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Metal Oxide and Activated Carbon as Photocatalyst for Waste Water Treatment

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Abstract. Nanoparticles of metal oxide have great potential in the photocatalytic system for removal of heavy metals in wastewater. The usage of titanium dioxide (TiO2) as photocatalyst has gained much attention because of its unique properties compared to others metal oxide. The usage of activated carbon (AC) as adsorbent from agricultural wastes such as coconut shell, cotton stalks and rice husk (RH) has recently used nowadays due to it is characteristic and low cost. Besides, it can reduce the abundant of wastes from open burning occurs and also can minimizing air pollution. The combination of photocatalyst-absorption process has been introduced in photocatalytic activity via dip-coating techniques without involving the filtration process. This technique has seeking more attention of researchers for removal of heavy metals such as cadmium (Cd), chromium Cr) and copper (Cu) in industrial wastewater treatment.

1. Introduction

Environmental pollution has been occurring because of the developmental activities such as growing in manufacturing, transportation and construction that produce a large amount of wastes. These wastes may lead to pollution of soil, water, air and oceans that affects our environment and human being. In this review, we focus on method of treatments specifically for industrial wastewater to overcome the water pollution issues. The water pollution occurs due the present contaminants and its amount not suitable in daily life used such as cooking, drinking, bathing and other uses that usually influenced by human activities [1]. Thus water pollution limits the fresh water resources in the whole world due to climate change, gaining in population and urbanization where demands for water increased [2].

Wastewater treatment is the important process to treat the polluted water into the fresh or safe water that can be used for living life purposes. Nowadays, the rapid development in paper, electronics [3] and dye industries [4] as well as metal plating facilities [5] affects the water resources quality mainly for drinking supply. Typically, the wastewater from these industries are highly toxic due to the presence of heavy metals which were directly or indirectly discharged into the environment [6]. Consequently, contaminated industrial wastewater with heavy metals risk human health and aquatic ecosystems as well as serious environmental problems [5]. For example, in Saudi Arabia, the major heavy metal contaminants from industries are Arsenite (As), Cadmium (Cd), Cobalt (Co), Chromium (Cr), Lead (Pb) and Zinc (Zn). These heavy metals are very dangerous even exposure at very low concentrations because it can cause cancer, brain damage, accumulative poisoning and destroy liver. The Cr itself is highly toxic, carcinogenic and mutagenic. The mutagenic of Cr inhibits mitotic process of plants [2]. Mostly Cr are found in tannery industrial wastewater. Then, Pb, Nickel (Ni) and Copper (Cu) [8] also can cause harmful for kidney, sensory system, liver, brain, reproductive system, sterility, capillary damage, stillbirths and causes neonatal deaths [7-9].

Thus to protect human life and prevent any consequence due to contaminated wastewater with heavy metals, the specific standards of water has been introduced in the many of developed countries. Even though high end treatment of industrial wastewater is expensive [6] but many technologies have been developed such as photocatalytic, adsorption, membrane filtration, precipitation, electrochemical and ion-exchanged techniques [7]. Various models of photocatalytic cell have been developed such as photocatalytic reactor using CFD (Computational fluid dynamics) simulation, electrospinning of mesoporous zinc oxide (ZnO) nanoporous for photocatalytic activity [10] and immobilized titanium dioxide (TiO_2) nanofilm on the substrate [11]. The model of photocatalytic cell that was proposed in this paper is immobilizing of TiO_2 and adsorbent via dip-coating technique. Mainly the advantages of this models are both of adsorption and photocatalysis process will occur simultaneously during treating the wastewater without involves the filtration process [12-13]. In general, photocatalytic methods were widely applied for water purification, air production, antibacterial activity and degradation of organic pollutants in wastewater.

2. Metal Oxide as Photocatalyst

Typically, photocatalytic cell consists of photocatalyst, adsorbent, adhesive and substrate. Generally, a photocatalytic cell is able to perform photocatalysis activity which involves capabilities of metal oxide or metal oxide nanoparticles such as titanium oxide that used to remove heavy metals from wastewater [14]. In photocatalysis, both light and catalyst were used simultaneously to help and rapidly increase a chemical reaction where it can decompose organic pollutants. There are two types of photocatalyst which are homogeneous or heterogenous. The homogenous photocatalyst are having similar phase of matter between photocatalyst and targeted medium that involves complexation process between catalyst and heavy metals. While heterogenous photocatalyst involves different phase of matter between photocatalyst and targeted medium. Thus degradation of pollutants occurs via photocatalysis process through irradiation of UV light [15]. Different type of metal oxides and adsorbents were variously studied in heterogenous photocatalyst. Many of nanomaterials adsorbents was developed due to the ability of removing contaminants from wastewater by enhancing the efficiency and capacity of adsorption. There are variety of membrane that acts as adsorbents in photocatalytic cell. The combination of both metal oxide and adsorbent shown high synergistic impact to clear the contaminated water [12].

Last few decades, the catalyst from metal oxide such as silica [7], ZnO, TiO_2 and zirconium dioxide (ZrO_2) has been used in the photocatalytic process for wastewater treatment. These metal has been proposed for hazardous pollutants removal like heavy metals such as Cd [15] due to environmental-friendly materials, efficient costly and have the capability for pollutants adsorption in low concentration (ppb) [14]. The average size of nano-particles which contains structure components with one dimension is less than 100 nm. The properties of these metal oxides are high surface area, reduce solubility and no secondary pollutants.

As known ZnO is as photocatalyst for heavy metals removal in the aqueous solutions [16]. ZnO is a potential photocatalyst in removal of heavy metals such as Cd [17] and Pb. For example, ZnO was act as photocatalyst to remove Cd from aqueous solution by using experimental-laboratory batch study [17]. ZnO features nanostructure with high sufficient surface area and its surface consists of many functional groups such as hydroxyl groups that can be active sites for adsorption activity and uptake positively charge ions [16]. ZnO possesses variety of nanostructures such as porous thin film, nanorods, nanosphere and nanowired [10]. However, nanorods structures is widely used as photocatalyst in removal heavy metals such as Cd and Pb. There are varieties of techniques to synthesis of ZnO such as hydrothermal synthesis, homogeneous precipitate and sol-gel method. But, the sol-gel method was usually proposed due to it has good crystalline structure of particles and has a narrow size distribution. Then, this method also was required simple operation and mild conditions.

TiO_2 is the common metal oxide in photocatalyst. TiO_2 features unique properties such as high stability, low cost, high surface activity, high refractive index and have strong catalyzing ability. TiO_2 is a strong photocatalyst due to its chemical stability and has high ability reactivity under ultraviolet (UV) light that is wavelength lower than 390 nm. The simple mechanism of the working of photocatalysis depends on the photoexcitation of electron in the catalyst that the holes (h^+) and released electrons (e^-) was created by irradiation from light (UV) in the conduction band [14]. Instead of heavy metals removal, TiO_2 can be combined to remove organic or inorganic pollutants in water and air. TiO_2 structure can be amorphous or crystalline that consists of anatase, rutile and brookite. But, the most stable phase of TiO_2 is the rutile structure compare to others.

Typically, TiO_2 particles is used heavy metal removal of wastewater. Thus TiO_2 can be synthesize via sol-gel technique, hydrolysis or hydrothermal. The synthesis of TiO_2 via sol-gel technique were carried out using titanium precursor in either acidic or alkaline condition to form the TiO_2 sol. The preparation of TiO_2 nanofilm is similar to TiO_2 particles but it undergoes a specific heat treatment such as the Ag/TiO_2 nanofilm was heat treated at 400 ºC to formed the nanoparticles of Ag that was dispersed on the TiO_2 surface [11]. Other than that, anodic oxidation technique was introduced from researchers that the temperature required is < 600 ºC to obtain a thicker film at low voltage oxidation and obtaining the smooth surfaces.

Recently, TiO_2 also has been used as composites compound with adsorbent such as the powder activated carbon (PAC) and TiO_2 that used in treatment of heavy metals wastewater. Thus TiO_2 and PAC will reduce overall cost, biologically and chemically inert, and increase it turn over frequency (TOF) [12].

3. Adsorbents

In removal of heavy metals such as Pb, Cu, iron (Fe) and Zn from electroplating industrial wastewater are using activated carbon (AC) produced from coconut shell as an adsorbent. Carbon nanotubes (CNT) also have been used as an adsorbent to remove Cd in wastewater due to its characteristics which are have large specific areas and high chemical stability but CNT requires high cost [9].

Adsorption process is a technique that purified wastewater for removing an organic and inorganic pollutants from industrial wastewater. This method also more economical to remove metal ions from wastewater [9]. Recently, AC is most commonly used as adsorbent that suitable for removal of pollutants due to high surface area that allows adsorption. Other than that, this absorbent was also used to obtain the treated water because of its properties like a good porosity structure that can remove pollutants in water [7].

AC have made from agricultural wastes such as rice husk (RH) [8], bamboo [18], cotton stalk [19] and coffee husk due to the microporous of plant structures and have long dispersion path through solid particle of adsorbents [8]. It is also can have commercially from supplier such as PAC. For example, AC from cotton stalks were used to remove heavy metals such as Cd, Pb and Cu in wastewater via mixed batch reactor. This method was proposed due to its good properties such as low cost and have high carbon contain beside it can reduce air pollution from burning the agricultural waste [19]. Then, the AC from bamboo was used to remove the heavy metals which are Pb and Cd due to it has renewable raw materials and less costly [18].

In most of Asian countries, the production of AC from RH has been proposed to reduce environmental pollution from abundant of agricultural waste due to low cost and it is effectively accessible materials. Thus, AC from RH mainly used as dye removal like methylene blue [4], metals removal such as Pb, Cu [8] Cd and Cr [2]. The RH content also can be sources of carbon based on containing high cellulose and lignin. This method was obtained the porosity of surface area of RH as an absorbent. Other than that, RH also is the suitable materials as an adsorbent that containing low ash, high carbon and silica contents.

There are some of researchers was used commercially AC in the photocatalytic studies such as PAC. For example, the magnetic PAC particles has been approached in magnetic field to be treated the wastewater. This process has occurred without involving filtration process, but there are limitations which are not sufficient in surface areas and porosity compared to be AC. Other than that, PAC also have used as adsorbent and TiO_2 as a catalyst without blending together because it will make the reducing of porosity. However, this method has disadvantage such as highly cost that mainly used on a large scale [13].

4. Adhesive

In most studies, the composite polymers were formed membrane for removal pollutants. It undergoes filtration process. The usage of polymer as adhesive used to form another layer after substrate for dip-coating method. Photocatalytic film has been proposed by using Ag_2O/TiO_2 modified chitosan-based photocatalytic film. This method showed the removal of organic pollutants due to the good adsorption capacity by modified chitosan [20]. Next, the other example of adhesive is epoxidized natural rubber (ENR) that was used as a polymer in the adsorption-photocatalyst process for dip-coated method. This method showed the ENR was blend together with PAC to coating the substrate [12-13]. This polymer widely used because its good properties such as low glass transition temperature, high strength and solubility parameter [21].

The other adhesive that has been proposed in photocatalytic activity is polyamide-amine-epichlorohydrin (PAE) which is this polymer was used with microfibrillated cellulose and nanoparticles of TiO_2 for photocatalytic activity via filtration process [22]. This paper will focus on photocatalytic activity that combining with adsorbent in the wastewater treatment for removal heavy metals without involving filtration process. This method also will use dip-coating techniques layer-by-layer of materials for removal of heavy metals such as Cu, Cd and Cr.

5. Substrate

Substrate typically used are quartz and glass slides that have formed self-assembled film. This film has good characteristics such as stable, has unique physical and chemical properties, particularly dense and electron transport properties. For example, both of the glycine betaine and cetyl-trimethyl ammonium bromide (CTAB) was using to be formed this film due to it is potential to absorb the Pb ion in wastewater [23].

In addition, the other substrate was determined is borosilicate glass slide. This substrate was used for removal COD efficiencies by using TiO_2. The synthesis TiO_2 via sol-gel process was using to be coated the borosilicate glass slide to form the film before undergo the photocatalytic activity [24].

6. Conclusion

To conclude, photocatalytic process is widely used to be treated the contaminated wastewater through metal oxides and absorbance. There are varieties of pathways to shows the physico-chemical parameters for metal oxide nanoparticles and activated carbon such as size, shape, porosity and surface area. This requires a good design of a photocatalytic cell.

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