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The investigation on ultrasonic degradation of acid fuchsine in the presence of ordinary and nanometer rutile TiO_2 and the comparison of their sonocatalytic activities

Jun Wang [a,*], Zhijun Pan [a], Zhaohong Zhang [b], Xiangdong Zhang [a], Yuefeng Jiang [a], Teng Ma [a], Fuyu Wen [a], Ying Li [a], Peng Zhang [a]

[a] *Department of Chemistry, Liaoning University, Shengyang 110036, PR China*
[b] *Department of Environment, Liaoning University, Shengyang 110036, PR China*

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Abstract

The ordinary and nanometer rutile titanium dioxide (TiO_2) powders were used as sonocatalysts for the degradation of acid fuchsine. A variety of factors affecting sonocatalytic degradation in the presence of ordinary and nanometer rutile TiO_2 were studied. The experimental results indicated that the degradation ratios of acid fuchsine in the presence of ordinary and nanometer rutile TiO_2 powders were much better than one without any TiO_2 under onefold ultrasonic irradiation. For ordinary and nanometer rutile TiO_2 powders, the sonocatalytic ability of ordinary rutile TiO_2 powder was more apparent than that of the nanometer rutile TiO_2 powder. The best degradation ratio of acid fuchsine can be obtained at the ultrasonic irradiation of 40 kHz frequency and 50 W power, 500 mg/L TiO_2 adding amount, pH = 3.0 and 20 mg/L acid fuchsine as the initial concentration. The experimental results indicated that the method of sonocatalytic degradation of organic pollutants in the presence of TiO_2 powder was an advisable choice for treating organic wastewaters for non- or low-transparent and fuscous dye wastewater.

Keywords: Sonocatalytic degradation; Acid fuchsine; Rutile titanium dioxide (TiO_2); Ordinary; Nanometer

1. Introduction

Because the structures of the organic dye compounds in common wastewaters ordinarily contain one or several benzene rings, these organic pollutants cannot be decomposed easily in traditional chemical and biological treatment methods [1–3]. In recent years, the method of photocatalytic degradation has been proposed to treat these dye wastewaters in the presence of ordinary or nanometer anatase titanium dioxide (TiO_2) powder as the photocatalyst all along and showed greatly obvious and satisfactory effects [4–9]. The semiconductor materials such as TiO_2 and ZnO can produce electron-cavity pairs having strong reduction and oxidation abilities under the irradiation of ultraviolet rays. These electron-cavity pairs can bring a series of reduction–oxidation reaction, which can destruct almost all organic pollutants [10–12]. However, as known to all, the penetrating ability of any light except X-ray into non- or low-transparent and fuscous dye wastewater is quite low, and the penetrating depth is only several millimeters. Hence, the utilization efficiency of ultraviolet light in photocatalytic degradation reaction is very low for those dye wastewaters. Fortunately, it was found that the penetrating ability of ultrasound is very strong for any water medium; the penetrating depth can reach up to 15–20 cm. Moreover, the ultrasound can usually be competent for catalyzing those chemical reactions that the ultraviolet and visible lights catalyze [13,14].

* Corresponding author. Tel.: +86 24 81917150; fax: +86 24 62202380.
E-mail addresses: wangjun890@126.com, wangjun890@sina.com (J. Wang).

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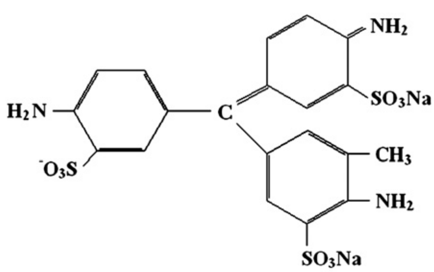
It has been reported that the sonocatalytic activities of TiO_2 powder are very obvious during the mineralization treatment of organic pollutants [15]. In this paper, the ultrasound with low frequency (20–80 kHz) and low power (30–50 W) was utilized as the irradiation source instead of ultraviolet light and the acid fuchsine as a model compound was treated in the presence of TiO_2 powder as sonocatalyst. Synchronously, the various affecting factors were studied on the sonocatalytic degradation of acid fuchsine and the sonocatalytic activities of ordinary and nanometer rutile TiO_2 powders were compared. The results indicated that the degradation effects of acid fuchsine in the presence of ordinary rutile TiO_2 powder were better than in the presence of nanometer rutile TiO_2 powder and without any TiO_2 catalyst. The method of sonocatalytic degradation has many advantages such as convenience, safety, economy and high efficiency, so this method has a better prospect in application.

2. Experimental

2.1. Materials

Acid fuchsine as a model compound was purchased from Shanghai Sanaisi Reagent Corporation. Water purified by a Milli-Q water system (Millipore) was used throughout the experiment. The TiO_2 powders (ordinary and nanometer rutile, Haerbin Chemistry Reagent Company, China) were used as sonocatalysts.



Structure of Acid fuchsine

2.2. Apparatus

Lambda-17 UV–vis spectrometer (Perkin–Elmer Company, US) and NMR (Varian Company, US) were used to inspect the sonocatalytic degradation processes of acid fuchsine. KQ-100 Controllable Serial-Ultrasonics apparatus (Kunshan Apparatus Company, China) was adopted to irradiate the solution of acid fuchsine and operated at ultrasonic frequency of 20–80 kHz and output power of 30–50 W through manual adjusting.

2.3. Procedure

The prepared acid fuchsine solution (20 mg/L) and (ordinary and nanometer rutile) TiO_2 powders (50 mg/L) were put into a self-made glass reactor (bottom area = 50 cm^2), the pH value was adjusted at 5.0, the ultrasound of 40 kHz frequency and 50 W output power was utilized to irradiate this mixed solution. After 60 min of ultrasonic irradiation, the UV–vis spectra were determined by UV–vis spectrophotometer in the wavelength range from 200 to 800 nm. In order to compare the degradation effects, the UV–vis spectra of the original and treated acid fuchsine solutions by onefold ultrasonic irradiation were also given as shown in Fig. 1. The maximal absorbencies of 10–50 mg/L acid fuchsine solutions abide by Lambert–Beer's law and the calibration curve of standard acid fuchsine solution is used to estimate the degradation ratio of acid fuchsine. The degradation ratio of acid fuchsine at intervals of 30 min within 180 min is shown in Fig. 2. Table 1 gives the relation of $-\ln([A]_t/[A]_0)$ or $1/[A]_t$ with the ultrasonic irradiation time, which can infer the reaction kinetics of the degradation process. The influences of initial concentrations (10–40 mg/L) of acid fuchsine, adding amounts (0–1000 mg/L) of TiO_2 powders, the initial pH (3–9) of acid fuchsine solution, reaction temperature (20–60 °C) and ultrasonic power (20–50 W) on the degradation of acid fuchsine were studied in this paper. These results are shown in Figs. 3–7, respectively. For validating the sonocatalytic activities of TiO_2 powders, the ^1H NMR spectra of the original and treated acid fuchsine solution in the presence of ordinary rutile TiO_2 powder under 60 min ultrasonic irradiation were also determined by NMR spectrophotometer as shown in Fig. 8. At last, for reviewing the sonocatalytic activities of reused TiO_2 powders, the degradation ratio of acid fuchsine in the presence of reused nanometer rutile TiO_2 powders within 60 min was also investigated and the results are shown in Fig. 9. All confirmed conditions were used throughout the experiment if there was no special demonstration.

3. Results and discussion

3.1. The UV–vis spectra of acid fuchsine

It could be found from Fig. 1 that the degradation extent of acid fuchsine in the presence of ordinary rutile TiO_2 powder was better than the ones in the presence of nanometer rutile TiO_2 powder and in the absence of any TiO_2 catalyst with

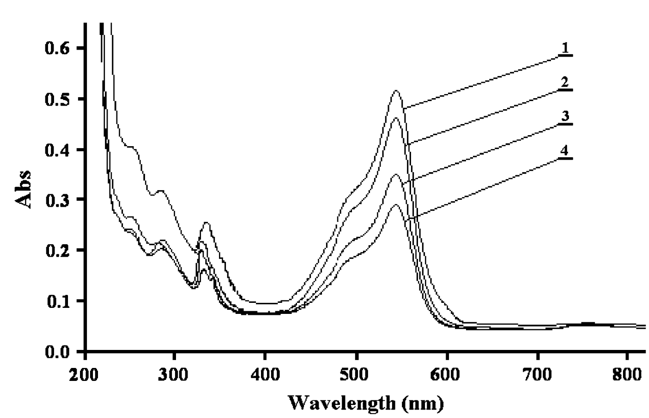


Fig. 1. UV–vis spectra of acid fuchsine. 1: Original solution; 2: only ultrasound; 3: ultrasound + nanometer rutile TiO_2; and 4: ultrasound + ordinary rutile TiO_2.

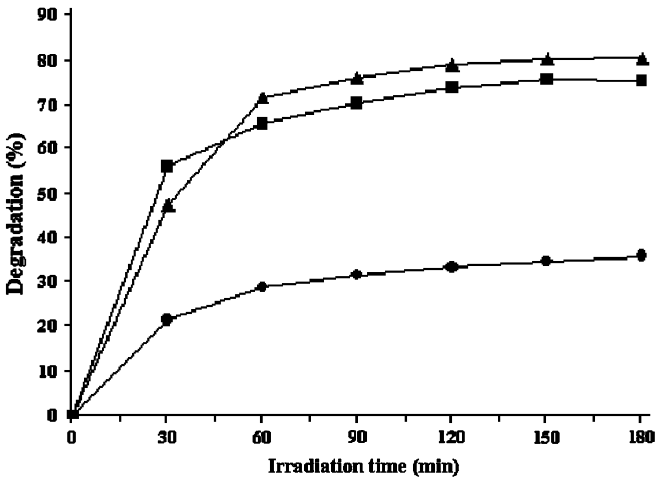


Fig. 2. Influence of irradiation time on degradation ratio. ▲: Ultrasound + ordinary rutile TiO_2; ■: ultrasound + nanometer rutile TiO_2; and ●: only ultrasound.

onefold ultrasonic irradiation and the order of degradation extents in three courses is ordinary rutile TiO_2, nanometer rutile TiO_2 and onefold ultrasonic irradiation. All results indicate that the TiO_2 powders have obvious sonocatalytic abilities for the degradation of acid fuchsine.

3.2. Effect of irradiation time on the degradation of acid fuchsine

The change of degradation ratios with ultrasonic irradiation time was reviewed for the mixed solution of 20 mg/L acid fuchsine and 50 mg/L TiO_2 (ordinary and nanometer) powders and the unmixed acid fuchsine solution without any TiO_2 powder under the ultrasonic irradiation of 40 kHz and 50 W. It can be observed from Fig. 2 that the degradation ratios of all the three courses increase gradually along with ultrasonic irradiation time, but the degradation ratios of acid fuchsine in the presence of ordinary and nanometer rutile TiO_2 powders are considerably higher than that of onefold ultrasonic irradiation. These results indicate that the degradation effects of acid fuchsine in the presence of TiO_2 (ordinary and nanometer rutile) catalysts combining with ultrasound are more obvious than that of using onefold ultrasound. In addition, as known to all, the catalytic activity of nanometer TiO_2 powder as a photocatalyst is remarkably much better than that of ordinary TiO_2 powder in the photocatalytic degradation of organic pollutants. However, for this work, at the beginning, the sonocatalytic activity of nanometer rutile TiO_2 powder is higher than that of ordinary rutile TiO_2 powder as with any familiar photocatalytic degradation, while it can be seen from Fig. 2 that their activities interconvert each other at 45 min of ultrasonic irradiation. Afterwards, the degradation ratios of acid fuchsine in the presence of ordinary TiO_2 catalyst become higher than the one in the presence of nanometer rutile TiO_2 catalyst at all times.

In addition, in order to infer the kinetics of the process of degradation, the data of $-\ln([A]_t/[A]_0)$ for first-order reaction and $1/[A]_t$ for second-order reaction according to irradiation time are all given in Table 1 for the three courses. It was thought that the degradation reaction of acid fuchsine should be a first-order kinetics reaction.

3.3. Effect of initial concentration on the degradation of acid fuchsine

A series of acid fuchsine solutions with different initial concentrations ranging from 10 mg/L to 40 mg/L were used for studying the influence on the degradation ratio of acid fuchsine. As shown in Fig. 3, the degradation ratios of acid fuchsine in all the three courses decrease with increasing concentration of acid fuchsine. And the degradation effects in presence of ordinary rutile TiO_2 is better than the ones of nanometer rutile TiO_2 and onefold ultrasound throughout in all experimental concentration ranges.

3.4. Effect of TiO_2 adding amount on the degradation of acid fuchsine

In order to optimize the adding amount of TiO_2 catalyst used for the highest degradation ratio of acid fuchsine, the researches about different adding amounts of TiO_2 powders were carried out under the ultrasonic irradiation of 40 kHz for 20 mg/L acid fuchsine solution. The degradation ratios of acid fuchsine in the presence of ordinary and nanometer rutile TiO_2 catalysts show similar change of trend in the range of TiO_2 adding

Table 1
Estimation of reaction kinetics of degradation process

Irradiation time (min)		0	30	60	90	120	150	180
Only ultrasound	$[A]_t$	0.528	0.404	0.376	0.362	0.352	0.346	0.339
	$-\ln([A]_t/[A]_0)$	0	0.268	0.340	0.377	0.405	0.423	0.443
	$1/[A]_t$	1.894	2.745	2.725	2.762	2.841	2.890	2.950
Ordinary rutile TiO_2	$[A]_t$	0.528	0.234	0.151	0.123	0.11	0.102	0.095
	$-\ln([A]_t/[A]_0)$	0	0.814	1.252	1.457	1.569	1.644	1.715
	$1/[A]_t$	1.894	4.274	6.623	8.130	9.091	9.804	10.526
Nanometer rutile TiO_2	$[A]_t$	0.528	0.210	0.181	0.157	0.139	0.135	0.130
	$-\ln([A]_t/[A]_0)$	0	0.922	1.07	1.213	1.335	1.364	1.402
	$1/[A]_t$	1.894	4.762	5.525	6.369	7.194	7.407	7.692

Standard curve equation of acid fuchsine: $A = 0.0211C$.

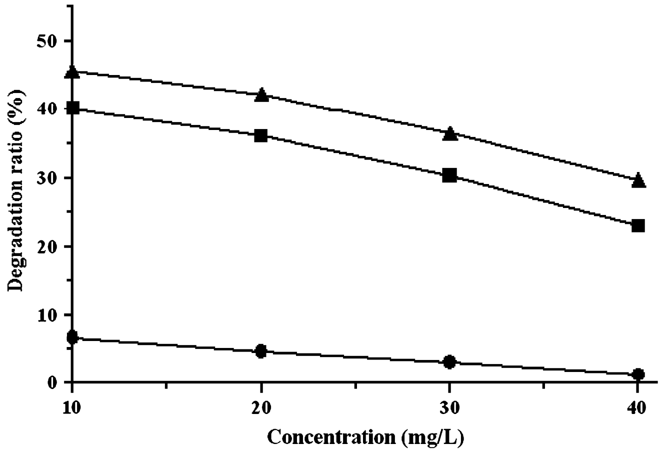


Fig. 3. Influence of initial acid fuchsine concentration on degradation ratio. ▲: Ultrasound + ordinary rutile TiO_2; ■: ultrasound + nanometer rutile TiO_2; and ●: only ultrasound.

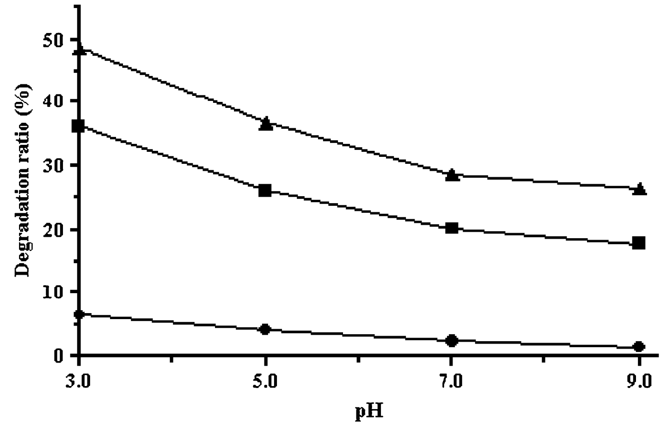


Fig. 5. Influence of changing pH value on degradation ratio. ▲: Ultrasound + ordinary rutile TiO_2; ■: ultrasound + nanometer rutile TiO_2; and ●: only ultrasound.

amounts starting from 250 mg/L to 1000 mg/L. The degradation ratios become high along with the increase in TiO_2 catalysts at low TiO_2 adding amount and then begin to decline, so the best degradation ratio appears at about 500 mg/L as shown in Fig. 4.

3.5. Effect of acidity on the degradation of acid fuchsine

The influences of acidities on the sonocatalytic degradation of acid fuchsine were studied in the range between pH = 3.0 and 9.0, the results are shown in Fig. 5. It was found that the degradation ratios of acid fuchsine in the presence of ordinary and nanometer rutile TiO_2 powders fleetly decrease with the increase in pH values, while it slowly declines under onefold ultrasonic irradiation. Hence, the treatment of some organic pollutants like acid fuchsine in molecular structure adopting sonocatalytic degradation method should be performed in slightly high acidic medium in order to obtain the perfect degradation ratio.

In general, for most organic compounds the degradation ratios increase with pH value increasing in the photocatalytic degradation reaction in the presence of TiO_2 powders. It is because the •OH radicals are easily produced when the cavities capture electron from OH^- anion in basic medium. However, the negative charges exist generally on the surfaces of TiO_2 particles when the pH values are higher than the isoelectric point (about 6.8) of TiO_2, the positive charges appear when the pH values are lower than the isoelectric point of TiO_2. The acid fuchsine with three sulfonic groups ionize effortlessly in liquid solution and is negatively charged. The acid fuchsine anions are adsorbed in high acidic medium by TiO_2 particles with positive charges on the surface and then decomposed by the cavities of TiO_2 particles directly or indirectly. Hence, the reason for the high degradation ratio can be explained by the effect of the distribution of positive charges on the surface of TiO_2 particles.

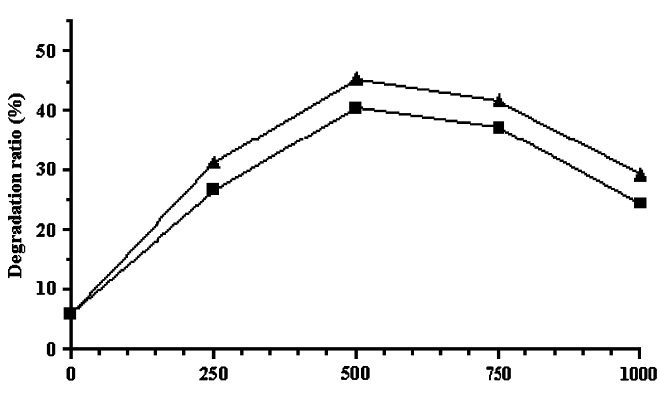


Fig. 4. Influence of TiO_2 adding amount on degradation ratio. ▲: Ultrasound + ordinary rutile TiO_2 and ■: ultrasound + nanometer rutile TiO_2.

3.6. Effect of temperature on the degradation of acid fuchsine

The effect of temperature in reaction system on the degradation of acid fuchsine was discussed in the range of 20–60 °C, the results are shown in Fig. 6. It was found that the degradation ratios of acid fuchsine all increase rapidly with the temperature heightening in the presence of ordinary and nanometer rutile

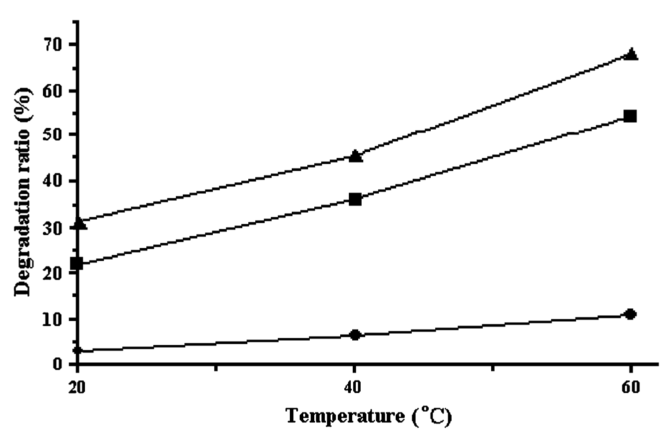


Fig. 6. Influence of temperature on degradation ratio. ▲: Ultrasound + ordinary rutile TiO_2; ■: ultrasound + nanometer rutile TiO_2; and ●: only ultrasound.

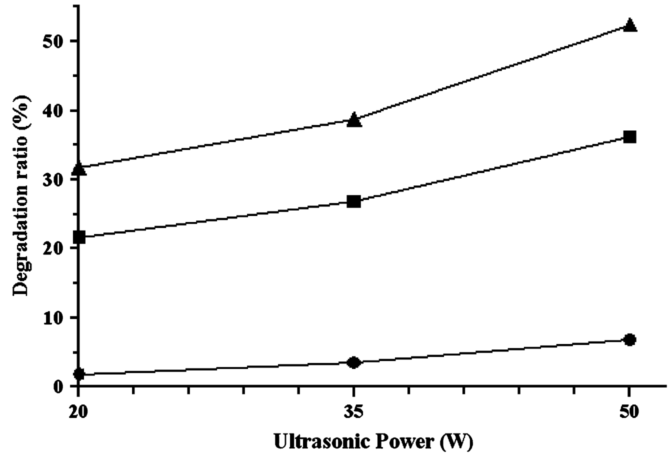


Fig. 7. Influence of ultrasonic power on degradation ratio. ▲: Ultrasound + ordinary rutile TiO_2; ■: ultrasound + nanometer rutile TiO_2; and ●: only ultrasound.

TiO_2 powders as well as in the absence of any TiO_2 catalyst with onefold ultrasonic irradiation. The degradation ratios increase from 31.2% to 65.8% and from 21.3% to 54.6% for ordinary and nanometer rutile TiO_2 powders, respectively, when the temperature rises from 20 °C to 60 °C, while the degradation ratio in the case of onefold ultrasonic irradiation increases from 3.7% to 11.3% in the same conditions.

In general, the reaction between organic pollutants and $^{\bullet}OH$ radicals does not depend on the change of temperature. Otherwise, the high temperature in aqueous solution goes against the production of $^{\bullet}OH$ radicals because of the escape of gas and vapor bubbles. Hence, in this experiment it can be inferred that the acid fuchsines in aqueous solution are mainly decomposed by the cavities on the surface or in the inner of TiO_2 particles by the ultrasonic irradiation.

3.7. Effect of ultrasonic power on the degradation of acid fuchsine

The research results shown in Fig. 7 indicate that degradation ratios of acid fuchsine increased gradually along with the increasing of ultrasonic power from 20 to 50 W. Moreover, the

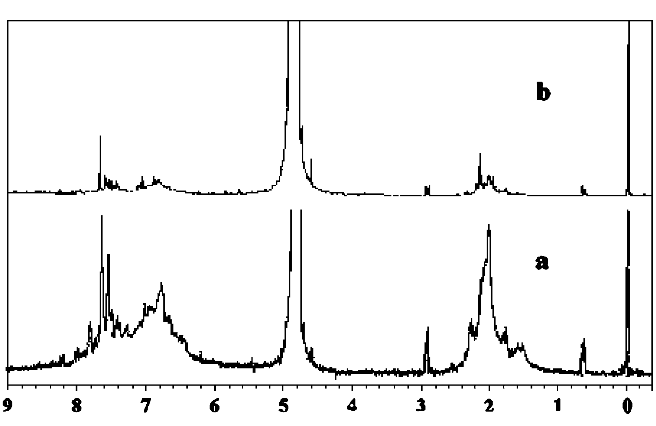


Fig. 8. ^1H NMR spectra of acid fuchsine under ultrasonic irradiation. a: 0.0 min and b: 40.0 min.

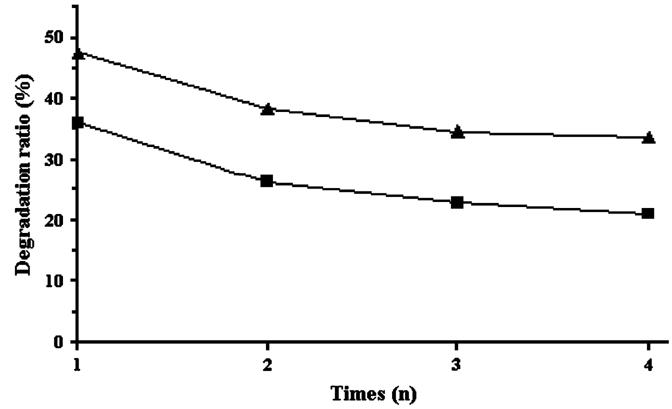


Fig. 9. Influence of reused times on degradation ratio. ▲: Ultrasound + ordinary rutile TiO_2 and ■: ultrasound + nanometer rutile TiO_2.

degradation ratio in the presence of ordinary rutile TiO_2 powder is higher than the ones in the presence of nanometer rutile TiO_2 powder and in the absence of any TiO_2 catalyst with only ultrasonic irradiation.

3.8. The ^1H NMR spectra of acid fuchsine

In addition, in order to explore the degradation mechanism and search the intermediate products of acid fuchsine under ultrasonic irradiation in the presence of ordinary rutile TiO_2 powder, the determination of ^1H nuclear magnetic resonance (^1H NMR) at different moments was conducted. It is a pity that the evidences of intermediate products were not found markedly after 40 min of ultrasonic irradiation as shown in Fig. 8. There are probably two aspects that can account for this fact. Firstly, the accumulative amount of the intermediate products is too low to be found; secondly, once the acid fuchsine molecules in aqueous solution touch the surface of TiO_2 particles, they are immediately oxidated and then decomposed completely by the cavities on the surface or inner of TiO_2 particles.

3.9. Sonocatalytic activity of reused TiO_2 catalyst

As known to all, the important one for any catalyst is recycle, so the sonocatalytic activities of reused TiO_2 powder were studied. It was found that in the high acidic condition, the used TiO_2 catalyst can be separated easily from the solution, so it was washed out and heated at 120 °C and then reused in new experiments with fresh acid fuchsine solution. Fig. 9 showed that in the second experiment the sonocatalytic activity of TiO_2 catalyst became lower than the first time. But the declined extents after second use became small, in short, the reused TiO_2 catalyst retained its sonocatalytic activity to a greater or lesser extent.

4. Conclusion

The acid fuchsine in aqueous solution can be obviously degraded by the sonocatalytic reaction in the presence of both ordinary and nanometer rutile TiO_2 powders, but the sonocatalytic activity of ordinary rutile TiO_2 powder is better than that of nanometer rutile TiO_2 powder. Especially, the research results demonstrated the feasibilities of the method combining ultrasound with TiO_2 catalyst for treating non- or low-transparent wastewaters containing concentrated dye. The optimal degradation for a high degradation ratio of acid fuchsine is considered to be initial concentration of 20 mg/L acid fuchsine, adding amount of 500 mg/L ordinary rutile TiO_2 powder, ultrasonic irradiation of 50 W output power and 40 kHz frequency, pH = 3.0 and 40 °C. In addition, the TiO_2 powder as sonocatalyst can be reused through simple heat treatment. Hence, the research results indicate that this method has a perfect foreground.

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