

Sol-gel synthesis of nanocrystalline TiO_2 and the investigation of its photocatalytic activity for degradation of methyl orange

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Abstract

This work presents the successful preparation of titanium dioxide (TiO_2) by the sol-gel process in the presence of polyethylene glycol with a molecular weight of 200 g/mol (PEG200) and crystallized after treatment with hot water at 90°C. The photocatalytic decolorization of an azo dye model, methyl orange (MO) in aqueous medium was carried out in a reactor with two UV lamps, using titanium dioxide containing PEG200 as catalyst. We investigated the effect of operating conditions such as initial concentration of MO, the initial concentration of TiO_2 , the pH of the solution and the addition of NaCl on the degradation of the dye. It was found that the kinetic of degradation of MO depends on the initial dye concentration and initial concentration of TiO_2 . Moreover, the addition of NaCl did not favor the photodegradation of the dye.

Keywords: Nanocrystalline TiO_2 ; sol-gel; photocatalysis; decolorization; dye.

1. Introduction

Textile dyes as well as other industrial dyes are considered among the largest groups of organic compounds that cause different environmental problems. In fact, wastewater generated by the textile industry contains considerable amounts of loose dyes, including azo dyes and huge amounts of inorganic salts [1-3]. Azo dyes, characterized by nitrogen-to-nitrogen double bonds (N=N), constitute over 50% of all textile dyes and have been widely used in many industries: production of textiles, paints, cosmetics, pharmaceutical and ink, etc. [4-6]. Such colored dye wastes constitute a major threat to the surrounding ecosystems such as environmental pollution and health hazards. The toxicity and potentially carcinogenic nature of these substances and their manufacturing precursors represent an increasing danger in aquatic life [7, 8]. The increased and the stringent international environmental standards (ISO 14001, October 1996) have encouraged the need to develop novel treatment methods for converting organic contaminants, such as dye-containing effluents, to harmless compounds [9].

Several studies have been carried out on the issues of biological, physical and chemical treatment of dye-containing effluents. Bio-treatment of azo dyes is, in general, ineffective, due to their resistance to aerobic degradation. Furthermore, the azo dyes that undergo reductive cleavage through anaerobic biological treatments

potentially generate carcinogenic aromatic amines in the process [10, 11]. Physical methods such as flocculation, reverse osmosis, and absorption on activated charcoal are non-destructive and merely transfer the pollutants to other media, thus causing secondary pollution [12, 13]. Chemical destruction of dyes may be accomplished by using chlorine or ozone. These chemical treatments have yielded encouraging results of color and organics removal, but the required dosages are often too high to be economically feasible [6].

Recently, photocatalytic processes have received a great deal of attention, particularly for the complete destruction or mineralization of the toxic and non-biodegradable compounds to carbon dioxide and inorganic constituents in both water and gas phases [14]. Among the photocatalysts applied, titanium dioxide is the most popular one due to the peculiarities of its chemical inertness, its suitable band gap energy, its non-photocorrosion and non-toxic influence on the microorganisms [15]. Owing to the policies of efficient utilization of solar energy, high quantum efficiency and operation suitability, the current research works on the photocatalytic processes have focused on the designs and constructions of new light energy sources, photochemical reactors, preparations of novel photocatalysts and their supports [16]. Irradiation of TiO_2 semiconductor by light with energy equal to or greater than its band gap energy leads to excitation of an electron from the valence band to the conduction band. Charge separation is then formed. The electrons in the conduction band behave as a cathode

and promote the reduction reactions of oxidized compounds with potentials positive to that of the lowest conduction band level. On the other hand, positive holes (h⁺) are generated in the valence band. The holes show high affinities for electrons and behave as an anode to oxidize the reduced compounds with potentials negative to that of the highest valence band level or to oxidize the adsorbed H₂O or OH⁻ to hydroxyl radical (HO[•]). Hydroxyl radicals are very reactive neutral species, which react rapidly and non-selectively with the contaminants preadsorbed on titanium dioxide surface. Accordingly, HO[•] is the chief oxidant for photocatalytic degradation in wastewater treatment [17].

The catalyst used in our work is the same catalyst used previously [18] in the form of thin films of TiO₂ produced by a method of coating by sol-gel immersion in the presence of polyethylene glycol PEG200 to degrade the domoic acid. However, in this investigation, we use this catalyst in the powder form to degrade another pollutant which is methyl orange. The aim of this study is to show the importance of heterogeneous photocatalysis for the degradation of industrial dyes. In this context, the present investigation focuses on the photocatalytic efficiency effects of titanium dioxide, prepared by the sol-gel method in the presence of polyethylene glycol (PEG200) and crystallized at a temperature of 90°C, on the degradation of an azo dye methyl orange in synthetic solution in order to be applied in the depollution of a real effluent from the textile industry..

2. Experimental details

The investigated Using titanium tetra-n-butoxide (TTB), as the starting material, colloidal TiO₂ nanoparticles were prepared by a sol-gel method. In a typical preparation procedure, TTB was dissolved in a small amount of ethanol and stirred for 30 min. Then, a mixture of water containing HCl and ethanol was poured and stirred into the transparent solution to promote hydrolysis. Finally, an organic polymer (PEG) was slowly added to this solution and stirred for one hour. The sol-gel solution was prepared in the presence of PEG of molecular weight 200.

The photocatalytic oxidation of methyl orange in TiO₂ suspension under UV illumination from 60 watt UV lamps was investigated in order to evaluate the photocatalytic activity of the prepared TiO₂ nanoparticles. MO, a well-known acid-base indicator, was chosen as a simple model of a series of common azo dyes, largely used in the industry. For each measurement, 1.5 g/L of photocatalyst was added into a 100 mL photochemical reactor containing 70 mL of 15 mg/L MO. Before photoreaction, the suspension was stirred in the dark for 60 min to attain the adsorption-desorption equilibrium for MO and dissolved oxygen on the surface of TiO₂, and then exposed to the UV light. After a defined irradiation time, a small quantity of solution was filtered through 0.45 nm filters to

remove the catalyst before analysis. The absorbance of the residual MO in the solution was measured with a UV-visible spectrophotometer (JENWAY 6405) at 475 nm, which is the maximum absorption of MO.

3. Results and discussion

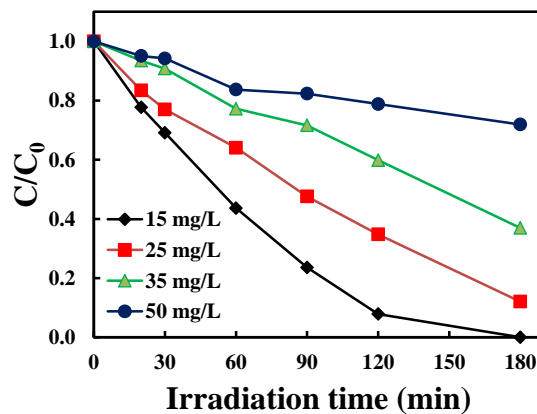
3.1. Photocatalytic degradation and dark adsorption

The reaction bowl was exposed to UV light irradiation for 12 h in the absence of TiO₂. We noticed that photodegradation of MO is very negligible (only 16%), indicating that MO has a good photostability under the UV light irradiation. Under the experimental conditions and in the presence of 1.5 g/L TiO₂, approximately 84% of the initial concentration of the dye was removed after 120 min.

3.2. Effect of initial dye concentration

The effect of initial MO concentration in water on the photocatalytic effectiveness of the process was examined. Since the characteristic dyes concentrations in wastewater from textile industry lies in the range 0.01–0.05 g/dm³ [19], the photocatalytic oxidation of methyl orange were conducted for solutions with various methyl orange concentrations from 15 to 50 mg/l at its natural pH with the constant catalyst loading 1.5 g/L. Figure 1 shows the obtained results.

Figure 1. Effect of initial concentration on the photo-



decolourisation of MO: catalyst dose = 1.5 g/L; time = 180 min and pH = pH natural.

It is observed that with the increasing the initial dye concentration, the decolorization efficiency of methyl orange decreases. This behavior is different from that obtained for the degradation of CCl₄ for which the degradation increases with increasing the initial concentration [20]. The degradation rate is directly proportional to the probability of formation of hydroxyl radicals (OH[•]) on the catalyst surface and the probability of hydroxyl radicals reacting with the dye molecules [21, 22]. As the initial dye concentration increases, more and more dye molecules are adsorbed onto the TiO₂ surface.

It is believed that the large amount of adsorbed dye has an inhibitory effect on the reaction of the dye molecules with photogenerated holes or hydroxyl radicals due to the absence of any direct contact between them [23]. As the dye concentration is increased, the dye molecules also absorb light and the photons never reach the surface of the photocatalyst, which decreases the efficiency of photodegradation.

Several experimental results [24] indicate that heterogeneous photocatalytic oxidation of various dyes are well described by a pseudo-first-order kinetic for diluted solutions. The photocatalytic decolorization of methyl orange follows pseudo-first-order kinetics. Figure 2 illustrates a good linearity between $\ln(C_0/C)$ versus t plot for each MO concentration values studied. C_0 is the initial concentration of MO and C is the concentration of MO (mg/L) at time t . The first order rate constants were found to be 9.977×10^{-3} , 6.607×10^{-3} , 1.926×10^{-3} and 0.885×10^{-3} for dye concentrations 15, 25, 35 and 50 mg/L, respectively. The rate constant values were found to decrease with increased MO concentration

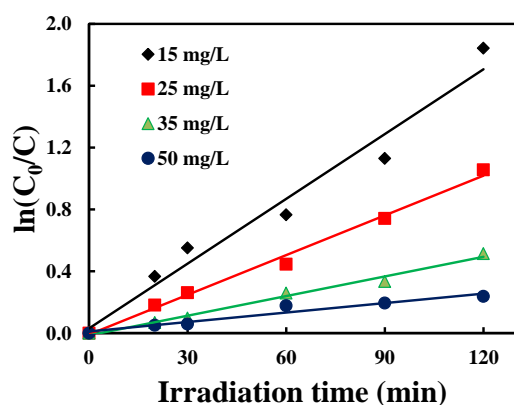


Figure 2. Kinetics of photocatalytic MO photo-decolourisation: catalyst dose = 1.5 g/L; [MO] = 15, 25, 35 and 50 mg/L.

3.3. Effect of pH

It is reported that the pH of a solution is an important parameter in the photocatalytic degradation of organic compounds due to the fact that pH influences the surface charge of the semiconductor, thereby affecting interfacial electron transfer and, therefore, the photoredox process [25]. Figure 3 illustrates the photo-decolourisation of MO at different pH (3, 7, 9), which clearly shows that the best results were obtained in acidic solution, 98.58% (pH = 3), 91.85% (pH = 9) and 56.42% (pH = 7) after 120 min of irradiation.

The possible explanation of these results is the amphoteric behaviour of semiconducting titanium dioxide and the change of its surface charge properties with the changes of pH values [19] near its point of zero charge (pH_{pzc}), according to the following reactions:

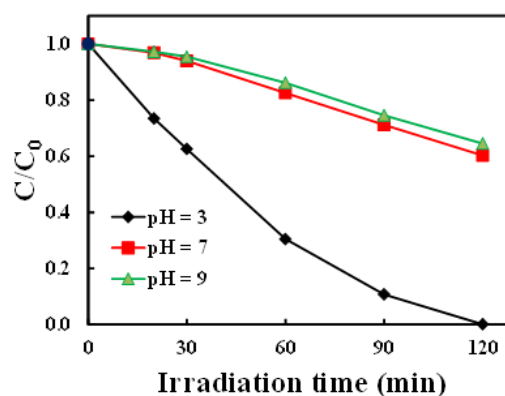


Figure 3. Effect of pH on MO photo-decolourisation: catalyst dose = 1.5 g/L; [MO] = 15 mg/L, irradiation time = 120 min.

Hence, pH changes can influence the adsorption of dye molecules at TiO₂ surfaces, an important step for the photo-oxidation to take place. For nanocrystalline titania, the pH_{pzc} is around 5.8–6.8 [19]. Thus, when $pH < 6$, a strong MO adsorption is observed on TiO₂ particles resulting from the electrostatic attraction of positively charged TiO₂ with the dye. In the present case the highest degradation rate was achieved at pH = 3. In alkaline solution, the MO molecules are negatively charged and their adsorption is also expected to be affected by an increase in the density of TiO groups on the semiconductor surface. Thus, due to Coulombic repulsion, substrate is scarcely adsorbed [26, 27]. At high pH, hydroxyl radicals are so rapidly removed that they do not have the ability to react with dyes [26]



3.4. Effect of catalyst dosage

The effect of different dosages of TiO₂ on the photocatalytic degradation of MO was investigated for different concentrations varying from 0.5 to 2 g/L. Figure 4 shows the obtained results.

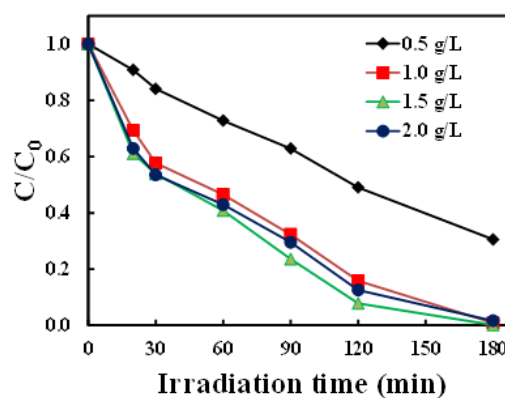


Figure 4. Effect of catalyst amount on the photo-decolourisation of MO, [MO] = 15 mg/L and pH = 3.

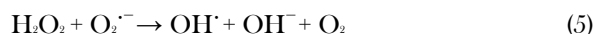
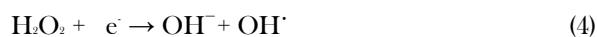
It can be observed from Figure 4 that the photocatalytic degradation increases with increasing the amount of catalyst, the reaction was retarded at high TiO₂ dosages. In fact, as the concentration of the catalyst is increased the number of photons absorbed and the number of dye molecules adsorbed are increased with respect to an increase in the number of photocatalyst. However, it is well known that for high concentration of TiO₂ particles, the scattering light has a practical limit above which the degradation rate will decrease due to the reduction of the photonic flux within the irradiated solution [28]

3.5. Effect of H₂O₂

The addition of hydrogen peroxide to the photooxidation process increases the concentration of OH[•], since it inhibits the electron-hole recombination, according to the following equation:



In the photocatalytic degradation process, the role of H₂O₂ is twofold. It accepts a photogenerated electron from the conduction band and thus promotes the separation of charges (equation (4)). It also forms OH[•] radicals via superoxydes according to the following equations :



The addition of H₂O₂ is known to increase the rate of photocatalytic degradation with higher quantum yield of formation of OH[•] [29]. Therefore, the rate of degradation should be improved. However, for high doses, H₂O₂ is a powerful OH[•] trapper [30] as described by the following equations:



The obtained results are shown in Figure 5.

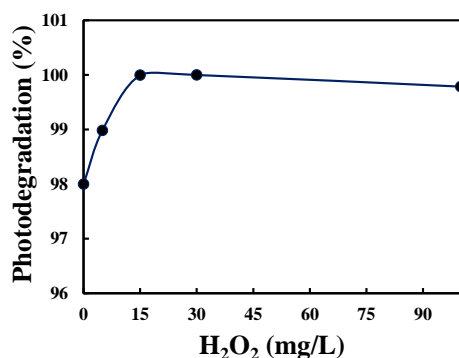


Figure 5. Effect of H₂O₂ concentration on the photodecolourisation of MO.

It can be seen that the photocatalytic degradation of MO initially increases with increasing H₂O₂ concentration up to 100 mg/L, and then finally decreases. This negative effect of high concentration of H₂O₂ may be due to the formation of OH₂[•]; when the H₂O₂ concentration is higher, the formed OH₂[•] is significantly less reactive than OH[•] [31].

3.6. Effect of NaCl

In typical textile effluents, about 70–120 g/L of NaCl is present. The role of NaCl on the degradation rate is studied at a pH of 3, a dye concentration of 15 mg/L, a TiO₂ catalyst loading of 1.5 g/L and an irradiation time of 180 min. The obtained results depicted in Figure 6 show that the rate of degradation slightly decreases with increasing NaCl concentration. Inhibition effects of anions could be due to the reaction of positive holes and hydroxyl radical with anions that behaved as h_{vb}⁺ and OH[•] radical centers (Eqs. (8) and (9)) resulting in prolonged color removal. The adsorbed anions might compete with MO dye for the photo-oxidizing species on the surface and prevent the photocatalytic degradation of the dyes. Formation of inorganic radical anions (Cl[•], ClOH^{•-}) under these circumstances is possible:

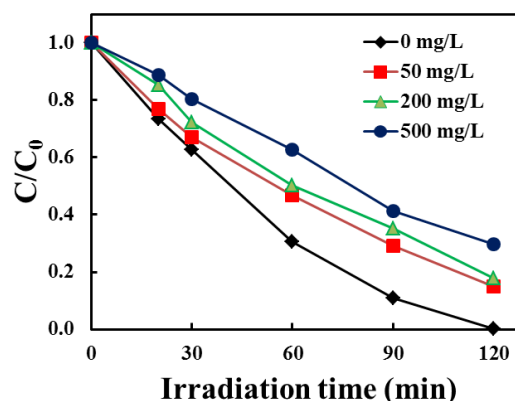


Figure 6. Effect of NaCl concentration on the photodecolourisation of MO.

4. Conclusion

The most important conclusions can be summarized in the following.

- Nanocrystalline anatase TiO₂ has been successfully prepared by the sol-gel method, using PEG as a structure-directing agent and a hot water treatment of 90°C;
- Dye absorption is a primary necessity to degradation.

- Nanocrystalline TiO₂ is efficient for the degradation of MO from aqueous solution.

-The addition of hydrogen peroxide improves the photodegradation rate. However, at higher concentration the H₂O₂ would quench the OH[•] and decrease the rate of the reaction.

- The photocatalytic decolorization of MO can be explained in terms of Langmuir-Hinshelwood kinetic model.

- Degradation of MO is favored under acidic conditions.

- The presence of Cl⁻ anion leads to an increase of the effectiveness of the photocatalytic degradation

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