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CHARACTERIZATION OF NATURAL ZEOLITE FOR ADSORPTIVE REMOVAL OF ANTIBIOTICS FROM AQUEOUS SOLUTION

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ABSTRACT

The persistent existence of antibiotics in sewage wastewater treatment plants in recent years has emerged as a serious concern. In this study, natural zeolite (NZ02) obtained from China was employed as an adsorbent to remove tetracycline (TC) from aqueous solution. The characterization results show that the NZ02 consists of quartz, clinoptilolite-Na and heulandite having the CEC of 62.18cmol/kg and the surface area of 36.646m^2/g. Adsorption results show that the maximum adsorption capacity of TC on NZ02 was 19.30mg/g and the equilibrium data followed theLangmuir adsorption isotherm model.

1. INTRODUCTION

In recent years, there are other emerging contaminants in wastewater such as endocrine-disruptive and pharmaceutical compounds (Liu et al., 2009). The fact is that the rise of antibiotics in wastewater due to its' extensive use in veterinary and healthcare medicine has stirred up the awareness starting from scientists and researchers to public (Rizzo et al., 2013). Traces of antibiotics had been detected at several regions at all parts of the world (Cha et al., 2006; Dinh et al., 2011; Zou et al., 2011). Even though only a minute amount of antibiotics present in wastewater, it would lead to the spread of resistant microbes (Akiyama and Savin, 2010).

A various kinds of technologies have been used to remove antibiotics in water including reverse osmosis, nanofiltration, chlorination, ozonation, ultraviolet disinfection and adsorption by activated carbon. The usage of reverse osmosis and nanofiltration has been increasing but the membranes are prone to fouling and malfunction if they are in contact with oxidizing agent (Homem and Santos, 2011). Chlorination is an alternative way to treat antibiotics containing wastewater but there is a significant concern that the chlorinated byproducts might be formed which might be more dangerous than the antibiotics (von Gunten et al., 2006).Similarly, ozonation technology does not seem to be practical due to difficulty in pH control and the high possibility of the formation of biologically active chemical components (Ding et al., 2012; Homem and Santos, 2011).On the other hand, ultraviolet disinfection is less effective in removing antibiotics and requires more energy than ozonation(Michael et al., 2013).

Adsorption process is commonly used industrially to remove organic pollutants. The tetracycline removal capacity of 65.471 mg/g by activated carbon was reported (Rivera-Utrilla et al., 2013). Despite of the excellent performance of activated carbon, it is costly and difficult to be regenerated (Crisafully et al., 2008).Thus, natural zeolite is a potential to be an alternative for activated carbon to remove antibiotics in aqueous solution via adsorption process. In contrast to activated carbon, natural zeolite exists abundantly in nature and is a low-cost material (Wang and Peng, 2010). In addition, it could be easily modified to widen its' adsorption range (Rakić et al., 2013). Considering the effectiveness of natural zeolite in removing organic micropollutants from the environment, we proposed to employ natural zeolite to serve as an adsorbent in the removal of antibiotics from aqueous solution (de Ridder et al., 2012; Grieco and Ramarao, 2013).

2. MATERIALS AND METHODS

2.1 Chemicals

Tetracycline (Calbiochem, EMD Chemicals) was selected as the target antibiotics as it is one of the most commonly used antibiotics in the world(Wan et al., 2010).

2.2 Natural Zeolites

Natural zeolite (NZ02) obtained from China having particle size of 200-mesh sieve was used in this study. Before use, the NZ02was washed with double distilled water and dried at 105°C for 24 hours to remove any impurities. It was later kept dried in a desiccator.

2.3Characterization of natural zeolites

Fourier transform infrared spectroscopy (FTIR)(Model Nicolet IS5, Thermo Fisher Scientific, USA) was used to analyze the functional groups inherited by the NZ02. The cation exchange capacity (CEC) of the NZ02 was measured based on the British Standard (1995). The surface morphology of the NZ02 was studied by scanning electron microscopy (SEM) (S4 800/FEI-quanta-200F) and the BET analysis was done by conducting nitrogen adsorption/desorption (NAD) analysis carried out at 77.3K (Micromeritics model ASAP 2000, USA). The mineralogical analysis was done by powder X-ray diffraction (XRD) analyzer (model Bruker-D8 Advance) using Ni filtered Cu-Kα radiation (40 kv, 40 mA). The elemental composition of NZ02 was determined by X-ray fluorescent (XRF) spectrometer (JEOL model JSX-3400R, Japan).

2.4TC adsorption experiments

The TC adsorption experiments were conducted in batch adsorption experiment at the temperature of 303K. First, 50mL of TC solutions with known concentration was poured into capped 125mL conical flask followed by introducing 50mg of NZ02and then shaken in a shaker at the constant speed of 200rpm until equilibrium state was reached. Due to the fact that the TC is light sensitive, all the TC solutions were sealed with aluminum foil.

The adsorption capacity of the TC, q_e (mg/g) was computed using Eq. 1,

$$q_e = \frac{C_i - C_e}{M} xV \qquad (1)$$

where C_i and C_e is the initial and equilibrium concentration of TC (ppm), respectively. M is the mass of NZ02 (g) and V is the volume of TC solution (L).

The adsorption kinetic experiments were conducted by using 250mL, 50ppm of TC with 250mg of NZ02. A portion of the samples were taken out to be analyzed at selected time intervals.

Adsorption equilibrium experiments were performed with initial concentrations of TC ranging from 1 to 50ppm. The adsorption was left for 2 hours which was proved to be sufficient for the process to reach equilibrium. In order to study the influence of pH on the adsorption performance, the pH of the solutions was varied by using either 0.1M HCl or NaOH solution.

2.5Analysis

Nylon syringe filter (0.80µm) was used to separate the NZ02 particle from the solution before the remaining TC concentration determination using a UV-VIS spectrophotometer (Perkin Elmer, Lambda 35) spectrophotometer at the wavelength of 366nm.

3. RESULTS AND DISCUSSION

3.1Characterization of natural zeolites

The FTIR spectrum of NZ02was recorded in the wavelength between 4000 and 500 cm^{-1}as shown in Fig. 1. The band at 3601cm^{-1} is due to the isolated OH^- stretching, the band at 1631 cm^{-1} is assigned to OH^- bending, the band at 1006 cm^{-1} is due to the Ti-O stretching vibration. The band at 792 cm^{-1} is assigned to the exchangeable cations. The CEC determined by the exchange between Ba^{2+} and Mg^{2+} was 62.18cmol/kg.

The SEM image of the NZ02 is illustrated in Fig. 2. The material consists of spherical and rough particles which is suitable to be utilized as adsorbents. The BET surface area, pore volume and average pore diameter of the NZ02 were 36.646m^2/g, 0.044cm^3/g and 4.754nm, respectively. Based on Fig. 3, the results of XRD reveal that the main minerals of NZ02 consist of quartz, clinoptilolite-Na and heulandite. In addition, the results obtained from XRF are arrayed in Table 1 which shows that the main oxides of NZ02 are silica followed by aluminum oxide.

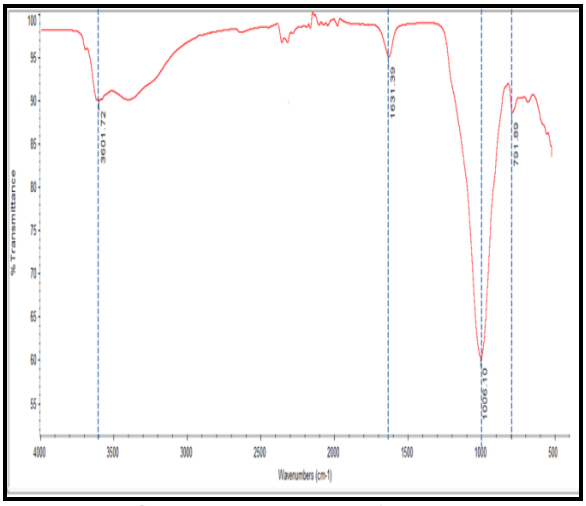

Fig. 1 FTIR spectra of NZ02.

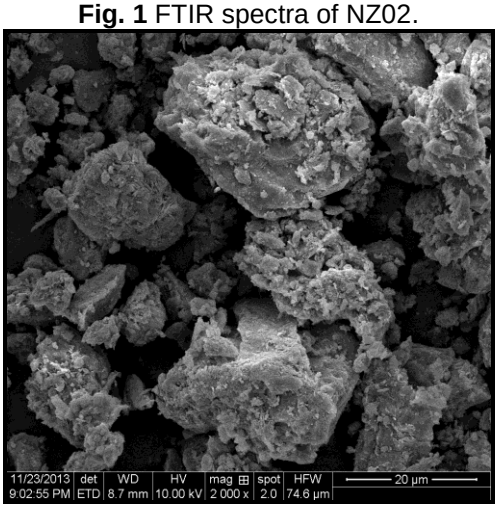

Fig. 2 SEM image of NZ02.

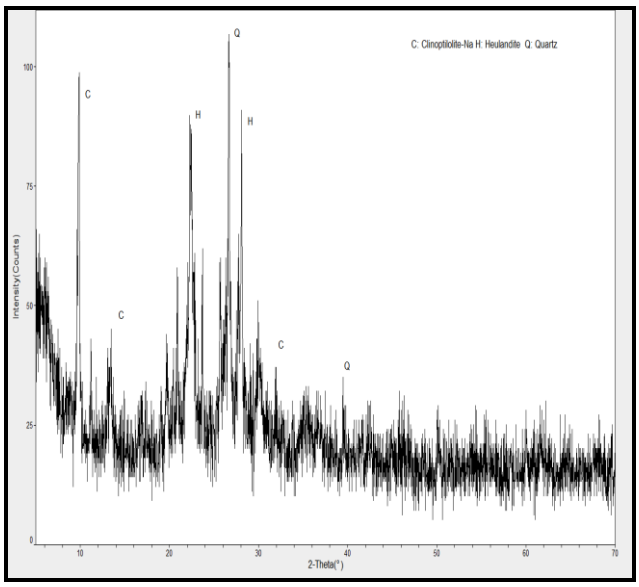

Fig. 3 XRD patterns of NZ02.

Table 1 Oxide compositions of NZ02.

Chemical	wt. %
Al_2O_3	30.57
SiO_2	52.41
K_2O	3.98
CaO	5.33
Fe_2O_3	5.90
TiO_2	0.53
P_2O_3	1.26

3.2 Adsorption isotherm and equilibrium time

The adsorption isotherm was determined to measure the adsorption capacity of the zeolite. The results which are demonstrated in Fig. 4 show that the Langmuir model could fit the experimental data better than the Freundlich model. Therefore, the NZ02 has homogeneous surface with uniform distribution of adsorption sites. The time taken for the adsorption process to reach equilibrium was 2 hours as indicated in Fig. 5.

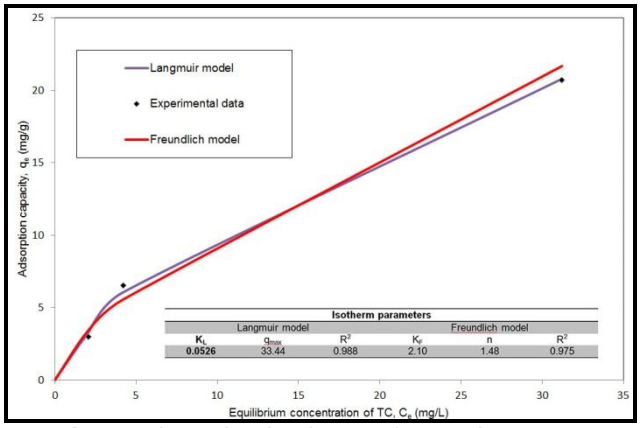

Fig. 4 Adsorption isotherm of TC using NZ02.

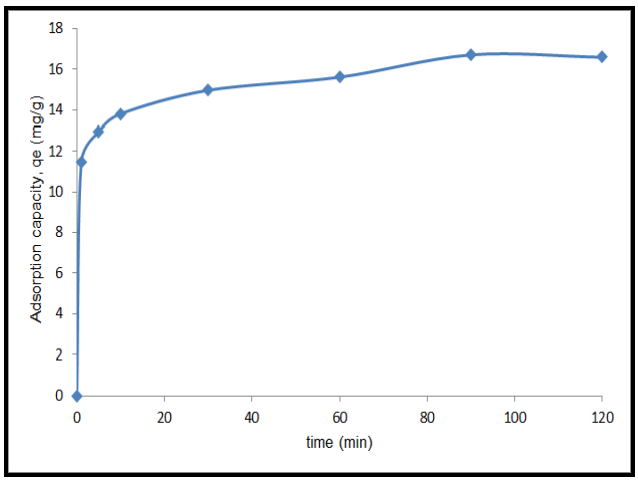

Fig. 5 Equilibrium time of TC adsorbed onto NZ02.

3.3The effect of pH

The adsorption capacity of TC at pH 5, 7, 8 and 10 is illustrated in Fig. 6.The maximum adsorption capacity of TC occurred at pH between 7 and 8 which was about 19mg/g.

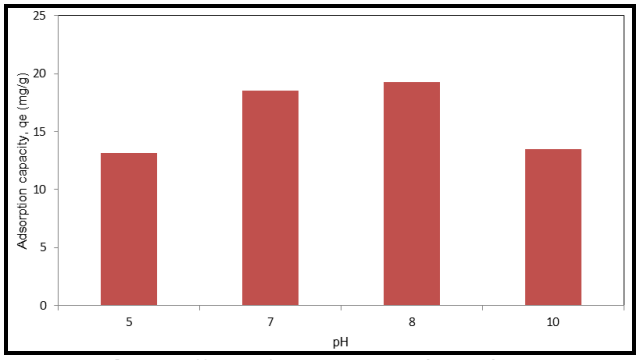

Fig. 6 Effect of pH on TC adsorption.

4. CONCLUSIONS

The characterization results of the natural zeolite (NZ02) shows that it has the potential to remove TC from aqueous solution in which the parameters such as pH, initial TC concentration and contact time affecting the removal performance. The optimum pH was observed between pH 7 and 8 having adsorption capacity of about 19mg/g, equilibrium time of 2 hours and the equilibrium data followed the Langmuir isotherm model.

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