

# Performance evaluation of powdered activated carbon for removing 28 types of antibiotics from water

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## Abstract

Currently, the occurrence and fate of antibiotics in the aquatic environment has become a very serious problem in that they can potentially and irreversibly damage the ecosystem and human health. For this reason, interest has increased in developing strategies to remove antibiotics from water. This study evaluated the performance of powdered activated carbon (PAC) in removing from water 6 representative groups of 28 antibiotics, namely Tetracyclines (TCs), Macrolides (MCs), Chloramphenicols (CPs), Penicillins (PNs), Sulfonamides (SAs) and Quinolones (QNs). Results indicate that PAC demonstrated superior adsorption capacity for all selected antibiotics. The removal efficiency was up to 99.9% in deionized water and 99.6% in surface water at the optimum conditions with PAC dosage of 20 mg/L and contact time of 120 minutes. According to the Freundlich model's adsorption isotherm, the values of  $n$  varied

among these antibiotics and most were less than 1, suggesting that the adsorption of antibiotics onto PAC was nonlinear. Adsorption of antibiotics followed well the pseudo-second-order kinetic model ( $R^2 = 0.99$ ). Analysis using the Weber-Morris model revealed that the intra-particle diffusion was not the only rate-controlling step. Overall, the findings in this study confirm that PAC is a feasible and viable option for removing antibiotics from water in terms of water quality improvement and urgent antibiotics pollution control. Further research is essential on the following subjects: (i) removing more types of antibiotics by PAC; (ii) the adsorption process; and (iii) the mechanism of the competitive adsorption existing between natural organic matters (NOMs) and antibiotics.

**Keywords:** antibiotics, adsorption, powdered activated carbon, kinetics, water treatment

## **1 Introduction**

In recent years, the occurrence and impacts of antibiotics in the aquatic environment have led to grave concerns about their ecological safety and health impacts given that the demand for high quality drinking water is increasing. Many studies have reported that a variety of antibiotics are present in wastewater effluents (Brown et al., 2006; Watkinson et al., 2007; Li et al., 2013; Golovko et al., 2014), surface and groundwater (Watkinson et al., 2009; Chen and Zhou, 2014; Jiang et al., 2014), some of which have even been detected in water treatment plants and drinking water supplies throughout the world (Ye et al., 2007; Yiruhan et al., 2010). The antibiotics of sulfamethoxazole, trimethoprim, and ofloxacin were detected at concentrations ranging from 110 to 470 ng/L in treated effluent at a large wastewater treatment plant (WWTP) in Albuquerque - New Mexico (Brown et al., 2006). At a WWTP in Brisbane (Australia), antibiotics (ciprofloxacin, sulphamethoxazole, lincomycin and trimethoprim) were detected in both influents and effluents with 100% frequency. Of the detected antibiotics, the concentration of ciprofloxacin was highest in influent and effluent with the mean value of 0.6 mg/L and 0.6µg/L, respectively (Watkinson et al.,

2007). Watkinson et al. (2009) also observed that the macrolide, quinolone and sulphonamide antibiotics were most prevalent in WWTP effluents with the concentration up to a maximum of 3.4 µg/L. Li et al. (2013) investigated the occurrences of 22 antibiotics in a wastewater reclamation plant in Beijing (China). They discovered that quinolones were the dominant antibiotics with 4916 ng/L in influents and 1869 ng/L in secondary effluents. In the study by Golovko et al. (2014), the target compounds of 10 antibiotics were investigated in a WWTP. Specifically, these were norfloxacin, levofloxacin, ciprofloxacin, azithromycin, erythromycin, clarithromycin, trimethoprim, sulfapyridine, sulfamethoxazole, and sulfasalazine. The maximum concentrations of 10 antibiotics varied from 0.069 µg/L to 3.09 µg/L in wastewater treatment plant (WWTP)'s influents and from 0.018 µg /L to 2.31µg/L in WWTP's effluents.

According to the study results of Watkinson et al. (2009), the antibiotics of macrolide, quinolone and sulphonamide were detected with the detection frequency of 15% - 83% in the low ng/L range up to 2 µg/L in the surface waters of six investigated rivers. In addition, the mean concentrations of oxytetracycline was up to 13640.9 ng/L in surface water and 8325.8 ng/L in groundwater from the Wangyang River (China), having a detection frequency of 100% (Jiang et al., 2014). In the Huangpu River, sulfonamides indicated the highest concentrations of 34-859 ng/L in water samples (Chen and Zhou, 2014).

In drinking waters, some antibiotics including sulfamethoxazole (3.0-3.4 ng/L), macrolides (1.4-4.9 ng/L), and quinolones (1.2-4.0 ng/L) were detected by Ye et al. (2007). Four fluoroquinolone antibiotics (norfloxacin, ciprofloxacin, lomefloxacin, and enrofloxacin) were detected in tap water at high rates in Guangzhou (77.5%) and Macao (100%), ranging respectively from 1.0 to 679.7 ng/L and 2.0 ng/L to 37.0 ng/L (Yiruhan et al., 2010).

Although the concentrations of antibiotics in the aquatic environment were generally low ( $\mu\text{g/L}$  or  $\text{ng/L}$  level), their impact on ecosystem function and potential to endanger people's health cannot be neglected (Constanzo et al., 2005, Ahmed et al., 2015). Since antibiotics are being increasingly detected in the aquatic environment, finding efficient and effective approaches to remove them from water supplies is critical. Normally, antibiotics cannot be effectively removed (only 5%) using conventional water treatment processes, for example coagulation, flocculation, sedimentation and filtration (Adams et al., 2002). However, they can be removed using oxidation processes such as chlorination and ozonation. Despite free chlorine, chlorine dioxide and ozone could effectively remove some antibiotics such as sulfonamides, macrolides, carbadox, and trimethoprim from surface water (>90%), while the formation of certain oxidation by-products and their activity and toxicity still require more research (Adams et al., 2002; Westerhoff et al., 2005). Regarding membrane filtration, only nanofiltration (NF) and reverse osmosis (RO) can reject antibiotics (Snyder et al., 2007; Nghiem et al., 2005; Radjenovic et al., 2008). For instance, the concentration of trimethoprim decreased from 265  $\text{ng/L}$  to 25  $\text{ng/L}$  after RO treatment (Snyder et al., 2007). Sulfamethoxazole can be rejected by NF membrane with the mean value of 21  $\text{ng/L}$  in groundwater dropping to below 2  $\text{ng/L}$  in permeate of NF. Nevertheless, the rejection of antibiotics by NF and RO depends on the physico-chemical properties and characteristics of the membranes (Nghiem et al., 2005; Radjenovic et al., 2008).

Adsorption is another viable method for treating antibiotics. Both powdered activated carbon (PAC) and granular activated carbon (GAC) have been used to remove the selected antibiotics from water (Adams et al., 2002; Kim et al., 2010; Genç and Dogan, 2015). Based on the findings of Adams et al. (2002), the percentage removed was more than 90% for the antibiotics (carbadox, sulfachlorpyridazine, sulfadimethoxine, sulfamerazine, sulfamethazine, sulfathiazole and trimethoprim) with a PAC dosage of 50  $\text{mg/L}$  in deionized water. Genç and Dogan (2015) found

PAC (0.0125 g in 50 mL) removed 87% ciprofloxacin at an initial concentration of 20 mg/L at 22 °C, while GAC of 2g/L can remove more than 90% trimethoprim with an initial concentration of 50 mg/L (Kim et al., 2010).

Rivera-Utrilla et al. (2009) investigated the removal of nitroimidazole antibiotics by adsorption on activated carbon (AC), and their results showed AC could eliminate nitroimidazoles efficiently from surface and groundwater (e.g. the adsorption capacity ranging from 1.04 mmol/g<sub>AC</sub> to 2.04 mmol/g<sub>AC</sub>). Carabineiro et al. (2012) compared the adsorption capacity of ciprofloxacin using three types of carbon-based materials (AC, carbon nanotubes and carbon xerogel). They found that the maximum adsorption capacity of AC (230 mg/g<sub>AC</sub><sup>-1</sup>) was much higher than the other two materials (112 and 135 mg/g<sub>AC</sub><sup>-1</sup> for carbon xerogel and carbon nanotubes, respectively). The removal of fluoroquinolones antibiotics such as ciprofloxacin and norfloxacin was also investigated by adsorption on microporous AC, and results indicated that maximum removal percentages of more than 96% were achieved (Ahmed et al., 2014)

Despite the types and concentrations of antibiotics in the aquatic environment vary from place to place, the levels of some antibiotics in the surface water are very high with concentration up to 150 µg/L being documented in the US (Kolpin et al., 2002). As reviewed by Lapworth et al. (2012), maximum concentrations for the most commonly detected antibiotics in groundwater were reported over the 40-10<sup>4</sup> ng/L range. A recent study by Ngumba et al. (2016) showed that the maximum concentration in the river waters (Kenya) of three antibiotics (sulfamethoxazole, trimethoprim, ciprofloxacin) was 13,800 ng/L. Therefore it is important to investigate the occurrence of antibiotics in water sources in a certain region to: firstly, control antibiotics pollution; and secondly, treat water. Recently, Li et al. (2014) discovered that 28 selected antibiotics were prevalent in four water reservoirs in North China with the highest concentration of 73.66 ng/L (florfenicol).

To date, although some evaluation studies on the removal of antibiotics using AC and other absorbents (e.g. zeolite, aluminum oxide, mesoporous silica spheres etc.) were carried out, only a limited number of antibiotics were involved in the investigations (Adams et al., 2002; Braschi et al., 2010; Chen and Huang, 2010; Xu et al., 2011; Gao et al., 2012; Zhang et al., 2013; Wu et al., 2013; Martucci et al., 2013; Martins et al., 2015). Moreover, the adsorption kinetic is essential to determine the rate of adsorption, especially for designing a water treatment plant. Nonetheless, only in recent times have a few studies on adsorption of antibiotics on AC focused on this problem (Kim et al., 2010; Méndez-Díaz et al., 2010; Rivera-Utrilla et al., 2013; Genç and Dogan, 2015). Hence, this study aimed to quantify the adsorptive capacity and adsorption rates of 28 selected antibiotics using PAC. The experimental data were also interpreted with kinetic and isotherms models so that the antibiotic adsorption onto PAC could be better understood.

## **2 Materials and Methods**

### **2.1 Chemicals and Materials**

The 28 selected antibiotics used can be divided into 6 groups, including 4 Tetracyclines (TCs), 4 Macrolides (MCs), 3 Chloramphenicols (CPs), 1 Penicillins (PNs), 13 Sulfonamides (SAs), 3 Quinolones (QNs) (Table 1). Physico-chemical properties of antibiotics are listed in Table 1. Oxytetracycline, Thiamphenicol, and Kitasamycin were obtained from the Institute of Biomedical Research (China), while Chloramphenicol and Sulfapyridine derived from the Institute of Metrology (China). Others were purchased from J&K Scientific (China). All the compounds were at least reagent grade (>95% purity).

The PAC used in this study was obtained from Shanxi Xinhua Active Carbon Factory (China) with an average pore size of 3.03 nm, specific surface area of 852.94 m<sup>2</sup>/g, iodine adsorption value of 903 mg/L, methylene blue adsorption of 142 mg/L and particle size of 200 mesh (75 μm) (more than 95% passing). Firstly, the PAC was washed with deionized water and then dried at 105°C for 2 hours and cooled to room temperature (25 ± 1°C) in the dryer. A slurry of PAC (1000 mg/L) was prepared using deionized water and stored at 4°C, and mixed by ultrasonic oscillation for 30 min prior to use. The 0.45 μm glass microfiber filters (Millipore, USA), were soaked for over 2 hours in 200 mL deionized water, and then kept at 4°C in the refrigerator.

**Table 1** Physico-chemical properties of 28 antibiotics used in the study

Group	Compound	Acronym	Molecular mass	LogK <sub>ow</sub> <sup>a</sup>	pKa <sup>a</sup>
Tetracyclines (TCs)	Oxytetracycline	OTC	460.45	-0.9	3.27
	Tetracycline	TC	444.43	-1.30	3.3
	Chlortetracycline	CTC	478.88	-0.62	3.3
	Doxycycline	DXC	444.44	-0.02	n/a <sup>b</sup>
Macrolides (MCs)	Erythromycin	ETM	733.92	3.06	8.88
	Roxithromycin	RTM	837.05	2.75	n/a <sup>b</sup>
	Kitasamycin	KIT	785.98	3.077	n/a <sup>b</sup>
	Spiramycin	SPI	843.05	1.456	n/a <sup>b</sup>
Chloramphenicols (CPs)	Thiamphenicol	TAP	356.22	-0.33	n/a <sup>b</sup>
	Florfenicol	FF	358.21	n/a <sup>b</sup>	n/a <sup>b</sup>
	Chloramphenicol	CAP	323.13	1.14	n/a <sup>b</sup>
Penicillins (PNs)	Penicillin G	PNG	373.49	1.83	n/a <sup>b</sup>
Sulfonamides (SAs)	Sulfadiazine	SDZ	250.28	-0.09	6.5 <sup>c</sup>
	Sulfamerazine	SMR	264.30	0.14	8.0 <sup>c</sup>
	Sulfamethazine	STZ	278.33	0.89	7.59
	Sulfameter	ST	280.30	0.41	n/a <sup>b</sup>
	Sulfamonomethoxine	SMMX	280.30	0.7	7.2 <sup>c</sup>
	Sulfamethizole	STL	270.33	0.54	5.5 <sup>c</sup>
	Sulfamethoxazole	STX	253.27	0.89	8.8 <sup>c</sup>
	Sulfamethoxypyridazine	STPD	302.28	n/a <sup>b</sup>	n/a <sup>b</sup>
	Sulfachlorpyridazine	SCPD	284.73	0.31	5.5 <sup>c</sup>
	Sulfacetamide	STM	214.24	-0.96	7.59
	Sulfapyridine	SPD	249.29	0.35	8.43
	Sulfadimethoxine	SDMX	310.33	1.63	5.9 <sup>c</sup>
	Sulfaguanidine	SPGD	214.24	-1.22	11.25

Quinolones (QNs)	Oxolinic acid	OLA	261.23	0.94	6.87
	Nalidixic acid	NDA	232.23	1.59	8.6
	Flumequine	FMQ	261.25	1.6	n/a <sup>b</sup>

LogK<sub>ow</sub>: Octanol/water partition coefficient.

pKa: Acidic equilibrium constant.

<sup>a</sup> Values obtained from U.S. National Library of Medicine: <http://toxnet.nlm.nih.gov/>.

<sup>b</sup> Not available.

<sup>c</sup> Values obtained from Li et al., 2014.

## 2.2 Sampling and Sample Preparation

The surface water (pH=7.1±0.1) was directly collected from Yixingbu Station in Tianjin Xinkaihe Water Treatment Plant, China. The sampling water was the mixture of 28 antibiotics spiked into the surface water, and the initial concentration of each antibiotic in all adsorption experiments was 5000 ng/L.

Following collection, the water samples were filtered through 0.45 µm glass microfiber filters. Sample volumes of 500 mL were adjusted to pH 2.0-3.0 and to them was added 0.5 g disodium ethylenediamine tetraacetate (Na<sub>2</sub>EDTA). The target antibiotics were then concentrated through a solid phase extraction (SPE) with Oasis HLB cartridges (6 mL/500 mg, Waters, USA) and a 12 position vacuum manifold (HSE-12D). After that, antibiotics were eluted in a test tube by three 4 mL methanol and evaporated under nitrogen sparge. Finally, the sample was reconstituted to a final volume of 1 mL with 10% methanol (v/v) and transferred to an amber autosampler vial for LC-MS/MS analysis. Detailed information is documented in our previous study (Li et al., 2014). All adsorption experiments were conducted at room temperature (25±1°C).

## 2.3 Analytical Methods

The LC system was an ACQUITY Ultra Performance liquid chromatography (UPLC) (Waters, Milford, USA). An ACQUITY BEH C18 (2.1 mm×50 mm i.d., 1.7 µm, Waters, USA) chromatograph column was employed and operated at 24°C. The



injection volume was 10  $\mu$ L. Acetonitrile (phase A), ultrapure water with 0.1% (v/v) formic acid (phase B1) and ultrapure water (phase B2) were served as mobile phases at flow-rate of 0.3 mL/min. The set-up of the gradient programs of the UPLC is shown in Tables S1 and S2.

The mass spectrometer was a Quattro Premier XE (Waters, USA) equipped with an electrospray ionization (ESI) source. The antibiotics were ionized in positive ion mode except for thiamphenicol, florfenicol and chloramphenicol which used a negative ion mode. Both positive and negative ions were acquired in the multiple reactions monitoring (MRM) mode. The temperature of the heated capillary was 350°C, and the source voltage was 2.8 kV. High purity nitrogen was used as the desolvation gas and the cone gas at the flow rates of 600 L/h and 75 L/h, respectively. High purity argon was utilized as the collision gas with the collision cell pressure being  $5 \times 10^{-3}$  mbar. The potential of the entrance and exit of the collision cell were set at 0 V and 1 V, respectively. Target antibiotics were identified based on the precursor ion and the two most intensive product ions, together with the retention time (Table S3). Details on this have been documented elsewhere (Li et al., 2014).

#### **2.4 Quantification and Quality Control**

A calibration curve was generated across a wide range of concentrations (1.5-500ng/L) with the correlation coefficients greater than 0.99. The limits of quantifications (LOQs) were determined as signal-to-noise ratio of 10 ranging from 0.1 to 1.0 ng/L. Recovery experiments with spiked samples of surface water from sampling sites were performed to determine the method's precision and accuracy. The range of recoveries was from 67.58% to 133.30%, and the relative standard deviation (RSD) values ranged from 0.60% to 12.29% (in Table S4).

#### **2.5 Adsorption equilibrium**

The PAC of 5, 10, 15, 20, 30 and 50 mg/L was added to six 600 mL water samples in 1L Erlenmeyer flasks respectively. Thereafter, the samples were continuously stirred

in the magnetic stirrer (HJ-6D, China) at speed 300 rpm. After 48-hour agitation, the samples were collected by vacuum filtration for analysis.

The adsorption capacity  $q_t$  (ng/mg) at time  $t$  (min) was computed using the following equation:

$$q_t = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where,  $C_0$  (ng/L) is the initial concentration of the antibiotics,  $C_e$  (ng/L) is the residual antibiotic concentration,  $V$  (L) is the volume and  $M$  (mg) is the weight of PAC.

The antibiotics adsorptive removal efficiency  $\eta$  (%) was calculated as follows:

$$\eta = \frac{C_0 - C_e}{C_0} \times 100\% \quad (2)$$

The Freundlich model was applied to evaluate the adsorption isotherms (Kim et al, 2014):

$$q_e = K_F C_e^n \quad (3)$$

where,  $q_e$  (ng/mg) is the adsorption capacities at equilibrium,  $K_F$  ( $\text{ng}^{1-n}\text{L}^n\text{mg}^{-1}$ ) and  $n$  constitutes the Freundlich adsorption parameters.

## 2.6 Adsorption kinetics

For adsorption kinetics, six 600 mL water samples in 1L Erlenmeyer flask water with PAC dosage of 20mg/L were stirred continuously at 25°C. Water samples were collected at 10, 20, 30, 60, 120, 180 min from six flasks for analysis, respectively.

As the 28 selected antibiotics studied in the research belong to different types, their adsorption to PAC may reveal different removal rates. To analyze the adsorption data further, the adsorption kinetics models, such as pseudo-first order model (Eq. (4)) (Ho, 2004, 2006), pseudo-second-order model (Eq. (5)) (Ho and McKay, 1998) and Elovich model (Eq. (6)) (Ho, 2006; Aroua et al., 2008), were chosen to evaluate and explain the adsorption kinetics. In this paper, moreover, the rate-controlling step of the adsorption process was investigated with the intra-particle diffusion model (Weber

and Morris, 1962) (Eq. (7)).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

where,  $q_t$  (ng/mg) is the adsorption capacity at time  $t$  (min),  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of pseudo-first-order adsorption.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{and} \quad h = k_2 q_e^2 \quad (5)$$

where,  $h$  (ng/mg min) is the initial adsorption rate, and  $k_2$  (mg/ng min) is the pseudo second-order rate constant of adsorption.

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (6)$$

where,  $a$  is the initial adsorption rate (ng/mg min) and  $\beta$  (mg/ng) is the desorption constant.

$$q_t = K_d t^{1/2} + C \quad (7)$$

where,  $K_d$  ( $\text{ng/mg min}^{1/2}$ ) is the intra-particle diffusion rate constant and values of  $C$  provide a clue concerning thickness of the boundary layer.

## 2.7 Effect of natural organic matters on PAC adsorption

The adsorption experiments were conducted using both surface water and deionized water to investigate the effect of natural organic matters (NOMs) on removal of antibiotic. The concentrations of turbidity and DOC in surface water were  $2.52 \pm 0.92$  NTU and  $2.98 \pm 1.09$  mg/L, respectively. The PAC was added at a dosage of 20 mg/L and the solutions were mixed for 120 min prior to sampling. Sample analysis was conducted as described for the adsorption equilibrium and kinetics experiments. The adsorption experiments were conducted in triplicate.

## 3 Results and discussion

### 3.1 Adsorption equilibrium

The removal efficiencies of 28 antibiotics at different dosages in surface water are shown in Table 2 with the standard deviation being less than 5%. Results indicated that removals of the antibiotics were enhanced by increasing PAC dosage; subsequently the removal efficiency rose from 70% to 100%. However, the removal efficiencies differed slightly when PAC dosage varied from 20 mg/L to 50 mg/L. Although higher PAC dosage could result in more of the antibiotics being removed, it also increased the cost of water treatment. Therefore, 20 mg/L of PAC was selected as the optimal dosage in this study for removing antibiotics from water with the adsorption capacity being greater than 220 ng/mg.

**Table 2**

Removal efficiency of 28 antibiotics at different dosages of PAC

Group	Compound	Removal efficiency at different dosages (%)					
		5mg/L	10mg/L	15mg/L	20mg/L	30mg/L	50mg/L
TCs	OTC	85.4	94.7	95.9	98.3	98.9	99.0
	TC	89.6	96.4	97.9	99.2	99.3	99.4
	CTC	94.9	97.9	99.1	99.7	99.8	99.8
	DXC	89.6	96.8	97.4	98.9	99.2	99.3
MCs	ETM	92.3	93.3	95.4	96.5	97.5	97.5
	RTM	85.1	88.5	92.3	95.9	95.9	97.0
	KIT	90.4	93.5	97.8	99.8	99.9	100.0
	SPI	87.5	93.7	97.4	99.9	100.0	100.0
CPs	TAP	92.6	95.9	97.1	99.4	99.4	99.7
	FF	88.1	93.8	97.3	99.2	99.6	100.0
	CAP	88.9	93.3	95.6	98.8	99.4	99.8
PNs	PNG	76.3	86.4	91.3	96.8	99.4	99.5
SAs	SDZ	75.9	80.8	84.9	91.1	93.9	96.8
	SMR	80.4	83.9	88.1	92.8	96.4	96.9
	STZ	76.9	84.6	88.1	95.4	96.9	98.6
	ST	74.6	82.4	86.8	95.2	98.3	98.8
	SMMX	76.9	82.6	87.5	93.9	96.2	96.7
	STL	73.2	78.4	84.2	90.2	93.7	94.7
	STX	72.9	76.0	81.5	88.0	90.8	92.1
STPD	82.6	90.7	93.1	98.2	99.2	99.3	

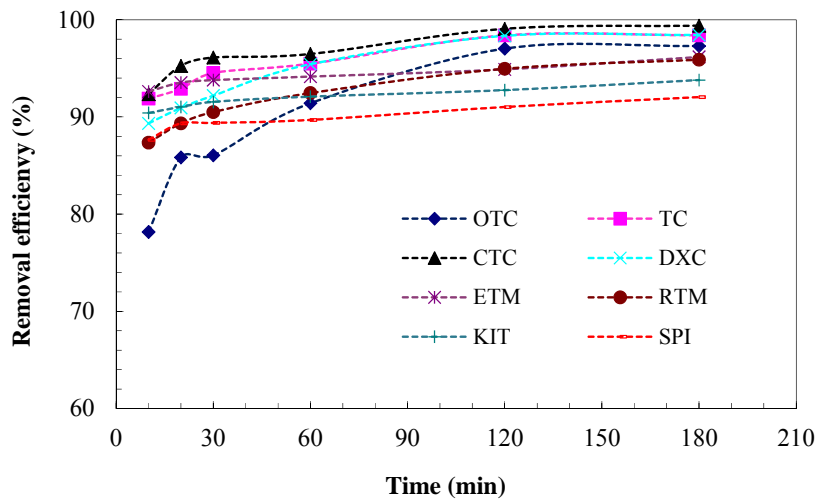
	SCPD	75.6	81.5	88.3	94.9	96.8	98.9
	STM	76.5	80.1	84.3	89.9	91.0	92.0
	SPD	81.0	88.2	93.6	97.8	98.8	99.0
	SDMX	78.8	82.3	87.6	92.2	96.8	97.7
	SPGD	80.7	89.5	93.6	97.5	98.9	99.1
QNs	OLA	93.4	98.5	99.1	99.9	100.0	100.0
	NDA	72.5	88.1	90.8	98.6	99.5	99.9
	FMQ	82.1	93.4	96.9	99.6	100.0	100.0

The parameters of the Freundlich model are given in Table S5. The Freundlich model was fitted to the adsorption data with  $R^2 > 0.9$ , and could reasonably describe the adsorption of antibiotics onto PAC. According to the results of the adsorption isotherm, most values of  $n$  were less than 1, which suggests the adsorption of antibiotics onto PAC was nonlinear and heterogeneous. The values of  $n$  obtained varied from the different antibiotics, possibly because the moieties of the adsorbate molecule influencing the adsorption of different antibiotics onto PAC (Kim et al, 2014).

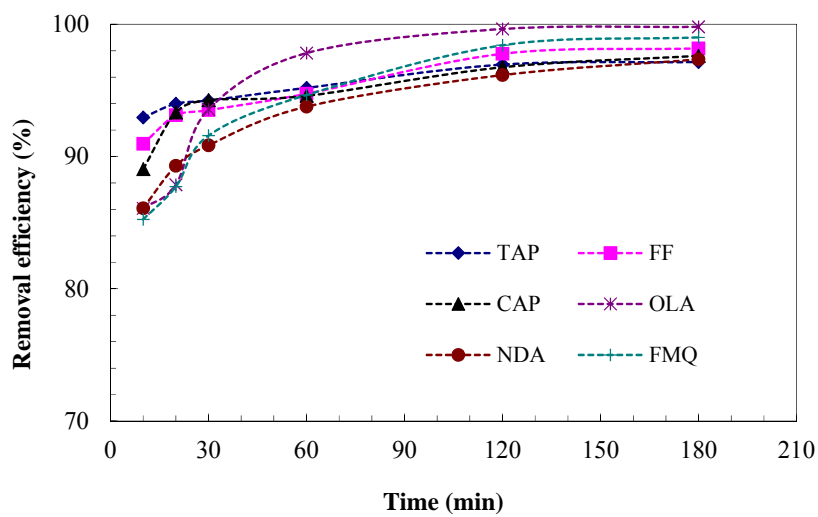
### 3.2 Adsorption kinetics

Previous studies have reported that hydrolysis of most studied antibiotics either does not occur or has a half-life of more than 16 hours under typical environmental conditions (pH=6.0-8.5; temperature = 20-25°C) ( Loftin et al., 2008; Białk-Bielin'ska et al., 2012). Consequently, these 28 antibiotics remained hydrolytically stable under current experimental conditions and could mainly be removed by PAC adsorption. Fig. 1 depicts the removal percentage changes of antibiotics with contact time. Results showed that the concentrations of 28 selected antibiotics decreased rapidly during the first 10 min, and more than 70% of each antibiotic was removed. Afterwards, the adsorption rate fell while the concentration of antibiotics decreased slowly. Correspondingly, the adsorption capacity was up to 249 ng/mg and 250 ng/mg at 120 min and 180 min, respectively. From 120 to 180 min, the residual concentrations of antibiotics did not change except that the removals of SMR, STL, STX and SDMX

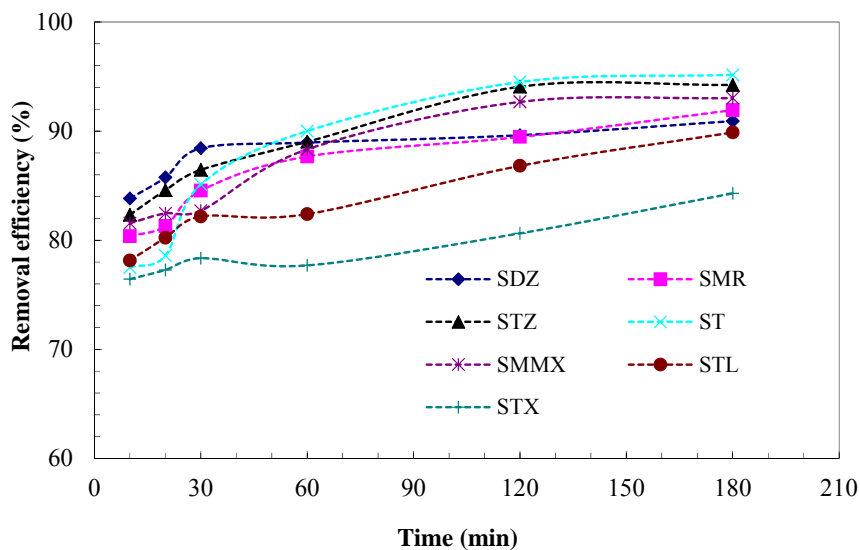
were slightly better at 180 min. Therefore, the results suggested that 120 min was suitable contact time for the antibiotic adsorption to PAC.



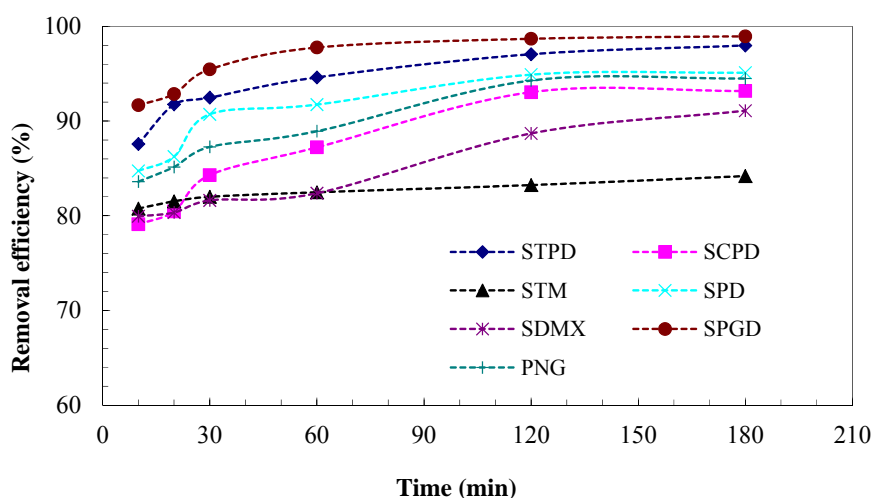
a. Removal efficiency of OTC, TC, CTC, DXC, ETM, RTM, KIT and SPI



b. Removal efficiency of TAP, FF, CAP, OLA, NDA and FMQ



c. Removal efficiency of SDZ, SMR, STZ, ST, SMMX, STL and STX



d. Removal efficiency of STPD, SCPD, STM, SPD, SDMX, SPGD and PNG

Fig.1. Removal efficiency of 28 selected antibiotics versus contact time at PAC dosage of 20mg/L

All kinetic parameters and correlation coefficients  $R^2$  are summarized in Table S6. As can be seen from Table S6, the values of  $R^2$  were very low based on the pseudo-first-order model and the experimental  $q_e$  values differed greatly from the corresponding values derived from the equation. Hence, the adsorption of antibiotics onto PAC did not follow the pseudo-first-order model, which suggested that the

external diffusion was not the determining step in the adsorption process. Conversely, the adsorption kinetics data fitted well with both the pseudo-second-order and Elovich models according to  $R^2$  values. Moreover, the second-order model indicated significantly higher  $R^2$  values (0.9989-0.9999), as well as better consistency of the experimental and theoretical  $q_e$  values when compared to the pseudo-first-order and Elovich models. Thus, the antibiotics adsorption can be simulated more appropriately by the pseudo-second-order kinetic model, which indicated that chemisorption controlled the adsorption (Aroua et al., 2008). Additionally, although the Elovich model is an empirical equation and does not predict any definite mechanism, it is useful in describing adsorption rate and the concentration changes. As the Elovich constant  $\alpha$  can represent the initial rate of adsorption, MCs and CPs demonstrated higher initial adsorption (up to 87% and 89%, respectively) than other groups of antibiotics at the beginning of the kinetic experiments due to their higher  $\alpha$  values. The rate-controlling step affecting the kinetics of adsorption was analyzed by the intra-particle diffusion model (Weber-Morris). Generally, the adsorption process includes three steps: the external surface adsorption; the gradual equilibrium stage with intra-particle diffusion dominating; and a final equilibrium stage with the intra-particle diffusion starting to slow down. If the plot  $q_t$  compared with  $t^{1/2}$  has a zero intercept ( $C=0$ ), the intra-particle diffusion is an important controlling factor in determining the kinetics of the process (Rauthula and Srivastava, 2005; Aroua et al., 2008). According to Table S6, obtained high  $C$  values varying from 182.38 to 229.86 suggested the intra-particle diffusion was not the predominant mechanism. Therefore, both external and intra-particle diffusion controlled the adsorption process of antibiotics onto PAC.

### **3.3 Performance of PAC adsorption under two water scenarios**

The results of the PAC adsorption experiments showed that the percentage removals of 28 selected antibiotics ranged from 96.5 to 99.9% and 86.8 to 99.6% in deionized water and surface water, respectively (Table 3). Under the surface water scenario, to a small extent the removal efficiency declined. This could be explained by the NOMs



in surface water competing for adsorption sites (direct site competition) and/or hindered diffusion of the antibiotics into carbon pores (pore blockage/constriction) (Ando et al., 2010), which reduced the antibiotics' adsorption capacity.

Furthermore, the removal of SAs decreased more than other antibiotics, which indicated NOMs in surface water exerted a greater influence on the removal of SAs. NOMs consist of a mixture of humic substances, polysaccharides, aminosugars, proteins, peptides, lipids, small hydrophilic acids, and others (Matsui et al., 2012). The humic substances are the main fractions of NOMs in natural surface water which consist of three major functional groups, these being carboxyl, methoxyl and phenolic hydroxyl, whereas all SAs possess amino and sulfonamide groups (Bajpai et al., 2000). It is probable that the carboxyl group of NOM interacted with the SAs amino group which in turn affected the adsorption of SAs onto PAC. However, the adsorption competition mechanisms between NOM and antibiotics are complex and need further research. Overall, PAC could adsorb more than 217 ng/mg for the six groups of 28 selected antibiotics under deionized and surface water scenario at a PAC dosage of 20 mg/L and 120 min.

**Table 3**

The removal efficiency of 28 antibiotics by PAC in deionized water and surface water

Group	Compound	Removal efficiency (%)	
		deionized water	surface water
TCs	OTC	99.8	97.6
	TC	99.9	99.0
	CTC	99.9	99.5
	DXC	99.9	98.5
MCs	ETM	99.8	96.3
	RTM	99.9	95.1
	KIT	99.9	99.6
	SPI	99.8	91.7
CPs	TAP	98.9	98.4
	FF	99.2	98.5
	CAP	99.2	98.4
PNs	PNG	99.9	96.2

SAs	SDZ	99.6	97.5
	SMR	99.7	90.6
	STZ	99.8	94.6
	ST	99.9	95.5
	SMMX	99.9	93.6
	STL	99.8	90.8
	STX	99.8	86.8
	STPD	99.9	97.2
	SCPD	99.9	93.2
	STM	98.0	87.0
	SPD	99.8	96.8
	SDMX	99.9	89.3
	SPGD	96.5	96.9
	QNs	OLA	99.9
NDA		99.7	98.4
FMQ		99.9	98.7

### 3.4 Comparisons of the antibiotics' adsorption performance

In this study, PAC exhibited a high adsorption capacity for 28 selected antibiotics. Based on the literature, the adsorption performance of various adsorbents was compared for these 28 antibiotics (Table 4). It can be seen that PAC has a high removal efficiency ranging from 65 to 100 % at a dosage of 20 mg/L and more than 90% at a dosage of 50 mg/L, respectively. Furthermore, some other adsorbents such as zeolite, mesoporous silica spheres, aluminum oxide and graphene oxide have been used to remove the antibiotics, and demonstrated different levels of removal efficiency. For example, Braschi et al. (2010) reported that zeolite had the maximal adsorption capacity of approximately 15.1% zeolite dry weight for SCPD removal. The rattle-type magnetic mesoporous silica spheres exhibited the adsorption capacity of 0.034 mmol/g and 0.079 mmol/g for STZ and TC, respectively (Xu et al., 2011). Aluminum oxide could remove 43% TC while graphene oxide could reject more than 71.4% TC and OTC from water (Chen and Huang, 2010; Gao et al., 2012). However, since these adsorbents were only employed to remove single or binary antibiotics, the feasibility of them removing other groups of antibiotics has not yet been confirmed, and more research is needed. Furthermore, considering the antibiotic types, the

adsorbents' dosages and experimental conditions, although it is difficult to make a fair evaluation through the data shown in Table 4, PAC can function as a good adsorbent for removing antibiotics without toxically active products compared to other adsorbents, for example aluminum oxide (Chen et al., 2010; Rivera-Utrilla et al., 2013).

**Table 4**

The removal efficiency or adsorption capacity of antibiotics with various adsorbents

Antibiotics	Absorbent	Water type	Adsorbent dosage	Removal efficiency or adsorption capacity ( $q_e$ )	Reference
SCPD	PAC	Surface water	10, 20, and 50 mg/L	10 mg/L: 49 - 73% 20 mg/L: 65 - 100% 50 mg/L: > 90%	Adams et al. (2002)
	A highly dealuminated faujasite zeolite (Y) (200 SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> ratio)	Water	a zeolite: antibiotic solution ratio of 1mg: 2mL.	>90%	Braschi et al. (2010)
	A high silica mordenite	Distilled water	Mordenite added with a zeolite: antibiotic solution ratio of 1 mg: 2 mL.	Maximal adsorption capacity of about 15.1% zeolite dry weight	Martucci et al. (2013)
STX	PAC	Surface water	20 mg/L	93.2%, $q_e$ : 235 ng/mg	This work
	PAC	Natural water	5 mg/L	About 35%	Snyder et al. (2007)
	Carbon nanotubes	Distilled water	40 mg/L	$q_e$ : 62.8 mg/g	Tian et al. (2013)
	Waste based carbon	Ultrapure water	2.0 g/L	$q_e$ > 110 mg/g	Calisto et al. (2015)
SPD	PAC	Surface water	20 mg/L	86.8%	This work
	Carbon nanotubes	Distilled water	40 mg/L	$q_e$ : 82.4 mg/g	Tian et al. (2013)
STZ	PAC	Surface water	20 mg/L	96.8%	This work
	PAC	Surface water	10, 20, and 50 mg/L	10 mg/L: 49 - 73% 20 mg/L: 65 - 100% 50 mg/L: > 90%	Adams et al. (2002)
	A highly dealuminated faujasite zeolite (Y) (200 SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> ratio)	Water	a zeolite: antibiotic solution ratio of 1mg: 2mL	>90%	Braschi et al. (2010)
	rattle-type magnetic mesoporous silica spheres	Deionized Ultrapure water	0.002 g $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /mSiO <sub>2</sub> spheres	$q_e$ : 0.0342 mmol/g	Xu et al. (2011)

TC	PAC	Surface water	20 mg/L	94.6%, $q_c$ : 238 ng/mg	This work
	Aluminum oxide	Water	0.8-3.5g/ L of $Al_2O_3$	43%	Chen and Huang (2010)
	Rattle-type magnetic mesoporous silica spheres	Deionized ultrapure water	0.002 g $\gamma$ - $Fe_2O_3$ /mSiO <sub>2</sub> spheres	$q_c$ : 0.0791 mmol/g	Xu et al. (2011)
	Graphene oxide (GO)	Water	0.544 mg/mL GO stock solution	> 71.4%, the ideal maximum adsorption capacity of 313 mg/g	Gao et al. (2012)
	BSA/ $Fe_3O_4$ microspheres	Ultrapure water	BSA/ $Fe_3O_4$ microspheres (200 mg) added into 100 mL of solution	92.07%	Zhang et al. (2013)
	Carbon nanoparticles made from vine woo	Distilled water	0.4 g/L	74-88%	Pouretedal and Sadegh (2014)
OTC	NaOH-activated carbon	Distilled water	25mg/50mL	70-100%	Martins et al. (2015)
	PAC	Surface water	20 mg/L	99.0%, $q_c$ : 247 ng/mg.\	This work
	Aluminum oxide	Water	0.8–3.5g/Lof $Al_2O_3$	43-57%	Chen et al. (2010)
	Graphene oxide	Water	0.544 mg/mL GO stock solution	>71.4%, the ideal maximum adsorption capacity of 212 mg/g	Gao et al. (2012)
NDA	PAC	Surface water	20 mg/L	97.6%, $q_c$ : 244 ng/mg	This work
	Montmorillonite (SAz-1) and kaolinite (KGa-1b)	Deionized water	0.1 g of clay and 20.0 mL of NDA solution	$q_c$ : 1.11 and 0.9 mg/g, respectively	Wu et al. (2013)
SDMX	PAC	Surface water	20 mg/L	98.4%, $q_c$ : 246 ng/mg	This work
	PAC	Surface water	10, 20, and 50 mg/L	10 mg/L: 49 - 73% 20 mg/L: 65 - 100% 50 mg/L: > 90%	Adams et al. (2002)
SMR	PAC	Surface water	20 mg/L	89.3%, $q_c$ : 233 ng/mg	This work
	PAC	Surface water	10, 20, and 50 mg/L	10 mg/L: 49 - 73% 20 mg/L: 65 - 100%	Adams et al. (2002)

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				50 mg/L: > 90%	
	PAC	Surface water	20 mg/L	90.6%, $q_c$ : 235 ng/mg	This work
ETM	BSA/Fe <sub>3</sub> O <sub>4</sub> microspheres	Ultrapure water	BSA/Fe <sub>3</sub> O <sub>4</sub> microspheres (200 mg) added into 100 mL of solution	98.98%	Zhang et al. (2013)
	PAC	Surface water	20 mg/L	96.3%, $q_c$ : 238 ng/mg	This work
CAP	BSA/Fe <sub>3</sub> O <sub>4</sub> microspheres	Ultrapure water	BSA/Fe <sub>3</sub> O <sub>4</sub> microspheres (200 mg) added into 100 mL of solution	96.4%	Zhang et al. (2013)
	PAC	Surface water	20 mg/L	98.4%, $q_c$ : 246 ng/mg	This work
PNG	Carbon nanoparticles made from vine woo	Distilled water	0.4 g/L	74-88%	Pouretedal and Sadegh (2014)
	PAC	Surface water	20 mg/L	96.2%, $q_c$ : 246 ng/mg	This work

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## **4 Conclusions**

This study investigated the removal of six groups of antibiotics (TCs, MCs, CPs, PNs, SAs, QNs) using PAC. The specific findings are as follows:

- PAC exhibited the high adsorption capacity for all selected antibiotics and these antibiotics were effectively removed from water.
- Based on the adsorption isotherms, the adsorption of antibiotics onto PAC was nonlinear and heterogeneous.
- NOMs in surface water exerted greater influence on the removal of SAs than others.
- The kinetics data suggested the adsorption process was governed by the pseudo-second-order reaction.
- It was observed that both the external surface adsorption and intra-particle diffusion were controlling factors in the antibiotic adsorption onto PAC.

It can be conclusively stated that PAC is an efficient and promising adsorbent for removing antibiotics from water.

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