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HOMOGENEOUS PHOTOCATALYTIC DEGRADATION OF ACID ALIZARIN BLACK USING HYDROGEN PEROXIDE

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ABSTRACT

Photocatalytic degradation of acid alizarin black (AAB) dye (C.I. 21725) in aqueous solution was investigated using UV light in the presence of hydrogen peroxide (H_2O_2) as a catalyst at different operating conditions. The operating conditions were concentration of catalyst dosage (0.1, 0.2 and 0.3 mL of 30 % H_2O_2), initial concentration of AAB dye (100, 150 and 200 mg/L) and pH (3.3, 6.84 and 10.8). It was found that the increasing of catalyst concentration enhanced the dye decolourisation. Hydrogen peroxide exerted positive effects on the AAB removal whilst the initial concentration of AAB negatively affected its removal. It was also found that the removal efficiency of AAB increased with the pH value close to neutral (pH 7), while a reversed trend was observed at acidic and basic medium.

KEY-WORDS: *Photocatalytic, AOPs, catalyst, wastewater,* H_2O_2.

INTRODUCTION

Many modern techniques of treatment have been used over the last few decades to treat and purify water. Ozonation and photolysis techniques, for example, have been used successfully to degradate and reduce a range of organic and biological pollutants (Rice and Browning, 1981, Rice and Hoff, 1981, Barakat et al., 2005). However, stronger oxidant are produced (i.e. radicals) when these techniques are combined with some additives such as hydrogen peroxide and catalysts, and these processes together with additives are called Advanced Oxidation Processes (AOPs) (Glaze et al., 1987). AOPs are typically based on redox reactions as a result of gaining and losing electrons by radicals and organic molecules, respectively (Rice and Netzer, 1983). Among AOPs, in recent years, homogeneous photocatalysis methods have received a great attention in degrading or reducing organic pollutant (Al-Ekabi et al., 1991).

It is estimated that, in textile industries, more than 10 % of the dye is lost during the process of dyeing and discharged as effluent (Weber and Stickney, 1993). Since the existence of small quantities of dyes (even bellow 1 part per million) is clearly visible, the discharge of those coloured water pollutants in the environment is a considerable non aesthetic pollution source. Through hydrolysis, oxidation or other chemical reactions taking place in the phase of wastewater, wastes of dyes can also produce dangerous by-products and eutrophication (Zollinger, 1991, Tang et al., 1997). Therefore, dye effluents decolourisation has received increasing attention. In liquid phase, addition of hydrogen peroxide (H_2O_2), as oxidant, is an accepted technique to accelerate photocatalytic oxidation. For photocatalytic oxidation of water phase, the hydrogen peroxide effect was extensively investigated. Addition of moderate H_2O_2 concentration was found to be significantly accelerate degradation of dyes and aromatic compounds (Barakat et al., 2005, Mart'yanov et al., 1997, Balcioglu and Inel, 1996, Dionysiou et al., 2004). This study outlines the results achieved for the degradation of acid alizarin black (AAB) in the presence of H_2O_2. Various operating parameters were studied in this research including initial AAB concentration, amount of H_2O_2 and pH.

METHODOLOGY

Materials

Acid alizarin black (AAB) was purchased from Hopkin and Williams LTD, UK and used as received. A stock solution of AAB (1000 mg/L) was prepared on a daily basis in distilled water and other concentrations (100, 150 and 200 mg/L) were prepared by dilution the stock solution of AAB. The prepared stock solution was covered by aluminum foil and kept in dark. Hydrogen peroxide (H_2O_2) was purchased from ALPHA, India and used as received without further treatment. UV lamp with 254 nm (12 watt) was purchased from SEMTEC, China.

Experimental procedures

A closed semi-batch reactor, as shown in **Fig. 1**, was used in this study. A 500 mL, at a specific concentration, of the AAB solution was charged into the reactor, this solution prepared from the stock solution by dilution. 30 % of H_2O_2 at a spesific volume (0.1, 0.2 and 0.3 mL) was added to the AAB solution. The volume of the reactor was 600 mL. It is made from PYREX glass and fitted with a sample port. The reactor was equipped with a plunging tube in which a SEMTEC 12 watt lamp was placed horizontally. A glass syringe with 5 mL volume was used, at a specific schedule, to collect samples. The pH values (3.23, 6.84, and 10.8) of these solutions were adjusted using 0.1M of NaOH and 0.1M of HNO_3. The pH of the solution was determined using pH meter (EUTECH, Malaysia). Visible spectrophotometer (Jenway, 6700) was used to analyse the collected samples.

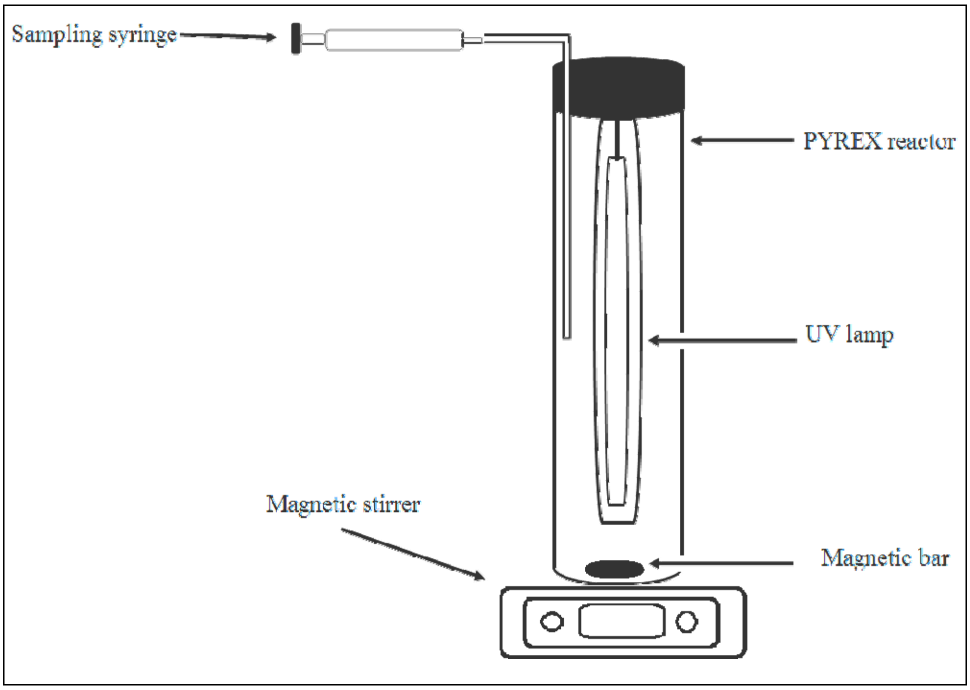

Fig. (1) *Photocatalytic reactor*

RESULTS AND DISCUSSION

Effect of initial H_2O_2 concentration

The effect of H_2O_2 concentration on AAB decolourisation was studied and the results are shown in **Fig.2**. The figure shows the decolourisation of AAB solution in the presence of H_2O_2. The other experiment conditions were kept constant (AAB concentration was set to 100 mg/L, pH 6.84, and room temperature 24^{o}C). Various volume of H_2O_2 (0.1, 0.2 and 0.3 mL) were used. **Fig. 2** also shows how the increasing catalyst amount increases the removal efficiency. After 30 min reaction time, the decolourisation rate of AAB increased when the amount of H_2O_2 increased, due to the formation of highest amount $OH^{\bullet}$ radicals when more H_2O_2 volume was used.

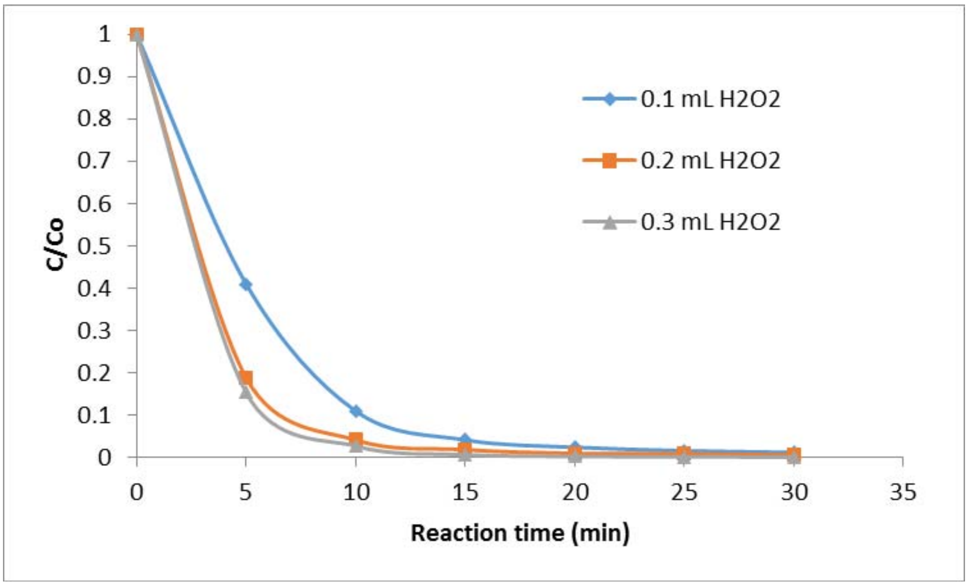

Fig. (2) *AAB removal by using different amount of H_2O_2 at 30 min ($[AAB]_o$ = 100 mg/L, Temperature= 24 ^oC, Volume = 500 mL, pH= 6.84)*

After 5 min of the reaction (see **Fig. 3**), the removal percentage of AAB increased and reached 59 %, after using 0.1 mL of H_2O_2. However, the removal percentage enhanced and reached 81 % and 84.5 % when the volume of H_2O_2 increased to 0.2 and 0.3 mL, respectively. The removal efficiency of AAB was recorded the highest removal percentage when 0.3 mL of (H_2O_2)wasused.

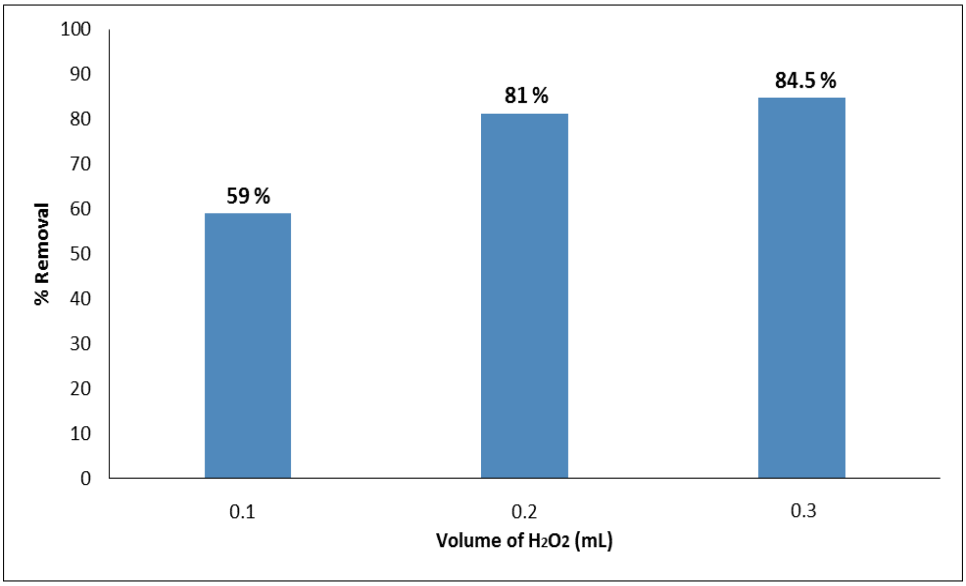

Fig. (3) *AAB removal percentage at various amount of H_2O_2 at 5 min ($[AAB]_o$ = 100 mg/L, Temperature= 24 ^oC, Volume = 500 mL, pH= 6.84)*

Effect of initial AAB concentration

The effect of initial AAB concentration on the decolourisation rate of AAB was studied using UV light in the presence of H_2O_2. The results show that increasing the initial concentration of AAB reduced the decolourisation rate (see **Fig. 4**). The rate constant, **k'**, was found to decrease linearly with increased initial AAB concentration. When AAB concentration increased from 100 to 200 mg/L, the decolourisation percentage of AAB at 5 min reaction time decreased from 81 % to 21 %, respectively (see **Fig. 5**). The dye loss, according to the following equation, was observed as a function of time and data were fitted to a pseudo first order rate model (Bali et al., 2004, Esplugas et al., 2002).

$$\ln\left(\frac{C}{C_o}\right) = -k't$$

The plot of ln (C/C_o) versus time gives a straight line with **k'** = - slope (**k'**, as seen from figure, depends on the H_2O_2 concentration), so the reaction follows a pseudo-first order scheme. Table 1 and Table 2 show the effect of dye concentration and amount of H_2O_2 on rate constant.

Table (1): Effect of AAB concentration on a pseudo-first order kinetic for the degradation of AAB

[AAB] (mg/L)	k' (min^{-1})	R^2
100	0.2483	0.9608
150	0.1511	0.9808
200	0.0844	0.994

Table (2): Effect of H_2O_2 amount on a pseudo-first order kinetic for the degradation of AAB

H_2O_2 Volume (mL)	k' (min^{-1})	R^2
0.1	0.1953	0.984
0.2	0.2327	0.9608
0.3	0.3052	0.9865

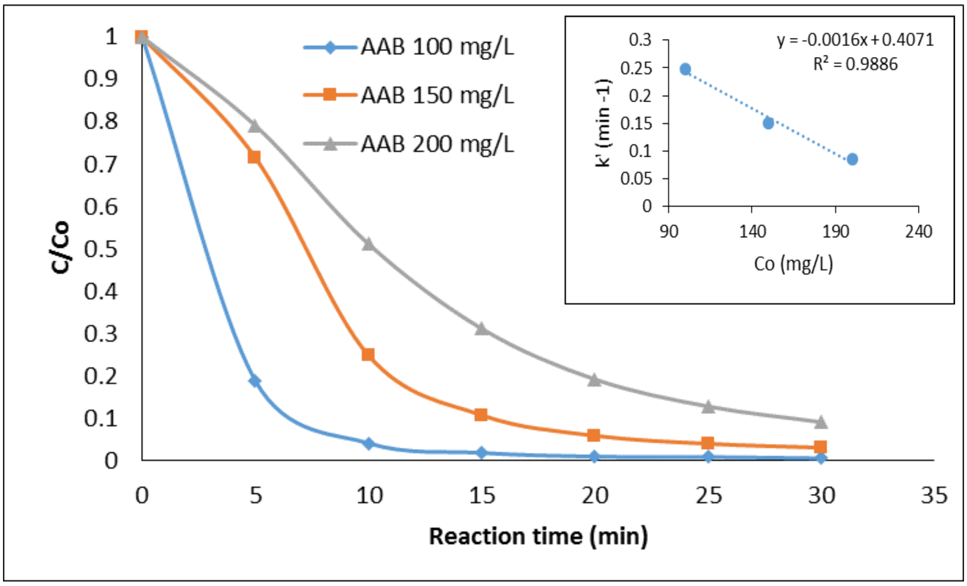

Fig. (4): *Effect of initial AAB concentration on solution decolourisation at 60 min (Temperature= 23 °C, Volume= 500 mL, pH= 6.84)*

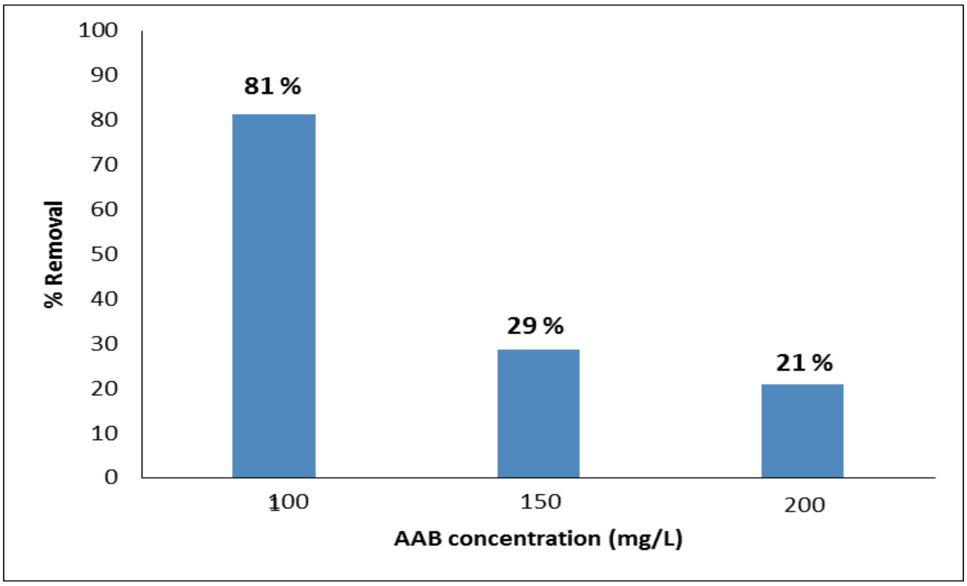

Fig. (5) *AAB removal percentage at various concentrations of AAB at 5 min (Temperature= 23 ^oC, Volume = 500 mL, pH= 6.84)*

Effect of pH

The process of AAB removal is higher at pH close to 7 compared to AAB removal in acidic and basic medium. As shown in **Fig. 6**, the removal percentage improved from 94 to 97 % when pH changed from 3.3 to 6.84, respectively. However, the improvement decreased from 97 to 95.4 % when pH increased from 6.84 to 10.8, respectively.

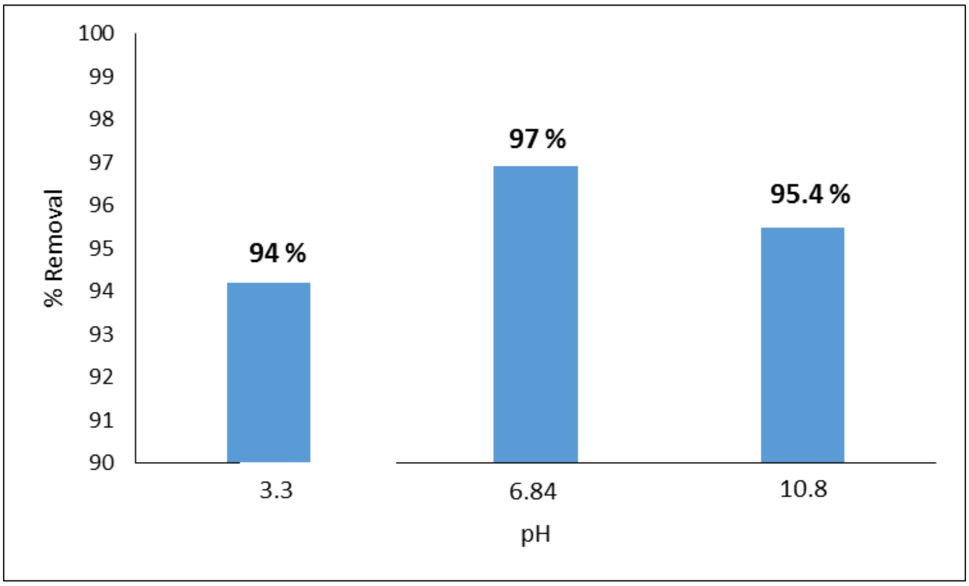

Fig. (6) *Effect of pH on AAB removal percentage at 30 min (Temperature= 23 ^oC, Volume = 500 mL)*

CONCLUSIONS

Photocatalytic degradation, in the presence of H_2O_2, of AAB under different operating conditions was studied in this research. The operating conditions were initial dye concentration, amount of H_2O_2 and pH. The most effective improvements on the degradation of AAB were recorded with initial AAB concentration of 100 mg/L. It was also found that the increasing of H_2O_2 quantity enhance the reaction rate of AAB decolourisation. The removal efficiency of AAB was favourable in the neutral medium more than the acidic and basic medium. The removal percentage reached the maximum value at pH close to 7.

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تێکچوونا بویاغا ترشێ ئەلیزارینێ رەش برێکا هاندەرێ روناهیێ ب کارئینانا ژوور ئوکسیدی هایدروجین

پوخته:

دڤێ ڤەکولینێدا تێکچوونا بویاغا ترشێ ئەلیزارینێ رەش (AAB, C.I. 21725) برێکا هاندەرێ روناهیێ هاتە کرن دناڤ ئاوێتەکێ ئاڤی دا بکارئینانا تیشکا سەر بنەفشیدا وب هەبوونا ژوور ئوکسیدی هایدروجین(H_2O_2) وەك کاریگەرەکێ هاندەر لبن جەند کردارێت جیاواز. باردوخێن کاری یێن ڤێ ڤەکولینێ پێك دهاتن (0.3, 0.2, 0.1ملیلتر ژ 30% H_2O_2) ژپەیتێ کاریگەری دگەل پەیتێ سەرەتایی ب (100, 150, 200ملغم/ لتر) یێ بویاغا AAB و pH ێ ئاوێتەی (٣.٣، ٦.٨٤، ١٠.٨). هاتە دیتن ژڤێ ڤەکولینێ ب زێدەکرنا پەیتێ هاندەری هاریکارییێ دکەت لسەر ژێبرنا رەنگێ بویاغا AAB. هاندەرێ ژوور ئوکسیدی هایدروجینی هندەك ئەنجامێن پوزەتیڤانە دان لسەر ژێبرنا بویاغا AAB لێ ب بکارئینانا پەیتێ سەرەتایی یێ AAB کارتێکرنەکا نێگێتیڤانە کر لسەر ژێبرنا ڤێ بویاغێ. هەروەسا هاتە دیتن ئەف هاندەرە دشێت ژێبرنا بویاغا AAB زێدەکەت دکەل بەهایێ pH نێزیك بیت بو هاوتا (pH 7)، بەلێ دێ دیار بیت بێچەوانەیە دناڤەندا ترش و تفتی دا.

تدهور التحفيز الضوئي لصبغة حامض أليزارين الأسود بإستخدام بيروكسيد الهيدروجين

الخلاصة

تم دراسة تدهور التحفيز الضوئي لصبغة حامض أليزارين الأسود (AAB, C.I. 21725) في المحلول المائي بإستخدام الأشعة فوق البنفسجية وبوجود بيروكسيد الهيدروجين(H_2O_2) كعوامل محفزة في حالة ظروف مختلفة. وكانت ظروف العمل لهذه الدراسة هي (٠.١، ٠.٢، ٠.٣ مليلتر من ٣٠ ٪ H_2O_2) لجرعة المحفز والتركيز الأولي (١٠٠، ١٥٠، ٢٠٠ ملغم/ لتر) لصبغ ال AAB و pH المحلول (٣.٣، ٦.٨٤، ١٠.٨). وقد وجد في هذه الدراسة أن زيادة تركيز المحفز يعزز من إزالة اللون لصبغة AAB . بيروكسيد الهيدروجين أعطت نتائج إيجابية في إزالة صبغة ال AAB في حين أن التركيز الأولي ل AAB تأثرت سلبياً في إزالة هذه الصبغة. تبين أيضا أن كفاءة إزالة صبغة ال AAB زادت مع قيمة pH قريبا إلى متعادل (pH 7)، في حين لو حظ السلوك العكسي في الوسط الحامضي و القاعدي.