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Photocatalytic degradation of Asucryl Red (GRL) in aqueous medium on heat-treated TiO_2 powder – effect of analytical parameters and kinetic modeling

Moussa Abbas[a,*], Mohamed Trari[b]

[a] *Laboratory of Soft Technologies and Biodiversity, Faculty of Sciences, University M'hamed Bougara, Boumerdes 35000, Algeria, Tel. +213 552408419; Fax: +213 21 24 80 08; email: moussaiap@gmail.com*
[b] *Laboratory of Storage and Valorization of Renewable Energies, Faculty of Chemistry (USTHB), BP 32-16111 Algiers, Algeria, email: mtrari@usthb.dz*

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ABSTRACT

Water loaded with Asucryl Red (GRL) dye is frequently discharged into natural receiving environments at relatively high concentrations, which can have serious consequences on the ecosystem if adequate treatment operations are not undertaken. The adsorption and photocatalytic degradation of GRL, selected as a model organic pollutant, has been investigated in aqueous suspension of TiO_2 powder as photocatalyst under UV-lamp irradiation. The experiments were carried out to investigate the factors influencing the photocatalytic degradation, initial GRL concentration (5–25 mg/L), TiO_2 mass (0.2–1.2 g), pH 2–10 and NaCl ionic strength (0.2–1.6 g/L). The experimental results showed that the efficiency of the photocatalytic process strongly depends on the pH while the initial rate of the photocatalytic reaction is proportional to the catalyst dose, but above a certain value, it becomes constant and sometimes decreases. The adsorption is an important parameter controlling the apparent kinetic constant of the degradation. The photocatalytic degradation rate was favored for high concentrations of the solution in agreement with the Langmuir–Hinshelwood (L–H) model. The degradation rate was found to be pH and temperature-dependent with a high degradation rate at high temperatures. The TiO_2 photocatalyst has a better activity for GRL degradation, compared to the various commercial catalysts already available in the literature.

Keywords: Photocatalytic degradation; Asucryl Red; TiO_2 powder; Kinetics; Modeling

1. Introduction

Our earth needs urgent actions to save the environment from all pollutants such as heavy metals, organic compounds, pesticides, drugs, and dyes, generated by heavy manufacturing industries and complex technological activities. These environmental pollutants pose serious toxic risks to microorganisms and represent a real threat to aquatic life and human beings. Dyes constitute one of the larger groups of pollutants in wastewaters and their releases come mainly from the textile and other industries. The discharge of highly colored wastewaters in the ecosystem involves environmental problems like aesthetic pollution, even a small amount of dye, and perturbation of aquatic life. The dyes can be fatal, and some of them carcinogenic and can lead to reproductive, developmental, neuron and acute toxicity [1]. It has also been established that the dyes leads to tumors at the site of application [2]. When administered intravenously

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* Corresponding author.

to determine the potency of the urinary collecting system, they cause mild to severe hypertension, cardiovascular and respiratory effects in patients. It may also provoke gastrointestinal irritations with nausea, vomiting, and diarrhea [3]. The tests of the dye revealed long-term toxicity in mice [4] and short-term toxicity in the pig [5]. Thus, keeping the toxicity in view, various attempts have been made for the removal of indigo carmine from wastewater. Apart from adsorption over chitin and chitosan [6] and charcoal from extracted residue of coffee beans [7], electrochemical [8], biological [9] and photochemical [10] techniques have also been explored. Among these attempts, the photocatalytic treatment remains an attractive alternative for the removal of soluble organic compounds. Contrary to physical processes, such as coagulation and adsorption, which merely transfer the pollutants from wastewaters to other media and cause secondary pollution, the photocatalysis can mineralize the organic compounds to carbon dioxide, water, and inorganic salts. Moreover, it does not require expensive oxidants and can be carried out at mild temperatures. However, the obligation to separate the small catalyst particles from the suspension after treatment limits the process development. Dyes are used in industries of paper, cosmetics, food, textiles, pharmaceuticals, as well as in medical diagnostics [11]. Annual production approaches 700.000 tons, of which 140.000 tons are discharged as effluents without any control or post-treatment [12]. Therefore, their elimination is a main environmental problem in the water treatment and several dyes are very toxic and difficult to biodegrade [13,14]. The chemical complexity and diversity of dyestuffs make conventional treatments often inefficient [15]. In this respect, advanced oxidation processes are currently under development for the degradation of recalcitrant organic molecules [16]. Heterogeneous photocatalysis with POAs is an emerging alternative and TiO_2 is very popular for the removal of soluble organic compounds. This technique leads to a high degree of mineralization at room temperature and atmospheric pressure [17]. The principle of the photocatalysis (Fig. 1) is based on the activation of TiO_2 by UV light ($h\nu \geq E_g$), resulting in the generation of electron (e^-)/hole (h^+) pairs, by excitation of electrons from the valence band (VB) to the conduction band (CB). The electron reduces the oxygen adsorbed on the TiO_2 surface, while the hole, reacts with surface OH^- ions to form oxidizing hydroxyl radicals ($OH^\bullet$), responsible for the degradation of pollutants, or by adsorption onto activated carbon [18–23]. This study aims to analyze the feasibility of discoloration of Asucryl Red (GRL) a recalcitrant dye using as TiO_2 photocatalyst. The factors that influence the photocatalytic dye removal were investigated.

2. Experimental studies

2.1. Materials and methods

The immobilized photocatalyst used in this study was a commercial TiO_2 purchased from Ahlstrom firm (France). It consists of PC500 Titania by Millennium Inorganic Chemicals (Hunt Valley, Maryland United States) (Anatase > 99%, specific surface area 350–400 m^2/g, mean crystallites size (5–10 nm). The physicochemical properties

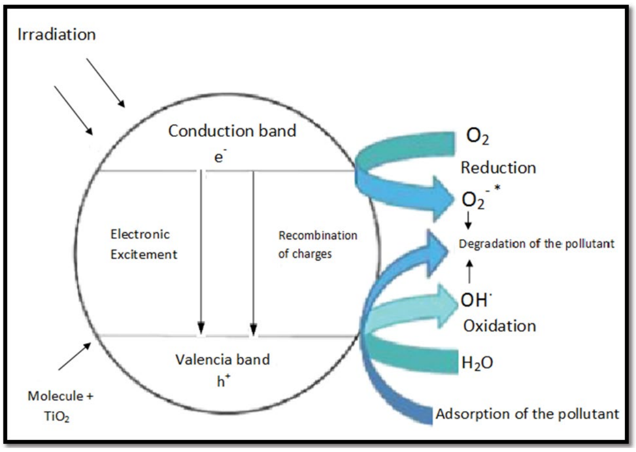
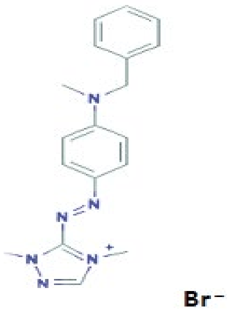


Fig. 1. Principal of heterogeneous photocatalysis.

Table 1
Physicochemical properties of GRL

Dye	Name sales representative	Gross formula	Molecular Weight (g/mol)	λ_{max} (nm)	CI	Supplier
Red Basic 46	Red Asucryl (GRL)	$C_{18}H_{21}N_6Br$ 	400,9	532	110825	AZUTEX

IUPAC name: N-benzyl-4-[(2,4-dimethyl-1,2,4-triazol-4-ium-3-yl)diazenyl]-N-methylaniline;bromide of GRL are gathered in Table 1. Solutions were prepared by dissolving the required quantity of GRL in distilled water. The pH was adjusted to a given value in the range (2–10) by the addition of HCl or NaOH (1 N), measured with a Schott Titroline (TE96) pH-meter. All photocatalytic tests were performed at room temperature under atmospheric pressure; 200 ml of a solution containing GRL of initial concentration C_0, to which 0.1 g of TiO_2 was added. The prepared solutions were stirred for 30 min in the dark and then exposed to UV lamp at time intervals ranging from 20 to 160 min. In the end, the solutions were filtered with a syringe equipped with a filter (porosity = 0.45 µm). GRL absorption measurements were performed with a UV-Visible spectrophotometer (λ_{max} = 532 nm) and the removal rate, defined as the efficiency of the adsorption reaction, is given:

$$R = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

where C_0 is the initial concentration of the GRL solution (mg/L) and C_t the concentration the time t.

2.2. Thermal treatment of TiO_2 powder

Titanium is a metal, so by definition is a reduced simple body, its usual oxide is chemically speaking TiO_2 which is one of the most used materials in our everyday life. Titanium dioxide represents 70% of the total volume of global pigment production, it is widely used as a bleaching agent in products such as that of paint, plastic, paper, ink, food, etc. To date, titanium dioxide appears to represent the photo-active solid that has given the best results in the photodegradation of pollutants in both the liquid and liquid phases gas phase. Its stability under different experimental conditions, its low price, and its harmless character are the advantages of this material. The photocatalytic treatment was realized in a double-walled cubic PVC cell which contains a magnetic stirrer, a UV lamp emitting at two wavelengths separately of 254 and 365 nm; the system was placed in a dark room. The TiO_2 powder was placed in a porcelain crucible and heated at 850°C for 1 h in a Vecstar Ltd. furnace equipped with a temperature control system under ambient air at a heating rate of 10°C/min.

3. Results and discussion

It is convenient to note that the photocatalytic process is focused on the generation of (e^-/h^+) pairs by illumination with visible or UV light, depending on the nature of the semiconductor ($h\nu > E_g$). Both electrons and holes migrate in opposite directions to the catalyst surface of the semiconductor where the redox reactions take place with the adsorbed azo dyes through radicals. The oxidizing radicals could attack the azo dyes and convert them partially into CO_2, H_2O, and nontoxic inorganic molecules. So, the formation of free radicals is essential for oxidizing dye and the photodegradation of GRL onTiO_2 gave encouraging results. The pH is a parameter that determines the surface properties of solids and the state of the pollutant as a function of its pKa and characterizes the water to be treated. Its effect on the photocatalysis is important to evaluate the effectiveness of the technique for water loaded with pollutants.

In general, when a compound is partially ionized or carrying charged functions, it is necessary to consider the electrostatic interactions that occur with TiO_2. Indeed, according to the zero charge point (pHpzc) of the solid, the surface charge of the solid depends on pH. Thus, for TiO_2, the surface is positively charged below pHpzc (= 6.5), and negatively charged above pHpzc (Fig. 2) [23].

3.1. Influence of the initial GRL concentration on photodegradation in the presence of TiO_2 catalyst

Water loaded with organic pollutants is frequently discharged into natural receiving environments, often at high concentrations, and can have serious consequences on the ecosystem. It would then be interesting to study the influence of the variation in the initial concentration C_0 on the effectiveness of photocatalytic degradation. The mass of TiO_2 was fixed at 0.1 g. The effect of the initial GRL concentration C_0 of on the photocatalytic degradation efficiency was studied for various C_0 (10, 15, 20 and 25 mg/L) Fig. 3 shows that the elimination rate decreases, while the ratio C/C_0 increases. The results indicate that the degradation efficiency of GRL decreases with augmenting the initial concentration C_0. This observation can be explained by the availability of active sites on the TiO_2 surface and the possibility of penetration of UV light throughout the surface of the catalyst in the solution causing an increase of $OH^\bullet$ radicals that contribute to the degradation of GRL. The degradation kinetic strongly decreases at higher concentrations. High concentrations form screen of GRL weakens the photons flux reaching because of the strong adsorption by the dye itself, thus reducing the number of $OH^\bullet$ radicals. When a photocatalyst is exposed to solar radiation, several active species are generated, namely: holes (h^+), electrons (e^-), hydroxyl radicals (OH^-) and superoxide radicals ($O_2^{\bullet-}$). The photodegradation can occur by one or more active species whose overall mechanism on TiO_2 is as follows:

$$TiO_2 + h\nu \rightarrow h^+_{BV} + e^-_{BC} \text{ (BC: Conduction band)} \tag{I}$$

$$O_{2ads} + e^-_{BC} \rightarrow O_2^{\bullet-} \tag{II}$$

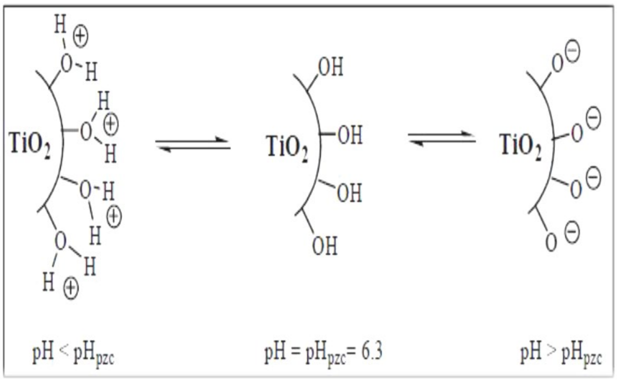


Fig. 2. pH_{PZC} of TiO_2.

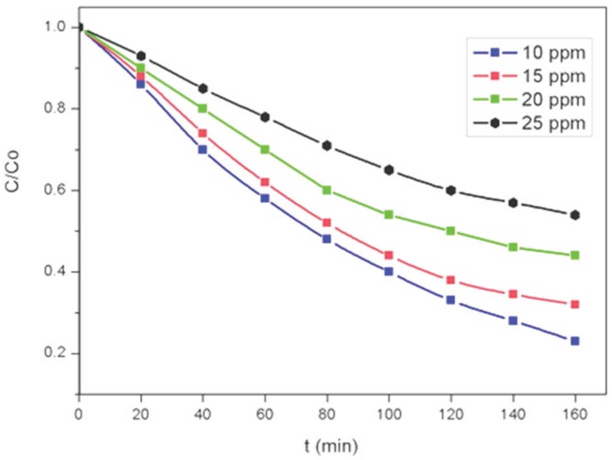


Fig. 3. Effect of initial GRL concentration on the photodegradation efficiency.

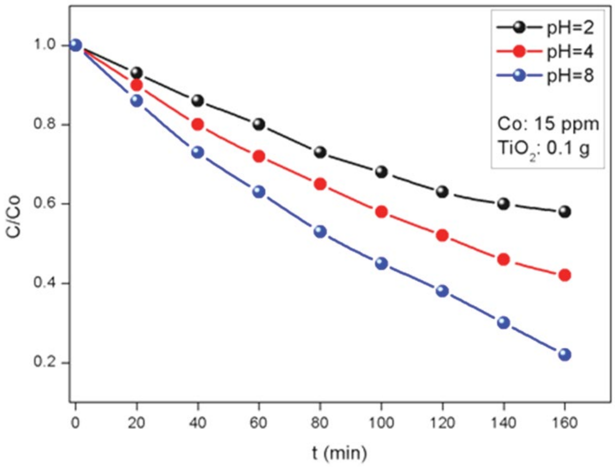


Fig. 4. Effect of initial pH on the photodegradation of GRL.

$$2O_2^{\bullet -} + 2H_2O \rightarrow H_2O_2 + 2OH^- + O_2 \quad \text{(III)}$$

$$O_{2ads} + e^-_{BC} + H^+ \rightarrow H_2O_2 \quad \text{(IV)}$$

$$2H_2O_{2ads} + e^-_{BC} \rightarrow OH^- + OH^\bullet \quad \text{(V)}$$

$$H_2O_{ads} + h^+_{BV} \rightarrow OH^\bullet + H^+ \text{ (BV: Valence band)} \quad \text{(VI)}$$

$$^\bullet OH_{ads} + h^+_{BV} \rightarrow OH^\bullet \quad \text{(VII)}$$

$$\text{Polluants} + (OH^\bullet, O_2^{\bullet -}, h^+) \rightarrow \text{by-products} \rightarrow CO_2 + H_2O + \text{mineral salts} \quad \text{(VIII)}$$

The efficiency of the photocatalytic reaction generally decreases with increasing initial concentration C_0. A high concentration C_0 leads to an increasing number of molecules of the pollutant adsorbed on the surface, thus reducing penetration photons; which decreases the efficiency of photodegradation.

3.2. Influence of pH

The initial pH of the solution can affect the photodegradation efficiency of dyestuffs; its effect for a solution (15 mg/L) GRL was studied in the presence of TiO_2 (0.1 g) for pH values 2, 4, 6, 6, 8 and 10 by addition of HCl or NaOH (Fig. 4) The pH for which the surface charge of TiO_2 is zero corresponds to pHpzc. The reactions of the surface of the photocatalyst are as follows:

$$TiOH + H^+ \rightarrow TiOH_2^+ \qquad pH < 6.5 \quad \text{(IX)}$$

$$TiOH + HO^- \rightarrow TiO^- + H_2O \qquad pH > 6.5 \quad \text{(X)}$$

The TiO_2 surface is positively charged in acidic solution related to the fixation of protons and negatively in basic medium due to their loss. The surface charge influences the dye adsorption and therefore can promote or limit the degradation. The adsorption of positively charged molecules is difficult in acidic medium and becomes favorable in basic electrolyte and vice versa for negatively charged compounds.

The ratio C/C_0 decreases and the degradation rate increases when the pH increases as a function of illumination time. At pH 8 (76%) degradation is accomplished within 160 min, indicating that TiO_2 has the best photocatalytic activity at this pH. Above pH10, the photodegradation is slowed down, due to the shielding effect caused by the cluttering of ions on the catalyst surface, thus preventing the light penetration. In the basic environment, there is a significant augmentation of the elimination rate, due to an increased number of $OH^\bullet$ ($h^+ + OH^- \rightarrow OH^\bullet$).

In a basic medium, the OH^- favors a combination with the photo holes (h^+) in the valence band (BV), which are likely to degrade the organic GRL. Moreover, the reduction of the yield at acid pH can be explained by the effect of the mobility of GRL molecules toward the photo-electrochemical sites of TiO_2 which depends on its surface charge. The latter is positively charged in an acid medium, depending on the load of the pollutant and pH.

3.3. Influence of TiO_2 mass on photodegradation of the dye

The photodegradation of GRL solution (15 mg/L) was studied at pH 8 by varying the mass of TiO_2 (m = 0.05, 0.1, 0.15, 0.20, and 0.25 g) (Fig. 5). For a certain catalyst mass, the reaction rate reaches an optimum and this limit depends on the geometry of the photo-reactor and operating conditions. The microstructure (grain size, porosity, specific surface area) and optical properties (absorption coefficient) play important roles in photocatalysis.

The maximal oxidation rate corresponds to the amount of TiO_2 for which all GRL molecules are eliminated. For large catalyst quantities, the reaction rate decreases due to saturation of the absorption sites for photons or by loss of light by diffusion and scattering. The ratio C/C_0 of GRL decreases with augmenting the TiO_2 mass while the elimination rate increases. C/C_0 decreases from 0.40 to 0.19 mg/L for a TiO_2 mass ranging from 0.05 to 0.20 g. For m = 0.2 g, the elimination rate is maximum for a minimal C/C_0. Therefore, 0.2 g is the maximum amount of TiO_2 for which all particles are

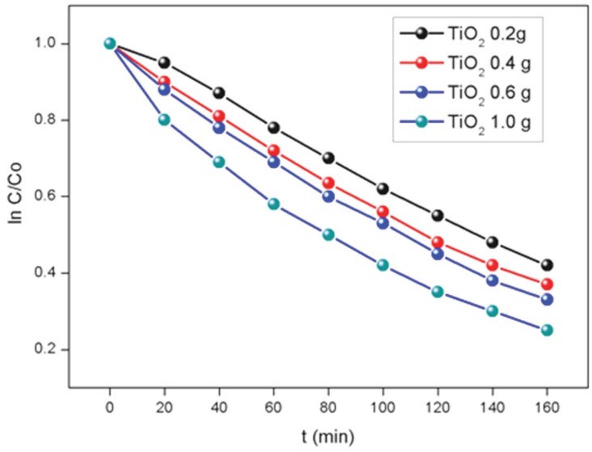


Fig. 5. Effect of TiO_2 mass on the photodegradation efficiency.

illuminated. For larger quantities (m = 0.25 g), a shielding effect of the particles occurs, which masks much of the photosensitive surface.

The initial rate of the photocatalytic reaction is proportional to the catalyst dose, but above a certain value, it becomes constant and sometimes decreases. This limit value corresponds to the maximum quantity of the catalyst for which all particles, exposed on the surface, are illuminated.

3.4. Influence of ionic strength on the photodegradation of GRL by TiO_2

The addition of NaCl leads to a decrease in the C/C_0 ratio up to a concentration of 1.2 g/L (Fig. 6). In addition, it enhances the GRL elimination because it promotes the association of the particles adsorbent/GRL, with the formation of new porosity and further surface sites where the GRL is trapped. The degradation efficiencies for the various parameters studied are gathered in Table 2. According to numerous works [24,25], the photocatalytic degradation rate of most organic compounds is described by the pseudo-first-order kinetic.

Studies have shown that pollutant degradation by heterogeneous photocatalysis follows rather the L–H model [26–28], where the degradation rate is proportional to the fraction of the catalyst surface covered by the substrate molecules. The L–H model is given by the following equation:

$$r = \frac{-dC}{dt} = \frac{K_r \cdot K \cdot C}{1 + K \cdot C} \quad (2)$$

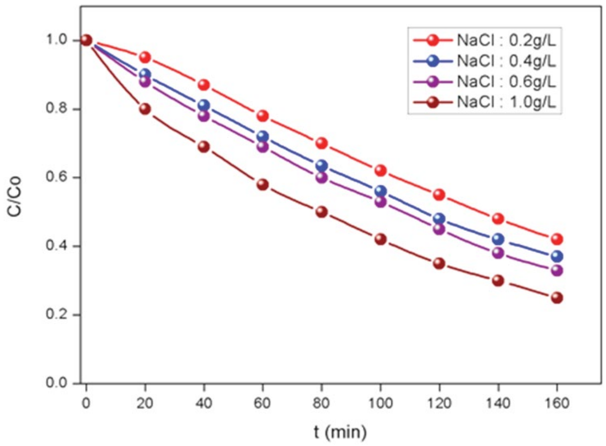


Fig. 6. Effect of ionic strength on the photodegradation efficiency.

For low concentrations ($C < 10^{-3}$ M), the term $K{\cdot}C$ is negligible in front of 1. Therefore, the reaction follows a pseudo-first-order kinetics [29] and Eq. (1) becomes as follows:

$$r = \frac{-dC}{dt} = K_r \cdot K \cdot C = K_{\text{app}} \cdot C \quad (3)$$

The integration of Eq. (3) gives:

$$\text{Ln}\, K_{\text{app}} \frac{C}{C_0} = K \cdot t \quad (4)$$

The initial rate (r_0) is given by:

$$r_0 = \frac{K_r \cdot K \cdot C}{1 + K \cdot C} = K_{app} \cdot C_0 \quad (5)$$

r: photodegradation rate (mg/L min); r_0: initial rate of photodegradation (mg/L min); C: pollutant concentration at time t (mg/L); K_r: constant of the adsorption equilibrium (mg/L min); K: kinetic constant of L–H (L/mg); $K_{app} = K_r.K$ apparent speed constant (min^{-1}), it is affected by the concentration C_0.

The plot ln (C_0/C) vs. t for different initial concentrations C_0 of GRL and various catalyst amounts are shown in Figs. 7 and 8 (Inset). The photocatalytic degradation follows perfectly the pseudo-first-order kinetic for C_0 values of 5 and 25 mg/L, the constants K_{app}. for different C_0 and catalyst amounts are reported in Tables 3 and 4. The effect

Table 2
Degradation efficiencies obtained for the various parameters studied

pH	*R* (%)	m-TiO_2 (g)	*R* (%)	NaCl (g/L)	*R* (%)	C_0 (mg/L)	*R* (%)
2	43.62	0.05	60.10	0.2	58.60	10	76.85
4	58.79	0.1	64.50	0.4	61.59	15	65.85
6	62.81	0.15	72.10	1	74.95	20	55.91
8	76.75	0.20	80.50	1.2	70.01	25	46.11
10	70.59	0.25	74.13	1.6	67.85		

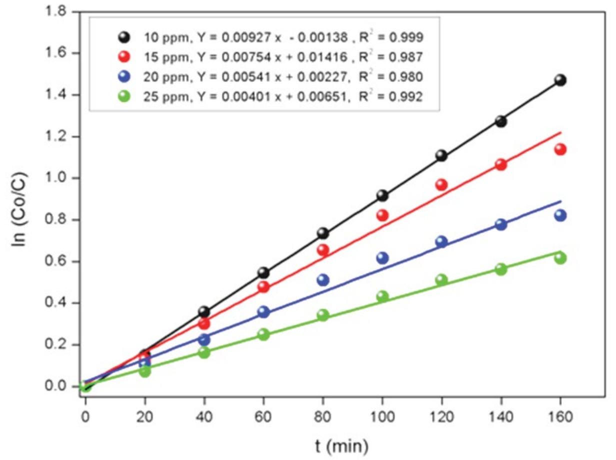


Fig. 7. First-order degradation kinetics at different concentrations.

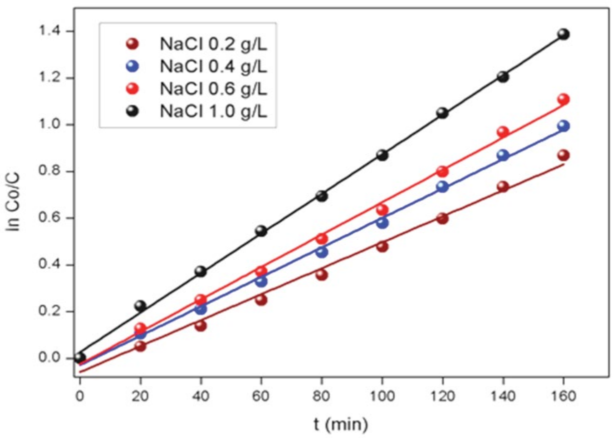


Fig. 8. First-order degradation kinetics at different catalyst amount.

Table 3
Determination of coefficients of degradation

C_0 (mg/L)	10	15	20	25
K_{app} (mg/L min)	0.011	0.0075	0.0057	0.0046
R^2	0.999	0.987	0.989	0.992
K_{ad} (L/mg)	0.4016	K_e (mg/L min)	0.1274	

of GRL concentration C_0 on the initial rate of degradation is shown in Fig. 4. The figure indicates that the rate of discoloration increases with increasing C_0 which corresponds to L–H adsorption model. A linear expression can be occasionally obtained from equation 5 by plotting the reciprocal initial rate constant against C_0 [30]. The plot of $1/K_{\text{app}}$. against C_0 (Fig. 9, Inset) gives a linear relationship.

$$\frac{1}{K_{\text{app}}} = \frac{1}{K_r} \cdot C_0 + \frac{1}{K_r \cdot K} \tag{6}$$

Table 4
Pseudo-first-order rate constants for the degradation of GRL at different catalyst amount

Catalyst amount (g)	K_{app} (min^{-1})	R^2
0.4	0.0063	0.996
0.6	0.0069	0.996
1.0	0.0084	0.998
1.2	0.0096	0.989

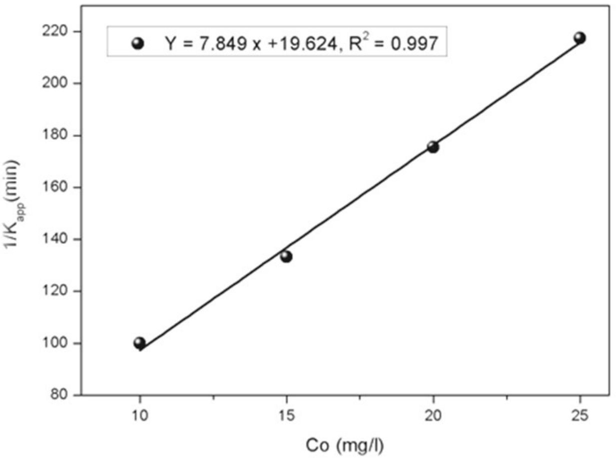


Fig. 9. Application of Langmuir–Hinshelwood model.

From the values of the slope ($1/K_r$) and the intercept ($1/K_r$ K), the constants $K{\cdot}C$ and K for the photocatalytic degradation of GRL are respectively 7.849 mg L min^{-1} and 19.624 L/mg (Table 1).

4. Conclusion

The photodegradation at different Asucryl Red concentrations leads to the conclusion that low concentrations result in better elimination rates. The basic medium gives encouraging results, especially at pH 8 and the optimal mass of TiO_2 of 0.2 g. The photodegradation at different NaCl concentrations showed that the elimination rate increases with augmenting the salt concentration up to 1.2 g/L above which there is a decrease in the rate, probably due to the congestion caused by these ions, which prevent the organic species to reach the photocatalytic sites. The efficiency of the photocatalytic processes was found to depend strongly on the solution pH.

The photocatalysis is effective as a method of dye degradation, with the system TiO_2/UV. It is focused on the generation of (e^-/h^+) pairs and both charge carriers migrate to the catalyst surface of semiconductor in the presence of the adsorbed azo dyes, where the redox reactions take place. The oxidizing radicals attack the azo dyes and convert them partially into CO_2, H_2O, and inorganic molecules.

The photocatalytic degradation was affected by the initial GRL concentration with respect to Langmuir–Hinshelwood kinetic model. TiO_2 has a better photoactivity for the degradation of (Asucryl Red) compared to the some commercial catalysts.

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Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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