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Photocatalytic Degradation Of Textile Dyes By Immobolized TiO_2 In Presence Of UV Irradiation

Corresponding Author

Noureddine Barka
Department of Chemistry,
Faculty of Sciences,
BP: 8106 Hay Dakhla,
Agadir, (MOROCCO)

Co-Authors

Ali Assabbane[1], Yhia Ait ichou[1], Abederrahman Nounah[2]
[1]Department of Chemistry, Faculty of Sciences. BP: 8106 Hay Dakhla, Agadir, (MOROCCO)
[2]Laboratory of Environment Sciences, EST Sale, BP.227, Sale-Medina, (MOROCCO)

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ABSTRACT

Immobilized Titanium dioxide (TiO_2) was used for the investigation of the photocatalytic degradation of Methyl Orange (MO) used as model pollutant compound, and Rhodamine B (RhB) as a potentially pollutants in aqueous solutions. The photocatalyst consist on Ahlstrom non-woven paper coated with photocatalytic titanium dioxide (Millennium PC500 anatase) and mineral specific surface extender (SiO_2 and zeolite UOP 2000). The process consists on recovering inside a batch reactor with a film of the photocatalyst and using UV lamp as irradiation source. It was found that there was a low adsorption in the dark and in the presence of the photocatalyst, also no degradation was observed for MO when the solution placed under UV irradiation without the photocatalyst, but a low degradation ratio was observed for RhB. The experimental results show that the rate of degradation follows pseudo-first kinetic order with respect to MO and RhB concentration.

KEYWORDS

Photocatalytic degradation;
Immobilized
TiO_2 Photocatalyst;
Methyl orange;
Rhodamine B;
Non-woven paper;
Batch reactor.

INTRODUCTION

Colour is the first indicator of contamination to be recognised in wastewater. Many industries, such as textile, tanning, printing, food, cosmetics, etc, use organic compounds as dyes to colour their final products. In the dyeing section of a textile industry, about 1000 L of water are used for every 1000 Kg clothes processed[1]. The presence of these species in water, ever at very low quantities, is highly visible and undesirable, their presence in aquatic systems reduce light penetration witch retard photosynthetic activity and also has a tendency to chelate metal ions producing micro-toxicity to fish and other organisms[2]. The toxicity and mass production of dyes leads to the necessity of treatment. The typical methods of treating dye wastewater include biological treatment, chemical coagulation, activated carbon adsorption, and others. The major difficulty in treating textile wastewater containing dyes is the ineffectiveness of biological processes. As for physical processes, such as coagulation and adsorption, they merely transfer the pollutants from wastewater to other media and cause secondary pollution[3].

Based on the use of solar energy, the photocatalytic treatment is a more attractive alternative for the removal of soluble organic compounds; it can give the complete mineralization of organic compounds to carbon dioxide, water and mineral acids. For the degradation process tow methods are favoured, suspended photocatalyst in aqueous media, and immobilized on support materials. In view of practical engineering, the immobilized photocatalyst should be preferred, to avoid downstream treatment (particle-fluid separation and/or photocatalyst recycling)[4]. This has led to a major attempt to immobilize the photocatalyst on support including ceramic[5], glass fiber[6], glass, quartz and stainless steel[7], activated carbon[8] and others. However, these efforts have not produced materials which meet all demands of photocatalytic activity. Importantly, the photocatalytic degradation efficiency of immobilized TiO_2 is often lower than that of the suspended particles[9].

In the present study an estimation of the performance of TiO_2 coated on Ahlstrom non-woven paper in the photocatalytic degradation of Methyl Orange and Rhodamine B in batch reactor. The decolourization efficiency was compared with the suspended TiO_2.

EXPERIMENTAL

Materials

The Methyl Orange was purchased from Merck (France), his molecular formula is $C_{14}H_{14}N_3NaO_3S$, and his structure is given in figure 1 (a), it's generally used as model compound and it is very cited in the literature. The Rhodamine B was purchased from Exciton (USA) and used as received. It consists of green crystals or reddish-violet powder, its molecular formula is $C_{24}H_{31}ClN_2O_3$ (mol wt: 479.02), it's highly soluble in water and organic solvent, and its colour is fluorescent bluish-red. The Rhodamine B has been used as a dye, especially for paper, and as biological stain. However, it has been found to be potentially toxic and carcinogenic[10]. The Rhodamine B structure is given in figure 1 (b). Solutions were prepared by dissolving requisite quantities of the dyes without further purification in distilled water. The aqueous solution concentrations of dyes were determined using a Jenway 6405 UV/Visible spectrophotometer. The wavelengths of maximum adsorption are 485 nm and 554nm respectively for Methyl Orange and Rhodamine B. The absorption measured was converted to a concentration through the standard-curve method.

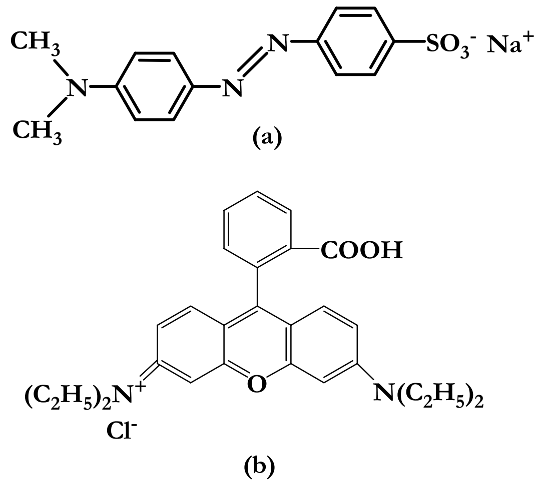

Figure 1: The molecular structure of MO (a) and Rhodamine B (b)

Photocatalytic reactor

The experiments were carried out using a cylindrical batch reactor opened at air, 8cm in diameter and 12 cm in working height (Figure 2). The water jacket has a diameter of 5cm contain the UV lamp and permit the water circulation. The photoreactor was recovered inside with the photocatalyst, witch consist on Ahlstrom non-woven paper (natural and synthetic fibres 254 µm of

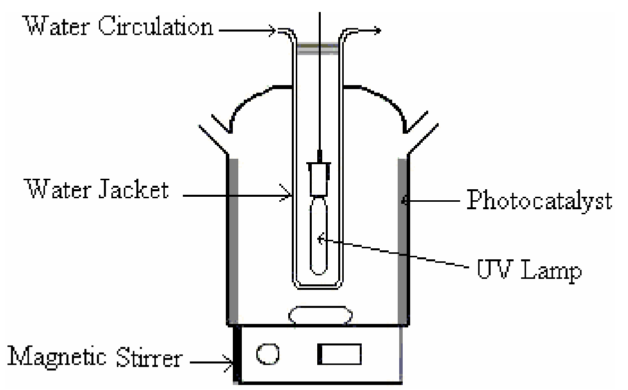

Figure 2: The schematic diagram of the photocatalytic reactor

thickness) coated with 18 g m^{-2} of Millennium PC500 titanium dioxide (anatase> 99%, surface area 350 to 400 m^2 g^{-1}, crystallites mean size = 5-10 nm) and mineral specific surface extender: SiO_2 (20 g m^{-2}) and UOP2000 zeolite (surface area 2000 m^2 g^{-1}) in order of 2 g m^{-2}. The reactor was exposed to a luminous source composed of a HPK 125w UV lamp (the wavelength maximum of the light source was 365 nm) placed in axial position inside the water jacket. The reactor was initially loaded with 500mL of aqueous solution and maintained in low continuous mixing by means of a magnetic stirrer.

RESULTS AND DISCUTION

Persistence of MO and RhB under UV irradiation

In the same operator conditions used for the photocatalytic degradation, the photolytic degradation was studied using 500 ml of MO and RhB at 12 mg L^{-1}. The solution was irradiated with a HPK 125w UV lamp without photocatalyst in the same photoreactor. Figure 3 shows the kinetic of disappearance over time. It appears that after 9 h of irradiation time, we note that, no degradation was observed for MO but a low diminution of the concentration of RhB was observed, and from this quantity we can negligee the interference of the photolytic degradation with the photocatalytic degradation.

Preliminary adsorption in the dark

The photocatalytic degradation rate depends generally on the amount of adsorbed molecules on the surface of the photocatalyst. Figure 4 shows the variation of the concentration of MO and RhB over time in the dark and in the presence of the photocatalyst with an initial concentration of 12 mg L^{-1}. the figure indicate that the adsorbed quantities those not except 5% of the initial quantity in the solution, this result can be explained by the reduction of available specific surface area resulting from the agglomeration of the photocatalyst particles during fixation. The figure indicates that the adsorption of RhB is slightly bigger than that of MO.

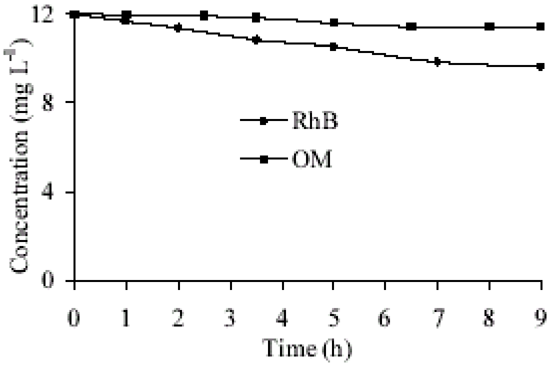

Figure 3: Photolytic degradation of MO and RhB under UV irradiation

Kinetic analysis

The decolourisation of MO and RhB solutions over time was investigated at an initial concentration of 12 mg L^{-1}, the result was shown in figure 5. The figure shows that the degradation rate of RhB was grater than that of MO in the beginning of the

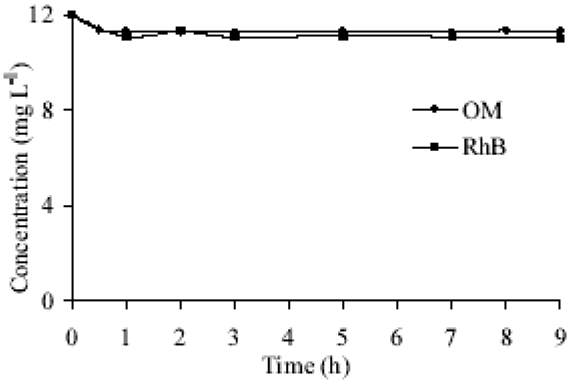

Figure 4: Preliminary adsorption in the dark of MO and RhB

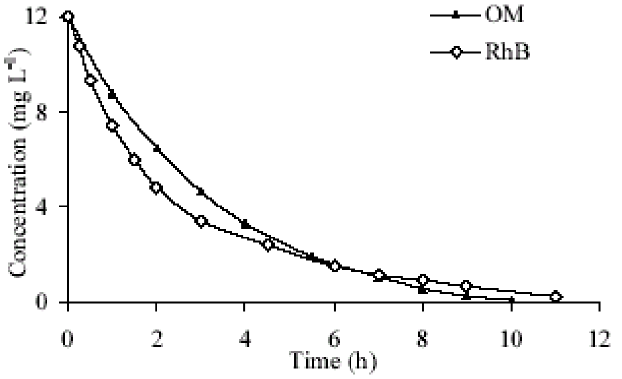

Figure 5: Variation of MO and RhB concentrations versus irradiation time

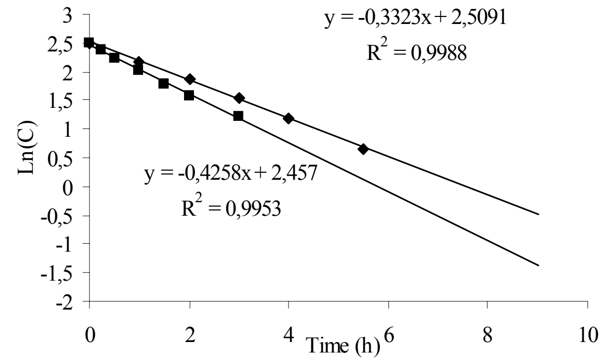

Figure 6: plot of Ln(C) versus irradiation time

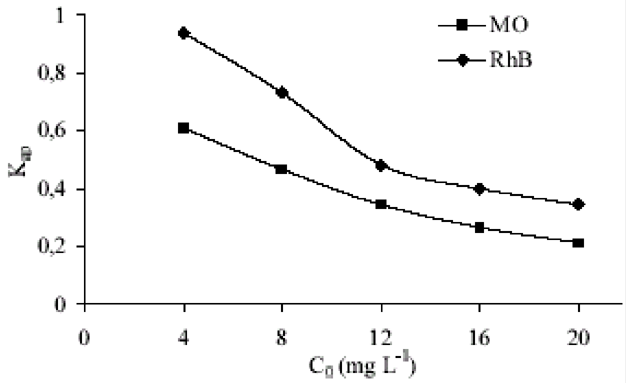

Figure 7: Variation of the apparent rate constant of degradation versus initial concentration of MO and RhB

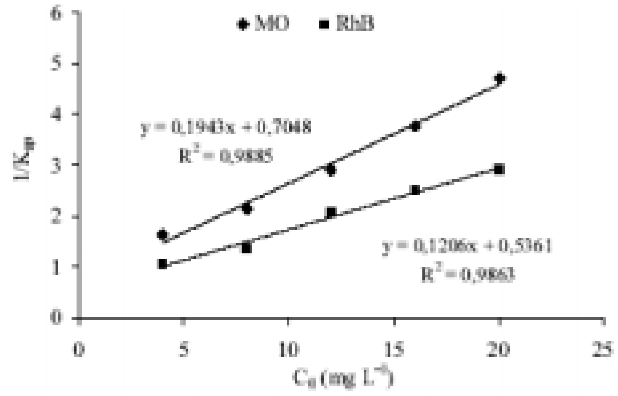

Figure 8: Plot of reciprocal of pseudo-first order rate constant against initial concentration of MO and RhB

process of the photocatalytic degradation and becomes so lower with the increase of the irradiation time. The decrease of the constant rate of decolouration of the RhB solutions can be explained by competitive adsorption/degradation of reaction intermediate with the RhB molecules witch could be grater than in the case of MO. The plot of Ln(C) versus time (h) in figure 6 gives a straight line during the first 6h of the degradation of MO and first 3h of the degradation of RhB, witch justify that the photocatalytic degradation rate R prove to be described as a pseudo-first order reaction kinetics with respect to MO and RhB concentrations according to the following equation:

$$\mathbf{R = k_{ap}\,[C]} \qquad (1)$$

Where R is the rate of the photocatalytic degradation and k_{ap} the apparent rate constant

The effect of initial concentrations on the initial rate constant k_{ap} was shown in figure 7. The figure indicates that k_{ap} decrease with increasing initial concentration of MO and RhB when others parameters are kept unchanged. The variation of reciprocal of pseudo-first order rate constant against initial concentration is shown in figure 8. The figure shows a linear relation ship between $1/k_{ap}$ and $[C]_0$ witch correspond to Langmuir -Hinshelwood model.

Langmuir-Hinshelwood model

$$k_{ap} = \frac{k_c K_{ads}}{1 + K_{ads}[C]_0} \qquad (2)$$

Where, K_{ads} is the adsorption equilibrium constant, and k_c a constant depending on the others factors influencing the process.

The linear transformation is:

$$\frac{1}{k_{ap}} = \frac{1}{k_c}[C]_0 + \frac{1}{k_c K_{ads}} \qquad (3)$$

The plot of $1/k_{ap}$ against $[C]_0$ gives the values of the slope ($1/k_c$) and the intercept ($1/k_cK_{ads}$). From there, k_c values for MO and RhB were found to be respectively 8.292 mg L^{-1} h^{-1} and 5.146 mg L^{-1} h^{-1}, and K_{ads} values were found to be 0.225 L mg^{-1} and 0.276 L mg^{-1} respectively for MO and RhB. Normally, k_c must be the same for the two dyes, since it only depends on the operative conditions, this difference can be due to the contribution of the photolytic degradation on the process.

Reproducibility of the photocatalytic activity of TiO_2 coated paper

In the goal to evaluate the reproducibility of the photocatalytic activity of the photocatalyst, tow experiments were performed in the photoreactor without changing the photocatalyst, which was just rinsed with pure water between experiments. Another experiment was later performed after changing the photocatalyst. The experiments results for MO and RhB are shown in figure 9 and figure 10, witch indicate that the reproducibility of disappearance rates varies less. This result shows that the photocatalyst can be used several times without loss of efficiency. However, it is necessary to take care in the manipulation of the paper to avoid all liberation of the powder

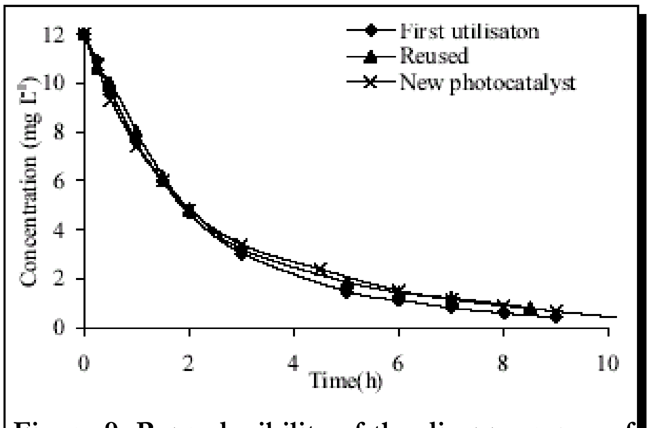

Figure 9: Reproducibility of the disappearance of RhB with the same photocatalyst reused and a new one

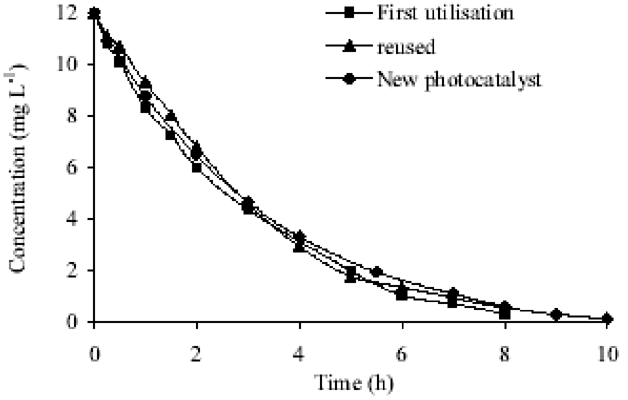

Figure 10: Reproducibility of the disappearance of MO with the same photocatalyst reused and a new one

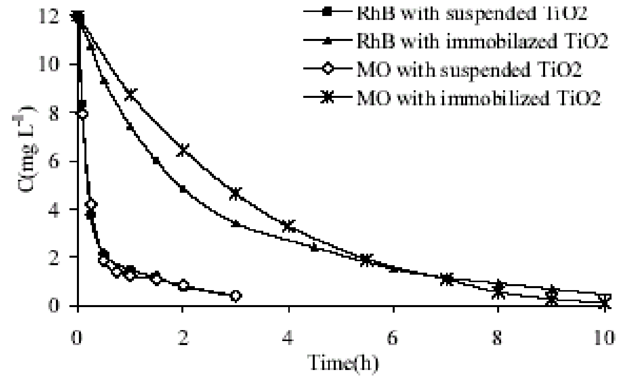

Figure 11: Comparison of the degradation efficiency of immobilized photocatalyst with suspended TiO_2

Comparison of decolorizing efficiency with suspended TiO_2

In other to compare the degradation efficiency of the immobilized photocatalyst with suspended TiO_2, the same reactor systems and UV light source were used with TiO_2 powder (Degussa-25). The experiment were carried out with 1g L^{-1} of suspended TiO_2 witch correspond to the same quantity immobilized in the working surface of paper (11 cm × 25 cm) at the ratio of 18 g L^{-1}. The result obtained is shown in figure 11. The figure indicates that about 85% of dyes disappear in the first hour of the process. However, the same percentage needs about 6h in the case of the immobilized TiO_2. Several factors were targeted as potential contributors to this lower performance of the immobilized photocatalyst:

(1) reduction of available specific surface area resulting from the binding with the supporting surface;

(2) significant radiation extinction (adsorption and scattering) by the support; or

(3) catalyst agglomeration (surface clumping) during fixation. However, this process had the advantage to avoid the finale tedious filtration and photocatalyst recycling.

CONCLUSION

The photocatalytic degradation of two model pollutants chosen has been performed with immobilized TiO_2 photocatalyst on non-woven paper. The photocatalytic degradation can be explained in terms of Langmuir-Hinshelwood kinetic model. The photocatalytic degradation is directly related to the adsorbed quantities of the pollutants. The photocatalytic efficiency of immobilized TiO_2 is often lower than that of suspended Degussa P25. however, this process could be a promising method for colour removal from textile wastewater as it can avoid the tedious final filtration of Titania in slurries and permit the photocatalyst recycling

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