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ORIGINAL PAPER

Removal of dexamethasone from aqueous solutions using modified clinoptilolite zeolite (equilibrium and kinetic)

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Abstract The aim of this study was to remove a known pharmaceutics, dexamethasone, from an aqueous solution using clinoptilolite zeolite (CP). CP is a natural, versatile and inexpensive mineral, which has been investigated and applied in the last few decades. Herein, the experiments were carried out in the common conditions of a batch system in room temperature, and the effects of some parameters such as pH of the solution, initial concentration of dexamethasone, adsorbent dose and contact time were studied. Kinetic and isotherm of adsorption processes of dexamethasone on CP were surveyed in the current study. Results revealed that the maximum efficiency (78 %) occurred in pH = 4. The adsorption process followed a pseudo-second-order kinetic model as well as Freundlich and Sips isotherm models fitted with the experimental data well.

Keywords Dexamethasone · Clinoptilolite zeolite · Removal efficiency · Isotherm and kinetic model

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Introduction

Glucocorticoids are one of the most important groups of pharmaceuticals, which are widely incorporated in the treatment of diseases in humans and animals (Reid 2000; Schäcke et al. 2002). Nowadays, overuse of different pharmaceutics, especially glucocorticoids in hospitals and medical centers, and unfortunately no use of some effective procedures in the treatment of effluents lead to an increase in the concentration of hazardous chemicals in wastewaters (Sui et al. 2010; Herrero et al. 2012). One of the most commonly used glucocorticoids is dexamethasone (Arsand et al. 2013; Herrero et al. 2012). The structures of dexamethasone are presented in Fig. 1. This structure is one of the chemicals which cannot be efficiently removed from hospital wastewater using conventional on-site treatment methods (Schäcke et al. 2002; Sim et al. 2010). Untreated effluents infiltrate into the underground water and finally enter to living organisms bodies (Jafari et al. 2011). Although dexamethasone has extensive effects in the treatment of various diseases, it can cause many adverse effects. This compound leads to some serious health risks such as weakening the immune system and also amplifies the risk of suffering from infectious diseases. Recently, due to the adverse effects that may cause some harsh irreversible problems, the researchers of environmental issues have suggested a variety of techniques for the removal of pharmaceuticals from wastewater (Kummerer 2001; Heberer 2002).

Among the common processes for purification, the removals of contaminants through using the adsorption technology on natural materials have gained much interest during recent decades (Elwakeel and Guibal, 2015a, b; Sharma et al. 2011; Amuda and Ibrahim, 2006). In the adsorption mechanism, attractive forces play the main role

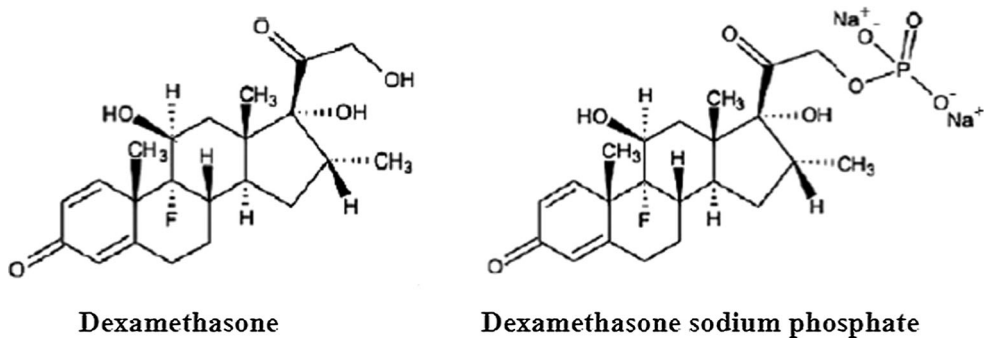

Fig. 1 Dexamethasone structures

between adsorbent and adsorbate functional groups. Intermolecular forces depend on different factors such as nature of adsorbent, adsorbate and contact area.

Natural adsorbents such as agricultural wastes and natural zeolites have been considered as high efficiency and environmental friendly adsorbents (Jaishankar et al. 2014). For instance, a number of studies have been investigated, such as removal of chromium (VI) using sunflower waste (Jain et al. 2009a), adsorption of metal ions by olive waste (Fiol et al. 2006), removal of copper by pine cone shell (Blazquez et al. 2012), Cu(II) onto coconut shell (Acheampong et al. 2013), cadmium (II) onto loquat leaves and canola residuals (Al-Dujaili et al. 2012; Amouei et al. 2014), thorium by brown algae (Keshtkar and Hassani 2014), removal of Cu(II) and Pb(II) by coffee grains (Cerino Cordova et al. 2013).

Natural zeolites which mainly consist of oxygen, silicon and aluminum are abundant and have different kinds. The chemical structure of zeolite consists of AlO_4^{5-} and SiO_4^{4-} units which are linked to each other by sharing oxygen atoms (Wibowo et al. 2011). This unique arrangement provides a special porous structure that has total negative charge. Zeolites have a number of characteristics such as dewatering, ion exchange capacity, low density and removal capability for organic and inorganic pollutants. These properties result in the use of zeolites for the removal of numerous contaminants from aqueous solutions such as cationic surfactants (Li 2007), basic dyes (Li et al. 2015), chromate (Ghiaci et al. 2004), Cr(VI) and As (V) (Yusof and Malek, 2009), cadmium (Vasylechko et al. 2003) and arsenic (Chutia et al. 2009; Malekpour et al. 2009).

Clinoptilolite is one of the most abundant zeolites and can be served in different applications such as aquaculture, agriculture, poultry, environments and medicine (Malekpour et al. 2009) due to cost-effectiveness in view point of industrial usages. The CP with the high selective affinity uniquely suited to various applications of wastewater treatment.

In this study, CP with the simplified formula of $(K_2, Na_2, Ca, Mg)_3\ Al_6\ Si_{30}\ O_{72}.\ 24H_2O$, specific surface area 43.91 cm^2/g, pore diameter 0.018 μm and pore volume 0.1717 cm^3/g was evaluated as a novel, inexpensive and efficient natural zeolite for removal of dexamethasone from aqueous solutions in different conditions.

Materials and methods

Preparation of adsorbent

In this study, the modified CP is used as natural adsorbent for the removal of dexamethasone from aqueous solutions. For preparation of the adsorbent, the materials were initially washed with distilled water and the dust was removed (Dianati Tilaki et al. 2014). Then, it was crushed into fine particles with an electric mill, and the American Standard Testing and Materials (ASTM) sieves were used finally, particles that were approximately below 500 microns were selected (Vasylechko et al. 2003). In the next step, for removing impurities from the zeolite surface and activation of the zeolite, the materials were washed with a sulfuric acid 2M solution (Maleki et al. 2015). In this stage, 3 g of zeolite were added to 100 ml sulfuric acid 2M solution mixed for 2 h on a shaker with 180 rpm. After 2 h, zeolite particles were filtered using Whatman membrane filter (0.45 microns) and washed several times with distilled water so that the pH effluent reached to 7. In the final step, the zeolite powder was placed in an oven (at 100 °Centigrade) for 12 h to remove moisture, and then, it was placed in the desiccators (Chutia et al. 2009).

Reagents

The stock solution of sodium phosphate dexamethasone (100 mg/l) was prepared by dissolving dexamethasone (4000 mg/l) in distilled water, and then, the desired concentrations were provided through diluting the stock solution.

Experimental plan

Experiments were done in the batch system in a laboratory scale and in room temperature (25 °C). The effects of several parameters such as pH solution (4, 7, 9), initial concentration of dexamethasone (5, 10, 20, 40 mg/l), adsorbent dose (0.1, 0.3, 0.5 g/50 ml) and contact time (15, 30, 45, 60, 90, 120 min) were investigated. The nitric acid and sodium hydroxide 2M solutions were used to adjust the pH of the solution. A shaker (by speed of 180 rpm) was used to mix the samples, and after the desired time lapsed, a centrifuge was used to separate the liquid phase from the solid one. After sampling from the liquid phase, the dexamethasone concentration was measured using UV spectrophotometer double beam, PG instrument model. The measurement was taken according to the standard methods of water and wastewater examinations (APHA et al. 2012). All experiments were repeated at least three times, and the relative error was about 2.5 %.

Results and discussion

Effect of pH on adsorption

In each adsorption process, the pH of the solution is one of the effective parameters owing to its direct influence on the adsorbent surface properties and ionic forms of contaminant in the solution. The type and ionic state of functional groups on the surface of the adsorbent and adsorbate are important factors that affect the dependence level of the adsorption process on pH. In the present study, for determining the effect of pH on adsorption efficiency, the adsorption process was performed in three conditions including acidic, neutral and alkaline in pH 4, 7 and 9, respectively. As shown in Fig. 2, the removal efficiency of dexamethasone through modified zeolite was increased by decreasing pH and the maximum removal efficiency was obtained in pH = 4.

There is a reverse correlation between the pH and number of H^+ ions on the adsorbent surface. In acidic condition in which the pH is low, the number of H^+ ions on the adsorbent surface is high, so electrostatic attraction increases between positively charged adsorbent surface and negatively charged dexamethasone ions. In neutral and alkaline conditions (pH $\geq$ 7), the number of H^+ ions is low. In these cases, OH^- ions and contaminant anions compete together for placing on adsorbent surface, so the removal efficiency decreases (Khalfaouei and Meniai 2012).

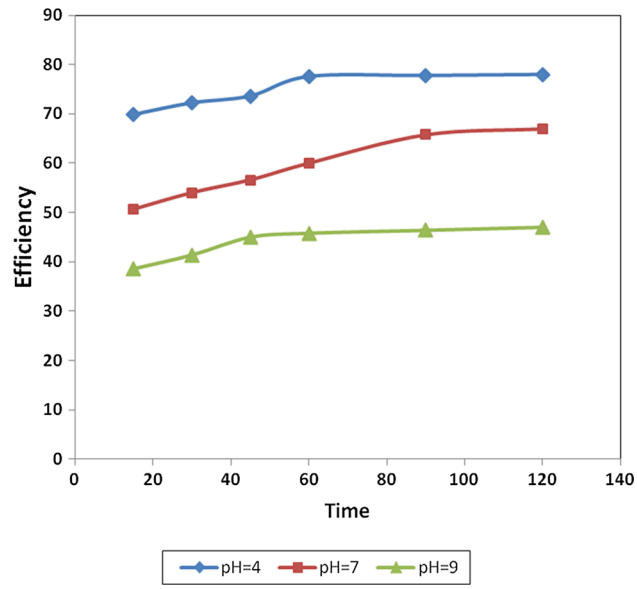

Fig. 2 Effect of pH on dexamethasone removal. Dexamethasone concentration = 5 mg/l and adsorbent dose = 0.5 g

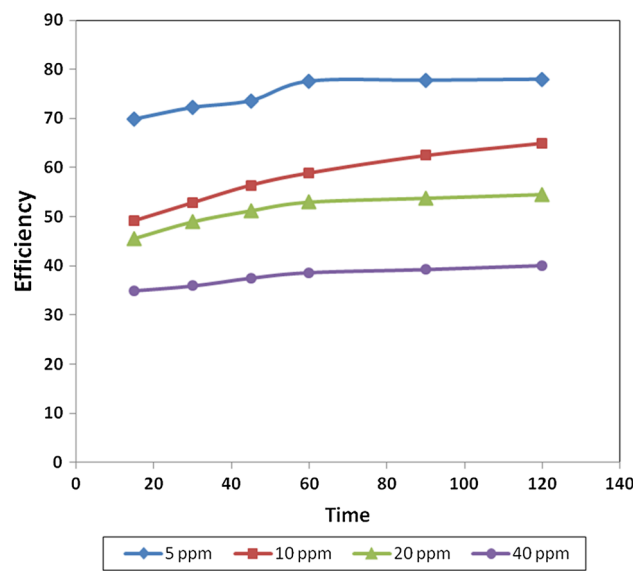

Fig. 3 Effect of initial concentration on dexamethasone removal. pH = 4 and adsorbent dose = 0.5 g

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. As shown in Fig. 3, by increasing the initial concentration, the removal efficiency was decreased, while the adsorption capacity was increased (Jain et al. 2009a). At low concentrations, the ratio of the available surface to the initial concentration is large; therefore, the removal efficiency is high. However, when the adsorbate concentration increases, this ratio reduces, so the removal efficiency decreases, too (Jain et al. 2009b; Jalali and Aboulghazi, 2013).

Effect of adsorbent dose on adsorption efficiency

In this study, the effect of adsorbent dose on removal efficiency was investigated through varying the adsorbent dose (0.1, 0.3 and 0.5 g/50 ml) in the aqueous solutions. Results in Fig. 4 demonstrate that when adsorbent dose increases, removal efficiency increases but adsorption capacity decreases (Bhaumik et al. 2011; Lian et al. 2013). The increase in removal efficiency can be explained as when the adsorbent dose is increased, the number of exchangeable sites and the amount of surface area are increased, too. The decrease in adsorption capacity may be owing to the overlapping of adsorption sites resulted from overcrowding of adsorbent particles (Garg et al. 2004).

Scanning electron microscopy (SEM)

The surface morphology of the adsorbent before and after the adsorption process was conducted with the help of SEM. As represented in Fig. 5a, an electron micrograph of native CP shows that its surface is irregular and porous, and there is a good probability for dexamethasone to be adsorbed into these pores. It is evident from the SEM of dexamethasone-loaded CP (Fig. 5b) that its surface has become shiny due to the deposition of dexamethasone ions after adsorption (Jain et al. 2009b).

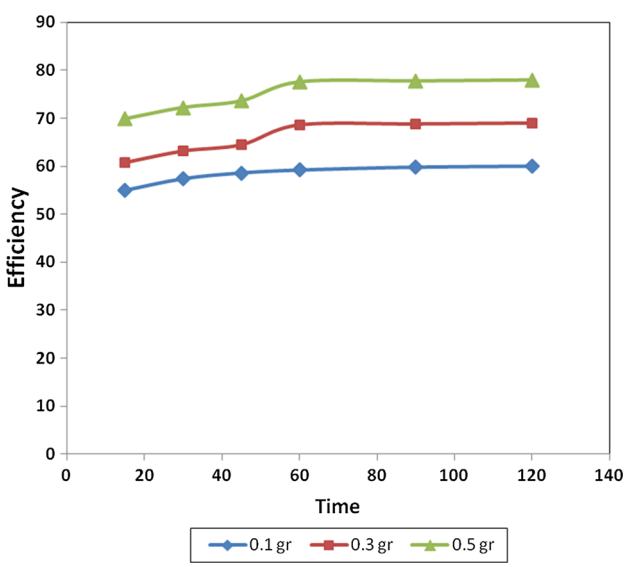

Fig. 4 Effect of adsorbent dose on dexamethasone removal. Dexamethasone concentration = 5 mg/l and pH = 4

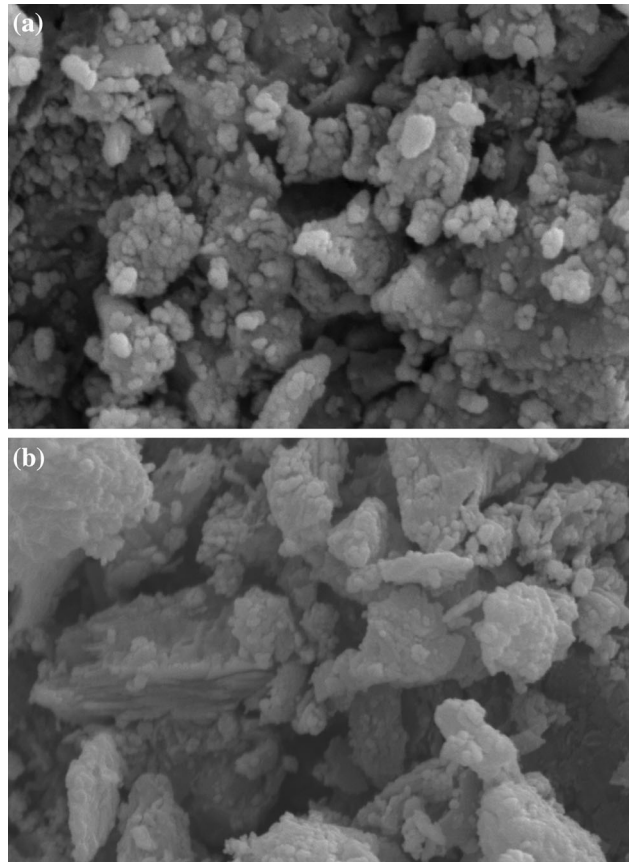

Fig. 5 SEM photographs of modified CP (**a**) and dexamethasone-loaded modified CP (**b**)

Sorption kinetics

The kinetic of adsorption demonstrates the rate of dexamethasone removal by the adsorbent, and this rate determines the equilibrium time. Kinetic models were used to characterize the mechanism of adsorption and specify the adsorbent performance. This model depends on different factors such as physical and chemical properties of the adsorbent and mass transfer process. In this study, the kinetic of the adsorption process was analyzed using pseudo-first-order and pseudo-second-order equations given below:

$$\ln(q_e - q_t) = \ln(q_e) - kt \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k} + \frac{t}{q_e} \quad (2)$$

As shown in Fig. 6, the correlation coefficient (R^2) in the pseudo-first-order model is relatively low; therefore,

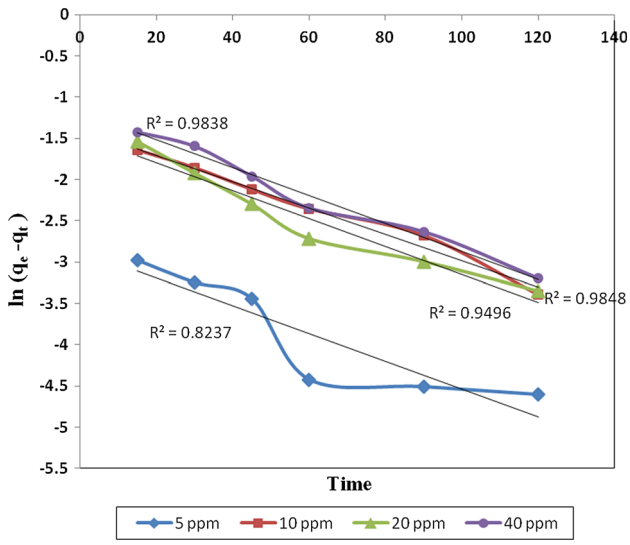

Fig. 6 Pseudo-first-order kinetic model

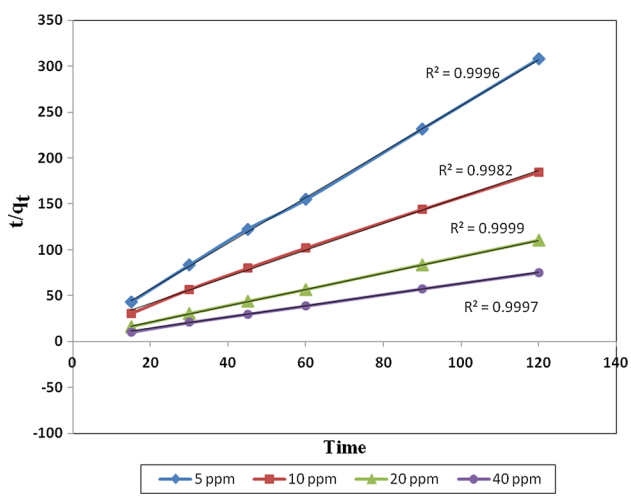

Fig. 7 Pseudo-second-order kinetic model

this model is inappropriate. Considering Fig. 7, it is obvious that the correlation coefficient is very high in the pseudo-second-order model; therefore, this model presents a suitable dexamethasone removal through CP zeolite.

In the adsorption process, there is a logic that the adsorbate removed from the solution is found in or on the adsorbent. Therefore, in this study, we can determine the retention of dexamethasone using modified zeolite with a simple mass balance as below:

$$q = \frac{V(C_i - C_{eq})}{M} \tag{3}$$

where q (mg/g) is dexamethasone retention by the adsorbent, V (L) is the volume of liquid phase, C_i and C_{eq} (mg/l) are the initial and equilibrium concentrations of the dexamethasone, respectively, and M (g) is the mass of the adsorbent.

Sorption isotherm

Adsorption isotherms express the relationship between adsorption capacity (q) and final concentration of adsorbate (C_{eq}) and provide important data for designing adsorption systems. In the present study, four isotherms including Freundlich, Langmuir, Temkin and Sips were used to describe sorption equilibrium data.

The Freundlich isotherm assumes that the adsorbent has a heterogeneous surface and the removal of contaminant ions occurs using multilayer adsorption. In this isotherm, the removal efficiency, because of having multilayer adsorption, rises with the increase in contaminant concentration (Jain et al. 2009a). The linearized Freundlich model is expressed as:

$$\ln(q_e) = \ln(k_f) + \frac{1}{n}\ln(C_e) \tag{4}$$

where q_e (mg/g) is adsorption capacity at equilibrium, and C_e (mg/L) is the equilibrium concentration of dexamethasone in the solution. All factors that affect the adsorption process are incorporated in k_f and n constants. Values of k_f and n were calculated from the intercept and slope of the plot of ln (q_e) versus ln (C_e) and are illustrated in Table 2.

The Langmuir model assumes that the adsorbent has a homogeneous surface and removal of contaminant ions occurs using monolayer adsorption and there is no interaction between adsorbed ions (Jain et al. 2009a). The linearized Langmuir model is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m k} + \frac{C_e}{q_m} \tag{5}$$

where q_e (mg/g) is adsorption capacity at equilibrium, q_m (mg/g) is the maximum adsorption capacity and C_e (mg/L) is the equilibrium concentration of dexamethasone in the solution, whereas k is the Langmuir constant. The values of q_m and k were calculated from the slope and intercept of the plot of C_e/q_e versus C_e and are reported in Table 2.

In the Langmuir isotherm, there is an essential characteristic that can be explained in terms of a dimensionless constant separation factor (R_L) defined as:

$$R_L = \left(\frac{1}{1 + kC_i}\right) \tag{6}$$

where C_i (mg/L) is the initial concentration of dexamethasone, and k is the Langmuir constant. R_L is a positive number and determines the feasibility of the adsorption process (Jain et al. 2009a). For a favorable adsorption in

Table 1 R_L for different concentrations at optimal conditions (pH = 4, 0.5 g zeolite)

C_i (mg/l)	R_L
5	0.552
10	0.381
20	0.235
40	0.133

Table 2 Freundlich, Langmuir, Temkin and Sips parameters at optimal conditions (pH = 4, 0.5 g zeolite)

Freundlich model	
k_f	0.372
n	2.15
R^2	0.996
Langmuir model	
q_m	1.976
k	0.162
R^2	0.982
Tempkin model	
A_T	1.96
b_T	6272.33
R^2	0.966
Sips model	
k_S	1.54
a_S	4.128
β_S	0.465
R^2	0.996

each initial concentration of the contaminant, the R_L values must be between 0 and 1 (Jain et al. 2009b). The R_L values for adsorption of dexamethasone on modified CP in different concentrations are represented in Table 1.

The Temkin isotherm model assumes that the heat of adsorption of all molecules decreases linearly rather than logarithmically with coverage because of the interactions between the adsorbent and adsorbate and the adsorption is characterized by a uniform distribution of binding energies (Kundu and Gupta, 2006). The linearized form of the Temkin isotherm can be expressed by the following equation:

$$q_e = \frac{RT}{b_T}\ln(A_T) + \frac{RT}{b_T}\ln(C_e) \quad (7)$$

where 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 values of A_T and b_T were calculated from the slope and intercept of the plot of q_e versus ln C_e and are reported in Table 2.

The Sips isotherm model is a combination of the Langmuir and Freundlich models. When the adsorbate concentration is low, it follows the Freundlich model, but at high adsorbate concentrations, it leads to the Langmuir model and predicts a monolayer adsorption. The linearized form of the Sips isotherm can be represented by the following equation:

$$\ln\frac{k_S}{q_e} = -\beta_S \ln C_e + \ln a_S \quad (8)$$

where 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 of adsorbate affect the equation parameters (Foo and Hameed, 2010). The values of a_S and β_S were calculated from the intercept and slope of the plot of $\ln(\frac{k_S}{q_e})$ versus ln C_e and are reported in Table 2.

Conclusion

Due to resistant structure of dexamethasone against the biological degradation and its low concentration in hospital wastewater, the decomposition of this compound by conventional wastewater treatment plants is very difficult. In the current study, the use of modified CP as a natural adsorbent for the purpose of removing dexamethasone from aqueous solutions was investigated. The high removal efficiency, natural and inexpensive, not production of sludge and other harmful substances for the environment (environmental friendly), are the advantages of this adsorbent. The removal efficiency depends on the pH solution, initial concentration of dexamethasone, adsorbent dose and contact time. The experimental data were fitted with the Freundlich and Sips models well. Maximum removal of dexamethasone was occurred in pH = 4 with 0.5 g CP.

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