CHAPTER I
INTRODUCTION

The widespread presence of dyestuff, toxic compounds and pathogenic organisms in water poses a serious problem. There are available for treatment of adulterated water such as physical, chemical, and biological methods (Reife & Freeman, 1996). However, it has critical process in the complete destruction of contaminants like, dye pollutants, non-biodegradable organic pollutants (Herrera *et al.*, 2001). Hence, photocatalytic processes has been considered as alternative choice for wastewater treatment (Agustina *et al.*, 2005)

Photocatalytic reactions via semiconductor as photacatalysts has shown a high effective in the photooxidation of many organic pollutants present in the water including dyes (Bansal *et al.*, 2010), herbicides (Vulliet *et al.*, 2003), insecticide (Guan *et al.*, 2008), halocarbons (Chatterjee *et al.*, 2006) under UV or sun light. In addition, the decomposition of pathogenic organisms namely viruses, fungus, bacteria by photocatalytic chemistry has been reported (Blake *et al.*, 1999). The degradation pollutants mechanism of photocatalytic reactions under light energy source (hv) is as follows

$$\text{Photocatalyst} + h\nu \rightarrow h^+ + e^- \quad (1)$$

$$h^+ + H_2O \rightarrow H^+ + OH^\bullet \quad (2)$$

$$e^- + O_2 \rightarrow O_2^{\bullet-} \quad (3)$$

$$O_2^{\bullet-} + O_2^{\bullet-} + 2H^+ \rightarrow O_2 + H_2O_2 \quad (4)$$

$$O_2^{\bullet-} + e^- + 2H^+ \rightarrow H_2O_2 \quad (5)$$

$$O_2^{\bullet-} + H^+ \rightarrow {}^\bullet OOH \quad (6)$$

$$H_2O_2 + e^- \rightarrow OH^- + OH^\bullet \quad (7)$$

$$O_2^{\bullet-}/{}^\bullet OOH/\ {}^\bullet OH/\ h^+ + \text{Pollutants} \rightarrow \text{degradation products} \quad (8)$$

When photocatalyst absorbs photon of energy greater than or equal to the band gap energy, an electron is then promoted from from valence band to conduction band resulting in creating electron vacancy or hole (h^+). After charge separation process of Photocatalyst by photon hole transform water molecules into OH free

radicals. Moreover electron can react with oxygen to create superoxide and then superoxide creating hydrogen peroxide and hydroperoxyl radical afterward hydrogen peroxide reacts with electron to generate hydroxyl ions and hydroxyl radical. (Rush *et al.*, 1985; Hoffmann *et al.*, 1995; Bahnemann *et al.*, 2004). Essentially, hydroxyl radical ($^{\bullet}OH$), holes (h^{+}), superoxide ($O_2^{\bullet-}$) and hydroperoxyl radical ($^{\bullet}OOH$) are highly reactive intermediates that will act concomitantly to oxidize large variety of organic pollutants and bioaerosols (Jacoby *et al.*, 1996; Sleiman *et al.*, 2007).

One of the most photocatalysts that has drawn much attention due to its great properties is Titanium dioxide (TiO_2) i.e. chemical inertness, long-term stability against corrosion, cost effectiveness, low toxicity and powerful oxidant (Hoffmann *et al.*, 1995). Dinder *et al.*, (1996) reported the photodegradation phenol capacity of TiO_2 is superior to that ZnO and Fe_2O_3. Sohrabi *et al.*, (2010) reported the order of photocatalytic activity of various photocatalysts was: $UV/H_2O_2/TiO_2$ > $UV/H_2O_2/Fe_2O_3$ > $UV/H_2O_2/ZnO$ > $UV/H_2O_2/SnO_2$. Therefore, TiO_2 has been performed along with its photocatalytic application for water treatment (Malato *et al.*, 2002). The crystallographic forms of TiO_2 exist in three forms (anatase, brookite and rutile) Brookite is extremely difficult to synthesize in the laboratory but both anatase and rutile can be readily prepared (Childs *et al.*, 1980). It is well known that anatase is usually used as a photocatalyst to treat various wastewaters due to its high photocatalytic activity (Kraeutler *et al.*, 1978; Rao *et al.*, 1980; Tetsuro *et al.*, 2007). Kwon *et al.*, (2004) prepared TiO_2 thin flims via sol-gel process using different alkoxide precursors including titanium isopropoxide, titanium propoxide, titanium ethoxide and titanium butoxide. All specimens exhibited crystals of the anatase phase with a very tiny amount of brookite phase. Pekakis *et al.*, (2006) were testing for two crystalline forms of TiO_2, anatase and rutile, was found that anatase more photocatalytic activity than rutile.

The attempt to enhance its photocatalytic activity of TiO_2 was decreasing the particle size and increasing the surface-to-volume ratio (Anpo *et al.*, 1987; Chae *et al.*, 2003). Consequencely, impregnation of nano-sized TiO_2 on larger nano-supporting structure has been investigated for the recovery the photocatalytic efficiency of TiO_2. To illustrate, Robert *et al.*, (1999) prepared TiO_2 supported on glass-fibre and studied on photocatalytic degradation of benzamide. Qiu *et al.*,

(2008) synthesized TiO_2 nanotubes from electrospun fiber templates. Moreover, Im *et al.*, (2010) improved photodegradation properties and kinetic models of a solar-light-responsive TiO_2 when incorporated into eletrospun hydrogel fibers. Recently, the interested nanofiber investigated as matrix for synthesizing nanoparticles is bacterial cellulose (BC). For instance, Maneerung *et al.*, (2008) impregnated silver nanoparticles into BC, Li *et al.*, (2009) synthesize CdS nanoparticles on BC nanofibers. Hu *et al.*, (2010) synthesized ZnO nanoparticles based on BC.

Bacterial cellulose (BC) has the same chemical structure as plant cellulose that are polysaccharide consisting of a linear chain of β(1→4) linked D-glucose units and have strong intramolecular and intermolecular hydrogen bonding between the individual chains; nevertheless, BC is superior to that plant cellulose because it more purity which free of lignin and himicellulose. BC is produced by acetic bacterium such as *Acetobacter xylinum* cultivated in stationary conditions using a culture medium containing carbon and nitrogen sources. It is non-toxic mat presents in non-woven network fibrous structure with diameter less than 100 nm and constitutes to be a three-dimensional multilayers linked together with nanofibers bring about generating micro-porous structure accordingly, BC provides large surface area (Czaja *et al.*, 2004). as well as BC sheet obtained from BC pellicle is high-strength material which has high dynamic Young's modulus, close to 30 GPa. (Nishi *et al.*, 1990) Moreover, another advantage of BC has much more surface hydrophilicity in chemical structure (hydroxyl and ether groups) than plant cellulose (Li *et al.*, 2009) that is useful for hydrolysis reaction so as to synthesizing TiO_2 photocatalyst nanoparticles on BC.

Owing to these unique properties of BC, in the present study BC produced by *Acetobacter xylinum* was used as an organic nanofiber template for ameliorating photocatalytic activity of TiO_2. Bacterial cellulose is not only a non-toxic material but also has many advantages being beneficial for synthesizing of TiO_2, including hydrophilicity in chemical structure which is useful for hydrolysis reactions and porous structure with high surface area due to its fibrilar diameter in nanoscale (Bielecki *et al.*, 2005, Czaja *et al.*, 2006).