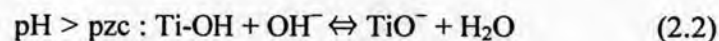# CHAPTER II

LITERATURE REVIEWS

Al-Bastaki (2003) compared the efficiencies of UV/TiO_2 and membrane processes (reverse osmosis (RO) and ultrafiltration (UF)) in the treatment of secondary and tertiary treated domestic wastewater, in terms of abilities to remove parasites and reduce COD. Both processes resulted in complete removal of parasites from secondary and tertiary effluent samples. COD was reduced by 64%, 86% and 50 % for UV/TiO_2 with RO, and UF processes, respectively.

Houas and coworkers (2000) investigated the photocatalytic degradation of methylene blue in aqueous suspensions of TiO_2. In addition to a prompt removal of the color, TiO_2 photocatalyst was able to oxidize the dye and brought about an almost complete mineralization of carbon, nitrogen, and sulfur into CO_2, NH_4^+, NO_3^- and SO_4^{2-}. These results suggest that TiO_2 photocatalyst may be employed as a method for treatment of diluted wastewater in textile industries.

Lachheb and coworkers (2002) studied the photocatalytic degradation of five dyes in aqueous suspensions of TiO_2. The dyes studied were alizarin S, crocein orange G, methyl red, congo red, and methylene blue. They investigated the influence of pH upon adsorption and photodegradation. For all dyes, except for OG, increasing the pH favored their adsorption. The pH simultaneously affected both the surface state of titania and the ionization state of organic molecules. For pH's higher than the point of zero charge (pzc) of titania, the surface becames negatively charged and for pH's less than the pzc, the surface was positively charged, according to the following equilibria:

$$pH < pzc : Ti\text{-}OH + H^+ \Leftrightarrow TiOH_2^+ \qquad (2.1)$$
$$pH > pzc : Ti\text{-}OH + OH^- \Leftrightarrow TiO^- + H_2O \qquad (2.2)$$

Since methylene blue is a cationic dye, its adsorption was favored on a negatively charged surface. By contrast, crocein orange G has its adsorption inhibited at high pH

because of the negatively charged sulfonate group. Nevertheless, the pH had little influence the kinetics of disappearance because protons did not intervene in the rate limiting step of the photocatalytic system.

Chakrabarti and coworkers (2004) studied the effect of air flow rate on photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst. The oxygen required for scavenging electrons generated by UV radiation came from the air bubbled through the liquid. For the dyes, the extent of photocatalytic degradation increased with increase in the air flow rate. The removal of COD also increased as air flow rate increased. The air flow rate was also sufficient to keep ZnO suspended in the liquid. An increase in the air flow rate increased the supply of oxygen by means of enhanced turbulence, gas holdup, gas–liquid interfacial area, and the mass transfer coefficient. Therefore, the number of hydroxyl and superoxide radicals produced also increased. Hence, the degree of photodegradation increased with increasing air flow rate. In addition, possible breakage of the particles due to attrition at a larger air flow rate may generate a larger catalyst surface area, thereby increasing the rate of degradation.

Daneshvar and coworkers (2004) studied the effect of oxygen concentration to the photocatalytic degradation of Acid Red 27 in UV/TiO$_2$ process. The rate limitation step of the photocatalytic degradation was the recombination of photogenerated hole-electron pairs. The adsorbed oxygen on the surface of TiO$_2$ prevented the recombination process by trapping electrons. The positive influence of oxygen concentration in photocatalytic system could be related to enhancing the separation of photogenerated electron-hole pairs, thereby increasing hydroxyl radical concentration.

Bizani and coworkers (2006) studied effect of pH on the photocatalytic decolorization and degradation of dye solutions and wastewaters in the presence of titanium dioxide. The pH was one of the most important parameters that could affect the photo-oxidation process. The effect of the solution pH on the degradation rate could be attributed to the modification of electrical double layer of solid–electrolyte interface, which consequently affected the adsorption-desorption processes and the

separation of the photogenerated electron–hole pairs on the surface of semiconductor particles. However, the strong adsorption dramatically reduce the active centers on the surface of catalyst, leading to a decrease, in absorption of the light quanta by the catalyst. This could cause the initial rate of the decolorizarion to be lower in strongly adsorbed dye solutions. Moreover, strong adsorption created a multilayer of dye molecules around the catalyst particles and as a result these molecules were not in direct contact with the catalyst, so they did not participate in the photo-oxidation process.

Das and coworkers (2006) studied the effect of initial concentration of methylene blue on the photocatalytic decolorisation over titania pillared zirconium phosphate (ZrP) and titanium phosphate. With increase in the concentration of methylene blue, the light absorbed by the substrate was more than that absorbed by the catalyst. So at higher concentration, the percentage of photodegradation decreased.

Ling and coworkers (2004) studied the effect of dissolved oxygen and the reaction temperature on the degradation of phenol and methylene blue using immobilized TiO_2 film. The significant role of oxygen in photocatalytic reaction was the prevention of the recombination of electron–hole pairs. Dissolved oxygen in water raised quantum efficiencies partly by inhibiting electron–hole recombination [Chen et al., 2000]. Air bubbling was the simplest way to supply sufficient amount of oxygen due to limited solubility of oxygen in water [Villacres et al., 2003; Salaices et al., 2004]. Reaction temperature had no significant effect on photodegradation of methylene blue. The photocatalytic oxidation process did not require heating as it was initiated by photonic activation. The true activation energy was very small or even zero. Literatures reported activation energies ranging from 5 to 20 kJ/mol [Chen et al., 2000]. These values are quite close to that for a hydroxyl radical reaction, suggesting that the photodegradation of most organic pollutants may be governed by hydroxyl radical reaction.

Sun and coworkers (2006) studied the effect of solution pH to the photocatalytic degradation of orange G (OG) using nano-sized $Sn(IV)/TiO_2/AC$ photocatalyst. The pH value of OG solution has significant influence on the

photocatalytic activity of the catalysts, which controls the production rate of hydroxyl radical. The photodegradation of OG was the most efficient in acidic solution and the optimal pH was at 2.0. The lower the pH value, the higher the energy level of valence bond. Consequently, TiO_2 had higher activity in oxidating organic pollutants. At pH lower than 2.0 the degradation efficiency also decreased because in OG dye, the azo linkage ($-N=N-$) is particularly susceptible to electrophilic attack by •OH radical. Besides, with the rise in pH, the –OH on the surface of TiO_2 could be replaced by –ONa, and the catalytic activity of TiO_2 decreased as a result.

Sahoo and coworkers (2005) studied the effect of initial dye concentration on the photodegradation of methyl red at different concentrations in the range of 10-50 ppm. The percent degradation gradually decreased with an increase in initial dye concentration. As the initial concentration of the dye increases, the color of the reaction mixture became more intense, thereby preventing the light from reaching the surface of the catalyst. Consequently, the degradation efficiency of the dye decreases as the dye concentration increases.