isotherms

1-1-1. Langmuir isotherm

The Langmuir adsorption isotherm has been the most widely used in many pollutants adsorption processes and is a successfully applied sorption isotherm for the sorption of a solute from a liquid solution [13]. The saturated monolayer isotherm can be expressed as

$$q_e = \frac{q_m K C_e}{1 + K C_e} \tag{1}$$

where C_e is the equilibrium concentration; q_e is the amount of Cd adsorbed per unit mass of Canola residue; q_m is q_e for a complete monolayer, a constant related to sorption capacity; and *K* is a constant related to the affinity of the binding sites and energy of adsorption.

1-1-2. Freundlich isotherm

Freundlich isotherm is an empirical equation describing adsorption onto a heterogeneous surface.

The Freundlich isotherm can be represented as [14]:

$$q_e = K C_e^{1/n} \tag{2}$$

where *K* and *n* are the Freundlich constants related to the adsorption capacity and

adsorption intensity of the sorbent, respectively.

1-1-3. Temkin isotherm

The derivation of the Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm [15] can be represented as:

$$q_e = A + B \ln C_e \quad (3)$$

where *A* and *B* are isotherm constants.

1-2. Kinetic model

1-2-1. Pseudo first kinetic model

The pseudo-first-order equation is given as [16]

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (4)$$

where k_1 is the rate constant of pseudo-second-order adsorption and q_t is metal adsorbed at time t. Integrating this equation for boundary conditions for t=0, q=0 gives

$$q_t = q_e(1 - \exp(k_1 t)) \quad (5)$$

1.2.2. Pseudo second kinetic model

The pseudo-second-order equation based on adsorption equilibrium capacity can be expressed as [17]:

$$\frac{dq}{dt} = k_1(q_e - q_t)^2 \quad (6)$$

Integrating this equation for boundary conditions for t=0, q=0 gives

$$q_t = \frac{k_1 q_e^2 t}{1 + k_1 q_e t} \quad (7)$$

1-3. The error analysis

In order to confirm the fit model for the adsorption system, it is necessary to analyze the data using error analysis. The calculated expressions of some error functions are as follows [18]:

(1) The sum of the squares of the errors (ERRSQ):

$$SSE = \sum (q_c - q_e)^2 \quad (8)$$

(2) The sum of the absolute errors (EABS):

$$EABE = \sum |(q_c - q_e)| \quad (9)$$

(3) The average relative error (ARE):

$$ARE = \frac{100}{n} \sum \left| \frac{q_c - q_e}{q_e} \right| \quad (10)$$

(4) Nonlinear chi-square test (χ^2)

$$\chi^2 = \sum \frac{(q_c - q_e)^2}{q_e} \quad (11)$$

Where *n* is the number of experimental data points, q_c is the predicted (calculated) and q_e is the experimental data.

2. Experimental

2-1. Preparation of biosorbent

This is an experimental study in which the Canola residue is used as biosorbent in the removal of cadmium from aqueous solution. The residues from Canola were collected in the agricultural lands at harvesting season. The residues were washed with purified water to remove dust, then left to dry completely in the sun. The dried materials were crushed into fine particles with an

electric mill. In order to eliminate color and contamination, fine particles were mixed with distilled water at ratio of 1 to 5 and then heated at 100°C for 5 hours by heat rate 31500 J. Next, the samples were filtered by Whatman membrane filter (0.45 microns) and washed several times with distilled water and placed in oven (at 80°C) for 8 hours until the moisture was removed. After drying, the adsorbent was milled again to smaller particles with electric mill. The ASTM sieve was used for particle sizing that was approximately less than 200 micron and then particles were placed into impermeable plastic bags [19, 20].

2-2. Reagents

In this study, stock solution of cadmium (1000 mg/l) was provided by dissolving cadmium nitrate ($CdN_2O_6.4H_2O$) in deionized water and then the desired concentrations were prepared by diluting the stock solution.

2-3 .Experimental plan

Experiments were conducted in Batch system (Erlen Mayer 150 ml) in the laboratory scale. This study investigated some factors such as pH (2, 4, 6, 7), contact time (5, 10, 15, 30, 45, 60, 120 minutes), the initial concentration of cadmium (15, 30, 60 mg/l) and the dose of adsorbent (0.2, 0.6, 1 g /100 ml). In order to determine adsorption equilibrium content, 0.6 g Canola powder was mixed with 100 ml sample containing 30 mg/l cadmium for 24 hours. The nitric acid and NaOH 0.1N were used to adjust the pH of the solution. In order to increase the accuracy and precision of the results, 200 samples were carried out in triplicate. A shaker (Model FL 83) at speed of 120 rpm was used in order to mix the samples. The samples were filtered by Whatman 0.45 microns. The filtrates were transmitted to polyethylene containers and pH was kept in acidic condition by nitric acid (pH= 2). Cadmium concentrations in the storage samples were measured by using Atomic absorption Spectrophotometer (PG-instrument 99s0). The measurements were performed according to the standard methods for water and wastewater examination (21).

3. Results and discussion

3-1. Influence of pH on the biosorption

In order to evaluate the efficiency of the cadmium adsorption of the Canola powder over different ranges of pH (2, 4, 6, and 7), a series of experiments were carried out. Usually cadmium containing waste water has acidic to neutral pH, so in this study the samples were investigated in pH 2, 4, 6, and 7 (Fig. 1). The results showed that the efficiency of cadmium removal by Canola adsorbent was raised by increasing pH.

3-2. Influence of initial cadmium concentration on the biosorption

In order to investigate the effect of initial cadmium concentration, 1 gram Canola adsorbent was utilized in 100 ml of cadmium solution (with soluble concentrations of 15, 30 and 60 mg/l) over 30 minutes at pH=6 and the results were presented in Fig. 2. The effect of initial cadmium concentration on adsorption efficiency showed that increasing initial concentration decreased the adsorption rate, but the efficiency is high. This phenomenon is due to the saturation of the

active sites of the adsorbent. Higher initial concentration can create a significant driving force that can overcome the mass transfer resistance. These results are similar to the results of Mahvi et al. [21]. So for the initial concentrations of 15, 30, and 60 mg/l, removal efficiencies were 90, 93 and 99 percent respectively.

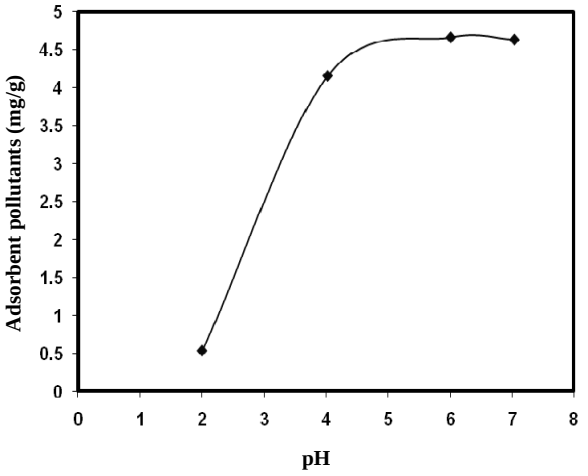

Figure 1. Effect of initial pH on absorbed cadmium with a constant concentration of 30mg/l (adsorbent dose= 0.6 g).

3-3. Influence of contact time on the biosorption

In this stage, the effect of different contact times was investigated in pH =6, adsorbent dose rate (0.2, 0.6, 1 g in 100 ml) and cadmium concentration of 60 mg/l. The results showed that by increasing contact times, the removal rate rises, so the maximum cadmium removal occurs in the initial 5 minutes of adsorbed process. The adsorption rate of cadmium decreases along with increasing the contact time, this phenomenon is due to the saturation of the active sites of adsorbent (Figs. 2 and 3).

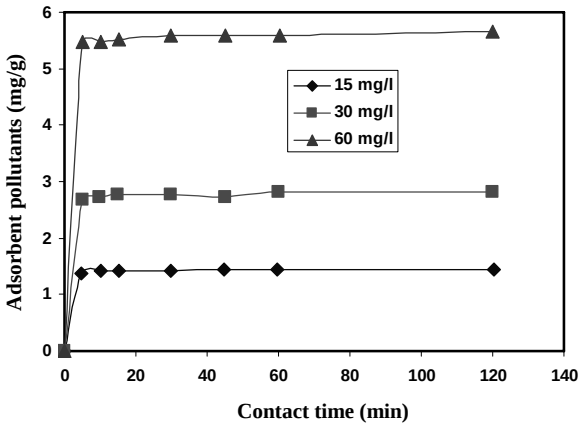

Figure 2. Effect of initial cadmium concentration on cadmium removal (Contact time 120min, pH = 6, adsorbent dose 1 g in 100 cc).

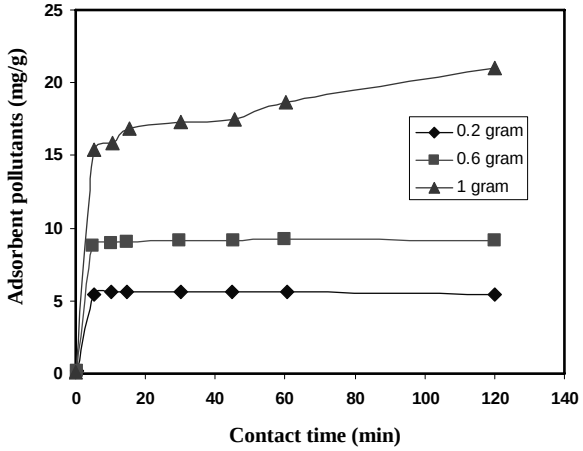

Figure 3. Effect of contact time on cadmium removal (Contact time 120 min, pH=6, the initial concentration of 60 mg of cadmium per liter).

The effect of adsorbent dose (0.2, 0.6 and 1g) in cadmium concentration of 60 mg/l at pH=6 was investigated in different contact times. The results indicate that by increasing the dose of adsorbent, the removal rate generally increases, so removal of cadmium in amounts of 0.2, 0.6 and 1 g of adsorbent in 120 min was 64, 92 and 95 percent, respectively (Fig. 4). In this study, adsorption equilibrium time was determined 15 min, so that after this time, adsorption rate of Cadmium by Canola adsorbent was stable.

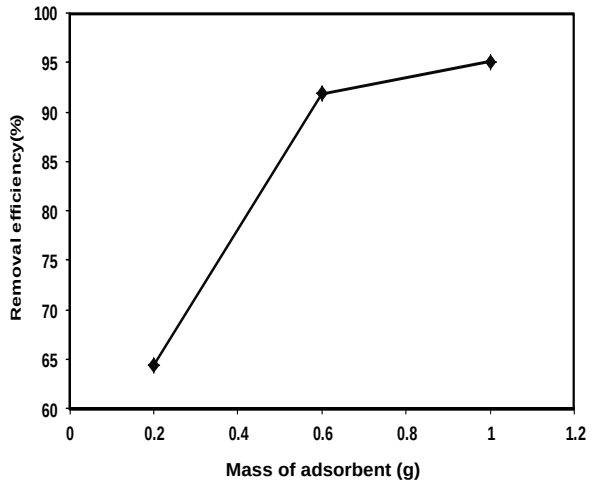

Figure 4. Effect of adsorbent mass on cadmium removal (initial cadmium concentration of 60 mg per liter, contact time: 120 minute, pH =6).

3-4. Determination of biosorption isotherm parameters about Cd/ Canola system

The retention of a metal ion (cadmium) by biosorbent can be evaluated by a simple mass balance following the logic that metal removed from the solution is found in or on the solid biomass:

$$q_e = \frac{V\,(C_i - C_{eq})}{M} \qquad (12)$$

Where C_i and C_{eq} (mg/l) are the initial and equilibrium concentration of the solute, respectively, q is metal retention by the biosorbent (mg / g), V (L) is the volume of liquid phase, M *(g)* is mass of adsorbent.

The analysis requires equilibrium to better understand the adsorption process. In this study, the Langmuir, Freundlich and Temkin models were applied. An adsorption isotherm is specified by certain constants whose values express the surface properties and affinity of the adsorbent. It can also be applied to understand the adsorption capacity of adsorbent.

The linear regressive method of least squares is used for finding the parameters of the isotherms. The nonlinear regressive method of least sum squares of difference between calculated data and experimental data was used to determine the isotherm parameters. The isotherm parameters and coefficients of determination from linear and nonlinear method were all listed in Table 1, 2, 3 and 4, respectively. The Freundlich model describes the saturation behavior of the adsorbent model from Table1, 2, 3 and 4.

Table 1. Isotherm parameters for Cd adsorption onto Canola residue from linear method.

Freundlich	n=0.689	K=5.284	$R^2 = 0.98$
Langmuir	$q_m = 8.733$	$K = 0.357$	$R^2 = 0.9141$
Temkin	$B = 0.136$	$A = -1.0701$	$R^2 = 0.9781$

Table 2. Isotherm parameter of Freundlich for Cd adsorption onto Canola residue from nonlinear method.

Freundlich			
	K	***n***	**OF**
ERRSQ	4.822	0.662	0.7166
ARE	4.85	0.658	9.924
EABS	4.85	0.658	1.219
X^2	4.96	0.697	0.1983

Table 3. Isotherm parameter of Langmuir for Cd adsorption onto Canola residue from nonlinear method.

Langmuir			
	q_m	***K***	**OF**
ERRSQ	2.8011	0.8911	0.4564
ARE	1.8013	1.1686	8.1292
EABS	1.8013	1.1686	0.9132
X^2	3.4927	0.7716	0.1533

Table 4. Isotherm parameter of Temkin for Cd adsorption onto Canola residue from nonlinear method.

Temkin			
	B	***A***	**OF**
ERRSQ	7.146	2.587	7.73
ARE	4.436	3.078	13.93
EABS	7.969	2.642	3.435
X^2	6.228	2.788	1.009

In order to determine different isotherms and their ability to correlate with experimental results, the fitted plots from each isotherm were shown with the experimental data for adsorption of Cd onto Canola residue in Figs. 5-9.

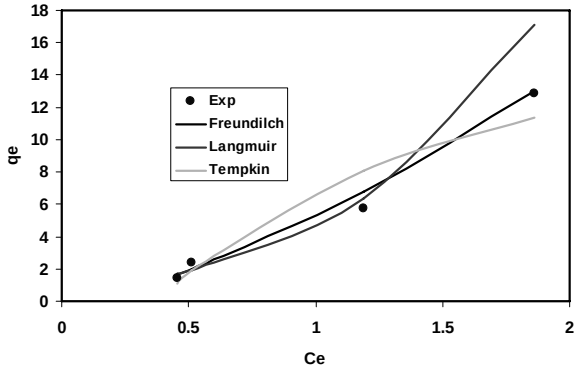

Figure 5. The experimental points and linear fitted curves from isotherms.

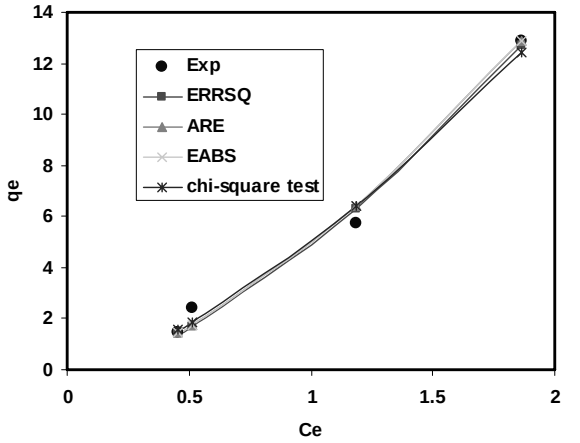

Figure 6. The experimental points and nonlinear fitted curves from Freundlich isotherm.

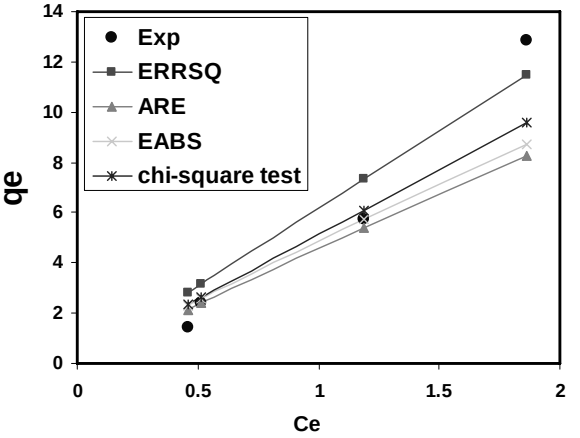

Figure 7. The experimental points and nonlinear fitted curves from Langmuir isotherm.

The values of ERRSQ, ARE, EABS, and χ^2 about Freundlich model from linear method or nonlinear method were smallest among the three isotherms, respectively. So it could be concluded that the model was the best to fit the experimental data according to Figs. 7, 8 and 9 and error values. Among the three isotherms, the Temkin equation was the poorest fit according to values of ERRSQ, ARE, EABS, and χ^2 from nonlinear method. According to Figs 7 and 8, using each of the error analyses gives different results, so it shows that error functions for nonlinear regressive method are important.

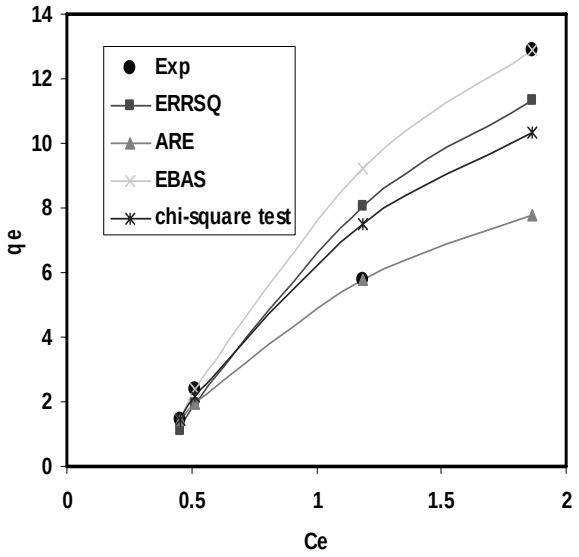

Figure 8. The experimental points and nonlinear fitted curves from Temkin isotherm.

3-5. The biosorption kinetic

The values of different errors from linear method and nonlinear method about first and pseudo-second-order model were both listed in Tables 5-10 respectively. Comparison of experimental points and fitted points was also shown in Figs. 9 and 10. First-order-kinetic model was shown in Fig. 9 and second-order-kinetic model was shown in Fig. 10.

Table 5. Pseudo-second-order and first-order parameters for Cd onto Canola residue from linear method ($C_0 = 15 mg/L$, $m_{adsorbent} = 0.2$).

	q_e	k_1	R^2
First order	0.4688	0.0113	0.9398
Second order	5.9204	0.297	0.9995

Table 6. Pseudo-second-order and first-order parameters for Cd onto Canola residue from linear method ($C_0 = 30 mg/L$, $m_{adsorbent} = 0.2$).

	q_e	k_1	R^2
First order	5.779	0.0181	0.9488
Second order	12.82	0.0208	0.9991

Table 7. Pseudo-second-order and first-order parameters for Cd onto Canola residue from linear method ($C_0 = 60 mg/L$, $m_{adsorbent} = 0.2$).

	q_e	k_1	R^2
First order	4.033	0.0161	0.9457
Second order	20.704	0.0137	0.9994

Table 8. Pseudo-second-order and first-order parameters for Cd onto Canola residue from nonlinear method ($C_0 = 15 mg/L$, $m_{adsorbent} = 0.2$).

First order	q_e	k_1	**OF**
ERRSQ	6.8673	0.3406	1.4934
ARE	6.8562	0.2393	4.4758
EABS	6.85	0.331	2.069
X^2	6.899	0.2972	0.3149
Second order			
ERRSQ	7.3040	0.0729	3.2184
ARE	7.382	0.0387	8.767
EABS	6.971	0.1795	3.1739
X^2	7.452	0.0538	0.686

Table 9. Pseudo-second-order and first-order parameters for Cd onto Canola residue from nonlinear method ($C_0 = 30 mg/L$, $m_{adsorbent} = 0.2$).

First order	q_e	k_1	**OF**
ERRSQ	13.432	0.3484	5.924
ARE	13.300	0.2455	4.6
EABS	13.30	0.3758	3.761
X^2	13.491	0.303	0.636
Second order			
ERRSQ	14.24	0.029	13.33
ARE	14.328	0.02	9.307
EABS	13.504	0.1058	6.64
X^2	14.52	0.0285	1.4121

Table 10. Pseudo-second-order and first-order parameters for Cd onto Canola residue from nonlinear method ($C_0 = 60mg/L$, $m_{adsorbent} = 0.2$).

First order	q_e	k_1	OF
ERRSQ	18.198	0.2613	9.748
ARE	18.501	0.204	5.164
EABS	18.501	0.2041	6.7182
X^2	18.246	0.242	0.699
Second order			
ERRSQ	19.7447	0.0188	10.889
ARE	18.501	0.2041	5.1649
EABS	16.79	0.1064	14.979
X^2	20.133	0.015	0.9935

From Fig. 9 and 10 can be seen that EABS error analysis is the best to fit biosorption kinetic model with the experimental data, while ARE is the worst to fit the experimental data.

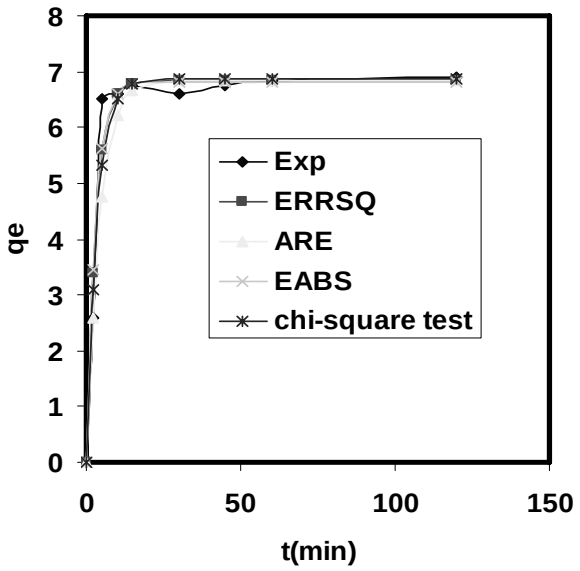

Figure 9. The experimental points and nonlinear fitted curves from first-order-kinetic model.

From Tables 5-7, we can conclude that pseudo second kinetic model is better than pseudo first kinetic model, but from Tables 8-10 and Fig. 9 and 10 we can conclude that pseudo first kinetic model is better than pseudo second kinetic model

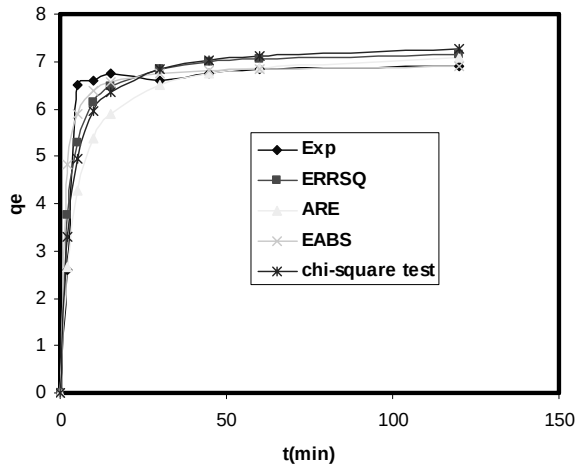

Figure 10. The experimental points and nonlinear fitted curves from second-order-kinetic model.

Comparison of difference between values of equilibrium adsorption quantity (q_e) from experiment and calculation (obtained from linear method or nonlinear method), some of the values of differences from experiment and linear method are larger, and some are opposite. So it cannot be concluded whether linear method or nonlinear method is better from the difference.

3-6. Adsorption thermodynamics

In the design of sorption systems, two types of thermodynamic properties, namely the directly measurable properties like tempera-

ture, equilibrium constant and properties which cannot be measured directly such as entropy, S, and free energy, G, are required. Thus, to establish the thermodynamic properties which cannot be directly measured, the famous thermodynamical relation known as Gibbs free energy, G, was used. The Gibbs free energy and entropy is used to decide the nature of sorption chemical reactions or the nature of sorption process.

The change in Gibbs free energy, which is a function of temperature, is given by:

$$\Delta G = \Delta H - T\,\Delta S \tag{13}$$

The change in free energy can be calculated using the constant, K_L, that is related to the energy of adsorption:

$$\Delta G = -RT \ln K_L \tag{14}$$

The calculated thermodynamic parameters for the sorption of cadmium by Canola such as K_L, ΔG, ΔH and ΔS are 2.735, 6.8 KJ/mol, 36.33 KJ/mol and 0.1 KJ/mol K respectively.

4. Conclusions

The efficiency of cadmium removal from aqueous solution by Canola plant residues as a natural biosorbent was evaluated. The effect of parameters such as contact time, pH, cadmium concentration and adsorbent doses were analyzed. In general, the best efficiency of cadmium removal by Canola residues was obtained at pH=6, dose adsorbent of 1 mg/ g and initial concentration of cadmium of 60 mg/l. The present study showed that the three isotherms, Langmuir, Freundlich and Temkin equation could represent the equilibrium adsorption of Cd onto Canola residue. The kinetic process can be predicted by pseudo-second-order and first order model. Both linear method and nonlinear method were suitable to predict the adsorption process.

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