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Application of direct and indirect oxidation techniques for degradation of some colored organic pollutants in aqueous solution

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Abstract

Although humans need dyes as they play an effective role in industry, including the textile industry or the cosmetics industry such as shampoo and soap, as well as a colorant agent in food industry, they may make negatively affect the environment, especially water pollution, which leads to the deterioration of public health where dye is an Endocrine Disruption chemical (EDC) which make hormonal imbalance for human so it considers toxic and carcinogenic. The main role in this work is removing dyes through a successful treatment. It is known that dyes have high chemical stability so traditional treatment is ineffective method but AOPs appears its ability on eliminating of dye by mineralization and convert dye to substance like carbon dioxide, water and some inorganic salts. Novacron-Deep red S-B is a textile dye that can be removed with some factors like UV/H_2O_2, Ozone(O_3), Fenton Process (Fe^{2+}/ H_2O_2) and photocatalysis by using Fe_3O_4 catalyst, each factor is using alone or make synergistic effect between them. Furthermore, magnetite has been prepared with a green method by using green tea leaves then make characterization for it by X-Ray-Diffraction (XRD) and scanning electron microscope (SEM).

Keywords: Novacron Deep Red S-B, UV/H_2O_2, Ozone(O_3), Fenton Process, AOPs.

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1. Introduction

No one can deny that Water pollution is one of the most important global challenges and is regards as one of the planet's biggest current challenges where the World Health Organization (WHO) has declared that eighty percent of human illnesses are water-borne [1]. Generally, water pollution arises as a result of existence of different substance which have specific biological, physical and chemical nature [2], form one of the factors that cause water contamination is Prescence of some coloring organic substance in water because of industries. Annually, the synthetic dyes that responsible of degree of color are produced about 7×10^7tones with over ten thousand tons of such dyes used by textile industries [3] These Colored compounds defined as dyes, its specific color depend on chromophore groups like azo, nitro, anthraquinone or methine and auxochrome groups like NH_2, SH and OH that can increase the degree of color [4] So dyes can be categorized into different types according to chemicals structure and based on its application such as acid dyes which considers azo chromophoric systems, has distinct groups like triphenylmethane, anthraquinone, or copper phthalocyanine and this dye can apply on wool an nylon at PH ranges from 3-7 [5], basic dyes often forms from hydrochloride salts that can make logically cations by losing Cl^- anions then producing cations, this type involve compounds monoazoic, azine and diazoic and is distinguishable with its strong colour brightness and intensity and this dye is suitable for silk and nylon [6], direct dyes that comprises from mainly azo compounds (disazo, trisazo and polyazo), Phthalocyanine, Stilbene, Miscellaneous dyes like thiazole and qinoline and this dye doesn't require binder or mordant, this type is suitable for direct dyeing of cotton without the use of a mordant [7], sulfur dyes which consists from bridge of sulfur compounds and its forms represents as sulphide, disulphide and polysulphife that link with some chromophoric groups like thianthrenes, thiazone or thiazole and this type is amorphous colloidal materials and has high molecular weight usually used to dye cotton and has a preference for cellulosics [8], Vat dyes are pigments that doesn't soluble in water and its general chemical composition made up of one or more carbon atoms pairs doubled to an oxygen atoms, vat dyes have three classes as shown conjugated dicarbonyl, Indogoid and Anthraquinonid, vat dyes is suitable for fibres due to its ability of adsorption the diffusion [9], reactive dyes consist of four groups S-F-T-X, where S-group indicates to solubilizing group for water like (COONa or SO_3Na), F-group indicates of chromophore groups which often an azo group, metal-complex azo, triphenyl dioxazine or anthraquinone, T-groups indicates for some linking group to attach reactive system (X-groups) that is accountable for forming covalent bond with cellulose fiber [10], disperse dye is partially soluble in water, it comprises between multiple chromophore where sixty percent of azo group, about twenty five percent anthraquinone dye and the rest is composition among nitro dyes, quinophthalone, naphthoquinone, methine and naphthoquinone, this dye usually uses for acrylic, polyesters and polyamide [11] and mordant dye class includes dyes that need a mordant (adhesive agent) to dye the fabric directly rather than bond directly, for example Tannic acid is utilised as a mordant for basic dyes, whereas metal ions are employed for acid dyes [12].

2. Treatment of dyes

Composition of most color organic dye is benzene, aniline, anthraquinone, naphthalene or benzidine compounds, all of these consider the major ingredient used to make dye which can form chelation (Organic-complexes) with salts, metals and other element during production processes and this leads to making toxic organic wastewater due to contain high color with high chemical stability and high COD [13] which needs to further treatment by the following procedure physical such as adsorption process which uses some materials like zeolites that can eliminate on Rhodamine B, alumina that can remove disperse dye from water or activated carbon [14], Biological methods or bioremediation considers commercially viable, and produces less sludge than alternative methods, in general this technique depend on using bacterial under specific condition from aerobic and anaerobic to degrade azo-bond in textile [15] and chemical methods that use Advanced oxidation processes “AOPs” which have different techniques that can be effected for removal of water-residue dye [16].

3. Advanced Oxidation processes ”AOPs”

This terminology or this expression of “AOP” was originally suggested in 1980 as a way to clean drinkable water, initially this technique depend on radical like sulfate radicals (SO_4^{--}) or hydroxyl radical ($HO^{\bullet}$) which are enough to do making purification process for wastewater [17]. Mechanism of these processes can be done in two steps; the first steps is producing of oxidant agent (in-direct or direct process) and the second step is oxidizing of organic pollutants by oxidative agent as shown in the next figure(1) [18].“AOPs” have been proved its efficiency for removal of chemical that compound called Endocrine Disruption chemicals which may be present in water as a result of using herbicides, pesticides or dyes, EDCs are a family of substances that imitate or hinder the normal functions of the endocrine system in humans and animals, including secretion, transport, binding and cause hormonal dysregulation [19], From are the most basic feature processes that used in “AOPs” are Photolysis Process (H2O2/UV) [20],Photocatalysis [21], ozonation [22], Sonolysis [23], Fenton Processes [24] and electrochemical processes that involve electrooxidation [25], electro coagulation [26] and electro flotation [27].

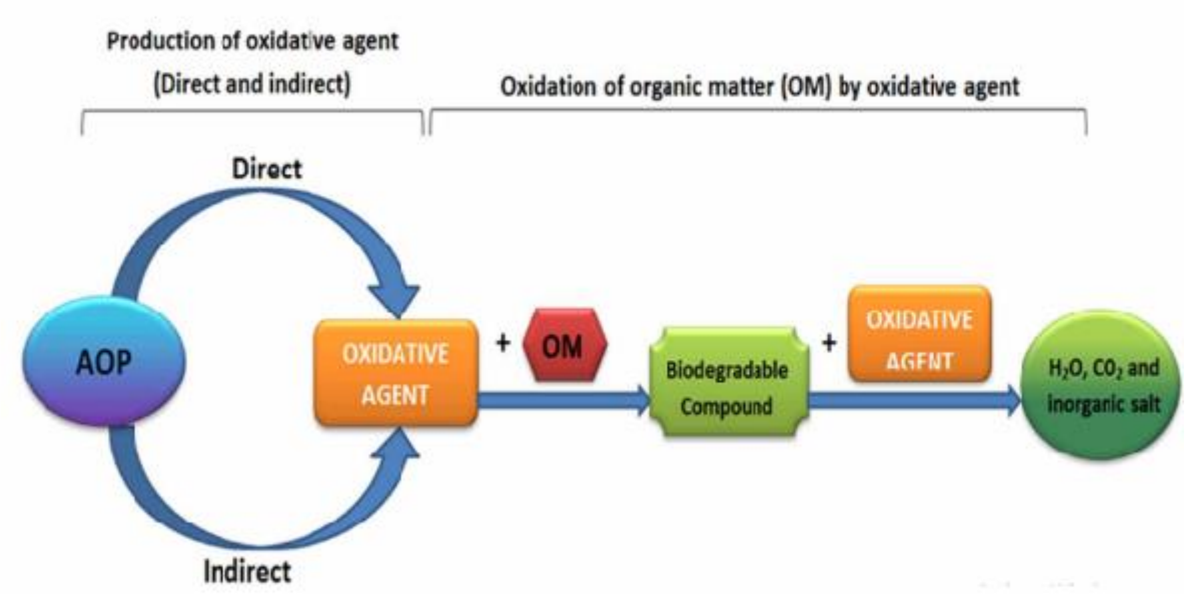


Figure (1). General mechanism of AOPs in remediates wastewater.

4. Experimental

4.1. Materials

Every chemical compound has been used is grade and not for further purification. ferrous sulphate heptahydrate (FeSO4·7H_2O) 98 % that used as a source for Fe^{2+} and Hydrogen peroxide (H_2O_2) its concentration (30%w/w) that used a source for hydroxyl radical $HO^{\bullet}$. Novacron Deep red S-B (Textile dye) purchased from commercial market to be using for this investigation as a probing pollutant.

4.2. Apparatus

PH meter genway (3510), a Hot plate magnetic stirrer(LHMS-A20) used for stirring solution and adjusting temperature, Sartorius Balance and UV-visible spectrophotometers that measures absorption is Jasco (V-630), ozone generator (GL-3189A) used as a source for ozone gas (O_3) with a capacity 600 mg/h, X-Ray Diffraction (XRD) pattern that using for recording is the Rigaku Miniflex 600 diffractometer with Cu Ka-radiation and scanning electron microscope (SEM) that using for images of surface morphology is BED-C 10.0KV, Jeol, equipped with EDX unit.

4.3.Decolorization study

This study was investigated under normal visible light irradiation and UV-Visible light. UV light source is UV lamp (45 cm in length and 15 w, Osram) placed in photochemical reactor between two mirrors to concentrated radiation that can be emitted equal 254nm when exposed at low pressure. Most of reactions have been done on the sample solution with different concertation at different time and volume is constant =25 ml in a beaker glass. The degradation takes place when start the reaction during applying of some factors of different AOPs like UV/H_2O_2, O_3, Fenton reaction (Fe^{2+}/H_2O_2) and Photocatalysis process by using magnetite or combination between different factor. Finally, the efficiency of degradation of dye was calculated through the following equations: removal percent% $= \frac{A_0-A_t}{A_0} \times 100$, where A_0 is the initial and A_t is final absorbance of treatment.

4.4. Preparation sources of iron.

4.4.1. preparation sources of iron for Fenton Processes

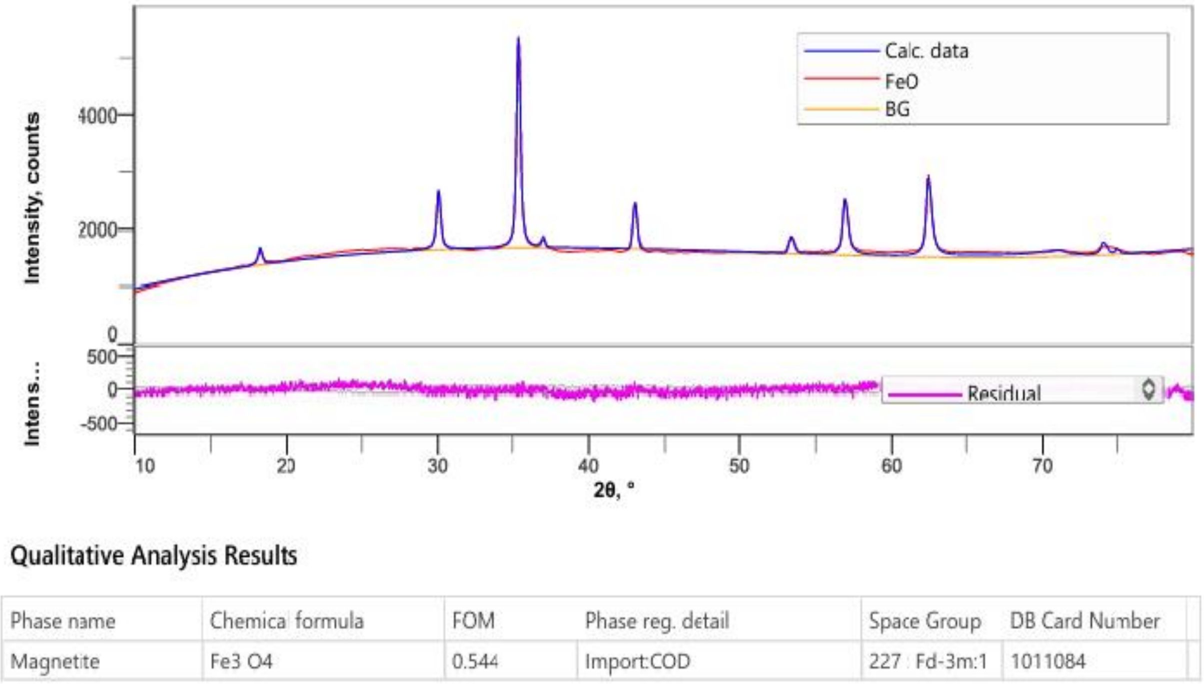
Preparation of Fe (II) as a source for Fenton process with 0.0179 Molar from ferrous sulphate heptahydrate.

4.4.2. Preparation of Fe (III) as catalyst and source for Fenton like process

The creation of iron nanoparticles in nanotechnology by using green tea leaves and ferrous sulphate heptahydrate ($FeSO_4.7H_2O$). In this study, the green tea source has been purchased from the market (Lipton company). Firstly, prepare concentrated green tea by heating; after that, filter the solution to react with 0.0769 M of $FeSO_4.7H_2O$ in distilled water. In the addition step, the percent between the iron solution and green tea is 1:2, and during addition, the ph must be kept in the range of 8-10, the temperature must be warm and gentle with a temperature approximately between 55°C and 60°C, and the addition must be drop by drop with a constant rate of stirring regulation. All the precaution steps can be controlled in the reaction due to its vital role in the shape, size, and phase of the producing catalyst. Fe-NPs will precipitate in a black form of particles in the solution; after that, using a centrifuge at 4500 rpm for ten minutes with a repeated cycle for the solution to separate nanoparticles alone, then washing them with distilled water, and putting these particles in a desiccator to dry the catalyst and make it ready for characterization and usage.

4.5. General Characterization of catalyst by XRD Card.

When making data analysis or data information, card of XRD show an identification phase that proves the Prescence of magnetite (Fe_3O_4) as the dominant Phase and give number of FOM equals 0.544 and this number expressed as numerical value which often between zero and one and indicates the degree of similarity between the simulated pattern that observed in XRD analysis and the reference where FOM is more than 0.5 so consider good agreement and acceptable results as well as XRD can determine space group from its type (Fd-3m) and can calculate the crystal size by using Scherer equation through determination of strongest peak and angle (2θ). The crystal size of GT-Fe NPs (Fe_3O_4) ≈ 31.9nm.



Qualitative Analysis Results

Phase name	Chemical formula	FOM	Phase reg. detail	Space Group	DB Card Number
Magnetite	Fe3 O4	0.544	Import:COD	227 : Fd-3m:1	1011084

Figure (2). Peak profile view of magnetite from XRD Card.

Tabel (1). show phases and Theta reflections (2θ) of magnetite.

Nom.	2θ, °	Decay (ηL/mL)	Decay (ηH/mH)	Size, Å	Phase Name	Chemical Formula
1	**18.21 (2)**	**1.4 (3)**	**1.1 (2)**	**316 (35)**	Magnetite: 1 1 1	Fe_3O_4
2	**30.029(11)**	**0.94 (12)**	**0.84 (12)**	**296 (10)**	Magnetite: 2 2 0	Fe_3O_4
3	**35.387(4)**	**0.63 (4)**	**0.85 (5)**	**315 (4)**	Magnetite : 3 1 1	Fe_3O_4
4	**36.998(12)**	**0.3 (7)**	**0.0 (9)**	**428 (84)**	Magnetite: 2 2 2	Fe_3O_4
5	**43.006(15)**	**0.0 (2)**	**0.0 (2)**	**292 (10)**	Magnetite: 4 0 0	Fe_3O_4
6	**53.37 (3)**	**0.0 (4)**	**0.9 (3)**	**286 (25)**	Magnetite: 4 2 2	Fe_3O_4

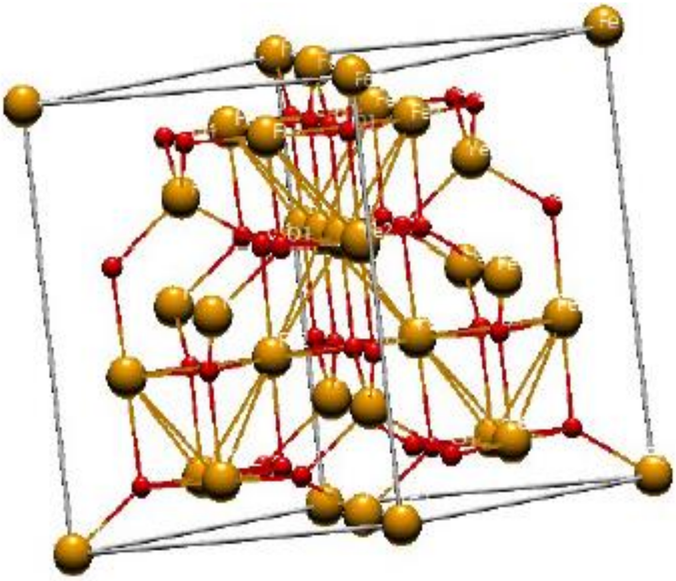


Figure (3). show magnetite in 3-D. by XRD.

4.6. Characterization of catalyst by SEM.

The SEM analysis reveals that the nanoparticles (NPs) are arranged in cluster-like formations, which can be correlated with the crystallographic information obtained from the XRD analysis as shown in figure (4).

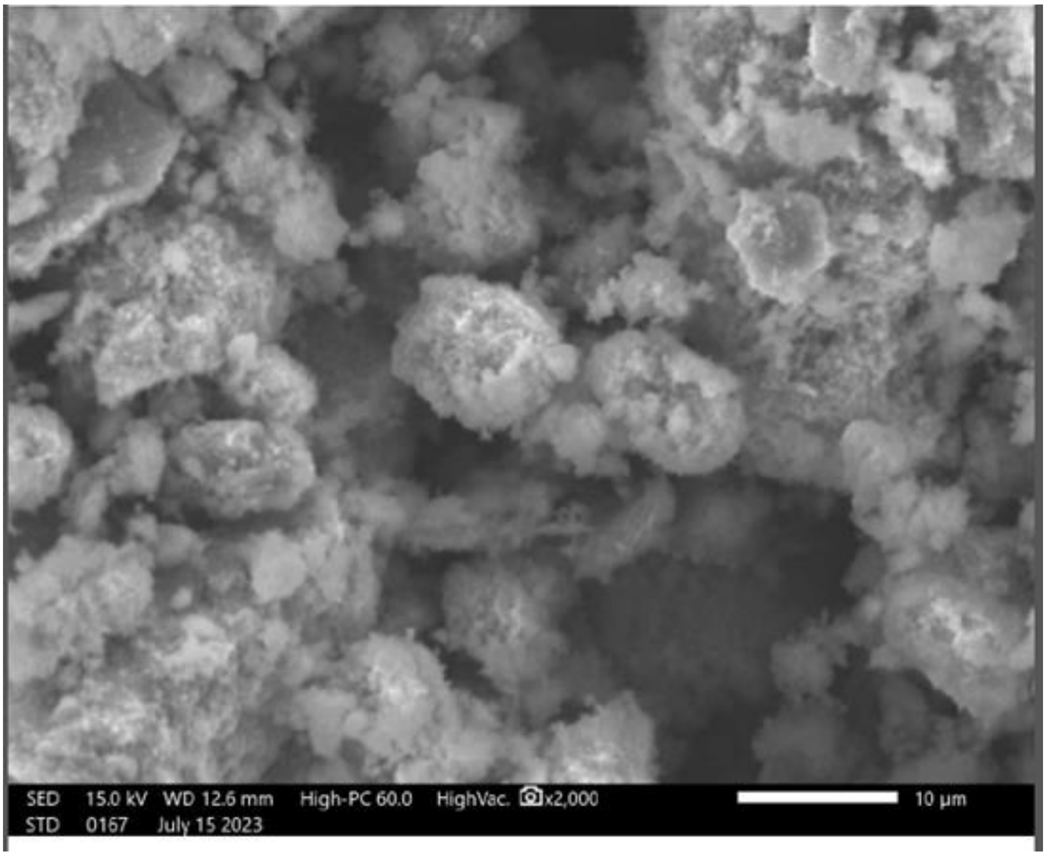


Figure (4). show nano magnetite under SEM.

5. Results and Discussion

5.1. H_2O_2 & H_2O_2/UV systems

Hydrogen Peroxide or hydrogen Peroxide with Ultraviolet Radiation (UV) (H_2O_2/UV) consider one of the most utilized processes in advanced oxidation processes (AOPs) to achieve wastewater treatment, especially for getting rid of persistent organic pollutants like colorant agent (Pigment and dyes). Hydrogen peroxide is strong oxidizing agent, on the other hand H_2O_2 may loss its reactivity at absence of catalyst or additional energy such as UV radiation.

The difficulty is that the colour that stays behind because of the dye employed might upset the ecosystem of the water that receives it. Main role of hydrogen peroxide

When H_2O_2 is used only to treat 25 mg/L solution of Novacron Deep Red S-B, the removal of the dye was very low (less than 6%) after about one hour of continuous treatment and there is no destruction removal of color by UV radiation only. So, the experiment was repeated in the presence of varying amounts of H_2O_2 (0.5, 1.0, 2.0 and 3.0 mmol) under UV radiation. The effect of H_2O_2 dose is presented in Figure (5). Increasing H_2O_2 dose cause a decrease in the removal efficiency. The best dose of hydrogen peroxide is 0.5 mmol, which results in 99.15% removal.

makes oxidization reaction for dyes that contain a lot of electrons due to Prescence of aromatic rings in it, although of occurrence the oxidation reaction, this reaction rate considers slow in behavior of reaction rate. When uses UV-radiation with hydrogen peroxides, this process can enhance the speed of reaction (oxidation reaction) due to generation a lot of potent oxidizing hydroxyl radical which attack organic pollutant as a result of cleavage of hydroxyl radicals as the following equations [28].

$$H_2O_2 \overset{UV}{\rightarrow} 2HO^{\bullet} \quad (1)$$

$$H_2O_2 \leftrightarrow HO_2^- + H^+ \quad (2)$$

$$RH + HO^{\bullet} \rightarrow H_2O + R^{\bullet} \rightarrow \text{further-oxidation} \quad (3)$$

Enhancing removal of dye increases as a result of particularly when exposing it under UV radiation by the increasing concentration of hydrogen peroxide as a result of improvement of degradation rate (speed up the breakdown of colors), the implantation of that is back to number of generated of hydroxyl that increasing with increasing amount of hydrogen peroxide.

The first case take place at low or moderate concentration of hydrogen peroxide; the relationship is directly proportional between of hydrogen peroxide and generated hydroxyl attack organic pollutant and this called “optimization state” but in the second case at higher concentration the relationship become invers due to scavenging of $HO^{\bullet}$ that quench when adding excess of H_2O_2 as the following [29].

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \qquad (4)$$

From the above equation, this reaction can be reduced the number of hydroxyl radical which is responsible for degradation of organic pollutant where a new less reactive species such as $HO_2^{\bullet}$ is formed by utilizing excess of H_2O_2 and this leads to reducing in the efficiency removing of dye.

In H_2O_2/UV system, the relationship between hydrogen peroxide and concentration of dye is inverse relationship and this can effect on removing of dye, this means if the initial of dye increase, this will lead to decreasing of the efficiency of removal with constant operational conditions.

The reason of inverse relationship between dye concentration and H_2O_2 may be come back to number of molecules of dyes where at high concentration, the number of molecules can make hindrance or blocking of UV radiation, they will make competition between dye and number of released hydroxyl radical from hydrogen peroxide as happens in Figure (6). This phenomenon called “water matrix” and this is among this method's biggest drawbacks [30].

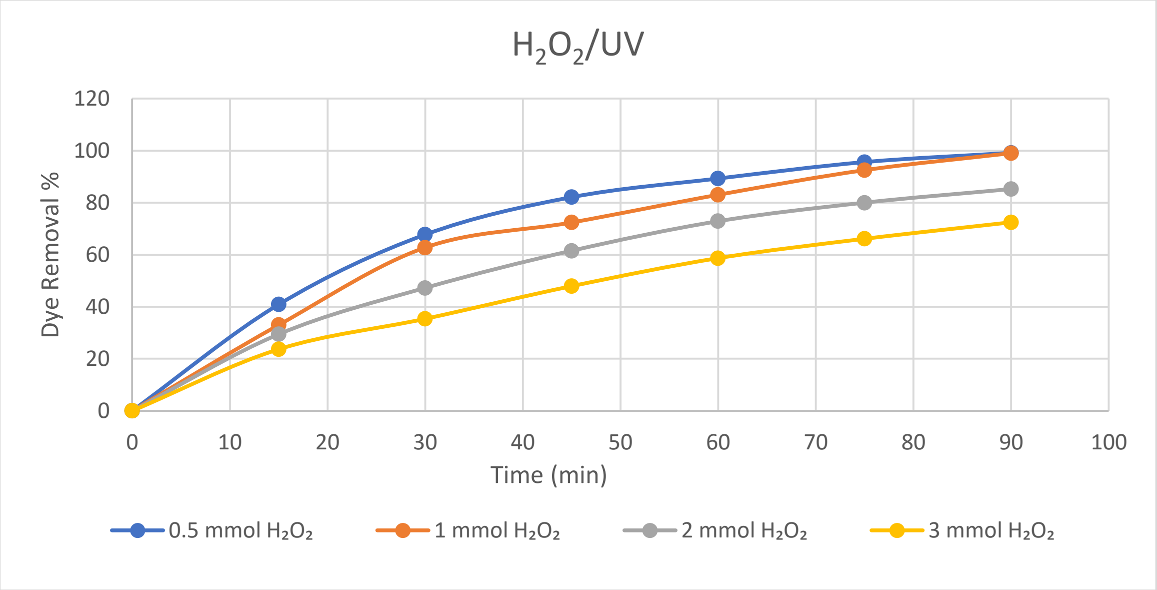


Figure (5). Effect of H_2O_2 dose on degradation of Novacron Deep Red S-B dye under UV radiation with concentration 20 mg/L dye.

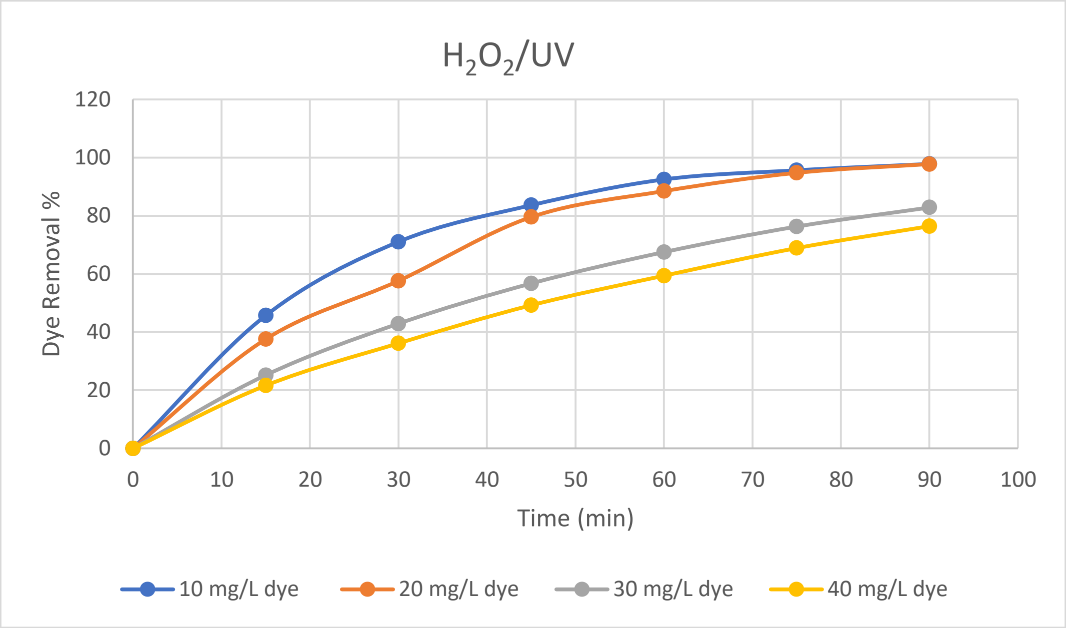


Figure (6). Relation between Novacron Deep Red S-B dye initial concentration and removal percent under UV radiation [Different Concentration of dye + H_2O_2 = 0.5 mmol].

Moreover, the kinetic of reaction changes in accordance with concentration of hydrogen peroxide in which behavior of reaction follows pseudo-first-order kinetics at low concentration of dye but at high concentration of organic pollutant the reaction will tends or shift to zero order kinetics, sequency the removal efficiency decreases due to reaction depending on few numbers of quantum yield of hydroxyl radicalsthat generate from hydrogen peroxide [31].

Degree of PH has also an effect in UV/H_2O_2 system which can inhibition, acceleration of removal efficiency and in some times at specific scale PH may take the same behavior (pH significantly affect the color degradation in within specific range with the same behavior of removal) on removal of organic pollutant and this depend on time of media (basic or acidic), for example basic media may decompose and give this anion which can react with non-selective way with hydrogen peroxide as the next equation.

$$HO_2^- + H_2O_2 \rightarrow H_2O + O_2 + OH^- \qquad (5)$$

This can reduce number of hydroxyl radical, further more this anion can react with released radical

$$HO^{\bullet} + HO_2^- \rightarrow H_2O + O_2^{\bullet -} \qquad (6)$$

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \qquad (7)$$

Also, solvent that is related to degree of Ph can be effect on basic nature of molecular structure like occurrence of tautomerism phenomena or protonation phenomena (effect of PKa) that can change of intensity of the maximum absorption band [32].

When studying the effect of Ph with four points (3, 5, 8, 10), it is noted that at Ph = 3 is the best removal while removal decrease at alkaline media Ph (8 and10) that are the least of removal percentage as Figure (4). Degradation became slow in alkaline media as a result of reducing hydroxyl radical [33].

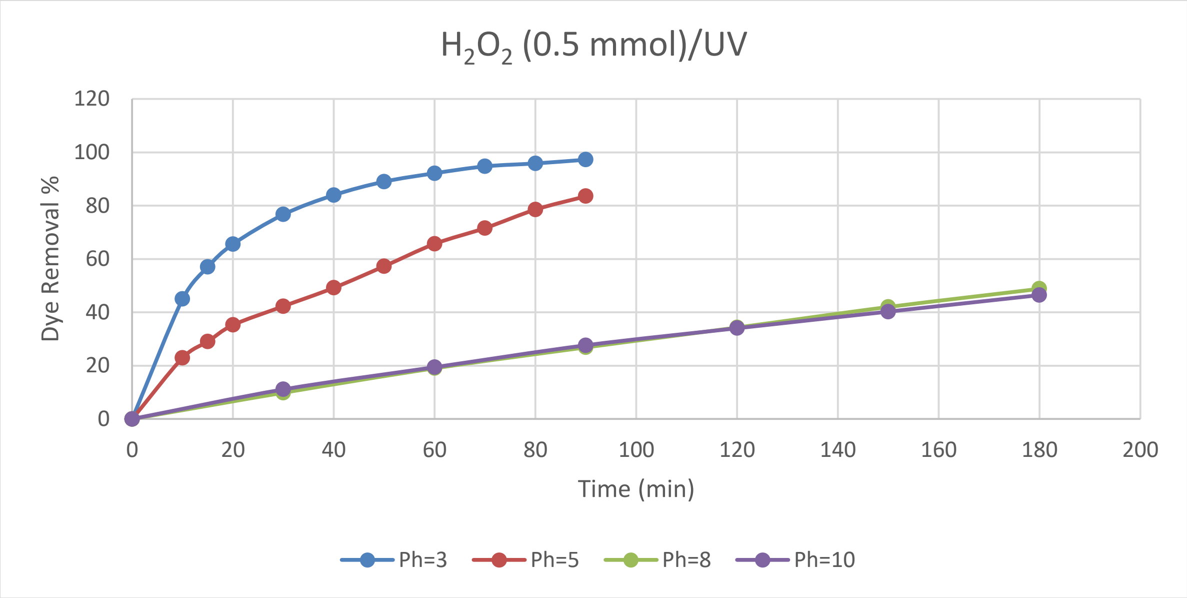


Figure (7). Effect of ph on H_2O_2/UV system reaction for removal of Novacron Deep Red S-B dye [100 mg/L of dye + 0.5 mmol (hydrogen peroxide)].

5.2. Fenton and Fenton-like systems

Fenton Processes (Fenton, Photo Fenton, Fenton like or hybrid Fenton) consider one of the most efficient ways for solving water contamination that happens due to Prescence chemical pollutant like organic dyes and endocrine disrupting chemicals (EDCs). This type of AOPs (Fenton processes) produce powerfully oxidizing radical species (mostly $OH^{\cdot}$) at temperatures and pressures that are close to ambient which is non selective then attacks the chromophoric group and can fully decompose organic contaminants into non-toxic components like carbon dioxide, H2O and inorganic salts "Mineralization". Generally, Fenton reactions take place

when ferrous ion (Fe^{2+}) activates H_2O_2 to produce hydroxyl radical via next complex reaction [34].

Fenton process reaction

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-} \qquad (8)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \qquad (9)$$

Photo Fenton reaction that uses UV radiation to improve the overall $HO^{\cdot}$ production by photo reduction of Fe^{3+} to Fe^{2+}.

$$Fe\,(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO^{\bullet} + H^{+} \qquad (10)$$

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet} \quad (11)$$

The effect of Fe (II) dose on Novacron Deep Red S-B dye removal is shown in Figure (8). The increase of Fe (II) from 1.79×10^{-3} mmol to 7.16×10^{-3} mmol causes a corresponding increase in dye removal from 67.75% to 86.28%, respectively.

The main role of Fe(II) is making as a catalyst in Fenton processes that makes the generation of hydroxyl radical which can plays as oxidizing species for organic dye So the reason of increasing removal of dye because the increasing of concentration of Fe^{2+}, this leads to increase of producing $HO^{\bullet}$ [35].

In the Photo-Fenton process, it is more efficient than the Fenton process because UV light can facilitate the reduction of Fe^{3+} to Fe^{2+} and still produce hydroxylation as well as direct photolysis of hydrogen peroxide, for these reasons, Photo-Fenton is more favor than Fenton for removing the organic pollutants.

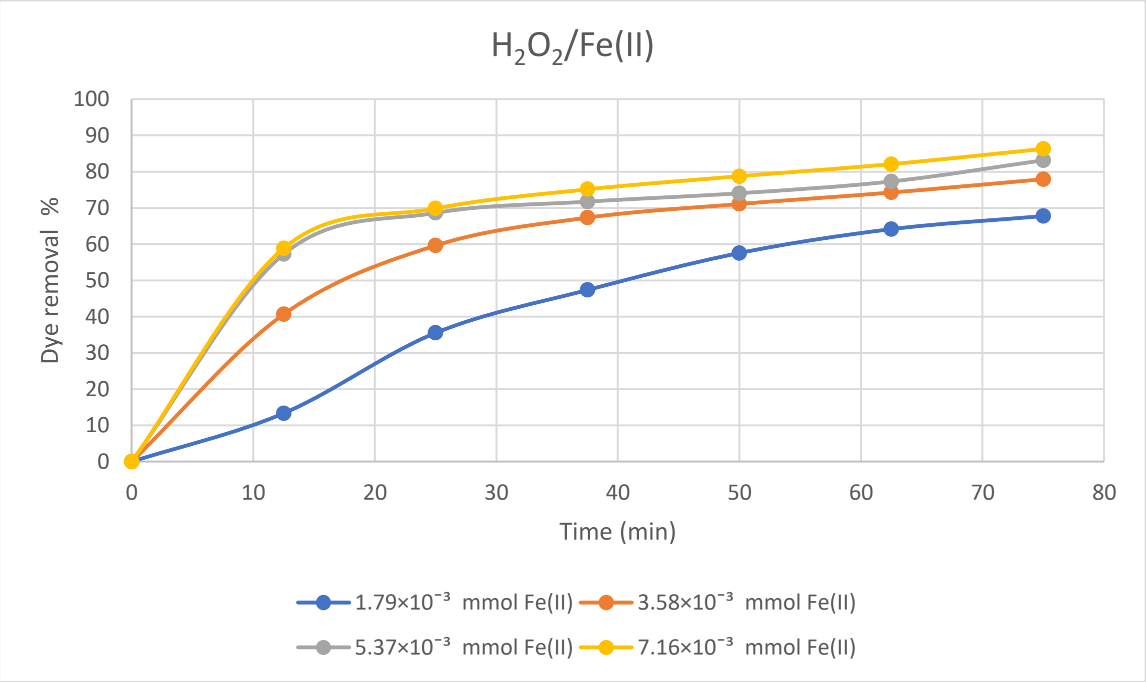


Figure (8). Effect of Fe (II) dose on dye removal in Fenton reaction.

[dye =100 mg/L, H_2O_2 = 2 mmol].

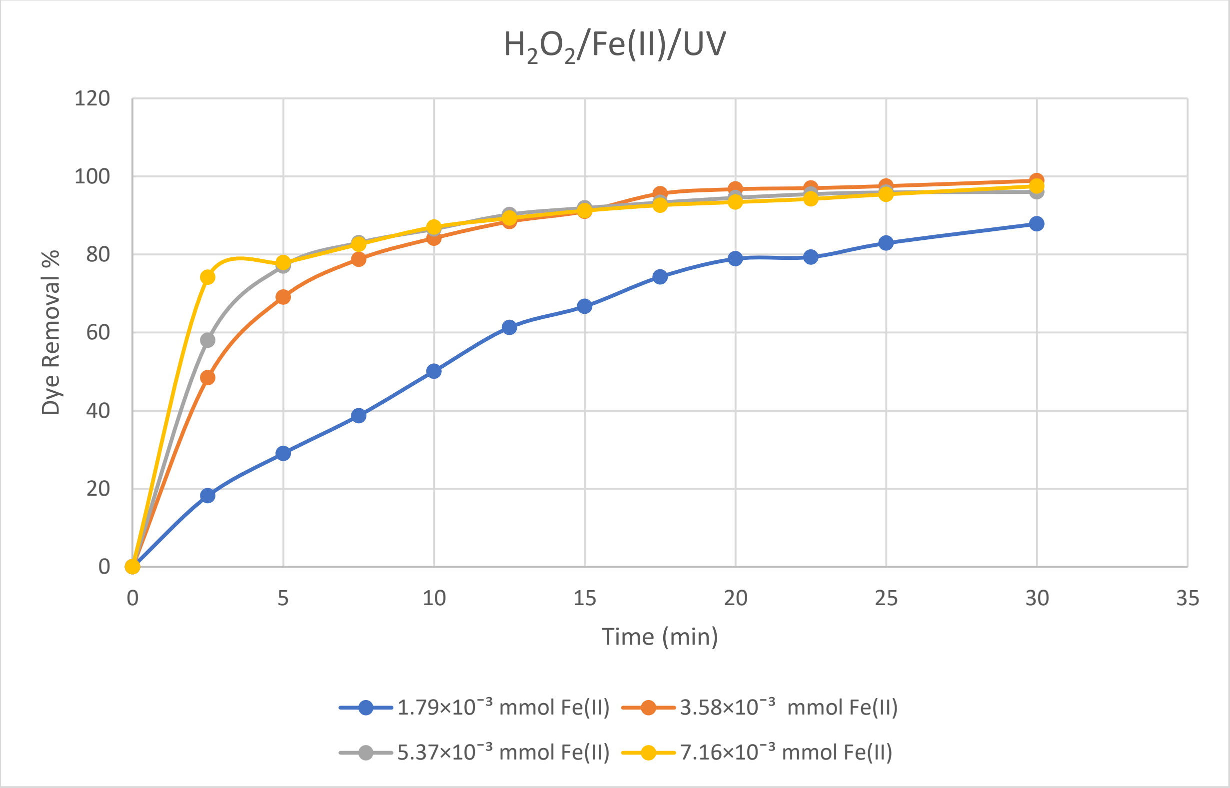


Figure (9). Effect of Fe(II) dose on dye removal in Photo-Fenton reaction. [dye=100 mg/L, H_2O_2 = 2 mmol].

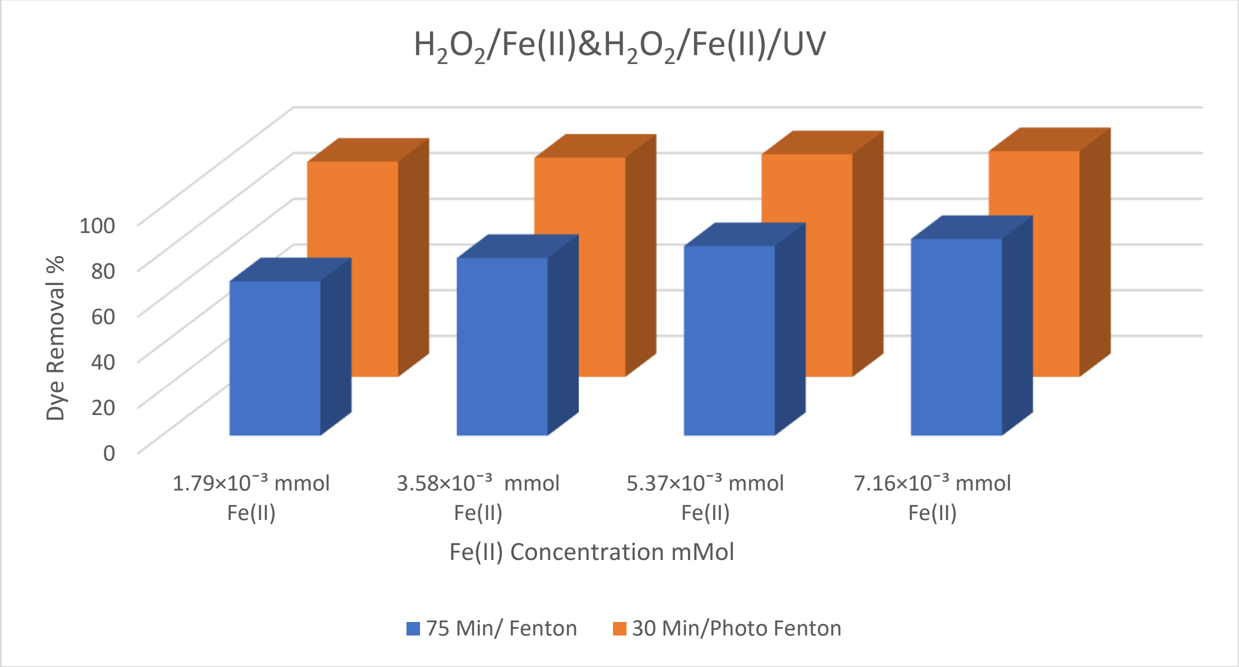


Figure (10). Comparison between Fenton and Photo-Fenton reactions for degradation of Novacron Deep Red S-B dye at different doses of Fe (II).

Effect of PH on dye, the results that have been studied of degree of PH (3,5,8,10), showed at PH=3 is optimal and the best results where PH at 3> 5> 8>10.

The explanation of that PH that using to treat wastewater at the range between (2-4), it is formed a greater number of Fe $(OH)^+$ and its activity is higher than Fe^{2+} in Fenton Processes and above PH=3 the reason of decreasing in removal percentage of color come back to the coagulation of hydroxo complex of Fe^{3+} formed during the reaction [36, 37].

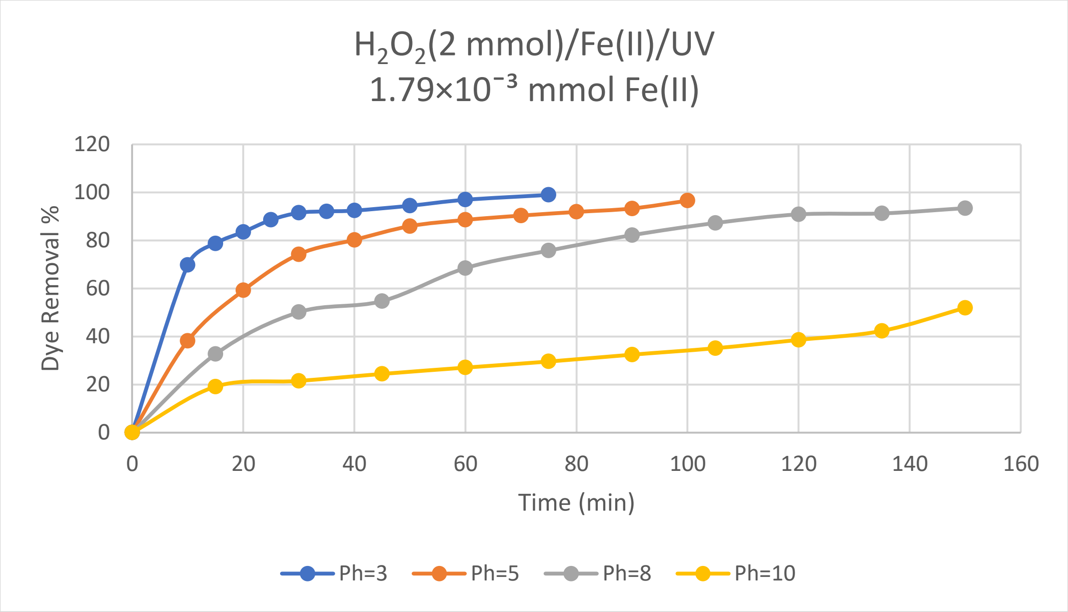


Figure (11). Effect of ph on Fenton reaction for removal of Novacron Deep Red S-B under UV radiation [dye=100 mg/L, H_2O_2=2 mmol, 1.79×10^{-3} mmol Fe (II).

In another set of experiments, trivalent iron nanoparticles like iron oxide-Magnetite (Fe_3O_4) were used as catalyst because it considers efficient catalysts. NPs Fe_3O_4 plays a vital role in the AOPs for the degradation of organic contaminants, especially when combined with hydrogen peroxide (H_2O_2) and this process is often referred to as a modified or heterogeneous.

Fenton-like reaction that is defined as a solid iron mineral or metal ion-organic ligand complexes can be used to replace the dissolved iron (Fe^{2+}) [38].

NPs Fe_3O_4 as heterogenous Fenton like can be represented as following equation [39].

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2^{\bullet} + H^+ \quad (12)$$

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + HO^{\bullet} + OH^- \quad (13)$$

In above equation, first step shows the combining between iron (III) and hydrogen peroxide and this step consider as an intermediate step for generation the iron (II) to begin Fenton reaction and producing hydroxyl radical.

Magnetite (Fe_3O_4), hematite (Fe_2O_3), akageneite ((β-FeOOH), goethite (α-

FeOOH), ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$), greigite (Fe_3S_4), or zero-valent iron nanoparticles are examples of iron-based substance or iron minerals in nanoparticulate form. These materials are characterized with high surface-to-volume ratio and compact size which makes it possible for pollutants in wastewater to be effectively oxidized as well as this type of iron-based materials is more efficient than Fe^{2+} in the application of AOPs, because it produces less sludge (can be separated by magnetic sedimentation), requires less hydrogen peroxide (Fenton-based AOPs, reducing the dosing of oxidants), and releases Fe (II) gradually (high activity), environmentally friendliness, morphological diversity and have cost reduction.

Fenton process can be controlled with some factor like Ph, initial dose of catalyst and initial dose of hydrogen peroxide. The optimum degree of Ph in Ph that used for iron-based nanomaterials as catalyst is Ph ranges between (2.5-4) where at this acidic value Fe^{3+} has higher solubility to Fe^{2+} [40, 41], the following experiments depend on fixed value of Ph=3 and change the other variables.

The effect of adding different concentrations of H_2O_2 to a fixed amount of magnetite nanoparticles (about 0.2 g/L) on dye removal was followed and presented in Figs. 8 and 9 without and with the effect of UV radiation, respectively. As shown in Figure (12), an increase in H_2O_2 concentration decreases the removal percent.

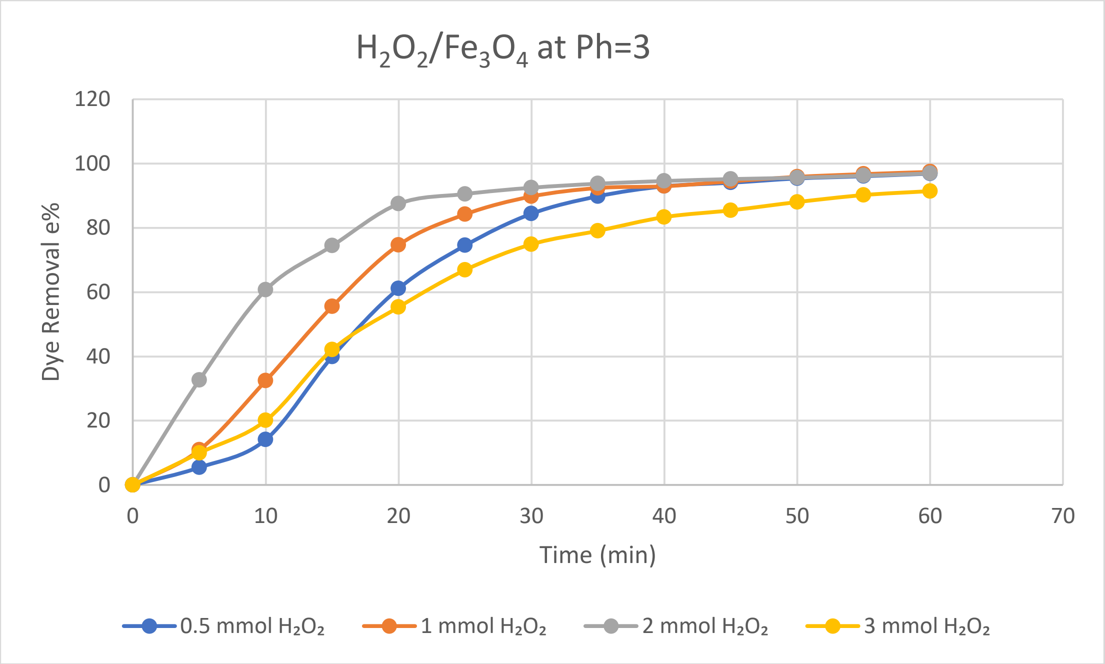


Figure (12). Effect of different concentrations of H_2O_2 on dye degradation=[20 mg/L] in the presence of magnetite at Ph=3.

When H_2O_2 levels rise, excess H_2O_2 molecules scavenge hydroxyl radicals to produce perhydroxyl radicals, which further slows down the dye removal process, which has lower oxidation potential [42].

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \quad (14)$$

This reaction reduces the number of radicals available for oxidizing the dye.

Figure (13) illustrates the effect of UV radiation on dye removal. Compared to the H_2O_2/Fe_3O_4 system shown in Figure (12), the presence of UV light significantly enhances the degradation rate, reducing the total reaction time from approximately 60 minutes to just 30 minutes. For comparison, the removal percents of each set of experiments at equilibrium are shown in Figure (14). These results show extent of the impact of UV-radiation rate of cleavage of H_2O_2.When hydrogen peroxide (H_2O_2) is exposed to UV radiation, particularly UV-C light (wavelength ~254 nm), it undergoes photolytic cleavage, producing hydroxyl radicals directly [43].

$$H_2O_2 + hv \rightarrow 2HO^{\bullet} \quad (15)$$

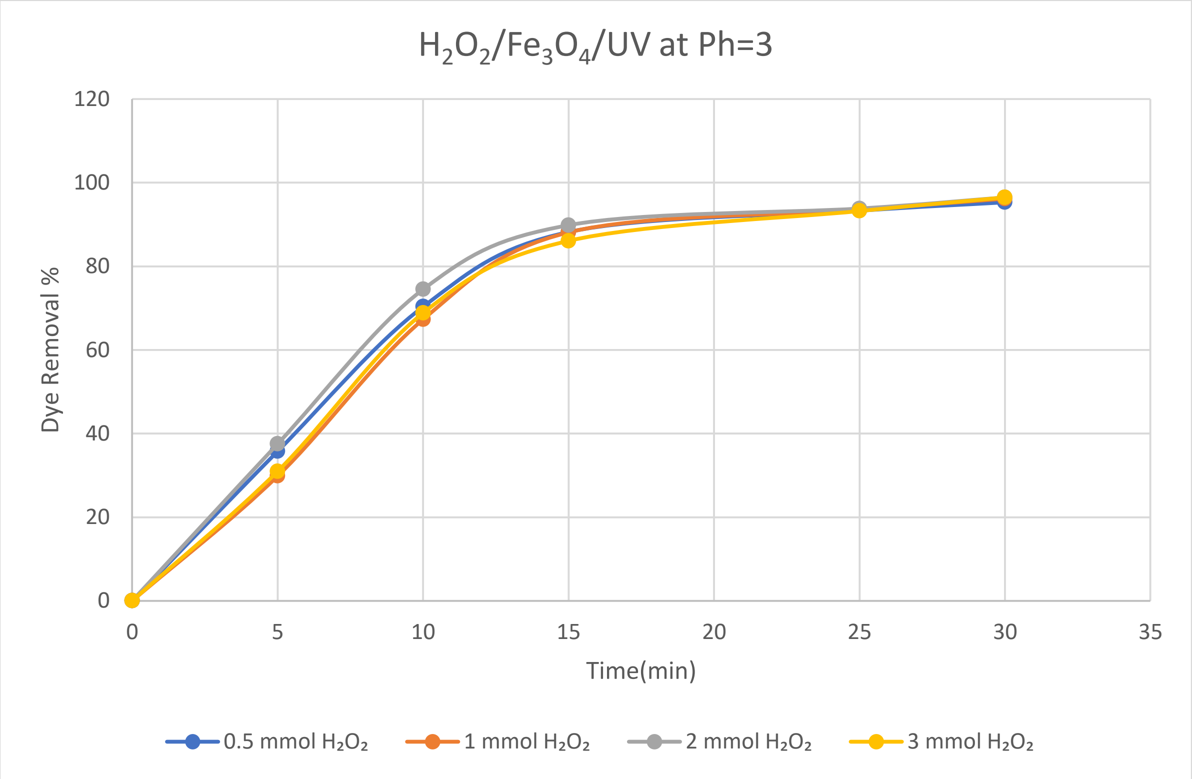


Figure (13). Effect of different concentrations of H_2O_2 on dye degradation[20 mg/L] in the presence of magnetite at Ph=3 under UV radiation.

degradation [20 mg/L] in the presence of magnetite at Ph=3 under UV radiation where concentration of dye=100 mg/L was examined in the absence and presence of UV radiation and the results are shown in Figures. (13 and 14)

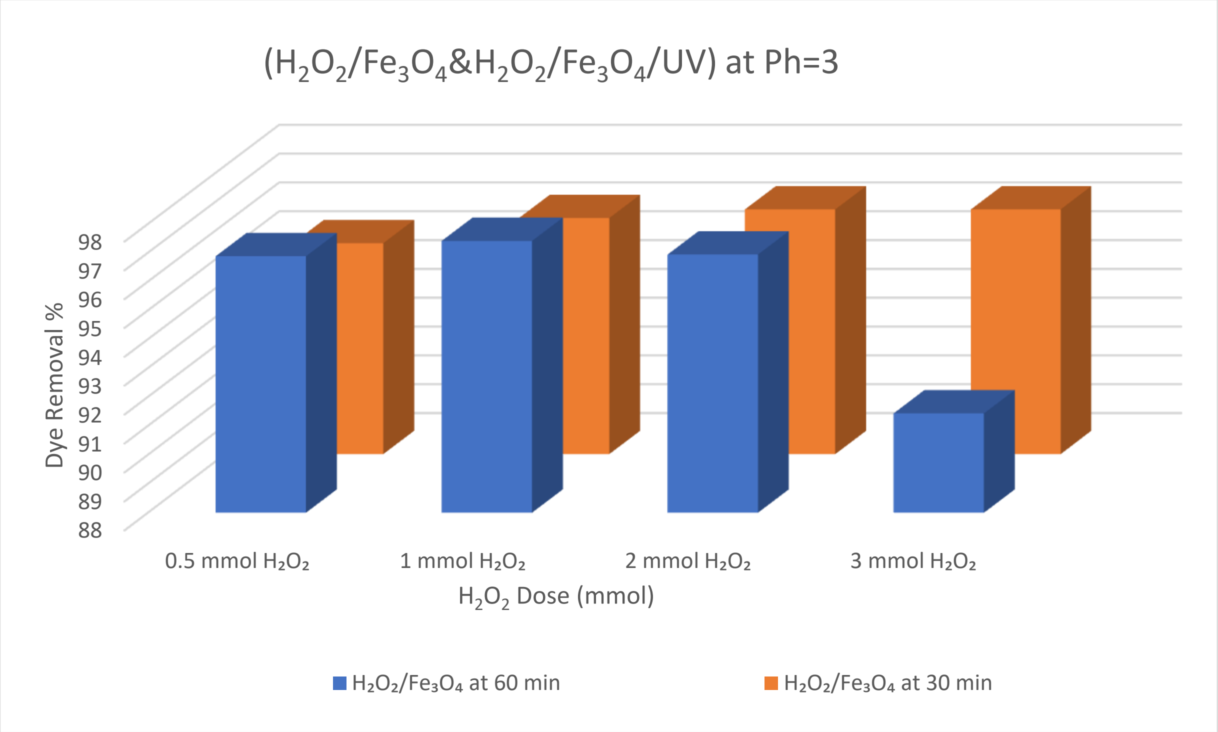


Figure (14). Comparison between the effect of different concentrations of H_2O_2 on dye degradation in the presence of Fe_3O_4 without and under UV radiation at Ph=3.

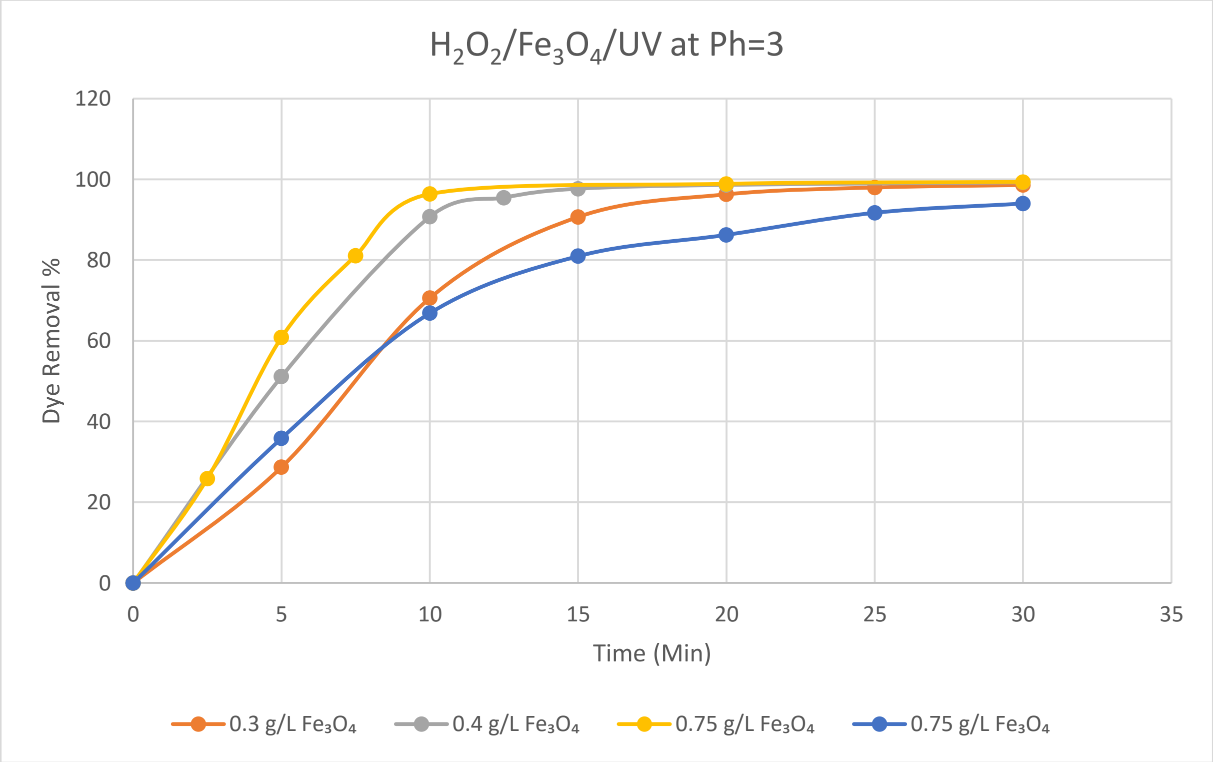


Figure (15). Effect of different doses of Fe3O4 of on dye degradation=100 mg/L in the presence of constant concentration of H2O2=2 mmol

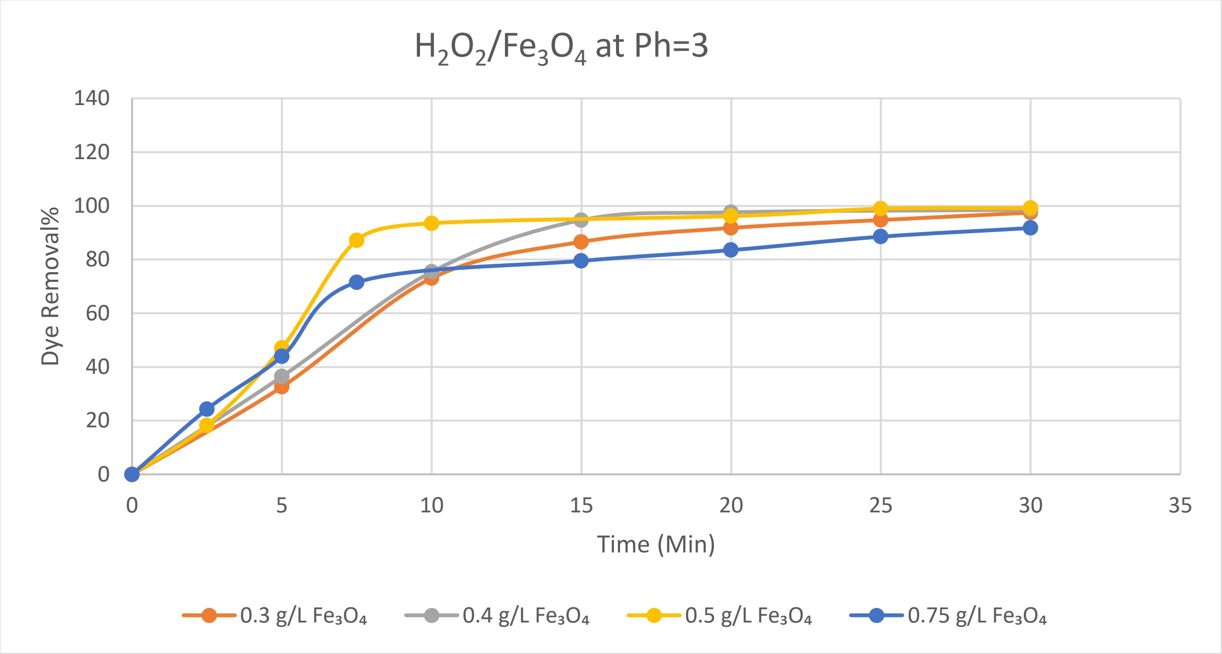


Figure (16). Effect of different doses of Fe_3O_4 of on dye degradation=100mg/L in the presence of constant concentration of H_2O_2= 2mmol under UV radiation.

According to the findings, there was a discernible rise in dye decolorisation from 0.3 to 0.5 g/l of catalytic load increment, when increasing of catalytic dose =0.75 g/L followed by a decrease in degradation capacity.

When the catalyst's surface increased, more active sites were created, which led to an initial rise in dye degradation. But the dye degradation reducing was noted with an increase in catalyst because the scattered nanoparticles reduce the generation of $HO^{\bullet}$ (scavenging of hydroxyl radicals) by blocking light penetration through a screening effect [44].

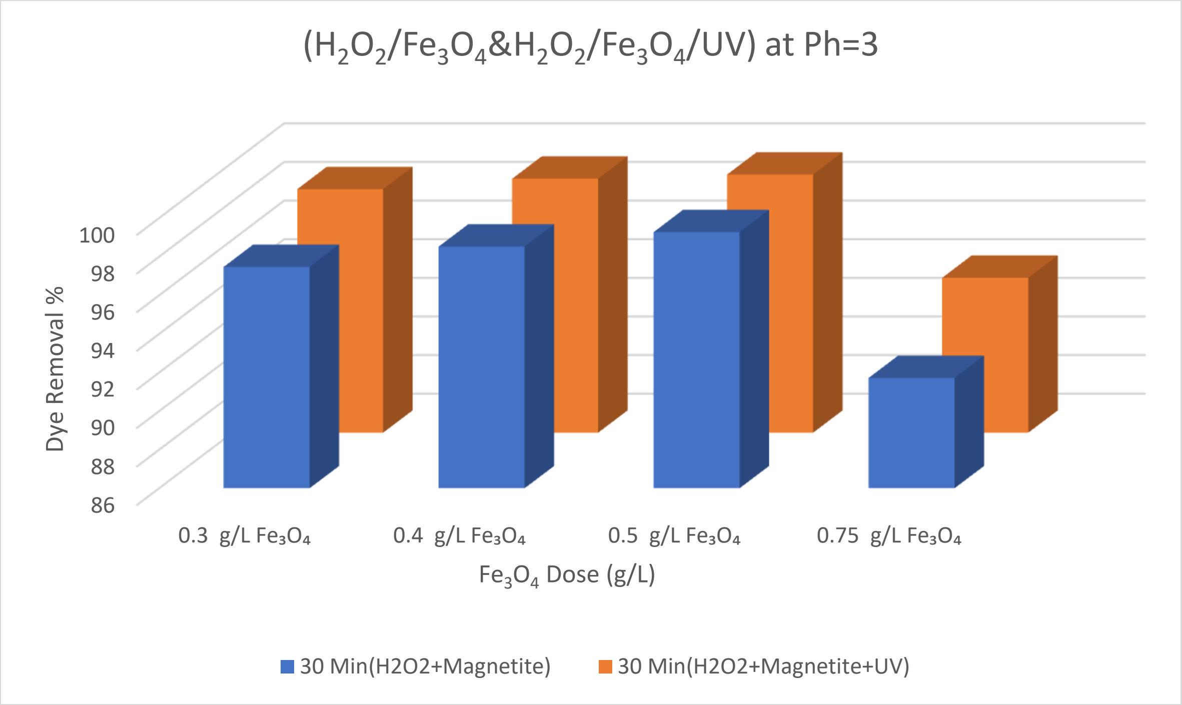


Figure (17). Comparison between the effect of different doses of Fe_3O_4 on dye degradation in the presence constant concentration of H_2O_2 without and under UV radiation (after 30 min).

At studying the behavior of this degradation in the absence and Prescence of UV effect, the difference can be noticed from the beginning of the reaction until the middle of the reaction more clearly, but in the final degradation the

two-reaction become almost are equals, this may be because of the rate of dye degradation is directly affected by another factor (such as the rate of diffusion of contaminants to the catalyst surface which means relation between adsorbate and adsorbent, or the rate of reaction between the radicals and the dye), adding UV may not make a significant difference.

5.3. O_3 and related systems

Ozone is a potent oxidizing agent an it has oxidant potential about 2.07 V so O_3 can treat wastewater organic pollutant like dye and residual color then can mineralized of these chemical dye [45].

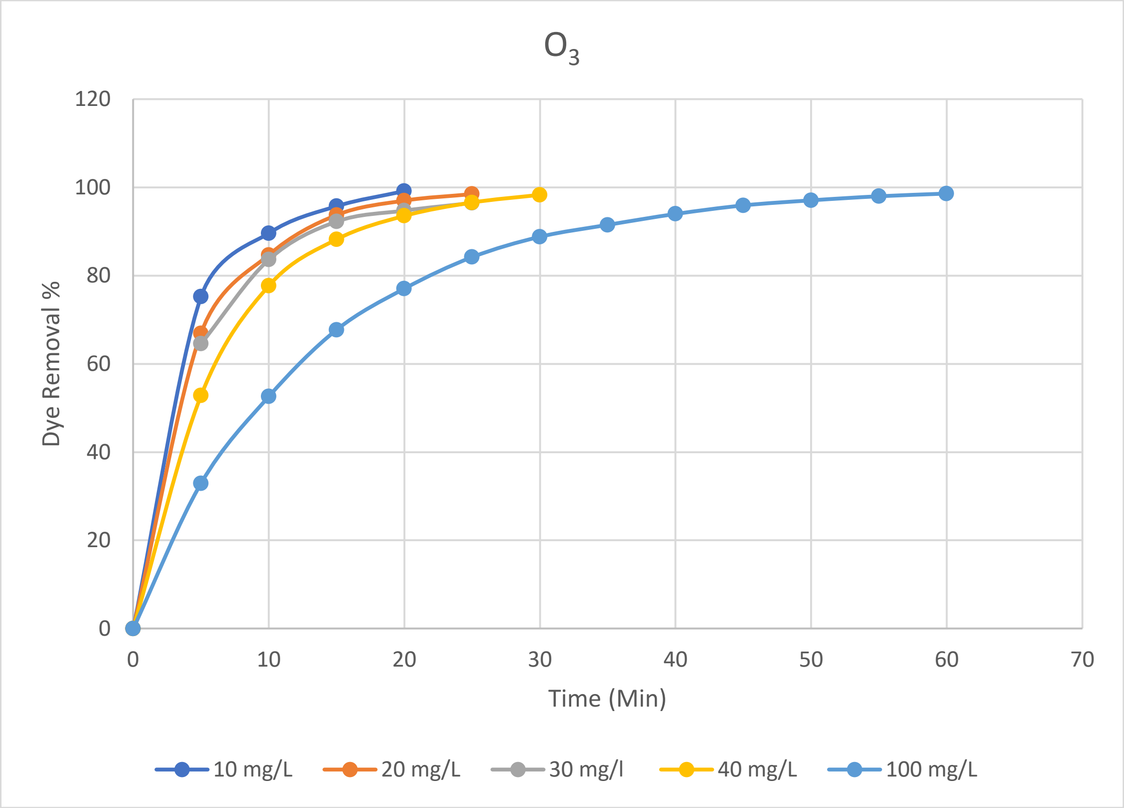
5.3.1. O_3 and O_3/UV

Ozone molecule has triatomic from oxygen, hybridization type from SP^2, the movement of electron and geometry help ozone to open the tricyclic ring then react with organic molecule that present in water and can oxidize these contaminants by a free radical that arise due to break down of ozone [46]. On the other hand the combination between UV and O_3 may enhance this system

(O_3/UV) because excited oxygen atoms O(^{1}D) that produced which combine with water and convert to hydroxyl radical[47].

The effect of ozone bubbling in different concentrations of Novacron Deep Red S-B dye (10 – 100 mg/L) is shown in Figure (18). The removal percent decreased with increasing dye concentration, and the rate of degradation also was slowed by increasing dye concentration. The decrease in dye removal percentage with increasing dye concentration during ozonation is primarily because the available radicals available from ozone are not enough to react with all dye molecules, which leads to a lower percentage of the dye being removed, even if the total mass removed increases where $r=\frac{dc}{dt}$ [48].

When the same experiments were performed under the effect of UV radiation, it was observed that removal efficiency was slightly increased and (as shown in Figure 19). O_3 with UV form hydroxyl radical more than ozone alone. The comparison of experimental data obtained for ozonation and photo-ozonation processes are shown in Figure (20)



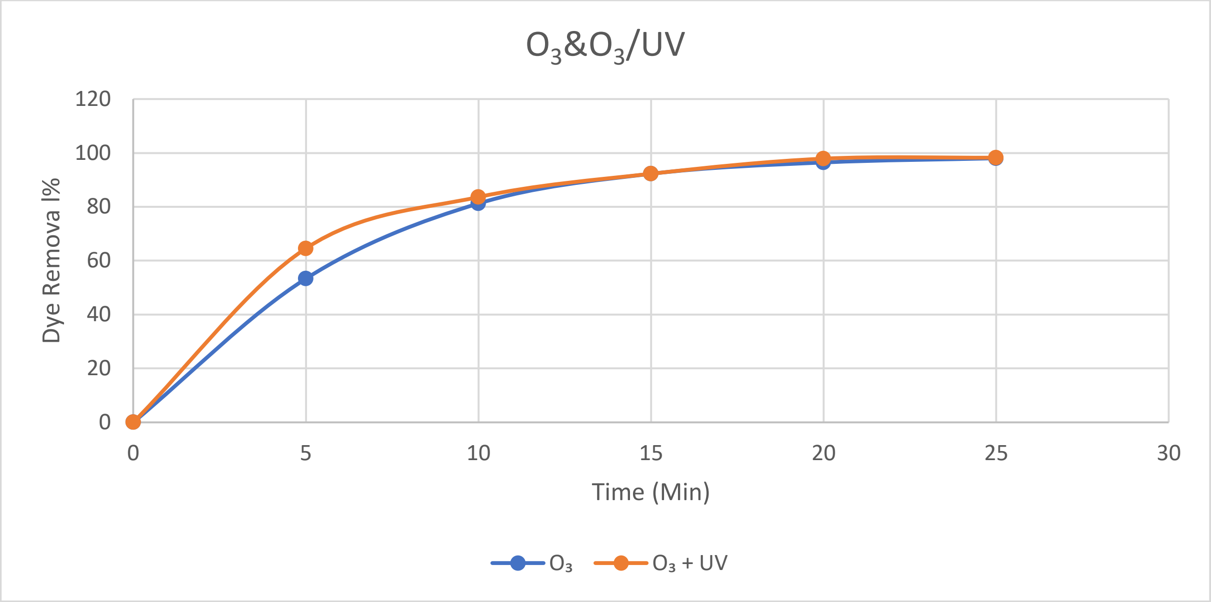


Figure (18). Effect of ozone on degradation of different concentrations of Novacron Deep Red S-B dye [Direct O_3+ Different Concentration of dye].Figure (19). Effect of ozone on degradation of the same concentrations[30 mg/L] of Novacron Deep Red S-B dye.

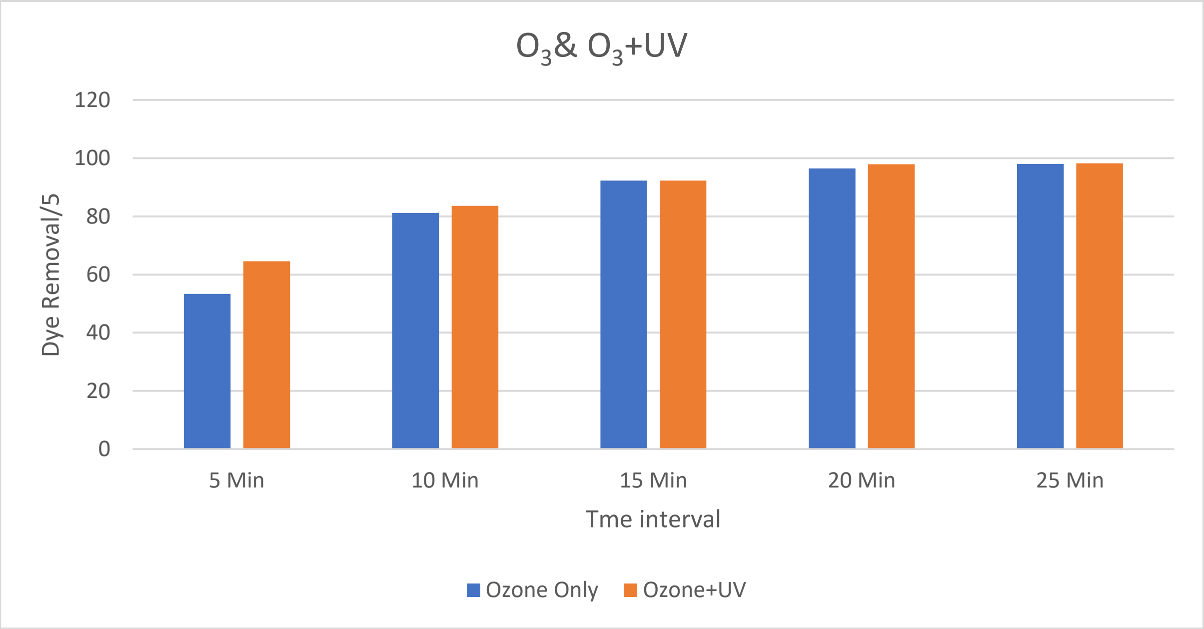


Figure (20). Comparison between the effect of ozone on degradation of different interval of time [5,10,15,20,25 Min] for the same concentration [30mg/L] of Novacron Deep Red S-B dye without and under UV radiation.

5.3.2. (O_3/H_2O_2) and. ($O_3/H_2O_2/UV$)

O_3 with H_2O_2 enhance the production of generated $HO^{\bullet}$[49], those hydroxyl radicals are more non-selective and reactive than ozone itself, leading to complete mineralization of dye molecules but when add Photolysis to peroxone system it will increase the number of active radical in some intermediate pathways so pollutant (suppose compound M) can inhibit or promote this reaction, inhibition takes place when exposes radicals or disrupts its work and may form intermediate stable compound that reduces of decomposition or promotion about facility of chain reaction [50].When hydrogen peroxide was coupled with ozone for 50 mg/L of Novacron Deep Red S-B dye, without and under the effect of UV radiation, the percent of removal and its rate were increased, Figure (21).

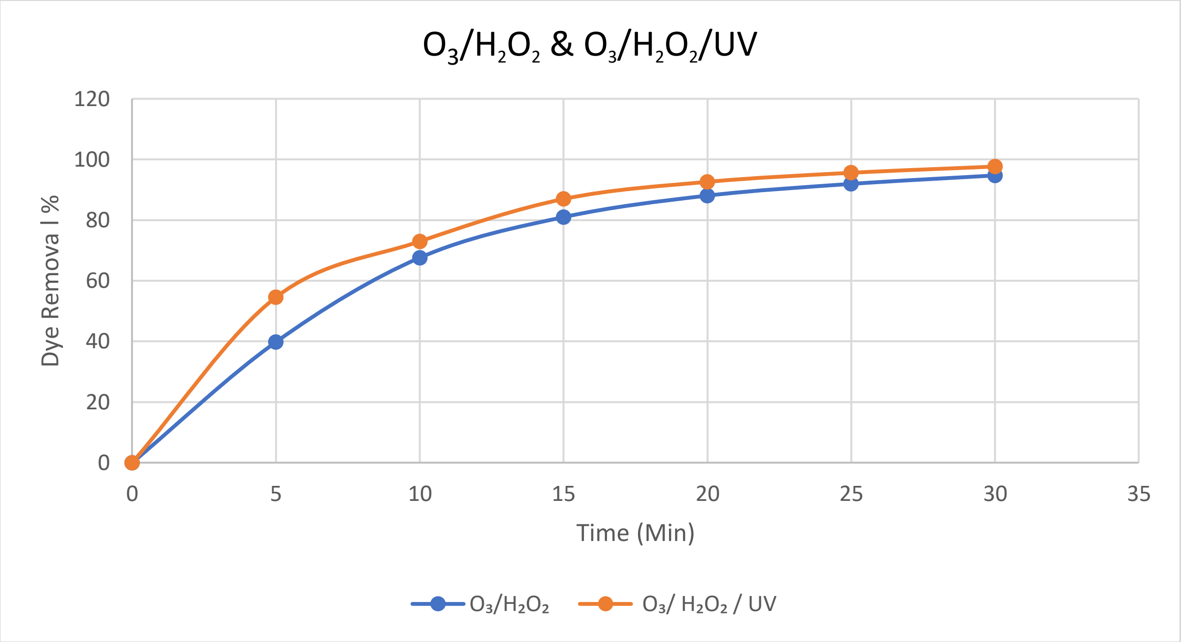


Figure (21). Comparison between Peroxone and photo-peroxone [H_2O_2 = 0.5 Mmol, Dye=50 mg/L].

When comparing between reaction, the results showed that photo-peroxone is better than peroxone where in the end of reaction, the removal percent in photo-peroxone can enhance the removal percent by over 3% at the same time of reaction.

5.3.3. Heterogenous catalytic ozonation process (COP)

This type a promising efficient system for removal pollutant from water and wastewater. The basic idea In a heterogeneous COP, the catalyst might improve the ozonation reactions in many ways: the first probability is the interaction of functional group (for example oxygen atom may attach to hydrogen then form hydroxyl group), these radical may react with ozone on the on the catalyst's surface and generates very reactive oxidant species with much higher oxidation potential than molecular ozone through a chain of reactions, the second probability the catalyst offers a surface on which the desired substance and molecular ozone may react instead of propagation and the third probability, the catalyst can adsorb the compound in the solution which ultimately interacts with ozone that has dissolved [51].

The study of experiment is highly efficient for removing elevation levels of dye in few times with few times in comparison two other system of ozone as well as it shows the effect of UV-radiation where UV can increase the reaction rate of reaction.

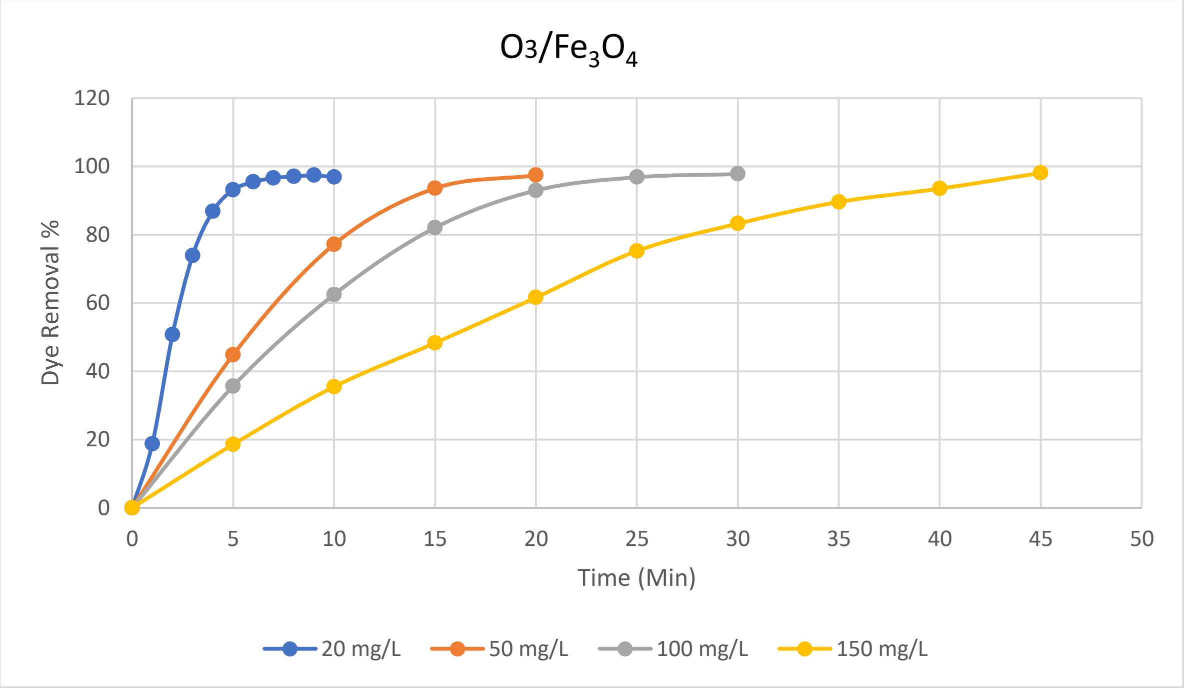


Figure (22). Removal of different concentrations of Novacron Deep Red S-B dye by ozonation in the presence of Catalyst magnetite [different Concentration + 0.2 g/L].

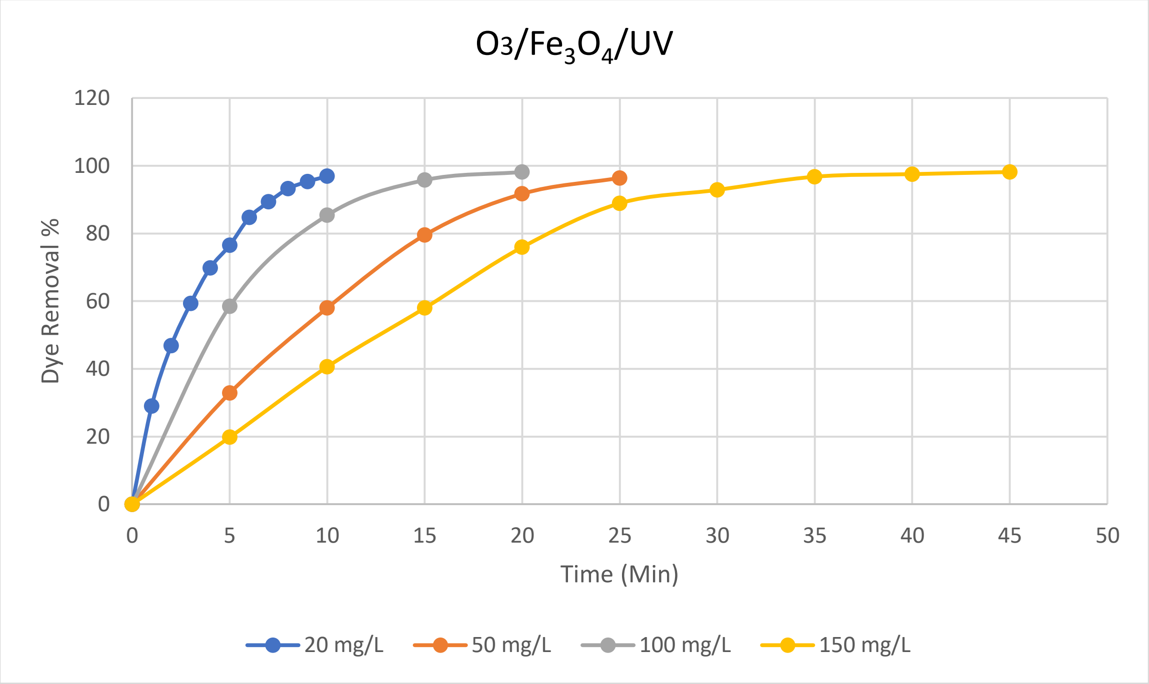


Figure (23). Removal of different concentrations of Novacron Deep Red S-B dye by ozonation in the presence of Catalyst magnetite under effect of UV [different Concentration + 0.2 g/L].

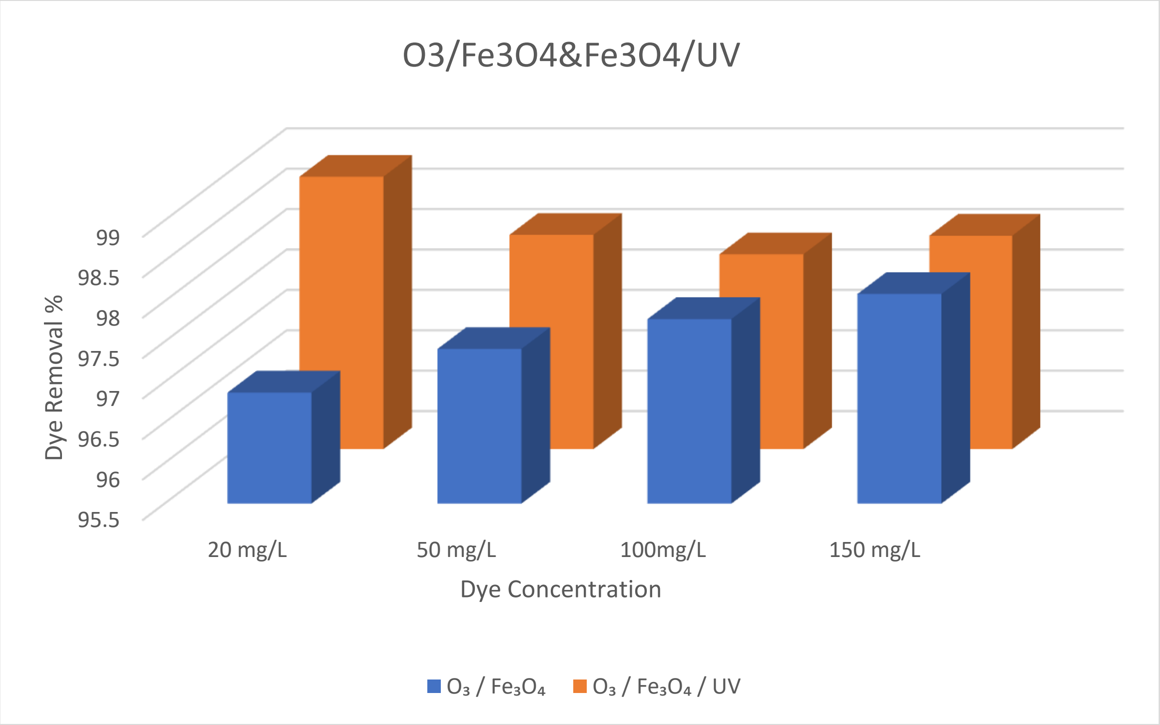


Figure (24). Comparison between removal percents of Novacron Deep Red S-B dye by O_3/Fe_3O_4 system in the absence and presence of UV radiation.

For optimization the O_3/Fe_3O_4 system, different doses of Fe_3O_4(0.3, 0.4, 0.5g/L) were added to the system. The results obtained showed little increase of the removal percents by increasing Fe_3O_4 dose, Figure (25). The same experiments were repeated in the presence of UV radiation which resulted in increasing the removal rates and dye removal percents, Figure 26.

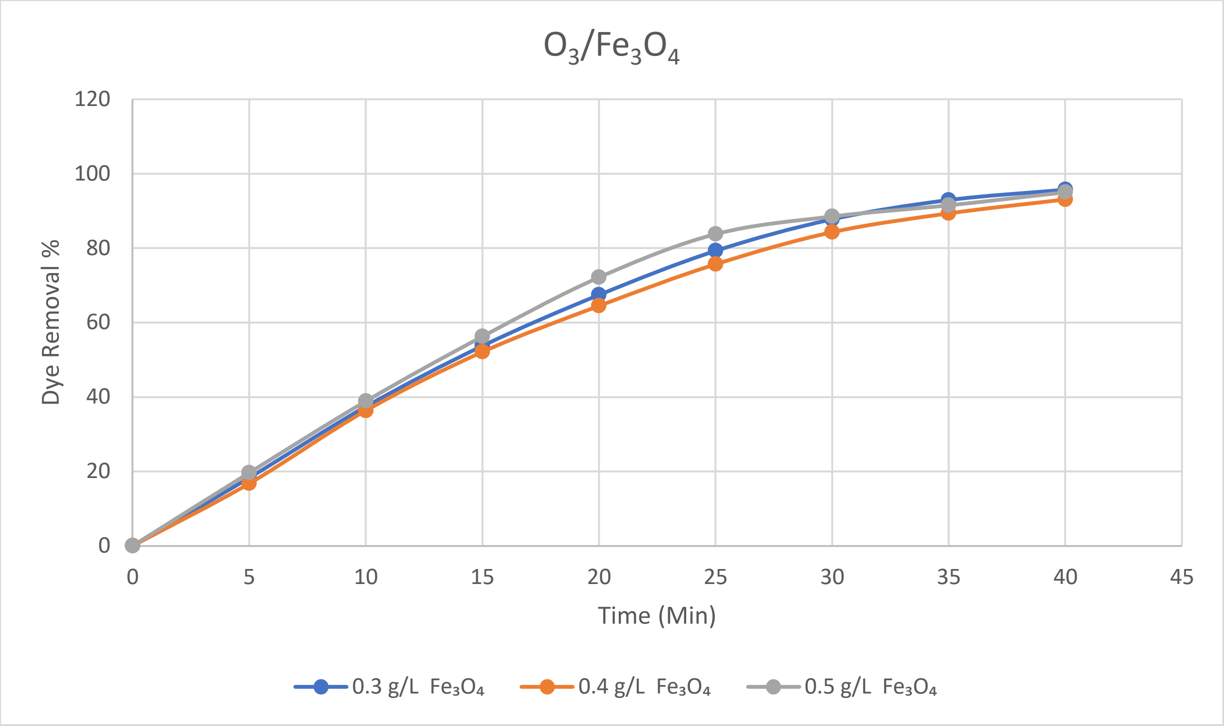


Figure (25). Effect of different dose Fe_3O_4 with O_3 for removal Novacron Deep Red and its concentration=150 mg/L dye.

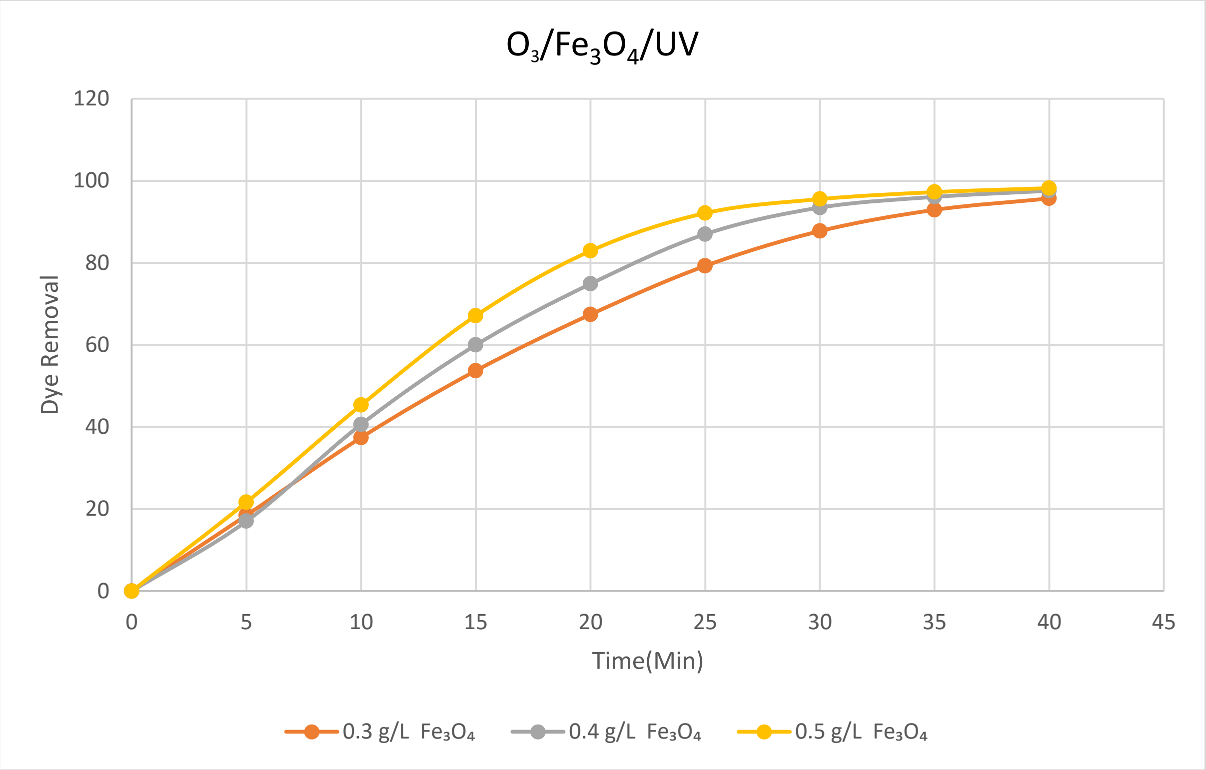


Figure (26). Effect of different dose Fe_3O_4 with O_3 for removal Novacron Deep Red and its concentration=150 mg/L dye under UV-Radiation.

6. Conclusion

This study investigated the efficiency of using AOPs by various direct and indirect oxidation techniques for the removal Novacron Deerp Red S-B textile dye in aqueous solutions and the work successfully employed UV/H_2O_2, ozonation (O_3, O_3/UV, O_3/H_2O_2, O_3/H_2O_2/UV) and Fenton processes that involving homogenous Fenton and heterogenous Fenton processes.

The study proved the efficiency of synthesized Magnetite (Fe_3O_4) catalyst that prepared with green synthesis. Dye efficiency removal was achieved 99.15% with 0.5mMol of hydrogen peroxide. The degree of Ph=3, was found to be optimal for maximizing dye removal efficiency, effect of ultraviolet radiation increases the rate of degradation reaction and higher initial of dye concentration decrease of removal %.

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