



Rapid adsorption of acetochlor and metolachlor from aqueous solution onto solid waste coal fly ash

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ABSTRACT

Coal fly ash (FA) as the solid waste was applied to explore the adsorption of acetochlor and metolachlor (herbicides). The effects of initial pH, contact time, temperature, and dosage of FA were explored. The physical and chemical characteristics of FA were analyzed by scanning electron microscopy, X-ray diffraction, and Fourier transform infrared spectroscopy. The adsorption kinetics of FA to acetochlor and metolachlor were most consistent with the pseudo-secondary model of other kinetic models, with R^2 values as high as 0.999 and the equilibrium time were attained after 10 and 15 min, respectively. Additionally, the maximum removal efficiencies of acetochlor and metolachlor (10 mg/L) by FA were 91.25% and 73.65%, respectively. Langmuir isotherm (for acetochlor, $R^2 = 0.9980$; for metolachlor, $R^2 = 0.9913$) was considered to be the better matched one than Freundlich, Dubinin–Radushkevich, and Brunauer–Emmett–Teller. The values of the saturated adsorption quantity got for acetochlor and metolachlor on FA calculated by the Langmuir model were 42.12 and 19.38 mg/g, respectively. The values of the saturated adsorption quantity predicted by the three-dimensional prediction model based on the pseudo-secondary dynamics were 42.76 and 16.57 mg/g, respectively, which were consistent with the Langmuir model. Moreover, the results of this paper suggested that there were a coexistence with physical and chemical adsorption processes of these two herbicides and the physical adsorption was the primary adsorption process of metolachlor on FA, while chemisorption played a dominant role in that of acetochlor on FA. The main adsorption mechanism might be the hydrogen bond and ligand exchange based on complexation.

Keywords: Composition; Adsorption capacity; Hydrogen bond; Complexation; Ligand exchange

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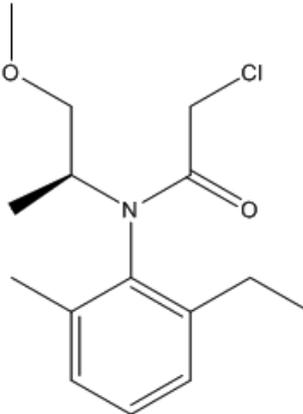
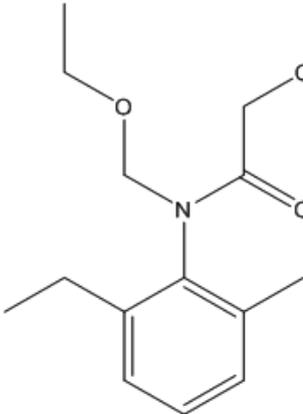
1. Introduction

Acetochlor, which is stable, non-volatile, and hydrophobic in nature, is the most representative pre-emergence selective systemic herbicide of amides. In addition, it has a certain water solubility [1–3]. Since its successful development, acetochlor has been one of the most important and widely used herbicide varieties in the world, especially in China with annual use of more than 10,000 tons [4,5]. Acetochlor is primarily utilized in weed control of corn, peanut, soybean, cotton, and other dryland crops [6]. The large application of guanamine acetochlor has caused global pollution [7,8], and there is evidence that acetochlor can be classified as endocrine disruptor (CEDC) [9]. Due to the potential genotoxicity of acetochlor, it is classified as a B2 carcinogen, and its use range is limited [10]. As another amide herbicide, metolachlor is one of the commonly used herbicides in sugarcane fields and gradually become the most commonly used chloroamide herbicide in corn fields with the use of over 30,000 tons every year in the mid-1990s in United States [11,12]. Trace amounts of metolachlor are toxic to both human beings and animals [13,14]. Their chemical structures and properties are shown in Table 1. In recent years, the adsorption method with low cost, high operability, and no secondary pollution has been widely used to remove herbicides in aqueous environments and soils. For acetochlor, researchers carried out three different biochar adsorption tests on acetochlor. The results showed that the biochar made from rice husks had the strongest adsorption capacity for acetochlor. The comparison showed that the adsorption properties of biochar to acetochlor was the result of the combined effects of biochar surface area and carbonization degree [4]. Some scholars have explored the adsorption of acetochlor on biochar at different temperatures. It was found that the adsorption of acetochlor on high temperature biochar was mainly affected by aromatic carbon components, and pore filling effect may be one of the main effects affecting the adsorption of acetochlor by biochar [3]. Another group of researchers studied the adsorption of acetochlor on organobentonite. The results showed that the arrangement of the modifiers of bentonite interlayer dominated the adsorption and release process. Increasing the amount of modifier in a certain range can enhance the interlayer spacing of organobentonite and the adsorption capacity of acetochlor [15]. In addition, the adsorption of acetochlor on modified montmorillonite [16], Mg-modified biochar [17], acidified black soil [18], OTMAC organobentonite, DTMAC organobentonite, and HTMAC organobentonite [19] were also studied by some scholars. For metolachlor, researchers studied the adsorption of metolachlor by periodic mesoporous organosilicas, the results suggested that the hydrophobic was the major mechanism in the adsorption of this herbicide as well as aromatic π - π interactions [20]. There were previously report about the biosorption of metolachlor on rice-straw-derived biochar, which shown that the adsorption capacity of metolachlor on D350 (rice-straw-derived biochar) prepared at the pyrolysis temperature of 350°C was significantly higher than that of straw raw material. Pyrolysis made the pore of the adsorption material developed gradually, the polarity decreased, the relative contribution of surface adsorption

increased, and the relative contribution of distribution decreased [21]. Generally speaking, among these adsorbents, it is hard to look for a kind of adsorbent which has many advantages such as fast adsorption equilibrium time and large adsorption capacity. Although there were many previously reported about the removal of acetochlor and metolachlor with different adsorbents, the adsorption of acetochlor and metolachlor by coal fly ash (FA) as an has rarely been reported.

FA is a mainly by-product from coal-fired power plants and coal combustion. The world's annual output of FA is estimated at 3.5 million tons/y [22–24]. It is estimated that by 2020, the accumulated reserves of FA will exceed 3 billion tons [25]. Its composition could change extremely based on the source of the coal and the combustion conditions [26,27]. FA has a certain morphological effect, micro-aggregate effect, and a pozzolanic effect [28]. It is generally dumped in landfills, but it has been widely used in road construction, cement production, zeolite synthesis, and other aspects [29]. At present, it is mainly used in cement and concrete industry, which can not only save the amount of cementitious materials, but also improve the working performance of concrete, the strength [30], and the freeze-thaw resistance [31]. In addition, a small amount of FA is also used in the study of geotechnical engineering [32], soil improvement [33]. However, the recovery and utilization of FA is far from enough, and its new application remains to be explored. In recent years, some scholars have studied the adsorption of pollutants by FA. There are some researchers studied the performance of the adsorption of sulfonated humic acid onto FA that was modified by microwave-assisted in solutions, which indicated that the adsorption properties of modified FA were greater than that of raw materials. Comparing the effects of adsorption of different factors, the initial pH of solution was the most critical factor [34]. Some researchers obtained an inexpensive mesoporous silica material by modifying FA as raw material, and the adsorption time of the material for sulfate was 5 min. The FA is a kind of cheap adsorbent that the adsorption capacity was 146.1 mg/g, three folds greater than that of commercial active carbon that previously reported [35]. Other research workers compared the tannic acid adsorption properties onto FA, NaOH treated FA, and chitosan modified NaOH treated FA and found that the saturated adsorption amount of chitosan/NaOH/FA composite was greater than that of FA and NaFA. Another group of researchers added a geopolymer monolith to FA to adsorb lead in wastewater, which was one of the first investigations concerning the use of geopolymeric monoliths as adsorbents [36]. On the applications of the FA, the powder FA was made into granular form as an adsorbent for removal pollutant in a sewage treatment plant [37]. In a word, FA in this experiment, as a kind of waste, has the characteristics of fast adsorption speed, large adsorption capacity, and strong regeneration capacity for pesticides and other pollutants in water. It is an excellent environmental adsorbent, which can be used as the raw material of ceramic membrane and the filling adsorbent of fixed bed adsorbents. It has a broad application prospect in wastewater treatment. Besides, there are few studies on FA adsorbing acetochlor and metolachlor have been reported.

Table 1
Chemical structure and properties of acetochlor and metolachlor

Types of pesticide	Metolachlor	Acetochlor
Structure		
Molecular formula	$C_{15}H_{22}ClNO_2$	$C_{14}H_{20}ClNO_2$
Molecular mass (g/mol)	283.8	269.8
$\text{Log}K_{ow}$	3.05	3.03
Water solubility (mg/L) (25°C)	530	223

In this work, FA were applied to remove acetochlor and metolachlor in aqueous solutions. The characterization of FA were investigated by using the X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transformed infrared (FT-IR) spectroscopy. This study explored the effects of the surface functional group of the FA and adsorption processes of the two herbicides. The effects of several factors, such as textural analysis of FA, adsorbent dosage, contact time, temperature, and initial pH were carried out. The adsorption kinetics and adsorption isotherms of acetochlor and metolachlor for FA were utilized to fit the data of batch experiments, analyze, and compare. In addition, the chemical adsorption mechanism of FA on acetochlor and metolachlor was studied. The inside mechanism of the adsorption of herbicides onto FA was discussed. The significance of the results not only makes the waste FA rich in resources, but also a newly high-efficiency adsorbent for extracting wastewater and soil from residual herbicides such as acetochlor and metolachlor.

2. Materials and methods

2.1. Materials

In this study FA came from coal-fired power plants of Harbin Hatou investment Co. Ltd, Harbin of China. The FA was washed with distilled water, then filtered and dried. Acetochlor (purity of 99%) was obtained from Shandong Binnong Technology Co. Ltd, Qingdao of China and metolachlor (purity of 99%) was obtained from Syngenta Crop Protection Co. Ltd, Suzhou of China.

2.2. Characteristics of FA

The surface structures of FA were observed and analyzed by SEM su8010 (IRAffinity-1S, IR Shimadzu, Japan). The phase

composition and structure of the FA samples were obtained at Bragg angles in the range from 10° to 70° by XRD (Phillips, Holland). The changes of surface functional groups pre- and post-adsorption of FA were analyzed by FI-IR IRPrestige-21 (Shimadzu Ltd., Tokyo, Japan). The chemical and elemental compositions of FA samples were determined by X-ray fluorescence spectroscopy (XRF 1800, Rigaku Co., Tokyo, Japan).

2.3. Procedures for the adsorption experiment

The effects of adsorption initial pH, time, temperature, and FA dosage were investigated. After equilibrium, the two herbicides were separated from FA by centrifuge (IEC 61010-2-020, KUBOTA, Japan) for 10 min at 4,500 rpm. The concentrations of acetochlor and metolachlor were determined by ultraviolet visible spectrophotometer V 1800 (Shimadzu Ltd., Tokyo, Japan) at 223 and 217 nm, respectively [20]. The concentration of acetochlor and metolachlor was calculated according to the Lambert-Beer law using the standard curve method. In the whole research phase, the pH increased from about 3.0 to about 11.0, the contact time increased from 0 to 80 min, adsorption temperature range was kept at 15°C–35°C, the initial acetochlor concentration increased from 10 to 80 mg/L, the initial metolachlor concentration ranged from 10 to 40 mg/L, and the dosage of FA range was 0.08–4.0 g/L. The experiments were carried out with 10 mg/L acetochlor solution, 10 mg/L alachlor solution, and FA to obtain adsorption equilibrium and kinetics. Extensive experiments were completed with 25 mL of different concentrations of acetochlor and metolachlor solutions to obtain the adsorption isotherms. The whole experiment was set up three groups of parallel tests and the three parallel experiments data was averaged. Blank samples without FA were used in each series of experiments to deduct the effects of microorganism and photodegradation.

2.4. Adsorption kinetics

Under fixed experimental conditions, several adsorption kinetics experiments were done with different contact time. The adsorption kinetics of FA was studied by three kinetic models: pseudo-first-order (PFO), pseudo-second-order (PSO), and intra-particle diffusion models. The kinetic rate equation can be expressed as:

$$\frac{dq_t}{dt} = (q_e - q_t)^n \tag{1}$$

where q_t (mg/g) and q_e (mg/g) are the adsorption capacity at time t (min) and the equilibrium adsorption capacity. k_1 and k_2 are the rate constant for 1 and 2 times of adsorption. The linearized integral form of the equation is:

PFO:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

PSO:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

Deform the Eq. (3):

$$q_t = \frac{tk_2 q_e^2}{1 + tk_2 q_e} \tag{4}$$

The initial adsorption rate h (mg/g/min) when t tends to 0 is defined as:

$$h = k_2 q_e^2 \tag{5}$$

Eq. (6) can be obtained by Eqs. (4) and (5):

$$q_t = \frac{t}{1/h + (1/q_e)t} \tag{6}$$

Intra-particle diffusion:

$$q_t = k_{diff} t^{0.5} + C \tag{7}$$

where C (mg/g) is a constant related to boundary layer thickness, and the k_{diff} (mg/g min^{0.5}) is a constant associated with the intra-particle diffusion rate.

2.5. Adsorption isotherm studies

In Eqs. (8)–(15), the parameters related the adsorption isotherm were obtained as follows:

The Langmuir’s linearization equation is:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{8}$$

Where q_m (mg/g) is the maximum adsorption capacity, K_L (L/mg) is the Langmuir constant, and C_e (mg/L) is the equilibrium concentration. q_e (mg/g) is obtained as:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \tag{9}$$

where V (L) is the solution volume, C_0 (mg/L) is the initial concentration, and m (g) is the mass of FA. The removal ratio of acetochlor and metolachlor by FA is calculated as:

$$\eta = \frac{(C_0 - C_e)}{C_0} \times 100\% \tag{10}$$

The value of R_L can be used to determine whether the adsorption tends to be conducive to the adsorption equilibrium [38] and is equal to:

$$R_L = \frac{1}{(1 + K_L C_0)} \tag{11}$$

The value of R_L , when $R_L = 0$, irreversible adsorption; $0 < R_L < 1$, favorable adsorption; $R_L = 1$, linear adsorption; $R_L > 1$, unfavorable adsorption. The Freundlich isotherm linear equation representation is:

$$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e) \tag{12}$$

where K_F (L/mg) is the empirical constant of Freundlich isotherm related to adsorption capacity and n is Freundlich constant. The adsorption process is favorable when $1/n$ value is from 0.1 to 0.5 [39].

The linear equation of Dubinin–Redushkevich (D–R) isotherm is expressed by:

$$\ln q_e = \ln q_m - K_D \varepsilon^2 \tag{13}$$

where ε is the Polanyi potential ($\varepsilon = RT \ln(1 + 1/C_e)$) and K_D (mg²/kJ²) is the activity coefficient related to the mean free energy of adsorption. R is the universal gas constant (8.314 J/mol K) and T represents the temperature of Kelvin.

Using Eq. (14), the free energy (E) of the adsorbate from solution onto the surface of the adsorbent is calculated:

$$E = \frac{1}{\sqrt{2K_D}} \tag{14}$$

The E (kJ/mol) value is used for determining whether it is physical adsorption or chemical adsorption. If it is between 8 and 16 kJ/mol, the adsorption process is chemical; when $E < 8$ kJ/mol, the process is depicted as physical adsorption.

The linear equation of the Brunauer–Emmett–Teller (BET) isotherm model is expressed by:

$$\frac{1}{q_e(1 - C_e/C_s)} = \frac{1}{q_m} + \frac{1}{q_m c} (C_s/C_e - 1) \tag{15}$$

where C_s (mg/L) is the saturated adsorption concentration, and c is a parameter related to the difference of adsorption thermal between the first layer and subsequent layers.

2.6. Desorption regeneration of FA

The experimental conditions are as follows: add 50 mg FA and 25 mL, 10 mg/L acetochlor, or metolachlor solution into 50 mL conical flask respectively, seal the bottle mouth with sealing film, conduct constant temperature oscillation for 1 h, temperature selection is 25°C, speed selection is 165 rpm. After the adsorption is complete, separate the adsorbent, wash it repeatedly with distilled water and dry it. The adsorbent is then added to a glass container containing 100 mL of distilled water and sealed, and the distilled water is the regeneration liquid. The vessel is then subjected to an ultrasonic oscillation for 2 h. Finally, the adsorbent after oscillation is collected, washed with distilled water, and dried for the next experiment, which needs to be repeated three times. The evaluation index of adsorbent regeneration capacity is based on the adsorption capacity and removal rate of acetochlor or metolachlor in each experiment.

3. Results and discussion

3.1. Characterizations of FA

FA was scanned by SEM. From Figs. 1a–c, the FA has rough surface structure and irregular porous. It was obvious that the irregular spherical particles with rough surface were sharply deformed into clumps which are heterogeneously distributed and highly disordered. The XRD pattern of FA (Fig. 1d) showed that quartz (SiO_2) was the main crystalline specie in the FA, while hematite (Fe_2O_3) and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) also existed. The results were consistent with the conclusions of previous works [26]. The amorphous phase of aluminosilicate might exist in XRD patterns with several halos centered approximately between 21° and $36^\circ(2\theta)$ [40]. The extremely wide reflection of the XRD pattern of FA at a low value of 2θ (10° – 20°) indicated the presence of amorphous materials. Fig. 1e shows FT-IR spectra of the adsorbent FA, adsorption products (adsorption of acetochlor and metolachlor in FA). By comparing the infrared spectra of FA with those of two adsorption products, it could be found that the spectra of FA adsorbed acetochlor and metolachlor have changed, indicating that FA has good adsorption capacity for the two herbicides. The main changes are as follows: (1) after the adsorption of these two herbicides, the absorption peak of the C=O stretching vibration of FA was shifted to a lower wavenumber, which might be due to the interference of C=O stretching vibration of acetochlor and metolachlor adsorbed on FA and (2) the framework vibration of Si–O–Si of FA shifted from 1,093.71 to 1,090.26 and 1,089.89 cm^{-1} [41], respectively, and the absorption peaks became weaker, which indicated that hydrogen bonding or surface complexation might occur between the two herbicides and FA. (3) The fingerprint region (800 – 400 cm^{-1}) of FA changed obviously after acetochlor and metolachlor were adsorbed. The peak of Al–OH stretching vibration (797.72 cm^{-1}) became weaker as well as the peak of M–O ($M = \text{Al}, \text{Si}$) bending vibration (475 cm^{-1}) [42], indicating that acetochlor and metolachlor could form complex with the cation of FA. These results are similar to those of the literature [43,44].

3.2. Effect of pH

The initial solution pH value as an important factor affecting the adsorption process were also studied [45,46]. The results of the effect of pH are shown in Fig. 2a, with the batch adsorption studies carried out and the pH changed from 3.0 to 11.0. Under the acidic condition, the amount of adsorption ratio was lower than that of the other conditions but gradually increased with the increasing pH values. Then, the adsorption ratio of FA to acetochlor increased faster while the adsorption ratio of FA to metolachlor hardly increased as the values of pH ranged from 7.0 to 11.0. These two herbicides belongs to non-ionic pesticides, and their molecules do not protonate at low pH and undergo cation exchange with FA. The increase of FA adsorption to acetochlor and metolachlor under alkaline conditions might be due to the fact that the electrostatics of the pesticide molecules or adsorption surfaces were changed to some extent, or the differentiation of pesticide molecules was affected by ionization and hydrolysis [47].

3.3. Effect of temperature

As shown in Fig. 2b, the experiments of the effect of temperature on adsorption were carried out at 15°C, 25°C, and 35°C. The results showed that the change of the adsorption ratio of the two herbicides on FA was opposite with the increasing temperature. The adsorption ratio of acetochlor on FA raised with the temperature raised, which showed that the process was endothermic, and increasing temperature was beneficial to the adsorption of acetochlor on FA. The result was similar to those reported by researchers [48]. Another hypothesis was that as the temperature increases, the approached sites, structure, and volume of the pores on the surface of the adsorbent were increased, which enhanced the adsorption properties of the adsorbents [49,50]. However, adsorption ratio of metolachlor on FA increased with the decrease of temperature, which indicated that the adsorption of metolachlor by FA was exothermic, which was consistent with the reports in the literature [47,51].

3.4. Effect of dosage of FA

As shown in Fig. 2c, effect of dosage on FA adsorbed herbicides were studied with doses of range 0.08–4.0 g/L. The adsorption ratio of these two herbicides increased rapidly as adsorbent dose increased, and the adsorption ratio was not increased considerably when adsorbent doses were higher than 1.2 g/L. When the dosage of FA was about 2.0 g/L, the adsorption ratio of acetochlor and metolachlor reached the maximum (91.25% and 73.65%), respectively. Increasing the dosage of adsorbent, the adsorption sites of adsorbent could not be full-scaled used and made some adsorption sites approached so that the adsorption capacity of the two herbicides per unit of FA gradually reduced. In general, the surface area and available sites are usually related to the amount of adsorbent [34]. As the increase of dosage, the adsorption capacity of it would be a corresponding increase. Comparing with the lower dosage of FA, there are faster adsorption processes of acetochlor and metolachlor onto FA of higher dosage. There are previously reported obtained the similar conclusions [52].

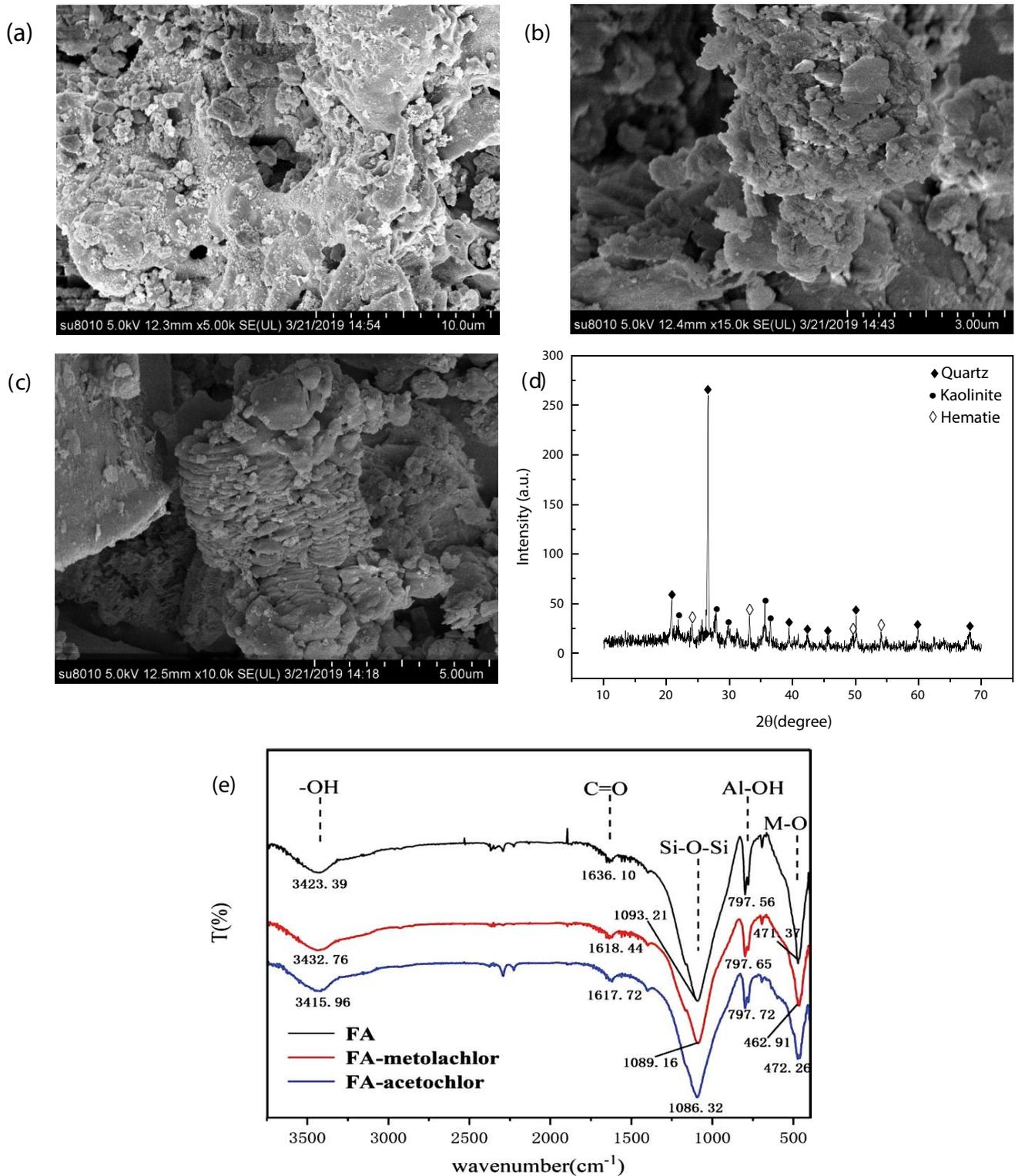


Fig. 1. (a–c) SEM images of FA, (d) XRD pattern of FA, and (e) FTIR patterns for FA and adsorption products.

3.5. Adsorption kinetics

The effect of contact time under certain conditions was investigated. As shown in Fig. 3a, the adsorption rate was rapidly increasing at the beginning of adsorption process and

gradually decreased with lengthening of contact time until adsorption equilibrium. The equilibrium time of acetochlor was about 10 min and the equilibrium time of metolachlor was about 15 min. This was because the mass concentration of the two herbicides in the solution was high at the beginning

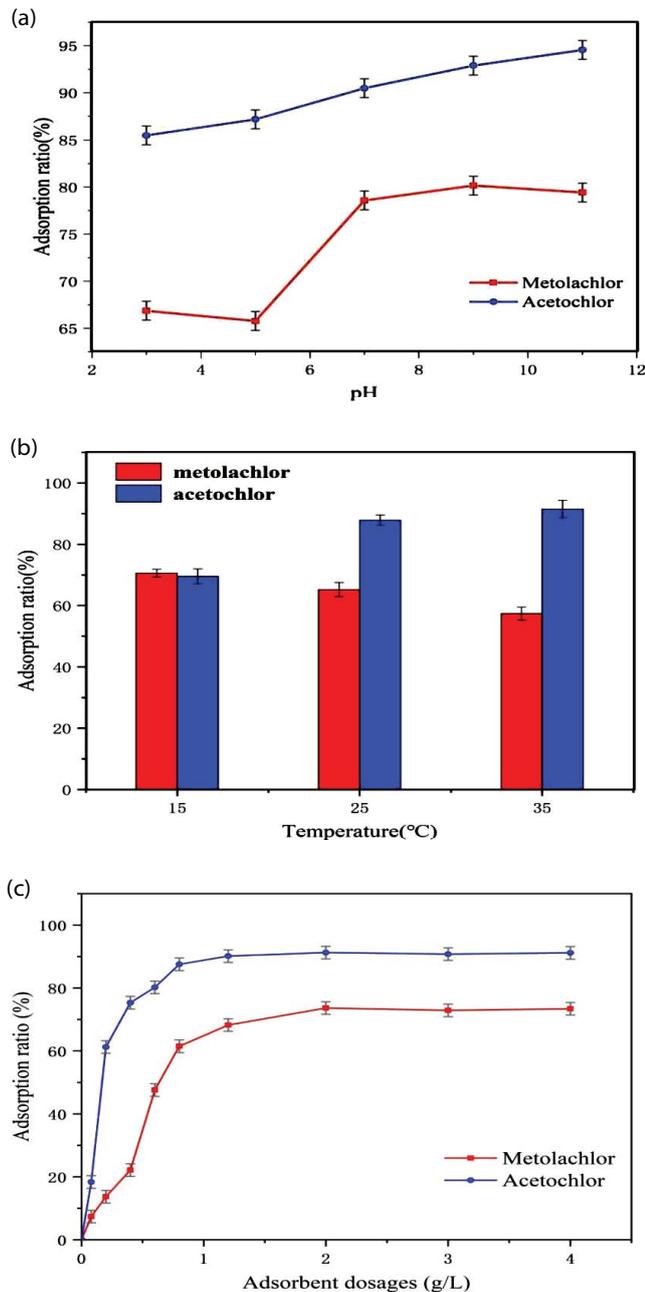


Fig. 2. (a) Effect of solution pH on the adsorption of acetochlor and metolachlor by FA (concentration of 10 mg/L, temperature 25°C, 15 min equilibrium time, and adsorbent dose of 2.4 g/L), (b) effect of temperature on the adsorption of acetochlor and metolachlor by FA (the concentration of 10 mg/L, 15 min equilibrium time, and adsorbent dose of 2.4 g/L), and (c) effect of dosage of FA on the adsorption of acetochlor and metolachlor (concentration of 10 mg/L, temperature 25°C, and the equilibrium time of 15 min).

time, and there were a large amount of available adsorption sites of FA. As the adsorption proceeding, the decreasing adsorption rate gradually decreased due to the adsorption sites were gradually occupied by contaminants.

PFO, PSO, and intra-particle diffusion model were applied to fit the experimental data (as shown in Figs. 3b–d). In Table 2, the R^2 of PSO model obtained was higher than 0.999, and q_e that obtained by calculated was similar with that of experimental, which showed that the PSO model was well fitted to the adsorption data. A similar conclusion were obtained by previously research [53].

Adsorption kinetics experiments at a different initial concentration of herbicides were carried out. Linear regression of q_e , h , and C_0 was carried out to obtain higher regression coefficients (>0.9987). Therefore, q_e and h could be represented by C_0 respectively, and the corresponding logarithmic function about C_0 was obtained. The values of q_e and h were substituted into Eq. (6). The relationship between q_t , C_0 , and t of acetochlor and metolachlor can be expressed as Fig. 4. This prediction model can be used to derive the q_t at any given C_0 and t [54]. The adsorption amount of FA to acetochlor increased rapidly with t and C_0 while the adsorption amount of FA to metolachlor increased slowly with t and C_0 . The experimental data was basically consistent with the predicted value of the formula. The predicted maximum adsorption amount of acetochlor ($q_m = 42.76$) was very close to that obtained by Langmuir ($q_m = 42.12$). So was the adsorption of metolachlor on FA.

On the other hand, the R^2 of PFO is lower than that of PFO model. The result of kinetic demonstrated the adsorption process has both physical adsorption and chemical adsorption. Therefore, the adsorption equilibrium could be reached in a short time, which was consistent with experimental observations [55].

In addition, as the R^2 value for intra-particle diffusion model obtained was very high ($R^2 > 0.957$), the intra-particle diffusion model is proceeding in two steps, which illustrated that adsorption of acetochlor and metolachlor onto FA happen in two steps. The adsorption process occurred on the surface of adsorbents in the first step, while in the second step, the adsorbates penetrate through the pores of the adsorbents [56]. The values of $k_{id,1}$ and $k_{id,2}$ (Table 2) were the rate parameters for first step and second step respectively. The lower the rate parameter values were, the greater the diffusion of the two herbicides in the pores of the adsorbent. The intercepts values C were in the range of 0.195–3.897 mg/g, indicating that the thickness of the boundary layer had smaller values.

3.6. Adsorption isotherm

The curves of the isotherms of acetochlor and metolachlor remove by FA at 25°C and solution pH 7.0 are shown in Fig. 5, which illustrated adsorption properties of adsorbent was increased as the increasing concentration of the two herbicides while equilibrium was reached. The q_m of acetochlor and metolachlor obtained by experiment were 42.12 and 19.38 mg/g, respectively. The Langmuir, Freundlich, D–R, and BET model were established. The theoretical parameters of the isotherms used are shown in Table 3.

The Langmuir model presumes the monolayer adsorbents and occurs on the specific homogeneous sites of the adsorbent [57]. The results showed that the correlation coefficients of the Langmuir isotherm model of acetochlor

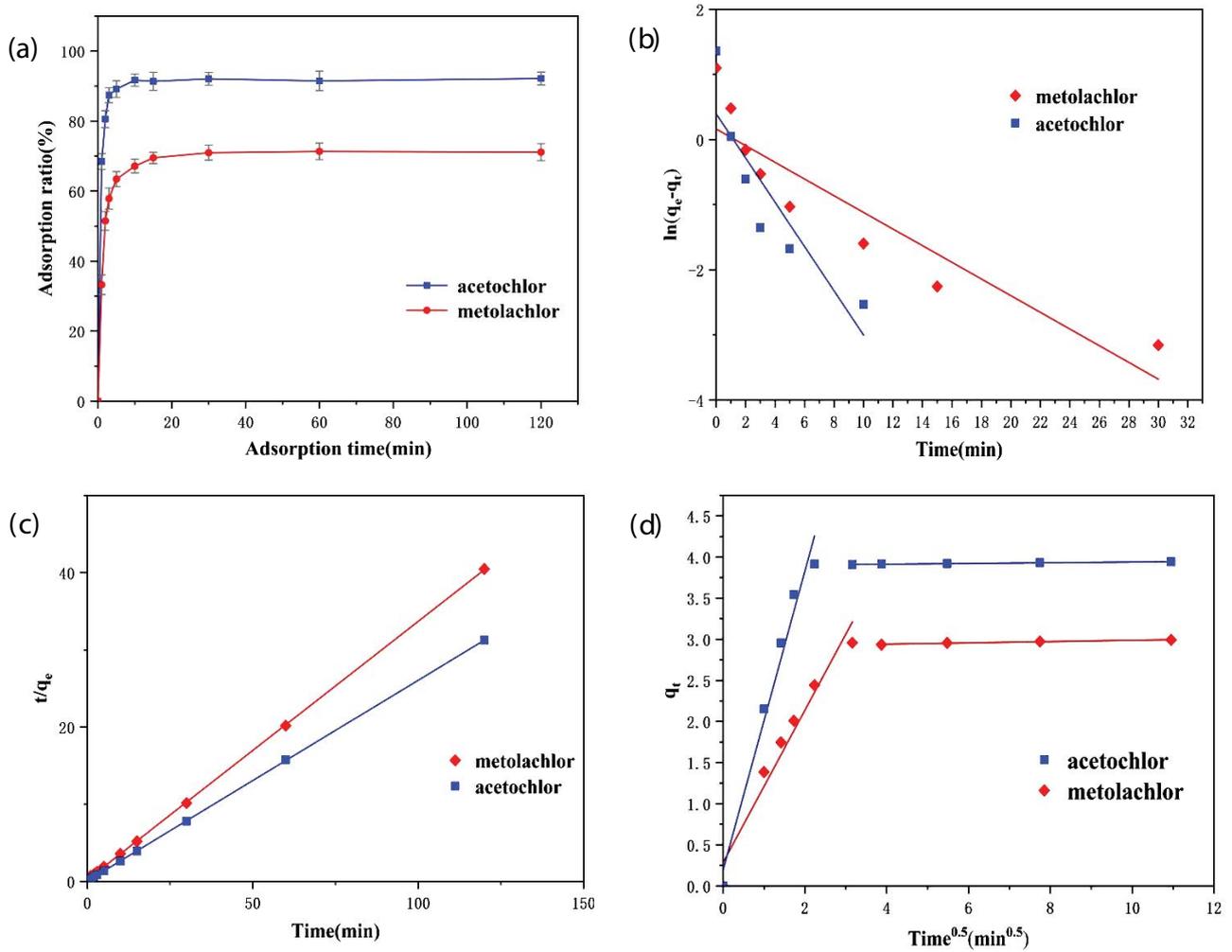


Fig. 3. (a) Effect of adsorption time of acetochlor and metolachlor by FA, kinetic model of acetochlor, and metolachlor on FA: (b) pseudo-first-order, (c) pseudo-second-order, and (d) intra-particle diffusion model.

Table 2

Parameters of pseudo-first-order, pseudo-second-order, and intra-particle diffusion kinetics models for acetochlor and metolachlor onto FA at 25°C

Types of pesticides		Metolachlor	Acetochlor
$q_{e,exp}$ (mg/g)		2.935	3.974
Pseudo-first-order model	k_1 (1/min)	0.128	0.340
	$q_{e,cal}$ (mg/g)	1.176	1.485
	R^2	0.8413	0.7974
Pseudo-second-order model	k_2 (g/mg min)	0.500	1.248
	$q_{e,cal}$ (mg/g)	2.987	3.844
	h	4.466	18.447
	R^2	0.9992	0.9994
Intra-particle diffusion model	$k_{id,1}$ (mg/g(min ^{0.5}))	0.925	1.816
	C_1	0.285	0.195
	R^2	0.9691	0.9913
	$k_{id,2}$ (mg/g(min ^{0.5}))	7.840×10^{-3}	4.280×10^{-3}
	C_2	2.910	3.897
	R^2	0.9572	0.9741

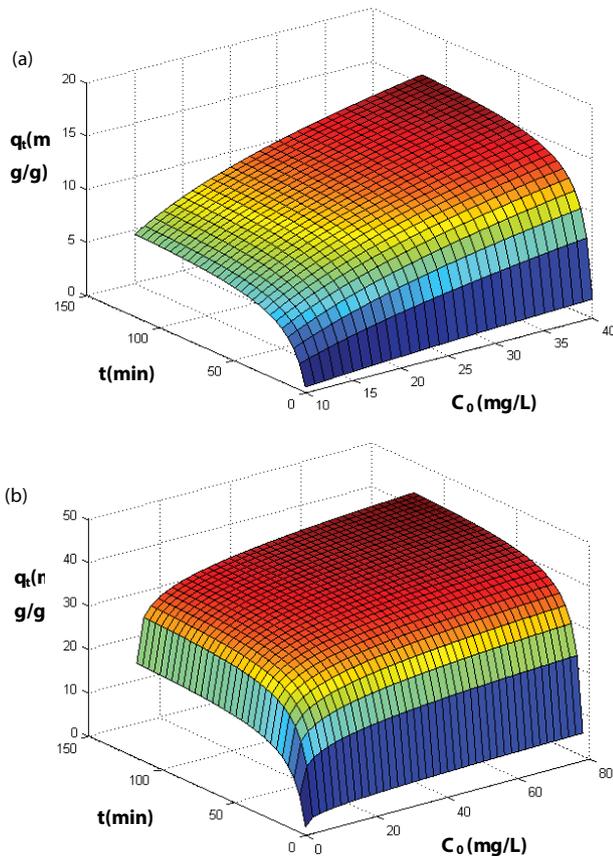


Fig. 4. Comparison of experimental data points given by symbols and the surface predicted by the model given Eq. (6) ((a) for metolachlor and (b) for acetochlor).

and alachlor were 0.991 and 0.997, respectively, which were higher than other models. The large value of K_L denoted two herbicides molecules had a greater affinity for FA and a stable adsorption complex were produced. The R_L values of acetochlor and metolachlor obtained in this study were 0.0039 and 0.136, respectively, indicating that the adsorption of these two herbicides onto FA favorable.

The Freundlich isotherm describes that the adsorption is multilayered and occurred with a heterogeneous surface [58]. As shown in Table 3, the R^2 value of acetochlor and metolachlor for Freundlich isotherm obtained was very low, which suggested that the Freundlich isotherm could not describe the process of these two herbicides remove by FA.

The D–R isotherm is utilized to explain the adsorption behaviors. The adsorption process may be a physical process or an ion-exchange process, which depends on the main free energy data [59]. E appears in different ranges and means different results. When the value of E is between 8.0 and 16.0 kJ/mol indicating the adsorption process is ion exchange [60]. When $E < 8.0$ kJ/mol means physisorption [61], chemical adsorption dominates when E is in the range of 20–40 kJ/mol [62]. From Table 3, the values E of acetochlor and metolachlor were 6.79 and 28.49 kJ/mol, respectively, it seemed that physical adsorption was the primary adsorption process of metolachlor on FA, while chemisorption played an important part in adsorption process of acetochlor on FA.

Table 3

Parameters of acetochlor and metolachlor adsorption isotherms fitted with Langmuir, Freundlich, D–R, and BET models

Types of pesticides		Metolachlor	Acetochlor
Langmuir	q_m (mg/g)	19.38	42.12
	K_L (L/mg)	0.1260	3.6360
	R^2	0.9913	0.9980
Freundlich	K_F (mg/g)(L/mg) ^{1/n}	4.825	33.188
	$1/n$	0.332	0.070
	R^2	0.8562	0.7443
D–R	q_m (mg/g)	16.549	42.806
	K_D (mg ² /KJ ²)	8.738×10^{-4}	4.485×10^{-5}
	R^2	0.9081	0.9192
BET	q_m (mg/g)	19.85	35.06
	c	47.97	–16,892.53
	R^2	0.9841	0.0002

The BET isotherm model can also be used for the adsorption of porous solids in the liquid phase [63]. It is generally used to describe multilayer adsorption, which belongs to physical adsorption based on Van der Waals force [64]. As shown in Table 3, the R^2 value of metolachlor obtained was very high, while R^2 value of acetochlor was only 0.0002, which showed that adsorption process of metolachlor may be more in line with multi-molecular layer adsorption and physical adsorption.

From adsorption isotherm, the adsorption capacity of acetochlor (42.12 mg/g) is about two times that of metolachlor (19.38 mg/g). The maximum adsorption amount of various adsorbents to acetochlor were compared as shown in Table 4. Compared with the adsorbents of other literatures, the adsorption capacity of FA from this work is higher. Besides, the adsorption equilibrium time of acetochlor in FA (10 min) is very short. Therefore, in this study, FA could be utilized as a highly effective adsorbent to remove acetochlor from solution.

3.7. Desorption regeneration of FA

In order to explore the reusability of FA, acetochlor, and metolachlor adsorbed on FA surface were desorbed by ultrasonic vibration, so as to remove the pollutants attached on FA surface and pore diameter. As shown in Fig. 6, after three desorption regeneration cycles, the removal efficiencies of FA to acetochlor and metolachlor decreased from 91.25% and 73.65% to 75.45% and 60.84%, respectively. The results showed that the adsorption properties of FA on the above two pesticides decreased slightly after ultrasonic vibration reuse. However, considering that FA is a cheap and easy to get substance in this study, it has the advantages of low cost and secondary utilization of waste, when FA is reused, the amount of FA can be increased appropriately to achieve the best adsorption performance.

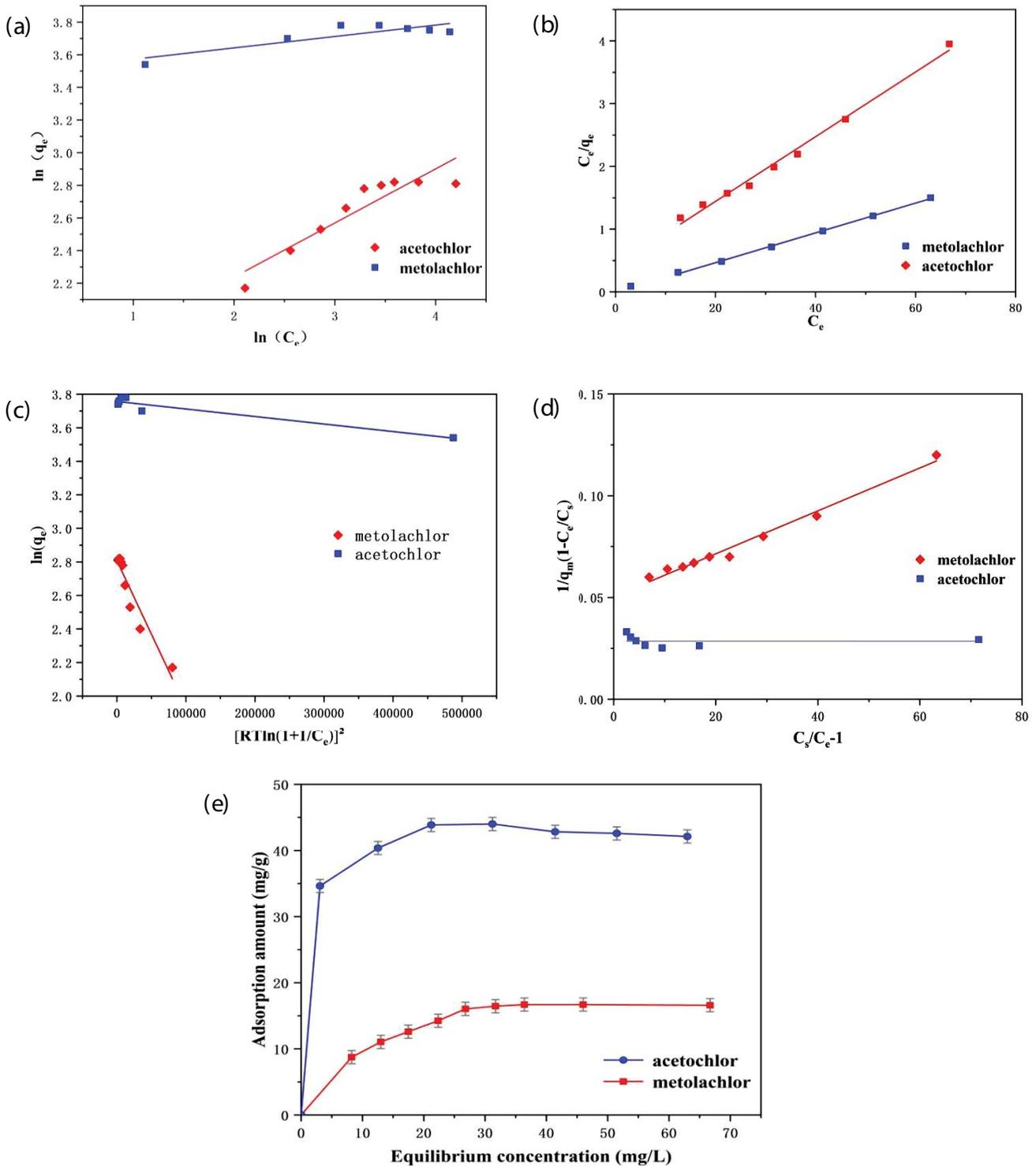


Fig. 5. Adsorption isotherm of acetochlor and metolachlor on FA (a) Freundlich, (b) Langmuir, (c) D–R, and (d) BET, and (e) adsorption isotherm curve of acetochlor and metolachlor on FA (adsorbent dose = 2.0 g/L, shaking time 15 min).

3.8. Adsorption mechanism

The adsorption mechanism of acetochlor and metolachlor on FA is complicated, which is controlled by the surface properties of FA. As the non-ionic pesticide, the

driving force of these two herbicides on FA maybe not electrostatic [1,65], indicating that the adsorption mechanism is probably not an ion exchange. On the other hand, for FA, it is similar in composition and structure to mineral clay in the soil. Particularly, from the XRD (Fig. 1d) and

Table 4
Maximum uptake capacity and adsorption equilibrium time for the adsorption of acetochlor onto various adsorbents

Adsorbents	Equilibration time	q_m (mg/g)	References	Mechanisms
Acidified black soil	>>60 min	0.586	[18]	Physical adsorption
Modified montmorillonite	>>60 min	3.3	[16]	Electrostatic adsorption and hydrophobic interaction
Pig manure biochar	>>60 min	10	[3]	π - π interaction and pore filling interaction
DTMAC organobentonite	60 min	14	[15]	Hydrophobic interaction
HTMAC organobentonite	60 min	15		
Mg-modified biochar	<30 min	27.4	[17]	π - π interaction and hydrogen bond
FA	10 min	42.12	This study	Hydrogen bond and ligand exchange
OTMAC organobentonite	3 min	45	[19]	Hydrophobic interaction
DTMAC organobentonite	20 min	70		
HTMAC organobentonite	20 min	91		

Table 5
Chemical composition of FA in various literatures and that of Kaolinite

Adsorbents	FA [41]	FA [76]	FA [34]	FA [36]	FA [This study]	Kaolinite [77]
SiO ₂ (%)	63.10	50.95	44.70	60.46	55.64	47.64
Al ₂ O ₃ (%)	16.9	36.10	20.80	21.50	27.21	36.18
Fe ₂ O ₃ (%)	4.40	3.91	4.06	4.30	3.84	0.44
CaO (%)	3.50	2.94	13.19	7.63	3.12	0.87
K ₂ O (%)	3.27	2.23	–	1.25	1.75	0.90
MgO (%)	0.80	0.70	–	0.82	0.64	0.87
TiO ₂ (%)	0.34	1.06	–	1.53	0.91	0.37
Na ₂ O (%)	4.57	–	–	0.19	–	0.90

Table 5, the crystal structure and composition of FA was similar to that of kaolinite (consisting of tetrahedral SiO₄ layer and octahedral AlO₂(OH)₄ layer which are two inter-linked layers) [66]. Therefore, analogous to the adsorption mechanism of kaolinite, the main adsorption mechanism of FA might be ligand exchange, which is the result of the interaction of complexation, chelation, and hydrogen bond [67]. According to the result of the FT-IR spectra, C=O of acetochlor, and metolachlor might be the important binding site. The framework vibration of Si–O–Si of FA shifted from 1,093.71 to 1,090.26 and 1,089.89 cm⁻¹, and Al–OH stretching vibration bond (about 797.72 cm⁻¹) became weak, indicating that the ligand exchange might occur between active sites of the two herbicides and Al–OH of FA. As shown in Fig. 7, the exchange between acetochlor and metolachlor and hydroxy of Al–OH occurred and active sites of the two herbicides (N≡, C=O) formed complex with the cation of aluminum ion [44,68]. In addition, the peak of M–O (M = Al, Si) bending vibration (475 cm⁻¹) became weaker, which showed that active sites of the two herbicides might interact with the hydroxyl groups in the structure of M–O through hydrogen bond [69–71]. Besides, some scholars have also reported that FA can adsorb some organic compounds through ligand exchange [72].

From the D–R isotherm model and adsorption kinetics, the values E of acetochlor and metolachlor were 6.79 and 28.49 kJ/mol, respectively, and the adsorption kinetics data of these two herbicides onto FA had a great fitting by the

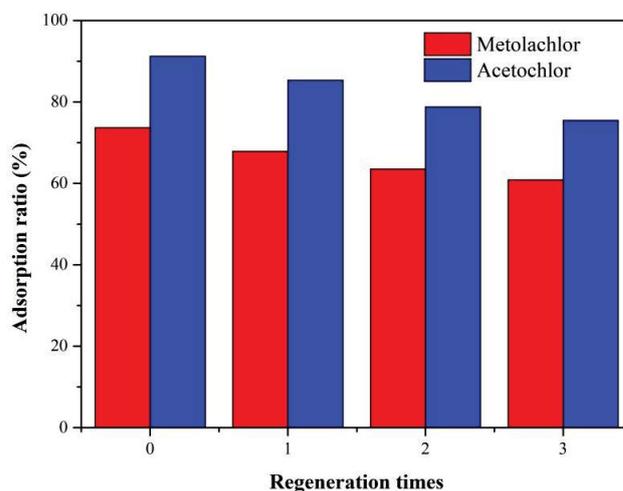


Fig. 6. Experimental of regenerative adsorption of acetochlor and metolachlor by FA.

PSO model. The results showed that adsorption process of the two herbicides was a combination of chemical and physical adsorption and the physical adsorption was the primary adsorption process of metolachlor on FA, while chemisorption dominates adsorption process of acetochlor on FA [47,48,73].

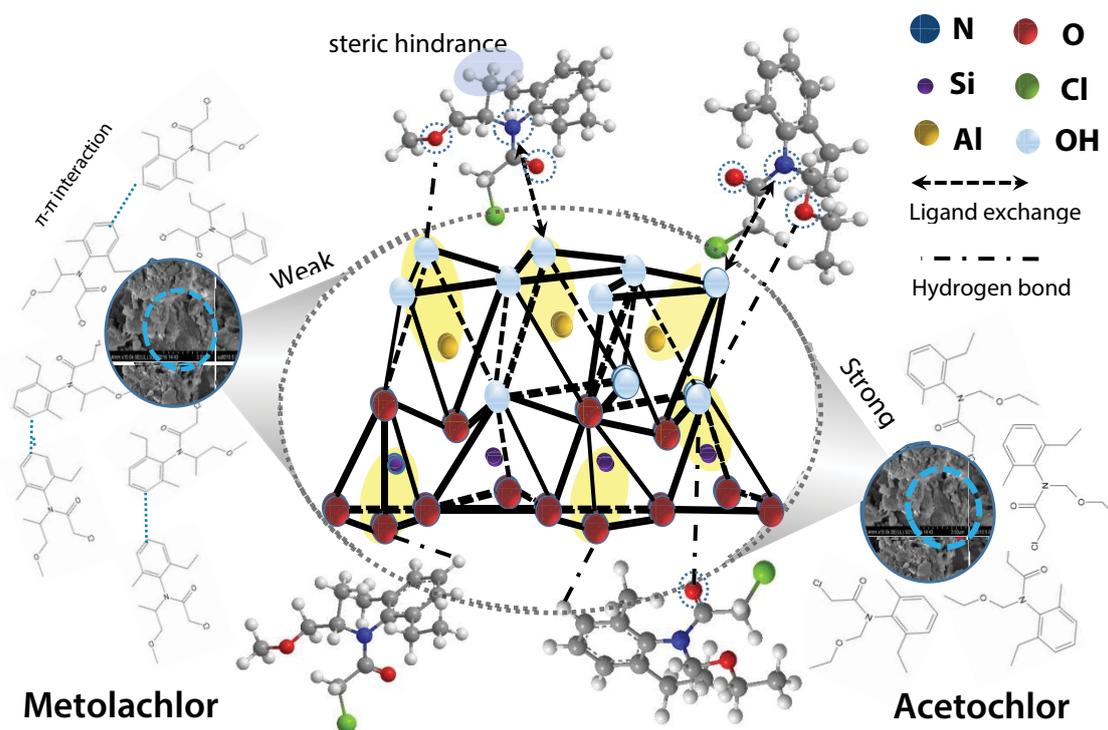


Fig. 7. Mechanism of hydrogen bonds and ligand exchange for acetochlor and metolachlor adsorption on FA.

Moreover, the structure of acetochlor is very similar to that of metolachlor except that one amide N substituent of acetochlor is $-\text{CH}_2\text{OC}_2\text{H}_5$ (ethoxymethyl), while the corresponding substituent of metolachlor is $-\text{CH}(\text{CH}_3)\text{CH}_2\text{OCH}_3$ (1-methoxyisopropyl), which suggested that the steric hindrance of $-\text{CH}(\text{CH}_3)\text{CH}_2\text{OCH}_3$ makes the metolachlor molecule have poor coplanarity and the degree of conjugation is weaker than that of acetochlor molecule [74]. On the other hand, because the solubility of acetochlor (223 mg/L) is less than that of metolachlor (530 mg/L), its hydrophobic interaction is stronger than metolachlor [75]. Above results may be the reason why the adsorption capacity of acetochlor (42.12 mg/g) is about two times than that of metolachlor (19.38 mg/g).

4. Conclusions

The potential and adsorptive properties of solid waste FA as an adsorbent to remove acetochlor and metolachlor from aqueous solution were investigated. From the adsorption kinetics and adsorption isotherm, the adsorption of acetochlor and metolachlor on FA was well fitted for the Langmuir isotherm model and PSO kinetic models with intra-particle diffusion model. Particularly, adsorption process of metolachlor might be more in line with multi-molecular layer adsorption and physical adsorption while chemisorption plays an important part in adsorption process of acetochlor on FA. FA displays strong adsorption capacities for acetochlor and the saturated adsorption amounts of acetochlor by FA was 42.12 mg/g. The adsorption equilibrium could arrive at 15 min. The adsorption mechanism are the hydrogen bond and ligand exchange.

The results demonstrates that solid waste FA has a great potential to be a low-cost and environmentally friendly adsorbents for acetochlor and metolachlor removal in wastewater treatment.

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