CALCIUM ALGINATE IMMOBILIZED TiO_2/ZnO BEADS FOR THE REMOVAL OF COPPER

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Bachelor of Science with Honours

(Resource Chemistry)

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Calcium alginate immobilized TiO_2/ZnO beads for the removal of copper

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A thesis submitted in partial fulfilment of the requirements for the Degree of
Bachelor of Science with Honours
(Resource Chemistry)

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List of Abbreviations

Advanced oxidation process	AOP
Calcium alginate	Ca-alginate
Calcium chloride	$CaCl_2$
Copper	Cu
Equation	Eq.
Flame atomic absorption spectrometer	FAAS
Hour	h
Minute	min
Nitric acid	HNO_3
Reactive oxygen species	ROS
Scanning electron microscope	SEM
Sodium alginate	Na-alginate
Sodium hydroxide	NaOH
Titanium dioxide	TiO_2
Ultraviolet	UV
Zinc oxide	ZnO

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Calcium alginate immobilized TiO_2/ZnO the beads for removal of copper

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ABSTRACT

This study was conducted to prepare calcium alginate (Ca-alginate) beads by immobilizing hybrid photocatalysts namely titanium dioxide, TiO_2 and zinc oxide, ZnO. The calcium alginate beads were prepared by encapsulating different ratios of TiO_2 and ZnO and their efficiency was further tested for the removal of copper (Cu) from water by using ultraviolet (UV) irradiation. Dark adsorption study was done without UV irradiation to determine the extent of Cu adsorption on the surface of the beads. The results showed that Cu was removed better in the presence of UV up to 90% than in the dark condition which was only about 55%. Suspended photocatalyst showed slightly higher photocatalytic activity compared to the immobilized photocatalyst in the removal of 60 ppm Cu. The effect of pH on Cu removal has been studied and the maximum removal efficiency of Cu was 98.7% at pH ~7. In the recycling study, Ca-alginate immobilized TiO_2/ZnO beads demonstrated good removal efficiency of Cu in all three cycles of use. Thus, the potential of Ca-alginate immobilized TiO_2/ZnO beads as an environmentally friendly catalyst can be further developed for heavy metals removal from contaminated water.

Key words: Ca-alginate, copper removal, photocatalyst, immobilization, photocatalysis

ABSTRAK

Kajian ini dijalankan untuk menyediakan manik kalsium alginat (Ca-alginat) diiimmobilisasi dengan hibrid fotomangkin iaitu titanium dioksida, TiO_2 dan zink oksida, ZnO. Manik kalsium alginat yang mengandungi TiO_2 dan ZnO dalam nisbah yang berbeza telah disediakan untuk menilai kecekapan penyingkiran kuprum (Cu) dari air dengan menggunakan sinaran ultraviolet (UV). Kajian penjerapan gelap telah dijalankan tanpa sinaran UV untuk menentukan tahap penjerapan Cu pada permukaan manik. Hasil kajian menunjukkan bahawa penyingkiran Cu adalah lebih baik dengan sinaran UV (90%) berbanding dengan keadaan gelap (55%). Fotomangkin yang terampai menunjukkan aktiviti fotopemangkinan yang lebih tinggi sedikit berbanding fotomangkin yang diimobilisasi dalam penyingkiran 60 ppm Cu. Kesan pH dalam penyingkiran Cu telah dikaji dan kecekapan penyingkiran Cu yang maksimum adalah 98.7% pada pH ~7. Dalam kajian kitar semula, didapati manik Ca-alginat diimobilisasi dengan TiO_2/ZnO menunjukkan kecekapan penyingkiran Cu yang baik dalam kesemua tiga kitaran kajian. Oleh itu, potensi manik TiO_2/ZnO-Ca alginat sebagai pemangkin mesra alam boleh diperkembangkan lagi dalam penyingkiran logam berat untuk rawatan air.

Kata kunci: *Ca-alginat, penyingkiran kuprum, fotomangkin, immobilisasi, fotopemangkinan*

Chapter 1: Introduction

1.1 Research Background

Heavy metals are toxic and cause adverse effects to the environment especially the aquatic environment. There are many types of heavy metals present in the earth which are mainly the transition elements, metalloids, lanthanides and actinides. The common sources of heavy metal contamination are usually from the mining and industrial wastes. Heavy metals can be directly or indirectly released to the environment.

Copper (Cu) is regarded as a heavy metal. Trace amount of Cu is essential in all living organism but exceeding the required amount will become toxic to the body (Wright & Welbourn, 2002). Short term exposure of copper leads to gastrointestinal distress and long term exposure may cause liver or kidney damage (Abdel-Ghani & El-Chaghaby, 2014).

Concerning this, numerous approaches have been studied for the removal of heavy metals such as chemical precipitation, coagulation, membrane filtration, adsorption, ion-exchange, solvent extraction and electrochemical treatment technologies (Dushenkov et al., 1995; Kurniawan et al., 2006). However, some of these approaches have their own drawbacks. For example, chemical precipitation lead to a high production of sludge and its disposal causes long-term environmental effects (Aziz et al., 2008).

Advanced oxidation processes (AOPs) is a method which is based on the *in-situ* generation of non-selective and highly reactive oxygen species (ROS) such as hydroxyl radical (•OH), superoxide anion radicals ($\bullet O_2^-$) and hydrogen peroxide (H_2O_2) (Comninellis et al., 2008). According to Topkaya et al. (2014), AOPs have turn out to be an evolving technology because of their efficiency in the degradation of organic

compounds. Among various AOPs, heterogeneous photocatalysis using semiconductors such as TiO_2 and ZnO have been commonly applied in wastewater treatment. TiO_2 and ZnO are widely used as photocatalyst due to their excellent photocatalytic activity, non-toxicity and wide availability. In the presence of ultraviolet (UV) light irradiation, TiO_2 and ZnO are very effective catalyst due to their similar wide band gap of 3.2 eV at room temperature (Topkaya et al., 2014).

In the water treatment, TiO_2 and ZnO have been generally applied in the suspended form. The suspended form of photocatalysts would have a better interaction with the heavy metal ions compared to the immobilized form (Fatin et al., 2012). However, application of suspended form of photocatalysts in large scale of water treatment is impractical due to a high cost of post-filtration process and recycling, time consuming and the strong absorptions between the catalyst particle and dissolved pollutants limits the penetration depth of UV light (Mahmoodi et al., 2007). Therefore, immobilized photocatalysts are more practical to be used in the removal of heavy metal as it can be easily separated from solution after treatment. Immobilization of photocatalyst has been carried out using various solid supports such as zeolites, silica, quartz, activated carbon, fiberglass and polymer (Leung, 2009).

Alginate is a natural adsorbent that is used for the removal of heavy metals. Alginate gels have a semi-permeable membrane where diffusion of low molecular weight of water-soluble molecules can occur (Albarelli et al., 2009). Alginates are able to bind to metal ions through carboxyl groups (Siegel & Siegel, 1973). The most common immobilization method for adsorption is entrapment and cross-linking with polymeric matrices such as calcium alginate, polysulfanone, polyacrylamide and polyvinylalcohol (Fosso-Kankeu & Mulaba-Bafubiandi, 2014). Calcium alginate gel has been chosen in this

study because it is effective, low cost, can be easily prepared and has an open lattice structure for the fast diffusion of metal ions (Leung, 2009). The preparation of calcium alginate beads are done due to their gel forming properties in the existence of multivalent cations (Wu et al., 2010).

So far, only a limited number of studies have been carried out to investigate the study on immobilization of photocatalyst for the removal of heavy metal (Liu et al., 2005). To the best of our knowledge, no studies have been done on the removal of Cu using Ca-alginate immobilized with hybrid photocatalysts, TiO_2 and ZnO. Therefore, this research was carried out to study the removal efficiency of Cu using TiO_2/ZnO-Ca alginate beads.

1.2 Problem statement

The suspended form of photocatalyst shows a high efficiency in the removal of heavy metal as compared to the immobilized form because after immobilization the active surface area will be reduced (Albarelli et al., 2009). However, it is not economical to use the powder form of photocatalyst because the process of separation is expensive. Therefore, the immobilized system would be a much better option to be used. Existing studies have mainly focused on the immobilization of a single photocatalyst in calcium alginate. In this research, hybrid photocatalysts, TiO_2 and ZnO were immobilized by varying their ratios in calcium alginate to study their effectiveness for the removal of Cu under UV irradiation.

1.3 Objectives

The objectives of this study are to:

i) prepare TiO_2/ZnO-Ca alginate beads by varying the ratios of TiO_2 and ZnO.

ii) characterize the prepared TiO_2/ZnO-Ca alginate beads by using scanning electron microscope (SEM).

iii) determine the removal efficiency Cu using the prepared TiO_2/ZnO-Ca alginate beads under UV irradiation.

Chapter 2: Literature Review

2.1 Heavy metal: Copper

Heavy metals are potentially hazardous to both human and environment. Heavy metals are non- biodegradable and most of them have a high toxicity level. According to Fu and Wang (2011), specific gravity of heavy metals is greater than 5.0 and their atomic weights are between 63.5 to 200.6. Elements that can be regarded as heavy metal include lead, copper, cadmium, chromium, nickel, arsenic, and zinc. Ingestion and exposure of heavy metals beyond the allowed concentration can cause serious health effects (Barakat, 2010).

Cu has a broad range of industrial application especially in the alloy industry whereby alloys contain Cu as a principal metal. Besides, Cu is also used widely used in electrical industry, machinery, printing, dyes, construction industry, electroplating and transportation. The main source of Cu pollution is through the discharge of untreated waste water to water bodies from copper wire mill, fungicides and insecticides industry (Joshi et al., 2011).

Cu usually exist in the environment as Cu(II) but also as Cu(I). Traces of Cu compound are essential in all living organism but exceeding the required amount will become toxic to the body (Wright & Welbourn, 2002). Cu can cause some serious consequences such as hematemesis, convulsions, Wilson disease and may also be fatal (Fu & Wang, 2011). Application of copper salt on the skin is corrosive and may lead to papulovesicular eczema, a chronic skin rash (Joshi et al., 2011).

2.2 Photocatalysis

Photocatalysis is the acceleration of photoreaction in the presence of a catalyst and can be included as one of the advanced oxidation process (AOP) (Topkaya et al., 2014). One of the essential technologies that are now emerging is the photocatalysis reaction assisted by semiconductors such as TiO_2 and ZnO. Photocatalysis using metal oxides is initiated by the absorption of photons with energy equivalent or greater than the band gap of the semiconductor producing electron-hole (e^-/h^+) pairs (Joshi et al., 2011). This process does not yield any toxic intermediates and suitable for cleaning water environment with low to medium concentration of contaminants (Fatin et al., 2012).

Photocatalytic degradation mostly uses UV irradiation as an energy source which requires large input of electric power to generate radiation; however in tropical countries like Malaysia, intense sunlight is available which is a safe and cost effective source of UV (Fatin et al., 2012).

When the UV light is illuminated on the semiconductor surface-aqueous media, the interaction forms photo-excited electron-hole pairs (Samarghandi et al., 2007). The space-charge makes the photo-generated electrons and holes to keep on separated or recombine to release heat by a trapping mechanism in the vicinity of the solid-liquid interface. The formation of •OH and $\bullet O_2^-$ radicals, the main decomposer of the molecules occurs due to the "trapped" holes and electrons on the hydroxylated semiconductor surface (Topkaya et al., 2014). Through a series of chain reactions, the radicals will react with the aqueous phase pollutant molecules or with the surface adsorbed which brings about decomposition by altering their molecular structures (Topkaya et al., 2014). The schematic diagram of the photocatalytic process on the surface of the semiconductor nanoparticles for the degradation of organic dyes (Singh et al., 2013) is as shown in Figure 2.1.

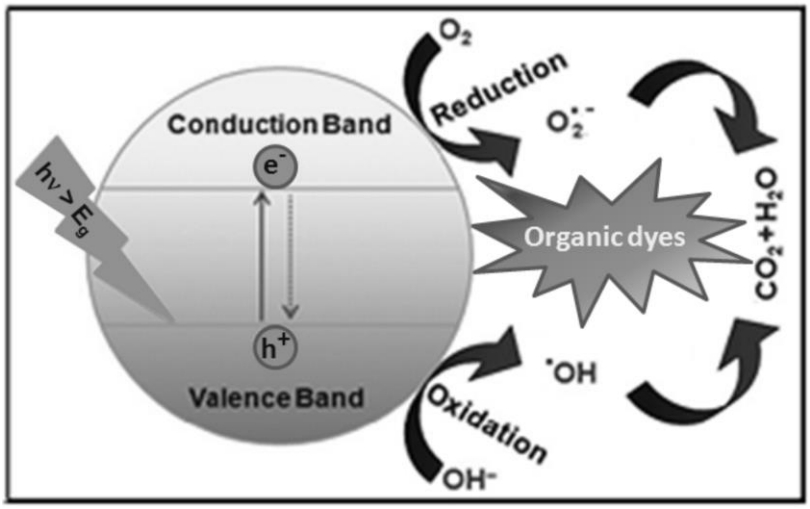

Figure 2.1: Schematic diagram on the photocatalytic process on the surface of the semiconductor nanoparticles for the degradation of organic dyes (Singh et al., 2013).

2.3 Properties of zinc oxide

ZnO is a naturally occurring oxidic compound which appears to be a white powder, insoluble in water and has a band gap energy of 3.2 eV (Lam et al., 2012). ZnO has been emerging as a potential photocatalyst for environmental remediation and removal of pollutants. The nanostructure of ZnO provides a good photocatalyst due to their high surface area, large amount of oxygen vacancy, mesoporous structure, excellent photocatalytic lifetime, high quantum efficiency and it has many surface active sites for the adsorption of heavy metals (Singh et al., 2013). ZnO act as a multifunctional material which has a high chemical stability, high electro coupling coefficient, high photostability and a wide range of radiation absorption (Bacaksiz et al., 2008; Segets et al., 2009). ZnO is known for its low toxicity, biocompatibility and biodegradability (Kolodziejczak-Radzimska & Jesionowski, 2014). The advantage of ZnO over TiO_2 is that it absorbs a large portion of the solar spectrum (Lam et al., 2012).

Some studies have shown a superior degradation efficiency of the photocatalytic mechanism mediated by ZnO (Chen, 2007). Certain modification technique can be applied to ZnO to improve its photocatalytic activity properties. A research has been conducted on the surface modification of ZnO by depositing palladium, Pd, with appropriate content on their surfaces to improvise their photocatalytic reaction (Liqiang et al., 2004).

2.4 Properties of titanium dioxide

TiO_2 is an excellent photocatalyst and a powerful adsorbent for the removal of heavy metals. Wang et al. (2013) stated that TiO_2 based materials has a unique property due to its electronic and optical properties. TiO_2 have a high chemical stability, low cost, low toxicity and are insoluble in water (Li Puma et al., 2008). Crystal phase, crystallinity, surface area and porosity influence the photocatalytic activity of TiO_2. The desirable phase for photocatalysis would be the anatase phase with a band gap of 3.2 eV (Li Puma et al., 2008; Joshi et al., 2011). Upon irradiation, TiO_2 particle can act as an electron acceptor or donor for molecules in the surrounding medium (Joshi et al., 2011).

TiO_2 has a structure characterized by electron filled valence band and empty conduction band which is separated by a band gap and it is due to this structure, irradiation with UV leads to the formation of hydroxyl radical and photogeneration of electron-hole pairs (Wahyuni et al., 2011). Furthermore, studies on Cu(II) removal from its solution through photocatalytic reduction in the presence of TiO_2 has also been reported (Wahyuni et al., 2011).

TiO_2 has been used in photocatalytic degradation of various organic pollutants such as chlorophenol, phenol and azo dyes found in wastewater (Tang et al., 1997; Antoniou & Dionysiou, 2007). The diffusion of the organic pollutant and accessibility to the active

centers on the surfaces throughout the TiO_2 materials is an advantage from the large internal surface area and mesoporosity (Wang et al., 2013).

2.5 Immobilization technique

The term immobilization in this project is defined as the attachment or entrapment of TiO_2/ZnO particles into the Ca-alginate matrix. The suspended TiO_2 has been reported to provide better results than those which are in the immobilized form. The reduction in the surface area after immobilization makes the efficiency of the immobilized adsorbent to decrease (Jeon et al., 2002). However, the use of the suspended adsorbent is impractical as the separation becomes difficult from treated water. Adsorbents that are normally used in the removal of heavy metals are clay minerals, activated carbon, metal oxides, zeolites, biomass, agricultural wastes and polymeric matrices (Qu, 2008). Immobilized TiO_2 is economically beneficial where it actually removes the post-process filtration step to get rid of the powder photocatalyst from the treated water for disposal (Albarelli et al., 2009).

Many techniques has been developed for immobilizing photocatalysts onto a solid support which includes sputtering, spray coating, dip coating from suspension, electrophoretic deposition and sol-gel-related methods (Khataee et al., 2011). The types of solid supports that are used to immobilize photocatalyst are glass rings, activated carbon, silica, aluminium, stainless steel and other support materials (Rezaee et al., 2008). A novel adsorbent by immobilizing TiO_2 on molecular imprint chitosan matrix has been synthesized and used to adsorb heavy metal ions (Li et al., 2008). Another study also reported that calcium alginate immobilized TiO_2 beads showed excellent heavy metal

removal efficiency after ten adsorption/desorption cycles when being used to elute lead (II) and cadmium (II) ions (Leung, 2009).

2.6 Alginates

Alginate (Figure 2.2), the salt of alginic acid is a natural polymer which is extracted from the brown seaweed and widely used as a component for entrapment. It is cheap, non-toxic, efficient and often used as a polymeric matrix (Kimling & Caruso, 2012). Alginate contains alternating blocks of 1→4 linked α-L-guluronic and β-D-mannuronic acid residues. The alginate with monovalent ions (ammonium and alkali metals) are soluble whereas the alginate itself and with bivalent or polyvalent metal ions (except Mg^{2+}) are insoluble (Percival & Mc Dowell, 1981). The most abundant functional group found in the alginate polymer is the carboxylic groups which enhances the adsorption of metal ions (Fourest & Volesky, 1995). Besides that, sulfonic acid and hydroxyl groups are also found abundantly in alginates.

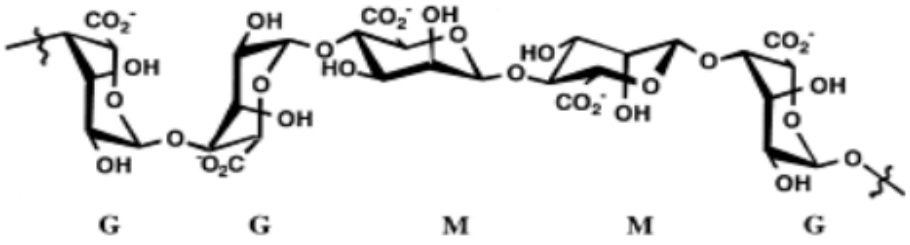

Figure 2.2: The molecular structure of alginate molecules, G: α-L-guluronic and M: β-D-mannuronic acid (Dumitriu, 2004).

The main property of alginates is that in the presence of calcium or divalent cations, they will form a structure of cross-linked chains known as the ‘egg-box model’ (Rees & Welsh, 1977). Calcium ions are mostly preferred because of its non-toxicity properties. Each divalent calcium ions binds to two carboxyl groups of adjacent alginate molecules forming hydrogels (Kumar & Chandrasekaran, 2003). The advantages of calcium alginate beads are due to its natural origin, presence of carboxyl groups, hydrophilicity and biodegradability (Gok & Aytas, 2009).

Ca-alginate can be used as a green support for TiO_2 immobilization and is a new environmentally friendly immobilization system for a large scale of water treatment (Harikumar et al., 2013). According to a research conducted by Escudero et al. (2009), the entrapment of a waste metal hydroxide in calcium alginate beads improved the adsorption of arsenic by 60%.