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Highly adsorptive removal of oxytetracycline in water environment using polyanion modified alumina nanoparticles

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ABSTRACT

In this study, adsorptive removal of an antibiotic oxytetracycline (OTC) using polyanion poly(2-acrylamide-2-methylpropane sulfonic acid), PAMPs modified α-Al_2O_3 nanoparticles (PAMNA) was investigated. Surface modification of α-Al_2O_3 nanoparticles by PAMPs enhanced the removal efficiency of OTC significantly from 35.5 to 90.7 %. The optimum conditions for adsorptive removal of OTC using PAMNA were found to be pH 4, contact time 120 min and adsorbent dosage 20 mg/mL. Under selected conditions, the removal efficiency of OTC using PAMNA was greater than 90 % while the maximum adsorption capacity reached 140.2 mg/g. After three regenerations, the removal efficiencies of OTC were still higher than 75 %. The results of adsorption isotherms of OTC on PAMNA and the surface charge change of PAMNA indicate that both electrostatic and non-electrostatic interactions control OTC adsorption on PAMNA.

Introduction

Contamination of water is a severe form of pollution that can be difficult to eliminate [1]. An antibiotic is a type of pharmaceutical compound that is commonly used in modern medical field and veterinary industry. Oxytetracycline (OTC) is one of the most stable antibiotics that belong to tetracycline family. The OTC is widely used in agricultural activities due to the low cost and high make broad spectra against bacteria [2]. The OTC in sewage sludge and wastewater plants was actually rather high [3]. In addition, the presence of many organics and pharmaceutical residues in the natural environment can influence the OTC removal from aqueous solution. Therefore, the removal of OTC in water environment by different techniques attracted intense studies in the field of environmental research [4]. There are many techniques for removal of antibiotics such as advanced oxidation [5], and photocatalysis [6], membrane bioreactor [7] and adsorption [8-10]. It is evident that adsorption is an effective method and preferable for developing countries by using low cost adsorbents.

Alumina (Al_2O_3) is a popular adsorbent that is easy to collect and manufacture from natural minerals [4]. The alpha alumina (α-Al_2O_3) is the most stable form among various alumina phase. However, α-Al_2O_3 with small specific surface area and low charge density that is low potential for an antibiotic removal when used directly. To enhance the removal efficiency, the α-Al_2O_3 surface

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needs a modification with environmentally friendly chemicals such as negatively charged polyanion. The poly(2-acrylamide-2-methylpropane sulfonic acid) (PAMPs) is a strong polyanion that is applicable for modifying α-Al_2O_3 surface [11]. In the present work, for the first time, we investigate adsorption of OTC using PAMPs modified α-Al_2O_3 for purpose of water treatment.

Experimental

Materials

The α-Al_2O_3 nanoparticles was fabricated by the solvo-thermal technique by following the procedure in our previously published paper [12] while polyanion PAMPs was synthesized according to the research [11]. Oxytetracycline hydrochloride (OTC) with high purity of 98%, was purchased form Tokyo Chemical Industry (Japan). Other chemicals including NaCl, HCl, and NaOH are analytical reagents (Merck, Germany). Deionized water was used to prepare all aqueous solutions. An HI 2215 pH meter (Hanna, USA) was used to monitor pH of solutions.

Surface modification of nano α-Al_2O_3 by PAMPs

A stock solution of 1000 mg/L PAMPs was prepared by dissolving 0.2500 g of PAMPs into a 250 mL volumetric flask and filled up with deionized water. The PAMPs solution, α-Al_2O_3 nanoparticles and NaCl solution were mixed and adjusted to pH 4 before filling the final amount of 10 mL in 15 mL Falcon tubes to form PAMPS modified nano α-Al_2O_3 (PAMNA).

Adsorption study

A 10 mg/L of OTC was added to PAMNA adsorbent in 15 mL Falcon tubes before adjusting the pH solution and shaking for various contact time. To optimize the best conditions, the effective parameters for OTC removal, such as adsorbent dose, pH, and contact time, were systematically investigated by changing one parameter while the other factors remained constant. Each parameter that affects the removal of an antibiotic was inspected at least three times.

All adsorption isotherms experiments were performed under optimal pH, adsorbent dosage, and contact time conditions. The adsorbent was separated by using a refrigerated centrifuge (MR23i, JOUAN, France) at 10.000 rpm for 10 min after achieving equilibrium. A spectrophotometer (UV-1650 PC, Shimadzu, Japan) was used to quantify the OTC concentrations at a wavelength of 355 nm.

The removal efficiency (%) of OTC was determined by the following equation:

$$Removal\ efficiency\ (\%) = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i (mg/l) and C_f (mg/l) are initial and final concentrations of OTC, respectively.

The adsorption capacities of OTC on PAMNA were calculated by using the equation:

$$\Gamma = \frac{C_i - C_e}{m} \times 1000 \quad (2)$$

where Γ is the adsorption capacity of OTC (mg/g), Ce is the equilibrium concentration of OTC (mg/L), m is the adsorbent dosage (mg/mL).

The surface charges of α-Al_2O_3 after PAMPs modification and OTC adsorption at pH 4 in 1 mM NaCl were evaluated by measuring ζ potential using a Zetasizer Nano ZS (Malvern, England) by Smoluchowski's equation using the electrophoretic mobility measurements [13].

Results and discussion

Adsorptive removal of OTC using nano α-Al_2O_3 without and with PAMPs modification

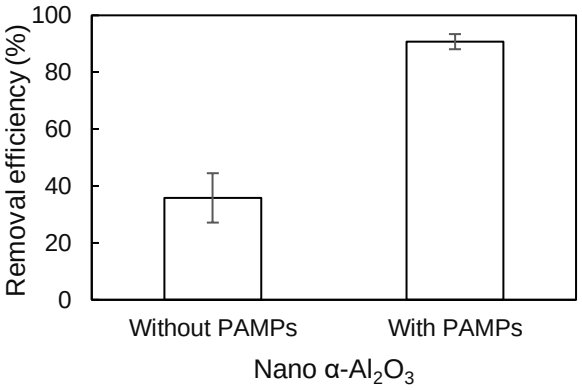

Figure 1: Adsorptive removal of OTC removal using nano α-Al_2O_3 without and with PAMPs modification. Error bars show standard deviations of triples

Polyanion, PAMPs with a concentration of 1000 mg/L was used to modify the surface of nano α-Al_2O_3 in 0.01 M NaCl at pH 4. The PAMPS adsorption on nano α-Al_2O_3 surface is controlled by both electrostatic and nonelectrostatic interaction so that adsorption at high NaCl concentration is promoted. It implies that the high

numbers of PAMPs loops and tails were adsorbed layer on nano α-Al_2O_3 with these conditions [11]. As a result, the surface charge of nano α-Al_2O_3 is high negative which can enhance adsorption of OTC.

Figure 1 indicates that the removal efficiency of OTC in 0.001 M NaCl (pH 4) with initial concentration of 10 mg/L increased from 35.5 to 90.7 % when used PAMPs modified nano α-Al_2O_3 (PAMNA). Because the OTC removal efficiency using PAMNA is much higher than that using raw nano α-Al_2O_3, further studies of OTC adsorption only focuses on PAMNA material.

Adsorption of OTC using PAMNA

Effect of pH

The pH is an important factor in adsorption of OTC on PAMNA because pH strongly influences to charging behavior of OTC while surface charge of PAMNA is pH independent. The effect of pH was investigated the range of 3.0-10.0 under contact time 120 min, adsorbent dosage 20 mg/mL. Figure 2 shows that the removal efficiency of OTC using PAMNA decreased with increasing pH. In the pH range of 4 to 10, the species of OTC changed from zwitterionic to negative form since OTC had two values of pKa of 3.3 and 7.3. As a result, the removal efficiency of OTC was decreased with increasing pH from 4 to 10, especially at pH> 7. At pH 3, the dissolution of nano α-Al_2O_3 could take place so that OTC removal was reduced. Therefore, the optimum pH for OTC removal using PAMNA was 4 and was kept for further study.

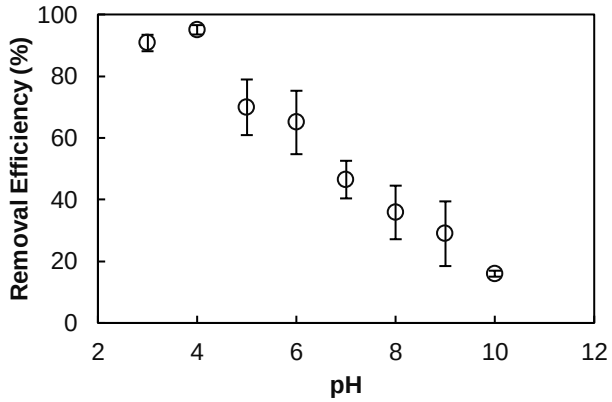

Figure 2: Effect of pH on OTC removal using PAMNA (C_{OTC} = 10 mg/L, contact time 120 min, and adsorbent dosage 20 mg/mL). Error bars show standard deviations of triples

Effect of contact time

Contact time highly influences the adsorption equilibrium. The adsorptive removal of OTC using PAMNA was carried out at pH 4 and 20 mg/mL while the adsorption time increased from 10 to 180 min.

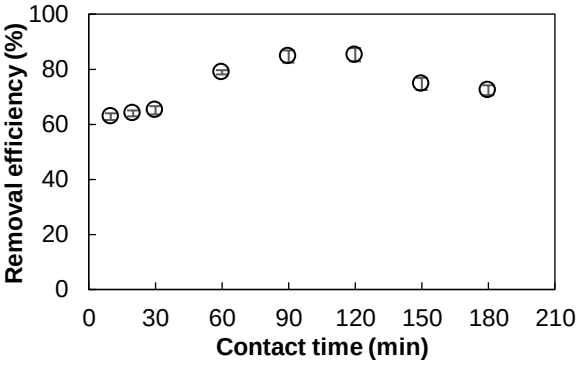

Figure 3: Effect of contact time on OTC removal using PAMNA (C_{OTC} = 10 mg/L, pH 4, and adsorbent dosage 20 mg/mL). Error bars show standard deviations of triples

As seen from Figure 3, the OTC removal using PAMNA increased with increasing contact time from 10 to 120 min. The highest removal efficiency was found to be about 90 %. After 120 min, OTC removal slightly decreased due to the desorption process under long time of shaking. The contact time in our case is much shorter than that of the adsorptive removal of OTC using maize straw-derived biochar [14]. Therefore, contact time of 180 min is suitable for removal of OTC using PAMNA.

Effect of adsorbent dosage

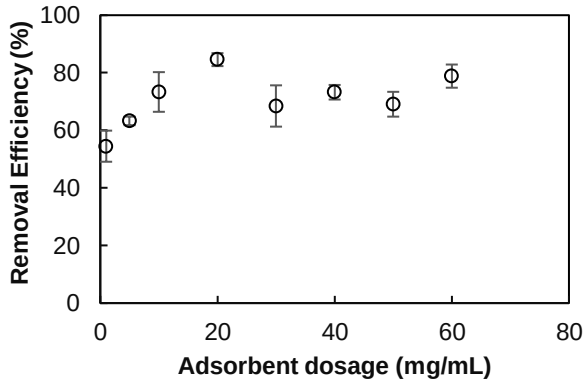

Figure 4: Effect of PAMNA dosage on OTC removal (C_{OTC} = 10 mg/L, pH 4, and contact time 120 min). Error bars show standard deviations of triples.

Figure 4 shows the removal efficiency of OTC using PAMNA when the dosage increases from 1 to 60 mg/mL.

As can be seen in Figure 4, the OTC removal increased with adsorbent dosage increase from 1 to 20 mg/mL. Higher dosage than 20 mg/mL may induce the fast

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coagulation of nanoparticles [15]. The fast coagulation may decrease the interaction between OTC molecules and PAMNA surface. Thus, OTC removal seems to be decreased. Therefore, optimum PAMNA dosage was 20 mg/mL and it is kept unchanged for further research.

Adsorption isotherms and mechanisms

Adsorption isotherms of OTC on PAMNA at two NaCl concentrations while other experimental conditions were fixed at pH 4, contact time 120 min and adsorbent dosage 20 mg/mL. The initial concentrations of OTC were ranged from 5 to 2000 mg/L. We used Langmuir model to fit experimental data of OTC capacity on PAMNA. Table 1 shows that OTC adsorption capacity increased when the increasing NaCl concentration from 1 to 10 mM. An increase in NaCl concentration makes a decrease in electrostatic attraction between the positive OTC species and the negatively charged PAMNA surface due to the presence of high concentration of competitive counter ions; but the adsorption capacity increase from 55.5 to 140.2 mg/g.

Table 1: The parameters for OTC adsorption isotherms on PAMNA at two NaCl concentrations fitted by Langmuir model

Parameter	NaCl concentration (mM)	
	1	10
Γ max (mg/g)	55.5	140.2
K_L (L/g)	0.032	0.040
R^2	0.9905	0.9707

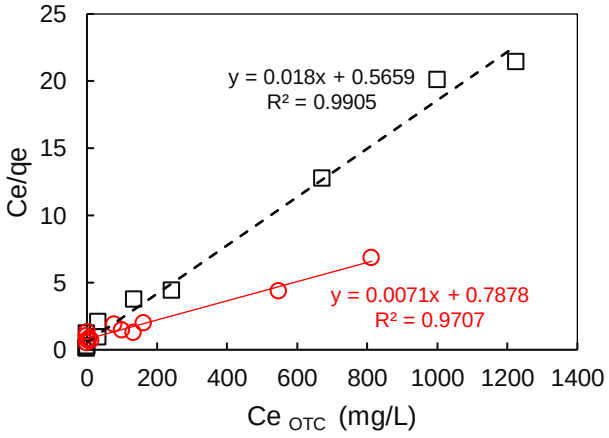

Figure 5: The Langmuir linear fit for OTC adsorption isotherms on PAMPs modified α-Al_2O_3 (PAMNA) at two NaCl concentrations

The maximum adsorption capacity of PAMNA in our case is much higher than other adsorbents [2]. The Langmuir model can fit experimental data well with R^2 > 0.97 (Figure 5). The maximum adsorption capacity of OTC in our case for is much higher than other studies. This result suggests that other interactions such as lateral and hydrophobic between polymer chains and hydrocarbon in OTC molecules.

The adsorption mechanism of OTC on PAMNA is also discussed in based on surface charge change by ζ potential (Figure 6).

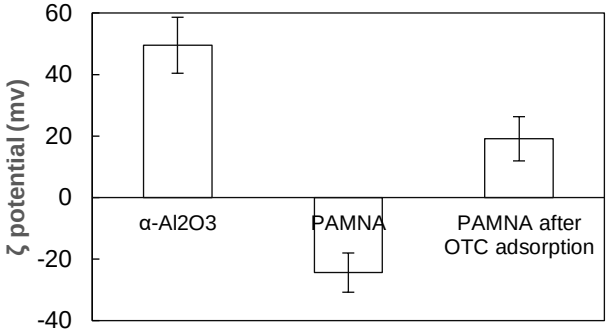

Figure 6: The ζ potential of nano α-Al_2O_3, PAMPs modified α-Al_2O_3 (PAMNA) and PAMNA after OTC adsorption in 1 mM NaCl (pH 4)

Figure 6 reveals that the ζ potential of nano α-Al_2O_3 dramatically changed after surface modification with PAMPs and after OTC adsorption. Since PAMPs is a strong polyanion, the α-Al_2O_3 surface charge reversed from positive (ζ = 49.5 mV) to negative (ζ = -24.4 mV). It implies that the charge reversal occurred in the presence of more loops and tails. Nevertheless, after OTC adsorption with the positive species of OTC (at pH 4) [16], the negative charge of PAMNA was decreased so that the ζ potential reversed again to positive charge (ζ = 19.1 mV).

The results of surface charge changes and adsorption isotherms indicate that OTC is highly adsorbed on PAMNA by both electrostatic and non-electrostatic interactions.

Reuse of adsorbent

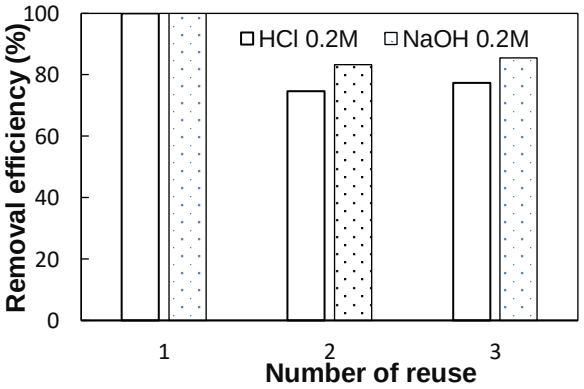

Figure 7. The removal efficiency of OTC using PAMNA after three regenerations

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The reuse of adsorbent is important to evaluate the performance and application in reality. To evaluate reuse potential of PAMNA, we used 0.2 M NaOH and 0.2 M HCl to desorb OTC, then the adsorbent was remodified with PAMPs residue under the optimum condition [11]. The removal efficiencies of OTC using the reused PAMNA are shown in Figure 7.

Figure 7 shows that the removal efficiencies of OTC using PAMNA after three regenerations were slightly decreased but the they were still higher than 75 %. There results again indicate that PAMNA is reusable and high performance for OTC removal in water environment.

Conclusion

We have investigated adsorption of an antibiotic OTC on PAMPs modified α-Al_2O_3 nanoparticles (PAMNA). Adsorptive removal efficiency of OTC increased sharply to 90.7 % The effective conditions including pH, contact time, adsorbent dosage for OTC removal using PAMNA were optimized and found as 4, 120 min and 20 mg/mL, respectively. The maximum adsorption capacity of OTC using PAMNA was 140.2 mg/g. By evaluating adsorption isotherms and the surface charge change, we demonstrate that both electrostatic and non-electrostatic interactions are driving forces for OTC adsorption on PAMNA in water environment.

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