



CHAPTER I INTRODUCTION

Methyl orange (MO) or acid orange 52 (AO 52) is one of azo compounds. Azo compounds are an important class of synthetic dyes, and they are characterized by the presence of one or more azo group ($-N=N-$) bound to aromatic rings (Liu *et al.*, 2005). MO is commonly used as coloring agent in many applications, such as textile, paint, ink, plastic, and cosmetic industries. The release of this coloring agent definitely causes the environmental problem. One of the most commonly found problems is wastewater problem. The wastewaters in the environment are a considerable source of non-aesthetic pollution, and dangerous by-products can originate through oxidation, hydrolysis, or other chemical reactions taking place in the wastewaters (Konstantinou *et al.*, 2004).

Several techniques have been developed to remove dye pollutants. Physical methods (such as adsorption), biological methods (such as biodegradation), and chemical methods (such as chlorination and ozonation) are the most frequently used methods for treatment of dye-containing wastewaters. The conventional processes for treatment of these effluents are insufficient to purify the significant quantity of wastewaters generated from the different operations of textile dyeing and washing. Some methods, such as combined coagulation, electrochemical oxidation, and active sludge, have recently been examined and proved to be effective. Other methods, such as flocculation, reverse osmosis, and adsorption on activated carbon, have also been investigated. The disadvantage of these methods is incomplete destruction of the pollutant compounds, since they just transfer the compounds present from aqueous to another phase, thus causing secondary pollution problem. Consequently, regeneration of adsorbent materials and post-treatment of solid-wastes, which are expensive operations, are required (Lachheb *et al.*, 2002 and Konstantinou *et al.*, 2004).

Photocatalysis, one of advanced oxidation processes (AOPs), is an efficient technique for water and air purification due to its several advantages. Firstly, it destroys the pollutants by decomposing or transforming into less harmful substances in the

presence of UV and near-UV illumination. Secondly, non-toxic material can be used as semiconductor photocatalyst, such as titanium dioxide (TiO_2). Thirdly, this process can be operated at room temperature and atmospheric pressure. Finally, the photocatalytic process is receiving increasing attention because of its low cost due to the use of sunlight as the source of irradiation, also implying environmental cleaning process. The TiO_2 -composed photocatalytic system appears as the most emerging technology for destroying dye pollutants because TiO_2 photocatalyst is largely available, inexpensive, and non-toxic, and shows relatively high chemical stability. So far, attempts to significantly enhance the photocatalytic efficiency of TiO_2 have been made either by coating and doping with transition and noble metals, such as copper (Rao *et al.*, 2003), gold (Arabatzis *et al.*, 2003), iron (Carneiro *et al.*, 2005), and silver (Sokmen *et al.*, 2001, Vamathevan *et al.*, 2001, and Rupa *et al.*, 2007), or by chemically modifying with carbon (C) or nitrogen (N), such as $n\text{-TiO}_{2-x}\text{C}_x$ or $n\text{-TiO}_{2-x}\text{N}_x$. Therefore, the charge separation in the photocarrier generation can be enhanced, and the energy needed for photoexcitation is reduced, both of which allow modified titanium dioxide to absorb light efficiently and to initiate the reaction rapidly. The primary photocatalytic processes occur upon irradiation of light with energy greater than or equal to the band gap of photocatalyst, and the electrons and holes are then generated and trapped on the photocatalyst surface, subsequently producing reactive oxygen species, such as OH^\bullet and $\text{O}_2^{\bullet-}$ radicals, to decompose organic dye pollutants (Ioannis *et al.*, 2003, and Yang *et al.*, 2004).

Because the photocatalytic decomposition of azo dye by using nanocrystalline mesoporous-assembled TiO_2 has not been extensively investigated, this research was focused on this kind of photocatalyst. The mesoporous-assembled TiO_2 nanocrystal is very interesting to be used for the photocatalytic decomposition of azo dye because it possesses very small physical dimensions, large surface area and pore volume for reactant accessibility, uniform pore size distribution, and high volume fraction of atom located at the surface, which are very helpful for this application. The experimental investigation was performed on the photocatalytic decomposition of MO, a model azo dye, using mesoporous-assembled TiO_2 nanocrystal synthesized by a sol-gel process with

the aid of structure-directing surfactant, without and with impregnated Pt nanoparticles, as compared with commercially available non-mesoporous-assembled TiO₂ powders. Various synthetic and reaction parameters, such as calcination condition for photocatalyst preparation, initial dye concentration, hydrogen peroxide concentration, initial solution pH, and Pt loading content, were studied on the photocatalytic MO decomposition performance.