



Nano-photocatalytic Mineralization and Disinfection for Water Reclamation: From Catalyst Engineering to Process Optimization and Modelling

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“The important thing in science is not so much to obtain new facts as to discover new ways of thinking about them” - *Sir William Bragg*

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ABSTRACT

In this thesis, a feasible photocatalytic technology for water treatment was explored using a *bottom-up* approach in four separate research and developmental stages. These include (1) the synthesis, characterizations and photocatalytic activity (PCI) evaluation of a thin nanocrystals layer of titanium dioxide (TiO_2) immobilised onto modified mesoporous kaolin clay; (2) optimization and kinetics study of the photocatalytic reaction with recalcitrant organic dye Congo red (CR); (3) optimization and kinetics study of the photocatalytic disinfection with surrogate *Escherichia coli* and (4) assessment of a sequential batch reactor (SBR) mode for semi-continuous removal of dissolved pharmaceutical organic matters from secondary municipal wastewater.

A modified two step sol-gel approach was used to immobilise layered of TiO_2 nanocrystals onto structurally stable kaolin ($\text{TiO}_2\text{-K}$) particles for enhanced physical properties. The $\text{TiO}_2\text{-K}$ demonstrated a superior settling ability, adsorption capacity, PCI and stability compared to other conventional TiO_2 particles. Microscopic characterizations revealed that the modified kaolin provides a delaminated sandwich silica structure which minimizes chemical intercalation and further promotes high external surface area for heterocoagulation with microporous TiO_2 nanocrystals. Thermal regeneration cycles for the photocatalysts lifespan study examines that the PCI of $\text{TiO}_2\text{-K}$ was improved over six treatment cycles, as a result of the change in average TiO_2 nanocrystals size and porosity.

The real operational performances of the $\text{TiO}_2\text{-K}$ photocatalysts for the organic degradation in water were investigated in a self-designed laboratory scale annular slurry photoreactor (ASP) system. The effect of key operational factors for the ASP system, such as $\text{TiO}_2\text{-K}$ loading, pH, aeration rate and CR concentration were investigated. Results show that pH was the most significant factor that affects the adsorption and photocatalytic reactions in the ASP system. The point of zero charge (PZC) for the $\text{TiO}_2\text{-K}$ particles was found to shift towards more basic extent of 9.5, resulting in a detrimental PCI when the ASP was operated at $\text{pH} > \text{PZC}$ ($\text{TiO}_2\text{-K}$). The optimum operating conditions of the ASP was found to be 6.0 g L^{-1} $\text{TiO}_2\text{-K}$ loading, pH 7.0, 7.5 L min^{-1} aeration rate and 40 mg L^{-1} CR concentration. Under

these optimum ASP conditions, the CR was completely photo-degraded in 4 h along with 80% reduction in chemical oxygen demand (COD) of the LC/MS-identified intermediates species.

Owing to the lack of understanding and predictive in the singular optimum ASP condition, the Taguchi method was employed to collectively optimise the operating factor; determine the synergistic factor interactions and key influential factors, and further develop an empirical response surface model for the PCI prediction. From the Taguchi experiments, the photo-oxidation kinetics of CR exhibited saturation kinetics and thus, the Langmuir-Hinshelwood (L-H) model was applied. The Taguchi method predicted the optimum L-H apparent first order rate constant of $3.46 \times 10^{-2} \text{ min}^{-1}$ under the ASP operating conditions of 8.0 g L^{-1} $\text{TiO}_2\text{-K}$, pH 5.0, 7.5 L min^{-1} aeration rate and 40 mg L^{-1} CR. Analysis of variance revealed that the CR concentration is the most significant factor, while pH appears to be the least significant one. The aeration rate in ASP was determined to have a significant synergistic effect on the $\text{TiO}_2\text{-K}$ loading from the 3-D response surface plot.

When the photo-oxidation of CR was referenced to the anatase titanate nanofiber (TNC) with PZC of 4.6, it was observed that the ASP operation was constrained by a narrow functional pH range. The optimum ASP operating conditions with slurry TNC were 4.0 g L^{-1} TNC loading, pH 3.0, 5 L min^{-1} aeration rate and 60 mg L^{-1} CR, resulting in a degradation rate of $3.47 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$. Subsequent Taguchi analysis found that the low PZC (TNC) has a profound effect on the synergistic interaction with its loading concentrations. The 3D response plots showed that the low PZC (TNC) could be compensated with a high TNC loading at $\text{pH} > \text{PZC (TNC)}$ and low aeration rate for optimal conditions. The Taguchi method predicted that the optimum ASP operating conditions were 6.0 g L^{-1} TNC, pH 9, 5.0 L min^{-1} aeration rate and 20 mg L^{-1} CR. Analysis of variance shows that the pH, aeration rate and CR concentration were the significant factors, while TNC loading is the least significant one.

The PCI for both photocatalysts were also tested against the photo-disinfection of *Escherichia coli* (ATCC 11775) as the surrogate indicator in the batch ASP system. In both investigations, the photocatalytic inactivation kinetics was found to exhibit non-linearity in the enumerated bacteria against irradiation time. The modified Hom model was used to fit a sigmoidal-shape bacterial survivor curve with strong shoulder and tailing characteristics.

Using the TNC, the dissolved oxygen level in the open ASP system was found to be constantly replenished and further affects the photocatalytic inactivation kinetics. An L-H mechanistic model was proposed to determine oxygen transfer limitation in the photocatalytic disinfection process at different TNC loadings. A Fe^{2+} up to 1.0 mg L^{-1} could initiate the residual disinfecting effect (RDE) of the photocatalytic reaction in the ASP, with constant dissociation of hydrogen peroxide (H_2O_2) to hydroxyl radicals (OH^\cdot). The RDE was diminished with increasing COD values. To effectively suppress the bacterial regrowth, the dissolved organic carbon should be well suppressed below 16 mg COD L^{-1} .

Finally, the ASP system was operated as a SBR mode to allow semi-continuous treatment of the secondary municipal wastewater spiked with pharmaceutical Carbamazepine (CBZ) compound. A microfiltration module of $0.2 \mu\text{m}$ in porosity was fitted parallel to the reactor light source. The effects of key factors such as SBR cycles, nitrate (NO_3^-), phosphate (PO_4^{3-}), COD and photocatalysts on the effective photocatalytic CBZ removal were investigated. When the CBZ was degraded in the presence of high molecular weight effluent organic matter (EOM) in wastewater, the photocatalytic reaction appeared to have a preferential attack on the EOM that subsequently lower the degradation efficiency of CBZ. Other than this, the PO_4^{3-} in the wastewater showed a detrimental effect of photocatalyst fouling and deactivation on both TiO_2 catalysts used, resulting in a strong catalyst deactivation, and fouling of the catalysts. The deactivation and fouling are site specific and do not completely retard the photoactivity of the catalysts used. The sequential batch-annular slurry photoreactor (SB-ASP) was effectively operated up to two SBR cycles at catalyst loading (1 gL^{-1}) without any photocatalyst replacement, as the semi-continuous operation allows simultaneous water discharge and UV photocatalyst reactivation phase.

DECLARATIONNAME: Meng Nan ChongProgram: PhD (Chemical Engineering)

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1. **M.N. Chong**, B. Jin, C.W.K. Chow, C. Saint. Recent developments in photocatalytic technology for water treatment: A review. Submitted to *Water Research*.
2. **M.N. Chong**, V. Vimonses, S. Lei, B. Jin, C. Saint, C. Chow. 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.
3. V. Vimonses, **M.N. Chong**, B. Jin. Evaluation of the physical properties and photodegradation ability of titania nanocrystalline impregnated onto modified kaolin. Submitted to *Microporous and Mesoporous Materials*.

4. **M.N. Chong**, S. Lei, B. Jin, C. Saint, C. Chow. 2009. Optimisation of an annular photoreactor process for degradation of Congo red using a newly synthesized titania impregnated kaolinite nano-photocatalyst. *Separation and Purification Technology* 67:355-363. Copyright for this paper belongs to Elsevier B.V.
5. **M.N. Chong**, B. Jin, H.Y. Zhu, C. Chow, C. Saint. 2009. Application of H-titanate nanofibers for degradation of Congo red in an annular slurry photoreactor. *Chemical Engineering Journal* 150:49-54. Copyright for this paper belongs to Elsevier B.V.
6. **M.N. Chong**, B. Jin, C. Chow, C. Saint. 2009. A new approach to optimise an annular photoreactor system for the degradation of Congo red: Statistical analysis and modelling. *Chemical Engineering Journal* 152:158-166. Copyright for this paper belongs to Elsevier B.V.
7. **M.N. Chong**, H.Y. Zhu, B. Jin. 2010. Response surface optimization of photocatalytic process for degradation of Congo red using H-titanate nanofiber catalyst. Accepted by *Chemical Engineering Journal* 156:278-285. Copyright for this paper belongs to Elsevier B.V.
8. **M.N. Chong**, B. Jin. Photo-disinfection activity and kinetics of Escherichia coli using novel titania impregnated kaolinite catalyst. Submitted to *Chemical Engineering Journal*.
9. **M.N. Chong**, B. Jin, H.Y. Zhu, C. Saint. Bacterial inactivation kinetics, regrowth and synergistic competition in a photocatalytic disinfection system using anatase titanate nanofiber catalyst. Submitted to *Journal of Photochemistry and Photobiology A: Chemistry*.
10. **M.N. Chong**, B. Jin, C. Saint. Kinetic and mathematical modelling for the photocatalytic inactivation of Escherichia coli in an annular slurry photoreactor using titanate nanofiber catalyst. Submitted to *Chemical Engineering Journal*.

11. M.N. Chong, B. Jin, C.W.K. Chow, H. Zhu, C. Saint. Assessment of sequential batch photoreactor system for the removal of Carbamazepine from secondary municipal wastewater: Impacts of effluent organic matter and inorganic ions. Submitted to *Environmental Science and Technology*.

Signature..... Date.....

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PREFACE

This thesis contains nine chapters, of which six chapters (Chapter 2, 4, 5, 6, 7 and 8) comprise the main body. In Chapter 1, a general introduction to this project and thesis is outlined. Chapter 2 contains a comprehensive literature review, which has been submitted for publication. Chapter 3 is a general introduction to the experimental materials and methods used in this study. Specific details of the methods are given in the relevant chapters. This project aimed to develop and utilize new TiO₂ photocatalysts for the integration with an annular photoreactor system for the treatment of wastewaters. The research outcomes and findings are presented thoroughly in Chapters 4 to 8. In Chapter 4, the research focuses on the synthesis, characterisation and application of nanocrystalline titania impregnated onto modified kaolinite clay (TiO₂-K) for enhanced catalyst recovery and adsorption capacity. The durability and physical changes in the structure of the catalyst over repetitive use in water treatment was also identified. In Chapter 5, the photocatalytic activity of two different self-made photocatalysts (i.e. TiO₂-K and titanate nanofiber catalyst (TNC)) on sub-micron immobilizers were evaluated and compared in an annular slurry photoreactor (ASP) system. The influence of different photoreactor operational factors on the photooxidation rate of Congo red was studied. However, the optimized operating conditions as obtained from the studies were seen to be rather frail due to a lack of data on the factor interactions and correlations. In Chapter 6, a relatively new multi-variable optimization approach based on response surface optimization was employed to statistically identify the most significant factors, factor interactions and correlations for the two photocatalysts used. These two photocatalysts showed different isoelectric properties. The TNC catalyst with low point of zero charge experienced higher operational obligations from the factor interactions. In Chapter 7, the photo-disinfection using both photocatalysts was also evaluated under different operational conditions of the ASP system. The photo-inactivation rate of bacterial *Escherichia coli* (ATCC 11775) was evaluated using different disinfection rate models. It was observed that with the thin fibril morphology of the titanate nanofiber catalyst, an additional limiting term of dissolved oxygen should be introduced to the denominator of the mechanistic Langmuir-Hinshelwood equation. Furthermore, the residual disinfecting effect of the TNC catalyst with different ferric ion concentration was assessed and it was found that the underlying bacterial regrowth mechanism depends on the organic carbon level in water.

Chapter 8 demonstrated the possibility of using the ASP system in a sequential batch reactor (SBR) operation mode for the semi-continuous treatment process of secondary wastewater containing Carbamazepine, a pharmaceutical compound that usually penetrates through the biological activated sludge treatment. The influence of catalysts, SBR cycle, organic matter and inorganic ions on the photo-degradation performance for removal of Carbamazepine and chemical oxygen demand was assessed. Finally Chapter 9 draws the conclusions from each individual published paper and results chapters and discusses the possible future prospects for continued work in this area.

Chapters of 4, 5 and 6 have been partially published in refereed academic journals. The remaining in Chapter 2, 4, 5, 6, 7 and 8 have also been submitted for consideration of publication in different refereed academic journals. All the papers are closely related to the research field of this work.