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Adsorption characteristics of 2,4-dichorophenoxy acetic acid onto surfactant modified titania nanoparticles

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ABSTRACT

The present study investigated adsorption of 2,4-dichorophenoxy acetic acid (2,4-D) on titania (TiO_2) nanoparticles with surface modification by cationic surfactant, cetyltrimethylammonium bromide (CTAB). Titania nanoparticles which were successfully synthesized by sol-gel method, were characterized by X-ray diffraction (XRD) and Transmission electron microscopy (TEM). Surface modification of TiO_2 with CTAB enhanced the removal of 2,4-D significantly. Some effective conditions affect to the removal of 2,4-D using CTAB modified TiO_2 such as pH and adsorbent dosage were systematically studied and found to be 5 and 10 mg/mL, respectively. Adsorption mechanisms of 2,4-D onto CTAB modified TiO_2 was suggested based on the change in surface charge after adsorption.

Introduction

The environmental concerns for frequent occurrence of toxic organic substance such as herbicides in ground and surface waters have been addressed [1]. The 2,4-dichlorophenoxyacetic acid (2,4-D) which is one of the phenoxyacetic acid herbicides, is widely used for control of broadleaf weeds in grain croplands, forests, domestic lawns, commercial turfs, and aquacultures [2]. Normally, 2,4-D exists in anionic form in aqueous solution due to its low pKa (2.73). The negative charged 2,4-D species are particularly considered because they are very weakly retained onto the soils. On the other hand, they can easily move into solution, leading to the contamination in water environment. Adsorption is one of the effective techniques that is thoroughly studied for removal of 2,4-D from aqueous solution. Many researches have been investigated the adsorptive removal of 2,4-D using various materials such as mineral [3], activated carbon [4] and polymeric adsorbent [5].

Among various metal oxides material, titania (TiO_2) has been found as one of the best and the most widely investigated material for photocatalyst. Based on the fundamentals of photocatalysis and surface characteristics, TiO_2 nanomaterials indicate many advantages. The TiO_2 is versatile, economical, stable, abundant, non-toxic, and environmentally friendly [6]. However, the photocatalytic performance of TiO_2 is largely dependent on its optical and electronic structures, morphological properties, crystallinity, particle size, and surface chemistry [7-9]. In addition, its

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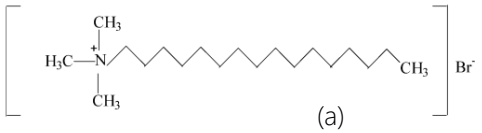
low quantum efficiency and wide band gap makes a limit in its applications in the visible light region. In order to enhance the activity and sensitivity of TiO_2 at longer wavelength, many modification techniques have been studied including metal and nonmetal doping, or surface modification [7, 10]. Not so many study removal of contaminants using TiO2 by adsorption technique comparing with photocatalyst. To the best of our knowledge, adsorption of organic pollutants on TiO_2 with surface modification by surfactant has not been studied.

In the present work, for the first time, we investigated the adsorptive removal of 2,4-D using TiO_2 nanoparticles with modification by cationic surfactant CTAB. The synthesized TiO_2 nanoparticles were characterized by X-ray diffraction (XRD), and Transmission electron microscopy (TEM). Some effective conditions to 2,4-D adsorption on TiO_2 nanoparticles including pH, adsorbent dosage and ionic strength were thoroughly studied.

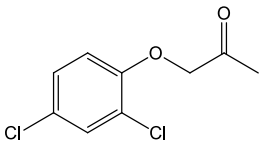
Experimental

Materials

The 2,4-Dichlorophenoxyacetic acid (2,4-D) crystal with purity >97.0% and cetyltrimethylammonium bromide (CTAB) with purity >98.0 % were supplied by Tokyo Chemical Industry was used without further purification. The chemical structures of 2,4-D and CTAB are indicated in Figure 1a and 1b, respectively. Tetrabutylorthotitanate (TBOT) ($C_{16}H_{36}O_4Ti$, Merck, Germany) was used to synthesize TiO_2 nanoparticles. Ionic strength and pH were prepared and adjusted by the addition of KCl, HCl, and KOH (p.A, Merck, Germany). Other chemicals with analytical grade were purchased from Merck



(a)



2,4-Dichlorophenoxyacetic acid

(b)

Figure 1: Chemical structures of Cetyltrimmoniumbromide (CTAB) (a) and 2,4-Dichlorophenoxyacetic acid (2,4-D) (b)

An ultrapure water system (Labconco, USA) with a resistivity of 18.2 MΩcm was used to produce ultrapure water in preparing all aqueous solutions. Solution pH was measured using an HI 2215 pH meter (Hanna, USA).

Synthesis of TiO_2 nanoparticles from TBOT

The TiO_2 nanoparticles were fabricated by sol-gel method according to our previously published paper [11].

Characterization methods

The TiO_2 nanoparticles were characterized by XRD, and TEM. The XRD pattern was conducted on a Bruker D8 Advance X-ray Diffractometer while the TEM image was collected by Hitachi High-Technologies Corporation S4800-NIHE, Japan.

Adsorption studies

All adsorption experiments were carried out by batch mode in 15mL Fancol tubes at room temperature controlled by an air conditioner at 25 ± 2℃.

The conditions of CTAB modification onto TiO_2 nanoparticles were carried out with contact time 120 min, 1mM KCl, at various pH solutions from 3-11 and using adsorbent dosages from1 to 50 mg/mL.

The effects of pH, and adsorbent dosage on 2,4-D adsorption were investigated. The ultraviolet spectroscopy (UV) method using a spectrophotometer (UV-1650 PC, Shimadzu, Japan) was used to determine all 2,4-D concentrations before and after adsorption.

Results and discussion

Characterizations of TiO_2 nanoparticles

The synthesized TiO_2 nanoparticles from TBOT was characterized by XRD, and TEM.

The XRD pattern of TiO_2 nanoparticles is shown in Figure. 2.

Figure 2 shows that the large peaks which occurred at 2θ=25.265° were observed in the XRD pattern of synthesized TiO_2-NPs. Many previous reports indicated that the TiO_2 anatase phase had peaks at 25.3°, 37.8°, and 48.1°, while the rutile peaks are at 2θ = 27.5°, 36.2°, and 54.4°[6, 12]. The appeared peaks of synthesized TiO_2 nanoparticles in the present study

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were encountered at 2θ = 25.3°, 37.8°, and 48.1°and some lower pic at 2θ = 27,2; 36,2; 54,3. Therefore, the XRD pattern confirms that the phase of TiO_2 in our case is mainly the anatase and the phase of rutile was also found in a much smaller quality.

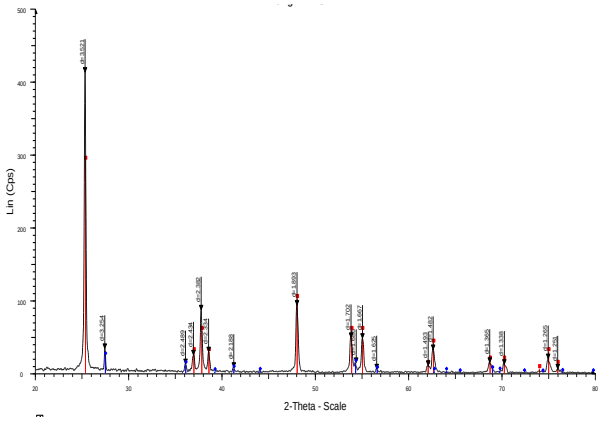

Figure 2: XRD pattern of synthesized TiO_2 nanoparticles

The TEM image of TiO_2 nanoparticles in Figure. 3 show that TiO_2 particles have sphere with the average diameter of around 30 nm.

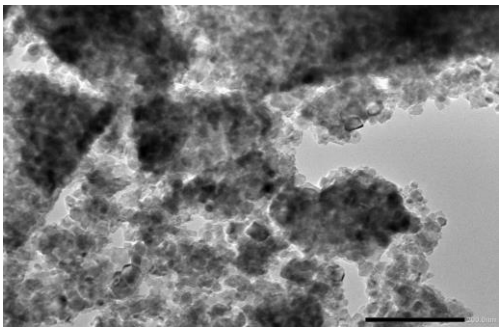

Figure 3: TEM image of TiO_2 nanoparticles

Based on XRD and TEM results, we confirm that TiO_2 nanoparticles with the phase of anatase were successfully synthesized from TBOT by sol- gel method.

Adsorption of 2,4-D on CTAB-modified TiO_2 nanoparticles

Figure 4. shows the adsorption ability of TiO_2 nanoparticles with and without CTAB modification at solution pH=4 and 5. It exhibits that the original material has a limited ability to 2,4-D treatment with the highest removal about 28.18% at pH 4 and 18.07 % at pH 5. At different pH, adsorption ability of raw TiO_2 material decreased dramatically to around 10%. Meanwhile, the adsorption ability of TiO_2 nanoparticles with CTAB modification is nearly doubled that of original material (54.69 %) at pH 4 and it rises significantly to above 92% at pH 5.

The result indicates that CTAB-modified TiO_2 plays a much better 2,4-D adsorption ability under the same experimental condition.

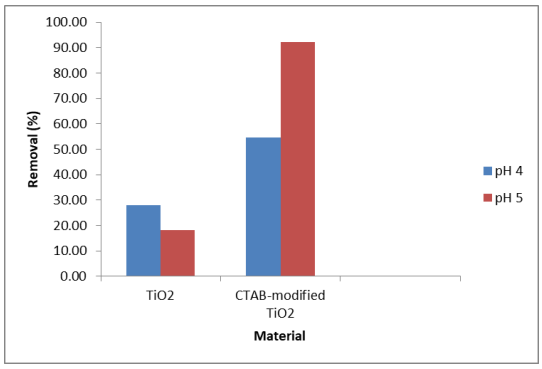

Figure 4: The 2,4-D adsorption onto original nanotitanium and CTAB-modified TiO_2 ($C_{i,2,4\text{-}D}$ = 5 ppm, and 1 mM KCl). Error bars show standard deviations of three replicates

Effect of pH

Solution pH is one of the most important factor for 2,4-D adsorption because pH strongly affects to surface charge of TiO_2 nanoparticles and charged species of 2,4-D. Since 2,4-D has pK_a= 2,73 [5] that is lower the point of zero charge (PZC) of TiO_2 nanoparticles (about 5.6)[9]. Therefore, optimal pH should be under PZC. In this study, pH 5 shows the highest removal efficiency, at 85.18%.

Our results indicate that surface charge of TiO_2 nanoparticles is strongly changed to be highly positive after CTAB modification. This phenomenon suggests that negative species of 2,4-D are suitable for adsorption onto CTAB modified TiO_2 surface due to the electrostatic force.

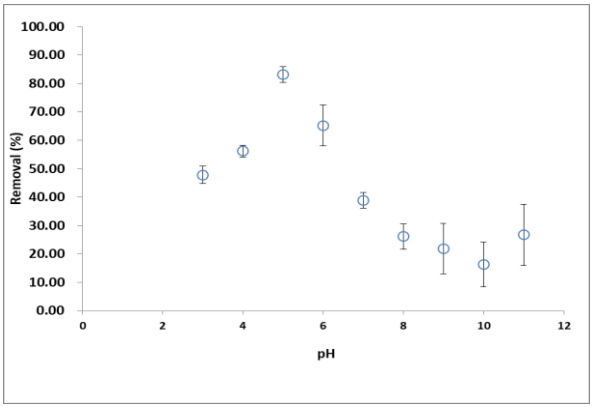

Figure 5: Effect of pH on 2,4-D adsorption onto CTAB-modified TiO_2 nanoparticles ($C_{i,2,4\text{-}D}$ = 5 ppm, and 1 mM KCl). Error bars show standard deviations of three replicates

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Effect of adsorbent dosage

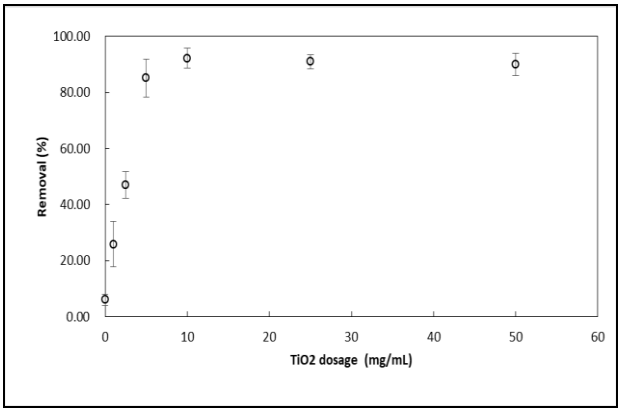

Figure 6: Effect of adsorbent dosage on 2,4-D adsorption onto CTAB modified TiO_2 ($C_{i,2,4\text{-}D}$ = 5 ppm, pH 5, and 1 mM KCl). Error bars show standard deviations of three replicates

The adsorbent dosage highly influences to the total surface area and surface charge density so that it is an important factor for adsorption. The influence of CTAB-modified TiO_2 dosage is indicated in Figure 6 in which the amount of adsorbent was studied in range 1-50 mg/mL. Figure 6 shows that the removal of 2,4-D increased with increasing adsorbent dosage from 1 to 10 mg/mL then changed insignificantly.

The increase in removal of 2,4-D is due to the increase of adsorption sites that can remain the state of unsaturated during the adsorption process. The appropriate adsorbent dosage is found to be 10 mg/mL and it is fixed for further studies.

Adsorption mechanisms of 2,4-D onto CTAB-modified TiO_2

In this part, the adsorption mechanisms of 2,4-D onto CTAB-modified TiO_2 are discussed in detail by evaluating the ζ potential change. According to previous reports, the ζ potential of TiO_2 at pH 5 was slightly positive [6, 9, 13, 14]. However, after modification with CTAB, the increase in surface charge was obtained with highly positive of synthesized CTAB-modified TiO_2 (ζ=+29.4 mV) due to the presence of high number of cationic surfactant molecules $C_{16}H_{33}(CH_3)_3N^+$ to form micelles. Interestingly, after 2,4-D adsorption, the ζ potential found to be +32.6 mV, indicating that the net charge of CTAB-modified TiO_2 increased slightly. In other word, the 2,4-D adsorption onto positively charged CTAB-modified TiO_2 surface by non-electrostatic interactions because 2,4- D exists in negative species. If electrostatic attraction induces 2,4-D adsorption, the decrease in ζ potential would be found. In our case, 2,4-D adsorption was controlled by the interaction of 2,4-D molecules and CTAB micelles therefore the change in surface charge was small.

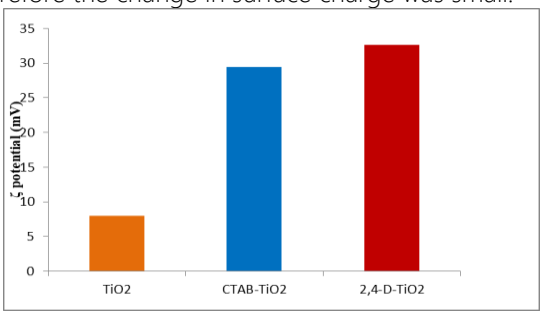

Figure 7: The ζ potential of synthesized TiO_2, CTAB-modified TiO_2 and CTAB-modified TiO_2 after adsorption of 2,4-D (at pH=5 and 1 mM KCl)

Conclusion

Adsorption of 2,4-D onto CTAB-modified TiO_2 nanoparticles was investigated in this study. The synthesized TiO_2 nanoparticles contained the dominant anatase phase with average diameter of around 30 nm. Surface modification of TiO_2 nanoparticles by CTAB induced a significant increase in the removal of 2,4–D using TiO_2 nanoparticles. The optimum conditions for removal of 2,4-D using CTAB modified TiO_2 nanoparticles were found to be pH 5, adsorbent dosage 10 mg/mL. Based on surface charge change after adsorption, we indicate that the adsorption of 2,4-D onto TiO_2 nanoparticles with surface modification by CTAB was mainly controlled by non-electrostatic interaction.

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