



Rapid adsorption of tetracycline from aqueous solution on fly ash

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ABSTRACT

In this study, we use fly ash (FA), which is considered as the solid waste, to explore its absorption capacity of tetracycline (TC). We chose one kind of FA, which is obtained from factory, to use in the experiment. The effect of adsorbent dosages, pH, contact time, adsorption kinetics and isotherm were studied. The physical and chemical characteristics were analyzed by scanning electron microscopy, Fourier-transform infrared spectroscopy. As for adsorption kinetics of the FA, it is mostly consistent with the pseudo-second-order model, and the equilibrium time was attained after about 20 min. Besides, the maximum removal rate of TC by FA was about 87%. In this study, we found that Brunauer–Emmett–Teller model was the best fitted one compared with Langmuir isotherm model and Freundlich isotherm model, which indicated that it was a multi-molecular adsorption process. Also through the adsorption and characterization experiment, we suggested cation exchange was the major mechanism of TC adsorption on FA.

Keywords: Antibiotic contamination; Ion exchange; Pollutant removal; Solid waste

1. Introduction

Globally, the average total annual use of antibiotics is approximately 200,000 tons [1]. Tetracycline (TC) is one of the most widely used class of veterinary and human antibiotics [2]. However, the majority of TC cannot be absorbed by the animals or humans to which they are applied [3]. In the process of biological metabolism, the vast majority of TC is discharged through feces and urine directly from the body and, ultimately, into the water environment, which

leads to water pollution [1]. Furthermore, TC may cause bacterial resistance, resulting in ecological destruction and threatening human health through bioaccumulation in the food chain [4–6]. Therefore, it is vital to develop economical, efficient and environmentally friendly technologies to remove TC from wastewater.

For removing TC in water, different technologies have been developed, such as microbial degradation [7], photocatalytic degradation [8–11], advanced oxidation [12], membrane separation [13,14]. But corresponding to these

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methods there are some defects, such as photocatalytic degradation easy cause secondary pollution [15], advanced oxidation efficiency is high, but can't realize the recycling the TC and the cost is high, at the same time, the degradation process of intermediate risk needs to be evaluated [16], and membrane separation, although have a very good effect on intercept to TC, high energy consumption and membrane pollution [17]. Adsorption was an old but clean, simple, and efficient process to remove aqueous pollutants [18–21]. Since the application of the adsorption method in the removal of organic pollutants in water is low cost, efficient and convenient to use [22,23], more and more attention has been drawn to it [24]. Many adsorbents, such as activated carbon [25], bamboo charcoal [26], clay [27], polymers and particles [28], have been used to remove TC from water.

Nowadays, there has been an increasing interest in the utilization of natural materials and industrial wastes, which can be taken as an alternative to traditional adsorbents [29,30]. Fly ash (FA), fine ash collected from the flue gas after coal combustion, is the main solid waste discharged from coal-fired power plants [31,32]. It is generally captured from flue gas by electrostatic precipitators or other particle filtration equipment before the flue gases reach the chimneys [33,34]. FA consists of both amorphous aluminosilicate material and crystalline phases, mainly α -quartz (SiO_2), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), hematite ($\alpha\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4) [35]. FA is counted as an irritant that accounts for air pollution and also poses disposal difficulties [36]. Nowadays, the reuse of FA has attracted wide attention. Expect some important areas of FA application, such as concrete production, road basement material, waste stabilization/solidification, cement clinkers and more recently geopolymers concrete, some scholars have focused their attention on the adsorption of pollutants by modified FA [31,37]. Scholars studied the adsorption behavior of zeolite X which was synthesized by hydrothermal method with coal FA pretreated by alkaline fusion and centrifugal extraction on Cu^{2+} ion, and found that the thermodynamic parameters indicated that adsorption process is spontaneous and endothermic [38]. Liu et al. [39] prepared FA into $\text{CeO}_2\text{-CuO/FA}$ by liquid phase impregnation at room temperature, which improved the adsorption efficiency of SO_2/NO . Also, scholars studied the adsorption properties of FA modified by HCl on Cu^{2+} , Ni^{2+} , Cr^{6+} in heavy metal wastewater [40]. In our previous study, we utilized FA to remove metolachlor and acetochlor and showed a good adsorption ability [41]. Its saturated adsorption capacity can reach 19.18 mg g^{-1} for metolachlor and 42.12 mg g^{-1} for acetochlor. However, the behavior for adsorbing TC on FA has a few reports.

This work focused on the influence of the adsorption properties of TC antibiotics. The influence of adsorption time, initial pH value and adsorbent dosages on the adsorption properties of TC antibiotics were investigated. The adsorption kinetics and adsorption isotherms of TC for FA were analyzed. The formation mechanism and stability of the functional sets on the surface of FA were investigated by using the chemical properties and structure characteristics. Based on the interaction between FA and TC, the adsorption mechanism of surface functional groups of FA was analyzed. The results of the research can not only make many kinds of waste FA resourceful, but also provide a

new method for the clearness of wastewater containing TC, which is of great practical significance.

2. Materials and methods

2.1. Materials

The adsorbent (FA) of this study was obtained from coal-fired power plants of Harbin Hatou Investment Co., Ltd. FA collected directly from the bottom of the boiler. A certain amount of FA obtained before was weighed in the laboratory and was washed in a boiling water bath with distilled water for 10 min, then filtered by filter paper. Repeated washing ten times until pH was nearly neutral. Immerse the FA in distilled water and heat it to 100°C with a constant temperature water bath to remove the oily substances that may be contained. Then it was dried in an oven for 24 h and filtered with 30 mesh sieves after drying. The adsorbents were held in a thermostatic chamber at 60°C for 48 h. TC (>96% purity) was obtained from Tianjin Ding Guo Biotechnology Co., Ltd. The purity of all chemicals was an analytical reagent.

2.2. Physical and chemical characteristics of FA

The surface structure of adsorbent was analyzed by using a scanning electron microscopy (SEM) Se3400 N (Hitachi Ltd., Tokyo, Japan). The surface functional groups of FA were analyzed by Fourier-transform infrared spectroscopy (FTIR) IRPrestige-21 (Shimadzu Ltd., Tokyo, Japan). The contents of basic functional group and acidic functional groups (carboxylic group, lactonic group and phenolic group) of FA surface were determined by acid base neutralization. The oxygen functional set on the surface of FA can be quantitatively analyzed according to the reaction between acid or base and surface oxidation [40]. The basic groups are neutralized by addition of HCl solution and the acidic groups are neutralized by addition of NaOH, Na_2CO_3 , or NaHCO_3 solutions. Among them, NaOH solution ($\text{pK} = 15.74$) can neutralize carboxylic group, lactonic group and phenolic group, and Na_2CO_3 solution ($\text{pK} = 10.25$) can neutralize carboxylic and lactonic groups, whereas NaHCO_3 solution ($\text{pK} = 6.37$) neutralizes only carboxylic group. In the experiments, FA were respectively (0.5 g) put in the conical flask added 25 mL NaOH (0.1 mol L^{-1}), Na_2CO_3 (0.05 mol L^{-1}), or NaHCO_3 (0.1 mol L^{-1}) solution with constant temperature oscillation for 24 h under 25°C . Among them: (1) The number of basic groups was equal to the amount of HCl solution consumed. (2) The number of acidic groups was equal to NaOH solution consumption. (3) The amount of carboxylic group was equal to the consumption of NaHCO_3 solution. (4) The amount of phenolic group was equal to NaOH solution consumption minus the amount of Na_2CO_3 solution consumption. (5) The amount of phenolic group base was equal to the Na_2CO_3 solution consumption minus the NaHCO_3 solution consumption. The point of zero charge (pH_{pzc}) of the adsorbents FA was determined to use the pH drift methods [42]. The speciation drawing of TC as use of pH was taken from the methods of some scholars [43,44]. The solution speciation's of TC were modeled under different experimental conditions followed Chen's method [45]. Elemental analyses were carried out for FA using analyzers CORDER MT-6 (Yanagimoto Co., Ltd., Japan).

2.3. Adsorption kinetics studies

The control mechanism of the adsorption process is described by two kinetic models of pseudo-first-order and pseudo-second-order models. The adsorption capacity is calculated by the following equation:

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

where q_e is the amount of TC ions adsorbed per unit weight of adsorbents (mg g^{-1}), C_0 is the initial concentration (mg L^{-1}) of TC ions in solution, C_e is the equilibrium concentration (mg L^{-1}) of TC in solution, V is the adsorbate solution volume (L), and W is the adsorbent weight (g).

The kinetic rate equation is as follows:

$$\frac{dq_t}{dt} = (q_e - q_t)^n \quad (2)$$

where q_e and q_t correspond to the amount of TC adsorbed per unit mass of adsorbent (mg g^{-1}) at equilibrium and at time t , respectively. k_n is the rate constant for n th order adsorption (k_n units are $1/\text{min}$ for $n = 1$ and $\text{g mg}^{-1} \text{min}^{-1}$ for $n = 2$). The linearized integrated forms of the equations are shown as follows:

First-order kinetics ($n = 1$) and second-order kinetics ($n = 2$):

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

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

The straight-line plots of $\ln(q_e - q_t)$ against t and of t/q_t against t were used to determine the rate constants and correlation coefficients (R^2) for the first and second-order kinetic models, respectively. The fitting equation was selected based on the linear regression, R^2 , and the calculated q_e values.

2.4. Adsorption isotherm models

Three isotherms models: Langmuir, Freundlich and Brunauer–Emmett–Teller (BET) model were used to fit experimental data to analyze the adsorption behavior between TC and FA.

The Langmuir isotherm model equation is as follow:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (5)$$

where q_m (mg g^{-1}) is the maximum adsorption amount and K_L (L mg^{-1}) is the Langmuir constant related to the adsorption energy.

The Freundlich isotherm model formula is as follow:

$$\ln q_e = \ln K_F + \frac{1}{n} C_e \quad (6)$$

where K_F is the adsorption capacity per unit concentration, and n^{-1} is the adsorption intensity. $n^{-1} < 0$, the adsorption is irreversible; $0 < n^{-1} < 1$, the adsorption is desirable; $n^{-1} > 1$, the adsorption is undesirable.

BET two constant formula:

$$V = \frac{V_m \cdot C_p}{(p_0 - p) \left[1 + \frac{(C-1)p}{p_0} \right]} \quad (7)$$

where V_m is the saturated adsorption capacity mL g^{-1} when the surface is covered with a monolayer, C constant, V is the total volume of adsorbate, p_0 is the saturated vapor pressure of the condensate, p is the pressure, x is the relative pressure (p/p_0).

When adsorption occurs on a porous material, the number of adsorption layers is limited. If there are only n layers, the BET three-constant formula can be obtained:

$$V = \frac{V_m C_x}{(1 + C_x)} = V_m \frac{\left(\frac{C}{p_0}\right)^p}{1 + \left(\frac{C}{p_0}\right)^p} = V_m \frac{bp}{1 + bp} \quad (8)$$

When $n = 1$, BET evolves into the Langmuir single molecule adsorption equation. In the above formula, x is the relative pressure (p/p_0).

2.5. Procedure for the adsorption experiment

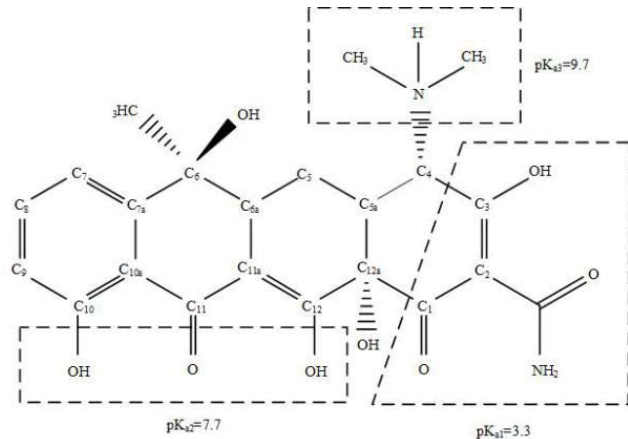
The influence of several parameters, such as contact time, adsorbent dose and the initial pH were investigated. Adsorption kinetics data were obtained by using 25 mL liquids containing TC (10 mg L^{-1}) solution and 150 mg adsorbent at a rotational speed of 150 rpm for 1 h in a shaker. Adsorption isotherms data were obtained by using the different concentrations of TC were adsorbed by FA. After equilibrium, the centrifuge (IEC61010-2-020, KUBOTA, Japan) was used to separate the TC solution from the adsorbents at 4,500 rpm for 10 min. The concentration of TC was determined with ultraviolet visible spectrophotometer V-1800 (Shimadzu Co., Tokyo, Japan) at 276 nm wavelength. The concentration of TC was calculated using a standard curve based on the Lambert–Beer law. In the whole experiment, the pH was adjusted with 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH. Throughout the study, the contact time of FA was studied from 0 to 1 h, the pH was adjusted from 3.0 to 11.0, the initial TC concentration ranged from 10 to 150 mg L^{-1} , and the dosage of adsorbent is $1.0\text{--}8.0 \text{ g L}^{-1}$. Adsorption temperature was kept at 25°C , at a rotational speed of 150 rpm in a shaker. Each treatment has three replicates and the average of the three tests was determined.

3. Result and discussion

3.1. Characterization

The chemical structure and properties of TC are shown in Table 1. TC is a hermaphrodite molecule with three

Table 1
Chemical structure and properties of tetracycline hydrochloride

CAS Registry Number	64-75-5
Chemical structure	
Chemical formula	$C_{22}H_{24}N_2O_8 \cdot HCl$
Molar mass	480.9 g mol^{-1}
Solubility in water	0.041 mol L^{-1}
λ_{max}	362 nm

corresponding pK_a values (3.3, 7.7 and 9.7) [46]. The main components of FA are SiO_2 , Al_2O_3 , and Fe_2O_3 , they make up about 85% of FA. To investigate the pore structure of FA, we used SEM to scan this adsorbent. The result is shown in Fig. 1. In Fig. 1 we can see that the pore structure of FA surface is rough and has some irregular porous. It is apparent that irregular spherical particles had a rough surface that was full of non-uniformly distributed and highly disordered agglomerates. And from other studies, we could see that the crystal structure and composition of FA were similar to that of kaolinite (consisting of two inter-linked layers, tetrahedral SiO_4 layer and octahedral $AlO_2(OH)_4$ layer) [47].

The FTIR of FA is shown in Fig. 2. TC has multiple polar/ionizable functional groups, including phenol, alcohol, ketone and amino groups, which makes TC completely soluble in water but insoluble in non-polar hydrophobic phase [48]. Among them, the peak nearby 470 cm^{-1} can be attributed to Si–O and Al–O bending vibration, the peak nearby 780 cm^{-1} can be attributed to Al–OH stretching vibration bond, and the peak nearby $1,093 \text{ cm}^{-1}$ can be attributed to framework vibration of Si–O–Si [49]. The main changes are as follows: (1) After the adsorption, the absorption peak of the C=O stretching vibration of FA was shifted to a lower wave number, which might due to the interference of C=O stretching vibration after FA adsorbed TC. (2) The framework vibration of Si–O–Si of FA shifted from $1,093.89$ to $1,093.11 \text{ cm}^{-1}$ [50], and the absorption peaks became weaker, which indicated that hydrogen bonding or surface complexation might occur between TC and FA. (3) The fingerprint region ($800\text{--}400 \text{ cm}^{-1}$) of FA changed obviously after TC was adsorbed. The peak of Al–OH stretching vibration (797.16 cm^{-1}) became weaker as well as the peak of Al–O and Si–O bending vibration (469.73 cm^{-1}) [51], indicating that TC might have a complex

reaction with the cation of FA. Also in the FTIR spectrum of the FA after adsorption, the peak OH stretching was transferred from $3,431$ to $3,428 \text{ cm}^{-1}$, and the appearance of the new band at $1,895 \text{ cm}^{-1}$ (COH) was clearly observed. These results indicate that the oxygen-containing groups of FA may play an important role in the adsorption process by forming hydrogen bonds between the amino groups of TC [52]. In addition, a change in the spectrum in the range of $1,617\text{--}1,612 \text{ cm}^{-1}$ indicates that π -electron-involved due to the strong electron-withdrawing ability of the ketone group, the conjugated ketene structure of the TC molecule can exhibit a π -electron acceptor, and adsorption bonding. It strongly interacts with the polarization-rich electronic structure of biochar as a π -electron donor.

3.2. Adsorption kinetics

The adsorption rate of adsorbents can be determined by many factors, including its structure, adsorbent dosages, pH value. As a result, it is important to both experiment and practical application to decide the adsorption equilibrium time. The effect of contact time is shown in Fig. 3a. It shows that the adsorption rate increased rapidly at the beginning and then slowed down until adsorption equilibrium reached. This is because at the initial stage, the mass concentration of the adsorbents is high in the solution and the adsorption sites were more. During the adsorption process, the adsorption sites were gradually occupied and the adsorption rate decreased. The equilibrium time of the adsorbent is about 20 min, which is pretty short compared with other adsorbents [34]. It indicated that the adsorption is a process dominated by chemical adsorption. And the short equilibrium time makes FA a potential adsorbent in practice.

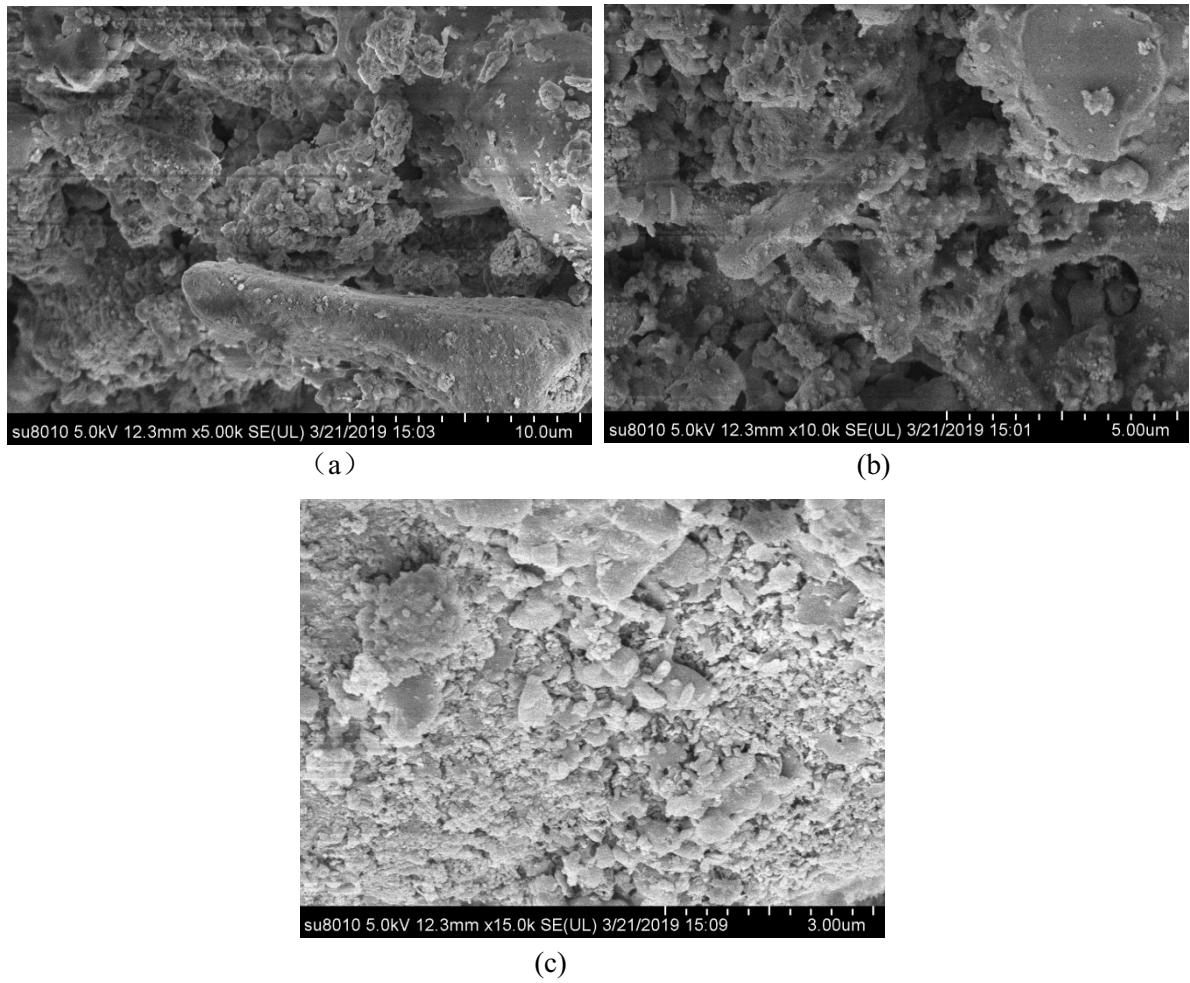


Fig. 1. (a–c) SEM images of FA under different magnifications and angles.

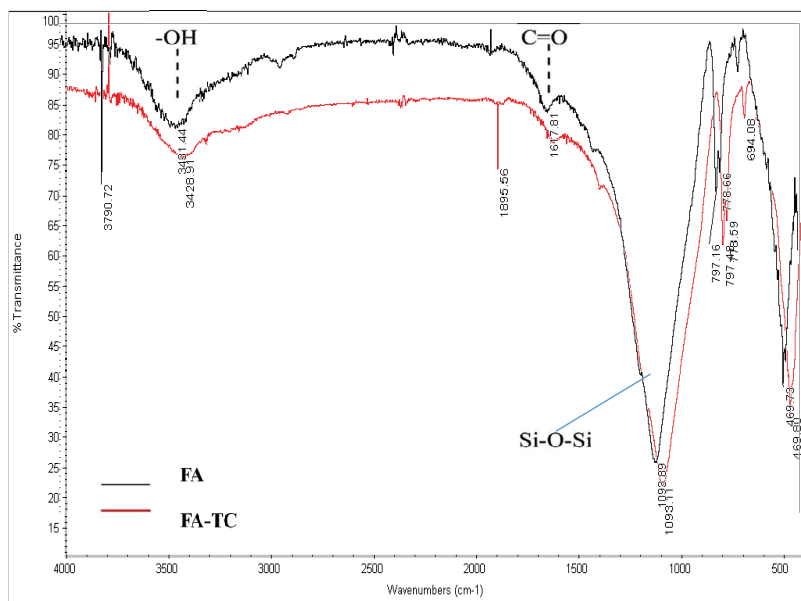


Fig. 2. The FTIR spectrograms of FA before and after TC adsorption.

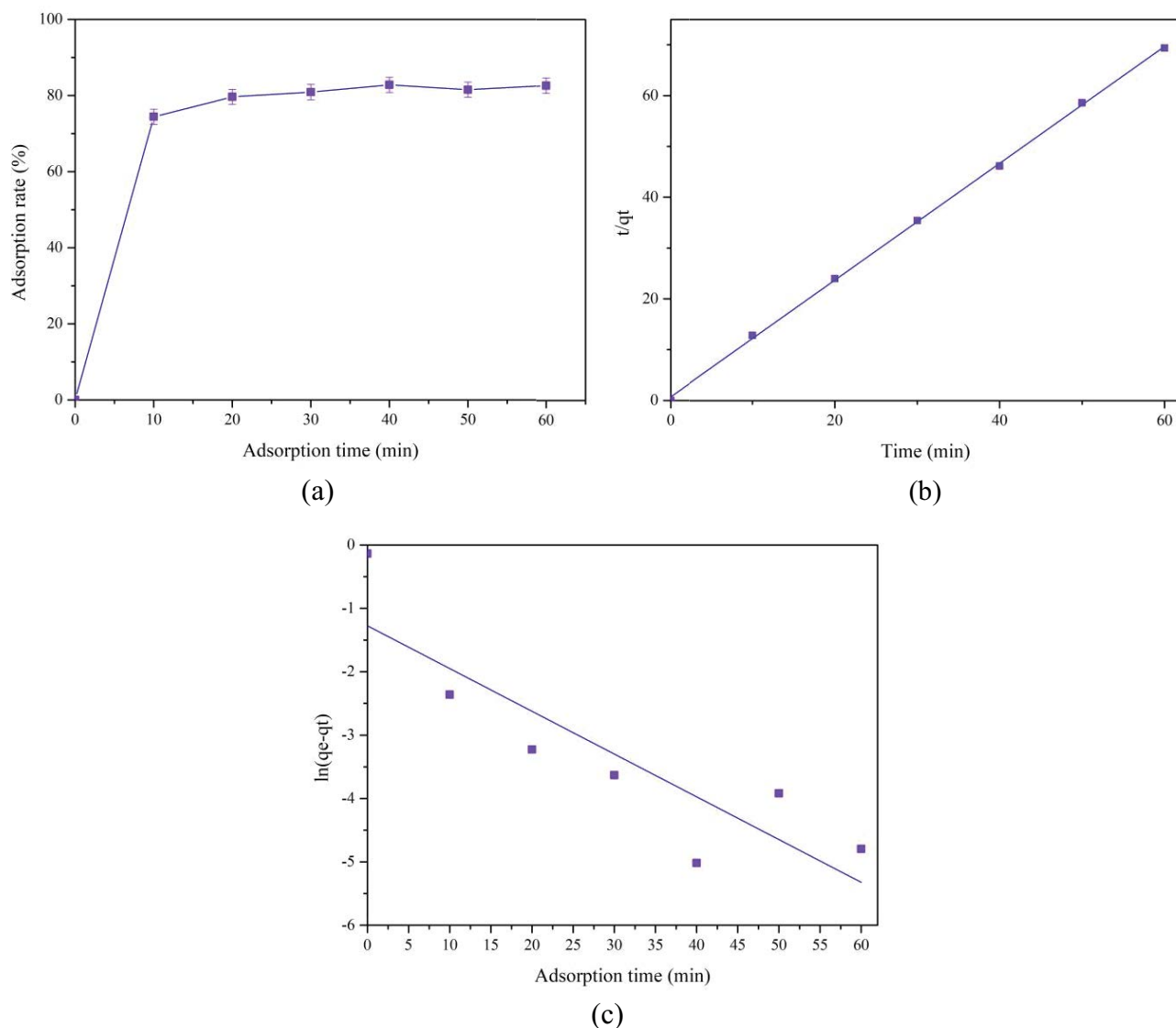


Fig. 3. (a) Effect of adsorption time of TC by FA (0–1 h); kinetic model of TC on FA: (b) pseudo-first-order and (c) pseudo-second-order.

The pseudo-first-order model and pseudo-second-order model were applied to fit the experimental data. As is shown in Table 2, the R^2 of pseudo-second-order had a much higher degree of fitting compared with the pseudo-first-order, and the $q_{e,cal}$ calculated by pseudo-second-order was similar to that of experimental, which shows that the pseudo-second-order model was fitted to the adsorption data. As we can see, the adsorption equilibrium could be reached in a short time. The pseudo-second-order model assumes that the adsorption process is two stages of rapid adsorption and slow adsorption, and the FA adsorption reaction process is consistent with this assumption [53]. Since the pseudo-second-order kinetic model is based on the assumption that the adsorption rate is controlled by the chemical adsorption process, the FA adsorption kinetics may be jointly controlled by the number of adsorption active sites (adsorption reaction) and the network structure of the adsorbent (internal diffusion). It can be

seen that the pseudo-secondary mechanical equation can simulate the adsorption kinetics of TC on FA [54].

3.3. Effect of adsorbent dosages

The effects of dosage of FA on TC were tested from 1.0 to 8.0 g L⁻¹, as shown in Fig. 4. With the dosages of adsorbents increasing, the adsorption ratio increased quickly. While the adsorbent dosage was higher than 6.0 g L⁻¹, the adsorption rate wasn't increased as it was considered to be. For the FA, we can see that when the adsorption ratio reached the maximum (88%), the adsorbent dosage is 8.0 g L⁻¹. For further experiments, we found that a small amount of adsorbent has a limited adsorption capacity in a higher concentration of TC solution, but then we can see that as the amount of adsorbent added increases, the adsorption removal rate also increases rapidly (Fig. 4). The adsorption sites increase with the dosage of the

Table 2
Parameters and correlation coefficients of pseudo-first-order and pseudo-second-order

Types of pesticides	TC	
Pseudo-first-order model	K_1 (1/min)	0.0675
	$q_{e,cal}$ (mg g ⁻¹)	0.279
	R^2	0.722
Pseudo-second-order model	$q_{e,cal}$ (mg g ⁻¹)	0.870
	K_2 (1/min)	1.83
	R^2	0.9997
	$q_{e,exp}$ (mg g ⁻¹)	0.865

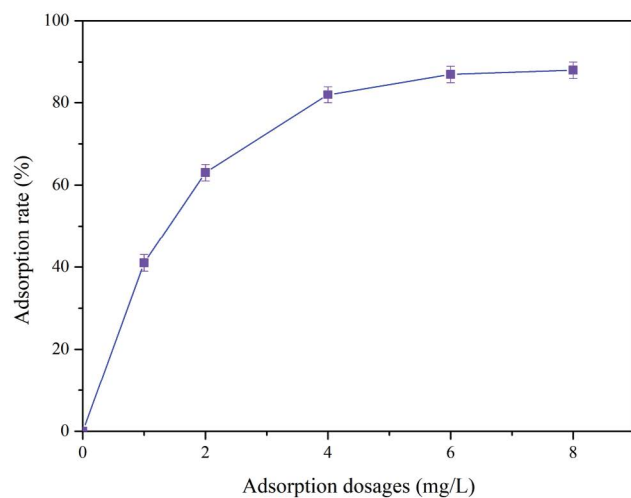


Fig. 4. Effect of adsorption dosage of TC by FA (0–8 mg L⁻¹).

adsorbent, so the removal rate of the adsorbate increases accordingly. In general, the surface area and available sites are usually relative to the adsorbent amount [29]. However, the adsorbent dosage exceeds the optimum amount, and the removal rate remains stable [7]. The phenomena were similar to the adsorption research of TC reported previously [55,56].

3.4. Effect of pH

The pH value can affect both the presence of the adsorbate in the solution and the surface of the adsorbent [57]. The results of the effect of pH are shown in Fig. 5a, with the pH ranged from 3.0–11.0. Although the adsorption removal rates are quite different, the removal ability of the adsorbent shows the same trend when the pH changes. Under alkaline condition, the adsorption rate was much lower than that of other conditions. We can see that, along with the increasing pH values, the adsorption rate gradually decreased. The final pH after the adsorption reaction was measured and the difference between the initial pH (pH_i) of the solution and the final pH (pH_f) was calculated, as is shown in Fig. 5b. The dissociation constants of TC in water were pK₁ = 3.3, pK₂ = 7.7, and pK₃ = 9.7. When the pH of the TC solution is lower than 3.3 (pK₁),

Table 3
Parameters of TC adsorption isotherms fitted with Langmuir, Freundlich and BET models

Models	TC	
Langmuir	q_m (mg g ⁻¹)	5.26
	K_L (L mg ⁻¹)	0.108
	R^2	0.968
Freundlich	K_F ((mg/g)(L/mg) ^{-1/n})	1.75
	1/n	2.23
	R^2	0.0910
BET	q_m (mg g ⁻¹)	5.85
	K	45.7
	R^2	0.998

the main form of TC in water is TCH³⁺; when the pH of the solution is between 7.7 (pK₂) and 9.7 (pK₃), TC will exist in the form of TCH⁻ and TC²⁻ [58], and the proportion of negative charge in TC molecules increased. The pH value also affects the surface charge of FA, which leads to a strong repulsion between TC and FA. According to the results of better adsorption effect in the presence of a large number of cations, we can preliminarily infer that electrostatic interaction may play an important role in the adsorption process. As a result, within the tested pH range, when the pH value of the solution was acidic, FA may have the best adsorption effects on TC. The trend presented in this research was similar to the earlier study [59]. In the study of adsorption of non-ionic compounds on FA, the trend is different from this study [41]. Fig. 5c shows the point of equal charge of FA, which is about 6.6 < 7.0. This indicates that the FA surface is negatively charged.

3.5. Adsorption isotherm

The isotherms curves of TC remove by FA at 25°C and pH 7.0 are shown in Fig. 6, which shows that as equilibrium concentration of the TC increasing, adsorption properties of FA was increased until equilibrium was reached. The saturated adsorption capacity (q_m) obtained by experiment was 4.06 mg g⁻¹, and Freundlich, Langmuir, and BET model were figured out. The theoretical parameters of the used isotherms are listed in Table 3. The Freundlich isotherm can describe heterogeneous adsorption [59]. As it is shown in Table 3, the correlation coefficient (R^2) value of TC for Freundlich isotherm was 0.910, which isn't high enough, thus the adsorption process of TC by FA couldn't be well described by Freundlich model.

The Langmuir equation is the monolayer adsorption of a uniform surface, the energy relationship represented by the Langmuir equation is: The heat of adsorption does not change with adsorption, and the energy of each adsorption point does not change. This is obviously ideal adsorption [60]. We could see that the R^2 of the Langmuir isotherm model was 0.9680, which indicated Langmuir model suits the adsorption of FA well. The large value of K_L (0.1076 L mg⁻¹) showed that TC may have a great affinity for FA.

The BET isotherm model is mostly used to study the surface adsorption of solids on gases and liquid, and it is

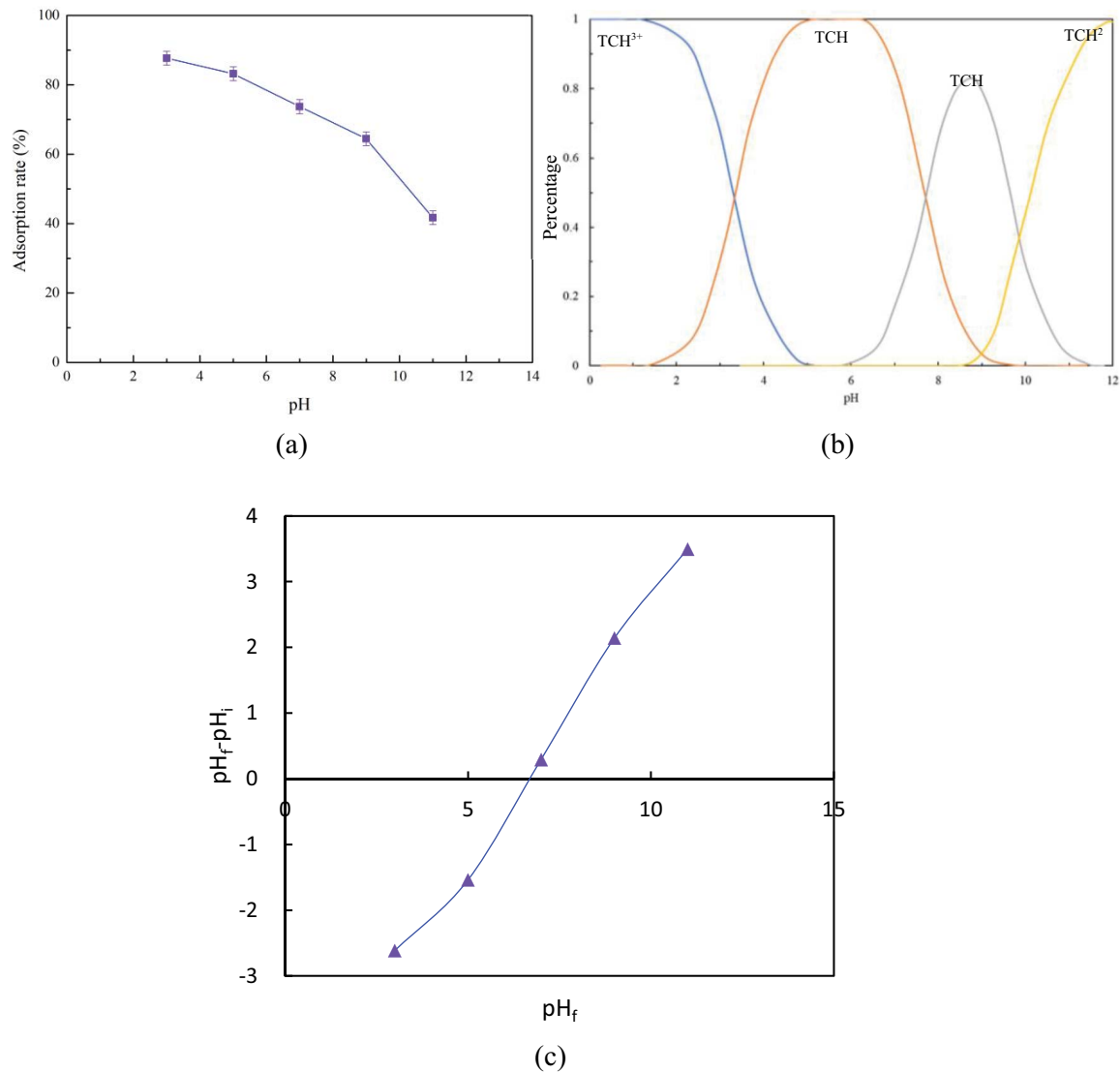


Fig. 5. Effect of pH: (a) adsorption capacity under the influence of pH, (b) exist form of FA under different pH and (c) determination of p*H*_{pzc} of FA.

applied to the surface adsorption phenomenon of research solutions [57]. It is generally used to describe multilayer adsorption, which belongs to physical adsorption based on van der Waals forces [61]. As it is shown, the *R*² value was 0.9976, which is higher than Langmuir model (0.9680). As a result, the process of adsorption can be seen as a BET adsorption process.

3.6. Adsorption mechanism

Scholars have a lot of experiments on TC adsorbents. The adsorption capacity of FA is compared with other adsorbents, and the results are shown in Table 4 [62–65]. By comparison, we found that the removal rate of TC by some adsorbents is not high, which is related to the number of adsorption sites of different materials. It also shows that FA has a better utilization efficiency of adsorption sites and can be used as a TC adsorbent in practice. At the

same time, different researchers choose different pH conditions for the adsorption of TC on different adsorbents. This is because the ionic (molecular) form of TC changes greatly at different pHs. This feature also provides many different methods for TC adsorption. Therefore, under different environments, the choice of TC adsorbent needs to be further studied.

The adsorption mechanism of TC is very complicated and is greatly affected by FA. Through the analysis of kinetics and isotherm model, we can see that the whole adsorption process includes both physical and chemical adsorption process, and chemical adsorption is dominant. Cation exchange and complexation should be the main mechanism.

Analysis of the adsorption isotherm model found that the adsorption process is very suitable for the BET model and can be regarded as a multi-molecule adsorption process. That is to say, after the adsorbent surface is filled with TC, the adsorption can continue due to the van der Waals force

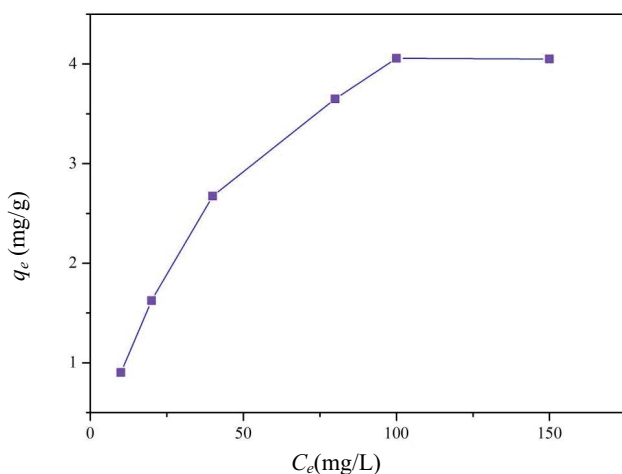


Fig. 6. Adsorption isotherm of TC on FA.

of TC itself. Which becomes a process of multi-molecular layer adsorption. The whole adsorption process has physical adsorption based on van der Waals force. At the same time, the fitting effect of FA to TC adsorption process and Langmuir isotherm model has reached a high level, indicating that TC is first adsorbed to the FA surface through the monolayer adsorption process assumed by the Langmuir model, and this process is Occurs on the surface of a homogeneous medium, and then undergoes a process of multi-molecular layer adsorption under the influence of Van der Waals force. The overall multi-molecular layer adsorption process can also explain the result of fitting with the Freundlich model ($R^2 = 0.9100$).

Through the analysis of adsorption kinetics, it is found that the adsorption process is more suitable for pseudo-secondary kinetics than the first-order kinetics, which proves that the adsorption process is mainly controlled by chemical adsorption [64]. And adsorption reaches equilibrium in a short time, which also shows that chemical adsorption is the main mechanism. Chemical adsorption generally requires a relatively short time, and the rapid adsorption of TC by FA also provides a good choice for practical applications.

The FA and the TC molecules are adsorbed by the intermolecular attraction force, and the chemical adsorption is mainly due to the Si–O–Si bond and Al–O–Al bond. The polarized molecules (TC) and the secondary positively

charged aluminum silicate, calcium silicate and silicic acid in the FA produce dipole-dipole bond adsorption, are an ion exchange process or formation of ion pairs [68]. From the increase in the adsorption rate of FA under acidic conditions, and the point of equal charge (Fig. 5c), we could charge that the adsorption of TC on FA is enhanced by the exchange of cation ligands and cation bridges under acidic conditions. In addition, the electrolyte has a large effect on the adsorption of TC, which further illustrates that electrostatic interactions such as ion exchange play an important role. However, because the surface charge is generally not high, the q_m of FA for TC is not high. In this study, the main adsorption mechanism is the cation exchange and complexation between Si, Al and other elements in FA and TC, which also makes the entire adsorption process faster and can reach equilibrium in a short time.

In addition, through the changes of the FTIR spectrums before and after adsorption, it can be milled that there is hydrogen bonding in the adsorption process, and the π – π electron interaction in the carbon–oxygen bond and the interaction exists throughout the adsorption process (Fig. 7).

4. Conclusion

We investigated the potential and adsorptive properties of this kind of FA as an adsorbent to remove TC. The adsorption kinetics and adsorption isotherm indicated that the adsorption of TC on the adsorbent was fitted for BET isotherm model. Therefore, adsorption process of TC may be multi-molecular layer adsorption. The adsorption equilibrium arrived at about 20 min, which is an extremely rapid process. FA can perform well when you need a high adsorption rate. The adsorption process is mainly controlled by cation exchange and complexation, hydrogen bonding, physical adsorption, and π – π electron interaction also contributed to the adsorption. As we could see from the result, FA could be an environmental-friendly and effective adsorbent to remove TC and contribute to relieving antibiotic contamination, and it still has the potential to be discovered.

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Table 4
Adsorption ratio and pH for the adsorption of TC onto various adsorbents.

Adsorbents	pH	Adsorption ratio (%)	References
Sludge-based adsorbent	Natural pH	37	[54]
Montmorillonite (MMT)	8	42	[55]
Cow manure biochar (CMBC700)	3	48	[56]
Spent coffee ground (SCG500)	7	60	[57]
FA	9	64	This study
Sodium dodecyl sulfate modified montmorillonite (SDS-MMT)	8	69	[55]
Magnetic sludge-based adsorbent	Natural pH	70	[54]

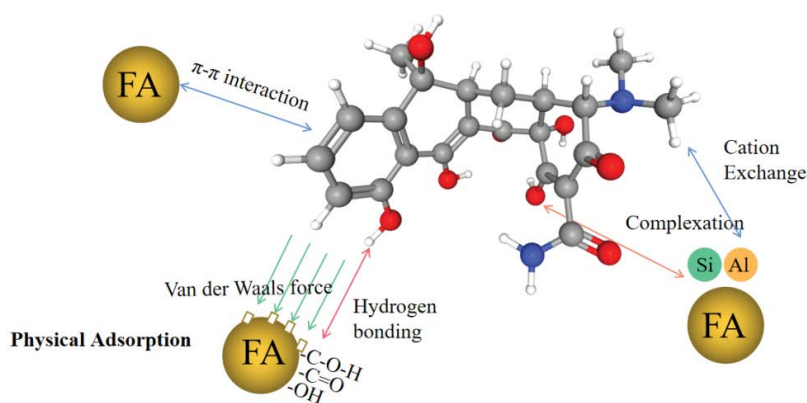


Fig. 7. The adsorption mechanism of TC on FA.

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