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A novel method treating organic wastewater: Air-bubble cavitation passing small glass balls

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ABSTRACT

Here, a novel degradation method, air-bubble cavitation induced by air-bubble passing small glass balls, was provided to effectively degrade organic pollutants in wastewaters. In order to demonstrate its universality, the degradation of various dyes (Methyl Orange (MO), Rhodamine B (RM-B), Congo Red (CG-R), Azo Fuchsin (AF) and Acid Red B (AR-B)) was carried out. Meanwhile, the effect of operating parameters such as air-bubbling time, dye initial concentration, NaCl addition amount and glass-ball size on the degradation were investigated. The results showed that the degradation ratio of Methyl Orange in aqueous solution reached 37.82% when the experimental conditions of 10 mg/L initial concentration, 3.0–3.5 mm glass-ball size, 4.5 L/min gas flow rate and pH = 6.0 were adopted with 3.0 h air-bubbling at room temperature (25.0 ± 0.2 °C). Under the same condition, the degradation ratios attained to 60.37%, 64.52%, 71.75% and 75.64%, respectively, for Rhodamine B, Congo Red, Azo Fuchsin and Acid Red B. In addition, the process of air-bubble cavitation and possible degradation mechanism of organic pollutants were discussed primarily. All experiments indicate that this method is an effective, energy saving and simple reaction device for the treatment of organic wastewaters. Hence the degradation by means of air-bubble cavitation is expected to be feasible and promising as an advisable choice for the treatment of organic wastewaters in future.

1. Introduction

In recent years, with the growth of population and the development of social economy, the discharged amounts of various pollutants are also growing rapidly. Especially, the pollutants caused by textile dyes and other industrial dyestuffs on water pollution have seriously threatened the survival of human being and the development of our society [1–3]. Therefore, it has begun to pay more attention to the problem of water pollution. The prevention of water deterioration and the protection of water resources have become a common human goal [4–6]. In water treatment, the cavitation technology as a method of harnessing refractory wastewater, not only removes toxic substances effectively, but also shows many other advantages including effective degradation, energy saving and simple reaction device. Hence, as one of the physical–chemical water treatment methods, it arouses more attention in recent years. At present, the cavitation is classified into four types based on the mode of generation, namely, ultrasonic cavitation, hydrodynamic cavitation, optic cavitation and particle cavitation [7,8]. Ultrasonic cavitation and hydrodynamic cavitation were two main means among the four types of cavitations for treating wastewaters in past study [8–10]. Whereas, optic and particle cavitations are typical single bubble cavitations, which fail to induce any physical or chemical change in the bulk solution [8]. However, owing to ultrasonic cavitation lacks comprehensive utilization of professional knowledge about related subjects, it is difficult to realize industrialization [11]. Hydrodynamic cavitation technology is still in its infancy stage and its degradation efficiency is relatively low, so it cannot yet be applied in practice on a large-scale [12].

In this work, a new cavitation method, air-bubble cavitation (induced by air-bubble passing glass balls), is presented. It is considered that during the rising process, original air bubbles are cut up heaps of times by small glass balls and become many small air bubbles. Two or several of them quickly recombine to a bigger one. When the inner wall tension between two bubbles reach a maximum limit, it breaks and collapses instantly. The cavitation happens and incidentally the high temperature, high pressure and high jet are produced locally, which induce H_2O and O_2 to form $^{\bullet}OH$ and $^{\bullet}O_2{}^{-}$ radicals with strong oxidation ability, respectively. Thus, the organic pollutants are degraded effectively by these reactive oxygen species (ROS). Here, Methyl Orange (MO) was chosen

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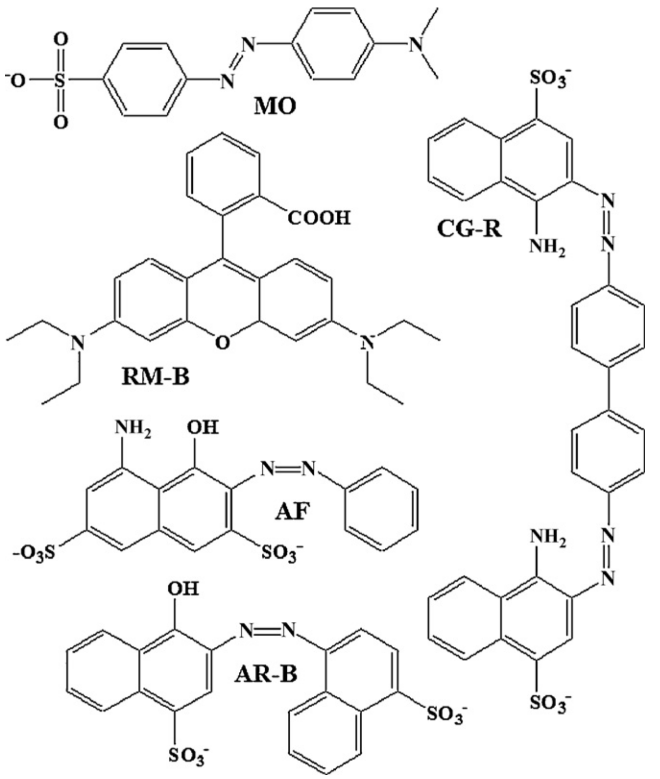

Fig. 1. Molecular structures of dyes used in this study.

as a model pollutant compound because it was a common dye and UV–vis spectrum was possibly used to monitor its degradation processes. Various influencing factors were studied on the degradation of MO through air-bubble cavitation. All experimental results indicated that the air-bubble cavitation was an effective, energy saving and simple reaction device method for wastewaters treatment.

2. Materials and methods

2.1. Materials

Methyl Orange (MO, analytical reagent, Aldrich, WI, USA) was purchased and chosen as a model compound. This compound shows yellow in basic medium and red in acidic medium, respectively. When MO is dissolved in water the UV–vis spectrum shows two absorption peaks at 275 and 460 nm, respectively. Other dyes (Congo Red (CG-R), Rhodamine B (RM-B), Azo Fuchsin (AF) and Acid Red B (AR-B), all analytical reagents, Tianjing Guangcheng Chemical Reagent Limit Company, China) were adopted to compare the degradation effect with MO and estimate the feasibility of air-bubble cavitation method. All other chemicals came from high purity Fluka or Aldrich products. The glass balls (1.0–1.5, 2.0–2.5, 3.0–3.5 and 4.0–4.5 mm sizes, ordinary grinding glass-ball, Zhejiang Yuyao Keyan Glass Ball Factory, China) were marinated in 1.0 mol/L hydrochloric acid (HCl) solution for 2 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 experimental result shows that such glass balls treated repeatedly hardly display the adsorption to MO. The water in this experiment was purified by a Milli-Q water system (Millipore) and was used throughout. Molecular structures of dyes used in this study were presented in Fig. 1.

2.2. Apparatus

UV–vis spectrophotometer (LAMBDA-17, Perkin-Elmer Company, USA) was used to inspect the degradation process and degree of dyes. The total organic carbon analyzer (TOC 1200, Thermo Electron Corporation, The Netherlands) was utilized to further analyze the degradation effect and degree of dye. High performance liquid chromatography (HPLC, Agilent-1100, Agilent Company, USA) was used to inspect the residuary dye and intermediate product. The Novpak-C_{18} chromatographic column is used in this experiment. The mobile phase is water and methyl alcohol (proportion 10:90, HPLC grade) and the flow rate of the solution is 1.0 mL/min. Air Pump (EP-9000, Guangdong Chuangxing Electronic Limit Company, China) was adopted to puff air into the solution of dyes, operating at output power of 5.6 W and gas flow rate of 4.5 L/min.

2.3. Procedure

The experimental procedure was as follows. The prepared 1000 mL MO solution 10 mg/L was put into self-made glass reactor filled with treated small glass balls. The amount of glass balls is three quarters of the reactor volume and the addition amount of MO solution is about 5.0 cm higher than the height of glass balls. Air was puffed from the bottom into the reactor. UV–vis spectra of the untreated and treated MO solution by air-bubble alone and air-bubble passing glass balls were all determined by UV–vis spectrophotometer in the wavelength range from 200 to 800 nm. The degradation ratio of MO in aqueous solution was calculated by the formula: Degradation ratio $(\%) = (C_0 - C_t)/C_0 \times 100\%$, where C_0 and C_t are the concentrations of MO solution at air-bubbling 0 and t time (min), respectively. The TOC removal was also determined to further explore the MO degradation effect. In order to check up the intermediate products and residuary dyes, HPLC (at 254 and 460 nm channel wavelength) of untreated and treated MO solution under different conditions were also determined, respectively.

Various factors influencing the degradation of MO were studied by multifold methods. The relationship between the degradation ratios and the air-bubbling time as well as the corresponding kinetics of degradation reactions was discussed. The influences of MO initial concentration (5.0–25.0 mg/L), NaCl addition amount (0–40 mg/L) and glass-ball size (1.0–1.5 to 4.0–4.5 mm) were also measured. For comparison, under same conditions the degradations of several dyes (MO, CG-R, RM-B, AF and AR-B) were reviewed. In addition, the process of air-bubble cavitation and possible degradation mechanism were provided and analyzed preliminarily.

All experimental conditions such as 10 mg/L MO initial concentration, 3.0–3.5 mm glass-ball size and 4.5 L/min gas flow rate at room temperature ($25.0 \pm 0.2\,^{\circ}C$) within 3.0 h air-bubbling, were unaltered throughout the investigation except for those special studies. The experimental equipment was provided as Fig. 2.

3. Results and discussions

3.1. UV–vis spectra, TOC and HPLC of MO solution during degradation

Fig. 3 shows that the original MO solution with 10 mg/L concentration has two main absorption peaks around 275 and 460 nm, respectively. They attribute to the electronic transitions of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ of benzene ring and azo bond in MO molecule, respectively. With the combined action of air-bubbling (4.5 L/min gas flow rate and 3.0 h air-bubbling) and the glass balls (3.0–3.5 mm size), the absorption peaks both declined obviously compared with that of original MO solution. It indicated that the method of air-bubble passing glass balls resulted in obvious degradation effect of MO.

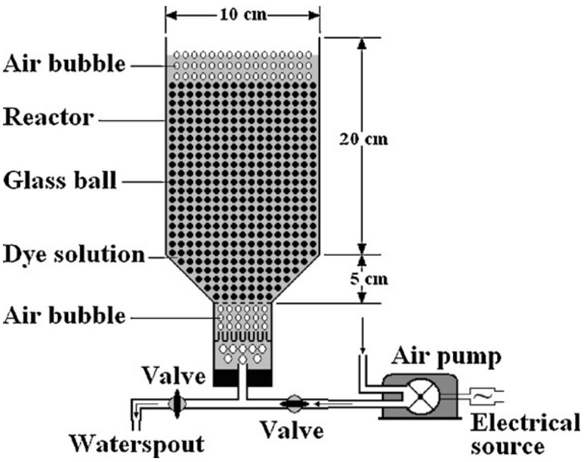

Fig. 2. Experimental equipment of degradation reaction.

Without glass balls, for air-bubble alone the absorption peaks of MO solution could also decline to a certain extent, but the decrease extent was very small. This showed that air-bubble alone cannot degrade MO effectively.

In addition, the degradation degree of MO in aqueous solution was also tracked through TOC determination. It was found that the degradation ratios based on the calculation of TOC were 35.16% and 7.64% for air-bubble alone and air-bubble + glass-ball, respectively, within 3.0 h air-bubbling. These were comparable with the results calculated according to the absorbance of UV–vis spectra. Hence, it was clearly seen that the MO in aqueous solution addition can be degraded effectively by using air-bubble cavitation method.

In order to explore the intermediate products and residuary dyes during the degradation process of MO in aqueous solution treated by air-bubble passing glass balls, HPLC of the treated solutions were determined at 254 and 460 nm channel wavelength, respectively. For comparison, HPLC of untreated (original) and treated MO solutions with air-bubble alone and air-bubble passing glass balls were also investigated. As shown in Fig. 4, for three courses the maximal peaks of the MO solutions all appeared at 1.41 min retention time for both 254 and 460 nm channel wavelength. And the peaks as height order was MO original solution > MO + air-bubble > MO + air-bubble + glass-ball. It meant that the azo bond and benzene ring of MO molecule was both destroyed by degrees. The maximal peaks at 460 nm had a little trend of changing two lower peaks, which indicated that the intermediates may be formed during the degradation process, but they were degraded largely at last by the method of air-bubble passing glass balls. The degradation process of MO in aqueous solution by air-bubble passing glass balls may produce hydroxyl ($^{\bullet}$OH) and superoxygenic anion ($^{\bullet}O_2^-$) radicals with strong oxidation ability, which can degrade the organic pollutants effectively.

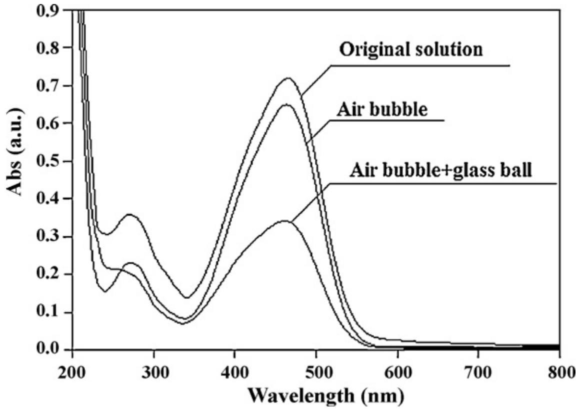

Fig. 3. UV–vis spectra of MO solutions under different conditions. (10 mg/L initial concentration, 4.5 L/min gas flow rate, pH = 6.0 solution acidity, 3.0 h air-bubbling and 25.0 ± 0.2 °C temperature).

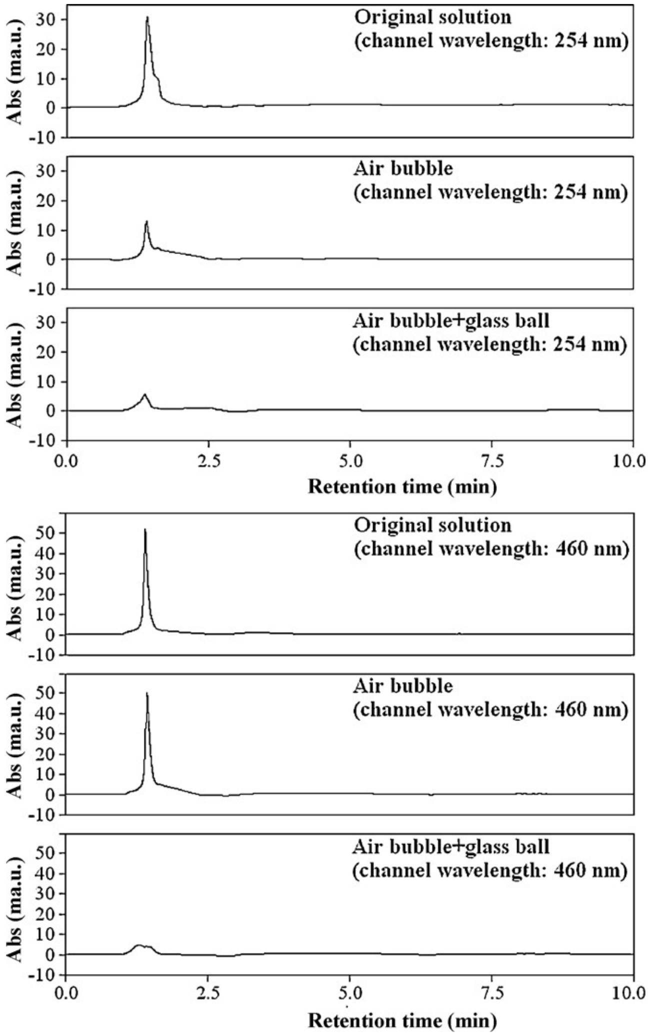

Fig. 4. HPLC of MO solutions at 254 and 460 nm channel wavelength under different conditions. (10 mg/L initial concentration, 4.5 L/min gas flow rate, pH = 6.0 solution acidity, 4.0 h air-bubbling and 25.0 ± 0.2 °C temperature).

3.2. *Effect of air-bubbling time and reaction kinetics on degradation of MO*

The degradation of MO dye in the presence of glass balls (3.0–3.5 mm) within 5.0 h air-bubbling at 1.0 h intervals were carried out for 10 mg/L MO solution and 4.5 L/min gas flow rate. As shown in Fig. 5a, the degradation ratios all rose along with the increase of air-bubbling time for three courses, which showed that the number of MO molecules was gradually reduced. Moreover, for 3.0 h air-bubbling in the presence of glass balls, the degradation ratio reached 37.82%. While air-bubbling 5.0 h, the degradation ratio exceeded 58.67%. Otherwise, without glass balls the degradation ratio was very low. Such as the degradation ratios were only 5.12% and 7.32%, when air-bubbling time were 3.0 and 5.0 h, respectively.

Fig. 5b shows all calculated values of $-\ln(C_t/C_0)$ were approximately linear with air-bubbling time (t) all through. That is, whether glass balls exist or not, the degradation processes of

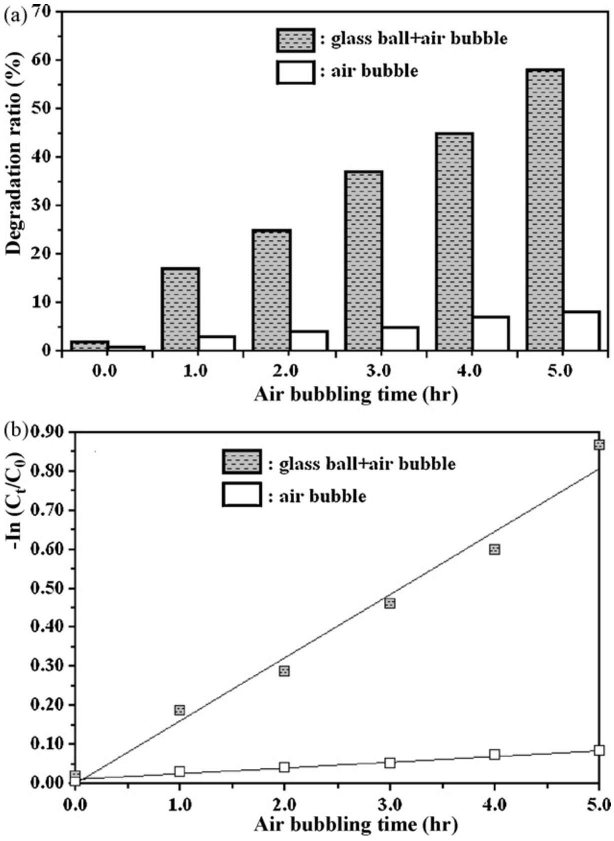

Fig. 5. Influence of (a) bubbling time and (b) reaction kinetics on degradation of MO. (10 mg/L initial concentration, 3.0–3.5 mm glass-ball size, 4.5 L/min gas flow rate, pH = 6.0 solution acidity and 25.0 ± 0.2 °C temperature).

MO in aqueous solution followed the pseudo first-order reaction kinetics. The rate constants were 0.1613 h^{-1} ($R^2 = 0.9813$) and 0.0151 h^{-1} ($R^2 = 0.9808$), respectively, corresponding in the presence and absence of glass balls, but the former is much faster than the later.

3.3. Effect of initial concentration on degradation of MO

The initial concentration of organic pollutants is an important parameter in wastewater treatment. If the initial concentration is too high, not only more time must be needed, but also the degradation is not complete. If the initial concentration is too low, it is difficult to degrade the organic pollutants due to they are far away from reaction activity field. Because the degraded amount of MO through air-bubble passing glass balls is limited in unit time, the fit initial concentration is necessary for effective degradation. As in Fig. 6, for 3.0 h air-bubbling, 4.5 L/min gas flow rate, 3.0–3.5 mm glass-ball size and pH = 6.0, in the range of 5.0–25.0 mg/L initial concentration, the MO degradation ratio decreased along with the raise of initial MO concentration. Considering the actual status, in this study, 10 mg/L was selected for initial concentration of MO solution throughout.

3.4. Effect of NaCl concentration on degradation of MO

In the process of dye production and printing, some organic salts as side products were often generated, like NaCl. Their presence may affect the degradation of organic pollutants. Thereby, altering NaCl concentration between 0 and 40 mg/L at 10 mg/L intervals, the effect of NaCl concentration on the degradation of MO was considered in this work. From Fig. 7, for 10 mg/L MO solution, 3.0 h air-bubbling, 4.5 L/min gas flow rate, 3.0–3.5 mm glass balls and pH = 6.0, at beginning the degradation ratio became low with the increase of NaCl concentration. However, when the NaCl concentration is beyond 20 mg/L, the degradation ratio begins to increase with the further raise of NaCl concentration. The reason is maybe that at the low concentration of NaCl or no NaCl, the free or exposed MO anions should be degraded by $^{\bullet}OH$ easily. However, along with the increase of NaCl concentration, more and more Na^+ ions gather around the MO anions, which causes the charge of MO anions to be neutralized and, and then, the MO anions are isolated. Thus, it makes MO to be degraded more difficultly. Moreover, with the further increase of NaCl concentration, the superfluous NaCl increase the surface tension and decrease the vapor pressure of aqueous solution, which helps in collapsing of the bubbles more violently, and resulting in a high degradation degree of organic pollutant.

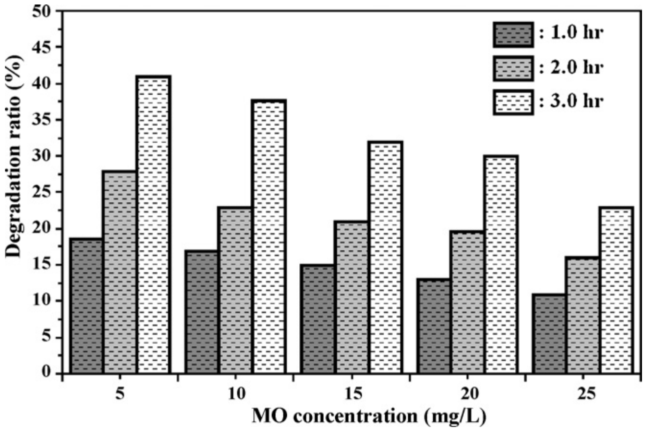

Fig. 6. Influence of MO initial concentration on degradation of MO. (3.0–3.5 mm glass-ball size, 4.5 L/min gas flow rate, pH = 6.0 solution acidity, 1.0–3.0 h air-bubbling and 25.0 ± 0.2 °C temperature).

3.5. Effect of glass-ball size on degradation of MO

It is understandable that glass-ball size decides both size and number of air bubbles. Even it influences the whole cavitation effect. Generally, too small size of glass balls can produce much more small size bubbles, but the cavitation effect may be influenced negatively owing to there is not enough space for bubbles to combine. However, the glass balls with too big size generate less but big air bubbles and only a few bubbles can combine, so that there is not obvious cavitation effect. Therefore, the first-rank

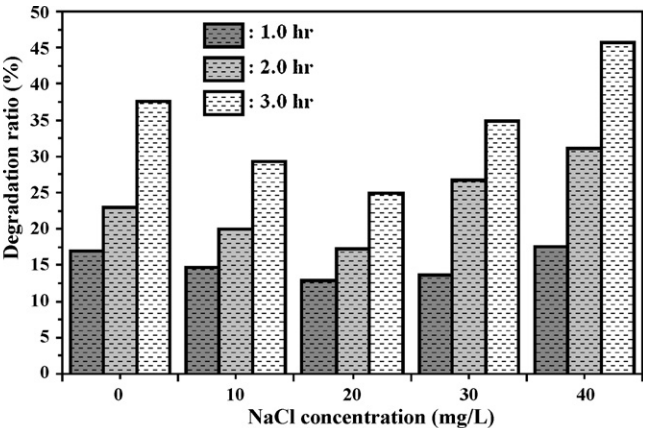

Fig. 7. Influence of NaCl concentration on degradation of MO. (10 mg/L initial concentration, 3.0–3.5 mm glass-ball size, 4.5 L/min gas flow rate, pH = 6.0 solution acidity, 1.0–3.0 h air-bubbling and 25.0 ± 0.2 °C temperature).

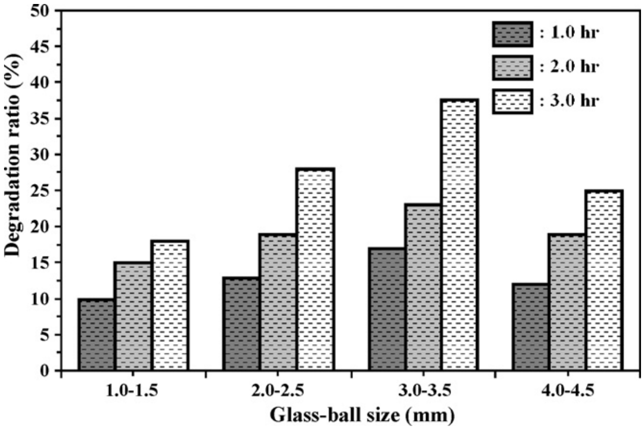

Fig. 8. Influence of glass-ball size on degradation of MO. (10 mg/L initial concentration, 4.5 L/min gas flow rate, pH = 6.0 solution acidity, 1.0–3.0 h air-bubbling and 25.0 ± 0.2 °C temperature).

glass-ball size is sought to achieve the highest degradation ratio. As shown in Fig. 8, the degradation ratio increases along with the accretion of glass-ball size from 1.0–1.5 to 3.0–3.5 mm. But when the glass-ball size surpass 3.0–3.5 mm, the degradation ratio decrease obviously. These demonstrated that there was a dependent relationship between cavitation effect and the glass-ball size in a certain range.

3.6. Comparison of degradation of some dyes

Fig. 9 shows the comparison of the degradation ratios of some organic dyes (MO, RM-B, CG-R, AF and AR-B). Obviously, these dyes can be degraded effectively by the method of air-bubble passing glass balls, which indicated that this method was a widespread treatment technology for many organic pollutants in wastewaters. The order of degradation ratios was as following: AR-B > AF > CG-R > RM-B > MO. The reason is that dyes like azo dyes with the simple structure were more easily to be degraded, whereas the dyes like the hetero-atom tricyclic compounds with complicated composition and structure were considerably difficult to be degraded.

3.7. Possible degradation mechanism of dyes during air-bubble passing glass balls

All experimental results showed that air-bubble cavitation induced by air-bubble passing glass balls can effectively degrade some organic dyes, such as MO, RM-B, CG-R, AF and AR-B, in aqueous solution. However, as the present work reports the utilization of air-bubble cavitation for treating various wastewaters for the first time, there have not yet been a satisfactory explanation on the process of air-bubble cavitation and a ready-made mechanism on the degradation of organic pollutants up till now. Here, the possible cavitation process and degradation mechanism were provided. Integrating all corresponding knowledges, perhaps, the following two points of view, namely “ultrasound-like cavitation” and “hydrodynamics-like cavitation”, should be borrowed to explain the phenomena of air-bubble cavitation and the degradation of organic pollutants in aqueous solution. As shown in Fig. 10, during rising process, an air-bubble is hampered by some glass balls with appropriate sizes and then split into two or several smaller air bubbles. In order to reduce the surface tension and energy, these small air bubbles have a recombination trend to come back to original bubble or form one bigger bubble. At this time, the interfacial tension between tangent two bubbles becomes bigger and bigger. That is, the interface becomes thinner and thinner until it ruptures. Because of the abrupt rupture, as shown as in Fig. 11a, large amounts of energies as light and heat forms were released, meanwhile, going with high pressure and fast jet. This phenomenon is similar to ultrasonic cavitation [13,14].

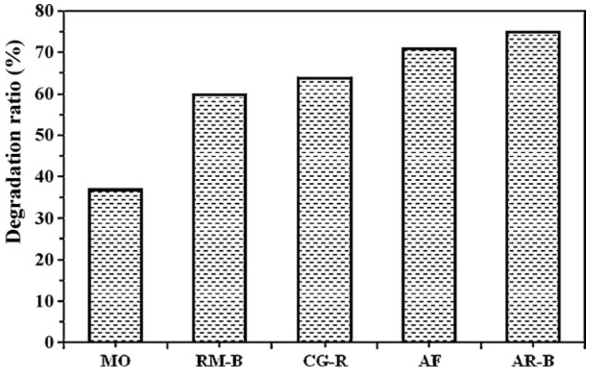

Fig. 9. Comparison of degradation of some dyestuffs. (10 mg/L initial concentration, 3.0–3.5 mm glass-ball size, 4.5 L/min gas flow rate, pH = 6.0 solution acidity, 3.0 h air-bubbling and 25.0 ± 0.2 °C temperature).

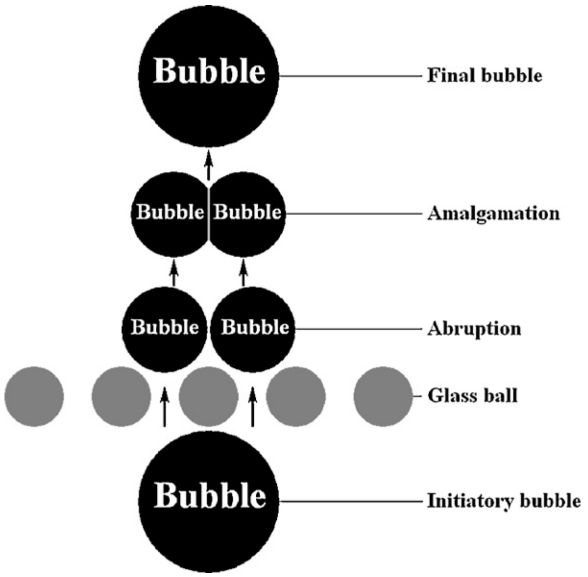

Fig. 10. Ascending process of air-bubble passing glass balls in water.

On the other hand, as shown as in Fig. 11b as the interface between coterminous two air bubbles disappears suddenly, the circular fringe of fracture zone outspreads and then fluctuates inside and outside until reaching to balance state. During outstretched process at upright direction, the constriction of the combined bubble at horizontal direction results in the reduction of pressure in the space around the bubble. When the inner pressure achieves and exceeds a critical value (vapour pressure of solvent) the cavitation effect occurs. This process is similar to the hydrodynamics somewhat.

Like the ultrasonic or hydrodynamic cavitation, the air-bubble cavitation can also produce strong light and high heat. Generally, the high temperature, high pressure and intense turbulence generated by cavitation effect can directly destroy the organic pollutants in aqueous solution [15,16]. Because of existence of plenitudinous oxygen (O_2), it is similar to the combustion that the organic pollutants are gradually decomposed and become carbon dioxide (CO_2) and water (H_2O) finally. Otherwise, under the actions of strong light and high heat, the H_2O molecule splits and becomes hydroxyl radical ($^{\bullet}OH$) and hydrogen radical ($^{\bullet}H$). And then the $^{\bullet}H$ reacts with O_2 producing superoxygenic anion radical

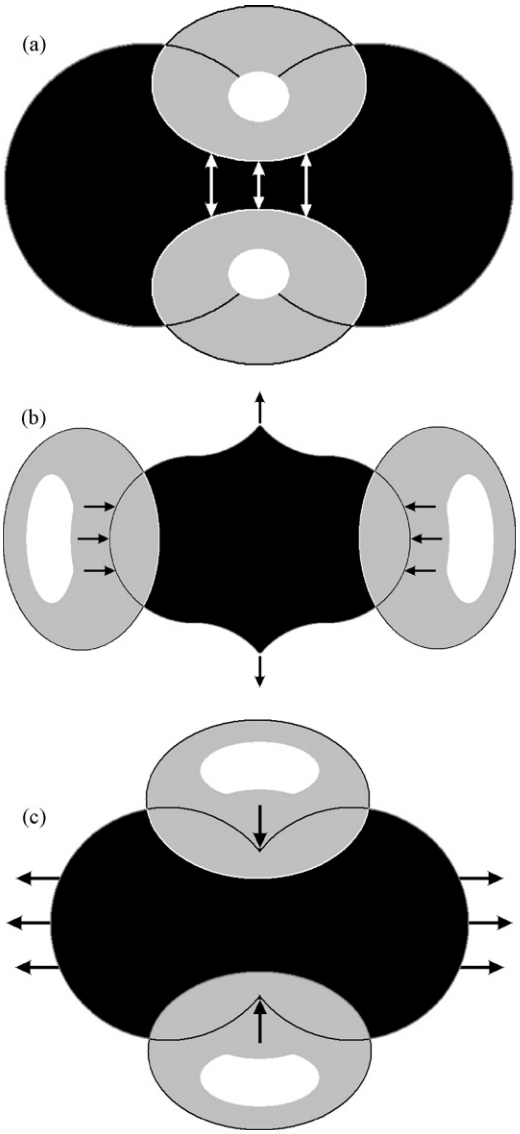

Fig. 11. Cavitation effect during cracking of air bubbles. (■): air bubbles; (▨): cavitation area; (□): cavitation center.

($^\bullet O_2^-$). Because of strong oxidizing property, these active oxygen species can also degrade organic pollutants in aqueous solution. In a similar way, as shown in Fig. 11c, when the bubble oscillates, the expansion generates up and down, the same cavitation happens.

To sum up, these processes including the formation, growth and collapse of microbubbles, leads to the generation of high temperature, high pressure and strong jet action locally, which can cause organic pollutants decompose and degrade. Therefore, here we call the method of air-bubble passing glass balls as air-bubble cavitation. Of course, the detailed mechanism on the air-bubble cavitation needs to be further and specially studied.

4. Conclusions

(1) Air-bubble passing glass balls can effectively degrade MO in aqueous solution. The degradation process follows pseudo first-order reaction kinetics.
(2) The effects of air-bubbling time, MO initial concentration, NaCl addition amount and glass-ball size on the degradation of MO were investigated systematically. Under the experimental conditions, such as 10 mg/L initial concentration, 3.0–3.5 mm glass-ball size, 4.5 L/min gas flow rate, pH = 6.0 solution acidity, 5.0 h air-bubbling and 25.0 ± 0.2 °C temperature, the degradation ratio can be over 58.64%.
(3) Through the degradation of some other dyes, it was proved that the air-bubble cavitation was a far-ranging method for treating organic pollutants.
(4) The degradation phenomenon of organic pollutants caused by air-bubble passing glass balls is attributed to air-bubble cavitation effect. In degradation process, the $^\bullet$OH and $^\bullet O_2^-$ radicals could be formed, which induced the organic pollutants to be degraded effectively.
(5) Anyway, all experimental results indicated that the air-bubble cavitation was an effective, energy saving and simple reaction device method for treating organic wastewaters. Hence, it is hoped that the method of air-bubble cavitation could become a kind of practical value and large-scale wastewater treatment method on the basis of further study.

Acknowledgments

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