Treatment of Raw Dye Wastewater by Using Novel
Process Ultrasonic Irradiation with Fenton Oxidation

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Treatment of raw dye wastewater mainly containing methyl orange was conducted by using Fenton oxidation and liking ultrasonic irradiation with Fenton oxidation (*i.e.*, US-Fenton) in the present work. The effect of varying initial pH, hydrogen peroxide and ferrous species dosage on chemical oxygen demand (COD) and colour removal efficiencies was determined and the change of UV/Visible absorption spectra with reaction time was also measured to investigate the decomposition of organic chemical compounds containing aromatic rings. The results showed that enhancement effect of ultrasonic irradiation on Fenton oxidation was obvious, displaying a good synergistic effect in treating dye wastewater. When COD concentration and colour value were 3020 mg/L and 2060, respectively in the influent, those removal efficiencies were 93.7 and 95.9 % in the US-Fenton system (significantly higher than that in Fenton system) under the optimum condition including initial pH of 3, H_2O_2 of 6.0 mmol/L and Fe^{2+} of 0.8 mmol/L, electric output power of 250 W and electric frequency of 20 kHZ. Before oxidation in the US-Fenton system, the absorption spectrum of dye wastewater was characterized by three main bands including two in UV region with maximum absorption at 210 and 280 nm respectively and the other in visible region with that of 465 nm and the visible maximum absorption band disappeared after oxidation, suggesting the fragmentation of organic chemical compounds containing aromatic rings during the ultrasonic irradiation and Fenton oxidation process. These results suggest that the process linking ultrasonic irradiation with Fenton oxidation may provide an economical and effective alternative for treatment of dye wastewater or non-biodegradable industrial wastewater.

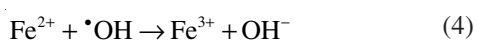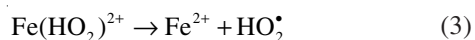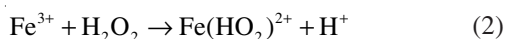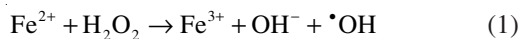**Keywords: Dye wastewater, Fenton oxidation, Ultrasonic irradiation, COD removal, Colour removal.**

INTRODUCTION

Dyes are extensively used in paper, leather and textile industries that generally produce large volumes of dye wastewater typically characterized by high chemical oxygen demand (COD) and intense colour, which may cause serious toxicities to water life as well as undesirable colours to water bodies and even harm to public health[1]. Organic pollutants degradation and colour removal are two important research tasks in dye wastewater treatment. Due to existence of complicated chemical structures such as aromatic amine, phenyl and azo compounds in dye wastewaters, it is commonly considered to be non-biodegradable or very low biodegradable[2]. Thus, dye wastewaters treatment, including colour removal and organic pollutants biodegradation, were unsatisfactory in conventional wastewater treatment processes (*i.e.*, biological oxidation treatment) because of its refractory to degradation.

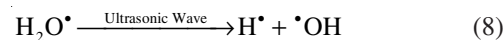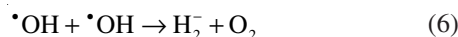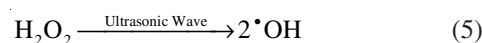For the treatment of non-biodegradable industrial wastewaters, in some cases, advanced oxidation processes (AOPs) have been reported to be a preferable alternative to the conventional biological oxidation treatment process[3-6]. In an AOP, degradation of non-biodegradable pollutants can be highly treated by hydroxyl radical (•OH) displaying non-selectivity and high reactivity in attacking ring-conjugated double bonds, such as C=N, C=C and N=N[7], which can mineralize a wide range of organic chemical compounds[8]. In particular, Fenton's oxidation process, among various AOPs, is widely considered as one of the most promising methods for treatment non-biodegradable pollutants[9-11] due to its high oxidation potential, easy operation and inexpensive chemical reagents, *i.e.*, hydrogen peroxide and ferrous species[12,13]. More importantly, the Fenton's oxidation reaction is not influenced by wastewater characteristic, such as biodegradability, toxicity and salinity[14,15]. Degradation of non-biodegradable organic compounds with Fenton's oxidation method has been proven to be an efficient process in treating carpet dyeing wastewater[16], textile wastewater[17] and landfill leachate[18], which had a good removal performance for both COD and colour. During the Fenton's oxidation

process, $^{\bullet}$OH was generated by both Fe^{2+} and H_2O_2 according to the eqn. 1, which has a strong oxidation capacity (only lower than fluorine) and can non-selectively react with various organic chemical compounds[19]. As a result, organic pollutants can be degraded by $^{\bullet}$OH. And then, reactions of eqns. 2 and 3 were induced by ferric species (Fe^{3+}) and H_2O_2, where the reaction (eqn. 1) can be propagated by the reproduction of Fe^{2+}, as expressed in eqn. 3[13]. Although the removal of COD and colour during the Fenton oxidation process seems satisfactory, an obvious drawback may hinder its application in non-biodegradable pollutants treatment, where a large amount of sludge containing Fe^{3+} was generated during the Fenton oxidation process, greatly decreasing the organic compounds removal efficiency[6,20]. This may contribute to the following two reasons: 1) rate constants of eqns. 2 and 3 are just 3.1 and 2.7 mmol L^{-1} s^{-1} respectively, which were significantly lower than that of the eqn. 1 (76 mol L^{-1} s^{-1}), leading to the fact that Fe^{2+} was consumed more rapidly than it was regenerated; 2) Fe^{2+} can be oxidized by $^{\bullet}$OH produced in the homogeneous catalyst reaction (eqn. 1) with a rather high rate constant of 3.75×10^8 mol L^{-1} s^{-1}, as expressed in eqn. 4[21]. Thus, to obtain a good COD and colour removal performance during the Fenton oxidation reaction, much more Fe^{2+} would be needed to promote the reaction of eqn. 1 and also moderate the $^{\bullet}$OH (eqn. 4), which leads to large formation of Fe^{3+} sludge and it should be separated and properly treated to minimize the adverse effect on the Fenton oxidation reaction. The oxidized rate of Fe^{2+} is remarkably higher than its regenerated rate during the Fenton reaction and therefore, it is rather important to enhance the capacity of Fe^{2+} reproduction.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe(HO_2)^{2+} + H^+ \qquad (2)$$

$$Fe(HO_2)^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet} \qquad (3)$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \qquad (4)$$

To overcome the disadvantage mentioned above, the combination of Fenton with ultrasound (US) or ultraviolet light (UV) has been developed to promote the regeneration of the catalyst (Fe^{2+}), thus greatly enhancing the oxidation capacity of Fenton process, which was also called as a Fenton-based technology, $i.e.$, US-Fenton and UV-Fenton[22-24]. Compared with UV-Fenton, US-Fenton may be more attractive due to its obvious advantages such as low cost, convenient operation, strong catalytic capacity and environmental friendly. During the ultrasonic irradiation, numerous cavitation bubbles were generated by passing through of ultrasonic wave into solution, where transient collapse of cavitation bubbles can produce some species with strong oxidization capacity [hydrogen radicals ($H^{\bullet}$), hydroxyl radicals ($^{\bullet}$OH) and hydroperoxyl radicals ($HO_2^{\bullet}$)], as described in eqns. 5-8[5,25] due to the formation of extremely high temperature and pressure in the local micro-environment[26]. Moholkar[27] found that transient collapse of cavitation bubbles can create a high temperature of 5000 K and pressure as high as 500 bar. Based on the mechanisms of recalcitrant chemical compounds removal by US, non-biodegradable pollutants can be indirectly oxidized by oxidization species mentioned above or/and directly pyrolyzed during the

collapse of cavitation bubbles[28], displaying combination of physical with chemical effects.

$$H_2O_2 \xrightarrow{\text{Ultrasonic Wave}} 2{}^{\bullet}OH \qquad (5)$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2^- + O_2 \qquad (6)$$

$$H^{\bullet} + O_2 \rightarrow H_2O^{\bullet} \qquad (7)$$

$$H_2O^{\bullet} \xrightarrow{\text{Ultrasonic Wave}} H^{\bullet} + {}^{\bullet}OH \qquad (8)$$

The present study was to treat raw dye wastewater collected from Chemical Dye Industrial Factory, Fengyang, China by using Fenton oxidation system and a combination process of ultrasonic irradiation with Fenton oxidation ($i.e.$, US-Fenton). Our specific objectives were: (1) to compare the effectiveness of Fenton and US-Fenton on COD and colour removal; (2) to investigate whether ultrasonic irradiation has a synergistic effect on Fenton oxidation process; (3) to determine the optimal operational parameters, such as initial solution pH, H_2O_2 dose and Fe^{2+} dose. Moreover, Change of UV/visible absorption spectra with reaction time during the COD and colour removal process was further analyzed. These results obtained from this study, linking US with Fenton's oxidation process, may serve as a new suggestion for the treatment of dye wastewaters or non-biodegradable industrial wastewaters.

EXPERIMENTAL

Experimental setup and operation: A schematic diagram of the experimental setup designed by our research team is shown in Fig. 1 (hereinafter referred to as US-Fenton reactor), operated in batch test, mainly consisting of a Fenton's oxidation reactor and an ultrasonic irradiation reactor. In Fenton or US-Fenton system, raw dye wastewater, collected from Chemical Dye Industrial Factory, Fengyang, China, was treated with varying initial solution pH, H_2O_2 dosage and Fe^{2+} dosage to investigate the optimum parameters and demonstrate the synergistic effect of ultrasonic irradiation on Fenton oxidation process. The US-Fenton reactor was performed according to the following operational procedures: (1) raw dye wastewater was introduced into the Fenton's oxidation reactor with a working volume of 3.5 L and Fe^{2+} salt (ferrous sulfate used here) and H_2O_2 (wt. 30 % solution) were added to the Fenton's oxidation reactor with a high stirring rate of 220 rpm; (2) 0.5 M HCl was used for adjusting the pH to desired value; (3) And then, Fenton's oxidation reaction was conducted for 3 h with a slow stirring rate of 40 rpm; (4) 15 mL solution sample was collected for monitoring the COD and colour after completing Fenton's oxidation reaction; (5) effluent from the Fenton's oxidation reactor was pumped to the subsequent ultrasonic irradiation reactor, where a ultrasonic generator (KSB0D, made in Ninno Kesheng Instrument Co., China) was used for 3 h with the fixed electric output power and frequency of 250 W and 20 kHZ respectively and solution samples were also collected for analysis of colour and COD concentration after completing ultrasonic irradiation.

Samples analysis: Water samples collected from the effluent of Fenton's oxidation reactor and US reactor were immediately filtered through 0.45 μm membrane filters and COD concentration and colour in solution were then monitored to compare the operational performance of organic removal
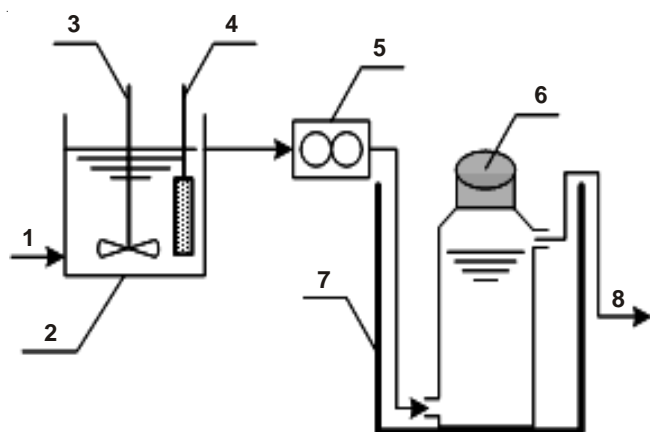
Fig. 1. A combination process of Fenton's oxidation with ultrasonic irradiation for dye wastewater treatment; 1-influent, 2-Fenton's oxidation reactor, 3-stirrer, 4-pH meter, 5-flowmeter, 6-glass bottle, 7-ultrasound generator, 8-effluent

Fig. 3. Effect of pH on COD and colour removal efficiency by Fenton and US-Fenton systems (Conditions: H_2O_2 conc. = 6.0 mmol/L, Fe^{2+} conc. = 0.6 mmol/L, electric output power = 250W and electric frequency = 20 kHZ)

in Fenton and US-Fenton systems. COD was analyzed according to the standard method (formulated by Ministry of Environmental Protection of China, 2002). Measurement of pH was performed by using a pH meter analyzer (S20, Mettler-Toledo, Switzerland). Raw dye wastewater, discharged from Chemical Dye Industrial Factory, Fengyang, China, mainly contained Methyl Orange ($C_{14}H_{14}N_3SO_3Na$, its chemical structure as shown in Fig. 2) and so, colour was determined by measuring the absorption at 465 nm using an UV spectrophotometer (UV-1750, Shimadzu, Japan), where COD concentration and colour in raw dye wastewater were 3020 mg/L and 2060, respectively.
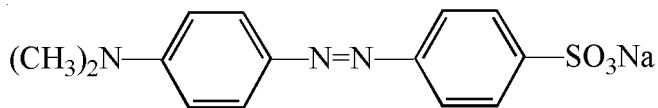

Fig. 2. Chemical structure of methyl orange

RESULTS AND DISCUSSION

Effect of pH on COD and colour removal performance in Fenton and US-Fenton systems: Initial tests were performed with varying solution pH (ranging from 2 to 8) at a constant addition of H_2O_2 of 6.0 mmol/L and Fe^{2+} of 0.6 mmol/L to assess the effect of pH on COD and colour removal performance by using Fenton and US-Fenton systems, as shown in Fig. 3. The result shows that pH had an obvious influence on COD and colour removal efficiency in both Fenton and US-Fenton systems. It is observed that as the solution pH was increased, COD and colour removal efficiency were firstly increased slightly and then dropped significantly, where the COD and colour removal efficiencies was rather high in the pH range of 2-3 through those decreased a little when pH fell from 3 to 2 and the maximum COD and colour efficiencies of 76.9 % and 91.6 % in Fenton system and 91.2 and 96.6 % in US-Fenton system, respectively were achieved at a pH of 3. For pH > 3, COD and colour removal efficiencies in both Fenton and US-Fenton systems decreased obviously with an increase of pH, where those declined to 37.5 % and 45.8 % in Fenton system and 43.2 % and 66.3 %, respectively, as the pH
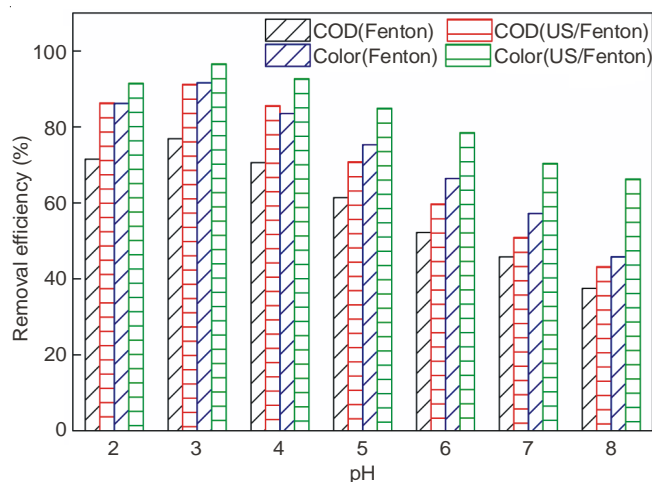
increased up to 8. These indicated that a high solution pH had a negative effect on decolourisation and COD removal of organic pollutants in Fenton and US-Fenton systems, which may be contributed to its influence in determining the oxidation ability of •OH, the stability of H_2O_2 and the species of dominant iron ions (Fe^{2+} or Fe^{3+})[29].

There was a significant difference in COD and colour removal efficiencies between Fenton and US-Fenton when pH values were set ranging from 2 to 8, as illustrated in Fig. 3. In all batch tests, the COD and colour removal efficiencies in US-Fenton system were higher than that in Fenton system, displaying beneficial effect of ultrasonic irradiation on Fenton oxidation process, which may be mainly due to the extra production of •OH by US[30], as expressed in eqns. 5 and 8. Similar results were also found in other reports about the degradation of organic compounds by the combination of US with Fenton[4,5,23]. It was noted that ultrasonic irradiation can greatly facilitate the colour removal efficiency at a relative high pH. For example, colour removal efficiency was 66.3 % in US-Fenton system while that was only 45.8 % in Fenton when pH increased up to 8 studied here, suggesting that ultrasonic irradiation do improve the degradation of non-biodegradable pollutants.

Effect of hydrogen peroxide dosage on COD and colour removal performance in Fenton and US-Fenton systems: Fig. 4 compares the effect of H_2O_2 dosage on the degradation of dye wastewater containing methyl orange by both Fenton system and US-Fenton system with the pH of 3 and Fe^{2+} dosage of 0.6 mmol/L, where the addition of H_2O_2 in 7 batch tests were 1.5, 3.0, 4.5, 6.0, 7.5, 9.0 and 10.5 mmol/L, respectively. Both in Fenton and US-Fenton systems, COD and colour removal efficiencies increased rapidly with the increasing of H_2O_2 addition up to 7.5 mmol/L. However, further increasing the H_2O_2 dosage can't significantly enhance the degradation of organic pollutants and even had a slight decrease in COD removal efficiency, which may be due to the fact that an excessively high concentration of H_2O_2 in solution may result in the two side reactions occurrence of eqns. 9 and 10, leading to the extra consumption of Fe^{2+} and •OH by H_2O_2 or HO_2•[31].
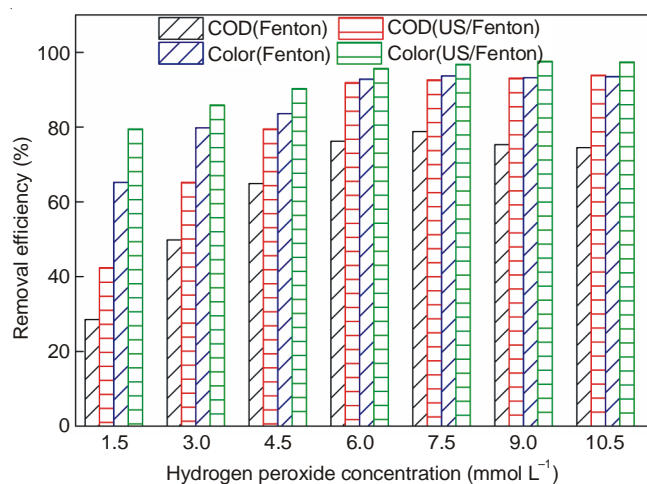
Fig. 4.   Effect of hydrogen peroxide dosage on COD and colour removal efficiency by Fenton and US-Fenton systems (Conditions: Fe^{2+} conc. = 0.8 mmol/L, pH = 3, electric output power = 250W and electric frequency = 20 kHZ)
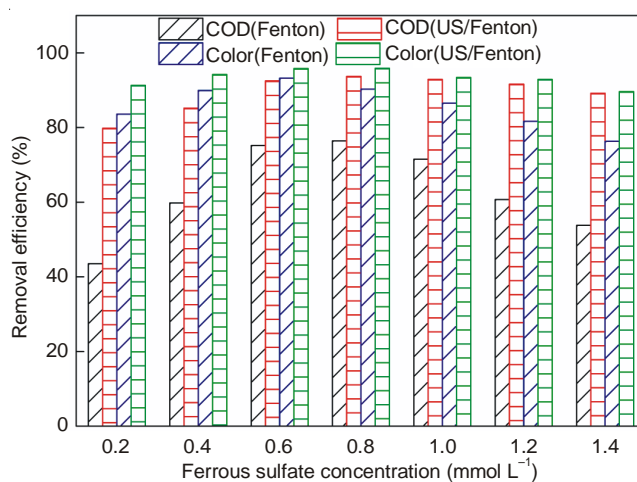
Fig. 5.   Effect of ferrous species dosage on COD and colour removal efficiency by Fenton and US-Fenton systems (Conditions: H_2O_2 conc. = 6.0 mmol/L, pH = 3, electric output power = 250W and electric frequency = 20 kHZ).

This result is in agreement with the report of Chu *et al.*[15] showing inhibition of excessively high H_2O_2 dosage on degradation of organic chemical compounds in coking wastewater by using iron powder and hydrogen peroxide. A low addition of H_2O_2 dosage into solution (such as 1.5 mmol/L) would lead to the less production of $^{\bullet}OH$, obviously decreasing the COD and colour removal efficiencies both in Fenton and US-Fenton systems. Compared with Fenton oxidation process, however, up to more 13.9 % COD and 14.3 % colour removal efficiencies can be achieved with the US-Fenton system. This suggests that ultrasonic irradiation displayed significant enhanced effect of degradation of dye wastewater in the US-Fenton system, which was probably mainly due to the following reason. A nucleus with high temperature (up to thousands degree) and pressure (up to hundreds of atmosphere) can be generated during the collapse of cavitation bubbles in a microsecond range, leading to production of a large amount of reactive species, such as $^{\bullet}OH$[32], as shown in eqns. 5 and 8.
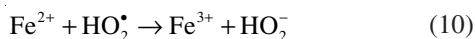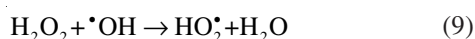
$$H_2O_2 + {^{\bullet}OH} \rightarrow HO_2^{\bullet} + H_2O \qquad (9)$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^- \qquad (10)$$

Effect of ferrous species dosage on COD and colour removal performance in Fenton and US-Fenton systems: Ferrous species dosage on COD and colour removal performance in Fenton and US-Fenton systems were also investigated in the following batch tests, by varying the addition of Fe^{2+} from 0.2 to 1.4 mmol/L while keeping the addition of H_2O_2 dosage and pH constant at 6.0 mmol/L and 3 respectively, where the results are illustrated in Fig. 5. There was little difference in COD and colour removal efficiencies between Fenton system and US-Fenton system when the addition of Fe^{2+} dosage was beyond 0.8 mmol/L and the difference became more obvious as it was over 0.8 mmol/L.

Both in Fenton and US-Fenton systems, increasing of Fe^{2+} dosage ranging from 0.2 to 0.8 mmol/L caused an increase of COD and colour removal efficiencies and with the further increase of Fe^{2+} addition up to 1.4 mmol/L, the COD and colour removal efficiencies decreased slowly in Fenton system, probably due to the faster consumption of $^{\bullet}OH$ with Fe^{2+} (eqn. 4),

while it barely changed in US-Fenton system, suggesting that effect of Fe^{2+} dosage on COD and colour removal performance in US-Fenton system were less than that in Fenton system, in particular for colour removal. A colour removal efficiency of over 90 % can be stably achieved with the variation of Fe^{2+} dosage ranging from 0.2 to 1.4 mmol/L.

Fig. 5 also indicates that good COD removal performance can be obtained in US-Fenton system when Fe^{2+} concentration was as low as 0.4 mmol/L. At this time, COD removal efficiencies were 85.2 %, which were 25.4 % higher than that in Fenton system. This may be due to the fact that ultrasonic irradiation promoted the decomposition of H_2O_2 to generate $^{\bullet}OH$ (eqn. 5) although a low addition of Fe^{2+} dosage may hinder the reaction of Fe^{2+} with H_2O_2 to produce $^{\bullet}OH$ (eqn. 1), leading to a less production of sludge containing Fe^{3+}.

Change of UV/visible absorption spectra with reaction time in US-Fenton system: As discussed above, ultrasonic irradiation had an obvious enhanced effect on Fenton oxidation for treatment of dye wastewater, suggesting the combination of US with Fenton may have a competitive advantage over only Fenton system when treating non-biodegradation pollutants. To investigate the change of molecular and structural characteristics during the treatment of dye wastewater by using US-Fenton system, the change in representative UV/visible absorption spectra with reaction time were recorded before and after oxidation, as shown in Fig. 6, where the concentrations of Fe^{2+}, H_2O_2 and pH in solution were kept in 0.8 mmol/L, 6.0 mmol/L and 3, respectively with the reaction time of 60 min. At a general glance, there were significant differences in main absorption bands between before and after oxidation by US-Fenton, where before oxidation, the absorption spectrum of dye wastewater was characterized by three main bands including two in UV region with maximum absorption at 210 and 280 nm respectively and the other in visible region with that of 465 nm and the visible maximum absorption band disappeared after oxidation. The maximum absorption peak at 465 nm may be associated with a chromophore consisting of two aromatic rings connected by the azo bond[33]. According to the report by Zhang *et al.*[34], the disappearance of visible
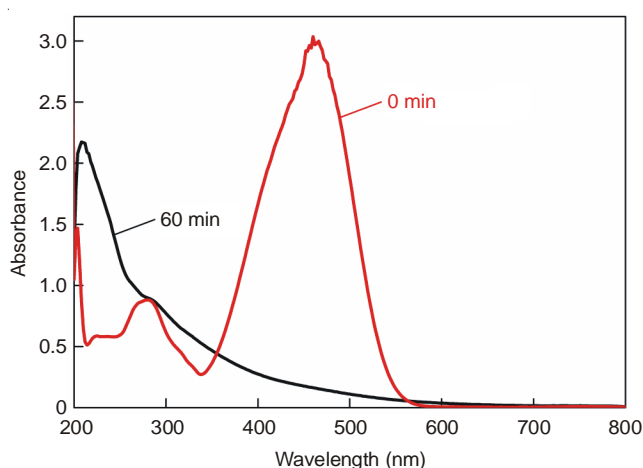
Fig. 6. Change of UV/visible absorption spectra with reaction time in US-Fenton system (Conditions: H_2O_2 conc. = 6.0 mmol/L, Fe^{2+} conc. = 0.8 mmol/L, pH = 3, reaction time = 60 min, electric output power = 250W and electric frequency = 20 kHZ)

band was probably due to the fragmentation of organic chemical compounds containing aromatic rings; in addition, the enhancement of peak at 210 nm or 280 nm was regarded as an evidence of intermediates formation during the oxidation process by US-Fenton system.

Conclusion

The performances of colour and COD removal from raw dye wastewater mainly containing methyl orange were investigated by using Fenton oxidation process and combining of Fenton oxidation with ultrasonic irradiation (*i.e.*, US-Fenton) in this study. According to the experimental results, it can be concluded that the enhancement effect of ultrasonic irradiation on Fenton oxidation was significant when treating dye wastewater. In particular, at a low concentration of Fe^{2+} in solution (such as 0.4 mmol/L), COD removal efficiencies were 85.2 % in US-Fenton system, which were 25.4 % higher than that in Fenton system. The colour and COD removal efficiencies were greatly dependent on initial pH, H_2O_2 and Fe^{2+} concentration in solution, where the optimum pH of 3, H_2O_2 of 6.0 mmol/L and Fe^{2+} of 0.8 mmol/L were determined to obtain a good colour and COD removal performance in the US-Fenton system when electric output power and electric frequency of ultrasonic irradiation were set at 250 W and 20 kHZ respectively. Based on the results above, the proposed process linking ultrasonic irradiation with Fenton oxidation may be an effective and economical technology, probably being a promising method for dye wastewater or non-biodegradation industrial wastewater.

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