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TiO_2-MoO_3 as Photocatalyst for Azo and Triphenylmethane Dyes Decolouration

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Abstract: TiO_2-MoO_3 was first used as catalyst to oxidize propylene to acetone. The by-products of this reaction were acetic acid, acetaldehyde and carbon dioxide. The decolouration performances of TiO_2 and TiO_2-MoO_3 for the oxidation of azobenzene in aqueous suspensions irradiated with UV light at 365 nm were studied at pH 3 and 10. At pH 3 complete decolouration of azobenzene dye was obtained after 30 min of irradiation in the presence of TiO_2-MoO_3 whereas in the presence of TiO_2 the time of complete decolouration was 55 min. Subsequent study using TiO_2-MoO_3 as photocatalyst was the study of the kinetic rate constants of azo and triphenylmethane dyes decolouration. The results were as followed: 0.4535, 0.6832, 0.8512 and 0.9946 m for methyl green, fast green, crystal violet, malachite green respectively at the same concentration of 0.05 mM. The kinetic rate constants for azo dyes were: azobenzene 0.2909 m (C_0 = 0.032 mM), methyl orange 0.5497 min^{-1} (C_0 = 0.04 mM) and p-methyl 0.8168 m (C_0 = 0.1 mM). These results showed that using TiO_2-MoO_3 as photocatalyst the decolouration was rapid and total after irradiation time of 30 min whatever the azo or triphenylmethane dyes.

Key words: Textile dyes, photodecolouration, wastewater treatment, photocatalysis

INTRODUCTION

Industrial wastewaters treatments are still today the main cause of organic pollutions in the natural environment followed by the agricultural pollution sector and the urban wastes. Great efforts are however made within the last few years to solve the environment pollution problem such as the development of less consumption water processes, the recycling of water within the existing processes and the modernisation of exploitation systems (Bousselmi *et al*., 2004). The textile industries' sewage is part of the most ill treated wastewaters and that sewage is characterised by strong colouration, high pH variation, high chemical oxygen demand and bio-toxicity increase with regard to bacteria (Tripathy *et al*., 1995; Fang and Chan, 1997; Arslan, 2001; Walker and Weatherley, 2001). According to the World Health Organisation (WHO), 80% of the world population diseases like gastro-enteritis, malaria and river blindness are directly caused by water (Desjardins, 1997). The health of living organisms alters slowly, their life expectancy is shortened and their lineage can be affected by malformations with increased probability of catching cancer. This does not only concern aquatic fauna, but man also unconsciously swallows these toxins through food products like the meat of those living organisms, plants, fruits and vegetables. The aniline dyes like azobenzene (C_6H_5-N = N-C_6H_5) are the most important family, both at the level of application (Danish Environmental Protection Agency (Depa, 2000; Bauer *et al*., 2001) and the multiplicity of the studied structures. More than one

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million of dyes annually produced in the world are azo dyes representing 70% by weight. Azo dyes, due to their poor exhaustion properties as much as 30% of initial dye applied remain unfixed and end up in effluents. The compounds belonging to the triphenylmethane family are known to be genotoxic for bacterial and mammalian cells. (Haveland-Smith and Combes, 1981; Rao, 1995; Cho *et al*., 2003; Culp *et al*., 2002) established that green malachite, which is commonly used in textile industries, is a highly cytotoxic substance for mammalians. It is estimated that 10-20% of these dyes are also lost into wastewater during dyeing process. In spite of the highly cytotoxicity and genotoxicity of these textile dyes for bacterial and mammalian cells the biological treatment processes of wastewater are proven that they can be used for various type of wastewater including textile wastewater (Jacob *et al*., 1998; Nigam *et al*., 1998; Conneely *et al*., 1999; Pointing and Vrijmoed, 2000; McMullan *et al*., 2001; Wesenberg *et al*., 2002; Bour *et al*., 2002; Coulibaly *et al*., 2003; Oufdou *et al*., 2004; Méndez-Paz *et al*., 2005; Wijetunga Somasiri *et al*., 2006). The biological treatment processes, physico-chemical treatment processes such as absorption and coagulation/flocculation using lime, alum and polyelectrolyte are inoperative on bio-refractory and soluble dyes or produce amount of sludge giving handling and disposal problems (Pagga and Brown, 1986). According to Wijetunga *et al*. (2006) when it is possible the biological treatment processes of wastewater are at relatively low cost compared to advanced techniques of oxidation (TOAS). The advanced techniques of oxidation (TOAS) such as UV-hydrogen Peroxide systems (Muruganandham and Swaminathan, 2004; Alshamsi *et al*., 2007), UV-ozone systems (Arslan *et al*., 2001; Li *et al*., 2003), UV-TiO_2 systems (Giusoppe *et al*., 2003; Yu *et al*., 2006; Jae-Kyu *et al*., 2006), UV-TiO_2-Mx systems (Linda Zoua *et al*., 2006). The novel oxide photocatalytic complexes (Jingfei Luan *et al*., 2006) and the solar photo catalysis (Bauer *et al*., 2001; Bousselmi *et al*., 2003; Abramovi *et al*., 2003) greatly showed their efficiency in the oxidation of organic compounds including bio-refractory organic pollutants. Moreover, the oxidation through ozone and hypochlorite are efficient decolouration methods, but they are not desirable due to a generation of secondary pollution from chlorine residue. Either the biological or the advanced techniques of oxidation (TOAS), the proper treatment technology (Addou *et al*., 2004) should be used before discharging the industrial wastewater mainly the coloured textile wastewater into natural biotic environment. The present study concerns the performance study of TiO_2-MoO_3 as photocatalyst to the degradation or decolouration of textile wastewater containing azo and triphenylmethane dyes known to be cancer producing compounds and constitute about 65% of industrial dyes market.

MATERIALS AND METHODS

Materials

The following dyes of high purity were used as received: methyl red, crystal violet, methyl green, fast green (Acros), methyl orange (Merck), azobenzene, malachite green (Aldrich). Analytical reagent grade nitric acid, ammoniac solution, ammonium molybdate and acetonitrile of chromatographic grade were purchased from sigma France. Doubly distilled water was used through out. TiO_2 catalyst was nanometer titanium dioxide (Degussa P25) mainly anatase (80%) with a surface area of 44 $m^2 g^{-1}$ and TiO_2-MoO_3 catalyst was prepared using TiO_2, concentrated nitric acid (HNO_3), 0.5N NH_4OH and ammonium molybdate $(NH_4)_6Mo_7O_{24}$. $4H_2O$. The UV/VIS spectra measurements were recorded with Spectrophotometer Spectronic GENESYS 2PC UNI/NRE/GPA/106 (USA).

Photochemical Reactor

The experimental device is presented in Fig. 1. It is an open parallelepiped reactor having four cells of (4×4×3 cm) made of PVC. The depth of the dye solutions in each cell was 1 cm. The UV lamp (Bioblock) 230 V, 50 Hz with emitting radiation of 365 nm and average intensity of 8 mwcm was located 3 cm above the dye solutions as presented in Fig. 1.

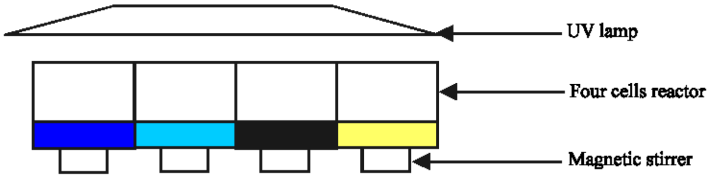

Fig. 1: Schematic diagram of photocatalytic reactor

Table 1: Rate constants of photocatalytic decolouration of azo and triphenylmethane dyes using TiO_2-MoO_3 photo catalyst (0.8 g L^{-1})

Dyes	Kobs (mm^{-1})	R^2	10-4 (mol L^{-1})
Malachite green	0.9946	0.9686	0.5
Crystal violet	0.8512	0.9971	0.5
Fast green	0.6832	0.9908	0.5
Methyl green	0.4535	0.9707	0.5
P-methyl red	0.8178	0.9368	1.0
Methyl orange	0.5497	0.9267	0.4
Azobenzene	0.2909	0.9522	0.32

Catalyst's Preparation

Present study is carried out with two catalysts TiO_2 and TiO_2-MoO_3 whose preparations can be made according to the supercritical fluid dry method (SCFD) (Zhang *et al*., 2005), the ultrasonic nebulization and flame hydrolysis of a mixed ethanol solution of molybdenyl acetylacetonate and dipropoxy-titanium-bis(acetylacetonate) (Lee *et al*., 1993) or the simplified following impregnation method described by (Davidov, and Sheppar, 2003). For the TiO_2-MoO_3 catalyst, dissolve 25 g of TiO_2 into 100 mL of concentrated nitric acid (solution 1) then, add a solution of 0.5N NH_4OH to obtain a pH 1. Dissolve 2 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ into 500 mL of distilled water at 70°C (solution 2). Mixed the two solutions and maintain the mixture at a temperature of 50°C during 5 h. To keep the mixture's PH constant, periodically add the 0.5N NH_4OH. After 5 h, evaporate the mixture at 100-110°C. The residue obtained should be dried at 130-140°C during 10 h and then, burnt for 3 h at a temperature of 250-300°C. After cooling, grind the obtained powder and again burnt it at 550°C (in the air) for 10 h. After cooling, the sample should be compressed and made into pastilles. Before the study of the catalyst's activity, the pastilles should be broken into pieces of 2.5 mm.

For the TiO_2 catalyst the preparation principle is the same as that of the TiO_2-MoO_3 catalyst except that here, solution 2 is not added.

Procedure

Solutions containing the following initial concentrations of azo dyes, methyl orange (0.04 mM), p-methyl red (0.1 mM), azobenzene (0.032 mM) and triphenylmethane dyes, malachite green (0.05 mM), crystal violet (0.05 mM), methyl green (0.05 mM) and fast green (0.05 mM) were examined (Table 1). The reacting mixture was prepared by suspending the required amounts of catalyst in distilled water and by adding a desired amount of dye. The initial pH value was adjusted by using H_2SO_4 or NaOH solution. The resulting aqueous suspension containing the dye, the catalyst powder was stirred in an open reactor with UV lamp switched off. After 30 min an aliquot was taken and the UV lamp switch on. The aliquot was then filtered through 0.45 µm fisher brand filter to separate the catalyst. The spectrum of the non-irradiated dye was recorded between 300 to 700 nm. The concentration C_0 of the non irradiated solution of the dye and the concentration Ci of the unreacted dye after a period of irradiation were determined by comparing the absorbance A_0 (at the wavelength of the maximum absorbance (310 nm with TiO_2 and 370 nm with TiO_2-MoO_3) of the non irradiated solution to the absorbance A_i of an irradiated solution after a fixed intervals of time. The quantity of catalyst was 0.5 g L^{-1} TiO_2 or TiO_2-MoO_3.

RESULTS AND DISCUSSION

Effect of the Nature of Catalyst and the pH on Azobenzene Dye Decolouration

From observation of Fig. 2a and b, it can be noticed that the peak of absorption of non-irradiated dye in the presence of TiO_2 is different of the peak of non-irradiated dye in the presence of TiO_2-MoO_3 (307 and 370 nm, respectively). These two parent peaks were used to evaluate the dye decolouration. It can be seen in Fig. 2c and d that at pH 3 in the presence of TiO_2 incomplete decolouration or degradation was obtained and a new peak at 325 nm appears indicating an intermediate decolouration or degradation product whereas complete decolouration or degradation of azobenzene was achieved by using TiO_2-MoO_3 photo catalysts. At pH 10 (Fig. 2e, f) both the two photo-catalysts undergo intermediate decolouration or degradation products. These preliminary results allow us to choose pH 3 and TiO_2-MoO_3 for azo and triphenylmethane dyes decolouration.

Kinetic Studies of Azo Dye Decolouration Using TiO_2 and TiO_2-MoO_3

In the studies above, pH 3 was chosen according to complete decolouration of azo dye at this pH. The experiments were done at a fixed time of 30 min. To confirm the selection of the efficient photo

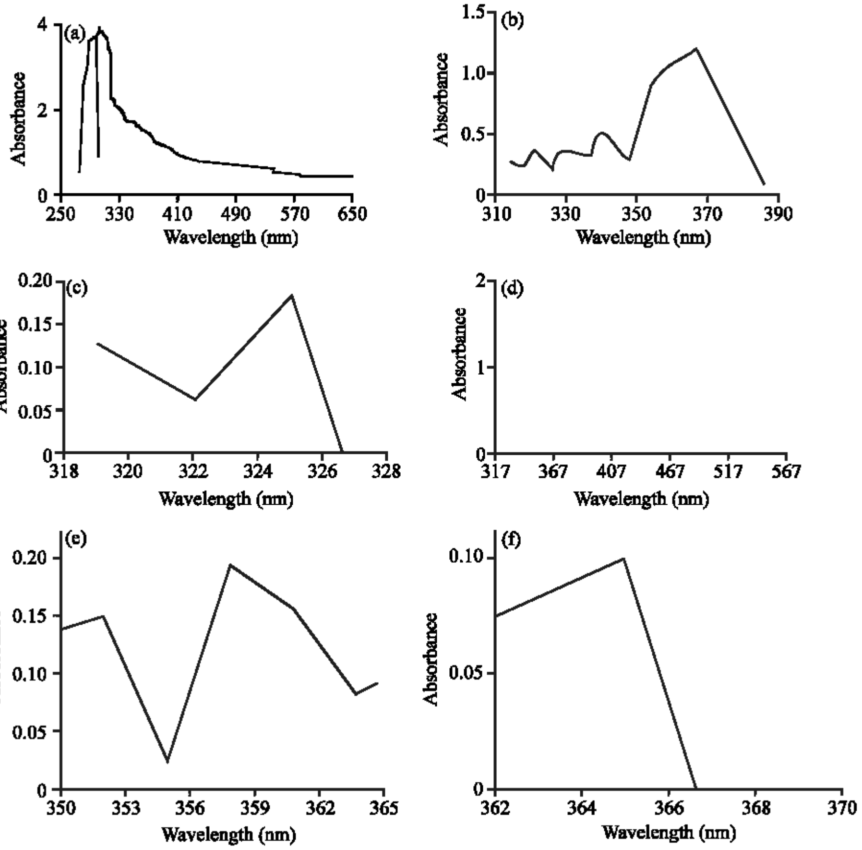

Fig. 2: Spectrograms of irradiated and non-irradiated azobenzene dye solution at pH 3 and pH 10 in the presence of TiO_2 and TiO_2-MoO_3, (a) 30 min non irradiation TiO_2, (b) 30 min of irradiation TiO_2-MoO_3 (c) 30 min of irradiation pH 3, 365 nm TiO_2, (d) 30 min non irradiation pH 3, 365 nm TiO_2-MoO_3, (e) 30 min of irradiation pH 10, 365 nm, TiO_2 and (f) 30 min of irradiation pH 10, 365 nm, TiO_2-MoO_3

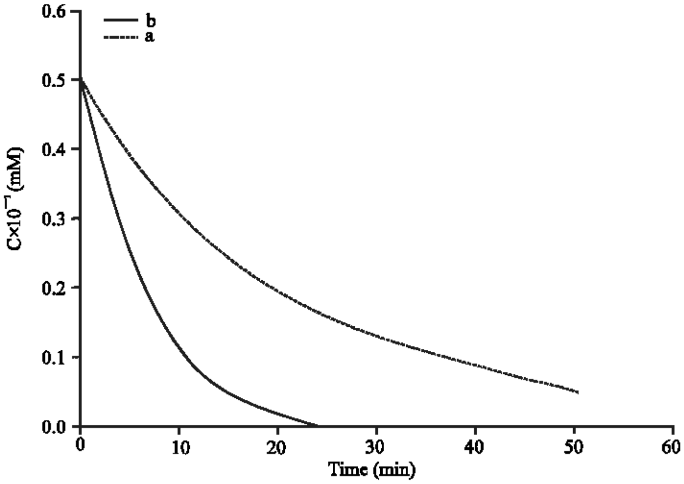

Fig. 3: Effect of (a) TiO_2 and (b) TiO_2-MoO_3 catalysts at pH 3 on azobenzene dye photo-decolouration kinetic

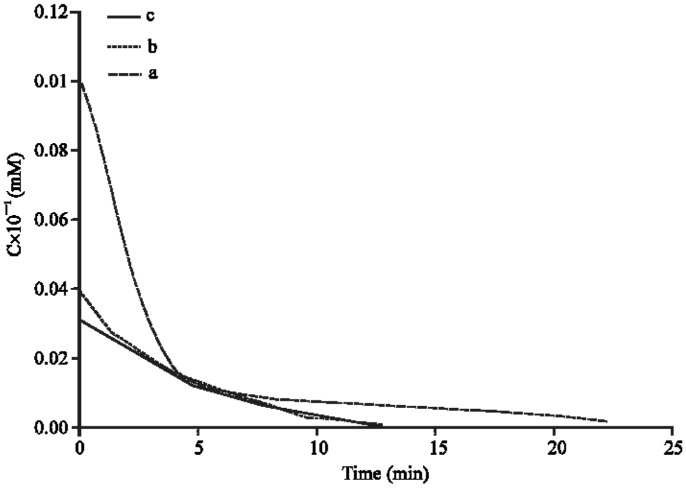

Fig. 4: Photocatalytic decolouration of azo dyes at pH = 3 azobenzene (C_0 = 0.032 mM) (a), p-methyl red (C_0 = 0.1 mM) methyl orange (C_0 = 0.04 mM)

catalyst, the kinetic studies of azo dye at pH 3 in the presence of TiO_2 and TiO_2-MoO_3 was performed. Figure 3 presents the decolouration of azo dye at pH 3 in the presence of both photo-catalysts. After 30 min of irradiation, azo dye in the presence of the TiO_2-MoO_3 catalyst is completely decolorized whereas in the presence of TiO_2 complete decolouration is obtained after 55 min. In addition to this, it can be noticed in accordance to Fig. 3 that the decolouration rate of dye is higher in the presence of TiO_2-MoO_3 than in the presence of TiO_2. TiO_2-MoO_3 catalyst as compared to TiO_2 has a better photocatalytic activity for the pollutants decolouration at pH 3.

Kinetic Studies of Azo and Triphenylmethane Dyes Decolouration Using TiO_2-MoO_3

Figure 4 shows that the p-methyl red and methyl orange decolouration are completely achieved after 17 min whereas azobenzene decolouration requires 25 min when initial concentrations

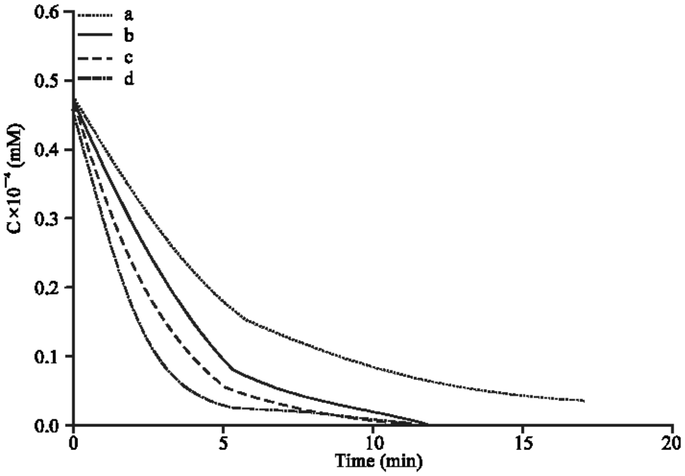

Fig. 5: Photocatalytic decolouration of triphenylmethane dye solutions $C_0 = 0.5\times10^{-4}$ M, pH= 3 malachite green (d) crystal violet (c), methyl green (a), fast green (b)

ranged between 0.03 to 0.1 mM. After 25 min of irradiation, the solution of the azobenzene dye, which is initially yellow-orange, becomes colourless. Azo dyes are characterized by nitrogen-nitrogen double bonds (-N = N-) that determine the colour of the dye and their associated chromophores and auxochromes. The cleavage of azo bonds certainly leads to decolouration of the dye. This result is similar to that which is obtained through solar photocatalytic degradation of the same dye (Mansouri *et al*., 2007).

The four triphenylmethane dyes show similar kinetic behaviour (Fig. 5). The methyl green is less reactive than the other dyes. Green malachite and crystal violet decolouration is achieved after 15 min whereas fast green and methyl green decolouration is achieved after 25 and 30 min, respectively for the studied concentrations.

In order to compare the course of photo decolouration of azo and triphenylmethane dyes at ambient temperature, the apparent rate constants were calculated. It is known from the literature (Silwia Moza *et al*., 2005; Giuseppe *et al*., 2003) that photo catalytic oxidation of organic pollutants follows Langmuir-Hinshelwood kinetics. This kind of reaction usually is represented by Eq. 1.

$$-dC/dt = kc \qquad (1)$$

After integration is obtained:

$$C = C_0 \exp(-kt) \qquad (2)$$

where, C_0 is the initial concentration of dye, C is the concentration of dye after t min of irradiation and k is the rate constant depending on the reaction conditions. k values were obtained from Eq. 3 witch is the linear transforms of Eq. 2

$$\mathrm{Ln}\,(C_0/C) = f(t) \qquad (3)$$

CONCLUSION

The photocatalytic of azo and triphenylmethane dye decolouration using TiO_2-MoO_3 exhibited the typical kinetic behaviour previously reported for most organic compounds (Jingfei *et al*., 2006; Taicheng *et al*., 2001). The pH plays an important function on the kinetic of the photo catalytic decolouration of azo and triphenylmethane dyes in presence of TiO_2 or TiO_2-MoO_3. A comparison between the TiO_2 and TiO_2-MoO_3 photo catalyst performances suggested that TiO_2-MoO_3 used as a catalyst for the degradation of 1,4-dichlorobenzene (Lee *et al*., 1993) was the best photocatalyst than the TiO_2 and can constituted an excellent alternative for the decontamination of wastewater by organics dyes in open photo reactor at ambient temperature. The photochemical catalysis in ecological and economical point of view has a significant advantage compared to classic processes of water treatment.

The study presented herein clearly demonstrates that TiO_2-MoO_3 photocatalytic methods are promising for aromatic decolouration or degradation of effluents however further studies in optimization of photodegradation will be needed to conclude the best irradiation conditions such as initial concentration of dye, concentration of photocatalyst, reaction temperature, optimal time of photodegradation. The experimental results of photocatalytic decolouration of azo and triphenylmethane dyes show that photodecolouration or photodegradation technology of wastewaters is more effective process than coagulation/flocculation technology.

As perspectives, identification of intermediates in photocatalytic degradation process, the study of the photocatalytic regeneration and possibility of continuous treatment operation for long period of time and the construction of a prototype reactor will be conducted in the future because the main objective of the applied science findings is reached when transferring the result into industrial application.

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