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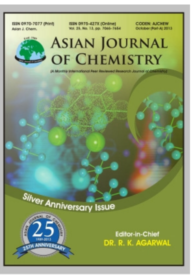

Treatment of Polyaniline Wastewater by Fenton Reagent

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This paper describes a simple method using Fenton reagent for treating the wastewater from the preparation of polyaniline. The method employs the absorption of UV-visible spectroscopy as a quantitative indicator of the byproducts. Some factors *e.g.*, reactive time, temperature, pH and the concentration of $FeSO_4 \cdot 7H_2O$ and H_2O_2 were investigated. The study shows that the optimum conditions for treating the wastewater were the 1:1 concentration ratio of $FeSO_4 \cdot 7H_2O$ to H_2O_2, reaction time 50 min, temperature 19 ºC, pH 1.1. After the Fenton process, some solid $CaCO_3$ and active carbon were used to obtain near-neutral and colourless water. The experimental results demonstrated that the chemical oxygen demand (COD) value of water sample is 1512 and 56 mg L^{-1} for pre- and post-treatment, respectively. The removal efficiency of the COD is more than 96 %.

Key Words: Polyaniline, Wastewater treatment, Fenton reagent, UV-visible spectroscopy, Chemical oxygen demand.

INTRODUCTION

Polyaniline (PANI) is unique among conducting polymers in its wide applied range of the metal anti-corrosion coatings, antistatic materials, electrode materials of the lithium battery, high-temperature material, solar energy materials, *etc.*[1-5]. Polyaniline is typically synthesized by oxidizing aniline monomer either electrochemical[6-8] or chemical ways[9,10]. However, during the synthesis process, a large amount of the wastewater containing unreacted acid, unreacted aniline monomers, inorganic salts and other byproducts (*e.g.*, ADPA, benzidina, hydrazobenzeno, azobenzeno, benzoquinone and hydroquinone)[11] is produced, which will be able to pose severe harm for human health and the environment. To the best of our knowledge, there are few studies about the treatment of polyaniline wastewater[12,13]. Therefore, the study on polyaniline wastewater treatment is most significant.

Fenton reagent, a strong oxidizing agent, has obvious effect on oxidizing a lot of difficult degraded organic compounds[14-18] due to the generation of hydroxyl radicals during the decomposition of H_2O_2 in the catalyst of Fe^{2+} [19-21]. Compared to other traditional oxidants, the hydroxyl radical has a higher oxidation potential and is able to oxidize almost all organic contaminants into nitrogen, carbon dioxide and water in aqueous solution as well as the advantages of rapid reaction, mild condition and non pollution[22-26]. Based on the reaction mechanism of Fenton reagent and polyaniline wastewater system, we suggest that the degradation process of the organic component is as follows[27-30]:

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

$$^{\bullet}OH + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O \qquad (2)$$

$$\text{Organic component} \xrightarrow[H^+]{^{\bullet}OH/HO_2^{\bullet}} CO_2 + H_2O + N_2 \qquad (3)$$

The work presented in this paper first describes the application of Fenton treatment and ultrasonic treatment of activated carbon to the degradation of the byproducts in polyaniline wastewater and the results the high removal efficiency of chemical oxygen demand (COD) and colourless water through assistance of the suitable amount of active carbon and solid $CaCO_3$. Compared with alone Fenton treatment, the combination of the Fenton treatment with ultrasonic treatment of activated carbon is favour to improve the overall treatment process efficacy.

EXPERIMENTAL

All the reagents used were analytical grade and were used as received without any further purification. Aniline, ammonium persulfate [$(NH_4)_2S_2O_8$], hydrochloric acid, ferrous sulfate heptahydrate, hydrogen peroxide (30 % H_2O_2), active carbon, $CaCO_3$ were obtained from Sinopharm Chemical Reagent Co., Ltd. All the solutions were prepared with double distilled water.

Preparation of polyaniline wastewater: 200 mL of 1 mol L^{-1} HCl solution was mixed with 4.57 mL aniline with continuous stirring, followed by the dropwise addition of 11.41 g $(NH_4)_2S_2O_8$ in 50 mL above hydrochloric acid solution to start chemical polymerization of aniline in the aqueous medium. After stirring 5 h at room temperature, 200 mL purple-red wastewater was obtained by filtration. It should be noted that the purple-red wastewater contained unreacted HCl, residual aniline monomers, inorganic salts and colourful organic by products.

Treatment of wastewater: 10 mL of the raw polyaniline wastewater were treated using Fenton reagent in certain conditions noted below (Figs. 2-6). The filtrate is pale yellow after full reaction. Then some solid $CaCO_3$ and active carbon were added to the filtrate in the ultrasonic condition. They were respectively used to adjust the pale yellow filtrate to near-neutral and adsorb residual organic components. The byproduct in filtrate was analyzed by UV-visible spectrophotometer (Shimadzu UV-2550). The pH of solutions were adjusted with 1.0 mol L^{-1} NaOH and recorded with a PHS-25A pH meter (Shanghai Kanghua Biochemistry Instrument CO., LED).

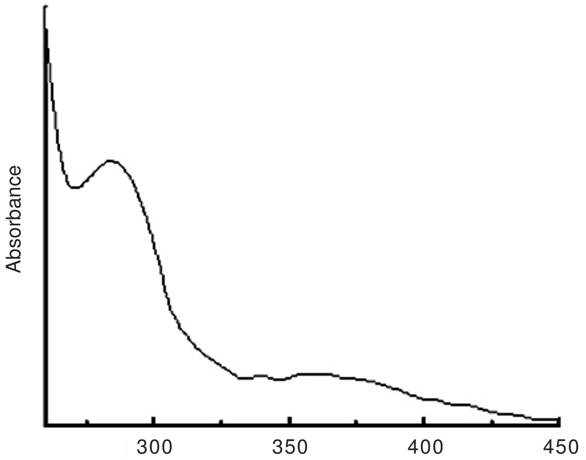

Fig. 1. UV-VIS spectroscopy of raw polyaniline wastewater

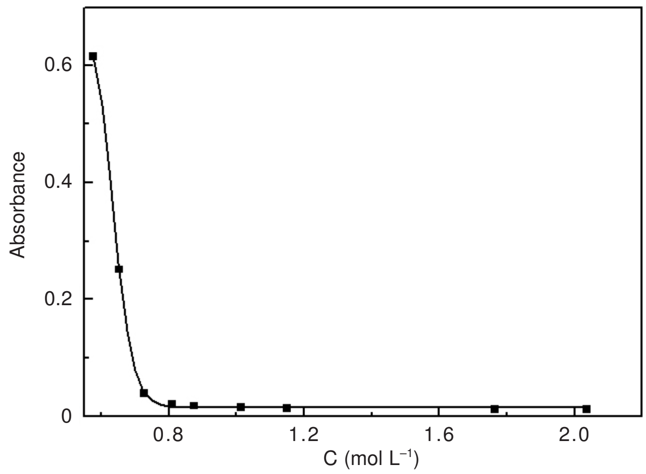

Fig. 2. Effect of the H_2O_2 concentration. (10 mL raw polyaniline wastewater, 0.9 mol L^{-1} $FeSO_4 \cdot 7H_2O_2$, 30 min, 15 °C)

Measurement of chemical oxygen demand (COD): 1 mL of the raw or treated wastewater was diluted to 100 mL due to the high concentration of organics and then 20 mL of which was used to measure COD by $K_2Cr_2O_7$ method with blank sample of double distilled water.

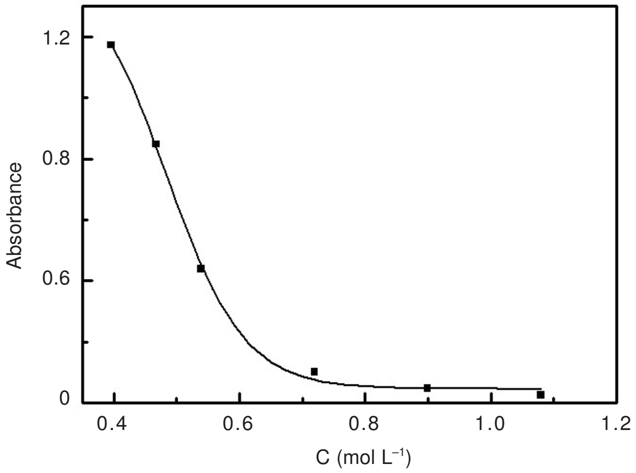

Fig. 3. Effect of the $FeSO_4 \cdot 7H_2O$ concentration. (10 mL raw polyaniline wastewater, 0.8 mol L^{-1} H_2O_2, 0.5 h, 15 °C)

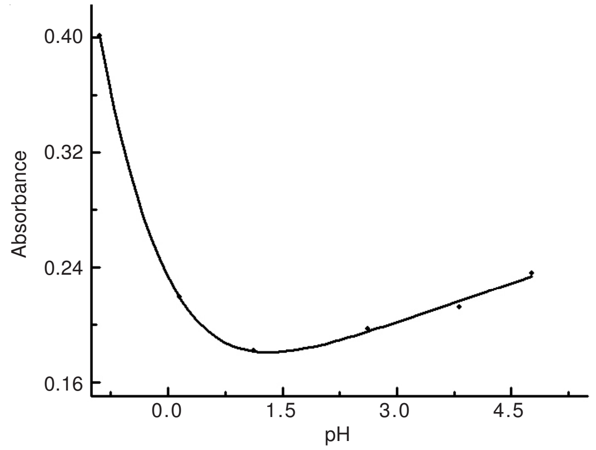

Fig. 4. Effect of pH. (10 mL raw polyaniline wastewater, 0.8 mol L^{-1} H_2O_2 and $FeSO_4 \cdot 7H_2O$, 0.5 h, 15 °C)

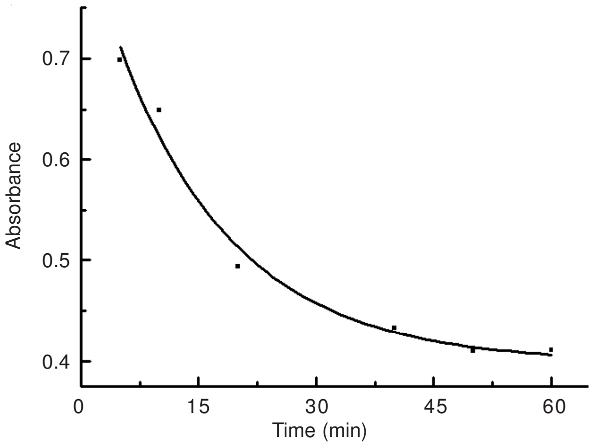

Fig. 5. Effect of reaction time. (10 mL raw polyaniline wastewater, 0.8 mol L^{-1} of H_2O_2 and $FeSO_4 \cdot 7H_2O$, 15 °C, pH 1.1)

RESULTS AND DISCUSSION

UV-Visible spectroscopy of polyaniline wastewater: Fig. 1 shows UV-visible spectroscopy of the raw polyaniline wastewater. The absorption spectrum is obtained over a range of 270-450 nm with a strong absorption at 285 nm, which is generally consistent with the result of a previous study[12]. The

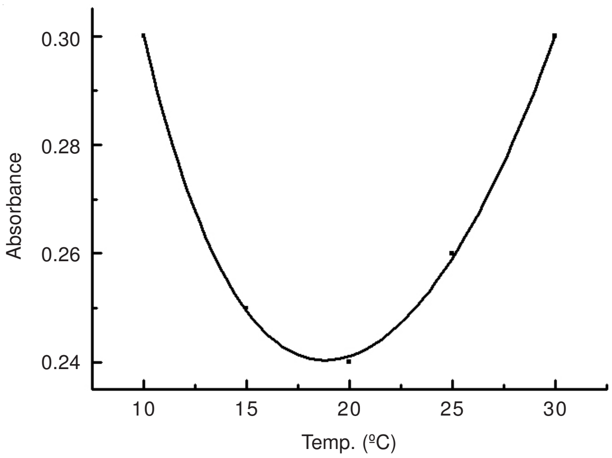

Fig. 6. Effect of temperature. (10 mL raw polyaniline wastewater, 0.8 mol L^{-1} of H_2O_2 and $FeSO_4·7H_2O$, reaction time of 50 min, pH 1.1)

absorbance at 285 nm could be monitored by UV-visible spectroscopy and indirectly revealed the concentration of the organic byproducts (*e.g.*, ADPA, benzidine, hydrazobenzene, azobenzene, benzoquinone and hydroquinone) in the polyaniline wastewater.

Effect of the H_2O_2 concentration: The effect of H_2O_2 concentration on the absorbance of the treated wastewater is shown in Fig. 2. The absorbance of the treated wastewater rapidly decreases with the increasing H_2O_2 concentration in the concentration range of 0.6-0.8 mol L^{-1}. However, when the H_2O_2 concentration is over 0.8 mol L^{-1}, the absorbance barely changes and remains at near 0.0. This is a sign that the reducible substances in the wastewater are in its minimum concentration. Therefore, 0.8 mol L^{-1} H_2O_2 would be a suitable concentration.

Effect of the $FeSO_4·7H_2O$ concentration: The effect of $FeSO_4·7H_2O$ concentration on the absorbance of the treated wastewater is shown in Fig. 3. It can be seen that the absorbance of the treated wastewater rapidly decreases with increasing $FeSO_4·7H_2O$ concentration below 0.7 mol L^{-1}, which may be attributed to the formation of large amounts of hydroxyl radicals and the removal of organic byproducts with increasing Fe^{2+} concentration. However, when the $FeSO_4·7H_2O$ concentration is over 0.8 mol L^{-1}, the absorbance does not decrease and remains at near 0.0. This is due to the rapid and complete degradation of the organic byproducts in the given condition. During the treatment process, the large amounts of brown flocs were suspended in the supernatant. Then these flocs were coagulated, precipitated out and filtered. Such a coagulation/precipitation action perhaps constitutes an important part of colour and COD reduction of the Fenton process. These flocs could be adsorption and co-precipitation by ferric flocs and/or precipitation ferric hydroxides[31]. Thus, the optimal concentration of $FeSO_4·7H_2O$ is 0.8 mol L^{-1}, which is almost same with that of H_2O_2.

Effect of pH: The effect of pH on the absorbance of the treated wastewater is shown in Fig. 4. The absorbance of the treated wastewater is rapidly decreasing with increasing pH below 1.1 and then has a slow increase above pH 1.1. The pH 1.1 is optimum with a minimum absorption. It is the reason for the generation of hydroxyl radicals and the existing form of Fe^{2+} being associated with pH. When pH value was too high, the generation rate of hydroxyl radicals will be restrained; when pH value is too low, it will break up the equilibrium between Fe^{3+} and Fe^{2+} and influence the oxidation[32].

Effect of reaction time: Fig. 5 shows the relationship between reaction time and the absorbance of the treated wastewater. The absorbance of the treated wastewater is markedly decreasing with increasing time until *ca.* 0.5 h, then reduces very slowly and becomes almost stable after 1 h. The treatment time is strongly dependent on both the generation rate of hydroxyl radicals and the degradation rate of the organic byproducts in the wastewater. When the reaction time is too short, it will be incomplete reaction. Hence, 50 min is proposed as optimum reaction time.

Effect of temperature: Fig. 6 presents the relationship between reaction temperature and the absorbance of the treated wastewater in the solution containing 0.8 mol L^{-1} H_2O_2 and 0.8 mol L^{-1} $FeSO_4·7H_2O$ with pH 1.1 for 50 min. For the general chemical reaction, molecular average kinetic energy and the reaction rate of a reaction increase with increasing temperature. However, the disintegration of H_2O_2 would be bad to forming hydroxyl radical and also reduce the degradation efficiency of the polyaniline wastewater. The results indicate that the optimum temperature is at *ca.* 19 ºC.

Discolouration and COD of water sample: The colour of the water samples for pre- and post-treatment is shown in Fig. 7. After treated using Fenton reagent, the brown flocs were formed and removed by filtered. The colour of the water samples was changed from the purple-red (Fig. 7a) of the raw wastewater to the pale yellow (Fig. 7b), which is attributed to the oxidation of the iron ion exposed in the air after the removal of brown flocs.

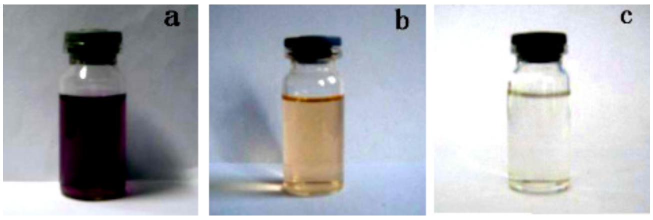

Fig. 7. Photograph of raw wastewater (a) and the treated water by Fenton reagent and $Ca(OH)_2$ (b) and the further treated water by active carbon (c)

In order to adjust pH of the treated water and remove iron ion, sulfate ion and so on, a suitable amount of solid $CaCO_3$ was added in the pale yellow solutions until pH (6-8) was reached. We chose $CaCO_3$, it is mainly due to its ability of neutralizing the acid and precipitating iron ion and sulfate ion. The COD value of the water samples deceased from 1512-56 mg L^{-1} with a removal efficiency of 96 % through the previous process.

Granular and powdered active carbons for water treatment typically exhibit a heterogeneous pore structure, in which micropores, mesopores and macropores are contained and is widely employed for the removal of organic pollutants. Consequently, some granular and powered active carbon of 1:1 was used to remove the residual components of the treated water samples to obtain colourless and clear water (Fig. 7c).

The ultimate COD value of the treated water (56 mg L^{-1}) meets the level 1 national sewage discharge standard (GB18918-2002).

Conclusion

As mentioned before, the polyaniline wastewater can be easily treated by Fenton method and the concentration of the byproducts in the wastewater could be indirectly monitored by means of UV-visible spectrometry. According to the experimental results, the optimal condition for the wastewater treatment is 0.8 mol L^{-1} H_2O_2, 0.8 mol L^{-1} $FeSO_4\cdot 7H_2O$, 50 min and 19 ºC. The COD value of the raw wastewater and further treated water are, respectively, 1512 and 56 mg L^{-1} with the COD removal efficiency is more than 96 %. This work offers potential application of the large-scale polyaniline wastewater treatment and will significantly contribute to water purification and reducing the emissions of organic pollutants.

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