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ADSORPTION OF CIPROFLOXACIN FROM AQUEOUS ENVIRONMENT BY USING SYNTHESIZED NANOCERIA

ADSORPCJA CIPROFLOKSACYNY ZE ŚRODOWISKA WODNEGO ZA POMOCĄ ZSYNTEZOWANYCH NANOCZĄSTEK TLENKU CERU

Abstract: Antibiotics are widely detected emerging contaminants in water environments and possess high potential risks to human health and aquatic life. However, conventional water treatment processes cannot remove them sufficiently. To develop innovative nanoadsorbents for effectively remove antibiotic contaminants from water environment, nanoceria were prepared via in situ precipitation method, and evaluated their adsorption capacity for a model antibiotic, ciprofloxacin (CIP). The properties of the prepared nanoceria were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and vibration sample magnetization (VSM). The effect of various operating parameters such as pH, initial CIP concentration, contact time, and adsorbent dosage on adsorptions of CIP were studied in batch experiments. Maximum adsorption capacity of the nanoceria was 49.38 mg/g at the conditions of pH 5, initial CIP concentration of 200 mg/dm³ and adsorbent dosage of 0.2 g/dm³, when 95.43 % of the CIP was removed. For adsorption kinetics, both pseudo-first-order and pseudo-second-order models can well describe the experimental data, indicating that the adsorption process was controlled by both physical diffusion and chemical interaction. For adsorption isotherms, the Freundlich model could fit the experimental data better than the Langmuir and Temkin models, suggesting a multilayer adsorption process. The thermal dynamics study showed the absorption process was spontaneity, exothermic, and irreversible. Finally it was concluded that the nanoceria can be used effectively for CIP removal.

Keywords: ciprofloxacin, cerium oxide nanoparticles, adsorption of ciprofloxacin, isotherm model, antibiotic pollutants, thermodynamics studies

Introduction

Today, the drugs in the environment have been considered as emerging contaminants and have attracted more and more attentions. They were used in treatments of infections and curing the microbial, viral, fungal and parasites agents for 70 years [1]. Antibiotics are a big branch of pharmaceutical substances, which consisted of 15 % of total drugs consumptions [2]. Annual application of antibiotics is 100,000 to 200,000 Mg per year [3]. Antibiotics are in human body in very low concentration and large parts of them are excreted by urine and feces. In addition, the wastewater produced by pharmaceutical

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industry contain large amounts of antibiotics, and the inappropriate treatment of such wastewater will result in serious water pollution [4]. Different concentrations (1-100 µg/dm³) of antibiotics were observed in underground water, surface water and lakes. Significant amount of antibiotics were even found in liver of trout and brain of shrimps [5]. Their presence resulted in bacterial drug resistance in low concentration, and threat the human healthy [6]. In addition to their chemical pollution, they showed high stability and diffusion ability [7]. Therefore, antibiotics have been the most concerned by the scientific community and the public in recent years. Ciprofloxacin (CIP) is a typical synthetic antibiotic, which belongs to fluoroquinolones, and it is used to treat the urinary tract infections, certain type of infectious diarrhea, and respiratory tract infections. The fluorine atom in structure of CIP resulted in high stability of this antibiotic [8]. It is shown that more than 95 % of CIP would not be decomposed during the uptaking and it found its way to sewage [9].

The antibiotics show the lower biodegradability, high toxicity, carcinogenicity and mutagenicity, and they increase the allergic reactions and induce the population increase of antibiotic resistance bacteria in human and animals [10, 11]. Different methods have been developed to treat antibiotic pollutants including coagulation, reverse osmosis, absorption on active carbon, ozonation, advanced oxidation systems like Fenton or photo-Fenton, ultrasonic degradation, pre-oxidation with UV lamp, and biofiltration [12, 13]. However, coagulation and centrifuge made a secondary pollutant, and biological methods were time-consuming and had low efficiency [14]. The antibiotic presence in wastewater prevents bacterial activity [15]. In addition, they cause toxicity in microorganisms that are used in filtration and produce high biomass [10]. Advanced oxidation process needs high energy and it was not often used because of economic limitation.

Surface adsorption is the most effective method in purification of sewage as it provides the advantages of simple design, easy to manage, high efficiency, less sludge production and environment friendly [16, 17]. The boom in nanoscience and nanotechnology offers opportunities to develop innovative techniques in removing the pollutants from aqueous solutions using iron, titanium, manganese and cerium oxides nanoparticles. Nanoparticles can provide high special surface for chemical reactions and absorption of organic compounds. Cerium oxide nanoparticles (CeO₂-NPs) are effective nanoadsorbents because of high special surface, physical and chemical properties and electrical charges, and have been investigated for adsorbing various pollutants including heavy metals [18], dyes [19], and nutrients [20]. Yet, the adsorption information of CeO₂-NPs for antibiotics are limited. To this end, CeO₂-NPs were synthesized and evaluated their adsorption capacity for the model antibiotic CIP from aqueous environment. Adsorption kinetics, equilibrium isotherm and thermodynamics have been systematically studied. The operating parameters such as initial pH of solution, adsorbent dosage, initial pollutant concentration and contact time on the adsorption capacity of CeO₂-NPs for CIP removal have also been investigated and optimized.

Materials and methods

Chemicals and reagents

Ciprofloxacin (molecular weight 367.8 g/mol, purity higher than 99.6 %, molecular formula C₁₇H₁₈FN₃O₃, and acidity coefficient pK_a = 5.7) was supplied by Sigma-Aldrich, USA. Stock of CIP with concentration of 1.000 mg/dm³ was prepared in double distilled

water. The chemical structure CIP is provided in Figure 1. Sodium hydroxide (NaOH, 98 %) and hydrochloric acid (HCl, 37 %) used in the study were of analytical grade and were supplied by Sigma-Aldrich.

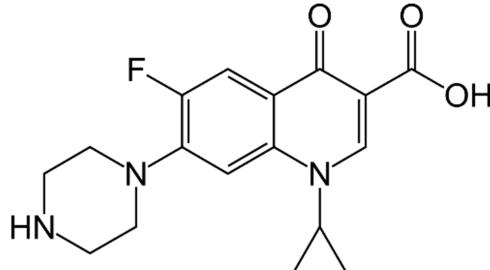


Fig. 1. Chemical structure of ciprofloxacin

Preparation and characterization of nanoadsorbent

To prepare of CeO₂-NPs, 11.235 g of cerium nitrate (Ce(NO₃)₃·6H₂O) was dissolved in 50 cm³ of distilled water and then stirred for 20 min. Meanwhile, 0.0323 g of xanthan gum was dissolved in 60 cm³ of distilled water and stirred for 20 min to achieve a clear xanthan gum solution. Afterwards, the cerium nitrate solution was added to the xanthan gum solution, and stirred for 40 min. In this solution a 3 M ammonia solution was slowly added under stirring until the pH value 9 is reached. The particle was collected by centrifugation at 5000 rpm for ten minutes. The centrifuged particles were washed with water and again subjected to centrifugation at 5000 rpm for 4 min. The centrifuged sample, dried for 24 h at room temperature, was powdered using mortar and pestle.

The microstructure analysis of CeO₂-NPs was performed using transmission electron microscopy (TEM) (Philips CM-12 Model). The X-ray diffraction (XRD) pattern of CeO₂-NPs was obtained on a D8 powder X-ray diffractometer with Cu *Kα* radiation (Bruker, Billerica, MA, USA). The magnetic property of CeO₂-NPs was confirmed by vibration sample magnetization (VSM) tool.

Antibiotic adsorption experiments

In order to remove CIP, the adsorption experiment by CeO₂-NPs was conducted in a 250 cm³ Erlenmeyer on a shaker. A 50 cm³ of CIP stock with different concentrations (20-100 mg/dm³) and pH values (3-11) were prepared using distilled water. The pH were adjusted with HCl and NaOH. CeO₂-NPs were added to solution and the mixture was shaking on a shaker. The samples were taken at set time intervals, filtered using Whatman filter paper (0.45 μm), and then subjected to CIP measurement on a spectrophotometer (CE-1021, Shimadzu, Tokyo, China) at the absorbance of 276 nm. The adsorption capacity of CIP on CeO₂-NPs (q_e [mg/g]) and removal efficiency (Re [%]) were calculated using the following equations [21]:

$$q_e = \frac{(C_o - C_e)V}{M} \quad (1)$$

$$Re = \frac{(C_o - C_e)}{C_o} \cdot 100 \% \quad (2)$$

where C_0 and C_e were initial and equilibrium concentration of CIP in aqueous phase [mg/dm³], V was solution volume [dm³] and M was the mass of CeO₂-NPs [g]. Each experiment was replicated twice, and the mean values were reported.

Results and discussion

Characterization of CeO₂-NPs

Figure 2 presents the TEM image of CeO₂-NPs. The range of diameters of CeO₂-NPs are about 40-90 nm. Figure 3 shows the XRD spectrum of CeO₂-NPs. The XRD peaks located at angles (2θ) of 28.57°, 33.09° and 47.48° are corresponding to (111), (200) and (220) planes of the CeO₂-NPs. Other peaks found at 2θ of 56.35°, 59.12°, 69.37°, 76.67° and 79.11° are corresponding to (311), (222), (400), (331) and (420) planes of CeO₂-NPs that can be indexed as the fluorite cubic structure (JCPDS #00-034-0394). The average crystallite size (D) of CeO₂-NPs was calculated by the Scherer formula:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (3)$$

where K is a dimensionless shape factor and has a typical value of about 0.9, λ is the wavelength of Cu $K\alpha$ (1.542 Å), β is the full width at half maximum (FWHM) of the line, and θ is the diffraction angle using (311) plane reflection from the XRD pattern. The calculated crystallite size of CeO₂-NPs is 34.21 nm with a lattice parameter of 5.4204. In addition, the VSM curve (Fig. 4) confirms the magnetic properties of CeO₂-NPs, which is in agreement with the reported results in literature [22].

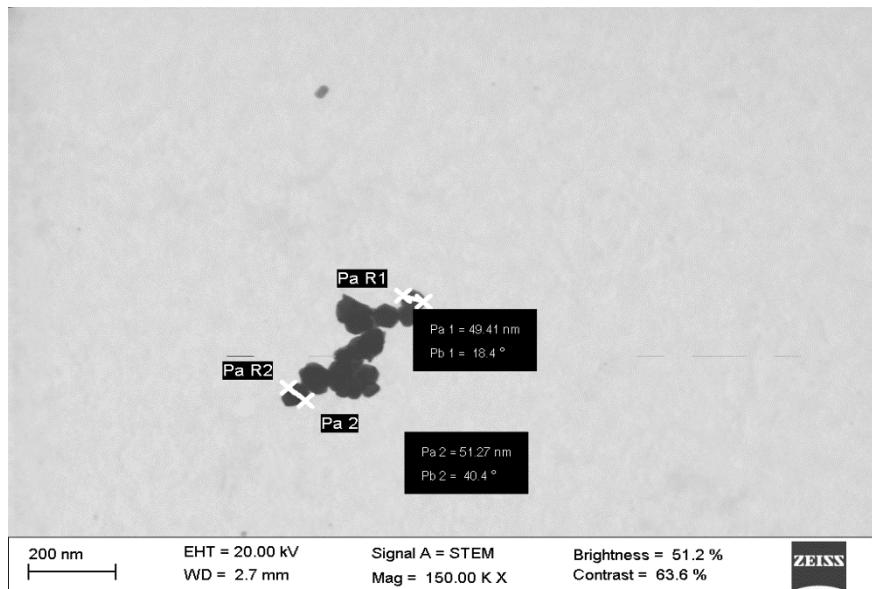


Fig. 2. TEM image of cerium oxide nanoparticles

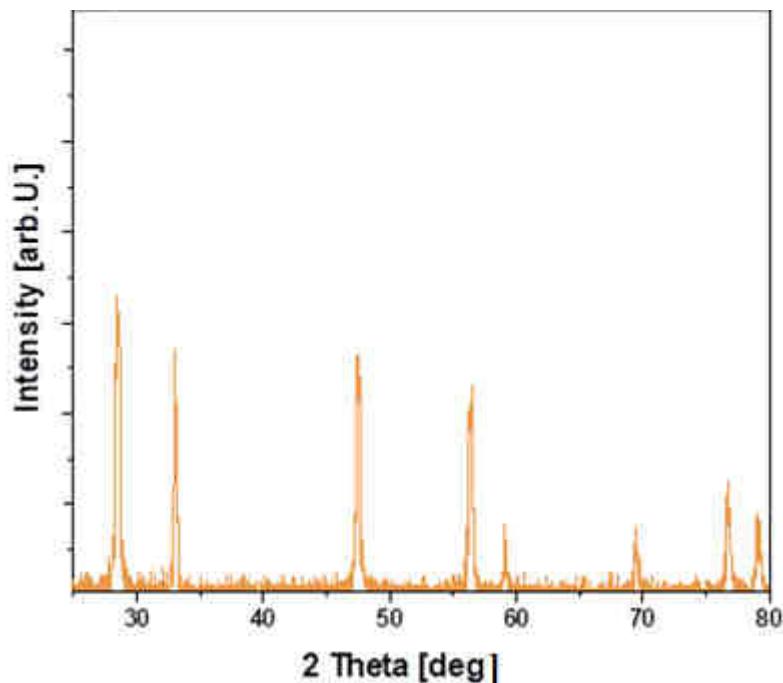


Fig. 3. XRD spectrum of cerium oxide nanoparticles

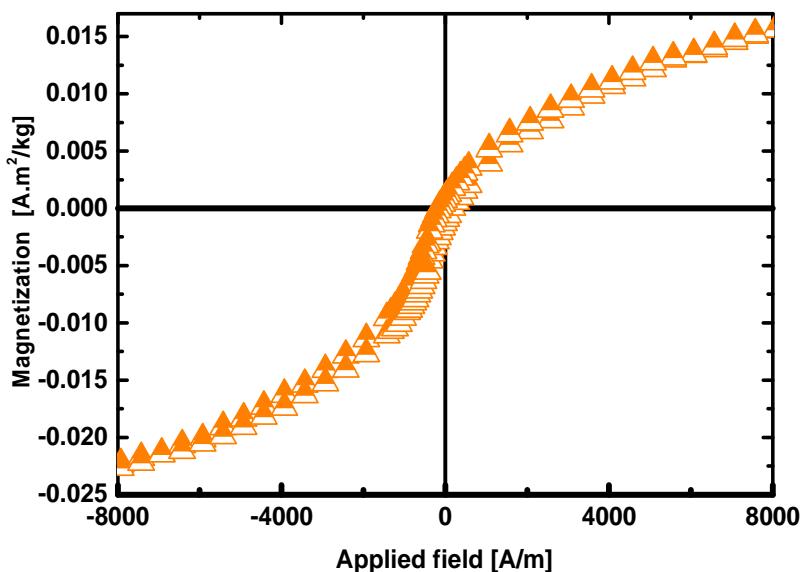


Fig. 4. M-H loops of cerium oxide nanoparticles

Adsorption kinetics

Adsorption of CIP onto CeO₂-NPs over time is displayed in Figure 5. It is observed that CeO₂-NPs could quickly capture CIP from aqueous solution. The adsorption mainly occurred in the first 20 min and could rapidly reach equilibrium within 80 min for an varying initial CIP concentration from 20 to 200 mg/dm³. The equilibrium adsorption capacity was ranged from 4.78 to 49.85 mg/g. Pseudo-first-order and pseudo-second-order models are used to analyze the kinetics results, which are expressed as [23]:

pseudo-first-order models:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

pseudo-second-order model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where q_t and q_e [mg/g] are the adsorption capacities of CIP at time t [min] and equilibrium, respectively. k_1 [min⁻¹] and k_2 [g/mg·min] are the rate constants of the pseudo-first-order and pseudo-second-order kinetic models, respectively. Table 1 lists the parameters for the two kinetic models. Obviously, both models can well describe the adsorption kinetic results, indicating that the adsorption of CIP onto CeO₂-NPs was controlled by both physical diffusion and chemical interaction.

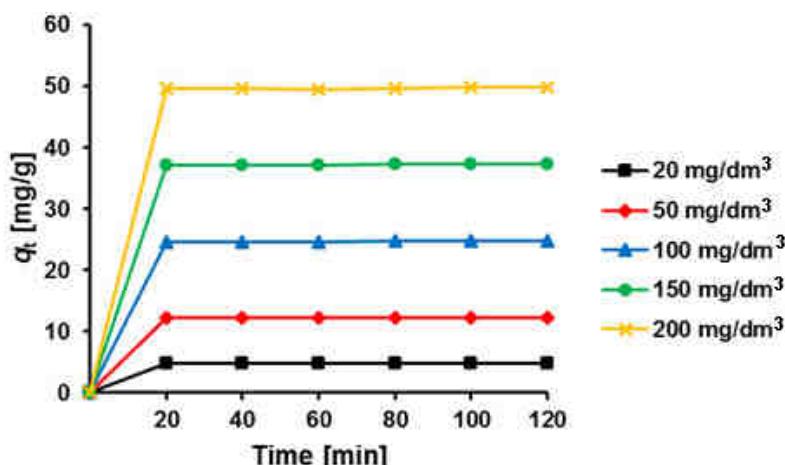


Fig. 5. Adsorption kinetics of ciprofloxacin onto cerium oxide nanoparticles. Experimental conditions: CeO₂-NPs dosage 0.2 g/dm³, initial CIP concentration 20-200 mg/dm³, pH = 5

Table 1
Kinetic parameters for adsorption of ciprofloxacin by cerium oxide nanoparticles

Kinetic model	Parameters	Initial CIP concentration [mg/dm ³]				
		20	50	100	150	200
Pseudo-first-order model	q_e [mg/g]	4.78	12.25	24.72	37.21	49.72
	k_1 [min ⁻¹]	0.342	0.259	0.322	0.326	0.315
	R^2	0.9999	0.9999	0.9999	0.9999	0.9999
Pseudo-second-order model	q_e [mg/g]	4.80	12.30	24.84	37.40	49.98
	k_2 [g/(mg·min)]	0.965	0.309	0.139	0.089	0.067
	R^2	0.9999	1.0000	1.0000	1.0000	1.0000

Adsorption isotherms

Isotherms usually showed the relation between adsorbed antibiotic mass per gram of absorbent and residual antibiotic concentration in solution in equilibrium condition. Figure 6 presents the adsorption isotherm results. The adsorption equilibrium models were used to show the adsorption equilibrium and measurement of the adsorption rate in different conditions. These models showed how absorbed molecules in solid and liquid phases will distribute in equilibrium condition, so they provided comprehensive and complete view about mechanism, surface properties and absorbing condition [24, 25]. The most important adsorption isotherm models were Langmuir model, Freundlich model, and Temkin model.

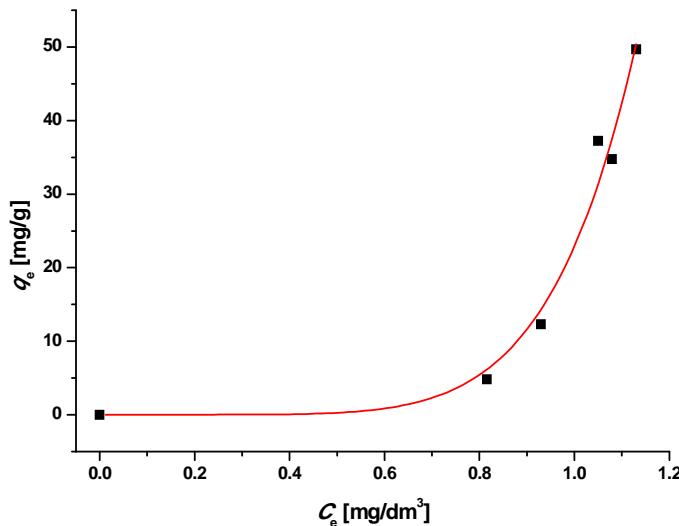


Fig. 6. Adsorption isotherm of ciprofloxacin onto cerium oxide nanoparticles with Freundlich model fitting. Experimental conditions: CeO₂-NPs dosage 0.2 g/dm³, initial CIP concentration 20-100 mg/dm³, pH = 5

The Langmuir isotherm model was based on solid scientific assumptions. It is assumed that adsorbates (atoms, molecules or ions) will bind to determined and uniform sites on absorbents surface and the monolayer absorption process will happen. The model can be expressed as below [21]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

where q_e and C_e are adsorption capacity [mg/g] and concentration of adsorbates at equilibrium, K_L is Langmuir constants, and q_m is the maximum adsorption capacity [mg/g]. The Langmuir equation could be calculated in linear condition using q_m and K_L with drawing the curve $1/q_e$ versus $1/C_e$ [23]:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \frac{1}{C} \quad (7)$$

The Freundlich isotherm assumes an exponentially decaying sorption site energy distribution. This is an experimental model and is applicable to non-ideal sorption on heterogeneous surfaces as well as multi-layer sorption and is expressed by the following equation [25]:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (8)$$

where K_F and $1/n$ are the Freundlich constants that are related to the adsorption capacity and the adsorption intensity, respectively. The Freundlich constants can be obtained by drawing the $\log q_e$ versus $\log C_e$ based on experimental data in light to linear equation [23]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (9)$$

In order to validate the adsorption isotherm model used in the study, in addition to coefficient of determination R^2 , the parameters of Marquardt's percent standard deviation (*MPSD*), Hybrid error function (*HYBRID*), and relative error $\Delta q_e [\%]$ were also evaluated, which can be described as follows [26]:

$$MPSD = 100 \sqrt{\frac{1}{n-p} \sum_{i=1}^n \left(\frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right)_i^2} \quad (10)$$

$$HYBRID = \frac{100}{n-p} \sum_{i=1}^n \left[\frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,exp}} \right]_i \quad (11)$$

$$\Delta q_e = 100 \sqrt{\frac{\sum |(q_{e,exp} - q_{e,cal})/q_{e,exp}|^2}{n-1}} \quad (12)$$

where in two equations, n is the observations in the experiments, p is the number of parameters in the model, $q_{e,exp}$ is the observation of the batch experiment i , and $q_{e,cal}$ is estimated from the equation for the corresponding.

Table 2
Isotherm model parameters and error evaluation for adsorption of ciprofloxacin onto cerium oxide nanoparticles

Model	R^2	Parameters		<i>HYBRID</i>	<i>MPSD</i>	$\Delta q_e [\%]$
Langmuir	0.930	$q_m = 1.85 \text{ mg/g}$	$K_L = 0.04 \text{ dm}^3/\text{mg}$	768	38.72	37.68
Freundlich	0.946	$1/n = 0.14$	$K_F = 1.30$	785	40	38.98

The isotherm model parameters with the various error functions used in the present study are given in Table 2. According to R^2 , *MPSD*, *HYBRID* and $\Delta q_e [\%]$, Freundlich isotherm model exhibited the best fit. Figure 6 presents the fitting curve of the Freundlich equation on the isotherm data. Therefore, the adsorption of CIP onto CeO₂-NPs was a multilayer adsorption process, and the adsorption occurred at a heterogeneous surface [26]. Moreover, $1/n$ values between 0 and 1 indicated a good adsorption [23].

Adsorption thermodynamics

Three basic parameters for thermodynamic study include standard enthalpy (ΔH°), Gibbs free energy (ΔG°) and standard entropy (ΔS°), which can be evaluated by the following equations [23, 25]:

$$K_C = \frac{q_e}{C_e} \quad (13)$$

where K_c is the equilibrium constant [dm^3/g], q_e is the amount of adsorbed CIP on CeO_2 -NP at equilibrium [mg/g], and C_e is the equilibrium concentration of the CIP in the solution [mg/dm^3].

$$\Delta G^\circ = -RT \cdot \ln K_c \quad (14)$$

where R is the universal gas constant (8.314 [J/mol · K]), and T is the temperature [K].

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (15)$$

The ΔH° and ΔS° values are derived from linear plot against $1/T$, which are from the slope and intercept, respectively.

The adsorption kinetics of CIP onto CeO_2 -NPs were critically investigated at 298, 308 and 318 K, respectively, and the thermodynamic parameters were calculated as shown in Table 3. All the values of ΔG° was negative and it showed that the absorption process by CeO_2 -NPs was spontaneity. The decrease of ΔG° happened with increase in temperature, indicating that the increasing temperature resulted in increase of spontaneity. The negative ΔH° indicated the adsorption process were exothermic. According to Le Chatelier's principle, increasing the temperature reduced the reaction rate, and it was followed by reducing the maximum adsorption capacity. The positive ΔS° showed the regularity at solid/solution interface decreased during absorption, and the reaction was irreversible [27].

Table 3
Thermodynamic parameters for the adsorption of ciprofloxacin onto cerium oxide nanoparticles

T (K)	ΔG° [kJ/mol]	ΔS° [kJ/mol · K]	ΔH° [kJ/mol]
298	-1213.6	0.003	-1212.6
308	-1036.5		
318	-1021.4		

Experimental conditions: CeO_2 -NPs mass 0.2 g, initial CIP concentration 200 mg/dm³, pH 5

Effect of pH

The pH is an important parameter that influences on surface charges of absorbents, ionization degree of different pollutants and separation of application groups on absorbent active sites. Effect of different pH (3-11) in adsorption of CIP on CeO_2 -NPs was shown in Figure 7. Upon increasing the pH from 3 to 5, the removal efficiency of CIP significantly increased from 95 to 99 %. While pH was higher than 5, the removal efficiency was slightly reduced. The adsorption capacity showed the similar trend. The effect of pH on the adsorption of CIP depends on point of zero charge (pH_{pzc}) and pK_a parameters. The pK_a for CIP was 5.7 and the pH_{pzc} of CeO_2 -NPs was 7.8 [28, 29]. In acidic condition, both CIP and CeO_2 -NPs have positive charges, which hinders the contact between CIP and CeO_2 -NPs by charge repelling.

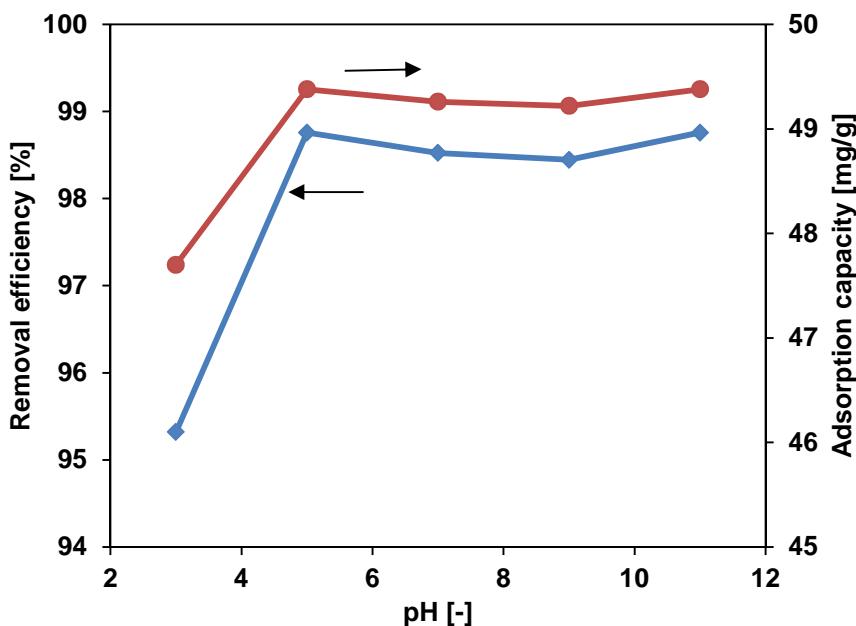


Fig. 7. Effect of pH on adsorption of ciprofloxacin onto cerium oxide nanoparticles. Experimental condition: CeO₂-NPs dosage 0.2 g/dm³, initial CIP concentration 50 mg/dm³, contact time 60 min

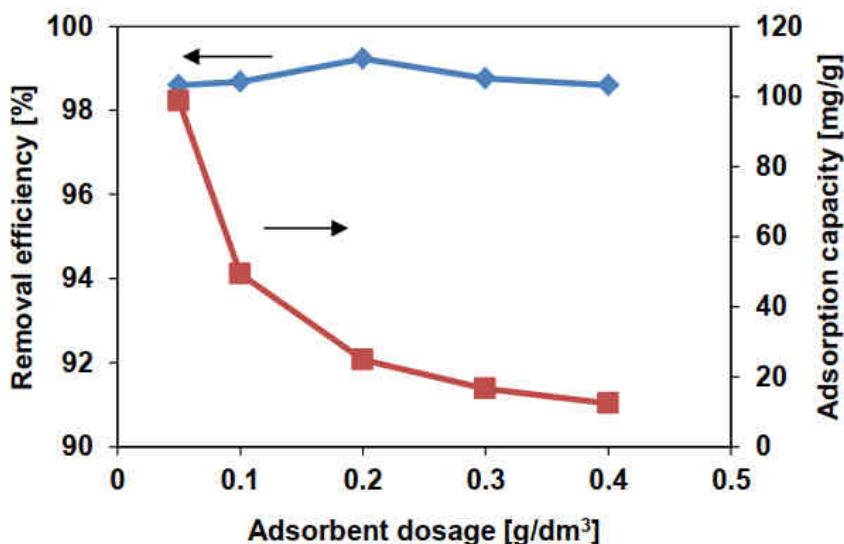


Fig. 8. Effect of adsorbent dosage on ciprofloxacin adsorption onto cerium oxide nanoparticles. Experimental condition: initial CIP concentration 50 mg/dm³, pH 5, contact time 45 min, ambient temperature

Effect of adsorbent dosage

The adsorbent dosage is an important parameter in determining the adsorbent capacity of CIP onto CeO₂-NPs. To study the effect of adsorbent dosage in removing CIP, 0.05-1 g/dm³ CeO₂-NPs were used to conduct the adsorption experiments at conditions of initial CIP concentration of 50 mg/dm³, pH = 5, contact time of 45 min, and ambient temperature. According to the results shown in Figure 8, with increase of CeO₂-NPs dose from 0.05 to 0.4 g/dm³, the removal efficiency of CIP first increased and reached the maximum value of 99.22 % at the CeO₂-NPs dose of 0.2 g/dm³ with an adsorption capacity of 24.8 mg/g, and then gradually decreased. The increase of removal efficiency of CIP is related to the increased active surface of CeO₂-NPs with the increase in adsorbent dosage [30]. However, continuously increasing the adsorbent dosage would induce the agglomeration of nanoparticles that shelters the available adsorption sites. The maximum absorption capacity was 98.62 mg/g with the minimum adsorbent dosage of 0.05 g/dm³, and it gradually decreased with increasing the adsorbent dosage.

Effects of contact time and initial ciprofloxacin concentration

The effects of contact time and initial CIP concentration on removal efficiency of CIP was studied in experimental conditions of contact time 20-120 min, pH = 6, CeO₂-NPs dose 0.2 g/dm³, and initial CIP concentration 50-200 mg/dm³, and the results are shown in Figure 9. It was found that increasing the contact time slightly increased the removal efficiency. The limited enhancement is because the fast adsorption process occurred in the first 20 min, and after that the adsorption slowly approached to equilibrium. At a fixed contact time, increased the initial CIP concentration promote the removal efficiency. In fact, the increase of initial CIP concentrations provides an important driving force to overcome the mass transfer resistance of the CIP between the solid phases and the aqueous phases, so increasing initial concentrations would enhance the adsorption efficiency [31].

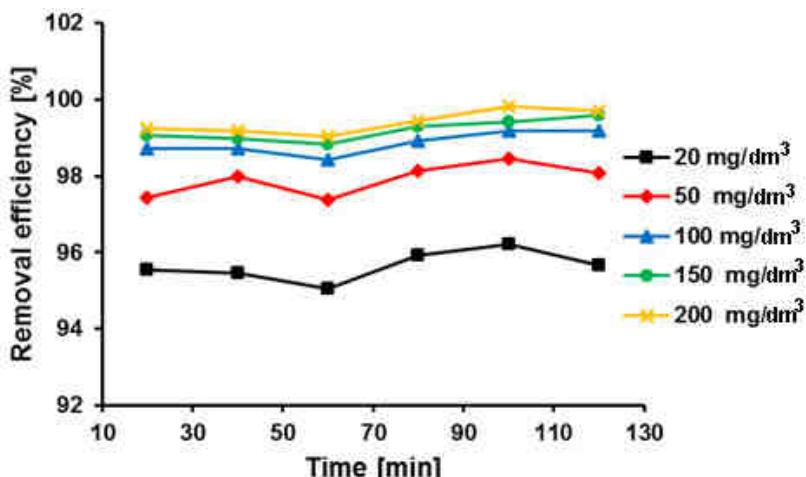


Fig. 9. Effects of contact time and initial ciprofloxacin concentration on removal efficiency of ciprofloxacin by cerium oxide nanoparticles. Experimental conditions: contact time 20-120 min, pH 6, CeO₂-NPs dose 0.2 g/dm³, initial CIP concentration 50-200 mg/dm³

Conclusions

This study comprehensively investigated the adsorption of CIP onto CeO₂-NPs. For adsorption kinetics, both pseudo-first-order and pseudo-second-order models can well describe the experimental data, indicating that the adsorption process was controlled by both physical diffusion and chemical interaction. For adsorption isotherms, the Freundlich model could fit the experimental data better than the Langmuir and Temkin models, suggesting a multilayer adsorption process. The thermal dynamics study showed the absorption process was spontaneity, exothermic, and irreversible. In addition, the effects of various operating parameters were investigated, and the optimum conditions were determined as follows: initial CIP concentration 200 mg/dm³, pH 5, CeO₂-NPs dose 0.2 g/dm³, and contact time 80 min.

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