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Review

Activated carbon adsorption of quinolone antibiotics in water: Performance, mechanism, and modeling

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ABSTRACT

The extensive use of antibiotics has led to their presence in the aquatic environment, and introduces potential impacts on human and ecological health. The capability of powdered activated carbon (PAC) to remove six frequently used quinolone (QN) antibiotics during water treatment was evaluated to improve drinking water safety. The kinetics of QN adsorption by PAC was best described by a pseudo second-order equation, and the adsorption capacity was well described by the Freundlich isotherm equation. Isotherms measured at different pH showed that hydrophobic interaction, electrostatic interaction, and π - π dispersion force were the main mechanisms for adsorption of QNs by PAC. A pH-dependent isotherm model based on the Freundlich equation was developed to predict the adsorption capacity of QNs by PAC at different pH values. This model had excellent prediction capabilities under different laboratory scenarios. Small relative standard derivations (RSDs), i.e., 0.59%–0.92% for ciprofloxacin and 0.09%–3.89% for enrofloxacin, were observed for equilibrium concentrations above the 0.3 mg/L level. The RSDs increased to 11.9% for ciprofloxacin and 32.1% for enrofloxacin at μ g/L equilibrium levels, which is still acceptable. This model could be applied to predict the adsorption of other chemicals having different ionized forms.

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Introduction

The extensive use of antibiotics has been paid more and more attention in the fields of medicine, public health and environmental protection. The majority of antibiotics are poorly metabolized and thus excreted by humans or animals, and can directly enter natural waters in large quantities

(Gobel et al., 2005; Baquero et al., 2008). Also, traditional wastewater treatment processes cannot remove these chemicals efficiently (Westerhoff et al., 2005). The presence of antibiotic residues in the environment has constituted an emerging threat to human health and ecology, through entering water supplies, promotion of antibiotic-resistant bacteria and disturbance of ecological balance (Sanderson

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et al., 2004; Rizzo, 2012; Harnisz et al., 2015; Osinska et al., 2016).

Quinolones (QNs) are a category of antibiotics sharing the structure of 4-quinolyl. QNs have been detected in aquatic environments throughout the world. The most commonly used antibiotics are ciprofloxacin (CIP), ofloxacin (OFL) and norfloxacin (NOR). The residual concentration of CIP was found to be as high as 600 ng/L in the effluent of a wastewater treatment plant in Spain (Reverte et al., 2003). The average concentrations of OFL and NOR from four wastewater treatment plants in the U.S. were 470 ng/L and 400 ng/L, respectively (Brown et al., 2006). The extremely high concentrations of 100,000 ng/L of CIP and 7600 ng/L of OFL were reported in the wastewater of a hospital in Sweden (Huang et al., 2011).

In China, QN pollution in aquatic environments may be even more severe (Bu et al., 2013; Sui et al., 2015). Zhang et al. (2015) reported that the proportion of QN usage (17%) among all antibiotics in China was higher than in the U.S. (<8% for humans, <10% for animals) and other countries. Specifically, Zhang et al. (2015) reported that the maximum detected concentrations of several QNs (such as CIP, OFL, and NOR) in aquatic environments (not including wastewater) in China were as high as 7560 ng/L, and the average concentration of all detected QNs was 303 ng/L. The reported QN concentrations in aquatic environments from Italy (9 ng/L), U.S. (up to 120 ng/L), and Germany (20 ng/L) are much lower than that in China.

The use of granular activated carbon (GAC) or powdered activated carbon (PAC) has been proven to be an effective technology for the removal of bulk organic matter as dissolved organic carbon (DOC) (Mckay et al., 1985). GAC and PAC can also remove various organic pollutants in water, including odorants (Li et al., 2015a), disinfection by-product precursors (Chen et al., 2015; Liao et al., 2015), and organic chemical spills (Zhang and Chen, 2009; Zhang et al., 2011).

Adams et al. (2002) reported that PAC adsorption was effective in removing several antibiotics, including carbadox, sulfachlorpyridazine, sulfadimethoxine, sulfamerazine, sulfamethazine, sulfathiazole, and trimethoprim. More recently, Putra et al. (2009) demonstrated that 30 g/L of PAC could remove 95% of 317 mg/L amoxicillin from pharmaceutical wastewater. The study of Peng et al. (2012) concluded that 0.6 mg/L PAC could reduce the ofloxacin and norfloxacin from 100 to 1 $\mu\text{mol/L}$ at pH 7.0 ± 0.2 .

Adsorbents other than AC have been used to remove QNs from water. Peng et al. (2012) studied the adsorption of NOR and OFL by carbon nanotubes (CNT) and found that the adsorption was affected by hydrophobic effects and molecule structure. Yang et al. (2012) showed that the two main mechanisms for NOR and CNT adsorption by porous resins were hydrophobicity and micropore-filling. Neutral pH generally benefited NOR adsorption by these adsorbents. Ötker and Akmeahmet-Balcioğlu (2005) used natural zeolite to remove enrofloxacin (ENR) from water, and reported that the adsorption capacity increased with decreasing pH. Yao et al. (2013) applied sludge-derived biochar to adsorb gatifloxacin, and reported a correlation between the adsorption capacity and the volatiles content of the sludge source. However, these studies are still too limited and inconsistent to enable understanding of the mechanism of adsorption and

development of a model to predict the adsorption behavior of QNs.

This study evaluated the relationship between the molecular structure of QNs and their PAC adsorption behavior at different pH levels. Moreover, a pH-dependent isotherm model (PIM) for the investigation of QN adsorption was introduced. This model was first developed based on the Freundlich adsorption isotherms obtained by experimental data at different pH values (Li et al., 2015a). This model is able to predict the adsorption capacity in pH range of 0–14 and assists in understanding the mechanisms of QN adsorption onto PAC. However, there are still many improvements that can be made for the model, such as verification of ng/L level adsorption and competitive adsorption by organic matters.

1. Materials and methods

1.1. Chemicals and reagents

The PAC used in this study was prepared by grinding Filtrasorb-400 (Calgon Corp., USA) into powder with a diameter of 200 mesh (about 40 μm). Six QNs with large-scale application in China were studied. All of the QNs used were purchased from Dr. Ehrenstorfer GmbH Corporation (Augsburg, Germany). Their basic properties are shown in Table 1.

1.2. Adsorption kinetics and isotherm experiments

The procedure used for PAC adsorption kinetic experiments followed that described by Lin et al. (2015). During these experiments, 1.0 mg/L of each QN was spiked into bottles, and then 8 mg/L of PAC was added in each bottle. All solutions were prepared with Milli-Q water (Millipore Corp., Billerica, MA, U.S.A.). The bottles were then shaken well at $25 \pm 2^\circ\text{C}$ at the pH of the isoelectric point of the QNs (adjusted by 1 mmol/L orthophosphate buffer [PBS] solution). Samples were taken at defined time intervals in the range of 0–48 hr and filtered by 0.45 μm polytetrafluoroethylene (PTFE) membrane filters (Millipore Corp, Cork, Ireland) to remove the PAC particles. Then, the residual QN concentrations were analyzed.

The adsorption isotherms were determined using the bottle point method at $25 \pm 2^\circ\text{C}$ according to Lin et al. (2015). For each set of samples, the solution pH was strictly controlled by a PBS solution buffer according to the pK_a values of the QNs. Then, PAC with dosages of 4 to 20 mg/L was added to the bottles. The bottles were shaken well for 48 hr to guarantee adsorption equilibrium had been achieved. Samples were taken from the bottles and filtered through PTFE membrane filters to remove the PAC particles. Then, the residual QN concentrations were determined.

1.3. Quinolone analysis

The concentrations of the six QNs were determined by a high pressure liquid chromatograph (HPLC, Model 1290, Agilent Technologies, U.S.A.) coupled with a tandem mass spectrometer (MS–MS, model 6460, Agilent Technologies, USA) according to Liao et al. (2013). A C18 chromatographic column of (2.1 \times

100 mm, Agilent Technologies, USA) was used. Optimum separation was achieved using gradient elution. The mobile phase consisted of A: 0.1% formic acid and B: acetonitrile. The injection volume was 10 μ L and the flow rate was 0.3 ml/min. All of the compounds were eluted within 10 min. The detection was conducted using an ESI+ ion source and scanned under Multi-Reaction Monitor (MRM) mode. More spectroscopic details are given in Supporting Information Table S1.

2. Models for adsorption kinetics and isotherm

2.1. Kinetic equations

The kinetic equations used in this study are shown as Eqs. (1) and (2).

$$\text{Pseudo first-order equation: } q_t = q_e \left(1 - \frac{1}{e^{k_1 t}}\right) \quad (1)$$

$$\text{Pseudo second-order equation: } q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (2)$$

where, q_t (g/g) is the adsorption capacity at time t (min); q_e (g/g) is the adsorption capacity or carbon loading of PAC at equilibrium; and k_1 (sec^{-1}) and k_2 (sec^{-1}) are the kinetic parameters for the pseudo first and second-order equations, respectively.

2.2. Isotherm equations

Eqs. (3) and (4) show the adsorption models used in this study.

$$\text{Freundlich: } q_e = K_f C_e^{\frac{1}{n}} \quad (3)$$

$$\text{Langmuir: } q_e = q_m \frac{b C_e}{1 + b C_e} \quad (4)$$

where, q_e (mg/g) is the adsorption capacity or carbon load at equilibrium; C_e (mg/L) is the solute concentration of adsorbate at equilibrium; K_f ((mg/g)/(mg/L) $^{1/n}$) and $1/n$ are the Freundlich equation constants; q_m (mg/g) is the maximum adsorption capacity of carbon load at the highest equilibrium concentration; and b (L/mg) is the Langmuir constant.

2.3. Isotherm prediction model

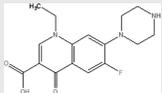
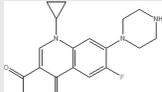
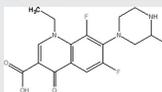
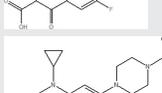
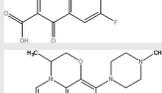
A pH-dependent isotherm model (PIM) was previously developed by our group for a sulfonamide adsorption study (Li et al., 2015b). It is well known that different species of QNs will exist in certain proportions at a given pH. A hypothesis was adopted that the total adsorption capacity at a certain pH is the sum of the adsorption capacities for the individual species present. Thus, the following equations could be obtained.

$$q_e = K_f C_e^{\frac{1}{n}} = q_e^+ + q_e^{\pm} + q_e^- + q_e^0 \quad (5)$$

$$q_e = K_f C_e^{\frac{1}{n}} = K_f^+ C_e^{+\frac{1}{n}} + K_f^{\pm} C_e^{\pm\frac{1}{n}} + K_f^- C_e^{-\frac{1}{n}} + K_f^0 C_e^{0\frac{1}{n}} \quad (6)$$

Table 1 – Properties of quinolones.

pH_{PZC} and pK_a values were acquired from the website: www.chemicalize.org

Name	pH_{PZC}	pK_a	Molecular weight	Formula
Norfloxacin (NOR)	7.2	5.8	319.3	
Ciprofloxacin monohydrochloride (CIP)	7.2	5.8	367.8	
Lomefloxacin hydrochloride (LOM)	7.2	5.6	387.8	
Sarafloxacin hydrochloride (SAR)	7.2	5.7	421.8	
Enrofloxacin (ENR)	6.2	5.7	359.4	
Ofloxacin (OFL)	5.8	5.7	361.4	

pH_{PZC} : point of zero charge, pH at which the QN has no net charge.

pK_a : logarithm of acid dissociation constant K_a , only pK_a between 0 and 14 are listed.

$$q_e = K_f^+ (C_e \delta^+)^{\frac{1}{n^+}} + K_f^\pm (C_e \delta^\pm)^{\frac{1}{n^\pm}} + K_f^- (C_e \delta^-)^{\frac{1}{n^-}} + K_f^0 (C_e \delta^0)^{\frac{1}{n^0}} \quad (7)$$

where q_e is total adsorption capacity; and $q_e^+/q_e^\pm/q_e^-/q_e^0$ is the capacity for different species of cations/zwitterions/anions/neutral molecules.

The capacity for each species could be described by the Freundlich equation.

' $\delta^+/\delta^\pm/\delta^-/\delta^0$ ' is the percentage of each species at a given pH, which could be calculated according to pK_a (Fig. 1).

For a given pH, the calculation of K_f^+ , K_f^\pm , K_f^- , K_f^0 and n^+ , n^\pm , n^- , n^0 was accomplished by a computer-aided ergodic trial calculation.

2.4. Computer ergodic trials for the most optimum solution of the PIM model

The computer-aided ergodic trial calculation was carried out by Matlab 7.1 (Mathworks, Inc., Natick, USA). The code was written by the authors, as shown in the Appendix. The values for eight PIM parameters (shown in Eq. (7)) were determined using the random sampling method by Matlab 7.1 with the $1/n$ range of 0.1–0.5 and the K_f range of 0–400. For each set of random values of the eight parameters, the adsorption capacity was calculated according to Eq. (7). Then, the calculation result was compared with the experimental result of capacity under given equilibrium concentrations. The sum of deviations for all experimental results was obtained to evaluate the model. The random sampling was stopped after 500,000 trials, which is sufficiently large. The trial results were ranked by the sum of deviations, and the set of parameters with the smallest sum was regarded as the final parameters for the PIM model. In some cases, the trial with the smallest sum was not reasonable, the trial with the next smallest sum was chosen as the most optimum solution.

3. Results and discussions

3.1. Adsorption kinetics

The results of the adsorption kinetic experiments are shown in Fig. 2. The adsorption curves of all QNs reached equilibrium after 30–40 hr, with a removal of 80%–96%. Therefore, a sufficiently long adsorption time of 48 hr was set for isotherm studies and other tests.

The pseudo first-order and the pseudo second-order model were used to fit the kinetic experiment data, as shown in Table 2.

Both the pseudo first-order and pseudo second-order models fit the results very well, as shown in Table 2. The pseudo second-order model was slightly better according to the correlation coefficients. It can be inferred that the multi-step adsorption process simulated by the pseudo second-order model could reflect the experimental data better (Qiu et al., 2009).

3.2. Adsorption isotherms

The Freundlich model and the Langmuir model were used to fit the isotherm results of the six QNs, as shown in Table 3 and Appendix A Fig. S1. The pH used for measurement of the isotherms was $(pK_{a1} + pK_{a2}) / 2$, where the maximum quantities of zwitterions and neutral molecules exist. Under these conditions, the maximum QN removal could be achieved by PAC adsorption.

The Freundlich isotherm equation fit the experiment data better ($r^2 > 0.94$) than the Langmuir isotherm equation ($r^2 > 0.73$). The Langmuir model was established according to the hypothesis that the adsorption sites are uniformly distributed, absorption on the adsorbent forms a monolayer, and there is no adsorbate transmigration on the adsorbent surface. The Freundlich model assumes a heterogeneous adsorbent surface, where the stronger binding sites are occupied first (Hamdaoui and Naffrechoux, 2007). The parameter of the Freundlich model, K_f , is an approximate measure of adsorption capacity. Actually, K_f equals

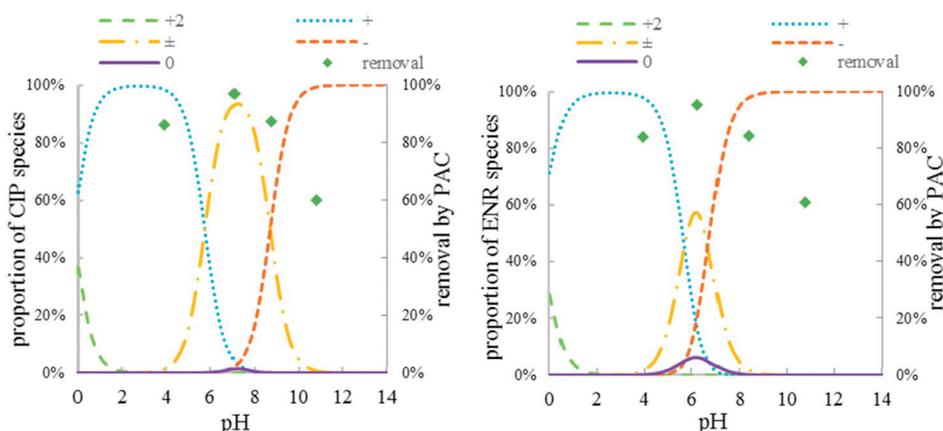


Fig. 1 – Species distribution of CIP and ENR at different pH and their removal by PAC. Initial QN concentrations = 2 mg/L; PAC dosage = 8 mg/L; temperature = 25°C. The legend of +2, +, ±, – and 0 represent the divalent cation, monovalent cation, zwitterionic species, monovalent anion and neutral compound, respectively. The diamond symbols show the removal of QN by PAC.

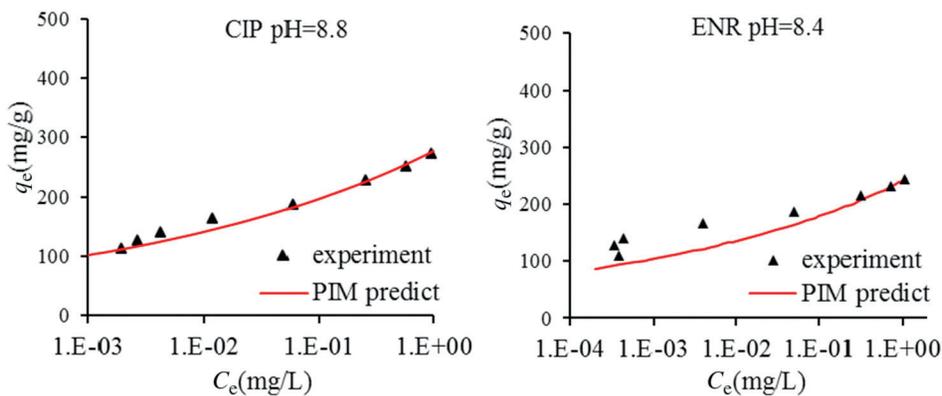


Fig. 2 – Validation of the adsorption model at weakly alkaline pH.

the adsorption capacity when the equilibrium adsorbent concentration is 1. The parameter $1/n$ in the model represents the heterogeneity of adsorption on sites on the sorbent (Tan et al., 2008). From the result, we may conclude that the surface is heterogeneous and that multilayer adsorption possibly occurred during QN adsorption by PAC.

3.3. pH influence on adsorption

In order to elucidate the influence of pH on adsorption behavior, further studies were conducted with CIP and ENR, as they are widely used and representative QNs. Table 4 shows the adsorption isotherms of CIP and ENR under different pH conditions: acidic (3.9), neutral (7.1/6.2), alkaline (10.8) and weakly alkaline (8.4/8.7). We evaluated the stability of these two QNs under these pH conditions, and no hydrolysis or other reaction was observed (as evidenced in Appendix A Table S2). The results demonstrated that the Freundlich model fits the experimental data better than the Langmuir model. A pH-dependent isotherm model (more detail in Section 3.4) based upon the Freundlich equation was developed to predict the adsorption capacity of QNs by PAC at different pH values.

As shown in Table 4, QNs presented the highest adsorption capacities at neutral pH, where the neutral molecules predominated. When the pH decreased, the adsorption capacity decreased slightly. When pH increased over 10, the adsorption capacity reduced greatly.

The change of adsorption capacity could be explained by the distribution of different species of QNs at different pH values. Fig. 1 shows the proportion of different species of CIP and ENR over the pH range of 0–14. The removal of CIP and ENR by PAC adsorption under four pH conditions is also shown in Fig. 1.

Under acidic conditions (pH 2–5), the QN molecule exists as a monovalent cationic ion (CIP^+ , ENR^+) due to protonization of the pyrazine ring. Under alkaline conditions (pH > 9), the QN molecule has negative charge (–) due to the deprotonation of a carboxyl group. Under neutral conditions (pH = 6–8), CIP exists as the zwitterion (CIP^\pm) with a deprotonated carboxyl group ($-COO^-$) and a protonated pyrazine ring ($PR-H^+$). Under neutral conditions (pH = 6–8), part of ENR exists as the zwitterion (ENR^\pm with $-COO^-$ & $PR-H^+$) and the rest as the neutral molecule (ENR^0). Under extreme acidic conditions (pH < 0), which is beyond the pH range of this study, ENR takes on two positive charges.

It can be concluded that the hydrophobic interaction mainly contributes to QN adsorption onto PAC (Yang et al., 2012). As indicated by Fig. 1, QN will ionize under pH conditions below 5 or over 9, and become less hydrophobic, impairing the adsorption capacity. In addition, the functional groups on the PAC surface will take on different charges under different pH conditions and may also attract or repel QNs. The pH at point of zero charge (pH_{PZC}) of this PAC has been measured as 9.5 (Lin et al., 2015). Therefore, under acidic or alkaline conditions, both QNs and PAC surface have the same charge, and the electrostatic

Table 2 – Kinetics model parameters for the adsorption of quinolones onto PAC.

Quinolones	Pseudo First-order			Pseudo Second-order			Adsorption capacity from experiments $q_{e,exp}$ (mg/g)
	k_1 (min ⁻¹)	q_e (mg/g)	r^2	k_2 (g/(mg·min))	q_e (mg/g)	r^2	
NOR	19.10×10^{-3}	118	0.95	18.80×10^{-5}	125	0.98	124
CIP	6.73×10^{-3}	121	0.96	5.85×10^{-5}	135	0.97	127
LOM	4.20×10^{-3}	184	0.99	2.60×10^{-5}	205	1.00	190
SAR	3.45×10^{-3}	116	0.98	3.21×10^{-5}	131	0.99	120
ENR	5.07×10^{-3}	88.3	0.98	0.61×10^{-5}	99	0.99	93.5
OFL	5.22×10^{-3}	99.0	0.99	5.92×10^{-5}	110	0.99	104

Note: pH = 7.0, Temperature = 25°C, PAC = 8 mg/L, initial QNs = 1 mg/L.

Table 3 – Adsorption isotherms for quinolones onto PAC.

Quinolones	Freundlich			Langmuir		
	K_f	$1/n$	r^2	b	q_m	r^2
NOR	318	0.132	0.99	878.40	237	0.82
CIP	346	0.140	0.94	482.72	289	0.86
LOM	512	0.166	0.98	153.25	413	0.86
SAR	328	0.132	0.99	1280.22	236	0.76
ENR	368	0.136	0.97	3125.45	275	0.73
OFL	295	0.106	0.98	2530.65	230	0.85

Note: pH = 6.2 for ENR, pH = 5.8 for OFL, pH = 7.0 for other QNs; temperature = 25°C.

Table 4 – Adsorption isotherms of CIP and ENR at different pH.

	pH	Freundlich			Langmuir		
		K_f	$1/n$	r^2	b	q_m	r^2
CIP	3.9	329.09	0.151	0.98	669.88	291.96	0.67
	7.1	342.71	0.130	0.97	536.04	287.53	0.84
	8.8	255.16	0.114	0.99	365.21	237.44	0.82
	10.8	180.04	0.137	0.91	125.09	168.51	0.95
ENR	3.9	262.11	0.111	0.99	1107.13	224.2	0.69
	6.2	368.40	0.136	0.97	3125.45	275.46	0.73
	8.4	238.95	0.079	0.96	3425.38	213.02	0.78
	10.8	158.11	0.079	0.95	7000.26	142.19	0.67

repulsion force will hinder the adsorption to some extent. However, the functional groups on the PAC surface only influence a part of the adsorption sites and are not the dominant factor for QN adsorption.

It should be noted that under acidic or alkaline conditions, this PAC still has an adsorption capacity for QNs that is over 50% of the maximum capacity under the optimum pH. This phenomenon can be explained as follows. First, the hydrophobic polycyclic aromatic ring is the main target for AC adsorption, although the carboxyl or nitrogen groups will become charged under certain pH conditions. Thus, the adsorption capacity will not decline very much under either acidic or alkaline conditions. Second, the π - π dispersion force may contribute greatly to adsorption. The fluorine group on the benzene ring of CIP or ENR withdraws electrons from the polycyclic aromatic ring and leads to an electron-depleted region serving as a π -electron acceptor.

Thus, there should be a high density of π -electrons on the AC surface that will serve as a π -electron donor.

3.4. Development of the prediction model of QN adsorption at various pH

In this study, the PIM model based on the Freundlich equation was developed first to predict the adsorption behavior of CIP or ENR under various pHs. The modeling results for CIP and ENR can be expressed by Eqs. (8) and (9):

$$\text{CIP: } q_e = 253(C_e\delta^+)^{0.13} + 91(C_e\delta^\pm)^{0.17} + 100(C_e\delta^-)^{0.13} + 241(C_e\delta^0)^{0.46} \quad (8)$$

$$\text{ENR: } q_e = 195(C_e\delta^+)^{0.10} + 72(C_e\delta^\pm)^{0.19} + 126(C_e\delta^-)^{0.11} + 242(C_e\delta^0)^{0.46} \quad (9)$$

The model was validated by the isotherm measurements at certain pH, as shown in Fig. 2 and Table 5. For CIP, the PIM model presented an average deviation of about 5.0%, with a maximum of 11.9% and minimum of 0.6%. For ENR, the PIM model presented an average deviation of about 14.7%, with a maximum of 32.1% and minimum of 0.09%. It can be concluded that the model performs better for QN equilibrium concentration C_e above 0.3 mg/L. In this range, the predicted deviation was below 1% for CIP and 4% for ENR, respectively, and exhibited fairly good applicability. Further investigation is needed to improve the performance of the PIM model at lower concentration levels of QNs.

It should be noted the residual QN concentrations after PAC adsorption in this study were in the range of $\mu\text{g/L}$ to mg/L (as shown in Table 5). This is higher than the levels of dozens to hundreds of ng/L found in aquatic environments, as described in the Introduction section. This difference was due to the level of detection (LOD) of the LC-MS/MS, which was at the $\mu\text{g/L}$ level. Generally, isotherm curves can be used to estimate the adsorption performance beyond the experimental range to some extent (Suffet, 1980). For dilute solutions of $\mu\text{g/L}$ to ng/L , the partition of chemicals between the AC phase and liquid phase could possibly follow the same model. Thus, the estimation of isotherms in the upper range of ng/L could lead to acceptably small error. We will try to improve the LOD of QNs and determine the isotherms at lower concentrations as well as the applicability of our model in real source water as the next research steps.

Table 5 – Deviation between the PIM prediction result and experimental data.

QN	Items	Equilibrium concentration and prediction derivation					
CIP	C_e (mg/L)	0.0042	0.012	0.059	0.25	0.57	0.95
	Measured capacity (mg/g PAC)	140.9	163.4	187.8	227.6	252.2	273.6
	Predicted capacity (mg/g PAC)	124.2	144.0	181.6	225.5	254.6	275.2
	Absolute deviation (mg/g PAC)	16.7	19.4	6.2	2.1	2.4	1.6
	Relative deviation (%)	11.9	11.9	3.28	0.9	0.9	0.6
ENR	C_e (mg/L)	4.5×10^{-4}	0.0039	0.05	0.31	0.73	1.07
	Measured capacity (mg/g PAC)	139.5	166.3	185.7	215.1	230.6	243.4
	Predicted capacity (mg/g PAC)	94.8	121.3	164.0	206.7	231.1	243.2
	Absolute deviation (mg/g PAC)	44.7	45.0	21.7	8.4	0.5	0.2
	Relative deviation (%)	32.1	27.0	11.7	3.89	0.21	0.09

4. Conclusions

The adsorption behavior of six QNs by PAC was investigated in this study. Both the pseudo first- and second-order models fit the kinetic results well. The multi-step simulation of the adsorption process by the pseudo second-order model was used as it better reflected the experimental conditions. The Freundlich model correlated with the data better than the Langmuir model. The adsorption capacity varied greatly under different pH conditions. The hydrophobic interaction, electrostatic interaction, and π - π electron interaction were regarded as the main influencing factors on adsorption capacity. A pH-dependent isotherm model based on the Freundlich isotherm equation was established to predict the adsorption capacity at different pH. This model is able to predict the adsorption capacity in the pH range of 0–14 with high accuracy. However, the applicability of this model in real source water with ng/L levels of QNs needs to be verified in future work.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org.10.1016/j.jes.2016.09.010>.

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