Development of Multifunctional Nanomaterials and Adsorption - Photocatalysis Hybrid System for Wastewater Reclamation

Vipasiri Vimonses

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"Success is not final, failure is not fatal: it is the courage to continue that counts" – *Sir Winston Churchill*-

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ABSTRACT

This thesis study aimed to develop multi-functional nano-catalyst and porous adsorbents from low-cost and locally available materials, and then implement this into an Adsorption-Photocatalysis hybrid system for wastewater reclamation. The project involves two major technological practices for wastewater treatment: adsorption and photocatalysis. For each technology, a specific functional nanomaterial has been developed and investigated regarding their removal capability for a pilot-scale water treatment process. The experimental studies include: 1) evaluation and characterisation of the natural clay minerals that deliver the most suitable properties for adsorption performance and immobilisation of titanium dioxide (TiO_2); 2) synthesis, modification, and characterisation of the clay mixtures as alternative adsorbents, and titania immobilised onto modified porous kaolin as the photocatalyst; 3) evaluation and optimisation of their removal capability, kinetics and mechanisms toward different surrogate indicators of both nanomaterials via the batch and continuous water treatment system; and 4) integration of the adsorption-photocatalysis hybrid system as a major technical outcome for the treatment and reclaimantion of wastewater.

Three Australian natural clay minerals, bentonite, kaolins, and zeolite, were investigated to gain understanding of their physiochemical properties as well as their adsorption capabilities towards Congo red (CR) dye as a chemical surrogate indicator. Microscopic characterisations revealed the variation of the layered structures among clays, resulting in the differences in their adsorbent-adsorbate interaction profiles. The removal capacities of the clays were evaluated through the adsorption isotherms and kinetic studies, where it was found that Na-bentonite showed the best removal performance, followed by kaolin and zeolite. Thermodynamic and pH effect studies indicated that dye adsorption by the studied clays was a spontaneous and exothermic reaction, while pH conditions appeared insignificant. Further investigation has been emphasised on using different natural kaolins, in which the recyclability of these clay minerals was also taken into account. These results depicted a very high thermal stability of the kaolin structure. Repetitive recycled kaolin trials revealed good recovery of dye removal efficiency even

after five experimental tests. This study demonstrated the potential employment of these natural clays as alternative adsorbents for wastewater treatment.

To improve the removal efficiency of these natural clays as an economically viable adsorbent for wastewater treatment, a physical modification of the clay minerals was adopted in this present work. A feasible technical approach of combination and calcination of these natural clay materials to improve dye removal efficiency was developed to compromise the indigenous weakness of individual clays. The application of a mixture of clay minerals would be able to compromise the indigenous constraints of the individual clays. An optimisation study using calcium hydroxide or slaked lime as an additional calcium source for the clay mixture was included. Different characterisation methods, i.e. differential temperature analysis (DTA) coupled with thermogravimetric analyser (TG), scanning electron microscopy (SEM), and x-ray diffraction (XRD), were applied to comprehend the changed properties of the adsorbents during calcination treatment. The clay mixture and lime showed superior decolourisation, over 10–20 times to those of bentonite, kaolin and zeolite, at the optimum thermal condition at 300°C for 1.5 h. The great enhancement in dye removal efficiency was the contribution of the combination of an adsorption/precipitation mechanism. The instant precipitation of dissolved Ca ions with dye molecules illustrated the major contributor to dye removal, followed by the constant adsorption. The adsorbent mixture possessed the potential for recovery by heat treatment, of which their removal capacity was found comparable to the fresh materials even after the 5^{th} cycle.

The application of the adsorbent mixture was investigated in a pilot scale implementation, in which the laboratory scale fluidised-bed reactor (FBR) was developed in our research group. Optimisation of the operating parameters influencing pollutant removal performance of the FBR system, i.e. adsorbent loading, aeration rate, reaction time etc. was undertaken to facilitate the continuous operating scheme. The removal performance of oxyanion phosphate and nitrate in wastewater effluent, as well as their interference effect on dye elimination was also determined. The results revealed that the very effective elimination of CR and phosphate as complete removal can be

achieved, while the reduction of nitrate became less extensive due to the difference in their removal mechanisms, i.e. adsorption and precipitation etc. The feasibility of using the FBR system in the wastewater treatment was also investigated. Several municipal primary effluent samples were treated using the FBR system in continuous operation mode. The results showed an average 10-15% and 20-40% reduction of the nitrate and chemical oxygen demand (COD), respectively, while 100% phosphate removal was obtained over the experimental period. This study demonstrated that the FBR system with the formulated clay-lime mixture can be a cost-effective alternative treatment process for large-scale application in the wastewater industry.

Another advanced technology, heterogeneous photocatalysis, was used in this study to improve the quality of treated wastewater. A modified two-step sol-gel method was developed to synthesise a titanium dioxide impregnated kaolin (TiO_2-K) nanophotocatalyst, in which various parameters affecting the sol-gel formation and photocatalyst preparation were optimised. Further detailed investigation was carried out to improve the clay surface function prior to the impregnation. The natural kaolin was subjected to a series of acidic-alkali treatments to delaminate the clay structure, followed by thermal treatment. This clay pre-modification was designed to increase the specific surface area available for heterocoagulation with the microporous titania particles. Characterisation and photocatalytic activity of the TiO_2-K catalyst were performed by different microscopic techniques, i.e. XRD, SEM, TEM, UV-diffuse reflectance etc., and CR degradation, respectively. We examined thermal regeneration cycles of the catalyst lifespan, where the improvement of the photocatalytic activity was observed as a result of the change in average titania nanocrystal size and their porosity. This TiO_2-K exhibited a superior removal capability over the commercial TiO_2 in terms of initial adsorption and catalyst recovery. The self-settling capability of this catalyst can facilitate its separation after photooxidation treatment.

Finally, the integration of adsorption and photocatalysis techniques was investigated as an alternative hybrid system for municipal wastewater treatment. The primary and secondary biological effluents were preliminary treated by the FBR system with the synthesised clay-lime mixture before being subjected to an annular slurry photoreactor

(ASP) using the TiO_2-K catalysts. The formulated clay-FBR system demonstrated a prevailing removal efficiency towards PO_4^{3-}, NO_3^- and suspended solids; whereas the TiO_2-K-ASP showed superior degradation of dissolved organic content. This hybrid treatment approach demonstrated a synergetic enhancement for the chemical removal efficiency, and might be able to be employed as a feasible alternative treatment process for wastewater reclamation.

DECLARATION

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

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1. **V. Vimonses**, S. Lei, B. Jin, C.W.K. Chow, C. Saint. 2009. Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay materials. *Chemical Engineering Journal.* 148: 354-364. Copyright for this paper belongs to Elsevier B.V.

2. **V. Vimonses**, S. Lei, B. Jin, C.W.K. Chow, C. Saint. 2009. Adsorption of congo red by three Australian kaolins. *Applied Clay Science*. 43: 465-472. Copyright for this paper belongs to Elsevier B.V.

3. **V. Vimonses**, B. Jin, C.W.K. Chow, C. Saint. 2009. Enhancing removal efficiency of anionic dye by combination and calcination of clay materials and calcium hydroxide. *Journal of Hazardous Materials.* 171: 941-947. Copyright for this paper belongs to Elsevier B.V.

4. **V. Vimonses**, B. Jin, C.W.K. Chow, C. Saint. 2010. Insight into Removal Kinetic and Mechanisms of Anionic Dye by Calcined Clay Materials and Lime. *Journal of Hazardous Materials.* 177: 420-427. Copyright for this paper belongs to Elsevier B.V

5. **V. Vimonses**, B. Jin, C.W.K. Chow, C. Saint. 2010. Development of a pilot fluidised bed system with a formulated clay-lime mixture for continuous removal of chemical pollutants from wastewater. *Chemical Engineering Journal.* 158: 535-541. Copyright for this paper belongs to Elsevier B.V

6. M.N. Chong, **V. Vimonses**, S. Lei, B. Jin, C. Chow, C. Saint. 2009. Synthesis and characterisation of novel titania impregnated kaolinite nano-photocatalyst. *Microporous and Mesoporous Materials.* 117: 233-242. Copyright for this paper belongs to Elsevier B.V.

7. **V. Vimonses**, M.N.Chong, B. Jin. 2010. Evaluation of the Physical Properties and Photodegradation Ability of Titania Nanocrystalline Impregnated onto Modified Kaolin. *Microporous and Mesoporous Materials*. 132:201-209. Copyright for this paper belongs to Elsevier B.V.

8. **V. Vimonses**, B. Jin, C.W.K. Chow, C. Saint. An Adsorption-Photocatalysis Hybrid System as Alternative Wastewater Treatment by Multi-Functional-Nanoporous Materials. *Water Research*. 44: 5385-5397. Copyright for this paper belongs to Elsevier B.V.

Vipasiri Vimonses

Signed..... *Date*.....

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PREFACE

This present project aimed to develop an adsorption-photocatalysis hybrid process for wastewater reclamation using multifunctional clay materials. This thesis contains nine chapters, of which Chapter 2, 4, 5, 6, 7 and 8 are the main content. Chapter 1 provides a general induction and objectives of the project, whilst the general overview of the clay minerals and their current applications in water and wastewater treatment is illustrated in Chapter 2. Chapter 3 presents the experimental and analytical methodologies used in this study. More specific details are also explained in relevant chapters. The research outcomes and important findings are presented thoroughly in Chapters 4 to 8. Chapter 4 reports physiochemical properties of the natural clay minerals and their adsorption capacities. This also encompasses microscopic characterisations of the clay materials and examination of their adsorption behaviours through adsorption isotherms and kinetic models. Chapter 5 focuses on the development of alternative clay-based adsorbents that can deliver high removal efficiency towards organic and inorganic contaminants. A feasible physical approach includes optimisation of clay-lime mixture composition and their thermally treated condition. The adsorbent mixture demonstrated a significant enhancement in removal efficiency owning to a combination of adsorption/precipitation processes as a prime mechanism for dye removal. Chapter 6 describes application of the optimised clay-lime mixture in the mini-pilot scale operation. A lab designed fluidised-bed reactor (FBR) system was developed. We studied the influence of different operating parameters on the removal capacity in a continuous scheme, such as adsorbent loading, aeration rate, adsorbent re-loading time etc. We examined the removal of nominated oxyanions, i.e. phosphate and nitrate, prior to the practice of primary wastewater effluent in the FBR system. The obtained result indicated an excellent removal of anionic dye and phosphate nutrient; while the nitrate and COD removal was moderately achieved due to a different dominant mechanism. The following chapter, focussed on an application of the heterogeneous photocatalysis process for degradation of organic contaminants. A modified two-step sol-gel approach was used to immobilise layeres of titania nanocrystal onto a core kaolin substrate. Raw kaolin was preliminarly treated with a series of acid-alkali modifications to promote a delaminated sandwich silica structure, providing a high external surface area for TiO_2

immobilisation. The synthesised titanium dioxide impregnated kaolin (TiO_2-K) nanophotocatalyst demonstrated a superior adsorption capacity, settling ability and structural stability, in relation to other commercially available TiO_2 particles. In Chapter 8, the integration of adsorption and photocatalysis treatment for real wastewater effluents is reported. The consecutive treatment of adsorption through the clay –lime mixture FBR system, followed by the photooxidation via an annular slurry photoreactor (ASP) system using the synthesised TiO_2-K nanocatalyst was investigated. The adsorption-photocatalysis hybrid system revealed a synergetic enhancement for the contaminant removal efficiency. Complete elimination of phosphate content was obtained in the adsorption stage; while moderate nitrate removal was obtained from the hybrid treatment. The corresponding COD reduction during the photodegradation was further investigated by the advanced high performance size exclusion chromatography technique, where it revealed the shift of apparent molecular weight of the dissolved organic contaminants toward the smaller molecular weight region. This present study demonstrated that this adsorption-photocatalysis hybrid technology can be used as a feasible alternative treatment process for wastewater reclamation. Lastly, the results and conclusions from each individual chapter are given, in conjunction with further discussions of the future perspectives for continued work in this area.

This thesis has been prepared as a series of publications, of which Chapters 4, 5, 6, 7 and 8 have been published in referred international academic journals. The remaining Chapter 2 will be submitted for publication in a refereed journal. All the publications are closely relevant to the research area of this present work.