



Degradation of methyl orange through synergistic effect of zirconia nanotubes and ultrasonic wave

Jianling Zhao*, Xixin Wang, Libin Zhang, Xiaorui Hou, Ying Li, Chengchun Tang

School of Material Science and Engineering, Hebei University of Technology, Dingzigu Road 1, Tianjin 300130, China

ARTICLE INFO

Article history:

Received 21 October 2010
Received in revised form 24 January 2011
Accepted 25 January 2011
Available online 1 February 2011

Keywords:

Synergistic degradation
Zirconia nanotubes
Ultrasonic wave
Methyl orange

ABSTRACT

Zirconia nanotubes with a length of 25 μm , inner diameter of 80 nm, and wall thickness of 35 nm were prepared by anodization method in mixture of formamide and glycerol (volume ratio = 1:1) containing 1 wt% NH_4F and 1 wt% H_2O . Experiments showed that zirconia nanotubes and ultrasonic wave had synergistic degradation effect for methyl orange and the efficiency of ultrasonic wave increased by more than 7 times. The decolorization percentage was influenced by pH value of the solution. Methyl orange was easy to be degraded in acidic solution. The decolorization percentage of methyl orange reached 97.6% when degraded for 8 h in 20 mg/L methyl orange solution with optimal pH value 2. The reason of synergistic degradation effect for methyl orange might be that adsorption of methyl orange onto zirconia nanotubes resulted in the easy degradation of the methyl orange through ultrasonic wave.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Azo dyes are the largest group of colorants used in industry for color printing, textile dyeing, etc. [1]. However, the production and use of azo dyes result in environmental pollution due to the color visibility and the toxicity of certain dyes [2]. Various methods such as adsorption, biodegradation, photocatalytic and Fenton degradation can be used for the treatment of dyes [3–5]. The main disadvantages of these methods include high cost, secondary pollution or low efficiency, etc.

The method of ultrasonic irradiation is usually used to treat dyestuff wastewaters owing to its advantages such as cleanness and non-secondary pollution [6–8]. However, ultrasonic method usually needs lots of energy and long reaction time [9]. Therefore, one of the important research contents is to improve the efficiency of ultrasonic waves.

Zirconia is widely used as adsorbent or carrier in treatment of environmental pollution due to its excellent properties [10,11]. The morphology of zirconia has a great influence on its performance. Among various morphologies, zirconia nanotubes have attracted considerable attention due to large surface area and specific tubular structure. Recent years, zirconia nanotubes have been prepared by anodization method which has such advantages including simple technique, low cost, high yield and easy for industrial production [12–14].

In this paper, zirconia nanotubes were prepared by anodization method and then degradation of methyl orange through joint action of zirconia nanotubes and ultrasonic wave was studied in detail. Results showed that zirconia nanotubes and ultrasonic wave had synergistic degradation effect for methyl orange and the efficiency of ultrasonic wave increased substantially.

2. Experimental details

2.1. Preparation of zirconia nanotubes

Zirconia nanotubes were prepared by anodizing a zirconium foil in mixture of formamide and glycerol (volume ratio = 1:1) containing 1 wt% NH_4F and 1 wt% H_2O . Zirconium electrode was anode and platinum electrode was cathode, the distance between the two electrodes was 2 cm. Voltage increased from 0 V to 50 V in 10 min slowly, and was kept constant at 50 V for 3 h. After the experiment, the sample was ultrasonically dispersed for 30 min in concentrated hydrochloric acid solution and rinsed with water, then calcined at 600 °C for 2 h.

2.2. The degradation experiment of methyl orange

10 mg zirconia nanotubes were added into 25 mL methyl orange solution which was at a certain pH value and concentration. Ultrasonic degradation experiments were carried out under different conditions (Fig. 1). The concentration of methyl orange solution was measured through T6 UV-vis spectrophotometer (Pgeneral, China). The decolorization percentage was calculated according to the concentration change before and after degradation.

* Corresponding author. Tel.: +86 22 60204805; fax: +86 22 60204129.
E-mail address: zhaojl02@mails.tsinghua.edu.cn (J. Zhao).

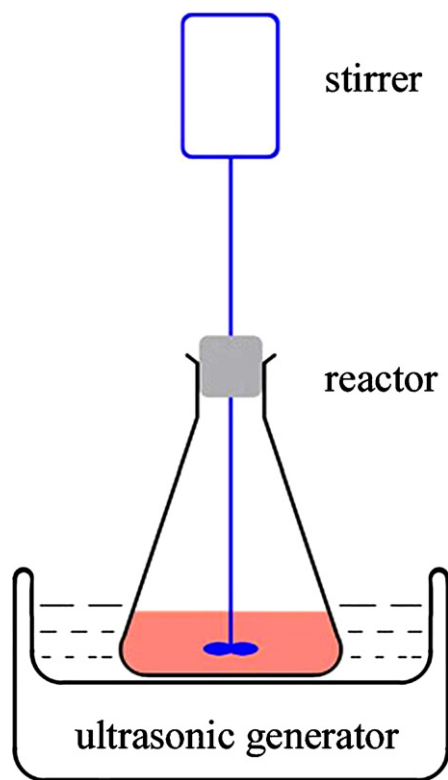


Fig. 1. Schematic diagram of experimental setup.

2.3. Measurement and characterization

The morphologies of zirconia samples were observed through Philips XL 30 TMP scanning electron microscope and Philips Tacnai F20 transmission electron microscope. Zirconia nanotube samples before and after adsorption of methyl orange and the zirconia nanotube samples after decolorization of methyl orange solution were characterized through Fourier transform infrared spectroscopy (FTIR, WQF-410, China). Ultrasonic wave was obtained through SG28-300 ultrasonic generator with a frequency of 28 kHz and power density of 0.5 w/cm^2 (Zhangjiagang ultrasonic electrical Co., China).

3. Results and discussion

3.1. Morphologies of zirconia nanotubes

Fig. 2 shows the morphologies of zirconia nanotubes prepared by anodization method. The average inner diameter of these nan-

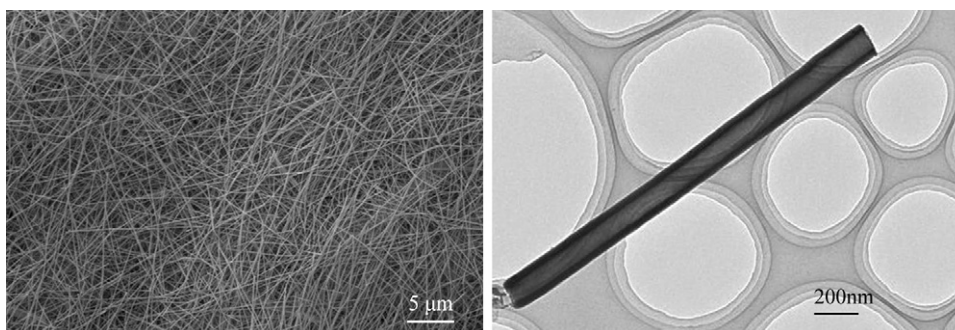


Fig. 2. Morphologies of zirconia nanotubes prepared by anodization.

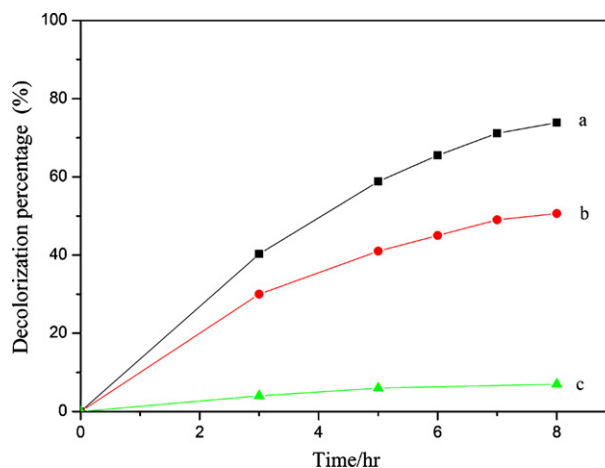


Fig. 3. Decolorization of methyl orange through synergistic effect of zirconia nanotubes and ultrasonic wave (C_0 : 20 mg/L, pH: 4.5); (a) crystallized zirconia nanotubes, (b) uncrystallized zirconia nanotubes, (c) without zirconia nanotubes.

otubes was determined to be $\approx 80 \text{ nm}$, wall thickness of $\approx 35 \text{ nm}$, and length of $\approx 25 \text{ }\mu\text{m}$.

The as-anodized samples are amorphous. When calcined at 600°C , the samples have two mixed crystal forms of tetragonal and monoclinic phase, while monoclinic phase is the dominant phase.

3.2. Synergistic effect of zirconia nanotubes and ultrasonic wave

The decolorization experiments of zirconia nanotubes and ultrasonic wave were conducted in 20 mg/L methyl orange solution when the pH value was 4.5. Fig. 3 shows the results. The decolorization percentage increased obviously due to the joint actions of zirconia nanotubes and ultrasonic wave. The performance of crystallized zirconia nanotubes is superior to that of the uncrystallized zirconia nanotubes (Fig. 3a and b). Without zirconia nanotubes, decolorization percentage of methyl orange is rather limited (Fig. 3c). Results show that zirconia nanotubes and ultrasonic wave have synergistic degradation effect for methyl orange and efficiency of ultrasonic wave increased by more than 7 times due to the use of zirconia nanotubes.

In order to study the adsorption of methyl orange, zirconia nanotubes were dipped into methyl orange solution for a certain time, then separated, rinsed with water and dried at $60\text{--}70^\circ\text{C}$. Infrared analysis of zirconia nanotube samples before and after adsorption of methyl orange and the zirconia nanotube samples after decolorization of methyl orange solution were conducted and shown in Fig. 4.

In the infrared spectrum of zirconia nanotubes (Fig. 4a), a broad absorption band at 1110 cm^{-1} illustrates the existence of hydroxyl groups at the surface of zirconia nanotubes. In the infrared spec-

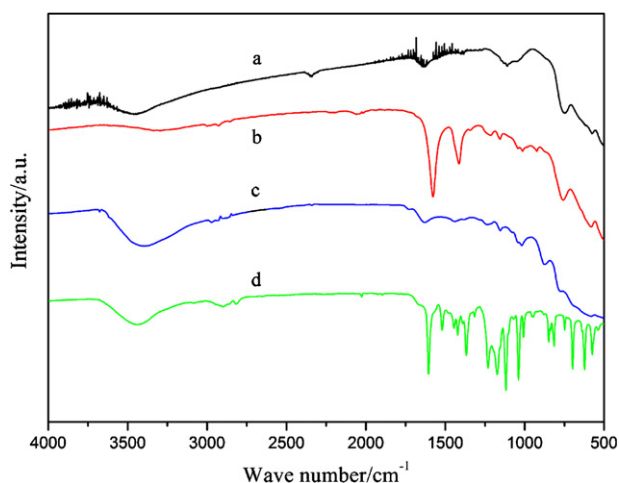


Fig. 4. Infrared spectra analysis of zirconia nanotubes (a), zirconia nanotubes adsorbed with methyl orange (b), zirconia nanotubes after decolorization of methyl orange solution (c), methyl orange (d).

trum of zirconia nanotubes adsorbed with methyl orange (Fig. 4b), relative strength of the absorption peaks changed greatly compared with that of methyl orange (Fig. 4d). Two wide strong absorption peaks at 1578 cm^{-1} and 1414 cm^{-1} , together with the absorption peaks below 1414 cm^{-1} become much weaker in Fig. 4b. The peak positions in Fig. 4b have moved compared with Fig. 4d, which indicates that zirconia nanotubes have strong adsorption effect to methyl orange and result in the change of electric cloud distribution within the molecules. In the infrared spectrum of zirconia nanotubes after decolorization of methyl orange solution (Fig. 4c), there is hardly adsorption peaks at 1578 cm^{-1} and 1414 cm^{-1} , which indicates that the decolorization of methyl orange solution was not due to physical adsorption, but due to degradation of methyl orange.

During the synergistic degradation process of methyl orange, zirconia nanotubes adsorb methyl orange molecules in the solution. Ultrasound can generate strong impact and cavitation effect on the surface of zirconia nanotubes, and then generate HO^\bullet free radical. The HO^\bullet can oxidize the adsorbed methyl orange and result in the degradation of methyl orange [15–17].

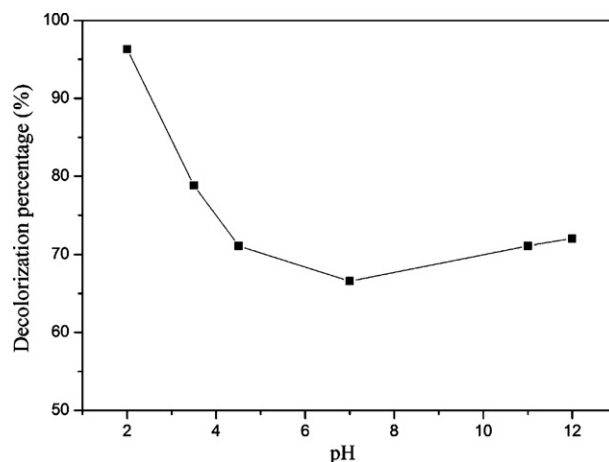


Fig. 5. The influence of pH value on decolorization percentage (C_0 : 20 mg/L, t : 7 h).

3.3. Influential factors of decolorization percentage

The pH value of methyl orange solution has great influence on the decolorization percentage. Fig. 5 shows the influence of pH value on decolorization percentage when reaction time is 7 h and the concentration of methyl orange solution is 20 mg/L. Methyl orange is more easily degraded in acid solution and the decolorization percentage decreases with increase of pH value. In alkaline solution, the decolorization percentage increases slightly with the increase of pH value. When the pH value is 7, the decolorization percentage is the lowest.

There are two main reasons for the strong influence of pH value. On the one hand, surface hydroxyl group of zirconia is acidic to a certain degree and in acidic solution, the surface hydroxyl group exists in the form of $-\text{OH}$, while in alkaline solution, the surface hydroxyl group exists in the form of $-\text{O}^-$. The structure change would affect the adsorption of methyl orange onto zirconia nanotubes.

On the other hand, the molecular structure of methyl orange changes in solution with different pH values. The proportion of azo structure increases with the increase of the solution pH value, and the proportion of quinoid structure increases with the decrease of the solution pH value. According to the experimental results, quinoid structure may be more likely to be degraded.

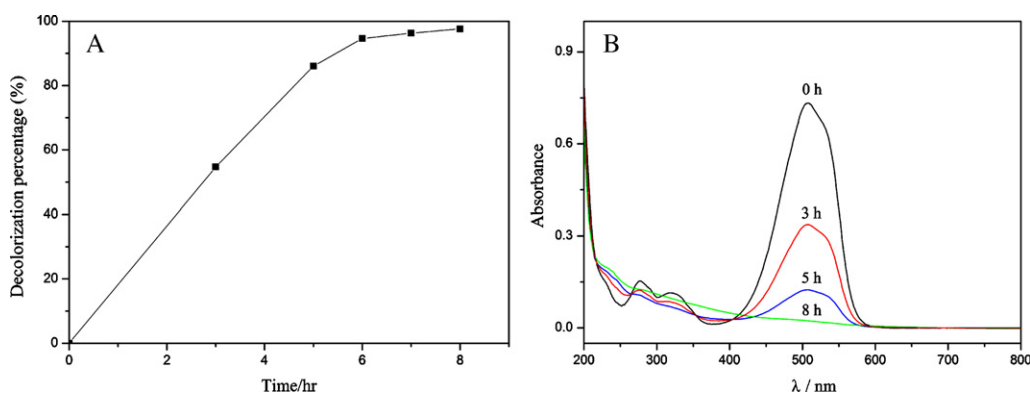
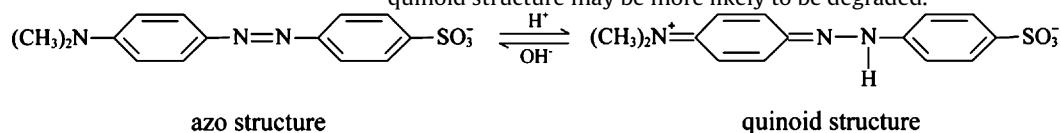


Fig. 6. The influence of decolorization time (C_0 : 20 mg/L, pH: 2.0).

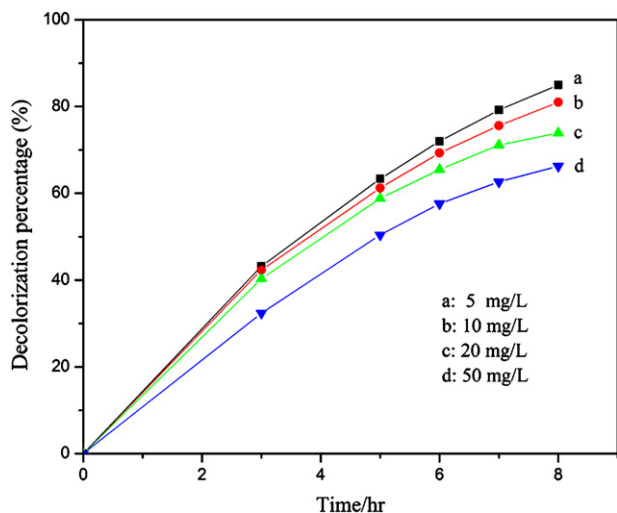


Fig. 7. The influence of solution concentration (pH: 4.5).

Reaction time influenced the decolorization percentage a lot. Fig. 6A shows the decolorization percentage changing curve vs. time when the pH value is 2. The decolorization percentage increases with the extension of time, reaches 94.6% after 6 hours, and increases to 97.6% after 8 h. Fig. 6B gives the UV–vis absorption spectra of original methyl orange solution and methyl orange solution after degradation for 3, 5 and 8 h. Methyl orange has a strong characteristic peak at 510 nm and two weak absorption peaks at 280 nm and 320 nm. These absorption peaks become weak and disappear along with the extension of reaction time while the intensity of absorption peak between 220 nm and 240 nm increases. The UV–vis results indicate that methyl orange was degraded during the process, which is in agreement with the IR analysis.

In addition, decolorization percentage is directly affected by the solution concentration. Under same conditions, the decolorization percentage decreases with the increase of the solution concentration (Fig. 7).

4. Conclusion

Zirconia nanotubes with a length of 25 μm , inner diameter of 80 nm, and wall thickness of 35 nm were prepared by anodization in mixture of formamide and glycerol (volume ratio = 1:1) containing 1 wt% NH_4F and 1 wt% H_2O . Experiments show that zirconia nanotubes and ultrasonic wave had synergistic degradation action for methyl orange and the efficiency of ultrasonic wave increased by more than 7 times. The decolorization percentage of crystallized zirconia nanotubes is higher than that of uncrystallized zirconia nanotubes. The synergistic decolorization percentage was affected by pH value of the solution. In acidic solution the methyl orange was easy to be degraded. When pH value was 2 and the solution concentration was 20 mg/L, the decolorization percentage of methyl orange reached 94.6% after degradation for 6 h

and reached 97.6% after 8 h. Under the same conditions, the decolorization percentage decreases with the increase of the solution concentration.

The synergistic degradation effect of zirconia nanotubes and ultrasonic wave can be ascribed to that the absorption of methyl orange onto zirconia nanotubes would lead to easy degradation of methyl orange through ultrasonic wave.

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 50972036) and Support Program for Hundred Excellent Innovation Talents from the Universities and Colleges of Hebei Province.

References

- [1] A. Rehorek, M. Tauber, G. Gubitza, Application of power ultrasound for azo dye degradation, *Ultrason. Sonochem.* 11 (2004) 177–182.
- [2] J. Hong, H. Emori, M. Otaki, Photodecolorization of azo dyes by extracellular metabolites under fluorescent light and influence of operational parameters, *J. Biosci. Bioeng.* 100 (2005) 192–196.
- [3] I.T. Peternel, N. Koprivanac, A.M.L. Božić, H.M. Kušić, Comparative study of UV/TiO₂, UV/ZnO and photo-Fenton processes for the organic reactive dye degradation in aqueous solution, *J. Hazard. Mater.* 148 (2007) 477–484.
- [4] G. Annadurai, R. Juang, D. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, *J. Hazard. Mater.* 92 (2002) 263–274.
- [5] E. Bae, W. Choi, Highly enhanced photoreductive degradation of perchlorinated compounds on dye-sensitized metal/TiO₂ under visible light, *Environ. Sci. Technol.* 37 (2003) 147–152.
- [6] E. Psillakis, G. Goula, N. Kalogerakis, D. Mantzavinos, Degradation of polycyclic aromatic hydrocarbons in aqueous solutions by ultrasonic irradiation, *J. Hazard. Mater.* 108 (2004) 95–102.
- [7] G. Tezcanli-Guyer, N.H. Ince, Degradation and toxicity reduction of textile dyestuff by ultrasound, *Ultrason. Sonochem.* 10 (2003) 235–240.
- [8] M. Inoue, F. Okada, A. Sakurai, M. Sakakibara, A new development of dyestuffs degradation system using ultrasound, *Ultrason. Sonochem.* 13 (2006) 313–320.
- [9] M.T. Taghizadeh, A. Mehrdad, Calculation of the rate constant for the ultrasonic degradation of aqueous solutions of polyvinyl alcohol by viscometry, *Ultrason. Sonochem.* 10 (2003) 309–313.
- [10] L.A. Rodrigues, L.J. Maschio, R.E. Silva, M.L.C.P. Silva, Adsorption of Cr(VI) from aqueous solution by hydrous zirconium oxide, *J. Hazard. Mater.* 173 (2010) 630–636.
- [11] I.A. Salem, Kinetics of the oxidative color removal and degradation of bromophenol blue with hydrogen peroxide catalyzed by copper(II)-supported alumina and zirconia, *Appl. Catal. B: Environ.* 28 (2000) 153–162.
- [12] H. Tsuchiya, J.M. Macak, L. Taveira, P. Schmuki, Fabrication and characterization of smooth high aspect ratio zirconia nanotubes, *Chem. Phys. Lett.* 410 (2005) 188–191.
- [13] J. Zhao, X. Wang, R. Xu, F. Meng, L. Guo, Y. Li, Fabrication of high aspect ratio zirconia nanotube arrays by anodization of zirconium foils, *Mater. Lett.* 62 (2008) 4428–4430.
- [14] J. Zhao, R. Xu, X. Wang, Y. Li, In situ synthesis of zirconia nanotube crystallines by direct anodization, *Corros. Sci.* 50 (2008) 1593–1597.
- [15] M.M. Tauber, G.M. Gubitza, A. Rehorek, Degradation of azo dyes by oxidative processes—Laccase and ultrasound treatment, *Bioresour. Technol.* 99 (2008) 4213–4220.
- [16] S.N. Nam, S.K. Han, J.W. Kang, H. Choi, Kinetics and mechanisms of the sonolytic destruction of non-volatile organic compounds: investigation of the sonochemical reaction zone using several OH monitoring techniques, *Ultrason. Sonochem.* 10 (2003) 139–147.
- [17] K. Okitsu, K. Iwasaki, Y. Yobiko, H. Bandow, R. Nishimura, Y. Maeda, Sonochemical degradation of azo dyes in aqueous solution: a new heterogeneous kinetics model taking into account the local concentration of OH radicals and azo dyes, *Ultrason. Sonochem.* 12 (2005) 255–262.