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Adsorption Thermodynamics of Adsorptive Removal of Tetracycline on Lanthanum Modified Magnetic Composite

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ABSTRACT

Lanthanum is one of the rare earth elements, which exhibits potential high adsorption capacity for a series of organic and inorganic pollutants. In this research, a lanthanum modified magnetic adsorbent La-modified Fe_3O_4 was prepared by chemical co-precipitation and used for adsorptive removal of tetracycline (TC) from aqueous solution. At the adsorbent dosage of 5 mg in 50 mL solution, the uptake of TC achieved as much as 83.29 mg/g. The equilibrium adsorption data were fitted by Langmuir, Freundlich, Temkin, Redlich-Peterson and Koble-Corrigan models. The R^2 values of Freundlich, Redlich-Peterson and Koble-Corrigan models were higher than those of Langmuir and Temkin models. This indicates the chemisorption occurring on heterogeneous adsorbent surface. At 298, 308 and 318 K, the q_{max} values by Langmuir model were of 110.4, 145.9 and 176.0 mg/g, respectively. Thermodynamic analysis indicates that $\Delta H°$ and $\Delta S°$ were 29.83 KJ/mol and 124 $J \cdot mol^{-1} \cdot K^{-1}$, respectively. This demonstrates that the adsorption process was spontaneous and endothermic in nature.

INTRODUCTION

Tetracyclines (TC) were first found in 1940s, which have been the second most widely used chemicals due to their cheapness and excellent bacteriostasis (Mathers et al. 2011). In the past decades, it has been used widely in the therapy of human, animal infections and feed. Accordingly, it was detected in all kinds of water such as surface water, ground water, and drinking water. Nowadays, it remains a big challenge to remove TC from wastewater because of its properties such as persistence, carcinogenicity and refractory biodegradation. TC wastewaters usually present neutral or negatively-charged properties due to their complex structure, so the conventional techniques such as sedimentation, flocculation and coagulation were not ideal from the practical point of view (Shao et al. 2012). Therefore, it is of great significance to remove tetracycline efficiently from aqueous solution.

Adsorption is an economic and eco-friendly technique, which is being widely used in the removal of refractory compounds from wastewater. Up to now, various sorbents have been reported. Activated carbon is one of the most common adsorbents, but its costliness and difficult regeneration limit its usage (Li et al. 2013). Therefore, several workers have investigated the low-cost adsorbents for TC removal, including montmorillonite (Parolo et al. 2008), goethite (Zhao et al. 2011), graphene oxide (Gao et al. 2012) and modification of biochar (Liu et al. 2012). Although there are many kinds of adsorbents, regenerative utilization is still a crucial issue. At present, high gradient magnetic separation (HGMS) develops rapidly, which performs efficiently for separating some magnetic materials. Therefore, it is actually a good choice to prepare some magnetic adsorbents for the removal of TC. Shao et al. (2012) have synthesized $MnFe_2O_4$/activated carbon magnetic composite to remove tetracycline. Gupta et al. (2011) have investigated the adsorption capacity of composite adsorbent containing iron oxide and carbon nanotubes. Fe_3O_4 modified activated carbon is also an excellent adsorbent material (Yang et al. 2008). Fe_3O_4 nanoparticles processes magnetic and large specific surface area, which are widely used as adsorption materials. Additionally, it has been found that lanthanum is often used to modify adsorptive materials due to its good adsorption capacity for a series of organic and inorganic pollutants. Xie et al. (2008) have synthesized lanthanum hydroxide materials to remove the phosphate from water. After lanthanum modification, the adsorption capacity of lanthanum modified diatomite achieved as much as 469.7 mg/g of phosphate uptake (Li et al. 2015).

In this research, La-modified Fe_3O_4 nanoparticles were prepared by a simple chemical co-precipitation method. The prepared La-modified Fe_3O_4 nanoparticles were tentatively applied for adsorptive removal of TC from aqueous solution. Effect of adsorbent dosage was investigated. Adsorption isotherm data were simulated by Langmuir, Freundlich, Temkin, Redlich-Peterson and Koble-Corrigan models to discuss the adsorption mechanism involved. Also, thermodynamic analysis was conducted and thermodynamic parameters including ΔG°, ΔH° and ΔS° were calculated.

MATERIALS AND METHODS

Chemicals: All chemicals were of analytical grade and used without further purification. Tetracycline (TC) was purchased from Hefei Biological Science and Technology Co., Ltd. (Anhui Province, China). The solutions were prepared by dissolving a certain amount of reagents with deionized (DI) water.

Adsorbent preparation: The magnetic lanthanum modified Fe_3O_4 sample was prepared by a chemical co-precipitation method. Briefly, a solution containing $FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$ with a molar ratio of 2:1 and $La(NO_3)_3 \cdot 6H_2O$ was added to the DI water and heated to 70°C. The mixture was then co-precipitated by dropwise addition of NaOH solution until the pH~11. Then the solution was cooled in air to room temperature and then magnetically separated. The precipitate was washed with DI water to neutralize the pH. The prepared lanthanum-modified Fe_3O_4 was dried at 80°C overnight and stored in desiccators before use. The prepared lanthanum modified Fe_3O_4 is denoted as La-modified Fe_3O_4.

Batch adsorption studies: A stock TC solution (500 mg/L) was diluted to get the desired concentration with DI water. A series of 100 mL conical flasks were used for adsorption tests. For the effect of adsorbent dosage, a certain amount of La-modified Fe_3O_4 was added into 50 mL of solution with a TC concentration of 25 mg/L. For isothermal study, 20 mg of La-modified Fe_3O_4 was added into 50 mL solution with TC concentration range from 15 to 200 mg/L. These mixtures were shaken at 120 rpm for 24 h to achieve adsorption equilibrium. All the samples were collected and filtered through a 0.45 μm pore-size membrane before analysis.

Analysis of TC: The concentration of TC was measured by UVmini-1240 spectrophotometer (Shimadzu, Japan) to monitor emissions at the wavelength of maximum adsorption (360 nm) (Figueroa et al. 2004). The adsorption capacity was calculated using the following equations:

$$q_e=(C_0-C_e)V/W \quad ...(1)$$

$$q_t=(C_0-C_t)V/W \quad ...(2)$$

Where, q_e and q_t (mg/g) are the adsorption capacity at equilibrium and time t (min); C_0 is the initial TC concentration, while C_e and C_t (mg/L) are the concentrations of TC at equilibrium and t (min), respectively; V (L) is the volume of solution, and W (g) is the mass of La-modified Fe_3O_4.

RESULTS AND DISCUSSION

Effect of adsorbent dose on TC adsorption: The adsorbent dosage is one of the fundamental parameters that directly affect the removal of TC from aqueous solution. Effect of the dosage of La-modified Fe_3O_4 on TC adsorption was investigated, and the results are illustrated in Fig. 1. It was found that the uptake of TC at the adsorbent dosage of 5, 10, 20, 40 and 60 mg achieved 83.29, 61.81, 45.65, 30.01 and 20.56 mg/g, respectively. The TC uptake decreased with increasing adsorbent dosage. Usually, the dispersion of adsorbent in aqueous solution is uniform. Almost all the active sites are fully exposed, and the number of active sites available for adsorption increases by increasing the adsorbent dose. The increase in the concentration of adsorption sites may lead to a lower adsorption capacity (Zubair et al. 2017). The dosage of La-modified Fe_3O_4 was selected to be 20 mg for the following tests.

Adsorption isotherm: The adsorption isotherm is an essential way of predicting adsorption mechanism and behaviour. The experimental isotherm data for TC adsorption onto La-modified Fe_3O_4 was fitted by Langmuir, Freundlich, Temkin, Redlich-Peterson and Koble-Corrigan adsorption isotherm models. The simulated curves at three temperatures are presented in Fig. 2 and the fitting parameters are listed in Table 1.

Langmuir isotherm has been frequently used to analyse the equilibrium adsorption experimental data. It is appropriately used to describe the monolayer adsorption between the adsorbate and the surface of adsorbent (Langmuir 1916). The non-linear form of Langmuir adsorption isotherm is:

$$q_e = \frac{q_m k_L C_e}{1+k_L C_e} \quad ...(3)$$

Where q_e (mg g^{-1}) is the adsorption capacity at equilibrium, q_m (mg g^{-1}) is the maximum adsorption capacity, k_L (L mg^{-1}) is a constant related to the affinity of the binding sites and energy of adsorption.

Freundlich isotherm is applicable to describe the multilayer adsorption onto a heterogeneous surface. It is commonly expressed as (Freundlich 1906):

$$q_e = k_F C_e^{\frac{1}{n}} \quad ...(4)$$

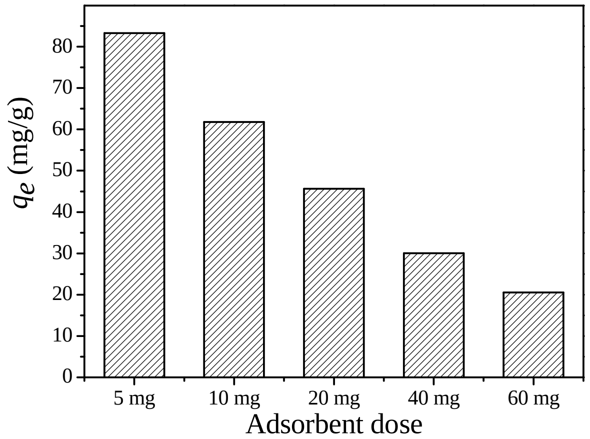

Fig. 1: Effect of adsorbent dosage on the adsorption of tetracycline adsorption.

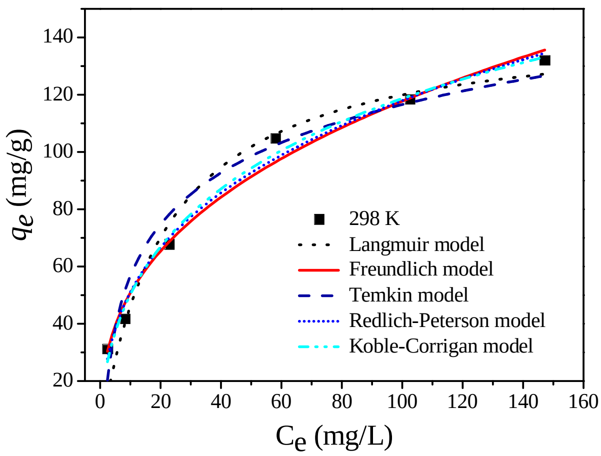

Fig. 2: Adsorption isotherms of the TC adsorption at 298 K.

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

The derivation of the Temkin isotherm assumes that the heat of adsorption of all molecules in the layer decreases linearly with the coverage of adsorbent surface. The Temkin isotherm can be presented as (Fu et al. 1994):

$$q_e = A + B\ln C_e \qquad \text{...(5)}$$

Where, A and B are Temkin constants.

Redlich-Peterson isotherm is a three-parameter equation, which combines the features from Langmuir and Freundlich isotherms. It can be used in a wide concentration range, including the homogeneous or heterogeneous systems. The model is expressed as (Foo & Hameed 2010):

$$q_e = \frac{AC_e}{1 + BC^g_e} \qquad \text{...(6)}$$

Where, A ($L.g^{-1}$) and B ($L.mg^{-1}$) are the Redlich-Peterson isotherm constants, g is the Redlich-Peterson isotherm exponent.

Koble-Corrigan isotherm is another three-parameter empirical model. It is also related to Langmuir and Freundlich isotherm models and expressed as (Han et al. 2005):

$$q_e = \frac{AC^n_e}{1 + BC^n_e} \qquad \text{...(7)}$$

Where, A, B and n are the Koble-Corrigan parameters, respectively.

From Fig. 2, it is observed that the five isotherm models fitted the equilibrium data well at 298 K. As presented in Table 1, the correlation coefficient (R^2) of Freundlich model at 288 K, 298 K and 308 K were 0.976, 0.984 and 0.981, respectively. The R^2 value by Redlich-Peterson was higher than 0.973, while it was 0.987 for Koble-Corrigan model. The R^2 values were lower than 0.960 calculated by Langmuir and Temkin models. Obviously, these three models including Freundlich, Redlich-Peterson and Koble-Corrigan are comparatively better to describe the experimental data than those of Langmuir and Temkin models. Meanwhile, the optimal Freundlich model indicates the chemisorption as heterogeneous. By Langmuir model, the calculated q_{max} for TC at 298, 308 and 318 K achieved 110.4, 145.9 and 176.0 mg/g, respectively. The q_{max} gradually increased with the increase in reaction temperature, which demonstrated an endothermic process. Therefore, the La-modified Fe_3O_4 shows a great adsorption capability for practical water purification.

Thermodynamic analysis: Thermodynamic parameters can provide additional support to the findings from isotherms, which is associated with standard free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°). These thermodynamic parameters were calculated by the following equations (Yuan et al. 2009):

$$\Delta G^0 = -RT\ln K_0 \qquad \text{...(8)}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad \text{...(9)}$$

$$\ln k_0 = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad \text{...(10)}$$

According to the actual adsorption experimental data, Fig. 3 expresses the plot between $\ln(q_e/C_e)$ versus q_e and Fig. 4 presents the plot between ΔG° versus T. From Fig. 4 we can get the calculated values of ΔH° and ΔS° from the slope and intercept. The calculated values of ΔH°, ΔS° and ΔG° were listed in Table 2.

Table 1: Adsorption isotherm parameters fitted by the Langmuir, Freundlich, Temkin, Redlich-Peterson and Koble-Corrigan models.

	Nonlinear fitting parameters		
	288 K	298 K	308 K
Langmuir			
q_{max}(mg/g)	110.4	145.9	176.0
k_L(L/mg)	0.046	0.046	0.055
R^2	0.953	0.950	0.959
Freundlich			
k_F(mg/g)	17.49	21.83	28.56
n	2.85	2.73	2.79
R^2	0.976	0.984	0.981
Temkin			
A	-6.31	-3.22	5.08
B	20.58	26.00	30.39
R^2	0.959	0.948	0.950
Redlich-Peterson			
A	18.71	47.39	42.90
B	0.719	1.755	1.066
g	0.724	0.674	0.709
R^2	0.973	0.980	0.980
Koble-Corrigan			
A	13.32	18.44	23.22
B	0.073	0.062	0.079
n	0.559	0.515	0.558
R^2	0.980	0.985	0.987

Table 2: Values of thermodynamic parameters for TC adsorption at different temperatures.

T/K	LnK°	ΔG° (KJ·mol^{-1})	ΔH° (KJ·mol^{-1})	ΔS° (J·mol^{-1}·K^{-1})
288K	2.519	-6.032	29.83	124
298K	2.875	-7.123	29.83	124
308K	3.327	-8.519	29.83	124

From Table 2, it was obviously found that ΔH° and ΔS° were 29.83 KJ·mol^{-1} and 124 J·mol^{-1}·K^{-1}, respectively. Meanwhile, the positive value of ΔH° revealed that TC adsorption onto La-modified Fe_3O_4 was an endothermic process. The increase in reaction temperature is conducive to the adsorption process, which was consistent with the aforementioned experimental results. Meanwhile, the positive value of ΔS° is related to the increased randomness during the adsorption. The ΔG° values were negative at 288 K, 298 K and 308 K, indicating the spontaneous process in nature. Additionally, ΔG° decreased slightly with the increase of temperature from 288 K to 308 K, which further indicated the rise of temperature would benefit the adsorption.

CONCLUSION

Rare earth element lanthanum was innovatively used to modify nanao-Fe_3O_4 by a chemical co-precipitation method to prepare La-modified Fe_3O_4. At a dose of 5 mg, the

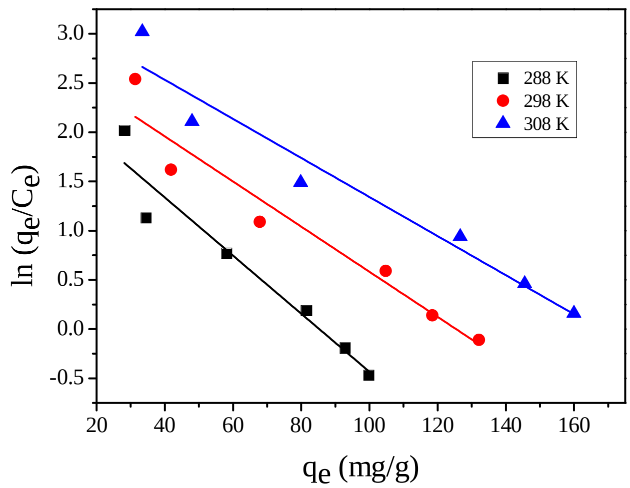

Fig. 3: Plots of ln(q_e/C_e) versus q_e for adsorption of TC onto La-modified Fe_3O_4 at different temperatures.

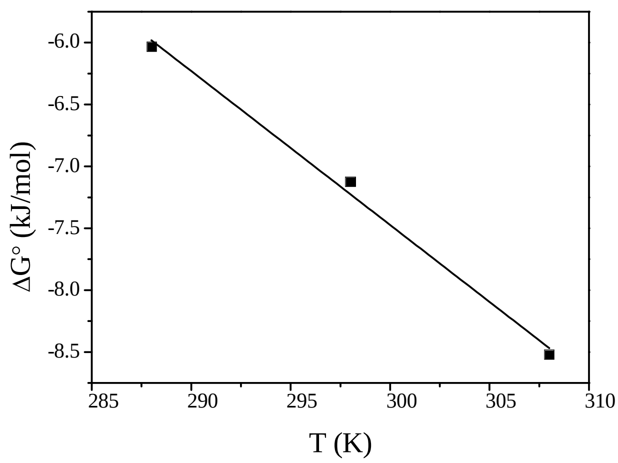

Fig. 4: Changes of free energy (thermodynamic calculations).

uptake of tetracycline achieved as much as 83.29 mg/g, indicating an excellent adsorption capability of the magnetic adsorbent. The equilibrium adsorption data were fitted by Langmuir, Freundlich, Temkin, Redlich-Peterson and Koble-Corrigan models. The R^2 values of Freundlich, Redlich-Peterson and Koble-Corrigan models were higher than those of Langmuir and Temkin models. This indicates the chemisorption might occur on the heterogeneous adsorbent surface. At 298 K, the q_{max} values by Langmuir model were of 145.9 mg/g. Thermodynamic analysis indicates that ΔH° and ΔS° were 29.83 KJ·mol^{-1} and 124 J·mol^{-1}·K^{-1}, respectively. This demonstrates the adsorption process was spontaneous and endothermic in nature.

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