Applied Surface Science xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Effect of temperature on the adsorption of sulfanilamide onto aluminum oxide and its molecular dynamics simulations

Ying-xue Ji [a], Feng-he Wang [a,*], Lun-chao Duan [a], Fan Zhang [a], Xue-dong Gong [b]

[a] Department of Environmental Science and Engineering, Nanjing Normal University, Nanjing 210023, PR China
[b] Department of Chemistry, Nanjing University of Science and Technology, Nanjing 210094, PR China

ARTICLE INFO

Article history:
Received 15 May 2013
Received in revised form 17 August 2013
Accepted 17 August 2013
Available online xxx

Keywords:
Sulfanilamide (SA)
Aluminum oxide
Adsorption
Temperature
Molecular dynamics simulation

ABSTRACT

The effect of temperature on the adsorption of sulfanilamide (SA) onto aluminum oxide was researched through batch adsorption experiments, and was then simulated using the molecular dynamics (MD) method. The results show that SA can be adsorbed effectively by the adsorbent of aluminum oxide due to their interactions between SA molecule and the surface of aluminum oxide crystal, and temperature is a key factor which influences the adsorption efficiency obviously. The removal ratio of SA at 298 K is the highest among the selected temperatures (293 K, 298 K, 303 K). MD simulations revealed the interactions between SA molecules and (0 1 2) surface of aluminum oxide crystal at molecular level. The SA molecule has clung to the (0 1 2) face of aluminum oxide crystal, and its structure is deformed during its combining process with the surface. Both binding energies (E_b) and deformation energies (ΔE_{deform}) in the SA-aluminum oxide system follow the same order as: SA-Al_2O_3 (298 K) > SA-Al_2O_3 (293 K) > SA-Al_2O_3 (303 K). Their deformation energies are far less than their non-bonding energies. Analysis of radial distribution functions (RDFs) indicates that SA can be adsorbed effectively by aluminum oxide crystal mainly through non-bond interactions. The simulation results agree well with the experimental results, which verify the rationality and reliability of the MD simulation. The further MD simulations provide theoretically optimal temperature (301 K) for the adsorption of SA onto aluminum oxide. The molecular dynamics simulation will be useful for better understanding the adsorption mechanism of antibiotics onto metal oxides, which will also be helpful for optimizing experimental conditions to improve the adsorptive removal efficiency of antibiotics.

1. Introduction

Various kinds of antibiotics have been used for the therapy of infectious diseases in human and livestock owing to their great therapeutic values for almost one hundred years [1]. Sulfonamides (SAs) are among those heavily used and widely detected antibiotics. Once applied to animals or humans, antibiotics are often poorly absorbed by living organisms, and most of them are excreted in forms of metabolites or parent chemicals [2,3]. When released to the soil, antibiotics may interact with different soil components, and/or be washed off into surface waters or be leached to ground waters, thus threat environmental and human health [3,4]. Even the chronic exposure to antibiotics can also exert pressure on the development of antibiotic resistant bacteria, and then minimize the effectiveness and therapeutic value of antibiotics [5–8]. Its environmental fate as well as the removal mechanisms, methods and conditions therefore deserves special attention.

Adsorption of antibiotics onto solid particles is the key process controlling their leaching and transport in environment [4]. Consequently, many studies have focused on the interactions between antibiotics and soils or soil components. Aluminum is the most abundant metallic element in the Earth's crust. Both the geographical features such as frequent heavy rains and high temperature in the humid tropics or human activity enhances the weathering process, which result in high aluminum oxide content in the soils [7,9]. Adsorption of antibiotics onto aluminum oxides may play an important role in controlling the mobility and spread of antibiotic contaminants such as sulfonamides (SAs), tetracyclines (TCs) and fluoroquinolones (FLQs). Recent studies have reported that strong interaction exists between TCs and aluminum oxide via both adsorption and transformation [10,11]. Studies on the adsorptive removal of SAs by clay minerals [12], the high-silica zeolite [13], multiwalled carbon nanotubes [14] or even soils [15] have been documented previously. However, investigations over the adsorption of SA onto aluminum oxides and the effect of temperature on the adsorption have not been reported yet. Comprehensive investigations of both experimental and theoretical aspects are thus needed to better understand its mechanism.

* Corresponding author. Tel.: +86 25 85481126; fax: +86 25 85481126.
E-mail address: wangfenghe@njnu.edu.cn (F.-h. Wang).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.08.067

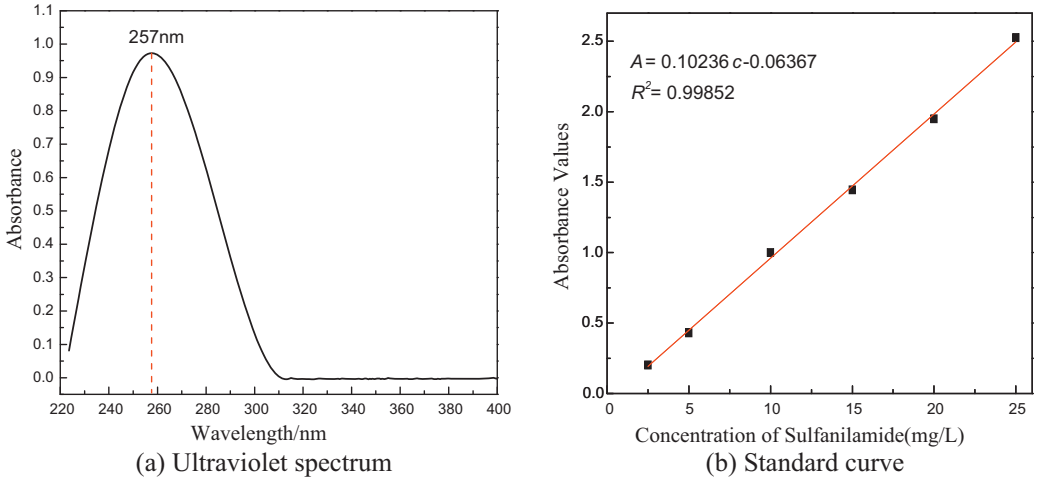

Fig. 1. Ultraviolet spectrum (a) and standard curve (b) for SA.

In this work, aluminum oxide was used as the adsorbent to remove the antibiotic SA from aqueous solutions, and batch adsorption experiments were carried out under various temperatures. Molecular dynamics (MD) simulations of the interactions between SA molecule and aluminum oxide crystal were performed, and the adsorption mechanism was dissected at molecular level using the COMPASS force field [16] and Discover module in Materials Studio 4.2 program [17,18]. Based on the reliability of the MD simulations, the program was sequentially used to explore the theoretically optimal temperature for the adsorption of SA onto aluminum oxide. Our study provides a new approach to elucidate the adsorption mechanism of antibiotics onto metal oxides, and to determine the optimal condition for improving the adsorptive removal efficiency.

2. Materials and methods

2.1. Materials

For the adsorption experiments, all chemicals were obtained from Sinopharm Chemical Reagent Co., Ltd, China. SA was at 99% of purity, and was used without further purification. The aluminum oxide used in this study was Al_2O_3(s) (powder) at analytical reagent grade. The reported surface area and site density of Al_2O_3(s) were 90.1 m^2/g and 3.81 sites/nm^2, respectively [19].

2.2. Batch adsorption experiment method

The initial and residual concentrations of SA in the aqueous samples were measured using a UV-vis spectrophotometer (UV-2550, Shimadzu, Japan). The absorbance values of SA samples were read at the wave length of 257 nm (shown in Fig. 1(a)). Standard curves were gained by measuring the absorbance values of synthetic standard solutions. All standard solutions were gained by diluting the stock solutions with distilled water. Concentration of the SA stock solution was 25 mg/L. The calibration plot of absorbance value versus concentration for SA showed a linear variation within its experimental concentration range (2.5–25 mg/L). Details are summarized in Fig. 1(b). The correlation coefficient (R^2) was greater than 0.99, indicating that the plot showed an ideal linear variation.

Aluminum oxide was selected as adsorbent for SA in the aqueous solution. Various amounts of aluminum oxide (4.0, 40, and 80 mg) were added into 250 mL stopper conical flasks containing 40 mL of the test solution (10 mg/L for SA). To be consistent with the MD simulations, batch adsorption experiments were carried out on a temperature-controlled orbital shaker (ZD-85A, Jintan Ronghua Instrument Manufacture Co., Ltd.) at 200 rpm under temperatures of 293 K, 298 K and 303 K, respectively. The time required for reaching the equilibrium condition was estimated by drawing samples and analyzing the residual concentrations of SA at the regular time interval (20 min) till values to be constant. Samples were collected with a disposable syringe and filtrated through a 0.45 μm disposable membrane filter. The concentration was calculated from the calibration plot above after measuring its corresponding absorbance value. The removal ratio of SA (r) from the solution was calculated with the following equation.

$$r = \frac{c_0 - c_t}{c_0} \times 100\% \quad (1)$$

In which c_0 is the initial antibiotic concentration (mg/L); c_t is the residual antibiotic concentration (mg/L).

2.3. MD simulation method

2.3.1. Model construction

The main growth face of aluminum oxide crystal, namely (0 1 2) face, was chosen in this study, and the simulated super cell of aluminum oxide crystal was built and extended from 2D to 3D periodic super cell, which was 14.277 Å × 15.385 Å × 9.735 Å in size. The total number of atoms was 252 (O = 162, Al = 90). Three-dimensional molecular structure of SA was built and optimized to the most stable configuration using molecular mechanics (MM) method and COMPASS force field [20]. Fig. 2 gives the 2D and 3D structures of SA conformation.

To investigate the interactions between SA molecule and the (0 1 2) face of aluminum oxide crystal, one molecular configuration of SA was placed on the aluminum oxide (0 1 2) face to construct the layer model. To eliminate the effect of periodic boundary condition on the system, the vacuum thickness in the system was set to 10 Å. Then the MM method was used to optimize the system to produce the initial configuration of the MD simulation, and the MD simulation was carried out with the Discover module. Considering the actual reaction process that there only existed interactions between atoms on the above two layers of aluminum oxide and the SA molecule, only these atoms were unconstrained while the other atoms in aluminum oxide were fixed during the simulation. The layer model is shown in Fig. 3(a).

2.3.2. Simulation method

All MD simulations were carried out in the NVT ensemble [21,22]. To investigate the effect of temperature on the adsorption process in the system, the temperature was set at 293 K, 298 K

Please cite this article in press as: Y.-x. Ji, et al., Effect of temperature on the adsorption of sulfanilamide onto aluminum oxide and its molecular dynamics simulations, Appl. Surf. Sci. (2013), http://dx.doi.org/10.1016/j.apsusc.2013.08.067