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Degradation of congo red induced by air-bubbles in the presence of nanometer TiO_2 powders

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ABSTRACT

In this work, a new cavitation degradation method induced by air-bubbles passing small glass balls combined with TiO_2 powders was provided to remove congo red (CG-R) in aqueous solution. And then the degradation process of CG-R was inspected by using UV–vis, total organic carbon analyzer, and high performance liquid chromatography technologies. The remarkably high degradation effect (about 98.89%) of CG-R can be obtained when the experimental conditions of 80 min air-bubbling time, 50 mg/L initial concentration, 1,000 mg/L anatase TiO_2 amount, 3.0–3.5 mm glass ball diameter, 4.50 L/min gas flow rate, and pH 6.0 solution acidity at 15.0 ± 0.2°C temperature were adopted. From the results it can be infered that there is a synergetic effect between air-bubbles passing small glass balls and TiO_2 powders in the degradation of CG-R dyes. Moreover, the catalytic activity of nanometer anatase TiO_2 powder was obviously higher than that of rutile TiO_2 powder during the degradation of CG-R dyes. The degradation of CG-R induced by air-bubbles passing small glass balls combined with TiO_2 powders follows the pseudo-first-order reaction kinetics. All experimental results indicate that this new method was a feasible and promising choice for the treatments of organic wastewaters.

Keywords: Nanometer titanium dioxide (TiO_2); Air-bubble; Small glass ball; Congo red dyes; Degradation

1. Introduction

Wastewaters from textile and yarn dyeing are one of the major environmental polluters. Dye components in such wastewaters can be a key source of environmental pollution [1]. Therefore, the elimination of dye effluents is considerably important in environmental remediation and has attracted close attention of many researchers in recent years. Many traditional physical and chemical techniques (adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation by chemical agents, etc.) can be used efficiently [1–6]. Nevertheless, they are customarily non-destructive methods and merely transfer contaminants from water to sludge. Thus, it easily causes secondary pollution. Besides, due to the presence of large numbers of aromatic compounds in dye molecules and the stability of modern dye, the conventional biological treatment methods are ineffective for decolorization and mineralization [7]. Hence, inexpensive and environment friendly alternative treatment methods are required. It has been well known that various advanced oxidation

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processes (AOPs), characterized by the production of ·OH radicals under mild experimental conditions, have emerged as a promising technology for the decomposition of organic pollutants [8,9]. Especially, among them, the ultrasonic cavitation and hydrodynamic cavitation have been attracting attention as new AOPs for the elimination of hazardous chemical substances in water [10–12].

Cavitation is the phenomenon of sequential formation, growth, and collapse of millions of microscopic vapor bubbles (voids) in the liquid. The collapse or implosion of these cavities creates local high temperature of 14,000 K roughly and pressure of about 10,000 atm or result in short-lived and local hot-spot in cold liquid. Thus, the cavitation serves as a means of concentrating the diffused fluid energy locally and creating a zone of intense energy dissipation in very short duration [13]. Hence, the cavitation technology, as a method of harnessing refractory wastewater, not only removes toxic substances effectively, but also shows many other advantages: effective degradation, energy saving, no secondary pollution, and simple reaction device. At present, the admitted cavitation phenomena should be classified into four types based on the mode of generation, namely ultrasonic, hydrodynamic, optic, and particle cavitations [14–18].

In the previous work, a new degradation method, being similar to ultrasonic and hydrodynamic cavitations, the air-bubble induced cavitation passing small glass balls was presented [19,20]. In addition, with regard to the removal of dye pollutants, TiO_2 photocatalysis and sonocatalysis have been used diffusely and efficiently [21]. In this work, in order to improve the method of air-bubble cavitation degradation, the effectiveness combined with nanometer TiO_2 powder, as an assisted catalyst, for degradation of congo red (CG-R) was investigated. Meanwhile, the effects of operating factors such as air-bubbling time, TiO_2 addition amount, initial concentration, glass ball size, and gas flow rate on the degradation of CG-R were also discussed. The catalytic activities of two phases of (anatase and rutile) TiO_2 powders were also compared. We predict that this new method could be applied in the treatment of industrial and organic dyes wastewater on a large scale on further studies.

2. Experimental section

2.1. Materials

CG-R (A.R. purity, Tianjin Kaiyuan Reagent Corporation, China) was purchased and chosen as the model organic pollutant. All other chemicals came from high purity Fluka or Aldrich products. The small glass balls (sizes of 1.0–1.5, 2.0–2.5, 3.0–3.5, and 4.0–4.5 mm, ordinary grinding glass ball, Shandong Yuyao Keyan Glass Ball Factory, China) were marinated in 1.0 mol/L hydrochloric acid solution for two days, and then taken out washing with secondary distilled water to neutral. After that they were marinated in secondary distilled water a day waiting for later utilization. The water purified by a Milli-Q water system (Millipore) was used throughout. The nanometer TiO_2 powders (anatase and rutile phases, Haerbin Chemistry Reagent Company, China) were heat treated for activation at 300 and 450°C, respectively.

2.2. Apparatus and instruments

Muffle furnace (SX2-4-10, Great Wall Furnace Company, China) was used to treat nanometer TiO_2 powders. The XRD and TEM of nanometer TiO_2 powders were determined by X-ray diffractometer (Rigaku Rint-2500, Rigaku Corporation, Japan) and transmission electron microscope (JEOL JEM-3010, Hitachi Corporation, Japan). UV–vis spectrometer (Cary 50, Varian Company, USA) was used to inspect the degradation process of CG-R. The total organic carbon analyzer (TOC-1200, Thermo Electron Corporation, The Netherlands) was utilized to further evaluate the degradation effect and degree of CG-R. High performance liquid chromatography (HPLC, Agilent-1100, Agilent Company, USA) was used to inspect the intermediate product and residual amount of CG-R. Air Pump (EP-9000, Guangdong Chuangxing Electronic Limit Company, China) was adopted to puff air-bubble into the CG-R solution, operating at output power of 5.6 W. The whole experimental apparatus is shown in Fig. 1.

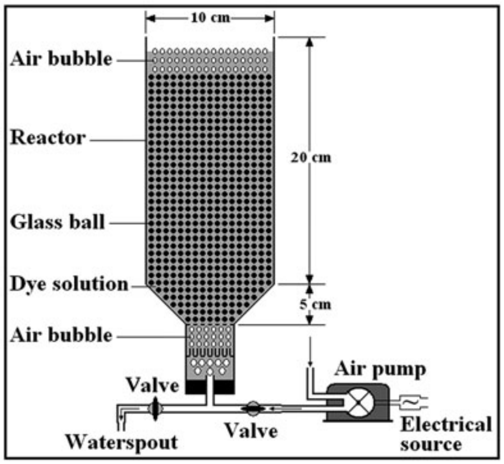

Fig. 1. Experimental equipment of the degradation reaction.

2.3. Procedure

About 700 mL CG-R solution and 700 mg heat-treated nanometer (anatase or rutile phase) TiO_2 powders were put into a 1,000 mL glass beaker. The mixed solution was stirred for 20 min to make a good dispersion of nanometer TiO_2 powder. Then, the suspension was put into a 2.5 L self-made glass reactor filled with small glass balls with a fixed size. The amount of small glass balls is four-fifths of the whole volume of the glass reactor and CG-R solution was 3.0 cm higher than the height of glass balls. Air was puffed from the reactor bottom into CG-R solution [22,23]. UV–vis spectra of the untreated and treated CG-R solution were determined by the UV–vis spectrometer in the wavelength range from 200 to 800 nm. TOC removal was also examined to further explore the CG-R degradation effect. In order to check up the degradation intermediate products of CG-R, HPLC was investigated at 497 nm channel wavelength at different conditions.

3. Results and discussion

3.1. UV–vis spectra, TOC, and HPLC of CG-R solution during degradation

Fig. 2(a) shows that the UV–vis spectra of original CG-R solutions provide three absorption peaks at 225, 342, and 497 nm, respectively. The degradation of CG-R was carried out in the conditions of 50 mg/L initial concentration, 1,000 mg/L nanometer anatase TiO_2 addition amount, 3.0–3.5 mm glass ball diameter, 4.50 L/min gas flow rate, pH 6.0 solution acidity, 15.0 ± 0.2℃ temperature and 60 min bubbling time. Due to the relatively high absorbance of 50 mg/L CG-R solution, the degradation ratio could not be calculated directly based on the absorbance change. So, before determination the tested CG-R solution was diluted five times, which makes the concentration to be reduced to about 10 mg/L. This concentration range obeys well the Lambert-Beer' law [20].

After air-bubbling, the CG-R solution in the presence of nanometer anatase TiO_2 powder displays much lower absorbance than those in the presence of nanometer rutile TiO_2 powder and in the absence of any catalyst. That is, the degradation ratio using nanometer anatase TiO_2 powder was much higher than those using nanometer rutile TiO_2 powder and without any catalyst. The corresponding degradation ratios were 27.35, 56.62, and 92.31%, respectively, for air-bubbling (60 min) + glass ball, air-bubbling (60 min) + glass ball + nanometer rutile TiO_2 powder, and air-bubbling (60 min) + glass ball + nanometer anatase TiO_2 powder. The results illuminate that all the azo bond, biphenyl, and naphthalene rings of CG-R molecules can be destroyed in a large degree through air-bubbles passing small glass balls in the presence of nanometer TiO_2 powder. Moreover, the nanometer anatase TiO_2 powder shows best catalytic performance. Due to the crystal type and structure, the nanometer anatase TiO_2 is easy to capture the CG-R dyes. And then these CG-R dyes are mainly oxidized by the holes on the surface of

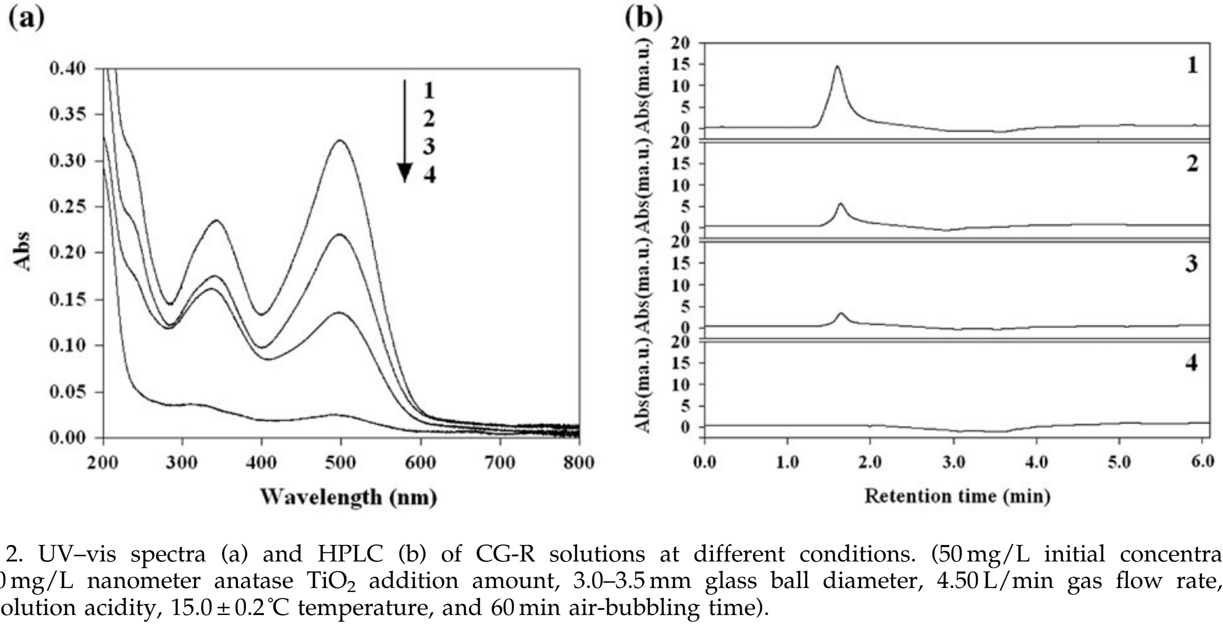

Fig. 2. UV–vis spectra (a) and HPLC (b) of CG-R solutions at different conditions. (50 mg/L initial concentration, 1,000 mg/L nanometer anatase TiO_2 addition amount, 3.0–3.5 mm glass ball diameter, 4.50 L/min gas flow rate, pH 6.0 solution acidity, 15.0 ± 0.2℃ temperature, and 60 min air-bubbling time).
(1) Original solution; (2) air-bubbling (60 min) + glass ball; (3) air-bubbling (60 min) + glass ball + nanometer rutile TiO_2 powder; and (4) air-bubbling (60 min) + glass ball + nanometer anatase TiO_2 powder.

nanometer anatase TiO_2 particles. For nanometer rutile TiO_2, under the action of air-bubble cavitation, the holes also generated on the surface of rutile TiO_2, but the oxidation ability of the holes is poor. Besides, the adsorption ability of nanometer rutile TiO_2 for CG-R dyes is also weak, it has hardly effect on the calculations of degradation rates [20]. Therefore, the nanometer anatase TiO_2 powder shows high photocatalytic activity.

For evaluating the degradation effect, the calculations of degradation rations based on the TOC removals of CG-R solutions were also performed. The TOC removal ratios of CG-R solutions were 20.21, 49.72, and 80.07%, respectively, for air-bubbling (60 min) + glass ball, air-bubbling (60 min) + glass ball + nanometer rutile TiO_2 powder, and air-bubbling (60 min) + glass ball + nanometer anatase TiO_2 powder. That is, the trend of TOC removals was perfectly consistent with above determined ones by using UV–vis spectra. By comparing with the trend which had not added catalyst previously, the TOC removal ratios of CG-R had an obvious increase after adding catalyst. Besides, the results also prove that adopting this method the CG-R dyes in aqueous solution can mostly be degraded. It also demonstrates that the catalytic activity of nanometer anatase TiO_2 powder is higher than that of nanometer rutile TiO_2 powder. Moreover, UV–vis absorbance analysis is a useful method to perform measurement and get preliminary information on the degradation rate of organic pollutants fast and easily. So, it was used in all later work.

In order to explore the intermediate products and degradation process, the HPLC of original and treated CG-R solutions was determined using channel wavelength at 497 nm which gives a maximum absorption peak in UV–vis spectra. As shown in Fig. 2(b), there is only one peak, namely, no other peaks appear. It indicates that no new intermediate product generated during degradation. The height order of four curves was original solution > air-bubbling (60 min) + glass ball > air-bubbling (60 min) + glass ball + nanometer rutile TiO_2 powder > air-bubbling (60 min) + glass ball + nanometer anatase TiO_2 powder. It can be inferred again that the catalytic activity of nanometer anatase TiO_2 powder was higher than that of nanometer rutile TiO_2 powder during the degradation of CG-R.

3.2. Effect of air-bubbling time and reaction kinetics on degradation of CG-R

The degradation process of CG-R dye in the presence and absence of nanometer TiO_2 powders was investigated within 80 min at 20 min intervals. As shown in Fig. 3(a), the degradation ratios of three columns all rose along with the increase of air-bubbling time. It indicates that the number of molecules for CG-R decreased gradually. At any air-bubbling time within 80 min, the order of degradation ratios is as follows: air-bubbling + glass ball < air-bubbling + glass ball + nanometer rutile TiO_2 powder < air-bubbling + glass ball + nanometer anatase TiO_2 powder. The highest degradation ratio (98.89%) is achieved at 80 min for nanometer anatase TiO_2 powder. Nevertheless, the considerably low degradation ratios in the presence of nanometer rutile TiO_2 powder and without any TiO_2 catalyst are 66.42 and 42.01%, respectively, at the same air-bubbling time. It has been well known that the catalytic activity of nanometer anatase TiO_2 powder remarkably excels the nanometer rutile TiO_2 powder in the photocatalytic degradations of various organic pollutants. Here, the similar results were also found. So, those

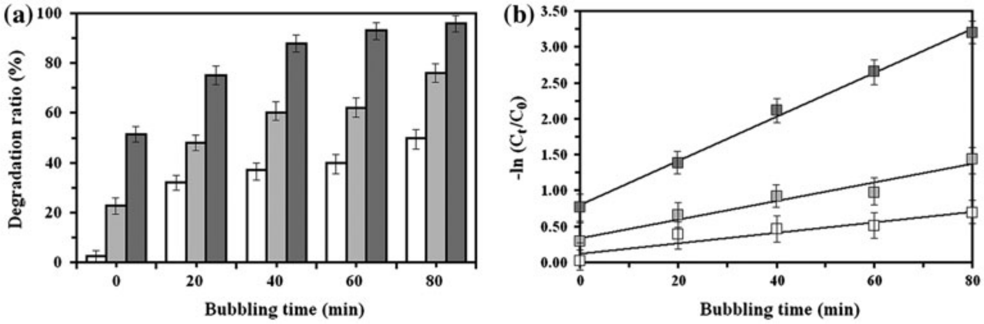

Fig. 3. Influence of air-bubbling time (a) and reaction kinetics (b) on degradation of CG-R. (50 mg/L initial concentration, 1,000 mg/L nanometer anatase TiO_2 addition amount, 3.0–3.5 mm glass ball diameter, 4.50 L/min gas flow rate, pH 6.0 solution acidity, and 15.0 ± 0.2℃ temperature.).
□: Air-bubbling + glass ball; ▨: air-bubbling + glass ball + nanometer rutile TiO_2 powder; ■: air-bubbling + glass ball + nanometer anatase TiO_2 powder.

wastewaters containing organic pollutants treated by photocatalytic technology also can be well done by the method of air-bubbles passing small glass balls combined with nanometer anatase TiO_2 powder.

The data of $-\ln(C_t/C_0)$ as a function were plotted versus air-bubbling time (t) for three courses. In fact, as shown in Fig. 3(b), all calculated values of $-\ln(C_t/C_0)$ are approximately linear with the air-bubbling time all through. That is, whether the two phases of nanometer TiO_2 powders exist or not, the degradation processes of CG-R dye all followed the pseudo-first-order reaction kinetics. The reaction rate constants are 0.0308 min^{-1} ($R^2 = 0.9964$), 0.0131 min^{-1} ($R^2 = 0.9515$), and 0.0073 min^{-1} ($R^2 = 0.9235$), respectively, corresponding air-bubbles passing small glass balls in the presence of nanometer anatase TiO_2 and rutile TiO_2 as well as in the absence of any catalyst. Apparently, the order is also air-bubbling + glass ball < air-bubbling + glass ball + nanometer rutile TiO_2 powder < air-bubbling + glass ball + nanometer anatase TiO_2 powder.

3.3. *Effect of initial concentration and TiO_2 amount on degradation of CG-R*

Different initial concentrations of CG-R solution ranging between 25 and 100 mg/L were used to review the effect on the degradation. Other experimental conditions were the same as mentioned above. As shown in Fig. 4(a), for both nanometer anatase and rutile TiO_2 powders, the best degradation ratio was obtained when the initial CG-R concentration of 50 mg/L was adopted. Afterwards, the degradation ratios fall slowly with further increase of CG-R concentration. Apparently, the proper dye initial concentration redounds to the degradation of organic pollutants. On the one hand, in high concentration solution, the adsorption of nanometer TiO_2 (anatase and rutile) powders to dye molecules attains saturation quickly. The relatively thick adsorption dye layer covers on the surface of nanometer TiO_2 particles, and then interdicts the transmission of the (heat and light) energy released by air-bubble cavitation. On the other hand, the superfluous dye molecules in aqueous solution absorb a part of (light) energy, which also weakens the catalytic activity of nanometer TiO_2 powder.

The reduction ratios of CG-R dyes, caused by degradation and adsorption, should depend on the additional amount of nanometer TiO_2 powders at a certain extent. Here, altering nanometer TiO_2 (anatase and rutile) addition amount between 500 and 1,250 mg/L, the influences on the degradation of CG-R dyes were reviewed. From Fig. 4(b), it was found that the degradation ratios both rose gradually as the nanometer (anatase and rutile) TiO_2 addition amount increase, but it began to decline slightly after 1,000 mg/L for anatase TiO_2 powder. Hence, it can be judged that the proper catalyst amount is of advantage to the degradation of CG-R dyes to a certain extent. It is because that the superfluous nanometer TiO_2 particles not only defilade one another, but also obstruct the transmission of the (heat and light) energy. Otherwise, because of the exorbitant adsorption caused by superfluous nanometer TiO_2 particles, almost all dye molecules are kept on the surface of nanometer TiO_2 particles. Therefore, the CG-R molecules weasel from being decomposed. It is also possible that the nanometer anatase TiO_2 powder with large surface area have strong adsorption ability. And that the excessive adsorption not only made CG-R molecules attain the protection, but also reduced the oxidation activity of nanometer anatase TiO_2 powder. While, for nanometer rutile TiO_2 powder, the CG-R dyes were mainly oxidized by the ·OH radicals generated by air-bubble cavitation. The ascending

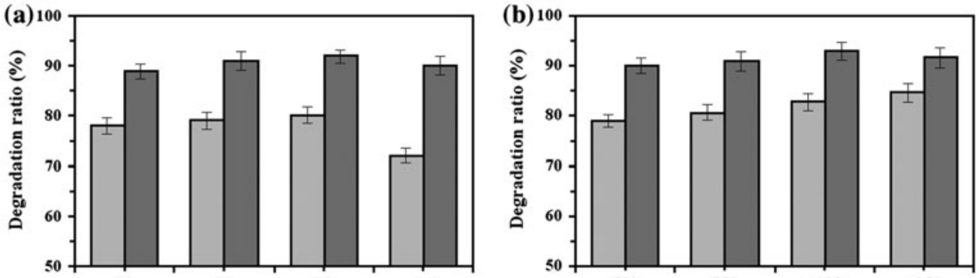

Fig. 4. Influence of initial concentration (a) and TiO_2 addition amount (b) on degradation of CG-R. (50 mg/L initial concentration, 1,000 mg/L nanometer anatase TiO_2 addition amount, 3.0–3.5 mm glass ball diameter, 4.50 L/min gas flow rate, pH 6.0 solution acidity, 15.0 ± 0.2 ℃ temperature, and 60 min air-bubbling time.)
▨: Air-bubbling (60 min) + glass ball + nanometer rutile TiO_2 powder; ■: air-bubbling (60 min) + glass ball + nanometer anatase TiO_2 powder.

addition amount of nanometer rutile TiO_2 powder will increase the number of the $\cdot$OH radicals. So, the degradation ratio increases gradually along with the increase of nanometer rutile TiO_2 addition amount all through.

3.4. Effect of glass ball size and gas flow rate on degradation of CG-R

The influences of glass ball size between 1.0–1.5 and 4.0–4.5 mm and gas flow rate between 2.25 and 13.25 L/min on the degradation of CG-R dye were investigated. Fig. 5(a) shows that, for both of nanometer anatase and rutile TiO_2 powders, the degradation rations increase along with the increase of glass ball diameter until 3.0–3.5 mm, and then slightly decrease. It indicates that the small glass balls with 3.0–3.5 mm diameter are propitious to the passing of gas flow, and then producing more suitable size of air-bubbles. Glass ball diameter may decide the size of the spitted air-bubbles, influencing their surface tension and surface energy. The too small glass balls can produce more small air-bubbles, which have large surface tension and easily release their energy retuning to original stable state, but they weaken the passing rate of gas flow. Conversely, the big glass balls cannot produce plenteous small air-bubbles, which abate the combination chance of air-bubbles. Hence, it is necessary to adopt a suitable diameter of glass ball for effective degradation of organic pollutants.

In addition, it can be considered that the gas flow rate also determines the number and size of small air-bubbles, and then influence their collision frequency and broken velocity. With slow air-bubbling, the air-bubbles around small glass balls can be naturally formed and broken, which is conducive to contact, collide, and burst of air-bubbles. Excessive speed, it is often too fast to make air-bubbles burst, that is, the air-bubbles are drilling through the small glass balls gaps without the possibility to combine a big air-bubble. As shown in Fig. 5(b), the degradation ratio of CG-R dye reached the maximum when the gas flow rate was 4.50 L/min. These demonstrated that there is a dependent relationship between degradation ratio and gas flow rate in a certain range.

3.5. Possible degradation mechanism of CG-R by air-bubbles passing small glass balls combined with nanometer TiO_2 powder

All the experimental results showed that the method of air-bubble cavitation induced by air-bubbles passing small glass balls in the presence of nanometer TiO_2 powders could effectively degrade CG-R in aqueous solution. In the previous work, the use of one-fold air-bubble cavitation for treating various wastewaters was reported [24]. However, the degradation process caused by air-bubbles passing small glass balls as well as the corresponding degradation mechanism has not yet been studied in detail. Here, unifying the previous work, the explanation about assisted air-bubble cavitation by nanometer TiO_2 powder was tentatively proposed.

In Fig. 6(a) it can be found that, because of the buoyant force, the formed air-bubbles must go up. At the same time, in rising process same small air-bubbles will become a big air-bubble since they knock against one another. And that the presence of small glass balls will aggravate this phenomenon. As shown in Fig. 6(b), in the specific process a big air-bubble was cut up to two or several small air-bubbles by small glass balls. For reducing the surface tension or

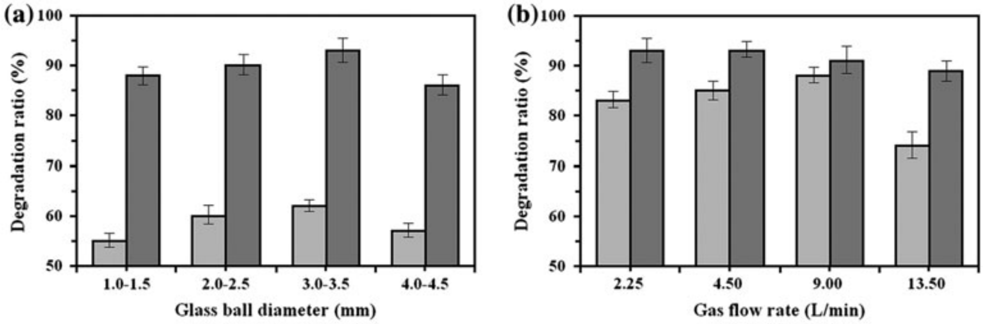

Fig. 5. Influence of glass ball size (a) and gas flow rate (b) on degradation of CG-R. (50 mg/L initial concentration, 1,000 mg/L nanometer anatase TiO_2 addition amount, 3.0–3.5 mm glass ball diameter, 4.50 L/min gas flow rate, pH 6.0 solution acidity, 15.0 ± 0.2 ℃ temperature, and 60 min air-bubbling time.)
░: Air-bubbling (60 min) + glass ball + nanometer rutile TiO_2 powder; ■: air-bubbling (60 min) + glass ball + nanometer anatase TiO_2 powder).

surface energy, these small air-bubbles have a recombination trend to become one bigger air-bubble. After two new bubbles touch, the tension of inner wall between both becomes bigger and bigger, and the thickness of inner wall also becomes thinner and thinner at the same time. At last, it fractures and collapses. Instantly, a great deal of energy in the form of light or heat is released [25,26]. As well known, cavitation is the phenomenon of sequential formation, growth, and collapse of millions of microscopic vapor bubbles (voids) in the liquid. Therefore, here we call this phenomenon as air-bubble cavitation. Being similar to ultrasonic and hydrodynamic cavitations, the air-bubble cavitation should also induce the formation of $\cdot$OH and $\cdot O_2^-$ radicals with strong oxidation ability, through the splitting of water (H_2O) molecules and reduction of $\cdot$H radicals to oxygen (O_2) gas, respectively. Naturally, these reactive oxygen species can degrade the CG-R in aqueous solution [25]. However, without recurring to other catalysts, the degradation efficiency is very low.

With regard to the degradation of CG-R caused by air-bubble cavitation combined with nanometer TiO_2 powders, maybe, the following two points of view, namely cavitation-luminescence excitation and cavitation-hot excitation, could be used to expound the reasons. Firstly, it has been well known that the cavitation can generally result in the formation of light with a comparatively wide wavelength range. Those lights whose wavelengths are below 375 nm [26], beyond all doubt, can excite the nanometer TiO_2 powders acting as photocatalyst. And then, the photogenerated electron-hole pairs are generated on the surface of nanometer TiO_2 particles. In general, the photogenerated electrons react with the oxygen (O_2) dissolved in solution, producing the $\cdot O_2^-$ radicals with high oxidative activity. And that, the photogenerated holes can bring into play the different roles according to different crystal forms of TiO_2 powder. For nanometer anatase TiO_2 powders, due to the relatively strong adsorption ability, as mentioned above, the holes can directly degrade the organic pollutants adsorbed on the surface. For nanometer rutile TiO_2 powders, due to the relatively low adsorption ability, the holes on the surface firstly react with water molecules and then produce the $\cdot$OH radicals, indirectly decomposing the organic pollutants in aqueous solution. That is, the holes generated on the surface of nanometer rutile TiO_2 particles indirectly degrade the organic pollutants in aqueous solution through $\cdot$OH radicals. The generation of $\cdot$OH radicals can be proved by the experiment of chemilluminutesescence [26]. In fact, that is the mechanism of photocatalytic degradation. Thus, in comparison, nanometer anatase TiO_2 powders display a higher catalytic activity than nanometer rutile TiO_2 powders in degradation process. Secondly, any cavitation occurs at millions of active locations and simultaneously generates many localized "hot spots" with a transient high temperature of about 14,000 K and high pressure of about 10,000 atm. Similarly, the temperature of "hot spot" produced by air-bubble cavitation in water medium can also achieve 1.0×10^4 and 3.0×10^4°C. Such high temperature sufficiently brings many holes producing $\cdot$OH radicals on the surface of nanometer TiO_2 powders. Of course, the detailed process of the air-bubble cavitation and corresponding degradation mechanism needs to be further and specially studied.

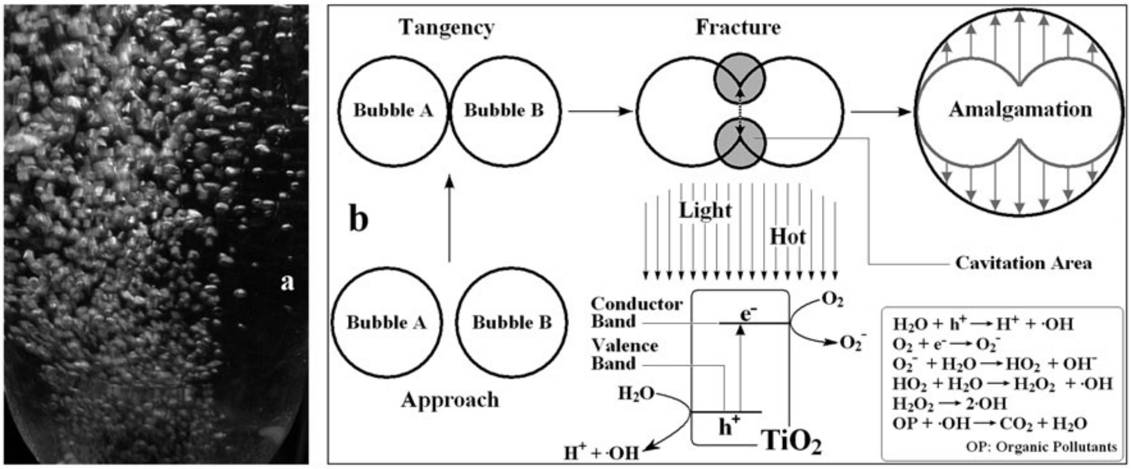

Fig. 6. (a) Rising process of air-bubbles and (b) possible process of air-bubble cavitation and degradation mechanism of organic pollutants in aqueous solution in the presence of nanometer TiO_2 powder.

4. Conclusions

The CG-R in aqueous solution can be obviously degraded by air-bubbles passing small glass balls in the presence of nanometer TiO_2 powders. Moreover, the catalytic performance of nanometer anatase TiO_2 powder is obviously better than that of nanometer rutile TiO_2 powder during the degradation of CG-R dyes. It can be learnt that the CG-R dyes are mainly oxidized by the holes on the surface of nanometer anatase TiO_2 particles and that the discoloration and degradation happen at the same time. For the nanometer rutile TiO_2 powder, the CG-R was mainly oxidized by the ·OH radicals generated by the excitation of air-bubble cavitation. Thus, the breakage of azo bond takes place primarily, and then the naphthyl rings are broken by ·OH radicals. In a word, all experimental results indicated that the air-bubble induced degradation of CG-R dyes in the presence of nanometer TiO_2 powders was inexpensive, no secondary pollution, simply setup and higher degradation rate method for treating non- or low-transparent organic wastewaters.

Acknowledgments

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