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Removing of Acid Red 1 Dye Pollutant from Contaminated Waters by UV/ TiO2/ H2O2 Process Using a Recirculating Tubular Reactor

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Abstract

Dyes are the most important materials in industries which are dangerous to ecological systems due to their toxic properties. This study investigated the photocatalytic efficiency of TiO_2 nanoparticles stabilized on a glass plate in order to remove Acid Red1 (AR1) dye in an aqueous solution under UV Light. In this research, the photocatalytic decomposition of the AR1 dye was carried out in a batch tubular reactor with a recirculating flow. Effective parameters on the process such as: the initial pH of the solution, the concentration of AR1, the distance of the lamp from the catalysts' surface, the concentration of H_2O_2, and the flow rate were studied. The morphological properties of the Titanium dioxide nanoparticles stabilized on the glass plate were investigated through SEM and AFM. The favorite dye removal efficiency for a solution containing 30 mg/L of AR1 was obtained in the pH of 2.5, H_2O_2 concentration of 10.12 mM, radiation time of 120 min, and the lamp-catalyst surface distance of 10 cm. In these conditions, the dye removal efficiency became approximately 99%.

Keywords: Photocatalytic; TiO_2 nanoparticles; dye removal, Acid red 1.

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Introduction

Nowadays, organic pollution has become one of the most pivotal environmental issues. Several industrial activities, particularly, the textile industries release hazardous materials, especially organics into the environment and give rise to extensively harmful effects on both humans and other species [1]. The use of polluted water resources for irrigation will cause soil contamination; hence, the treatment of this water remains a major challenge all over the world [2-4]. Several assorted methods, including electro-coagulation, chemical coagulation, membrane separation, adsorption, etc., are used for treating wastewater, that each has its own advantages and disadvantages.

Likewise, the method used for wastewater treatment depends on the types and sources of pollutants [5, 6]. Hence, it is important to develop technology capable of providing reliable, economical, and fast water treatment to mitigate these problems and ensure a safe and sustainable future [7, 8]. According to the World Bank’s estimation, around 20 percent of the industrial wastewater is produced by textile industries [9]. Dyes are mostly used in different industries and freely solved in water. About 10 to 20 percent of these toxic dyes are washed out by water, becoming harmful to flora and fauna [10] and causing some diseases in humans, such as nausea, skin irritation, lung problems, and so on. [11-14].

As compared to other water treatment approaches, advanced oxidation process (AOPs) is a method by which •OH radicals are produced. •OH radicals have stronger oxidation power than many other oxidants and are able to decompose organic compounds into less hazardous compounds, such as H_2O, CO_2, or HCl. AOPs have assorted methods in order to generate •OH radicals, e.g., using ozone, Fenton technology, electromagnetic beam, ultrasound, microwave, and photochemical techniques helped by the catalytic activity of metal oxides semiconductor to decompose pollutants of water.

UV/TiO_2 is a type of AOPs [15-17] which is an indirect and effective heterogeneous photocatalytic process using the energy of UV radiation [18]. TiO_2 is the preferred photocatalyst among other semiconductors, such as CdS, GaP, and ZnO for different reasons, including its economic availability, excellent photoactivity, low toxicity, and high stability in both acidic and basic media [19]. Many other semiconductors don't seem to be appropriate for environmental purification because they can be dissolved and produce toxic byproducts in solutions [20]. Despite its benefits, TiO_2 suffers from two main drawbacks, i.e., poor solar energy conversion and a high rate of charge recombination, which may decrease the quantum yield and waste a huge amount of energy. Dopants such as metals and nonmetals are used for solving this problem [21-23]. The TiO_2 process consists of five steps described below [24, 25]:

1- Eliminating organic pollutants from the liquid phase (water) to TiO_2 surface

2- Adsorption of organic pollutants on TiO_2 surface

3- Starting photocatalysis reaction on the TiO_2 surface

4- Eliminating degraded organic pollutants from the TiO_2 surface

5- Transferring the degraded pollutants to the bulk fluid

Numerous studies have suggested that the UV irradiation of TiO_2 leads to the development of reactive oxygen species, including hydrogen peroxide or hydroxyl radical, that are able to decompose organic pollutants into carbon dioxide, H_2O, and other mineral acids [26, 27]. This method has some advantages as compared to other methods. For instance, UV-Photocatalysis technology is more efficient, causes less pollution, and has fast kinetics. These unique characteristics have made it a preferred method over other ways in the past decades [28]. Furthermore, photocatalytic methods require minimal addition of chemicals and produce zero waste, accordingly.

The catalytic activity of TiO_2 is mainly influenced by its crystalline structure (Anatase, rutile, and Brookite) and morphology (nanoparticle, nanowire, nanotube, etc.). Anatase is known as the best form for photocatalytic activity because the Anatase phase has an energetic separation capability among the valence and conduction band through UV radiation. Molecular charge separation and excitation are the results of absorbing the photon energy from UV radiation by TiO_2. The conduction and valence band energies of the Anatase TiO_2 photocatalyst are -0.1 V and +3.1 V, respectively [29-33]. The conduction band energy of the TiO_2 photocatalyst is slightly higher than the reduction potential of O_2 (a predominant electron acceptor) which can ease the transfer of electrons from the conduction band to O_2. On the contrary, the valance band energy level is much lower than the oxidation potentials of most of the electron donors. Thus, the highly oxidative holes can be transferred to the TiO_2 surface adsorbing •OH and usually encourage the redox transformation of textile effluents [34]. The main purpose of the present lab study was to check the feasibility of treating the sewage polluted with the AR1 dye with the TiO_2/H_2O_2 photocatalyst process. A reactor was utilized, and the assorted parameters were surveyed for the optimization of the conditions for photodegradation. The originality of this paper lies in using TiO_2/H_2O_2 for degrading the AR1 azo dye.

Experimental

Chemicals

The Titanium dioxide nanoparticle was purchased from Degussa (Germany), H_2O_2 (30%) was obtained from Merck, and AR1 dye ($C_{18}H_{13}N_3Na_2O_8S_2$) was provided from Sigma Aldrich (USA). Its structure is shown in Figure 1:

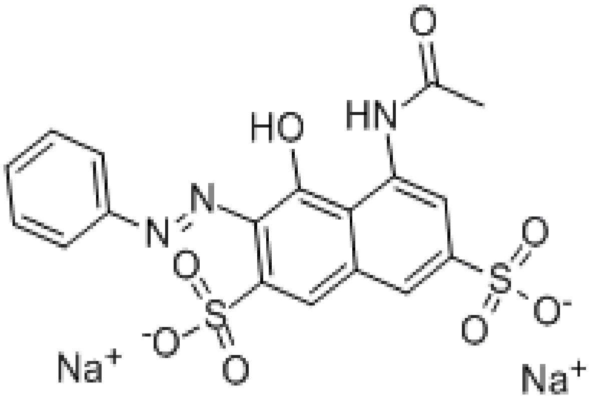


Figure 1. The structure of azo dye (AR1).

Reactor and Procedure

The proposed reactor consists of a cylinder glass with three glasses, coated by TiO_2 particles and located inside the reactor at a distance of just about 2 cm from each other. It also contains a pump and a plastic tank in order to store the solution. According to Figure 2, the reactor has a cylindrical chamber with a length of 35 cm and a diameter of 8 cm. The UV lamp was fixed adjacent to the reactor. The average UV intensity is about 15 W with an emission peak wavelength of approximately 254 nanometers and can change the organic materials into CO_2, H_2O, and other materials. The role of the pump is to assist the circulation of the wastewater through the reactor and storage tank. The effects of different experimental parameters, including pH, pollutant density, the distance of the UV lamp from catalyst surface, flow rate, amount of H_2O_2, and so on, were investigated. All experiments had been carried out at room temperature (23±2°C).

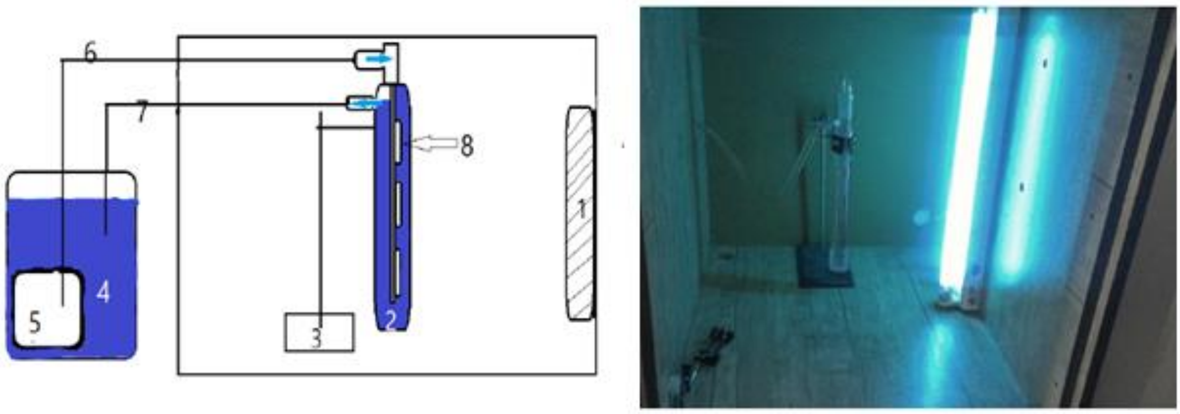


Figure 2. Experimental setup (1:UV Source, 2: Cylinder glass, 3: Stand, 4: Polluted water, 5: Water pump, 6 and 7: Suction lines, 8: Glasses coated by TiO_2 nanoparticles).

Sample Preparation

At first, the three glasses (1.5×4 cm) were put in the H_2SO_4 1 M solution due to the development of more porosity on the surface of the glasses. Then, they were rinsed with purified water several times. Completely dried, the TiO_2 suspension (10 g/L) was poured into the glasses, and finally, the glasses were put in an oven at 100 °C for three hours at 500 °C for four hours in a furnace to fixate the TiO_2 nanoparticles on the surface of the glasses. When rinsed with purified water, the glasses were attached to the reactor inside. Figures 3 and 4 show the SEM and AFM images of the TiO_2 nanoparticles on the glasses, respectively. They show the 2D and 3D images of the surface of the glasses filled with the TiO_2 nanoparticles uniformly. It is shown that the surfaces of the glasses are well-coated by TiO_2. The AFM morphology and roughness data of TiO2 nanoparticles on the glass plates are displayed in Table 1.

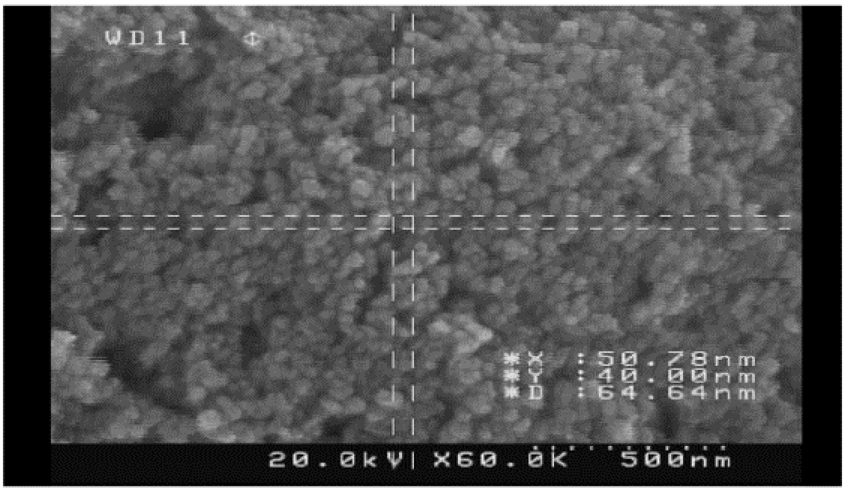


Figure 3. SEM of TiO_2 Nanoparticles on the glass plates.

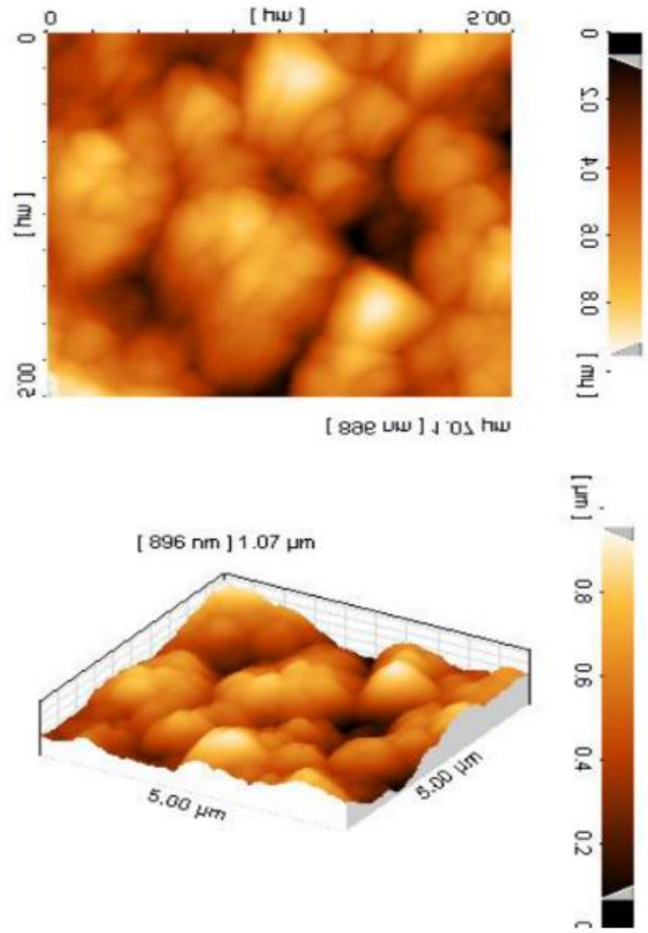


Figure 4. AFM of TiO_2 Nanoparticles on the glass plates.

Table 1. The AFM morphology and roughness data of TiO_2 nanoparticles on the glass plates.

Projected Area (μm^2)	RMS Roughness (nm)	Average Roughness (nm)	Surface Skewness, Ssk	Surface Kurtosis Sku	Ten Point Height, S10z (nm)	Maximum Peak Height Sp (nm)
25	159	128	0.065	2.75	77	1.07

Methods of analysis

The dye concentration measurement method was according to 2120C standard code. In this study, the UV-Visible spectrum was used to measure the AR1 concentration and determine the λ_{Max} for AR1. The absorbance curve of AR1 at 30 mg/L concentration in the range of 300-800 nm was used for determining the λ_{Max}. After determining the λ_{Max} of AR1, the absorbance values of the various concentrations of AR1 at 500 nm were measured. Then, the calibration curve was depicted, and the AR1 concentration was measured based on this curve in the surveys.

Procedure

In each step, 2 liters of the solution, which consisted of 30 mg/L AR1, was poured into the storage tank with a pump. Once turning on the pump and adjusting the flow rate, we let the solution pass through the reactor for 20 minutes in order to adsorption process the dye particles on the catalyst surface to achieve their balanced state. Then, a specified amount of H_2O_2 was added to the solution in the tank. The UV lamp was turned on to radiate to the solution. We took samples at specified times regularly and measured the residual pollutant by a spectrophotometer device in $\lambda = 500$ nm, and the concentration of the dye was determined with the help of the calibration curve. The degradation percentage (CR%) was calculated by Equation (1):

$$\mathrm{CR\%} = \frac{X_i - \mathrm{Xt}}{\mathrm{Xi}} \times 100 \quad (1)$$

Where Xi is the initial content, while Xt is the residual pollutant content (mg/L). The residual pollutant content was measured by a spectroscopic method.

Results and discussion

Effect of the pH range on the AR1 dye removal in the UV/TiO2/H2O2 process

Figures 5 and 6 reveal the removal percentage of AR1 within the reactor at different pH values (from 2.5 to 6.8). The result demonstrated that the reduction efficiency was improved when the pH of the solution decreased. Relatively, pH decrease leads to the generation of the TiOH2+ particles, which have a positive charge that assists the absorption of the AR1 dye with the –SO3- group. Hence, in an acidic circumstance, the AR1 azo dye will be absorbed by the TiO2 particles, therefore, the efficiency of dye removal will increase consequently.

In acidic pH, forming active radicals of hydroxyls on TiO2 particles surface takes place. As reported in previous studies, the effect of pH on the photodegradation of pollutants in solutions depends on several factors, including the ionization state of the TiO2 surface, the situation of valance band, conductive band of the photocatalyst, hydroxyl radicals, etc. [35-37]. It has been found that in acidic conditions, the TiO2 surface has a positive charge, and in basic conditions, it has a negative charge because the PZC of TiO2 varies between pH = 6-7.5. Thereby, if pH is over PZC, the catalyst surface becomes negatively charged, and the contaminants with positive charges will be adsorbed. However, if pH is less than PZC, the surface charge of the catalyst becomes positive, and the adsorption of the negatively charged pollutants will occur following increasing of the electrostatic attraction. Nevertheless, a suitable design for the pH control of photoreactions is so critical in every photocatalytic wastewater treatment process, and there's a significant relationship between the pH of the solution and the theoretical values of efficiency, which is well illustrated in Figure 6. Hence, pH = 2.5 was chosen as the best pH for the removal of AR1 during this study.

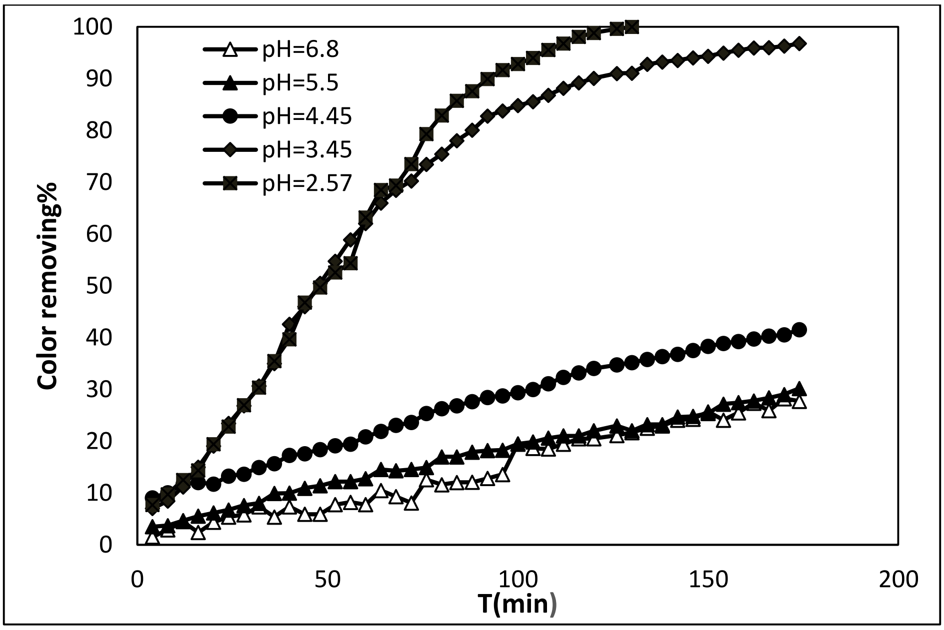


Figure 5. Effect of pH on the dye removal efficiency [AR1] = 30 mg/L, [H_2O_2] = 10.11 mM, flow rate = 70 mL/s, distance of UV lamp and catalyst = 20 cm, t = 120 min.

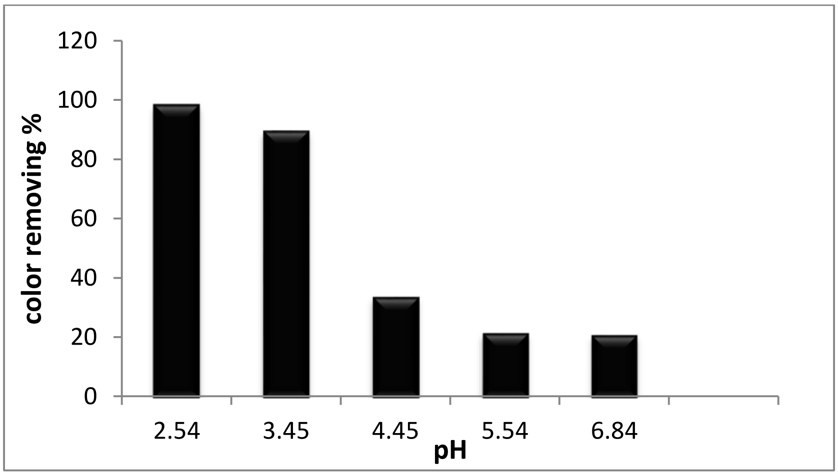


Figure 6. Dye removal efficiency in different pH [AR1] = 30mg/L, [H_2O_2] = 10.11mM, flow rate = 70 mL/s, distance of UV lamp and catalyst = 20 cm, t = 120 min.

Effect of H2O2 Concentration on the AR1 dye removal in UV/TiO2/H2O2

In this study, by increasing the concentration of H2O2, the efficiency of eliminating AR1 increases until a defined amount which gives the highest rate. A high H2O2 concentration increases the removal efficiency. This phenomenon can reasonably be explained based on increasing of hydroxyl radicals due to high H2O2 concentration and consequently enhancement of their reaction with the dye molecules.

As seen in Figures 7 and 8, above the H2O2 concentration of 10.11 mM, no enhancement to the degradation process occurs. Afterward, the elimination efficiency decreases when the H2O2 concentration exceeds 10.11 Mm. According to below equations, using an excessive amount of H2O2 can play a scavenger role and may decrease the mineralization rate. In higher concentrations, H2O2 reacts with hydroxyl radicals (•OH) and it can decrease the destruction amount of the AR1 azo dye. Hydroxyl radicals can produce hydroperoxyl radicals (HO2•), which are less reactive as compared to hydroxyl radicals. On the other hand, in lower concentrations of H2O2, H2O2 is disintegrated to hydroxyl radicals by UV radiation [38].

$$H_2O_2 + e^- \rightarrow \mathrm{O}H^- + \mathrm{O}H^\bullet \qquad (2)$$

$$H_2O_2 + hv \rightarrow 2\mathrm{O}H^\bullet \qquad (3)$$

$$H_2O_2 + \mathrm{O}H^\bullet \rightarrow H\mathrm{O}_2^\bullet + H_2O \qquad (4)$$

$$H\mathrm{O}_2^\bullet + \mathrm{O}H^\bullet \rightarrow H_2\mathrm{O} + \mathrm{O}_2 \qquad (5)$$

Therefore, the best amount of H2O2 in this process is about 10.11 mM in 120 min and pH = 2.5. Thus, there is a significant relationship between the amount of H2O2 and theoretical values of efficiency.

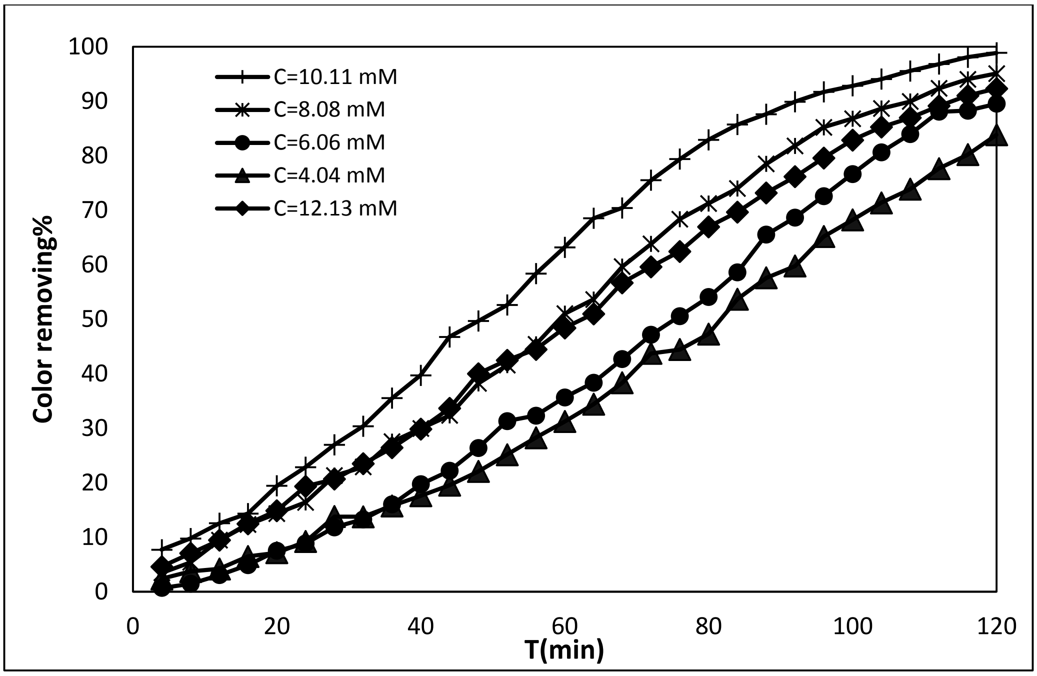


Figure 7. Effect of H2O2 concentration on the dye removal efficiency [AR1] = 30mg/L, flow rate = 70 mL/s, distance of UV lamp and catalyst = 20 cm, t = 120 min, pH = 2.5.

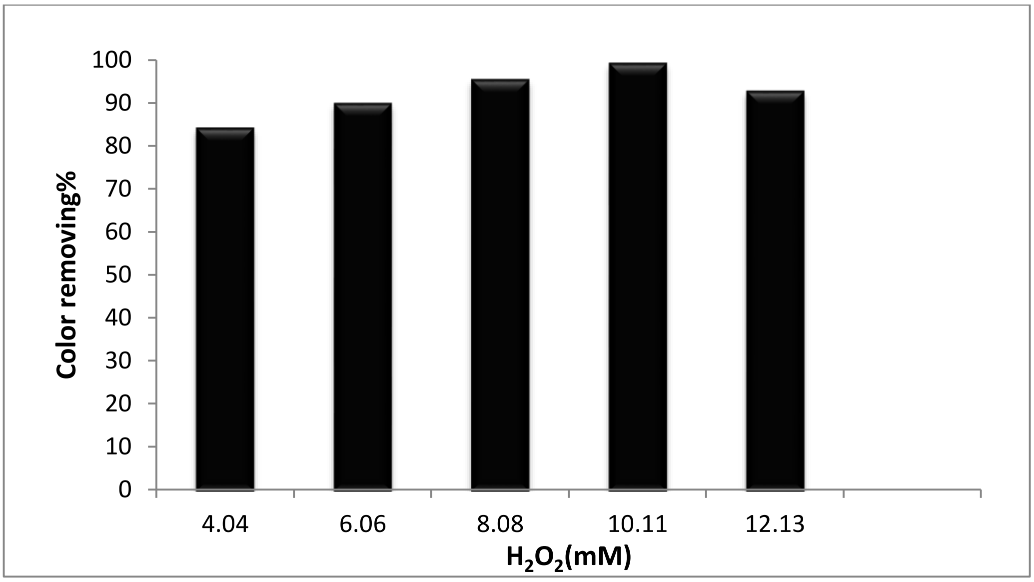
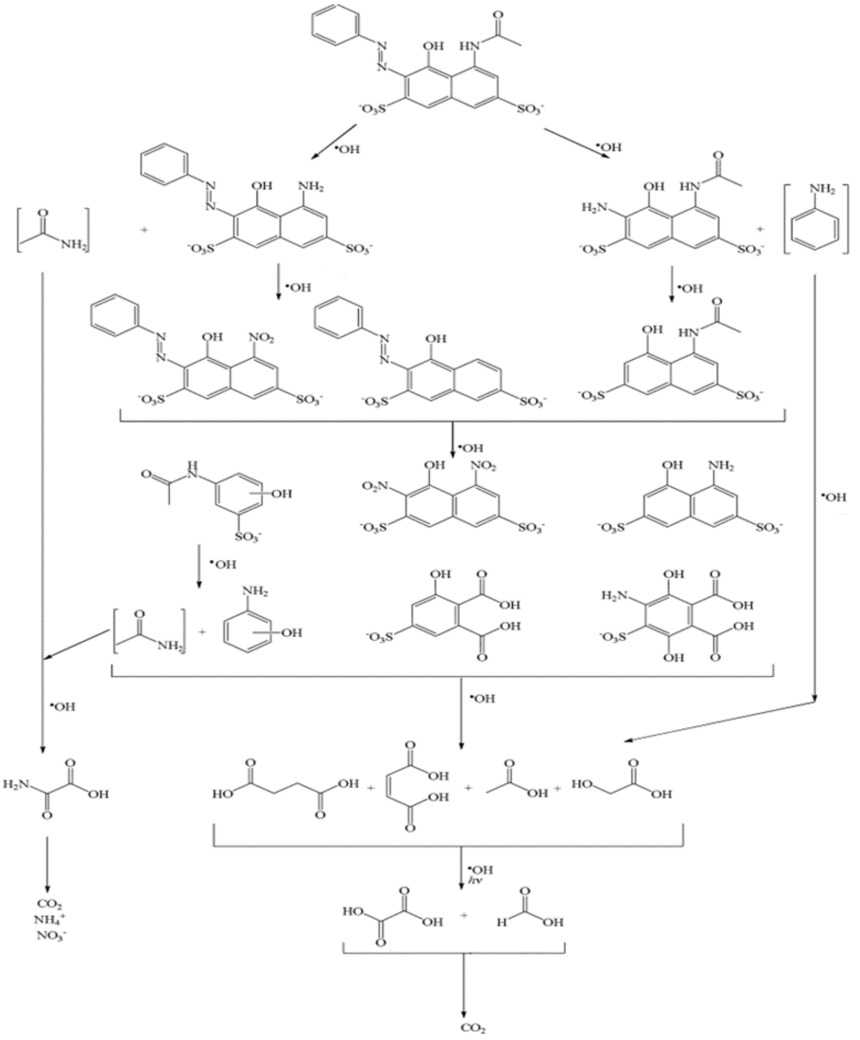


Figure 8. Dye removal efficiency in different concentration of H2O2 [AR1] = 30mg/L, flow rate = 70 mL/s, distance of UV lamp and catalyst= 20 cm, t = 120 min, pH = 2.5.

Generally, within the photocatalytic oxidation process, H2O2 particles play two pivotal roles and have special functions: the first function of H2O2 is to assist the separation of the charge by receiving electrons in the conduction band of TiO2, and the second is to produce oxidizing agents, including •OH. In higher concentrations and after the maximum range, the degradation of the pollutant began to decrease. The decrease in the efficacy of the process due to the rise of the H2O2 concentration could be for scavenging radicals. Additional H2O2 will begin reacting with the •OH radicals so as to create water molecules [39]. The mechanism of photocatalytic oxidation of AR1 dye is provided in Scheme 1.



Scheme 1. The mechanism of photocatalytic oxidation of AR1 dye.

Effect of distance of UV source and TiO_2 catalyst surface on the AR1 dye removal in $UV/TiO_2/H_2O_2$

It is clear that the efficiency of the removal decreases with an increase in the distance among the UV lamp and TiO_2 catalyst. According to Figures 9 and 10, in the distance of 10 cm, the removal efficiency surpasses the others due to enhancing the production of the •OH radicals as a result of UV radiation to the TiO_2 particles, leading to more oxidation of organic contaminants. Whereas in the distance of 30 cm, an increase in distance of the UV lamp and TiO_2 catalyst leads to the production of less •OH and thus the oxidation of organic pollutants.

Generally, the distances of the UV lamp and TiO_2 catalyst play key roles in the photocatalytic process. Since the goal of the experimental design was to determine the maximal dye degradation, 10cm was chosen as the best distance of the UV source and catalyst under optimal conditions. In this situation, the efficiency become nearly 100%.

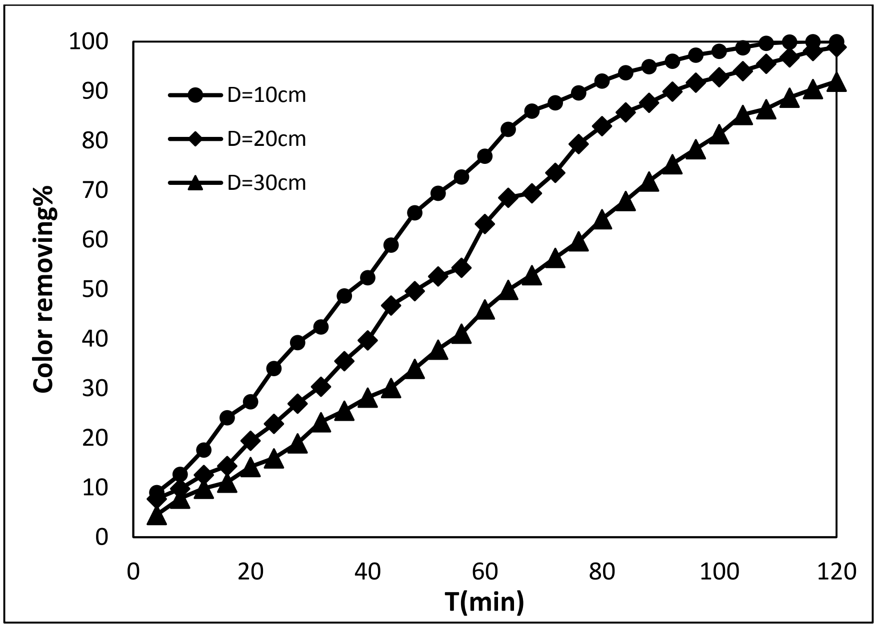


Figure 9. Effect of distance of UV source and TiO2 catalyst surface on the dye removal efficiency, [H2O2] = 10.11mM, [AR1] = 30mg/L, flow rate = 70 mL/s, t = 120 min, pH = 2.5.

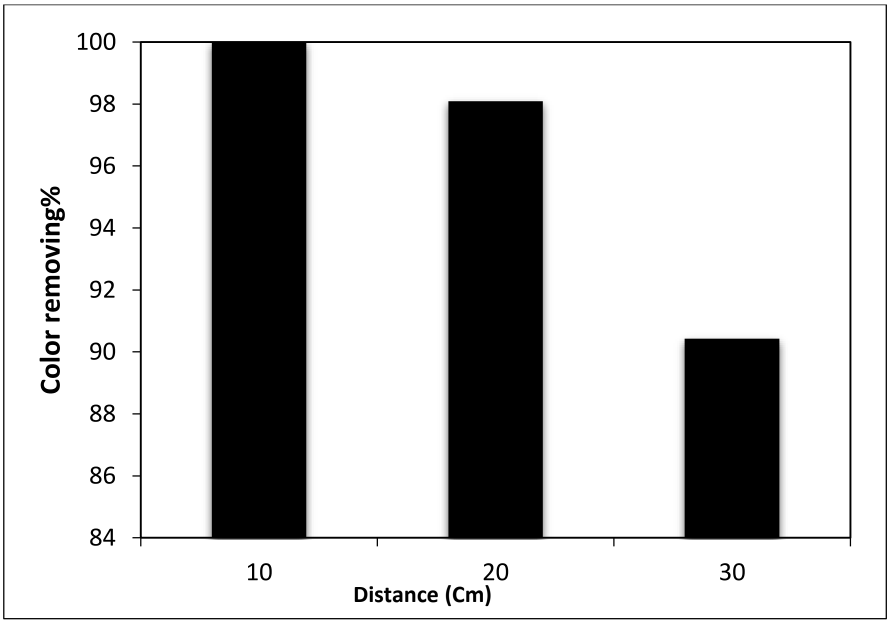


Figure 10. Dye removal efficiency in different distance of UV lamp and TiO2 catalyst surface, [H2O2] = 10.11mM, [AR1] =30 mg/L, flow rate =70 mL/s, t =120 min, pH = 2.5.

Effect of initial dye concentration of AR1 on the dye removal in UV/TiO2/H2O2

Figures 11 and 12 display the dye removal percentage with different initial concentrations at a diverse time. Accordingly, the removal percentage decreased with the rise of the organic pollutant. In general, when the amount of H2O2 is constant, the produced •OH radical is constant as well and makes the dye removal percentage decrease. Besides, in higher concentrations, photons, which are radiated from the UV lamp, cannot pass through the solution and reach the catalyst`s surface. As a result, the amount of the •OH radicals decrease. Generally, according to previous studies, the degradation rate increased by increasing the initial concentration of the organic pollutant to a level above a certain concentration, and the reaction rate started to decrease upon increasing the concentration [40-42].

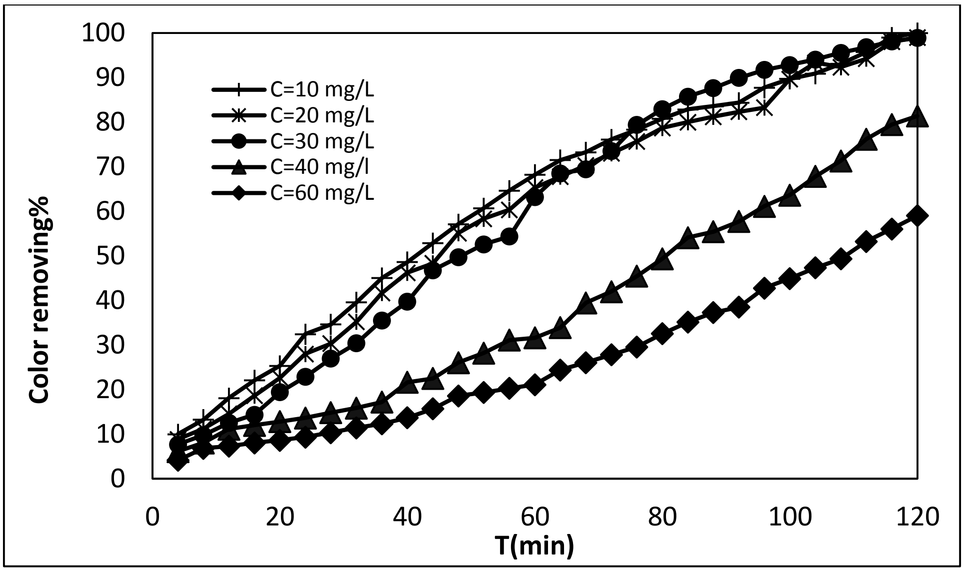


Figure 11. Effect of initial dye concentration on the dye removal efficiency [H2O2] = 10.11mM, flow rate = 70 mL/s, distance of UV lamp and catalyst = 10 cm, t = 120 min, pH = 2.5.

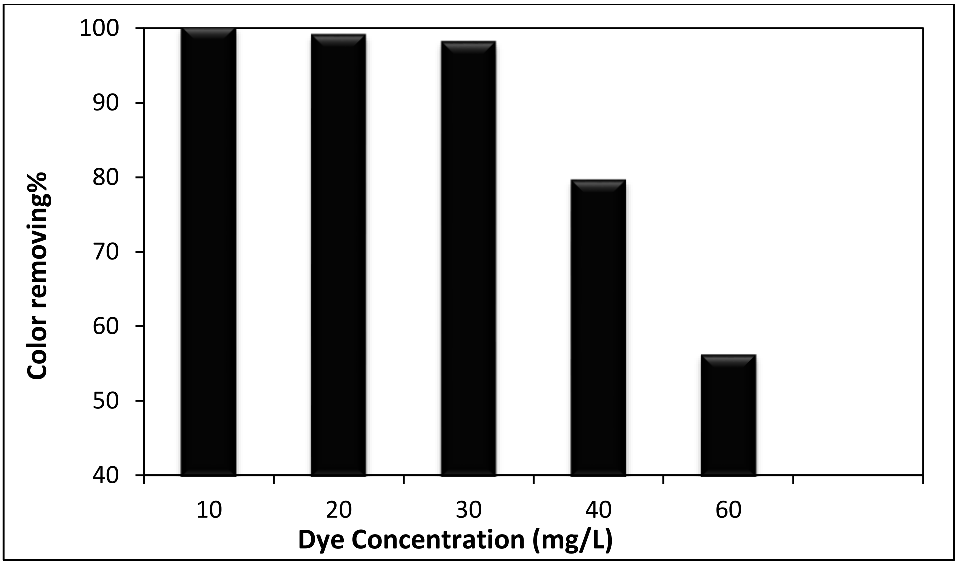


Figure 12. Dye removal efficiency in different initial dye concentrations [H2O2] = 10.11mM, flow rate = 70 mL/s, distance of UV lamp and catalyst = 10 cm, t = 120 min, pH = 2.5.

Effect of flow rate on the AR1 dye removal in UV/TiO2/H2O2

The flow rate has a distinguishing impact on the removal of AR1 efficiency. The result of the various flow rate on removing the AR1 in pH= 2.54, C= 30 mg/L, and H2O2 Concentration 10.11 mM was assessed by the change of the flow rate from 18 to 70 mL/s, and the final concentration of AR1 was measured by a spectrophotometer and calibration curve. The results displayed in Figures 13 and 14 reveal that in the flow rate of 18 mL/s, the removal efficiency of AR1 has decreased. It's noted that the removal gradient depends on the disposing of the wastewater near the catalyst surface and the UV radiation time. Hence, if the disposing time of the water, TiO2 catalyst, and UV radiation is shortened, the efficiency of the AR1 removal are going to be decreased.

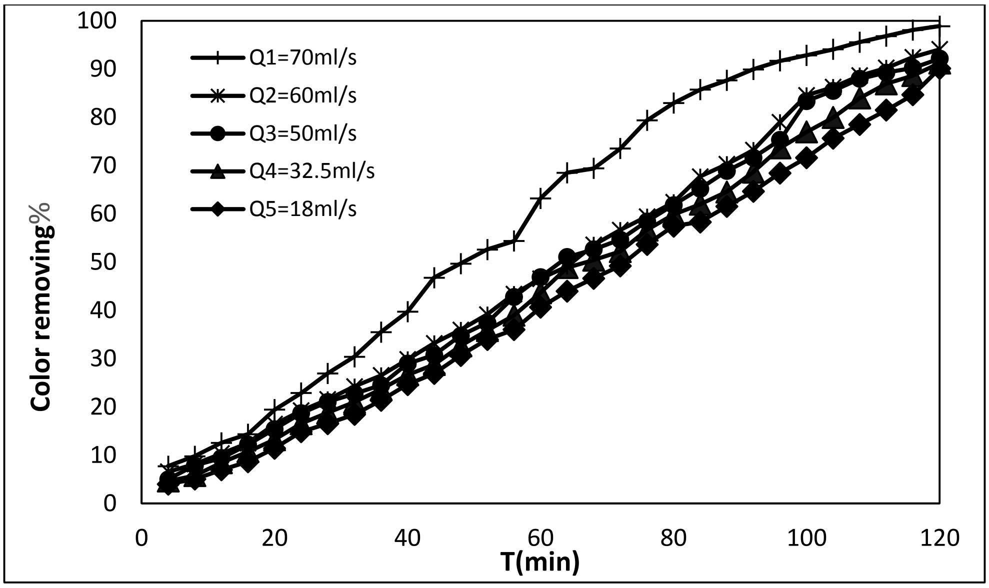


Figure 13. Effect of flow rate on the dye removal efficiency [H2O2] = 10.11mM, [AR1] = 30 mg/L, t = 120 min, pH = 2.5, distance of UV lamp and catalyst = 10 cm.

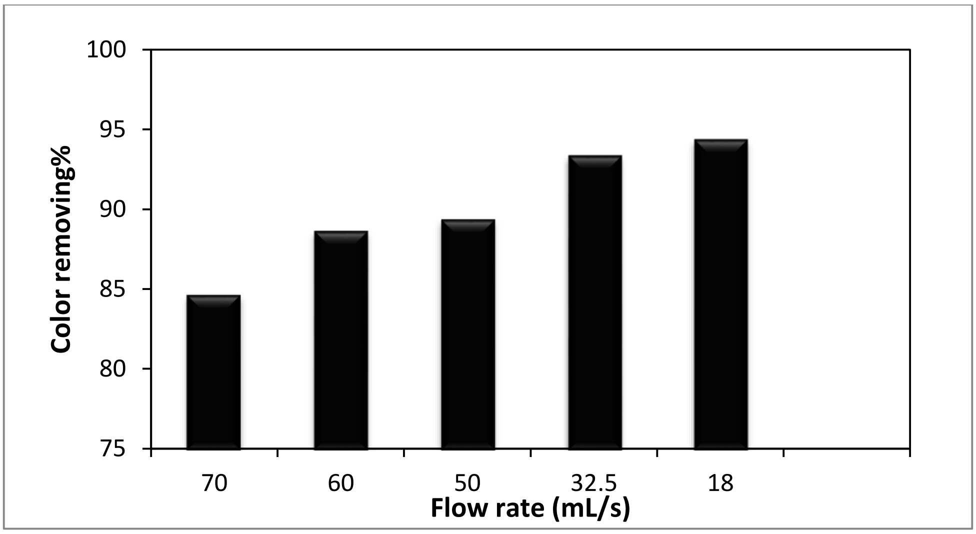


Figure 14. Dye removal efficiency in different flow rate [H2O2] = 10.11mM, [AR1] =30 mg/L, t =120 min, pH = 2.5, distance of UV lamp and catalyst =10 cm.

Survey of photocatalysis process for removing AR1 azo dye in presence and absence of TiO_2 and H_2O_2

For investigating the roles of H_2O_2 and TiO_2 on removing efficiency of AR1 azo dye, according to Figure 15, several different conditions were prepared as below:

1- Presence of TiO_2 and absence of H_2O_2

2- presence of h_2o_2 and absence of TiO_2

3- Absence of both H_2O_2 and TiO_2

4- Presence of both H_2O_2 and TiO_2

For this purpose, the effect of the absence of H_2O_2 and TiO_2 was investigated while other experimental conditions (the distance of UV and catalyst =10 cm, t = 120 min, pH = 2.5, flow rate: 70 mL/s) were fixed. As revealed in Figure 15, in the absence of H_2O_2 and TiO_2, the efficiency is zero due to the lack of the Hydroxyl radicals as effective factors in destroying the Azo dye. But in the presence of both TiO_2 and H_2O_2, the efficacy is around 99% since the electrons on the surface of the catalyst are stimulated, the electron-hole pairs are generated, and the hydroxyl radicals are produced. As a result, the presence of TiO_2 and H_2O_2 is required. Thereupon, in the absence of each one, the degradation of AR1 will not occur.

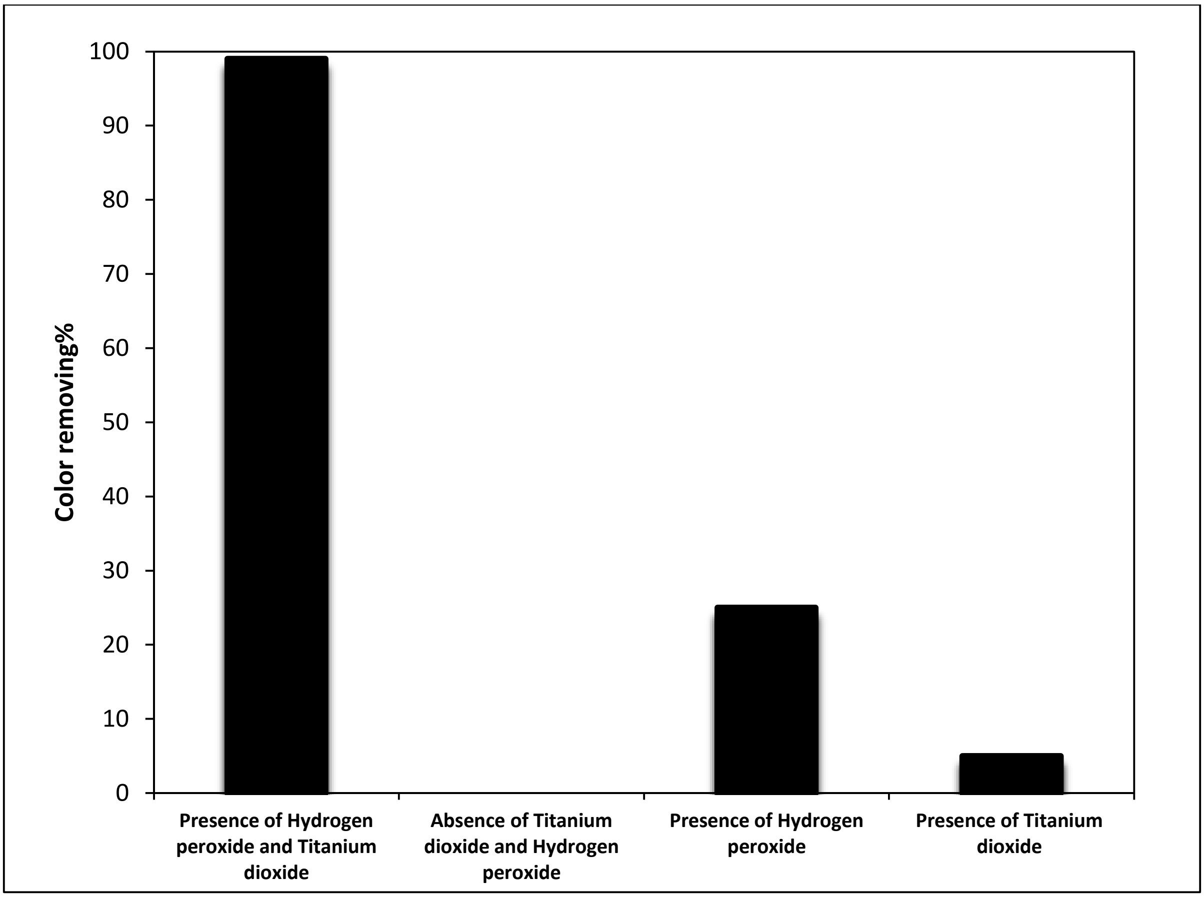


Figure 15. Photocatalytic process for removing AR1 azo dye in the absence and presence of TiO2 and H2O2, [AR1] = 30 mg/L, t = 120 min, pH = 2.5, distance of UV lamp and catalyst = 10 cm, flow rate = 70mL/s.

Determination of the rate constant of AR1 degradation in UV/TiO2/H2O2 process

Generally, there are two steps in heterogeneous photocatalyst process:

a) Adsorption of organic pollutant on photocatalyst and;

b) Photocatalysis reaction.

To determine the rate controlling and mass transfer mechanism, experimental kinetic data was correlated to linear form of the pseudo first order (Lagergren Model) and second order (Ho model) rate models. The R^2 values obtained from Figure 16 suggested that Lagergren Model was not befitted to the modelling of kinetic data. According to Figure 17, the extremely high value of the correlation coefficient about both adsorbents shows a good compliance of the data with the pseudo second order kinetic and therefore the constant of the reaction is 0.028 min-1.

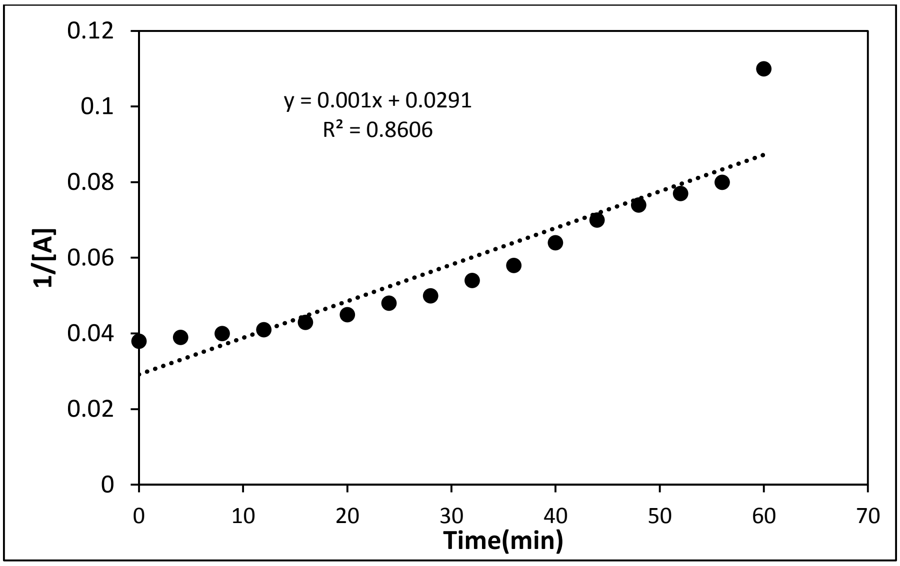


Figure 16. Pseudo first order kinetic of AR1 degradation in UV/TiO2/H2O2 process.

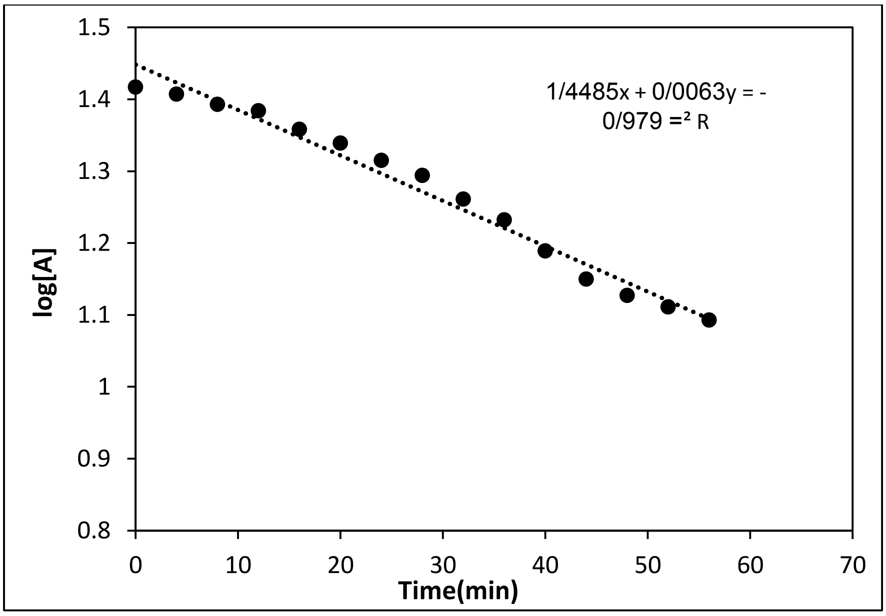


Figure 17. Pseudo second order kinetic of AR1 degradation in UV/TiO_2/H_2O_2 process.

Conclusion

In this work based on UV/TiO_2/H_2O_2 process, using a tubular reactor, a 100% efficiency was practically achieved for AR1 dye removal. This high efficiency indicates the high efficiency of the method in AR1 dye degradation from contaminated waters. The advantages of this method include low cost, high safety and efficiency, no need to separate the catalyst from the solution during the process. The operating variables, including pH, flow rate, the distance of UV source and catalyst, H_2O_2 concentration and initial dye concentration were investigated on the dye removal efficiency. As a result, under optimal conditions (pH = 2.5, flow rate = 70mL/s, distance UV lamp and catalyst = 10 cm, time = 120 min, [H_2O_2] = 10.11mM, [AR1] = 30 mg/L), the theoretical efficiency of the AR1 azo dye degradation can achieve up to 99%. Finally, the kinetics analysis confirmed a first-order reaction for the AR1 dye removal, and this photocatalytic process could be potentially employed in the removing of a pollutant from the environment.

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