*REMOVAL OF THIAZINE DYE AZURE A BY SONOLYSIS, SONOPHOTOLYISIS , AND SONOCATALYSIS

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ABSTRACT

This research is includes the efficiency of three methods of advanced oxidation processes and comparing them for decolonizing the textile dye Azure A in aqueous solution.These methods are ultrasound US only , ultrasound with ultraviolet (US / UV) and ultrasound with ozone (US / O_3). The aim is to determine the best method of treatment for mineralization of colour . All the experiments have been done by using sonoreactor only , sonoreactor with photoreactor and sonoreactor with ozone . The study includes the investigating effects of dye concentration , temperature , pH, light intensity and air flow rate . Complete degradation has been achieved in a somewhat short time 60 min . The maximum removal of color was found in higher pH and temperature where at T=308K the removal percentage are 34%,60.2%,and 98% and at pH=8 are 33%,59.5%,and 97.6% by three methods consecution. shown the removal rate that increase with decreases initial dye concentration , and also that the ratio of removal increases with rise of temperature , which decreases activated energy of reaction . It is noticed that activation energy value of removal dye are 13.8 , 9.95 , 8.15 KJ / mol at three methods successively . As far as pH is concerned , it appears that the ratio of removal decreased in acidic medium . Moreover , one can notice from the results with the increase of both air flow rate velocity and light intensity the ratio of removal increases . The decolonization reaction was found to follow first order kinetics with respect to the dye concentration .

Key Words: Thiazine Dye, Azure A, US,US/UV,US/O_3,Cavitation.

Chemistry classification : QD701-731

***The research is a part of on MSC. Thesis in the case of the second researcher**

INTRODUCTION

Ultrasound is a novel advanced oxidation process (AOP_S) that has emerged as an answer to the growing need for lower levels of contaminants in wastewater [1] . There are many studies in the literature reporting sonochemical removal of color from water and the corresponding operating parameters such as a frequency , power , pH , temperature , and dissolved gases [2-5] . Application of ultrasound in a solution leads to the acoustic cavitation phenomenon such as formation, growth, and collapse of bubbles (cavitation), accompanied by generation of local high temperature, pressure, and reactive radical species ($\dot{O}H$, $\dot{O}OH$) via thermal dissociation of water and oxygen. These radicals penetrate into water and oxidize dissolved organic compounds. Hydrogen peroxide (H_2O_2) is formed as a consequence of $\dot{O}H$ and $\dot{O}OH$ radical recombination in the outside of the cavitation bubble[6,7] . Recently ultrasound in combination with other methods has been used for the removal of dyes and other pollutants such as , ultrasound combined oxidation process [8], H_2O_2 / US , O_3 / US ,and UV / US , also concern the opportunities of treatment of specific types of waste e.g.

pharmaceutical or dying waste [9]. Photosonolysis consists on molecular splitting by the combined effect of photolysis and sonolysis phenomena . Sonolysis is produced by mechanical waves which induce cavitation phenomena in the water . Photolysis is produced due to the interaction between the water molecules and the sunlight radiation [10] . Ozone decomposition rate in water increase at pH rises for example at pH value 10, and Oxidation of organic spaces may occur due to a combination of reaction with molecular ozone and reactions with $OH^{\cdot}$ radicals[11] . The ozonation process has a high treatment cost also , there are a long number of advanced oxidation processes currently being investigated which use a sonochemical reactor alone and in combination with ozone and hydrogen peroxide[12]. When water is ozonated simultaneously with ultrasonic irradiation , ozone undergoes thermal decomposition in collapsing bubbles providing additional $OH^{\cdot}$ radicals[13].

EXPERIMENTAL PART

Materials and Instruments

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) . Electronic spectra were recorded on UV – vis spectrophotometer . Shimaduz model 1650 pc using 1cm glass cell . pH measurements were carried out using aPhilips pw 9421 pH meter(pH $\pm$ 0.001) . Ozone generator China MQ – 12083 , that generate an amount of gas 0.025 gm / min if the generator provided the only air and also generate the amount of supply 0.05 gm / min of the oxygen generator . Device for measuring low pressure mercury lamp Boland Philips , G6 T5 , 4 ,6 , 10 , 12 Watt .Fig.(1) shows that Azure A dye that used as a model of organic pollutant .

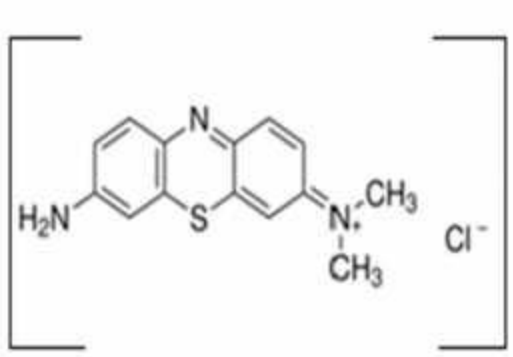


Fig.(1): Structural formula of Azure A dye

Preparation of dye solution and measurements

Studying the effect of different factors on the rate of removal by preparation different solution of dye and study each factor alone , all experiments were conducted at short time 60 min , fill the instrument generator ultrasound for ten minutes before the start of all experiments irradiation and then irradiating the dye solution for period of 60 min. then measuring absorbance for this concentration at λ_{max}=632nm Fig.(2) shows the spectrum of dye and Fig.(3) show calibration curve for Azure A dye .

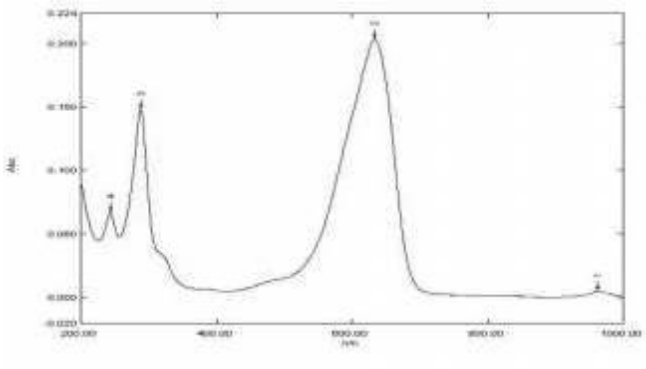


Fig.(2): UV-Visible absorption spectrum of Azure A at 298K,pH=6

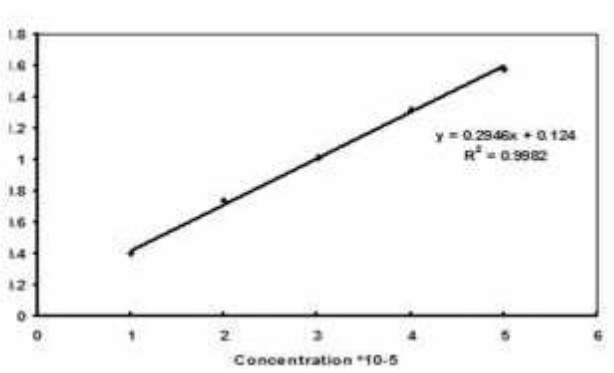
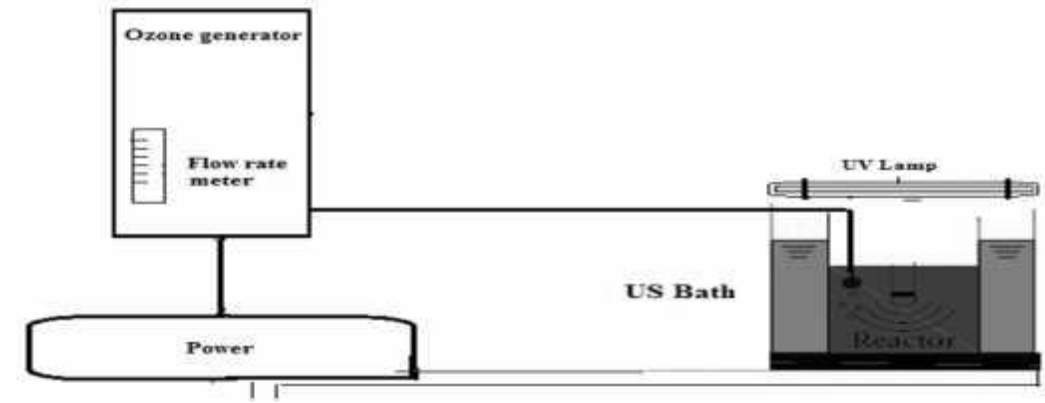


Fig.(3): Calibration curve of Azure A at 298K, pH=6

Sonoreactor

Powersonic –LUC-410 , this model built in microprocessor with thermometer with timekeeper between 0 – 99 min , with performed stainless steel baskets , capacity 10 liters , temperature range (ambient to 50^{o} 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 dye solution prepared with ultrasound and ultraviolet rays that are kept on the solution from the top and then treated solution with ultrasound and ozone, shown in Fig.(4) .



Scheme (4): Diagram of Sonoreactor

RESULTS AND DISCUSSION

Effect of concentration

The effect of different concentrations of dye where treated by ultrasound , ultrasound with ultraviolet , and ultrasound with ozone , proved that the percentage of removal decreases with increasing concentration of dye when treated by ultrasound only, also when treated with ultrasound and ultraviolet ,where it decreases susceptibility of UV radiation into force of solution to increase concentration[14] . Also at application ultrasound with ozone decreases the rate of removal Fig.(5) shows this effect.

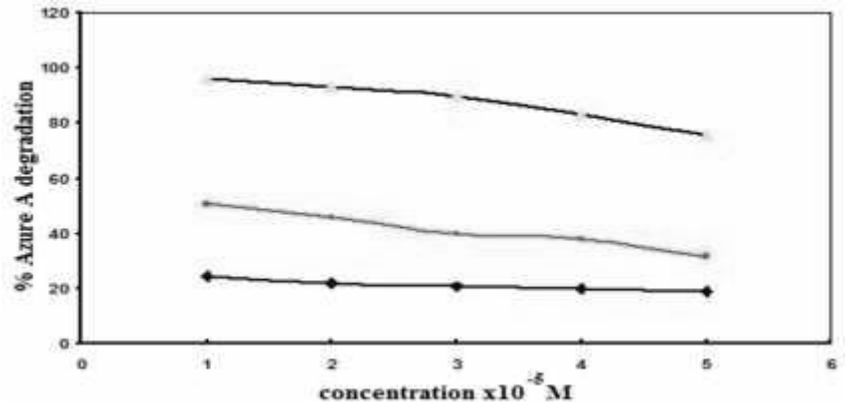


Fig.(5): Degradation of Azure A dye at different initial concentration at 298K, pH=6, 40kHz, I_o=19.30mW/cm^2,0.025 gm/min

According to kinetic study, the removal rate of dye is first order reaction is attributed to the dye concentration so the equ. 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 equ.(1) and Fig.(6)

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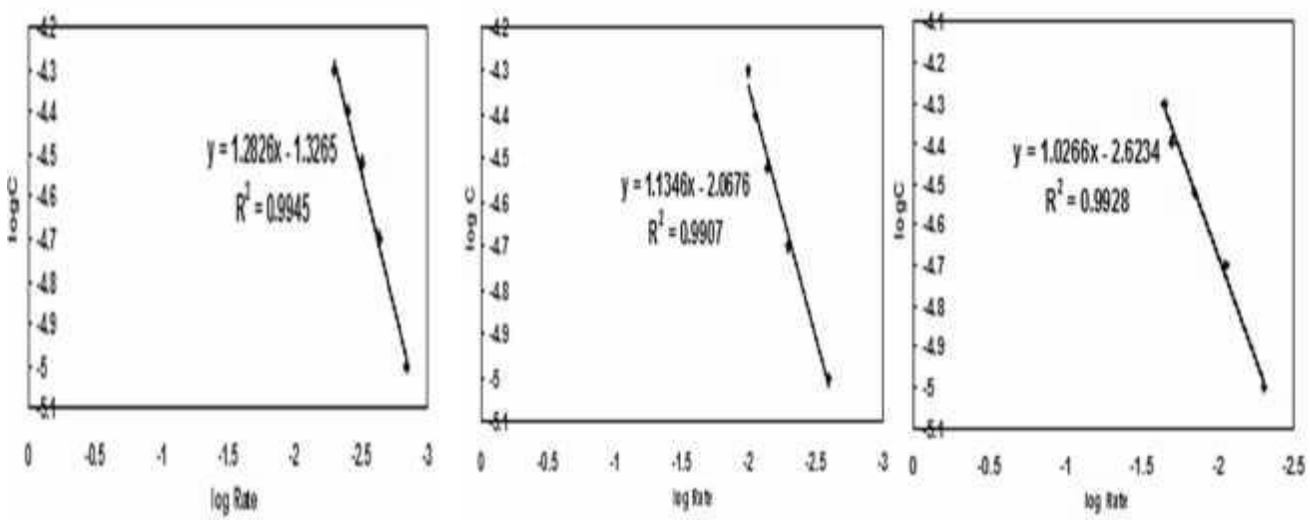
$$LogRate = Logk + nLogc \qquad \text{.....(1).}$$



(a) **(b)** **(c)**

Fig.(6): Relation ship between Log R, Log C for Azure A at 298K, pH=6, 40kHz, I_o=19.30 mW/cm^2, 0.025 gm/min at different methods : (a) US , (b) US+UV , (c) US+O_3

Effect of temperature

Throughout experiments, it is found that the effect of temperature on the rate of reaction is important as the rate of reaction increases gradually with temperature so that the removal ratio increases with temperature :

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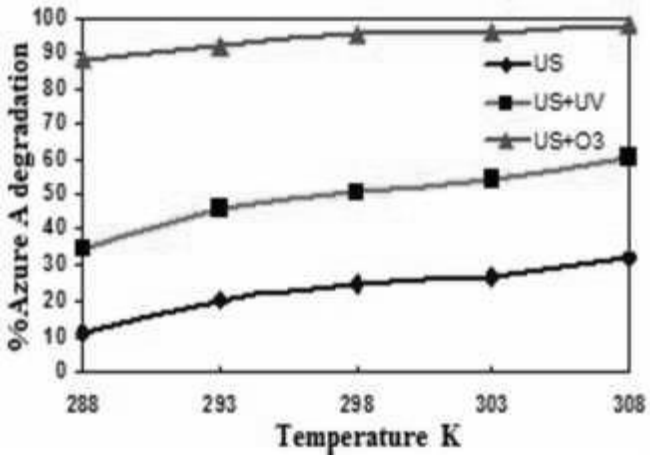
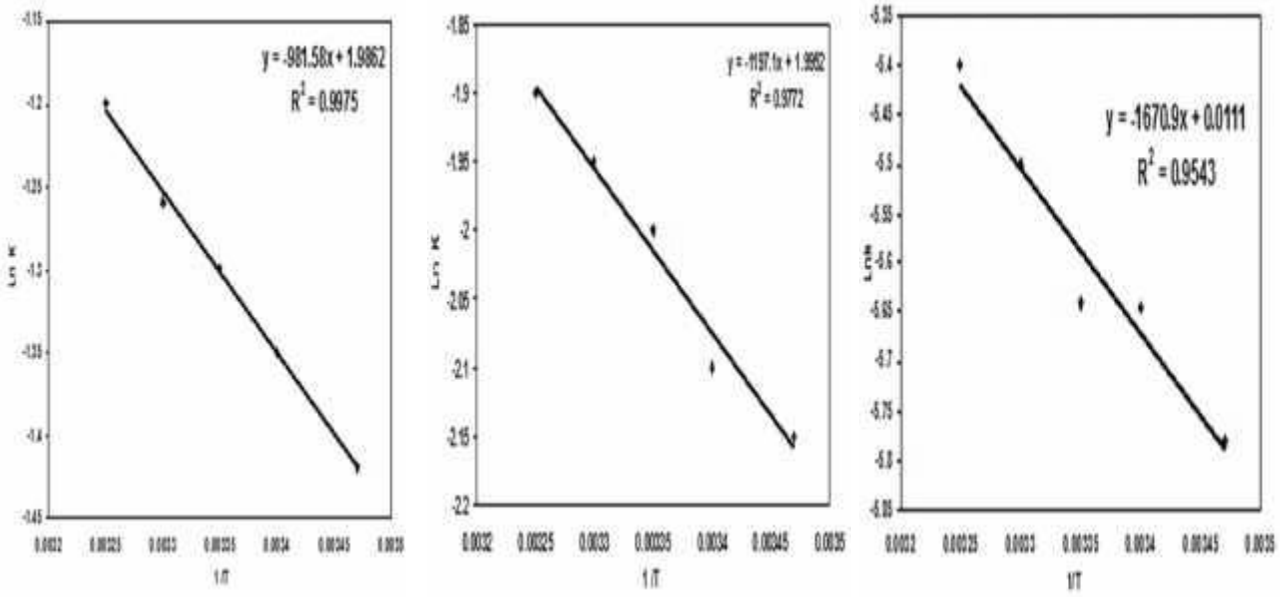
increase this effect show in Fig.(7), and Arrhenius equation was used to clarify the relationship between rate consistency and its temperature

$$\ln A = \ln k - Ea / RT \qquad \text{.....(2).}$$

Where:
k : is rate constant , A: Frequency factor , R: Gas constant , T: temperature . Fig.(8) show this effect.



Fig(7): Degradation of AA at different temperature and methods at pH=6,40kHz, I_o=19.30mW/cm^2,0.025gm/min



(a) (b) (c)

Fig(8): Arrhenius equ. For color removal Azure A pH=6,40kHz,I_o=19.30mW/cm^2, 0.025gm/min different methods: (a)US, (b)US+UV, (c)US+UV+O_3

3.3. Effect of initial pH

This study includes the effect of different values of pH function limited between 2-8 on solution ,It is found that the maximum rate of disintegration of the dye 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 . Sotelo and other [15] show that the solubility of ozone gradually decreases with initial pH increase and pH alteration for solution by HCl hydrochloric acid and NaOH, this effect show in Fig.(9)

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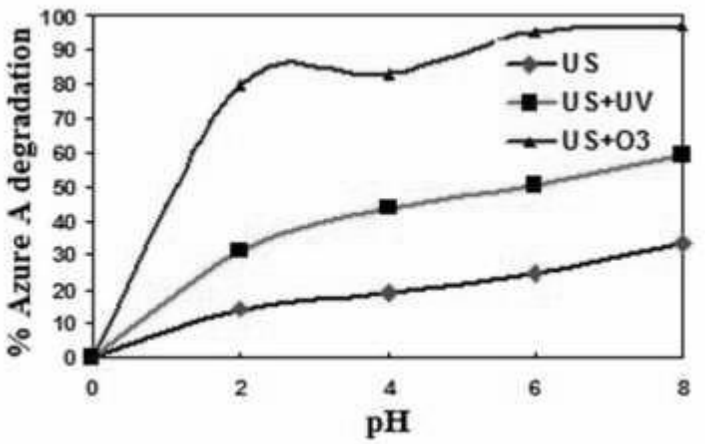

Fig(9): Degradation of Azure A Dye at different pH and methods at 298K, 40kHz, I_o=19.30mW/cm^2,0.025gm/min

3.4. Effect of Light intensity

The study include the effect of different values of light intensity on the removal of dye solution ,It is found that the maximum rate of disintegration of dye when the value of of light intensity I_o = 19.30 mW /cm^2 , rate removal of depended on number of photon internal in dye 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 increase in removal percentage [16]. In general , many researches showed that the removal rate of organic pollutants increase efficiency with the rise of light intensity[17-19]. This effect show in Fig. (10) compare with Fig.(11).

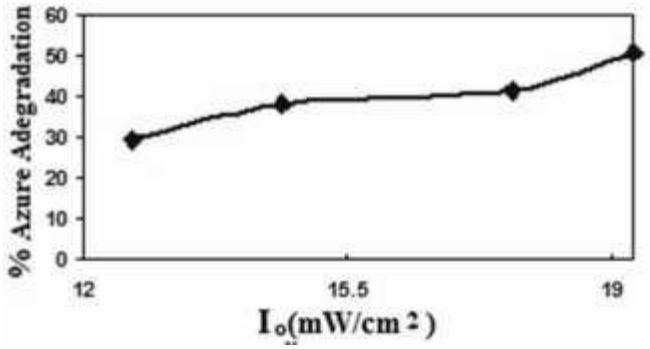

Fig.(10): Degradation of Azure A at different light intensity at US+UV method at 298K, pH=6

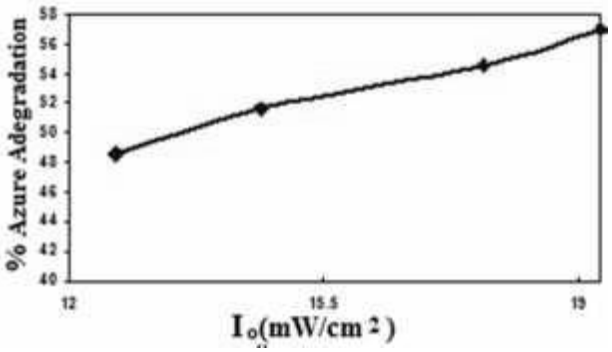

Fig.(11): Degradation of Azure A dye at different light intensity at UV+O_3 at 298K , pH=6

3.5. Effect of gas flow rate

The rate of oxidation increase with increase rate of air passed , The rate of color removal depended on ozone amount needed , which notice that the rate of gas reactive 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[20]. This effect shows in Fig.(12) in comparison with Fig.(13)

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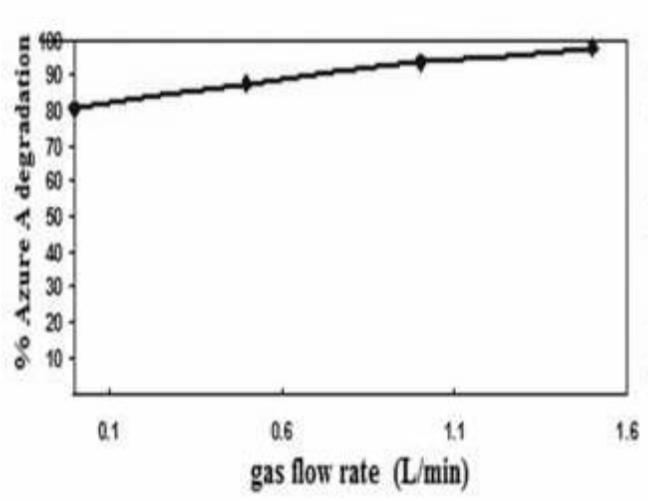


Fig.(12):Degradation of Azure A dye at different gas flow rate at 298K, pH=6

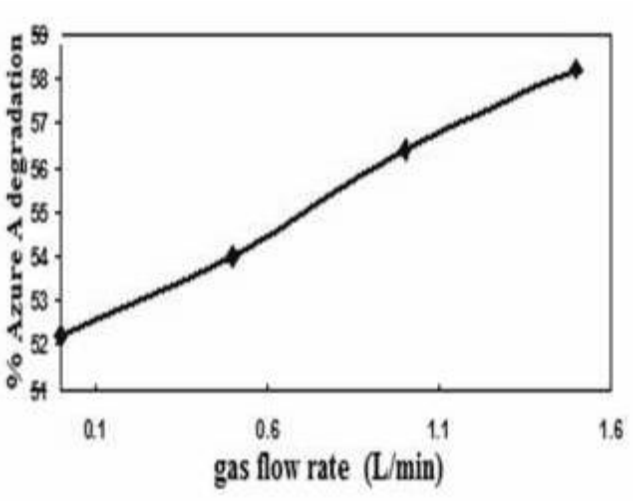


Fig.(13): Degradation of Azure A dye at different gas flow rate at US+O_3 method at UV+O_3 method at 298K ,pH=6

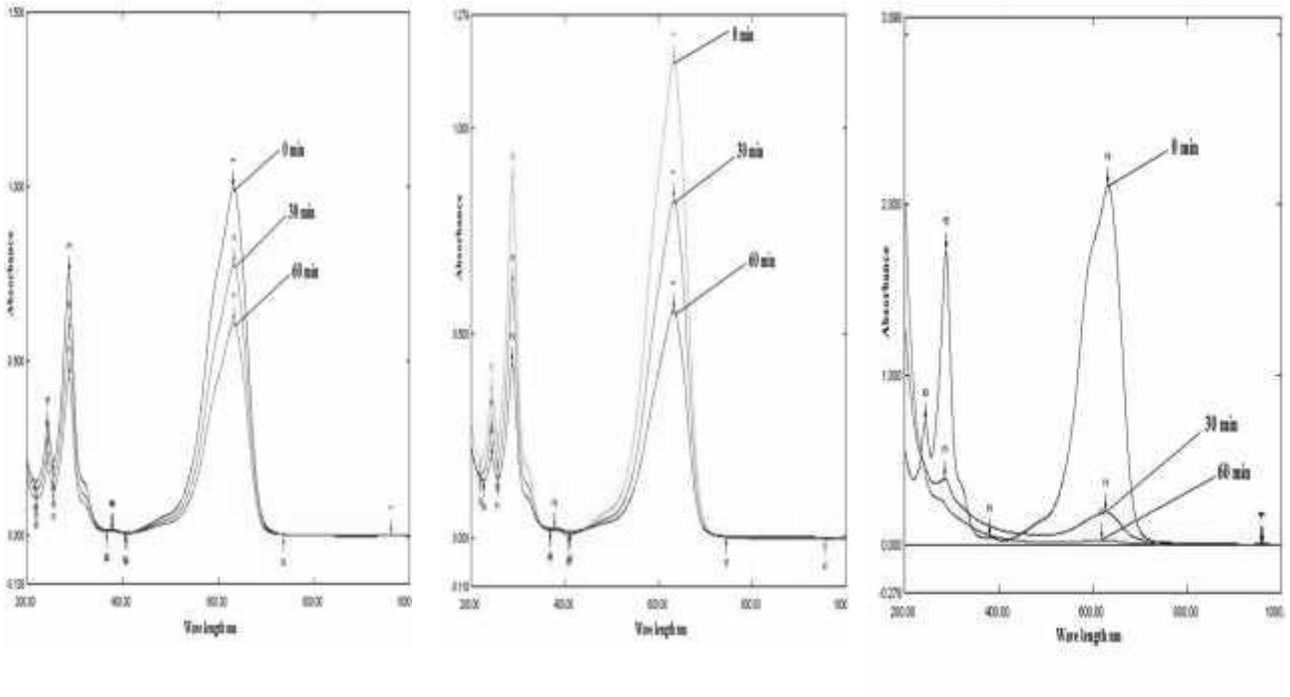
3.6. Electronic Spectra

The study includes more than electronic spectra in different case in three methods and at different pH range between 2-8 at treatment by ultrasound / O_3 method , This spectra record at max wave length λ_{max} = 632 of Azure A . All Figures show that the absorbance curve decrease with time of radiation increase but this happened in US /O_3 more than other methods and different in 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. Some of absorption spectrum appear isobestic point such as this case in Fig.15 (C). Isosbestic points are commonly met when electronic spectra are taken (a) on a solution in which a chemical reaction is in progress (in which case the which case the two absorbing components concerned are a reactant and a product, A+ B), or (b) on a solution in which the two absorbing components are in equilibrium and their relative proportions are controlled by the concentration of some other component, typically the concentration of hydrogen ions, e.g. an acid–base indicator.

$$A \rightarrow B + H^+_{aq} \qquad \text{.....(3).}$$

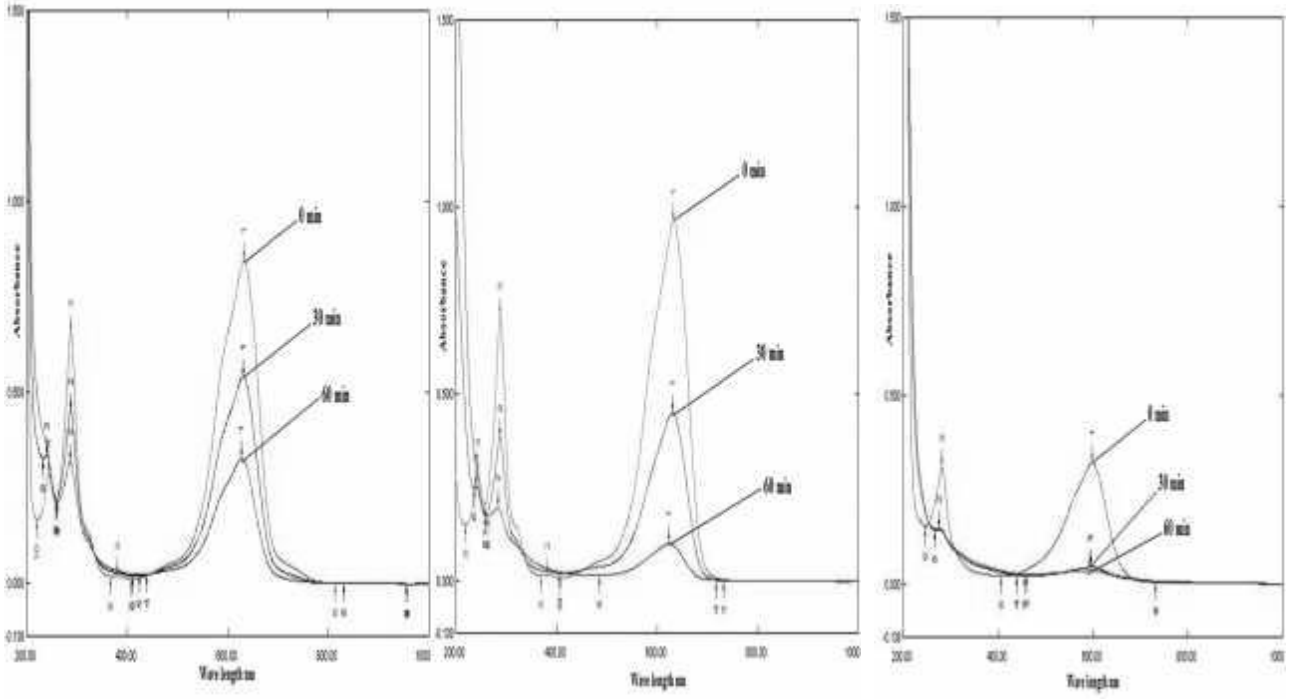
The effect may also appear (c) in the spectra of a set of solutions of two unrelated non-interacting components having the same total concentration .

Fig. (14) and(15) shows electronic spectra of Azure A in different methods and pH



(a) (b) (c)

Fig(14):UV-Visible absorption of Azure A dye under effect three methods: (a) US only,(b) US+UV, (c) US+O_3



(a) (b) (c)

Fig.(15): UV-Visible of Azure A dye under effect US+O_3 at three different pH
(a) pH=2,(b) pH=4,(c) pH=8

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*ازالة صبغة الثيازين (Azure A) بواسطة تقنية الموجات فوق الصوتية و تقنية الموجات فوق الصوتية والاشعة فوق البنفسجية و تقنية الموجات فوق الصوتية و الاوزون

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الخلاصة :

تضمن البحث الحالي دراسة كفاءة ثلاث طرق من طرائق الأكسدة المتقدمة و المقارنة فيما بينها في إزالة و تحطيم صبغة النسيج (Azure A) في المحلول المائي وهذه الطرق هي الموجوتية و الموجات فوق الصوتية مع الأشعة فوق البنفسجية و الموجات فوق الصوتية مع الأوزون . الهدف هو تحديد طريقة المعالجة المثلى لإزالة اللون . جميع التجارب أجريت باستخدام المفاعل الصوتي فقط ثم المفاعل الصوتي مع المفاعل الضوئي و المفاعل الصوتي مع الأوزن البحث دراسة تأثير كل من التركيز الابتدائي و درجة الحرارة و pH و شدة الضوء و سرعة الهواء . تحلة التامة في وقت قصير مقداره 60 دقيقة . الإزالة العظمى للون تحققت في pH قاعدية و ودرجة حرارة عالية حيث عند 308K كانت نسبة الإزالة هي 34% و 60.2% و 98% و في pH=3 كانت 33% و 59.5% و 97.6% بواسطة الطرق الثلاثة على التوالي . تبين ان سرعة الإزالة تزداد مع نقصان التركيز الابتدائي للصبغة وكذلك نسبة الإزالة تزداد بزيادة درجة الحرارة التي تقل طاقة التنشيط للتفاعل , و كانت قيم طاقة التنشيط لإزالة الصبغة 8.15 KJ/mol , 9.95 , 13.8 باستخدام الطرق الثلاثة.كذلك لوحظ إن نسبة الإزالة تقل في الوسط الحامضي بينما تزداد مع زيادة كل من سرعة السريان و شدة الضوء . و جد إن تفاعل الإزالة يتبع حركيات المرتبة الأولى نسبة إلى تركيز الصبغة .

الكلمات المفتاحية : اصباغ الثيازين , ازور A , US , US/UV , US/O_3 , التجويف.

* البحث مستل من رسالة ماجستير للباحث الثاني