Photocatalytic Degradation of Monoazo and Diazo Dyes in Wastewater on Nanometer-Sized TiO$_2$

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Abstract : Advanced oxidation processes (AOPs) have proved very effective in treatment of the various hazardous organic pollutants in water. The photocatalytic degradation of two azo dyes, monoazo dye Acid Orange 10(AO10) and diazo dye Acid Red114(AR114) present in wastewater were studied. Homogeneous photocatalytic degradation of the two azo dyes with UV/Visible/H$_2$O$_2$ process was investigated. The rates of disappearance of the two azo dyes were monitored spectrophoto-metrically at the visible maximum absorption wavelengths. It was found that the rate of decolorization rises by increasing the initial dosage of H$_2$O$_2$ up to a "critical" value at which it is maximum and beyond which it is inhibited. The rates of reactions follow pseudo-first-order kinetics. Also heterogeneous photocatalytic degradation of the two azo dyes with UV/Visible/TiO$_2$ (titanium dioxide) interface was investigated. The photocatalytic degradation rate depends on dye structure, dye concentration, TiO$_2$ loading and pH of the medium. The mechanism of the photodegradation process under UV-visible light illumination involves an electron excitation into the conduction band of the TiO$_2$ semiconductor leading to the generation of very active oxygenated species that attack the dye molecules leading to photodegradation .

Photocatalytic activity of TiO$_2$ was examined by focusing on its enhancement by electron scavengers in the photocatalytic decomposition of the two azo dyes. The electron scavenger employed was inorganic oxidant such as H$_2$O$_2$, adequate dose of H$_2$O$_2$ led to a faster degradation of the two azo dyes in the TiO$_2$ photocatalytic system. The fast decolorization of monoazo dye (AO10) than diazo dye (AR114) is an indication that, the number of azo and sulphonate groups in the dye molecule may be a determining factor for increasing the degradation rates. TiO$_2$ can be recycled at least twice without significant change in its efficiency. The photodegradation rates of the two recycled catalysts RC-1 and RC-2 were examined. [Journal of American Science. 2010; 6(11): 130-142]. (ISSN: : 1545-1003).

Keywords: Azo dyes; UV/H$_2$O$_2$ oxidation, Titanium dioxide; Photodegradation; Semiconductor.

1. Introduction

Environmental pollution on a global scale, as well as the lack of sufficient clean energy sources, have drawn much attention to the need for developing ecologically clean chemical technology, materials, and process [1-4]. Azo dyes, being the largest group of synthetic dyes, constitute up to 70% of all the known commercial dyes produced. Highly substituted aromatic rings joined by one or more azo groups characterize their chemical structures. These substituted ring structures make the molecules recalcitrant which the conventional wastewater treatment processes do not degrade. Being released into the environment, these dyes not only impart colors to water sources but also damage living organisms by stopping the reoxygenation capacity of water, blocking sunlight, and therefore disturbing the natural growth activity of aquatic life [5,6]. Thus, the color removal of textile wastewater is a major environmental concern [7].

In recent years, research in new non-biological methods has led to processes which actually destroy these pollutants in stead of simply extracting them from water (e.g., adsorption by active carbon, air stripping, etc.). It has been shown that the use of TiO$_2$, O$_3$, H$_2$O$_2$, and Fenton (a mixture of ferrous ion with H$_2$O$_2$) are more efficient in the photodegradation of organic pollutants in comparison to that of direct photolysis [8-10]. Among them, one of the common observations is that the enhancement of organic decomposition is due to the generation of powerful non-selective hydroxyl radical ($^\bullet$OH) produced in the process of photodegradation.

The efficiency of advanced oxidation processes for the degradation of recalcitrant compounds has been extensively studied [11-16]. Photocatalytic process, which utilizes TiO$_2$ semiconductor photocatalyst, has received increasing attention because of its low cost, non-toxicity, relatively high chemical stability of the catalyst, and the possibility of using sunlight as a source of irradiation [5,8,11,14]. However, it has a limitation that the quantity of $^\bullet$OH radicals cannot be increased infinitely because overdosing of TiO$_2$ scatters the light in the solution [8,17]. Therefore, new

developments of these technologies have focused on searching for better oxidants to increase the generation of radicals or to optimize the photodegradation process.

It was reported that the use of inorganic oxidants, such as H_2O_2, ClO_3^- BrO_3^-, and $S_2O_8^{--}$, in TiO_2 system increased the quantum efficiencies either by inhibiting electron-hole pair recombination through scavenging conduction band electrons at the surface of TiO_2 or by offering additional oxygen atom as an electron acceptor to from the superoxide radical ion ($\overset{\bullet}{O}_2^-$) [8,18]. According to the investigation on H_2O_2, adequate dose of H_2O_2 led to a faster degradation of organic compounds in the TiO_2 photocatalytic system [8,19]. However, the degradation was suppressed if excess H_2O_2 was used. This is due to the undesirable consumption of $\overset{\bullet}{}OH$ radical that was previously formed in the solution by H_2O_2, leading to generation of less-reactive $HO_2^{\bullet}$ radicals [8, 20]. Enhancement of TiO_2-catalyzed photodegradation of organic compounds by several inorganic oxidants was mainly attributed to the

increased electron scavenging from the extra oxidant sources [8,21].

Several studies of photocatalytic degradation of dyes have been reported [8,22,23]. Factors influencing the photodegradation rate of aqueous system have been studied in the subjects such as the initial concentration of dyes, the effect of pH values, dissolved oxygen contents and amounts of photocatalyst added to the aqueous solution [24,25].

This paper describes the kinetics of the color removal for two dyes, monoazo dye Acid Orange 10(AO10) and diazo dye Acid Red 114 (AR114) by homogeneous photocatalytic degradation in presence of (UV/Visible/H_2O_2), which is a 'friendly' oxidant and by heterogeneous photocatalytic degradation in presence of (UV/Visible/TiO_2) and enhancing the photocatalytic activity of TiO_2 by employing electron scavenger such as H_2O_2. Variable factors such as the initial dyes concentration, H_2O_2 does, TiO_2 loading and pH values have been studied. Moreover the efficiency of the recycled TiO_2 was examined

2. Materials and Methods
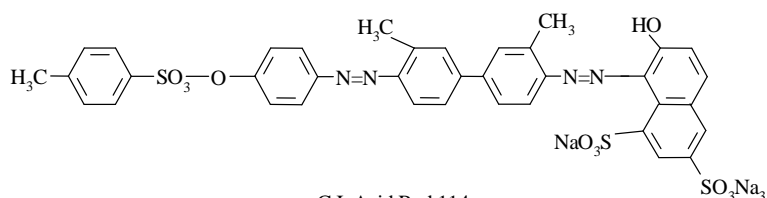
2.1. Materials

Two azo dyes, monoazo dye Acid Orange 10 (AO10) and diazo dye Acid Red 114(AR114) were obtained from Lingxian Shine Coating and .

auxilaries Co. LTD. were used without further purification. Their structure are drawn.
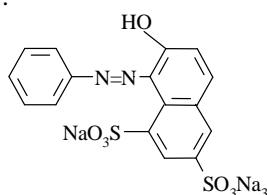
C.I. Acid Orange 10

(Mol. wt. 452.376 g and λ_{max} 478 nm)

C.I. Acid Red 114

(Mol. wt. 830.8308g and λ_{max} 514 nm)

Hydrogen peroxide (30% w/w) was obtained from Merck. Titanium dioxide P-25 from Degussa Corporation (70% anatase. 99.8% purity, average particle size 30 nm and specific surface of 50 m^2/g). It was dissolved in deionised water using (New water purification system, Human RO 180. RO, product).

2.2. Physical measurements

For the UV/Visible/H_2O_2 and UV/Visible/TiO_2 processes, irradiations were performed in a batch photoreactor. All experiments were conducted in a batch microsol light tester equipped with a pre-settable timer and water-cooling jacket (BS 1006 UK-TN) fitted with 400 W MB/U lamp show in Fig. (1) (made in England).

Fig. (1): Batch microsol photoreactor light tester

The pH values of the solution were adjusted, using microcomputer pH-vision DATALOGGER 6209; JENCO ELECTRONICS-LTD (made in U.S.A.). PH adjusted using dilute hydrochloric acid and sodium hydroxide solutions. Hydrochloric acid was chosen because its effected on the adsorption surface properties of the TiO_2 is negligible [26]. The absorption spectra were recorded with JENWAY-6300 UV-Visible spectrophotometer. The absorbance of solutions measured using a 1cm quartz cell (made in U.K.).
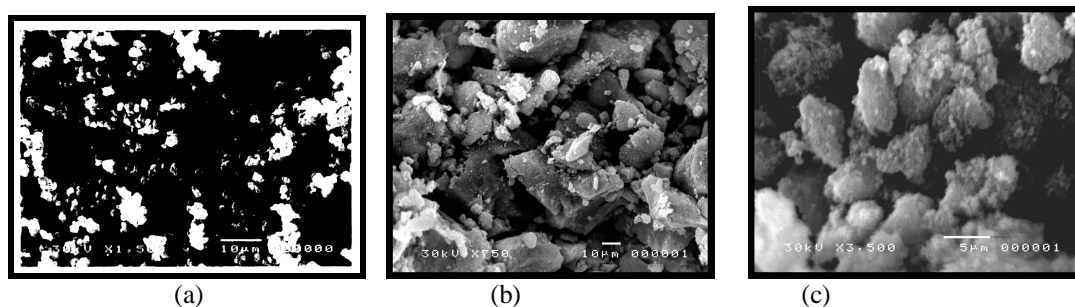
2.3. SEM analysis

Fig. (2): SEM micrograph of (a) TiO_2 and (b) (AO10) adsorbed on TiO_2 (c) (AR114) adsorbed on TiO_2

The SEM picture of pure TiO_2 and (AO10) and (AR114) adsorbed on TiO_2 are shown in Fig. (2). The SEM picture of pure TiO_2 Fig. 2a shows that, the size of titanium dioxide particles are uniform and needle-like particles [9]. In case of (AO10) and (AR114) agglomeration (particle-particle intera-ctions) is observed. The distribution of dye on the surface of TiO_2 is not uniform and SEM pictures Fig. 2b,c show that, dyes contain irregular shaped particles which are the aggregation of tiny crystals. However, it cannot be ruled out, that some dye particles are too small to be observed at the resolution of the used microscope [4,18]. The image from Fig. 2b, c reveals that, the presence of great agglomerates with particle size of monoazo dye (AO10) than diazo dye (AR114). From this result, it is clear that the morphology has been strongly influenced by the type of acid dye [27].

2.4. Photocatalytic degradation experiments

2.4.1. Homogeneous photocatalytic degradation

The experiments are carried out in a batch–type photoreactor. H_2O_2 is acts as photocatalyst and UV/Visible/light as illuminating light source. Reaction system is setup by adding the photocatalysts into 250 ml dye solutions prepared in appropriate concentrations using deionized water. The pH is adjusted to the desired values with HCl and NaOH.

Centrifug model 800 of a maximum speed 4000r/min is used for complete separation for the semiconductor particles used (TiO_2) from the sample solution. Scanning electron microscope (SEM) analysis is performed to identify the catalyst surface morphology using a JEOL-JSM-5400S scanning electron microscope (made in Japan). The SEM is measured in National Center for Radiation Research and Technology.

The dye solutions are stirred and divided to 5 ml samples and illuminated in a batch–type photo-reactor. At regular time intervals the dye concentrations are measured spectrophotometrically.

2.4.2. Heterogeneous photocatalytic degradation

Also the experiments are carried out in the same batch photoreactor. Pure TiO_2 powder adding into 250 ml dye solutions prepared in appropriate concentrations using deionized water. The pH also is adjusted to the desired values. The dye solutions are stirred and divided to 5 ml samples and illuminated in batch photoreactor. At regular time intervals the samples centrifuged and dye concentrations are measured spectrophotometrically.

3. Results and Discussion

3.1. Homogeneous photocatalytic degradation with H_2O_2

3.1.1. Effect of initial dye concentration.

Initial dye concentrations C_o were set in the range 1.0 x 10^{-5} to 1.0 x 10^{-4} M for both two azo dyes Acid Orange 10 and Acid Red 114. Photocatalysis were occurred in presence of 5mM H_2O_2 for both two azo dyes and pH 3.0. Initially, a large degree of removal is observed. This is due to fast decomposition of H_2O_2 producing the hydroxyl radicals.

Degradation of the dye is due to the hydroxyl radicals generated upon photolysis of hydrogen peroxide [28-30], following the reaction:

$$H_2O_2 + h\nu \longrightarrow 2\ {}^{\bullet}OH \qquad (1)$$
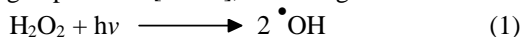
This radical is a very powerful oxidizer, able to react with inorganic as well with aliphatic or aromatic organic compounds [31,32].

According to the results of Shu et al., [28] the photooxidation reaction is pseudo-first-order with respect to azo dye concentration. This frequently occurs when the contaminant is very dilute in solutions. The kinetic constant can also be linked to the dye absorbance by Eq. (2).

$$\ln \frac{A}{A_o} = -kt \qquad (2)$$

Where : A_o and A are the initial and final absorbance values of solution before and after irradiation [33].

Moreover, decolorization of dye is mainly due to hydroxyl radicals generated. Azo bonds are more active: AO10 contain one azo bond and AR114 contain two azo bonds and degradation of this dyes are due to the initial electrophilic cleavage of its chromophoric azo (–N=N–) bond attached to naphthalene ring [34].

The values of photodegradation pseudo first order rate constants for different concentrations of dyes calculated from the linear plots of ln A/A_o against irradiation time are given in Figs. (3,4). Taking into account that, the life-time of hydroxyl radical is very short (only few nanoseconds), they can only react where they are formed [35]. Increasing the concentrations of AO10 and AR114 lead to decrease in the degradation rates see Fig. 4 and Table 1. However, the molar extinction coefficient of the two dyes are high (ε=16.9 x 10^3 and 18.3x10^3 liter mole^{-1} cm^{-1} for AO10 and AR114 respectively), so that a rise in its concentration induce an inner filter effect, i.e., incident light would largely be wasted for dye excitation rather than for the hydroxyl radical precursor excitation. Consequently, the solution becomes more and more impermeable to UV radiation. As the rate of hydrogen peroxide photolysis directly depends on the fraction of incident light absorbed by H_2O_2 molecules, the degradation rate slows down. The effect of direct UV/Visible irradiation was insignificant. The observed first order rate constants were 5.2 x 10^{-3} and 4.7 x 10^{-3} (min^{-1}) for AO10 and AR114 respectively. For reaction combined UV/Visible irradiation and hydrogen peroxide addition, the decolorization was extremely powerful than that of direct photolysis.
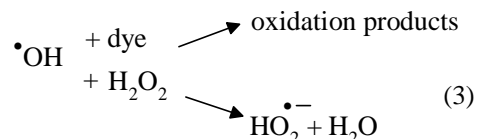
3.1.2. Effect of initial H_2O_2 concentration

The effect of varying the initial H_2O_2 concentration increase from 5mM to 100 mM for dye concentration 1.0 x10^{-5}M at pH 3.0 for both the two azo dyes AO10 and AR114. A very large excess of H_2O_2 in comparison to the dye was introduced in the solutions. Fig. 5, shows that, the initial hydrogen peroxide concentration strongly modifies the rates of degradation of the two azo dyes, Acid Orange 10 and Acid Red 114 in the UV/Visible/H_2O_2 processes [19,29].

At low hydrogen peroxide concentrations, formation of ${}^{\bullet}OH$ is the kinetic determining step. H_2O_2 cannot generate enough hydroxyl radicals and the oxidation rate is logically slow. Further, most of free radicals are directly consumed by the dye.

An increase of the hydrogen peroxide concentration up to 50 mM leads to an important rise in the solution discolouration rate (see Table (1)). On the other hand, further increase in the H_2O_2 concentration partly inhibits the oxidation rate. This hehaviour is proof of the existence of an optimal dosage in H_2O_2. We must underline the fact that hydroxyl radicals produced upon photolysis of hydrogen peroxide can react with dye molecules, but also with an excess of H_2O_2.

$$\begin{array}{l} {}^{\bullet}OH \quad \begin{array}{l} + \text{dye} \nearrow \text{oxidation products} \\ + H_2O_2 \searrow \\ \qquad\qquad HO_2^{\bullet -} + H_2O \end{array} \end{array} \qquad (3)$$

In the presence of high concentration of peroxide (>50 mM), we could expect that more ${}^{\bullet}OH$ radicals would be produced. However these radicals preferentially react with the excess of H_2O_2. This undesirable reaction competes with the destruction of the dye chromophore [36,37].

3.1.3. Effect of initial pH

To study the effect of pH on photode-gradation, experiments are conducted at 1.0 x 10^{-5}M dye concentration for the two azo dyes Acid Orange 10 and Acid Red 114 in presence of 50mM H_2O_2 dose at different initial pH values ranges from 1.0 to 11.0, the calculated pseudo first-order rate constants (Fig. 6) are given in Table (1). The results show that, high degradation rate constant values are observed at pH 3.0 for both two azo dyes and decrease significantly in alkaline media. Similar results have already been reported for azo dyes [35,36].

The high rate constant value observed at lower pH can be explained by the change in the molecule structure. The presence of labile H atom makes the molecule of dye especially vulnerable toward attack of ${}^{\bullet}OH$ radicals [36].

In alkaline medium, hydrogen peroxide undergoes decomposition leading to dioxgen and water rather than producing hydroxyl radicals under UV/Visible/irradiation [38]. Therefore the instantaneous concentration in $\dot{O}H$ is lower than expected. The base–catalyzed decomposition involves the HO_2^- anion: the conjugated base of H_2O_2 reacts with non-dissociated molecule of H_2O_2 according to Eq. (4).

$$HO_2^- + H_2O_2 \longrightarrow H_2O + O_2 + {}^-OH \quad (4)$$

Furthermore, the deactivation of ${}^\bullet OH$ is greater when the pH of the solution is high (the reaction of ${}^\bullet OH$ with HO_2^- being approximately 100 times faster than its reaction with H_2O_2 [30,38].

$$^\bullet OH + HO_2^- \longrightarrow H_2O + \dot{O}_2^- \quad (5)$$

$$H_2O_2 + {}^\bullet OH \longrightarrow H_2O + H\dot{O}_2^- \quad (6)$$
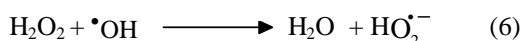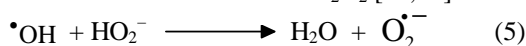
The reactivity of $H\dot{O}_2^-$ and its basic form $\dot{O}_2^-$ with organic compounds is very weak. They preferentially disproportionate producing some hydrogen peroxide and oxygen, according to the Eq. (7).

$$H\dot{O}_2^- + \dot{O}_2^- + H_2O \longrightarrow H_2O_2 + O_2 + {}^-OH \quad (7)$$
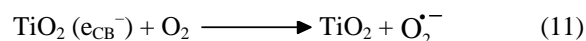
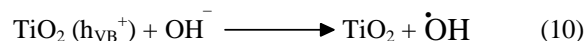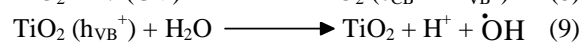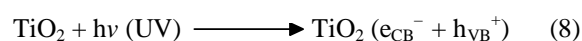3.2. Heterogeneous photocatalytic degradation
3.2.1. Photocatalysis of TiO_2 suspension containing azo dyes
 3.2.1.1 Photodegradability of the dyes

Initial control experiments are carried out in order to evaluate the photocatalysis viability in the degradation of the azo dyes AO10 and AR114 under the following conditions : (i) self photolysis of dye solution with   UV/Visible/light and (ii) under irradiation of UV/Visible/light with photocatalyst. Fig. (7) shows the change in absorption intensity on irradiation of an aqueous solutions of AO10 and AR114, in the presence and absence of titanium dioxide.

From the obtained results it is clear that the dyes are small decolorization to (i) direct photolysis of UV/Visible/light. Simultaneous irradiation and aeration in the presence of TiO_2 caused excellent decolorisation of the dyes [39,40]. This suggested that the photocatlytic activity of TiO_2 degussa P-25 is remarkable, and the photocatalytic degradation of these dyes under UV/Visible/light is significant [41-43]. This is due to the fact that when TiO_2 is illuminated with the light of $\lambda < 390nm$, conduction band electrons (e^-) and valence band holes (h^+) are generated. TiO_2 suspension is irradiated with light energy greater than its band gap energy (E_g, 3.2 eV).

The photogenerated electrons could reduce the dyes or react with electron acceptors such as O_2 adsorbed on the Ti(III) surface or dissolved in water, reducing it to superoxide radical anion $\dot{O}_2^-$. The photo-generated holes can oxidize the organic molecule to form R^+, or react with OH^- or H_2O oxidizing them into $\dot{O}H$ radicals. Together with other highly oxidant species (peroxide radicals) they are reported to be responsible for the heterogeneous TiO_2 photodecomposition of organic substrates as dyes. According to this, the relevant reactions at the semiconductor surface causing the degradation of dyes can be expressed as follows:

$$TiO_2 + h\nu \,(UV) \longrightarrow TiO_2 \,(e_{CB}^- + h_{VB}^+) \quad (8)$$

$$TiO_2 \,(h_{VB}^+) + H_2O \longrightarrow TiO_2 + H^+ + \dot{O}H \quad (9)$$

$$TiO_2 \,(h_{VB}^+) + OH^- \longrightarrow TiO_2 + \dot{O}H \quad (10)$$

$$TiO_2 \,(e_{CB}^-) + O_2 \longrightarrow TiO_2 + \dot{O}_2^- \quad (11)$$

$$\dot{O}_2^- + H^+ \longrightarrow H\dot{O}_2 \quad (12)$$

$$Dye + \dot{O}H \longrightarrow degradation\ products \quad (13)$$

$$Dye + h_{VB}^+ \longrightarrow oxidation\ products \quad (14)$$

$$Dye + e_{CB}^- \longrightarrow reduction\ products \quad (15)$$
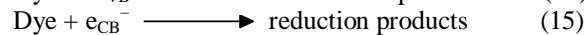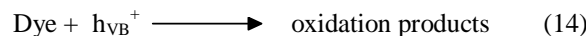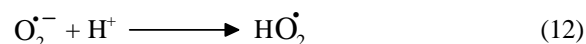
The resulting $\dot{O}H$ radicals, being a very strong oxidizing agent can oxidize most of azo dyes to the mineral end-products. Substrates not reactive toward hydroxyl radicals are degraded employing TiO_2 photocatalysis with rates of decay highly influenced by the semiconductor valence band edge position [44]. The role of reduced pathway (Eq. (15)) in heterogeneous photocatalysis has been investigated also in the degradation of several dyes but in a minor extent than oxidation [43,45].

3.2.1.2. Factors influencing the photocatalytic degradation
 3.2.1.2.1 Effect of initial dye concentration

The effect of initial concentration of the dyes on the rate of degradation was performed by varying the initial dye concentration from 1.0×10^{-5} to $1.0 \times 10^{-4}M$ at pH = 3.0 with constant loading of TiO_2(0.2 g/l) for both two azo dyes AO10 and AR 114.

The values of the first order rate constants calculated according to Eq. 2. are shown in Fig. (8) [15,43,45]. It is generally noted that the degradation rate reach to maximum level [$1.0 \times 10^{-5}M$] for both two azo dyes and a further increase in dyes concentrations lead to decrease the degradation rate of the dyes [46,47]. The rate of degradation relates to the probability of $\dot{O}H$ radicals formation on the

catalyst surface and to the probability of $\overset{\bullet}{O}H$ radicals reacting with dye molecules. The degradation efficiency of the dye decreases as the dye concentration increases further. The presumed reason is that at high dye concentrations the generation of $\overset{\bullet}{O}H$ radicals on the surface of catalyst is reduced since the active sites are covered by dye ions. Another possible cause for such results is the UV/Visible screening effect of the dye itself. At a high dye concentration, a significant amount of UV/Visible may be absorbed by the dye molecules rather than the TiO_2 particles and that reduce the efficiency of the catalytic reaction because the concentrations of $\overset{\bullet}{O}H$ and $\overset{\bullet}{O_2}^-$ decrease [40,48].

Moreover the major portion of degradation occurs in the region near to the irradiated side (termed as reaction zone) where the irradiation intensity is much higher than in the other side [49]. Thus at higher dye concentration, degradation decreases at sufficiently long distances from the light source or the reaction zone due to the retardation in the penetration of light.

Hence, it is concluded that as initial concentration of the dye increases, the requirement of catalyst surface needed for the degradation also increases [50].

3.2.1.2.2. Effect of TiO_2 loading

TiO_2 dosage is an important parameter that can affect the degradation rate. The initial reaction rates were found to be directly proportional to catalyst concentration indicating the heterogeneous regime. However, it was observed that, above a certain level of concentration the reaction rate decreases and becomes independent on the catalyst concentration.

In this work, the effect of TiO_2 loading on the photodegradation rate of the two azo dyes AO10 and AR114 has been examined by varying its amount from 0.05 to 0.2 g/l ([AO10]=[AR114]= 1.0x 10^{-5}M, pH = 3.0 for both two azo dyes). The linear plots of ln A/A_o against irradiation time (Fig. 9) and photodegradation rate constants for both two azo dyes are given in Fig. (10). Fig. (10) shows that, the rate of photodegradation increase with catalyst loading up to 0.2 g/l. Above this loading, increase in turbidity of the solution reduces the light transmission through the solution, so this work stopped at this level. While below this level, it is assumed that the catalyst surface and absorption of light by the catalyst are the limiting factors. Many authors have investigated the reaction rate as a function of catalyst loading under different experimental conditions [51]. The enhancement of the removal rate is due to (i) the increase in the amount of catalyst weight which increases the number of dye molecules adsorbed (ii) the increase in the density of particles in the area of illumination [34]. Thus higher amount of the catalyst may not be useful both in view of possible aggregation as well as reduced irradiation field due to increase in light scattering [52].

3.2.1.2.3. Effect of pH

The interpretation of pH effects on the efficiency of dye photodegradation process is a very difficult task because of its multiple roles. First, is related to the ionization state of the surface according to the following reactions,

$$TiOH + H^+ \longleftrightarrow TiOH_2^+ \qquad (16)$$
$$TiOH + OH^- \longleftrightarrow TiO^- + H_2O \qquad (17)$$
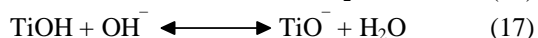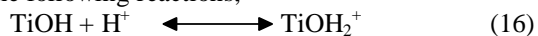
as well as to that of reactant dyes and products such as acids and amines. pH changes can be thus influence the adsorption of dye molecules onto the TiO_2 surfaces, an important step for the photocatalytic oxidation to take place [53]. Bahnemann et al. [54] have already reviewed that acid-base properties of the metal oxide surfaces can have considerable implications upon their photocatalytic activity. The point of zero charge (PZC) of the TiO_2 (Degussa P-25) is 6.8 [55]. Thus, the TiO_2 surface is positively charged in acidic media (pH<6.8), whereas it is negatively charged under alkaline conditions (pH> 6.8).

Second, hydroxyl radicals can be formed by the reaction between hydroxide ions and positive holes. The positive holes are considered as the major oxidation species at low pH whereas hydroxyl radicals are considered as the predominant species at neutral or high pH levels [48]. It was stated that in alkaline solution $\overset{\bullet}{O}H$ are easier to be generated by oxidizing more hydroxyle ions available on TiO_2 surface, thus the efficiency of the process is logically enhanced [42]. Similar results are reported in the photocatalysed degradation of acidic azo dyes and triazine containing azo dyes [50], although it should be noted that in alkaline solution there is a coulombic repulsion between the negative charged surface of photocatalyst and the hydroxide anions. This fact could prevent the formation of $\overset{\bullet}{O}H$ and thus decrease the photoxidation. Very high pHs have been found favorable even when anionic azo dyes should hamper adsorption on the negatively charges surface [56]. At low pH, reduction by electrons in conduction band may play a very important role in the degradation of dyes due to the reductive cleavage of azo bonds.

Third the TiO_2 particles tend to agglomerate under acidic condition and the surface area available

for dye adsorption and photon absorption would be reduced [53]. Hence, pH plays an important role both in the characteristics of textile waters and in the reaction mechanisms that can contribute to dye degradation, namely, hydroxyl radical attack, direct oxidation by the positive hole and direct reduction by the electron in the conducting band.

The wastewater from textile industries usually has a wide range of pH values. Generally, pH plays an important role both in the characteristics of textile wastes and generation of hydroxyl radicals [50]. Hence, attempts have been made to study the influence of pH in the degradation of the two azo dyes AO10 and AR114. The photocatalytic reactions are conducted at different pH values ranges from 1.0 to 11.0 and two dyes concentration [1.0×10^{-5}M] at catalyst loading of 0.2 g/l. All reactions followed an apparent first-order kinetics confirmed by the linear transform of ln $(A/A_o) = f(t)$. The rate constants of disappearance k in min^{-1} for two azo dyes AO10 and AR114 are illustrated in Fig. (11).

The results obtained in Fig. (11) indicated that, at pH<6 a strong adsorption of the two azo dyes on the TiO_2 particles is observed as a result of the electrostatic attraction of the positively charged TiO_2 with the dyes. At pH>6.8 as two azo dyes molecules are negatively charged in alkaline media, their adsorption is also expected to be affected by an increase in the density of TiO^- groups on the semiconductor surface. Thus, due to coulombic repulsion the dyes are scarcely adsorbed [42]. For the above reasons the photocatalytic activity of anionic dyes (mainly sulphonated dyes) reached a maximum in acidic conditions followed by a decrease in the pH range 7-11 [40,43,47].
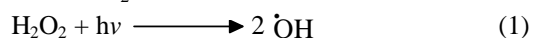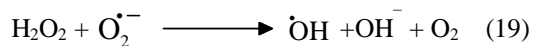
$$(dye–SO_3Na) \longrightarrow (dye–SO_3)^- + Na^+ \quad (18)$$
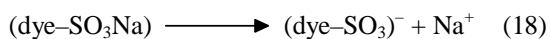
Moreover, the higher degradation rate at acid pH is seen also for UV/Visible/TiO_2 experiments due to the efficient electron-transfer process due to strong surface complex bond formation. This effect is less marked in neutral/basic pH solutions [57]. The inhibitory effect seems to be more pronounced in the alkaline range (pH=11-13). At high pH values the hydroxyl radicals are rapidly scavenged and they do not have the opportunity to react with dyes [58].

Since the influence of the pH is dependent on dye type and on properties of TiO_2 surface. This effect on the photocatalytic efficiency must be accurately checked before any application.
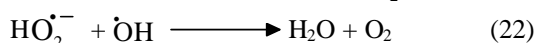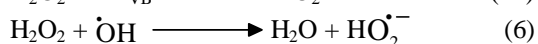
3.2.2. Photocatalysis of TiO_2 suspension with H_2O_2 containing azo dyes

It was observed that H_2O_2 addition was beneficial for the photooxidation of the two azo dyes AO10 and AR114 [46]. The reactive radical

intermediate $\overset{\bullet}{O}H$ formed from H_2O_2 by reactions with the photogenerated electrons can exert a dual function : as strong oxidant themselves and as electron scavengers, thus inhibiting the electron-hole recombination of the semiconductor surface [59] according to the following equations :

$$H_2O_2 + \overset{\bullet}{O_2}{}^- \longrightarrow \overset{\bullet}{O}H + OH^- + O_2 \quad (19)$$

$$H_2O_2 + h\nu \longrightarrow 2\overset{\bullet}{O}H \quad (1)$$

$$H_2O_2 + e_{CB}{}^- \longrightarrow \overset{\bullet}{O}H + OH^- \quad (20)$$

Moreover, the solution phase may at times be oxygen starved, because of either oxygen consumption or slow oxygen mass transfer. Peroxide addition thereby increases the rate towards what it would have been an adequate oxygen supply. However, H_2O_2 can also become a scavenger of valence band holes and $\overset{\bullet}{O}H$, when present at high concentration, [40].

$$H_2O_2 + 2 h_{VB}{}^+ \longrightarrow O_2 + 2H^+ \quad (21)$$

$$H_2O_2 + \overset{\bullet}{O}H \longrightarrow H_2O + H\overset{\bullet}{O_2}{}^- \quad (6)$$

$$H\overset{\bullet}{O_2}{}^- + \overset{\bullet}{O}H \longrightarrow H_2O + O_2 \quad (22)$$

As both $h_{VB}{}^+$ and $\overset{\bullet}{O}H$ are strong oxidants for dyes, the photocatalytic oxidation will be inhibited when H_2O_2 level gets too high. Furthermore, can be adsorbed onto TiO_2 particles to modify their surfaces and subsequently decrease its catalytic activity.

In this work, the effect of varying dose of H_2O_2 [5mM-100mM] in presence of constant weight of TiO_2 (0.05 g/l) was also studied in the presence of the two azo dyes ([AO10] and [AR114] = 1.0×10^{-5}M) at constant pH=3.0 Fig. (12). The results demonstrate that, the rate of photodegradation enhanced in presence of H_2O_2 with TiO_2 from 50mM H_2O_2 without TiO_2 (Fig. 5) to 10mM H_2O_2 in presence of 0.05 g/l TiO_2 for AO10 (Fig. 13), while the rate of photodegradation remain constant in both two cases at 50 mM H_2O_2, for AR 114 without TiO_2 (Fig. 5) and in presence of 0.15 g/l TiO_2 Fig. (13).

On the other hand, the effect of TiO_2 loading on the photodegradation rates of AO10 and AR114 has been examined by varying its amount from 0.05 to 0.20 g/l, ([AO10] =[AR114]=1.0×10^{-5}M), pH= 3.0, [H_2O_2]=10mM, 50mM for AO10 and AR114 respectively. The calculated photodegradation rate constants are given in Fig. (14). The results, demonstrate that the rate of photodegradation reached to maximum value, when loading by ([0.05 g/l TiO_2] and in presence of 10 mM H_2O_2 for AO10) compared to [0.20 g/l TiO_2] without H_2O_2 for the same dye Fig. (10). Also the rate of photodegradation of AR114 enhances in presence of H_2O_2 with TiO_2 from 0.20 g/l

TiO_2 without H_2O_2 Fig. (10) to 0.15 g/l TiO_2 in presence of 50 mM H_2O_2 Fig. (14).

Also the concentrations of the two azo dyes were increased in presence of H_2O_2 with TiO_2 from [1.0 x 10^{-5} M] to [5.0 x 10^{-5}M] for (AO10) and [1.0 x 10^{-4}M] for (AR114) in presence (0.05 g/l TiO_2 with 10 mM H_2O_2 for (AO10) and 0.15 g/l TiO_2 with 50mM H_2O_2 for AR114) at pH 3.0. The photodegradation rates reached to maximum at $75.4x10^{-3}$ (min^{-1}) for (AO10) and $42.9x10^{-3}$ (min^{-1}) for (AR114) Fig. (15). The effect of use TiO_2 with H_2O_2 on the pH values was fixed at pH 3.0 for both two azo dyes [1.0 x 10^{-5}M].

From the above results it was found that, there were optimum conditions for each process to obtain excellent degradation for each dye. The optimum conditions in presence of UV/H_2O_2 or UV/TiO_2 alone was 50 mM H_2O_2 or 0.20 g/l TiO_2 for both two azo dyes. These conditions were reduced in presence of UV/H_2O_2/TiO_2 to (10mM H_2O_2 and 0.05 g/l TiO_2 for AO10) and (50 mM H_2O_2 and 0.15 g/l TiO_2 for AR114) Fig. (16).

3.2.3 Efficiency of the recycled TiO_2

Photocatalysis is a clean technology, which normally dose not involve any waste disposal problem. The catalysts can be recycled. TiO_2 can be used at least twice without significant change in the efficiency [60]. The economy of the photocatalytic process depends upon how many times a catalyst can be reused without sacrificing its efficiency and the type of regeneration it requires.

The photodegration rates of the two recycled catalysts RC-1 and RC-2 were examined . RC-1 achieved 50.4 x 10^{-3} (min^{-1}) for (AO10) and RC-2 achieved 43.8 x 10^{-3} ($min)^{-1}$ for (AR114) compared to 73.2 x 10^{-3} and 42.9 x 10^{-3} ($min)^{-1}$ for (AO10) and (AR114) respectively obtained with the fresh catalyst under the same experimental conditions. The used catalyst was regenerated to get RC-1 first by treating with boiling distilled water till a colorless wash liquid was obtained and then by drying it in a hot air oven at a temperature of 90 to 100°C. RC-1 was heated in a muffle furnate at about 600°C to yield RC-2.

The decrease in the efficiency of the recycled catalyst may be attributed to the deposition of photoinsensitive hydroxides (Fouling) on the photocatalysts surface blocking its active sites.

Table (1): Photodegradation rates of (AO10) and (AR114) in presence of different parameters.

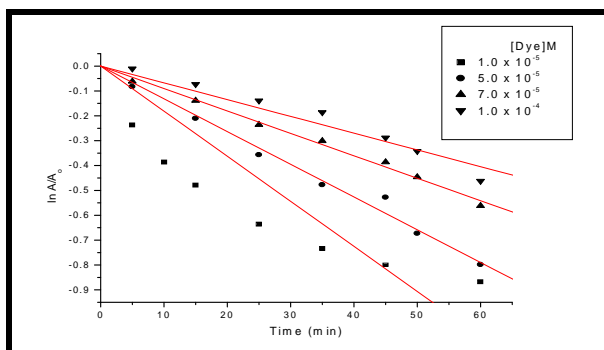| Parameters	$k(min^{-1})$ x 10^3	
	AO10	AR114
[Dye] M		
1.0 x 10^{-5}	18.1	13.0
5.0 x 10^{-5}	13.2	10.5
7.0 x 10^{-5}	9.0	9.6
1.0 x 10^{-4}	6.7	8.0
[H_2O_2]mM		
5	18.1	13.2
10	22.4	15.8
25	29.3	18.3
50	42.9	35.2
100	6.8	23.8
pH		
1	20.5	15.3
3	42.9	35.2
5	15.0	10.8
7	10.0	9.0
9	9.3	8.3
11	5.7	2.0

Fig. (3): Kinetics of photodegradation of (AO10) at different initial dye concentrations in presence of 5mM H_2O_2 and pH 3.0.
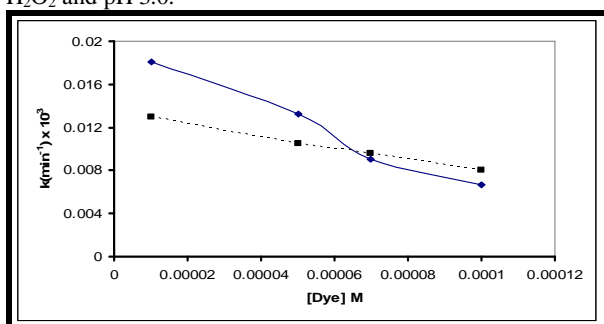

Fig. (4): Plot of k (min^{-1}) vs. [dye] for (—) [AO10] and (---) [AR 114] in presence of [5mM H_2O_2] for both (AO10) and (AR114) at pH 3.0.
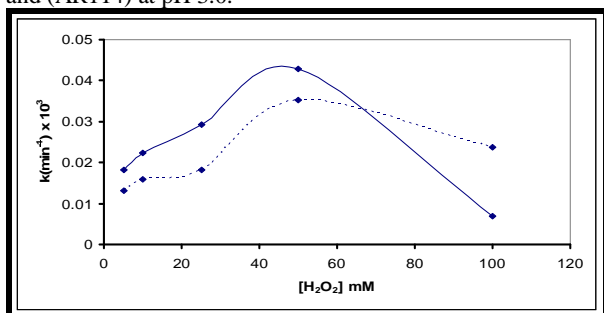

Fig. (5): Plot of k (min^{-1}) vs. [H_2O_2] for (—) [AO10] and (---) [AR 114] =1.0 x 10^{-5}M at pH3.0.
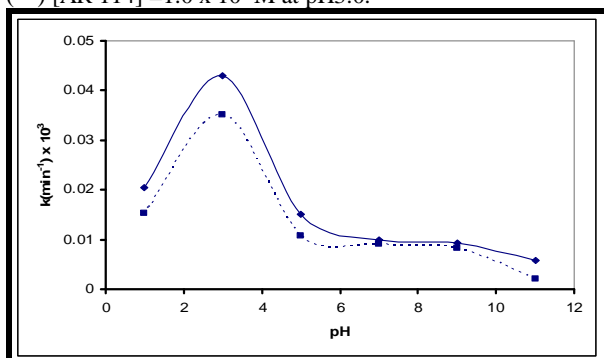

Fig. (6): Plot of k (min^{-1}) vs. pH for (—) [AO10] and (---) [AR 114] =1.0 x 10^{-5}M in presence of 50mM H_2O_2 for both (AO10) and (AR114).
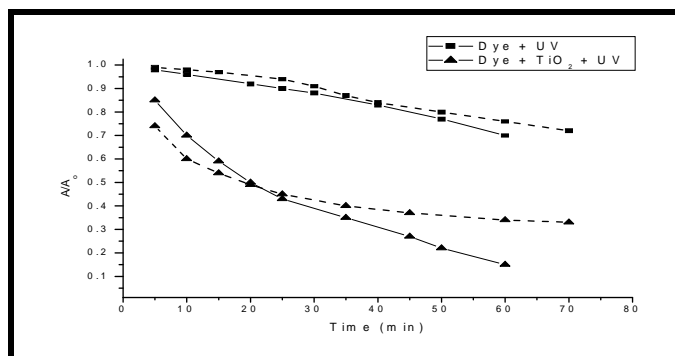

Fig. (7) :Plot of absorbance at λ_{max} (478, 514 nm)   vs. time for [AO10(—) and AR114 (---)] = 1.0 x 10^{-5} M at pH3.0.
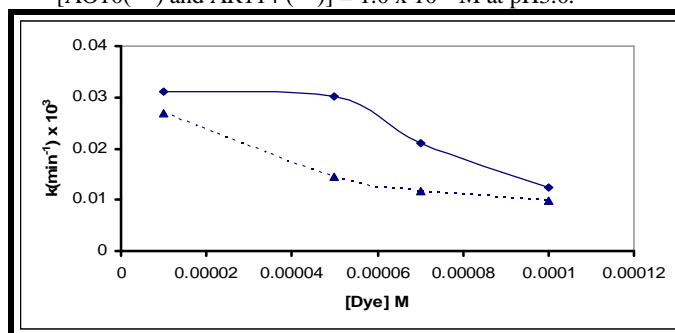

Fig. (8): Plot of k (min^{-1}) vs. [dye] for (—) [AO10] and (---) [AR 114] in presence of 0.2 g/l TiO_2 for both two azo dyes at pH3.0.
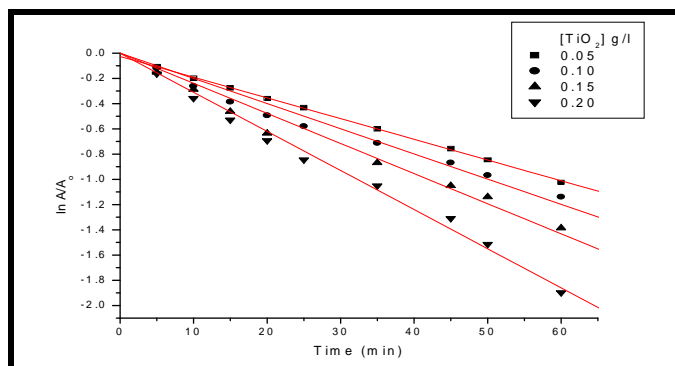

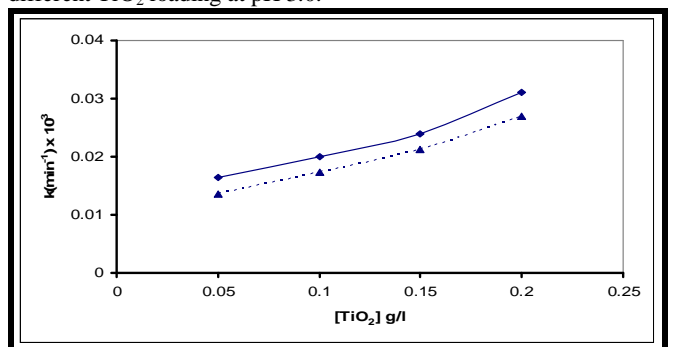**Fig. (9):** Kinetics of photodegradation of [AO10] = 0 x10^{5}M at different TiO_2 loading at pH 3.0.

Fig. (10): Plot of k (min^{-1}) vs. [TiO_2] for (—) [AO10] and (---) [AR 114] =1.0 x 10^{-5}M at pH3.0.
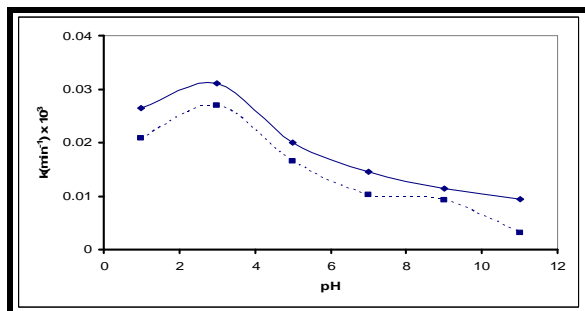
Fig. (11): Plot of k (min^{-1}) vs. pH for (—) [AO10] and (---) [AR 114] =1.0 x 10^{-5}M in presence of 0.2 g/l TiO$_2$ for both two azo dyes.
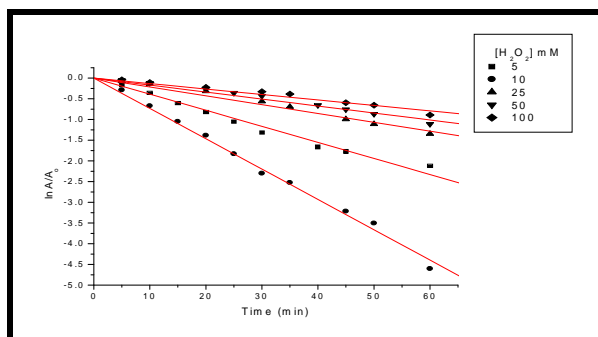

Fig. (12): Kinetics of photodegradation of [AO10] =1.0 x 10^{-5}M at different H$_2$O$_2$ concentrations in presence of 0.05 g/l TiO$_2$ at pH 3.0.
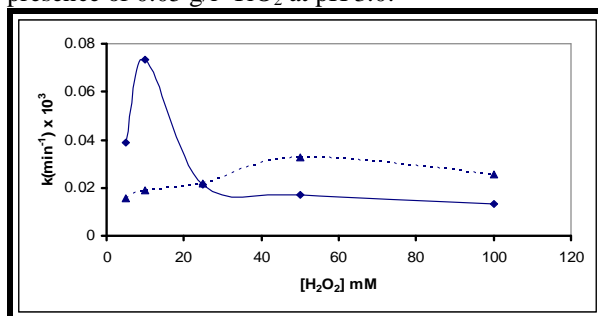

Fig. (13): Plot of k (min^{-1}) vs. [H$_2$O$_2$] for (—) [AO10] and (---) [AR 114] =1.0x10^{-5}M in presence of 0.05 g/l TiO$_2$ for (AO10) and 0.15 g/l TiO$_2$ for (AR114) at pH3.0.
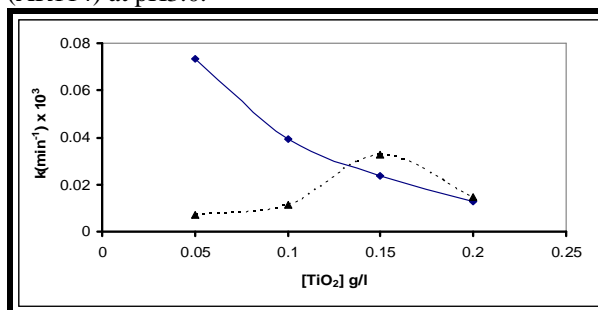

Fig. (14): Plot of k (min^{-1}) vs. [TiO$_2$] for (—) AO10 and (---) [AR 114] =1.0 x 10^{-5}M in presence of 10 mM H$_2$O$_2$ for (AO10) and 50mM for (AR114) at pH3.0.
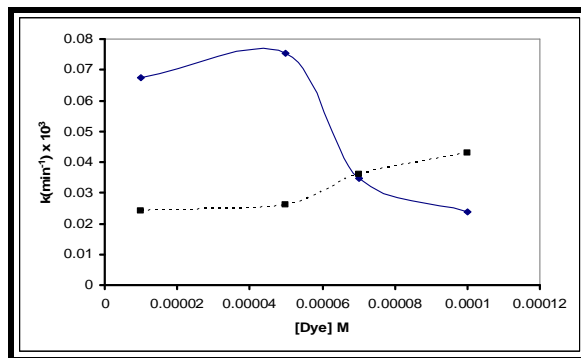

Fig. (15): Plot of k (min^{-1}) vs. [dye] for (—) [AO10] and (---) [AR 114] in presence of 0.05 g/l TiO$_2$ and 10mM H$_2$O$_2$ for (AO10) and 0.15 g/l TiO$_2$ and 50mM H$_2$O$_2$ for (AR114) at pH3.0.
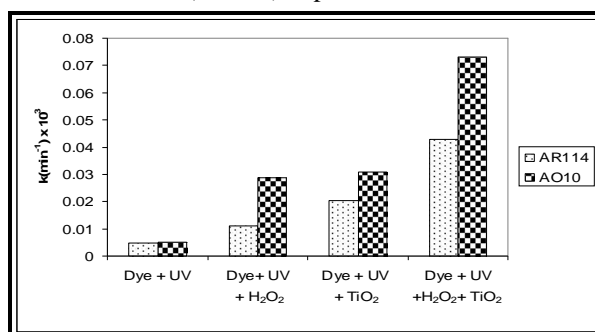

Fig. (16): Plot of k(min^{-1}) vs(AO10) and (AR114) at the best conditions for each process to obtain degradation at pH 3.0

4. Conclusion

The impact of H$_2$O$_2$ initial concentration in color removal kinetics under UV/H$_2$O$_2$ process for two azo dyes (monoazo dye (AO10) and diazo dye (AR114)) was investigated. The results prove that the pseudo-first order kinetic model is in good agreement with the experimental data. A set of parameters for the model depicting this degradation were determined. These parameters, will naturally vary with the operating conditions, such as (dye concentration, H$_2$O$_2$ dose, pH values). An increase in H$_2$O$_2$ dose leads to a faster degradation up to a critical value; at a higher ratio the degradation process become slower.

The photodegradation of the two azo dyes catalyzed by UV/TiO$_2$ was carried out with good results. Various parameters such as (dye concentration, TiO$_2$ loading, pH values) were tested. The photocatalytic degradation rates for the two dyes were enhanced in presence of UV/H$_2$O$_2$/TiO$_2$ at optimum conditions for each process and dye. The monoazo dye (AO10) was degraded faster than the diazo dye (AR114).

It may be postulated that, the dye color removal and degradation rates are proportional to the number of azo and sulphonic groups present in their molecules.

In summary, this work demonstrates that photocatalysis is a very effective technology for degrading Acid dyes with azo and sulphonic groups. Moreover, this technology can be utilized directly in dye baths before they are mixed with other textile effluents, which make their treatment difficult and costly due to dilution.

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