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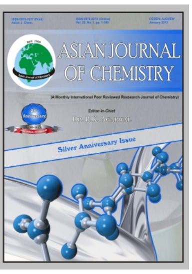

Ultrasound-Promoted Degradation of Acid Brown 348 by Fenton-Like Processes

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The combination of ultrasonic irradiation and Fenton-like's reagent is effective for the degradation of Acid brown 348 in aqueous solution. Furthermore, it can achieve better results than either Fenton-like reagent or ultrasound alone. Effects of the reaction conditions on the removal of Acid brown 348 from aqueous solution were observed under ultrasound irradiation. The best removal ratio was 96 % under the optimal conditions (pH 2.5, dosage of fly ash 2.5 g/L, H_2O_2 5.0 mM, the dye initial concentration 50 mg/L, temperature 40 ºC, reaction time 140 min, ultrasonic frequency 40 kHz). Based on the degradation compounds identified from LC-MS and UV-VIS studies, -N=N- bonds of the Acid brown 348 molecule were found to be broken. The wastewater from the factory was treated first by activated carbon absorption and then degraded with ultrasound/fly ash/H_2O_2, the removal efficiency of COD_{Cr} of dye wastewater was 95 %, whose degradation kinetic was well fitted Behnajady's model.

Key Words: Fenton-like reagent, Acid brown 348, Degradation, Ultrasound irradiation.

INTRODUCTION

The chemical structures of azo dyes are characterized by highly substituted aromatic rings joined by one or more azo groups (-N=N-) and the aromatic rings mostly substituted by sulfonate groups. These complex aromatic substituted structures make conjugated system and are responsible for intense colour, high water solubility and resistance to degradation of azo dyes under natural conditions[1,2]. Being released into the environment, these dyes not only impart colours to water sources but also damage living organisms by stopping the reoxygenation capacity of water, blocking sunlight and therefore disturbing the natural growth activity of aquatic life[3]. Thus, the colour removal of textile wastewater is a major environmental concern[4].

Fly ash, generated during the combustion of coal for energy production, is an industrial by-product which is recognized as an environmental pollutant. Because of the environmental problems presented by the fly ash, considerable research has been undertaken on the subject worldwide. A considerable amount of research has been conducted using fly ash for removal of organic compounds and mercury in air, dyes and other organic compounds in water[5]. Iron oxide (Fe_2O_3) is one of the constituent of fly ash, which can produce Fe^{3+} in acid solutions. In the presence of H_2O_2, Fe^{3+} can react with H_2O_2 to form $Fe\text{-}O_2H^{2+}$, which further decomposes to Fe^{2+}. Once Fe^{2+} was formed, it reacted with H_2O_2 and produced ·OH to form the Fenton-like process, by which wide range of organic pollutants in water and wastewater can be destroyed[3,6,7]. Recently, the degradation of Acid orange 3 and Direct black 168 by combination of the fly ash/H_2O_2 and ultrasound have been reported[7,8].

Acid brown 348 (AB-348) is a triazo dye widely used to dye protein/animal fibers such as wool, silk, mohair, angora, alpaca and some nylons and synthetics, whose toxicology is not fully investigated, itself may not be toxic. However, under anaerobic condition, azo dyes are cleaved by microorganisms to form potentially carcinogenic aromatic amines[4]. To the best of our knowledge, there has been no report on the degradation of Acid brown 348 from aqueous solution by combination of fly ash/H_2O_2 and ultrasound irradiation, we would like to report the results for the degradation of Acid brown 348 from aqueous solution by combination of fly ash/H_2O_2 and ultrasound irradiation.

EXPERIMENTAL

Acid brown 348 dye was obtained from Hebei Dingzhou Arpino LCD Material Co. Ltd. and used without further purification. The chemical structure is shown in Fig. 1. An aqueous solution of Acid brown 348 was prepared in laboratory by dissolving calculated amount of Acid brown 348 in distilled water.

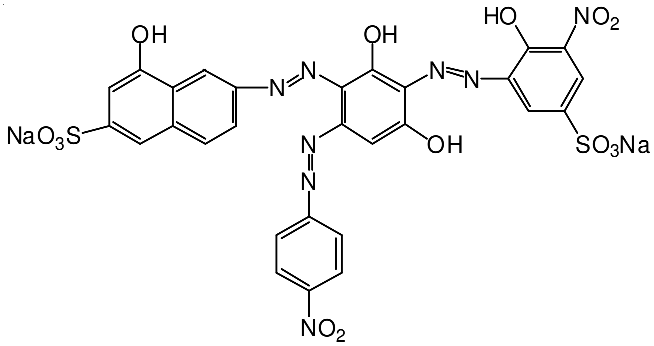

Fig. 1. Structure of Acid brown 348

Acid brown 348 industrial wastewater was obtained from Hebei Dingzhou Arpino LCD Material Co. Ltd., fly ash was provided by Baoding Thermal Power Plant in Hebei province, China. It was sieved form 200 meshes and was dried at 110 ºC for 2 h prior to use. Distilled water was used to make the dye solutions of desired concentration. Hydrogen peroxide (30 % w/w) was purchased from Tianjin Reagent Company, China. All other reagents were of analytical grade.

A pH meter (PHS-3C, Shanghai Hongyi Instrument Equipment Co. Ltd.) was employed for measuring pH values in the aqueous solutions. A TU-1901 double beam UV-VIS spectrophotometer (Beijing Purkinje General Instrument Co. Ltd.) was used to determine the dye concentrations. MS were determined on SHIMADZU (LC/MS-2010EA, UVD/ELSD) using CH_3CN and H_2O (0.05 % TFA) as mobile phase, the column type is Shim_pack XR-ODS with length 50 mm and internal 3 mm, the flow rate is 1 mL/min and the gradient is as follows. Time (min)/CH_3CN (%): 0/15, 1.70/100, 3.20/100, 3.33 /10, 3.60/stop. All the experiments were performed in Shanghai Branson ultrasonic cleaner (BUG 40-06, with a frequency of 40 kHz and a nominal power 250 W).

All experiments were carried out in the following manner. In each experimental run, 50 mL of aqueous solution of Acid brown 348, fly ash and H_2O_2 was mixed in a 100 mL conical flask, which was used as the reactor. The conical flask was located in the ultrasonic cleaner, where the surface of reactants was slightly lower than the level of the water in the cleaning bath and then the ultrasound irradiation started. The initial pH value was adjusted to a desired level by adding appropriate amounts of 1 M HCl. The temperature of the water bath was controlled by the addition or removal of water from ultrasonic bath. The mixture was irradiated for the period of time. The samples (7 mL) were taken out from the conical flask periodically using a pipette and were analyzed after centrifugation at 4,000 rpm for 15 min (sometimes, in order to decompose residual H_2O_2, which interferes with the COD and absorbance measurements, before each analysis, the samples containing H_2O_2 were treated with MnO_2 powder[9]). Blanks containing no Acid brown 348 were used for each series of experiments.

The dye concentrations were measured at a wavelength of 528 nm, which corresponds to the maximum absorbance of aqueous solutions of Acid brown 348. The dye removal ratio was calculated as follows (eqn. 1):

$$\text{Dye removal ratio (\%)} = (1-C_t/C_0) \times 100\ \% \qquad (1)$$

where, C_0 is the initial dye concentration, C_t is the dye concentration at contact time t. Each experiment was repeated three times. The standard deviations of the values were within 5 %. Chemical oxygen demand values were determined according to the method based on China Standard (GB 11914-89), which were conducted in accordance with ISO 6060[10].

RESULTS AND DISCUSSION

Effect of fly ash on the degradation under ultrasound: As shown in Fig. 2, in presence of fly ash, the degradation efficiency was 78 % comparing to 15 % without the catalyst. As we know, in acid solution fly ash can produce Fe^{3+} which can react with hydrogen peroxide to form $Fe\text{-}O_2H^{2+}$ (eqn. 3). With ultrasound irradiation, the decomposition rate of $Fe\text{-}O_2H^{2+}$ can be greatly enhanced (eqn. 4). Once Fe^{2+} was formed, it reacted with H_2O_2 and produced ·OH again, then a cycle mechanism was established[11,12], the more ·OH and the higher degradation efficiency achieved.

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \cdot OH + H_2O \qquad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{-}O_2H^{2+} + H^+ \qquad (3)$$

$$Fe\text{-}O_2H^{2+} \xrightarrow{\text{ultrasound}} Fe^{2+} + \cdot OOH \qquad (4)$$

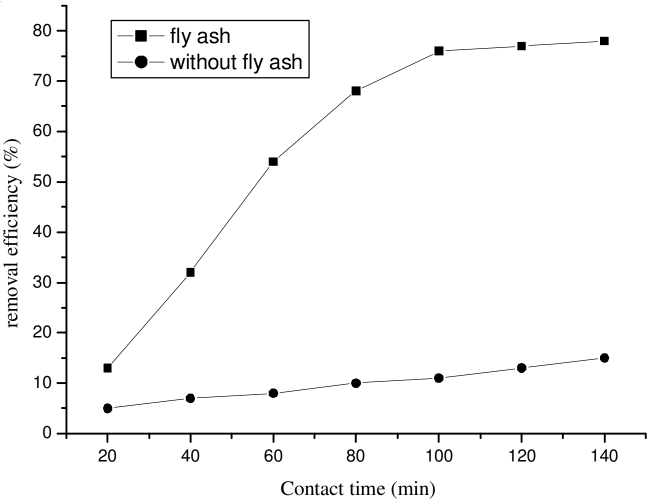

Fig. 2. Effect of fly ash on the degradation under ultrasound ; C_0 = 50 mg/L, concentration of H_2O_2: 4.8 mM, fly ash=2.5 g/L, pH = 2.5, T = 40 ºC, irradiation frequency: 40 kHz

Effect of ultrasound and stirring: As shown in Fig. 3, in the presence of ultrasound irradiation, the degradation efficiency of 84 % was achieved which was 27 % more than that with stirring (57 %) within 120 min. It is apparent that ultrasound can prompt the reaction to take place and give in higher degradation. One reason is that ultrasound can cause fly ash particle rupture, with a consequent decrease in particle size and increase in surface area available for reaction[13]. Secondly, ultrasonic irradiation accelerated heterogeneous reactions due to symmetric and asymmetric cavitations.

When cavitation occurs in a liquid near fly ash surface, the dynamics of cavity collapse changes dramatically. Close to a solid boundary, cavity collapse is very asymmetric and generates high-speed jets of liquid, which leads to the formation of micro-jets of dye solved in water that impinge on the catalyst surface resulting in the reaction promoting. The potential energy of the expanded bubble is converted into kinetic energy of a liquid jet that moves through the bubble's interior and

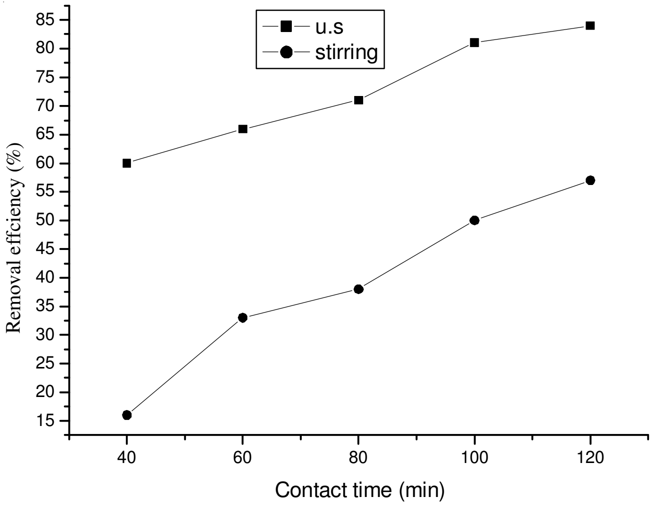

Fig. 3. Effect of ultrasound and stirring; $C_0 = 50$ mg/L, concentration of H_2O_2: 5.0 mM, fly ash = 2.5 g/L, pH = 2.5, T = 40 ºC, irradiation frequency: 40 kHz

penetrates the opposite bubble wall. These jets hit the surface of fly ash with tremendous force[14]. These phenomena increase the rate of mass transfer near the catalyst surface and induce the reaction to occur rapidly.

Degradation mechanisms of Acid brown 348 by fly ash/H_2O_2/ultrasound: Possible organic compounds formed during ultrasound/fly ash/H_2O_2 process which were analyzed by UV-VIS and LC/MS data and the result was presented in Table-1.

TABLE-1
DEGRADATION PRODUCTS OF AB 348 AFTER TREATMENT BY ULTRASOUND/FLY ASH /H_2O_2

m/z	Possible organic compounds
269	4-Hydroxy-6-nitronaphthalene-2-sulfonic acid
264	4-Hydroxy-3,5-dinitrobenzenesulfonic acid
200	3,6-Dinitrobenzene-1,2-diol
158	Naphthalene-1,4-dione
166	Phthalic acid
108	Cyclohexa-3,5-diene-1,2-dione or benzoquinone

The UV-VIS spectra of Acid brown 348 before and after degradation were compared. The disappearance of the absorption peak at 528 nm indicated cleavage of the corresponding bond of Acid brown 348 molecule. At the same time, the peaks at 210 nm emerged, which showed that some new products were formed in the reaction.

Based on the degradation compounds identified by mass spectra, reaction scheme of the degradation of Acid brown 348 was suggested as shown in Fig. 4. The ·OH attacked the -N=N- bond, leading to the cleavage of the -N=N- bond and the generation of 4-hydroxy-6-nitronaphthalene-2-sulfonic acid (*m/z*: 269), 3,6-dinitrobenzene-1,2-diol (*m/z*: 200) and 4-hydroxy-3,5-dinitrobenzenesulfonic acid (*m/z*: 264). The product 1,4-dinitrobenzene was not determined, possibly the ·OH attacked the C-N bond leading to the $-NO_2$ groups replaced by -OH to form hydroquinone[15], which was not captured, but its oxidation products benzoquinone (*m/z*: 108) was determined. The product 4-hydroxy-6-nitronaphthalene-2-sulfonic acid was further oxidized to benzoquinone. As the same mechanism, the 3,6-dinitrobenzene-1,2-diol (*m/z*: 200) and 4-hydroxy-3,5-dinitrobenzenesulfonic acid (*m/z*: 264) were oxidized to cyclohexa-3,5-diene-1,2-dione or benzoquinone, the 4-hydroxy-6-nitronaphthalene-2-sulfonic acid was changed into naphthalene-1,4-dione, then further was oxidized to phthalic acid. The result indicated clearly that Acid brown 348 was not mineralized completely.

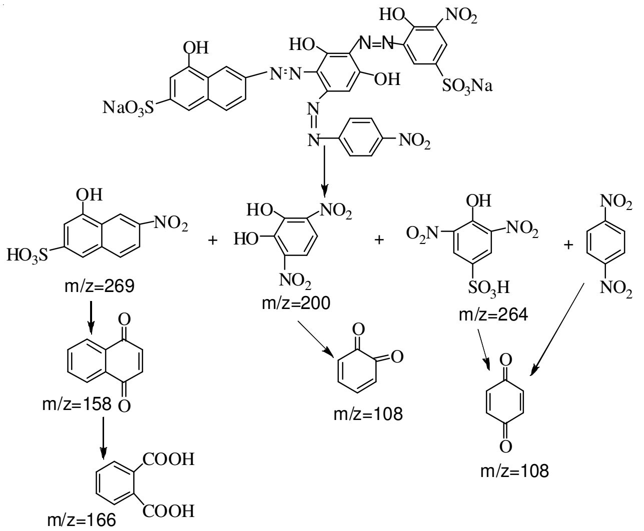

Fig. 4. Possible pathway of the degradation of Acid brown 348 by ultrasound/fly ash/H_2O_2

Effect of pH values on the degradation: The effect of the initial pH values on the degradation of Acid brown 348 by ultrasound/fly ash/H_2O_2 was investigated and the results were shown in Fig. 5. It was observed that the degradation of Acid brown 348 was significantly influenced by the pH value of the solution and the highest degradation efficiency was achieved at pH 2.5. The removal efficiency increased from 57 to 96 % as a consequence of the pH value decreasing from 4 to 2.5 within 140 min. When pH > 4.0, Fe^{2+}/Fe^{3+} will precipitate in the form of hydroxide which might result in the degradation rate to decrease. When pH < 2.5, the formation of $[Fe(II)(H_2O)]^{2+}$ occurs, which reacts more slowly with hydrogen peroxide and, therefore, produces less amount of reactive hydroxyl radicals thereby reducing the degradation efficiency[16]. In addition, the scavenging effect of hydroxyl radicals by hydrogen ions becomes important at a very low pH[17] and hydroxyl radical (·OH) could be consumed by the scavenging effects of H^+ (eqn. 5)[18], leading to less degradation efficiency. Hydrogen peroxide could capture a proton to form an oxonium ion $H_3O_2^+$ (eqn. 6) in the lower pH value, $H_3O_2^+$ will make hydrogen peroxide to be electrophobic and enhance its stability, which presumably reduces the reactivity of the reaction between hydrogen peroxide and ferrous ion[19].

$$^{\cdot}OH + H^+ - e^- \rightarrow H_2O \quad (5)$$

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \quad (6)$$

Effect of H_2O_2 dosage on the degradation of Acid brown 348: Increasing H_2O_2 load from 4 to 5 mM increased reaction performance (Fig. 6), because more radicals were formed. However, a significant improvement was not observed for a higher concentration (5.3 mM). Performance either in terms of ·OH degradation or in terms of mineralization dropped down for an excessive peroxide load due to the well-known hydroxyl radicals scavenging effect (eqn. 7)[20].

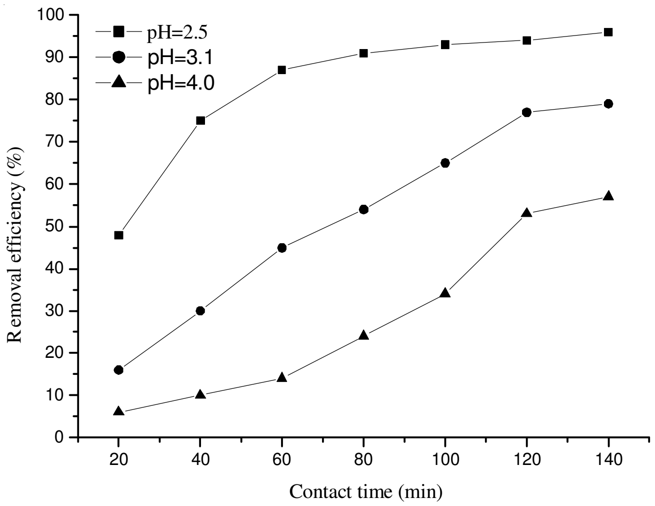

Fig. 5. Effect of initial pH values on the degradation of Acid brown 348; C_0 = 50 mg/L, concentration of H_2O_2: 5.0 mM, fly ash = 2.5 g/L, T = 40 °C, irradiation frequency: 40 kHz

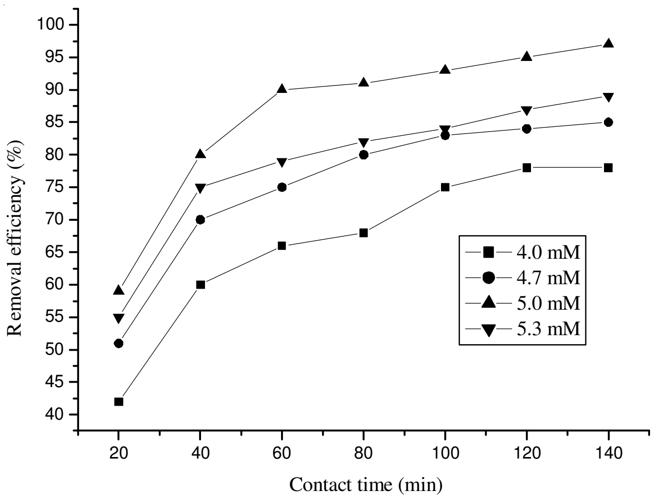

Fig. 6. Effect of H_2O_2 dosage on the degradation of Acid brown 348; C_0 = 50 mg/L, fly ash = 2.5 g/L, pH = 2.5, T = 40 °C, irradiation frequency: 40 kHz

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + {}^{\bullet}O_2H \qquad (7)$$

Such reaction reduces the probability of attack of organic molecules by hydroxyl radicals and caused the oxidation rate to drop. Although other radicals ($\cdot O_2H$) were produced, their oxidation potential was much smaller than that of the ·OH species[21]. Therefore, in the subsequent runs, 5.0 mM H_2O_2 was advisable.

Effect of Acid brown 348 concentrations on the degradation of Acid brown 348: With the initial Acid brown 348 concentration decreasing the degradation of Acid brown 348 increased (Fig. 7). A degradation efficiency of 96 % was achieved when dye concentration was 50 mg/L within 140 min. A higher concentration increased the number of dye molecules, but not the HO· radical concentration and so the removal rate diminishes.

Effect of temperature on the degradation of Acid brown 348: The rate of the redox reaction could be accelerated by increasing the reaction temperature. In the process, a higher temperature increased the reaction rate between hydrogen peroxide and the dye. Fig. 8 showed that at 40 and 50 °C the degradation efficiency was 93 and 89 %, respectively, which was higher than 84 % at 30 °C, but at 50 °C the degradation efficiency was less than that at 40 °C. In the subsequent runs, the reaction was carried out at 40 °C.

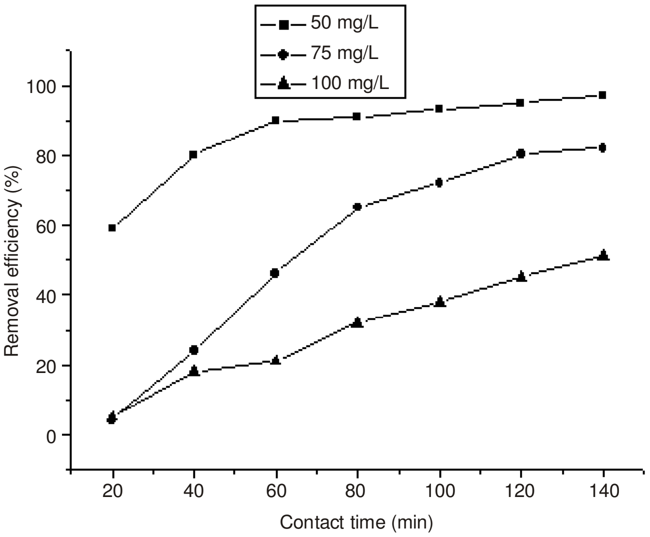

Fig. 7. Effect of Acid brown 348 concentration on the degradation; concentration of H_2O_2: 5.0 mM, fly ash = 2.5 g/L, pH = 2.5, T = 40 °C, irradiation frequency: 40 kHz

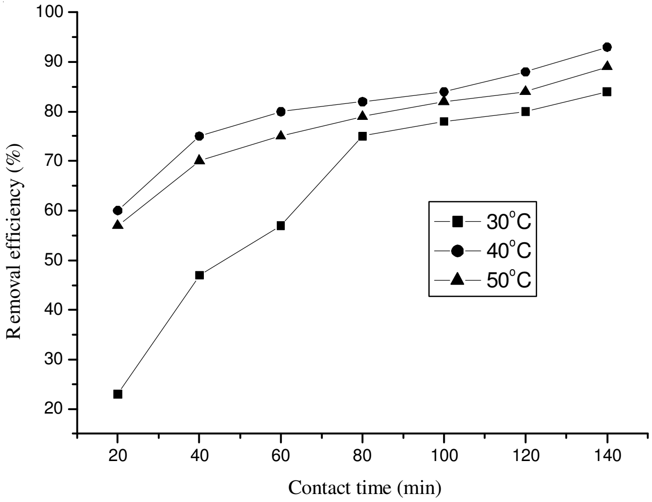

Fig. 8. Effect of temperature on the degradation of Acid brown 348; C_0 = 50 mg/L, concentration of H_2O_2: 5.0 mM, fly ash = 2.5 g/L, pH = 2.5, irradiation frequency: 40 kHz

Industrial effluent treatment: As shown in Fig. 9, the initial concentration of Acid brown 348 from factory wastewater was 44000 mg/L (A) and it decreased to 8700 mg/L (B) after adsorption by activated carbon. Further degradation under ultrasound/fly ash/H_2O_2 according to the optimum conditions selected above, concentration of Acid brown 348 decreased to 436 mg/L (C), the degradation efficiency of COD_{Cr} was 95 %.

A mathematical model, as shown in eqn. 8, was chosen to simulate the reaction kinetics[22].

$$\frac{C_t}{C_0} = 1 - \frac{t}{m + bt} \qquad (8)$$

where, C_t is the Acid brown 348 concentration at time t (min) and C_0 is the concentration of Acid brown 348 at time t = 0, b and m are two characteristic constants relating to the reaction kinetics and oxidation capacities (m = 88.67, b = 0.97).

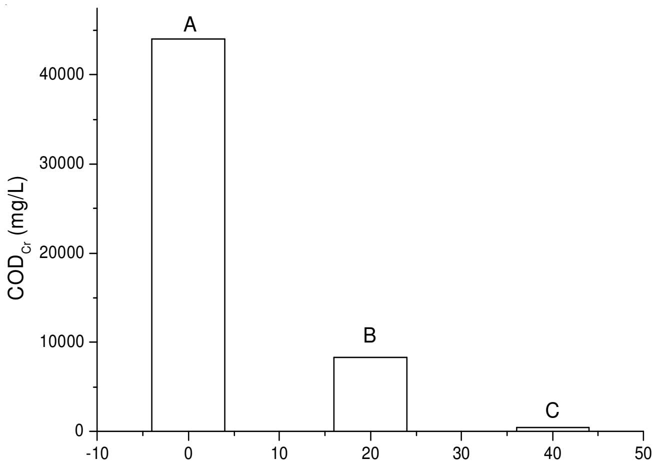

Fig. 9. COD_{Cr} value of the wastewater before and after advanced oxidation process; A. the initial factory wastewater B. after adsorption by activated carbon C. degradation of B

To solve the constants, eqn. 8 can be linearly to eqn. 9:

$$\frac{t}{1 - C_t / C_0} = m + bt \qquad (9)$$

By plotting $t/(1-C_t/C_0)$ *versus* t (Fig. 10), a straight line was obtained. As can be seen from Fig. 10, the corresponding results with high r^2 0.94 was observed. This indicated that the Acid brown 348 degradation kinetics was well described by the Behnajady's model in eqn. 9.

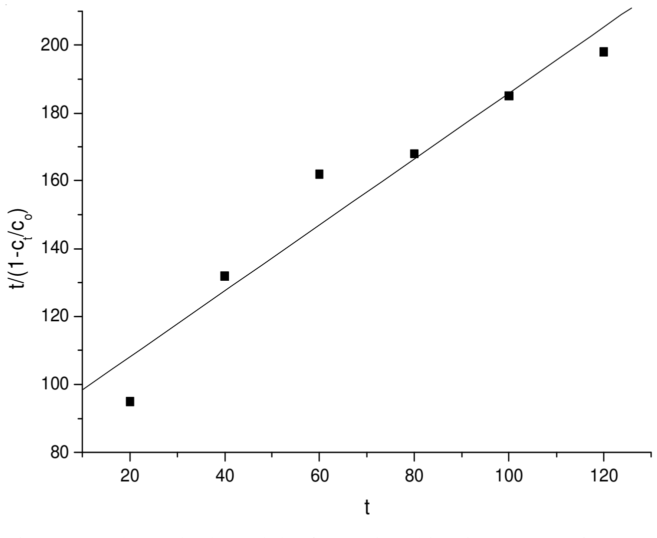

Fig. 10. Mathematical model of reaction kinetics; C_0 = 75 mg/L, concentration of H_2O_2: 5.0 mM, fly ash = 2.5 g/L, pH = 2.5, T = 40 ºC, irradiation frequency: 40 kHz

Conclusion

The combination of ultrasonic irradiation and Fenton-like's reagent was more useful for the degradation of Acid brown 348 in aqueous solution, which presents an enhancement in degradation ratio in comparison with either individual method. The optimum conditions for the degradation of Acid brown 348 in aqueous solution were: pH 2.5, H_2O_2 5.0 mM, concentration of dye 50 mg/L, fly ash 2.5 g/L, irradiation frequency 40 kHz, temperature 40 ºC. A degradation efficiency of 96 % was achieved within 140 min. In the combined procedure, some linkages of Acid brown 348 were broken, but complete mineralization does not occur. The simplicity of the procedure may be a significant advantage to degrade some dye wastewaters that are difficult to deal with using biological methods.

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