



Preparation of Adsorbent CeO₂-TiO₂ and Enhanced Adsorptive Removal of Tetracycline

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Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 12-11-2015
Accepted: 10-12-2015

Key Words:

CeO₂-TiO₂
Tetracycline
Adsorption
Kinetics
Isotherm

ABSTRACT

In order to enhance the adsorption performance of TiO₂, CeO₂ was tentatively introduced into the matrix of TiO₂ by sol-gel method. The prepared adsorbent CeO₂-TiO₂ was used for the efficient adsorptive removal of antibiotics tetracycline (TC). It was observed that the introduction of CeO₂ into TiO₂ matrix has improved the removal efficiency of TC by 57.6% compared to pure TiO₂. The uptake of TC was highly dependent on the solution pH conditions and the highest uptake of TC occurred under alkaline condition. Linear simulation method failed to discern which kinetic model was better to describe the kinetic data between pseudo-first-order and pseudo-second-order models. By nonlinear simulation, Elovich kinetic model was found to be the best model to describe the TC adsorption onto CeO₂-TiO₂, indicating that the pronounced diffusion-control process was the rate-determining step. The maximal adsorption capacity of the prepared sorbent was 59.3 mg/g using Langmuir isotherm model at 298 K. The uptake of TC increased with an increase in the reaction temperature, which demonstrates that the adsorption of TC was endothermic.

INTRODUCTION

In recent decades, advanced oxidation processes (AOPs) have become one of the focuses as AOPs are capable of effectively degrading almost all the organic pollutants whether in low and high concentrations (Andreozzi et al. 1999). AOPs such as photocatalytic and sonocatalytic oxidation processes are widely studied for the detoxification of organic pollutants (Konstantinou et al. 2004, Joseph et al. 2009). A number of catalysts are used in these catalytic oxidation processes. These catalysts play the key role as the oxidation processes occur on the interface of catalyst and solution. The first indispensable step for these oxidation processes is adsorption of organic pollutants onto the catalyst (Ishibashi et al. 2000, Hu et al. 2003, Li et al. 2009). For example, in photocatalytic oxidation processes, the overall degradation process of dye can be typically divided into three processes including the adsorption of dyes, surface reaction and desorption of final products. Apparently, the uptake of organic pollutants is crucial for the total degradation process. As a result, the adsorption capability of these catalysts used in the catalytic processes might determine the degradation performance of these catalysts to some extent.

TiO₂ is a well-known catalyst applied in photocatalytic and sonocatalytic oxidation processes. In this study, in order to improve the adsorption and catalytic performance of TiO₂, CeO₂ was successfully introduced into the matrix of TiO₂ by

sol-gel method. Adsorption performance of the prepared CeO₂-TiO₂ was studied systematically. The adsorption kinetics and isotherm were mainly investigated to better understand the adsorption behaviour. The influence of solution pH was also explored. These results could provide comprehensive insights to the degradation performance of catalysts in AOPs. Additionally, it is reported that most of antibiotics used eventually entered into rivers, lakes and other water bodies. Antibiotics have been even detected in potable water (Yang et al. 2011). Exposures to even low-level antibiotics could lead to significant consequences of the toxic effect. As such, antibiotics tetracycline was used as a target organic pollutant for the adsorption removal test.

MATERIALS AND METHODS

Chemicals: Tetracycline (TC) was purchased from Hefei Bomei Biological Science and Technology Co., Ltd (Anhui Province, China) and used without further purification. All the other chemicals used are of analytical grade. Deionized (DI) water was used to prepare solutions.

Adsorbent preparation: Adsorbent CeO₂-TiO₂ was prepared by the sol-gel route using tetrabutyl titanate and the cerium metal salts. Firstly, 50 mL tetrabutyl titanate was dissolved in 50 mL absolute ethanol under vigorous stirring. Then, 10 mL hydrochloric acid (37 wt.%) was added dropwise to the above solution. Another solution containing 50 mL etha-

nol, 20 mL H₂O, and cerium metal salts in the required stoichiometry was slowly added into the above solution. The mixture was hydrolyzed at room temperature for 40 min under vigorous stirring, and the transparent sol was obtained. The gel was prepared by aging the sol for 24 h at room temperature. The derived gel was dried at 373 K to remove the solvents and then fired in a muffle furnace at 723 K for 3 h and milled into powders for use. Pure TiO₂ was prepared in the same way.

Batch adsorption studies: A stock TC solution of 1000 mg/L was prepared by dissolving TC in DI water and then the solution was mixed in an ultrasonic bath for several minutes. Subsequently, the solution was stored in a brown volumetric flask and kept at room temperature in a dark place. For kinetic study, 1600 mg of CeO₂-TiO₂ was added into 1000 mL TC solution with an initial TC concentration of 25 mg/L. The mixed solution was stirred at a constant rate. The samples were collected at different time intervals. In other adsorption experiments, adsorptive removal of TC was performed in a series of 100-mL conical flasks containing 50 mL TC solution (25 mg/L). The dosage of CeO₂-TiO₂ or pure TiO₂ was 80 mg in 50 mL solution. These mixtures were shaken at 135 rpm for 24 h to achieve adsorption equilibrium. The adsorption temperature was kept at 298 K unless otherwise stated. The solution pH adjustment was conducted by adding diluted HCl or NaOH solution. All the solution pH values were maintained at neutral pH except for the pH effect study.

Analysis of tetracycline: Samples were collected and filtered through a 0.45 μm membrane before analysing. The concentration of the TC was determined by measuring the absorbance at a fixed wavelength (360 nm) (Figuroa et al. 2004) using a UVmini-1240 spectrophotometer (Shimadzu).

The removal efficiency of TC was calculated as:

$$\text{Removal efficiency} = (1 - C_t/C_0) \times 100\% \quad \dots(1)$$

Where C_t is the TC concentration at time t , and C_0 is the initial TC concentration.

RESULTS AND DISCUSSION

Comparison for the adsorption capability: The adsorption performance of TiO₂ and CeO₂-TiO₂ on TC removal was compared and the result is presented in Fig. 1. It can be observed that the removal efficiency for pure TiO₂ and CeO₂-TiO₂ achieved at 60 min were of 25.0% and 39.4%, respectively. Apparently, the introduction of CeO₂ into TiO₂ matrix has improved the removal efficiency of TC by 57.6%. This is expected to be especially helpful for the application of the CeO₂-TiO₂ in catalytic oxidation processes such as photocatalytic and sonocatalytic oxidation processes as the

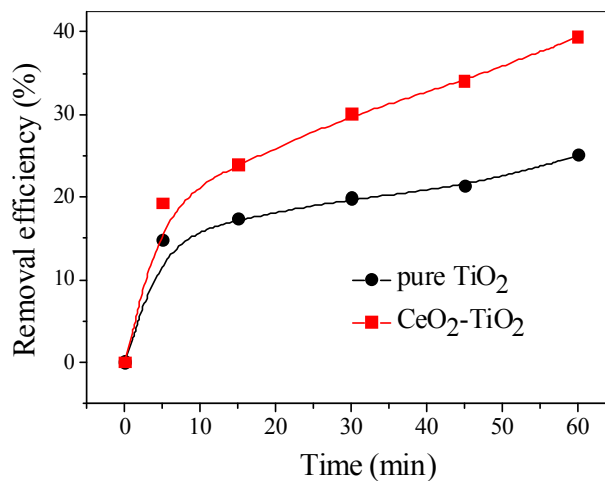


Fig. 1. Adsorption of TC on pure TiO₂ and CeO₂-TiO₂. Sorbent dosage 80 mg, 200 mL TC solution with a concentration of 25 mg/L, neutral solution pH.

uptake of pollutants onto the catalyst is the first indispensable step for decontamination. The enhanced uptake of TC could help the degradation of organic pollutants.

Adsorption kinetics simulated by linear kinetic models:

Adsorption kinetics for the uptake of TC onto CeO₂-TiO₂ was conducted at pH 5.0, 7.0 and 9.0, respectively, and the kinetic data are plotted in Fig. 2. As the adsorption could achieve equilibrium with 24 h, the adsorption duration was kept at 24 h in the following tests.

Both pseudo-first-order and pseudo-second-order kinetics models were used to fit the experimental data (Lagergren 1898, Ho & McKay 1999). The mathematical representations of the linear and non-linear models of pseudo-first-order and pseudo-second-order kinetics are given as:

$$q_t = q_e(1 - e^{-k_1 t}) \quad \dots(2)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \dots(3)$$

$$q_t = \frac{k_2 q_e^2 t}{(1 + k_2 q_e t)} \quad \dots(4)$$

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

Where q_e and q_t are the adsorption capacities (mg/g) of TC at equilibrium and at time t (min), respectively; and k_1 (min⁻¹) and k_2 (g/mg min) are the related adsorption rate constants for pseudo-first-order and pseudo-second-order model, respectively.

As illustrated in Fig. 2, both pseudo-first-order and

Table 1: Linear kinetic model parameters for the adsorption of TC onto CeO₂-TiO₂.

	Pseudo-first-order			Pseudo-second-order		
	q _e (mg/g)	k ₁ (min ⁻¹)	R ²	q _e (mg/g)	k ₂ (g/mg min)	R ²
pH=5.0	22.13	-0.00326	0.957	6.60	0.0315	0.994
pH=7.0	22.40	-0.00331	0.966	7.48	0.0318	0.994
pH=9.0	24.22	-0.00348	0.961	8.95	0.0307	0.996

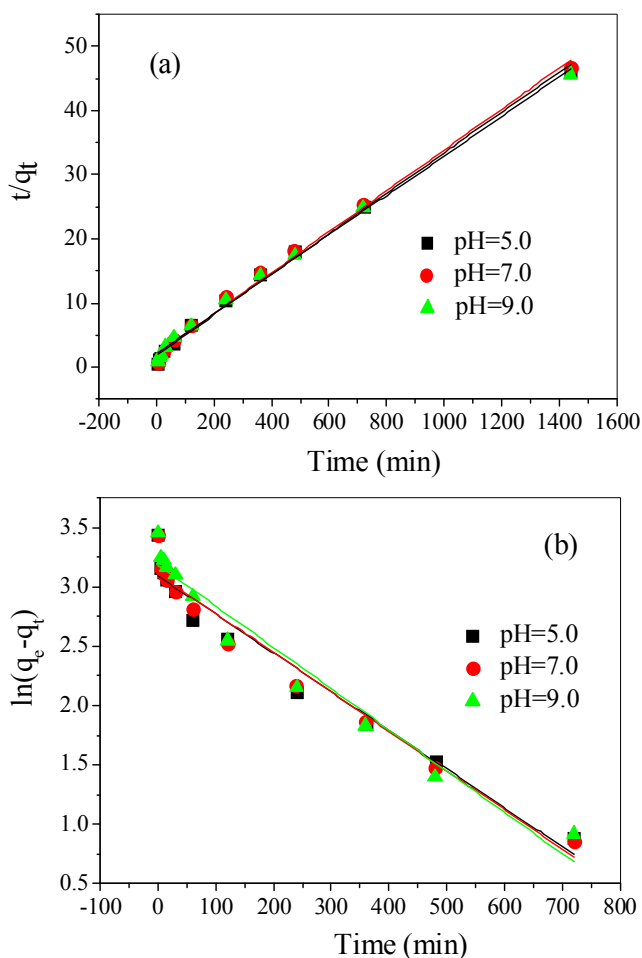


Fig. 2: Linear adsorption kinetics for pseudo-first-order (a) and pseudo-second-order (b) kinetic simulation of TC onto CeO₂-TiO₂.

pseudo-second-order kinetic model fitted the experimental data well from the fitted linear curves alone. Meanwhile, the related parameters for both kinetic models were listed in Table 1. At all the pH conditions, the values of correlation coefficient (*R*²) of pseudo-second-order model are higher than 0.994, which is a little higher than those of pseudo-first-order model. However, the calculated *q_e* values from pseudo-first-order model are much closer to the experimental

data than those of pseudo-second-order model. Thus, it is difficult to discern which kinetic model is better to describe the kinetics if only the linear kinetic simulation of pseudo-first-order and pseudo-second-order model was involved.

Adsorption kinetics simulated by nonlinear kinetic models: As the linear pseudo-first-order and pseudo-second-order model fails to better describe the experimental kinetics, nonlinear kinetic models were used to simulate the kinetic data. Typically, the adsorption process was a three-stage kinetic behaviour, an initial rapid stage (60 min), a slower second stage (60-180 min) and a slowest equilibrium uptake stage (Vadivelan & Kumar 2005). The driving force in the initial stage was the largest and most of the adsorption occurred within this stage.

Elovich model was also used for the non-linear simulation as well. The Elovich model can be written as (Kithome et al. 1988):

$$q_t = a \ln(t) + b \quad \dots(6)$$

Where *a* (g·mg/min) and *b* (mg/g) are constants.

The experimental kinetic data for TC adsorption at the three pH conditions were simulated by pseudo-first-order, pseudo-second-order and Elovich kinetic models using non-linear method, as illustrated in Fig. 3. Meanwhile, the parameters for the three models at pH 5.0, 7.0 and 9.0 were summarized in Table 2 for comparison. At pH 7.0, the *R*² values from the pseudo-first-order, the pseudo-second-order and the Elovich kinetic models are of 0.866, 0.934 and 0.984, respectively. Judging from the values of correlation coefficient (*R*²), it can be observed that Elovich model fitted the kinetic data better than pseudo-first-order and pseudo-second-order kinetic models at all the pH conditions examined. Additionally, the experimental data are quite in correlation with the fitted nonlinear kinetic curves of the Elovich model as well. Totally, The Elovich model is the best model to describe the TC adsorption onto CeO₂-TiO₂.

The Elovich model is used to describe chemisorption occurring on the solid-liquid interface. It was suggested that diffusion accounted for the Elovich kinetic pattern and the rate-determining step might be diffusional in nature (Aharoni et al. 1991, Pavlatou et al. 1988). As a result, the adsorption

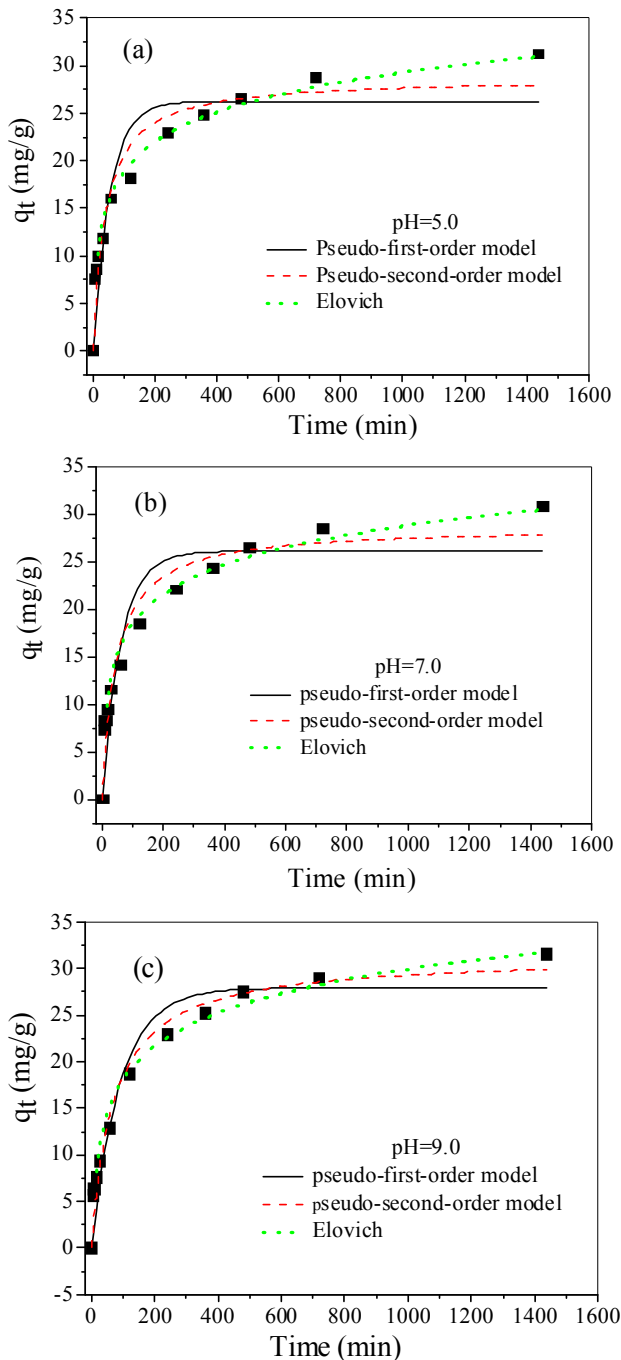


Fig. 3: Nonlinear adsorption kinetic simulation at pH 5.0 (a), 7.0 (b) and 9.0 (c) for the uptake of TC onto CeO₂-TiO₂.

of TC onto CeO₂-TiO₂ could be a chemisorption process in which the rate-determining step might be diffusion in nature.

Additionally, solution pH could affect the properties of both CeO₂-TiO₂ and TC molecules. As both CeO₂ and TiO₂ are metal oxides, it is expected that CeO₂-TiO₂ is positively-

Table 2: Nonlinear kinetic model parameters for the adsorption of TC onto CeO₂-TiO₂.

model	pH=5.0	pH=7.0	pH=9.0
Pseudo-first-order			
k_1 (min ⁻¹)	0.0185	0.0160	0.01095
q_e (mg/g)	26.24	26.09	27.90
R^2	0.866	0.866	0.933
Pseudo-second-order			
k_2 (g·mg/min)	0.00088	0.00077	0.00046
q_e (mg/g)	28.74	28.67	31.35
R^2	0.937	0.934	0.970
Elovich			
a	-1.881	-2.386	-5.528
k	4.512	4.513	5.136
R^2	0.988	0.984	0.978

Table 3: Langmuir and Freundlich isotherm parameters for the adsorption of TC onto CeO₂-TiO₂.

	Nonlinear method		
	288 K	298 K	308 K
Langmuir			
q_{max} (mg/g)	58.35	59.30	67.23
k_L (L/mg)	0.086	0.147	0.189
R^2	0.951	0.978	0.984
Freundlich			
k_F (mg/g)	13.30	17.15	21.42
n	3.381	3.827	4.157
R^2	0.973	0.978	0.914

charged under acidic conditions while negatively-charged under alkaline conditions due to the protonation and deprotonation of these oxides. By contrast, TC (H₂L) is an amphoteric compound with pK_a values at 3.3, 7.7 and 9.7 (Shao et al. 2012, Liu et al. 2012). Its predominant species are expected to be cation (H₂L⁺) at pH<3.3, zwitterions (H₂L⁰) at 3.3<pH<7.7, and negatively charged anions (HL⁻, L²⁻) at pH>7.7. As such, TC adsorption was highly dependent on solution pH, with the greatest adsorption occurring at pH 9.0 as presented in Table 2.

Adsorption isotherms: Isotherm studies for the uptake of TC onto CeO₂-TiO₂ were carried out at 288, 298 and 308 K. As shown in Fig. 4, both Langmuir and Freundlich models were used to fit the experimental data. The saturated monolayer Langmuir isotherm can be represented as (Langmuir et al. 1916):

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad \dots(7)$$

Where q_e is the amount of TC adsorbed onto the CeO₂-TiO₂ (mg/g), C_e is the equilibrium concentration (mg/L), q_m is the maximal adsorption capacity of the sorbent (mg/g)

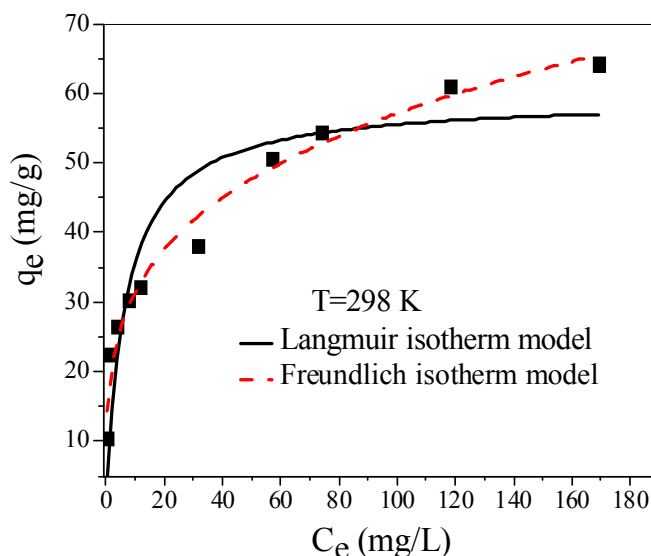


Fig. 4: Experimental points and fitted isotherm curves by Langmuir and Freundlich models.

and k_L is the equilibrium adsorption constant related to the affinity of binding sites (L/mg).

Freundlich isotherm is commonly written as (Freundlich et al. 1906):

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

Where k_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity of the sorbent, respectively.

As presented in Table 3, the Langmuir model is better to describe the isotherm data than the Freundlich model judged from the values of correlation coefficients (R^2). Using Langmuir model, the calculated maximal adsorption capacities for TC achieved 58.4, 59.3 and 67.2 mg/g at 288, 298 and 308 K, respectively. It is evident that the uptake of TC increased with an increase in the reaction temperature, indicating the endothermic nature of the adsorption process.

CONCLUSION

CeO₂-TiO₂ was successfully prepared by sol-gel method and used for the enhanced adsorptive removal of tetracycline (TC). The introduction of CeO₂ into TiO₂ has significantly enhanced the removal efficiency of TC. The uptake of TC was highly dependent on the solution pH conditions. It is difficult to discern which kinetic model is better to describe the kinetics if only the linear kinetic simulation of pseudo-first-order and pseudo-second-order model was involved. By nonlinear simulation, the Elovich model was found to

be the best model to describe the TC adsorption onto CeO₂-TiO₂, indicating the pronounced diffusion-control process was the rate-determining step. The maximal adsorption capacity of the prepared sorbent was 59.3 mg/g using Langmuir isotherm model at 298 K. Isotherm study indicated that TC adsorption was spontaneous and endothermic.

ACKNOWLEDGEMENTS

The authors thank for the foundation for university key youth teacher by Henan Province of China (2013GGJS-088).

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