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Degradation of Thiazine Dyes Azure B and C by Sonolysis, Sonophotolysis and Sonocatalysis

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The present research focuses on the application of advanced oxidation processes as sonolysis (US), sonophotolysis (US/UV) and sonocatalysis (US/O_3) for the degradation of thiazine dyes (Azure B and C) in aqueous solution. In this study, the concentration, temperature, pH, light intensity and gas flow rate on the dye decomposition were examined to find the optimum operating conditions of the treatment processes. Complete degradation was achieved in the relatively short time at 60 min irradiation. Faster decolourization was achieved at high pH and temperature. The degradation with sonocatalysis (US/O_3) was fastest. The best results were obtained from sonocatalysis (US/O_3) with efficiency more than 98 % of Azure B in comparison with Azure C 97 % at gas flow rate = 1.5 L/min and 0.025 g/min. The activation energy for both Azure dyes studied were decrease with temperature increase between 288-308 K. The decolourization of the dyes followed first order kinetics. Also both techniques sonophotolysis (US/UV/O_3) and photo oxidation (UV/O_3) were applied in optimums conditions to investigate the best removal of dyes. The results show that the best method for completely degradation of dyes at short time 10 min irradiation is sonophotolysis.

Keywords: Thiazine dye, Sonolysis, Sonophotolysis, Sonocatalysis, Degradation.

INTRODUCTION

Advanced oxidation processes (AOP's) refer to a set of chemical treatment techniques which are applied to oxidize pollutants in water and wastewater into CO_2 and H_2O and harmless inorganic products by generation high reactive and non selective species such as hydroxyl radicals[1]. Advanced oxidation processes (AOP's) are produced $^{\bullet}OH$ radicals from different reacting systems *e.g.*, ozone[2-4], hydrogen peroxide[5], ultrasonic[6], ultraviolet radiation[7], *etc.* these systems can be used individually or in different combination forms to generate the hydroxyl radicals[8]. One of the important advanced oxidation process is ultrasound[9,10]. These processes has been applied greatly for contaminant destructions polluted waters[11]. In recent years, ultrasound method both independent and combined, *e.g.*, UV/US[12], US/O_3[13], US/H_2O_2[14], US/UV/O_3[15] has been used for the treatment of dyes and other pollutants[16]. The effect of ultrasonic waves was studied by cavitation: the formation, growth and violent collapse of gas bubbles in the liquid[17-21]. The coupling of ultrasonic irradiation with ozonation of water increase in hydroxyl radicals production, ozone is decomposed thermoelectrically in the vapour phase where lead to an additional pathway[22,23].

EXPERIMENTAL

All chemicals were of highest purity from commercial suppliers such as B.D.H. and Aldrich. All chemical are used without additional purification. Sonoreactor (Powersonic LabTech model LUC-410), this model built in microprocessor with thermometer with timekeeper between 0-99 min, with performed stainless steel baskets, capacity 10 L, temperature range (ambient to 50 °C), frequency 40 kHz, power 500 W. Put the dye solution within the bath of ultrasound and then treated with it first without other factors and then treats solution with ultrasound and ultraviolet rays that are put on the solution from the top and then treated solution with ultrasound and ozone, shown in Fig. 1. Electronic spectra were recorded on UV-visible spectrophotometer Shimadzu model 1650 pc using 1 cm glass cell. pH measurements were carried out using Philips pw 9421 pH meter(pH ± 0.001). Ozone generator China MQ-12083, that generate an amount of gas 0.025 g/min if the generator provided the only air and also generate the amount of supply 0.05 g/min of the oxygen generator. Device for UV irradiation was low pressure mercury lamp Boland Philips, G6 T5, 4, 6, 10, 12 Watt. Fig. 2 shows structural formula of Azures B and C dye that used as a model of organic pollutant.

Preparation of dye solution: The effect of different factors on the rate of removal was investigated by preparation different solution of dyes and study each factor aloneness. All experiments were conducted at short time 60 min. Switch on the ultrasound generator for 10 min before the start of all experiments

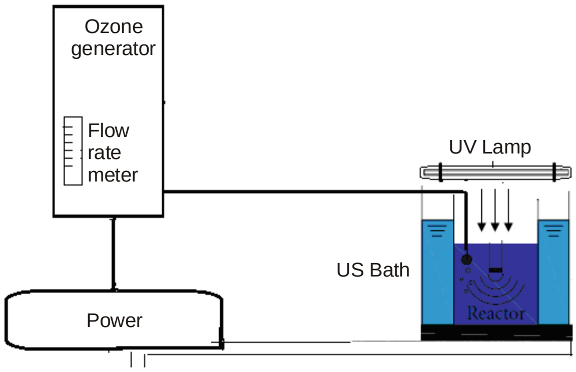

Fig. 1. Diagram of sonoreactor

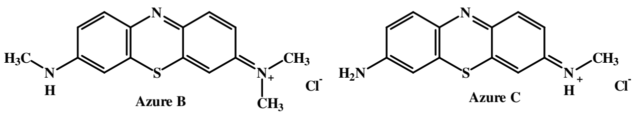

Fig. 2. Structural formula of Azure B and C dyes

irradiation and then irradiating the dye solution for period of 60 min, then the absorbance was measured at λ_{max} = 646.5 nm and 611.5 nm for Azure (B) and (C) respected Fig. 3 show the spectrum of dyes and Fig. 4 show calibration curve for Azure B and C dyes.

RESULTS AND DISCUSSION

Effect of concentration: The initial concentration of pollutant is important from an application view point. Hence the efficiency of different treatment process (US, US/UV, US/O_3) has been evaluated through the characterization of the initial and treated Azure B and C aqueous solution (Fig. 5). It is evident from the figures that the different initial Azure B and C dyes concentrations give different removal ratios. The removal ratio decreased with increasing initial concentrations of dyes by three methods because the irradiation decrease with initial concentration increase[24]. Ultrasound irradiation is the least efficient treatment after US/UV and US/O_3. So US/O_3 is the best efficient treatment than others methods. Azure B was investigated best ratio of removal than Azure C dye.

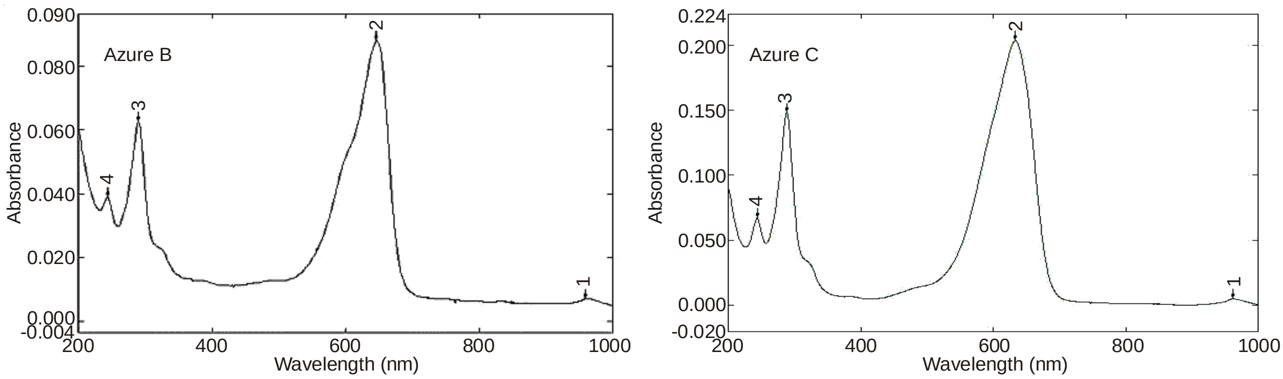

Fig. 3. UV-Visible absorption spectrum of Azure B and C dyes at 298 K, pH 6

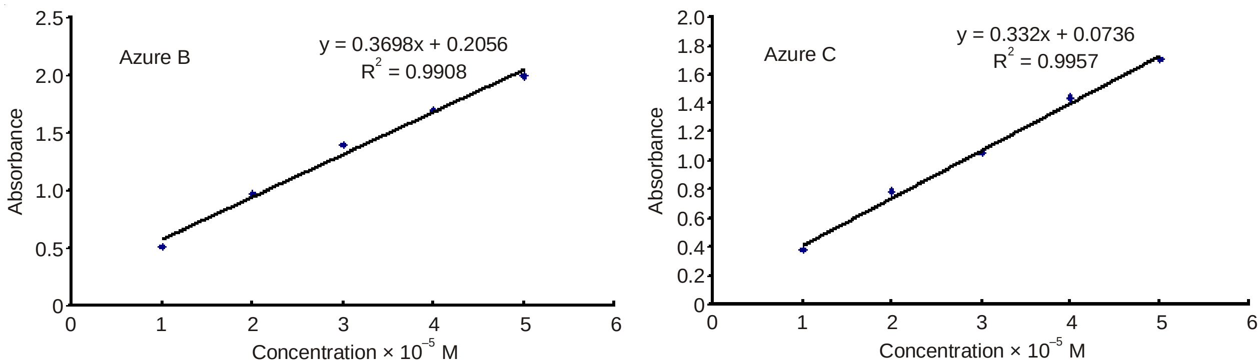

Fig. 4. Calibration curve of Azure B and C dyes at 298 K, pH 6

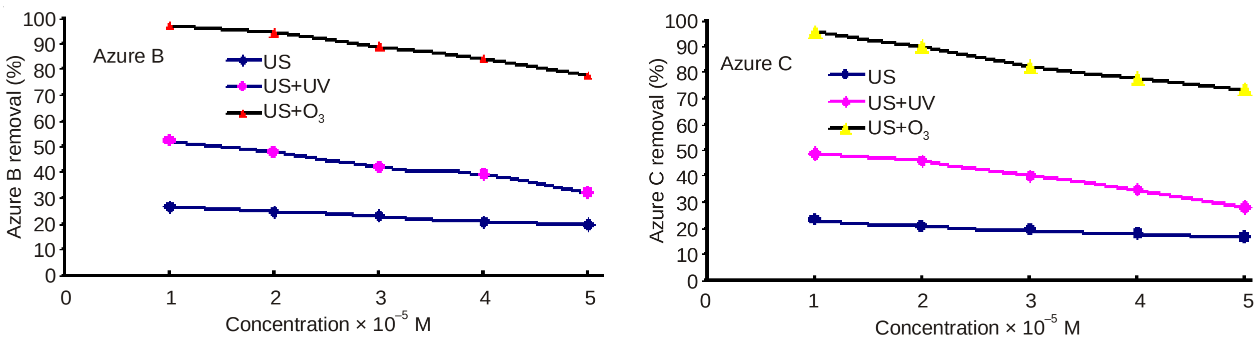

Fig. 5. Removal of Azure B and C dyes at different initial concentration at 298 K, pH 6, 40 kHz, I_o = 19.30 mW/cm^2, 0.025 g/min

According to kinetic studies, the removal rate of the dye is first order reaction attribution to the dye concentration so the eqn. 1 can be used in the following from, where can be linked values of rate constant 'k' with different dye concentration 'c' and determine reaction order 'n' as described by eqn. 1 and Figs. 6 and 7.

$$\log \text{rate} = \log k + n \log c \qquad (1)$$

Effect of temperature: Through out experiments it is found that the effect of temperature on the rate of removal is important as the rate of reaction increases gradually with temperature (Fig. 8). Arrhenius equation was used to clarify the relationship between rate consistency and its temperature:

$$\ln k = \ln A - E_a/RT \qquad (2)$$

where, k: is rate constant, A: frequency factor, R: gas constant, T: temperature. Figs. 9 and 10 show this effect.

Effect of initial pH: This study includes the effect of different values of pH function limited between 2-8 on Azure B and C dyes solution, are found that the maximum rate of disintegration of the dyes solution when the value of pH = 8, with the increase of initial pH,the rate of reaction increases so that rises efficiency for colour removal in three methods used. So that the rate of removal of Azure B dye more than Azure C in different pH. Sotelo *et al.*[25] showed that the solubility of ozone gradually decreases with initial pH increase and pH alteration for solution by HCl and NaOH (Fig. 11).

Effect of light intensity: It has been found that the maximum rate of disintegration of dyes when the value of light intensity $I_o = 19.30$ mW/cm^2, removal rate depends on number of photon internal in dyes solution this return to ability of photon breaking chromophoric band in dye molecular so that the number of photon internal to dye molecular increase with increase light intensity used in treatment process lead to

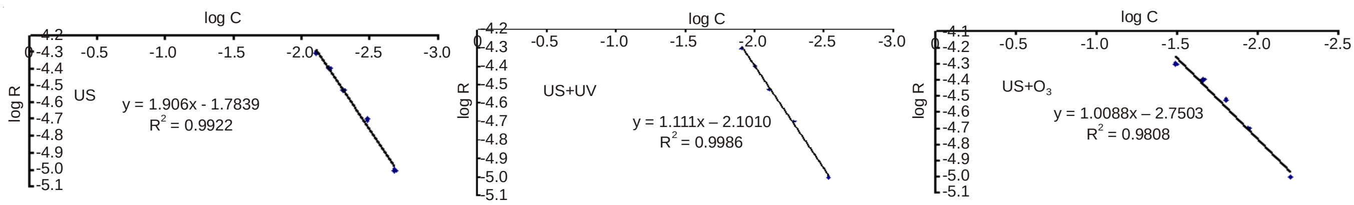

Fig. 6. Relation ship between log R, log C for Azure B at 298 K, pH 6, 40 kHz, I_o = 19.30 mW/cm^2, 0.025 g/min at different methods

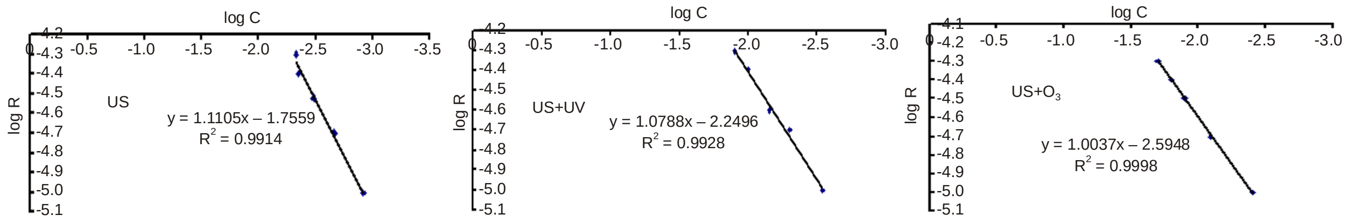

Fig. 7. Relationship between log R, log C for Azure C at 298 K, pH 6, 40 kHz, I_o = 19.30 mW/cm^2, 0.025 g/min at different methods

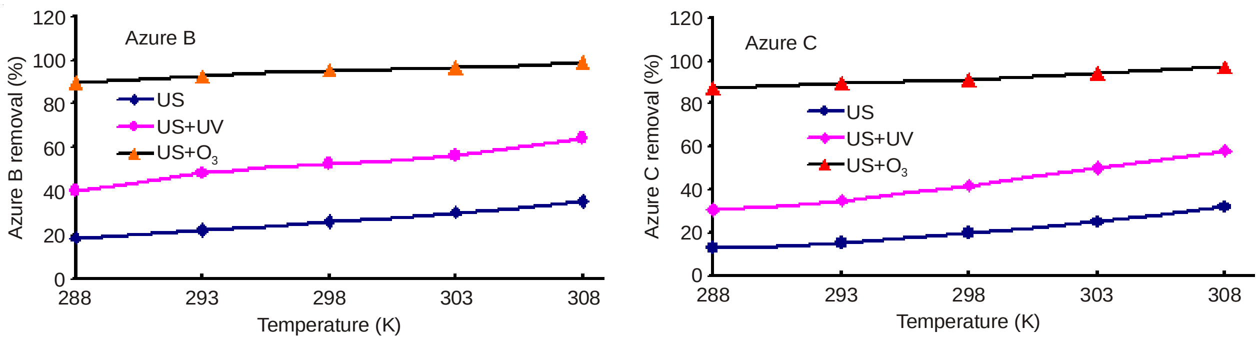

Fig. 8. Removal of Azure B and C dyes at different temperature and methods at pH 6, 40 kHz, I_o = 19.30 mW/cm^2, 0.025 g/min

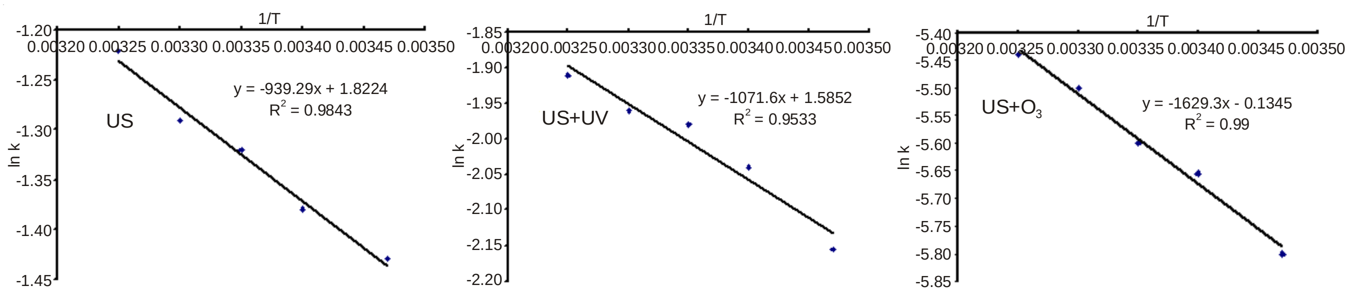

Fig. 9. Arrhenius eqn. Azure B at different methods at pH 6, 40 kHz, I_o = 19.30 mW/cm^2, 0.025 g/min

increase in removal percentage[26]. In general, many researches[27-29] showed that the removal rate of organic pollutants increase efficiency with the rise of light intensity. This effect shown in Fig. 12.

Effect of gas flow rate: Rate of colour removal depended on ozone amount required, which notice that the rate of reactive gas play important role in ozone product. Air is the gas used in this research for increase ozone product and when increase air flow rate increase oxygen amount internal to the instrument so that increase ozone generation. Gas properties presence of soluble gases will result in the formation of larger number of cavitation nuclei. However, higher gas solubility would cases more gas molecules to diffuse into cavitational bubble, causing its collapse to be less violent[30] (Fig. 13).

Effect of combined US/UV/O_3 in optimums conditions: This includes the combination effect of ultrasound, ultraviolet and ozone (US/UV/O_3) on the rate of removal of dyes. The results showed that the rate of removal of dyes solution reach to summit at short time 10 min irradiation, comparison with each method alone. This effect is showed in Fig. 14, which clarified that the degradation of Azure B is faster than Azure C.

Effect of combined UV/O_3 in optimums conditions: The combination between ultrasound and ozone increased the rate of removal of dyes. Complete degradation of dyes has been

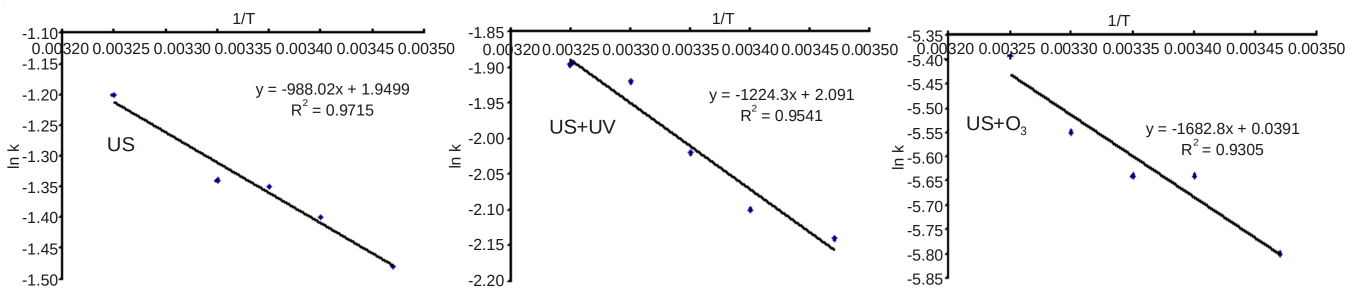

Fig. 10. Arrhenius eqn. Azure C at different methods at pH 6, 40 kHz, I_o = 19.30 mW/cm², 0.025 g/min

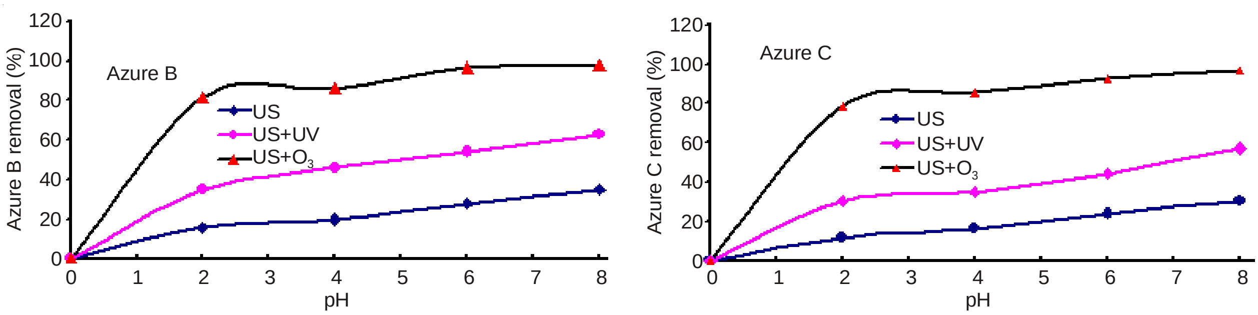

Fig. 11. Removal of Azure B and C at different pH at 298 K, 40 kHz, I_o = 19.30 mW/cm², 0.025 g/min

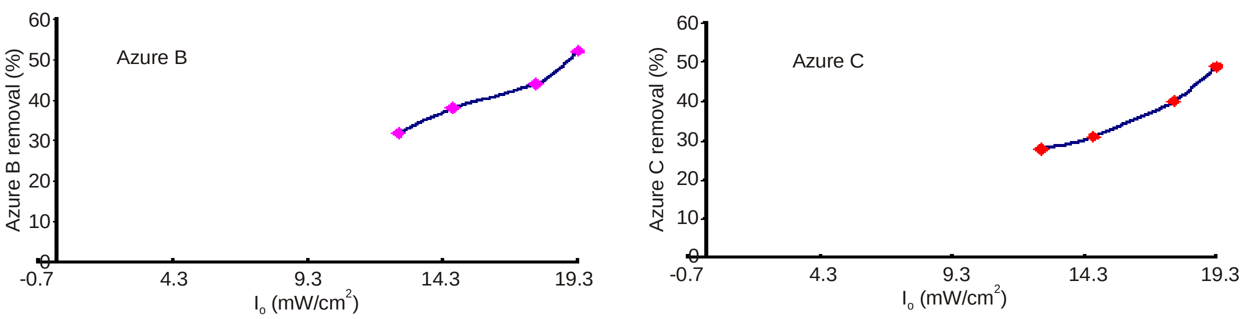

Fig. 12. Removal of Azure B and C dyes at different light intensity at US + UV method at 298 K at pH 6

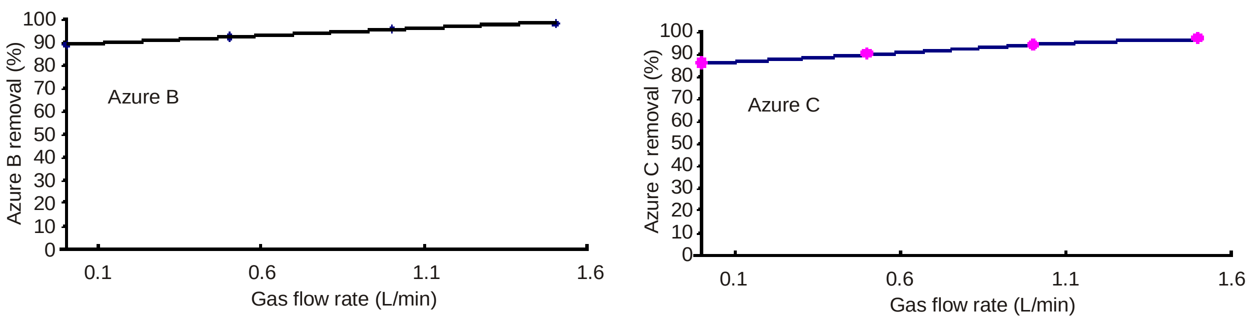

Fig. 13. Removal of Azure B and C dyes at different light intensity at US + UV method at 298 K at pH 6

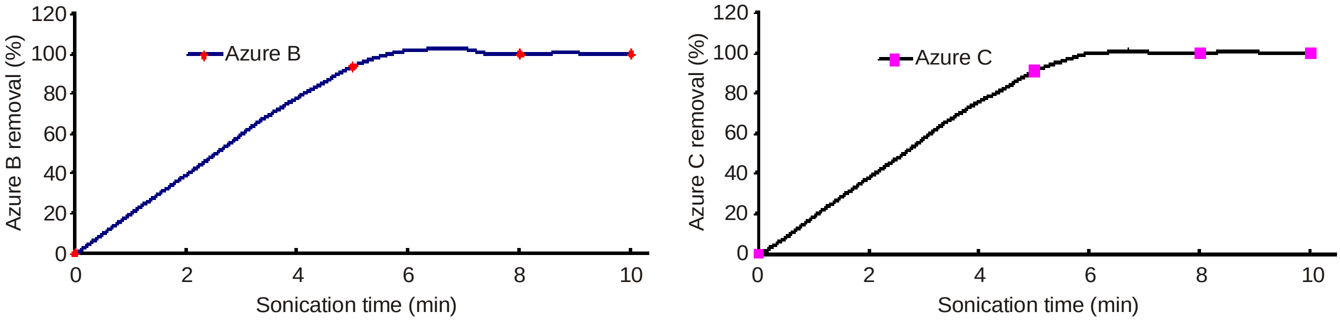

Fig. 14. Degradation of Azure B and C dyes at US/UV/O_3 at pH 8, 308 K, 1 × 10^{-5} M, 1.5 L/min, 19.30 mW/cm^2

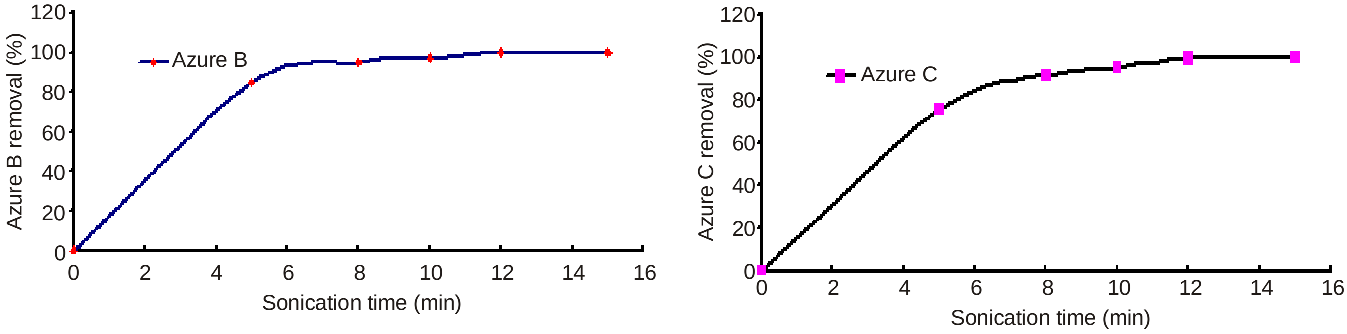

Fig. 15. Degradation of Azure B and C dyes at UV/O_3 at pH 8, 308 K, 1 × 10^{-5} M, 1.5 L/min,19.30 mW/cm^2

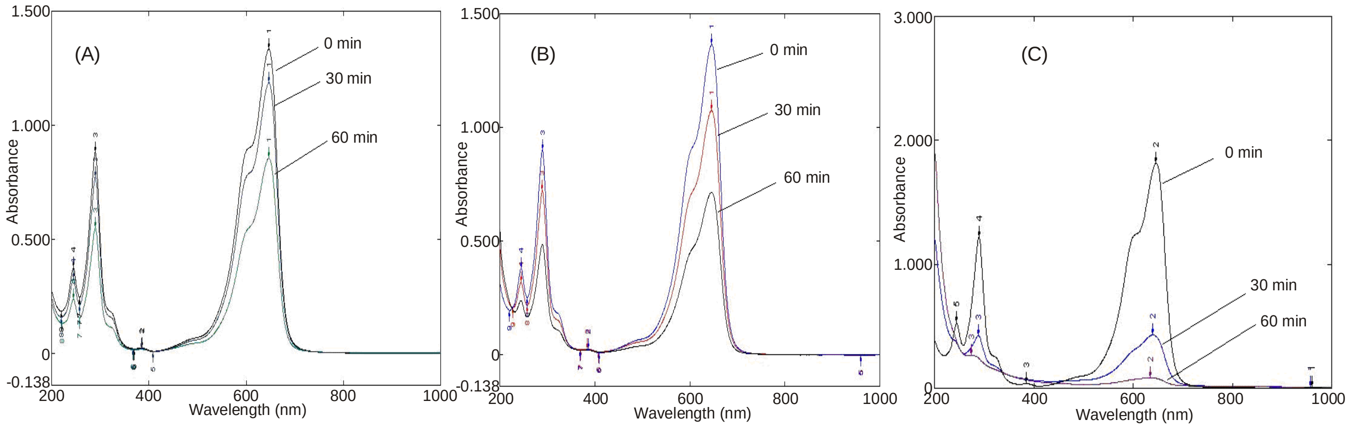

Fig. 16. UV-visible absorption of Azure B dye under effect three methods (A) US only, (B) US + UV, (C) US + O_3

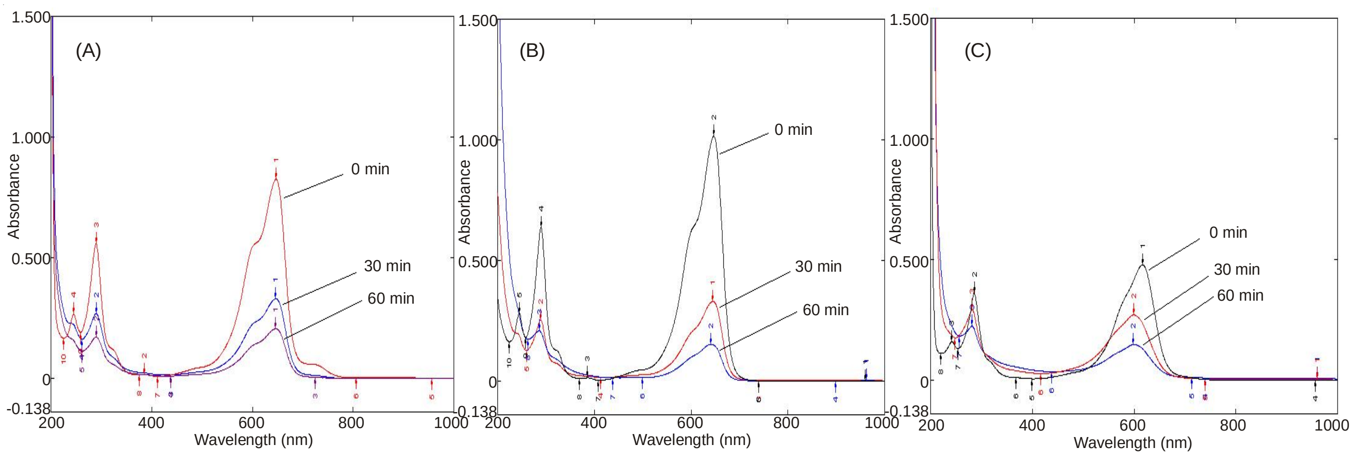

Fig. 17. UV-visible of Azure B dye under effect US + O_3 at three different pH (A) pH 2, (B) pH 4, (C) pH 8

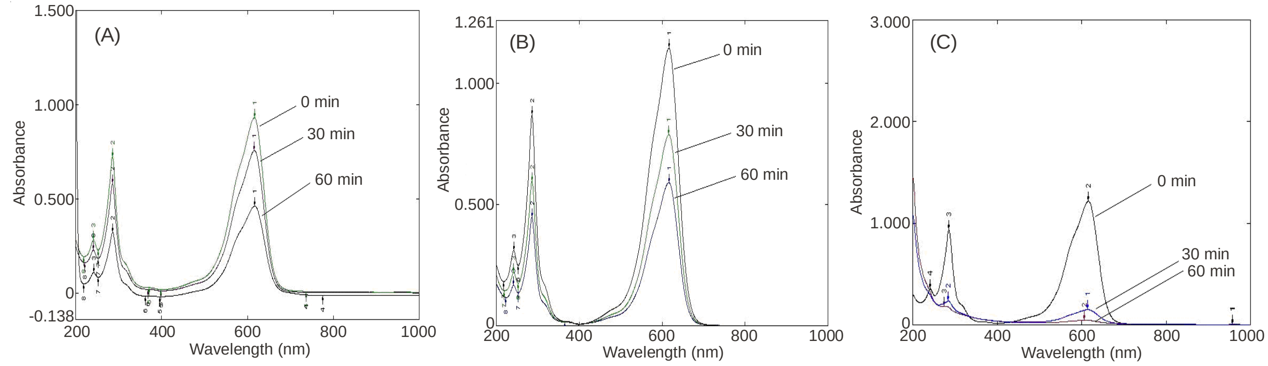

Fig. 18. UV-visible absorption of Azure C dye under effect three methods (A) US only, (B) US+UV, (C) US+O_3

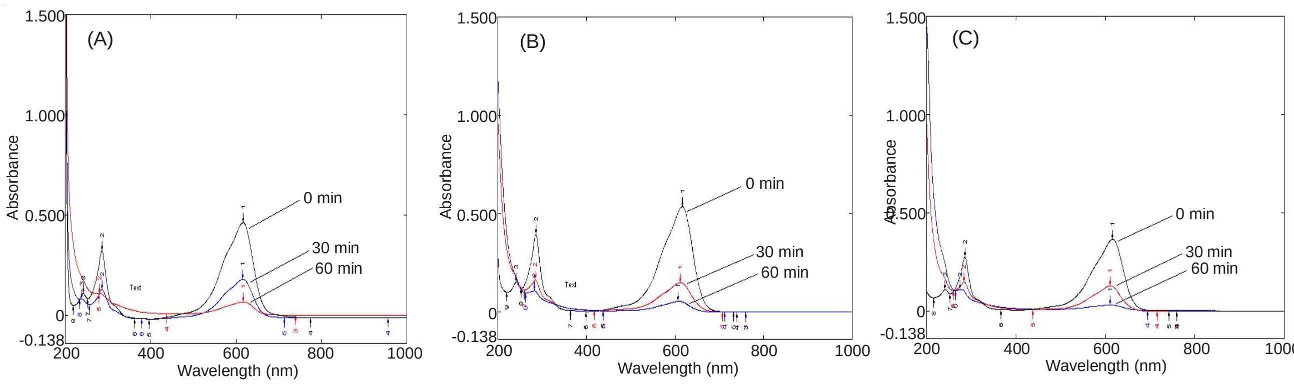

Fig. 19. UV-visible of Azure C dye under effect US + O_3 at three different pHs (A) pH 2, (B) pH 4, (C) pH 8

investigated in period short time 15 min irradiation. The results showed that the degradation of Azure B is faster than Azure C (Fig. 15).

Electronic spectra: The study included more than electronic spectra in different case in three methods and at different pH range between 2-8 at treatment by US/O_3 method. This spectra recorded at wavelength λ_{max} = 646.5 of Azure B and at λ_{max} = 611.5 nm of Azure C. All Figures show that the absorbance curve decrease with time of radiation increase but this happened in US/O_3 more than other methods at different pH medium such as in pH = 2 decreasing of absorbance less than pH = 4 and 8, but in pH = 8 more than decreasing in absorbance curve. Hence, it is clear that the decreasing of absorbance curves for both dyes in basic medium are more than in acidic medium. Some of absorption spectrum appear isobestic point. Figs. 16-19 show the electronic spectra of Azure B and C in different methods and pH.

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