Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2013, 5(11):578-582

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Research on selected antibiotics removal from water through powder activated carbon adsorption

Jianguang Liu[1*], Ruichao Xu[1], Chunyang Zhang[3], Wuchang Song[2], Ni Zhang[1], Xiangfeng Jia[1], Haifeng Wang[1] and Qiuyue Sun[1]

[1]School of Municipal and Environmental Engineering, Shandong Jianzhu University, Jinan, China
[2]Urban Water and Waste Water Monitoring Center of Shandong Province, Jinan, China
[3]School of Thermal Engineering, Shandong Jianzhu University, Jinan, China

---

ABSTRACT

The powdered activated carbon (PAC) adsorption to remove trace contaminant antibiotics from water was studied. The results showed that the PAC adsorption feature of selected antibiotics complied with Freundlich adsorption isotherm model. PAC has high performance in removing antibiotics in water. When the concentration of antibiotics in the water is about 489ng/L and the dosage of PAC is24mg/L, the removal rates of sulfamethoxazole, sulfadimidine, erythromycin, oxytetracycline and tetracycline through PAC adsorptionwere79.84%, 80.05%, 94.62%, 83.32% and 96.88% respectively.

Keywords: Water treatment, Antibiotic, Powdered activated carbon, Adsorption, Pharmaceuticals.

INTRODUCTION

In recent years, antibiotics have been detected in aquatic environments in many countries and regions[1-5], and long-term consumption of water that contains trace antibiotics and other drugs poses a threat to human health[6]. Attention has been drawn to this problem worldwide. The production and use of antibiotics in china is in severe abuse[7-9], and antibiotics pollution in water environment is more serious in china than in developed countries. Studies show that antibiotic had been detected in the Pearl River in Guangzhou, Shenzhen River, the Yellow River and other rivers in china, and that most of the antibiotics content level is higher than developed countries [10-12]. In recent years, antibiotics and other drugs have been detected in drinking water in the United States, Canada, Germany, France, Finland and other developed countries[13-16]. This exposes efficiency issue of the drinking water treatment process for pharmaceuticals removal as well as human health risks caused by trace drugs in drinking water.

Rooklidge [17]studied the treatment effect of the multi-stages and filter for four antibiotics(μg/L level) in drinking water. The results show that Tellabsneomycin and trimethoprim treatments are better with removal rate reaching 99.9%. Conversely, the removal rates of lincomycin and sulfa are only 4%and25%. Adams[18]used the ion exchange method to research the treatment effect for trimethoprim and sulfa antibiotic in river (μg/L concentrations), and the results show that they would rapidly go through the strong acid cation exchangers in column hence the removal rate is only 21%~58%.Currently,there are other ways to remove antibiotics, such as bioremediation[19], biological treatment, advanced oxidation technology and adsorption. Powdered Activated carbon (PAC) has a high specific surface area and rich gap structure, and is widely used in water treatment as a good adsorption material. The characteristics and performance of PAC for removing antibiotics in water were studied, which can provide reference for removal of the typical antibiotics in source water.

EXPERIMENTAL SECTION

2.1Experimental materials

Adsorbed material is powdered activated carbon which has a diameter of less than 0.074mm (200 sieve) derived from coal. Pure water was made with pure ultrapure water system. Methanol solution is HPLC grade. The antibiotics were conserved in refrigerator at -20℃. Standard stock solution of antibiotics was 1mg/L and further diluted with pure water to a concentration required of the experiment.

2.2 Characteristics analysis of PAC

Surface area, pore volume and pore sizes of powdered activated carbon were determined by specific surface area and pore size analyzer (V-sorb 2800p, Gold APP Instrument Corporation China).

2.3 Analysis of antibiotics concentration

500mL water samples were filtered through 0.45μm cellulose acetate membrane and then added 0.1gNa_2EDTA, and adjusted the pH to 3.0. Solid phase extraction columns (6mL, 500mg, Waters Oasis HLB) were used to extract the antibiotics from water sample. The columns were activated by washing with 5mL methanol and 5mL pure water at a flow rate of 1mL/min. 500mL water samples flowed through the column at a flow rate of 5mL/min. The columns were dried by vacuum draw. The antibiotics were eluted with 6mL methanol solution into 10mL centrifuge tubes, the flow rate through the columns is 1mL/min. After the methanol solution in the centrifuge tubes were purged with N_2 to near dryness at room temperature, the volume was made up to 200μL with water-methanol (70:30) solution and solution were transferred into 1.5mL amber screw vials. The antibiotics were analyzed with HPLC-MS/MS (HPLC-tandem mass spectrometry: High Performance Liquid Chromatography, Agilent 1200.TripleQuadrupolemass Spectrometer model, Agilent 6410.USAAgilent Technology Co., Ltd. PC -420Dsolid phase extraction device).

2.4 Operation procedure of adsorption test

Powdered activated carbon sample was immersed in pure water for24 hours, and then placed in to an oven to dry at 105℃ until a constant weight is reached. Powdered activated carbon sample and water samples were put into Erlenmeyer flasks. The water samples in each flask were of the same volume and the antibiotic concentration is about 489ng/L. The flasks were placed on a shaker in the constant temperature box. All water samples were filtered through 0.45μmcellulose acetate membrane before the residual antibiotic concentration was measured.

2.5Freundlich adsorption isotherm model

The adsorption capacity of activated carbon is represented by adsorption capacity,

$$q = \frac{V(C_0 - C)}{M} = \frac{X}{M} \quad (1)$$

Where q -activated carbon adsorption capacity, per unit weight of the adsorbent material adsorbed antibiotic weight, ng/mg; V -water sample volume, L; C_0, C -concentration of antibiotics in water samples of raw water and adsorption equilibrium ng/L; X -adsorbed weight, ng; M -activated carbon dosage, mg;

In this experiment, Freundlich equation was fitted to antibiotic adsorption isotherms. Freundlich equation is below:

$$q = K \bullet C^{\frac{1}{n}} \quad (2)$$

where q -activated carbon adsorption, ng/mg; C -equilibrium concentration of the adsorbed substance ng/L; K, n-constants related to temperature and pH of the solution, the nature of the adsorbent and the adsorbed matters.

RESULTS AND DISCUSSION

3.1 Characteristics of PAC

The detection results of surface area, pore-volume, and pore size of activated carbon powder are shown in Table 1.

Table1Basic properties of activated carbon

Name	BET Specific surface area（m^2/g）	Pore-volume (cm^3/g)	Aperture (nm)
PAC	1054.7372	0.5919	2.2447

It can be seen from table 1 that the PAC has rich pore structure and high specific surface area.

3.2 Effects of PAC dosage to adsorption

Sulfamethoxazole was used in the test. The dosage of PAC for six 1000mL erlenmeyer flasks was 10, 20, 40, 60, 80 and 100mg respectively. The water sample volume in each erlenmeyer flask was 1000mL, with a sulfamethoxazole concentration of about 489ng/L. The temperature of water sample was20℃. All flasks were shaken for 1h on the shaker. Every water sample should be filtered through 0.45μm cellulose acetate membrane, residual antibiotic concentration was measured and the results are shown in Fig.1.

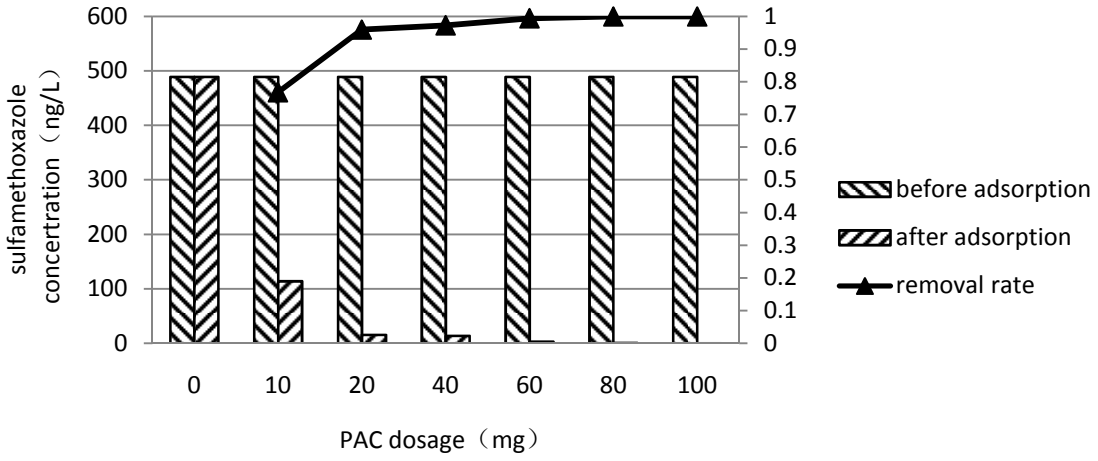

Fig.1 Sulfamethoxazole concentrations for different PAC dosage

The Fig.1 shows that the removal rate of sulfamethoxazole increases along with powdered activated carbon dosage. When the dosage of PAC is 10mg/L, the removal rate of sulfamethoxazoleis76.71%. While the dose of PAC is not less than20mg/L, the removal rate of sulfamethoxazole is more than 95%. The blank experiment was set up to correct the loss of trace antibiotics during experimental procedure. The result shows that PAC has better adsorption performance for sulfamethoxazole.

3.3 Effects of PAC adsorbed time

Sulfamethoxazole was selected in the experiment. Four Erlenmeyer flask (1000mL) were used. Three Erlenmeyer flasks were added 10mgPAC, while the fourth was not. In each of Erlenmeyer flask with the same volume of water sample (1000mL).The temperature of water samples was20℃. The three flasks with PAC were shaken on a shaker for 0.5h, 1h and 2h respectively. The water samples should be filtered through 0.45μmcellulose acetate membrane before the residual antibiotic concentration was detected. The sulfamethoxazole concentration of blank water sample is 476.23ng/L. Other results are shown in Fig.2.

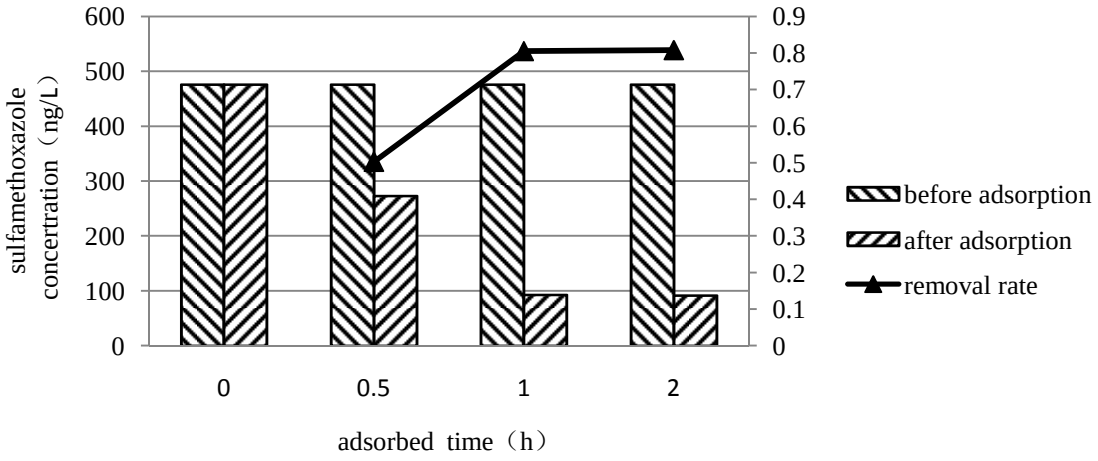

Fig.2 Sulfamethoxazole concentrations in different adsorption time

The Fig.2 shows that the removal rate of sulfamethoxazole increases with increase in the adsorption time. When the oscillation time is 1h, the removal ratereaches80.53%. The increase extent is not significant when being shaken up to 2h, with a removal rate of 80.78%. The duration of PAC adsorption equilibrium for sulfamethoxazole is 1h.

3.4 Effect of kinds of antibiotics

Five kinds of antibiotics were selected in the experiment. The dose of PAC in six1000mL Erlenmeyer flasks are 0mg, 2mg, 6mg, 12mg, 18mg and 24mgrespectively for the adsorption test of each antibiotic. The volume of water samples is the same in all experimental Erlenmeyer flasks(1000mL).The temperature of water was20℃The flasks were shaken for 1h on the shaker. Every water sample should be filtered through 0.45μmcellulose acetate membrane before the concentration of residual antibiotics was detected. The results were shown in Fig.3.

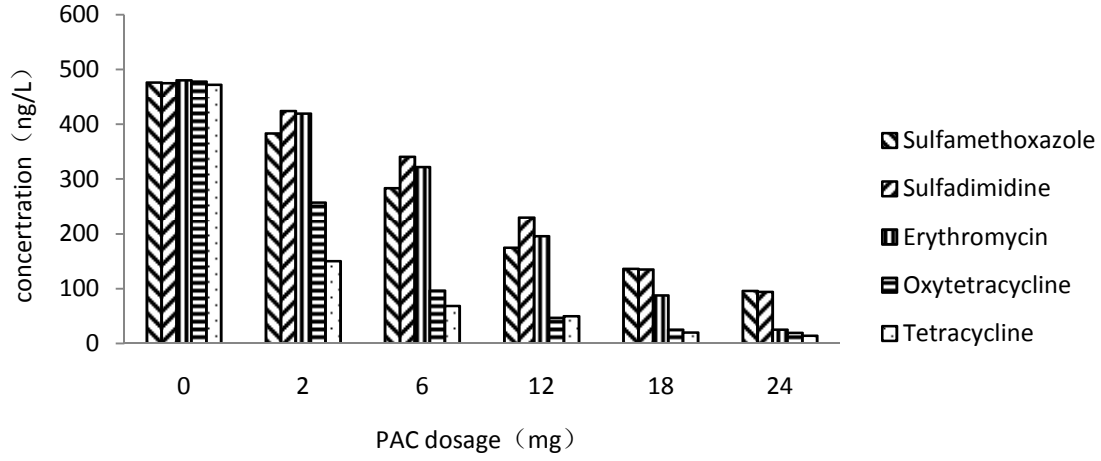

Fig.3 PAC adsorption equilibrium of antibiotic concentration

From Fig.3, it can be seen that the equilibrium concentration of antibiotics in water samples decreases with increase in PAC dosage. PAC has excellent capability in antibiotics removal. The removal rates of all tested antibiotics increased with raise in PAC dosage within a certain range. When PAC dosage is 24mg/L, the maximum removal rate of sulfamethoxazole, sulfadimidine, erythromycin, oxytetracycline and tetracyclinereached79.84%, 80.05%, 94.62%, 83.32%and 96.88% respectively.

3.5 PAC Adsorption capacity for antibiotics

Based on the tests above (3.4), the adsorption capacity of PAC for antibiotics were calculated using the activated carbon adsorption formula (1).The results were shown in Fig.4.

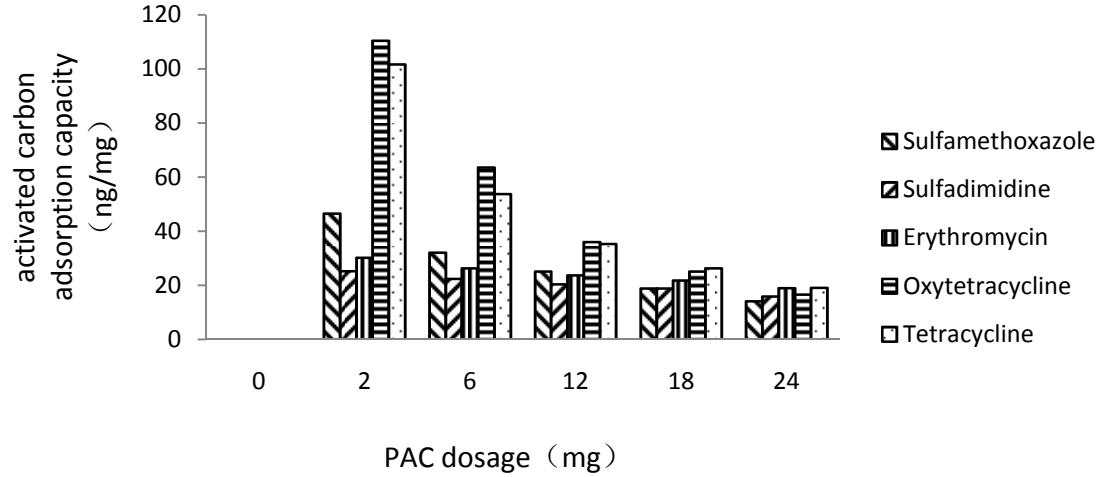

Fig.4 PAC adsorption capacity of the typical antibiotics

From Fig.4, it can be seen that the adsorption quantity per unit mass of PAC decreases along with the decline of antibiotic concentration in adsorption equilibrium condition. Furthermore, it can be seen that the capacity of PAC adsorption for different kind of antibiotics is not alike with same PAC dosage. The adsorption capacity of PAC for tetracycline and oxytetracycline is higher than other antibiotics, which may be due to the presence of a large number of hydroxyl groups in both antibiotics molecular structure as well as much acidic oxygen-containing groups in PAC surface.

3.6 Adsorption isotherm model

Calculated results of the test comply with the Freundlich model. The Freundlich model parameters calculated are

shown in Table2.

Table 2AntibioticsFreundlich adsorption isotherm parameters

Antibiotics	Freundlich adsorption isotherm parameters		
	K	n	R^2
Sulfamethoxazole	1.17	0.23	> 0.9
Sulfadimidine	1.18	0.15	> 0.9
Erythromycin	1.25	0.14	> 0.9
Oxytetracycline	1.12	0.57	> 0.9
Tetracycline	1.19	0.63	> 0.9

In the table 2, it is more reasonable to use the Freundlich model to represent adsorption isotherm for antibiotic adsorption. All the correlation coefficients (R^2) are greater than 0.9. The experimental results showed that Freundlich adsorption isotherm parameters for different types of antibiotics are different. The parameter K for Sulfa antibiotics (including sulfamethoxazole and sulfadimidine) and tetracycline antibiotics (including oxytetracycline and tetracycline) is approximate. The reason may be their similar molecular structure. The greater K value indicates that the PAC adsorption rate for antibiotics is larger [20]. PAC adsorption rate for erythromycin is highest, while adsorption rate for sulfonamide and tetracycline is not much different. The smaller the value of parameter n[20], the faster the PAC adsorption saturates, and the easier the antibiotics is to be adsorbed. The rate of adsorption saturation of PAC for sulfa and erythromycin antibiotics is faster than tetracycline.

CONCLUSION

By studying the PAC adsorption for selected antibiotic substances in water, the following conclusions can be drawn. (1) PAC has high performance in removing some typical antibiotics. When the concentration of antibiotics in the water is about 489ng/L, the PAC dosage is 24mg/L, the adsorption removal rate of sulfamethoxazole, sulfadimidine, erythromycin, oxytetracycline and tetracycline was 79.84%, 80.05%, 94.62%, 83.32% and 96.88% respectively. (2) The Adsorption features of PAC for antibiotics comply with the Freundlich adsorption isotherm model. The adsorption characteristics of PAC for different types of antibiotics are different. The adsorption capacity of PAC for tetracycline and oxytetracycline is higher than other antibiotics.

Acknowledgement
This work was supported by National Natural Science Foundation of China (51278285), Shandong Provincial Natural Science Foundation of China (ZR2010EM019) and National Science and Technology Major Project of china (2012ZX07404-003).

REFERENCES

[1] G Hamscher; B Priess and H Nau. *Archiv fur Lebensmittelhygiene*, **2006**, 57, 97–101.
[2] DW Kolpin; ET Furlong; MT Meyer. *Environ. Sci. Technol*., **2002**, 36, 1202–1211.
[3] AL Batt; DD Snow and DS Aga. *Chemosphere*, **2006**, 64, 1963–1971.
[4] AYC Lin;TH Yu and CF Lin. *Chemosphere*, **2008**,74,131–141.
[5] S Managaki; A Murata and H Takada. *Environ. Sci. Technol*., **2007**,41, 8004–8010.
[6] A Bendesky and C Menéndez. *Mutat. Res*., **2002**, 511(2), 133–144.
[7] QX Zhou; Y Luo and ME Wang. *Journal of Chemical Ecology*, **2007**, 2(3), 243-251.
[8] BJ Richardson; PKS Lain and M Martin. *Marine Pollution Bulletin*, **2005**, 50(9), 913-920.
[9] WH Xu; G Zhang and SC Zou. *Environmental Science*, **2007**, 28(8), 1779-1783.
[10]YC Liu; WH Xu and LL Yu. *Journal of Instrumental Analysis*, **2006**, 25(2), 1-5.
[11] JP Ye; SC Zou and GZhang.*Ecological Environment*, **2007**, 16 (2), 384-388.
[12] QX Yang; XM Li and ZJ Jia. *Tech. Equip. Environ. Pollut. Control*, **2006**, 7(12), 57-60）.
[13] TA Temes; MMeisenheimer and D Medowell. *Environ. Sci. Technol*., **2002**, 36(17), 3855-3863.
[14] P Westerhoff; Y Yoon and S Snyder. *Environ. Sci. Technol*., **2005**, 39(17), 6649-6663.
[15] GA Loraine and ME Pettigrove. *Environ. Sci. Technol*., **2006**, 40 (3), 687–695.
[16] S Mompelat; B L Bot and O Thomas. *Environ. Int*., **2009**, 35(5), 803-814.
[17] SJ Rooklidge and JR Miner. *American Water Works Association J*., 2**0**05, 97(12), 92-100.
[18] C Adams; Y Wang and K Loftin. *Environ. Eng.*, **2002**, 128(3), 253-260.
[19] MP Das; M Bashwant; K Kumar and J Das. *J. Chem. Pharm. Res*., **2012**, 4(2), 1061-1065.
[20] W Wu and XH Zhao. *Water Supply and Drainage*, **2012**, 38(5), 133-136.