Adsorption of Navy Blue on Titanium Dioxide Photocatalyst by Using Metallic Nanoparticles

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Abstract: Dyes have the largest range of colors that can readily change our taste. Dyesnecessarily havethe ability to be soluble to a maximum extent or fractionally where it is being applied. Industries are setting free million tons of dyes as a hazardous and toxic discharge. Dyes produced a toxic effect to the global world.(TiO_2) Titanium dioxide is a notable substance for the researchers due to its biocompatibility, chemical structure stability, optical, electrical, and physical properties. The efficiency of titanium dioxide was improved by doppingTiO_2 with copper using visible light irradiation. CuO/TiO_2anatase and Degussa P25 were used to degrade Navy blue dye and havehighphotocatalytic effectiveness in the evacuation of natural contaminants. The amount of debasement of dye as an element of time indicated that the efficiency of degradation is different for both P25 Degussa and $CuO/TiO_2$4 wt.%anatase for the same dye. The adsorption of color at its normal pH is higher because of the low negative surface charge on Cu-TiO2 when contrasted with Degussa P25on which the adsorption is less due to the relatively more negative charge on the surface. Decomposition of (NB) was investigated using different concentrations (25, 49, 76, 124, and 149) mg L^{-1} of Degussa P25 and 4 wt.%CuO/TiO_2 and. The total degradation (100%) of dye was investigated at 125 mgL^{-1} with 4 wt. % CuO/TiO_2after 80 minutes. The debasement rate is relative to the measure of OH•/O2•-radicals that are shaped on a superficial levelof the photocatalyst. However, when the same amount of catalyst concentration is used, the active site quantity remains the same. This optimization value of catalyst can be illustrated on the development of $OH^•/O_2^{•-}$ radicals, as at higher convergence of catalyst progressively dynamic locales are accessible for OH•/O2•-radicals, which increases the adsorption on catalyst surface of dye and ultimately increases the rate of debasement. This factor can be attributed to two reasons, first due to penetration of light in the solution as less light reaches to the catalyst or accumulation of more TiO_2 that causes less degradation rate. Secondly, by increasing the interaction of particles in solution consequently increase the deactivation ratio of activated particles by particle collisions at the ground state, so the ratio of debasement decrease. The results revealed that the amount of dye adsorbed on 4 wt.%CuO/TiO_2 catalyst surface was higher than the absorption on the Degussa P25 surface.

Keywords: TiO_2 Nanoparticles, Photocatalyst, Navy Blue, Adsorption

1. Introduction

Every fabric has a specific color range. Besides its constitution, if the fabric is not colored suitably, commercially, it is not theright product. In early times the fabric was dyed with organic dyes. But they imparted a limited and dull shading range. No matter how low color fastness, they give when placed in sunlight and wash them. Subsequently, they required a mordantfor thepreparationof the dye complex to fix dye and fabric together so that dyers can work tediously. Synthetic dyewas discovered in 1856by W. H. Perkins andgave a range of dyes that quicklygive brilliant shades [1]. Historically the application of naturally occurring dyes has been found dating back to 3500 BC and was abstracted from fruits, flowers, vegetables, particular insects, and fish products. Therefore dyes use has increased extensively inthe industry today. The natural or syntheticcolored and aromatic organic compounds that are attracted to the substrate to which it has been applied is known as a "Dye." Mainly dyes are usedin aqueous. Sometime mordant is used to enhance the ability of the dye on the surface of the substrateon which the dye is being applied. In the very first stage, the use of color to find the specific components inthe tissue part can be achieved with dyes. Though there are some other sources, Dyes still has the most extensiverange of colors that can readily change our taste. They are being used for different materials i.e., inleather, textiles, and plastic, food, and paper industries as a liquid. The main characteristic of the dye is that they necessarilyhave the ability to soluble to the maximum extent or fractionally where it is being applied. Like other chemicals, dyes also follow the same rule, i.e., particular dyes may have a toxic effect, mutagenic or carcinogenic, and can be harmful to the health [2].

Natural dyes are gaining much more interest inthe entire world in every field of life due to their less toxic and harmful effects in the environment as compared to synthetic dyes. Around 80% dyestuff attach with the fabric while 20% drained out and goes in the wastewater and cause serious problem both for plants and human beings. Industriesare setting free million tons of dyes as a hazardous and toxic discharge, including organic and color compounds from dying and textile substances. The wastewater coming from the textile sector is most pollutant than any other industry, both in terms of the volume coming and composition of effluents [3]. Moreover, these effluents create a severe problem not only the human life but also for the aquatic environment asthe water gets turbid and polluted for all the water bodies like lakes, canals, and rivers, etc. and makes it non-biodegradable [4]. At the same time, these pollutants cause problems for light penetration and photosynthesis due to highly toxic and mutagenic so effects the irrigation as well. Industries are setting free million tons of dyes as a hazardous and toxic discharge. Dyes produced a harmfulimpact on the global world [5].

It prohibitsthe entry of sunlight required for the mechanism of photosynthesis. This obstructs the oxygen transfer process on the air-water surface. Dissolved oxygen deficiency in water is the most real problem of material waste, as broke up oxygen is essential in marine life. The texture of the soil hardens, and root penetration can be prevented. Dyes produced in the material, printing and paper enterprises may enter sewage and wastewateras a result becomes a significant source of pollution of waterways. In general numerous porous like materials have been used to remove harmful and toxic chemicals or dyes from the water, especially those which are easy to use, cost-effective, fast kinetics, full availability, and have high capacities [6] of adsorption. The possible methods are includedas activated carbons, nickel oxide nanoplates [7], clays [8], graphene oxides [9], andcomposites of hydroxyapatite with organic substrates etc [10].

Titaniaor (TiO_2) titanium dioxide is a renowned and famoussubstance for the researchers owing to its biocompatibility, chemical structure stability, optical, chemical, and physical stuff. Two primary factors limit its application: (1) the brisk recombination of a photograph created electron-opening (e−/h+) matches in TiO_2 that lessens its viability, and (2) the wideband hole (3.0–3.2 eV) of TiO_2 situated in the UV locale that causes the assimilation of just a little part of sun based light (under 5% of sun based vitality is radiated as UV illumination) [11].

Because of the rather wide band hole of titanium dioxide, it fundamentally assimilates bright illumination in the range shorter than 387 nm. Since UV light in the sun oriented light is under 5%, this can bring down the proficiency of titanium dioxide when daylight is applied as the wellspring of vitality. Henceforth, incredible exertion has been centered around growing new titanium dioxide-based photocatalyst with productive photograph reaction in the scope of visible light [12]. TiO_2 has been found in four different forms rutile, anatase, brookite and TiO_2 (B). Anatase TiO_2 is crystalline in nature that correlate with the tetragonal structure and shows excellent photocatalytic efficiency in ultraviolet irradiation for the elimination of pollutants in various industries and are used to degrade different dyes. Mostly the photocatalytic ability of titanium dioxide is found on the anatase planes [13, 14], however thermodynamically, the planes are secure and thus dominant in natural and synthesized anatase [15]. Rutile TiO_2 has a tetragonal crystal structure as well. These are used mainly in paints as white pigments. But the interfacial stage between rutile and anatase are observed as very efficient to enhance photocatalytic ability due to separation of charge carrier, consequently biphasic TiO_2 play very important role to improve the activity of photocatalyst [15]. Brookite TiO_2 belongs to orthorhombic crystalline structure. TiO_2 (B) is a monoclinic mineral and is a moderately new expansion to the Titania family.

The efficiency of titanium dioxide can be improved by dopingTiO$_2$ with other compounds like nitrogen, carbon, copper, and tungsten, etc., using visible light [16] irradiation. Magnesium-doped titanium dioxide (Mg + 2-TiO_2) [17] is also used when a weight percentage of magnesium is used to decompose different dyes. Another approach is the reduction of TiO2 to oxygen vacuum-rich TiO_2-x, an excellent

photocatalytic material for water partitioning, and serving as a robust model system [18].

It would be highly desirable to develop a TiO2-based photocatalyst that reacts to visible light. Several strategies have been reported to extend its adsorption range to the visible light spectrum by changing the band gap of semiconductors, including replacing the O atom in TiO2 with C or N, doping with metal elements such as Sb and V, and others with metal production of oxides or hydrogenated black-TiOx structures. Of these, the design of TiO2 by decorating plasma metal nanoparticles with Ag or Au is a particularly promising approach [8]. Additional efficiency and durability can be achieved by introducing anomalies in the lattice structure of the surface layer of titanium dioxide nanocrystals, allowing nanoformed TiO2 incorporated into outdoor building materials for infrared absorption, such as floor stones in Noxer blocks. Substrates that can be easily separated from treated water (Vohradsky and Ramsden, 2001). Photocatalytic destruction of organic matter is also used in photocatalytic antimicrobial coatings.

2. Material and Method

2.1. Preparation of Catalyst

Titanium dioxide TiO_2 anatase and copper chloride $CuCl_2$, both of these compounds were acquired from Sigma Aldrich, and Degussa P25 was purchased from Evonikenterprises. To control the pH of experiments, NH_4OH and 0.1 M HCl were used. The analytical grade of chemicals was used in all the reactions without any further purification. Precipitation-deposition and impregnation method [19] were used to deposit the Copper on TiO_2. 1 g amount of TiO_2 and 3, 5, 9 % wt. of $CuCl_2$ salt were solved gently in 100 mL of distilled water for 24 h atordinary temperature so that Cu ions can deposit on TiO_2. Then by using the NH_4OH solution, the pH of the solution was set at 8.5. After that, the solution was stirred for one hour at 80°C and was kept at room temperature for two days to get stabilized. The solution then filtered through (Whatman; Grade 2) and the precipitates that were obtained washed using deionized water repeatedly. Then the final catalysts were allowed to dry for threehr at 90°C, and annealing was done at 400°C for 2 hours.

Table 1. General characteristics of dye.

Dye Name	Navy Blue
Molecular formula	C39 H23 Cl Cr N7 O12 S. 2 Na
C. I number	Blue 172
Molecular weight	947.13
λ max (nm)	585

2.1.1. Photodegradation Experiments

The synthetic textile Navy Blue HE2R 1 (NB) dye was acquired from the SundarEnterprises textile garment region, Raiwind. The reactions were carried out in a Pyrex glass beaker, which was set under the UV light irradiating lamp. UV–vis spectrophotometer (Agilent Technologies carry 60 UV-Vis) was utilized to check the debasement or removal of dye. Generally, during the reaction time, 1 mL dye sample

was drawn with the help of a micropipette after 10 min. The sample was centrifuged and filtered to observe the removal of catalyst from the dye mixture. The maximum wavelength (λ max) of dye was used to measure absorbance. The efficiency of dye degradation was evaluated using the following Equation.

$$\text{Efficiency (\%)} = [A_0\text{-}A_t/A_0] \times 100$$

Here, A_0 is the basic absorbance of dye mixture before the reaction, and 'A_t' is the absorbance of dye during the reaction at the time 't.' In general, 5 mg L^{-1} amount of dye solution was reacted with an optimized amount of catalysts (125 mg L^{-1}) in 250 mL solution. (Cu reinforced TiO_2 and Degussa P25) for 2 hours in UV light illumination at neutral pH 6.5 of dye in the presence of continuous air to assist the progress of oxygen supply for the effective oxidation process of dyes. The temperature was maintained at room temperature during the whole experiment [20].

Several parameters were studied during the reactions like results of irradiation and catalyst, the impact of dye adsorption with and without UV light irradiation, the effect of primary dye ratio, and the effect of catalyst concentration. Different examinations were performed using the same conditions to investigate the results of the catalyst by reducing the irradiation time from 120 min to 80 min.

The ability of relative catalyst concentration for dye degradation was measured using the same conditions, but the solution was agitated and placed in the place without light for 30 min. To avoid any complication for photocatalytic dye degradation, a small-time interval was used in diffused light. The solution of the same catalyst concentration was prepared to find the optimized amount of dye using the same conditions. Keeping other parameters constant, the effect of catalyst concentration was determined by varying the catalyst amount from 25 milligram L^{-1} to 150 milligram L^{-1} [21].

2.2.2. Study of the Effects of Irradiation

Adsorption activity of the dye on the surface of the catalyst was determined for 4 wt.% (CuO/TiO_2) and Degussa P25 separately. To check absorbance, two solutions were prepared in the 1-liter flask and shifted into two beakers using 5 mg L^{-1} of dye concentration and 125 milligram L^{-1} of each catalyst (4 wt.%CuO/TiO_2 and Degussa P25) amount. Then 1 mL sample from each solution was taken with the help of micropipette and shifted into the spectrophotometer cell. The absorbance of both solutions was checked using UV–vis spectrophotometer (Agilent Technologies cary 60 UV-Vis). And then, both beakers of dye solutions were placed one after the other under UV light for 30 min to study the effect of UV irradiation at room temperature. After 30 minutes, 1 mL sample from each solution was taken, and absorbance at the maximum wavelength (λ max) was checked by using UV–vis spectrophotometer (Agilent Technologies cary 60 UV-Vis) to check the results of irradiation [22].

2.2.3. Study of the Effects of Catalyst

Withrespect to the check effect of photocatalysts, dye solutions with different catalyst solutions were prepared.

First of all, a 1-liter flask was taken, and the resolution of NB dye was prepared using its optimized amount (5 mg L^{-1}) with water, and then this solution was taken into 250 mL beaker. Then the optimized concentration of TiO_2 (125 mg) catalyst without any amount of copper was taken in 250-milligram beaker of dye solution. The mixture was then stirred for half-hour and placed under the irradiation of UV lamp for 2 hours. After 2 hours, 1 mL solution from the beaker was taken in the sample cell, and absorbance was checked using (Agilent Technologies carry 60 UV-Vis). In the second 250 mL beaker of dye solution, (125 mg) amount of (2 wt. % CuO/TiO_2) catalyst was taken, stirred, and placed in the UV light irradiation for 2 hours and absorbance was checked [23]. The same procedure was repeated for 4 wt. % CuO/TiO_2, 8 wt. %CuO/TiO_2, and Degussa P25 catalysts and absorbance of all the solutions were checked after 2 hours to check the effect of a catalyst on dye using different amount of copper with TiO_2. The value of catalyst type and their degradation efficiency is given in Table 2.

Table 2. Value of catalyst type and their.

Experiment No.	Catalyst type	Degradation efficiency
1	Anatase	34.32
2	2 wt. % CuO/TiO_2	59.93
3	4 wt. % CuO/TiO_2	76.82
4	8 wt. % CuO/TiO_2	43.23
5	Degussa P25	64.94

2.2.4. Study of the Effects Of Absorbance

Two solutions were made using 25 mg of 4 wt.%CuO/TiO_2 and Degussa P25 separately in a one-liter flask with deionized water. Then 200 mL solutions of each catalyst added into two different beakers. Later on, the effect of adsorption of dye on catalysts was determined by adding a pre-determined amount of (5 mg) of Navy Blue HE2R 1 (NB) dye in both above beakers and placed under dark conditions for 30 minutes. After 30 minutes, both solutions were purified, and the relative amount of adsorbed dye was determined by calculating the amount of dye on the surface of filtered catalysts with the help of weighing balance [24].

2.2.5. Optimization of Catalyst Concentration

To determine the optimized amount for the decomposition of dye, various concentration (24, 49, 74, 100, 125 and 150) milligram L^{-1} solutions of catalyst (4 wt.% CuO/TiO_2 and Degussa P25) were prepared in the standard 1-liter flask, using the optimized concentration of dye (5mg L^{-1}) for each catalyst. Then each catalyst concentration solution from the flasks was taken in 250 mL beaker using (5mg L^{-1}) dye solution and stirred for 30 min. Later on, each beaker was placed under the irradiation of UV light for 80 min. After 80 min 1 mL sample from each concentration solution beaker was taken into the cell using micropipette and absorbance was checked with the help of UV–vis spectrophotometer (Agilent Technologies cary 60 UV-Vis). All catalyst concentration values and results are given in Table 2.

Table 3. Catalyst concentration & Adsorption efficiency.

Experiment	The concentration of	Adsorption efficiency

No.	Catalyst (5mg L^{-1})	4 wt.% CuO/TiO_2	Degussa P25
1	25	71.46	62.22
2	50	78.53	66.84
3	75	83.96	72.01
4	100	87.07	73.50
5	125	98.87	78.26
6	150	88.04	64.67

2.2.6. Optimization of Dye Concentration

To check the effect of the rapid increase in basic dye concentration upon its degradation rate, solutions of various concentration (5, 10, 15, 20 and 25mg L^{-1} of Navy Blue HE2R 1 (NB) dye were prepared in the 1-liter flask, using the optimized amount of catalyst (125 mg L^{-1}) for each dye solution. Then each dye solution from the flasks was taken in 250 mL beaker using (125 mg L^{-1}) amount of catalyst solution and was allowed to stir for 30 min. Later on, each beaker was placed under the irradiation of UV light for 80 min. After 80 min, 1 mL sample from each dye solution was taken into the cell using micropipette and absorbance was checked with the help of UV–vis spectrophotometer (Agilent Technologies cary 60 UV-Vis). All the values of different dye concentrations and their results are given in Table 3.

Table 4. Values of dyes and their adsorption effeciency.

Experiment No.	Initial Dye Concentration (mg L^{-1})	k_d (min $^{-1}$)	
		CuO/TiO_2	P25
1	5	0.9564	0.6450
2	10	0.4435	0.3237
3	15	0.2391	0.2051
4	20	0.1928	0.1592
5	25	0.1041	0.082

3. Results and Discussions

3.1. Effect of Irradiation

Figure 1. Shows the absorption spectrum of Degussa P25 and 4 wt.%CuO/TiO_2anatase effects on (NB) dye in an aqua solution under the irradiation of UV light for 80 minutes. The results of UV–vis absorption spectrum shows an apparent reduction in the absorbance of dye which is the indication that the primarychromophore of dye has been degraded [19]. The amount of degradation of dye as a role of time is shown in Figure 2, which shows that the efficiency of degradation is different for both Degussa P25 and 4 wt.%(CuO/TiO_2) anatase for the same dye. Using Degussa P25, the efficiency of dye degradation was found upto 60%, as shown in Figure 2a. However, the debasement efficiency of dye with 4 wt.%CuO/TiO_2 was found upto 75%, as shown in Figure 2.
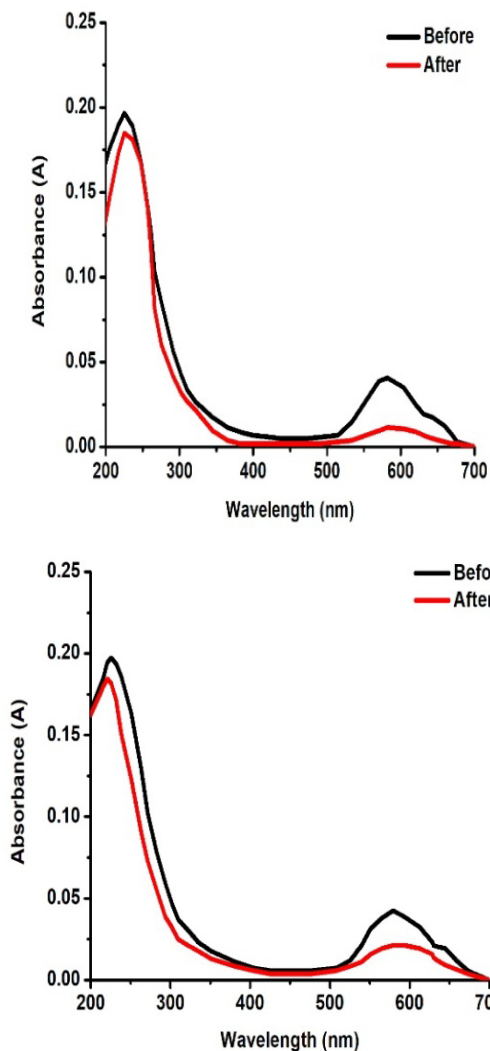
Figure 1. Alterations in the UV–vis absorption spectrum of NB dye aqueous solutions after half-hour irradiation on Degussa P25 (left) and 4 wt.% CuO/TiO$_2$ (right).
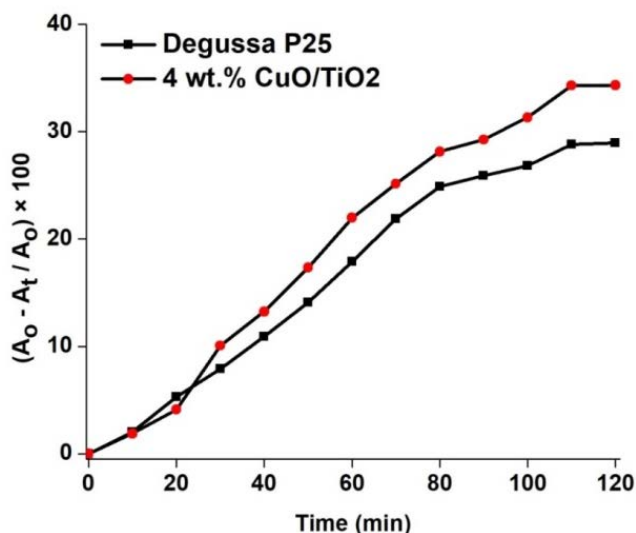

Figure 2. Photo degrading efficiency (%) of NB dye as a role of time up to 120 minutes (C$_0$ = 5 mg L^{-1}; Catalyst concentration = 25 mg L^{-1}; pH = 6.5)

(a) at Degussa P25 (b) on the surface of 2 wt.% Cu2O-CuO/TiO2-TiO2.

3.2. Effect of Adsorption

The ratio of degradation of a dye inthe variousphotocatalytic process depends upon the capability of dye absorbance on the surface of the catalyst [3]. This effect was calculated by adding a pre-determined amount (5 mg) of NB in 25 milligram L^{-1} of both catalysts (4 wt.% CuO/TiO$_2$ and Degussa P25) to get the dye adsorbed on the catalyst surface for 30 min in dark conditions. After 30 minutes, both solutions were filtered, and the relative amount of adsorbed dye was determined by calculating the amount of dye on the surface of filtered catalysts with the help of weighing balance. The results revealed that the amount of dye adsorbed on 4 wt.%CuO/TiO$_2$ catalyst surface was higher than the absorption on the Degussa P25 surface, as shown in Figure 3.
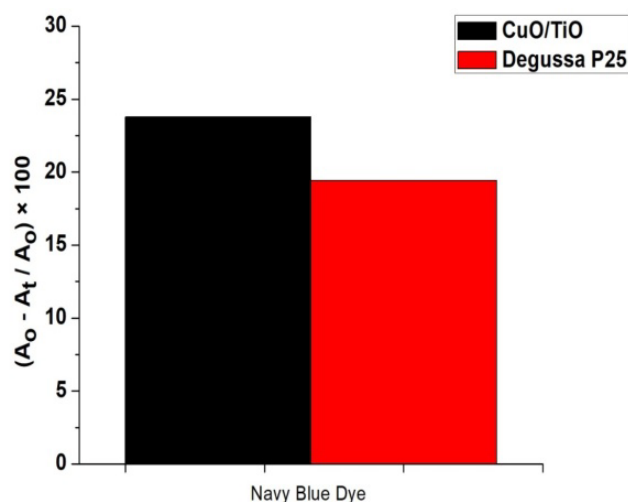

Figure 3. Adsorption efficiency of NB dye at Degussa P25 and 4 wt.%CuO/TiO$_2$ after 30 min under dark conditions (Catalyst concentration = 25 mg L^{-1}; dye concentration = 5 mg L^{-1}).

The high efficiency of dye adsorption can be demonstrated based onthe natural pH of dye that was found to be 6.5. The point of zero charges (pzc) of TiO$_2$ is pHpzc = 6.8 [4]. Generally, zero point charge (ZPC) of TiO$_2$ decreases with the loading of metal due to potential energy barrier (Schottky barrier) formation, consequently depletion of an electron occurs on TiO$_2$ and so, OH groups increases on the surface. The ZPC of copper metal loaded titanium dioxide (Cu-TiO$_2$) usually found in the range of 5.6 - 6.1 [25]. At a pH value of a solution higher than its pHpzc, the catalyst surface carries a negative charge [5]. So, the adsorption of dye at its natural pH is higher due to low negative surface charge on Cu-TiO$_2$ as compared to Degussa P25 on which the adsorption is less due to the relatively more negative charge on the surface [5].

3.3. Effect of Catalyst Concentration

Decomposition of (NB) was investigated using different concentrations (25, 50, 75, 125, and 150) mg L^{-1} of 4 wt.%CuO/TiO$_2$ and Degussa P25. The results revealed that 125 mg L^{-1} was the optimum catalyst dose of 4 wt. % Cu2O-

CuO/TiO2 and Degussa P25 to degrade the dye effectively, as shown in (Figure 4). The total degradation (100%) of dye was investigated at 125 mgL^{-1} with 4 wt. %CuO/TiO$_2$after 80 min.

This optimization value of catalyst can be illustrated on the production of OH$^•$/O$_2^{•-}$ radicals, as a higher concentration of catalyst more active sites, are available for OH$^•$/O$_2^{•-}$ radicals, which increases the adsorption of dye on catalyst layer and ultimately increases the rate of degradation [7]. By increasing further catalyst doze above optimized amount, the degradation rare decreases. This factor can be attributed to two reasons, first due to penetration of light in the solution as less light reaches to the catalyst or accumulation of more TiO$_2$ that causes less degradation rate [8]. Secondly, by increasing the interaction of particles in solution results in the increase of deactivation rate of activated particles due to particle collisions at the ground state, so the rate of degradation decreases [9].
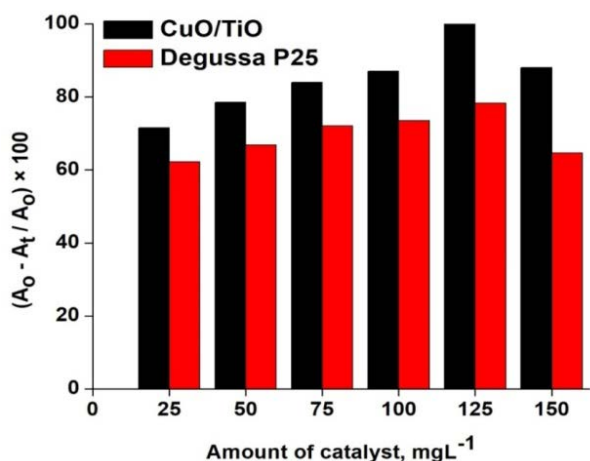

Figure 4. *Effect of varying catalyst concentration on the rate of NB dye photo degradation after 80 min of UV irradiation ($C_0 = 5$ mg L$^-$1; pH = 6.5; t = 80 min).*
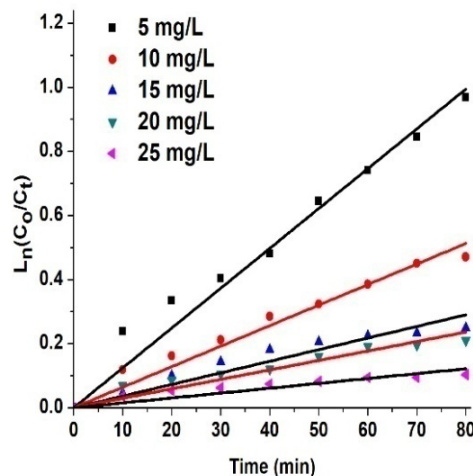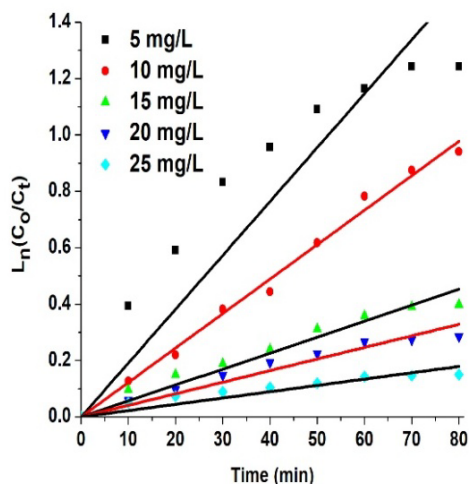
3.4. Effect of Dye Concentration

Figure 5. *Pseudo-first-order Ln (C_o/C_t) plots of varying NB dye concentration versus irradiation time representing the effect of increasing dye concentration on degradation rate. (Left) CuO/TiO$_2$ and (Right) Degussa P25.*

To check the effect of various concentration of initial dye on its degradation rate different concentration solution (5, 10, 15, 20 and 25) mg L^{-1} of Navy Blue HE2R 1 (NB) dye were prepared in 250 mL water using the optimized amount (125 mg L^{-1}) of 4 wt.%CuO/TiO$_2$ and Degussa P25 and irradiated with UV light for 80 min. The results showed that 5 mg L^{-1} is the optimum amount of dye for 4 wt.% Cu2O-CuO/TiO2 and Degussa P25 catalysts, as shown in (Figure 5).

Value of rate constant (kd) of each dye was evaluated using the following two formulas.

$$C_t = C_o \exp(-k_d t) \qquad (1)$$

$$\text{or } \ln C_o/C_t = k_d t \qquad (2)$$

Here, C_t is the absorbance of dye at a definite time t, and C_o is the absorbance of initial dye. k_d is the pseudo-first-order kinetic rate constant (min^{-1}) for the degradation process, and 't'is the time of degradation. The degradation rate is proportional to the amount of OH•/O$_2$•$^-$ radicals that are formed on the surface of photocatalyst, although when the same amount of catalyst concentration is used, the active site quantity remains the same [10]. So, as the dye concentration increases, they block the active sites more for the generation of OH•. Also, the increase in dye concentration causes more dye molecule absorbance on the surface of photocatalyst that reduces the light radiation. As a result, low light intensity reducesphotocatalytic degradation [14].

4. Conclusion

Industries are setting free million tons of dyes as a hazardous and toxic discharge, including organic and color compounds from dying and textile substances. Most of these dyes are highly toxic and poisonous for the health of human being indirectly or directly. The wastewater coming from the textile sector is most pollutant than any other industry, both in terms of the volume coming and the composition of effluents. Titaniaor titanium dioxide (TiO$_2$) is a very

renowned and is a well-known substance for the researchers due to its biocompatibility, chemical structure stability, optical, chemical, and physical properties. In general numerous porous like materials have been used to remove harmful and toxic chemicals or dyes from the water, especially those which are easy to use, cost-effective, fast kinetics, wide availability, and have high capacities [6] of adsorption. The possible methods are including activated carbons, nickel oxide nanoplate, clays, graphene oxides, and composites of hydroxy apatite with organic substrates. Additional efficiency and durability can be achieved by introducing anomalies in the lattice structure of the surface layer of titanium dioxide nanocrystals, allowing nanoformed TiO2 incorporated into outdoor building materials for infrared absorption, such as floor stones in Noxer blocks. Substrates that can be easily separated from the treated water. These are used mainly in paints as white pigments. But the interfacial stage between rutile and anataseisconsidered as very efficient to enhance photocatalytic ability due to separation of charge carrier; consequently, biphasic TiO_2 playsa significant role in improving the activity of photocatalyst.

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