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Bentonite for ciprofloxacin removal from aqueous solution

Nevim Genç, Esra Can Dogan and Meral Yurtsever

ABSTRACT

Ciprofloxacin hydrochloride (CIP) is the second generation of fluoroquinolone antibiotics whose residues are found in wastewater and surface water. CIP has high aqueous solubility under different pH conditions and high stability in the soil system. In this study, bentonite was used as a potential sorbent for the removal of CIP from aqueous solutions using batch experiments. The effects of various parameters such as contact time, pH, adsorbent dosage, agitation speed, ionic strength and initial concentration of CIP in aqueous solution on the adsorption capacity were investigated. The optimum contact time, pH, agitation speed and adsorbent dosage were found to be 30 min, 4.5 pH, 150 rpm and 2.5 g L^{-1}, respectively. When the ionic strength was increased from 5 to 50 mM, the adsorption of CIP decreased from 97.8 to 93.4%. The isotherm adsorption data fitted well with the Langmuir model, K_l and q_e were found to be 0.27 L mg^{-1} and 147.06 mg g^{-1}, and the data fitted well with the pseudo-second order kinetics, whereby k was found to be 2.19 g mg^{-1} h^{-1}.

Key words | adsorption, bentonite, CIP removal

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INTRODUCTION

Pharmaceuticals are a class of chemicals used for diagnosis, treatment (cure/mitigation), alteration, or prevention of disease, and maintaining the health condition or the structure/function of the human body. Most pharmaceutical compounds are introduced into water bodies by domestic sewage or industrial wastewater, hospitals and health centers. Usually, these drugs are found in the environment in the μg L^{-1} or ng L^{-1} concentration ranges (Ribeiro *et al.* 2011). There is little information about the extent of environmental occurrence, transportation, ultimate fate, effects and removal of pharmaceuticals. A significant reduction in the aqueous phase was observed for most pharmaceuticals during their treatment through wastewater treatment plants. The processes which have been proposed to be responsible for this reduction are sorption and biodegradation (Githinji *et al.* 2011).

Among the pharmaceuticals, antibiotics are among the most widely used. If the antibiotics are not degraded or eliminated during sewage treatment, they will reach surface water, groundwater and, potentially, drinking water. Ciprofloxacin hydrochloride (CIP), one of the commonly used fluoroquinolones, was found in wastewater and surface water with concentrations of several hundred ng L^{-1} (Wang *et al.* 2011). CIP has been reported in concentrations between 0.7 and 124.5 μg L^{-1} in hospital effluent (Githinji *et al.* 2011). CIP can adsorb on sewage sludge with concentrations up to 2.42 mg kg^{-1} and accumulate in soil after the application of fertilizers which are made from sewage sludge containing CIP (Li *et al.* 2011). Even at low concentrations, CIP could still be toxic to some microorganisms. Thus, from a risk assessment point of view, CIP might be considered as an environmental hazard (Wu *et al.* 2010).

Both adsorption and photodegradation strongly influence CIP fate in aquatic systems, although it appears that the dominant mechanism depends upon the ambient particulate organic carbon level (Cardoza *et al.* 2005). Amphoteric pharmaceuticals are released to the environment within treated wastewater and medicated aquaculture feed, and also through land disposal of livestock wastes and municipal biosolids. These wastes are rich in dissolved organic carbon, which may bind and potentially enhance pharmaceutical transport in the environment (Carmosini & Lee 2009).

Although some antibiotics were found to be eliminated to some extent by the wastewater treatment process, the removal routes (biodegradation, adsorption, volatilization or hydrolysis) are still not very clear. Li and Zhang found

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that biodegradation and adsorption were the major removal processes for the target antibiotics, where volatilization and hydrolysis were negligible (Li & Zhang 2010). In freshwater and saline sewage system, CIP removal efficiencies were 90.8 and 52.8%, respectively. The overall percent difference in the effluent and influent concentrations of CIP, sulfamethoxazole, tetracycline, and trimethoprim antibiotics changes at secondary removal processes and ranges from 33 to 97% (Batt *et al.* 2007).

Values for CIP's acid dissociation constants pK_{a1} and pK_{a2} are 6.1 and 8.7, respectively. The cationic form CIP^{+} predominates due to protonation of the amine group in the piperazine moiety when the solution pH is below 6.1. When the solution pH is above 8.7, the anionic form CIP^{-} prevails due to loss of a proton from the carboxylic group. When solution pH is between 6.1 and 8.7, the zwitterionic form CIP^{0} resulting from the charge balance of the two groups mentioned above is the dominant species (Wu *et al.* 2010). The molecular structure of CIP and its ionic forms as a function of pH are shown in Figure 1.

CIP has a molecular weight of 331.4 g mol^{-1} (Githinji *et al.* 2011). Important physicochemical properties of CIP are water solubility of 11,480 mg L^{-1} and log K_{ow} of 0.28 (Wu *et al.* 2009). The octanol–water partition coefficients (K_{ow}) can be utilized to assess the hydrophobic adsorption for uncharged molecules (Golet *et al.* 2003). In this way, uncharged antibiotics with $pK_{ow} < 2.5$ are considered to have low adsorption potential (Rogers 1996). Considering their zwitterionic characteristics, it could be concluded that the adsorption of fluoroquinolones on activated sludge was mainly affected by the electrostatic force rather than hydrophobic interaction (Golet *et al.* 2003).

Up to now, several reports have been published related to the adsorption of CIP to natural materials or components of natural materials (activated carbon (Carabineiro *et al.* 2012); activated charcoal and talc (Ibezim *et al.* 1999); montmorillonite (Wu *et al.* 2010; Wu *et al.* 2012); soil (Carrasquillo *et al.* 2008; Vasudevan *et al.* 2009; Conkle *et al.* 2010); 2:1 dioctahedral clay minerals (Wang *et al.* 2011); kaolinite (Li *et al.* 2011); modified coal fly ash (Zhang *et al.* 2011); aerobically digested biosolid (Wu *et al.* 2009); sawdust (Bajpai *et al.* 2012); magnetite (Rakshit *et al.* 2013)).

In adsorption technology, inorganic adsorbents are often utilized since they offer advantages due to their stability compared with the radioactive and thermal treatments which are necessary to induce the complete degradation of adsorbates, and therefore the regeneration of exhausted adsorbents is possible (Martucci *et al.* 2012).

Adsorption behavior of pharmaceuticals in water is controlled by adsorbent properties, pharmaceutical properties (e.g., water solubility, hydrophobicity, and acid/base properties), and water characteristics (e.g., pH, ionic strength, cations, anions, and natural organic matter) (Bui & Choi 2010). Cation exchange capacity was considered as the key soil factor influencing the extent of CIP adsorption at pH values between 3 and 8. However, the conclusion of the study performed by Wu *et al.* (2010) was based on the fact that CIP exists in cationic form in acidic solution, in which CIP adsorption was high. It is expected that the ionization behavior significantly influences CIP sorption to adsorbent components (Gu & Karthikeyan 2005).

The main aim of this study was to evaluate the efficiency of bentonite in removal of CIP from aqueous solutions by the adsorption process. The adsorption mechanism was proposed according to the results of the effect of operating variables, the adsorption kinetics and the adsorption isotherm.

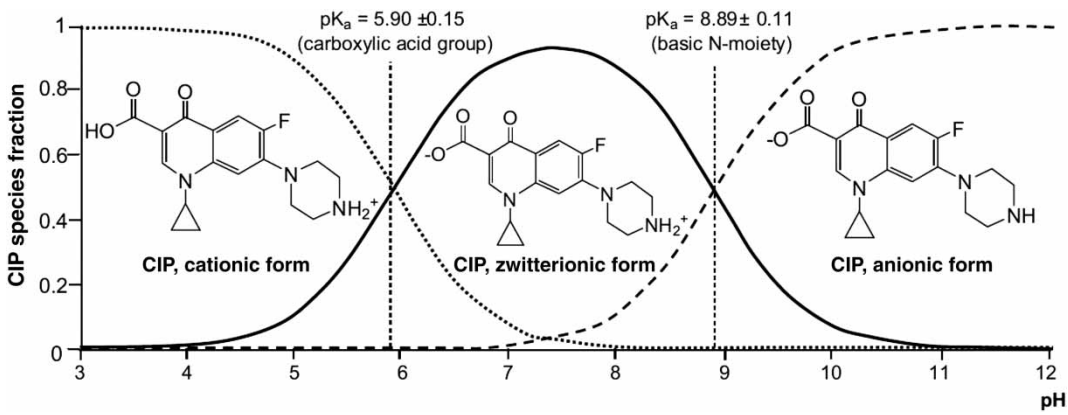


Figure 1 | Molecular structure of CIP and its ionic forms as a function of pH, pK_a values (Carabineiro *et al.* 2012).

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MATERIALS AND METHODS

Materials

The bentonite that has been used was obtained from Çankırı, Turkey. Its particle size is less than 0.6 mm. CIP with a purity higher than 99% was obtained from the Sanovel pharmaceutical company of Turkey. Limit of fluoroquinolonic acid is less than 0.2% (w/w). Particle size distribution on 20 ASTM is 0.24%.

Batch ciprofloxacin hydrochloride adsorption experiments

The adsorption experiments were performed in a wide variety of conditions including different pH, bentonite dosages, agitation periods, initial CIP concentrations, and ionic strength. An IKA model shaker was used in all adsorption experiments. For all adsorption experiments, 0.125 g bentonite was dispersed in 50 mL CIP solution in a 100 mL flask and the solutions were shaken at 150 rpm for 30 min. The initial pH values of the CIP solutions (about pH = 4.5) were not adjusted. The initial concentration was 500 mg L^{-1} for kinetic studies and 50–500 mg L^{-1} for adsorption isotherm. The equilibrium time for kinetic studies was 5, 10, 15, 20, 30, 45, 60, 150, and 210 min. For the pH adsorption edge experiment, the pH value was varied from 2 to 8. pH adjustments were made by using 1 M HCl or 1 M NaOH. The effect of ionic strength on the CIP adsorption was determined using inert electrolyte KCl solutions (0–50 mM). For the effect of bentonite dosage on the CIP adsorption, dosage was varied from 2.5 to 7 g L^{-1}; for the effects of agitation speed, rpm was varied from 100 to 300. After mixing, all solutions were filtered through 0.45 μm mesh size filters.

Analysis

The concentrations of CIP in the residual solutions were analyzed by means of a UV spectrometer (Hach-Lange DR 5000). The wavelength used to analyze the concentrations of the CIP was 340 nm. The calibration curve was established with 10 standards between 5 and 100 mg L^{-1} with the coefficient of determination of 0.9932. The adsorption capacities were calculated according to a mass balance of CIP in the solutions and were represented in units of miligrams of CIP per gram of adsorbent. The adsorption capacities at equilibrium were calculated according to Equation (1):

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

where q_e and C_e are the CIP amount adsorbed (mg g^{-1}) and the residual concentration (mg L^{-1}) at equilibrium, respectively; C_0 is the initial concentration of CIP (mg L^{-1}); V and m are the volume of CIP solution (L) and the mass of adsorbent used (g), respectively.

In order to compare the applicability of both the Langmuir and Freundlich models quantitatively, a data analysis was carried out using correlation analysis by utilizing least square method, and the average relative standard error (ARSE) is calculated by Equation (2) (Zhang *et al.* 2011):

$$\mathrm{ARSE} = 100 \times \sqrt{\frac{\sum_{i=1}^{n} \left[\left(q_{e,exp} - q_{e,cal}\right)/q_{e,exp}\right]^2}{(n-1)}} \quad (2)$$

Total organic carbon (TOC) was measured using a procedure described in ASTM D4129-98 (2000) and pH adjustments were performed in a Testo pH meter. A Jeol model JSM-6060LV scanning electron microscope (SEM) was used to take micrographs of the raw bentonite and CIP-adsorbed bentonite. SEM photographs were taken at different magnifications (in the range of × 400–5000).

RESULTS AND DISCUSSION

First of all, it was observed that CIP was adsorbed on bentonite. The surface morphology of natural bentonite is given in Figure 2. As can be seen from Figure 2, the raw bentonite has a flaky and porous structure.

In Figure 3, TOC percentage removal was plotted against time, and it was observed that TOC removal of 65.4% at initial 5 min had increased to 96% at 10th minute.

Effect of contact time

Figure 4(a) shows the effect of contact time on the adsorption of CIP for 500 mg L^{-1} initial concentration in solution. It was clear from Figure 4(a) that the adsorption was basically fast in the first 5 min and up to 30 min. The amount of CIP adsorbed was 91.2, 98.3, 98.7 mg g^{-1} at 5th, 30th, 210th minutes respectively (Figure 4(a)). It was observed from contact time curves that the equilibrium time was 30 min. This is the reason why the optimum

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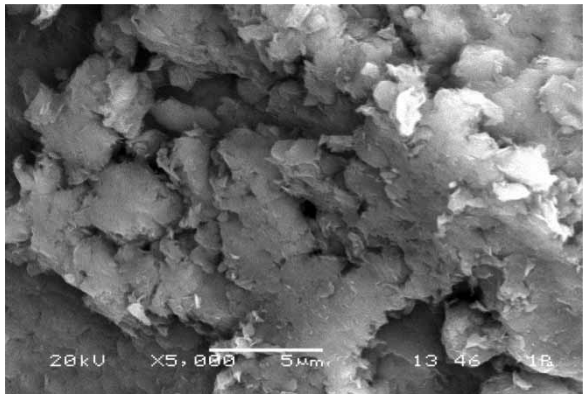


Figure 2 | The SEM micrograph of natural bentonite at mag. × 5,000.

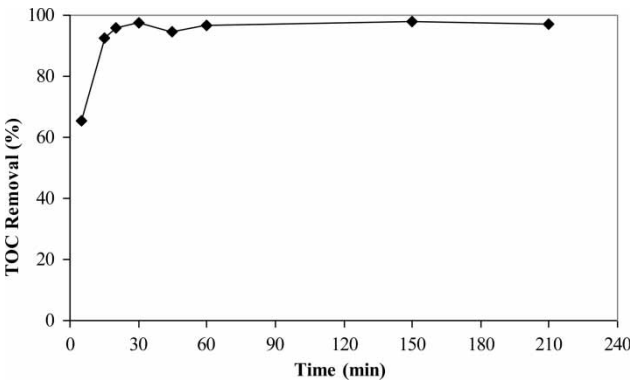


Figure 3 | The variation of TOC removal as a function of time.

contact time was considered to be 30 min in all the experiments.

As can be seen from Figure 4(a), the adsorption was rapid in the first 30 min. However, at some point in time, when the amount of CIP being adsorbed onto the adsorbent was equal to the amount of CIP being desorbed from the adsorbent, the adsorption process reached a dynamic equilibrium and the adsorption amount remained approximately constant, and thereafter desorption of CIP was observed. Figure 5 shows the absorbance data versus the wavelengths for different contact times. Wavelength scanning of CIP solutions showed that prolonged contact times such as 60 and 150 min resulted in desorption of small amounts of adsorbed CIP (see Figure 5). This is the reason why the optimum contact time was 30 min.

Effect of pH

The major mechanism of CIP adsorption was the cation exchange under ambient pH conditions. Solution pH had strong influence on the amount and the species of CIP adsorbed. Both cationic and zwitterionic forms of CIP could be adsorbed significantly. At high pH complexation with the interlayer, cation exchange may become the dominant mechanism for CIP uptake (Wu *et al.* 2010). When solution pH was above its pK_{a2} (8.7), adsorption of CIP greatly reduced due to the net repulsion between the negatively charged adsorbate surfaces and the CIP anion (Wang *et al.* 2010). The interactions between CIP and kaolinite experimentally confirmed that cation exchange was the dominant mechanism of CIP adsorption on kaolinite (Li *et al.* 2011).

In this study, at an initial CIP concentration of 500 mg L^{-1}, the amount of CIP adsorption reduced from 99 mg g^{-1} at a pH value of 2–4.5 to 81 mg g^{-1} at a pH value of 7.5 (Figure 4(b)).

During the course of this study, the sorption process of Enrofloxacin on montmorillonite was also investigated. The results showed that the sorption process was initiated by the interaction of hydrated protons on montmorillonite surfaces with diverse moieties of Enrofloxacin molecules, depending on the pH value. The sorption mechanisms of Enrofloxacin were mainly cation exchange at acidic condition, charge neutralization at neutral condition, and proton transfer at alkaline condition (Yan *et al.* 2013). Mechanisms of CIP removal by nano-sized magnetite were investigated by Rakshit *et al.* (2013). The observed bell-shaped sorption envelope for CIP could be explained by the combined pH dependencies of the CIP speciation and the magnetite surface charge. At acidic pH values both CIP and magnetite were positively charged, limiting the CIP ability to interact with the magnetite surface. As the pH increased from 4.0 to 6.0, proportions of neutral CIP increased, making the interaction with the positively charged magnetite more feasible. Above pH value of 6.5, both CIP and magnetite became more negatively charged with the increasing pH, which resulted in a decreased adsorption. There was also a similar trend in the adsorption of CIP on bentonite.

Effects of adsorbent dosage

In general, increase in adsorbent dosage provides better removal efficiency. The effect of bentonite dosage on CIP removal was tested by using different amounts of bentonite in the range of 2.5–7 g L^{-1}. Figure 4(c) shows the effect of dosage on the q_e values. As can be seen from the figure, better adsorption efficiencies were obtained at 2.5 g L^{-1}.

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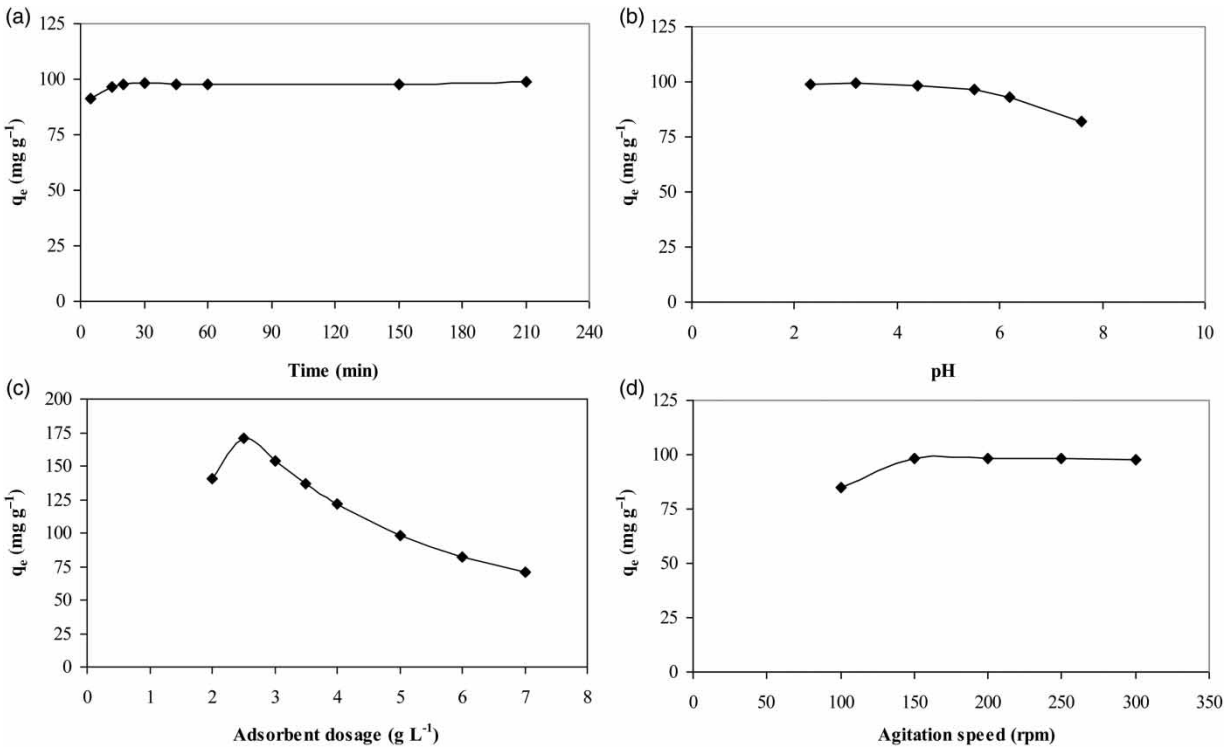


Figure 4 | The variation of q_e as a function of contact time (a), pH (b), adsorbent dosage (c) and agitation speed (d).

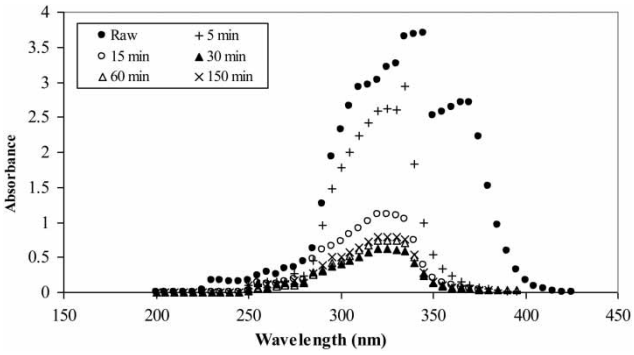


Figure 5 | Scanning wavelength versus different contact time.

Effects of agitation speed

The equilibrium adsorption capacity is presented in Figure 4(d) for different agitation speeds. Higher removal efficiencies were obtained with the increase in agitation speed. The q_e value increased from 84.64 to 98.52 mg g^{-1} by increasing the agitation speed from 100 to 150 rpm; 150 rpm was determined as the optimum agitation speed for the adsorption.

Effect of ionic strength

Possible mechanisms of CIP-like compounds' adsorption on minerals were identified as cation exchange, cation bridging and surface complexation (Vasudevan *et al.* 2009; Bui & Choi 2010; Wang *et al.* 2010).

Figure 6 shows the percentage of CIP adsorption on bentonite at different ionic strengths (0–50 mM). As the ionic strength was increased from 5 to 50 mM, the percentage of CIP adsorbed decreased from 97.8 to 93.4%. There is

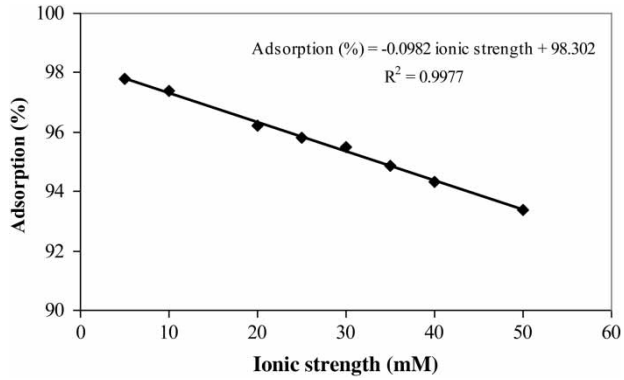


Figure 6 | Variation of CIP removal as a function of ionic strength.

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competition between CIP, for sorption sites, and a larger quantity of K^+, for adsorption sites, on bentonite due to the cationic form of CIP when solution pH value is below 6.1. The adsorption of pharmaceuticals is also based on their pK_a value. For example, an increase of ionic strength lowered the adsorption of uncharged sulfamethazine to montmorillonite but increased the adsorption of anionic sulfamethazine (Gao & Pedersen 2005).

Adsorption kinetics

The kinetics data of CIP adsorption on bentonite were fitted to the pseudo-second order model (Equation (3)). Equation (3) can be converted into the linear form as in Equation (4):

$$q_t = \frac{kq_e^2 t}{1 + kq_e t} \tag{3}$$

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \tag{4}$$

where k (g mg^{-1} h^{-1}) is the rate constant of adsorption, q_e (mg g^{-1}) is the amount of CIP adsorbed at equilibrium, q_t (mg g^{-1}) is the amount of CIP adsorbed on the surface of the adsorbent at a time, t, and kq_e^2 is the initial rate of adsorption (mg g^{-1} h^{-1}). The initial rate of 21.428 mg g^{-1} h^{-1} was obtained when the data were fitted to Equation (4) (Figure 7). The initial rate obtained was slower than the calculated values of 73,232 and 110,000 mg g^{-1} h^{-1} obtained from CIP adsorption on montmorillonite by Wu *et al.* (2010) and Wang *et al.* (2011), respectively, whereas it was much faster than the adsorption on rectorite (250 mg g^{-1} h^{-1}), on illite (110 mg g^{-1} h^{-1}) (Wang *et al.* 2011), and on kaolinite (552.4 mg g^{-1} h^{-1}) (Li *et al.* 2011).

The q_e value obtained was 99 mg g^{-1} compared with 725 mg g^{-1} for adsorption on montmorillonite, rectorite and illite (Wang *et al.* 2011). In this study, the rate constant was obtained as 2.19 g mg^{-1} h^{-1} by using the experimental data. This rate constant was higher than the obtained 0.2 and 0.3 g mg^{-1} h^{-1} values for adsorption on rectorite and illite, respectively (Wang *et al.* 2011). The large variation of CIP adsorption efficiency was often related to the relative contents of different components in clay minerals obtained from the different geographical areas.

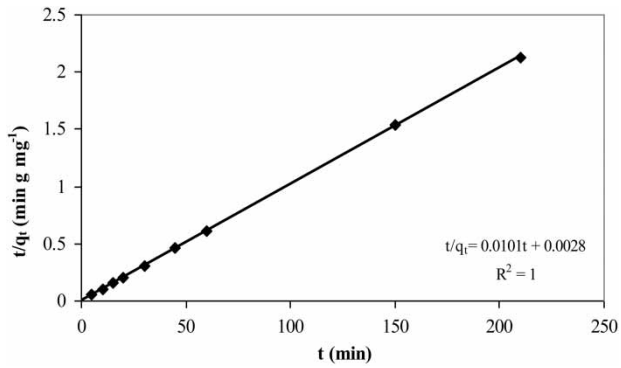


Figure 7 | Adsorption kinetics of CIP on bentonite.

Adsorption equilibrium of CIP on bentonite

Adsorption isotherms were simulated by the Freundlich model and Langmuir model, given in Equations (5) and (6):

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{5}$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_l} \left(\frac{1}{C_e} \right) \tag{6}$$

where K_f and n are parameters indicating the capacity and intensity of adsorption, respectively. The parameter n can be described as the surface site heterogeneity. Generally, an n value closer to 0 indicates that the surface is heterogeneous, whereas an n value near 1 indicates a homogeneous surface (Rakshit *et al.* 2013). The magnitude of the n value gives an indication of the favorability of the adsorption. Values of n greater than 1 show the favorable nature of adsorption (Daneshvar *et al.* 2002). K_l is the Langmuir adsorption constant (L mg^{-1}) and is related to the free energy of adsorption, and q_m is the monolayer adsorption capacity of the adsorbent (mg g^{-1}), i.e. the maximum amount that can be adsorbed. The K_l constant and n coefficient indicate that adsorbent performs well as a molecular filter for antibiotics (Martucci *et al.* 2012).

In order to determine if the adsorption process is favorable or unfavorable, a dimensionless constant separation factor or equilibrium parameter, R_l, is defined according to Equation (7):

$$R_l = \frac{1}{(1 + K_l C_0)} \tag{7}$$

where the R_l value indicates the adsorption process is irreversible when R_l is 0; favorable when R_l is between 0 and 1; linear when R_l is 1; and unfavorable when R_l is greater than 1. The corresponding parameters of bentonite are summarized in Table 1.

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Table 1 | Langmuir and Freundlich isotherm parameters

Isotherm models	
Langmuir	
q_m (mg g^{-1})	147.06
K_l (L mg^{-1})	0.27
R^2	0.9392
R_l	0.0105–0.007
ARSE (%)	3.77
Freundlich	
K_f	44.88
n	2.61
R^2	0.9006
ARSE (%)	5.06

The experimental isotherm data fitted well to the Langmuir equation, with a relatively high correlation value of 0.9392. However, a poor fit with low correlation value of 0.9006 was observed for the application of the Freundlich equation. Furthermore, the values of ARSE for the Langmuir model were all lower than those for the Freundlich model. Compared with the CIP adsorption capacity of 1.443–1.580 mg g^{-1} on modified coal fly ash (Zhang *et al.* 2011), 112 and 231 mg g^{-1} on carbon xerogel and activated carbon, respectively (Carabineiro *et al.* 2012) and 6.3 mg g^{-1} on kaolinite (Li *et al.* 2011), bentonite exhibited a much higher adsorption capacity for CIP. In this study, R_1 value was in the range of 0.0105–0.007, indicating a 'favorable adsorption' and strong binding between the CIP and the relevant adsorbent. R_1 value was calculated in the range of 0.032–0.23 for the chemically prepared carbon adsorbent from date palm leaflets by El-Shafey *et al.* (2012) and 0.0485–0.290 for adsorption of CIP on modified coal fly ash at 30 °C by Zhang *et al.* (2011).

Table 2 presents a comparison of the maximum adsorption capacities (q_m) of CIP on various adsorbents. It is clear from this comparison table that the commercial bentonite gave a high adsorption capacity for CIP.

Table 2 | CIP adsorption capacity of adsorbents

Adsorbents	q_m (mg g^{-1})	References
Modified coal fly ash	1.547	Zhang *et al.* (2011)
Montmorillonite	395	Wang *et al.* (2011)
	330	Wang *et al.* (2010)
	397.6	Wu *et al.* (2010)
Rectorite	135	Wang *et al.* (2011)
Illite	33	Wang *et al.* (2011)
Activated carbon	231 ± 6	Carabineiro *et al.* (2012)
Carbon xerogel	112 ± 8	Carabineiro *et al.* (2012)
Carbon nanotubes	135 ± 2	Carabineiro *et al.* (2012)
Kaolinite	6.297	Li *et al.* (2011)
Aluminum hydrous oxide	0.0136	Gu & Karthikeyan (2005)
Iron hydrous oxide	0.022	Gu & Karthikeyan (2005)
Chemically prepared carbon (wet and dry)	133.3 and 125.0	El-Shafey *et al.* (2012)
Bentonite	147.06	This study

CONCLUSIONS

The results of this study indicated that bentonite is an efficient material for the removal of CIP from aqueous solution. Laboratory experiments also confirmed that bentonite is able to adsorb CIP up to 99%.

The following conclusions can be made from the experimental results of CIP adsorption on bentonite.

- The optimum contact time, pH, agitation speed, adsorbent dosage were found to be 30 min, 4.5, 150 rpm, 2.5 g L^{-1}, respectively.
- The isotherm adsorption data fitted well with the Langmuir model; K_l and q_e were found to be 0.27 L mg^{-1} and 147.06 mg g^{-1}, respectively.
- The kinetic data fitted well with the pseudo-second order kinetics; k was found to be 2.19 g mg^{-1} h^{-1}.
- The increase of ionic strength resulted in a decrease in the adsorption of CIP on bentonite.
- The data suggested that bentonite is more efficient than most of the adsorbents for removing CIP. Compared with the adsorption capacity of 1.443–1.580 mg g^{-1} on modified coal fly ash (Zhang *et al.* 2011), 112 and 231 mg g^{-1} on carbon xerogel and activated carbon respectively (Carabineiro *et al.* 2012), and 6.3 mg g^{-1} on kaolinite (Li *et al.* 2011), bentonite exhibited a much higher adsorption of CIP.
- This adsorption as well as its wide availability, low cost and stability, should encourage more detailed studies of bentonite as an alternative adsorbent concerning the removal of pharmaceutical drugs from aqueous solutions.

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