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Adsorption study on the removal of ciprofloxacin in aqueous solution by an acidic ion exchange resin with bifunctional group

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Removal of fluoroquinolone antibiotic pollutants in the aquatic environment has become a research hotspot. In this work, two skeletal resins and four acidic ion exchange resins have been used as adsorbent materials to evaluate their adsorption properties for fluoroquinolone antibiotic ciprofloxacin (CIP) in aqueous solution. Compared with other materials, the sulfonic-phosphoric acid-based bifunctional resin S9570 has shown the best adsorption performance for CIP. The effect of solution pH on the adsorption of CIP by S9570 has been further explored, and the optimal adsorption capacity has been obtained at pH 4.0. The adsorption kinetics and thermodynamics of S9570 for CIP have been investigated in details. The high fits of the pseudo-second-order and intraparticle diffusion equations indicate that these two models can better describe the adsorption process of S9570 for CIP which has been jointly controlled by chemical adsorption and intraparticle diffusion steps and has been accompanied by weak or intermediate initial adsorption behaviour. The best fit results of Langmuir has indicated that there exists a monolayer adsorption on the surface of the S9570.Thermodynamic parameters suggest that the adsorption is an endothermic, spontaneous process with increased randomness at the solid-liquid interface. Through this evaluation of resin adsorption materials, it has been proved that the adsorbent material has good reusability and anti-interference performance.

Keywords: Acidic ion exchange resin, Bifunctional group, Ciprofloxacin, Kinetics, Thermodynamics

The report from ESAC (European Surveillance for Antimicrobial Consumption) points out that quinolone antibiotics have become one of the three commonly used antibiotics in the world[1]. The third-generation fluoroquinolone antibiotics have widely used due to their excellent pharmacokinetic properties, strong antibacterial properties, broad antibacterial spectrum, high bioavailability, long half-life, and inability to be metabolized in the body. However, most fluoroquinolone antibiotics cannot be completely metabolized and decomposed in humans and animals, and are excreted into the environment in the form of prototype and active metabolites through feces and other excretions[2]. Once discharged into the environment without treatment, it is easy to cause enrichment, and then enter the human body through the food chain, causing serious impact on human health. As a representative drug of fluoroquinolone antibiotics[3], ciprofloxacin (CIP) has become one of the ten emerging contaminants due to its rapid increase in use in recent years[4]. Therefore, the removal of CIP pollutants in the water environment has become a research hotspot. CIP in wastewater mainly comes from pharmaceutical, medical, aquatic, animal husbandry and other fields. The removal methods of this antibiotic include biodegradation method[5], membrane separation technology[6], advanced oxidation technology[7] and adsorption method. Compared with other technologies, adsorption method is widely used due to its advantages of low cost, safety and controllability, simple design and operation, and no secondary pollution[8-18]. As a common type of adsorbent materials in adsorption methods, resins have been used in the adsorption removal of fluoroquinolone antibiotics in wastewater[8-11]. This research mainly involved the use of skeleton[8] and modified resin as adsorbent materials[9-11] to adsorb and remove antibiotics from the wastewater in the pH range of 3~10[19]. However, most studies has removed antibiotics through the hydrophobic action under neutral conditions, such as skeleton resins[8] melamine-urea-formaldehyde modified resin[9], and tertiary amino, quaternary amino and sulfonic acid modified ion exchange resins[10]. The others relied on the hydrogen bonding under acidic conditions, such as polymaleic anhydride modified resins[11]. The adsorption effects of the above studies are all general, and the ion

exchange characteristics of the resins have not rationally utilized. In particular, the sulfonic acid modified ion exchange resin does not give full play to its strongly cationic exchange properties under acidic conditions, so that antibiotics could be removed by stronger electrostatic action. Therefore, it is necessary to develop a more efficient adsorption method suitable for the removal of fluoroquinolone antibiotics in acidic wastewater *via* using ion exchange resins.

Ion exchange resins are divided into acidic and basic ion exchange resins. Among them, basic ion exchange resins have great limitations in practical applications due to their poor thermal stability. Considering the structural characteristics of CIP molecule, we speculate that the acidic ion exchange resin and basic ion exchange resins and the antibiotic will have opposite charges within a certain acidity range, respectively. Therefore, the difference in electro negativity between them can be used to promote the mutual adsorption of the two through electrostatic interaction, thereby efficiently removing CIP in the wastewater.

Although CIP concentrations in practical wastewater are among at the ng/L~ mg/L levels[20-22], the research concentrations in the literatures are all focused on the level of mg/L in order to evaluate the maximum adsorption capacity of various materials to CIP[8-11]. In this study, to screen the resin with optimal adsorption performance, higher concentration level of mg/L has been selected for study. The adsorption properties of two skeleton resins (XAD7HP and XAD1180) and four acidic ion exchange resins (IRC747, IRC748, FPC23 and S9570) for CIP molecules have been evaluated to screen out the optimal adsorption material. The effect factors such as *p*H and initial concentration of CIP solution, temperature and rotating speed etc. have been investigated, respectively. The adsorption kinetics and thermodynamics of CIP onto the adsorption material have been further examined to reveal potential mechanisms involved in the adsorption process.

Experimental Section

Materials and reagents

XAD7HP, XAD1180, IRC747, IRC748, FPC23 were provided by Rohm & Hass. S9570 was provided by Purolite. CIP (98%) was purchased from Shanghai McLean Biochemical Technology Co., Ltd.. HCl, HAc, NaAc, NaOH, KOH, KH_2PO_4 and other analytical grade reagents were all purchased from Xi'an Chemical Reagent Factory. All the solutions were prepared with ultrapure water.

Study on the adsorption of the resins for CIP molecules

Preparation of CIP-containing simulated solution

2.7218 g of KH_2PO_4 was dissolved and diluted to 2 L with ultrapure water, further pH was adjusted to 4 with HCl solution.0.2 g of CIP was added to the prepared KH_2PO_4 solution, then diluted to 2 L with ultrapure water to obtain a 100 mol/L CIP simulated solution.

Adsorption of the resins for CIP molecules

0.05 g of XAD7HP, XAD1180, IRC747, IRC748, FPC23, S9570 resins were added to 50 mL of CIP simulated solutions (100 mg/L), respectively. The mixture solutions were shaken at the speed of 200 rpm under 298 K for 24 h. The supernatant liquids of the mixtures were taken to be measured absorbance A at the wavelength of 276.5 nm with an ultraviolet spectrophotometer. The concentrations of CIP were derived *via* A-C standard curve. The equilibrium adsorption capacity and removal rate were calculated with Eqs (1) and (2):

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

$$R(\%) = \frac{C_o - C_e}{C_o} \times 100 \quad \ldots(2)$$

Where, q_e is the equilibrium adsorption capacity (mg/g), R is the removal rate (%), C_o is the initial concentration of CIP(mg/L), C_e (mg/L) is the equilibrium concentration of CIP(mg/L), V is the volume of the solution(L), m is the mass of the resin (g). Each sample was repeated for three times.

Effect of simulated solution pH on the adsorption of S9570 for CIP molecules

0.05 g of S9570 resins were added to 50 mL of CIP simulated solutions (*p*H 4, 5, 6, 7, 8, 9), respectively. The mixture solutions were shaken at the speed of 200 rpm under 298 K for 24 h. The adsorption parameters q_e and R were obtained as described above.

Adsorption kinetics of S9570 for CIP molecules

Adsorption kinetic experiments

0.05 g of S9570 resins were added to 50 mL of CIP simulated solutions with the different concentrations (50, 100 and 150 mg/L) at *p*H 4, respectively. The mixture solutions were shaken at different temperatures (298, 303, 308 and 313K) with the different speeds (100 and 200 rpm). Supernatant samples were periodically taken out at intervals of 10, 20, 30, 40, 60, 75, 100, 120, 140, 160, 180, 200, 240, 280, 320, 360,

480, 600 and 720 min. The adsorption parameter q_e was obtained as described above.

Adsorption kinetic equations

Pseudo-first-order kinetic equation

The pseudo-first-order kinetic equation is only applicable to describe the initial process of adsorption, but not the entire process, the expression [23] is as follows:

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

Where, k_1 is the rate constant (1/min), t is the adsorption time (min), q_t is the adsorption capacity at time t (mg/g).

Pseudo-second-order kinetic equation

The pseudo-second-order kinetic equation can well describe the entire adsorption process and is widely used in various adsorbent-adsorbate systems[24], the expression is as follows:

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

$$h = k_2 {q_e}^2 \quad \ldots(5)$$

Where, k_2 is the rate constant (g/mg·min), h is the initial rate (mg/g·min), k_2 and $q_e$can be obtained from the slope and intercept of Eq. (4), individually.

Intraparticle diffusion equation

The Weber-Morris intraparticle diffusion equation is used to describe the control step in the reaction. Through the intraparticle diffusion rate constant, the control step of the reaction can be determined to describe its adsorption kinetic data[25], the expression is as follows:

$$q_t = k_i t^{1/2} + C_i \quad \ldots(6)$$

Where, k_i is the intraparticle diffusion constant (mg/g·min$^{1/2}$), $C_i$is the characteristic parameter of intraparticle diffusion, $C_i < 0$, the thickness of the liquid film hinders the intraparticle diffusion process;$C_i = 0$, intraparticle diffusion is the only control step in the adsorption process;$C_i > 0$, there is a rapid adsorption stage within a short period of time when the adsorption process starts[26]. k_i and C_i can be obtained from the slope and intercept of Eq. (4), individually.

Feng-Chin Wu[27] studied the fast initial adsorption behavior based on the intraparticle diffusion equation, and defined the initial adsorption factor R_i as follows:

$$R_i = 1 - \frac{C_i}{q_e} \quad \ldots(7)$$

$R_i = 1$, no rapid initial adsorption; $0.9 < R_i < 1$, weak initial adsorption; $0.5 < R_i < 0.9$, intermediate initial adsorption; $0.1 < R_i < 0.5$, strong initial adsorption; $R_i < 0.1$, the adsorption process is completed within a short time.

Adsorption thermodynamics of S9570 for CIP molecules

Adsorption thermodynamic experiments

0.04, 0.05, 0.06, 0.07, 0.08 and 0.09 g of S9570 resins were added to 50 mL of CIP simulated solutions (100 mg/L, pH 4), respectively. The mixture solutions were separately shaken at the speed of 200 rpm under 298, 303, 308 and 313 K for 12 h. The adsorption parameter q_e was obtained as described above.

Adsorption thermodynamic models

Langmuir isotherm model

The model assumes: (1) the surface of the adsorbent is uniform; (2) the adsorbate only acts on the active sites on the outer surface of the adsorbent, and there is no force between the adsorbate molecules, which belongs to a simple monolayer adsorption. The linear expression of the model is as follows[28]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad \ldots(8)$$

$$R_L = \frac{1}{1 + K_L C_0} \quad \ldots(9)$$

Where, q_m is the saturated adsorption capacity of the monolayer(mg/g), K_L is the Langmuir isotherm constant (L/mg). q_m and $K_L$can be determined from the slope and intercept of Eq. (8). R_L is the feature separation coefficient. $R_L = 0$, irreversible adsorption; $0 < R_L < 1$, favorable adsorption; $R_L = 1$, linear adsorption; $R_L > 1$, unfavorable adsorption[29].

Freundlich isotherm model

The model proposes that it can be used to describe whether the surface of the adsorbent is uniform or not, especially when the adsorbate is adsorbed on the adsorbent with non-uniform surface at low concentration. The linear expression of the model is as follows[30]:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad \ldots(10)$$

Where, n is the characteristic constant , K_F is the Freundlich adsorption constant (mg/g). n and K_F can be obtained from the slope and intercept of Eq. (10).

Temkin isotherm model

The model assumes that the adsorbent surface is not uniform, which can reflect the interaction between adsorbate and adsorbate. The linear expression of the model is as follows[31]:

$$q_e = B_T \ln C_e + B_T \ln K_T \quad \ldots(11)$$

Where, B_T is the Temkin constant , K_T is the equilibrium constant (g/mg).B_T and K_T can be obtained from the slope and intercept of Eq. (11).

Thermodynamic parameters

$$K_0 = \frac{q_e}{C_e} \quad \ldots(12)$$

$$\ln K_0 = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad \ldots(13)$$

$$\Delta G = \Delta H - T\Delta S \quad \ldots(14)$$

Thermodynamic parameters can be estimated from Eq. (12-14)[32]. By plotting $\ln K_0$ against $1/T$, ΔH and ΔS can be calculated from the slope and intercept of Eq. (13), then ΔG can be calculated from Eq. (14).

Evaluation on the adsorption property of S9570 for CIP molecules

Effect of interfering ions on the adsorption of S9570 for CIP

0.01 mol/L KCl, K_2SO_4, KNO_3, $KHCO_3$, NaCl, $CaCl_2$, $CuCl_2$, $FeCl_3$, $NiCl_2$, $ZnCl_2$ were added to the CIP simulation solutions (100 mg/L pH=4), separately, then the obtained solutions were add with 0.0500 g of S9570. The mixture solution was shaken at the speed of 200 rpm under 313 K for 12 h until the adsorption equilibrium. The adsorption parameter q_e was obtained as described above.

Adsorption reusability of S9570 for CIP

0.5 g of S9570 was added to 50 mL of 100 mg/L CIP solution (pH 4). The mixture solution was shaken at the speed of 200 rpm under 313 K for 12 h until the adsorption equilibrium. The adsorption parameter q_e was obtained as described above. Then CIP molecules on the material were desorbed with 2 mol/L HCl solution[33]. Five consecutive cycles of adsorption-desorption experiment were performed to evaluate the adsorption reusability of S9570 for CIP. Each sample was repeated for three times.

Results and Discussion

Study on the adsorption of the resins for CIP molecules

Evaluation and screening of the resins based on their adsorption properties for CIP molecules

In this study, two skeletal resins and four acidic ion exchange resins have been chosen as adsorbent materials to compare their adsorption properties for CIP. The particle size and exchange capacity of six resins are equivalent, so the purpose of this work is to focus on the influence of the resin matrix type, functional group type on the adsorption effect for CIP. The adsorption effects of the resins for CIP have been judged by parameters q_e and R.

XAD7HP and XAD1180 are skeleton resins without functional groups, the difference between the two is only the matrix. Comparing the adsorption effect of these two resins for CIP, as shown in Fig. 1 (b), although the PAA-type XAD7HP shows slightly better, the adsorption effects of the two skeleton resins on CIP are all poor. Compared with skeleton resins, the adsorption effects of four acidic ion exchange resins for CIP are much more significant, indicating that functional groups play a key role. As for the two weak acid resins, the adsorption effect of IRC748 containing CH_2COOH-NH-CH_2COOH is more significant than that of IRC747with -CH_2-NH-CH_2-PO_3Na_2.The adsorption effects of IRC748 and IRC747 are not as good as that of strong acid type FPC23 with -SO_3H. The strong-weak acid complex S9570 with -SO_3H & -H_2PO_3 bifunctional group has the best adsorption effect. As we know, the order of functional group acidity for these resins is: -SO_3 H&-H_2PO_3> -SO_3H >CH_2COOH-NH-CH_2COOH>-CH_2-NH-CH_2-PO_3Na_2[34]. The consistency of the experimental results with this order shows that the stronger the acidity of the resin functional group, thus the stronger the electronegativity, and the better the adsorption effect. Therefore, S9570 resin has been chosen as an optimal adsorption material for the follow-up research.

Effect of pH on the adsorption of S9570 for CIP molecules

As shown in Fig. 2, CIP molecule is an amphoteric compound which can exist in various forms such as cationic, zwitter ionic and anionic in solution. From the distribution curve of CIP, pH < pK_{a1}, it mainly exists in the form of positively charged CIP^+; pK_{a1}< pH < pK_{a2}, mainly existing in the form of electrically neutral CIP; pK_{a2}< pH, mainly existing in the form of negatively charged CIP^-. As shown in Fig.1(a), among

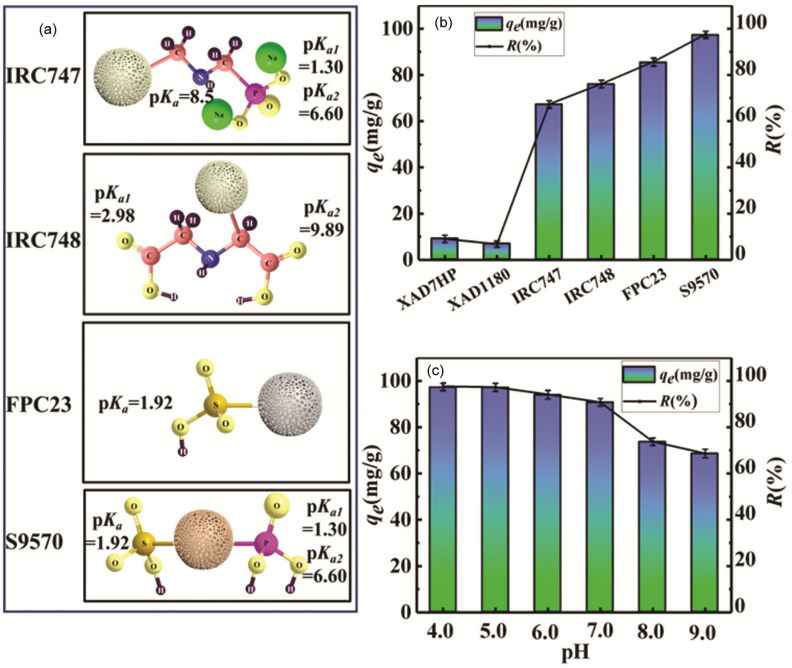

Fig. 1 — Effect of resin structure on adsorption (a) Resin structure; (b) Adsorption properties of the resins for CIP molecules and (c) Effect of *p*H on the adsorption of S9570 for CIP.

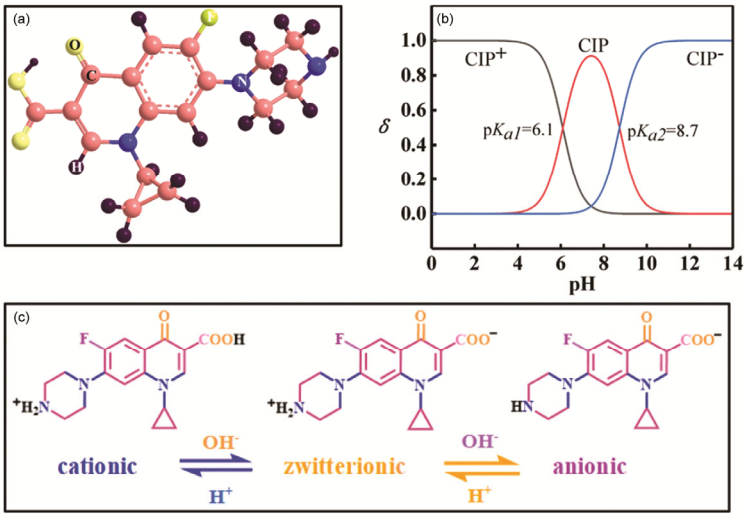

Fig. 2 — Structure and dissociation of CIP (a) Structure of CIP; (b) CIP distribution curve and (c) Dissociation of CIP.

the functional groups of S9570, -SO_3H is a strong acid group, which can be completely dissociated under the pH investigated; While -PO_3H_2, which is a weak acid, can only be partially dissociated. Compared with the dissociation strength of -SO_3H, it is negligible. Therefore, the negative charge of S9570 resin does not change much under the whole pH range investigated, and mainly depends on the dissociation of -SO_3H. Obviously, the ion exchange characteristic between S9570 and CIP mainly depends on the positive charge of CIP.

As shown in Fig. 1(c), in the range of pH 4.0~9.0, the smaller the pH, the better the adsorption effect of S9570 material for CIP, and the optimal adsorption capacity and removal rate of the material for the antibiotic molecules are obtained at pH 4. This is mainly because the positive charge of CIP increases significantly with the decrease of pH, especially when the pH value is between 4.0~6.0, the positive charge is the most significant (Fig. 2(b)). At low pH, the oppositely charged difference between S9570 and CIP is the largest. As a result, cation

Table 1 — Kinetics parameters of S9570 for CIP molecules.

		Pseudo-first-order				Pseudo-second-order			
		$q_{e,exp}$	$q_{e,cal}$	$K\times10^{-3}$	R^2	$q_{e,cal}$	$K_2\times10^{-4}$	h	R^2
T(K)	293	88.99	38.58	8.25	0.916	93.11	3.94	3.42	0.999
	303	91.58	39.11	7.81	0.901	95.88	3.72	3.42	0.999
	308	94.05	45.26	8.84	0.942	98.91	3.46	3.38	0.999
	313	96.64	40.76	7.37	0.897	101.01	3.49	3.56	0.999
C_0(mg/g)	50	47.18	25.27	9.04	0.943	49.63	6.62	1.63	0.999
	100	96.64	40.76	7.37	0.897	101.01	3.49	3.56	0.999
	150	144.02	93.07	8.14	0.979	154.32	1.47	3.49	0.999
RS(rmp)	100	89.99	75.18	7.27	0.993	99.01	1.43	1.41	0.996
	200	96.64	40.76	7.37	0.897	101.01	3.49	3.56	0.999

Table 2 — Intraparticle diffusion parameters of S9570forCIP molecules.

		k_{i1}	k_{i2}	C_{i1}	R_{i1}	R_{i1}^2	Initial behavior
T(K)	293	6.97	0.42	3.70	0.96	0.972	Weak
	303	7.11	0.47	3.89	0.96	0.971	Weak
	308	7.15	0.51	4.43	0.95	0.962	Weak
	313	7.39	0.56	4.99	0.95	0.949	Weak
C_0(mg/g)	50	2.62	0.34	9.54	0.80	0.988	Intermediate
	100	7.39	0.56	4.99	0.95	0.949	Weak
	150	9.71	1.48	5.91	0.96	0.975	Weak
RS(rmp)	100	4.87	1.88	5.42	0.94	0.985	Weak
	200	7.96	0.63	1.71	0.98	0.958	Weak

exchange property between them is more pronounced, thus exhibiting the best adsorption capacity and removal rate. In the following research, pH 4 as the optimal pH is chosen for adsorption removal of CIP molecules.

Adsorption kinetics of S9570 for CIP molecules

In general, the pH value, reaction temperature, initial concentration and rotating speed of the solution can affect removal effect of the material for CIP molecules. Through the optimization of the pH value in the previous stage, the effects of the other three factors have mainly investigated in the kinetic study. Three kinetic equations have beene used to fit the experimental data, the results are shown in Tables 1 and 2.

Compared with the pseudo-first-order kinetic equation, the fits of the pseudo-second-order kinetic equation are much better. The R^2 values of the equation are all above 0.99, which are obviously better than the former. At the same time, the calculated values ($q_{e,cal}$) of the equation parameters are basically consistent with the experimental values ($q_{e,exp}$), indicating that the equation can better describe the adsorption process of CIP by S9570. Based on the assumption of this equation[35], we speculate that there exists an electron transfer and shared chemisorption process between S9570 and CIP molecules through electrostatic interaction, hydrogen bond or Π-Π conjugated bond[10].

The fitting of the intraparticle diffusion equation shows double linearity, indicating that the adsorption process involved multiple stages. The first line represents the external diffusion of CIP molecules onto the S9570 adsorbent material, while the second line represents the diffusion from the interlayer into the interior of the S9570 particles[36]. From Table 2, the k_{il} values of the first stage are higher, indicating the existence of a fast external diffusion process as a result of electrostatic interaction between S9570 and CIP molecules. The lower k_{i2} values in the second stage illustrate the slow process of CIP molecules diffusing within the particles, indicating that most of the active sites of S9570 have been occupied by CIP molecules, few of active sites are left thus the less steeper slops are observed. Therefore, intraparticle diffusion limits the speed of the entire adsorption process and becomes the main rate-limiting step[37]. $C_{i1}> 0$, implying that there is a rapid adsorption phase within a short time of the beginning of the adsorption process[26], which is consistent with the above conclusion.$0.8 < R_{i1} < 1$, indicating that the process has a weak or intermediate initial adsorption behavior[27].

Based on the above analyses, pseudo-second-order and intra-particle diffusion equations are more

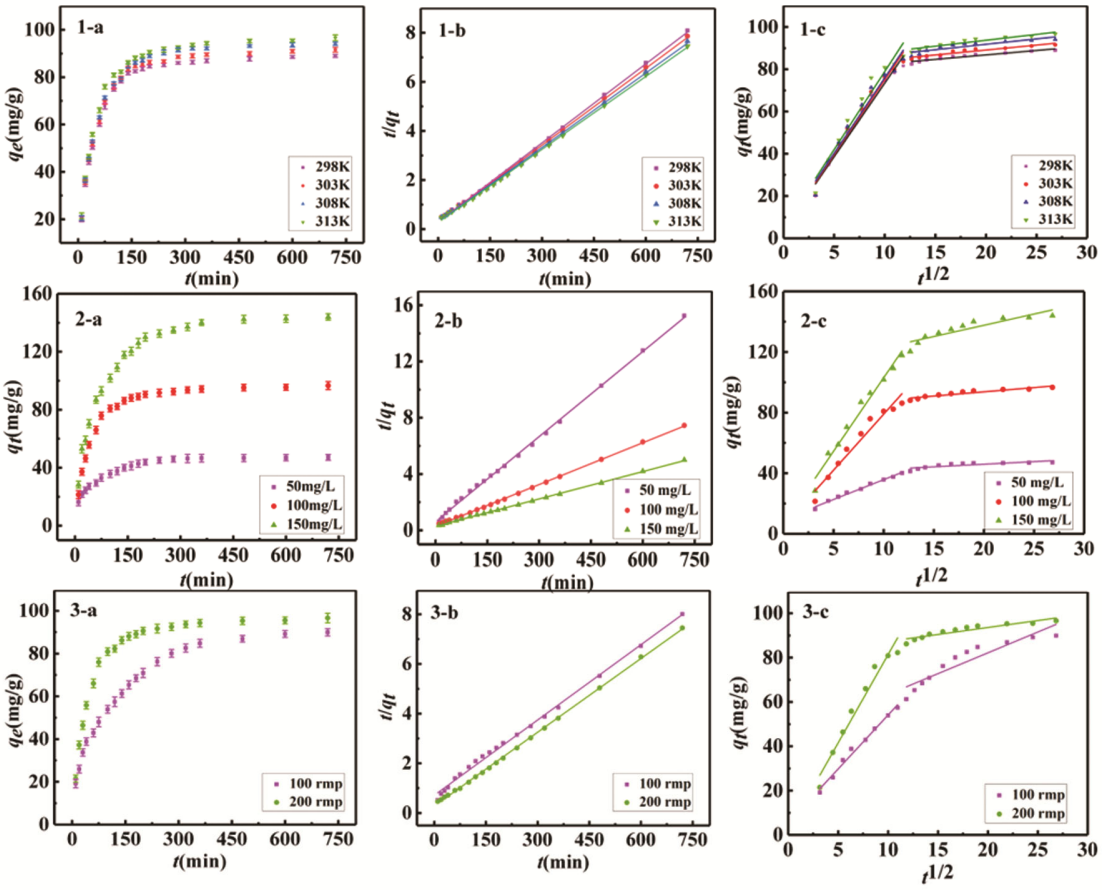

Fig. 3 — Adsorption kinetics of S9570 for CIP (1) Effect of the temperature; (2) Effect of the initial concentration and (3) Effect of the rotating speed (a) Kinetics curve (b) Pseudo-second-order; (c) Intraparticle diffusion;

suitable to describe the adsorption behaviors of S9570 material for CIP molecules.

Effect of the temperature on the adsorption of S9570 for CIP molecules

As shown in Fig. 3 (1-a; 1-b; 1-c) and Tables (1-2), when the temperature increases, the adsorption equilibrium time decreases, q_e increases slightly, k_2 and h increase to a certain extent, and k_i also increases slightly. The variation of the above adsorption parameters with temperature indicates that the adsorption process of CIP by S9570 is endothermic. However, small changes also infer that the endothermic process is not particularly significant, that is, the effect of the temperature is weak.

Effect of the initial concentration on the adsorption of S9570 for CIP molecules

As shown in Fig.3 (2-a; 2-b; 2-c) and Tables (1-2), when the concentration of the CIP solution is increased from 50 to 150 mg/L, the q_e values significantly increase, $q_{e,exp}$ increases from 41.78 to 144.02 mg/g, and $q_{e,cal}$ also increases from 49.63 to 154.32 mg/g. This phenomenon indicates that the increase of the initial concentration leads to the enhancement of the adsorption driving force due to the increase of the number of CIP-activated molecules. This can also be seen from the change of k_{i1} values. In addition, S9570 has an intermediate initial adsorption behavior for CIP molecules at low concentration, but a weak initial adsorption behavior at high concentration, implying that the adsorption of S9570 for CIP is a process with a gradually weakening adsorption rate.

Effect of the rotating speed on the adsorption of S9570 for CIP molecules

As shown in Fig. 3 (3-a; 3-b; 3-c) and Tables (1-2), with the increase of rotating speed, the time required to reach equilibrium will be relatively shorter, q_e will increase slightly, and k_2, h and k_{i1} will all increase, indicating that the movement of CIP molecules can be accelerated with the increase of rotating speed, thereby improving the adsorption of S9570 for CIP molecules to a certain extent and shortening the time to reach equilibrium.

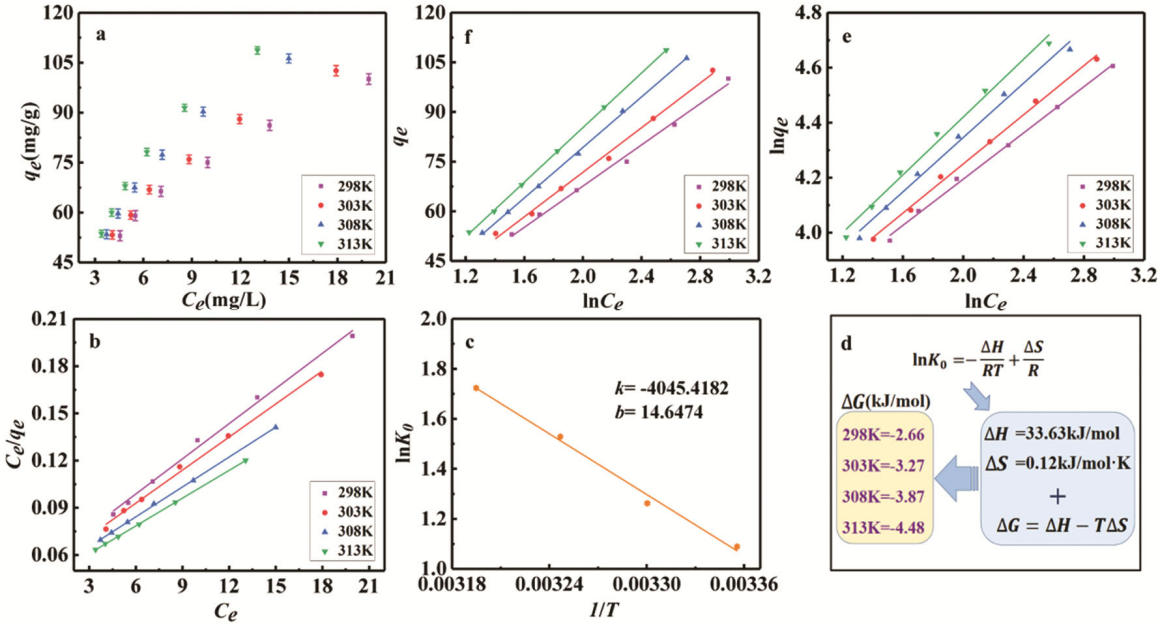

Fig. 4 — Adsorption thermodynamics of S9570 for CIP (a) Adsorption isotherms; (b) Langmuir model; (c) lnK_0~1/T curve; (d) Thermodynamic parameter; (e) Freundlich model and (f) Temkin model.

Table 3 — Isotherm parameters at different temperatures.

isotherm model	T (K)	Regression equation	Parameter				
			R_L	K_L	q_m	R^2	AIC
Langmuir	298	y=0.00745x+0.05412	0.0014	7.26	134.23	0.995	-22.21
	303	y=0.00700x+0.05094	0.0014	7.28	142.86	0.996	-26.12
	308	y=0.00633x+0.04630	0.0014	7.31	157.98	0.999	-31.04
	313	y=0.00588x+0.04324	0.0014	7.35	170.07	0.999	-34.68
			K_F		1/n	R^2	AIC
Freundlich	298	y=0.42020x+3.35385	28.61		0.42	0.997	1.93
	303	y=0.44695x+3.35565	28.66		0.45	0.997	2.50
	308	y=0.49409x+3.35735	28.71		0.49	0.992	3.24
	313	y=0.52573x+3.36853	29.04		0.53	0.990	3.67
			K_T		B_T	R^2	AIC
Temkin	298	y=31.12023x+5.38020	1.19		31.12	0.995	70.82
	303	y=33.64334x+4.51777	1.14		33.64	0.996	71.65
	308	y=38.15641x+2.98957	1.08		38.16	0.999	72.73
	313	y=41.20990x+2.86918	1.07		41.21	0.999	73.37

From the effects of three factors on the adsorption of CIP molecules by S9570, it can be seen that the effect of initial concentration is the most significant, followed by rotating speed, while the effect of temperature is the least, indicating there exists a weak endothermic process. Under the optimized adsorption conditions (313 K, 150 mg/g, 200 rmp, pH 4.0), the $q_{e,exp}$ and $q_{e,cal}$ values can be reached as high as 144.02 and 154.32 mg/g, respectively.

Adsorption thermodynamics of S9570 for CIP molecules

Experiment and model fitting of adsorption thermodynamics

The adsorption isotherm describes the equilibrium adsorption relationship of the adsorbate in the solid-liquid two phase under a constant temperature condition. Fig. 4(a) presents the adsorption isotherms of S9570 material for CIP molecules at different temperatures. Langmuir, Freundlich and Temkin isotherm models were used to investigate the adsorption thermodynamics between S9570 and CIP, the isotherm parameters at different temperatures were calculated. The results are shown in Fig. 4 (b, e, f) and Table 3.

From Table 3, the correlation coefficient R^2 values of the three models are not significantly different, so it cannot be effectively judged by the parameter R^2.

Akaike Information Criterion (*AIC*)[38], a new standard, has been adopted to judge the fitting goodness of three models. The smaller the *AIC* value, the better the fitting effect. The *AIC* values of the Langmuir model are the smallest, indicating that this model is more suitable for describing the adsorption thermodynamic process of S9570 for CIP molecules. The result shows that the surface of the S9570 is uniform, and the adsorption of the material for CIP is a monolayer saturated adsorption. With the increase of temperature, the monolayer saturated adsorption capacity q_m of CIP increases from 134.23 to 170.07 mg/g, and K_L increases also, indicating that high temperature is beneficial to the adsorption of S9570 for CIP molecules. This conclusion is consistent with that of the kinetic experiments. $0 < R_L < 1$, indicating that the adsorption of the material for CIP is a favourable and spontaneous process[28].

Parameters of adsorption thermodynamics

To further clarify the thermodynamic characteristics of the adsorption process ofS9570 for CIP molecules, thermodynamic parameters such as enthalpy change (ΔH), entropy change (ΔS) and standard Gibbs free energy (ΔG) at different temperatures have been calculated. The results are shown in Fig.4(c, d).

From Fig.4(c, d), $\Delta H > 0$, indicating that the adsorption of S9570 for CIP molecules is an endothermic process, which is consistent with the previous kinetic and thermodynamic conclusions, that is, the adsorption capacity of the material for CIP increases with the increase of temperature. $\Delta S > 0$, implying that during the adsorption process of S9570, the disorder of the solid-solution interface increases as a result of the replacement of CIP molecules by a large number of water molecules on the surface of the adsorbent material[39]. $\Delta G < 0$, inferring that the adsorption of S9570 for CIP is a spontaneous process[40] due to the adsorption stronger enough to overcome the potential barrier. This conclusion is consistent with that of parameter R_L. In addition, the absolute value of ΔG increases with the increase of temperature, suggesting that the increase in the activation energy of CIP molecules is beneficial to overcome the potential barrier[41].

Adsorption mechanism of S9570 for CIP molecules

From the kinetic conclusion, there exists an electron transfer and shared chemisorptions between S9570 and CIP molecules. Combining the electronegativity of the S9570 material ligand functional group and the CIP molecule at pH 4.0, we speculate that the adsorption mechanism between them is shown in Fig. 5.

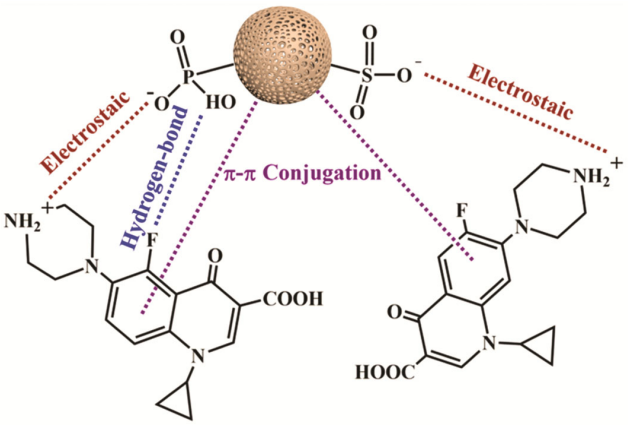

Fig. 5 — Adsorption schematic of S9570 for CIP molecules.

Under the acidic condition, $-SO_3H$ and $-PO_3H_2$ on the S9570 material are dissociated into negatively charged $-SO_3^-$ and $-HPO_3^-$, respectively, which can have electrostatic adsorption with positively charged CIP^+. At the same time, the hydrogen atom in the functional group $-HPO_3^-$ and the fluorine atom in CIP undergo hydrogen bond adsorption, and there is a Π-Π conjugation between the benzene ring on the adsorbent skeleton and the benzene ring in CIP[10]. It can be seen that the adsorption and removal of S9570 material for CIP molecules is mainly based on the electrostatic interaction, and also accompanied by the synergistic effect of hydrogen bonding and Π-Π conjugation.

Evaluation on the adsorption property of S9570 for CIP molecules

Effect of interfering ions on the adsorption of S9570 for CIP

The effect of interfering ions on S9570 for CIP adsorption is possibly caused by the competition partition of CIP molecules in the liquid-solid two-phase (the interfering ions in the solution and functional groups on the solid adsorbent), as well as the charged properties of interfering ions.

As shown in the Fig. 6 (a), anions have almost no effects on the adsorption process of S9570 for CIP due to the electrostatic repulsion between negatively charged S9570 and anions together with the electronegativity of the anions. HCO_3^- is protonated to be H_2CO_3 at pH=4, which has no effect on the adsorption process. For Cl^-, SO_4^{2-} and NO_3^-, the electronegativity order is $SO_4^{2-} > Cl^- > NO_3^-$, and the greater the electronegativity, the greater the influence on the adsorption process. Therefore, the interference effects of various anions are consistent with the experimental results.

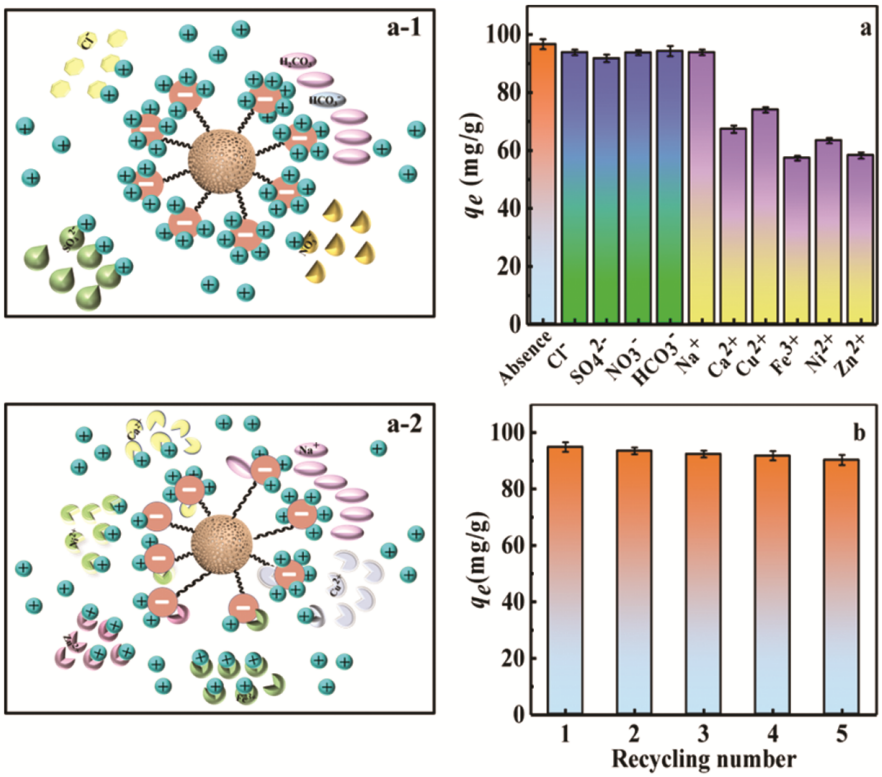

Fig. 6 — Evaluation of resins (a) Effect of interfering ions on the adsorption of S9570 for CIP ; (a-1) Anion; (a-2) Cation and (b) Reusability of S9570 material

Table 4 — Adsorption comparison of CIP by different methods.

Resin		Antibiotic	M_{CIP}: M_{Resin} (mg/g)	q_e (mg/g)	Ref.
Functional group	Interaction				
None	Hydrophobic	CIP	1 : 0.005	63.75	[8]
$-SO_3H$	Hydrophobic	CIP	1 : 0.010	20.00~30.00	[10]
$-N^+(CH_3)_3$	Hydrophobic	CIP	1 : 0.010	90.00~95.00	[10]
$-N(CH_3)_2$	Hydrophobic	CIP	1 : 0.010	90.00~95.00	[10]
$-C_2H_2(CO)_2O$	Hydrogen-bond	CIP	1 : 0.025	35.57	[11]
$-SO_3H$ &$-H_2PO_3$	Electrostatic, Hydrogen-bond, Π-Π Conjugation	CIP	1 : 0.007	144.02 154.32	This work

It is impossible to generate electrostatic adsorption between cations and positively charged CIP molecules, but they can be adsorbed through coordination interaction. The metal ion Na^+ without empty valence orbitals has almost no effect on CIP adsorption by resin. Ca^{2+}, Cu^{2+}, Fe^{3+}, Ni^{2+} and Zn^{2+} containing empty valence orbitals can reduce the adsorption effect. On the other hand, cations can also be adsorbed to negatively charged S9570 by electrostatic interaction. Obviously, the interference ability of cations is much more than that of anions.

Adsorption reusability of S9570 for CIP

In order to reduce the production cost of the industrial adsorbent and secondary pollution, the recovery and recycling of the adsorbent is very important. The effect of S9570 material adsorption-desorption cycle times on the adsorption capacity of CIP molecules is shown in Fig. 6 (b). It can be seen that the adsorption effect slightly decreases from 94.85 to 90.26mg/g after 5 consecutive cycles of adsorption-desorption. However, the material still has a good adsorption and removal effect for CIP, and its adsorption performance can still reach 95% of the initial adsorption capacity, indicating

that the adsorbent has good reusability and economic feasibility.

To asses S9570 material involved in this work, the adsorption and removal effects of CIP molecules by this material and other similar resin-based adsorbents reported in literatures are listed in Table 4.

Compared with the existing methods, S9570 adsorbs CIP molecules mainly through electrostatic interaction due to its strong ion exchange property. When the mass ratio of CIP to the adsorption material is only 1 : 0.0067 mg/g, $q_{e,exp}$ and $q_{e,cal}$ values even can attain as high as 144.02 and 154.32 mg/g respectively, indicating that a small amount of S9570 can achieve efficient adsorption and removal capacity. It follows that the adsorption material and method involved at present work have more superior application prospects.

Conclusion

In this study, the composite acid-type resin S9570 with bifunctional group has been used as a novel adsorption material. Under acidic condition, the material utilizes the synergistic effect of electrostatic interaction as the main and hydrogen bonding & Π-Π conjugation as a supplement to adsorb and remove the fluoroquinolone antibiotic CIP.

The adsorption of S9570 for CIP molecules is a monolayer adsorption process controlled by both chemisorption and intraparticle diffusion, which is a spontaneous, endothermic one with increased disorder at the solid-liquid interface.

S9570 still has a good adsorption and removal rate of CIP in the presence of interfering ions, especially anions, and also has excellent reusability. Compared with the existing resin methods, the present work has obvious advantages in the removal of CIP from wastewater. The adopted adsorption material and mechanism has ensured that the method is an efficient way for adsorbing and removing CIP from wastewater, good reusability and economic feasibility. It is foreseeable that this method provides a promising new idea for removing other fluoroquinolone antibiotics including CIP.

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