Sonocatalytic degradation of azo fuchsine in the presence of the Co-doped and Cr-doped mixed crystal TiO$_2$ powders and comparison of their sonocatalytic activities

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ABSTRACT

In order to degrade some pollutants effectively under ultrasonic irradiation, the Co-doped and Cr-doped mixed crystal TiO$_2$ powders, with high sonocatalytic activity, were prepared as sonocatalyst. The Co-doped and Cr-doped mixed crystal TiO$_2$ powders as sonocatalyst were prepared through sol–gel and heat-treated methods from tetrabutylorthotitanate, and then were characterized by XRD and TG–DTA technologies. In order to compare and evaluate the sonocatalytic activity of the Co-doped and Cr-doped mixed crystal TiO$_2$ powders, the low power ultrasound was as an irradiation source and the azo fuchsine was chosen as a model compound to be degraded. The degradation process was investigated by UV–vis, TOC, ion chromatogram and HPLC techniques. The results indicated that the sonocatalytic activity of Cr-doped mixed crystal TiO$_2$ powder was higher than that of Co-doped and undoped mixed crystal TiO$_2$ powder during the sonocatalytic degradation of the azo fuchsine in aqueous solution. These results may be of great significance for driving sonocatalytic method to treat non- or low-transparent industrial wastewaters.

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1. Introduction

In general, titanium dioxide (TiO$_2$) powder has been known to exist in three main polymorphic phases: rutile, anatase and brookite. All of them have the same fundamental structural units of octahedron, but their arrangements are different [1]. It is well known that the TiO$_2$ has many interesting physical properties. Since the pioneering work of Fujishima and Honda [2], some researchers began to use the TiO$_2$ powder as photocatalyst to degrade organic pollutants under ultraviolet irradiation [3–5]. However, because the TiO$_2$ powder as photocatalyst must be excited by ultraviolet light and the photogenerated electrons and holes recombine easily, its application is limited. At the present time, many methods have been used to solve these problems. For example, in order to extend the absorption threshold of TiO$_2$ powder, the effects of some transition metal ions as dopants such as Fe, V, Cr, Co and Ni were already investigated [6–10].

However, because of low penetrating ability of any light, it is very difficult to treat those non- or low-transparent wastewaters using photocatalytic degradation method. Whereas, the penetrating ability of ultrasound is very strong for any water medium and its penetrating depth can ordinarily attain to 25–30 cm. An ultrasonic irradiation might be used as an alternative energy source for formation of hydroxyl ($^\bullet$OH) radical. Hence, the ultrasonic irradiation has been proposed as one of the techniques for degradation of hazardous organic compounds [11]. In general, the ultrasonic irradiation results in the formation and collapse of microscale bubbles and generating local high temperature and high pressure. These bubbles are thought to work as the reaction field and to promote the degradation reaction. Much research has been done to degrade the organic pollutants [12–14].

The aim of this work is to provide a new degradation method for organic pollutants, which is the combination of Co-doped or Cr-doped mixed crystal TiO$_2$ and ultrasonic irradiation, to treat various wastewaters. In order to compare the sonocatalytic activity between the Co-doped and Cr-doped mixed crystal TiO$_2$ powder, azo fuchsine was chosen as a model compound to be degraded. It was found that Cr-doped mixed crystal TiO$_2$ powder behaved higher sonocatalytic activity than that of Co-doped mixed crystal TiO$_2$ powder under ultrasonic irradiation. The results showed that the ultrasonic irradiation in the presence of Co-doped and Cr-doped

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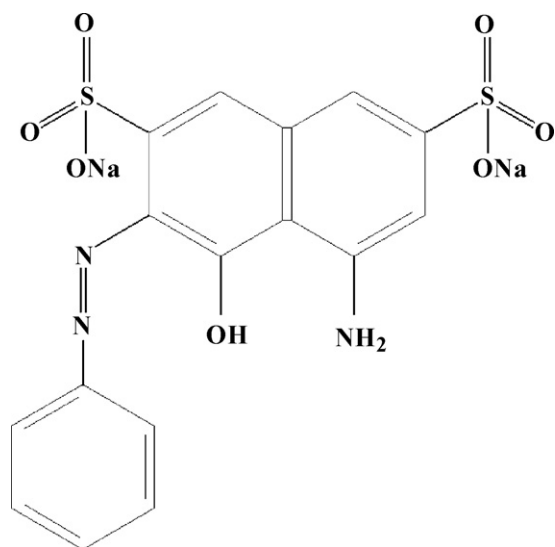*E-mail addresses:* wangjun890@126.com, wangjun890@sina.com (J. Wang).

Fig. 1. Molecular structure of azo fuchsine.

mixed crystal TiO$_2$ powders was a feasible method to treat the dye wastewater. The molecular structure of azo fuchsine is shown in Fig. 1.

2. Experimental

2.1. Materials and apparatus

Tetrabutylorthotitanate (Ti(OBu)$_4$, SP, Shanghai Chemistry Reagent Corporation, China); chromic nitrate and cobalt nitrate (Cr(NO$_3$)$_3$·9H$_2$O and Co(NO$_3$)$_3$·6H$_2$O, AR, Tianjing Tianhe Chemistry Reagent Corporation, China); ethyl alcohol (CH$_3$CH$_2$OH, AR, Beijing Chemistry Reagent Corporation, China); hydrochloric acid (HCl, GR, 30–38% content, Beijing Chemistry Reagent Corporation, China); azo fuchsine (C$_{16}$H$_{11}$N$_3$O$_7$S$_2$Na$_2$, AR, Shanghai Xinzhong Chemistry Reagent Corporation, China). SX2-4-10 Muffle furnace (Great Wall Furnace Company, China); 101-1 oven (Shanghai Experiment Apparatus Company, China); D8ADVANCE XRD diffractometer (Bruker Company, Germany); TGA/SDTA851^e Thermal analysis instrument (Mettler-Toledo Group, USA); LAMBDA-17 UV-vis spectrometer (Perkin-Elmer Company, USA); the total organic carbon (TOC) apparatus (TOC 1200, Thermo Electron Corporation, The Netherlands); KQ-100 ControllableSerial-Ultrasonics apparatus (40 kHz, 50 W, Kunshan apparatus Company, China); ICS-90 ion chromatogram (DIONEX Company, USA); Agilent-1100 high performance liquid chromatography (Agilent Company, US).

2.2. Preparation of Co-doped and Cr-doped mixed crystal TiO$_2$ powder

In this paper, the Co-doped and Cr-doped mixed crystal TiO$_2$ powders used as sonocatalyst were prepared by adopting sol–gel and heat-treated method. Ti(OBu)$_4$ was used as TiO$_2$ source and Cr(NO$_3$)$_3$·9H$_2$O and Co(NO$_3$)$_3$·6H$_2$O were used as Cr^{3+} and Co^{3+} dopants, respectively. Otherwise, the ethyl alcohol as solvent and the hydrochloric acid as catalyst were selected for preparation. The preparation process was as follows. Firstly, 50 mL Ti(OBu)$_4$ and 160 mL ethyl alcohol were mixed together and the mixed solution was stirred for 1.0 h. Afterwards, cobaltic nitrate solution and chromic nitrate solution with given concentration (the atomic ratio of Co and Cr to Ti is 0.25%) were added to the mixed solution in drops. At the same time, hydrochloric acid was also added for controlling the solution pH value to prevent the formation of TiO$_2$ precipitates. The finally mixed solution was placed for a moment to form wet gel. Then the wet gel was dried at 100 °C for 10.0 h in the oven to form dry gel powder. Last but not least important, the dry gel powder was heated at 600 °C for 3.0 h in the muffle furnace and the nano-sized Co-doped and Cr-doped mixed crystal TiO$_2$ powders were obtained after adequate rubbing.

2.3. Characterization of Co-doped and Cr-doped mixed crystal TiO$_2$ powder

The crystallization behaviors of the xerogel powder were monitored with a thermogravimetric-differential thermal analysis (TG–DTA) instrument. It was performed in the presence of Ar atmosphere (flowing rate 20 mL min^{-1}) from room temperature to 800 °C at a heating rate of 10 °C min^{-1}. X-ray diffraction (XRD) patterns obtained on an X-ray diffractometer with Cu Kα radiation with a scan rate of 2.0 °C min^{-1} were used to compare the difference between Co-doped and Cr-doped mixed crystal TiO$_2$ powders and undoped TiO$_2$ powder.

2.4. Sonocatalytic degradation reaction procedure

In a conical flask 50 mg Co-doped or Cr-doped mixed crystal TiO$_2$ powder was mixed with 50 mL of azo fuchsine solution (10 mg L^{-1}), and the mixed solution was stirred for 2.0 h without any irradiation in order to attain the adsorption equilibrium. Then a small amount of the mixed solution was taken out and centrifuged. The separated supernatant azo fuchsine solution was used for determining UV–vis spectra. Then, the mixed solution was placed inside an ultrasonic apparatus used as irradiation source. Total ultrasonic intensities and frequencies were adjustable for 20/30/50 W and 20/40/80 kHz, respectively. The mixed solution was sampled at a definite interval time for tracking the process of azo fuchsine degradation. For comparison, all the experiments were done under same conditions. Such as initial azo fuchsine concentration was 10 mg L^{-1}, addition amount of TiO$_2$ powder was 1000 mg L^{-1}, initial pH was 10.0, solution temperature was about 20.0 ± 0.2 °C, ultrasound frequency was 40 kHz and power was 50 W. The experimental setup is shown in Fig. 2.

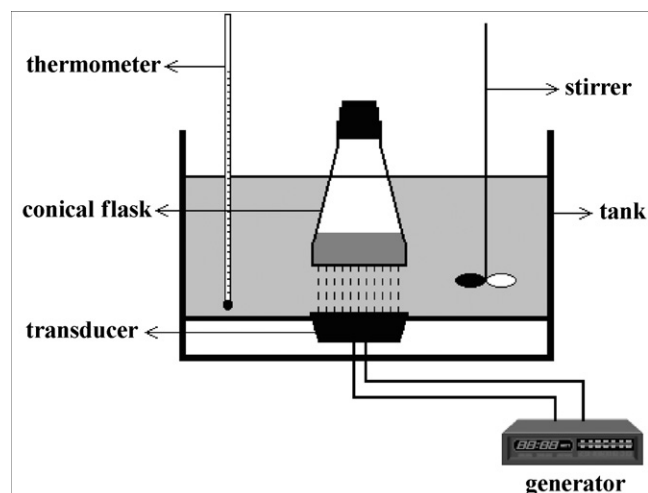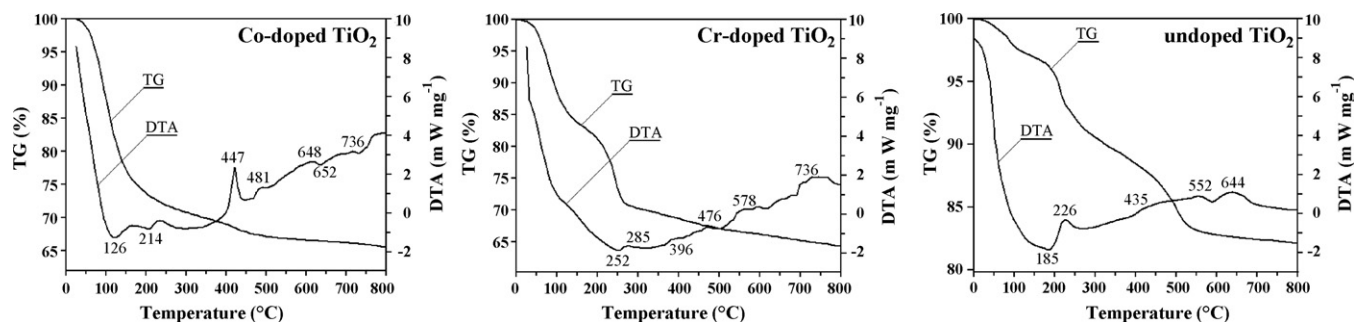**Fig. 2.** Schematic illustration of experimental setup.

Fig. 3. TG–DTA patterns of Co-doped TiO$_2$, Cr-doped TiO$_2$ and undoped TiO$_2$ powders.

3. Results and discussion

3.1. Thermal analysis of various TiO$_2$ dry gel powders

Fig. 3 shows the TG–DTA curves of (0.25%) Co-doped TiO$_2$, (0.25%) Cr-doped TiO$_2$ and undoped TiO$_2$ dry gel powders. The TG–DTA curve of Co-doped TiO$_2$ dry gel powder is mainly divided into three stages. The first stage occurs in the temperature range from room temperature to 126 °C. There is an endothermic peak. This is attributed to the evaporation of the physically absorbed water and alcohol molecules. The second stage happens at 447 °C, where there is an exothermic peak, but it is attributed to the combustion of organic compounds including butanol. The third stage presents between 481 °C and 736 °C, which shows several endothermic peaks. It should be attributed to the decomposition and combustion of un-hydrolyzed tetrabutyl titanate. In addition, after 736 °C, there is an exothermic peak. This process should belong to the phase transformation of TiO$_2$ powder from anatase to rutile. That is, the last exothermic peak between 749 °C and 800 °C reveals that all sub-stable anatase phase have already become stable rutile phase. Correspondingly, for (0.25%) Cr-doped and undoped TiO$_2$ dry gel powder, the similar course occurs throughout the whole process. However, from TG–DTA curves, it can be found clearly that the exothermic reaction temperature (644 °C) of undoped TiO$_2$ powder is lower than that (736 °C) of Co-doped and Cr-doped TiO$_2$ powders. It is the reason why, due to the presence of Co^{3+} and Cr^{3+} ions, the phase transformation of TiO$_2$ powder from anatase to rutile is restrained somewhat. For this reason, when the temperature reached 600 °C, there was more anatase phase TiO$_2$ in the mixed crystal TiO$_2$, so the sonocatalytic activities of Cr-doped and Co-doped TiO$_2$ are higher than that of undoped TiO$_2$.

3.2. The XRD of Co-doped, Cr-doped and undoped TiO$_2$

Fig. 4 represents the XRD patterns of Co-doped, Cr-doped and undoped TiO$_2$ powders. Comparing the XRD patterns, it can be found that the diffraction peaks belonging to anatase phase in
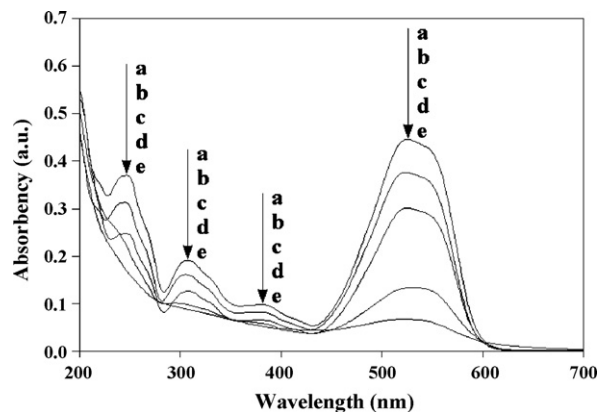

Fig. 5. The UV–vis spectra of azo fuchsine solution under different conditions: (a) original solution, (b) onefold ultrasound (120 min), (c) ultrasound (120 min) + undoped TiO$_2$, (d) ultrasound (120 min) + Co-doped TiO$_2$ and (e) ultrasound (120 min) + Cr-doped TiO$_2$.

Co-doped and Cr-doped TiO$_2$ powders are stronger than corresponding ones in undoped TiO$_2$ powder. However, the diffraction peaks belonging to rutile phase in Co-doped and Cr-doped TiO$_2$ powders are lower than corresponding ones in undoped TiO$_2$ powder. According to the quantitative equation: $\beta_R = 1/[1 + 0.8(I_A/I_R)]$ and $\beta_A = 1/[1 + 1.26(I_R/I_A)]$ (I_A, diffraction intensity of anatase phase; I_R, diffraction intensity of rutile phase), the Cr-doped mixed crystal TiO$_2$ powder contains 65.4% anatase phase and 34.4% rutile phase. The Co-doped mixed crystal TiO$_2$ powder contains 55.56% anatase phase and 44.05% rutile phase. While the undoped TiO$_2$ powder does 28.65% anatase phase and 71.43% rutile phase. It can be concluded that the Cr^{3+} and Co^{3+} ions as dopants not only restrain the crystallization of rutile phase TiO$_2$ but also cumber the transformation from anatase phase to rutile phase. Otherwise, in the XRD pattern there are not the peaks of Cr^{3+} and Co^{3+} ions as dopants. One probable reason is that the content of doped Cr^{3+} and Co^{3+} ions is so low that it cannot be detected by XRD. The other is
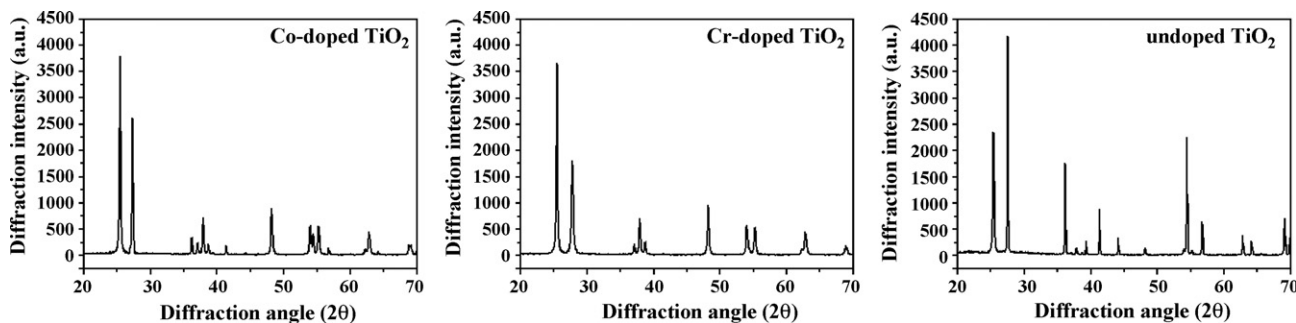

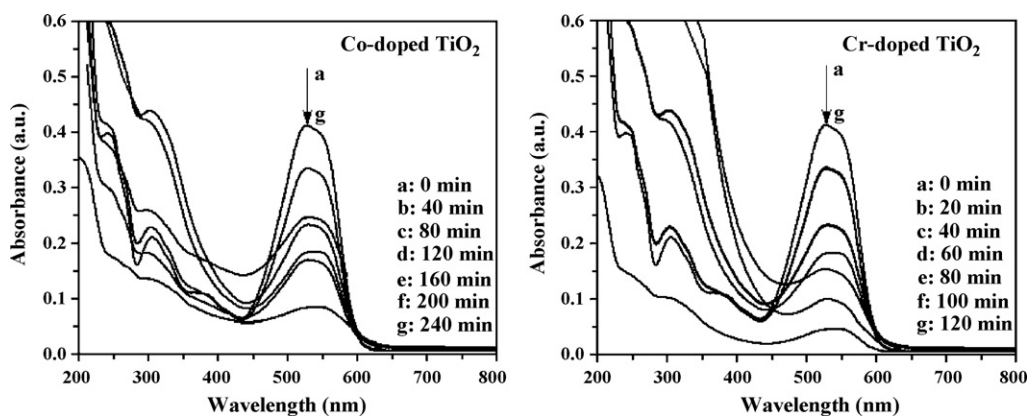**Fig. 4.** XRD patterns of Co-doped TiO$_2$, Cr-doped TiO$_2$ and undoped TiO$_2$ powder.

Fig. 6. The UV–vis spectra of azo fuchsine solution with ultrasonic irradiation time in the presence of Co-doped and Cr-doped mixed crystal TiO$_2$ powder.

that the radius of Ti^{4+} (0.68 Å), Cr^{3+} (0.64 Å) and Co^{3+} (0.74 Å) ions are very similar to each other and all the iron ions maybe insert the crystal structure of TiO$_2$ particles, and locate at interstices or occupy some of the titanium crystal lattice sites, forming an iron–titanium oxide solid solution.

3.3. The UV–vis spectra of azo fuchsine solution under various conditions

The 50 mL prepared azo fuchsine solution (10 mg L^{-1}) and 50 mg Cr-doped mixed crystal TiO$_2$ powder (1000 mg L^{-1}) were put into a glass reactor (50 cm^2 bottom area), the pH value of the mixed solution was adjusted to 5.0, and then irradiated with the ultrasound of 40 kHz frequency and 50 W output power. In order to exhibit the degradation of azo fuchsine, the UV–vis spectra of the original and treated azo fuchsine solutions were determined by UV–vis spectrophotometer at 120 min in the wavelength range from 300 nm to 800 nm. The determined results were shown in Fig. 5. It can be found that the degradation ratio order is as follows: original solution < onefold ultrasound < ultrasound (120 min) + undoped TiO$_2$ < ultrasound (120 min) + Co-doped TiO$_2$ < ultrasound (120 min) + Cr-doped TiO$_2$. And it can indicate from Fig. 5 that the azo fuchsine molecules were degraded mostly under ultrasonic irradiation in the presence of Cr-doped mixed crystal TiO$_2$ powder.

3.4. The effect of ultrasonic irradiation time on sonocatalytic degradation of azo fuchsine

The experimental conditions in the presence of Co-doped mixed crystal TiO$_2$ were same as that in the presence of Cr-doped mixed crystal TiO$_2$. The results were shown in the Figs. 6 and 7(a). It can

be found that the peak at 536 nm declined along with the ultrasonic irradiation time rising. But after 240 min, the peak did not completely disappear. It indicated that the degradation effect in the presence of Cr-doped mixed crystal TiO$_2$ is better than that in the presence of Co-doped mixed crystal TiO$_2$.

In addition, in order to infer the sonocatalytic activities of the Cr-doped mixed crystal TiO$_2$ and Co-doped mixed crystal TiO$_2$, the reaction kinetics were also studied. Here, the data of $-\ln(C_t/C_0)$ for first-order reaction as a function of irradiation time (t) was calculated. In fact, as shown in Fig. 7(b), the results indicate that all calculated values of $-\ln(C_t/C_0)$ are approximately linear with the irradiation time all through. That is, the sonocatalytic degradation processes of azo fuchsine in these four systems conform to pseudo-first-order kinetics reactions. Moreover, it also can be found that the ultrasonic degradation effect in the presence of Cr-doped mixed crystal TiO$_2$ is better than that in the presence of Co-doped mixed crystal TiO$_2$.

3.5. The effect of catalyst addition amount on sonocatalytic degradation of azo fuchsine

The addition amount of the catalyst is one of the important parameters for the catalytic activity. The more moderate addition amount of catalyst was used, the higher catalytic activity was obtained. So the effect of addition amount of various TiO$_2$ powders was investigated in the range of 0–1250 mg L^{-1} at 250 mg L^{-1} interval under 80 min ultrasonic irradiation. The results were shown in Fig. 8. It can be found that the degradation ratios rise along with the increase of catalyst addition amounts for both Cr-doped and Co-doped mixed crystal TiO$_2$ powders. Considering the cost and adsorption, in this work, 1000 mg L^{-1} was adopted as optimal addition amount of TiO$_2$ catalyst.
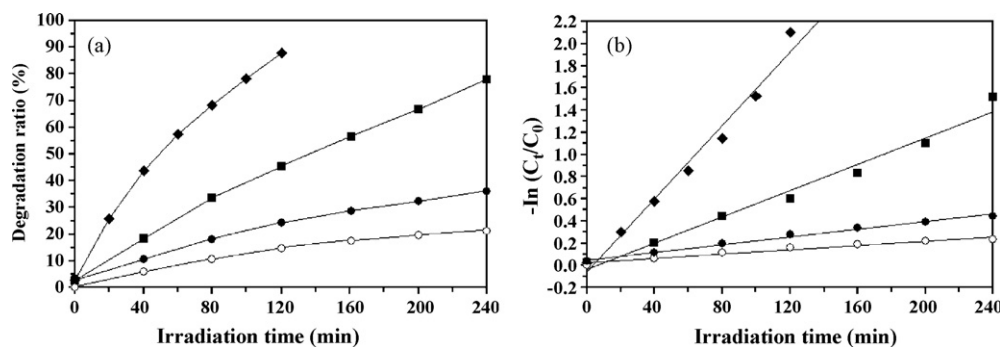

Fig. 7. The influence of (a) ultrasonic irradiation time and reaction kinetics and (b) on sonocatalytic degradation of azo fuchsine: (■) ultrasound + Co-doped TiO$_2$, (♦) ultrasound + Cr-doped TiO$_2$, (●) ultrasound + undoped TiO$_2$ and (○) onefold ultrasound.
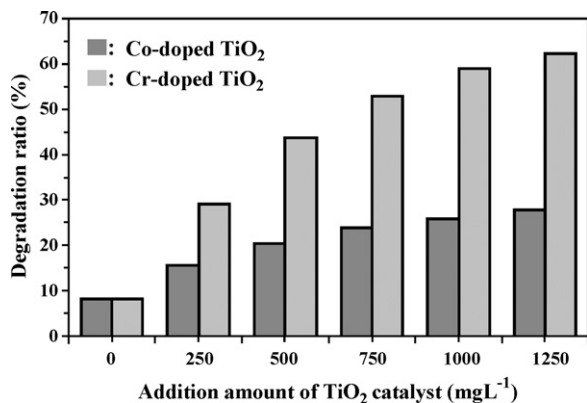
Fig. 8. The influence of catalyst addition amount on sonocatalytic degradation of azo fuchsine.
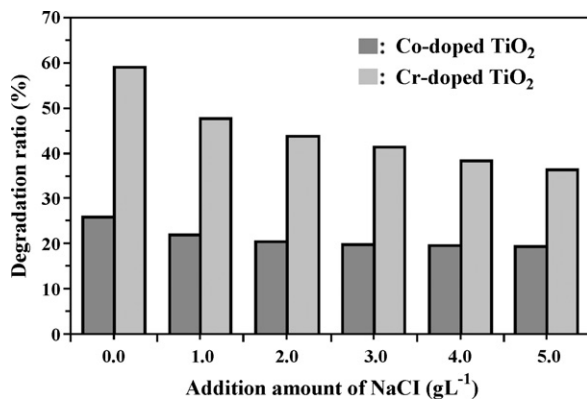

Fig. 9. The influence of NaCl addition amount on sonocatalytic degradation of azo fuchsine.

3.6. The effect of inorganic ion kind and amount on sonocatalytic degradation of azo fuchsine

In order to simulate industrial wastewater, some inorganic ions were put into the azo fuchsine solution. The effects of Cl^- and CO_3^{2-} as the object inorganic ions were investigated, and the results were shown in Figs. 9 and 10, respectively.

As shown in Fig. 9, it can be found that the degradation ratio of azo fuchsine decreased as the NaCl addition amount increased in the presence of Cr-doped and Co-doped mixed crystal TiO_2 powders under 80 min ultrasonic irradiation. Nevertheless, the decrease of the degradation efficiency in the presence of Cl^- anion may be due
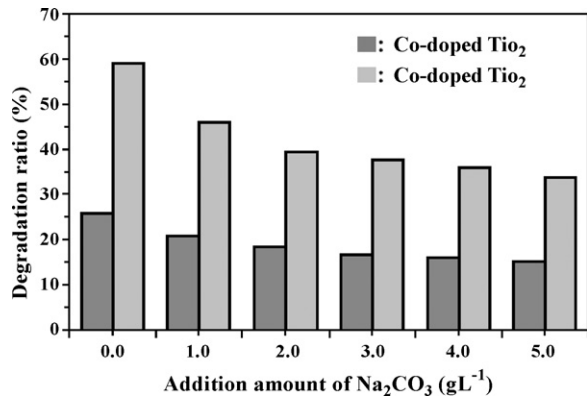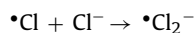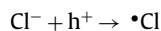

Fig. 10. The influence of Na_2CO_3 addition amount on sonocatalytic degradation of azo fuchsine.

to the catching properties of the chloride ion for holes. The process is shown in the following equations:

$$Cl^- + h^+ \rightarrow {}^\bullet Cl$$

$${}^\bullet Cl + Cl^- \rightarrow {}^\bullet Cl_2^-$$

The reaction of dye molecule with the hole has to compete with these supererogatory reactions. The chloride radical anions can also block the reactive sites of the surface of TiO_2 particles.

The effect of Na_2CO_3 on the sonocatalytic degradation of azo fuchsine is shown in Fig. 10. It can be found that the degradation ratio also decreased as the addition amount of Na_2CO_3 increasing in the presence of Cr-doped and Co-doped mixed crystal TiO_2 powders under 80 min ultrasonic irradiation. In fact, this decrease of the degradation efficiency is due to the scavenging property of carbonate ion for hydroxyl (${}^\bullet OH$) radicals [15]. The process is shown in the following equations [16,17]:

$${}^\bullet OH + CO_3^{2-} \rightarrow OH^- + {}^\bullet CO_3^-$$

$${}^\bullet OH + HCO_3^- \rightarrow H_2O + {}^\bullet CO_3^-$$
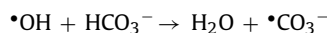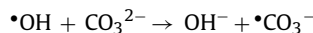
Thus the ${}^\bullet OH$ radical as oxidant decreases gradually with the increase of CO_3^{2-} anion and consequently there is a significant decrease in sonocatalytic degradation. In addition, the surplus CO_3^{2-} ions are disadvantage for the degradation of azo fuchsine because of electrostatic repulsion between them.

3.7. Ion chromatogram and HPLC of azo fuchsine solution during sonocatalytic degradation

In order to compare the different sonocatalytic activities of the Co-doped and Cr-doped mixed crystal TiO_2 powders, the ion chromatogram and the HPLC of treated azo fuchsine solutions were investigated.

After 80 min ultrasonic irradiation, the ion chromatogram of azo fuchsine solution in the presence of Co-doped and Cr-doped mixed crystal TiO_2 powders, were investigated and the results were shown in Fig. 11. It clearly proves that the sulphur and nitrogen heteroatoms in azo fuchsine molecule, after sonocatalytic degradation, are converted into the simple and innocuous inorganic NO_2^-, NO_3^- and SO_4^{2-} anions, whose peaks appear at 8.627 min, 14.370 min and 18.560 min in ion chromatogram, respectively. But the amount
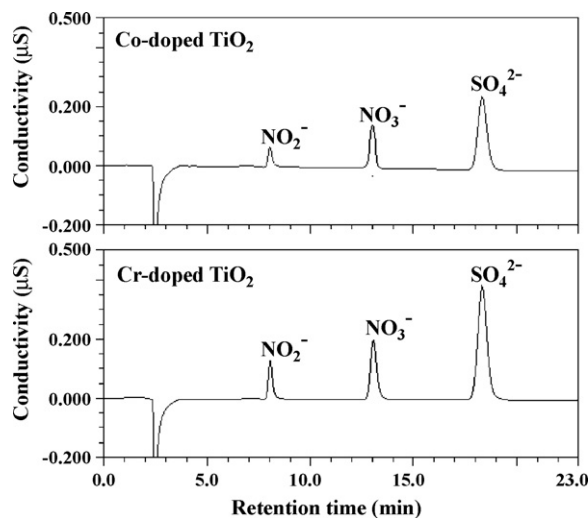

Fig. 11. Ion chromatogram of azo fuchsine solution under ultrasonic irradiation in the presence of Co-doped and Cr-doped mixed crystal TiO_2 powder.

of the inorganic anions in the presence of Cr-doped mixed crystal TiO_2 powder was slightly bigger than that in the presence of Co-doped mixed crystal TiO_2 powder. It indicated that the sonocatalytic activity of the Cr-doped mixed crystal TiO_2 powder was higher than that of the Co-doped mixed crystal TiO_2 powder. However, the peaks corresponding to NO_2^- and NO_3^- anions seem to be much lower compared with the theoretic content of nitrogen atom in azo fuchsine molecule. The following reasons may be used to explain this phenomenon. Firstly, during sonocatalytic degradation, at beginning the partial azo bond and $-NH_2$ group in azo fuchsine molecule are decomposed and then reduced to NH_4^+ cation, which did not appear in ion chromatograms. Secondly, as the azo fuchsine molecules in aqueous solution are gradually degraded, a series of nitrogen oxides (NO_x) and nitrogen gas (N_2) are also produced. Some volatile nitrogen oxides and nitrogen gas escape from reaction system, which also results in the low peak of the NO_2^- and NO_3^- anions. Of course, this is a perfect manner removing organic pollutants from wastewater.

As shown in Fig. 12, it can be found from the HPLC that the azo fuchsine in aqueous solutions were degraded under ultrasonic irradiation for 80 min in the presence of Co-doped and Cr-doped mixed crystal TiO_2 powders. But the declined extents of them were different. It also indicated that the sonocatalytic activity of Cr-doped mixed crystal TiO_2 powder was higher than that of Co-doped mixed crystal TiO_2 powder.

From ion chromatogram and HPLC, it can be found that the sonocatalytic activity of Cr-doped mixed crystal TiO_2 powder is higher than that of Co-doped mixed crystal TiO_2 powder. The reasons may be as follows: the high catalytic activity of prepared samples may be ascribed to small crystal size, high specific surface area as well as their mesoporous structure. The beneficial effect of Cr^{3+} under ultrasonic irradiation may be explained by considering the efficient separation of sonoexcited electrons and holes. It is well known, the Cr^{3+} capturing an electron to Cr^{2+} is more difficult than that of Co^{3+} to Co^{2+} in solution, but the oxidation process of Cr^{2+} to Cr^{3+} is easier than that of Co^{2+} to Co^{3+}. So the Cr^{2+} is relatively easy to be oxidized to Cr^{3+} in solution under ultrasonic irradiation, where less oxygen exists, because most oxygen have reacted with electrons excited by ultrasound. Due to the favorable circular system between Cr^{2+} and Cr^{3+} consuming electrons, holes remained on the surface of TiO_2 particles react with H_2O adequately and gen-
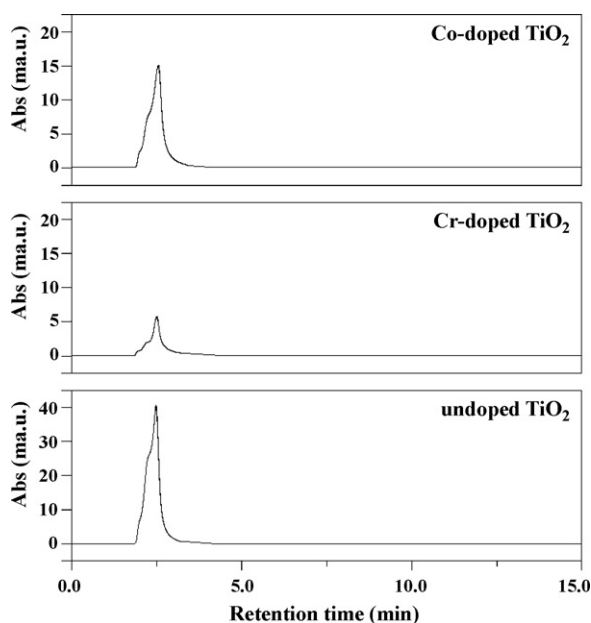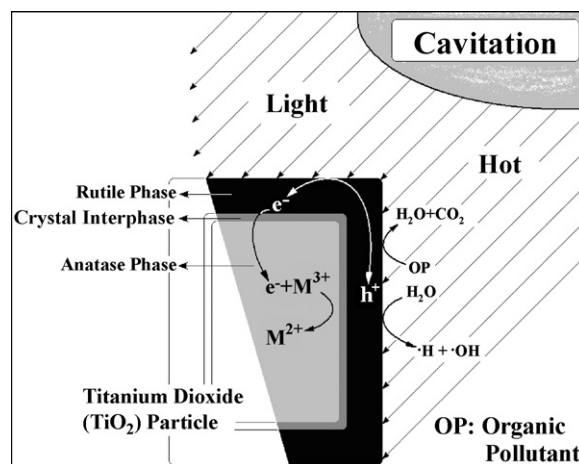

Fig. 13. Possible degradation process and mechanism of organic pollutants in the presence of M-doped mixed crystal TiO_2 powder.

erate $^\bullet$OH radicals with strong oxygen ability, which can degrade organic compounds effectively. So the Cr-doped mixed crystal TiO_2 powder has high sonocatalytic activity. And the order of degradation ratios is as follows: Cr-doped mixed crystal TiO_2 > Co-doped mixed crystal TiO_2 > undoped crystal TiO_2.

3.8. Possible sonocatalytic degradation mechanism

Until now, there has been no established mechanism and satisfactory explanation on the sonocatalytic degradation of organic pollutants in the presence of various TiO_2 catalysts. Possible process of sonocatalytic degradation of azo fuchsine in the presence of metal-doped mixed crystal TiO_2 powder under ultrasound irradiation is shown in Fig. 13. Perhaps the following three aspects, namely, sonoluminescence, "hot spot" and oxygen atom escape may be accepted to explain the sonocatalytic degradation process of azo fuchsine and other organic pollutants in aqueous solution. Firstly, it has been well known that the ultrasonic irradiation can result in the formation of the light with a comparatively wide wavelength range because of acoustic cavitation. Those lights below 375 nm in wavelength can excite the TiO_2 particles to act as a photocatalyst. And then a great deal of $^\bullet$OH radicals with high oxidation activity should form on the surface of TiO_2 particle. In fact, that is the reaction mechanism of photocatalytic degradation. Secondly, as well known, the temperature of "hot spot" produced by acoustic cavitation in aqueous medium can reach $10^5\,^\circ$C or $10^6\,^\circ$C, such high temperature sufficiently causes electrons to escape from the surface of TiO_2 particle and produces many holes. Similarly, these holes can decompose those organic pollutants adsorbed on the surface of TiO_2 particles directly or indirectly degrade them in aqueous solution through the $^\bullet$OH radicals resulting from the reaction of holes or electrons and H_2O molecules. Of course, the precise mechanism of sonocatalytic degradation is to be further investigated.

4. Conclusion

Through degradation of azo fuchsine in aqueous solution, it can be found that both Cr-doped and Co-doped mixed crystal TiO_2 powders exhibit the higher sonocatalytic activity than that of undoped TiO_2 powder. The corresponding order is Cr-doped mixed crystal TiO_2 powder > Co-doped mixed crystal TiO_2 powders > undoped TiO_2 powder. Concretely, the azo fuchsine in aqueous solution can be obviously degraded under ultrasonic irradiation in the presence of Cr-doped and Co-doped mixed crystal TiO_2 powders. The research results demonstrate

Fig. 12. HPLC of azo fuchsine solution under different conditions.

the feasibilities of the sonocatalytic degradation of azo fuchsine and other organic pollutants in wastewater. Especially, this method is applicable for those non- and low-transparent wastewaters. Hence, it has a corking applied foreground in future.

Acknowledgements

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