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Study of Fe_2O_3/H_2O_2 Fenton-like Oxidation and Mineralization of Anion Surfactant

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Abstract. Fe_2O_3/H_2O_2, a kind of Fenton-like agent, was used to degrade an anion surfactant, sodium dodecyl benzene sulfonate(SDBS)，in an aqueous solution. Through a number of batch degradation experiments under various conditions, it was found that the reactivity of the system increased by increasing temperature. The SDBS degradation ratio will increase by, respectively, increasing H_2O_2 concentration and Fe_2O_3 dosage at some extent, but too high H_2O_2 concentration or Fe_2O_3 dosage will decrease the degradation efficiency. pH value has some influences on the reactivity of the system; from 2 to 10, the system maintains high efficiencies all the time. It also can be seen that Fe_2O_3/H_2O_2 Fenton-like reaction almost has the same efficiency as homogeneous Fenton reaction, while the former has a widely pH range (2-10), and Fe_2O_3 can be separated easily and has no secondary pollutants.

Introduction

Anion Surfactant is a kind of surfactant most common used. It can restrain and kill the microorganisms and restrain the degradation of other organic toxic substances. And it also can bubble at the surface of water to hinder water oxygenate and make water quality worse, even be eutrophication, if it were discharged directly into water body.

Fenton's reagent [$Fe(II)+H_2O_2$], a widely used and studied catalytic treatment system, has been applied to treating various wastes such as those found in the textile and chemical industries[1]. In order to enhance the efficiency of degradation, many methods, such as microwave[2], photo and UV[3,4], electric[5,6], ultrasound[7], etc., were combined with Fenton method. However, in these homogeneous Fenton systems, the catalysts of iron ions are dissolved in water. Although these homogeneous catalysts are generally very efficient for degradation of organic compounds, their separation and reuse are rather difficult at the end of treatment. A kind of secondary pollutants, the ferric ions is generated. The removal of iron ions from the treated water needs a large amount of chemicals and manpower, which will increase the cost of treatment[8].

To overcome this disadvantage, several studies have been conducted to explore heterogeneous catalysts for substitution of deliquescent Fe(II) reagent. Some researchers put mineral-catalyzed Fenton-like system forward to treat organic pollutants. The catalysts used in the Fenton-like system were natural iron-bearing earth materials[9]. The catalyst loaded with irons also has received many attentions. The catalyst loaded with irons can be reused for further runs and extend the range of pH for Fenton oxidant[10-15].

In the present paper, the interest has been focused on the Fenton process for degradation of Sodium dodecyl benzene sulfonate(SDBS)，with Fe_2O_3 as catalyst. The affecting factors, such as temperature, contact time, catalyst dosage, H_2O_2 concentration, were studied.

Experimental

Material and Equipment. Fe_2O_3, H_2O_2(30%), $CHCl_3$, NaOH, HCl, and methylene blue supplied by their manufacturers was all analytical pure.

Degradation methods. Sodium dodecyl benzene sulfonate(SDBS)，a common anion surfactant, and molecular weight of 497.02, was selected as model pollutant. Its structure is show in Figure 1. The SDBS concentrations were measured using a WFZ-UV-2100 type ultraviolet-visible spectrophotometer by methylene blue spectrophotometry. In water solution methylene blue can be combined with SDBS to form blue complex clathrate, which is easily extracted by chloroform, then colorimetric estimated with organic phase (chloroform) at λ of 665nm. The degradation ratio, i.e. the removal degree of SDBS can be calculated using the equation of $\eta=(C_0-C_t)/C_0\times100\%$, where C_0 is the initial concentration of SDBS wastewater and C_t is the concentration at contact time t. In order to check the reproducibility of the results, random tests were done under different experimental conditions.

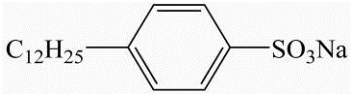

Figure 1 Structure of sodium dodecyl benzene sulfonate

Results and discussion

Influences of Time on SDBS Degradation. Figure 2 shows SDBS degradation ratio changes along with time. The experimental condition is: T=20℃，pH=5，$[SDBS]_0$=40mg/L，$[H_2O_2]_0$=0.588mol/L，$M(Fe_2O_3)$=2g/100ml. It can be seen from figure 2 that the concentration of SDBS decreased very fast at the beginning, then the curve became smooth. 60mins later, the degradation ratio can reach to 90%.

Influences of H_2O_2 Concentration on SDBS Degradation. Figure 3 shows the SDBS degradation ratio versus different H_2O_2 concentration conditions. The experimental condition is: T=20℃，pH=5，t=60min，$[SDBS]_0$=40mg/L，$M(Fe_2O_3)$=6g/100ml. The data indicate that the SDBS degradation ratio dose not increase with the H_2O_2 concentration increasing, which suggests more H_2O_2 concentration doesn't lead to higher degradation ratio. It is because that too more H_2O_2 will react with·OH, which is really effective in the process of degrading SDBS. The Fenton process involves the reactions are as below[16]:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HOO\cdot \qquad k_1=0.01\sim0.02 M^{-1}s^{-1} \qquad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + \cdot OH \qquad k_2=76 M^{-1}s^{-1} \qquad (2)$$

$$Fe^{3+} + HOO\cdot \rightarrow Fe^{2+} + H^+ + O_2 \qquad k_3=1.2\times10^6\ M^{-1}s^{-1} \qquad (3)$$

$$Fe^{2+} + \cdot OH \rightarrow Fe^{3+} + OH^- \qquad k_4=3.2\times10^8\ M^{-1}s^{-1} \qquad (4)$$

$$H_2O_2 + \cdot OH \rightarrow H_2O + HOO\cdot \qquad k_5=3.3\times10^7\ M^{-1}s^{-1} \qquad (5)$$

$$\cdot OH + \text{organics} \rightarrow \text{intermediates} \rightarrow CO_2+H_2O \qquad k_6=10^7\sim10^{10}\ M^{-1}s^{-1} \qquad (6)$$

From the reactions, we can see that too more H_2O_2 will react with·OH, which is really effective in the process of degrading SDBS. So, the adequate H_2O_2 concentration leads to higher system reactivity.

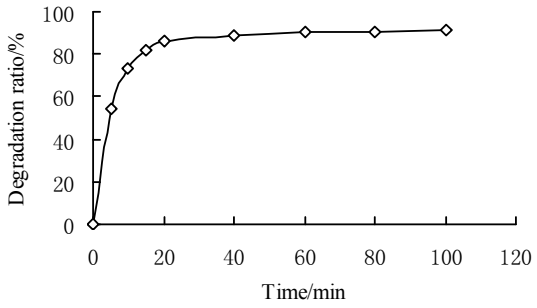

Figure 2 Effect of time on the SDBS degradation

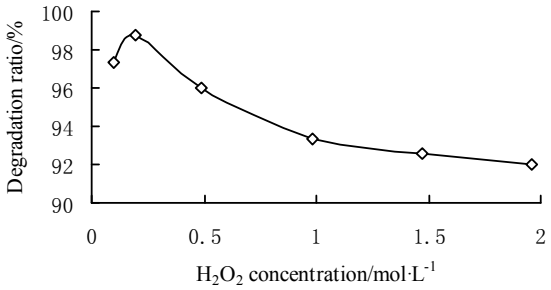

Figure 3 Effect of hydrogen peroxide concentrations on the SDBS degradation

Influences of Fe_2O_3 Catalyst Dosage on SDBS Degradation. The experimental condition of figure 4 is: T=20℃，t=60min，pH=5，$[SDBS]_0$=40mg/L，$[H_2O_2]_0$=0.588mol/L。Figure 4 suggests that it was not that the more the catalyst, the higher the degradation ratio. And 6g/100ml was a optimum dosage. The more active Fe sites on the catalyst surface for accelerating the decomposition of H_2O_2, and more Fe ion leaching in the solution, leading to an increase in the number of OH radicals. But too more catalyst will not help to produce more OH radicals, for H_2O_2 dosage is not change.

Influences of pH Value on SDBS Degradation. Figure 5 shows that at the adopted experimental conditions there is a dependence of the system reactivity upon the pH of the solution. The behavior of SDBS degradation is different at acidic, neutral and alkaline pH. At faintly acidic and neutral pH (5 and 6), the SDBS degradation ratios are higher than those at acidic and alkaline pH (2, 4, 8 and 10). However, the SDBS degradation ratios can reach to above 85% within 60 min at every pH value we adopted. The Fe_2O_3 catalyst can extend the range of pH for Fenton oxidant.

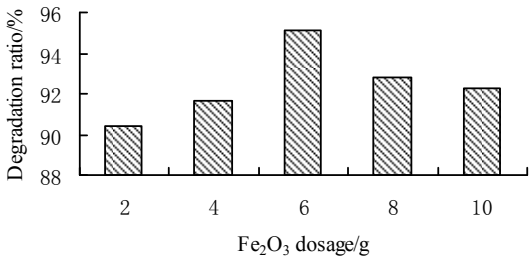

Figure 4 Effect of Fe_2O_3 dosage on the SDBS degradation with H_2O_2

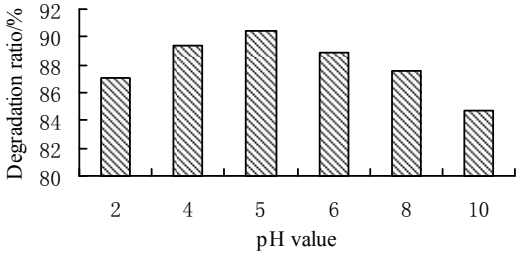

Figure 5 Effect of pH on the SDBS degradation

Influences of Temperature on SDBS Degradation. The effect of reaction temperature on the degradation of SDBS was studied, and the results are presented in Figure 6. The reactivity of the system increases by increasing reaction temperature. This is because faster catalysis of H_2O_2 at a higher temperature results in the increase in the number of OH radicals. Another possible reason put forward to interpret this phenomenon is that a higher temperature can provide more energy for the reactant molecules to overcome reaction activation energy.

Comparative experiment. Fe_2O_3-catalyzed Fenton-like reaction was compared with homogeneous Fenton reaction (Fe^{2+}/H_2O_2), and the result is shown in Figure 7. The experimental condition is: (1) both H_2O_2 and Fe_2O_3 (T=20℃, pH=5, $[SDBS]_0$=40mg/L, $[H_2O_2]_0$=0.392mol/L and Fe_2O_3 dosage=2g/100ml)and (2) both H_2O_2 and Fe^{2+} (T=20 ℃, pH=3, $[SDBS]_0$=40mg/L, Fe^{2+}/H_2O_2=1/5). It can be seen that Fe_2O_3-catalyzed Fenton-like reaction almost has the same efficiency as homogeneous Fenton reaction, while the former has a widely pH range, and Fe_2O_3 catalyst can be reused and has no secondary pollutants.

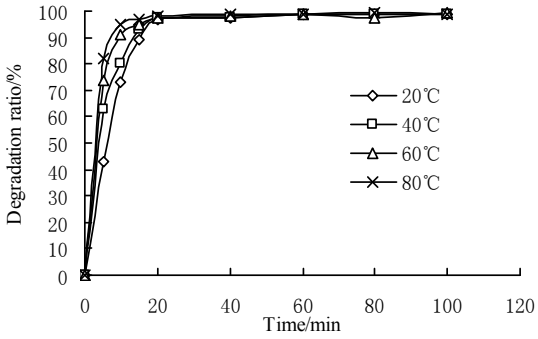

Figure 6 Effect of reaction temperature on the SDBS degradation

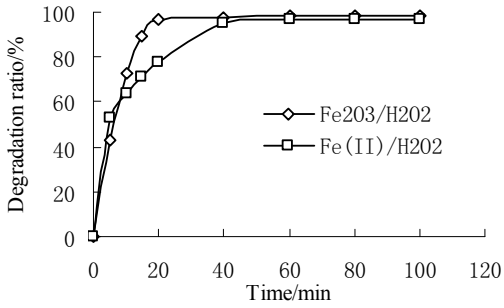

Figure 7 Comparative analyses for the SDBS degradation ratios under different contact time

Conclusions

Sodium dodecyl benzene sulfonate (SDBS) in an aqueous solution can be effectively degraded by Fe_2O_3-catalyzed Fenton-like system in the presence of H_2O_2. A number of batch degradation experiments under various conditions strongly indicated that: (1) The reactivity of the system increased by, respectively, increasing Fe_2O_3 dosage and H_2O_2 starting concentration at some extent, and decreased beyond the extant; (2) pH value will influence reactivity of the system, but not too much. From 2 to 10, the system maintains high efficiencies (above 85%) all the time; (3) The degradation ratio and speed of SDBS increased along with increasing temperature; (4) Through experiments, the optimum condition can be obtained that H_2O_2 concentration is 0.196mol/L, contact time is 60min, Fe_2O_3 dosage is 6g/100ml, solution pH is 5 and temperature is 80℃. Under the optimum condition, the degradation ratio can come up to 99%. Compared with homogeneous Fenton′s reagent, due to unique advantages of easy separation of heterogeneous catalyst from the treated wastewater, high catalytic reactivity at a wider pH range and lower H_2O_2 concentration, repeating usage and absence of secondary pollutants, Fe_2O_3 catalyzed Fenton-like system would be a promising method for degradation of hard-to-degrade organic wastewater.

Acknowledgements

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References

[1]YU HuanYan, Murari PRASAD, HE XiuLan, SHAN LianWei, QI ShuYan, 2009. Discoloration of Rhodamine B dyeing wastewater by schorl-catalyzed Fenton-like reaction. Sci. in China Series E: Technol. Sci. 52(10),3054-3060

[2]J. Sanz, J. I. Lombrana, A.M. De Luis, M. Ortueta, F. Varona, 2003. Microwave and Fenton's reagent oxidation of wastewater. Environ. Chem. Lett., 1, 45-50

[3]Moraes, J.E.F., Quina, F.H., Nascimento, C.A.O., Silva, D.N., Chiavone Filho, O., 2004. Treatment of saline wastewater contaminated with hydrocarbons by the photo-Fenton process. Environ. Sci. Technol. 38, 1183-1187

[4]Panagiotis Bouras, Panagiotis Lianos., 2008. Synergy Effect in the Combined Photodegradation of an Azo Dye by Titanium dioxide Photocatalysis and Photo-Fenton Oxidation. Catal. Lett. 123, 220-225

[5]Anna Da Pozzo, Paola Ferrantelli, Carlo Merli, Elisabetta Petrucci, 2005. Oxidation efficiency in the electro-Fenton process. J. Appl. Electrochem. 35, 391-398

[6]G. R. Agladze, G. S. Tsurtsumia, B.I. Jung, J. S. Kim, G. Gorelishvili., 2007. Comparative study of chemical and electrochemical Fenton treatment of organic pollutants in wastewater. J. Appl. Electrochem. 37, 985-990

[7]Jun Liang, Sergey Komarov, Naohito Hayashi, Eiki Kasai, 2007. Recent trends in the decomposition of chlorinated aromatic hydrocarbons by ultrasound irradiation and Fenton's reagent. J. Mater. Cycles. Waste Manag. 9, 47-55

[8]Cheng, M., Ma,W., Li, J., Huang, Y., Zhao, J., Wen, Y.X., Xu, Y., 2004. Visible-light-assisted degradation of dye pollutants over Fe(III)-loaded resin in the presence of H_2O_2 at neutral pH values. Environ. Sci. Technol. 38, 1569-1575.

[9]Matta R, Hanna K, Chiron S. 2007, Fention-like oxidation of 2,4,6-trinitrotoluene using different iron minerals. Sci. Total Environ., 385: 242-251.

[10]B. Muthukumari, K. Selvam, I. Muthuvel, M. Swaminathan. 2007. Photoassisted hetero-Fenton mineralization of azo dyes by Fe(II)-Al_2O_3 catalyst, J. Chem. Eng.,153: 9-15.

[11]Feng, J., Hu, X., Yue, P.L., 2004a. Novel bentonite clay-based Fenanocomposite as a heterogeneous catalyst for photo-Fenton discoloration and mineralization of Orange II. Environ. Sci. Technol. 38, 269-275.

[12]Feng, J., Hu, X., Yue, P.L., 2004b. Discoloration and mineralization of Orange II using different heterogeneous catalysts containing Fe: a comparative study. Environ. Sci. Technol. 38, 5773-5778

[13]Jianxin Chen, Lizhong Zhu. 2006, Catalytic degradation of Orange II by UV-Fenton with hydroxyl-Fe-pillared bentonite in water. Chemosphere., 65: 1249-1225.

[14]Jianxin Chen, Lizhong Zhu. 2010, Oxalate enhanced mechanism of hydroxyl-Fe-pillared bentonite during the degradation of Orange II by UV-Fenton process. J. Hazard. Mater., doi:10.1016/j.jhazmat.2010.10.071

[15]Tania R. Giraldi, Cezar C. Arruda, Geraldo M. da Costa, Elson Longo, Caue Ribeiro. 2009, Heterogeneous Fenton reactants: a study of the behavior of iron oxide nanoparticles by the polymeric precursor method. J. Sol-Gel Sci. Technol., 52:299-303

[16]Shou-Qing Liu, Shi Cheng, Lian-Rong Feng, Xiao-Mei Wang, Zhi-Gang Chen. 2010, Effect of alkali cations on heterogeneous photo-Fenton process mediated by Prussian blue colloids. J. Hazard. Mater., 182:665-671