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Sonocatalytic degradation of methyl orange in the presence of (nanometer and ordinary) anatase TiO_2 powders

WANG Jun*, GUO Bao-dong, ZHANG Zhao-hong, ZHANG Xiang-dong, WU Jing, LI Hong

(Department of Chemistry, Liaoning University, Shenyang 110036, China. E-mail: wangjun890@sina.com)

Abstract: The nanometer and ordinary anatase titanium dioxide(TiO_2) powders were adopted as the sonocatalysts for the degradation of methyl orange used as a model compound for the first time. It was found that the sonocatalytic degradation effect of methyl orange in the presence of TiO_2 powder were much better than that without TiO_2, but the sonocatalytic activity of the nanometer anatase TiO_2 particle was obviously higher than that of ordinary anatase TiO_2 particle. Although there are many factors influencing sonocatalytic degradation of methyl orange, the experimental results showed that the best degradation ratio of methyl orange could be obtained when the experimental conditions were: initial concentration 15 mg/L, nanometer anatase TiO_2 adding amount 750 mg/L, ultrasonic frequency 40 kHz, output power 50 W, pH = 3.0 and temperature 40℃ within 150 min. In addition, the catalytic activity of reused nanometer anatase TiO_2 catalyst was also studied and found to decline gradually comparing with initial nanometer anatase TiO_2 catalyst. All experiments indicated that the method of the sonocatalytic degradation of organic pollutants in the presence of TiO_2 powder was an advisable choice for non- or low-transparent organic wastewaters.

Keywords: titanium dioxide(TiO_2); sonocatalytic degradation; methyl orange; nanometer anatase; ordinary anatase

Introduction

In China even in all the world, the printing and dying industry create huge economy wealth and meet people need but the corresponding global environmental pollution also poses potential threat to environment (Daneshvar, 2004; Helena, 2003). The wastewaters from printing and dying process contain amounts of toxic substances that cannot be easily destroyed due to their stable conformation (Sarria, 2003; López, 2002). So conventional chemical and biological methods(Germán, 2004; Jin, 2001; Zhe, 2001) are not effective to treat the wastewaters. Recently, the technology of photocatalytic degradation has been proposed to treat organic wastewaters in the presence of anatase TiO_2 catalyst because of its good catalytic activity, a great achievement has been made during the practical application (Burrows, 2002; Siham, 2002; Zhang, 2003; Yao, 2004). However, it was also found that the method of photocatalytic degradation was not applicable to treat dye wastewaters with high chroma. The reason is that the penetration abilities of the lights used in the photocatalitic reaction for non-transparent and fuscous dye wastewaters are limited and the penetration depth is only several millimeters. In addition, the wavelength of the light treating wastewaters must be below 375 nm since the energy band gap (E_g) of anatase TiO_2 particle is about 3.2 eV (Gericher, 1979; Kormann, 1988). If the ultraviolet as well as visible lights are used for treating dye wastewaters integrating with TiO_2 catalyst, the utilization efficiency of light is quite low. But it can avoid these disadvantages to adopt ultrasound irradiation. As known to all, penetration ability of ultrasound is very strong for some water medium and its penetration depth can ordinarily attain 15—20 centimeters (Suslick, 1990). Moreover, ultrasound can usually be competent for catalyzing those chemical reactions that the ultraviolet and visible lights catalyze(Mason, 1998; Ince, 2001; Pétrier, 2000).

In this work, methyl orange was used as a model compound because it was the most common dye and possible to use UV-visible spectrum to monitor its degradation process. The various affecting factors were studied on ultrasonic degradation of methyl orange in the presence of TiO_2 powder treated heatedly. In addition, the nanometer and ordinary anatase TiO_2 powders were adopted as sonocatalysts and their catalytic activities were compared in detail. The results indicated the ultrasonic degradation effects on methyl orange were more obvious in the presence of nanometer anatase TiO_2 powder than in the presence of ordinary anatase TiO_2 powder and without TiO_2 powder. The method of sonocatalytic degradation has the characteristics such as convenience, safety, credibility and high efficiency, so it is hopeful that this method is extended and applied in the treatment of non- or low-transparent wastewaters on the basic of more research work.

1 Experimental

1.1 Materials

The nanometer and ordinary anatase TiO_2 powders were bought from Haerbin Chemistry Reagent Company. At first, the TiO_2 powders were heatedly treated at 200℃ and their XRD and TEM are shown in Fig.1 and Fig.2, respectively. The nanometer anatase TiO_2 powder is predominantly anatase (90% anatase and 10% rutile) and its density and size are about 3.56 g/cm^3 and 20—30 nm, respectively. The ordinary anatase TiO_2 powder is also predominantly anatase (90% anatase and 10% rutile) and its density and size are about 3.42 g/cm^3 and 100—200 nm, respectively. Methyl orange was purchased from Aldrich (Wisconsin, USA) and was the chose as a model compound. This compound is yellow in basic medium and red in acidic medium. When dissolved in water the UV-visible spectrum shows three maximum peaks and they appear at 275 nm, 325 nm and 495 nm, respectively. All other chemicals were high purity Fluka or Aldrich products. Water was purified by a Milli-Q water system (Millipore).

1.2 Instruments

VX-300 nuclear magnetic resonance (US Varian MERCURY company) and LAMBDA-17 UV-vis spectrometer (US Perkin-Elmer company) were used to inspect the degradation processes of methyl orange. KQ-100 Serial-Ultrasonics apparatus (Kunshan ultrasonics apparatus company) was used to irradiate the methyl orange solution, operated at ultrasonic frequency of 20—80 kHz and output power of 0—50 W.

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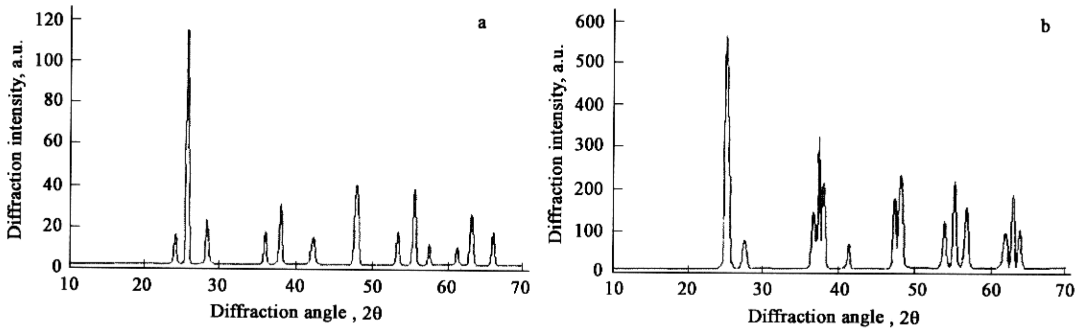

Fig.1 XRD of nanometer and ordinary anatase TiO_2 powders after treatment
a. nanometer anatase; b. ordinary anatase

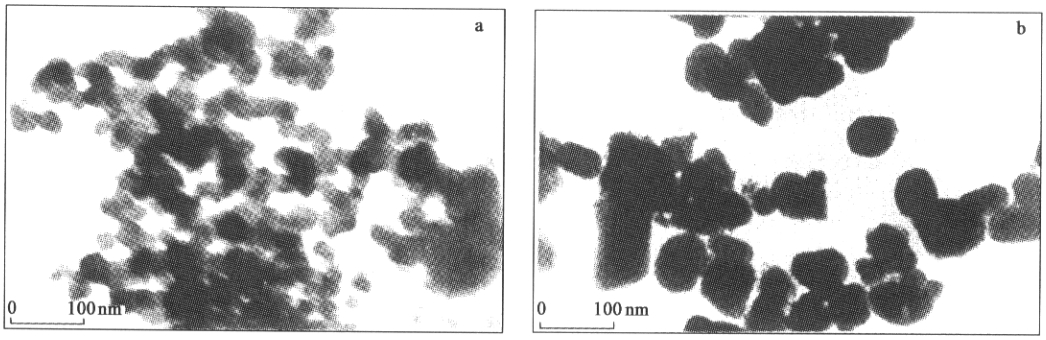

Fig.2 TEM of nanometer and ordinary anatase TiO_2 powders after treatment
a. nanometer anatase; b. ordinary anatase

1.3 Experimental methods

The prepared methyl orange solution and TiO_2 powder were put into a glass reactor (bottom area is about 50 cm^2) and the mixed solution (100 ml) was stirred to make good dispersion. The UV-vis spectra of the methyl orange solution before and during degradation were determined by the UV-vis spectrophotometer in the wavelength range from 200 to 700 nm as shown in Fig.3. The maximal absorbencies of 5.0—25.0 mg/L methyl orange solution abide by Lamber-Beer's law and the standard calibration curve is used to estimate the degradation ratio.

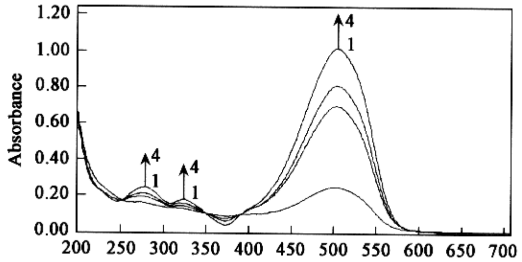

Fig.3 UV-visible spectra of original and degradative MO solutions
1. ultrasound + nanometer anatase TiO_2; 2. ultrasound + ordinary anatase TiO_2; 3. only ultrasound; 4. original

The degradation ratio and pH of methyl orange solution shown in Fig. 4 and Fig. 12 were determined at 30 min interval by UV-vis spectrophotometer and pH meter, respectively. The effects of initial methyl orange concentration, TiO_2 adding amounts, temperatures and pH, ultrasonic frequency and output power were measured and these results were given in Fig.6, Fig.7, Fig.8, Fig.9, Fig.10 and Fig.11. In order to check up intermediate products during the degradation, the different moment NMR of methyl orange dissolved in D_2O solvent were also determined as shown in Fig.5. At last, the sonocatalytic activities of reused TiO_2 were also investigated and the results were indicated in Fig.13. All experimental conditions were: TiO_2 adding amount 750 mg/L, initial methyl orange concentration 10 mg/L, pH = 3.0, ultrasonic frequency 40 kHz, output power 50 W and temperature of 40℃ within 90 min throughout the course of the investigation expect for those special studies.

2 Results and discussion

2.1 Effect of time

The degradation ratios at 30 min intervals were reviewed within 150 min. It was observed in Fig.4 that the degradation ratios of three courses all increased gradually along with time and a complete degradation of methyl orange was achieved at 150 min in the presence of nanometer anatase TiO_2 powder. The considerably low degradation ratios in the presence of ordinary anatase TiO_2 powder and in the absence of TiO_2 were obtained and they were only 58.76% and 19.23% at the same time, respectively. These results indicate that the degradation effects in the presence of TiO_2 catalysts together with ultrasound are more obvious than that of using one fold ultrasound. It has been well known that the catalytic activity of nanometer anatase TiO_2 as photocatalyst, in general, remarkably excels the ordinary anatase TiO_2 in the photocatalytic degradation of organic pollutants. Moreover, the technology of photocatalytic degradation for treating organic pollutants reaches the extent of practical application abroad. This work shows a same fact. Although the reason about the ultrasonic degradation in the presence of TiO_2 powder is not completely understood, at least the nanometer anatase TiO_2 should be adopted to act as catalyst of sonocatalytic degradation for treating non- or low-transparent wastewaters.

In addition, in order to explore the mechanism of sonocatalytic degradation and search the intermediate products of methyl orange, the NMR determinations at different

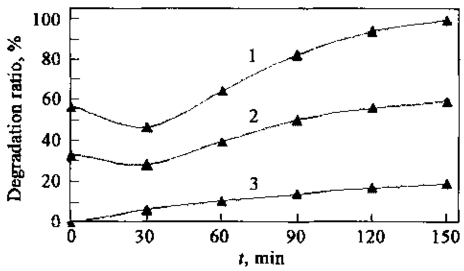

Fig.4 Effect of time on degradation ratio
1.ultrasound + nanometer anatase TiO_2; 2.ultrasound + ordinary anatase TiO_2; 3.only ultrasound

moment were conducted, however, the evidences of intermediate products were not found markedly in Fig. 5. There are probably two reasons that can account for this fact. Firstly, the accumulative amount of intermediate products is too low to be detected; secondly, once methyl orange molecules in solution touch the surface of TiO_2 catalyst, they are immediately oxidated and degraded completely by the $OH^{\cdot}$ radicals attached on the surface of TiO_2 catalyst. Nevertheless, it was seen that the amount of methyl orange became smaller and smaller at least.

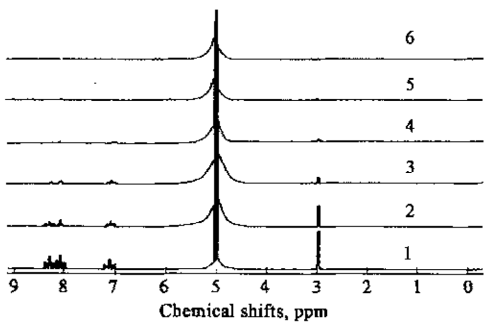

Fig.5 ^{1}H-NMR of methyl orange at different moment
1: 0 min; 2: 30 min; 3: 60 min; 4: 90 min; 5: 120 min; 6. 150 min

2.2 Effect of initial methyl orange concentration

Different initial methyl orange concentrations were used ranging from 5.0 mg/L to 25.0 mg/L. It was found that the best degradation ratio was obtained between 15.0 and 20.0 mg/L for nanometer anatase TiO_2 powder as shown in Fig.6, then the degradation efficiency andante decreased with increasing concentration of methyl orange. While the best degradation ratio in the presence of ordinary anatase TiO_2 powder appeared at the concentration between 10.0 and 15.0 mg/L. Perhaps it is owing to the higher adsorbability of nanometer anatase TiO_2 powder comparing with ordinary anatase TiO_2 powder, but the catalytic activity of ordinary anatase TiO_2 powder is not as good as nanometer anatase TiO_2 powder in any cases. In addition, the degradation ratio using one fold ultrasound slowly rises with increasing concentration of methyl orange from 5.0 mg/L to 25.0 mg/L.

2.3 Effect of TiO_2 adding amount

In order to optimize adding amount of TiO_2 catalyst, the following quantities were adopted starting from 250 mg/L to 1250 mg/L. It was found that the best results were obtained when adding amount of TiO_2 in solution was about 750 mg/L shown in Fig.7 for nanometer anatase TiO_2 powder, while the highest degradation ratio appeared at 1000 mg/L for ordinary anatase TiO_2 powder, which results from the differences between adsorb abilities of nanometer and ordinary anatase

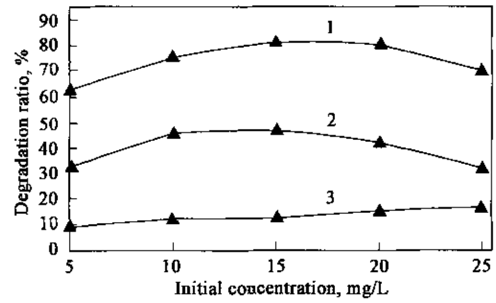

Fig.6 Effect of initial methyl orange concentration
1. ultrasound + nanometer anatase TiO_2; 2. ultrasound + ordinary anatase TiO_2; 3. only ultrasound

TiO_2 particles. According to these results, it can be known that the proper adsorption of TiO_2 particles can enhance the degradation ratio, but the excessive adsorption usually cuts down the degradation ability.

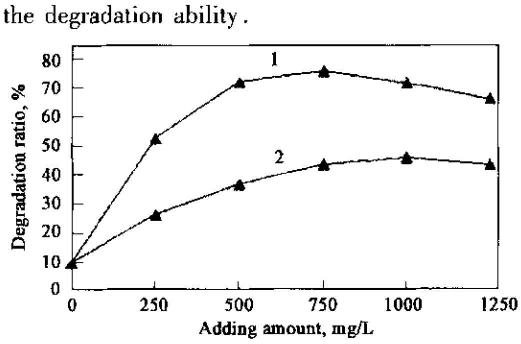

Fig.7 Effect of TiO_2 adding amount
1. ultrasound + nanometer anatase TiO_2; 2. ultrasound + ordinary anatase TiO_2

2.4 Effect of changing pH

The ultrasonic degradations of methyl orange solutions in the presence of nanometer and ordinary anatase TiO_2 powders as the sonocatalysts and in the absence of TiO_2 for comparison were studied in the pH range between 1.0 and 9.0. The relationship between the degradation ratio and the pH in solution is shown in Fig. 8. It can be found that the degradation ratios of methyl orange in the presence of nanometer and ordinary anatase TiO_2 powders fleetly decrease from pH = 1.0 to pH = 9.0. The degradation ratios of only using ultrasound without any TiO_2 catalysts are relatively high in acidic and basic solution, and then very low in neutral solution. The remarkable sonocatalytic degradation ratios in the presence of TiO_2 indicates that the treatments of the organic pollutants like methyl orange should be performed in high acidic medium in order to obtain the best degradation ratio. How the pH values affect the photocatalytic degradation of the organic pollutants in the presence of TiO_2 catalyst is variable and controversial. In general, it is expected that the degradation rate increases with pH value decreasing, which indicate the number of $OH^{\cdot}$ radical increase on the surface of TiO_2 particles in solution by trapping photo. In this case, the highest degradation ratio was also achieved in high acidic solution. How the degradation ratio at high and low pH values change can be explained by the integrative effects of adsorption and desorption. At low pH values, the surface of TiO_2 is positively charged and is capable of absorbing the molecule of methyl orange which is present in the form of unstable quinonoid formula at this pH values. At higher pH values, on the surface of TiO_2 there are superfluous negative charges those will lead to repulse to the methyl orange in solution, resulting in negligible adsorption.

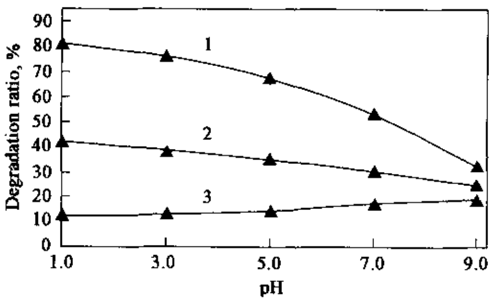

Fig.8 Effect of changing pH on degradation
1. ultrasound + nanometer anatase TiO_2; 2. ultrasound + ordinary anatase TiO_2; 3. only ultrasound

2.5 Effect of temperature

The effect of temperature on the degradation ratio was discussed in the range between 20℃ and 60℃. It can be seen in Fig. 9 that the degradation ratio of methyl orange increases rapidly with the temperature heightening in the presence of nanometer anatase TiO_2 powder. Obviously, the higher the temperature is, the quicker the degradation rate of methyl orange becomes. The degradation ratio increases by about 10% when the temperature rises from 20℃ to 40℃, while the degradation ratio increases upwards of 5% when the temperature rises from 40℃ to 60℃. The degradation ratio in the case of one fold ultrasound also increases with the hoist of temperature in solution, but the enhancement of degradation rate is slow, the degradation ratio increases by only 10% when the temperature rises from 20℃ to 60℃. However, the degradation ratio in the presence of ordinary anatase TiO_2 powder slightly increases in the range of 20℃ and 40℃, but it contrarily declines gradually with elevated temperature from 40℃ to 60℃. Perhaps, the adsorption ability of ordinary anatase TiO_2 becomes low and the cavitation effect is cut down at high temperature, which results in the seeming decline of integrative effect of degradation and adsorption on the surface of ordinary anatase TiO_2.

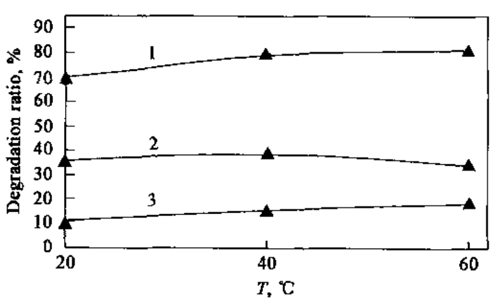

Fig.9 Effect of temperature on degradation ratio
1. ultrasound + nanometer anatase TiO_2; 2. ultrasound + ordinary anatase TiO_2; 3. only ultrasound

2.6 Effect of ultrasonic frequency

The results in Fig. 10 indicated that it could not satisfactorily elucidate the effect of ultrasonic frequency because the relationship between the ultrasonic frequency and cavity number excitated by ultrasound in the presence of TiO_2 catalyst is very complicated. Although the good degradation effects were obtained from the ultrasound of low frequency in the presence of anatase TiO_2, the best selection should be ones in the range between 40 and 80 kHz because they can be gained easily and their noises are smaller than the low frequency ultrasound during treating organic pollutants considering personal health.

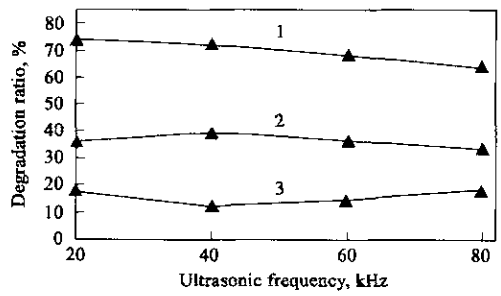

Fig.10 Effect of ultrasonic frequency
1. ultrasound + nanometer anatase TiO_2; 2. ultrasound + ordinary anatase TiO_2; 3. only ultrasound

2.7 Effect of ultrasonic power

In general, in the case of using one fold ultrasonic irradiation without TiO_2 catalyst, the degradation ratio becomes high with output power of ultrasound increasing. This is the reason that the power ultrasound is often used to treat some organic pollutants. The similar phenomena were found in the sonocatalytic degradation in the presence of ordinary anatase TiO_2 powder as shown in Fig. 11. The degradation ratio in the presence of nanometer anatase TiO_2 powder slightly rises with increasing output power of ultrasound at beginning, and then decreases slowly. The reasons may be as follows: firstly, the high output power provides the chances that the added $OH^{\cdot}$ radicals form; secondly, the ordinary anatase TiO_2 particles possess the suitable size with high sonocatalytic activity under the function of ultrasound; thirdly, the structure of nanometer anatase TiO_2 particles is destroyed to a certain extent, so the sonocatalytic activity of nanometer anatase TiO_2 powder becomes low.

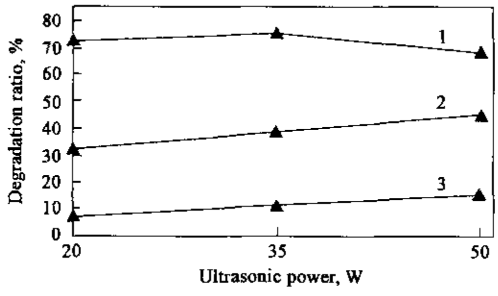

Fig.11 Effect of ultrasonic power
1. ultrasound + nanometer anatase TiO_2; 2. ultrasound + ordinary anatase TiO_2; 3. only ultrasound

2.8 Change of pH during degradation

In general, the pH of solution changed toward more acidity during ultrasonic irradiation because the organic pollutants gradually became NO_3^-, SO_4^{2-}, PO_4^{3-}, CO_2 and H_2O etc. along with the degradation. This is accordant with the photocatalytic degradation of organic pollutants in the presence of TiO_2 catalyst. It can be seen from Fig.12 that the pH of the methyl orange solution in the presence of nanometer anatase TiO_2 powder is lower than ones in the presence of ordinary anatase TiO_2 powder and without any TiO_2 at the same moment during the degradation, which implies methyl orange is gradually degraded. Perhaps, the pH change of solution can be used to judge the degradation degree of organic pollutants.

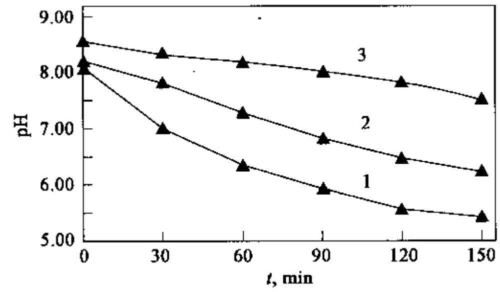

Fig.12 Different pH during degradation of methyl orange
1. ultrasound + nanometer anatase TiO_2; 2. ultrasound + ordinary anatase TiO_2; 3. only ultrasound

2.9 Sonocatalytic activity of reused TiO_2

Any catalyst after finishing its task is expected to reclaim and recycle by proper treatment. Accidentally, in the solution of pH = 3.0, the nanometer and ordinary anatase TiO_2 powders not only showed the high sonocatalytic activity, but also settled down completely and were separated easily from the solution. These TiO_2 deposits were washed with purified water and heated at 200℃ and then reused in new experiments with fresh methyl range solution. Fig.13 shows that the degradation ratios of methyl orange fall appreciably in the presence of used nanometer anatase TiO_2 powder in the second and third times experiments and then decline fleetly, which indicates its catalytic activities become low gradually. While, the ordinary anatase TiO_2 powder is different from the nanometer anatase TiO_2 powder and its catalytic activities heighten at beginning and gradually weaken afterward.

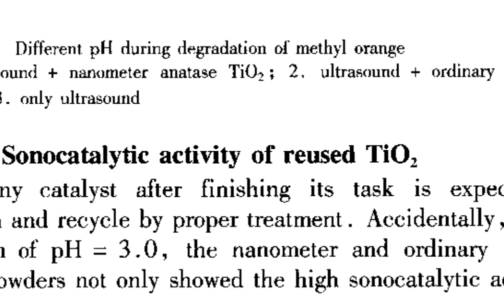

Fig.13 Effect of reused TiO_2 on degradation ratio
1. ultrasound + nanometer anatase TiO_2; 2. ultrasound + ordinary anatase TiO_2; 3. only ultrasound

2.10 Possible degradation mechanism

There have not been the ready-made mechanism and satisfying explanation yet on the sonocatalytic degradation of organic pollutants in the presence of TiO_2 up till now. Perhaps, the following two points of view, namely, sonoluminescence and "hot spot", should be accepted to explain the phenomenon of sonocatalytic degradation of methyl orange in the presence of TiO_2 catalyst. It has been well known that the ultrasonic irradiation can result in the formation of the light with a comparatively wide wavelength range. Those lights whose wavelengths are below 375 nm, beyond all doubt, can excite the TiO_2 particle acting as a photocatalyst and a great deal $OH^{\cdot}$ radicals with high oxidative activity form on the surface of TiO_2 particle. In fact, that is the mechanism of photocatalytic degradation. Otherwise, the temperature of "hot spot" produced by ultrasonic cavitations in water medium can achieve 10^5 ℃ or 10^6 ℃. So high temperature sufficiently brings the cavities producing $OH^{\cdot}$ radicals on the surface of TiO_2 particle. Of course, the detailed mechanism expects to be further and specially studied.

3 Conclusions

The methyl orange solution can be markedly degraded by the sonocatalytic reaction in the presence of anatase TiO_2 powder, furthermore, the sonocatalytic activity of nanometer anatase TiO_2 is obvious better than ordinary anatase TiO_2. The research results demonstrated the feasibilities of sonocatalytic degradation of methyl orange and other organic wastewaters. Especially, this method suits those non- and low-transparent wastewaters. The optimum degradation conditions for methyl orange solution are considered to be: initial methyl orange concentration 15—20 mg/L, adding amount 500—750 mg/L nanometer anatase TiO_2 power, ultrasonic frequency 20—40 kHz, output power 50 W, pH = 3.0 and 40℃ within 150 min. Furthermore, the catalytic activity of reused anatase TiO_2 was also studied and found to be lower than new TiO_2. The facts show that sonocatalytic degradation technology with huge development potential can have wide application prospect on the basic of further research.

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