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Al- Qadisiyah University
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KINETICS OF PHOTOCHEMICAL DEGRADATION OF AZURE DYES IN AQUEOUS SOLUTIONS BY USING ADVANCED TECHNOLOGIES

A thesis
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Abstract

In textile wastewater industry, Advanced Oxidation Processes (AOP'S) were used to degrading and removing of color from azure (A,B,C) dyes. The parameters studied were the effect of initial dye concentration, initial hydrogen peroxide dosage , temperature, Fenton reagent , pH and irradiation time . Photo experiments were conducted using the photoreactor. The light source of UV radiation is the Low Pressure Mercury Lamp-(LPML) and temperature 298K. The common used AOPs in drinking water treatment include UV/H_2O_2 process, UV/Ozone Process, UV/TiO_2 and Fenton's Reagent. Complete degradation was achieved in the relatively short time of 75 minutes irradiation. Faster decolourization was achieved at low pH and high temperature, the best results were obtained from photo Fenton's reagent. It has been found that the removal rate increased as the initial concentration of H_2O_2 and ferrous ion increase to optimum value and it has been found the increasing of removal percentage as the temperature increases with activation energy of (43.23 KJ/mole) from azure A dye in present UV light and activation energy for each azure B and C dyes (74.16 KJ/mole), (61.14 KJ/mole) in present UV. In present study the effect of all above effects on chemical oxygen demand(COD). The decolourization reaction was found to follow , first order kinetics with respect to the dye concentration. The experiments performed absence of UV radiation lead to enhance the

generation of hydroxyl radicals which drive the photooxidation processes. The results indicated that the (UV /H_2O_2/ Fe^{+2}) system gave the best way for removal. The highest removal was recorded from azure (A,B and C) dyes .

In this way , as the following table shows :

No	Dye	The best process	The highest removal
1-	A	98.1%	UV /H_2O_2/ Fe^{+2}
2-	B	99.1%	UV /H_2O_2/ Fe^{+2}
3-	C	98.8%	UV /H_2O_2/ Fe^{+2}

1-1 General Introduction

Textile industry is one of the most complicated industries among manufacturing industry(1).There are more than 100,000 different synthetic dyes available on the market, produced in over 700,000 tons annually worldwide(2). There are several classes of organic pollutants (organic dyes, pharmaceuticals, polycyclic aromatic hydrocarbons, polychlorinated pesticides, polychlorinated dibenzodioxins, and biphenyls) that by the seriousness of the risks they pose to environment and human health are considered priorities for environmental monitoring by the most important environmental agencies(3). Photo-oxidation technique is one of the important techniques that is used in many fields its high efficiency in the removal of the toxic effects of the environmental pollutants (4-5) . Another important problem of textile industry wastewater is the colored effluent because of the usage of large amounts of dyestuffs during the dyeing stages of the textile-manufacturing process and contains visible pollutants(6-7). The primary concern about effluent color is not only its toxicity but also its undesirable aesthetic impact on receiving waters. The main sources of wastewater normally come from cleaning water, pretreatment, dyeing and finishing process water non-contact cooling water and others(8). Thiazine dyes it is one of the cationic dyes which contains a group of base main that acquires a proton under acidic condition for the dye medium. It attaches to the tissues via ionic salt linkage with the acidic anion group in the tissue(9).

1-1-1 :Wastewater from Industry

Generally the term wastewater refers to any residual fluid released into the environment and that contains polluting potential. The equivalent term effluent, which means to spill, derives from the latin effluente (10). Textile effluent have a strong color , large amount of suspended solids , high chemical oxygen demand(COD) , high biological oxygen demand (BOD) and presence of metal ions(11-12). Major pollutants in textile wastewaters are high acidity, heat and other soluble substances main pollution in textile wastewater came from dyeing and finishing processes(13-14) .Different treatment processes included physical , chemical, and biological have been employed to treat various municipal and industrial wastewaters for example chemical (15). Biological, food(16), pharmaceutical(17), pulp and paper(18) ,dye processing and textile(19), and landfill leach ate effluents (20). Textile industry is one of the most water and chemical intensive industries worldwide due to the fact 200-400 liters are needed to produce 1 kg of textile fabric in textile factories (21-22) . During the last two decades, color removal from the textile industry has attracted considerable attention due to color visibility in receiving water and the toxicity of certain dyes. Without proper treatment of colored waste, these dyes may remain in the environment for a long time (23).It is clear that efforts to minimize the use of energy in the production of drinking water and wastewater services can potentially yield substantial energy savings (24).

Color removal from the textile wastewater has become an issue of interest during the last few years because of the toxicity of the dyes and more often the colored wastewater from the textile industries also decreases the visibility of the receiving waters (25). The textile dyes and dye intermediates with high aromaticity and low biodegradability have emerged as major environmental pollutants and nearly 10-15% of the dye is lost in the dyeing process and is released in the wastewater which is an important source of environmental contamination(26-27).Textile industry effluents can be classified as dangerous for receiving waters, which commonly contains high concentrations of recalcitrant organic and inorganic chemicals (28-29). Many industries have a need to treat water to obtain very high quality water for demanding purposes. Water treatment produces organic and mineral sludges from filtration and sedimentation. Textile industry produces large amounts of liquid by-products. Volume and composition of these wastewater can vary from one source to other source(30).

1-1-2 :Treatment of Industrial wastewater.

Treatment of wastewater is one of the biggest problems faced by textile. The most dyes can be easily treated if the conventional treatment methods are incorporated with the advanced oxidation processes which can break the complex structure of the dye and make it more a mixable to bio-degradation(31). The dyes in wastewaters present a significant problem in the wastewater treatment , due to the complex and varied chemical structure of these compounds along with other residual chemical reagents and impurities(32). There are several levels of wastewater treatment; these are primary, secondary and tertiary levels of treatment. Most municipal wastewater treatment facilities use primary and secondary levels of treatment, and some also use tertiary treatments(33).

Various physical, chemical and biological pre-treatment and post-treatment techniques have been developed over the last two decades to remove color from dye contaminated wastewaters in order to cost effectively meet environmental regulatory requirements(34). These traditional treatment methods require too many spaces and are affected by wastewater flow and characteristic variations. Also, either activated sludge process modifications when combinations of this process with physical or chemical processes can be found in most applications for the treatment of textile industry wastewater(35-37) .Textiles effluent contains dyestuffs, which are visible, even at low concentration(38). Chemical and biological treatments have been conventionally followed till now but these treatment methods have their own disadvantages such as the aerobic treatment process is associated with production and disposal of large amounts of biological sludge (39) . If these effluents are improperly treated, they will pose to serious threat to all species on earth because hydrolysis of the pollutants in wastewater can produce a great deal of toxic products. There are many ways for treating the textile effluent. The best combination of methods differs from plant to plant depending on the size, type of waste and degree of treatment needed(40) . Degradation of these no biodegradable organic compounds is not possible by conventional biological treatment processes. To overcome these problems advanced oxidation processes (AOP's) have been developed to generate hydroxyl free radicals by different techniques(41). In(1987) Glaze et al., define Advanced Oxidation Processes for water treatment as the processes that occur near ambient temperature and pressure which involve the generation of highly reactive radicals, especially hydroxyl radicals($^{\cdot}OH$)(42) . Table (1-1) act typical AOP system(43-44) :

Table (1-1) : Typical AOP system are listed

Homogeneous systems		Heterogeneous systems	
With irradiation	Without irradiation	With irradiation	Without irradiation
O_3/UV	O_3/H_2O_2	$TiO_2/O_2/UV$	Electro-Fenton
Electron beam	$O_3/(OH^-)$		
H_2O_2/UV	H_2O_2/Fe^{+2}(Fenton's)	H_2O_2/supported Fe^{+2}/UV	H_2O_2/supported Fe^{+2}/UV
		UV/TiO_2,ZnO, CdS	

Many processes such as photolysis, photo catalytic oxidation, ozonation, Fenton oxidation, wet air oxidation and membrane separation has been proposed for the degradation of these compounds even at low concentration(45-47). The various types of contamination of wastewater require a variety of strategies to remove the contamination(48-49).Also, treatment methods are often specific to the material being treated and some materials such as some detergents may be capable of biological degradation and in such cases, a modified form of wastewater treatment can be used(50). Toxic materials including many organic materials, metals (such as zinc, silver, cadmium, thallium, etc.) acids, alkalis, non-metallic elements (such as arsenic or selenium) are generally resistant to biological processes unless very dilute(51). Metals can often be precipitated out by changing the pH or by treatment with other chemicals and are resistant to treatment or mitigation and may require concentration followed by land filling or recycling(52). Dissolved organics can be incinerated within the wastewater by Advanced Oxidation Process. The following scheme the main classification of wastewater treatment methods:

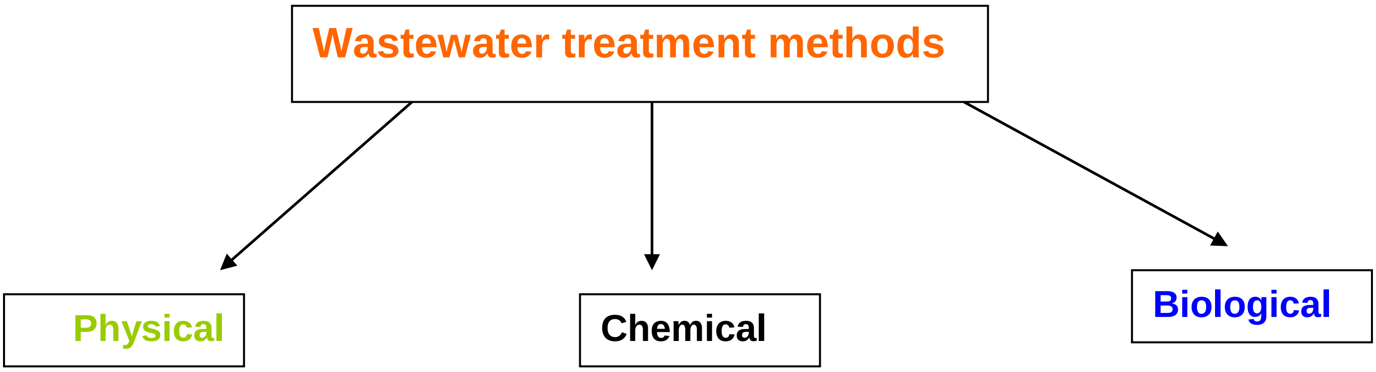


Figure (1-1): Treatment processes of Industrial wastewater .

1-1-2-1 :Physical methods

Adsorption is an effective method of lowering the concentration of dissolved dyes in the effluent resulting in color removal (53). The process of adsorption has an edge over the other methods due to it sludge free clean operation and complete removal of dyes even from dilute solution(54).

Existing physico-chemical advanced treatment technologies for example membrane processes is effective mean of removing pollutant from the wastewater, ion exchange, activated carbon adsorption etc. can only transfer pollutants from one phase the other phase rather than eliminating the pollutants from effluent body(55). Dye solutions, it is used in a combination with chemical or biological methods producing particles containing dye or dye degradation products with coagulation/precipitation or with some other chemical methods, or adsorption on various materials56).

The disadvantage here is a high sludge production therefore it is performed by adding a surface active ion of the opposite charge to the ion to be separated from the solution(57). Physical methods are employed mainly to separate large settle able and floating matter, clarify turbid solutions, recover and recycle valuable substances utilized in the main processes and separating inorganic materials(58).

1- 1- 2- 2: Biological methods

There are many types of biological treatment methods. A biological treatment presents a degradation of organic substances by microorganisms under aerobic or anaerobic conditions, and has been widely used and researched (59). Biological methods are generally cheap than those of chemical methods and simple to apply and are currently used to remove organic and color from dying and textile wastewater (60). It has been demonstrated that mixed bacterial cultures are capable of decolorizing textile dye solutions. Aerobic biological treatment option is ineffective removal for color removal from textile wastewater in most cases and the chemical coagulation and flocculation is also not effective for the removal of soluble reactive dyestuffs because many commercial dyestuff are toxic contain rising sludge and the structure of most commercial dye compounds are generally complex and inappropriate to remove pollutants from the total material, and pigmented polymers to the difficulty of analyzing these materials(61-62). The use of biological treatment is attractive due to its low operating cost but the residence time is very high relative to that of other processes. (63).

1- 1 -2- 3: Chemical methods

Chemical oxidation is the most commonly used method of decolourization, mainly due to its simplicity of application(64-65)..Chemical method includes coagulation or flocculation and oxidation. The main advantage of the conventional coagulation and flocculation is removal of the waste stream to removal of dye molecules from the dye effluent and don't molecules decomposition of dyes lead to even more potentially harmful and toxic aromatic compound(66). The oxidizing agent is usually hydrogen peroxide, which needs to be activated due to its stability in the pure form and it was removed the dye from the effluent with an aromatic ring cleavage of dye molecules(67). Chemical oxidation is the traditionally used technique for the removal of impurities such as taste, color and odor. Oxidants such as chlorine , ozone, chlorine dioxide and hydrogen peroxide are used for wastewater treatment. The choromophores that impart the colour are attacked by the oxidizing agents for the removal of colour (68) .

Physical and chemical treatment techniques are effective for colour removal but use more energy and chemical than biological processes(69). Advanced Oxidation Processes (AOP's) refer to a set of chemical treatment techniques procedures designed to remove organic and inorganic materials in water and waste water by oxidation (42). The advantages of

AOP's are their high treatment efficiencies ,fast reaction rates, hence relatively small reactors, and provided innovative ,cost-effective catalyzed chemical oxidation for treating pollutants in low or high concentration from contaminated soil, sludge and water, high flexibility and the possibility of incorporating them in to water recycling processes(70-72).

Over the last few years the tendency has been to carry out chemical oxidation in the presence of catalyst that serves as a generator of hydroxyl radicals . The oxidation potential of $^{\cdot}OH$ radical is 2.80v making it the most powerful oxidizing agent after fluorine (3.03v)(73). The main and short mechanism of AOPs can be defined in two steps: (a) the generation of hydroxyl radicals, (b) oxidative reaction of these radicals with molecules(74). AOPs can convert the dissolved organic pollutants to CO_2 and H_2O. Table (1- 2) shows hydroxyl radical as the second strongest oxidant(75-77) . The hydroxyl radical can oxidize a broad variety of organic substances such as dyes, pesticide, insecticide, et.(78-79). The use of hydroxyl radicals to promote chemical oxidation it is the common feature of all AOPs. Table (1- 3) shows several of the chemical oxidation technologies available.

Table(1- 2). Oxidizing potential for conventional oxidizing agents(75-77)

Oxidizing agent	Electrochemical oxidation potential (EOP), V
Fluorine	3.06
Hydroxyl radical	2.80
Oxygen (atomic)	2.42
Ozone	2.08
Hydrogen peroxide	1.78
Hypochlorite	1.49
Chlorine	1.36
Chlorine dioxide	1.27
Oxygen (molecular)	1.23

Table 3. Technologies used in the production of hydroxyl radicals(80)

Processes with ozone	Processes without ozone
Ozone at high pH (8-10)	H_2O_2 + UV
Ozone + UV	Photocatalysis (UV+ photo catalyst)
Ozone + H_2O_2	Ultrasound
Ozone + H_2O_2 + UV	Oxidation supercritical
Ozone + TiO_2	H_2O_2 + UV + iron salts (Foto-Fenton)
Ozone + TiO_2 + H_2O_2	H_2O_2 + iron salts (Fenton reagent)
Ozone + Ultrasound	

The oxidation of organic compounds in water with AOP's usually produces oxygenated organic products and low molecular weight acids that more biodegradable **(81)**. AOP's can be classified in two groups:

(1) Non-photochemical AOPs . (2) Photochemical AOPs.

1- Non-photochemical methods

There are four methods for generating hydroxyl radicals without using light energy. Ozonation, ozone/hydrogen peroxide , ozone+ catalyst and Fenton-process are widely applied and examined processes for the treatment of textile effluent.

A- Ozonation

Ozone has been used for the treatment of drinking water since 1903. Its produced oxidizing power. Ozone can generate hydroxyl radicals via catalytic decomposition of water, the oxidative power of an ozone generated hydroxyl radical is the same as those generated by Fenton's reagent . Ozone is a powerful oxidant agent for water and wastewater.

Once dissolved in water, ozone reacts with a great number of organic compounds in two different ways: by direct oxidation as molecular ozone or by indirect reaction through formation of secondary oxidants like hydroxyl radical (82). The removal of dyes by ozonation has various advantages as color removal is fast , no sludge or any toxic by products are produced(83) . The major disadvantage is that the half- life is short (20min) and effect salts , pH and temperature influence the stability of ozone. The effect of ozonation on the toxicity of the wastewater effluent depends on the type of dye being decomposed (84). The rate of ozone decomposition is favored by the formation of hydroxyl radicals at higher pH values. Ozone application can be generalized into two, a powerful disinfection and a strong oxidant to remove color and odour, eliminating trace toxic synthetic organic compounds and assisting in coagulation(85) . Ozone is well known and widely applied strong oxidizing agent for the treatment of both water and wastewater. The reaction between hydroxide ions and ozone leads to the formation of super-oxide anion radical O_2^- and hydroperoxyl radical HO_2^- by the reaction between ozone and the super-oxide anion radical the ozonide anion radical O_3^- is formed, which decomposes immediately giving ^{-}OH radical., three ozone molecules produce two $^{\cdot}OH$ radicals (86) .

$$3O_3 + OH^- + H^+ \rightarrow 2{}^{\cdot}OH + 4O_2 \qquad (1)$$

B- Ozone + hydrogen peroxide (O_3/H_2O_2)

The addition of both hydrogen peroxide and ozone can initiate the decomposition of ozone and enhances production lead to resulting in the formation of $^{\cdot}OH$ radicals(87) .

$$H_2O_2 \longrightarrow HO_2^- + H^+ \qquad (2)$$

$$HO_2^- + O_3 \longrightarrow HO^{\cdot}_2 + O_3^{\cdot -} \qquad (3)$$

In 1982 Staehlin and Hoigne have been observed when used acidic pH, H_2O_2 reacts only very slowly with O_3 but at pH values above 5 a strong of O_3 decomposition by H_2O_2(88). The combination of ozone and hydrogen peroxide is used to removal contaminants which oxidation is difficult and consumes large amounts of oxidant because of the high cost of ozone generation and this combined make the process economically feasible(89). Ozone / hydrogen peroxide has also been used to oxidize pesticides and other hazardous materials(90).As a result, the ozone decomposition rate will increase with increasing pH. Hydrogen peroxide is a relatively inexpensive, readily available chemical oxidant. Both of Korhonen and Tuhkanen are proved the advantages of ozone/hydrogen peroxide treatment for the control of microbiological growth in the white water system of the paper machine and able to reduce the acute toxicity of the effluents from the pulp and paper industry(91) ·. The capability of ozone to oxidize various pollutants by direct attack on the different bonds (C=C) bond (92), aromatic rings (93) is further enhanced in the presence of H_2O_2 due to the generation of highly reactive hydroxyl radicals (•OH).

C- Ozone + catalyst (O_3/CAT)

Ozonation reactions is to use heterogeneous or homogeneous catalysts . Several metal oxides and metal ions such as (Fe_2O_3, Al_2O_3–Me, MnO_2, Ru/CeO_2, TiO_2–Me, Fe^{2+}, Fe^{3+}, Mn^{2+}, etc.) lead to in the decomposition of the target compound has been achieved, the reaction mechanism in most remained unclear(94).In 1998 Cortes gave studied about advanced oxidation of chlorobenzenes in wastewater as well as in model solutions using iron and manganese ions as heterogeneous catalysts(95). In 1991 Paillard gave compared the efficiency of catalytic ozonation O_3/TiO_2 with plain ozonation and a combination of O_3/H_2O_2, Oxalic acid was chosen as a model compound(96). Both of Jans and Hoigne show that a few milligrams of activated carbon or carbon black per liter in ozone-containing water initiate a radical-type chain reaction that then proceeds in the aqueous phase and forms $^{\cdot}OH$ radicals(97).

D- Fenton system (H_2O_2/Fe^{2+})

The Fenton's process has its origin in the discovery reported in 1894 that ferrous ion strongly promotes the oxidation of tartaric acid by hydrogen peroxide (98). Fenton's reagent , a mixture of ferrous iron (catalyst) and hydrogen peroxide (oxidizing agent) ,has been known as a powerful oxidant for organic contaminants. The mechanism of the Fenton process is reported below(99-100) .

$$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+OH^{-}+HO^{\bullet} \qquad (4)$$

$$Fe^{2+}+HO^{\bullet} \rightarrow Fe^{3+}+OH^{-} \qquad (5)$$

$$HO^{\bullet}+RH \rightarrow H_2O+R^{\cdot} \qquad (6)$$

$$R^{\bullet} +Fe^{3+} \rightarrow R^{+} +Fe^{2+} \qquad (7)$$

Hydrogen peroxide decomposes catalytically by Fe(III) and generates again hydroxyl radicals. The use of $Fe(II)/H_2O_2$ as an oxidant for wastewater treatment is attractive due to the facts that: (1)- iron is a highly abundant and non-toxic element. (2)- hydrogen peroxide is easy to handle and environmentally benign(101). The result showed that efficient mineralization of the dye was achieved by the application of iron powder in combination with hydrogen peroxide . Other dyes that have been successfully removed by hydrogen peroxide are Reactive red 120 , Direct blue 160 and Acid blue 40 (102). At pH values <4.0, ferrous ions decompose H_2O_2 catalytically yielding hydroxyl radicals most directly while at pH values higher than 4.0, ferrous ions easily form ferric ions, which have a tendency to produce ferric hydroxo complexes. H_2O_2 is quite unstable and easily decomposes at alkaline pH (103). The Fenton process is very effective for ·OH radicals generation, it involves of one molecule of Fe^{2+} for each ·OH radical produced, demanding a high concentration of Fe(II) . One of the advantages of Fenton's reagent is that no energy input is necessary to activate hydrogen peroxide. (104).

1-2: Photochemical methods

Completion of oxidation reactions, as well as oxidative destruction of compounds to unassisted ozone or H_2O_2 oxidation, can be used by supplementing the reaction with UV radiation. In some reactions, the intermediate oxidation products remaining in the solution may be as toxic as or even more toxic than the initial compound and UV radiation could complete the oxidation to CO_2 and H_2O (105). Many organic contaminants absorb UV energy in the range of 200–300 nm and decompose due to direct photolysis or become excited and more reactive with chemical oxidants.

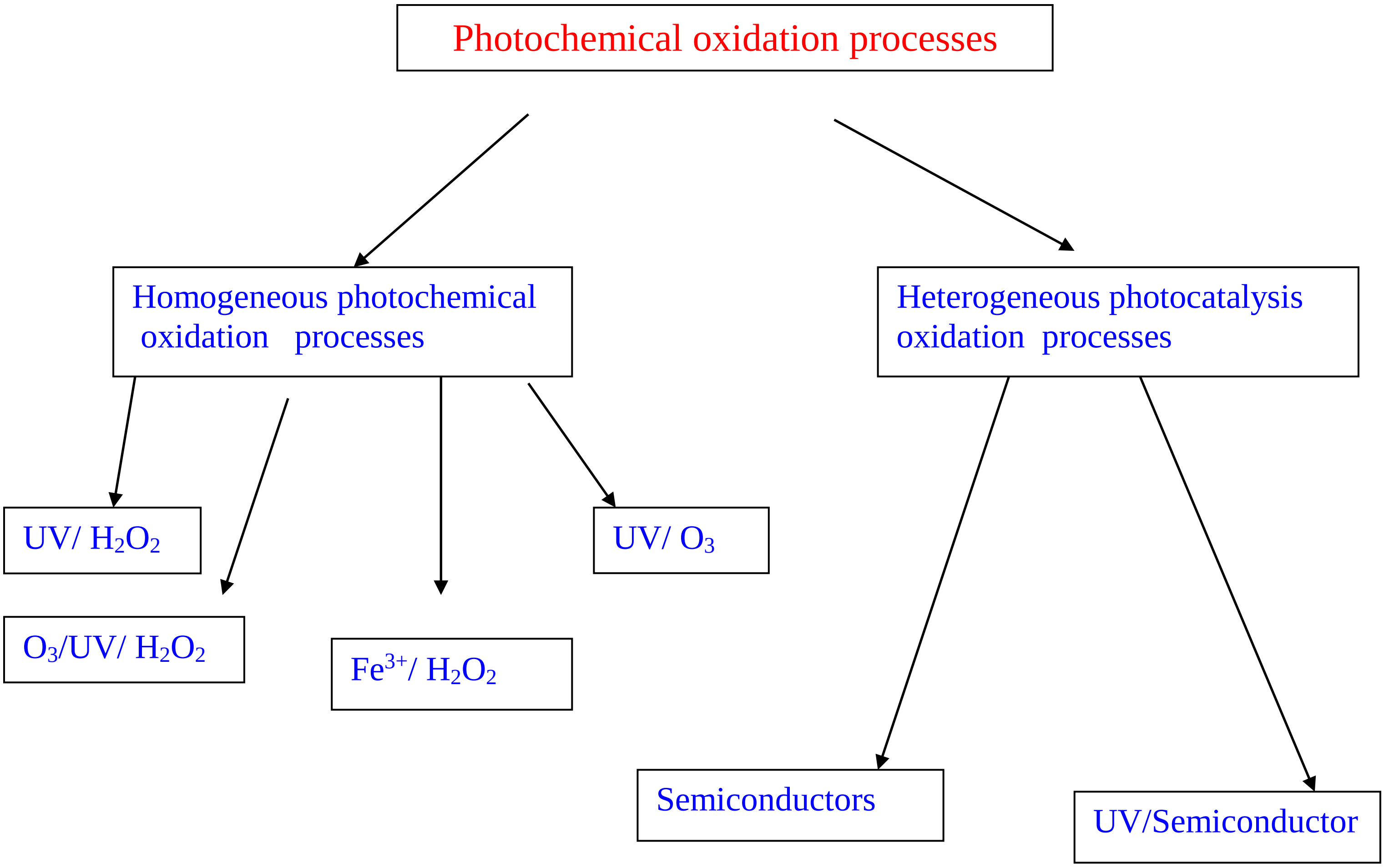


Figure (1-2): Photochemical oxidation processes.

1-2-1- Homogeneous photochemical oxidation processes .

The applications of homogeneous photo degradation (single-phase system) to treat contaminated water , involves the use of an oxidant to generate radicals, which attack the organic pollutants to initiate oxidation.

Many of the AOP's listed in Table 4 utilize the chemical, hydrogen peroxide. The oxidizing strength of hydrogen peroxide alone is relatively weak, but the addition of UV light enhances the rate and strength of oxidation through production of increased amounts of hydroxyl radicals.

Table(1- 4) :ct advantage and disadvantage from this methods of AOP’s (Homogeneous)(106-107):

Method	reaction	Disadvantage	Advantage
UV/H_2O_2	$H_2O_2 + hv \rightarrow 2HO$	- It cannot utilize solar light as the source of UV light due to the fact that the required UV energy for the photolysis of the oxidizer is not available in the solar spectrum	-Stable organic compounds with high molecular weights are broken down into smaller structures, which are more biodegradable, no sludge generation during any stage of treatment.
UV/O_3	$O_3+hv\rightarrow O_2+ O^{\cdot}$ $O^{\cdot}+H_2O\rightarrow 2^{\cdot}OH$	Absorbs λ < 300nm, a lesser component in solar radiation .	UV radiation could complete the oxidation reaction by supplement the reaction with it.
UV/H_2O_2/O_3	$O_3+H_2O_2+hv\rightarrow O_2+H_2 O_2$ $H_2O_2+hv\rightarrow 2^{\cdot}OH$	Absorbs λ < 300nm, a lesser component in solar radiation .	Increased rate of $^{\cdot}OH$ generation, it is the most effective and powerful method .
UV/H_2O_2/Fe^{+2} Photo Fenton	$H_2O_2+Fe^{+3} \rightarrow Fe^{+2}+^{\cdot}OH+OH^-$	1- Process is expensive. 2- Sludge generation . 3-Continuous supply of feed chemicals are required. 4- It is that the homogeneous catalyst, added as iron salt, cannot be retained in the process, thus causing additional water pollution	1- Effective decolorization of both soluble and insoluble dye and suitable for wastewater, which is resistant biological treatment. 2- It is that no energy input is necessary to activate hydrogen peroxide and a wide variety of dyes.

A- Hydrogen peroxide/UV (H_2O_2/UV) process.

Hydrogen peroxide is often used in advanced oxidation processes (AOP's) alone or together with other agents such as ozone and UV. H_2O_2 alone is ineffective in the treatment of textile wastewater at both alkaline and acidic pH (108), when mixture with UV irradiation, , H_2O_2 are photolysis to form two hydroxyl radicals ($2^{\bullet}OH$) which react with organic contaminants(109) . The use of hydrogen peroxide is cheaper than ozone generation, and the application of H_2O_2 is less complex than ozone(110).

Effect of initial hydrogen peroxide concentration this process includes H_2O_2 mixing with and without UV light. Ultraviolet radiation is used to cleave the (O-O) bond in hydrogen peroxide and generate the hydroxyl radical(111). The photolysis of hydrogen peroxide produces two hydroxyl radicals, but the decomposition of H_2O_2 by UV has a much lower extinction (absorption) coefficient of H_2O_2 by UV photolysis. The reactions describing UV/H_2O_2 processes are presented below(112) :

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet} \qquad (7)$$

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \qquad (8)$$

$$HO^{\bullet} + HO_2^{\bullet} \rightarrow H_2O + O_2 \qquad (9)$$

High concentrations of H_2O_2 making the H_2O_2/UV process less effective. Also, there are some factors effect of hydrogen peroxide such as temperature، pH, concentration of H_2O_2, lead to effect the production of hydroxyl radicals (113-114) . Galindo and Kalt (1998) documented the inverse relationship between the initial dye concentration and the efficiency of UV/H_2O_2 treatment(115).

B- Ozone/UV (O_3/UV) process.

In 2001 Rein documented ozonation of organic compounds does not completely oxidize organics to CO_2 and H_2O because remaining intermediate products in some solution after oxidation may be as toxic as or even more toxic than initial compound, therefore UV radiation could complete the oxidation reaction by supplement the reaction with it(94). UV lamp must have a maximum radiation in the range of 200-280 nm for an efficient ozone photolysis and low pressure mercury used for this process(76). There are various factors affect the oxidation rate of organic pollutants: pH, temperature, UV intensity , pollutant type and radical scavenger concentration(74).The O_3/UV process is more effective when the compounds of interest can be degraded through the absorption of the UV irradiation as well as through the reaction with hydroxyl radicals (116-117) .

Photolysis of ozone therefore appears only to be an expensive way to make hydrogen peroxide that is subsequently photolysis to ·OH radicals, and cleavage of H_2O_2. In 1982 Peyton gave demonstrated the efficiency of O_3/UV system for C_2Cl_4 elimination from water compared to ozonation and photolysis only(118). In (2003) Perkowski and Kos reported no significant difference between ozonation and O_3/UV in terms of colour removal(119).

C- Ozone–hydrogen peroxide–UV radiation (O_3/H_2O_2/UV)

The decomposition of ozone by addition of H_2O_2 to the O_3/UV process lead to this results are increased rate of $^{\cdot}OH$ generation (120-121). This method is considered to be the most effective and powerful method which provides a fast and complete mineralization of pollutants (122).

Efficiency of ozone/hydrogen peroxide/UV process is being much more higher with addition of hydrogen peroxide (123-124). Main short mechanism of O_3/ H_2O_2/ UV process is given below:

$$2\ O_3 + H_2O_2 \xrightarrow{\qquad} 2\ HO^{\cdot} + 3\ O_2 \qquad (10)$$

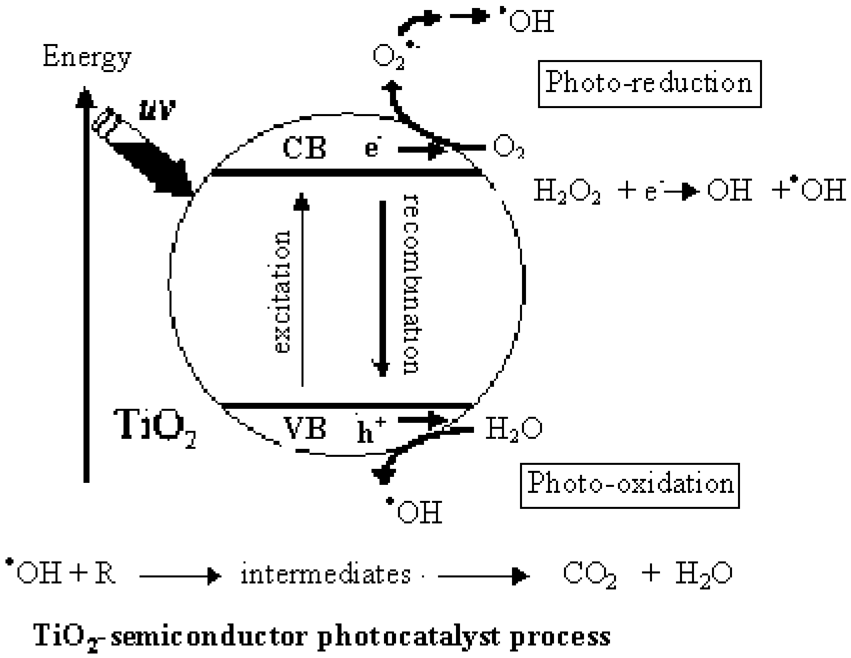
D- Photo-Fenton System

The combination of Fenton process with UV light, the so-called photo-Fenton reaction, had been shown to enhance the efficiency of Fenton process(125). Photo Fenton reaction gives faster rates and higher degrees of mineralization comparing to conventional Fenton process , and prefer Fenton process because this reaction can be driven by low energy photons and reduce the operational cost of the treatment**(126)**. It can be used to degrade many pesticides (127), harmful chemicals (128) and dyes. In 1934 Haber and Weiss studied Fenton’s reaction and concluded that this reaction can be expressed as a series of chain reactions with reaction pathways dependent on the concentration of the reactants(129). The efficiency of the Fenton reaction depends on the sample characteristics, pH, iron concentration, H_2O_2 dosage and the reaction time (130).

The oxidation of organic compounds in the Fenton's reaction is likely to occur in several steps:1 - Generation of $^{\bullet}OH$ radicals and their oxidative reaction with organic compounds. 2- Direct action of H_2O_2 toward the pollutant. $^{\bullet}OH$ scavenging due to Fe^{2+} ions and H_2O_2 , reaction of Fe^{3+} with H_2O_2 leading to regeneration of Fe^{2+} ions and formation of hydroperoxyl radicals (HO_2). 3- Reduction of Fe^{3+} to Fe^{2+} by $HO_2^{\bullet}$ (131)..

1-2-2-Heterogeneous photocatalysis

Widely applied Heterogeneous Photochemical Oxidation processes are semiconductor-sentized photochemical oxidation processes and to treated contaminated water by use of an oxidant to generate radicals. The process is heterogeneous because there are two active phases, solid and liquid. This process can also be carried out utilizing the near part of solar spectrum ($\lambda < 380$nm)(132).The oxidizing species ,either bound hydroxyl radicals or free holes, are generated as shown in Figure (1-3). Using photocatalysis, organic pollutants can be completely mineralized reacting with the oxidizers to form CO_2, water and dilute concentration of simple mineral acids.



Figure(1-3): General important events that take place on an irradiated semiconductor particle.

A- Semiconductors

Semiconductors are characterized by two separate energy bands: a low energy valence band (h^+_{VB}) and a high-energy conduction (e^-_{CB}) band. Each band consists of a spectrum of energy levels in which electrons can reside. The separation between energy levels within each energy band is small, and they essentially form a continuous spectrum. The energy separation between the valence and conduction bands is called the band gap(133). When a semiconductor molecule absorbs photons with energy equal or greater than its band-gap, electron in the valence band can be excited and then jump up into the conduction band (134). Semiconductors that have been used in environmental applications include TiO_2, strontium titanium trioxide, and zinc oxide , Fe_2O_3, CdS and ZnS can act as sensitizers for light-induced redox-processes due to the electronic structure of the metal atoms in the chemical combination. TiO_2 is generally preferred for use in commercial APO applications because of its high level of photoconductivity, ready availability, low toxicity and low cost(135).

B- UV/ Semiconductor System

The photo-catalyst titanium dioxide (TiO_2) is a wide band gap semiconductor (3.2 eV) and is successfully used as a photo-catalyst for the treatment of organic pollutants (136). Titanium dioxide, both in the forms of anatase and rutile, is one of the most widely used metal oxides in industry. Its high refractive index in the visible range permits preparation of thin films, and thus its use as a pigment material. TiO_2, the photon energy required to overcome the band gap energy and excite an electron from the valence band to the conduction band can be provided by light of a wavelength shorter than 387.5 nm. Simplified reaction mechanisms of TiO_2/UV process is given in following equations (eq. 12- eq. 15).

$$TiO_2 + h\upsilon \rightarrow e^{-}_{CB} + h^{+}_{VB} \qquad (12)$$

$$H_2O + h^{+}_{VB} \rightarrow OH^{\bullet} + H^{+} \qquad (13)$$

$$O_2 + e^{-}_{CB} \rightarrow O_2^{\bullet -} \qquad (14)$$

$$O_2^{\bullet -} + H_2O \rightarrow OH^{\bullet} + OH^{-} + O_2 + HO_2^{-} \qquad (15)$$

Main advantage of TiO_2/UV process is low energy consumption which sunlight can be used as a light source high stability, good performance$^{(137)}$

1-3- Ultraviolet Radiation Sources

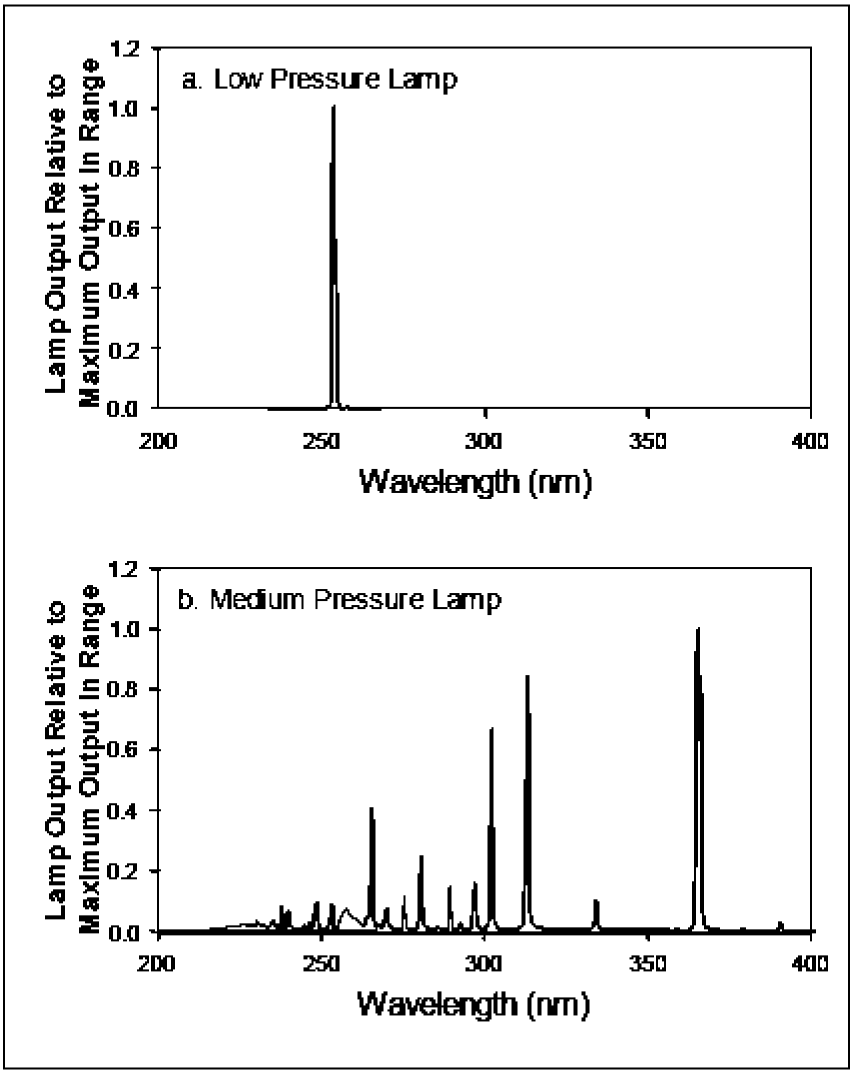
UV radiation is defined as the electromagnetic spectrum of wavelength between 10 and 400 nm. For UV photolysis application in water treatment because these radiations are adsorbed by water and generate highly reactive species for oxidation of pollutants in the water. The UV spectrum range of interest is the short term UV-C (200-280nm)$^{(138)}$. There is also UVB within (280-320) nm range and UVA within (315-400)nm$^{(139)}$. There are two kinds of UV lamps widely used in water treatment applications, which are low-pressure and medium/high-pressure mercury lamps. In this case, the glass tube contains mercury, while electricity is applied, the tube emits light . A spectral distribution of high-intensity, medium-pressure mercury lamps is presented in Figure (1-4).

There are many types of mercury lamps , including

1- Low-Pressure Mercury Lamp.

2- Medium-Pressure Mercury Lamp.

3- **High- Pressure Mercury Lamp**.



Figure(1-4) : UV output of LP (a) and MP (b) Mercury Vapor Lamps (140).

1- Low-Pressure Mercury Lamp.

Low pressure mercury lamps (LP Hg lamp) are highly efficient in providing short wavelength ultraviolet energy. This lamp is classified in group of Fluorescent and Germicidal lamps . In low-pressure mercury-vapor lamps only the lines at 184 nm and 253 nm are present but only the light at 253 nm is usable unless synthetic quartz is used to manufacture the tube as the line is otherwise absorbed(141). Generally speaking, this lamp is characterized the long-live and stability of the intensity of radiation generated during irradiation. The advantages of the low-pressure lamps are: 1-High electrical efficiency (30%), 2- Long life time (6000-10,000 hrs), and 3- Less fouling and the disadvantages are: 1- Low efficiency for direct photolysis of some pollutants; 2- More lamps are required for the same service; and 3- Potential high cost of used lamps disposal (large number)(142-143). Low-pressure mercury-vapor lamps usually have a quartz bulb in order to allow the transmission of short wavelength light. A lamp can then be used for the cleaning or modification of surfaces.

2- Medium-Pressure Mercury Lamp.

Medium-pressure mercury lamps (MPML) operate at higher pressures and temperatures than low-pressure lamps. The lamp lifetime is shorter than that of the low-pressure lamps, the range is about 3,000 to 4,000 hours(142). Medium pressure mercury lamps, often named as UV-lamps, belong to the general group of gas discharge lamps. In medium-pressure mercury-vapor lamps, the lines from 200–600 nm are present. The lamps can be constructed to emit primarily in the UV-A (around 400 nm) or UV-C (around 250 nm) and generate a broad spectrum output with strong peaks(144).Spectrum this lamp is characterized by multiple lines superimposed on a small continuum, which indicates that there is some radiation at all UV wave-lengths. The advantages of the medium-pressure lamps are: 1- Fewer lamps than low-pressure lamp systems, 2- Fast reaction , 3- Direct photochemical oxidation of some contaminant species and 4- Medium pressure mercury lamps provide a strong source of ultraviolet radiation for the polymerization of various materials. Also, the disadvantages are:1- Low electrical efficiency (5 to 20%),2- hence higher electrical costs, and 3- High heat output.

3-Xenon arc lamp.

The use of these lamps began in the forties , they were introduced in 1951 by Osram(145). Xenon arc lamps produce greater amounts of ultraviolet irradiation when it works , and Xenon have a strong spectral lines in the UV packages. It is the source of industrially working with electricity and is used to produce bright white light similar to sunlight(146). Used xenon lamps in flash lamps and curved glassware in the light bulbs filled with a special use which has a high efficiency and used produce lighting gives a strong convergence in the brightness of sunlight. There are types of this lamps including Xenon short – lamps (Xenon-mercury), which contain Xenon short and a small amount of mercury and Xenon lamp, as well as pure short that contains only xenon and have a nice close to the sunlight(147).

4- Fluorescent Lamps

The function of fluorescent lamp is similar to that of UV lamps in that a radius emerges as a result of the evaporation of mercury . However, difference is that the bulb of the fluorescent lamp is painted with phosphor so the radius of UV turns into the visible light, while the UV lamps are not painted with phosphor, so the emergent UV radius is generated(148).

Fluorescent lamps are considered to be capable of functioning under very low pressures and contain mercury vapor and other gases. Ultraviolet light is emitted and converted to visible light through the phosphor coating on the inside of the glass tube. These lamps last seven to 10 times longer than incandescent lamps and use a quarter of the electricity(149). In most cases, the air temperature near the lamp within a luminaire is greater than 25°C, resulting in light output and efficacy lower than manufacturer ratings for the lamp ballast system.

1-4- . COD , BOD and TOC.

Chemical oxidation technologies have been used for many years to degrade a wide range of pollutants in wastewater and drinking water(150). There are three type of COD test : the first type range (0-150)mg/L include river water , the second type range (150- 1500)mg/L include drainage water and three type range more than 1500mg/L include heavy wastewater . The COD test is widely used to measure the pollution associated with both biodegradable and no biodegradable organic matter present in wastewaters by using strong oxidation agents is a good option(151). .Factors influencing the COD removal were studied in the subjects such as the effect of the pH, initial concentration, catalyst variation and H_2O_2 concentration. Sheng and Chi documented COD removal depended on strength of dye waste, where COD reduction was slight from the medium and high dye waste(152). They were introduced in 2003 by Perkovski tested peroxone process on anthraquinone dye Acid Blue 62 and they found 60% colour removal efficiency(153). Biochemical Oxygen Demand (BOD) refers to the amount of oxygen that would be consumed if all the organics in one liter of water were oxidized by bacteria and protozoa. The BOD test takes 5 days to complete and is performed when BOD levels are high, dissolved oxygen levels decrease because the oxygen that is available in the water is being consumed by using a dissolved oxygen test kit(154). Generally COD is preferred to BOD in process control applications because COD results are more reproducible and are available in a few minutes or hours rather than five days and found that BOD increases while COD and TOC decreases. Total organic carbon (TOC) is the amount of carbon bound in an organic compound and is often used as a non-specific indicator of water quality or cleanliness of pharmaceutical manufacturing equipment. In 1970 TOC has been recognized as an analytic technique to measure water quality during the drinking water purification process.

1-5- quantum yield

Defined as the events number which occur per photon absorbed by the system OR as the amount (mol) of reactant or product formed per amount of photons (einstein) absorbed is central to homogeneous photochemistry(155) . The photo chemically defined quantum yield can be difficult to clarified experimentally in heterogeneous media and particularly for complex reactor geometries. The quantum yield Q can also be described by the relative rates of the radiative and non-radiative pathways, which deactivate the excited state:

$$Q= K_r \ / K_r + \Sigma K_{nr}$$

Where k_r and k_{nr} correspond to radiative and non-radiative processes, respectively. In this equation, Σk_{nr} describes the sum of the rate constants for the various processes that compete with the emission process(156).

There are two methods for relative quantum yield measurements:

1- a single-point method.

2- a comparative method.

1- The single-point method show the quantum yield is calculated by using the integrated emission intensities from a single sample and reference pair at identical concentration. While advantage in this method is getting results faster than the comparative method, easy and it is not always reliable due to the inaccurate measurement of the fluorophore absorbance but not always reliable .

2- The second method is the comparative method of Williams which involves the use of well characterized standard samples with known fluorescence quantum yields Φ_F values (157). The most reliable method for recording ΦF is the comparative method of Williams but provides much higher accuracy by calculating the slope of the line generated by plotting the integrated fluorescence intensity against the absorption for multiple concentrations of fluorophore. Quantum yield standards should be chosen to ensure maximum overlap of the absorption and emission between sample and reference (158) . Photo chemists have routinely determined quantum yields of reactant disappearance, product formation, light emission, and of various other events occurring in some photochemical process(159). Some quantitation methods are based on titrations which rely on color changes of an indicator solution while others use gravimetric, volumetric, spectrophotometer, or chromatographic methods for carbon quantitation. Quantum yield is the initial slope of the photosynthetic light response curve and represents the maximum efficiency of light utilization in photosynthesis. It has been extensively studied at the leaf level .

Photoreactors

Ultraviolet (UV) reactors are promising for the future of drinking water and wastewater treatment technology. We are engaged in offering wide range of UV reactirs. Our reactors are available in various specifications as per the requirements of clients(160). Development many types of reactors used in the photo and photochemical reactions that depend on the interactions in their work ، depending on pollutants are different reactors and different methods of treatment and that could lead to the formation of toxic compounds as by secondary(161). These reactors are demanded widely by clients due to its unique features like high durability, optimum performance, dimensional accuracy, speedy operations and flawless functioning. There are other types of reactors :

1- Annular Photo Reactor

The large quartz and borosilicate glass immersion wells used in the Immersion Well type Reactors (models QW2 and BW2 are used to contain irradiation lamps in the Annular Reactor. The Immersion Well is held in the centre of a rotating carousel assembly which holds up to 24 quartz or borosilicate glass tubes. Photoreactor clear in Figure (1-5) .

Figure (1-5): Annular Photo Reactor .

2- Photocatalytic Reactor.

Used Photocatalytic reactor for liquid phase toluene oxidation in presence of transition metal oxide doped TiO_2. Made of two layers of glass pyrex with two side holes lead to enter and exit the water for the purpose of cooling . The lamp is located user at the wavelength 365nm(162) . Shows in Figure (1-6).

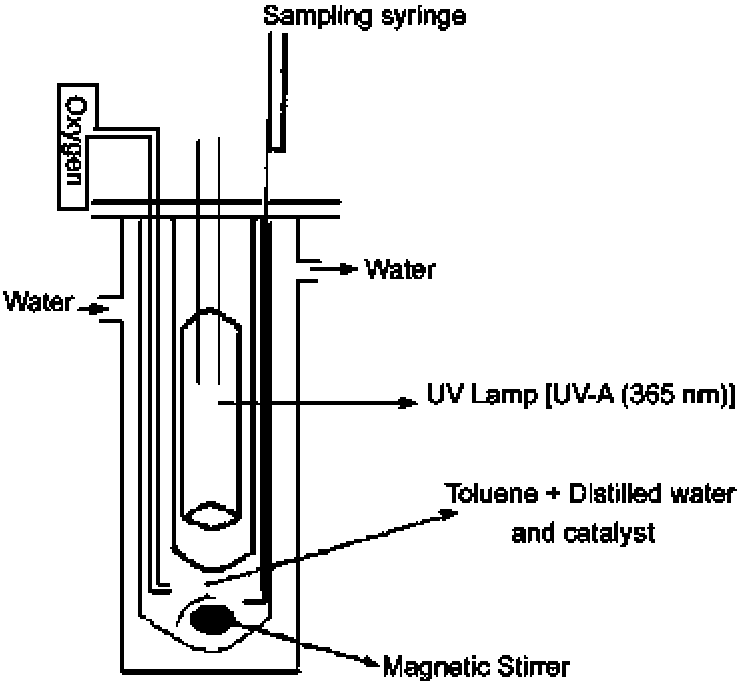


Figure (1-6): Photocatalytic Reactor.

3- The optical Mndda reactor .

Process is a promising low-cost technology that uses ultraviolet light to capture, oxidize, and enhance the removal of elemental mercury from the flue gas treatment systems of coal-fired power plants. Preliminary bench and field tests have achieved a greater than 90 percent oxidation and capture rate in simulated flue gas streams containing elemental mercury(163). Reactor shown in Figure (1-7) is the optical Mndda reactor, the reactor consists of two lamps of mercury low pressure with intensity 30 W, and at wavelength 254.

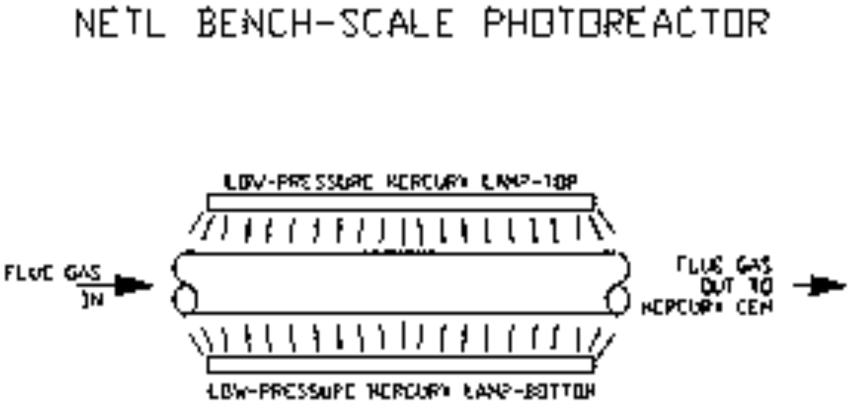


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Figure (1-7): Optical Mndda reactor.

The Aim of the Present Research .

That the main objective of this research is to study the efficiency of methods of photo-oxidation of azure dyes (A ,B ,C) using hydrogen peroxide , Fenton reagent and their impact in the degradation of the dye. The study involved use of ultraviolet light and measuring the rate of color removal. Study included the following factors :

1- Study the effect of dye concentration , pH, temperature and time at the rate of degradation.

2- Study the effect of the use different concentration of hydrogen peroxide in rate of degradation.

3- Study the effect of Fenton system , pH medium and effect of concentration hydrogen peroxide , ferrous ion concentration in the system on color ratio and degradation of dyes.

4- Study Chemical Oxidation Demand, Also study all of the following effects upon the dye concentration , the concentration of hydrogen peroxide , the Fenton system, and an acid function.

2- Material and methods.

2-1- Instruments .

No	Instrument	Model	Company, Source
1	UV-Visible Spectrophotometer	UV-1650	Shimadzu ,Japan
2	UV-Visible Spectrophotometer	7804C	Sunny, China
3	pH - meter	211-Instrument	Hanna, Romania
4	Hot- Plate	LMS-1003	Labtech, Korea
5	Oven	MemortLDO- 080N	Labtech, Korea
6	Electronic Balance	BL 210S	Sartorius Ag Gottingen ,Germany
7	Distil Water	WD-200 4F	Labtech, Korea
8	Water Bath	WB 710M	Optima, Japan
9	Low Pressure Mercury Lamp	G6 T5 (6 Watt)	Philips, Poland

2-2- Chemicals .

No	Structure formula	Company	Pure
1	H_2O_2 (30%)	B.D.H	
2	$FeCl_2.4H_2O$	B.D.H	
3	NaOH	B.D.H	
4	HCl	B.D.H	
5	H_2SO_4	B.D.H	98%

Dyes Used in this Study :

Azure(A, B and C) dyes were used in this study has been prepared these dyes and conducting experiments to remove the color. Table (1) refers to the properties of some dyes Azures.

Properties	Azure A	Azure B	Azure C
Empirical Formula	**$C_{14}H_{14}CLN_3S$**	**$C_{16}H_{18}CLN_3S$**	**$C_{13}H_{12}CLN_3S$**
Class	**Thiazine**	**Thiazine**	**Thiazine**
Source	**Aldrich**	**Aldrich**	**Aldrich**
Solubility in water	**Soluble**	**Soluble**	**Soluble**
Molecular Weight	**291.80**	**305.83**	**277.77**
Dye Content	**80%**	**89%**	**40%**
λ_{max}	**632nm**	**646.50nm**	**611.5nm**

Clarified shapes indicate the following structural formulas for each dye.

Figure (2-1): Structural formula of azure A dye.

[redacted]

Figure (2-2): Structural formula of azure B dye.

[redacted]

Figure (2-3): Structural formula of azure C dye.

2-3- Photoreactor.

Reactor consists of light in this research of low pressure mercury lamp inside the subject of a glass tube made of quartz tube placed inside a metal cylinder with two holes, there beside a container solution is placed in the dye solution is prepared, in which the two openings, one of the bottom of the container comes out of solution and passes to the pump then enters the lamp through the hole in the side of the hole and out the other side of the metal tube located inside the lamp and goes back to the container through the slot at the top. Connected this reactor inside laboratory and modification by changing the type of lamp . This reactor is characterized by :

1 - Simplicity of installation. 2- High efficiency of break down the pollutants of various kinds. 3 - low cost processing.

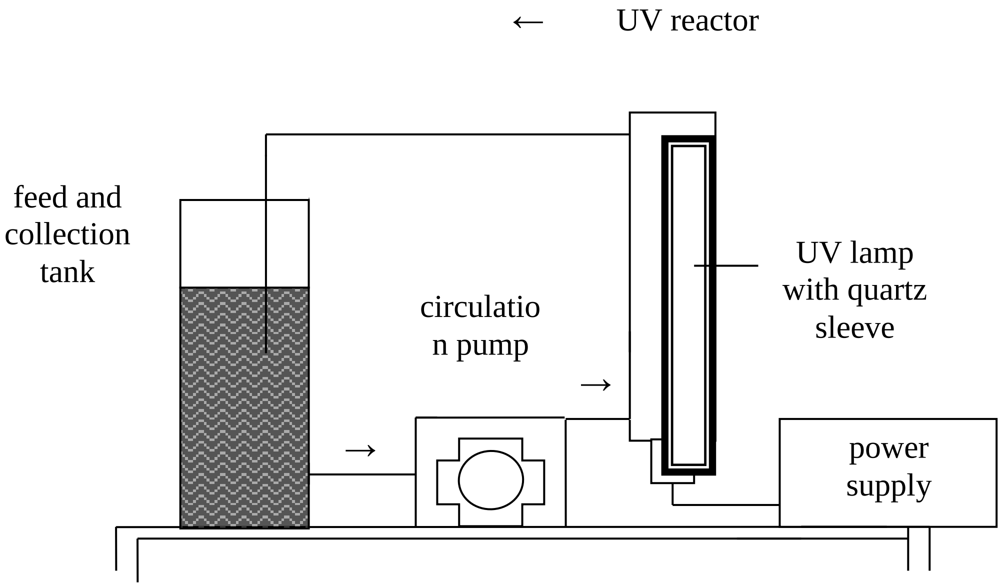


Figure (2-4): Photoreactor setup .

2- 4- The lamp

The lamp used in this research was the low pressure mercury lamp (LPML) is similar in construction to the fluorescent lights we see in the offices and homes everyday, Also the glass tube contains mercury; while electricity is applied, the tube emits light (142). Low pressure mercury lamps are highly efficient in providing short wavelength ultraviolet energy. Our low pressure mercury lamp technologies offer customers many solutions.

Technologies available include soft glass and quartz glass. To ensure that low intensity ultraviolet rays that fall on the solution Therefore, the lamp is surrounded by the cylinder from quartz glass. Finally surrounded the body of the lamp from the outside with metal cylinder contain tow holes one to enter the water from the pump distribution either to the other opening out to the water container assembly.

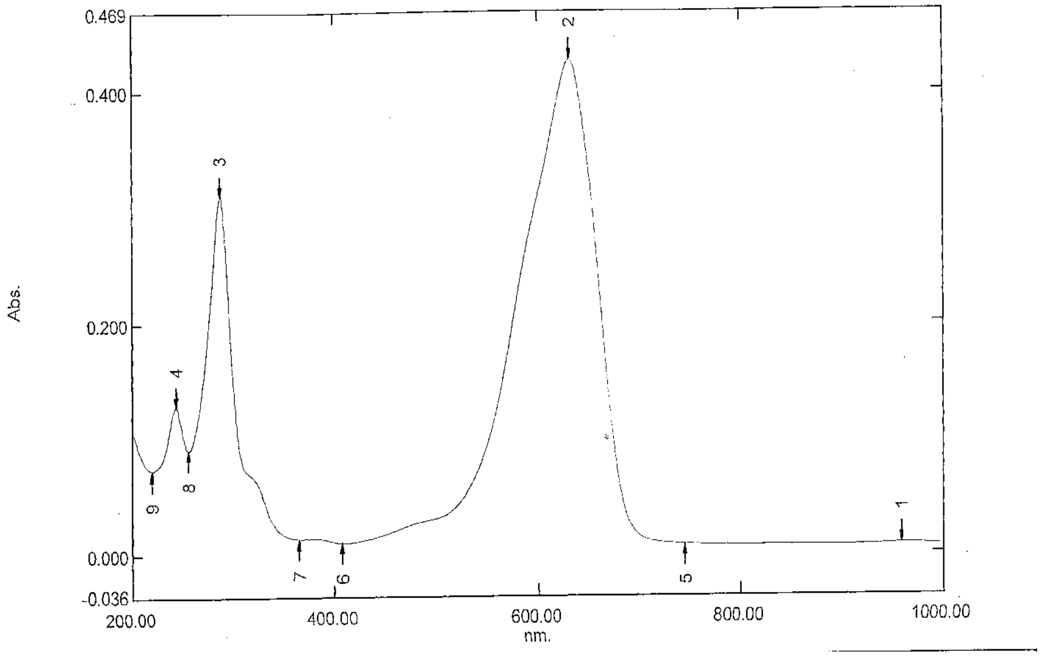
2-5- Methodology

2-5-1-Solutions Preparation

In this study, solutions of dyes were prepared azure (A, B and C) used . A solution concentration ($1x10^{-4}$M) results from this experiment, other solutions with ($1x10^{-5}$- $5x10^{-5}$M) were prepared from the resulted solution by taking weaning volume from the original solution which is prepared previously and diluting it by using the distilled water to reach the required volume. Then, moving this solution in order to be identical. The same way mentioned above were prepared each azure (B, C) dyes .

2-5-2-Determination of λ_{max} and Calibration Curves for three dyes.

The maximum wavelength of azure (A,B,C) dyes was specified by using Spectrophotometer in the range (200-800nm) ,and recording the spectra of absorption as shown in the Figures(2-5) to (2-7) . It is found that the highest absorbance of the azure A dye solution with($1x10^{-5}$ M) lies at wavelength(λ_{max} =632nm) , and prepared solution of azure B dye with ($1x10^{-5}$M)that found the highest absorbance at wavelength (λ_{max}=646.5nm). Wheel the solution of azure C dye with($1x10^{-5}$M) it is found the highest absorbance at wavelength(λ_{max} =611.5nm) .



Figure(2-5): UV-Visible spectrum of aqueous solution of azure A dye ($1x10^{-5}$ M), pH=6, T=293K.

The determination of calibration curve of the azure dyes which explains the relation between absorbance and concentration was prepared by using five successive concentration from the azure dyes for range between $1x10^{-5}$- $5x10^{-5}$M.Then, the absorbance of these concentrations are measured in the specified wavelength as Figure(2-8) to (2-10) .

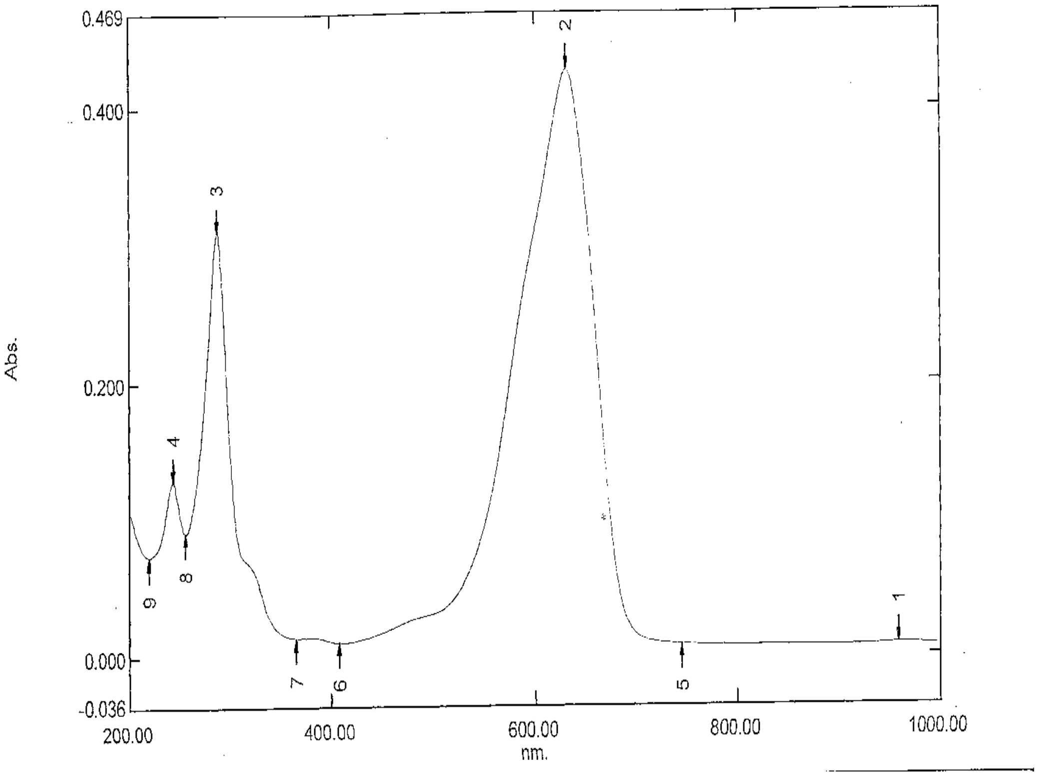


Figure (2-6): UV-Visible spectrum of aqueous solution of Azure B dye ($1x10^{-5}$ M), pH=6, T=293K.

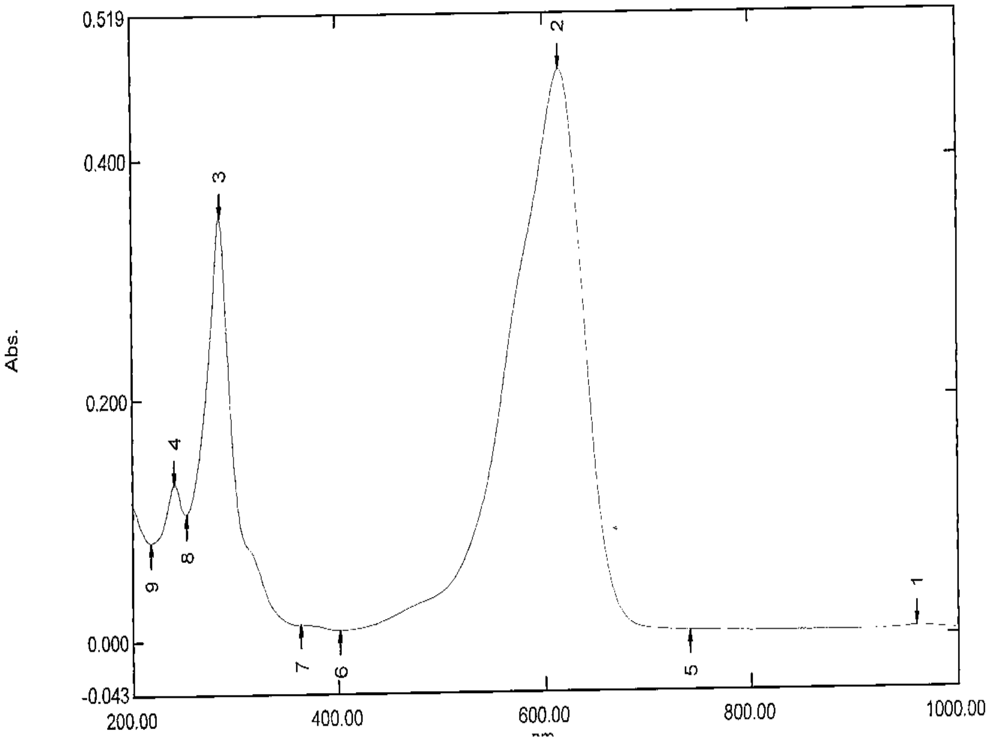
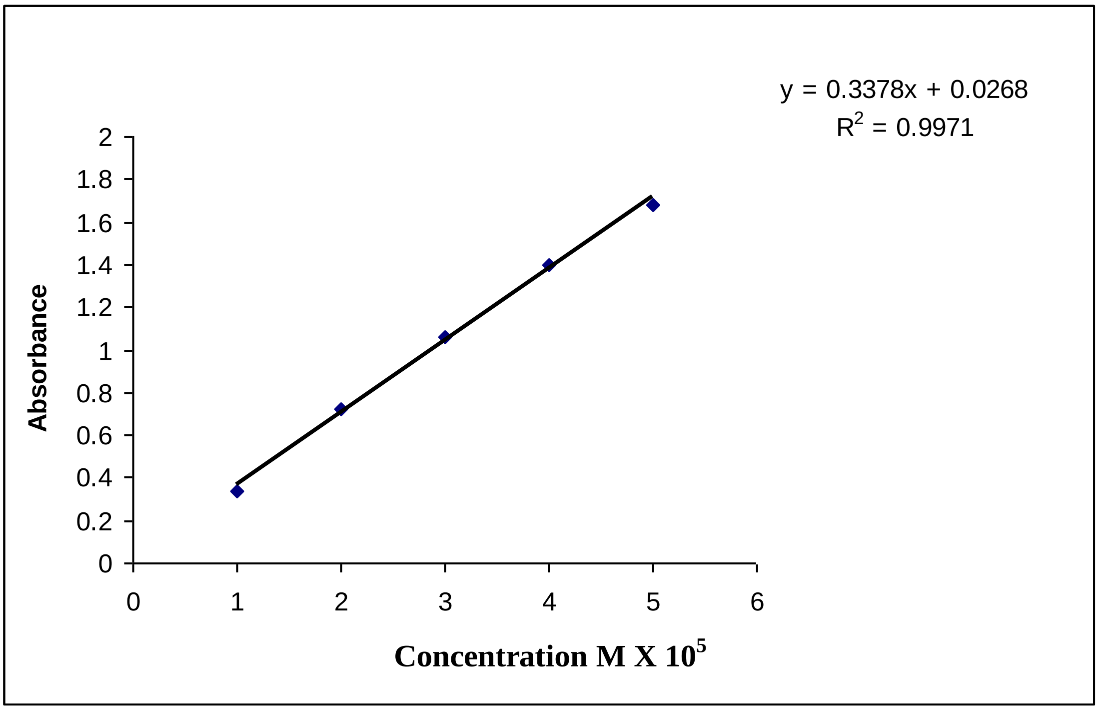
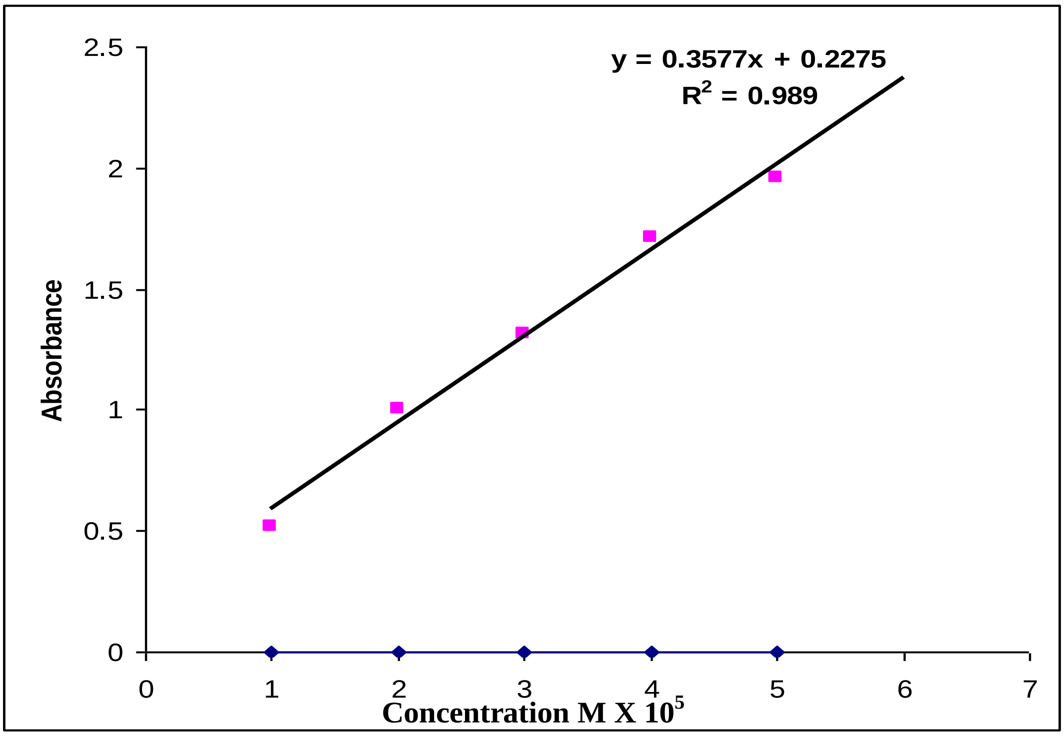


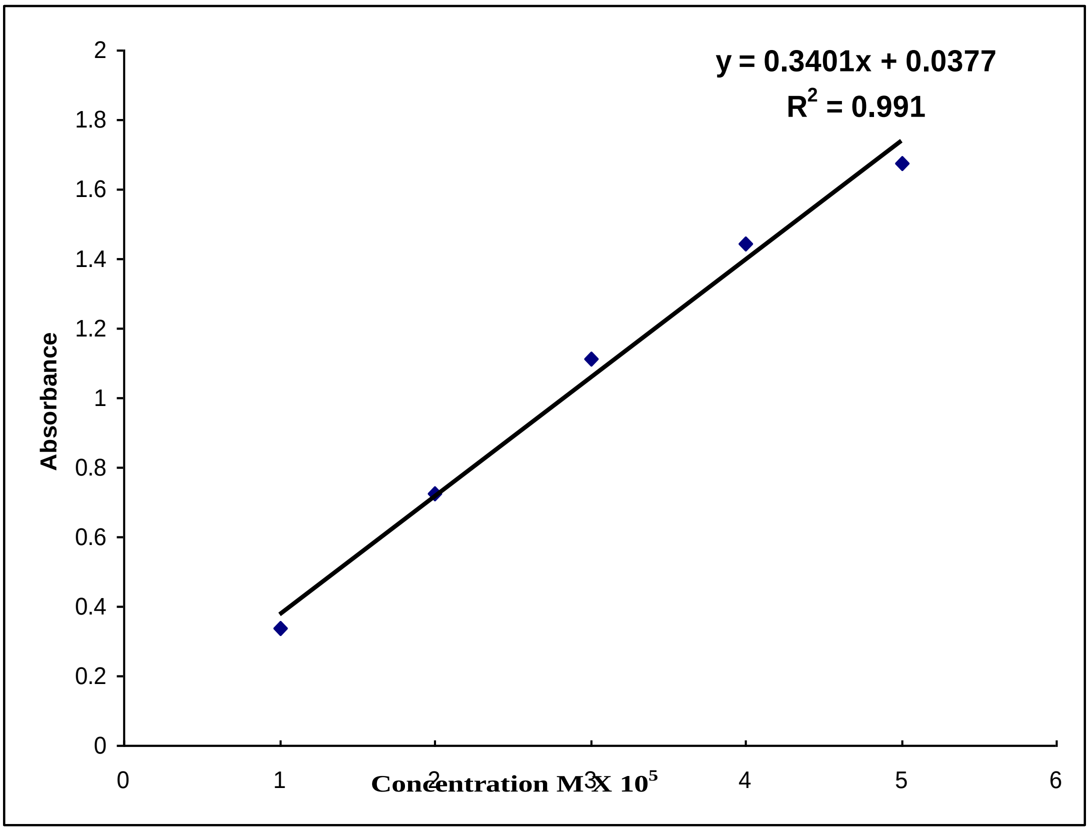
Figure (2-7): UV-Visible spectrum of aqueous solution of Azure C dye ($1x\ 10^{-5}$ M), pH=6, T=293K .



Figure(2-8):Calibration curve for azure A dye at pH=6,T=293k .



Figure(2-9):Calibration curve for azure B dye at pH=6,T=293k .



Figure(2-10):Calibration curve for azure C dye at pH=6,T=293k .

2-6- Irradiation of Dye Solutions.

Lamp was warming for ten minutes before the start of all photo experiment . All dye solutions were irradiated for a period of 75 minutes (the primary experiments indicated that the most of dye molecules are degraded or become colorless at the time near to this period).

2-7-Effect of Dye Concentration .

Five concentration were prepared from aqueous solution of the original dye in the range $1X10^{-5}$-$5X10^{-5}$M in distilled water, at temperature (293K). One liter of each concentration has been irradiated by using UV light in the Photoreactor for 75 minutes. The irradiation of one liter solution of dye azure A that was already prepared concentration $1x10^{-5}M$. At the samples of the models were taken within intervals each 15 minutes. After that, the absorbance was measured at each time at the λ_{max} of dye. Returned the same experiment but using azure B and C dyes with($1x10^{-5}M$)concentration has been irradiated by using UV light in the Photoreactor under the same time and condition. The absorbance was measured at the λ_{max} of dyes .

2-8-Effect of Initial Hydrogen Peroxide Concentration .

Five concentration were prepared from azure A dye concentration ($1x10^{-5}M$) and added different amount of hydrogen peroxide in the range (150-500mg/L),at pH=6,T=293K. The solutions were irradiated by using UV light in spectrophotometer for 75 minutes . The samples of the models have been taken for each 15 minutes, than the absorbance was measured at the λ_{max} =632nm. Returned the same experiments but using azure B and C dyes with ($1x10^{-5}M$)concentration has been irradiated by using UV light in the Photoreactor under the same time and condition. The absorbance was measured at the λ_{max} of dyes .

2-9- Effect of Initial pH.

Five concentration were prepared from azure A dye concentration ($1x10^{-5}M$) and added 500mg/L of hydrogen peroxide to solution of dye. The pH of solutions was adjusted by using NaOH and HCl at using different initial pH media ranges from 2,3,4,5,7,9,10and 12 ,than the solution was irradiated by using UV light for 75 minutes at T=293K. The samples of the models have been taken for each 15 minutes ,than the absorbance was measured at the λ_{max} of the dye . Returned the same experiments for each azure B and C dye with ($1x10^{-5}$M)concentration, and the pH of solutions was adjusted .The samples with drawn from the models and the absorbance was measured after irradiation for each azure B and C dyes.

2-10- Fenton's System .

A series of Fenton's solutions were prepared by mixing hydrogen peroxide (500mg/L) and Ferrous ion at the range 50-150mg/L at the pH equal of 4 and 293K.Other series of solutions were prepared by mixing hydrogen peroxide 150-500mg/L and Ferrous ion 150mg/L at pH equal of 4 and 293K. A third series of solution were prepared by using hydrogen peroxide 500mg/L , Ferrous ion 150mg/L at pH=(2-12) and 293K.The dye concentration was $1x10^{-5}$M ,all the solutions were irradiated for 75 minutes. After that ,the absorbance was measured of azure A at the wave length λ_{max} =632nm. Returned the same experiments for each azure B and C dye with ($1x10^{-5}$M)concentration and preparation a series of Fenton's solutions by mixing hydrogen peroxide (500mg/L) and Ferrous ion at the range (50-150mg/L) at the pH equal of 4 and 293K.Other series of solutions were prepared by mixing hydrogen peroxide (150-500mg/L) and Ferrous ion (150mg/L) at pH equal of 4 and 293K. A third series of solution were prepared by using hydrogen peroxide (500mg/L) , Ferrous ion (150mg/L) at pH=(2-12) and 293K. After that ,the absorbance was measured of azure B and C dyes at the λ_{max} of dyes.

2-11- Effect of Temperature .

Five concentration were prepared from azure A dye . The solution were irradiated at temperature range 298-318 and pH=6.The temperature was maintained by using regulator water bath. The degradation of dye was performed by irradiation presence UV light for 75 minutes, and the samples were withdrawn from the models for each 15 minutes. The absorbance was measured for azure A at the λ_{max} of dye. Returned the same experiments for each azure B and C dye with ($1x10^{-5}$M) concentration has been irradiated by using UV light in the Photoreactor under the same time and condition. The absorbance was measured at the λ_{max} of this dyes.

2-12- Chemical Oxygen Demand

In the COD test, the organic material concentration is calculated from the oxidant consumption necessary for the oxidation of the organic material. In the case of COD, a sample of waste water containing organic material is placed in contact with a very strong inorganic oxidant, a mixture of dichromate and sulphuric acid with silver sulphate as a catalyst. The temperature is increased to the point of ebullition of the mixture, resulting in an increase of the oxidation rate. After two hours (the standard duration of the test) oxidation of the organic compounds is virtually complete. The resulting COD value can be determined by means of a spectrophotometer by reading the concentration of formed chromium (Cr^{3+}) concentration. .

Samples of azure dyes (A , B, C) were treated with Thermo Low-range (0-150) COD test reagent in a Thermoreactor TR 300 COD Thermoreactor. A mixture of dichromate and sulphuric acid with dye solution from azure A the temperature is increased to the point of ebullition of the mixture، resulting in an increase of the oxidation rate, at 150 ^{o}C for two hours (the standard duration of the test oxidation of the organic compounds is virtually complete. Potassium dichromate has been found to be the most suitable oxidant. It is capable of oxidising a wide variety of organic substances almost completely to carbon dioxide and water. In this research we have by taking 3 ml of dye solution from azure A prepared and added to 3 ml of the solution of COD. Carried out study the effect of concentration dyes in range $1x\ 10^{-5}$– $5x10^{-5}$ M by taking 3 ml of a solution of azure (A,B,C) dyes before irradiation at pH= 6, and the temperature is equal to 298k and after 75 minutes of irradiation withdraw 3 ml of dyes solutions irradiated and added to 3 ml of the solution from COD . Then put in a Digester for two hours and after cooling measured using device (Lovibond, Vario LR). Then we studied the effect concentrations of hydrogen peroxide the extent of 100-500 mg/L then we have to withdraw 3 ml of dyes solutions (A,B,C) before and after irradiation was added to one tube of the solution COD and then placed in the device Digester for two hours and after cooling measured device. Also, studied the effect of pH was evaluated at pH media (2,3,4,5,7,9,10 and 12) and we have to withdraw 3 ml of a dyes solutions (A,B,C) before and after irradiation was added to one tube of the solution from COD and then placed in the device Digester for two hours and after cooling measured device . Then, study effect Fenton reagent on azure (A,B,C) dyes concentration ($1x10^{-5}$M) under the same condition include by using various concentration of ferrous in the range 50- 150m g/L in the presence of constant concentration of H_2O_2 500mg/L. Also, through experiments that were carried out using changing concentration of hydrogen peroxide ranging 100 – 500 mg/L at constant concentration of ferrous ion 150mg/L, and we have withdraw 3 ml of a dyes solutions (A,B,C) before and after irradiation was added to solution of COD and then placed in the device Digester for two hours and after cooling measured.

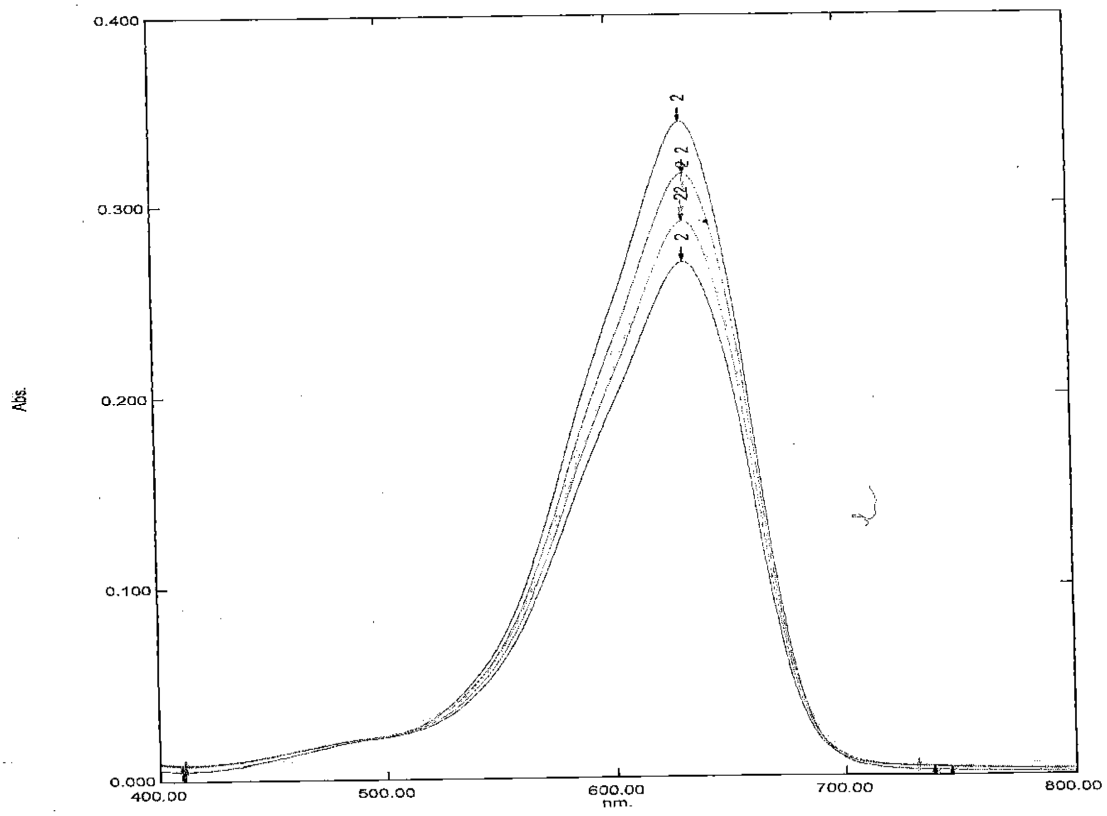

COD


COD
0-1500
COD
CSB
0-1500
ppm

RESULTS AND DISCUSSION

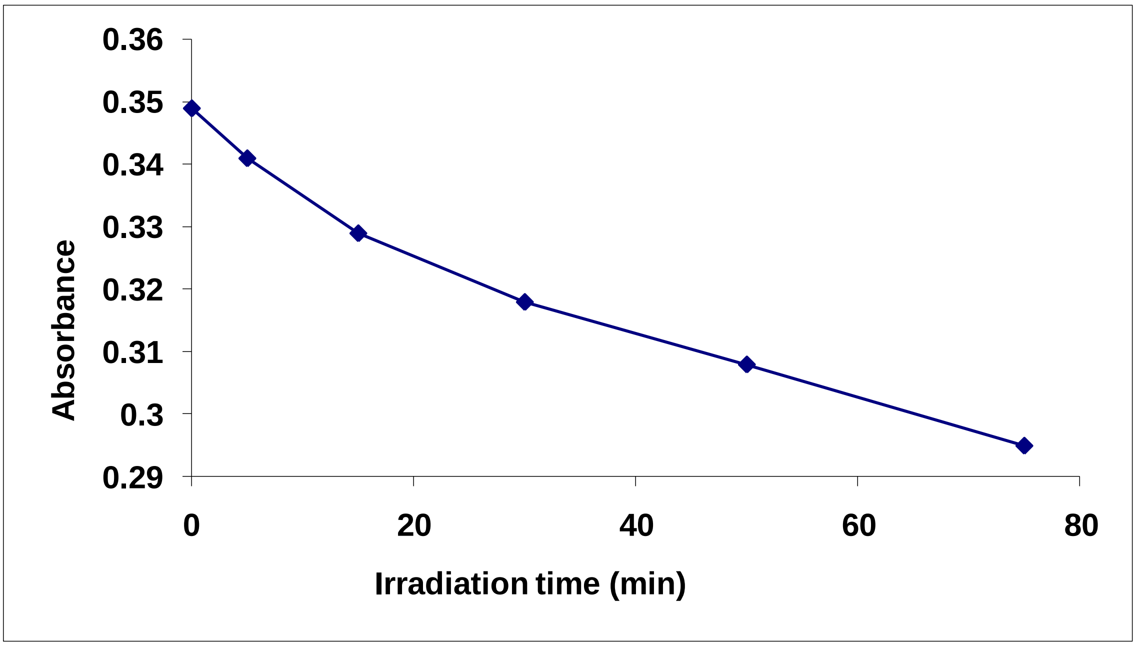
3-1- Effect of initial dye concentration

It has found in this study the effect of various initial dye concentration in the range $1x10^{-5}$-$5x10^{-5}$M on the degradation of azure A dye clear by using UV irradiation for 75 minute, and the samples with drawn from the solution for each 15 minutes . Also, the overall spectrum of dye decreases as the irradiation time increasing[(164)].As Figure(3-1) shows the results, the absorbance was measured for azure A at the λ_{max}=632nm.



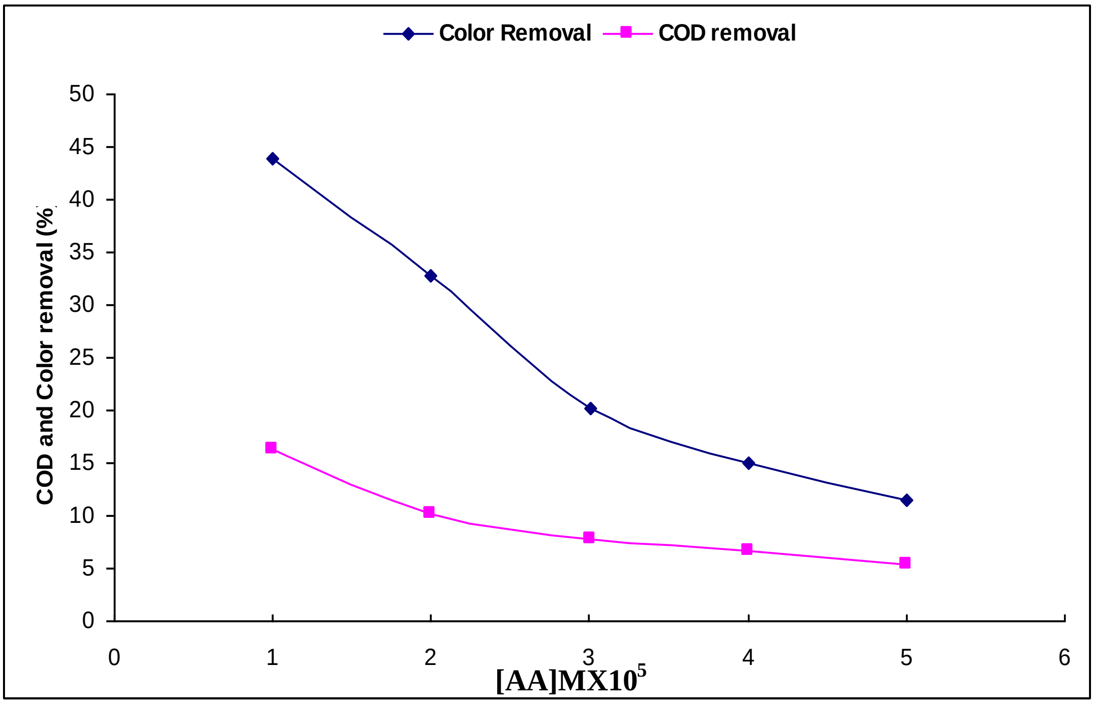
Figure(3-1):The UV-visible spectra of azure A dye solution($1x10^{-5}$M) as a function of irradiation time at pH=6, T=298k.

The results clarified the increasing in the initial concentration of dye lead to decreasing the color removal, because of the decreases penetration of photons entering into the solution and lowering the formation of hydroxyl free radicals in the solution(165). In this study show effect concentration of dye on ratio color removal during period different time under range 0-75 min in presence of UV irradiation from azure A dye concentration ($1x10^{-5}$M) ,determine absorption at this time. The results shown as Figure(3-2) the relation ship between absorbance and time irradiation. It is clear the dye concentration is decreases as long as the time increased.



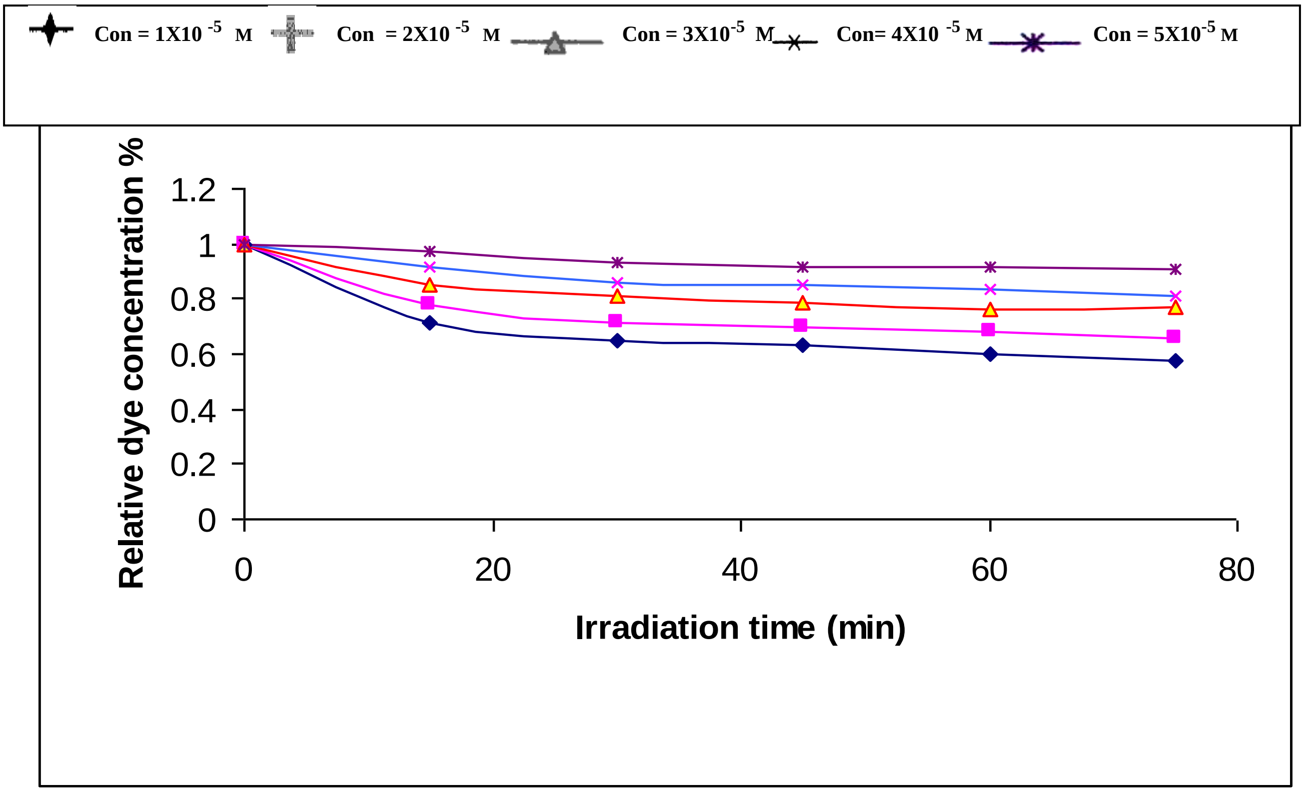
Figure(3-2): The absorption of dye at 632nm as a function of irradiation time. For azure A=$1x10^{-5}$M, pH=6,T=298k.

The percent of color removal decrease from 52% to 14% with increasing the concentration of dye from $1x10^{-5}$M to $5x10^{-5}$M in presence of UV irradiation ,and the results proved that the highest percentage of COD removal was obtained at the concentration $1X10^{-5}$M while , the lowest percentage was obtained at the concentration $5x10^{-5}$M. The results are shown in Figure(3-3).



Figure(3-3): Effect of dye concentration on color removal and COD removal of azure A at pH=6,T=298k .

Different initial dye concentration were used in the test and observed the effect on azure A color removal by using UV method. The results are shown in Figure(3-4). It is clear the higher dye concentration increased the absorption of UV radiation, lead to decreasing the availability if UV light for reactions.



Figure(3-4): Effect of different initial dye concentration on the color removal of azure A dye by using UV method at pH=6,T=298k.

The obtained results proved that the Photooxidation reactions of the Azure A dye is reactions of first order with respect to dye concentration , the coincident of the rapidity of reaction can be related with the absorption of the dye and can be calculated by using the law is called empirical method(134). Figure(3-5) shown relationship between Log R and Log C to determining order reaction. Also, the order total of reaction was calculated by :

1- With respect to H_2O_2 in the presence of dye

$$Rate_1/Rate_2=k[Dye]_1^x[H_2O_2]_1^Y/k[Dye]_2^x[H_2O_2]_2^Y \quad (8)$$

lead to order X equal (1) form azure A dye . When $[H_2O_2]$ constant while [Dye] change.

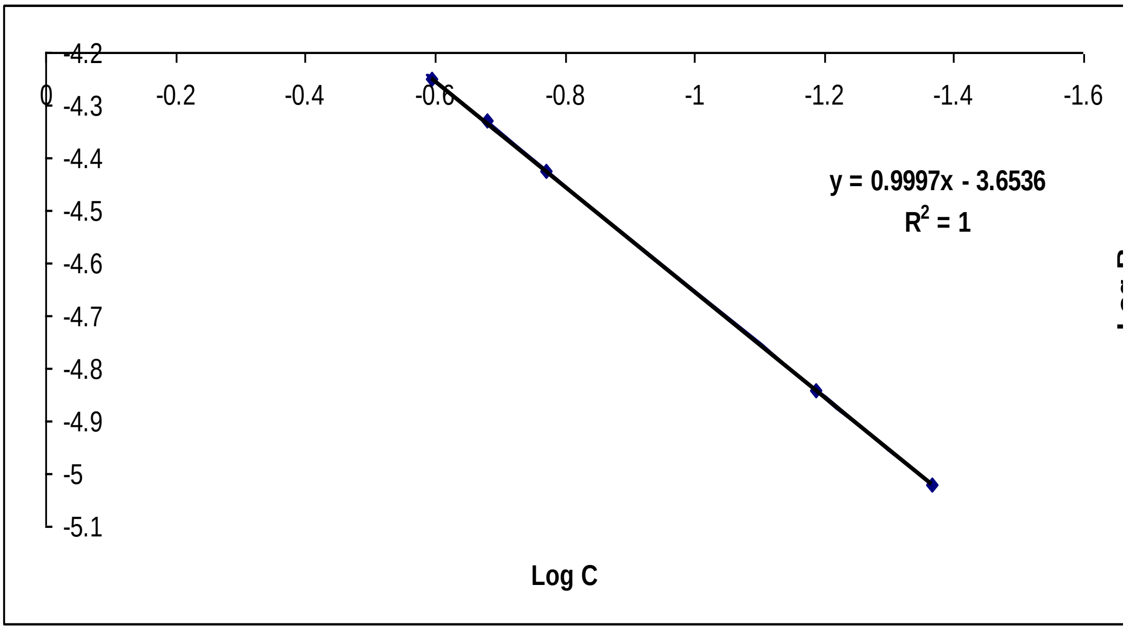
2- Effect of Fe^{+2} /H_2O_2 ,[Dye] by using the low

$$Rate_1/ Rate_2 = k\,[Dye]_1^x\,[Fe^{+2}]_1^z\ [H_2O_2]_1^Y / k\,[Dye]_2^x\,[Fe^{+2}]_2^z\ [H_2O_2]_2^Y \qquad (9)$$

lead to order X equal (1.02) form azure A dye . When [H_2O_2] and [Fe^{+2}] constant while [Dye] change, and Y equal (0.98) from [H_2O_2] When [Dye] and [Fe^{+2}] constant while [H_2O_2] change, and Z equal (0.96) from [Fe^{+2}] When [Dye] and [H_2O_2] constant while [Fe^{+2}] change.

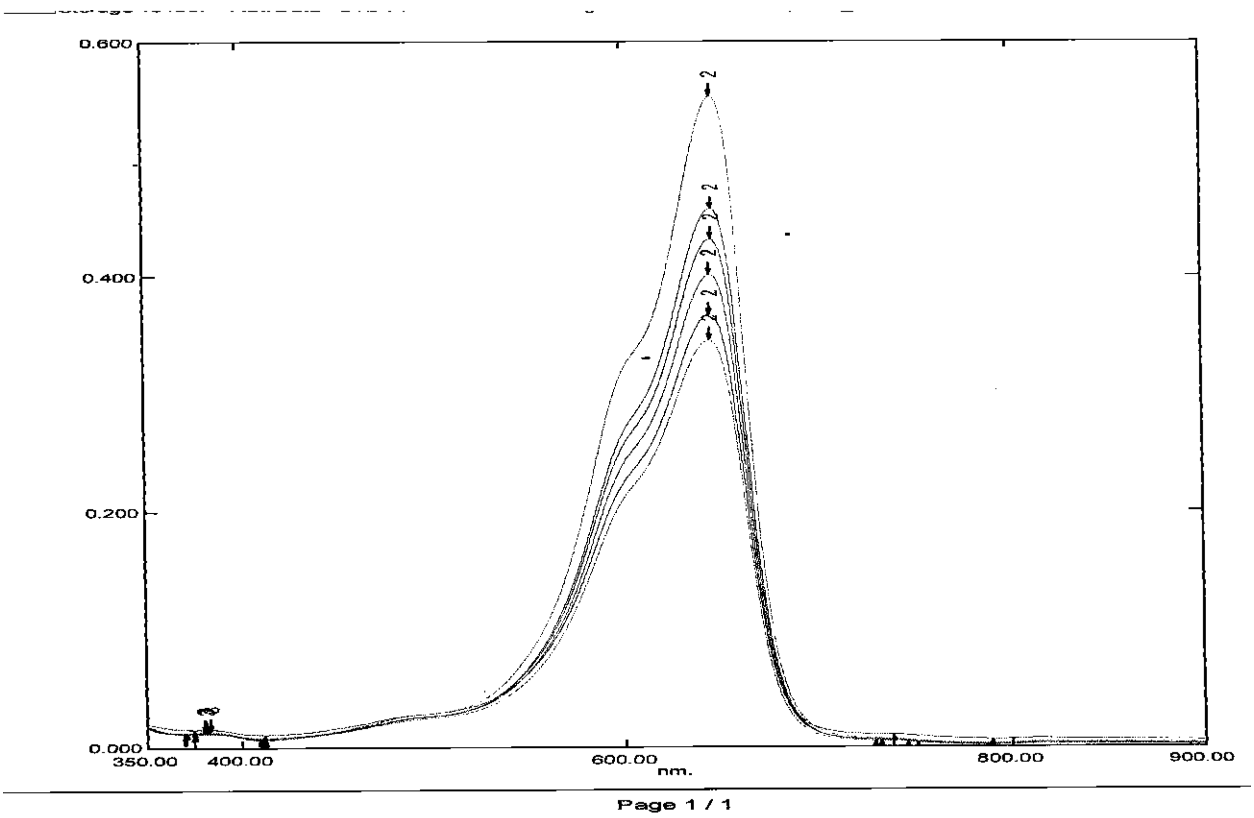
$$Log\ R= log\ k + n\ log\ C \qquad (10)$$

Where:
C: concentration of dye, n: order reaction, R: reaction rate, K: reaction rate constant.



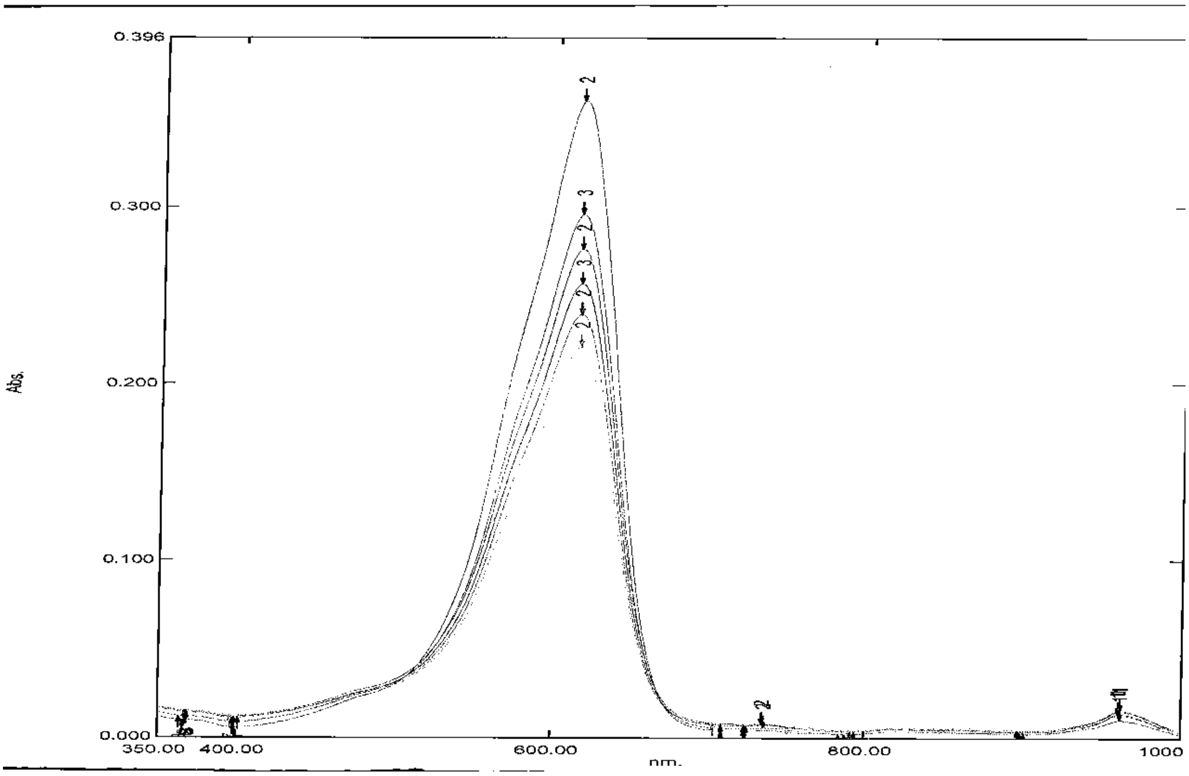
Figure(3-5): Relationship between Log R and Log C of oxidation of Azure A dye[AA]=1x10^{-5} M , pH=6, T=298k.

Returned the same experiments on azure B and C dyes after using UV irradiation for 75 minute, and the samples with drawn from the solution for each 15 minutes . Also, the overall spectrum of dye decreases as the irradiation time increasing as Figures(3-6)and (3-7) show. The absorbance was measured for azure B and C at λ_{max} of their.

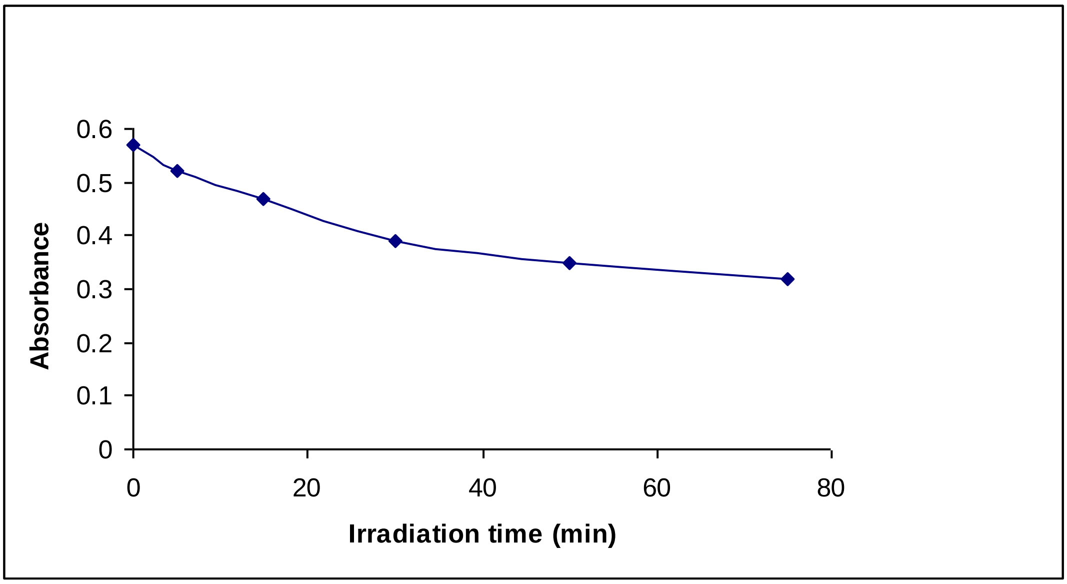


Figure(3-6):The UV-visible spectra of dye solution($1x10^{-5}$M) as a function of irradiation time at pH=6, T=298k.

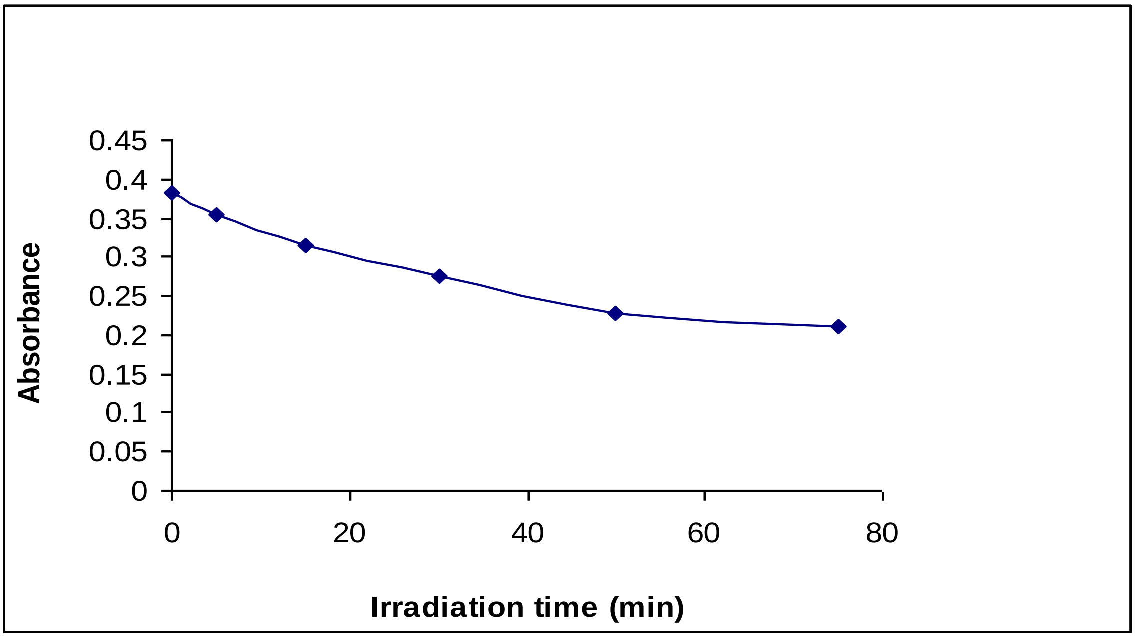
In this study show effect concentration of dye on ratio color removal was studied during period under range 0-75(min) in presence of UV irradiation form each azure B and C dyes concentration $1x10^{-5}$M ,determine absorption at this time. The results show as Figures (3-8), (3-9) the relation ship between absorbance and time irradiation.



Figure(3-7):The UV-visible spectra of dye solution(1x10^{-5}M) as a function of irradiation time at pH=6, T=298k.

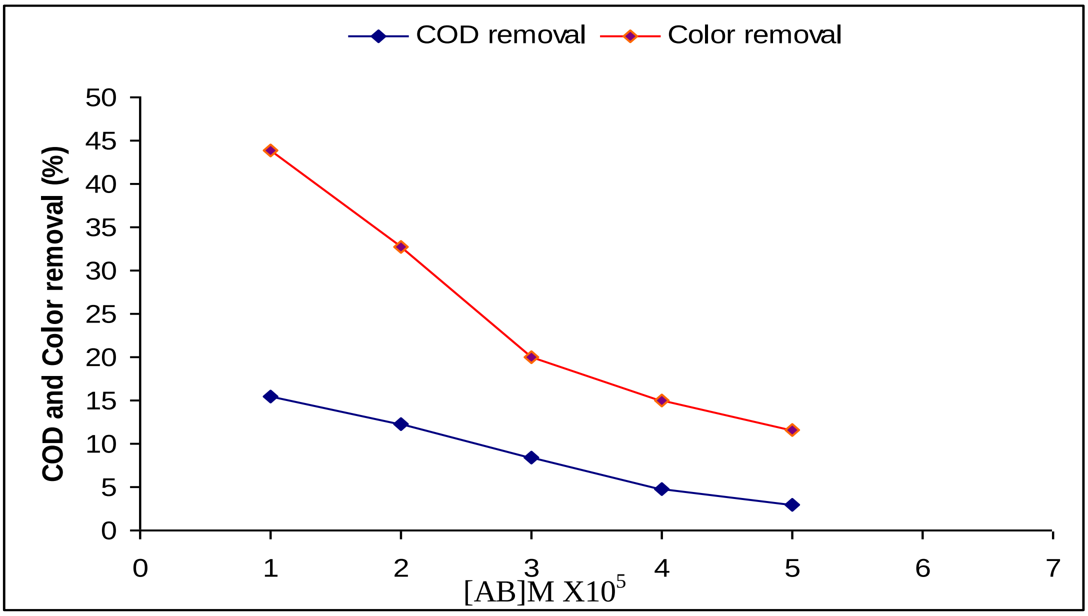


Figure(3-8): The absorption of dye at 646.5nm as a function of irradiation time . For azure B dye=1x10^{-5}M, pH=6,T=298k.

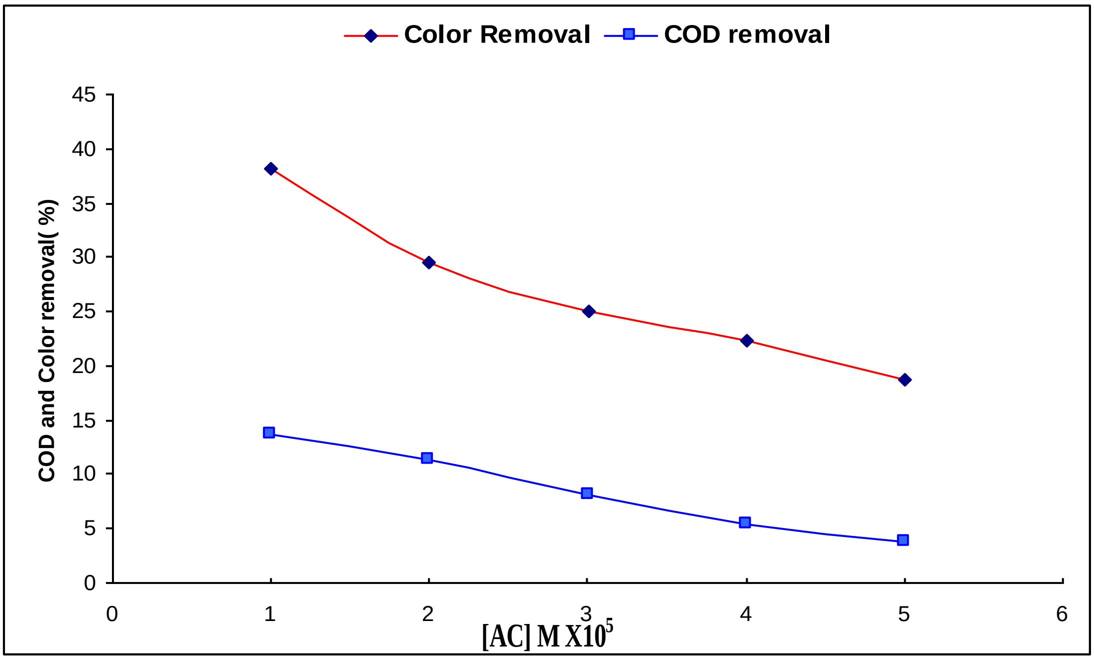


Figure(3-9): The absorption of dye at 611.5 nm as a function of irradiation time . For azure C dye=$1x10^{-5}$M, pH=6,T=298k.

The percent of color removal from azure B dye decrease from (43% to 12%) and azure C from (38% to 18%) with increasing the concentration of dye from $1x10^{-5}$ M to $5x10^{-5}$ M in presence of UV irradiation ,and the results proved that the highest percentage of COD removal was obtained at the concentration $1X10^{-5}$M while , the lowest percentage was obtained at the concentration $5x10^{-5}$M. The results are shown in Figures(3-10),(3-11). Can be explained by the difference in the effectiveness of the dyes to the absorbed radiation to several reasons, including different groups responsible for color and located in the structure of dyes lead to a change in the ability of the dye to absorb photons and to obtain degradation bonds .

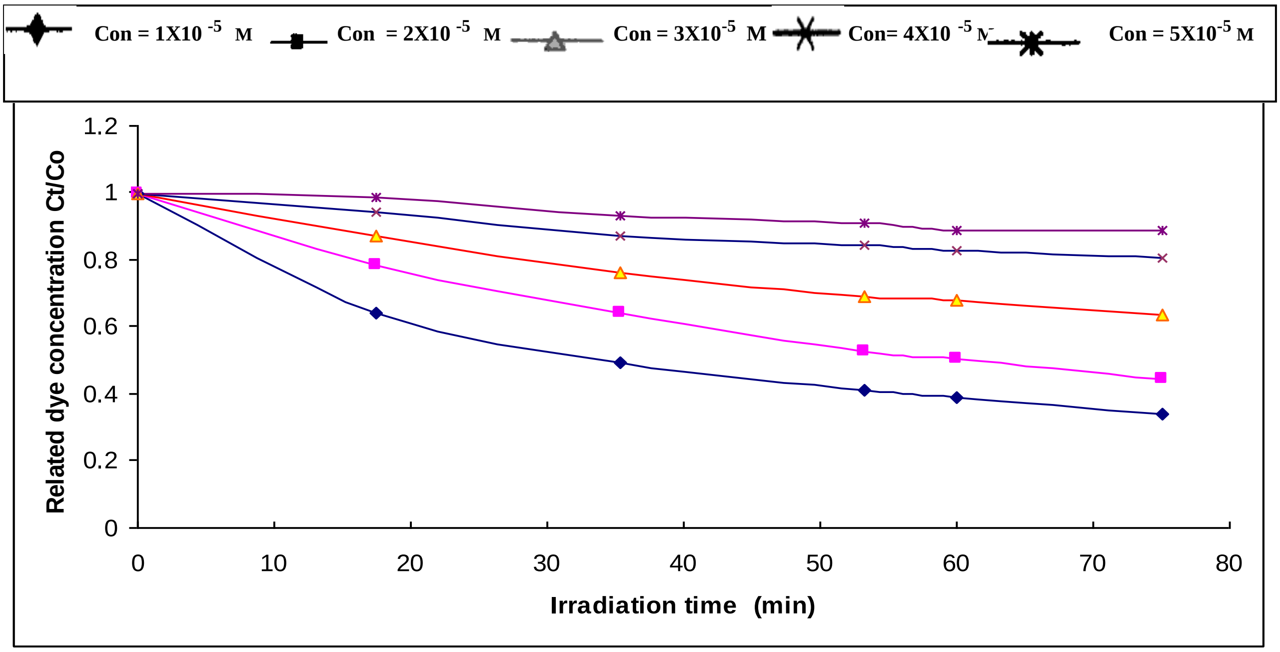


Figure(3-10): Effect of dye concentration on color removal and COD removal of azure B at pH=6,T=298k .

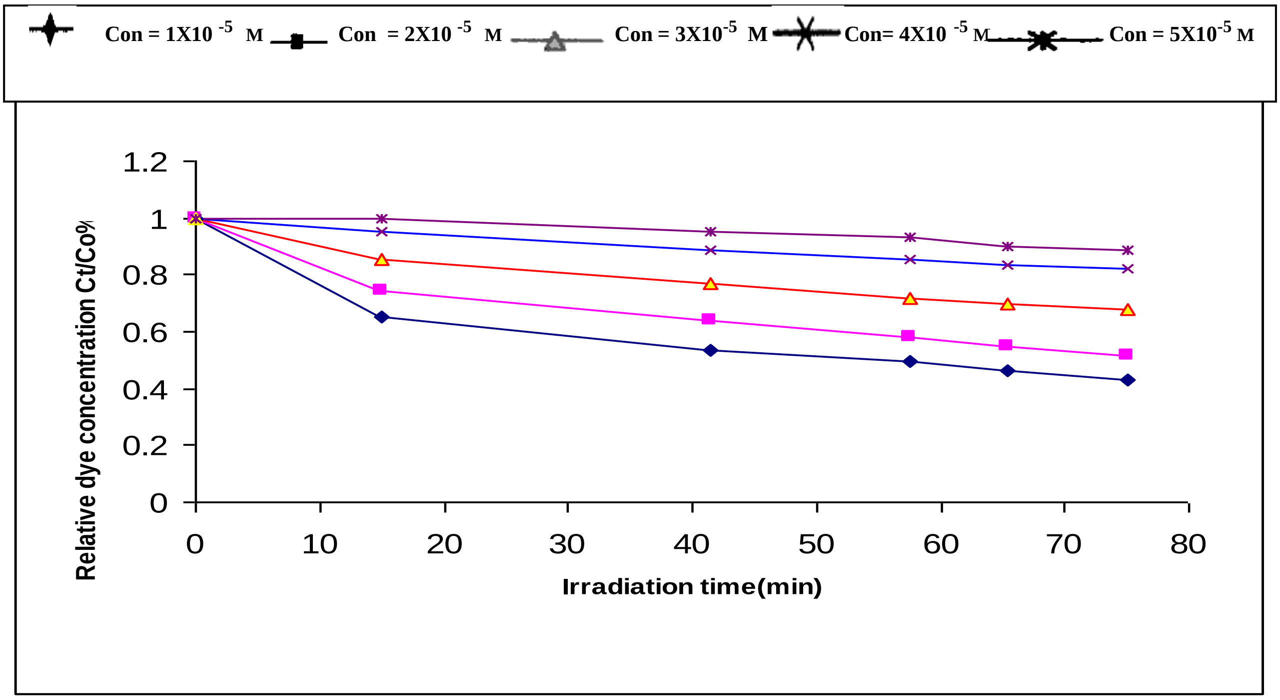


Figure(3-11): Effect of dye concentration on color removal and COD removal of azure C at pH=6,T=298k .

Different initial dye concentration were used in the study and observed the effect on azure(B , C) dyes color removal by using UV method. The results are shown in Figures(3-12),(3-13) .



Figure(3-12): Effect of different initial dye concentration on the color removal of azure B dye by using UV method at pH=6,T=298k.



Figure(3-13): Effect of different initial dye concentration on the color removal of azure C dye by using UV method at pH=6,T=298k.

The obtained results proved that the Photooxidation reactions of the Azure B and C dyes are reactions of first order with respect to dye concentration, the coincident of the rapidity of reaction can be related with the absorption of the dye and can be calculated by using the law is called empirical method. Figures(3-14)and (3-15) shown relationship between Log R and Log C to produced order reaction. Also, the order of reaction was calculated by :

3- With respect to H_2O_2 in the presence of dye

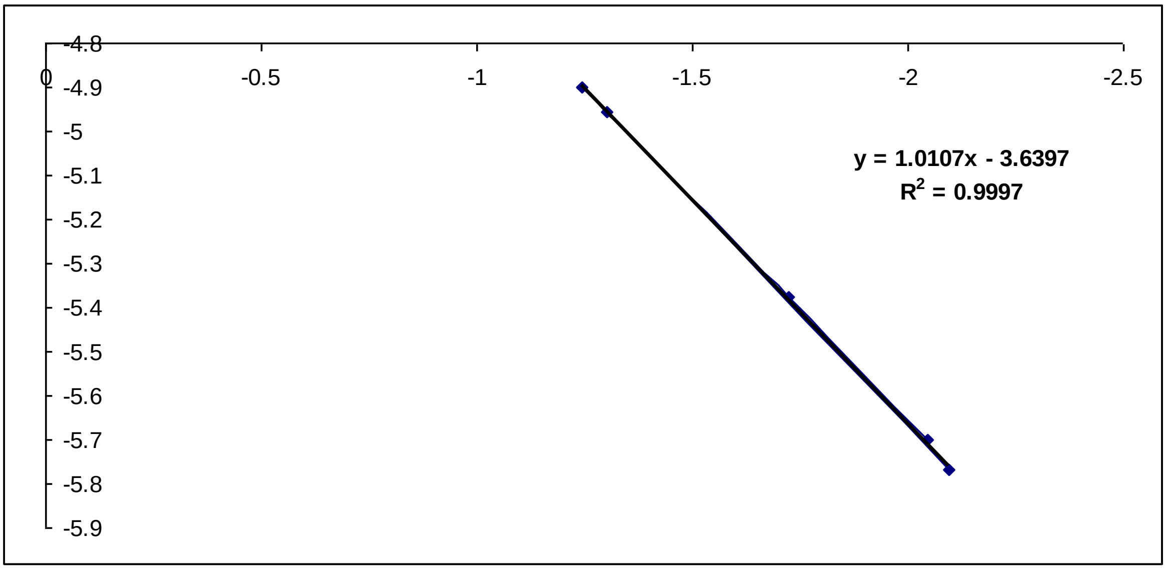
$$Rate_1/Rate_2=k[Dye]_1^x[H_2O_2]_1^Y/k[Dye]_2^x[H_2O_2]_2^Y \qquad (11)$$

lead to order X equal (0.91) form azure B and X equal (0.98) from azure C dye. When $[H_2O_2]$ constant while [Dye] change.

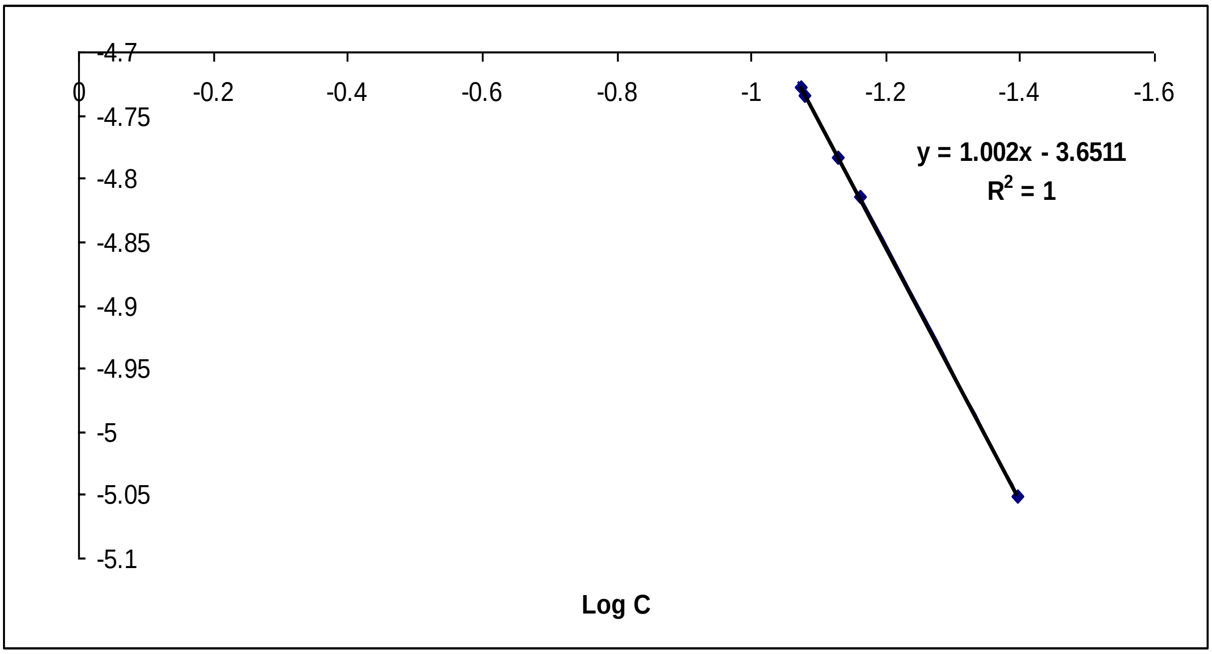
4- Effect of Fe^{+2} /H_2O_2 ,[Dye] by using the low

$$Rate_1/ Rate_2 =k [Dye]_1^x [Fe^{+2}]_1^z [H_2O_2]_1^Y / k [Dye]_2^x [Fe^{+2}]_2^z [H_2O_2]_2^Y \qquad (12)$$

lead to order X equal (1.01) form azure B dye. When $[H_2O_2]$ and $[Fe^{+2}]$ constant while [Dye] change, and Y equal (1.04) from $[H_2O_2]$ When [Dye] and $[Fe^{+2}]$ constant while $[H_2O_2]$ change, and Z equal (1.07) from $[Fe^{+2}]$ When [Dye] and $[H_2O_2]$ constant while $[Fe^{+2}]$ change from azure B dye. But order from azure C dye X equal (1.07) When $[H_2O_2]$ and $[Fe^{+2}]$ constant while [Dye] change, and Y equal (0.99) from $[H_2O_2]$ When [Dye] and $[Fe^{+2}]$ constant while $[H_2O_2]$ change, and Z equal (0.96) from $[Fe^{+2}]$ When [Dye] and $[H_2O_2]$ constant while $[Fe^{+2}]$ change from azure C dye.



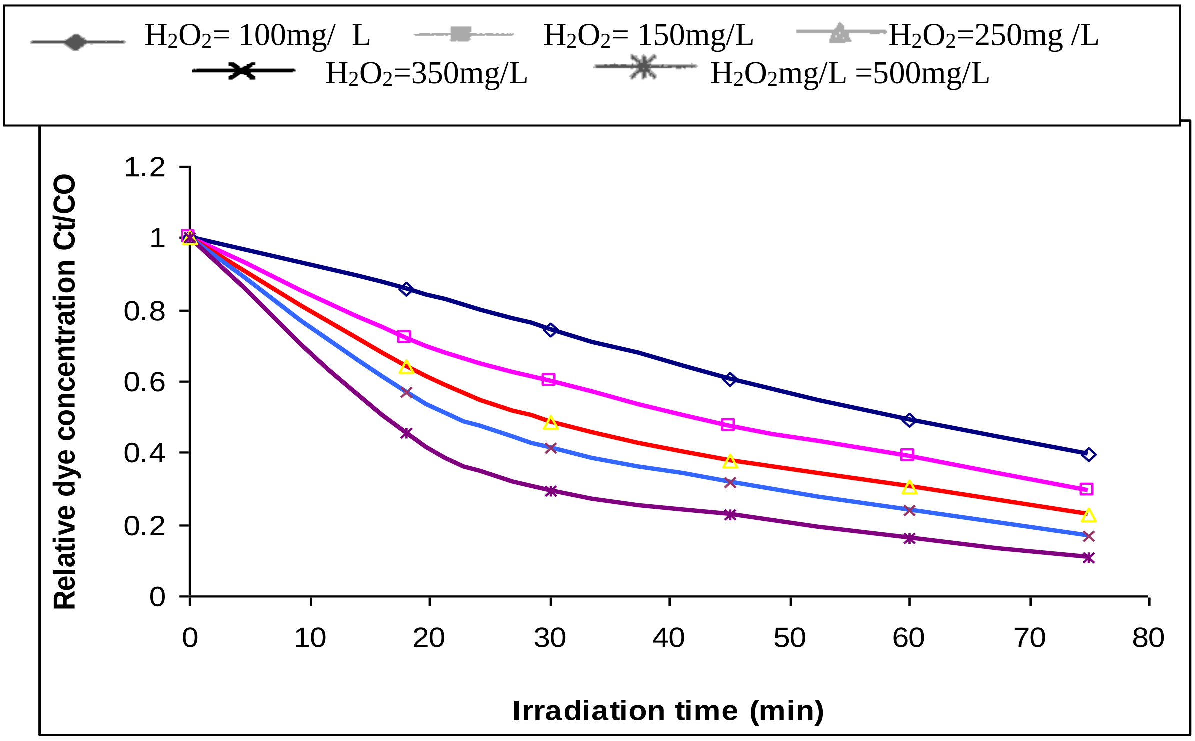
Figure(3-14): Relationship between Log R and Log C of oxidation of Azure B dye[AB]=1x10^{-5} M , pH=6, T=298k.



Figure(3-15): Relationship between Log R and Log C of oxidation of Azure C dye[AC]=1x10^{-5} M , pH=6, T=298k.

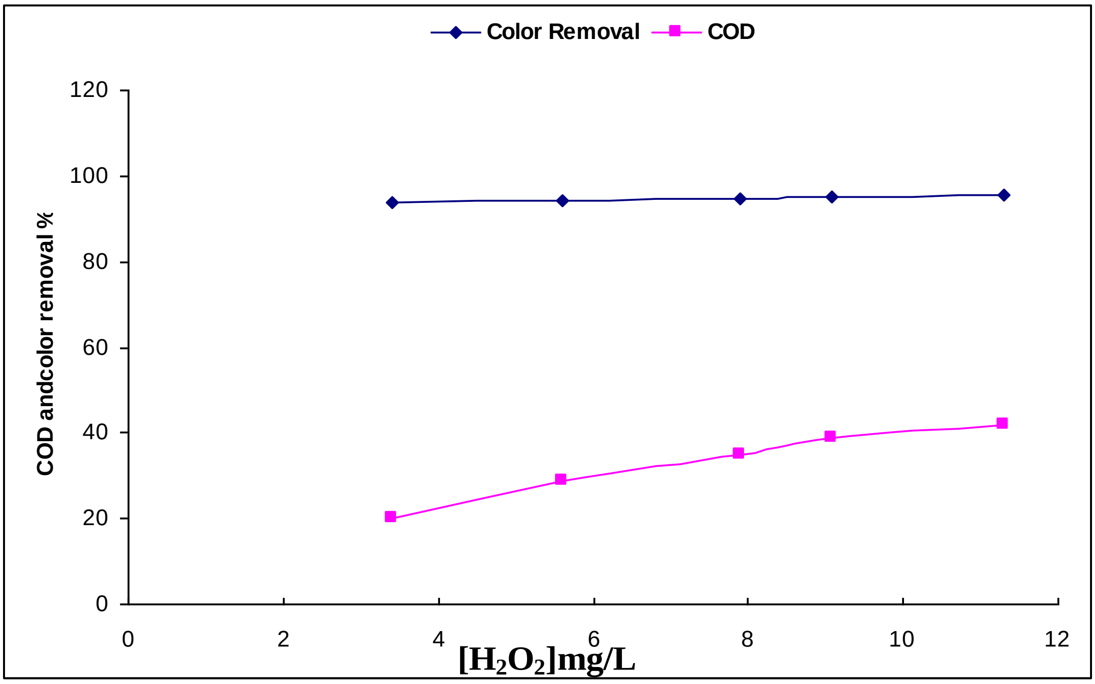
3-2- Effect of Initial Hydrogen Peroxide Concentration.

In the study observed the effect of different concentration of H_2O_2 at the range 100-500 mg/L clear on the decolourization in Photooxidation experiments presence UV light. These experiments carried out on azure A dyes with (1x10^{-5}M) concentration for 75min of radiation . Figure(3-16) shows the decolourization of azure A as a function of UV irradiation time for various initial H_2O_2 dosages. Color removal is decreased over time in the presence of UV / H_2O_2 light.



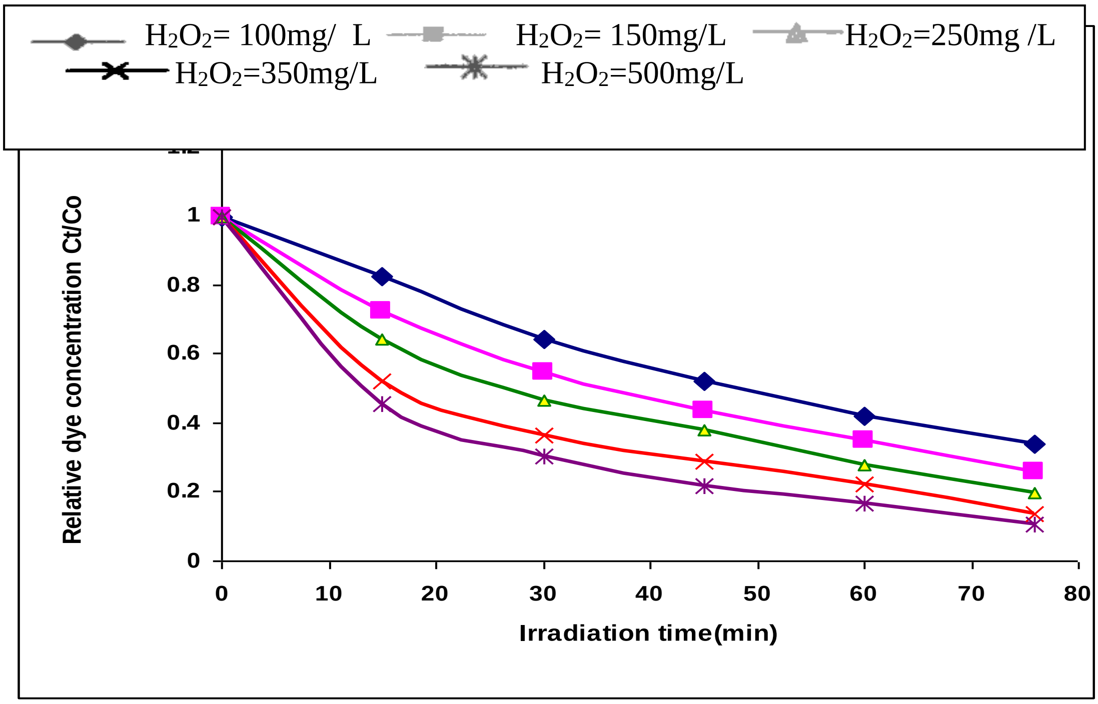
Figure(3-16): Effect of different initial H_2O_2 concentration on the color removal from azure A dye [AA]=1x10^{-5}M using UV / H_2O_2 method, pH= 6, T=298k .

The results showed the highest ratio decolorization of azure A was 95.8% using 500mg/L of H_2O_2, and the ratio decreased from95.8% to 93.4% when H_2O_2 concentration was reduce from 500-100mg/L respectively(115) . Also , the effect of H_2O_2 concentration on COD removal was investigated . We found that with increase of the hydrogen peroxide concentration the value of COD removal increase .The results are clarified in Figure (3-17).

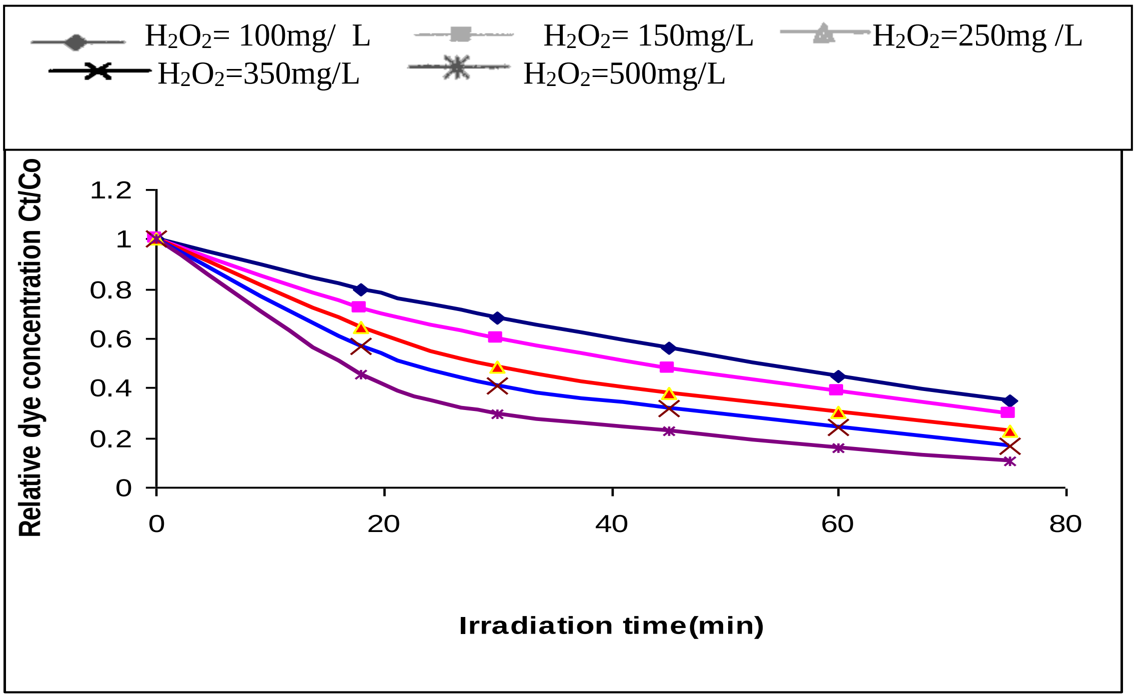


Figure(3-17):Effect of different initial H_2O_2concentration on COD and color removal from azure A dye ,[AA]=1x10^{-5}M,pH=6 at T=298k by using UV/H_2O_2 method**.**

While the effect of varying the initial H_2O_2 concentration was studied in the range 100-500 mg/L from each azure B and C dyes concentration 1X10^{-5}M and the results is shown in Figures (3-18)and (3-19) as the decolourization of azure B and C as a function of UV irradiation time. Color removal is decreased over time in the presence of UV / H_2O_2 light. The results are showed the highest ratio decolorization of azure B was 96.4% using 500mg/L of H_2O_2, and with the ratio decreases from96.4% to 94.2% but azure C recorder highest ratio decolorization 96.1 using 500mg/L of H_2O_2.

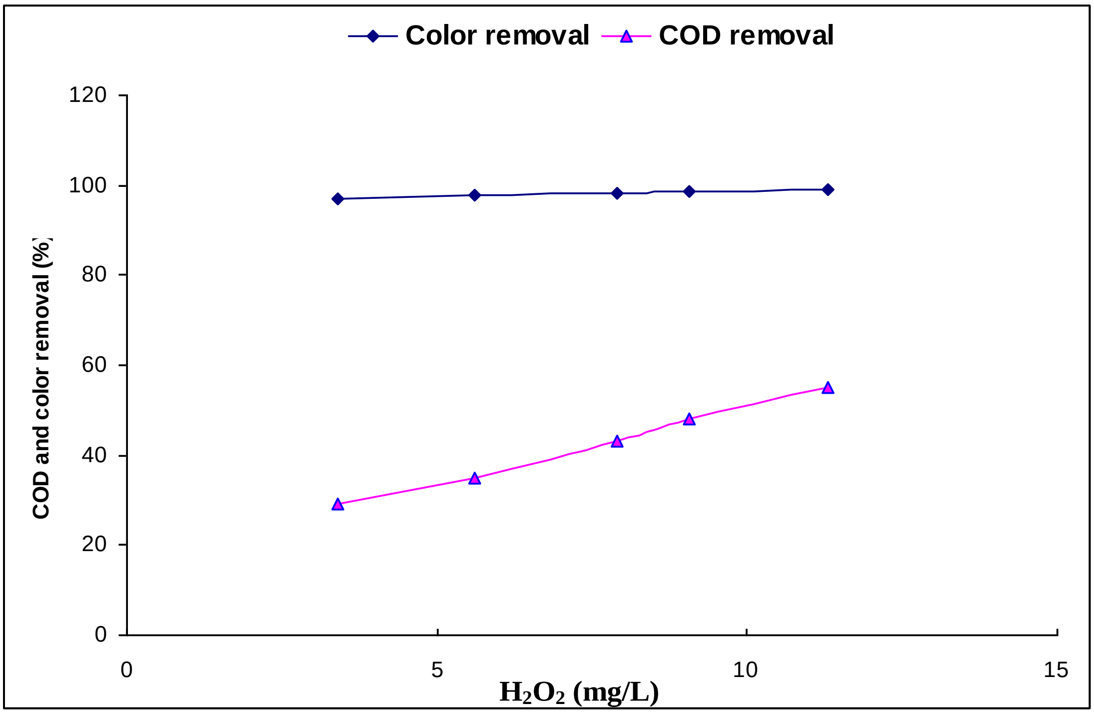


Figure(3-18): Effect of different initial H_2O_2 concentration on the color removal from azure B dye $[AB]=1x10^{-5}M$ using UV / H_2O_2 method, pH= 6, T=298k.

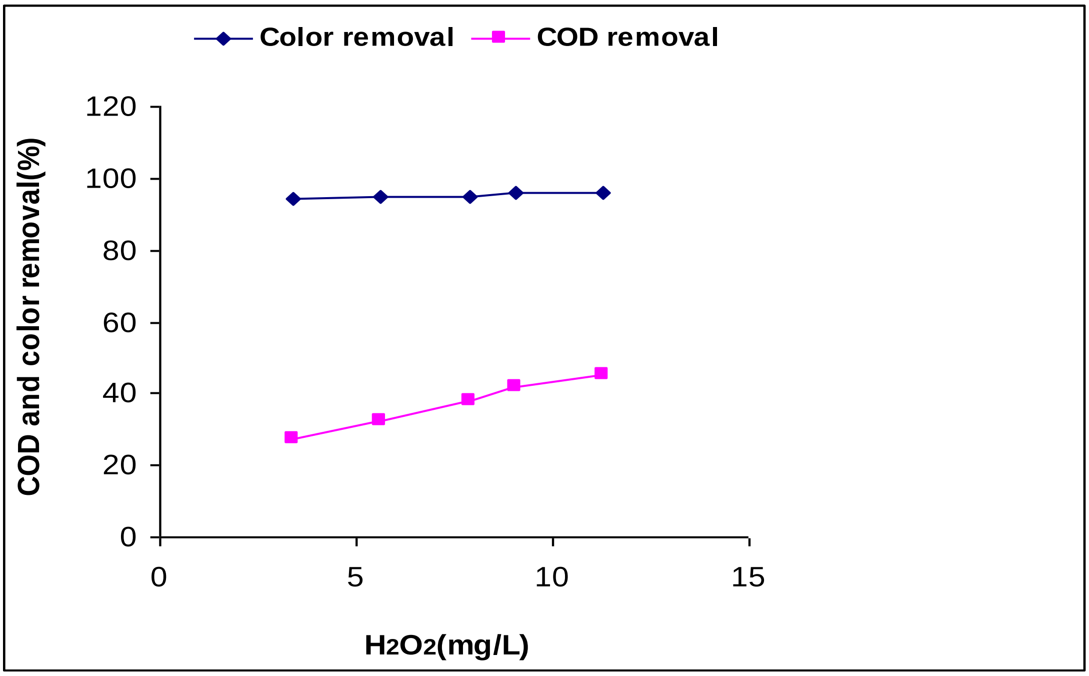


Figure(3-19): Effect of different initial H_2O_2 concentration on the color removal from azure C dye $[AC]=1x10^{-5}M$ using UV / H_2O_2 method, pH= 6, T=298 .

When H_2O_2 concentration was reduce from 500-100mg/L respectively. Investigate we study the effect of H_2O_2 concentration on COD removal from each azure B and C dyes . We found that with increase of the hydrogen peroxide concentration the value of COD removal increase . The results are clarified in Figures (3-20)to (3-21) At higher hydrogen peroxide concentration more $^{\bullet}OH$ was produced leading to a faster oxidation rate. Also, these free radicals preferred to react with the excess of H_2O_2 dosages(166).



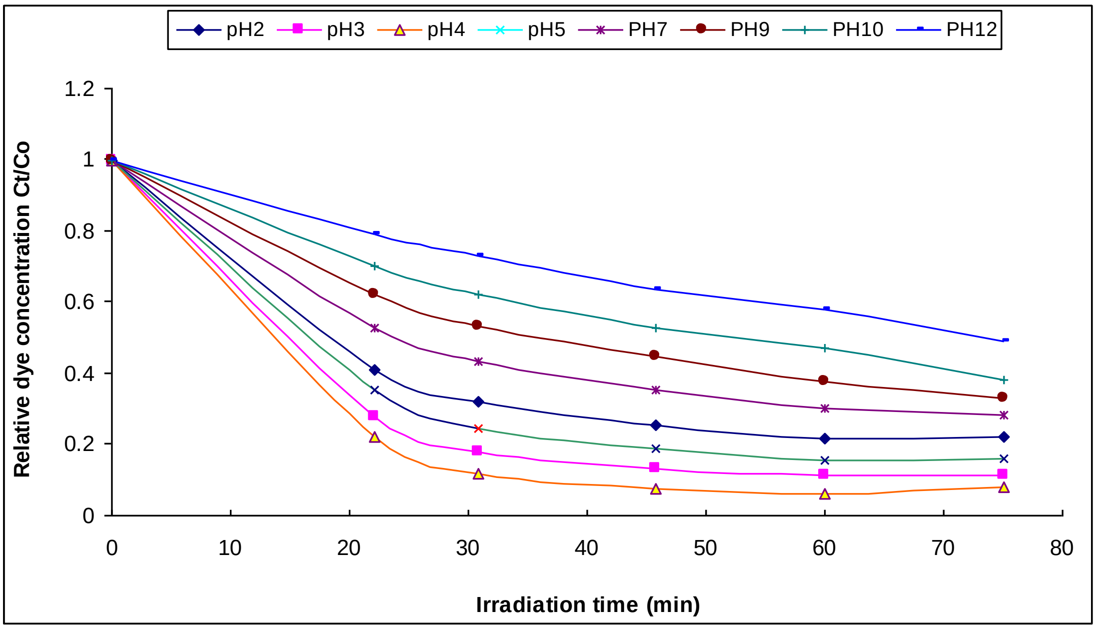
Figure(3-20):Effect of different initial H_2O_2concentration on COD and color removal from azure B dye ,[AB]=$1x10^{-5}$M, pH=6 at T=298k by using UV/H_2O_2 method.



Figure(3-21):Effect of different initial H_2O_2concentration on COD and color removal from azure C dye ,[AC]=1x10^{-5}M, pH=6 at T=298k by using UV/H_2O_2 method.

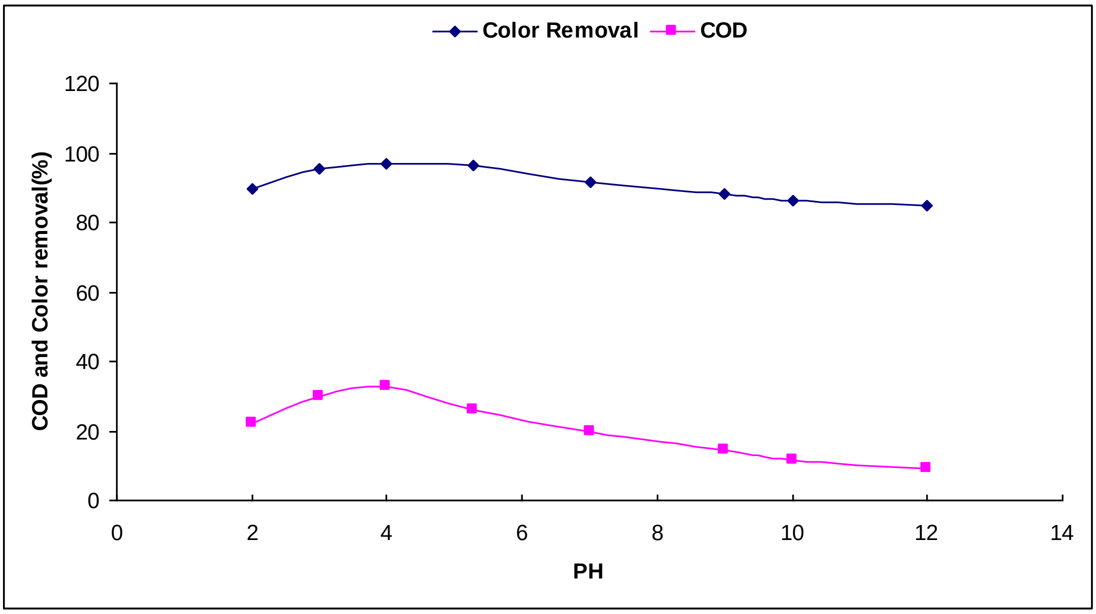
3-3-Effect of Initial pH

The effect of pH was evaluated at pH media (2,3,4,5,7,9,10 and 12) . From Figure(3-22) shows the gradient of relative dye concentration Ct/Co under increasing of irradiation time. The results deduced the high color removal was 96.8% under acidic medium at pH= 4 from azure A and low value was obtained in basic media was 89.6%. The increase of the rate of removing the color in low pH value due to more $^{\cdot}$OH radical generation changes in the structure of the molecule because of having a free hydrogen atom which makes the dye molecule exposed for attack by the hydroxyl radical in acidic conditions (167). Hydrogen peroxide undergoes decomposition in alkaline medium the removal was low because the generation of $HO^{\cdot}$ slowed down and decomposition of oxygen and water rather than producing hydroxyl free radicals under UV irradiation(168). The effect of different pH media on the color and COD removal of azure A dye by using the UV/H_2O_2 method was studied as show in Figure (3-23). The experiments are conducted at $1x10^{-5}$ M dye concentration in presence of 500mg/L H_2O_2 dose .

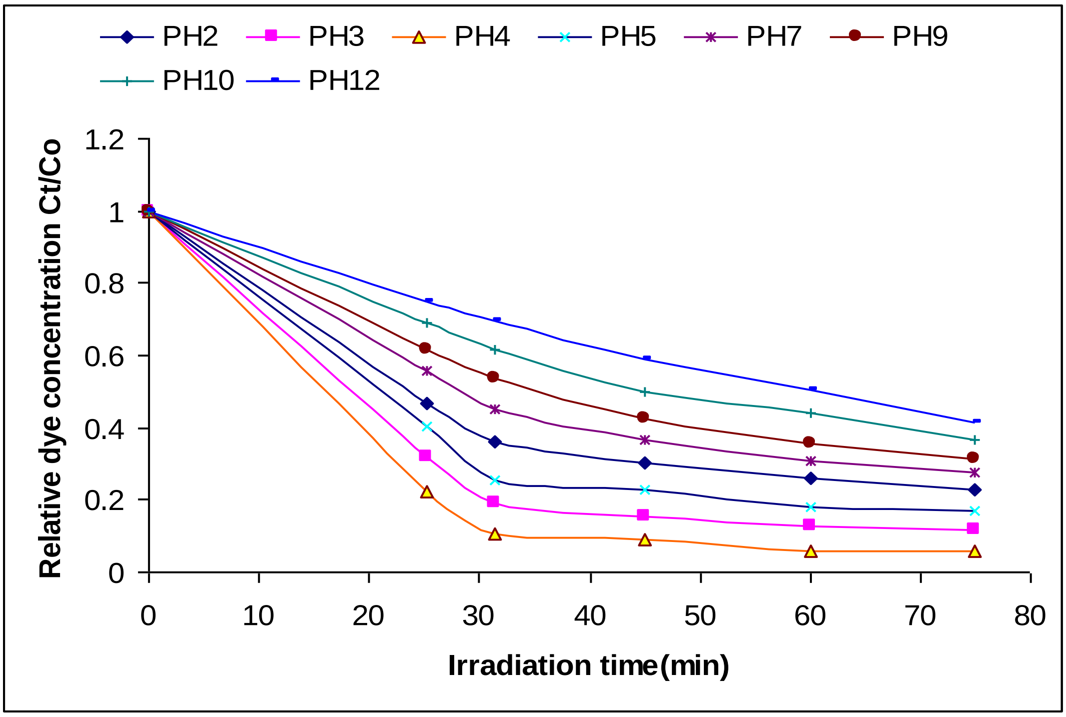


Figure(3-22):Effect of different pH value on color removal of azure A dye as function of irradiation time using UV/H_2O_2/ method,[AA]=$1X10^{-5}$M, ,[H_2O_2]=(500mg/L), T=298k.

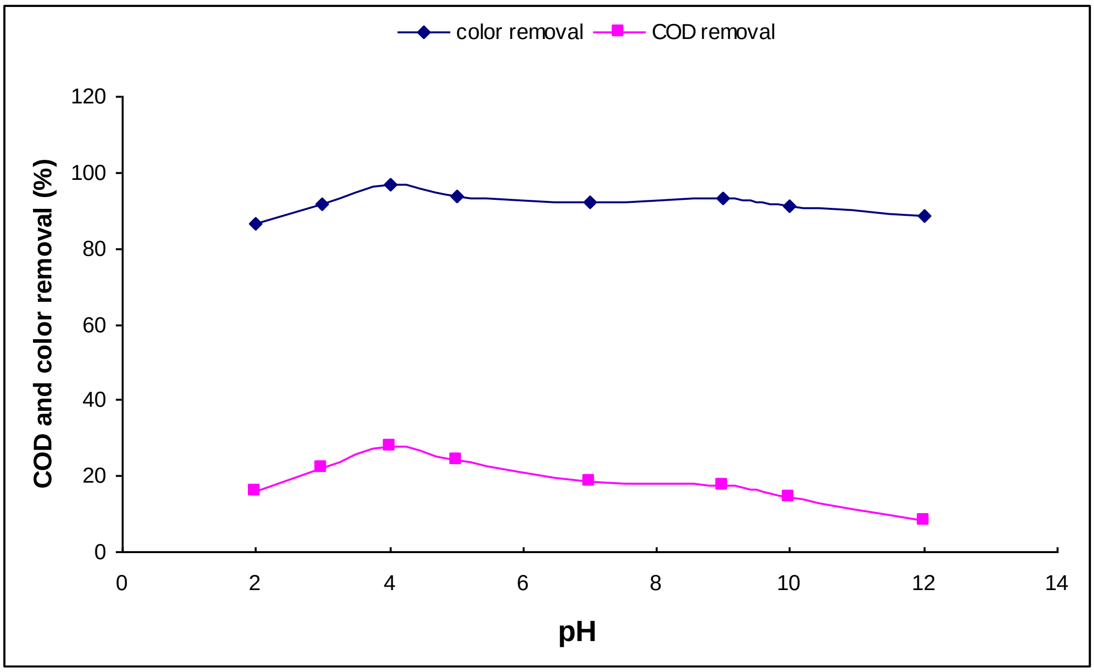
Returned the same experiments but using azure B and azure C dyes with ($1x10^{-5}$M)concentration, in presence of 500mg/L H_2O_2dose at different initial pH values ranges from 2 to 12, for 75 minutes observed the effect of pH on photo degradation is very important. The result is shown in Figure(3-24) , Figure(3-26) the high color removal of azure B 97.7% and azure C 97.4% are observed at pH 4 and decrease slightly in alkaline media in presence UV. Figure(3-25), Figure(1-27), show effect of different pH media on the color and COD removal of azure B and C dyes by using the UV/H_2O_2 method.



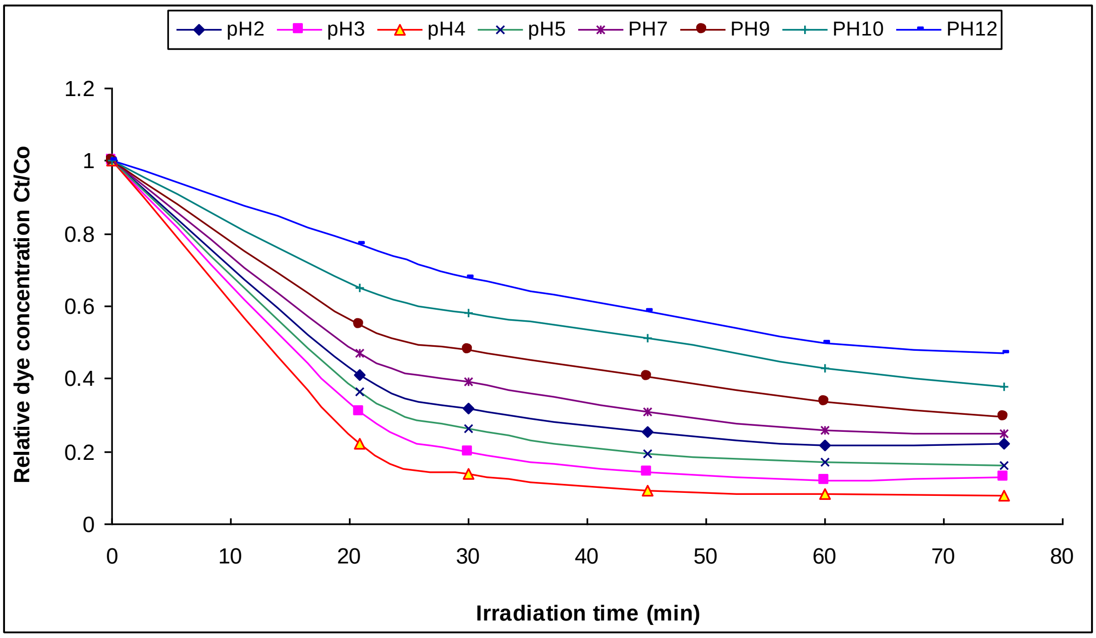
Figure(3-23):Effect of the initial pH on the COD and color removal from azure A dye[AA]=1x10^{-5}M,[H_2O_2]=(500mg/L),by using UV/H_2O_2 method, T=298K.



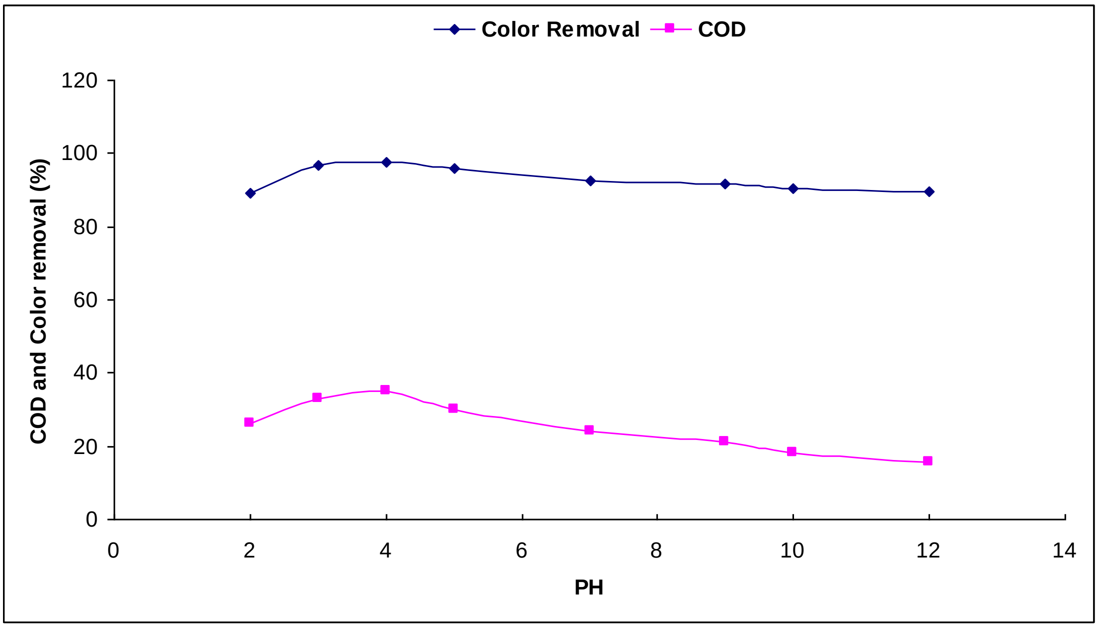
Figure(3-24):Effect of different pH value on color removal of azure B dye as function of irradiation time using UV/H_2O_2/ method, [AB]=1X10^{-5}, ,[H_2O_2]=(500mg/L), T=298k.



Figure(3-26):Effect of the initial pH on the COD and color removal from azure B dye[AB]=1x10^{-5}M,[H_2O_2]=(500mg/L),by using UV/H_2O_2 method, T=298K.



Figure(3-25):Effect of different pH value on color removal of azure C dye as function of irradiation time using UV/H_2O_2/ method, [AC]=1X10^{-5}, [H_2O_2]=(500mg/L), T=298k.

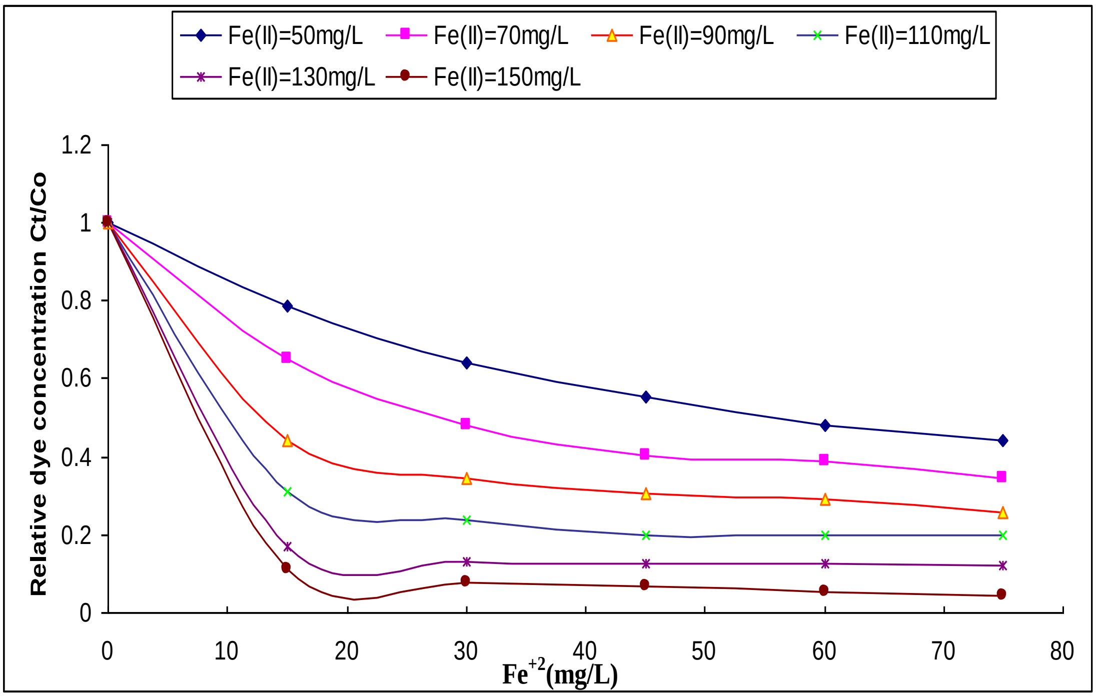


Figure(3-27):Effect of the initial pH on the COD and color removal from azure C dye[AC]=$1x10^{-5}$M,[H_2O_2]=(500mg/L),by using UV/H_2O_2 method, T=298K.

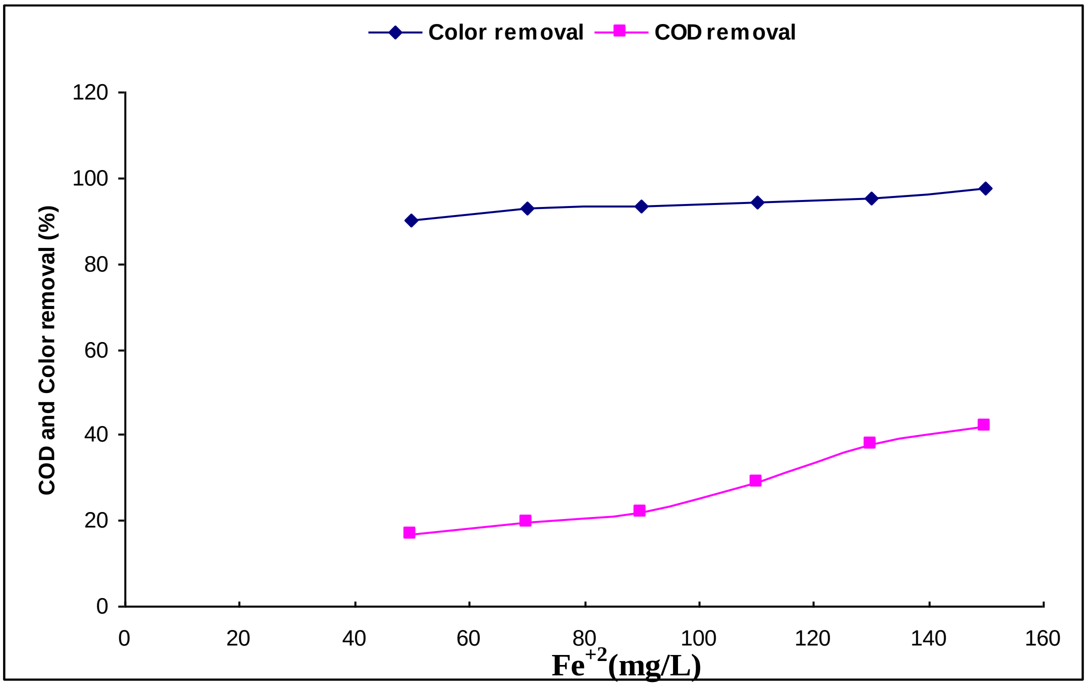
3-4- Fenton's system

3-4-1-Effect of Initial Ferrous ion Concentration

Carried out Fenton reaction on dye azure A concentration ($1x10^{-5}$M) under the same condition include by using various concentration of ferrous ion in the range 50- 150m g/L in the presence of fixed concentration of H_2O_2(500mg/L). Figure(3-28) show the decolourization of azure A as a function of UV irradiation time for various concentration of ferrous ion. In this study the effect of Fe^{+2} dosage in the Photo-Fenton oxidation process on the COD and color removal shown in Figure(3-29), higher dosages of Fe^{+2} lead to a high level of COD removal because a large amount of Fe^{+2} can promote the formation of OH through(169) .

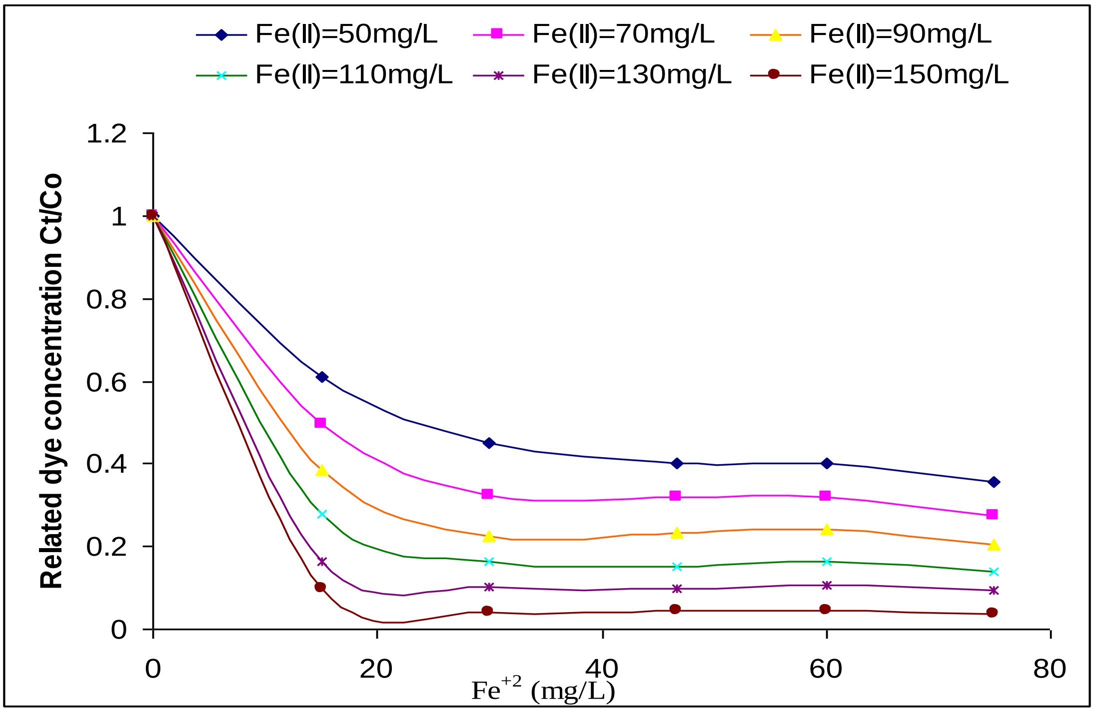


Figure(3-28):Effect of different Fe^{+2}concentration on the color removal of azure A dye as a function of irradiation time.[AA]=1X10^{-5}M**,** ,[H_2O_2]=(500mg/L), pH= 4, T=298k by using UV/ H_2O_2 / Fe^{+2} method.

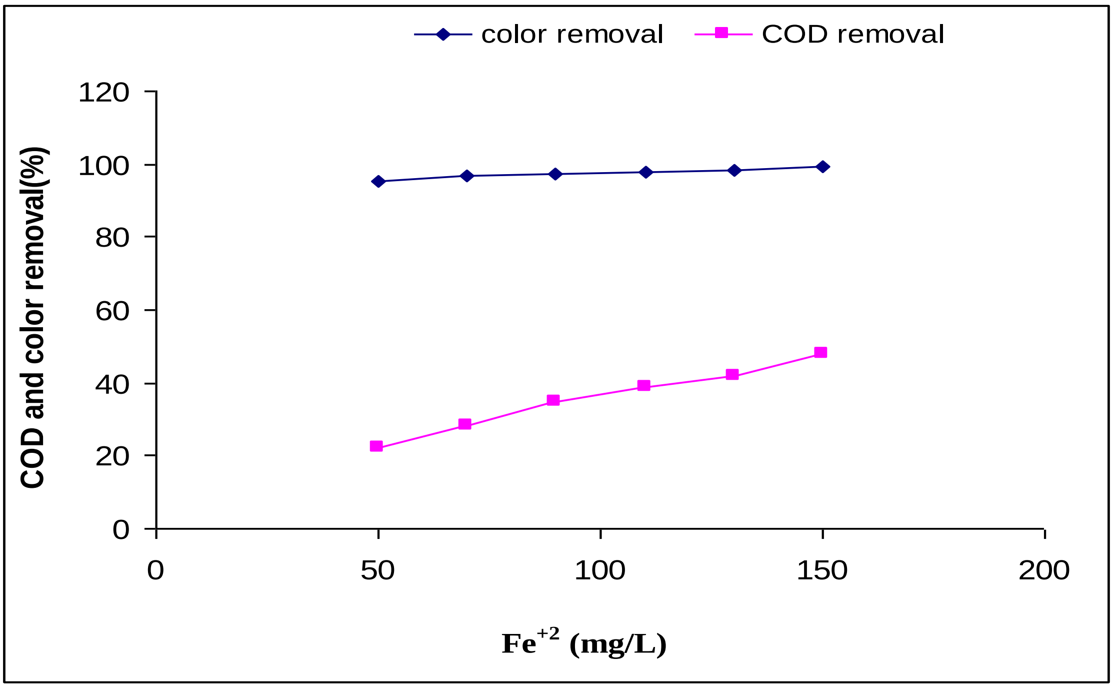


Figure(3-29): Effect of Fe^{+2} on the COD and color removal from azure A dye [AA] =1 X 10^{-5}M ,[H_2O_2]=(500mg/L), pH= 4 , T= 298K by using UV/ H_2O_2 / Fe^{+2} method.

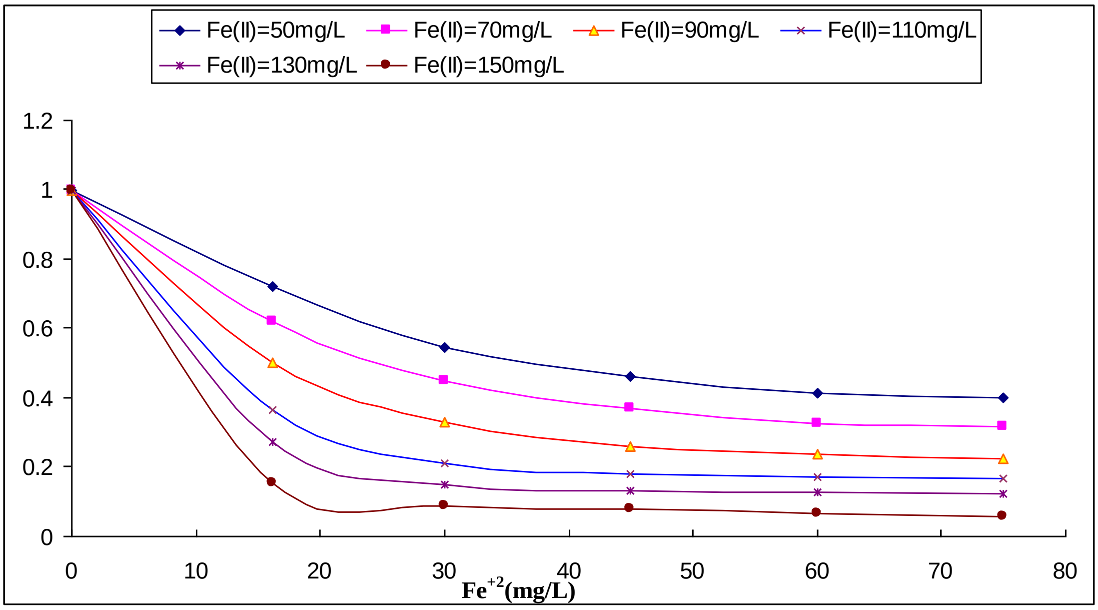
Returned the same experiments but using azure B and azure C dyes with ($1x10^{-5}$M)concentration, in presence of 500mg/L H_2O_2dose and using various concentration of ferrous ion, the rate of the degradation by H_2O_2 alone is extremely low for many dyes .Also addition of Fe^{+2} accelerate the generation of hydroxyl radical (170). Figure(3-30)and Figure(3-32) shows the decolourization of azure B and C dyes as a function of UV irradiation time . Figure(3-31)and Figure(3-33) shows the effect of Fe^{+2} dosage on the COD and color removal .



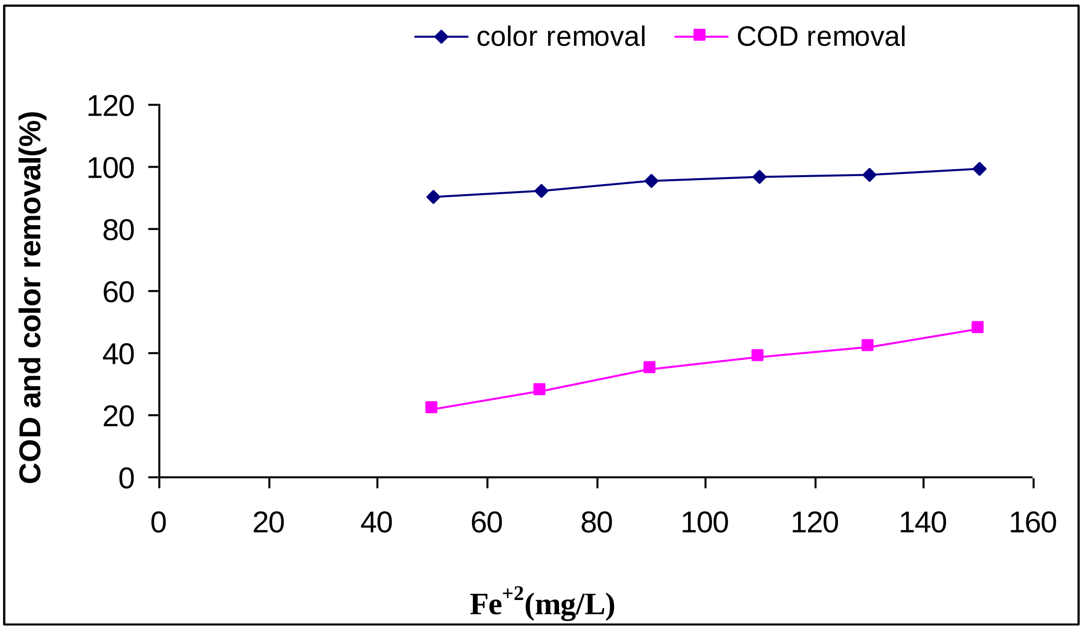
Figure(3-30): Effect of different Fe^{+2}concentration on the color removal of azure B dye as a function of irradiation time [AB]=1X10^{-5}, ,[H_2O_2]=(500mg/L), pH= 4, T=298k by using UV/ H_2O_2 / Fe^{+2} method.



Figure(3-31): Effect of Fe^{+2} on the COD and color removal from azure B dye [AB] =1 X 10^{-5}M ,$[H_2O_2]$=(500mg/L), pH= 4 ,T= 298K by using $UV/H_2O_2/Fe^{+2}$ method.



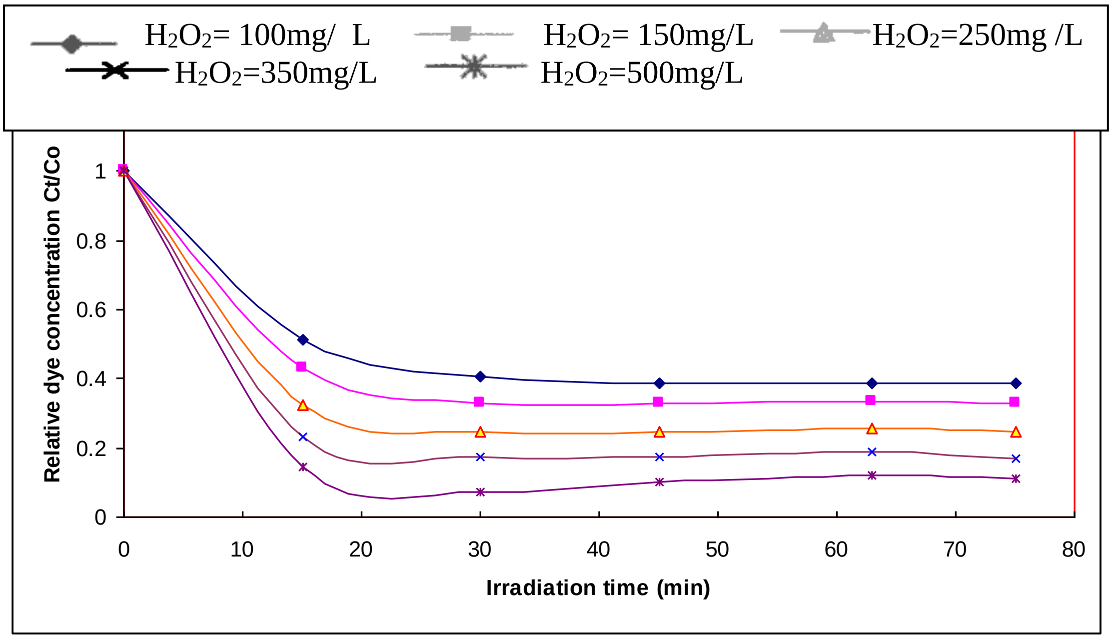
Figure(3-32): Effect of different Fe^{+2}concentration on the color removal of azure B dye as a function of irradiation time [AB]=1X10^{-5}, ,$[H_2O_2]$=(500mg/L), pH= 4, T=298k by using UV/ H_2O_2 / Fe^{+2} method.



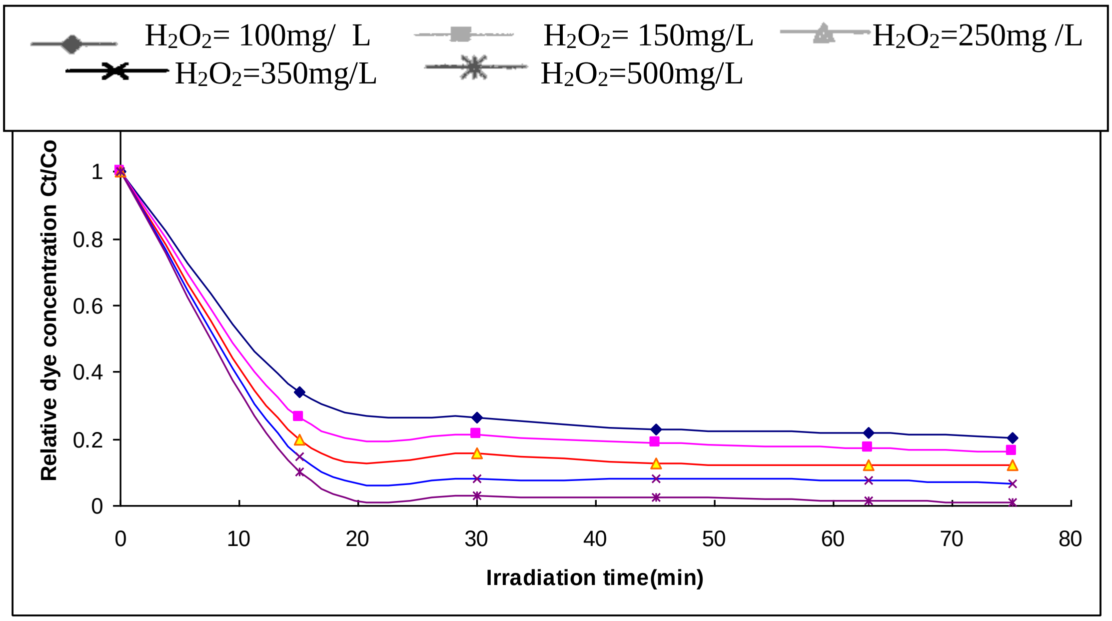
Figure(3-33): Effect of Fe^{+2} on the COD and color removal from azure C dye [AC] =1 X 10^{-5}M ,[H_2O_2]=(500mg/L), pH= 4 , T= 298K by using UV/ H_2O_2 / Fe^{+2} method.

3-4-2-Effect of Initial H_2O_2 Concentration

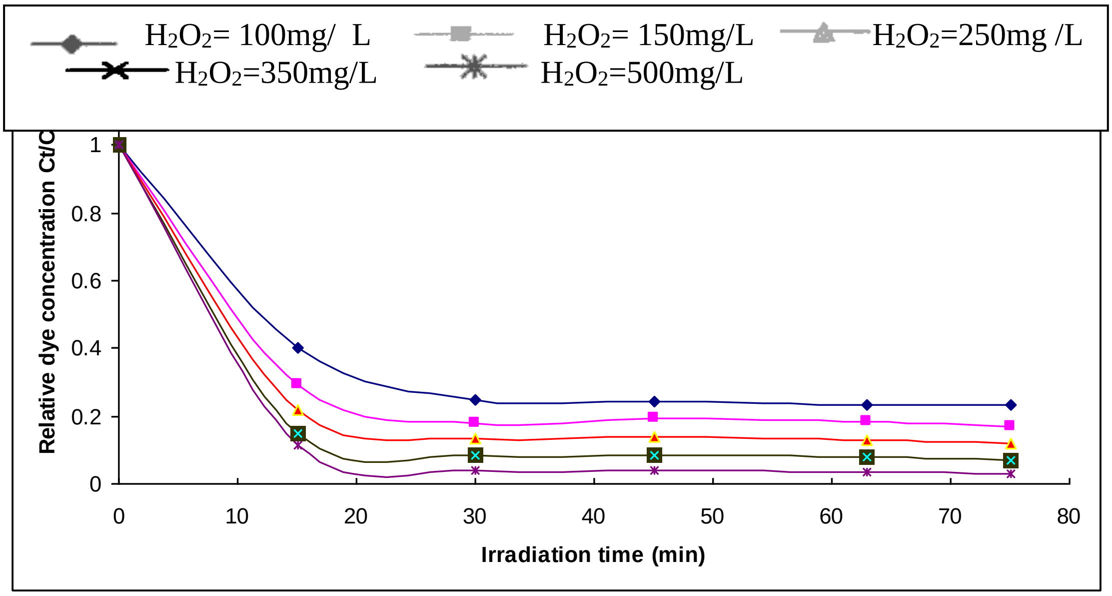
Concentration of hydrogen peroxide has important role in degradation of azure(A,B,C) dyes in Fenton systems . As it observed through experiments that were carried out using changing concentration of hydrogen peroxide ranging 100 – 500 mg/L at constant concentration of ferrous ion (150mg/L). This prove effectiveness of UV irradiation in color removal. As the H_2O_2 dosages increasing the removal percentage of color increased of azure A dye from 93.6%-98.1 and the COD increased from 26%-44% ,the removal percentage of color of azure B increased from 97%-99.1% and the COD increased from 33%-56% and the removal percentage of color of azure C increased from 94.2%-98.8% and the COD increased from 29.4%-52%. Figures (3-34), Figure (3-36), Figure (3-38), shows the color removal of azure dyes as a function of UV irradiation time for various initial H_2O_2 dosages. Figures (3-35), figure (3-37), figure (3-39), show effect of H_2O_2 on COD and color removal from azure dyes . The increasing of concentration of hydrogen peroxide effect in kinetic reaction, therefore the increasing of hydrogen peroxide concentration the ratio of degradation of pollutants increases because of increase quantity of generated hydroxide radicals and this conforms with many studies(166-171).



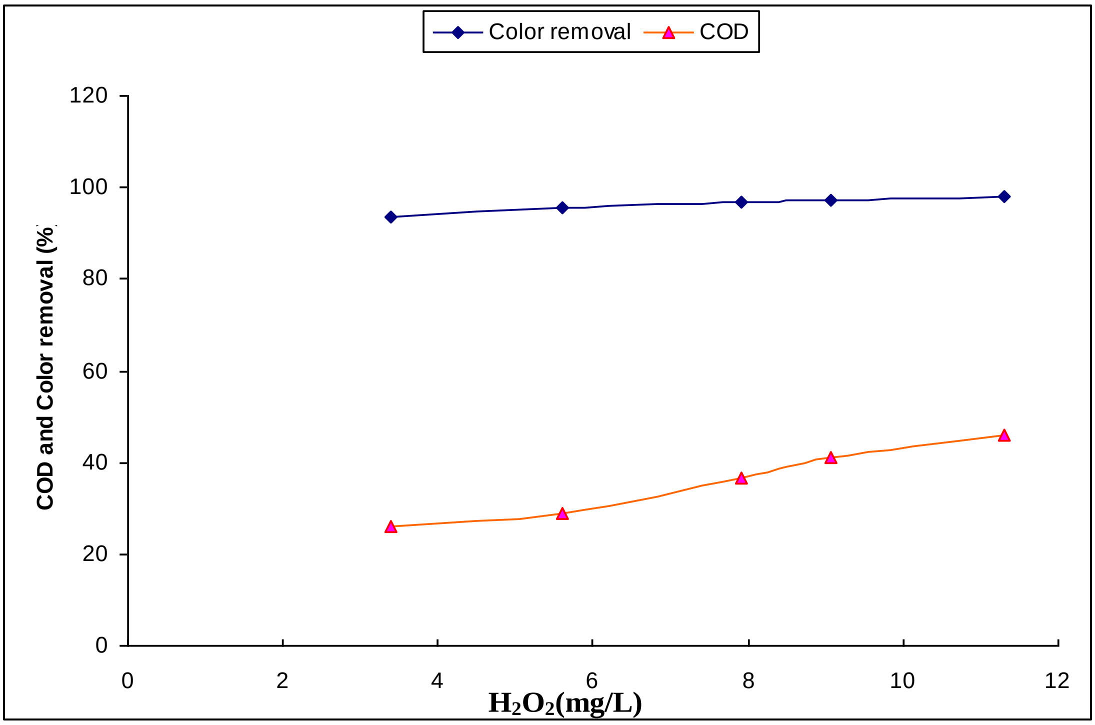
Figure(3-34): Effect of different initial H_2O_2 concentration on the color removal from azure A $[AA]=1X10^{-5}$ M, $[Fe^{+2}]=(150mg/L)$, ,$[H_2O_2]=(500mg/L)$, pH= 4, T=298k by using UV/ H_2O_2 / Fe^{+2} method.



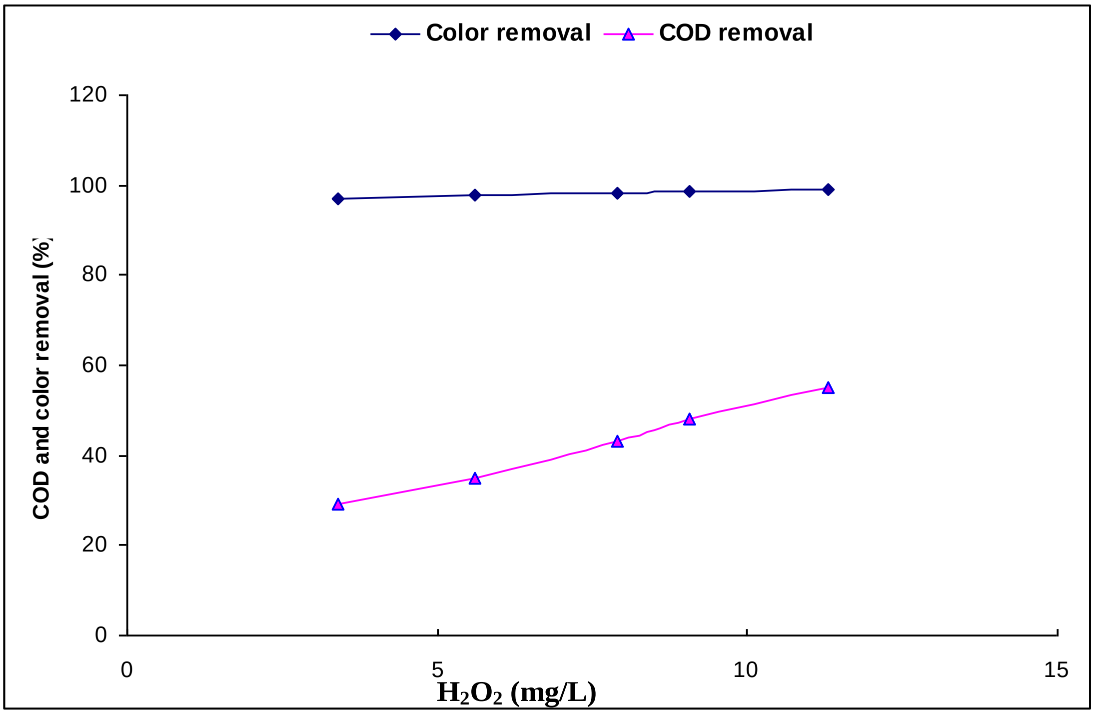
Figure(3-36): Effect of different initial H_2O_2 concentration on the color removal from azure B [AB]=1X10^{-5} M, [Fe^{+2}]=(150mg/L), ,[H_2O_2]=(500mg/L), pH= 4, T=298k by using UV/ H_2O_2 / Fe^{+2} method.



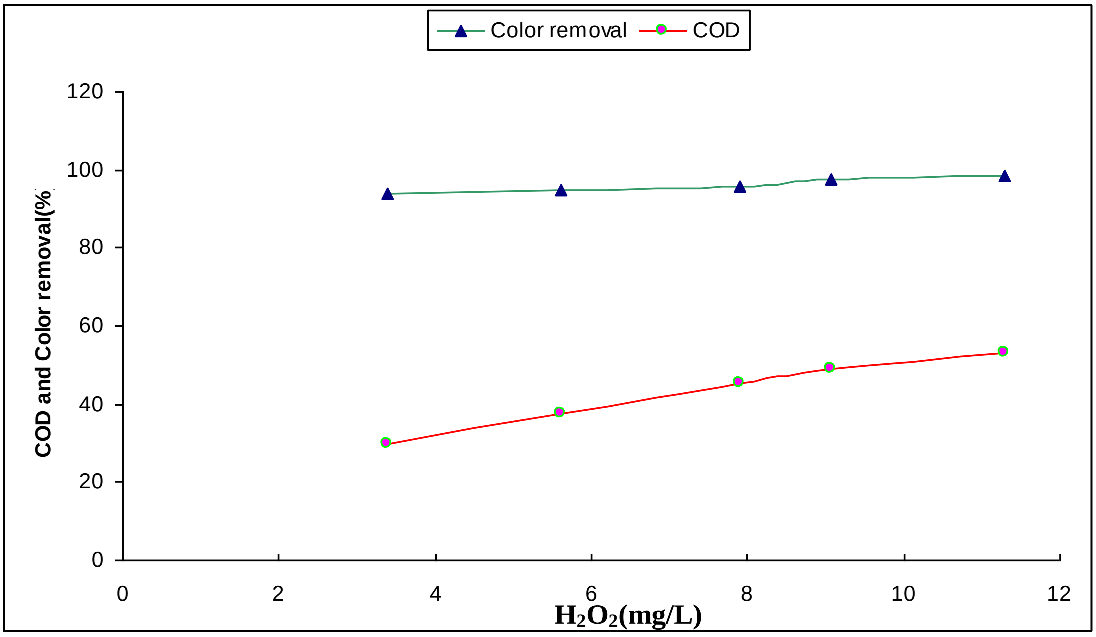
Figure(3-38): Effect of different initial H_2O_2 concentration on the color removal from azure C [AC]=1X10^{-5} M, [Fe^{+2}]=(150mg/L), ,[H_2O_2]=(500mg/L), pH= 4, T=298k by using UV/ H_2O_2 / Fe^{+2} method.



Figure(3-35): Effect of H_2O_2 on the COD and color removal from azure A dye [AA]=1X10^{-5}M ,[Fe^{+2}]=(150mg/L), pH= 4, T=298k by using UV/ H_2O_2 / Fe^{+2} method.



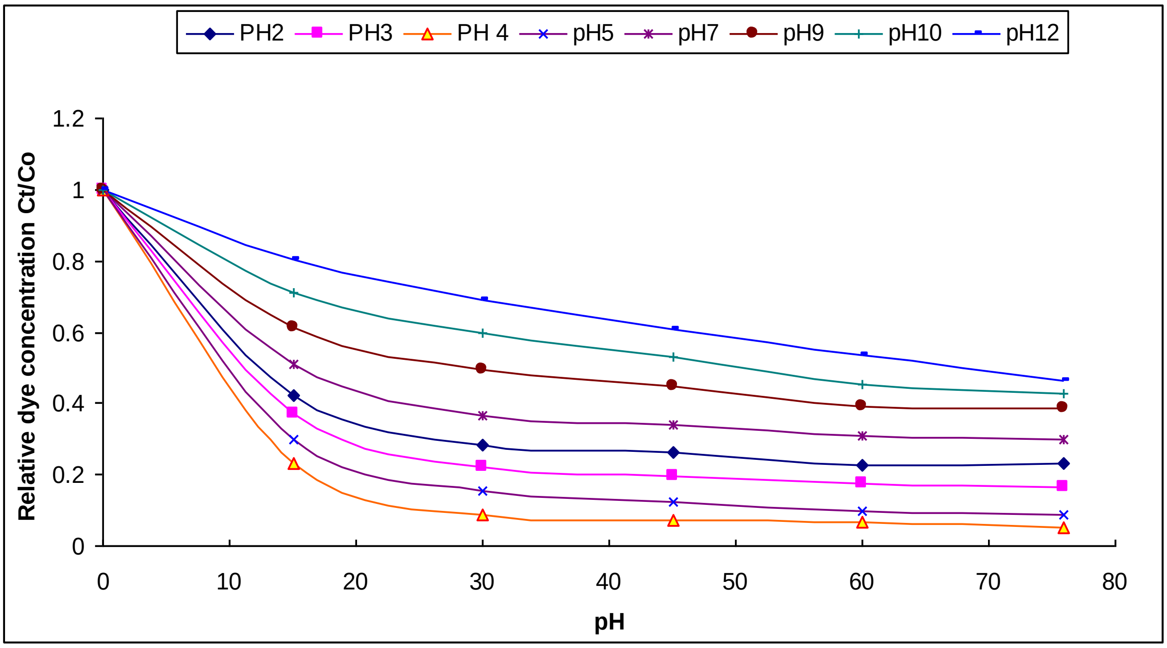
Figure(3-37): Effect of H_2O_2 on the COD and color removal from azure B dye [AB]=1X10^{-5}M ,[Fe^{+2}]=(150mg/L), pH= 4, T=298k by using UV/ H_2O_2 / Fe^{+2} method.



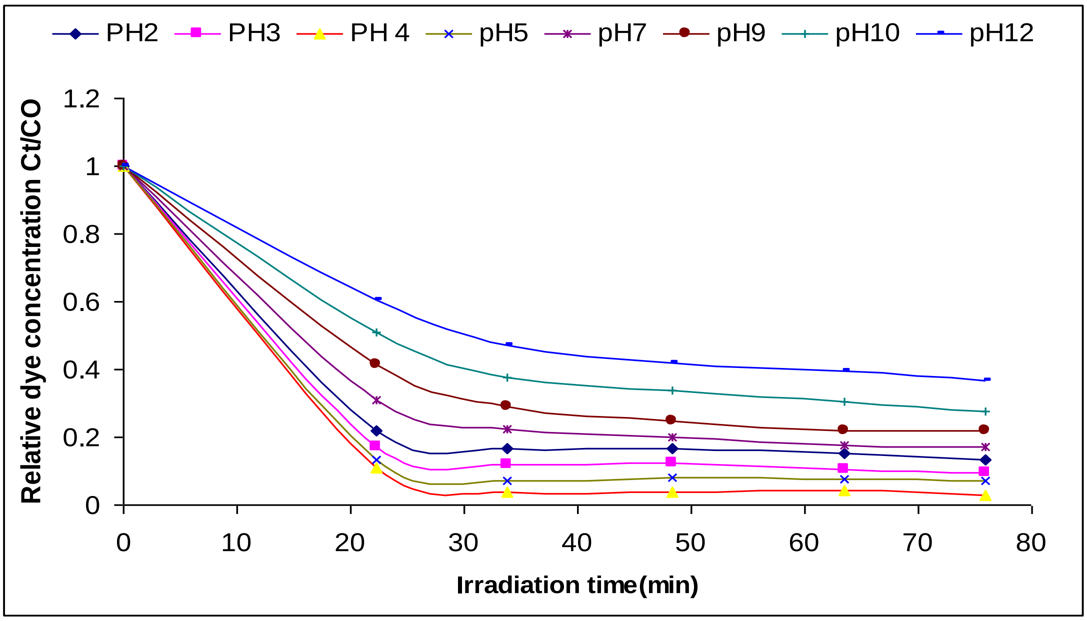
Figure(3-39): Effect of H_2O_2 on the COD and color removal from azure C dye $[AC]=1X10^{-5}M$,$[Fe^{+2}]=(150mg/L)$, pH= 4, T=298k by using UV/ H_2O_2 / Fe^{+2} method.

3-4-3- Effect of Initial pH

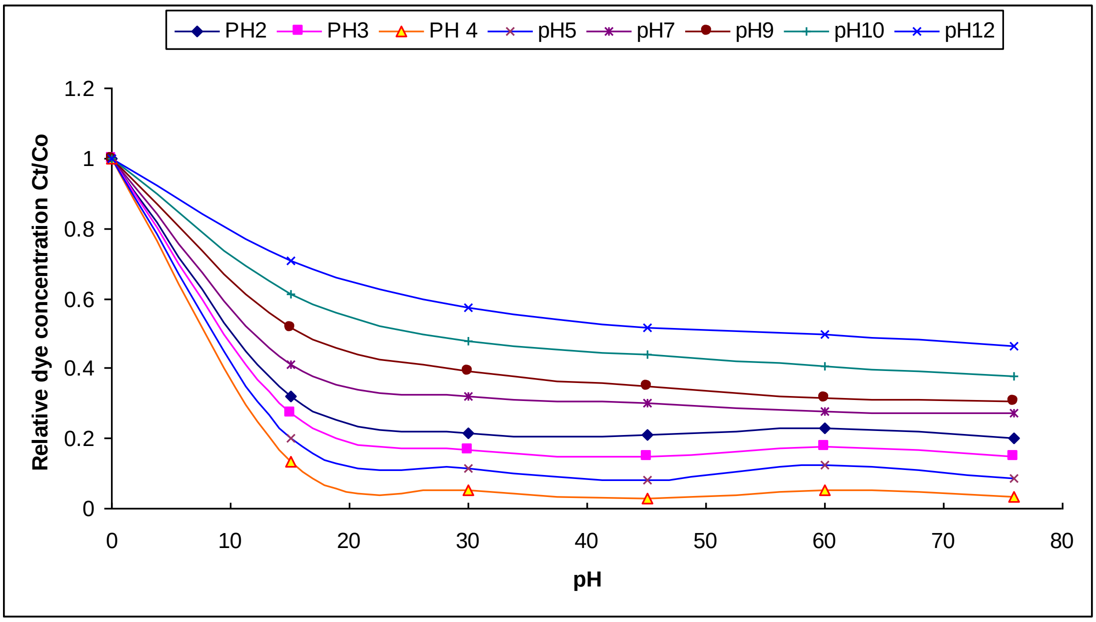
The results showed a clear effect of initial pH in oxidation reaction of azure (A,B,C) dyes. The high color removal was obtained under acidic media (due to more ·OH radicals generation) and low color removal in basic conditions (due to $Fe(OH)_3$ formation) and this conforms with many studies(172-173). The higher ratio color removal of azure dyes were obtained under acidic media at pH=4 under UV light and decreasing ratio in basic media. The higher decolourization rate demand reduce pH value because changing in molecular structure. From Figure(3-40), Figure(3-42)and Figure(3-44), it has been found that during 75 min of UV irradiation, the relative dye concentration Ct/Co was decreased as the pH value increased . The high color removal under acidic conditions is due to more $^{\bullet}OH$ generate, and low color removal at basic conditions because Fe^{+2} ions rapidly oxidized to Fe^{+3} ions formation $Fe(OH)_3$.



Figure(3-40):Effect of different pH value on color removal from azure A dye as function of irradiation time, $[AA]=1X10^{-5}M$, $[Fe^{+2}]=(150mg/L)$, pH= 4, T=298k using $UV/H_2O_2/Fe^{+2}$method, ,T=298k.

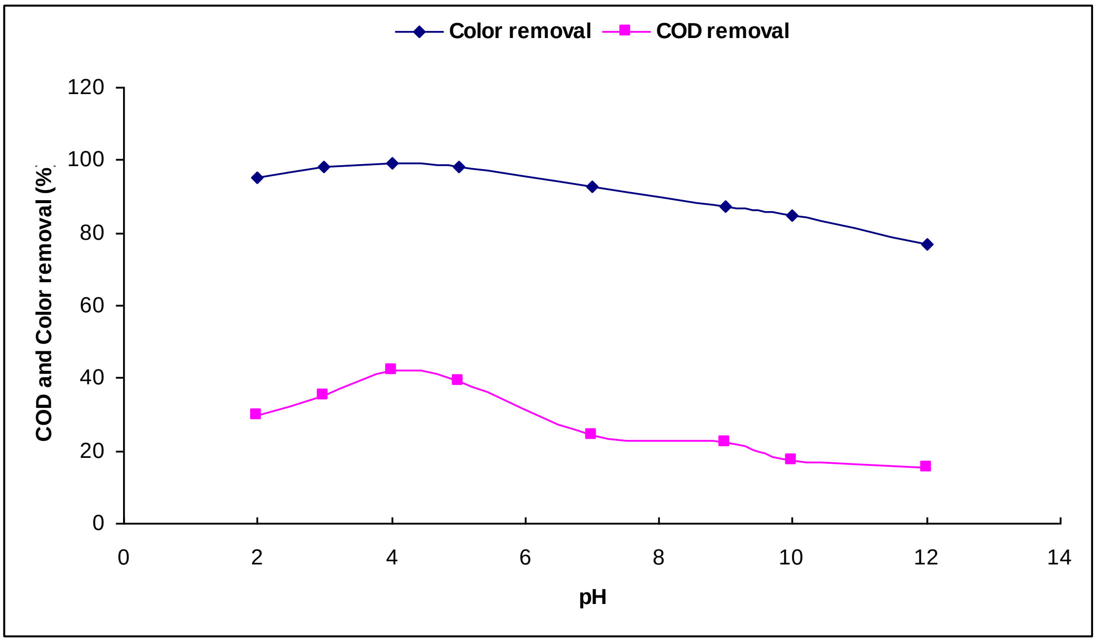


Figure(3-42):Effect of different pH value on color removal from azure B dye as function of irradiation time, $[AB]=1X10^{-5}M$, $[Fe^{+2}]=(150mg/L)$, pH= 4, T=298k using $UV/H_2O_2/Fe^{+2}$method, ,T=298k.

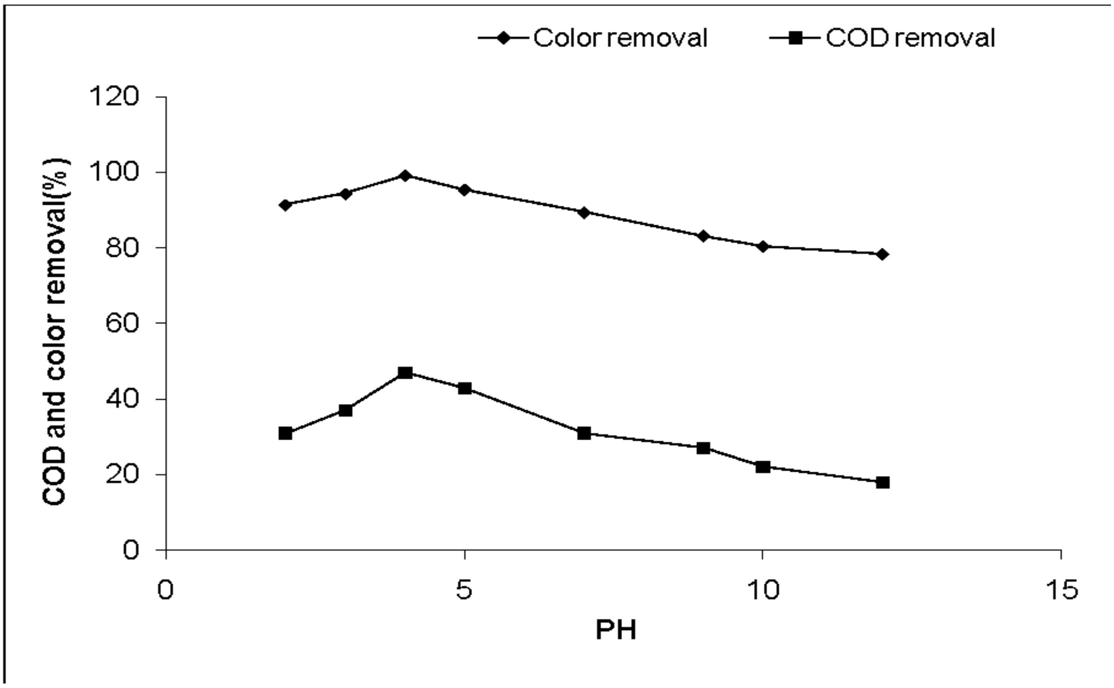


Figure(3-44):Effect of different pH value on color removal from azure C dye as function of irradiation time, [AC]=1X10^{-5}M, [Fe^{+2}]=(150mg/L), pH= 4, T=298k using UV/H_2O_2/Fe^{+2} method, ,T=298k.

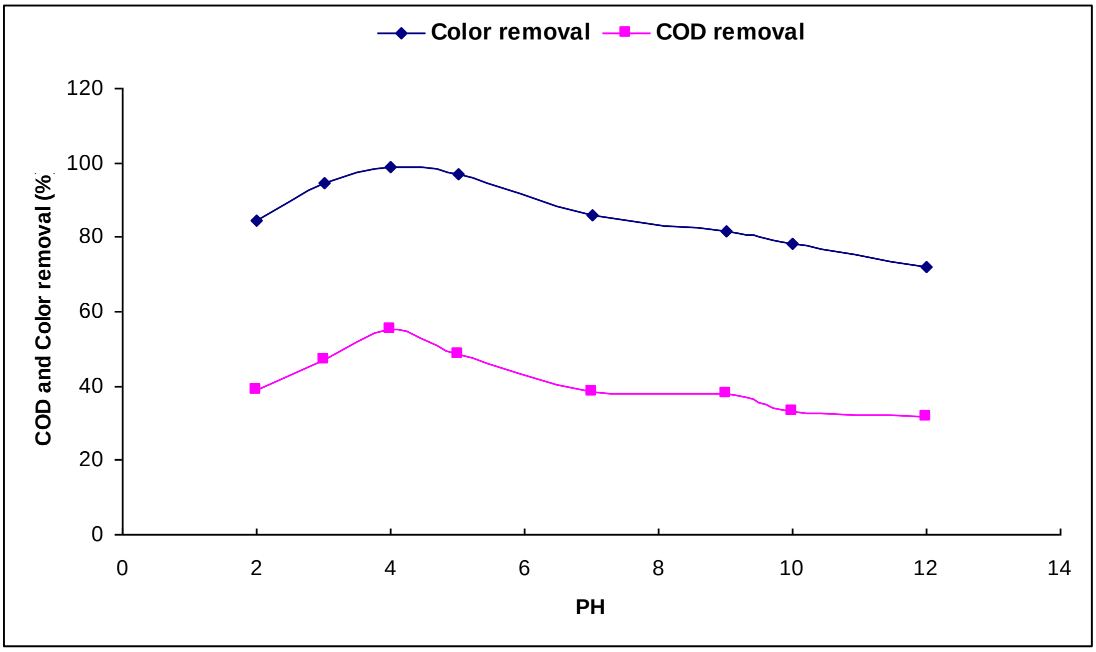
The COD reached the maximum removal after irradiation of dye 75 minutes at the initial pH value equal of 4 . In basic media the removal was low because the generation of$^{\cdot}$ OH slowed down due to the decomposition of H_2O_2 to H_2O and O_2(165). The results improved the highest ratio at the initial pH = 4 by the Photo - Fenton oxidation process must be adjusted either by HCl or NaOH at 4 acidic medium. This pH was consistent with some previous works(174). Figure (3-41), (3-43)and (3-45) show effect of initial pH on COD and color removal.



Figure(3-41): Effect of the initial pH on the COD and color removal from azure A dye[AA]=1x10^{-5}M,[H_2O_2]=(500mg/L), [Fe^{+2}]=(150mg/L), T=298K by using UV/H_2O_2/Fe^{+2} method.



Figure(3-43):Effect of the initial pH on the COD and color removal from azure B dye[AB]=1x10^{-5}M,[H_2O_2]=(500mg/L), [Fe^{+2}]=(150mg/L), T=298K by using UV/H_2O_2/Fe^{+2} method.



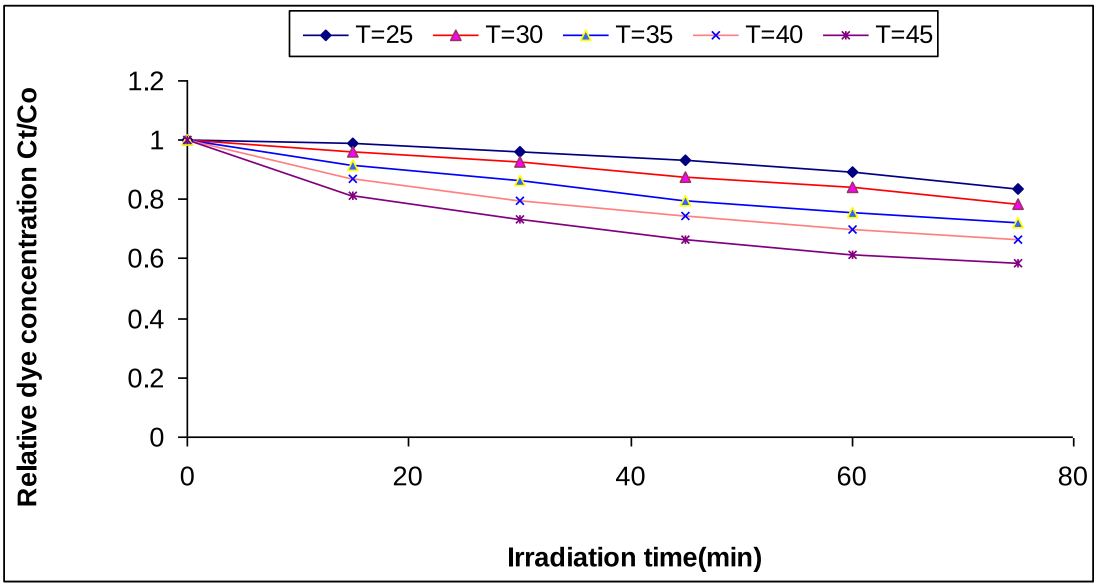
Figure(3-45):Effect of the initial pH on the COD and color removal from azure C dye[AC]=$1x10^{-5}$M,[H_2O_2]=(500mg/L), [Fe^{+2}]=(150mg/L), T=298K by using UV/H_2O_2/Fe^{+2} method.

3-5- Effect of Temperature .

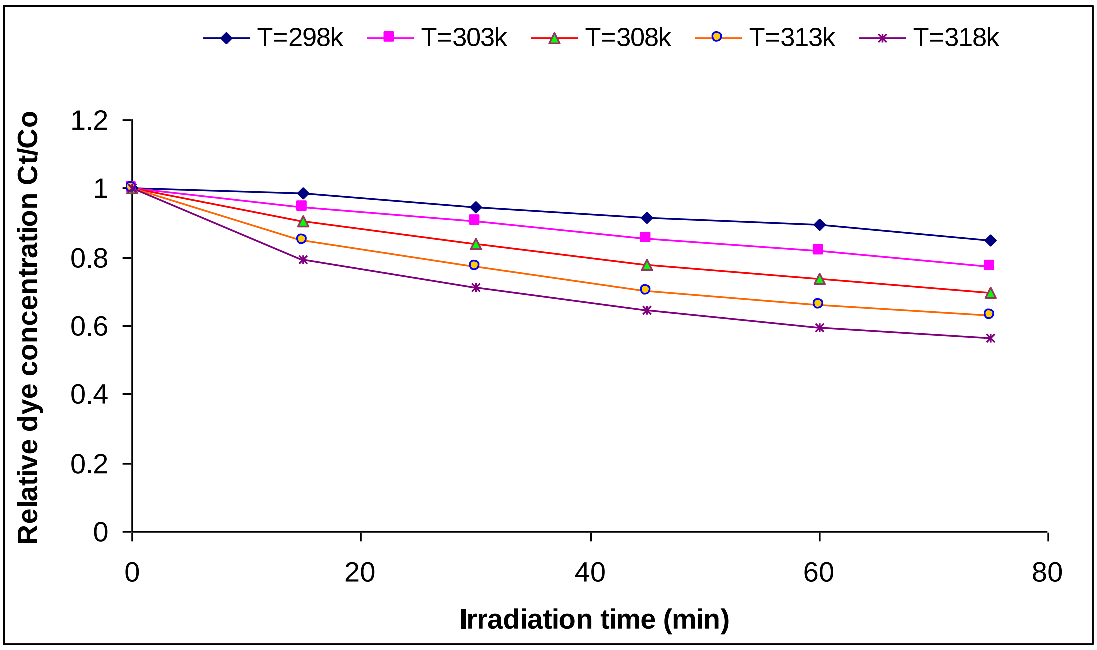
Temperature is an important kinetic factor on enhancing the color and COD removal percentage . The degradation of dyes were performed by irradiation the azure dyes (A,B,C) removal rate by using the UV method increased with increasing temperature of the system as shown in Figure (3-46),(3-47) and (3-48). High temperature increases the generation rate of $^{\bullet}$OH or directly affects the reaction rate with the dye molecule(175).

Given that the overall rate observed to be depended on availability of $^{\bullet}$OH, the experiments were carried out in a range between 298-318k and the results are clarified in the Figure (3-49), (3-50) and (3-51). In this study we found out that with the increase of the temperature the value of

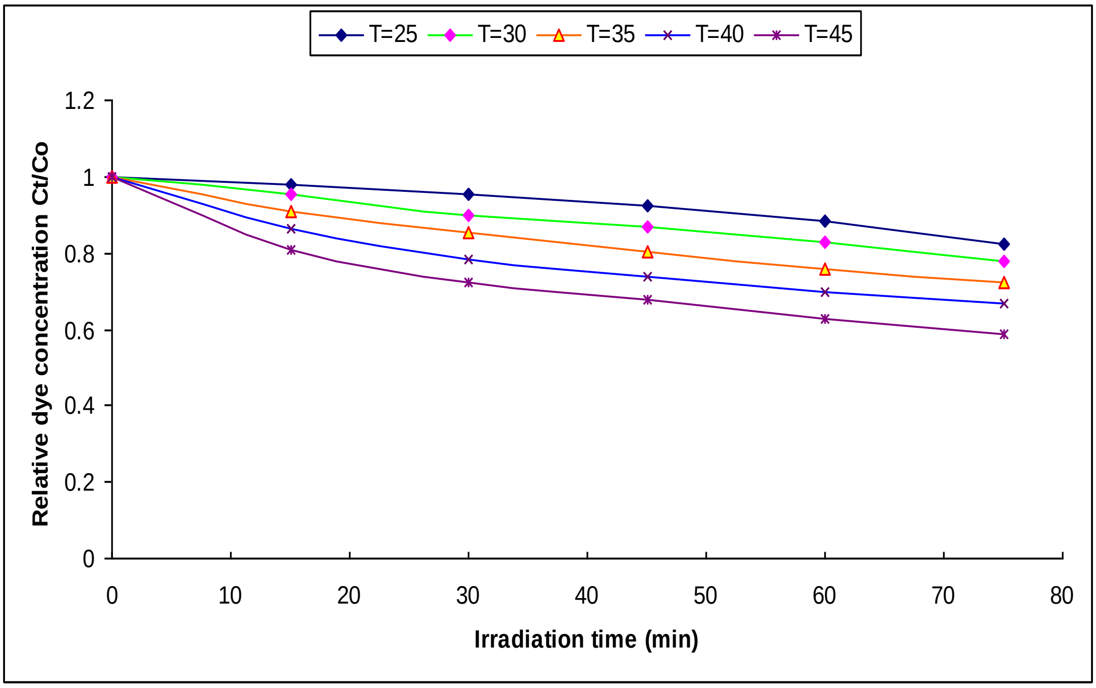
COD removal increases because a decrease in the oxygen amount demanding for oxidation. Also, Trillas et al., and Chen reported that raising the temperature of reaction enhances the rate of photocatalytic degradation significantly(176-177).



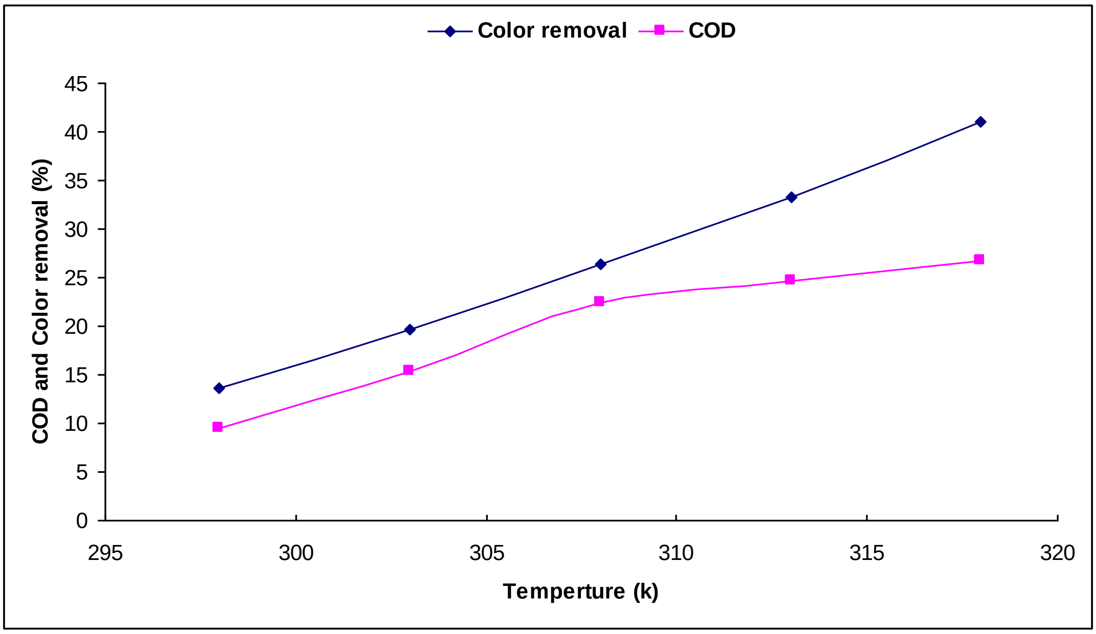
Figure(3-46): Effect of different temperature on the color removal of azure A using UV method. [AA]=$1x10^{-5}$M , pH=6 .



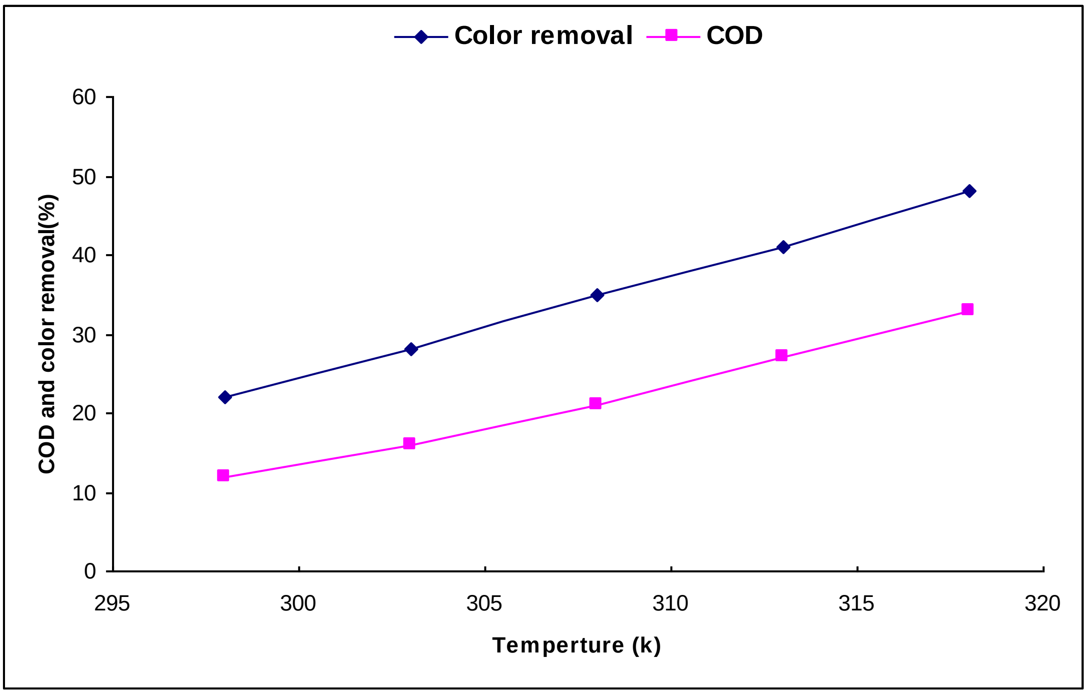
Figure(3-47): Effect of different temperature on the color removal of azure B using UV method. [AB]=$1x10^{-5}$M , pH=6 .



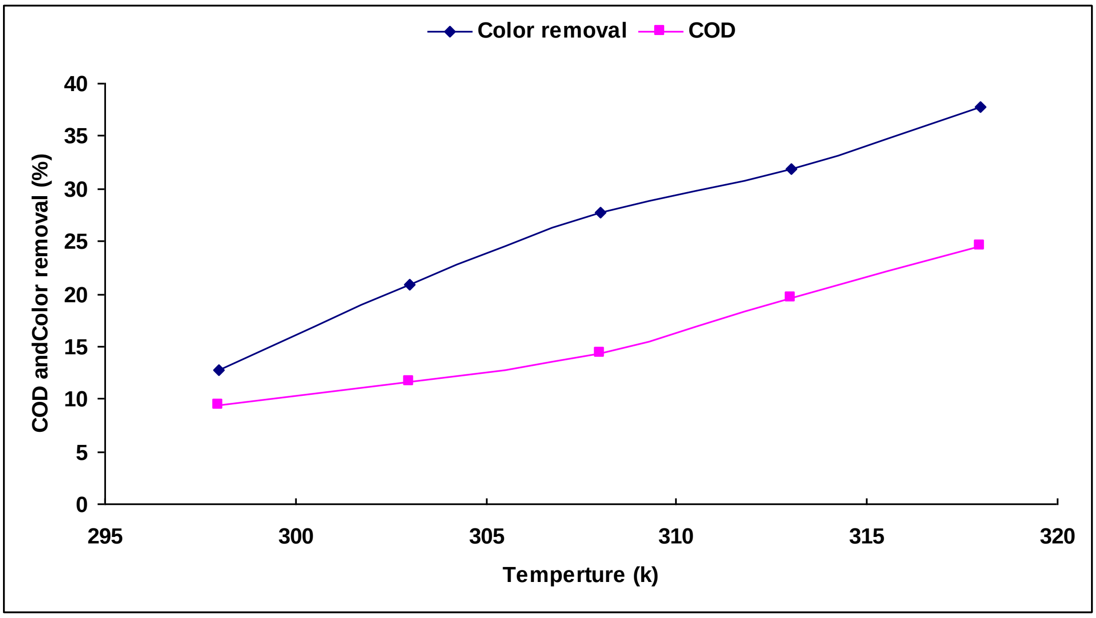
Figure(3-48): Effect of different temperature on the color removal of azure C using UV method. [AC]=$1x10^{-5}$M , pH=6 .



Figure(3-49): Effect of the temperature degree on color removal and COD of the [AA] =$1X10^{-5}$M at pH=6.



Figure(3-50): Effect of the temperature degree on color removal and COD of the [AB] $=1X10^{-5}M$ at pH=6.

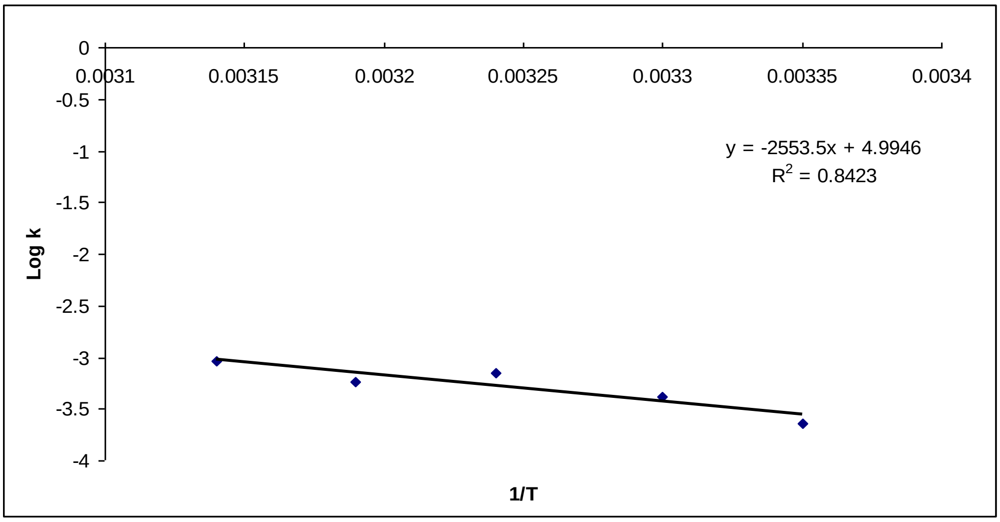


Figure(3-51): Effect of the temperature degree on color removal and COD of the [AC] $=1X10^{-5}M$ at pH=6.

The Arrhenius equation is used to describe the relationship between rate constants and temperature and draw this the relationship as show in Figures (3-52),(3-53)and (3-54)from the azure dyes (A,B,C).

$k = A\, e^{(-Ea/RT)}$ …………(8)

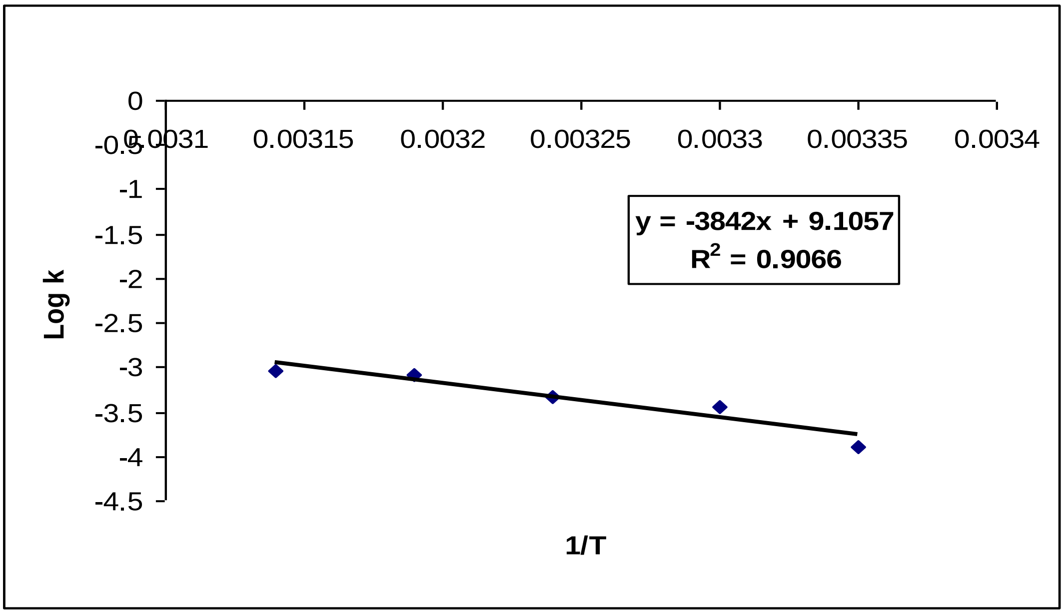
where: k : rate constant, A : frequency factor, Ea : activation energy, R : ideal gas constant.



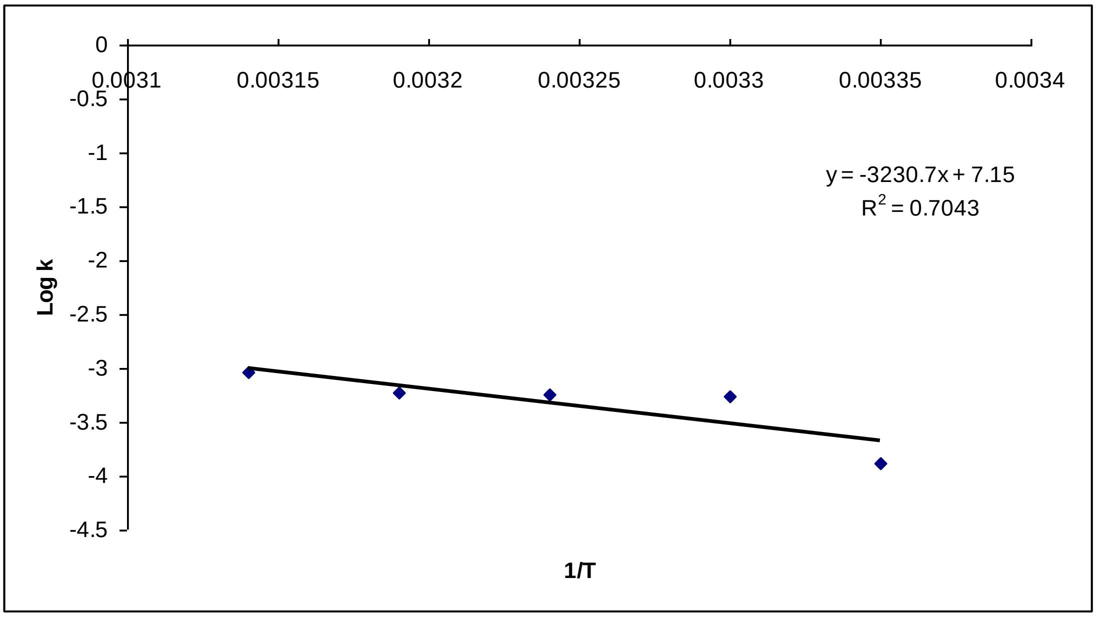
Figure(3-52): Arrhenius plot of color removal of dye.[AA]= $1x10^{-5}$ M, pH=6.

The activation energy Calculated from in plot was equal 43.23KJ/mole with the presence of light and alone dye .

The activation energy Calculated from in plot was equal 74.16 KJ/mole with the presence of light and alone dye .



Figure(3-53): Arrhenius plot of color removal of dye.[AB]= $1x10^{-5}$ M, pH=6.



Figure(3-54): Arrhenius plot of color removal of dye.[AC]= $1x10^{-5}$ M, pH=6.

Calculated the activation energy in plot was equal 61.14 KJ/mole with the presence of light and alone dye .

4-1- Conclusions :

1- The degradation was strongly influenced by various parameters, particularly the initial H_2O_2 dosage, dye concentration, pH, temperature as well as irradiation time.

2- The study showed that increasing the concentration of the dye reduces the speed of degradation , because high concentrations of the dyes reduce the ability of light penetration lead to reduces the speed of the degradation and the color removal of dyes .

3- The study showed that the effect of hydrogen peroxide concentration of the dyes clear in the absence of UV light. where the removal rate increases with increasing the concentration of hydrogen peroxide in order to increase the amount of hydroxyl radicals generated.

4- The photooxidation of azure dyes by using the UV/H_2O_2 is more effective in an acidic medium and low value was obtained in basic medium with the initial dosage of H_2O_2 ranging between 100-500 mg/L.

5- The study showed when carrying out reactions of Fenton's on azure dyes that the percentage removal increases with increasing the concentration of hydrogen peroxide and the concentration of ferrous ion in presence of UV light .Also, the presence of constant concentration of hydrogen peroxide and ferrous ion increased at pH=4.

6- Higher efficiencies of Color removal and COD removal in presence of Fenton's reagent was achieved at pH media (3,4) ,and high efficiencies were observed by increasing the concentration of Fe^{+2}.

7- The study showed that the effect of temperature in the percentage of color removal has given highest results, in presence of UV light so that the ratio increases with increasing temperature, which means that in presence of UV removal speed higher than in absence. Faster degradation kinetics ,higher Color removal and COD removal efficiency was observed at higher temperature 308K.

4-2- Recommendations :

1- Develop the use of catalytic oxidation technique for use in the treatment of pollution in the waters of rivers and the sea contaminated as well as petroleum products to take advantage of natural conditions of temperature and sunlight.

2- Design the size of the largest reactors for use in the treatment of industrial waste and the removal of organic dyes, pesticides and residues of plants kinds of medicine.

3- The focus of future studies of the use of systems with high efficiency and low cost by taking advantage of sunlight as a source of irradiation.

4- The possibility of coupling these methods with other methods of removing pollutants such as adsorption and chemical methods to achieve the best crash and removal of different pollutants.

5- Conduct advanced research using chlorine dioxide in study different pollutants.

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الخلاصة

في هذه الدراسة تم استعمال طرق الأكسدة المتقدمة Advanced Oxidation Processes AOP،S لغرض إزالة لون إصباغ الازور (A ، B ، C) . تضمنت هذه الدراسة تأثير تركيز الصبغة الابتدائي ، كمية بيرو كسيد الهيدروجين المستخدمة ، درجة الحرارة ، كاشف فنتون، المحلول ، وتأثير زمن التشعيع. تم إجراء التجارب الضوئية جميعها باستعمال مفاعل ضوئي مزود بمصدر للأشعة فوق البنفسجية هو مصباح زئبقي واطئ الضغط (Low Pressure - LPML) Mercury Lamp وبدرجة حرارة 298K. من الطرق الشائعة لعمليات الأكسدة الكيميائية المستخدمة في معالجة مياه الشرب هي process UV/H_2O_2 ، UV/Ozone، UV/TiO_2 و Fenton's Reagent. تحققت التجزئة التامة في فترة زمنية قصيرة نسبيا(75 دقيقة) من التشعيع. و أسرع إزالة للون في pH منخفضة وعند درجة حرارة عالية، وأفضل نتائج تم الحصول عليها باستخدام نظام فنتون الضوئي. بينت النتائج إن سرعة الإزالة تزداد بزيادة تركيز بيرو كسيد الهيدروجين وايون الحديدوز للوصول إلى القيمة الفضلى، ووجد إن نسبة الإزالة تزداد بزيادة درجة الحرارة مع طاقة التنشيط كما أن طاقة التنشيط لصبغة azure A تساوي (43.23 KJ/mole) بوجود الأشعة فوق البنفسجية أما للصبغتين الأخيرتين فكانت طاقة التنشيط لصبغة Azure B و azure C تساوي(74.16 KJ/mole) و (61.14 KJ/mole)على التتابع. في هذا البحث تم دراسة جميع التأثيرات المشار إليه أعلاه على الحاجة الكيميائية للأوكسجين (COD). تمت دراسة حركية تفاعل إزالة الإصباغ حيث أوضحت النتائج إن سرعة الإزالة تتبع حركيات المرتبة الأولى بالنسبة لتركيز الصبغة. دلت التجارب جميعا التي أجريت بوجود الأشعة فوق البنفسجية أهميتها ودورها في تحفيز

تفاعل أنتاج جذور الهيدروكسيل المسوؤلة عن بدء عملية الأكسدة الضوئية كذلك دلت النتائج أن طريقة فنتون هي الطريقة المثلى لإزالة اكبر كمية من الإصباغ مع تسجيل أعلى قيمة إزالة لإصباغ الازور الثلاثة والجدول الأتي يوضح ذلك .

ت	لإصباغ الازور	أفضل طريقة	أعلى نسبة إزالة منخفضة
-1	A	UV /H_2O_2/ Fe^{+2}	98.1 %
-2	B	UV /H_2O_2/ Fe^{+2}	99.1%
-3	C	UV /H_2O_2/ Fe^{+2}	98.8 %

وزارة التعليم العالي   والبحث العلمي

جامعة القادسية/ كلية التربية

حركيات التحطم الكيموضوئي لإصباغ الازور في محاليلها المائية بواسطة التقنيات المتقدمة

رسالة مقدمة إلى

مجلس كلية التربية / جامعة القادسية

وهي جزء من متطلبات نيل درجة الماجستير

في الكيمياء / الكيمياء الفيزياوية

من الطالبة

أزل شاكر وهيب السنجري

بكالوريوس كيمياء / 2002 م

أشراف

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