Open Journal of Inorganic Non-Metallic Materials, 2014, 4, 28-34
Published Online July 2014 in SciRes. http://www.scirp.org/journal/ojinm
http://dx.doi.org/10.4236/ojinm.2014.43005

Optimization of Conditions for the Photocatalytic Degradation of EDTA in Aqueous Solution with Fe-Doped Titanium Dioxide

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Received 19 May 2014; revised 17 June 2014; accepted 16 July 2014

Abstract

The conditions for photocatalytic degradation of ethylenediaminetetraacetic acid (EDTA) in aqueous solution with Fe-doped titanium dioxide (TiO_2) were optimized. The degradation efficiencies with Fe-doped TiO_2 were better, compared with those obtained with bare TiO_2 and Pt-doped TiO_2. The effect of various experimental factors, such as photocatalytic dosage, temperature, solution pH and light intensity on the photocatalytic degradation of EDTA by Fe-doped TiO_2 was investigated. The photocatalytic degradation treatment for the wastewater containing EDTA is simple, easy handling and low cost.

Keywords

EDTA, Fe-Doped TiO_2, Photocatalytic Degradation, Wastewater Treatment, Radioactive Liquid Waste

1. Introduction

The treatment of radioactive liquid waste from radiochemical plants and nuclear power plants become one of

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How to cite this paper: Sugiyama, T., Dabwan, A.H.A., Katsumata, H., Suzuki, T. and Kaneco, S. (2014) Optimization of Conditions for the Photocatalytic Degradation of EDTA in Aqueous Solution with Fe-Doped Titanium Dioxide. *Open Journal of Inorganic Non-Metallic Materials*, **4**, 28-34. http://dx.doi.org/10.4236/ojinm.2014.43005

urgent problems for the environmental safety. Ethylenediaminetetraacetic acid (EDTA; $C_{10}H_{16}N_2O_8$, CAS #60-00-4) has been widely used as a decontaminating agent in radiochemical and nuclear power plants. The addition of EDTA into the radioactive liquid waste can give the complexation of some of the precipitant cations, which results in the interference in their removal by the conventional treatment process such as chemical precipitation and ion exchange [1]-[9].

Since EDTA is stable, has low biodegradability, is rarely degradable by chlorine, is hardly retained by activated carbon fibers and is resistant to ozone treatment, it is a crucial step to perform a pretreatment step for the removal of EDTA for a better treatment of the liquid waste [1]-[9].

Recently, advanced oxidation method based on the photocatalysis has been employed successfully for the degradation of organic pollutants. For instance, the liquid waste containing bisphenol [10], phthalate [11] and agricultural chemicals (thiram [12]) has been treated with the photocatalytic degradation techniques. Recently, Nitoi *et al.* [9] have investigated the photocatalytic degradation of nitrobenzene in the aqueous solution with un-doped TiO_2 and Fe, Co and Ni-doped TiO_2 powders. In the studies, Fe-doped TiO_2 was very effective for the photocatalytic degradation of nitrobenzene.

Thus far, several studies have been reported for the photocatalytic degradation of EDTA with titanium dioxide (TiO_2) semiconductors [3] [7]. However, very few works related to the use of Fe-doped TiO_2 in the photocatalytic degradation of EDTA in the aqueous solution have been reported.

In the present work, the photocatalytic degradation of EDTA in the aqueous solution with Fe-doped TiO_2 has been investigated. Moreover, the treatment conditions such as the photocatalytic dosage, temperature, solution pH and light intensity have been optimized.

2. Experimental

2.1. Materials

Ethylenediaminetetraacetic acid disodium salts dihydrate used in the present study was purchased from Nacalai Tesque Inc., Kyoto, Japan (Grade > 99.5%). Three types of photocatalysts were obtained from Ishiraha Sangyo Kaisha, Ltd. 1) Bare TiO_2 (ST-01); particle size 7 nm, specific surface area 300 m^2/g, 2) Pt-doped TiO_2 (MPT-623); particle size 18 nm, specific surface area 60 m^2/g and 3) Fe-doped TiO_2 (MPT-625); particle size 15 nm, specific surface area 70 m^2/g. Laboratory pure water was obtained from an ultrapure water system (Advantec MFS Inc., Tokyo, Japan) resulting in a resistivity >18 MΩ·cm.

2.2. Photocatalytic Procedures

EDTA aqueous solutions were prepared with ultrapure water. Then, a 10 mL aqueous solution containing 0.1 mg/mL (0.268 μM) EDTA was put into a Pyrex glass reaction vessel (30 mL capacity). The photocatalyst powder was added into the solution to produce a given concentration of suspension. The experimental conditions for the optimization of treatment were shown in **Table 1**. The A 15 W black light (Toshiba Lighting & Technology Corp) with a maximum emission of 352 nm was applied as light source, which was positioned on the side of photoreactor. The light intensity was measured by a UV radiometer with a sensor of 320 - 410 nm wavelengths (UVR-400, Iuchi Co., Osaka, Japan), and the value was 1.0 mW/cm^2. The photocatalysts were continuously dispersed in the aqueous solution by a magnetic stirrer during the irradiation.

After the illumination, the photocatalyst was separated through the 0.45 μm Advantec membrane filter. The photocatalyst powders could be almost removed by the filtration. The amount of EDTA in the aqueous solution

Table 1. Degradation conditions.

EDTA	0.1 mg/mL, 10 mL
Photocatalyst	TiO_2, Pt/TiO_2, Fe/TiO_2
Photocatalyst dosage	0 - 20 mg/10 mL
Temperature	10˚C - 50˚C
Solution pH	3 - 8
Light intensity	0 - 4.5 mW/cm^2

was determined titrimetrically against standard Mg^{2+} using Erichrome Black T as indicator. The removal efficiency was calculated by applying the following equation:

$$\mathrm{DE}(\%) = \frac{C_0 - C_t}{C_0} \quad (1)$$

where C_0 is the original EDTA concentration and C_t the EDTA concentration after the treatment.

3. Results and Discussion

3.1. Effect of Doping Metal

In order to study the effect of doping metals on the photocatalytic degradation of EDTA in aqueous solution with TiO_2, Pt and Fe-deposited photocatalysts were evaluated for the improvement of degradation efficiency. The results are shown in **Table 2**. The illumination time was 60 min. The degradation efficiency with iron-doped TiO_2 was better compared with those obtained with bare and Pt-doped TiO_2. Other researchers [9] [13] have described the improvement of photocatalytic activity of 0.5 wt% Fe-doped TiO_2, which showed drastically the increases of charge-carrier lifetime to minutes and even hours beside undoped TiO_2 (average lifetime an electron/hole pair is approximately 30 ns). According to the estimation, Fe-doping may improve the photocatalytic degradation of EDTA in aqueous solution with TiO_2 semiconductors. Therefore, all subsequent experiments were performed with Fe-doped TiO_2.

3.2. Effect of Photocatalyst Dosage

To optimize the Fe/TiO_2 suspension concentration, the effect of photocatalyst dosages on the EDTA degradation in aqueous solution was investigated. The results are illustrated in **Figure 1**. With increasing the amounts up to 10 mg (1 mg/mL), the degradation efficiency increased. After the value, the efficiency became nearly flat. The increase in the efficiency appears to be owing to the increase in the total surface area, namely the number of active sites, available for the photocatalytic reaction as the dosage of photocatalyst increased. However, the Fe/TiO_2 photocatalyst was overdosed, the number of active sites on the Fe/TiO_2 surface may become nearly

Table 2. Effect of doping metal on the photocatalytic degradation of EDTA in aqueous solution.

Photocatalyst	Degradation efficiency (%)
TiO_2	68
Pt/TiO_2	73
Fe/TiO_2	91

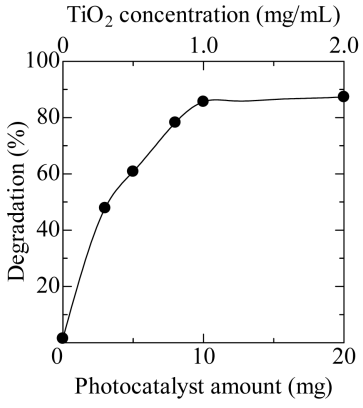

Figure 1. Effect of Fe/TiO_2 dosage on the photocatalytic degradation of EDTA in water. EDTA; 0.1 mg/mL, irradiation time; 60 min, temperature; 25˚C, light; black light 2.0 mW/cm^2.

constant due to the decreased light penetration, the increased light scattering and the loss in surface area occasioned by agglomeration (particle-particles interactions) at high solid concentration [14]. Therefore, 1.0 mg/mL (10 mg) of TiO_2 suspension concentration was adopted as the optimal amounts of photocatalyst for the sequential experiment.

3.3. Effect of Temperature

Little information dealing with the temperature effect on the photocatalytic degradation of pollutants in water by Fe/TiO_2 has been presented. Therefore, the effect of temperature on the photocatalytic degradation of EDTA in aqueous solution using TiO_2 was investigated in the range of 10˚C - 50˚C. The results are shown in **Figure 2**. The degradation efficiency of EDTA increased as the temperature increased up to 25˚C. Above the temperature, the efficiency curve was almost flat. In the photocatalytic degradation of imazaquin in the TiO_2 suspension [15], the effect of temperature was studied in the range 20˚C - 40˚C, and the rate constants increased with increasing temperature. Ishiki *et al.* [16] have evaluated the photocatalytic degradation of imazethapyr herbicide at TiO_2/H_2O interface. The temperature effect was investigated using a suspension between 20˚C and 40˚C, and the herbicide was more easily degraded at lower temperatures in the TiO_2 suspension, due to the decrease in the physisorption between the TiO_2 surface and the imazethapyr molecules. Therefore, various tendencies of the temperature effect seem to be observed for different target pollutants. All subsequent irradiations were performed at 25˚C because of the operating cost for the photodegradation system.

3.4. Effect of pH

The amphoteric behavior of most semiconductor oxides affects the surface charge of the photocatalyst. Therefore, the role of initial pH on the degradation efficiency for EDTA was investigated in the pH range 3 - 8, as illustrated in **Figure 3**. Although the degradation efficiency tended to increase with increase in pH up to around 6,

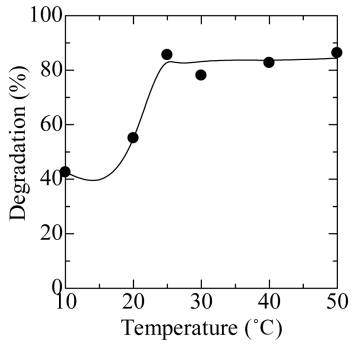

Figure 2. Effect of temperature on the photocatalytic degradation of EDTA in water with Fe/TiO_2. Fe/TiO_2; 1 mg/mL, EDTA; 0.1 mg/mL, irradiation time; 60 min, light; black light 2.0 mW/cm^2.

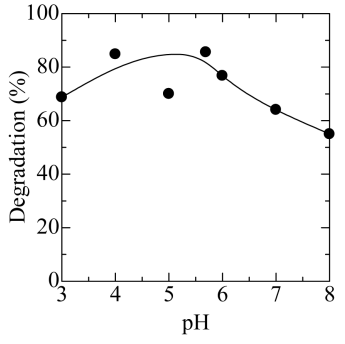

Figure 3. Effect of pH on the photocatalytic degradation of EDTA in water with Fe/TiO_2. Fe/TiO_2; 1 mg/mL, EDTA; 0.1 mg/mL, irradiation time; 60 min, temperature; 25˚C, light; black light 2.0 mW/cm^2.

the efficiency was roughly constant (approximately 80%). Above pH 6, the efficiency gradually decreased with pH. The pH value of zero point charge (zpc) pH_{zpc} of TiO_2 particles is equal to around six as Ti_{IV}-OH [17]. This means that the TiO_2 surface becomes positively charged, Ti_{IV}-OH_2^+, when the pH is lower than this value and becomes predominatly negative, Ti_{IV}-O^-, for a pH value above about six. Generally, the pH changes can have a non-insignificant result not only on the mode of adsorption of the EDTA substrate on TiO_2 surface, but also on the selectivity of the photodegradative reaction occurring on the particle surface since redox reactions are very sensitive to changes in the surface potential. In the pH range of 3 to 8, the EDTA chemical species and their metal complex species are anion in the solution. Therefore, the photocatalytic degradation of EDTA may be accelerated in an acid medium. Similar reaction has been suggested by a number of researchers. Consequently, 5.7 was selected for the optimal experimental conditions because of the unnecessary of chemical remediation including neutralization process.

3.5. Effect of Light Intensity

The effect of light intensity on the photocatalytic destruction of EDTA in water with Fe/TiO_2 was investigated. The results are illustrated in **Figure 4**. The degradation efficiency increased rapidly with increase in the light intensity up to 0.5 mW/cm^2, and then the efficiency increased gradually. Since the catalyst Fe/TiO_2 powders are suspended in a stirred solution, the light intensity will affect the degree of absorption of light by the catalyst surface. Ollis [18] reviewed the effect of light intensity on the kinetics of photocatalysis and stated that 1) at low light intensities, the rate would increase linearly with increasing light intensity; 2) at intermediate light intensities, the rate would depend on the square root of the light intensity; and 3) at high light intensities, the rate is independent of light intensity. Therefore, the results obtained in the photocatalytic degradation of EDTA in aqueous TiO_2 suspension were reasonable.

3.6. Reaction Mechanism

In the semiconductor Fe/TiO_2 material with a band gap (E_g), upon the illumination with radiation having an energy greater relative or equal to E_g, the promotion of an electron (e^-) from the valance band (VB) to the conduction band (CB) takes place. Concomitantly, the formation of a positive hole (h^+) in the VB occurs. Photogenerated electrons and holes can either undergo undesired recombination or migrate to the surface of the system, where they can initiate reactions with adsorbed species. Whereas holes in the VB are powerful oxidizing species that can produce hydroxyl radicals (•OH) from the reaction with H_2O, photogenerated electrons in the CB are involved in the formation of •OOH. These oxidizing species may attack the pollutant EDTA in the aqueous solution. The presence of the Schottky barrier can decrease the recombination of photogenerated electron-hole pairs consequently prolong their lifetime, and greatly enhance the photocatalytic activity of TiO_2. Iron loading can result in stronger Schottky barrier effect, and therefore shows better photocatalytic activity of TiO_2, as illustrated in **Figure 5** [19].

4. Conclusion

The optimization of photocatalytic degradation conditions of EDTA in water using Fe-doped TiO_2 was investi-

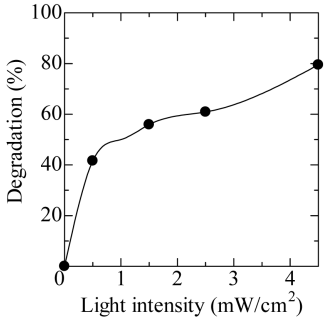

Figure 4. Effect of light intensity on the photocatalytic degradation of EDTA in water with Fe/TiO_2. Fe/TiO_2; 1 mg/mL, EDTA; 0.1 mg/mL, irradiation time; 60 min, temperature; 25˚C, light; black light.

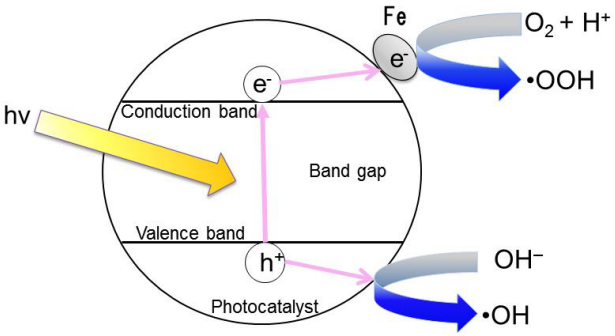

Figure 5. Schematic representation of the mechanism proposed for the photocatalytic degradation of EDTA over Fe/TiO_2.

gated. Fe-doped TiO_2 was very effective for the photocatalytic degradation of EDTA in aqueous solution, compared with bare TiO_2 and Pt-doped TiO_2. Since iron is one of cheap and convenient metals, the photocatalyic degradation technology developed may be applied into the treatment of radioactive liquid waste containing EDTA complexing agent.

Acknowledgements

The present research was partly supported by Grant-in-Aid for Scientific Research (C) 24510096 from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. All experiments were conducted at Mie University. Any opinions, findings, conclusions, or recommendations expressed in this paper are those of the authors and do not necessarily reflect the view of the supporting organizations.

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