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A comparative survey of linear and non-linear regression analysis on removal efficiency of clinoptilolite for sorption of dexamethasone from aqueous solutions

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ABSTRACT

The present study investigated the ability of clinoptilolite zeolite (CP) for removal of dexamethasone from aqueous solutions. The effects of some factors such as adsorbate concentration, adsorbent dosage, pH and contact time had been studied. Determination of dexamethasone was performed using UV-visible spectrophotometer. Four isotherm models including Freundlich, Langmuir, Tempkin and Sips were evaluated using linear and non-linear regression analysis. Results showed that in acidic condition (pH 4), the efficiency reached to maximum (57%) and linear regression had better performance for analyzing the experimental data. The Langmuir model is better than other isotherms to represent equilibrium data in both linear and non-linear methods.

Keywords: Dexamethasone; Aqueous solutions; Adsorption; Clinoptilolite zeolite; Isotherm

1. Introduction

Glucocorticoids are one of the most widely used pharmaceuticals in medical centers, so their concentration is high in wastewaters of medical centers [1,2]. Conventional treatment methods cannot remove them from wastewaters so they enter to the environment, willingly or unwillingly [2,3]. Environmental pollution is a serious risk for organisms. Dexamethasone is one of the most commonly used glucocorticoids in medical centers [4,5]. The empirical formula of dexamethasone is $C_{22}H_{29}FO_5$. This glucocorticoid has many positive and negative effects on different parts of the body.

Among different methods for removal of contaminants from aqueous solutions, adsorption on natural materials is a suitable method. Natural materials have appropriate potential for adsorption of contaminants from aqueous solutions. In a physical adsorption, attractive force between adsorbent and adsorbate functional groups has the main role. Natures of adsorbent, adsorbate, amount of contact surface and pH are some factors that affect the adsorption process. In recent years, some natural materials such as fruit wastes, plant wastes and especially zeolites due to low cost, abundance and suitable adsorption capacity have been considered as adsorbent for removal of contaminants from aqueous solutions [6]. It is also noteworthy to mention that a number of cases are the removal of chromium(VI) using sunflower stem wastes [7], biosorption of copper by pine cone shell [8], metal ions by olive stone wastes [9], Cu(II) onto coconut shell [10], cadmium(II) adsorption onto loquat leaves and canola residues [11,12], thorium removal by brown algae [13] and removal of Cu(II) and Pb(II) by coffee grains [14].

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Natural zeolites have different kinds and mainly consist of oxygen, silicon and aluminum. The chemical structure of zeolites includes AlO_4^{5-} and SiO_4^{4-} units, which are linked to each other by sharing oxygen atoms [15]. There are some characteristics in zeolites such as dewatering, ion exchange capacity, low density and removal capability for pollutants, which cause to use them for the removal of numerous contaminants from aqueous solutions. Clinoptilolite zeolite (CP) is one of the most abundant natural zeolites that have huge and various applicability in different areas such as aquaculture, agriculture, poultry, environments and medicine activities. Zeolites, especially CP, have high cation exchange capacity and selective affinity for contaminants. Some uses of zeolites to remove the contaminants from aqueous solutions and treatment of wastewaters are adsorption of chromate [16], cadmium [17], arsenic [18], phosphate [19], cephalexin [20], Co(II) [21] and photodegradation of furfural [22] and phenol [23] in wastewaters. In the current study, CP with the simplified formula of $(K_2,Na_2,Ca,Mg)_3Al_6Si_{30}O_{72}.24H_2O$ with pore volume 0.1717 cm^3/g and surface area 43.91 cm^2/g was used for dexamethasone removal from aqueous solutions.

In literature, the linear regression analysis has been frequently used to estimate the isotherm models parameters [24–26]. In linear regression, the least squares method is used for finding the parameters of the models by maximizing the values of coefficient of determination (R^2), but linear regression is criticized since it results in different linearized forms [27,28]. In recent years, several researchers have used non-linear regression to analyze isotherm models [29,30] for different adsorption processes such as the sorption of cadmium(II) ions by eucalyptus bark [31], basic dyes on sugarcane dust [32], arsenic onto iron oxide-coated cement [33] and brilliant green dye by rice husk ash [34]. In non-linear regression, the method of least sum squares of difference between calculated data and experimental data was used to determine the isotherm parameters. This method was performed using trial and error procedures with the help of solver add-in functions of Microsoft Excel software [28]. In this procedure, isotherm parameters were determined by maximizing R^2 and minimizing the values of sum squares of difference between calculated data and experimental data (sum of the squares of the errors [SSE]).

The present study investigated the parameters affecting the adsorption process of dexamethasone on CP. Four types of isotherm models were used for linear and non-linear regression analysis.

2. Materials and methods

2.1. Preparation of adsorbent

In this study, CP was used in the removal of dexamethasone from aqueous solutions. Preparation of adsorbent was done by several simple operations. Initially, an electric mill (Moulinex Turbomix) was used to crush the materials into smaller particles, and then the particles that were approximately less than 500 μm were selected using the American Society for Testing and Materials sieves. In next step, CP particles were washed several times with double distilled water to eliminate the impurities. In final step, CP powder was placed in oven (Memmert) at 80°C for 2 h in order to remove moisture, and then it was placed in desiccators (Pyrex) until being used for experiments.

2.2. Reagents

The stock solution of dexamethasone (100 mg/L) was prepared by dissolving dexamethasone (4,000 mg/L) in distilled water, and then the desired concentration was provided by diluting the stock solution.

2.3. Experimental plan

In this work, experiments were performed in batch system, in a laboratory scale and in room temperature (25°C). The effects of some factors such as initial adsorbate concentration (5, 10, 20 and 40 mg/L), adsorbent dose (0.2, 0.6 and 1 g/100 mL), pH solution (4, 7 and 9) and contact time (15, 30, 45, 60, 90 and 120 min) were investigated. Nitric acid 2M and NaOH 2M solutions were used to adjust the pH of solution. A shaker (IKA, Germany) was used to mix the samples during desired time, and after shaking, a centrifuge (Hettich, Germany) was used to separate the liquid phase from solid phase. After sampling from liquid phase, the dexamethasone concentration was measured using UV spectrophotometer double beam and PG Instruments (80+), UK. An UV spectroscopic scanning run (200–600 nm) was carried out with the reference solution to select the best UV wavelength for measurement of dexamethasone in an aqueous solution (241 nm). The analyses were performed using distilled water as blank [35]. The measurements were done according to the standard methods for water and wastewater examinations [36]. In order to increase the accuracy and precision of results, the experiments were conducted on triplicate, and the average contents were used, too.

3. Results and discussion

3.1. Adsorption isotherm

Adsorption isotherms explain the relationship between equilibrium adsorption capacity (q_e) and equilibrium final concentration of adsorbate (C_e) at constant temperature [37]. In the present study, equilibrium data were analyzed using linear and non-linear forms of four isotherms including Freundlich, Langmuir, Tempkin and Sips. The Freundlich isotherm assumes that the removal of contaminant ions occurs by multilayer adsorption and the adsorbent has a heterogeneous surface. In Freundlich isotherm, the removal efficiency of any compound enhances with the increase in contaminant concentration [7]. The linearized and non-linearized forms of Freundlich model are expressed as follows:

$$\mathrm{Ln}(q_e) = \mathrm{Ln}(k_F) + \frac{1}{n}\mathrm{Ln}(C_e) \tag{1}$$

$$q_e = k_F C_e^{\frac{1}{n}} \tag{2}$$

where q_e (mg/g) is equilibrium adsorption capacity, and C_e (mg/L) is the equilibrium concentration of adsorbate in solution. All factors that affect the adsorption process incorporated in k_F and n constants [38].

The Langmuir model assumes that the removal of contaminant ions occurs by monolayer adsorption and the

adsorbent has a homogeneous surface. The linearized and non-linearized forms of Langmuir model are represented by the following equations:

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{c_e}{q_m} \tag{3}$$

$$q_e = \frac{q_m k_L c_e}{1 + k_L c_e} \tag{4}$$

In above equations, q_e (mg/g) is equilibrium adsorption capacity; q_m (mg/g) is the maximum adsorption capacity and C_e (mg/L) is the equilibrium concentration of dexamethasone in solution whereas k_L is Langmuir constant.

The essential characteristic in Langmuir isotherm can be explained in terms of dimensionless constant separation factor (R_L), which is defined as follows:

$$R_L = \left(\frac{1}{1 + kc_i}\right) \tag{5}$$

where k is Langmuir constant, and C_i (mg/L) is initial concentration of dexamethasone. R_L determines the feasibility of the adsorption process and is a positive number. In each initial concentration, the R_L values must be between 0 and 1 for a favorable adsorption [7,39].

The Temkin isotherm model assumes that the heat of adsorption of all molecules decreases linearly rather than logarithmically with coverage [33]. The linearized and non-linearized forms of Temkin isotherm can be represented by the following equation:

$$q_e = \frac{RT}{b_T}\mathrm{Ln}(A_T) + \frac{RT}{b_T}\mathrm{Ln}(C_e) \tag{6}$$

$$q_e = \frac{RT}{b_T}\mathrm{Ln}(A_T C_e) \tag{7}$$

In above equations, q_e (mg/g) is equilibrium adsorption capacity; C_e (mg/L) is the equilibrium concentration of adsorbate in solution; R is universal gas constant (8.314 J/mol K) and T is temperature (298 K) whereas A_T and b_T are Temkin constants.

The Sips isotherm model is a combination of the Langmuir and Freundlich models. In low concentrations, it follows the Freundlich model while at high adsorbate concentrations, it leads to the Langmuir model. The linearized and non-linearized forms of Sips isotherm are shown in the following equations:

$$\mathrm{Ln}\left(\frac{k_s}{q_e}\right) = -\beta_s \mathrm{Ln}(C_e) + \mathrm{Ln}(a_s) \tag{8}$$

$$q_e = \frac{k_s C_e^{\beta_S}}{1 + a_s C_e^{\beta_S}} \tag{9}$$

where q_e (mg/g) is equilibrium adsorption capacity; C_e (mg/L) is the equilibrium concentration of adsorbate in solution and k_S (L/g); a_S (L/mg) and β_S are Sips isotherm model constants. The operating conditions such as pH solution, temperature and concentration influence on the equation parameters [40].

3.1.1. Determination of biosorption isotherm parameters

Each adsorption isotherm is specified by certain constants. These constants express the surface properties, affinity and adsorption capacity of adsorbent [12]. The retention of dexamethasone through biosorbent can be evaluated using a simple mass balance following the logic that the metal removed from the solution is found in or on the solid biomass:

$$q_e = \frac{V(C_i - C_e)}{M} \tag{10}$$

where q_e (mg/g) is equilibrium adsorption capacity; C_i and C_e (mg/L) are the initial and equilibrium concentration of adsorbate in solution, respectively; V (L) is the volume of liquid phase and M (g) is mass of adsorbent. In order to confirm the fit model for the adsorption system and to find the fitting degrees of isotherm with experimental data, it is necessary to analyze the data using error analysis. The calculated expressions of two error functions including the SSE and coefficient of determination (R^2) are as follows [12]:

$$\mathrm{SSE} = \sum\left(q_{\mathrm{cal}} - q_{\mathrm{exp}}\right)^2 \tag{11}$$

$$R^2 = 1 - \frac{\sum\left(q_{\mathrm{exp}} - q_{\mathrm{cal}}\right)^2}{\sum\left(q_{\mathrm{exp}} - q_{m\,\mathrm{exp}}\right)^2} \tag{12}$$

where q_{exp} (mg/g) is the amount of dexamethasone adsorbed by CP obtained from experiment, q_{cal} the amount of dexamethasone obtained by isotherm models and $q_{m\,\mathrm{exp}}$ the average of q_{exp} (mg/g).

3.2. Characterization of CP

Fourier transform infrared (FT-IR) spectrum of CP shown in Fig. 1 was obtained using a PerkinElmer instrument and KBr pellets. As shown, the CP spectrum indicates the hydrogen bonds about 3,680 cm^{-1}, and symmetric and asymmetric stretching vibrations of the OH groups are

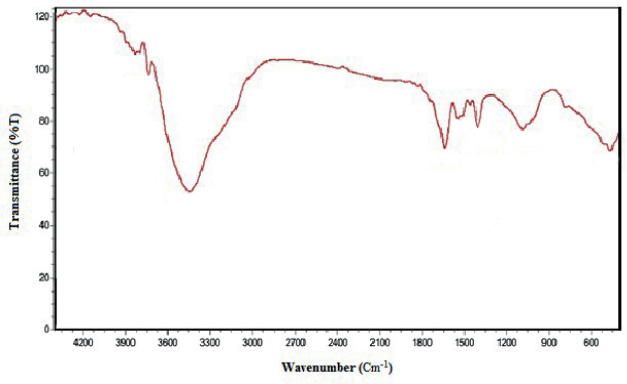

Fig. 1. FT-IR spectra of the CP.

around 3,450 cm^{-1}. The asymmetric stretching vibrations of the Si–O and Al–O bonds were at about 1,090 cm^{-1}. Bending vibrations of O–Si–O and O–Al–O peaks were located at 480 cm^{-1} [41].

The X-ray diffraction (XRD) analysis (Fig. 2) was performed with a Philips PW 1830 X-ray diffractometer with Cu Kα source (λ = 1.5418 Å) in a range of Bragg's angle (5°–70°) at room temperature. The results were compared with the database of the International Centre for Diffraction Data of Inorganic Substances and showed that the natural zeolite used in this experiment was clinoptilolite mineral [42].

3.3. Effect of contact time

In the current study, the experiments were done in different contact times (15, 30, 45, 60, 90, 120, 150 and 180 min) to study the effect of contact time on removal efficiency. As seen in Fig. 3, the results suggested that the removal efficiency increased with contact time and reached a maximum value at 120 min (equilibrium time).

3.4. Effect of pH on adsorption

In each adsorption process, pH is one of the most important parameters, which influences on the adsorbent surface properties as well as ionic forms of contaminant in the solution. In this study, for determining the effect of pH on the removal efficiency, experiments were performed in three states including acidic, neutral and alkaline in pH 4, 7 and 9, respectively. One of the reasons for choosing these values can be attributed to the pKa values of the considering compound in acidic, neutral and alkaline states. pKa was calculated based on the following equation:

$$\mathrm{pKa} = -\mathrm{Log}(Ka) \tag{13}$$

The following relationship is established between pH and pKa:

$$\mathrm{pH} - \mathrm{pKa} = \mathrm{Log}\frac{A^-}{HA} \tag{14}$$

While Ka is acid dissociation constant, [A^-] and [HA] are ionized and unionized concentration of chemical, respectively. Whenever pH is greater than pKa, the solubility of compound in water will be higher in amount, but if pH < pKa, depends on pKa, it will be in its none to semi-dissociated form. Therefore, choosing the accurate values of pH in which mentioned compound can be dissociated is very important. In neutral and alkaline states (pH ≥ 7), dexamethasone sodium phosphate (Fig. 4) has pKa equal to 6.4, but in acidic states due to the conversion of dexamethasone sodium phosphate to dexamethasone phosphoric acid (Fig. 5), the pKa1 and pKa2 values are 1.67 and 3.2, respectively. Therefore, the choice of pH values greater than 3.2 is suitable in acidic state.

The other reason for referring to the pH values can be attributed to the point of zero charge (pH_{PZC}) of CP. pH_{PZC} for a given mineral surface is the pH in which the surface has a net neutral charge. The pH_{PZC} of the used CP was about 9.

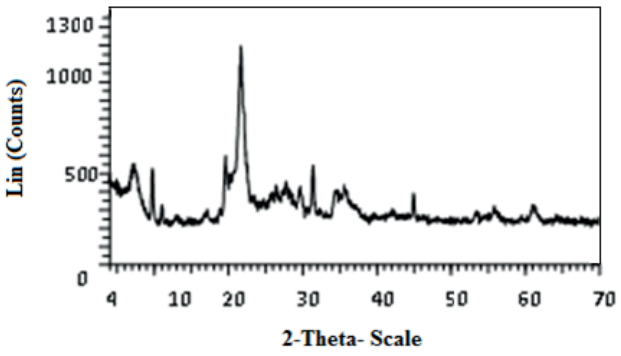

Fig. 2. XRD patterns of CP.

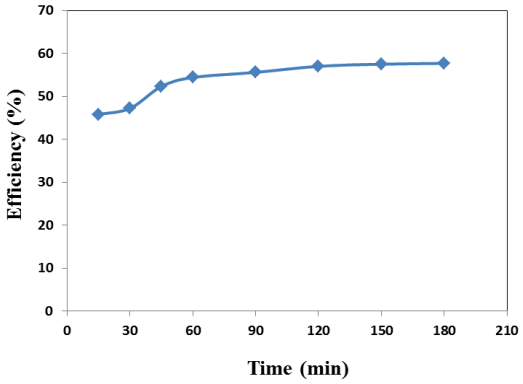

Fig. 3. Effect of contact time on removal efficiency (pH 4, dexamethasone concentration 5 ppm and 1 g CP).

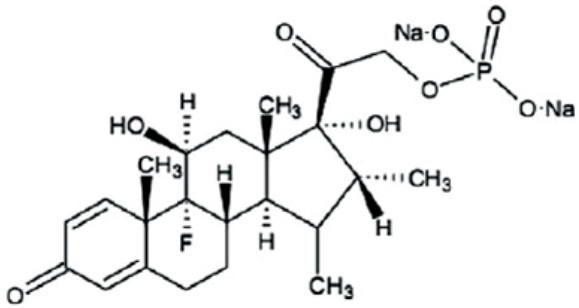

Fig. 4. Dexamethasone sodium phosphate.

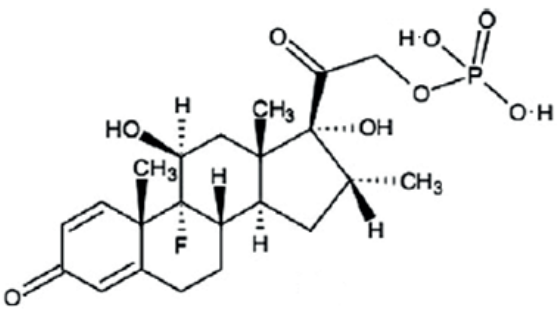

Fig. 5. Dexamethasone phosphoric acid.

When the pH values are smaller than pH_{PZC}, the charge of the CP is positive, and it is suitable for adsorption of negatively charged contaminants [43].

As indicated in Fig. 6, the removal efficiency of dexamethasone using CP was improved by decreasing the pH and maximum removal efficiency obtained in acidic condition (pH 4). There was a reverse correlation between the amount of pH and number of H^+ ions on the adsorbent surface. In acidic condition, when the pH is low and the number of H^+ ions on the adsorbent surface is high, so electrostatic attraction between positively charged adsorbent surface and negatively charged chemicals increases. In neutral and alkaline states (pH ≥ 7), the number of H^+ ions is low. In these cases, OH^- ions and contaminant anions compete together for placing on adsorbent surface, thus the removal efficiency decreases [44].

3.5. Effect of initial dexamethasone concentration on adsorption

In the current study, the experiments were done at different initial concentrations (5, 10, 20 and 40 mg/L) to determine the effect of initial dexamethasone concentration on removal efficiency. Fig. 7 represents that the removal efficiency is decreased by increasing the initial concentration, but adsorption capacity is increased [7]. There was a reverse correlation between initial concentration and removal efficiency. When initial concentration is low, the ratio of available surface to the initial concentration is high; as a result, the removal efficiency is high, too. However, since the concentration increases, this ratio decreases; hence, the removal efficiency decreases, too [39,45].

3.6. Effect of adsorbent dose on adsorption

Adsorbent dose is an important parameter, which affects the removal efficiency. In order to determine this effect, experiments were carried out using different dosage of adsorbent (0.2, 0.6 and 1 g/100 mL). As observed in Fig. 8, the results indicated that when adsorbent dose enhances, the removal efficiency increases but adsorption capacity decreases [46,47]. This phenomenon can be explained that the number of exchangeable sites and surface area are increased when the adsorbent dose is risen [48].

3.7. Scanning electron microscopy

The surface morphology of the adsorbent before and after the adsorption process was conducted with the help of scanning electron microscopy (SEM). As represented in Fig. 9(a), an electron micrograph of CP before adsorption process demonstrated that its surface is irregular and porous. This means that there was a good probability for dexamethasone to be adsorbed into these pores. It is evident from the SEM of dexamethasone loaded CP (Fig. 9(b)) that its surface has become shiny due to the deposition of dexamethasone ions after adsorption [39].

3.8. The linear and non-linear regression analysis

In this study, the linear and non-linear regression analysis was used to determine the best-fit isotherm. Four isotherms

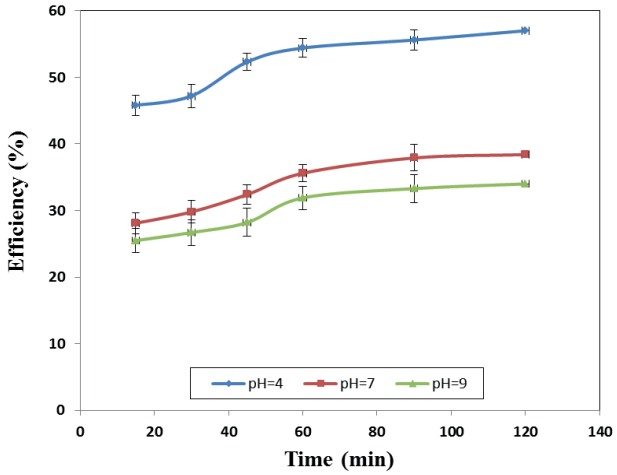

Fig. 6. Effect of pH on dexamethasone removal (dexamethasone concentration 5 ppm and 1 g CP).

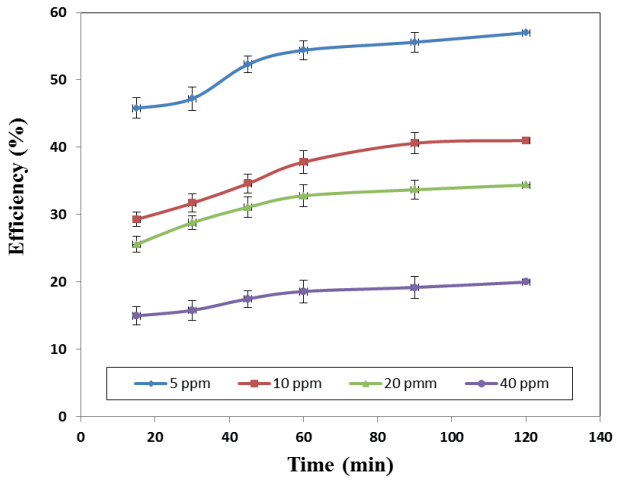

Fig. 7. Effect of initial concentration on dexamethasone removal (pH 4 and 1 g CP).

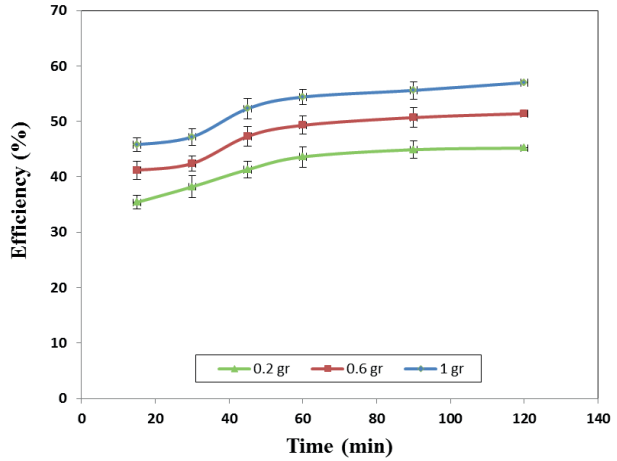

Fig. 8. Effect of adsorbent dose on dexamethasone removal (pH 4 and dexamethasone concentration 5 ppm).

including Freundlich, Langmuir, Temkin and Sips were used to describe sorption equilibrium data. The isotherm parameters, coefficients of determination and the values of error function from linear and non-linear method were listed in Tables 1 and 2.

As seen in Tables 1 and 2, the Langmuir model is better than other models to represent the equilibrium experimental data [39,49] in both linear and non-linear regression methods. In linear regression, the values of coefficients of determination are high [34,50]. The values of R_L for adsorption of dexamethasone on CP in different concentrations were reported in Table 3. As observed in Table 3, the values of *RL* are between 0 and 1; it means that this process is feasible and favorable. Non-linear regression of isotherm models is compared and shown in Fig. 10. As demonstrated in Fig. 10, Sips model is the poorest fit according to values of error functions.

4. Conclusions

In the present study, CP as a natural adsorbent was used to remove the dexamethasone from aqueous solutions. The effects of some parameters on removal efficiency were

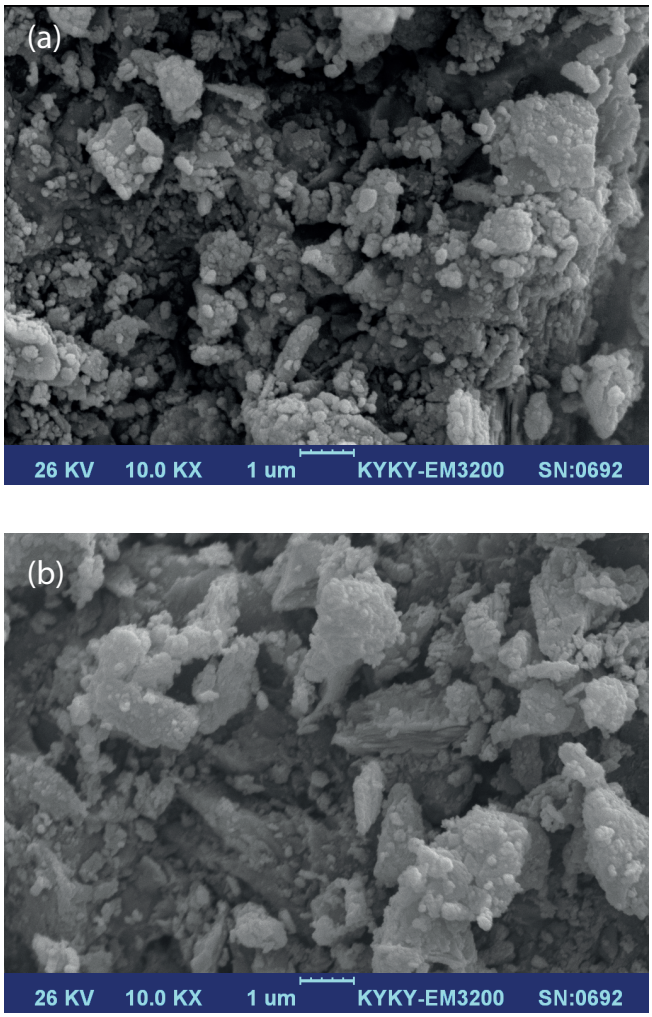

Fig. 9. SEM photographs of CP (a) and dexamethasone-loaded CP (b).

Table 1
Isotherm parameters for dexamethasone adsorption onto CP from linear method (pH = 4 and adsorbent dose = 1 g)

Freundlich	n	k_F	R^2
	2.463	0.105	0.959
Langmuir	q_m	k_L	R^2
	0.477	0.165	0.99
Temkin	A_T	b_T	R^2
	1.706	24,530.41	0.957
Sips	a_S	β_S	R^2
	14.526	0.404	0.96

Table 2
Isotherm parameters for dexamethasone adsorption onto CP from non-linear method (pH = 4 and adsorbent dose = 1 g)

Freundlich	n	k_F	SSE	R^2
	2.706	0.116	0.00268	0.937
Langmuir	q_m	k_L	SSE	R^2
	0.483	0.158	0.00152	0.964
Temkin	A_T	b_T	SSE	R^2
	1.736	24,485	0.00182	0.957
Sips	a_S	β_S	SSE	R^2
	5.163	0.535	0.0358	0.162

Table 3
R_L for different concentrations at optimal conditions (pH = 4 and adsorbent dose = 1 g)

Linear		Non-linear	
C_i (ppm)	R_L	C_i (ppm)	R_L
5	0.548	5	0.558
10	0.377	10	0.387
20	0.232	20	0.24
40	0.131	40	0.136

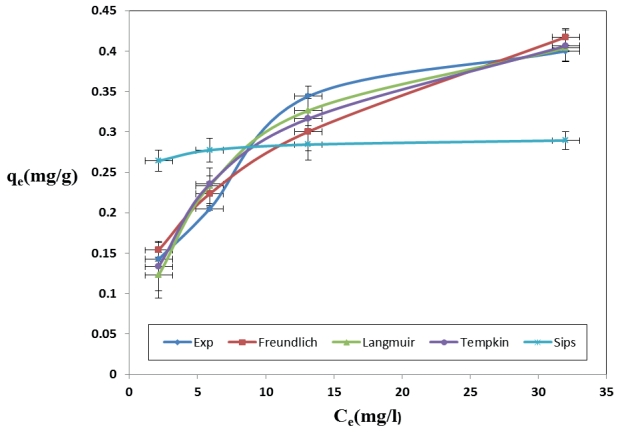

Fig. 10. The experimental points and non-linear fitted curves (pH 4 and 1 g CP).

investigated. Results showed that the maximum efficiency (57%) was found in pH 4 and the removal efficiency increased when the adsorbent dosage raised or initial concentration reduced. Values of coefficient of determination and least sum squares of difference showed that the performance of Langmuir model was better than other models and linear regression was better than non-linear regression to represent the equilibrium experimental data.

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