JOURNAL OF
Applied Polymer
SCIENCE

Preparation of metal ions impregnated polystyrene resins for adsorption of antibiotics contaminants in aquatic environment

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ABSTRACT: In this study, the strong-acid polystyrene resin D001 was modified by impregnation with metal ions Fe^{3+}, Cu^{2+}, and Zn^{2+} to prepare new kinds of sorbents. The modified D001 was characterized by N_2 sorption–desorption isotherms, X-ray powder diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The sorption performance of the metal modified resins for removal of antibiotics tetracycline (TC) and doxycycline (DC) from aquatic environment was investigated and excellent sorption capability with more than 98% removal ratio was observed for these resins after modification. Although these modified resins also presented pH-dependent sorption, they showed much better flexibility with pH fluctuation than those of the unmodified original D001, and extremely strong sorption capability was exhibited in a wide range of pH 2–8 for both TC and DC. Pseudo-second-order kinetic equation described the sorption process more reasonably than pseudo-first-order equation. Langmuir isotherm model provided the best match to the equilibrium data with monolayer maximum sorption capacity of 417–625 mg g^{-1} under 288–318 K. The sorption capacity decreased with the increase of ionic strength of NaCl. The main sorption mechanism was proposed to be surface complexation, cation bridge interaction and electrostatic attraction/competition between antibiotics and metal modified resins. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41803.

KEYWORDS: adsorption; resins; separation techniques

Received 18 July 2014; accepted 23 November 2014
DOI: 10.1002/app.41803

INTRODUCTION

The presence of pharmaceutical antibiotics in aquatic environments is considered to be a rising concern due to their potential risks to human and ecological health.[1,2] Antibiotics are difficult to be metabolized in human and animal bodies, and excrete continuously into the environment as active compounds.[3] Furthermore, antibiotics can be discharged into aquatic environments through other sources, such as the direct release of veterinary antibiotics in aquaculture, improper disposal of unused or expired antibiotics, and waste effluents from hospitals or manufactures. However, most traditional water and wastewater treatment technologies are ineffective or useless against such contaminants.[4] Studies show that antibiotics are detected in the higher $\mu g\ L^{-1}$ range in hospital effluents, lower $\mu g\ L^{-1}$ range in municipal wastewater and ng L^{-1} in surface, sea and ground waters.[5] As a result, relatively high densities of antibiotic-resistant bacteria are often found in the aquatic environment, posing a serious threat to public health in that currently available antibiotics may be ineffective in controlling more and more new types of infections.[6]

Tetracycline (TC) and doxycycline (DC), two typical tetracycline antibiotics group (TCs), are widely used as antimicrobials in human and veterinary medicines because of their broad-spectrum antimicrobial activities. Similar to other antibiotics contaminants, TC and DC residues in environment have caused potential problems due to increasing tetracycline resistant bacteria. Therefore, the efficient removal methods of these contaminants should be paid more attention. Up till now, the technologies of biodegradation,[7] advanced oxidation,[8] membrane filtration,[9] and sorption[10] have been developed for removal of the organic pollutants. Among which, the non-destructive method of sorption has been considered as one of the most economical, effective and attractive technologies to treat these persistent antibiotics.

Recent studies on the adsorbents are focused on sludge,[11] bentonite,[12] montmorillonite,[13] zeolite,[14] activated carbons,[15] carbon nanotubes,[16] graphene-like MoS_2,[17] metallic oxide,[18] or polymers.[19] Some of these adsorbents show good sorption ability at their original or natural forms, but some should be

Additional Supporting Information may be found in the online version of this article.

modified to display better sorption capacity. Researchers have indicated that metal ion (Cu^{2+} and Fe^{3+}) modified activated carbons can enhance the cephalexin removal from aqueous solution,[20] and Cu^{2+} grafted mesoporous SBA-15 displays more effective removal of naproxen than the original SBA-15,[21] and that the sorption capacity of TC on modified mesoporous MCM-41 increases dramatically after impregnation with zeolite.[22] The sorption behavior after modification is usually influenced by the grafting process and the choice of metal ions.

Polymer resins are good candidates for the design of antibiotics selective adsorbents due to their stable chemical structures, large surface areas, high porosity, low costs and easy regeneration. Polymer resins have demonstrated their potentials in the application in water purification, organic pollutants or heave metal removal, drug separation, and controlled drug delivery.[23–26] Recent studies have investigated some commercial hypercrosslinked resins, aminated polystyrene resins, macro/microporous resins and ionic exchange resins for adsorptive removal of antibiotics, such as sulfonamides,[27–29] tetracyclines,[30] norfloxacin,[18] nalidixic acid,[31] trimethoprim,[32] chloramphenical,[33] and vancomycin.[34] Modified polymer resins have also been engineered to remove pollutants from aqueous environment. Jia *et al.*[35] synthesized iron impregnated weakly basic resin D301 (Fe-D301) for the removal of 2-naphthalenesulfonic acid. Negrea *et al.*[36] designed Fe-III-loaded XAD7 resin containing di(2-ethylhexyl) phosphoric acid to remove As(V). To enhance the acid resistance and lipophilicity of the magnetic gamma-Fe_2O_3 particles, Zhang *et al.*[37] employed titanate to modify the resin to adsorb Ni^{2+}. Research group of Li has prepared some magnetic resins to investigate the sorption behavior and mechanism of contaminants (include antibiotics TC).[38,39] However, the designs of modified resins to enhance the sorption ability of antibiotics together with their mechanisms are still rare.

In the former research,[40] we investigated several commercial porous polystyrene resins for removing antibiotics TC and DC, and the strong-acid resins (for example, D001) showed good sorption ability only at extremely acidic condition of pH 2–3, which greatly restricted their further application. To increase the practicality in treatment of wastewater, metal modified D001 by impregnation with $Fe^{3+}/Cu^{2+}/Zn^{2+}$ was prepared and showed much better flexibility with pH fluctuation than those of the unmodified original D001. The sorption behavior for TC and DC was investigated through kinetics and thermodynamics studies. The mechanisms and predominant factors controlling the sorption were evaluated under deferent conditions (solution pH, ionic strength, and temperature).

EXPERIMENTAL

Materials

Tetracycline (TC) and doxycycline hydrochloride (DC) were obtained from Sigma–Aldrich Chemical (99% purity). The initial pHs of TC and DC aqueous solutions were 6.38 and 3.84, respectively. The strong-acid resin D001 was purchased from Nankai University Chemical Factory. The structures of sorbate (TC and DC) and sorbent (D001) were shown in Supporting Information Figure S1. HCl, NaOH, ethanol, $CuCl_2$, $FeCl_3$, and $ZnCl_2$ were supplied by Sinopharm Chemical Reagent (A.R. grade). Water used in the study was purified by distillation.

Characterization and Analysis

The surface area (BET method) was calculated by the nitrogen sorption-desorption isotherms at 77 K using a TriStar II 3020 surface area and porosity analyzer (Micromeritics Instrument). X-ray powder diffraction (XRD) patterns were recorded using a D/MAX-2550 diffractometer, equipped with a Cu Kα radiation source ($\lambda = 1.5418$ A). FTIR spectra were recorded in the range 400–4000 cm^{-1} using a Fourier transform infrared spectrometer. UV–vis diffuse reflectance spectra (UV–vis DRS) were recorded using a UV–vis diffuse reflectance spectrometer. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used to detect the uptake of Fe^{3+}, Cu^{2+}, and Zn^{2+} on the modified resins. For batch sorption experiments, the equilibrium concentration of TC or DC in the solution was measured in a 1-cm path-length quartz cuvette by UV–vis spectrometer (UV-2401 PC, Shimadzu, Japan) at 358 nm (TC) or 345 nm (DC). Linear calibration curves (absorbance versus concentration) were used to analyze the concentration with the correlation coefficient >0.999.

Preparation of Metal Modified D001

To remove impurities, the resin was first washed with distilled water, then rinsed with 1.0 mol L^{-1} NaOH, and finally washed with distilled water to pH 6–7. Next, the resin was rinsed with 1.0 mol L^{-1} HCl and again flushed with distilled water to reach neutral pH. Finally, the resin was stirred with ethanol for 4 h, and then vacuum desiccated at 325 K overnight. After these steps, the pretreated D001 resin was dipped into the mixture of HCl (0.5 mol L^{-1}) and $CuCl_2$ (0.05 mol L^{-1}) solution to be stirred at room temperature for 4 h and then stood for 48 h. The D001 resin modified with Cu^{2+} ion was therefore obtained and termed Cu/D001. Metal Fe^{3+} and Zn^{2+} modified D001 resins, Fe/D001 and Zn/D001, were prepared using the same method as that of Cu/D001 mentioned above, but exchanging $CuCl_2$ to $FeCl_3$ and $ZnCl_2$, respectively. To determine the uptake amount of Fe^{3+}, Cu^{2+}, and Zn^{2+} on the modified resins, the residual concentration (mmol L^{-1}) of metal ions in the metal halides solution were detected by ICP-OES after the resins being modified.

Sorption Experiments

Sorption experiments were obtained with a batch equilibrium procedure using 100 mL conical flasks in a thermostatic shaker bath at a preset temperature and a shaking speed of 130 rpm. The flasks were wrapped with aluminum foils to avoid photodegradation. For kinetics study, 50 mg of adsorbent were introduced into the flasks, which contained 50 mL TC or DC solutions at the initial concentration of 100 mg L^{-1}. At different sorption times at 298 K, 5 mL supernatant was aspirated and analyzed immediately. After quantification, which took around 30 s, the supernatant was reintroduced into the flasks. This procedure (separation, quantification and reintroduction) was repeated during several hours until the sorption equilibrium was reached. For pH dependent sorption, 10 and 20 mg adsorbents were introduced into TC or DC solutions and then adsorbed to equilibrium under 303 K, the solution pH was

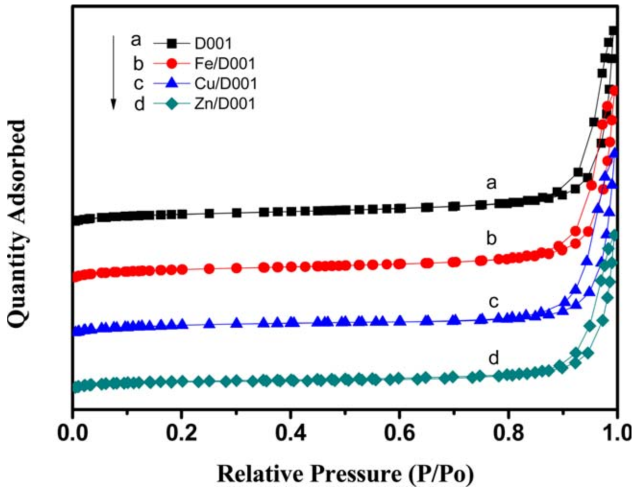

Figure 1. Adsorption and desorption isotherms of N_2 for M/D001 (M: Fe, Cu and Zn) and D001. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

changed from 2 to 11 using 0.02 mol L^{-1} HCl or NaOH. In ionic strength study, different amount of NaCl solid was added and dissolved in 80 mL TC or DC solution before adding 20 mg resins, the sorption underwent at 303 K till equilibrium. Sorption isotherm and thermodynamic studies were carried out with initial TC or DC concentrations of 20, 40, 60, 80, 100, and 120 mg L^{-1} under different temperatures of 288, 303, and 318 K, respectively.

The sorption capacity of TC or DC adsorbed onto resins at equilibrium and time t (h) was calculated using eqs. (1) and (2), respectively.

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

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

where q_e and q_t is the sorption capacity (mg g^{-1}) on the adsorbent at equilibrium and time t (h), respectively; C_0 is the initial adsorbate concentration (mg L^{-1}); C_e and C_t is the residual concentration (mg L^{-1}) of adsorbate at equilibrium and time t (h) in the solution, respectively; V is the volume of solution (L), and m is the mass of adsorbent (g).

Sorption Models of Kinetics and Isotherms

The sorption kinetic and isotherm models were of crucial importance in analyzing the sorption process and mechanism. In this study, two kinetic models: pseudo-first and -second order equations, and three isotherm models: Langmuir, Freundlich, and Tempkin were used to analyze the data of TC and DC sorption on the three metal impregnated resins M/D001 (M: Fe, Cu, and Zn). The original and linear forms of these models with their key parameters were listed in Supporting Information (Table SI).

RESULTS AND DISCUSSION

Characteristics of Adsorbents

The detection uptake of metal ions Fe^{3+}, Cu^{2+}, and Zn^{2+} on the modified resins was 1.2, 1.0, and 1.1 mmol g^{-1}, respectively. According to the introduced information about the commercial D001 resin, The total ion exchange capacity of the purchased D001 was above 4.1 mmol g^{-1}, which suggested that Fe^{3+}, Cu^{2+}, and Zn^{2+} may be loaded on a certain portion of ion-exchange groups of D001 resins by means of ion exchange.

Table I. Porous Structure Parameters of M/D001 (M: Fe, Cu, and Zn) and D001

Sample	BET surface area (m^2 g^{-1})	Pore diameter (nm)	Pore volume (cm^3 g^{-1})
D001	23.41	37.21	0.17
Fe/D001	23.82	35.92	0.16
Cu/D001	22.73	36.56	0.16
Zn/D001	19.43	38.40	0.14

The N_2 sorption-desorption isotherms and pore size distribution of the metal modified resins M/D001 (M: Fe, Cu, and Zn) and original D001 were shown in Figure 1. The textural properties of the four adsorbents were very similar. The sorption and desorption isotherms exhibited a hysteresis loop and a steep increase in nitrogen volume adsorbed at higher P/P_o, which suggested a relatively large contribution in mesopore and macropore range in the four adsorbents.[41] As shown in Table I, the four adsorbents displayed the BET surface area of 19.43–23.82 m^2 g^{-1} and the pore volume of 0.14–0.17 cm^3 g^{-1}.

Supporting Information Figure S2 showed wide-angle powder XRD patterns of M/D001 (M: Fe, Cu, and Zn) and D001. The XRD pattern of D001 indicated a broad diffraction peak centered at about $2\theta = 24°$, suggesting that the structure characteristic of D001 resin is amorphous. The XRD patterns of M/D001 (M: Fe, Cu, and Zn) samples were similar and no new peaks were obtained. Hence, after impregnation, no extra framework crystalline Fe, Cu and Zn species could be found on D001 resin.

The FTIR spectra of M/D001 (M: Fe, Cu, and Zn) and D001 were shown in Figure 2. The characteristic bands at about 1600,

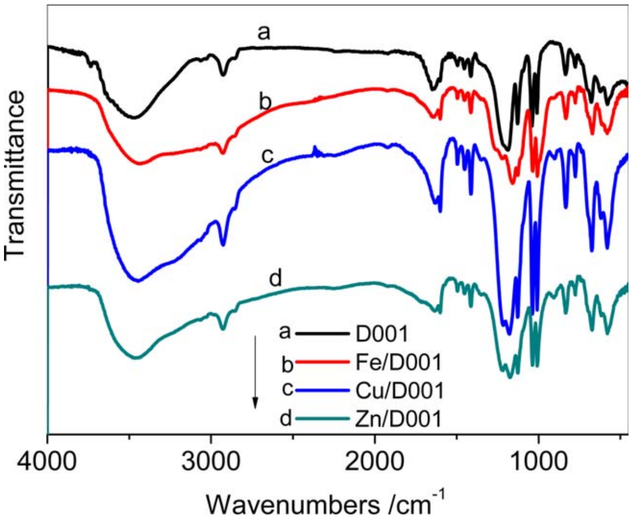

Figure 2. The FTIR spectra of M/D001 (M: Fe, Cu, and Zn) and D001. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

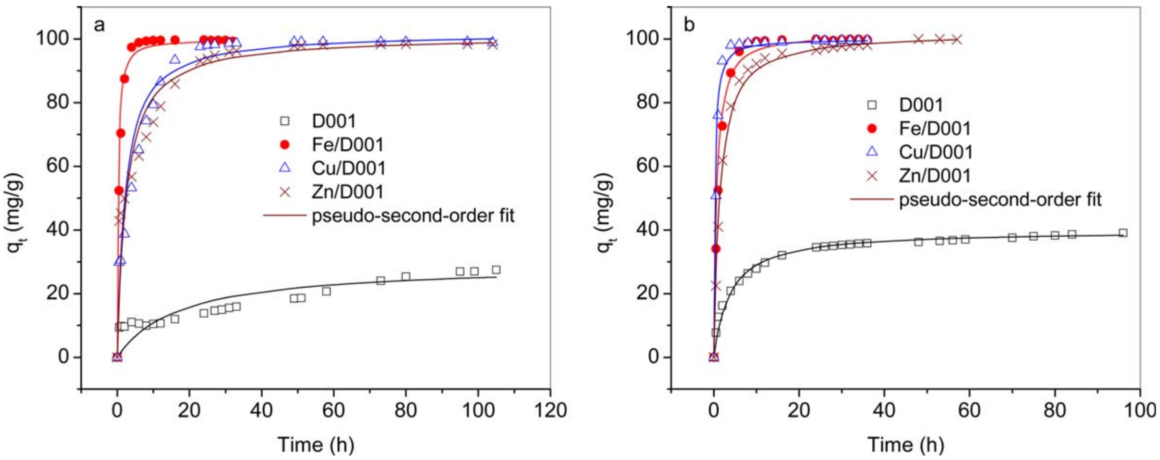

Figure 3. Sorption kinetics of TC (a) and DC (b) onto the four resins using pseudo-second-order model fit. ($m_{\text{sorbent}} = 50$ mg, $V_{\text{sorbate}} = 50$ mL, $C_0 = 100$ mg L^{-1}, pH = 7.0, $T = 298$ K). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1496, 1450, and 1411 cm^{-1} were the principal features of the resin structure.[42] This result demonstrated that the framework of D001 resin was stable during the modification process by metal ion. This result could be also proven by the XRD of the four adsorbents. Moreover, there were two bands at 1182 and 1039 cm^{-1} in the FTIR spectrum of D001, which was attributed to the asymmetric and symmetric stretching vibration of S=O.[43] On the other hand, the band at 1182 cm^{-1} in the FTIR spectra of M/D001(M: Fe, Cu and Zn) split into two absorption peaks, which appeared at 1160–1170 cm^{-1} and 1220 cm^{-1}, respectively. A new band at 900 cm^{-1} was found after the modification of metal ion on D001. These results indicated that the S=O had an interaction with Fe^{3+}, Cu^{2+}, and Zn^{2+}, which increased the nonequivalent of S=O.

Kinetics of Sorption

To define the sorption equilibrium time and analyze the rate during sorption process, the sorption kinetics of TC and DC onto three metal impregnated resins M/D001 (M: Fe, Cu, and Zn) and original D001 had been performed under pH 7.0. As seen from Figure 3, the modified resins displayed much better sorption performance both for TC and DC than the original resin. More than 98% of antibiotics were removed from the solution by metal modified resins. Although similar equilibrium sorption capacities were obtained on the three modified resins under experiment conditions, the sorption rate and the equilibrium time showed slight difference. For TC [Figure 3(a)], Fe/D001 displayed faster sorption than Cu/D001 and Zn/D001, around 90% sorption capacity was achieved in 2 h for Fe/D001, while it would take about 16 h for Cu/D001 and Zn/D001. The equilibrium time was around 24, 48, and 72 h for Fe/D001, Cu/D001 and Zn/D001, respectively. For the sorption of DC [Figure 3(b)], the sorption rate was in the order of Cu/D001 > Fe/D001 > Zn/D001, the time took for 90% sorption capacity was about 2, 4, and 8 h, while the equilibrium was 12, 24, and 48 h, respectively. The relatively fast sorption abilities of these metal modified resins exhibited another advantage compared to previously studied original resins (equilibrium time: 96 h for D201 and D370,[40] 15 days for XAD-7[32]).

Kinetics study with sorption kinetic models is crucial in understanding the sorption order and rate. The fitting results by pseudo-first and -second order models were shown in Figure 3 and Table II. It could be observed that pseudo-second-order model was more in agreement with the sorption data for both TC and DC on the modified resins than pseudo-first-order model. The correlation coefficient of pseudo-second-order model was significantly high ($R^2 > 0.9992$), and the equilibrium sorption capacity obtained from experimental data ($q_{e,\text{exp}}$) was approximately identical to those calculated by pseudo-second-order model ($q_{e,2}$). As a result, the sorption process of TC and DC on the modified resins could be illustrated by pseudo-second-order model, indicating that the sorption process gave a lot of credit to chemical interactions between antibiotics and adsorbents.[16] Beyond that shown in Figure 3, the sorption rate could also be reflected through the rate constant k_2, as well as the initial sorption rate h ($h = k_2 q_e^2$) and the half-equilibrium time $t^{1/2}$ ($t^{1/2} = 1/(k_2 q_e)$), which were given in Table II. As described above, the metal modified resins M/D001 (M: Fe, Cu, and Zn) exhibited much faster sorption for both TC and DC than original D001.

Effect of pH and Mechanism Analysis

In the sorption of amphoteric compounds, pH is considered to be one of the most important factors affecting the sorption performance, as it can alter the charge and species of the compounds as well as the sorbent surface properties.[44] TC and DC are amphoteric molecules with multiple ionizable functional groups, and may exist as cation, zwitterion, or anion forms at different pH conditions. In the case of TC (Supporting Information Figure S1), cationic form (TCH_3^+) mainly exists at pH below 3.3 due to the protonation of dimethyl-ammonium group. Its zwitterions (TCH_2^0) form appears at $3.3 < \text{pH} < 7.7$ by the loss of a proton from the phenolic diketone moiety. At $\text{pH} > 7.7$, TC transforms into anionic species (TCH^- at $7.7 < \text{pH} < 9.7$ or TC^{2-} at $\text{pH} > 9.7$) through the loss of protons from the tri-carbonyl system and phenolic diketone moiety.[22]

The effect of pH on the sorption of TC and DC onto the three metal modified resins and the original resin D001 was studied within the pH range of 2–11, and the results were depicted in Figure 4. For both TC and DC, all of the metal modified resins

Table II. Pseudo-First and Second-Order Kinetic Parameters for Sorption of TC and DC onto the Resins

			Pseudo-first-order model			Pseudo-second-order model				
Adsorbate	Resins	$q_{e,exp}$ (mg g^{-1})	$q_{e,1}$ (mg g^{-1})	k_1 (h^{-1})	R^2	$q_{e,2}$ (mg g^{-1})	k_2 (g mg^{-1} h^{-1})	h (mg g^{-1} h^{-1})	$t_{1/2}$ (h)	R^2
TC	Fe/D001	99.7143	23.2801	0.4099	0.8911	100.0000	0.0455	454.5455	0.2200	0.9999
	Cu/D001	99.1020	86.2888	0.1669	0.9964	102.0408	0.0047	49.2611	2.0714	0.9992
	Zn/D001	98.3878	56.8491	0.0955	0.9966	101.0101	0.0042	43.1034	2.3434	0.9993
	D001	27.4154	21.2085	0.0228	0.8959	29.2398	0.0020	1.7262	16.9386	0.9248
DC	Fe/D001	99.9240	54.2498	0.3907	0.9637	102.0408	0.0168	175.4386	0.5816	0.9997
	Cu/D001	99.5840	31.2244	0.5195	0.8572	100.0000	0.0476	476.1905	0.2100	0.9999
	Zn/D001	99.9940	32.7041	0.0900	0.8700	102.0408	0.0076	78.7402	1.2959	0.9999
	D001	39.0800	17.7574	0.0401	0.9311	39.8406	0.0068	10.7181	3.7171	0.9992

exhibited much better flexibility with pH fluctuation than the original D001 and showed excellent sorption performance in the studied wide range of pH, especially in the range of pH 2–8, where the amount adsorbed onto the modified resins were all above 200 mg g^{-1}. This result may be attributed to the change of the interacting forces between sorbate and sorbent by introducing metal active center to resin D001. Many studies have shown that TCs are capable of bounding with various multivalent metal cations such as Fe^{3+}, Al^{3+}, and Cu^{2+} to form strong complexes.[7,13,45,46] Because TC and DC possess multiple functional groups, such as enone, phenol and alcohol, which can be expected to form stable complex with the surface metals Fe^{3+}, Cu^{2+}, and Zn^{2+} of modified resins due to redistribution of electrons.[47] Therefore, we proposed a predominant interaction of surface complexation mechanism for the TC and DC sorption onto the metal modified resins.

The binding between the antibiotics and modified resins can be visualized comparing the FTIR spectra of antibiotics and antibiotics-loaded resins after sorption such as shown in Supporting Information Figure S3. TC showed characteristic peaks at 1653 and 1516 cm^{-1} assigned to the carbonyl and amino groups of the amide in ring A. The 1619 and 1586 cm^{-1} bands corresponded to the carbonyl stretching vibration in rings A and C, respectively. The 1456 cm^{-1} assigned to the C=C skeletal vibration, 1398 cm^{-1} corresponded to CH_3 deformation vibration, 1255 cm^{-1} assigned to C—N amine groups, and 1184 cm^{-1} which was attributed to the phenolic C=O stretching vibration.[45,48] The spectra of TC-loaded resins (TC-M/D001, M: Fe, Cu, and Zn) in Supporting Information Figure S3 were similar, suggesting that similar type of surface interaction might exist. It was clearly showed that the band of amide carbonyl and amino groups in ring A and the carbonyl groups in ring A and C of TC were changed and disappeared, and the peak intensity of 1160–1170 cm^{-1}, 1220 cm^{-1}, and 900 cm^{-1} which related the characteristic peaks of metal modified resins M/D001 (M: Fe, Cu, and Zn) discussed above (Figure 2) were decreased obviously. The obtained results indicated that tetracycline antibiotics were bound to the modified resins surface via strong complexation interactions and the complexation was probably occurring at the tri-carbonylamide (C-1:C-2:C-3 in ring A) and carbonyl (C-11 in ring C) functional groups. Other studies also provided evidence for the involvement of the tri-carbonylamide group of ring A and the O11:O12 oxygen to

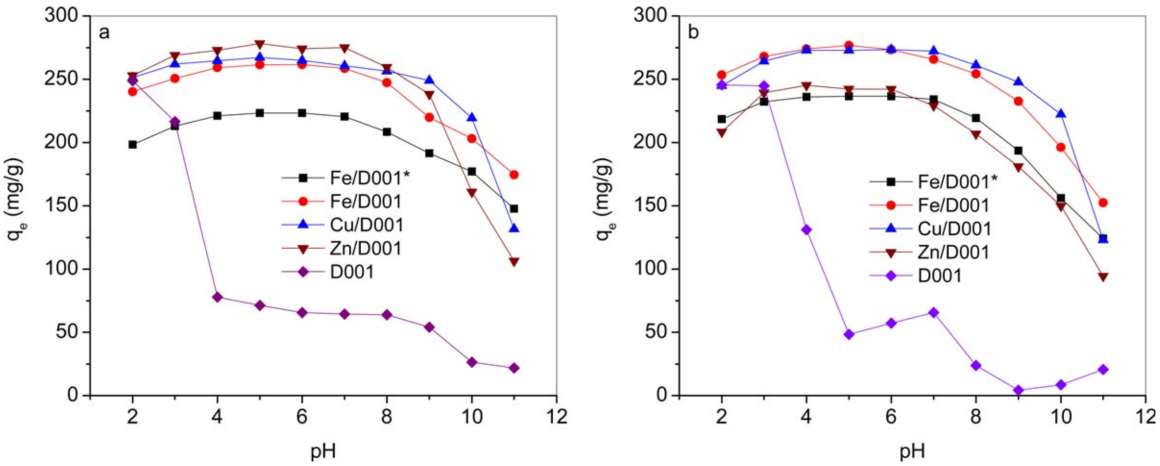

Figure 4. Effect of pH for sorption of TC (a) and DC (b) onto the resins ($m_{sorbent}$ =10 mg, $V_{sorbate}$ = 30 mL, C_0 = 100 mg L^{-1}, T =303 K. *:$m_{sorbent}$ =20 mg, $V_{sorbate}$= 50 mL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

form complexes with metal ions.[45,49] This complexation mechanism also can be interpreted by UV–vis DRS patterns (Supporting Information Figure S4) of TC and TC-load modified resins. Which showed the obviously shift of the peak in 358 nm after the antibiotics being adsorbed to the resins.

As shown in Figure 4, although a relatively weaker pH-dependent sorption was exhibited for M/D001 (M: Fe, Cu, and Zn) compared with D001, the sorption ability was still influenced by pH to a certain extent, and the trends were similar both for the three modified resins and for Fe/D001 under two diffident dose. Strong sorption occurred in the pH range of 4–7, where zwitterions forms of TC and DC existed. Above and below this range, where anionic or cationic species of sorbates existed, the sorption decreased gradually, especially when pH rose above 8. The observed pH effect on sorption suggested a certain importance of species in sorption, and the electrostatic interaction influenced the sorption process. As pH increased, the surface functional groups (i.e., sulfonic groups) of strong-acid resin D001 dissociated, resulting in higher negative charge densities on the surface. Meanwhile, the proportion of anionic species of TCs increased. Consequently, the electrostatic repulsion reduced the sorption amount of TCs onto the adsorbents, especially for the original D001, which contained lots of unmodified sulfonic groups. For M/D001 (M: Fe, Cu, and Zn), however, the sorption capacity was still higher than 100 mg g^{-1} as pH increased to 11, which implied other interactions were also involved, and the cation bridge interaction was proposed.

The metal atoms at the edge of modified resins could be protonated into the cation forms of Fe^{3+}, Cu^{2+}, and Zn^{2+}, some of which bonded in the diffuse interlamellar space. The "cation bridge" could have been formed when these edge sites cations (Fe^{3+}, Cu^{2+}, or Zn^{2+}) intercalated with the anionic functional group of TCs. This cation bridge interaction is generally very stable in aqueous environments.[50] Therefore, in the sorption of TCs onto Fe/D001, Cu/D001, and Zn/D001 under alkaline conditions, cation bridging probably played an important role.

Combining the above analyses, the sorption of TC and DC onto metal modified resins was predominated by the chemical force of surface complexation, the interactions of cation bridge, and the electrostatic interaction during the sorption.

Effect of Ionic Strength

The effect of ionic strength on the sorption of TC and DC onto the modified resins Fe/D001, Cu/D001, and Zn/D001 was studied under the background of 0–1% NaCl solutions. As shown in Figure 5, the trends were evident, and the sorption of TC and DC were all inhibited by the ions added in the solution. The extent of decrease in the sorption capacity on the resins was followed the order of Fe/D001 < Cu/D001 < Zn/D001.The sorption capacity of TC and DC decreased significantly when the amount of NaCl was increased from 0 to 0.1%, then it decreased slowly as the NaCl was further increased from 0.2 to 1%. For TC, the sorption capacity on Fe/D001, Cu/D001, and Zn/D001 declined by 29, 35, and 66%, respectively, as the NaCl was increased to 1% in the solution. While for DC the sorption capacity fell 36, 51, and 73% on Fe/D001, Cu/D001 and Zn/D001, respectively, under the background of 1% NaCl. The total extent of DC sorption capacity decrease on the three resins was relatively larger than that of TC's.

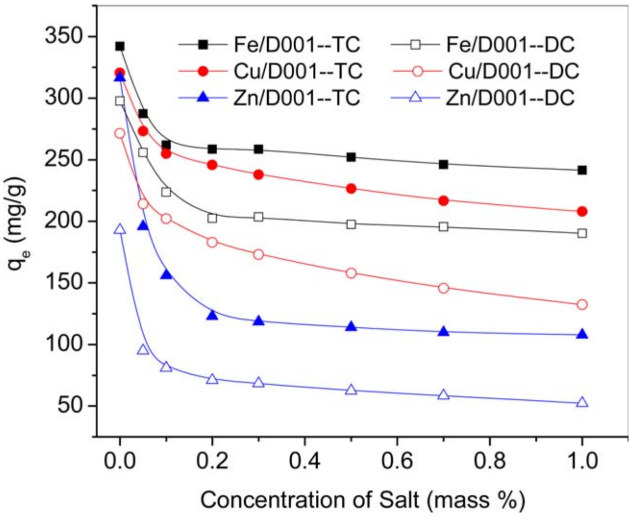

Figure 5. Effect of ionic strength (NaCl) for sorption of TC and DC onto M/D001 (M: Fe, Cu, and Zn) ($m_{\text{sorbent}} = 20$ mg, $V_{\text{sorbate}} = 80$ mL, $C_0 = 100$ mg L^{-1}, initial pH, $T = 303$ K). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The inhibitory effect of NaCl against TC and DC sorption onto the metal modified resins could be explained by the result of ion competition. On one hand, the chloride ions (Cl^-) competed metal active center on the sorbent with TC and DC molecules by forming metal chlorides with the Fe^{3+}, Cu^{2+}, or Zn^{2+} ions, which restrained the surface complexation between the metal cations and TCs, and thus decreased the sorption amount of TC and DC onto M/D001 (M: Fe, Cu, and Zn). On the other hand, the presence of sodium ions (Na^+) electrostatic attracted the negatively charged sulfonic groups of the resins, which competitively inhibited the cation species of TC and DC from sorption onto the resins. For DC especially, a large proportion of cation forms existed in the studied pH condition of 3.84 (initial pH), the electrostatic competition mechanism mentioned above might be responsible for its more extensive decrease in sorption capacity compared to TC (mainly as zwitterions form in the studied initial pH of 6.38).

Isotherms of Sorption

The sorption isotherms, which illustrate the changes in the sorption capacities on the sorbents (q_e) with equilibrium concentrations of sorbate in the solution (C_e), were critical for predicting the maximum sorption capacity and describing the surface properties and affinity of the adsorbents.[2] The equilibrium isotherms of TC and DC onto the metal modified resins M/D001 (M: Fe, Cu, and Zn) were studied by varying the initial concentration of sorbate under the temperature of 288, 303, and 318 K. Three typical isotherm models: Langmuir, Freundlich, and Tempkin were used to analyze the equilibrium data. The isotherm curves with their fitting results were shown in Figure 6. The isotherm constants and correlation coefficients R^2 obtained from the linear forms of isotherm models (described

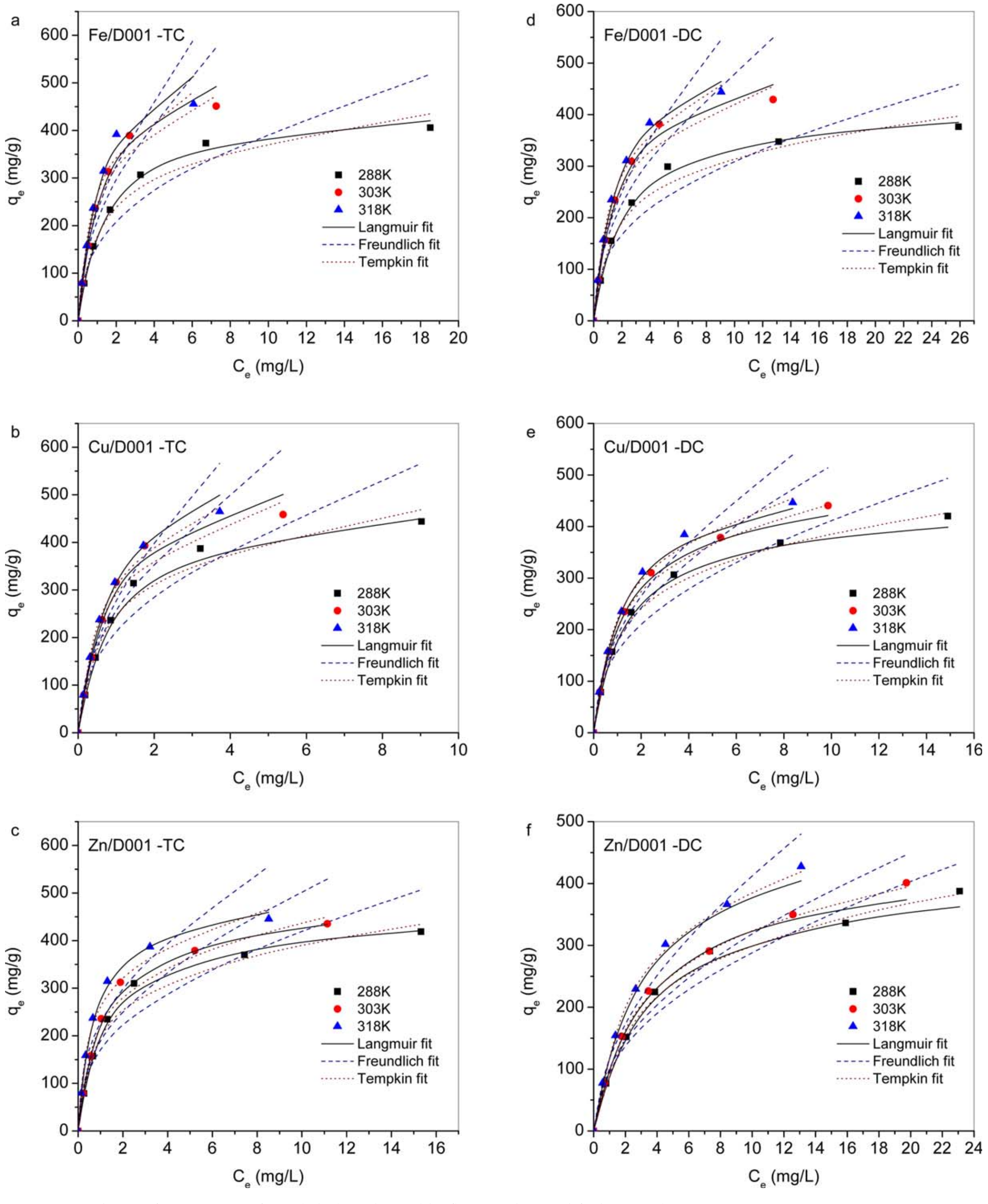

Figure 6. Sorption isotherms for sorption of TC (a,b,c) and DC (d,e,f) onto the modified resins ($m_{\text{sorbent}} = 20$ mg, $V_{\text{sorbate}} = 80$ mL, $C_0 = 20$–120 mg L^{-1}, initial pH, $T = 288$–318 K). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in Supporting Information Table SI) were summarized in Supporting Information Table SII.

The results showed that the three isotherm models correlated the sorption data in the order of Langmuir > Tempkin > Freundlich. Langmuir isotherm model fitted the equilibrium data best for TC and DC sorption onto the M/D001 (M: Fe, Cu, and Zn) with high R^2 (0.9991–0.9998). Langmuir was an ideal model which reflected uniform adsorbent surface and monolayer sorption on specific homogenous sites, so we proposed that the sorption of TC and DC onto the metal modified resins was highly possible to be monolayer and that the surface of the modified resins was uniform with homogenous active sorption sites. The Langmuir maximum sorption capacity was 417–625 mg g^{-1} (0.94–1.4 mmol g^{-1}) for TC and DC onto Fe/

D001, Cu/D001, and Zn/D001 under 288–318 K. As observed above, the uptake of Fe^{3+}, Cu^{2+}, and Zn^{2+} on the modified resins was 1.0–1.2 mmol g^{-1}, which having a certain correlation to this maximum uptake of antibiotics. This result suggested that the mental ions on the adsorbents took a critical part in the sorption process. On the basis of Langmuir dimensionless separation constant R_L ($R_L = 1/(1 + K_L C_0)$), which had values all lower than 1 and greater than zero as indicated in Supporting Information Table SII, the sorption of TC and DC onto the modified resins was favorable at the studied concentrations.[16] The Freundlich constant $1/n$ (0.386–0.536) values were all less than 1, also indicating the favorable feature of the sorption process.[20] In addition, Tempkin model fitted the sorption data with correlation coefficients R^2 range of 0.9731–0.9978, indicating a relatively good fit for the sorption. Tempkin model reflected the heat of sorption in the layer linearly decreased throughout the sorption process. It was a proper model for chemical sorption because of direct or indirect interactions (e.g., the strong electrostatic interaction) between the sorbents and sorbate. The good data fit given by Tempkin illustrated that strong chemical interactions might have taken place in the process of TC and DC sorption onto the modified resins. In addition, the sorption capacity of TC and DC increased slightly with the increase of temperature from 288 to 318 K, indicating favorable sorption at higher temperature and the endothermic feature of the sorption process.

Desorption and Recycling

Desorption of adsorbed TC from the TC-loaded metal modified resins M/D001 (M: Fe, Cu, and Zn) were studied using methanol, methanol/acetic acid (9 : 1, v/v), citric acid (0.1 mol L^{-1}) and NaCl (10%) as elution solvent, respectively. As shown in Supporting Information Figure S5, 11.9–21.3% TC were eluted by NaCl after 72 h of desorption process, while only 0.1–1.6% of desorption rate were obtained by the other three elution solvent. The poor desorption rate suggested that TC antibiotic bonded strongly onto the modified resins due to strong sorption interactions (e.g., the surface complexation). The change of TC removal efficiency by the regenerated adsorbents was also studied, and the result was shown in Supporting Information Figure S6. It was found that the efficiency of TC removal was still above 77% after five consecutive regeneration cycles.

Adsorption of TC in Environmental Matrix

To verify the potential application of M/D001 (M: Fe, Cu and Zn) in industry, two influent and effluent water samples obtained from one wastewater treatment plant (WWTPs), a lake water sample and a tap water sample were used to investigate the Fe/D001's adsorption performance within real environmental matrix that contains 0.005 and 0.05 g L^{-1} TC. As shown in Supporting Information Figure S7, the efficiency of TC removal by Fe/D001 was in the order of deionized water sample>tap water sample>effluent sample>lake water sample>influent sample. TC removal efficiency in the influent sample (>87%) decreased only 12% compared with that in deionized water. The obtained result indicated that the metal modified resins had good application prospect as adsorbents for tetracycline antibiotics removal from environmental water.

CONCLUSION

Based on the experimental results in batch studies, metal ions (Fe^{3+}, Zn^{2+}, and Cu^{2+}) modified D001 resins were proved to be effective adsorbents for the removal of TC and DC from aqueous solution. The modified D001 adsorbents were produced through original D001 resin impregnated with Fe^{3+}, Zn^{2+}, and Cu^{2+}. These metal modified resins exhibited excellent sorption capability under a broad pH range of 2–8 compared to the original D001. The kinetics of TC and DC sorption were well described by pseudo-second-order model. Sorption isotherms correlated the equilibrium data in the order of Langmuir > Tempkin > Freundlich. Langmuir provided the best fit for TC and DC sorption onto modified resins Fe/D001, Cu/D001, and Zn/D001 and showed high monolayer maximum sorption capacity of 417–625 mg g^{-1} under 288–318 K. The ionic strength with NaCl exhibited obvious inhibitory effect for the sorption. The interactions of surface complexation, cation bridging and electrostatic attraction/competition between sorbents and sorbate were proposed as the main mechanisms of TC and DC sorption onto metal modified resins.

ACKNOWLEDGMENTS

This work was financially supported by the National Nature Science Foundation of China (Nos. 21276117, 21376111), Natural Science Foundation of Jiangsu Province (Nos. BK20130513), A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions, Collabrative Innovation Center of Technology and Material of Water Treatment.

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