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Adsorption Performance of Tetracycline on Yellow River Sediment

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Pharmaceuticals and personal care products have aroused increasing concern throughout the world due to their wide occurrence in natural waters and direct threat to human beings. In this study, tetracycline , one of the pharmaceuticals and personal care products was selected as a target pollutant to check its adsorption behavior on Yellow river sediment. This will help understanding about its transportation in Yellow river and potential risk for human beings. Adsorption kinetics and isotherm tests were conducted for the sediments collected from Huayuankou (Zhengzhou city, China), the middle reach of Yellow river. Effect of solution pH and natural organic matters were also investigated. It was observed that solution pH had a dramatic influence on tetracycline adsorption while the maximal uptake of tetracycline achieved 40.8 mg/g at equilibrium pH 5. Elovich kinetic model could describe the adsorption kinetics better than pseudo-first-order and pseudo-second-order models. The isotherm data were well fitted by Langmuir, Freundlich, Toth and Redlich-Peterson models. The coexisting natural organic matter (humic acid) significantly inhibited the uptake of tetracycline onto Yellow river sediment.

Keywords: Adsorption, Yellow river sediment, Tetracycline, Kinetics, Isotherm.

INTRODUCTION

In the past decades, pharmaceuticals and personal care products have received increasing attention due to their likely occurrence in natural waters such as rivers, lakes, streams and even ground waters[1]. Some pharmaceuticals and personal care products may cause ecological harm including endocrine disruption and development of antimicrobial resistance. Their frequent exposure to environmental organisms and human beings will result in detrimental health effects that are actually irreversible[2]. Nevertheless, the health effects of small amounts of these chemicals (ng–μg/L) on humans over a lifetime of exposure are still unknown at this time. Consequently, there is a great need to discern and eliminate the adverse effect of pharmaceuticals and personal care products on humans and environment.

Tetracyclines are the second most widely used antimicrobial chemicals in the world, which are widely applied in human therapy and livestock industry[3]. An investigation on the fate of three antibiotics from the sulfonamide, tetracycline and macrolide groups was conducted in two consecutive years after pig slurry was applied to a field in arable production. The results reported a tetracycline content of 1691 μg/kg in soils[4]. This demonstrates the probable existence of tetracycline to a considerable extent in the soils. Meanwhile, as tetracycline molecules are usually neutral or negatively charged in environmental water, conventional water treatment techniques such as sand filtration, sedimentation, flocculation and coagulation are not so efficient for tetracycline removal as expected[5]. As a result, the transportation, transformation and removal of pharmaceuticals and personal care products become one of the fundamental environmental issues.

As tetracycline is expected to be ubiquitous in natural waters, its adsorption performance is fundamental for the predication of its natural content. A variety of natural minerals such as montmorillonite[6], palygorskite[7] and swelling clay minerals[8] have been selected for the adsorption of tetracycline. The adsorption performance varied according to the different natural minerals involved. Actually, compared with these natural minerals, the sediments from rivers and lakes play a more important role as they have a more direct access to tetracycline. In this study, the adsorption performance of tetracycline was investigated onto Yellow river sediment from Huayuankou of Zhengzhou City (Henan Province, China). Yellow river currently provides most of the source water for drinking water production throughout the city. Study on tetracycline adsorption kinetics and isotherm were conducted. Effect of solution pH and natural organic matter were investigated. These could help to evaluate the health risk of tetracycline.

EXPERIMENTAL

Tetracycline was purchased from Hefei Bomei Biological Science and Technology Co., Ltd (Anhui Province, China) and used without further purification. Other chemicals used were of analytical grade. Yellow river sediment was collected from Huayuankou of Zhengzhou City (Henan Province, China). Deionized water was used to prepare all solutions.

Adsorption of tetracycline on yellow river sediment: A stock tetracycline solution of 500 mg/L was prepared by dissolving tetracycline in DI water. It was stored in a refrigerator at 277 K and used within three days. The stock solution was diluted with DI water to prepare desired tetracycline solutions for the subsequent batch experiments.

Adsorptive removal of tetracycline was determined by batch experiments in conical flasks. For kinetic study, 200 mg of Yellow river sediment was added into 1000 mL tetracycline solution of 10 mg/L. In the tests of adsorption isotherm, pH and natural organic matter effect, 10 mg of the sediment was added into 50 mL tetracycline solution of 10 mg/L. These mixtures were shaked at 145 rpm for 24 h. The temperature was kept at a constant temperature 298 K unless otherwise stated. The solution pH adjustment was conducted by adding HNO_3 or NaOH solution. All the solution pH values were maintained at neutral pH except for the pH effect study.

Analyses: Samples were collected and filtered through a 0.45 μm membrane before analyzing. The tetracycline concentration of the samples was determined by measuring the absorbance at a fixed wavelength (360 nm) by an UVmini-1240 spectrophotometer (Shimadzu)[9].

RESULTS AND DISCUSSION

Effect of solution pH on tetracycline adsorption: The effect of solution pH was investigated for tetracycline adsorption on Yellow river sediment from pH 3 to 11 (Fig. 1). It demonstrates that tetracycline adsorption was strongly dependent on solution pH. Under acidic conditions, the adsorption of tetracycline increased dramatically with an increase in solution pH, while the tetracycline uptake decreased gradually with increasing pH under alkaline conditions. The maximal uptake of tetracycline achieved 40.8 mg/g at equilibrium pH 5. Similar tetracycline adsorption performance in a wide pH range was also observed by other study[10].

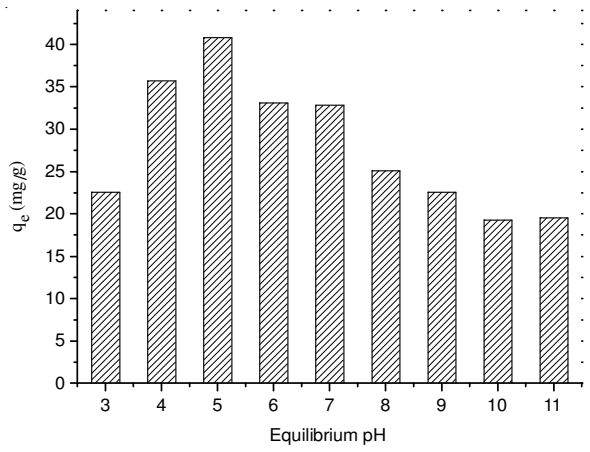

Fig. 1. Effect of solution pH on tetracycline adsorption on Yellow river sediment

Yellow river sediment mainly contains silicon and aluminium oxides, which could make the sediment more positively charged in acidic conditions while more negatively charged in alkaline conditions as illustrated by the following equations:

$$M\text{-}OH + H^+(aq) = M\text{-}OH_2^+ \text{ (acidic condition)} \quad (1)$$

$$M\text{-}OH = M\text{-}O^- + H^+(aq) \text{ (alkaline condition)} \quad (2)$$

On the other hand, tetracycline (H_2L) is an amphoteric compound with pKa values at 3.3, 7.7 and 9.7[11]. Its predominant species are expected to be cation (H_2L^+) at pH < 3.3, zwitterions (H_2L^0) at 3.3 < pH < 7.7 and negatively charged anions (HL^-, L^{2-}) at pH > 7.7. Under alkaline conditions, both tetracycline and the sediment are negatively charged and the repulsive force between them are expected to increase with increasing pH, which results in a decrease in tetracycline uptake. Under acidic conditions, a decrease in tetracycline uptake could be similarly expected to drop with decreasing solution pH. By contrast, at near neutral pH conditions, tetracycline molecules are zwitterions and their negative charge density increases gradually with the increasing pH. As a result, the repulsive force between tetracycline and the sediment is expected to be the weakest and tetracycline uptake could be the highest at near neutral pH conditions.

Adsorption kinetics: The results of kinetic study were fitted to pseudo-first-order, pseudo-second-order and Elovich models, while Elovich model fitted the data best at pH 7 (R^2 = 0.959), as illustrated in Fig. 2. The pseudo-first-order kinetic model can be expressed as[12]:

$$q_1 = q_e(1-e^{-k_1 t}) \quad (3)$$

The pseudo-second-order kinetic model can be expressed as[13]:

$$q_t = \frac{k_2 q_e^{\,2} t}{(1 + k_2 q_e t)} \quad (4)$$

where q_e and q_t are the adsorption capacities (mg/g) of the adsorbent at equilibrium and at time t (min), respectively; and k_1 (min^{-1}) and k_2 (g mg/min) are the related adsorption rate constants for pseudo-first-order and pseudo-second-order model, respectively.

The Elovich model can be written as[14]:

$$q_t = a \ln(t) + b \quad (5)$$

where a (g mg/min) and b (mg/g) are constants.

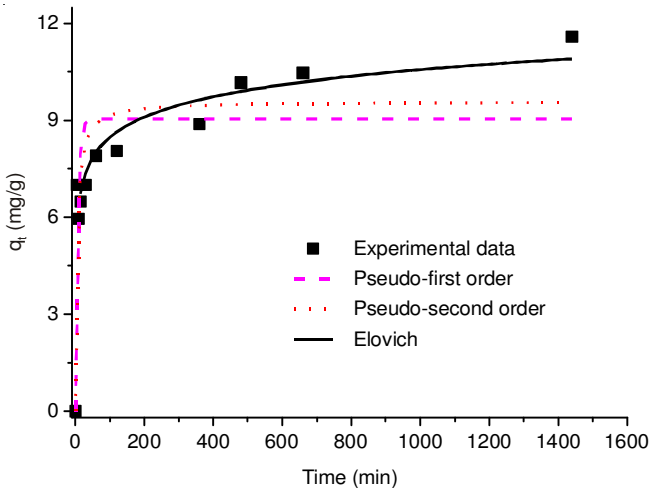

Fig. 2. Tetracycline adsorption kinetics on Yellow river sediment at pH 7

TABLE-1
ADSORPTION KINETIC PARAMETERS FOR TETRACYCLINE ADSORPTION ON YELLOW RIVER SEDIMENT AT DIFFERENT pH CONDITIONS

	pH = 5	pH = 7	pH = 9
Pseudo-first-order model			
k_1 (min^{-1})	0.10743	0.1453	0.09071
q_e (mg/g)	11.8409	9.045	8.947
R^2	0.859	0.713	0.913
Pseudo-second-order model			
k_2 (g mg/min)	12.3×10^{-3}	22.0×10^{-3}	13.2×10^{-3}
q_e (mg/g)	12.545	9.587	9.498
R^2	0.944	0.824	0.955
Elovich model			
b (mg/g)	5.012	4.286	3.084
a (g mg/min)	1.234	0.909	1.039
R^2	0.982	0.959	0.939

The adsorption kinetics was also investigated at pH 5 and 9 and the kinetic parameters for the three kinetic models are presented in Table-1. Obviously, Elovich model could describe the adsorption kinetics better than pseudo-first-order and pseudo-second-order models from the values of coefficient (R^2). Meanwhile, the highest adsorption capacity was observed at pH 5 while the uptake of tetracycline decreased from pH 5 to 9, which is consistent with the aforementioned result.

Adsorption isotherms: Adsorption of tetracycline is simulated by Langmuir, Freundlich, Toth and Redlich-Peterson models. The four isotherm models are listed below:

Langmuir isotherm[15]:

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (6)$$

where q_e is the amount of tetracycline adsorbed onto La-modified diatomite (mg/g), C_e is the equilibrium concentration (mg/L), q_{max} is the maximum adsorption capacity of the sorbent (mg/g) and k_L is the equilibrium adsorption constant related to the affinity of binding sites (L/mg).

Freundlich isotherm[16]:

$$q_e = k_F C_e^{\frac{1}{n}} \quad (7)$$

where k_F is roughly an indicator of the adsorption capacity and n is the heterogeneity factor, which has a lower value for more heterogeneous surfaces.

Toth isotherm is derived from the potential theory and is applicable to heterogeneous adsorption. Its expression is given as eqn.8[17]:

$$q_e = \frac{q_m C_e}{(K_{Th} + C_e^t)^{\frac{1}{t}}} \quad (8)$$

where K_{Th} [$(mg/L)^t$] is the Toth isotherm constant and t is the dimensionless constant, usually less than unity. The parameters K_{Th} and t are specific for adsorbate-adsorbent systems. The more the parameter t is away from unity, the more heterogeneous is the system.

The three-parameter Redlich-Peterson isotherm equation which has a linear dependence on concentration in the numerator and an exponential function in the denominator has been proposed to improve the fit by the Langmuir or Freundlich equation and is given by eqn. 9[18]:

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (9)$$

Fig. 3 illustrates the experimental points and non-linear fitted curves from isotherms for tetracycline adsorption on Yellow river sediment at 298 K. It is observed that the equilibrium data were fitted to four isotherm equations (Langmuir, Freundlich, Toth and Redlich-Peterson expressions) with R^2 values of 0.990, 0.982, 0.990 and 0.990, respectively. By comparing between the experimental data and fitted curves, it was found that the four isotherm models well predict the equilibrium adsorption behavior. As a comparison, the experimental data at 288 and 308 K were also simulated by the above-mentioned isotherms and the parameters are listed in Table-2. The data also indicates that the four isotherm models well described the tetracycline adsorption performance.

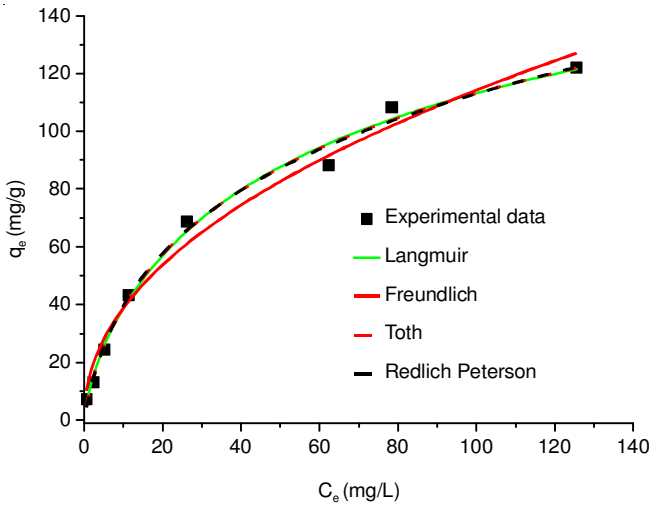

Fig. 3. Experimental points and non-linear fitted curves from isotherms for tetracycline adsorption on Yellow river sediment at 298 K

Effect of natural organic matter on tetracycline adsorption: Since natural organic matter (NOM) may have a high tendency to be adsorbed onto the surface of various materials, it might modify the properties of Yellow river sediment and block the adsorption sites[19-21]. Meanwhile, natural organic matter is ubiquitous in surface waters and its presence could interfere tetracycline adsorption to some extent. The effect of

TABLE-2
ISOTHERM PARAMETERS FOR TC ADSORPTION ON YELLOW RIVER SEDIMENT

	288 K	298 K	308 K
Langmuir			
q_{max}(mg/g)	153.194	205.351	311.949
k_L(L/mg)	0.0183	0.0440	0.0375
R^2	0.987	0.990	0.998
Freundlich			
k_F(mg/g)	6.4599	13.201	17.604
n	0.5670	0.4686	0.5059
R^2	0.977	0.982	0.982
Toth			
K_{Th}	55.521	3.9114	5.405
q_{max}(mg/g)	143.398	288.177	418.341
t	0.9819	0.4118	0.5004
R^2	0.986	0.990	0.990
Redlich-pererson			
A	2.3735	8.7579	11.261
B	0.0167	0.2173	0.1678
g	0.9998	0.7460	0.7526
R^2	0.986	0.990	0.991

natural organic matter, represented by humic acid, was investigated and the result is summarized in Fig. 4. It is observed that tetracycline removal efficiency decreased from 74.2 % without humic acid to 39.2 % in the presence of 0.001 M of humic acid. This demonstrates that the existence of humic acid significantly inhibited the uptake of tetracycline onto Yellow river sediment.

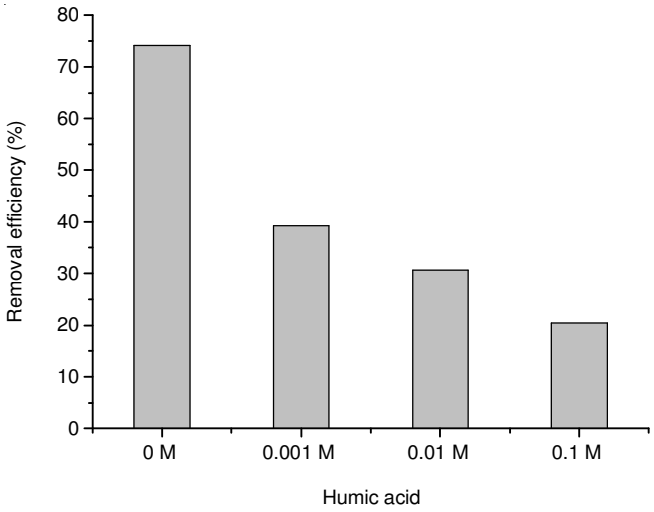

Fig. 4. Effect of natural organic matter on tetracycline adsorption

Conclusion

Tetracycline, one of the pharmaceuticals and personal care products detected in natural waters, was selected as a target pollutant to study its adsorption performance on Yellow river sediment. Adsorption of tetracycline was observed to be highly dependent on solution pH and the uptake of tetracycline at neutral pH condition was comparatively higher than acidic and alkaline conditions. Elovich kinetic model described the adsorption kinetics better than pseudo-first-order and pseudo-second-order models. The isotherm data were well fitted by Langmuir, Freundlich, Toth and Redlich-Peterson models. The coexisting natural organic matter significantly inhibited the uptake of tetracycline onto Yellow river sediment. This help understanding of the transportation of tetracycline in Yellow river and its health risk on humans.

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