Adsorptive removal of antibiotics from water using magnetic ion exchange resin

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ABSTRACT

The occurrence of antibiotics in the environment has recently raised serious concern regarding their potential threat to aquatic ecosystem and human health. In this study, the magnetic ion exchange (MIEX) resin was applied for removing three commonly-used antibiotics, sulfamethoxazole (SMX), tetracycline (TCN) and amoxicillin (AMX) from water. The results of batch experiments show that the maximum adsorption capacities on the MIEX resin for SMX, TCN and AMX were 789.32, 443.18 and 155.15 μg/mL at 25°C, respectively, which were 2–7 times that for the powdered activated carbon. The adsorption kinetics of antibiotics on the MIEX resin could be simulated by the pseudo-second-order model ($R^2 = 0.99$), and the adsorption isotherm data were well described by the Langmuir model ($R^2 = 0.97$). Solution pH exhibited a remarkable impact on the adsorption process and the absorbed concentrations of the tested antibiotics were obtained around the neutral pH. The MIEX resin could be easily regenerated by 2 mol/L NaCl solution and maintained high adsorption removal for the tested antibiotics after regeneration. Anion exchange mechanism mainly controlled the adsorption of antibiotic and the formation of hydrogen binding between the antibiotic and resin can also result in the increase of adsorption capacity. The high adsorption capacity, fast adsorption rate and prominent reusability make the MIEX resin a potential adsorbent in the application for removing antibiotics from water.

Introduction

Antibiotics have been widely used in veterinary and human medicine, but these compounds pose potential risks to human health and aquatic ecology when released into the environment (Watkinson et al., 2009). Now their residues have been detected worldwide in aquatic environment including surface, ground, and even drinking water (Nikolaou et al., 2007; Kim et al., 2010). Although the concentrations were generally reported to be in the range of ng/L to μg/L levels, long-term exposure even to the low level of antibiotics could induce chronic allergic reactions, toxic effects and potential development of antibiotic resistant bacteria (Boxall et al., 2003; Baquero et al., 2008).

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As conventional water treatment processes, such as coagulation, flocculation, sedimentation and ultraviolet irradiation, were relatively ineffective in eliminating antibiotics from water (Adams et al., 2002; Huerta-Fontela et al., 2011), some novel technologies including nanofiltration, reverse osmosis, advanced oxidation and adsorption have been developed in recent years. However, the use of membrane separation technologies is hampered by the problem of membrane fouling, and advanced oxidation processes may cause the formation of undesirable oxidation by-products, which hinder their popularization in water treatment plants. Adsorption is considered as an effective method to remove antibiotics from water. Activated carbon is the most widely used adsorbent in water treatment for the removal of organic micro-pollutants. Nevertheless, it is also known as a broad-spectrum adsorbent presenting lower selectivity for antibiotics (Choi et al., 2008), and high cost is needed to regenerate the activated carbon. Thus, more highly-selective and easily-regenerative adsorbents need to be explored for effectively removing antibiotics from water.

Magnetic ion exchange resin (MIEX) is a strong base anion exchange resin with iron oxide integrated into a macroporous, polyacrylic matrix, and is typically used with chloride as the exchangeable ion. In contrast to traditional anion exchange resins, the MIEX resin has a larger surface area due to the very small resin bead size. The average size in diameter of MIEX resin is 150–180 μm (2–5 times smaller than traditional resins), which may lead to fast adsorption of pollutants on the MIEX resin surface (Fearing et al., 2004; Hsu and Singer, 2010). Furthermore, the saturated resin can be easily regenerated using brine (Kitis et al., 2007). It was reported that the MIEX resin was effective in removing natural organic matter (NOM) from drinking water sources at relatively low dose (i.e., 5 mL/L), whilst bromide can be removed to different levels from water depending on the alkalinity and initial bromide ion concentration (Boyer and Singer, 2005). The adsorption efficiencies of MIEX resin for micro-pollutants from water were also studied. Humbert et al. (2008) evaluated the removal of two pesticides (i.e., atrazine and isoproturon) from surface water using a series of strong anion exchange resins. The results showed that the MIEX resin dosage of 8 mL/L only brought about the removal of 7% and 5% for atrazine and isoproturon, respectively. As for 2, 4-dichlorophenoxyacetic acid, a widely used herbicide on crops, the removal efficiency was greater than 80% at MIEX resin dosage of 1 mL/L (Ding et al., 2012). These results suggest that the removal efficiencies of micro-pollutants with MIEX resin are closely related to the characteristics of the target objects. To the best of our knowledge, the research about the removal of antibiotics by MIEX resin adsorption is still very limited.

This study aimed to investigate the adsorptive removal of three representative antibiotics from water using MIEX resin. The selected antibiotics were sulfamethoxazole (SMX), tetracycline (TCN) and amoxicillin (AMX), which were detected with high frequency in the aquatic environment (Heberer, 2002). The adsorption kinetics and isotherms of antibiotic on the MIEX resin were determined through batch experiments, and the removal mechanism was explored. In addition, the adsorption isotherms of these antibiotics on powdered activated carbon (PAC) were studied for comparison.
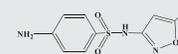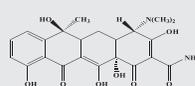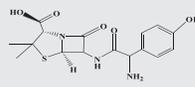
1. Materials and methods

1.1. Chemicals and materials

Three antibiotics (SMX, TCN and AMX) were purchased from Sigma-Aldrich (St. Louis, MO, USA). The organic solvents, methanol and acetonitrile, were of high performance liquid chromatography grade. Other chemicals were purchased from Beijing Chemical Reagents Company (Beijing, China) with analytical grade. The MIEX resin was virgin resin provided by Orica Watercare (Melbourne, Australia). The stock solution of antibiotics was prepared individually at a concentration of 100 mg/L in ultrapure water, which was produced by a Milli-Q system (Advantage A10, Millipore, Billerica, MA) with a resistivity of $\approx$ 18.2 MΩ. The major physicochemical properties of the selected antibiotics are provided in Table 1.

1.2. Experimental setup

To determine the adsorption kinetics of antibiotics on MIEX resin, batch experiments were conducted in magnetically stirred 100 mL glass conical flasks at room temperature of 25 ± 0.5°C. Each flask was added with 250 μL MIEX resin and 50 mL of an aqueous antibiotic solution at an initial concentration of 20, 100 and 500 μg/L, respectively. The solution pH was not controlled, which changed by less than 0.2 units after adsorption. A series of 1 mL of samples were taken out at pre-selected reaction times and were filtered through 0.22 μm PES syringe filters (Pall, USA). The residual antibiotic concentration was determined. Control experiments with 50 mL of aqueous antibiotic solution were conducted simultaneously in the absence of MIEX resin for comparison purposes. The adsorption isotherms were performed with a series of different initial antibiotic concentrations ranging from 100 to 5000 μg/L, the dose of MIEX resin and PAC were set as 5 mL/L and 20 mg/L, respectively. The adsorption experiment lasted for 30 min, which was sufficient to reach equilibrium. The effect of pH on the adsorption of antibiotics was evaluated with varying initial pH of solution from 3 to 11 by adding 0.1 mol/L HCl or 0.1 mol/L NaOH solution. All experiments were performed in duplicate.

Table 1 – Major physicochemical properties of the selected antibiotics.

Antibiotics	Chemical formula	Molecular weight	Molecular structure	pKa[a]	logK$_{ow}$[b]
SMX	$C_{10}H_{11}N_3O_3S$	253.28		1.85 ± 0.30 5.60 ± 0.04	0.89
TCN	$C_{22}H_{24}N_2O_8$	444.43		3.32 ± 0.10 7.78 ± 0.15 9.58 ± 0.15	-1.37
AMX	$C_{16}H_{19}N_3O_5S$	365.40		2.68 ± 0.10 7.49 ± 0.10 9.63 ± 0.10	0.87

[a] Goddard et al., 1996; Qiang and Adams, 2004.
[b] Machatha and Yalkowsky, 2005.

1.3. Analysis of antibiotics

The concentrations of selected antibiotics were determined by ultra-performance liquid chromatography–tandem mass spectrometry (UPLC–MS/MS, Waters, Milford, MA, USA) coupled with an Agilent Zorbax SB-C18 column (100 mm × 2.1 mm, 1.8 μm). Formic acid (0.2%, V/V) and acetonitrile were used as mobile phases A and B, respectively, with a total flow rate of 0.3 mL/min at 30°C. SMX, TCN and AMX were individually analyzed under an isocratic elution condition of 65:35, 85:15 and 80:20 (A:B), respectively. The injection volume was 5 μL. The mass spectrometer was operated under the positive electrospray ionization (ESI+) mode and the selected ion recording (SIR) mode was chosen to quantify the antibiotics. The other MS parameters were described in Appendix A Table S1 via our previous studies (Ben et al., 2008).

2. Results and discussion

2.1. Adsorption kinetics

As shown in Fig. 1, a rapid initial adsorption for all three antibiotics was observed in the first 10 min, and the initial rate of adsorption was greater for higher initial concentration
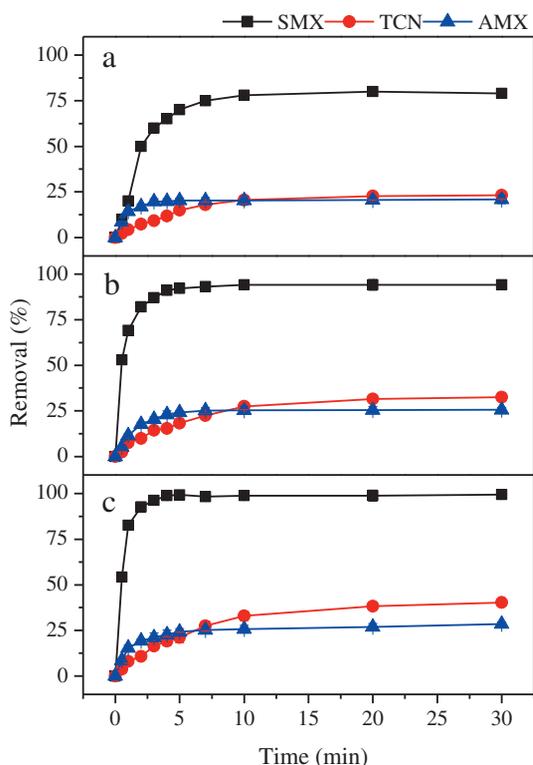

Fig. 1 – Removal of the selected antibiotics by magnetic ion exchange (MIEX) resin as a function of contact time. (a) $C_{o, antibiotic}$ = 20 μg/L; (b) $C_{o, antibiotic}$ = 100 μg/L; (c) $C_{o, antibiotic}$ = 500 μg/L. Experimental conditions: temperature = 25 ± 0.5°C, MIEX resin dosage = 5 mL/L, pH without any adjustment. Error bars represent the relative percent difference of duplicate experiments.

of antibiotics, thereafter, the adsorption rate decreased gradually. The adsorption equilibrium was reached at 30 min. The fast initial adsorption rate was attributed to the great availability of resin exchange sites. Along with the extension of adsorption time, the vacant sites on the surface of MIEX resin were mostly occupied, resulting in the decrease of the adsorption rate. Fig. 1 also indicates that the final removal efficiencies of MIEX resin for three antibiotics followed a descending order of SMX > TCN > AMX.

To further understand the adsorption kinetics of antibiotics using MIEX resin, experimental data were analyzed using pseudo-second-order model (Eq. (1)) (Ho and McKay, 1999):

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

where, k_2 (mL/(μg·min)) is the adsorption rate constant; and q_t (μg/mL) and q_e (μg/mL) represent the adsorbed concentrations of antibiotic at time t (min) and at equilibrium, respectively. Values of k_2 and q_e can be calculated from the plot of t/q_t against t. The initial adsorption rate h (μg/(mL·min)) can be obtained according to the following Eq. (2):

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

Table 2 shows the pseudo-second-order rate constants for the adsorption of three antibiotics. The linear correlation coefficients (R^2) were all above 0.99, clearly indicating that the pseudo-second-order kinetic model described the adsorption behavior of these antibiotics on the MIEX resin very well.

It is observed from Table 2 that at a certain dosage of MIEX resin, the adsorption rate (h) increased gradually with the increase of initial concentration of antibiotics, while k_2 value decreased. This result implies that the MIEX resin hosted faster adsorption rate when processing higher initial concentration of antibiotics. Higher concentration of antibiotics could bring about stronger driving force to accelerate the diffusion of antibiotics from the antibiotic solution onto absorbent (Özacar, 2003; Sun and Xu, 1997), leading to a higher h value.

As mentioned above, the adsorption rates of MIEX resin for different antibiotics exhibited a decreasing order for SMX, AMX and TCN, respectively. This was probably because of their different molecular weights, structures and hydrophobicity. Relatively lower molecular weight, simpler molecular structure and stronger hydrophobicity may increase the free energy of adsorbate from the polar aqueous solution, which was beneficial to the adsorption on the MIEX resin (Li and Sengupta, 1998).

The adsorption kinetic in water may be controlled by the external, interfacial or internal diffusion process (Qiang et al., 2013). The authors herein applied Eq. (3) to evaluate the intraparticle diffusion of antibiotics on MIEX (Weber and Morris, 1962):

$$q_t = k_{id} t^{1/2} + C \tag{3}$$

where k_{id} (μg/(mL·min$^{1/2}$)) is the intraparticle diffusion rate constant and C (μg/mL) is the intraparticle diffusion constant.

According to Eq. (3), if the kinetic process is dominated by the intraparticle diffusion, the plot of q_t versus $t^{1/2}$ should be a

Table 2 – Adsorption kinetic parameters fitted with pseudo-second-order equation for antibiotics on MIEX resin.					
		q_e (µg/mL)	k_2 (mL/(µg·min))	R^2	h (µg/(mL·min))
$C_{o,\ antibiotic} = 20$ µg/L	SMX	3.10	0.29	0.995	2.79
	TCN	1.68	0.10	0.994	0.28
	AMX	1.08	1.31	0.999	1.53
$C_{o,\ antibiotic} = 100$ µg/L	SMX	17.89	0.24	0.999	76.81
	TCN	9.99	0.02	0.996	2.00
	AMX	5.29	0.25	0.999	7.00
$C_{o,\ antibiotic} = 500$ µg/L	SMX	99.01	0.17	0.999	1666.51
	TCN	27.78	0.01	0.992	7.72
	AMX	21.10	0.14	0.999	62.33

straight line. As shown in Appendix A Fig. S1, the plots of q_t versus $t^{1/2}$ do not give linear forms within a poor correlation, indicating that the intraparticle diffusion was not a rate-limiting step.

2.2. Adsorption isotherms

The classic Langmuir isotherm model was applied to simulate the data of antibiotic adsorption on the MIEX resin and PAC, respectively. The isotherm equation is given as follow:

$$q_e = \frac{k_L q_m C_e}{1 + k_L C_e} \qquad (4)$$

where q_e (µg/mL) is the adsorbed concentration of antibiotic at equilibrium, q_m (µg/mL) is the maximum adsorption capacity, C_e (µg/L) represents the equilibrium concentration of antibiotic in aqueous solution, and k_L (L/µg) is the Langmuir constant.

Fig. 2 demonstrates that the adsorption isotherms for all the three antibiotics followed Langmuir isotherm over the concentration range studied. The model simulation parameters are listed in Table 3, where good regressions ($R^2 > 0.97$) were observed. The maximum adsorption capacities (q_m) of MIEX resin for SMX, TCN and AMX, which obtained by nonlinear curve fitting, were 789.32, 443.18 and 155.15 µg/mL, respectively. The adsorption capacities of PAC for the tested antibiotics obtained with this experimental configuration were lower as compared with MIEX resin, which were 104.12, 223.97 and 42.89 µg/mg for SMX, TCN and AMX, respectively. Besides higher adsorption capacities, MIEX resin also presented higher adsorption rates for the tested antibiotics than PAC (Appendix A Fig. S2).

2.3. Effect of pH

The pH value of solution affects the adsorption performance, since it can alter both the surface property of adsorbent and the speciation of the adsorbate in the solution (Abburi, 2003). The effect of pH on the adsorptive removal of these three antibiotics with MIEX resin is shown in Fig. 3. It can be observed that the adsorbed concentrations of tested antibiotics on the MIEX were around 20 µg/mL at pH 3. The removal of antibiotics increased with the increase of pH and the highest adsorbed concentrations were obtained at pH 7, which were 199.54, 48.12 and 42.07 µg/mL for SMX, TCN and AMX, respectively. As the pH further increased from 7 to

9, the adsorbed concentrations of antibiotics on the MIEX resin decreased thereafter. Finally, at pH = 11, the adsorbed concentrations were observed only a slight decrease because the further increase of pH had little impact on the speciation of antibiotics and the surface charge of MIEX resin.

2.4. Proposed adsorption mechanisms

According to the results of adsorption experiments, it can be observed that: (1) the adsorbed concentration of SMX on the MIEX resin was obviously higher than that of TCN and AMX, especially at neutral and alkaline conditions; (2) the adsorption concentrations of antibiotics on the MIEX resin under neutral condition was higher than that at acid and alkaline conditions, especially for SMX.

The major mechanism of anion exchange is proposed to explain the effect of pH on the adsorption of antibiotics, which concludes that the adsorption process of these antibiotics on MIEX resin may be predominated by sharing or exchanging the electrons between the active sites and antibiotics (Deng et al., 2009).

Under the neutral condition (pH = 7), the total SMX in solution consisted of more anionic form (90%) than TCN and AMX (20%–30%), as showed in Appendix A Fig. S3, which could occupy more ion exchange sites provided by the quaternary ammonium functional group on the surface of MIEX resin (Neale et al., 2010). Hence, the higher adsorption capacity of SMX than that of TCN and AMX is caused by the more effective ion exchange performance (Fig. 4a).

Moreover, the dissociation sites for SMX, TCN and AMX at pH = 7 were sulfamide group, phenolic hydroxyl group and carboxyl group, respectively (Qiang and Adams, 2004; Homayoonfal and Mehrnia, 2014). The deprotonated form of sulfamide group was a relatively stronger anion than that of phenolic hydroxyl group and carboxyl group (Chen et al., 2013). Hence, compared to TCN⁻ and AMX⁻, SMX⁻ tends to strongly bind with the quaternary ammonium compounds on the MIEX resin by electrostatic attraction.

When the pH value decreased from 7 to 3, the proportion of the neutral form for the antibiotics in the solution increased as the low $pK_{a,1}$ of 1.85, 3.32 and 2.68 for SMX, TCN and AMX, respectively, and some of them could not be removed by ion exchange. Another part of the cationic form for the antibiotics would greatly weaken the adsorption on the MIEX resin due to electrostatic repulsion force. So the adsorbed concentrations
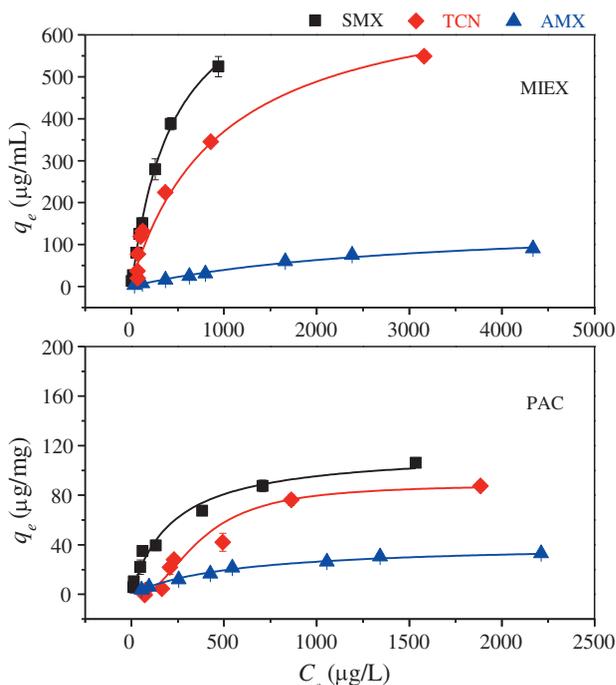
Fig. 2 – Adsorption isotherms of the selected antibiotics on MIEX resin and powdered activated carbon (PAC), respectively. Experimental conditions: temperature = 25 ± 0.5°C, MIEX resin dosage = 5 mL/L, PAC dosage = 20 mg/L, adsorption time = 30 min, $C_{o, antibiotic}$ = 100, 200, 500, 800, 1000, 2000, 3000, and 5000 μg/L, pH without any adjustment. Error bars represent the relative percent difference of duplicate experiments.

of three antibiotics on the MIEX resin decreased rapidly when the pH value decreased from 7 to 3.

With the pH value increasing from 7 to 11, the adsorbed concentrations of the antibiotics on MIEX resin decreased, which could be attributed to the competitive adsorption of hydroxyl ions for the active sites on MIEX resin. Additionally, the excess hydroxyl ions in strong alkaline condition make the surface of MIEX resin negatively charged, which restricts the adsorption of antibiotics onto the surface of MIEX resin due to electrostatic repulsion force (Crini et al., 2007). Other than the small drop (i.e., 16%) of adsorbed concentration of SMX with pH increase from 9 to 11, the adsorbed concentrations decreased rapidly by 60% and 43% for TCN and AMX, respectively. It is probably attributed to the formation of dianion (at the pH exceeded the $pK_{a,3}$) during the adsorption process, which may occupy more exchange sites on MIEX resin.

The three tested antibiotics contain hydrogen donor and acceptor, such as hydroxyl group, carboxyl group, sulfamide group and amino group, which may form hydrogen bonding with the polar functional groups (e.g., ketone and ammonium moieties) in the polypropylene polymer of the MIEX resin as illustrated in Fig. 4b. More hydroxyl groups gave a stronger hydrogen bonding interaction for the adsorption of TCN on the MIEX resin than AMX, which probably accounted for that the adsorbed concentration of TCN was a little higher than that of AMX under the same condition with MIEX at pH = 7.

Therefore, the adsorption capacity on the MIEX resin reflected a comprehensive balance among different influences induced by the physical–chemical mechanism of the target antibiotics (Hubicka and Kolodynska, 2001; Li and SenGupta, 2004).

2.5. Regeneration of MIEX

The MIEX resin contains a high proportion of magnetic iron oxide compounds, making fine resin beads agglomerate into larger, fast-settling particles (Humbert et al., 2007). Hence, the used MIEX resin could be easily separated from the treated water by gravity without external magnetic fields. The spent MIEX resins can be regenerated through reverse ion exchange, where contaminants were substituted by chloride ions (Bolto et al., 2004). In this study, the MIEX resin saturated with antibiotics was first regenerated with a 2 mol/L NaCl solution, and then applied to conduct the adsorption experiments. The results indicate that the regenerated MIEX resin showed negligible loss in its adsorption capacity even after seven test cycles (as shown in Appendix A Fig. S4).

3. Conclusions

This work investigated the adsorptive removal of three commonly-used antibiotics by MIEX resin. The results indicate that the antibiotic adsorption on MIEX resin was an initially rapid process and reached equilibrium within 30 min. Adsorption kinetics of antibiotics with MIEX resin fitted well with the pseudo-second-order model. The MIEX resin presented adsorption capacities of 789.32, 443.18 and 155.15 μg/mL for SMX, TCN and AMX, respectively. Compared to PAC, the MIEX resin showed higher adsorption capacities and adsorption rates for the tested antibiotics. The solution pH exerted a strong impact on the adsorption process and the highest adsorption removals of three tested antibiotics were obtained around neutral pH. Anion exchange is the major mechanism involved in the adsorption of antibiotics on the MIEX resin and the formation of hydrogen binding also enhances the adsorption. The MIEX

Antibiotics	MIEX			PAC		
	q_m (μg/mL)	k_L (L/μg)	R^2	q_m (μg/mg)	k_L (L/μg)	R^2
SMX	789.32	2.16×10^{-3}	0.998	104.12	7.10×10^{-3}	0.971
TCN	443.18	4.69×10^{-4}	0.993	223.97	2.61×10^{-3}	0.975
AMX	155.15	3.49×10^{-4}	0.978	42.89	1.64×10^{-3}	0.993

Table 3 – Parameters for the Langmuir equilibrium adsorption isotherms for antibiotics on MIEX resin and PAC, respectively.

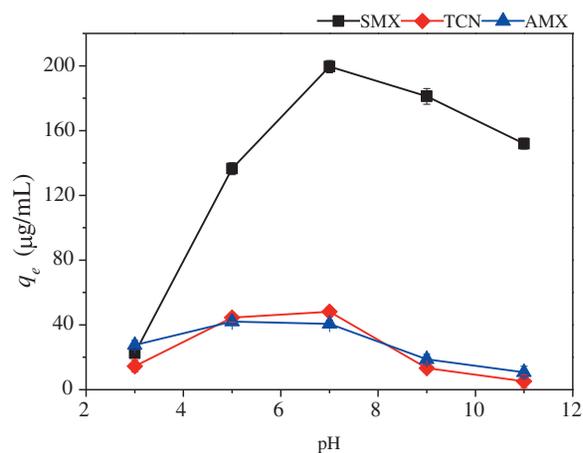**Fig. 3 – Effect of solution pH on the adsorption of selected antibiotics on MIEX resin. Experimental conditions: temperature = 25 ± 0.5°C, MIEX resin dosage = 5 mL/L, adsorption time = 30 min, $C_{o,antibiotic}$ = 1000 μg/L. Error bars represent the relative percent difference of duplicate experiments.**

resin can maintain high adsorption efficiencies for antibiotics after regeneration. Therefore, regarding the properties of fast separation, prominent reusability, together with the higher adsorption capacity and adsorption rate, MIEX resin could be a
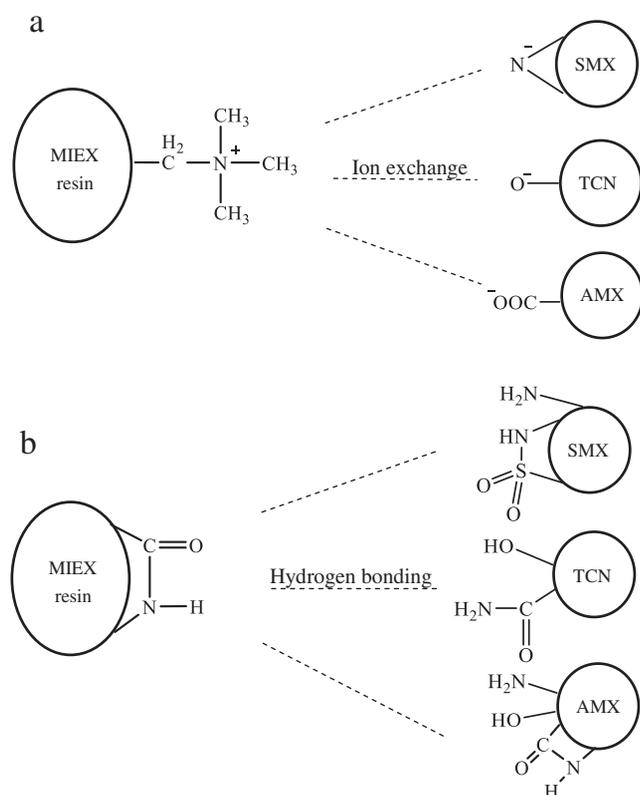

Fig. 4 – Proposed mechanisms for antibiotic adsorption on MIEX resin: (a) ion exchange, and (b) hydrogen bonding.

promising adsorbent to remove antibiotics in the water treatment process.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2016.03.017.

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