



Adsorption of Tetracycline on Activated Carbon and Graphite: A Comparative Study on the Mechanisms

J. CHEN^{1,2,*}, J.P. WANG^{1,2}, Z.H. FEI^{1,2} and G.C. ZHANG^{1,2}

¹Jiangsu Provincial Key Laboratory of Coastal Wetland Bioresources and Environmental Protection, Yancheng 224051, Jiangsu, P.R. China

²Institute of Applied Chemistry and Environmental Engineering, Department of Chemistry, Yancheng Teachers University, Yancheng 224051, Jiangsu, P.R. China

*Corresponding author: Fax: +86 515 88233188; Tel: +86 515 88233188; E-mail: keliernuonuo@yahoo.cn

(Received: 20 September 2011;

Accepted: 8 June 2012)

AJC-11570

The graphite and activated carbon were employed to simulate the black carbon with different surface properties. The adsorption of tetracycline on these adsorbents was investigated by method of static experiments. Related properties of the adsorbate and adsorbents were studied to support the adsorption mechanism exploration. The results suggested that H-bonding drives adsorption of tetracycline on the activated carbon, while hydrophobic force stands for adsorption of tetracycline on graphite.

Key Words: Tetracycline, Adsorption, Activated carbon, Graphite, Black carbon.

INTRODUCTION

Because the antibiotics in the environment might aid antibiotic-resistance of the microorganisms, they have drawn more and more attention, recently¹. The antibiotics are generally used as veterinary medicine, human infection medicine, aquaculture and husbandry growth promoters. Tetracyclines, a group of broad-spectrum antibiotics, rank secondly throughout the world, based on its production and usage². Tetracyclines have poor intake, with 25-75 % of the total dose leaving the organisms unmetabolized³. Thus, considerable amounts of tetracyclines were discharged into the environment during the application and production³. Tetracyclines were once thought to decompose readily, but they have been detected intact in multiple environmental samples.

The sorption is a key determinant of tetracyclines bio-availability, reactivity and mobility in the environment. It is an urgency to understand the interactions between tetracyclines and soils, sediments, aquatic particles^{1,4-6}. Thus, many studies have been conducted on tetracyclines adsorption properties employing typical adsorbents in the environment. As a geosorbent, the black carbon (BC) has been proved to influence the particles sorption behaviour in the environment⁷. However, less studies were designed to test the adsorption properties of tetracyclines on black carbon.

Based on current techniques for the isolation of black carbons, yet little was known about the potential effects on black carbon surface and adsorption properties⁸. Furthermore,

the black carbon surface properties vary considerable between the sample sources⁹. It is to say, the separation and representative of black carbon samples are problematic¹⁰.

So, activated carbon and graphite were used here to simulate the black carbon with different surface properties and the tetracycline was used as typicalness of tetracyclines. The study beginning with simplified simulators may be helpful to understand the role of black carbon on the fate of tetracycline in the environment.

The objectives of the current study were: (1) assessment of the adsorption properties of activated carbon and graphite for tetracycline, (2) interpretation of associated adsorption mechanism(s).

EXPERIMENTAL

Characteristics of the adsorbents and adsorbate: The activated carbon was from Calgon (Filter 400) and the graphite with the carbon element content about 99.99 % (EDS analysis result) was from Shandong, China. Before use, the activated carbon and graphite were first pulverized into 100 mesh powders and then allowed a 48 h treatment in 0.01 mol/L HCl solution. Then, they were rinsed to neutral with pure water, oven dried at 110 °C and stored in a desiccator.

The surface characteristics including SEM-EDS analysis (Quanta 200, FEI, Hillsboro, OR, USA and Sapphire CDU, EDAX Int, Mahwah, NJ, USA), the polar functional group concentrations¹¹, the pH_{PZC} ¹² and the specific surface area¹³ were evaluated for the activated carbon and graphite. The

effect of pH value on tetracycline (K_{ow}) was estimated by flask-shaking method¹⁴.

Adsorption experiments: The adsorption of tetracycline on the activated carbon and graphite were measured by batch experiments, including adsorption isotherm and the impacts of solution chemistry. Typically, the adsorbents were weighed and added to polypropylene tubes containing 40 cm³ tetracycline solution with desired concentration, ionic strength and pH. After equilibrium, the adsorbents were separated from the solutions by 0.45 μ m membranes. Concentration of tetracycline in the filtrate was analyzed by GBC 916 UV-VIS spectroscopy (GBC Scientific Equipment, Ltd., Victoria, Australia) at 280 nm wavelength¹⁵. And the McIlvaine solution was used to buffer the sample solutions containing tetracycline¹⁶.

RESULTS AND DISCUSSION

Characteristics of the adsorbents and adsorbate: Table-1 provides the physical and chemical properties of activated carbon and graphite. The activated carbon BET specific surface area is 894 m²/g, about 223 times of graphite's. In addition, there are plenty of functional groups located on the surface of activated carbon. But there is almost no polar group detected on graphite surface. This is in conformity of the EDS detection result that the carbon content is almost 100 %, so there is no heteroatom on the graphite surface.

TABLE-1
PROPERTIES OF ACTIVATED CARBON AND GRAPHITE

	Activated carbon	Graphite
Total basic sites concentration, [mmol/g]	0.34	-
Total acidic sites concentration, [mmol/g]	0.14	-
Phenolic, [mmol/g]	0.03	-
Lactonic, [mmol/g]	0.04	-
Carboxylic, [mmol/g]	0.07	-
pH _{PZC}	8.2	4.8
Specific surface area, [m ² /g]	894	4.0

The tetracycline's charging property is complicated due to its triple protonated nature. It was shown in Fig. 1 that tetracycline's major species is monovalent cation at pH < 3.3, neutral in pH 3.3-7.7, monovalent anion (-) in pH 7.7-9.7 and bivalent anion (2-) at pH > 9.7.

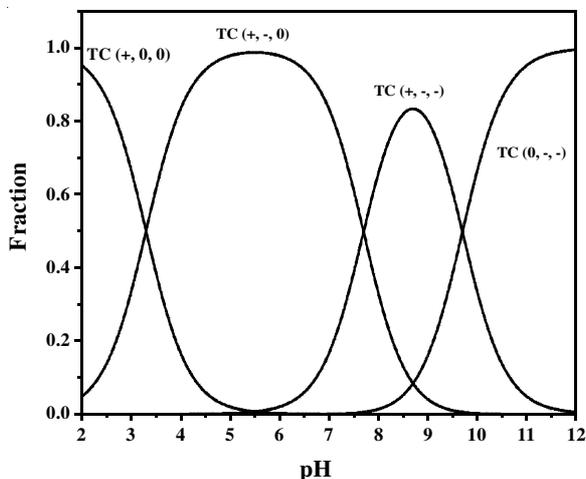


Fig. 1. Tetracycline's speciation distribution

In Fig. 2, the K_{ow} of tetracycline was presented as a function of pH. The K_{ow} of tetracycline increases with the increased pH and reaches its maximum at about pH 5-5.5, then decreases gradually. The trend of K_{ow} of tetracycline on pH resembles closely the distribution of tetracycline's neutral species (Fig. 1). The results suggested the neutral species of tetracycline (+, -, 0) is more hydrophobic than the others.

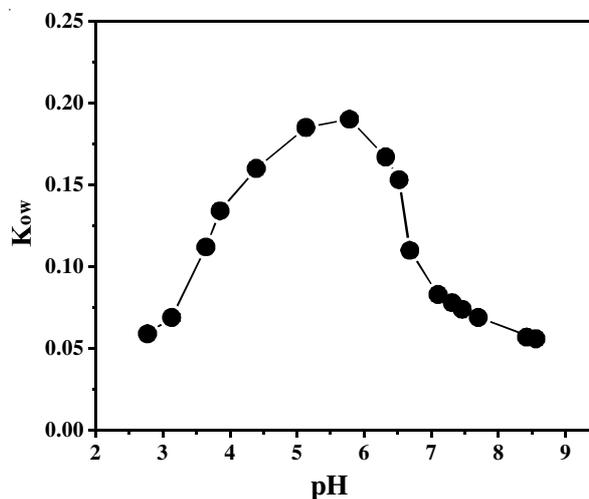


Fig. 2. K_{ow} of tetracycline on pH

Adsorption properties: It is shown in Fig. 3, divided into the adsorbents mass, the adsorption capacity of activated carbon (0.628 mmol/g) is much higher than graphite (15.0 $\times 10^{-3}$ mmol/g), while based on the adsorbents specific surface area, the adsorption capacity of graphite (5.48 $\times 10^{-6}$ mol/m²) exceeded activated carbon (0.703 $\times 10^{-6}$ mol/m²) obviously.

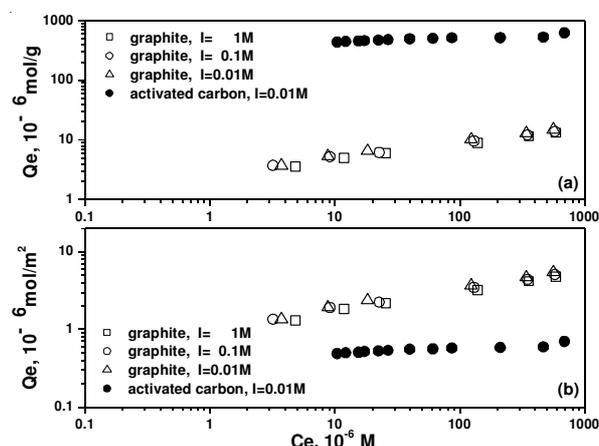


Fig. 3. Adsorption isotherms of tetracycline on graphite and activated carbon

Based on the adsorption capacities (q_m) of the adsorbents, the activated carbon exhibits much higher adsorption capacities than general environmental samples including bentonites, humic acid, peat, montmorillonites, hydrous oxides of Al and Fe (Table-2). It is to say, black carbon, a kind of geosorbent with the surface properties similar to that of activated carbon and graphite may play an important role in the fate of tetracycline presented in the environment.

Adsorption mechanisms: In fact, the adsorption is caused by the resultant force among the adsorbent surface, solvent

and adsorbate. The adsorption driving force and mechanism can be traced based on the experiment results.

TABLE-2
MAXIMUM ADSORPTION CAPACITIES OF TETRACYCLINE
ON DIFFERENT ADSORBENTS

Adsorbent	pH	q_m , [10^{-3} mol/g]
Hydrous oxides of Al ²⁺	5.3	0.16
Hydrous oxides of Fe ²⁺	5.3	0.12
Tannic acid-bentonite ¹⁷	6.1	0.210
Na- bentonite ¹⁷	6.1	0.078
Ca- bentonite ¹⁷	6.1	0.200
DDTMA- bentonite ¹⁷	6.1	0.038
Humic acid ¹⁸	4.55	0.155
Peat ¹⁸	4.55	0.120
Humic acid ¹⁸	6.14	0.075
Peat ¹⁸	6.14	0.060
Montmorillonite ¹⁸	5.0	0.540
Na-montmorillonite ¹⁸	5.5	0.112

About the activated carbon, the impacts of solution chemistry on the adsorption were presented in Fig. 4a. The ionic strength has no significant effect on the adsorption, but the solution pH gives a gentle negative impact, at the pH range of 3-9.8. The adsorption trend on pH was quite different from the K_{ow} general trend (Fig. 2). Hence, hydrophobic interaction is not the major driving force for the adsorption. Moreover, as discussed above, adsorption capacity is not a function of ionic strength. Generally, increasing ionic strength imposes negative impact on the adsorption stemming from electrostatic interaction¹⁷. Hence, the adsorption cannot be caused mainly by electrostatic interaction. This conclusion is drawn also based on the properties of activated carbon and tetracycline. The pH_{PZC} for activated carbon is shown in Table-1, the net charge on carbon's surface should reverse at pH 8.2. And the charging properties of tetracycline should change during the pH variation as shown in Fig. 1. In Fig. 4a, there is no charges interaction was found in the monotonic decrease of adsorption capacities on pH, while unexpected results were observed if concerning electrostatic interaction exclusively. For example, the higher adsorption capacities presented in acidic conditions, where both adsorbent and adsorbate charge alike.

The H-bonding was proposed as the potential major driving force for adsorption of tetracycline on activated carbon. For tetracycline molecule has oxygen and nitrogen polar functional groups. It was indicated that there are 11 H-bond acceptors and 8 H-bond donors in each molecule of tetracycline⁴. They are expected to form strong hydrogen-bonding with polar functional groups (Table-1) on activated carbon¹⁸. Part of these functional groups dissociate gradually with increasing aqueous pH. And the dissociation may cause the adsorption capacity decrease observed in Fig. 4a. So, the results can be explained reasonably with H-bonding interaction between functional groups on tetracycline molecule and activated carbon. Concerning the adsorption properties on graphite (Fig. 3 and 4b), the adsorption capacity of tetracycline is insensitive to ionic strength with the range form 0.01 to 1 mol/L. The adsorption capacity increases with raised pH from 3 to 4.5, the maximum adsorption capacity appears between pH 4.5-6.5 and then it decreases under increasing pH from 6.5 to 10.5.

So, firstly the major adsorption driving force is not the electrostatic interaction, the similar reason had been mentioned in the discussion of adsorption of tetracycline on the activated carbon. Secondly, the hydrophobic force was proposed as the potential major driving force for adsorption of tetracycline on the graphite. For there are significant correlation and similar trend observed among the neutral species (+, -, 0) distribution (Fig. 1), K_{ow} (Fig. 2) and the variation of adsorption of tetracycline (Fig. 4b). The maximums of the parameters mentioned above locate in the same pH range, 4.5-6.5. The adsorption capacity reductions in $pH < 4.5$ and $pH > 6.5$ may stem from the increase of the tetracycline water-solubility indicated by K_{ow} in Fig. 2. So, the results can be explained reasonably with the hydrophobic interaction among tetracycline, solvent and graphite.

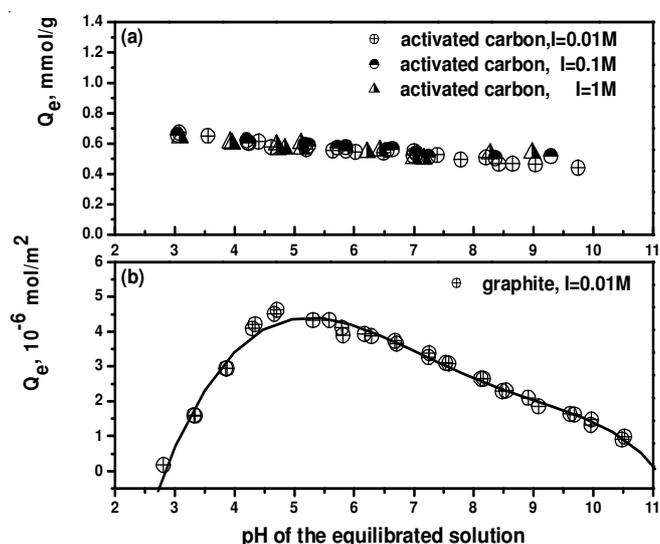


Fig. 4. Impacts of pH and ionic strength on adsorption of tetracycline

Conclusion

Activated carbon gives fairly high adsorption capacities of tetracycline and the adsorption capacities are not much impacted by ionic strength of the aqueous solutions, but negatively impacts are imposed by increasing aqueous pH. The potential driving force for tetracycline to adsorb on activated carbon might be the H-bonding between functional groups of activated carbon and the tetracycline. While in the case of graphite, the adsorption capacity, the K_{ow} and tetracycline species (+, -, 0) of tetracycline perform alike on pH. The major driving force for the adsorption is the hydrophobic force. The increase in water solubility of tetracycline can decrease the adsorption. Moreover, black carbon should play a special role in the fate of tetracycline, the surface properties may act as major determinant on the adsorption mechanism.

ACKNOWLEDGEMENTS

The authors express sincere gratitude to Jiangsu Provincial Key Laboratory of Coastal Wetland Bioresources and Environmental Protection (Grant Code: JLCBE09018), Jiangsu Provincial Department of Science and Technology (Grant No. BK2010037) for the financial support.

REFERENCES

1. R.A. Figueroa, A. Leonard and A.A. MacKay, *Environ. Sci. Technol.*, **38**, 476 (2004).
2. C. Gu and K.G. Karthikeyan, *Environ. Sci. Technol.*, **39**, 2660 (2005).
3. Z. Qiang, J.J. Macauley, M.R. Mormile, R. Surampalli and C.D. Adams, *J. Agric. Food Chem.*, **54**, 8144 (2006).
4. P. Kulshrestha, R.F. Giese and D.S. Aga, *Environ. Sci. Technol.*, **38**, 4097 (2004).
5. G. Hamscher, S. Sczesny, H. Hoper and H. Nau, *Anal. Chem.*, **74**, 1509 (2002).
6. N.S. Simon, *Environ. Sci. Technol.*, **39**, 3480 (2005).
7. K.J. Rockne, G.L. Taghon and D.S. Kosson, *Chemosphere*, **41**, 1125 (2000).
8. Y. Chun, G.Y. Sheng, C.T. Chiou and B.S. Xing, *Environ. Sci. Technol.*, **38**, 4649 (2004).
9. S. Kwon and J.J. Pignatello, *Environ. Sci. Technol.*, **39**, 7932 (2005).
10. J.J. Pignatello, S. Kwon and Y.F. Lu, *Environ. Sci. Technol.*, **40**, 7757 (2006).
11. H.P. Boehm, *Adv. Catal.*, **16**, 179 (1966).
12. M.V. Lopez-Ramon, F. Stoeckli, C. Moreno-Castilla and F. Carrasco-Marin, *Carbon*, **37**, 1215 (1999).
13. F. Rouquerol, J. Rouquerol and K. Sing, *Adsorption by Powders and Porous Solids*, Academic Press: London (1999).
14. A. Finizio, M. Vighi and D. Sandroni, *Chemosphere*, **34**, 131 (1997).
15. R.A. Figueroa and A.A. MacKay, *Environ. Sci. Technol.*, **39**, 6664 (2005).
16. P.A. Blackwell, H.C.H. Lutzhoft, H.P. Ma, B. Halling-Sorensen, A.B.A. Boxall and P. Kay, *J. Chromatogr. A*, **1045**, 111 (2004).
17. D.L. Sparks, *Environmental Soil Chemistry*, Academic Press: San Diego, edn. 2 (2003).
18. B.B. Sithole and R.D. Guy, *Water, Air, Soil Pollut.*, **32**, 315 (1987).