PHOTOCATALYTIC REMOVAL OF SOME TEXTILE DYES OVER SUSPENSION OF TITANIUM DIOXIDE AND IRRADIATION WITH SOLAR RADIATION

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ABSTRACT

The present work involves investigation of the photocatalytic removal of some textile dyeing using a suspension of titanium dioxide as a photocatalyst under irradiation with sunlight. Used textile dyes were direct blue, disperse blue, direct yellow, reactive yellow, disperse red, reactive blue, disperse yellow, and reactive red. All reactions were performed using 20 ppm of aqueous solution with a suspension of titanium dioxide of each dye under normal weathering conditions with under normal solar radiation. Photocatalytic removal of each dye was followed by measuring the optical intensity of each dye at its maximum absorption periodically. From the obtained results, it was found that the concentration of the used dyes was reduced with the time of irradiation. Photocatalytic activity of dye removal under the same reaction conditions fall in the following sequence: Reactive red > Disperse yellow > Reactive yellow > Direct yellow > Disperse blue > Direct blue.

Key words: Textile dyeing, Dyes removal, Photocatalytic processes, Titanium dioxide.

INTRODUCTION

In the last few years, there was much attention towards photocatalytic processes that are based on using light and photocatalyst semiconductors to perform photocatalytic processes. This type of processes is based initially on the photoexcitation of the particles of the used photocatalyst via absorption of light with a proper energy (Eg ≥ hν). Upon this process, valence band holes (h^+_{VB}), and conduction band electrons (e^-_{CB}) at each of valence band and conduction band respectively[1-3]. These holes and electrons are contributed in redox

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reactions with the pre-adsorbed species on the surface of the photocatalyst. Generally, photocatalytic systems are designed to fit purpose of the use[4,5]. For example, these systems can be used in the production of clean fuel, photocatalytic decomposition of water, and removal of pollutants from water as well as soil. Important example of using this system in removal of pollutants, is the use of heterogeneous photocatalytic system in the treatment of textile dyeing wastewaters[6-9]. It is well known that textile factories normally use huge amount of water especially in dyeing processes, and hence, the drain of this wastewater contains high concentrations of dyes, which is indicated by the deep color of the effluent wastewater[10,11]. The effluent wastewater contains high levels of the used dyes and most of these dyes are toxic and may be carcinogenic. Beside that, these dyes have rigid aromatic structure that enable these dyes to resist fragmentation under normal weather conditions. So that these wastewaters must be treated before charge into the ambient environment such as rivers, lakes, and soil[12,13].

Different methods and techniques can be used to approach this goal such as adsorption processes, biological methods, and chemical methods. Among these methods, advanced oxidation processes (AOPs) seem to be more efficient method in comparison with other biological and chemical methods. However, these AOPs methods are based on the formation of some active radical species such as $^{\bullet}OH$, $O^{\bullet-}$, $O_2^{\bullet-}$, and H_2O_2. These reactive species produce on the surface of the used photocatalyst upon reaction of H_2O and O_2 with positive holes and conduction band electrons[14-16]. Then these species are contributed in redox reactions with the adsorbed species on the surface[17]. The result of these reactions is the fragmentation of the organic molecules into the smaller fragments and some of volatile materials as well as inorganic molecules such as CO_2 and H_2O.

The main drawback of these AOPs is the high cost due to need large amount of electrical energy for operating of light sources, ozone generation as well as high cost for using ultra violet radiation in the excitation processes for these systems[18]. To overcome this problem, alternative approach can be achieved by using solar radiation in the excitation processes rather than using artificial UV sources. Solar radiation can be used with both; homogeneous and heterogeneous photocatalytic systems with some photocatalysts such as TiO_2, ZnO, CdS, Fe_2O_3 etc. These photocatalysts can absorb solar radiation while ozone and H_2O_2 can't absorb at wavelength more than 300 nm[19]. However, performance of this type of processes in air can enhance the efficiency of this process due to presence of oxygen. Presence of oxygen is essential for generation of the reactive species on the surface, and then these are utilized in redox reactions on the surface that leads to destruction of organic molecules into volatile and inorganic materials[20,21].

This work involves investigation of photocatalytic removal of eight of textile dyes that are used in Hilla Textile Factory using a suspension of titanium dioxide and under irradiation with direct sunlight under normal weathering conditions.
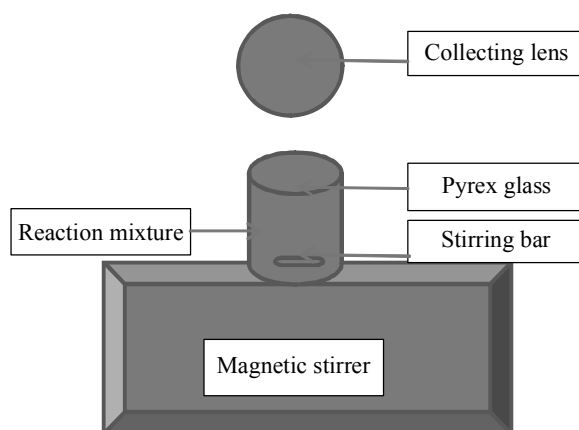
EXPERIMENTAL

Used materials

Titanium dioxide used in this study was P25 Degussa with a purity of 99.9% and a surface area of 50 m^2/g. Dyes used in this study were reactive red 31 (RR 31, λ_{max} = 500 nm, MF: $C_{30}H_{15}ClN_7Na_5O_{15}S_6$; MW: 992.14 g/mol), reactive yellow 145 (RY145, λ_{max} = 416 nm, MF: $C_{28}H_{20}ClN_9Na_4O_{16}S_5$, MW: 1026.25 g/mol), direct yellow 50 (DY50, λ_{max} 400 nm, MF: $C_{26}H_{18}N_4Na_2O_8S$, MW: 624.552659 g/mol), direct blue 80, (DB80, λ_{max} = 575 nm, MF: $C_{34}H_{22}N_4Na_4O_{16}S_4$, MW: 962.78 g/mol), disperse blue 56, (DB56, λ_{max} = 560 nm, MF: $C_{15}H_{13}BrN_2O_4$, MW: 365.18), disperse yellow 23, (DY23, λ_{max} = 478 nm, MF: $C_{18}H_{14}N_4O$, MW: 302.33 g/mol). All these dyes were provided by Sigma Aldrich and they were used without further purification.

Photocatalytic reactor

In this study, the used photoreactor was home made and it consists of Pyrex reaction flask, hot plate magnetic stirrer, and a collected lens with a focal length of 250 mm. The whole apparatus for this reactor is shown in Fig. 1.

Fig. 1: Schematic diagram of apparatus of photocatalytic degradation of some of textile dyes

Photocatalytic experiments

A solution of 20 ppm of each dye was prepared in this study. 100 mL of each dye solution was taken and to this solution, 0.10 g of TiO_2 was added in 200 mL Pyrex glass flask. The resultant mixture was stirred under normal air conditions using a magnetic stirrer until reaching equilibrium time for each dye. Then, this suspension was irradiated using normal sunlight radiation of solar spectrum. The ambient solar spectrum was collected and focused on the reaction vessel using a collecting lens with a focal length of 250 mm. For precise results, all experiments were conducted at the same time from 12 am to 2.00 pm at the same place in October from 2014. During irradiation, periodically, 2 mL of each sample was withdrawn and the solid materials were separated by centrifuge (3000 rpm). Then the absorbance of each supernatant liquid was recorded at wavelength of a maximum absorption of each dye using UV-Visible Shimadzu Spectrophotometer-SP21.

pH measurements

In order to investigate the effect of pH on the photocatalytic treatment for the used textile dyes, the pH value for each dye was recorded for stock dye and the dye after irradiation using pH-meter.

RESULTS AND DISCUSSION

Determination of adsorption equilibrium

To achieve equilibrium conditions, preliminary experiments were performed to find the required time that is sufficient to reach adsorption equilibrium for each dye over TiO_2. A solution of 100 mL of each dye was suspended with 0.10 g of TiO_2 without any light under a continuous stirring. The absorbance of each dye was followed periodically at λ_{max} of each dye until reaching equilibrium state. Equilibrium time for each dye was estimated and is shown in Table 1.

Table 1: Equilibrium time for each dye over suspension of TiO_2 under dark conditions

Used dye	Reactive red	Reactive yellow	Disperse yellow	Disperse blue	Direct yellow	Direct blue
Equilibrium time (min)	14	16	20	23	28	30

Photocatalytic dye removal

Photocatalytic dye removal over a suspension of TiO_2 and under irradiation with solar spectrum was followed by measuring absorbance of the used dye periodically and the obtained results are presented in Fig. 2.
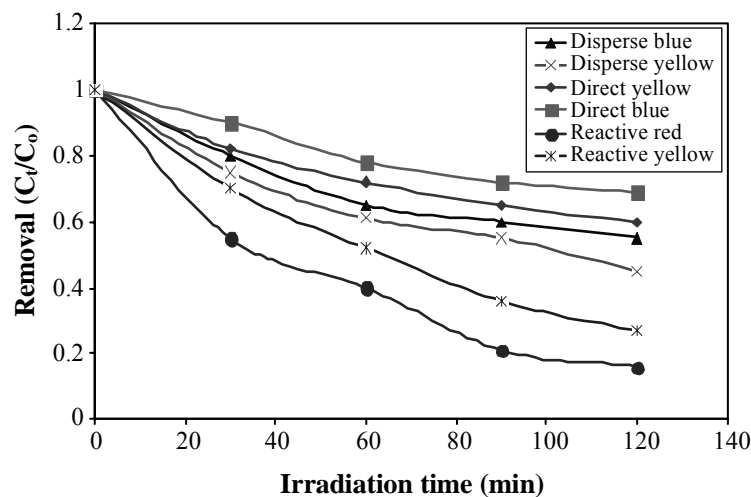
Fig. 2: Photocatalytic dye removal over TiO₂ suspension under irradiation with solar radiation

From these results, it can be seen that there was a progressive increase in the efficiency of dye removal over a suspension of TiO_2 and under irradiation with solar radiation. After 120 min of continuous irradiation, there was a considerable reduction in the concentration of all the used dyes. From these results, it is clear that reactive red dye was removed more in comparison with the other dyes, while most stable dye was direct blue[23].

This arises from the rigid structure of the dye and the high stability of the chromophoric groups in this dye, all these give this dye high stability towards irradiation conditions in comparison with the other dyes under the same reaction conditions[23]. However, the reduction of concentration of these dyes was followed as we started with same initial concentration for all dyes (20 ppm). The concentration after two hours was calculated by comparing initial concentration and absorbance C_o and A_o for each dye before irradiation with that after two hours of irradiation C_t and A_t, respectively as follows:

$$\frac{A_o}{A_t} = \frac{C_o}{C_t} \qquad\qquad\qquad …(1)$$

The remaining dye concentration under irradiation with a suspension of titania after 150 min of continuous irradiation are summarized in Table 2.

Table 2: Remaining dye concentration after 150 min of irradiation with solar spectrum over suspension of TiO_2

Used dye	Reactive red	Reactive yellow	Disperse yellow	Disperse blue	Direct yellow	Direct blue
Dye concentration after 150 min of irradiation (ppm)	0.86	1.05	3.59	5.20	5.70	5.90

Change of pH of dye solution with irradiation time

The change in pH for both; direct blue and reactive yellow dyes during photocatalytic reaction was investigated during progress of irradiation time. From the results, it was found that, pH value for direct blue was reduced from basic value (8.24) to neutral values with increasing irradiation time to reach (7.10) after 150 min of irradiation. On the other hand, the pH value of reactive yellow was changed from initially acidic value (6.6) to a neutral value around (6.96). It can be concluded from these results that the pH values of the treated dyes were changed to reach a pH value of water (around pH 7). However, this is very important point as the resulted water upon dye treatment has a pH values in the range of neutral water. These results may be considered to agree with the principles of Green Chemistry as they yield products that are friendly to the environment[24,25].

Table 3: Changes in pH values of the used dyes with progression of reaction time

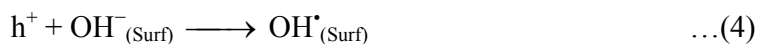| Used dye/irradiation time (min)	0	30	60	90	120	150
pH values of direct blue	8.24	7.81	7.59	7.43	7.22	7.10
pH values of reactive yellow	6.60	6.65	6.75	6.85	6.90	6.96

These results also help us to avoid adding acidic or basic materials to the produced water as in case of other treatment such as ozonation and chlorination methods, to make it neutral before afflation into the nearest ambient environment[26]. The obtained pH values for the used dyes with irradiation time is shown in Table 3.

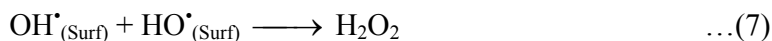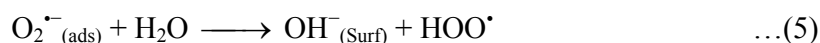**Proposed mechanism for photocatalytic degradation of dyes**

The available particles of the used photocatalyst would absorb this energy upon irradiation reaction mixture with a radiation with a proper energy; thus, producing valence band holes at the valence band and conduction band electrons at the conduction band as follows[27]:
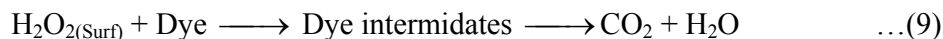
$$TiO_2 + h\nu \longrightarrow h^+ + e^- \qquad \qquad ...(2)$$

If these photogenerated species have enough time for charge transfer through the catalyst before recombination, e^- would react with preadsorbed electron acceptors such as adsorbed oxygen (O_2 ads), while positive hole h^+ would be trapped by surface hydroxyl groups:

$$e^- + O_{2(ads)} \longrightarrow O_2^{\bullet-}{}_{(ads)} \qquad \qquad ...(3)$$

$$h^+ + OH^-{}_{(Surf)} \longrightarrow OH^{\bullet}{}_{(Surf)} \qquad \qquad ...(4)$$

Hydroxyl radicals produced in this equation, can be also produced from other surface reactions such as dissociation of H_2O and H_2O_2 molecules that are adsorbed on the surface of the photocatalyst. Hydroxyl radical, and oxygen anion are very important powerful oxidation reagent, which can participate in the following surface reactions:

$$O_2^{\bullet-}{}_{(ads)} + H_2O \longrightarrow OH^-{}_{(Surf)} + HOO^{\bullet} \qquad \qquad ...(5)$$

$$O_2^{\bullet-} + H^+ \longrightarrow HOO^{\bullet} \qquad \qquad ...(6)$$

$$OH^{\bullet}{}_{(Surf)} + HO^{\bullet}{}_{(Surf)} \longrightarrow H_2O_2 \qquad \qquad ...(7)$$

Both hydroxyl and peroxide radicals play main role in photocatalytic dye fragmentation on the surface of the particles of the photocatalyst as follows:

$$OH_{\cdot(Surf)} + Dye \longrightarrow Dye\ intermidates \longrightarrow CO_2 + H_2O \qquad …(8)$$

$$H_2O_{2(Surf)} + Dye \longrightarrow Dye\ intermidates \longrightarrow CO_2 + H_2O \qquad …(9)$$

CONCLUSION

This study showed that solar radiation can be used in the photocatalytic dye removal from industrial wastewater. This can provide an alternative approach to avoid using artificial UV radiation sources as this type of radiation is harmful as well as requires high energy in operation with high cost. Reactive red dye was found to be most efficient dye in terms of removal efficiency while direct blue was the most stable dye under the same reactions conditions.

ACKNOWLEDGEMENT

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