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 5th 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

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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.

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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 preliminarily 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.

CHAPTER 1

INTRODUCTION

1. Background

The global population has grown significantly over the last century, this has lead to a great increase in the demand for water supply. The water shortage situation could develop into a global water crisis. Reliance on surface water bodies alone seems to be insufficient to respond to this rising demand, while heavy extraction of groundwater can lead to negative long term effects such as land subsidence. Seeking new reliable water sources, therefore, has turned into an urgent environmental issue. Treated wastewater is one of the promising alternatives as a reclaimed water source, which has drawn an interest over the last few years, especially in arid and semi-arid regions where water sources are limited. The treated wastewater is a readily available and reliable source, and recycling would reduce the extensive amount of water extracted from the environment [1]. The potential use of the treated wastewater can be varied significantly, depending upon the degree of treatment and more importantly on public acceptance. This practice has been carried out in many countries especially for irrigation purposes, e.g. agriculture, landscapes, and recreational areas [2].

Water quality is a crucial issue for reuse of the treated wastewater. Health hazards are the major restriction for the reuse of wastewater which leads to a higher stringency of the water quality requirement. Generally, the treated wastewater must at least meet minimum safety standards for specific reclaimed purposes. In general, conventional treatment processes, including primary and secondary treatments, are able to remove over 90% of chemical contaminants and up to 95-99% of microorganisms. However, direct reuse of this effluent cannot be practised without further treatment due to the presence of high organic content and pathogenic organisms [3-4]. The effluent from secondary treatment still contains some suspended, colloidal, and dissolved constituents as well as a variety of pathogens which are hazardous. Hence, consecutive tertiary treatment and disinfection processes are required to ensure the exclusion of pollutants, and that the water obtained is harmless. Traditional tertiary treatment such as deep filtration, macro-filtration and typical adsorbents can only partly remove the residuals, while the remaining pathogens are passed to the disinfection stage for final removal. To date, the currently available treatment technologies regarded as effective processes for reclaiming the municipal wastewater effluent are still experiencing a series of technical and economical challenges. This has lead to extensive research of advanced technologies that can overcome such inherent limitations.

Nanotechnology has become one of the most significant technologies of the 21st century. It encompasses a broad range of tools, techniques and applications based on a structure size between 1 and 100 nm. A unique aspect of nanotechnology is the enormously increased ratio of surface area to volume presented in many nanoscale materials, leading to new possibilities in surface-based science. Due to their small size and well-organised structure, nanoscale materials offer an alteration of physio-chemical properties of the corresponding bulk material properties, e.g. colour, strength, and thermal resistance etc., providing opportunities to be exploited in many industrial facets. Nanomaterials are considered as new functional materials used in industry based techniques and processes, such as cleaning-up industrial contamination, and improving energy production and uses.

Water purification is identified as a priority area for nanotechnology applications due to readily available appliances incorporating nanomaterials, and the public pressure for clean water requirement [5]. High quality treated water can be produced from this innovative technology for reuse purposes and with the benefit of not generating disinfection by-products. Over decades, a wide range of water treatments incorporating nanosciences have been studied such as nanofiltration membranes, nanoporous/filter materials, nanocatalysts, magnetic nanoparticles and nanosensors. Many technology developers stated that these nanotechnologies offer more cost-effective processes for removal of aqueous pollutants in wastewater [5].

Nanoporous materials are considered to be an alternative resource offering potential for the wastewater treatment industry. They show a specific capability in the removal of hazardous substances either through adsorption or size exclusion. The presence of nanopores facilitates their important uses in various fields such as ion exchange, separation, catalysis, sensing, biological molecular isolation and purification. The major advantages of using these materials over conventional or advanced membrane filtration are due to their low-cost and abundant availability, lower energy requirement for operation, and the capability of handling wastewater with high organic content. A number of publications have addressed the utilisation of nanoporous materials for removal of various pollutants such as organic and inorganic compounds, heavy metals, microorganisms etc. In some cases, the polluting adsorbates can be ultimately decomposed through thermal adsorbent regeneration. In addition to this, the applications of nanoporous materials have been recently extended into catalytic oxidation of water pollutants, in particular for degradation of recalcitrant or non-biodegradable compounds. The materials are commonly used either as an active catalyst itself or as a supported substrate due to their high surface area. It is suggested that the introduction of nanoparticles in heterogeneous catalytic processes can appreciably enhance the catalytic efficiency [6].

Among available nanoporous materials, natural clay minerals have received considerable attention as alternative low–cost materials due to being non-toxic, abundant, environmentally friendly and possessing multifunctional properties depending upon the types of clays. Zhou et al [7] suggested that the nano-structural layer and nano-sized layer space of the clay minerals can act as naturally occurring nanomaterials or as nano-reactors for production of nano-species, nanoparticles or nanodevices. However, in many instances, inherent downsides of the natural clays such as high impurities, heterogeneous functional surfaces, fragile molecular structure, as well as favourable interaction toward particular compounds etc, has limited their uses to certain applications. Such drawbacks can be minimised by adopting a physiochemical modification prior to utilisation, i.e. chemical grafting, sonication, mechanical grinding, acid–alkaline treatment, thermal activation etc.

Nevertheless, selecting appropriate types of clay together with suitable modification methods is considered as one of the technical challenges. Variation of the clay structures based on their types and origins could result in different performances and behaviours toward the treatments. Therefore, it is essential to gain in-depth information of the clay characteristics and their adsorption properties toward a targeted compound. This leads to a requirement of the adsorption isotherms and kinetic studies, where the removal performance and mechanisms of the clays can be determined. Furthermore, the significant effects of influential systematic parameters on the adsorption efficiency such as solution pH and temperature are also observed in many cases.

Despite being used as alternative adsorbents, the application of the clay and modified clays in the area of Advanced Oxidation Processes (AOPs) for water and wastewater treatment has gained much attention. The AOPs principle is based on the in-situ generation of highly reactive radicals (i.e. $OH^{\bullet}$, $O_2^{\bullet -}$ etc.) for oxidation of recalcitrant organic compounds and pollutants, pathogens and disinfection by- products [8-10]. Among these, heterogeneous titanium dioxide (TiO_2) photocatalysis in a slurry system (suspension of fine powdered TiO_2) has been widely studied, owing to its potential to mineralise a range of refractory organic pollutants at ambient temperature and pressure into innoxious substances [11]. However, a separation of the fine TiO_2 catalysts after treatment can be energy intensive and time consuming, resulting in a significant reduction in the benefits of this technique in water treatment industries. This technical constraint leads to development of an immobilised photocatalyst on an inert support to avoid costly separation processes after treatment. The titania immobilisation process often involves several intense chemical and thermal interactions, hence the clay porous materials that possess a highly stable structure are often in great demand as catalyst supports.

Other technical challenges commonly facing such nanotechnological applications in large scale wastewater treatment are the difficulty in process implementation and recovery of the materials after treatment. Since small size particles are often employed to deliver high adsorption/removal efficiency, the operating procedure can be complicated. In terms of engineering aspects, it is believed that such problems can be overcome by a well-designed reactor and optimised operating conditions. The appropriate design of an operating module incorporating proper arrangement of treatment processes could offer a better potential to deal with complicated wastewater sources. In this present work, an integration of adsorption and photocatalysis processes using an in-house developed multifunctional nanoporous material will be investigated to achieve a high quality of treated wastewater for reclamation.

2. Aims

The aim of this study was to develop multifunctional nanomaterials and an effective hybrid treatment system that could be employed as an alternative tertiary wastewater treatment process for reclaimed wastewater.

The project involves two major technological practices for wastewater treatment, i.e. adsorption and photocatalysis, which encompass four separate research and development stages. These 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 photocatalyst immobilised onto modified porous kaolin;

(3) Evaluation and optimisation of both nanomaterials for their removal capabilities, kinetics and mechanisms toward different surrogate indicators such as industrial dye and sewage wastewater via the batch and continuous water treatment system;

(4) Integration of the adsorption-photocatalysis hybrid system as the best available technical solution to treat reclamation wastewater.

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<u>CHAPTER 2</u>

LITERATURE REVIEW

APPLICATION OF CLAY MINERALS AS ALTERNATIVE ADSORBENTS AND PHOTOCATALYSTS FOR WATER AND WASTEWATER TREATMENT

1. Background

Clays and clay minerals have been widely utilised for many industrial practices, such as in geotechnology, agriculture, construction, engineering, process industries, and environmental applications [1-2]. The major utilisation of the clay minerals can be classified into two contrasting broad classes, i.e. based on their inertness and stability, and their reactivity and catalytic activity [3].

Among natural materials, clay minerals (aluminosilicates) have several important advantages over alternative adsorbents. They are inexpensive, abundantly available and non-toxic, and have good sorption properties and ion exchange potential for charged pollutants. They possess a wide pore size distribution, ranging from micro- (<20 Å) to mesopores (20-500 Å). The porosity of the minerals is formed from fractures in the particle surfaces, staggered layer edges, whereas voids are generated by overlapping of stacked layers and interlayer regions [4]. Incorporation of various species and nanoparticles into the interlayer space allows clay minerals to be utilised as new functional materials [5]. These clay mineral-based functional materials and nanocomposites demonstrate a great variety of applications for catalysis and adsorption, environmental remediation, and for manufacturing polymers, electronics and fuel cells in industries [2].

A number of clay minerals have been investigated and used as alternative low-cost materials for water and wastewater treatment, including sepiolite [6], kaolinite [7-9], montmorillonite [10], smectite [11], bentonite [8,12] and zeolite [8,13-14]. These clay minerals are of interest according to their variety of structural and surface properties, high chemical stability, high specific surface area and high adsorption capacity [15]. Also, such features allow the clays to be tailored to suit specific decontaminating purposes, which can bring about considerable advantages from an industrial application point of view.

In this chapter, an overview of the physiochemical properties of clay minerals will be discussed, including the current modification techniques employed to alter the clay properties to suit their target performance. Thereafter, the applications of these clay minerals in water and wastewater treatments will be focused, in particular as alternative low-cost adsorbents and catalytic supports for photocatalytic degradation, which are the objective of this study.

2. Physiochemical Properties and Characterisation of Clay Minerals

Depending upon the geographic source of origin, the physiochemical properties of clay minerals can be varied and is the main determining factor for their utilisation. The term “clay” is generally used to refer to aluminosilicate minerals whose particle sizes fall into a micron range, and possess cation-exchange properties [16]. With variety in the structural orientation, clays can be categorised into different groups. A phyllosilicate or sheet silicate is one of the most important groups for industrial applications, and is generally termed as “clay minerals”. The basic structure of the clay minerals consists of a tetrahedral sheet of polymerised silica and octahedral sheet of alumina. The alumina octahedra can polymerise in two dimensions by sharing four oxygen atoms, in which two oxygen atoms are left unshared, providing a negative charge of two. This negative charge is counterbalanced by hydrated cations, e.g. Na^+, Mg^{2+}, Ca^{2+} etc., which are located in the interlamellar space. Such interlamellar cations are typically exchangeable and their amount indicates the cation-exchange capacity (CEC) of the clay minerals [17]. Due to their extremely fine particles, the clay minerals tend to exhibit the chemical properties of a colloid [18-19]

In general, clay minerals are identified according to their magnitude of net layer charge, layer structure arrangement, and interlayer species [20]. The clays are placed alternately by tetrahedral and octahedral sheet structures, which are classified into different layer types. Such structures are distinguished by the number of tetrahedral and octahedral layers [19]. Diversities in such layered structures are categorised into different classes e.g. smectites (montmorillonite, saponite), mica (illite), kaolinite, serpentine, pylophyllite (talc), vermiculite and sepiolite [21]. The most common clay minerals used in the water and wastewater industries are classified into 3 different types, i.e. 2:1 and 1:1, and zeolite groups, which will be employed in this study.

The 2:1 type clay minerals consist of two silicon-oxygen tetrahedral sheets that sandwich an aluminium-oxygen-hydroxyl tetrahedral sheet (Fig.1a). There are three main mineral groups possessing this structure, i.e. illite, vermiculite, and smectite [22-23]. The isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral sheet and Mg^{2+} or Fe^{2+} for Al^{3+} in the octrahedral sheets could result in a negative surface charge on the clay. These charges are permanent and less subjective to pH changes, yet such pH sensitivities do vary with the type of the host clay [19]. This unbalanced charge can be compensated by exchangeable cations, i.e. Na^{+} or Ca^{2+}, which are relatively loosely held, giving rise to cation exchange properties. A second negative charge takes place as a result of dissociation of the hydrogen in various hydroxyl groups, including SiOH and AlOH groups, of which the dissociated propensity increases with an increase in pH. Another source of negative charge of the clays can be owing to their low coordination number edge atoms; these charges can be neutralised by compensation cations [19]. Such a layer structure of the clay allows expansion (swelling property) when it contacts water, which provides an additional mineral surface for cation adsorption [19]. Examples of common 2:1 clays used in chemical and industrial applications are montmorillonite and bentonite. Montmorillonite possesses a very large surface area, and hence has been the subject of most studies involving clay nanocomposites [24]. Bentonite can be divided into different types based on the dominant exchangeable cation, i.e. Na-bentonites and Ca-bentonites. It acquires unique properties, such as large chemically active surface area to volume ratio, a high cation exchange capacity and inter-lamellar surface possessing unusual hydration characteristics [25]. These features allow them to be modified by a range of different surface treatments such as organoclay [26], acid-alkali treatment [27] and grafting polymer [28]. The use of montmorillonite and bentonite based materials in water treatment have been widely reported, i.e. removal of Cr(VI) [26,29], Pb (II) [30], industrial dyes [8,12,31] , coagulation [32], flocculation [33] etc.

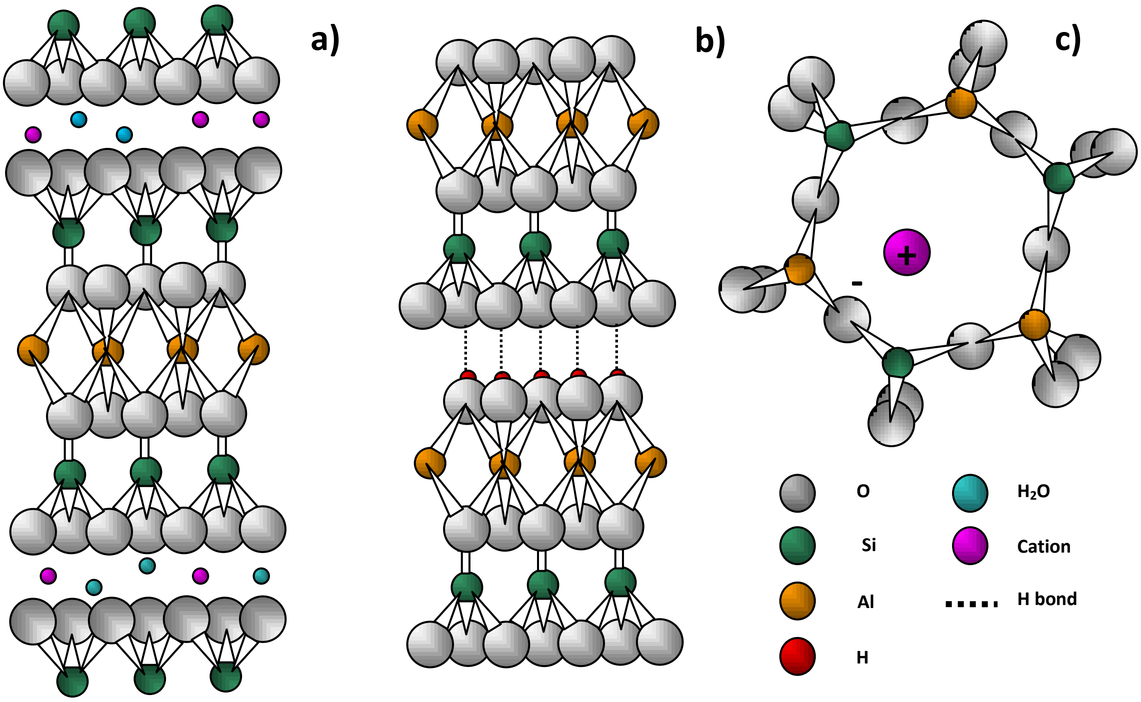

Figure 1: A diagram of clay mineral molecular structures a) Bentonite (Montmorillonite), b) Kaolinite and c) Zeolite [8]

In contrast, the 1:1 clay mineral refers to clays with a structure comprising as alternative layers of a tetrahedral silica sheet and an octahedral alumina sheet, where the layers are bound together by hydrogen bonds. Kaolinite is one of the most commonly known 1:1 clay minerals, which is classified as a phyllosilicated (sheet silicates) mineral with the chemical composition of $Al_2Si_2O_5(OH)_4$. The layers are tightly held together to form clay stacks with a basal spacing of around 7.1°A [34]. The lattice structure of kaolinite is nearly in perfect order and thus there is relatively low isomorphous substitution, leading to a limited swelling of kaolinite in water (Fig. 1b). Such ordered arrangement of the clay gives the kaolinite a rigid and chemically and thermally stable structure with a low expansion coefficient. Thus, most sorption activity tends to take place along the edges and surfaces of the clay structure [35].

Zeolite is very similar to the clay minerals in its composition, i.e. hydrated aluminosilicates, however they differ in their crystalline structure. This inorganic polymer represents the largest group of microporous materials, which have a high adsorptive selectivity feature. Zeolite is built by connecting SiO_2 and AlO_4 tetrahedra in a network formation of a cage-like structure as shown in Fig. 1c.

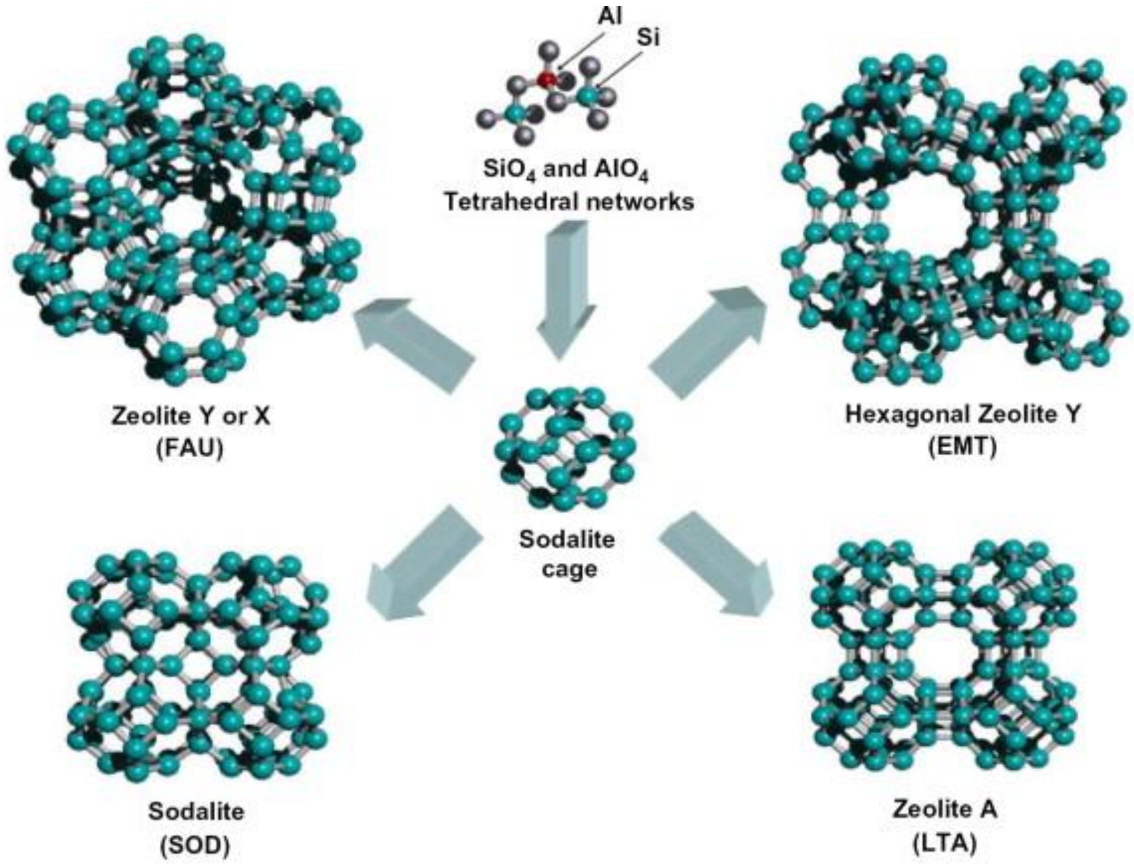

Figure 2: Framework structures of zeolites based on sodalite cage as a secondary building block [36]

Fig. 2 demonstrates the different framework structures of zeolites based on the sodalite cage as a secondary building block [36]. Their symmetrically stacked alumina and silica tetrahedral sheets lead to an open and stable three dimensional honey comb structure with a negative charge interconnected cages and channels with Brønsted and Lewis acid sites [19, 37-38]. These negative charges within the pores can be neutralised by positively charged ions, i.e. Na^+, which are exchangeable with certain cations in solutions such as heavy metals and ammonium ions [22, 39]. Variation of functional properties of zeolites enables them to be employed as adsorbents, molecular sieves, membranes, ion exchangers and catalysts in industrial applications for water/wastewater treatment, gas separation and dehydration processes [40]. However, the major use has been found in water and wastewater treatment [41].

Aluminosilicate zeolites are highly hydrophilic adsorbents owning to their electrostatic charged framework and abundance of extra-framework cations. Other factors contributing to their unique hydrophilicity include defect sites, surface nature, metal constitutions in the framework, and the amount of coke deposits [36]. The zeolites with medium and large pores are often used in catalysis to facilitate the diffusion of molecules reaching the catalytic active sites in the material pores. In contrast, those with a high concentration of cation exchange sites and small pores are more suitable for adsorption processes due to the molecular sieving effect. To date, there are more than 40 species of natural zeolites (with more than 100 species for synthetic ones) [42]. Among these, clinoptilolite, a mineral of the heulandite group, is the most abundant and frequently studied [43], and has been widely used for many industrial applications [14].

A number of researchers have evaluated the capacity of zeolites in removal of methylene blue dye in water [44], phenols and chlorophenols [45], and geosmin and methylisoborneol from drinking water [46]. In addition, the chemical and cage-like structural characteristics of zeolites make them very effective to eliminate toxic metal ions, e.g. Pb^{2+} [47], radionuclides and ammoniacal nitrogen from wastewater [41,43].

3. Modification of clay minerals

The physiochemical properties of clay minerals can vary, depending upon the geographic source of origin, and is the main factor determining their ultimate utilisation. These properties can be altered by several modification methods to enhance their functional ability and efficiency. Such alterations have been addressed in many publications and are summarised below.

3.1 Acid/Alkali treatment

One of the most common chemical methods for clay modification is known as acid activation. This modification involves the treatment of clay with concentrated inorganic acid, i.e. HCl or H_2SO_4. This process results in an increase in the clay specific surface area, porosity and surface acidity [48]. Important parameters for the acidification, which determine the properties of the products, include the nature and type of clay, acid concentration, temperature and activation time, etc. [17, 49]. In addition, this acid activation is believed to promote catalytic activity of the clay by increasing the number of Brønsted and potential Lewis sites.

Komadel and Madejová [50] stated that the acidification of clay minerals under controlled acid conditions can induce partial dissolution of other elements (i.e. Fe and Mg) within the clay structure. Such an acid attack preferentially occurs at the octahedral alumina sheet, while the tetrahedral sheet (i.e. SiO_4 and SiO_3OH) remains largely intact [51]. This dealumination leads to an increase in the silica to alumina ratio. The opposite was observed in alkali treatment which also resulted in dissolution of the most irregular (amorphous) mineral particles [52]. This alteration was confirmed by X-ray diffraction (XRD) diagrams where they showed severe destruction of the crystal lattice after acid treatment; while sharpening of the XRD reflection after alkali treatment was observed. A similar phenomenon was also addressed by Gupta and Bhattacharyya [53] where they demonstrated that the intensities of the characteristic XRD peaks can reduce upon acidification. Many studies observed the increase of porosity in the tens of nanometres range after acid treatment [54], in which these pores could be formed as cavities on basal or edge surfaces of the clay particles or as a result of a decrease in particle sizes due to partial dissolution of larger particles. The adsorption studies of the activated montmorillonite demonstrated a considerable improvement in adsorption capacity towards diazo acid dyes such as amido black [55] and methylene orange [56] after acidification by HCl. The increase in its adsorption capacity was due to the substitution of the Al^{3+} or Fe^{2+} of the clay by H^+ after acidification demonstrated by the specific surface area (BET) and XRD analysis. Chemical treatment under acid and alkali conditions can result in remarkable changes in pore behaviour of the clay minerals. It is recognised that the alteration can be more prevalent in nanosize pores than larger pores [54].

In general, both acid and alkali treatments can increase variations in surface charge, while the cation exchange capacity (CEC) is altered depending on the types of minerals and treatment methods. Acidification leads to an incremental increase in the amount of weakly acidic surface functional groups associated with a decrease in the amount of groups of stronger acidic character. Unlike alkali treatment, the amount of surface groups of intermediate acidity increases and that of low acidity decreases [57].

Jozefaciuk and Matyka-Sarzynska [27] studied the effect of acidification and alkalisation on nanopore properties of bentonite, biotite, illite, kaolin, vermiculite and zeolite by well-defined adsorption-desorption isotherms, where they found an increase in specific surface areas of the minerals under both conditions. However, Komarov [58] suggested that the impacts of acidic treatment were more pronounced for montmorillonite, whilst negligible change was observed in the case of kaolinite.

Guo et al [59] prepared decolourising ceramsites via acid-alkali treatment with H_2SO_4 and NaOH, followed by the thermal activation from different clays minerals, i.e. sepiolite, bentonite and palygorskite etc. They observed that clays possessing high Al_2O_3, Fe_2O_3 and MgO content demonstrated the best performance for dye and organic removal. This study also demonstrated the preliminary basic treatment followed by acid activation was found to enhance the overall decolourising performance through chemical flocculation with precipitated metal ions from the adsorbent.

The changes of surface and morphological properties of the treated clay after chemical modification can be examined via scanning electron microscopy (SEM) imaging. Melo et al [24] observed the surface alteration of kaolinite after chemical treatment with H_2O_2 and acid modification (Fig.3). They observed that the micro-size particles of the untreated clay are composed of individual platelets conglomerating into larger size particles. After treatment with H_2O_2, a separation of some discrete platelets was evidenced. This can be explained by the removal of organic matter, which contributes to a reduction of the agglomerating effect. Such chemical treatment also was found to increase the specific surface from 35.3 to 53.0 $m^2 g^{-1}$.

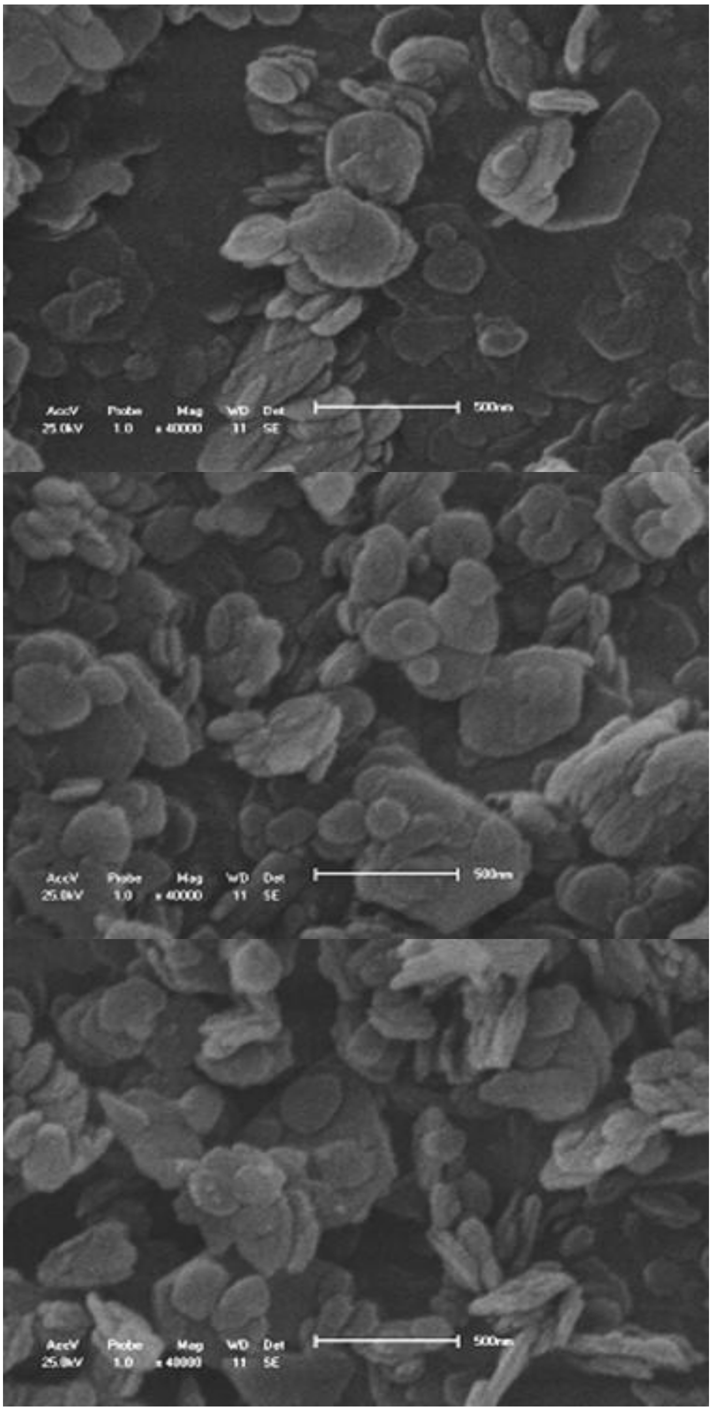

Figure 3: SEM images of a) untreated kaolinite, b) kaolinite after chemical treatment with H_2O_2, and c) kaolinite after chemical treatment using H_2O_2 and acid acidification with HNO_3 and H_2SO_4 [24]

3.2 Thermal treatment

Calcination is another well-known treatment method for the activation of clay adsorbents. Heating can bring about the modification of structure, physiochemical properties, and composition of the clay minerals, including strength, cohesion, consistency limits, water content, maximum dry density, internal friction angle, particle size, permeability and specific gravity etc. [60]. Additionally, the thermal treatment can assist stabilisation of the clay to maintain important permanent properties. These concomitant changes can be varied from one clay mineral group to the other, as well as the particle size and heating regime. Raising the temperature to dehydration stage leads to a loss of adsorbed water causing alteration of the macro- and microporosity of the clay minerals, resulting in the collapse of interlayer spaces and reduction of cation exchange capacity (CEC). Partial loss of the adsorbed and hydration water can increase hydrophilicity and surface acidity of the materials [61]. It is often that the heat treatment is preceded by other treatment methods, i.e. chemical modifications, to achieve better performance.

Heller-Kallai [61] suggested that thermal treatment of the clay materials can be carried out in different forms: i) without any admixtures or pre-treatment; ii) mixed with various reagents before heating, iii) after pre-treatment, i.e. acid activation; and iv) after pre-heating and pre-treatment, i.e. by acid activation and subsequent re-heating. The degree of thermal tolerance can vary depending upon the clay types. It is suggested that dehydration at a high temperature can cause the irreversible collapse of the structure. The clay platelets are bonded electrostatically. Therefore, dehydration of cations can result in a reduced adsorption ability of the clay [36]. For instance, the study by Joshi et al [61] revealed a gradual increase in the strength of the studied clays (kaolinite and bentonite), and clay sediment with an increase in heating temperature. Yet, such significant and permanent increase in their strength occurred only after dehydroxylation. By continuing heating to a temperature above the dehydroxylation stage, the clays became resistant to disintegration upon immersion in water. Thus, thermoanalytical measurement of the clay minerals is often performed to understand the stability of their structure against an elevated temperature gradient. The thermogravimetry/differential thermal analysis profiles of natural Na-bentonite, kaolin and zeolite are given in Fig. 4

[63]. It was found that the kaolin demonstrated the highest structural stability due to the strong bond between its aluminosilicate layers. In case of zeolites, dehydration at high temperatures (>200 ºC) is observed as a result of a strong interaction between the electrostatic charged framework with the water molecules [36].

In addition to this, an improvement in adsorption performance of the calcined clays was also reported in many publications. Guo et al [59] found that the decolourising of dye manufacturing effluent by ceramsites can be improved two-fold by raising the calcination temperature from 300 to 700 ºC.

The effects of thermal and chemical treatments on physical properties of kaolinites were also recently investigated by Melo et al [24]. Modification of the clay structure after heat treatment at 500 ºC for 5 h was evidenced by the changes of the XRD pattern, where they observed the formation of an amorphous phase in the thermally treated clay. This is related to the loss of hydroxyl groups, which cause a rearrangement of the original structure of kaolinite. Vieira et al [64] evaluated the morphological changes of the calcined bentonite and its adsorption efficiency toward nickel in the porous bed. The clay was treated at 500°C for 24 h to increase its mechanical resistance and to eliminate some impurities. They reported that the calcination led to an increase in the clay surface area and the development of micro and mesoporosity due to bonded water release and dehydroxylation.. This can cause a reduction in clay density compared with the untreated one; while the adsorption of nickel in clay pores resulted in a slight increase in actual density.

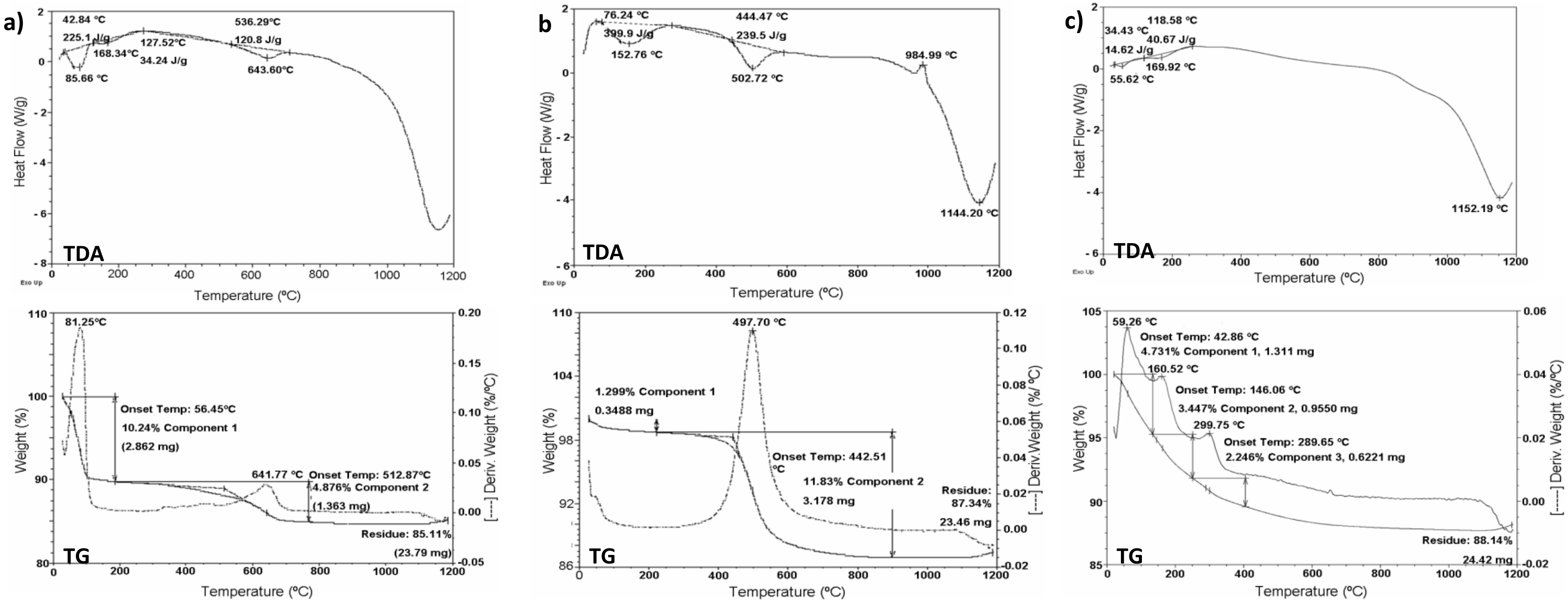

Figure 4: Differential thermal analysis (DTA- Heat flow against temperature profile) and thermogravimetric (TG- Weight loss against temperature profile) profiles of a) Sodium Bentonite, b) Kaolin, and c) Zeolies [63]

3.3 Surfactant modifications

In general, natural clays posses electrically charged and hydrophilic surface characteristics surface due to isomorphous substitution in their crystal lattice, and thus they are very efficient adsorbers of ions and polar molecules [65]. The application of clay for removal of non-ionic organic pollutants, on the contrary, is likely limited.

Surface modification using functional polymers is one of the most effective methods to alter the surface properties. This surface modification of the clay minerals is generally carried out by two main approaches: physical adsorption or chemical grafting of functional polymers to the surfaces of the clays [66]. The surface of clay minerals can be changed via the physical adsorption of specific functional polymers, resulting in improving the physical and chemical properties without rendering their structure. This physical attachment is usually controlled by thermodynamic criteria and therefore results in weak forces between the adsorbed polymers and the clay minerals, i.e. Van der Waals forces.

In contrast, chemical grafting of functional polymers can render the ability to control and alter the properties of clay mineral surfaces. The grafting method allows the polymer chain to be tightly bound onto the clay surfaces by covalent bonds via the condensation of functionalised polymers with reactive groups of the clays [66]. The grafting procedure can be carried out through different pathways. For instance, in case of 2:1 clay minerals, guest compounds can be intercalated from the vapour, liquid, and solid state [67]. Saline coupling agents are commonly used to prepare micro-composites based on clay, silica and fibre glass etc [68]. Once the clay mineral is grafted with organosilane, their hydrophilic surface becomes organophillic and can be easily dispersed in low-polarity compounds including polymers [69]. Shen et al [70] studied the grafting mechanism of saline onto montmorillonite for environmental remediation. They found that the grafting reaction from the silane vapour favoured intercalation of silane into the clay as compared to that of the aqueous phase. Recently, Wang et al [71] introduced a new grafting method, where polymer chains were grafted onto the surface of the clay silicate layers via high-dose gamma-ray irradiation. This method was suggested to simpler compared to conventional ones.

Clay surfaces modified with an organic ion surfactant are known as organoclay. This surfactant modification enables the transformation of organophilic surfaces to organophobic surfaces, and therefore the adsorption interaction towards organic compounds can be enhanced. The organoclay consists of alternate organic and inorganic layers. The organic layer, or the hydrophobic layer, will act as an organic phase for the reactable dissolved organic substances. The surface modification can be preceded by insertion of alkyl-ammonium cations or quaternized cationic surfactant into the interlamellar spacing to create a sorption zone for hydrophobic contaminants [72-73]. Characteristics of this zone can be altered using various surfactants, e.g. replacement of exchangeable cations with organic cations which have long-chain alkyl groups [74], a number of positive charges [75], structural aspects (number of alkyl branches, presence of aromatic moieties), and polarity index of the alkyl groups [76]. Through hydrophobic binding, the clay-organic complexes are efficient in adsorbing a variety of organic molecules from water.

The application of organoclays in adsorbing organics was first recognised by McBride et al [74]. They investigated the adsorption of 2,4-D compounds on Bentone 24, a montmorillonite ion exchanged with dimethyl benzyl octadecyl ammonium ions. Since then, the modified organoclays have been applied in a wide range of practical cases for organic pollution control, such as water purification [77], industrial wastewater treatment and remediation of contaminated ground water [78]. It is suggested that the organoclay can outweigh the conventional activated carbon in some circumstances, as the activated carbon is incapable of removing large molecules such as humic acid [79], and emulsified oil and greases [80]. Numerous studies have focused on using bentonite as a substrate for organoclay syntheses [12,81-82]. Özcan et al [12] introduced a large organic cation surfactant onto Na-bentonite to produce a Dodecyltrimethylammonium bromide-modified bentonite (DTMA-bentonite), which showed significant improvement for removing acid dye, which was approximately 11 times higher than the original clay. The adsorption efficiency of the organoclays for removal of organic pollutants in water has been evaluated and reported in many publications [83-84].

In addition to this, adsorption mechanisms of the organoclays towards organic compounds and various methods for improving their adsorption capacities have been extensively studied and proposed [85]. It is suggested that the degree and mechanism of the adsorption is greatly dependent on the molecular structure of the organic cation that is used to modify the clay surface [81].

Barlelt-Hunt et al [81] and Shen et al [86] proposed that if the organoclays are prepared with small organic cations, the contaminated organic compounds tend to be primarily adsorbed onto the hydrophobic siloxane surface of the modified clays. The adsorption capacity of this class of organoclays is enhanced by increasing the exposed siloxane surface [86-87].

The uses of natural clays as coagulation aids for improving the settling performance have been long known [77, 88-89]. Recently, the application of organoclays for coagulation treatment was also investigated. Jiang et al [90] developed a polymeric Al/Fe modified montmorillonite aiming to combine the advantages of good adsorption of the clay with excellent coagulation/adsorbing chemical character of the polymeric Al/Fe species [91]. This modified clay coagulant proved to have great affinity toward phenol [90], heavy metals (e.g. Pb, Cu, Cr) [92] and humic acids [93]. Jiang et al [32] examined the removal capability of this effective modified clay coagulant for wastewater treatment, where they found significant improvement in COD and colour removal performance.

To extend their exploitation in pollution control processes, the used organoclays have to be regenerated and recycled. The regenerating methods include biological degradation [94], photo-assisted oxidation [95], chemical extraction/desorption [82], and thermal desorption regeneration [96]. A brief review of the regenerating and recycling methods for organoclays was reported by Zhu et al [97], where the inherited advantages and limitations of individual techniques were also discussed.

4. Applications of clays in water and wastewater treatment processes

As mentioned above, the uses of clay materials in water and wastewater treatments can be varied significantly based upon their functional properties or modification methods to suit the removal purposes. However, in the work presented here, the utilisation of clays was exclusively focused on two application approaches i.e. as alternative adsorbents and as catalytic induced materials for advanced photocatalytic oxidation.

4.1 Clay minerals as low-cost adsorbents

In general, applications of the nanoporous materials are mainly emphasized on retaining contaminated compounds on the adsorbents, while the chemical degradation of components might not be predominant. The removal mechanisms of contaminated pollutants in water occur by either adsorption processes or sieve exclusion between the gaps of packed bed material. The native ion-exchange properties of clay materials exhibit a highly selective capability in removal of particular contaminants. The ionic charges on the clay surface can also increase the adsorption capacity by attracting oppositely charged polluting substances and convert them into harmless or easily removed forms. Such combination mechanisms allow them to handle a high load of pollutants.

The adsorption process is superior compared with other techniques for wastewater reuse in terms of initial cost, flexibility and simplicity of system design, ease of operation and application for many toxic compounds, and importantly no formation of hazardous substances [43]. The process draws more attention especially when the adsorbents are inexpensive and exceptional pre-treatment is not required. Available porous adsorbents according to their chemical compositions and technical characterisations are summarised in Table 1 [98].

Table 1: Classification of nanoporous materials [98]

Activated carbon is the most commonly used adsorbent in water and wastewater treatment industries due to its high effectiveness in removal of organic and inorganic pollutants. Granular activated carbon, for instance, is particularly effective in removal of large organic molecules from aqueous media [80]. However, there are some limitations associated with the use of activated carbon. Some evidence is presented that activated carbon suffers from slow adsorption kinetics and inefficient capacity [99]. Many authors have suggested that non-selective adsorption of activated carbon makes it less effective to remove organics in contaminated aqueous streams [100-102]. Hopman et al [103] stated that interference due to the presence of natural organic matter (NOM) can dramatically decrease the adsorptive capacity and bed life of the activated carbon. Also, slow rates of sorption and desorption of the absorbed substances are observed in studies [104]. Other major limitations of activated carbon are its high cost and impractical regeneration with massive loss of adsorbents. The increasing demand of an efficient and economical treatment technology has given rise to a search for alternative low-cost adsorbents to substitute the use of commercial activated carbon in the water and wastewater industry.

Among natural materials, clay minerals (aluminosilicates) provide several important advantages over other alternative adsorbents. The clays are inexpensive, abundantly available, non-toxic, and have promising adsorption properties and potential for ion exchange for charged pollutants. Varieties of clay minerals have been investigated as alternative low-cost adsorbents for wastewater treatment such as sepiolite [6], kaolinite [7-9], montmorillonite [10], smectite [11], bentonite [8, 12]] and zeolite [13-14]. These clay minerals are of interest according to their variety of structural and surface properties, high chemical stability, high specific surface area and high adsorption capacity [15]. These economically promising and technically feasible features make clay minerals promising alternative adsorbents for water treatment applications.

To investigate the adsorption capability of the clay adsorbents, the impact of several important parameters such as solution pH and temperature, as well as their adsorption characteristics need to be considered. The adsorption efficiency is often described by means of adsorption equilibrium isotherms and kinetic studies. Examples of common adsorption isotherms are given below.

4.1.1 Adsorption isotherms

Analysis of the adsorption isotherm is of fundamental importance to describe how adsorbate molecules interact with the adsorbent surface. Equilibrium studies determine the capacity of the adsorbent and describe the adsorption isotherm by constants whose values express the surface properties and affinity of the adsorbents. The relationship between equilibrium data and either theoretical or practical equations is essential for interpretation and prediction of the extent of adsorption [105].

Several adsorption isotherms have been investigated for the adsorption process and are summarised in Foo and Hameed [106]. Among those, the Langmuir [107] and Freundlich [108] models are the most common isotherms due to their simplicity and capability to describe experimental results in wide ranges of concentration. They also allow for the effect of surface heterogeneity for both multiple and single desorbing ions during the adsorption [109].

Freundlich isotherm

The Freundlich isotherm is employed to describe heterogeneous systems and reversible adsorption, and is not restricted to the monolayer formation:

$$q_e = K_F C_e^{1/n} \qquad (1)$$

Eq. (1) can be rearranged to obtain a linear form by taking logarithms:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (2)$$

where q_e is the amount of dye adsorbed per unit of adsorbent at equilibrium(mg g^{-1}), C_e is the concentration of dye solution at equilibrium (mg l^{-1}), K_F (mg$^{1-1/n}$ l$^{1/n}$ g^{-1}) and n are the Freundlich adsorption isotherm constants. K_F and $1/n$ values can be calculated from the intercept and slope of the linear plot between log C_e and log q_e.

Favourable adsorption by a material can be determined from the Freundlich constants. K_F is indicative of the adsorption capacity of the adsorbent, i.e. the greater the K_F value, the greater the adsorption capacity. The other Freundlich constant n is a measure of the deviation from linearity of the adsorption and is used to verify types of adsorption. It is suggested that if n is equal to unity, the adsorption is linear. Furthermore, an n value below unity indicates that the adsorption is a chemical process; whereas, an n value above unity is associated with favourable adsorption and a physical process [15].

Langmuir isotherm

The Langmuir equation is intended for a homogeneous surface and obeys Henry's Law at concentrations approaching zero. This adsorption isotherm is based on the assumption:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

The equation can be linearised to the following equation

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m} \frac{1}{C_e} \tag{4}$$

where q_m is the maximum amount of adsorption with complete monolayer coverage on the adsorbent surface (mg g^{-1}), and K_L is the Langmuir constant related to the energy of adsorption (l mg^{-1}). The Langmuir constants K_L and q_m can be determined from the linear plot of $1/C_e$ versus $1/q_e$.

Unlike the Freundlich isotherm, the Langmuir isotherm is based on the assumption that the structure of the adsorbent is homogeneous, where all sorption sites are identical and energetically equivalent. That is, the adsorption process should have an equal sorption activation energy and demonstrates the formation of monolayer coverage of the adsorbate molecule on the outer surface of the adsorbent.

The effect of isotherm shape is used to predict the favourability of an adsorption system under specific conditions. According to Hall et al [110], favourable adsorption of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L:

$$R_L = \frac{1}{1 + K_L\ C_i} \tag{5}$$

The values of R_L are basically classified into four groups, indicating the shape of the isotherm as follows:

R_L	Type of isotherm
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

4.1.2 Adsorption kinetics and mechanisms

The study of adsorption kinetics is markedly important since it provides informative reaction pathways and mechanisms involved in the adsorption process. The obtained kinetic rate is used to determine the feasible exploitation of the adsorbent. A slow adsorption rate often presents serious limitations for the practical application of the adsorption process.

Adsorption is a physio-chemical reaction process. The molecules adhere to a surface of adsorbents with which they come into contact, due to forces of attraction at the surface. The use of surface energy to attract and hold molecules can be carried out by either physical or chemical interaction. The adsorption mechanism occurs in three basic steps, which are film diffusion, pore diffusion, and adhesion of the solute molecules to the adsorbent surfaces. Film diffusion is the penetration of the solute molecule of the adsorbate through the particle's "surface film". Pore diffusion involves the migration of solute molecules through the pores to an adsorption site. Adhesion occurs when the solute molecule adheres to the pore surface. It is noteworthy that the rate of adsorption of a particular molecule depends upon its mobility in the solution phase, the sorbent pore structure, the particle size, and the hydrodynamics of contact between the solution and the particle phase [45].

Pseudo-first order model

Pseudo-first order equation or Lagergren's kinetics equation [111] is widely used for the adsorption of an adsorbate from an aqueous solution. This model is based on the assumption that the rate of change of solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid uptake with time.

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \qquad (6)$$

when $q_t = 0$ at $t = 0$, Eq. (6) can be integrated into following equation:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (7)$$

where q_t is the amount of dye adsorbed per unit of adsorbent (mg g^{-1}) at time t, k_1 is the pseudo-first order rate constant (min^{-1}), and t is the contact time (min). The adsorption rate constant (k_1) is calculated from the plot of log (q_e-q_t) against t.

Pseudo-second order model

Ho and McKay [112] presented the pseudo-second-order kinetic as:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \qquad (8)$$

Integrating Eq. (8) and noting that $q_t = 0$ at $t = 0$, the obtained equation can be rearranged into a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (9)$$

where k_2 is the pseudo-second order rate constant (g mg^{-1} min^{-1}). The initial adsorption rate, h (mg g^{-1} min^{-1}) at $t \longrightarrow 0$ is defined as

$$h = k_2 q_e^2 \qquad (10)$$

The h, q_e and k_2 values can be obtained by a linear plot of t/q_t versus t.

Intra-particle diffusion model

Adsorption is usually governed by either the liquid phase mass transport rate or the intraparticle mass transport rate, in which diffusive mass transfer is incorporated into the adsorption process. Weber and Morris [113] proposed the use of the intra-particle diffusion model to identify diffusion mechanisms of adsorption processes. The effect of intra-particle diffusion resistance on adsorption can be determined by the following relationship:

$$q_t = k_{id} t^{1/2} + I \tag{11}$$

where k_{id} is the intra-particle diffusion rate constant (mg g^{-1} $min^{-1/2}$). From Eq. (11), when adsorption mechanism follows the intra-particle diffusion model, a plot of qt against $t^{1/2}$ should give a linear line with slope k_{id} and intercept I. Values of I give information about the thickness of the boundary layer, i.e. the larger the intercept the greater the boundary layer effect.

During the adsorption process, there are a series of resistances to mass transfer involved in the reaction. These may be either 'external resistance', in which resistance is encountered by solute molecules as they diffuse through a solute film onto the adsorbent particle surface, or 'internal resistance', in which resistance is encountered by solute molecules as they diffuse through the liquid filling the pores on the way to the adsorption sites. The external resistance is characterised by the external mass transfer coefficient and the internal resistance can be assessed by internal pore and solid diffusivities. It is suggested that the multiple regions of the plot between q_t and $t^{1/2}$ usually represents the external mass transfer followed by intraparticle diffusion in macro, meso and micropores [114].

4.1.3 Other key parameters involved in clay adsorption performance

In general, pore and particle size, pore distribution, surface area and pore surface chemistry are the major factors for sorption processes. Tchobanoglous et al [115] suggested that the size distribution of the adsorbents is an important parameter which affects the kinetics of the ion-exchange process, since the rate of exchange is proportional to the inverse of the square of the particle diameter. Appropriate pore size distribution facilitates the adsorption process by providing adsorption sites and the appropriate channels to transport the adsorbate.

Other physio-chemical factors also significantly affect the adsorption performance. Solution pH has been identified as one of the most important parameters affecting adsorption of the clay. An impact of the initial pH on adsorption capacity is likely dependent on the surface properties of the absorbent and adsorbate. The presence of acidic and basic functional groups on the surface of the adsorbates is pH dependent [116]. A change in pH causes a variation in surface ionic charge of both adsorbate and adsorbent (zeta potential), resulting in electrostatic interaction as well as ion exchangeable capacity of sorption processes. In addition to this, the solubility/dissociation of adsorbent and adsorbate in the aqueous media also varies upon pH changes.

As previously discussed, the differences in pH sensitivities among clays can be attributed to the difference in their molecular structures. In the case of bentonite, the ion-exchange capacity mostly counts on substitutions within the lattice structure. These negative charges are known to be permanent and pH independent. Whereas, the negative charges of kaolin with low isomorphous substitution are mainly derived from the broken bonds around the edges and exposed hydroxyl basal, and relatively depend upon pH [117]. Additionally, the solution pH can significantly affect the surface charge of the adsorbent and the degree of ionisation and speciation of the adsorbate [15]. Since the clay minerals are mainly made of Al and Si, these oxides can be hydrolysed in aqueous solution, where the charge (positive or negative) is created on their surfaces. This charge was found to be proportional to the solution pH surrounding the oxide particles [118]. Vimonses et al [9] stated the favourable adsorption of anionic Congo red dye onto different kaolinites under acidic regions. They suggested that at lower pH, a high electrostatic attraction exists between negative charges of anionic dyes and positive charges of both kaolinite and its edges, thereby increasing the dye adsorption capacity. A contrasting interaction was observed in the case of cationic dye adsorption [31].

Another important parameter affecting the adsorption efficiency of adsorbents is temperature. Temperature plays a role in altering the adsorption and desorption rate as it manipulates the solubility of substances as well as the pore expansion of porous materials. In general, a low temperature leads to an increase in adsorption capacity except in the case of viscous liquids. However, in many cases, the introduction of heat can accelerate the adsorption efficiency. For instance, the adsorption of phenol on to the clay studied by Nayak and Singh [119] revealed the favourable adsorption at high temperature, indicating the apparent endothermic process. They explained that this phenomenon is due to a temperature effect linked with the presence of hydrogen bonding in phenolic compounds. The phenol is significantly soluble in aqueous solution due to the existence of extensive hydrogen bonding between the phenol molecule and water. At a high temperature, these hydrogen bonds are broken and cause phenol to be less soluble and exhibit a higher tendency to adsorb on the clay surface rather than remain in the solution [120].

The effect of temperature on adsorption processes can be determined through the following equations:

$$\Delta G^\circ = \Delta H^\circ - \Delta S^\circ T \qquad (12)$$

$$\Delta G^\circ = -RT \ln K_C \qquad (13)$$

By combining of Eq. (12) and (13), the van't Hoff equation can be written as:

$$\ln K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \qquad (14)$$

where K_C is the equilibrium constant, which is the ratio of the equilibrium concentration of the dye ions on the adsorbent to the equilibrium concentration of the dye ions in solution. R is the ideal gas constant (8.314 $\mathrm{Jmol^{-1}K^{-1}}$) and T is the adsorption temperature in Kelvin. Values of ΔG^{o} (kJ $\mathrm{mol^{-1}}$) at different temperatures were evaluated from Eq. (12). A plot of ln K_C versus $1/T$ should give a linear line, where values of ΔH^{o} (kJ $\mathrm{mol^{-1}}$) and ΔS^{o} (J $\mathrm{mol^{-1}}$ $\mathrm{K^{-1}}$) can be calculated from the slope and intercept of van't Hoff plots.

4.1.4 Organic removal

The adsorption capability of raw and modified clay minerals for organic removal from water and wastewater was reported in several publications [93,121]. In general, the natural clays are more prone to removal of ions and polar molecule pollutants due to their electrically charged and hydrophilic surface characteristics [65]. The application of clay for removal of non-ionic organic pollutants, on the contrary, is likely limited. For example, aluminosilicate zeolites exhibit a strongly hydrophilic capability in nature due to the presence of the intracrystalline void space of polar groups such as cations and hydroxyl groups. This “water like” property makes it unlikely to attract organic substances. Miguel et al [122] compared the removal efficiency of different adsorbents of manganese and different organic compounds using zeolites in a rapid small scale column. The results showed that all natural zeolites presented a very limited capacity to remove organic matter from solution. However, the affinity of zeolite to organic pollutants can be increased by regulating the surface properties of zeolite, i.e. alteration of Si/Al atomic ratio [123]. Namba et al [124] reported that a higher Si/Al ratio provided a more hydrophobic material surface, and hence showed better affinity for organic contaminants.

Therefore, the modified clays that possess strong hydrophobic surfaces, i.e. organoclays, play an important role in removal of trace pollutants such as VOCs, tannic acid, phenol, and 2,4,5-trichlorophenol, polycyclic aromatic hydrocarbons (PAHs) and toxic metals [72,125-127]. This hydrophobic selectivity toward contaminants has advantages over activated carbons which always suffer from non-selective capability and impaired effectiveness due to the presence of interfering constituents in water such as NOM.

It is suggested that the integration of clay minerals with polymeric metal species to form a new type of adsorbent can somewhat enhance organic removal. Liu and Gonzalez [121] observed a slight increase in humic acid adsorption on montmorillonite in the presence of bivalent metals in the system. They proposed that the bridging of bivalent metal ions between the clay and humic acids would be responsible as a dominant adsorption mechanism. Jiang and Graham [128] stated that, among polymeric metal species, the Al and/or Fe species are the most effective coagulants/adsorbents for removal of natural and synthetic organic impurities in drinking water treatment. This hypothesis was confirmed by Jiang and Cooper [93], where they demonstrated the order of adsorption affinity of the montmorillonite clays to humic acids as polymeric Fe/Al-modified > polymeric Al-modified > polymeric Fe –modified > unmodified natural clay.

Oladoja and Ademoroti [129] extended the application of the clay minerals to on-site wastewater treatment using a fortified soil-clay percolator column unit filled with kaolinite, illite, smectite and pebbles, where they reported 69-98% COD removal can be obtained. Beall [80] addressed the synergetic effect of the organo-clay adsorbent with a number of water treatment technologies. Upon concomitant application with activated carbon, this modified clay removed other molecules that bind the pores of the carbon, and therefore allowed the carbon to remove the organic traces more efficiently.

Sabah et al [130] explored a feasible employment of natural and activated sepiolites on the removal of cationic organic reagents, e.g. typical quaternary amines from aqueous solutions. They demonstrated that adsorption of the cationic surfactant was governed by the combination of different mechanism steps, i.e. preliminary ion-exchange between magnesium ions in the clay matrix and ammonium ions in the surfactant, followed by chain-chain interaction between hydrocarbon chains of the amine molecules through Van der Waals forces. However, they concluded that the untreated sepiolite is more beneficial for the adsorption of amines from wastewater since no significant increase in the adsorption capacity was observed by the acid-heat activated ones.

4.1.5 Dye removal

Among the alternative low-cost adsorbents, clay adsorption is considered as the most economical option for dye removal [131]. Over decades, the use of clay minerals such as bentonite, sepiolite, palygorskite etc. as principal raw materials have been investigated for decolourisation. As the adsorption of dyes on clay minerals is mainly dominated by ion-exchange processes this means the adsorption capacity can vary significantly with pH [43]. Al-Ghouti et al [132] examined the mechanism of dye adsorption onto diatomite, also known as diatomaceous earth. They found that the uptake occurs via physical adsorption (depending on particle size) and the presence of electrostatic interactions (depending on the pH). Amid clay species, montmorillonite has gained much interest since it occupies the largest surface area with the highest cation exchange capacity; while considered as low cost, being about 20 times cheaper than activated carbon [133]. In many cases, the adsorption capacity of cationic/basic dyes tends to exhibit much higher rates than those for anionic/acid dyes due to their cation-exchange properties with the clays [43]. Roulia and Vassiliadis [134-135] examined the adsorption behaviour of the cationic dye C.I. Basic Blue 41 onto montmorillonite, bentonite, raw perlite, and expanded perilte. Adsorption experiments demonstrated that the clays are more efficient adsorbents compared with the perlites, but their dye retention is subjective to an increase in pH and temperature. The differences in dye uptake mechanisms were also detailed by visible spectroscopy analyses. The results indicated that the adsorption of the dye molecules onto montmorillonite initially takes place at the surface via the formation of H-aggregates before migrating into the interlamellar space, leading to intercalation of the dye into the clay. The dye molecules between the silicate sheets might adopt different orientations and, eventually, become layered depending on the dye loading and the temperature. In the case of bentonite, a rapid insertion of the dye molecule into the interlamellar space was observed. Diffuse reflectance spectra revealed the presence of new species in acidic solutions of the dye, attributed to higher dye aggregates. H-aggregates of the dye were also identified in the perlitic samples.

Several reviews have addressed the significance of clay minerals for dye removal from textile wastewaters [43,131]. Guo et al [59] reported ceramsite prepared from palygorskite demonstrated a very high removal efficiency for dyeing wastewater, by which a decolourising amount of 635 mL g^{-1} and 81% COD reduction was achieved. Vimonses et al [8] preliminary study compared the adsorption capacity of several Australian natural clays for removal of Congo Red (CR) anionic dye. Adsorption tests showed that the Na-bentonite can deliver the highest removal efficiency over other studied clays. Their further investigation on the mixtures of sodium bentonite, kaolinite, and zeolite with lime demonstrated a great enhancement in the dye removal with the potential to recycle over 5 times [63].

A number of nanoclays, modified nanoclays, and montmorillonite were examined as adsorbents for anionic, cationic and non-ionic dyes. Yang et al [136] detailed the differences in adsorption capacity of these clays and dyes with respect to their structures, chemical and morphological properties, as well as their sorption forces. This study indicated that with certain modifications these nanoclays can become excellent adsorbents for anionic, cationic and non-ionic dyes. On the other hand, Juang et al [137] investigated the ability of acid-activated clay for the removal of basic, acidic, dispersed, direct and reactive dyes, where the highest adsorption capacity for basic dyes was observed.

China clay also showed the very efficient removal of Omega Chrom Red ME, particularly at acidic pH and low temperature conditions [138]. An interesting study was carried out by Choi and Cho [139], where they investigated the effectiveness of vermiculite extract solution as a coagulant and of vermiculite as an adsorbent for decolourisation of dye effluents. They found that the coagulation performance of vermiculite was controlled by the containing elements in the clay (e.g. Mg, Fe, Al, Ca, Si etc.), while adsorption of the basic dye (cationic blue) increased as the clay particle size decreased and temperature increased.

Eren and co-workers studied the adsorption equilibrium, kinetics and thermodynamic studies of a Basic Crystal violet dye by a manganese oxide-coated sepiolite [140]. The adsorption capacity of this modified-sepiolite was approximately 4 times higher than the raw clays, and the adsorption reactions were found to obey the Langmuir isotherm and pseudo-second order kinetics. It was suggested that the adsorption isotherm was likely to depend on the surface properties and affinity of the adsorbents. Table 2 illustrates the adsorption capacity of dyes on different clay materials.

Table 2: Dye adsorption capacity of different clay minerals

Clay Mineral	**Dye**	**Adsorption capacity (mg g^{-1})**	**Reference**
Kaolinite	Congo red	5.6	[9]
Bentonite	Congo red	158.7	[141]
Surfactant-modified montmorillonite	Congo red	350	[142]
Zeolite	Congo red	4.3	[8]
Ca-Bentonite	Congo red	85.29	[143]
Na-Bentonite	Acid Blue 193	67.1	[15]
DTMA-bentonite	Acid Blue 193	740.5	[12]
Acid-activated clay	Basic blue 69	394	[137]
Acid-activated clay	Basic blue 22	406.3	[137]
Modified- sepiolite	Crystal violet	319	[140]
Monmorillonite/$CoFe_2O_4$ composite	Methylene Blue	97.75	[31]

4.1.6 Heavy metal removal

Clay particles have large surface area to mass ratios with extensive negative exchange sites on their surfaces for metal adsorption. Several studies have documented the performance of clay minerals, such as montmorillonite, kaolinite, and illite, for the removal of toxic metals: Pb, Zn, and Ni [25]. The addition of clays into acid drainage treatment was found to reduce metals and resulted in producing more dense flocs, thereby increasing settling ability [14,30]. Adsorption of metals onto clay minerals involves two different mechanisms; i) an ion exchange reaction at permanent charge sites; and ii) formation of complexes with surface hydroxyl groups at the edge-sites.

It is suggested that clay minerals which possess natural hollow brick-like structures or fibrous clays, i.e. palygorskite ($Si_8Mg_5O_{20}(OH)_2(H_2O)_4{\cdot}4H_2O$) and sepiolite

($Si_{12}Mg_8O_{30}(OH)_4(H_2O)_4 \cdot 8H_2O$), provide great potential for retention of micro-pollutants such as heavy metal cations [144]. In addition to this, Iwata et al [145] suggested that the adsorption of metal ions is mainly affected by the degree of surface heterogeneity owing to the existence of crystal edges, broken bonds, imperfections on the surface, and organic matter content. Jiang et al [146] recently investigated adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) onto natural kaolinite clay, where they found that the adsorption capabilities of the kaolinite clay for the metal ions were in the order of Pb(II) > Cd(II) > Ni(II) > Cu(II) , and were more favourable at high pH conditions.

Gupta and Bhattacharyya [53] investigated the adsorption capacity of Pb(II) and Cd(II) from spiked water samples onto natural kaolinite, montmorillonite and their acid-activated forms. Many studies have been carried out on adsorption of heavy metals by zeolites [47, 147-148].

4.1.7 Nutrient and inorganic removal

Discharge of excess nutrients into the environment can lead to serious problems such as the eutrophication of rivers and deterioration of water bodies, as well as hazards to human health [149]. For instance, nitrogen compounds such as nitrates can form nitrosamines and nitrosamides that are potentially carcinogenic [150].

The removal of nitrogen by clay minerals has been extensively examined, particularly by zeolites [19, 151]. Clinoptilolite zeolite with typical channel dimensions of 3.9 x 5.4 Å showed excellent removal of ammonium (NH_4^+) from aqueous solution due to its selective ammonium-ion interaction and good sorption at low temperature [152-153]. It is suggested that the ammonium uptake takes place via either exchange with Na^+, Ca^{2+}, and K^+ ions or adsorption in pores of aluminosilicate systems [38,154]. Jorgensen [155] and Rožić et al [19] suggested that preliminary ion-exchange occurs when the concentration of ammonium is equal or lower than the concentration of exchangeable cations of the zeolites. Adsorption, thereafter, begins to predominate in the process with increased ammonium content. Aiyuk et al [151] also evaluated the capability of a natural zeolite for NH_4^+ removal as part of their low cost integrated wastewater treatment process, i.e. coagulation/flocculation, anaerobic degradation and zeolite ion-exchange system. This ion-exchange system can be regenerated by biological nitrification with comparative removal efficiency of the original. A similar study was conducted by Gersberg et al [89], where they used a column packed with clinoptilolite for removal of ammonia as a part of a clay-alum flocculation process for virus removal from municipal wastewater.

Rožić et al [19] revealed the rapid removal of ammoniacal nitrogen by zeolite and clay in the batch tests, in which an immediate increase in the solution pH after addition of the materials due to hydrolysis was observed. The cations in the zeolite and clay framework, i.e. Na^+, K^+, Ca^{2+}, and Mg^{2+}, are partially exchanged by hydronium ions, and release hydroxide ions that are responsible for the pH increase in the suspension [39]. It was concluded that the removal of ammonium ions was mainly governed by ion-exchange, while those of the clays was subject to ion-exchange and adsorption. In the same study, Rožić et al [19] also pointed out the important behaviours of the clays towards the removal of ammonium, where they reported that to enhance removal effectiveness the clays should be in liquid colloidal state (hydrated state). Chávez et al [156] studied the kinetics and equilibrium adsorption of Ba^{2+} by Ca-exchanged clinoptilolite tuff and montmorillonite clay, where they reported the Ba^{2+} uptake followed the Langmuir isotherm and pseudo-second order kinetic for both materials. In addition to this, the addition of clay in the shale precipitation/clay adsorption for water purification was reported to enhance the removal of ferric ions and uncharged organic matter [157].

Ma and Zhu [158] introduced a simultaneous removal of phosphate and phenanthrene by alum aided with surfactant-modified bentonite. The addition of a small amount of the modified clay was found to enhance the adsorption of organic pollutants and the removal of phosphate compounds. It was proposed that the removal mechanism involved cation exchange with the inner surface of the lamellar bentonite, resulting in an increase in lamellar spacing and hence the specific surface area available for the adsorption of phosphate ions. Bleiman and Mishael [159] developed new polymer-chitosan-montmorillonite composites for adsorption of selenium from drinking water. They demonstrated that under a high loading of polymer, the composites are positively charged, resulting in formation of a bilayer and partial clay exfoliation structures. Such structures can promote high selenate adsorption due to internal anion-exchange sites.

The presence of concentrated fluoride is another concern in drinking water, as excessive uptake of the fluoride can cause adverse health effects including dental or skeletal fluorosis [160]. Various publications have reported the use of low-cost clay minerals, i.e. bentonite, kaolinite and zeolite, for defluoridation of high mineral content water. However, a major limitation is their low adsorption capacity in this regard. Kamble et al [161] has recently developed the modified bentonite clay with electropositive atoms, such as lanthanum, manganese and potassium, to enhance the clay adsorption capacity for fluoride ions from water and wastewater.

4.1.8 Biological contaminant removal

Gersberg et al [89] investigated the effect of the clay on alum flocculation for virus removal from sewerage wastewater. They found that the addition of montmorillonite can achieve removal values of 1.5 logs (96.8%) for poliovirus and 1.8 logs (98.4%) for MS2 bacteriophage, which was slightly higher than that of 1.3 logs (95%) obtained by Dryden et al [162] in pilot-scale studies of poliovirus removal by alum coagulation of wastewaters alone. In the same study by Gersberg et al [89], the addition of clay was suggested to increase the floc density and therefore enhance their settling velocity.

Lund and Nissen [33] also reported that the addition of bentonite (1 gL^{-1}) into irrigation or river streams enabled the removal of coxsackievirus to 2-3 logs (99-99.9%), indicating the effectiveness of clay as an adsorbent/flocculent for improving the virological quality of the treated effluents. The adsorption of viruses by clay occurred upon a clay-cation-virus bridge, at which the virus could be removed along with the removal of clays [163]. It was also suggested that the degree of virus adsorption can be increased by aluminium ions, and was dependent on the concentration of cations, the presence of organic matter, and the surface charge density and geometry of the clay particle.

4.2 Clay minerals as catalysts and photocatalyst supports

The uses of clay minerals either as active catalysts or catalyst supports have been widely investigated for environmental remediation, e.g. decontamination of soil, underground waters, sediments and industrial effluents [8-9, 63, 164-165].

In water and wastewater treatment industries, advanced oxidation processes (AOPs) are one of the most promising innovative technologies for water purification and wastewater reclamation. The AOP principle is based on the in-situ generation of highly reactive transitory species, such as H_2O_2, $OH^{\bullet}$, $O_2^{\bullet-}$, O_3 etc., for oxidation of recalcitrant organic compounds and pollutants, pathogens and disinfection by-products [166-168]. The employment of clay minerals for such oxidation processes has also been documented extensively [169-173]. Montmorillonite, for instance, is the most important clay mineral for these applications. This is based on the fact that the acid forms of the clay provide environmentally friendly alternatives to liquid Brønsted acids [3], which are able to chemically interact with a range of contaminant compounds. Ravindranathan et al [174] firstly introduced a new approach to the preparation of metal supported montmorillonite catalysts via a polyol process, where ethylene glycol was used as a reducing agent. This process can be considered as a basic practice for the preparation of other fine metal particles supported on montmoritlonite. Duad and Hameed [175] successfully optimised preparation conditions for the iron (III) immobilized montmorillonite catalyst through an incipient impregnation method. Its catalytic activity was examined by the decolourisation of Reactive Black 5 dye in the presence of H_2O_2 in a Fenton-like oxidation process. Recent studies have also shown the potential of zeolites in degradation of organic substances through the catalytic oxidation process. It was found that acidic/protonic forms of zeolites exhibit an effective catalyst in many remediation applications [176-177]. Catalytic performance of these zeolites is related to the presence of strong Brønsted acid sites which are capable of oxidising chlorinated volatile organic carbons (VOCs) such as 1,2-dichloroethane, dichlorimethane and trichloethylene etc [178]. An increase in degradation capacity is associated with the development of strong acidity as a result of dealumination [176]. Such a dealumination process can be carried out by substitution of aluminium for silicon in the framework. It was also found that for some compounds catalytic activity was favoured by the microporous structure of zeolites due to confinement effects [178]. The surface properties result in a flexibility and suitability to various pollutants.

Among the developed AOPs, photocatalysis is believed to prevail over other techniques such as ozone, hydrogen peroxide and UV radiation due to its better control in terms of generating the reactive radicals while avoiding or minimising the formation of the potentially toxic by- products [179]. The photocatalytic process generally involves generation and use of powerful but relatively non-selective transient oxidizing species, primarily the hydroxyl radical ($OH^•$) and, in some cases, the singlet oxygen, O(1D), and superoxide radical [180]. Weast et al [181] reported that $OH^•$ posseses the highest thermodynamic oxidation potential among these oxidising agents using in conventional treatment systems (Table 3).

Table 3: Oxidation Potential of Several Oxidants in Water [181]

Oxidant	**Oxidation potential (eV)**
$OH^•$	2.80
$O(^1D)$	2.42
O_3	2.07
H_2O_2	1.77
Perhydroxy radical	1.70
Permanganate ion	1.67
Chlorine dioxide	1.50
Chlorine	1.36
O_2	1.2

In comparison to other semiconductor catalysts used in this process, titanium dioxide (TiO_2) is the most common photocatalyst due to its relative inertness, corrosion resistance, reduced toxicity, high photoactivity under the photon energy of $300 \text{ nm} < \lambda < 390 \text{ nm}$, high chemical and thermal stability [182-183].

4.2.1 Phocatalysis Mechanisms

Photocatalysis employs a light source and a catalyst to bring about a chemical reaction and generate highly reactive hydroxyl radicals ($OH^{\bullet}$) which then attack the organic pollutants in solution [184]. However, the reaction only occurs when catalysts absorb sufficient light with energy equal to or higher than their corresponding band gap. When a TiO_2 particle absorbs adequate energy from a photon of light ($E > E_{bg}$), an electron (e^-) of TiO_2 is then promoted from the valence band to the conduction band. This movement of the electron leaves a hole (h^+) in the valence band. These generated electrons and holes can either recombine, dissipating energy, or be available for redox reactions with electron donor or acceptor species adsorbed on the surface of TiO_2 or nearby in the electrical double layer surrounding the catalyst. The holes are suggested to be the main species responsible for degrading organic pollutants, either directly by oxidising organics adsorbed on the TiO_2 surface or indirectly by generating hydroxyl radicals to attack organics by reacting with water or OH^-. In this reaction, oxygen is introduced to react with the generated electrons to minimise recombination of the hole and the electron [184]. In addition, it is suggested that superoxide radicals may also participate in photooxidation mechanism. Such highly reactive species are able to effectively degrade a wide range of organic compounds including, aromatics and aliphatics, dyes, pesticides and herbicides [185]. The proposed photocatalytic reactions on TiO_2 are shown in Fig. 5.

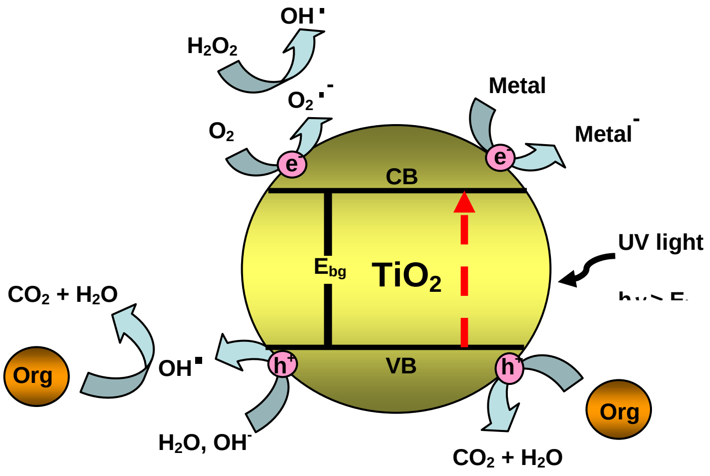

Figure 5: Schematic mechanism of TiO_2 photocatalysis

In general, photocatalytic degradation and mineralisation take place by an electron transfer reaction. The oxidation mechanisms can vary depending upon the physio-chemical properties of the organic compounds to be degraded by either the highly reactive $OH^{\bullet}$ species and active hole, or both. In the case where the reactive hydroxyl radicals become the predominant species, a high concentration of H_2O and OH^- molecules adsorbed on catalyst surface is essential [186]. This water adsorption potential can be promoted by the super hydrophilicity of TiO_2. Oxygen molecules, which act as the accepting species in the electron-transfer reaction in photocatalysis, subsequently generate hydroxyl radicals through the superoxide anion and its protonated forms. The presence of hydrogen peroxide (H_2O_2) in the aqueous medium increases hydroxyl radical concentration and consequently accelerates the degradation rate. However, there are some studies showing that the degradation rate can deteriorate when the H_2O_2 concentration is too high [187-188]. This could be due to the excess H_2O_2 in the system acting as a hydroxyl radical scavenger, which causes a decrease in the degradation rate [188]. It is suggested that the effect of hydrogen peroxide is dependent upon the H_2O_2/contaminant molar ratio [189].

When organic degradation takes place through the hole (h^+), equilibrium of the adsorption and desorption between the compounds and catalyst surface plays an important role. As a result, pH exhibits a significant influence on the surface properties. The effect of pH on photocatalysis is generally attributed to the surface charge of TiO_2 (of which the point of zero charge is about pH 5.5) and its relation with the ionic form of the organic compounds. This electrostatic interaction between catalyst surface and the organic substance subsequently either enhances or inhibits the photodegradation rate [188]. Other factors that influence the degradation rate are the concentration of catalysts and the pollutants to be treated. In general, photocatalytic degradation will increase as the catalyst load increases; however, this increase only continues up to a certain loading, where the optimum light absorption is reached. Above this level additional catalyst in the suspension will block the UV-light passage to other catalyst particles [190-191], resulting in a reduced degradation rate. Similar phenomena also occur when the concentration of the pollutant that can adsorb a portion of the activating light is too high. Due to photonic activation, the photocatalysis can take place at room temperature;

however, Herrmann [192] suggested that photocatalytic reaction would be more efficient in the range of 20-80°C, where the true activation energy E_t is nil and the apparent activation energy E_a is small. At a high or a low temperature, the activation and apparent activation energy would not be stable resulting in a less favorable adsorption mechanism of reactant. Other factors involved in the efficiency of photocatalysis degradation are retention time, light intensity, oxygen pressure etc.

The overall process can be summarized by the following reaction equation:

$$\text{Organic pollutants} + O_2 \xrightarrow[h\nu,\ \lambda \leq 387.5\text{ nm}]{TiO_2} CO_2 + H_2O \qquad [15]$$

4.2.2 Immobilisation of photocatalyst on clay supports

TiO_2 photocatalysis is generally employed in the form of a slurry or suspension in a so-called "heterogeneous process". This is due to the fact that the small particles of TiO_2 is able to deliver high removal efficiency, as a high ratio of catalyst surface area to volume of the particles results in enhanced pollutant/hydroxyl radical interaction. From a practical point of view, however, such heterogeneous photocatalytic water purification utilising commercial TiO_2 photocatalysts still faces a number of constraints that limit its feasible application, i.e. poor adsorption, low surface area, utilisation of a small fraction of sun light (2–3%), rapid recombination of electron–hole pair properties. In addition to this, its small particle size likely induces agglomeration of titania catalysts into larger particles, resulting in an adverse catalytic performance, and also confines the water purification to severely interrupted treatment cycles with elevated difficulty in solid catalysts recovery. The post-separation of catalyst can be a time consuming and costly process, resulting in great limitations in exploiting the TiO_2 to the best of its photoefficiency.

These constraints have invoked the exploitation of various forms of titania-supported photocatalysts, being synthesised via different chemical methods to achieve desirable physicochemical properties, photoactivity and stability for feasible photocatalytic water application [193]. Fabrication of the catalyst on a variety of supporting substrates such as silica gel, quartz optical fibres, glass fibres, cellulose membranes, polymer films etc. has been studied extensively to overcome the intricate separation [189]. Shan et al [182] suggested that an ideal support for a photocatalyst should meet several criteria, including: i) strong adherence between catalyst and support; ii) non-degradation of the catalyst reactivity by the attachment process; iii) provide a high specific surface area; iv) have a strong adsorption affinity towards the pollutants; and v) possess a physical configuration facilitating an ultimate liquid-solid phase separation [195-196].

Several catalyst preparation procedures have been developed to attach the TiO_2 on any appropriate support, i.e. via thermal treatment, chemical vapour deposition, and electrophoretic deposition etc. The titania coating film is one of the major "*in situ*" catalyst generation techniques, generally performed by the "sol-gel" method [197]. The sol-gel process involves an integrated series of physical and chemical transformations of titanium salt (usually an alkoxide) precursor in adequate solvent and/or acid-base conditions [195]. Deposition of TiO_2 thin films onto large catalyst supports, such as ferromagnetic cores or different silica materials have previously been shown to considerably improve the ease of particle recovery and adsorptive capacity [198]. In addition to this, porous materials that possess a thermally stable structure are often in great demand as catalyst supports. Layered silicate porous materials such as clay minerals are one of the most common supporting materials suitable for the preparation of particles with small diameter of a few nm range on the surface and in the interlameller space of clays in aqueous suspension [199]. The major advantage of this technique lies in their non-toxicity, low-cost and easy recovery from treated effluent. Fig. 6 demonstrates a schematic diagram of the heterocoagulation; disaggregation of the particles on the clay mineral lamellae [200]. Different types of clays have been intensively investigated as a support for TiO_2, this includes bentonite [201], sepiolite [202], montmorillonite [200], kaolinite [165,203], and zeolite [204].

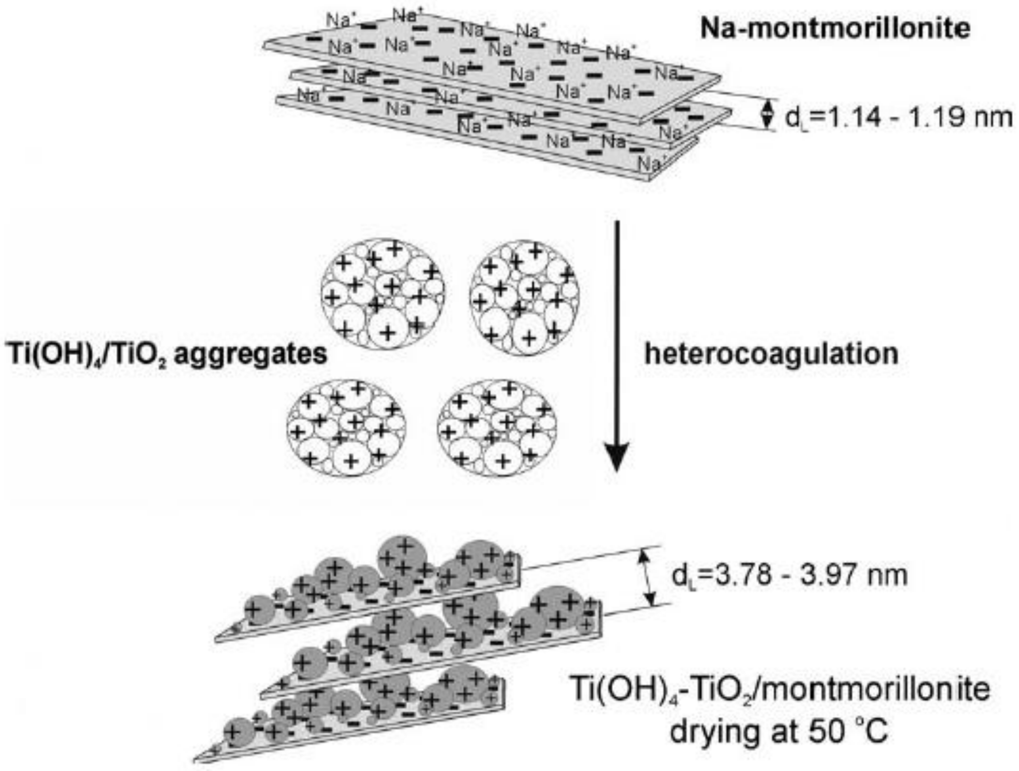

Figure 6: A schematic diagram of the heterocoagulation; disaggregation of the particles on the clay mineral lamellae [200]

An alternative form of titania incorporated into clay particles is known as TiO_2-pillared clay, where TiO_2 particles are introduced into 1 nm thick mineral layers [169-170]. The preparation of titania impregnated pillared clay minerals was first carried out by Sterte [171] and Yamanaka et al [172], in which the catalyst was prepared via ion-exchange between the positively charged colloidal particles of hydrated titanium and the charged-balancing cations between the layers [171-172]. Nevertheless, in some cases, the pore size of these pillared clays was found to be too small for large organic molecules to diffuse through the pores to access the active sites, leading to an adverse impact on the photocatalytic reaction [173]. Zhu et al [205] also pointed out a superior photocatalytic activity of mesoporous titania composites with large anatase crystals deposited on clay mineral fragments. The photocatalytic performance of the catalyst can be further enhanced by improving the dispersion of these materials in aqueous media. It is therefore suggested that the ideal catalyst particles should be adequately large for recovery, whilst tiny enough to be well dispersed in water [173]. Yang et al [173] lately developed new titania clay composites by direct reaction of $TiOSO_4$ with laponite, hectorite, beidellite and saponite under hydrothermal conditions, followed by washing steps with pure water and ethanol prior to calcination. It is reported that the ethanol washing can facilitate the formation of mesoporous structures with anatase nanocrystals attached on the fragments of clay mineral layers. Such an obtained structure allows the particles to be easily dispersed in water which can promote the diffusion of recalcitrant organic compounds to access and react on the anatase surface. This study revealed that the ethanol washed samples also possessed larger specific surface area and pore volume, resulting in 2-6 times higher photocatalytic activity than those without the washing step.

Fassier et al [206] studied the deposition of anatase titania on a fired clay substrate using a simple spraying technique followed by thermal treatment. Results showed that the photocatalytic activity of the titania coated fired clay catalyst was dependent upon the calcined temperature, which accounted for changes of the specific surface area and anatase/rutile ratio of the particles. Manova et al [207] recently introduced a new preparation technique for nanostructured titania-clay porous material by controlled hydrolysis and polycondensation of titanium (IV) isopropoxide in the presence of organoclays prepared from various layered silicate clays treated with cetyltrimethylammonium bromide. The materials not only demonstrated higher efficiency in 2,4-dichlorophenol degradation than those of a commercial TiO_2 catalyst, but also accommodated recovery of the catalyst from the reaction media after reaction. A combination of TiO_2-based photocatalysis and adsorption system using TiO_2 intercalated into the interlamellar space of the hydrophilic montmorillonite was also explored by Ilisz et al [208]. The TiO_2/monmorillonite adsorbent/catalyst was prepared by means of a heterocoagulation process and tested using 2-chlorophenol degradation. Advantages of this material lies between its high oxidation rate and concurring photocatalytic recovery without further regeneration.

Although the clay minerals are considered attractive as a catalyst support or substrate, in many cases natural clays should not be used directly for TiO_2 immobilisation. Chong et al [165] reported that the presence of different surface or lattice-bounded impurities might diffuse or otherwise affect the titania efficiency of the immobilised layer.

Changes in morphology and physiochemical properties of kaolin after a series of acidification-alkalization-thermal treatments have been reported [203]. This pre-treatment is considered critical in order to delaminate the clay layers to a flat surface with consistent distribution of micropores, resulting in an increase in surface area for ease of light accessibility and TiO_2 sol deposition. This is also to promote the subsequent heterocoagulation between the positively charged titania sol and clay particles.

Zhang et al [209] compared the supported catalytic performance of different silica based materials, where various parameters such as particle size, catalyst dose, support bonding and calcination temperature were considered. Xu and Langford [210] observed a higher photoactivity for titania supported zeolite, than those of silica and alumina. They concluded that the larger adsorption capacity of the zeolite and its unique structure are the major factors which may be responsible for photocatalytic enhancement. Ejhieh and Khorsandi [211] synthesised a modified NiS–P zeolite as photocatalyst for decolourisation of Eriochrome Black T, where they found the mineralisation of 40 mg L^{-1} of the dye was obtained under the optimum conditions of pH 9.1 and 0.8 g $L^{-1}$of catalyst loading.

In addition to monitoring the catalyst behaviour based upon their oxidation efficiency, different characterisation techniques have often been used to correlate titania coating structure and morphology with preparation methods and resultant catalyst system performance. Examples of morphology images of titania impregnated kaolin are illustrated in Fig.7. A summary of analytical techniques and their application for the characterisation of immobilised TiO_2 is given in Table 4.

Table 4: Analytical techniques for characterisation of immobilised TiO_2 photocatalyst

Spectroscopic Techniques	**Application**	**References**
Scanning electron microscopy (SEM)	Surface morphology, microstructure	[165,203,212]
Transmission electron microscopy (TEM)	Surface morphology, crystallinity	[165,203,173,212]
UV-Vis diffuse reflectance spectra	Characterise the optical absorption properties of a catalyst	[203,213]
X-ray diffraction (XRD)	Crystallographic structure	[95,165,200,203,209,212]
X-ray photoelectron spectroscopy (XPS)	Elemental composition, empirical formula, chemical state and electronic state of elements	[214]
Energy dispersive spectrometry (EDS)	Elemental analysis or chemical characterisation of a catalyst	[213]
Thermal gravimetric analyses (TGA)	Determination of the changes in weight comparative to change in temperature	[203]
Nitrogen adsorption-desorption	Specific surface area and pore size distribution	[165,200,203,173]
Zeta potential measurement	Determination of electric properties of interfacial layers in colloidal system	[215]
Particle size distribution		[165,200,203]
Fourier transform spectroscopy i.e. FTIR	Characterisation/identification of catalysts based on spectra analysis	[213]

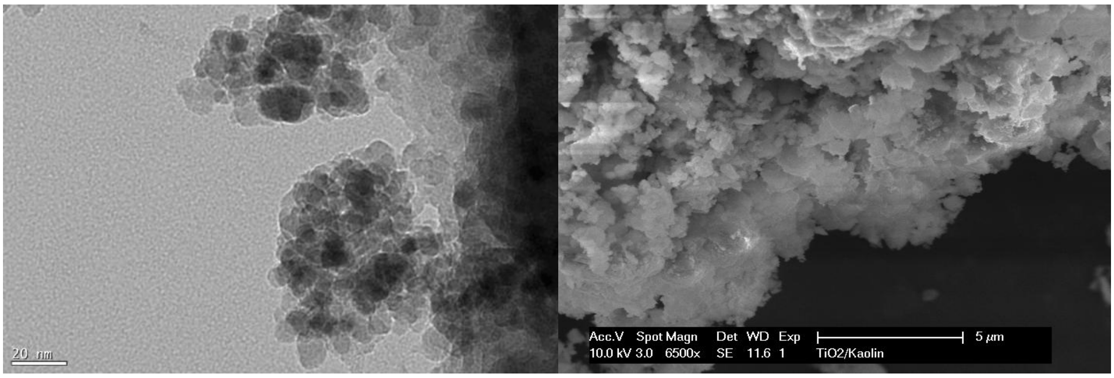

Figure 7: Electron microscopy images of titania impregnated kaolin a) TEM and b) SEM [198].

To date, little attention has been paid to how the physicochemical properties and photoactivity of the TiO_2 nanocrystals could be varied during the photocatalytic process, especially if the catalysts are repeatedly recovered and reused in a water purification system. In this present work, further investigation on the changes of physicochemical properties of the used titania impregnated kaolin photocatalysts during thermal regeneration were conducted, where the obtained results indicated that the layered TiO_2 nanocrystals on the core kaolin substrate remain in anatase TiO_2 form even after six thermal regeneration cycles [203]. Fig. 8 illustrates the structure stability of titania anatase/kaolin catalysts after several cycles of thermal treatment [203]. The stability in the layered TiO_2 nanocrystal structure can be attributed to the formation of Ti-O-Si bonds between the TiO_2 network and the siliceous side of kaolin particles during the course of synthesis. It was also known that the presence of Ti-O-Si bonds could suppress TiO_2 phase transformation from anatase to rutile, and thus directly influence its stability for catalytic applications [216-217]. In addition to this, the presence of kaolinite as a supported substrate would increase the firing temperature and light brightness colour of the catalysts [218]. This study pointed out the potential of the titania deposited clay to be efficiently reused.

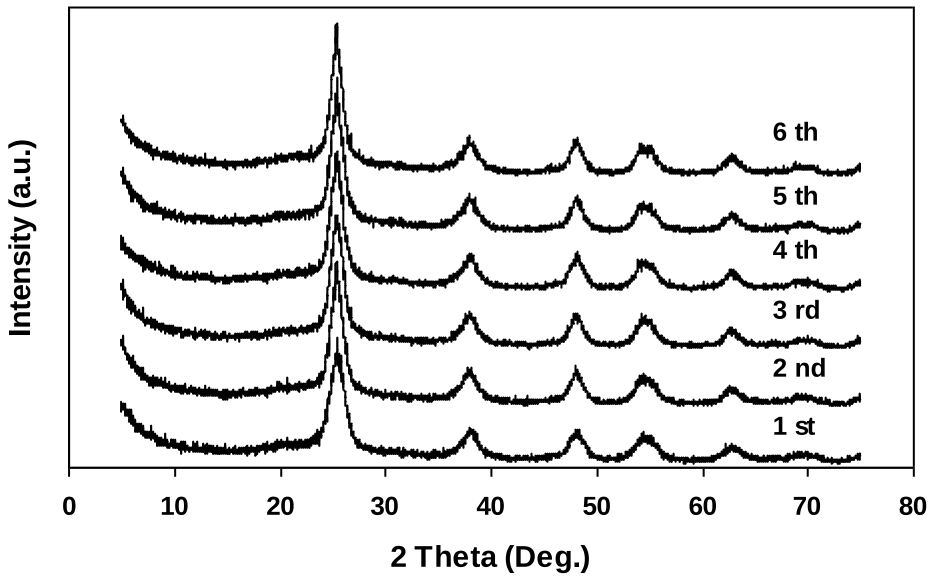

Figure 8: X-ray diffraction (XRD) of recycled TiO_2/K photocatalysts after several cycles of thermal treatment.

Improvement in catalytic activity and selectivity of catalytic processes can be achieved through the tailored-design of catalytic materials with microstructure and active site dispersion. As previously discussed, every clay mineral has unique properties that come with their inherent advantages and disadvantages. Therefore, an appropriate clay substrate in conjunction with immobilization method should be wisely selected based on the type of applications, the type of pollutants that are required to be degraded and consideration of the photoreactor design, in order to maximize the photocatalytic efficiency of the prepared catalysts for a longer working life.

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CHAPTER 3

EXPERIMENTAL MATERIALS AND METHODS

1. Materials

1.1 Clay materials

Five Australian clay minerals, sodium bentonite, kaolins (Q38, K15GR and Ceram), and zeolite, were employed as alternative adsorbents and substrates for TiO_2 nanophotocatalysts in this present study. Sodium bentonite contained a high montmorillonite content. Q38 is dry milled kaolin of good white colour, typically used in the manufacture of paints or products that require a white colour. K15GR is white kaolin clay generally used as a pigment extender in paints and as a functional filler in rubber compounds. Ceram is a white firing kaolin exhibiting ball clay properties. This Ceram kaolin consistently contributes high plasticity and green strength to ceramic bodies with excellent fired properties. All clays were obtained from Unimin Australia Ltd, and Escott zeolite was provided by Zeolite Australia Ltd. This zeolite contains clinoptilolite as the main crystalline component. Physico-chemical properties of each material are given in Table 1.

1.2 Congo Red

Congo Red (CR) [1-naphthalenesulfonic acid, 3,3´-(4,4´-biphenylenebis (azo)) bis(4-amino-) disodium salt] is a benzidine-based anionic diazo dye prepared by coupling tetrazotised benzidine with two molecules of napthionic acid [1]. The molecular structure of CR is illustrated in Fig. 1. In this present work, CR was chosen as an anionic dye surrogate indicator of industrial wastewater. The CR solution was prepared to the desired concentration by the addition of double-deionised water obtained from a Barnstead nanopure Diamond Water ion exchange system with 18.2 MΩ-cm resistivity.

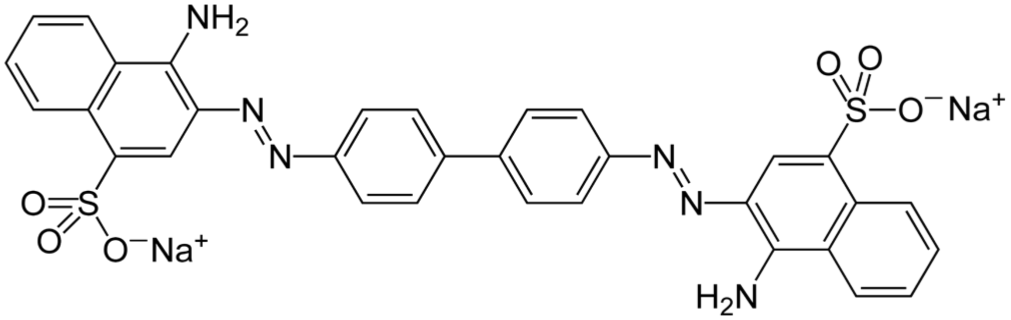

Figure 1: Molecular structure of congo red

Table 1: Physical and chemical properties of Australian clay materials

	Natural Clay Minerals				
Chemical Compound (%)	**Sodium Bentonite**	**Q38 Kaolin**	**K15GR Kaolin**	**Ceram Kaolin**	**Zeolite**
SiO_2	56.0	48.7	46.5	52.2	68.26
Al_2O_3	16	34.6	36.8	32.6	12.99
Fe_2O_3	4.6	0.9	0.9	0.6	1.37
CaO	0.9	0.1	0.6	<0.1	2.09
K_2O	0.4	1.2		0.4	4.11
TiO_2		1.3	0.8	0.9	0.23
MnO					0.06
MgO	3.3	0.4	0.3	0.3	0.83
Na_2O	2.9	0.2	0.1	0.2	0.64
P_2O_5					0.06
H_2O	10.0				
LOI	5.7	12.1	13.9	2.1	8.87
CEC	95meq/100g				120meq/100g
Particle size	D_{85} 75 µm	D_{99} 38 µm	< 53 µm	< 61 µm	D_{100}70 µm
Density	1.0 g cm^{-3}	0.6 g cm^{-3}	0.6 g/cm^3	0.7 g/cm^3	1.1-1.6 g cm^{-3}

1.3 Inorganic anions

Phosphate (PO_4^{3-}) and nitrate (NO_3^-) anions were selected as representative nutrients present in wastewater effluents. Phosphate and nitrate solutions were prepared from potassium dihydrogen orthophosphate (KH_2PO_4, VWR England) and potassium nitrate (KNO_3, Labchem Ajax Finechem Australia), respectively. The solution was made up to the desired concentration by the addition of double-deionised water obtained from a Barnstead nanopure Diamond Water ion exchange system with 18.2 MΩ-cm resistivity.

1.4 Wastewater Effluents

To simulate a wastewater treatment process, real wastewater from primary effluent and the secondary biological treatment via membrane bio-reactor (MBR) were employed in this study. The primary wastewater effluent from the Glenelg WWTP, Adelaide, Australia was collected and analysed in triplicate twice a week over a 2 week period. At this stage, large solid particles were removed through preliminary screening, followed by gravitational settling in a primary sedimentation tank. The secondary wastewater source was obtained from our laboratory scale MBR system (8 L capacity), which treated the primary effluent from the WWTP. A Zema® hollow membrane was used in the sequential batch MBR reactor, with a cycle of 1 h of wastewater recharge, 0.5 h of aerobic reaction and followed by 4 h of anaerobic digestion. The sludge retention time (SRT) used in the MBR was approximately 60 d. The treated effluents from the MBR were collected in a tank to ensure sufficient wastewater capacity for the subsequent adsorption and photocatalytic integration treatment. The wastewater quality of both the collected primary effluents from the WWTP and the secondary biologically treated effluents from the MBR system is given in Table 2.

Table 2: The quality of wastewater effluent following primary and secondary treatment.

Compositions	**Primary Effluent (mg L^{-1})**	**Secondary MBR Effluent (mg L^{-1})**
COD	285 - 315	13.5 - 22.0
PO_4^{3-}	21.7 - 23.8	19.9 - 20.3
NO_3^-	210 - 238	145.0 - 190

2. Synthesis and Characterisation of Multifunctional Nanomaterials

2.1 Formulated Clay - Lime Mixture Adsorbent

The clay-lime mixtures for the initial adsorption process, made-up of the sodium bentonite (15%), kaolin (10%), zeolite (5%), and lime (70%), were prepared and pre-activated according to the optimised conditions given in Chapter 5.1. The clay mixture was thermally treated at 300 ˚C for 1.5 h. and then kept in a desiccator until analysed.

2.2 Titania Impregnated Kaolinite Nano-Photocatalyst

The TiO_2-K catalyst particles were synthesized in accordance with the method developed by our research group [2, 3] and is detailed in Chapter 7. A summary of the catalyst preparation procedure is given in Fig. 2. A modified two step sol–gel method was used, where 25 mL titanium precursor was hydrolysed by 30 mL absolute ethanol. The resultant hydrolysed solution was then acid-catalysed under controlled acidic conditions. This was followed by heterocoagulation of the catalysed product with 10% (w/v) kaolinite suspension at 37˚C under constant overhead stirring for 4 h. The dry-milled kaolin clays were pre-treated by a series of acid-alkalization washes, followed by thermal treatment at 750^{o}C for 1 h before use. The clay particles were used as the inert carriers for the deposition of titania sol, enabling easy catalyst particle separation after water treatment. The heterocoagulated catalyst products were filtered and washed repeatedly with distilled water up to three times to remove any excess chemical impurities. The filter cake was dried in a conventional oven at 70±2˚C for 2-4 h, before being fired at 600°C for 3 h. The final TiO_2-K catalysts were ground to an appropriate particle size range before use.

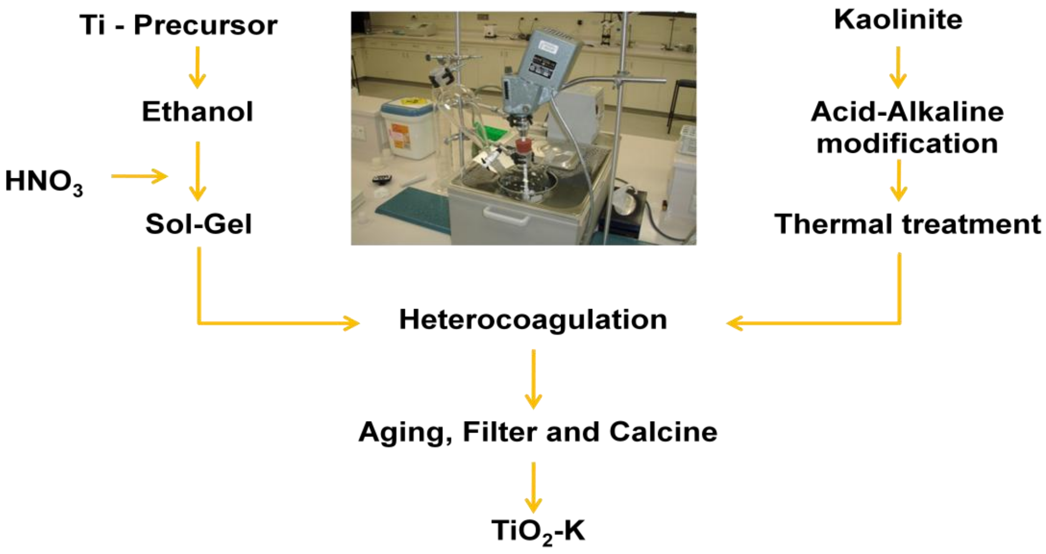

Figure 2: A summary of the titania impregnated kaolinite nano-photocatalyst preparation procedure.

2.3 Characterisation of the Multifunctional Nanomaterials

2.3.1 Differential Thermal Analysis and Thermogravimetric Analysis

Differential temperature analysis coupled with thermogravimetric analysis (DTA-TG) (TA Instruments) was performed on the natural clay minerals to obtain their weight loss profiles as a function of temperature. During the analysis, the raw clay samples were heat-treated from room temperature to 1200˚C at a ramping rate of 10˚C min^{-1} under anoxic conditions to avoid possible oxidation.

2.3.2 Static Particle Size Measurement

Particle size of the pre-treated kaolin was measured using a static light scattering laser diffraction particle sizer instrument (Malvern Mastersizer 2000), covering the detection range from 0.02 to 2000 microns. The kaolin particles were first dispersed in sodium pyrophosphate solution, with constant agitation and sonication until a stable dispersion was attained.

2.3.3 Electron Microscope Measurements

Morphological and surface characteristics of the mineral particles were analysed using scanning electron microscopy (SEM) (Philips XL30 SEM) at an accelerating voltage of 10 kV. A thin platinum coating was applied to the particle sample prior to analysis.

Transmission Electron Microscopy (TEM) was also performed in the case of TiO_2-K using Philips CM-100 TEM at an accelerating voltage of 100 kV. Before analysis, the TiO_2-K particles were minimally suspended in ethanol solution (ca. 0.01% w/v), followed by ultrasonic dispersion and subsequent immobilisation on copper measurement grids of 2 mm diameter.

2.3.4 Physical Surface Area and Pore Size Measurements

Brunauer- Emmett-Teller (BET) specific surface area and pore size measurements were performed using a Micromeritics gas adsorption analyser (Gemini Type 2375) at 77 ± 0.5 K in liquid nitrogen. Prior to the surface analysis, the sample vessels loaded with ca. 0.5–1.0 g were vacuum treated overnight at 105˚C and evacuation pressure of 50 mTorr. Nitrogen adsorption isotherms of the samples were then analysed for the specific surface area using the BET equation.

2.3.5 Powder X - Ray Diffractionometric Measurement

X-Ray Diffraction **(**XRD) measurements were performed using a Philips PW Diffractometer (Cu X-rays $\lambda = 1.54$ Å) over the range of 5–75° 2θ for all the samples. Samples were spiked with 10 wt% of zinc oxide before the diffractionometric analysis to facilitate determination of the amorphous phase to the amount of nanocrystals formed. In the case of the synthesised titania photocatalysts, the average crystallite diameter of the TiO_2 nanocrystals, Dhkl, was obtained using the Debye–Scherrer equation [$Dhkl = k\alpha/\beta \cos\theta$], where β is the line broadening, k is the crystalline shape with Warren's correction value for instrumental broadening of 0.89, and α and θ are the radiation wavelength and Bragg angle, respectively. A standard for the line broadening width based on a single anatase crystal of TiO_2 was used for calibration.

2.3.6 X-Ray Fluorescence Analysis

X-ray fluorescence analysis (XRF) was employed to perform elemental analysis for raw kaolin and the synthesised TiO_2-K nanophotocatalysts. Approximately 1g of the oven dried sample (105°C) was accurately weighed with 4g of 12-22 lithium borate flux. The mixtures were heated to 1050°C in a Pt/Au crucible for 20 minutes to completely dissolve the sample then poured into a 32mm Pt/Au mould heated to a similar temperature. The melt was cooled rapidly over a compressed air stream and the resulting glass disks were analysed on a PANalytical Axios Advanced wavelength dispersive XRF system using the in-house Silicates calibration program.

2.3.7 UV - Vis Diffuse Reflectance Analysis

The optical absorption characteristic of the resultant TiO_2-K composites was measured using a UV–Vis diffuse-reflectance spectroscopy. The diffuse-reflectance spectra were measured using a Varian Cary 5000 UV–Vis spectrophotometer between the wavelengths of 250 to 600 nm.

3. Experimental Procedure

3.1 Bench - Scale Operation

3.1.1 Bench - Scale Adsorption

Adsorption on the clay materials was initially carried out in a batch system to determine their removal capacity. A desired amount of the adsorbent was added to 50 ml of known concentration of CR solution. The pH was adjusted with 0.1 M HNO_3, and 0.1 M NaOH . The mixture was agitated at 150 rpm in a rotary shaker (Ratek OM 15 orbital mixer, Australia) at 30 ºC. Due to the high CR concentration, experiments were carried out over 24 hours to ensure that adsorptive equilibrium was obtained. The samples were withdrawn from the experimental flask at pre-determined time intervals until adsorption equilibrium was achieved. Then, the dye solution was separated from the adsorbent by centrifugation (Eppendorf Centrifuge 5415R, Germany) at 13,200 rpm for 20 minutes. The supernatants were then filtered using Millex VX filter (Millipore 0.45 μm) to ensure the solutions were free from adsorbent particles before measuring the residual dye concentration. All experiments were carried out in triplicate, and the average values were taken to minimise random error.

3.1.2 Bench - Scale Photocatalysis

Photoactivity of the resultant TiO_2-K was evaluated using CR at a standard photo-oxidation rate. An Aqueous solution of 57.4 µmol L^{-1} CR was photochemically reacted with TiO_2-K in a preliminary experiment. An 11W UV-C light (Davis Ultraviolet, Australia) was positioned centrally to a magnetically-stirred beaker that contained the reaction solution. The linear attenuation of the UV intensity at the reaction solution surface was determined to be 300 µW cm^{-2} using a radiometer. Prior to the photochemical reaction, the TiO_2-K was maintained in dark homogenisation for 0.5 h to ensure constant dispersion and mixing. Sampling was conducted every 1 h, and the supernatant was obtained for calorimetric measurement via centrifugation at 5000 rpm for 10 min. A control experiment to assess photolysis was also conducted in parallel. A single maximum wavelength of 496.5 nm was used with a path cell length of 1 cm in a UV-Vis spectrophotometer for analysing CR concentration. The CR concentrations were measured in triplicate and were evaluated as the average photo-oxidation rate.

3.2 Pilot - Scale Operation

3.2.1 Fluidised - Bed Reactor System

The Fluidised - Bed Reactor System (FBR) developed by Vimonses et al [4] was used for the formulated clay-lime mixture adsorption process in this study. The FBR cylinder reactor was fabricated using a poly(methyl methacrylate) plastic column with a detachable conical bottom for ease of cleaning and scheduled maintenance. A gas sparger with an average pore size of 45 µm was fitted to the detachable conical bottom. The pilot FBR reactor consisted of three sampling ports positioned in a vertical row. The first port on the top part of the reactor was assigned for influent feeding. The middle port was taken as a sampling point that was connected to the sand-bed column filtration. The last port was located at the bottom end of the reactor to ease the discharge of the effluent. The pressurized air was regulated by a flow meter (BOC, 1-15 L min^{-1}) to ensure constant aeration. To improve the hydrodynamic performance with homogeneous fluid flow of the FBR, a baffle ring was also provided just above the aeration disc to direct the flow of the solution in an up-flow mode through the reactor. This configuration provides a more direct and complete contact between the clay mixture and solution.

The suspension from the fluidized bed reactor was subsequently transferred to the glass column of 3 cm diameter and with 30 cm height packed with two different sizes of sand. The column was equipped with a sintered glass disc filter to support the bed and sealed with a stopper to facilitate the pressurized condition during filtration. The column bed was initially filled with 3 cm of coarse sand (0.425-1 mm) to avoid possible blockage of the disc filter and subsequently filled with 7 cm of finely granulated sand (0.125-0.355 mm). Such configuration of the sand column allowed the clay particles and particulates formed by precipitation to be retained within the bed, while the residual dissolved contaminants still easily passed through. From this packing practice, an average permeate flow rate of 10 mL min^{-1} could be obtained. The sand bed was set to be replaced when the column was half saturated to avoid the breakthrough condition, or when the flow rate was dropped to lower than 8 mL min^{-1} as a result of the particle blockage within the column bed. An image of the fluidized bed reactor and sand filtration column is displayed in Fig 3.

Figure 3: A laboratory-designed Fluidised-Bed Reactor System

3.2.2 Annular Slurry Photoreactor (ASP) System

A stainless steel-lined ASP designed by Chong et al [5] was a three-phase bubble column reactor, where the TiO_2-K particles were dispersed in the targeted water via bubble aeration. A detachable conical bottom was made to the ASP to prevent a reaction dead zone for the TiO_2-K catalyst, as well as promoting ease of cleaning and maintenance. At the lower end, a 45μm air sparger was fitted to provide homogeneous aeration for catalyst suspension and mixing. An UV-C light of 11W (Davis Ultraviolet, Australia) was positioned annularly within the quartz thimble to prevent direct contact with the reaction fluid, while allowing optimal UV transmission into the annulus reaction zone. The UV-C light was used for photonic excitation of the TiO_2-K catalyst alone. Samples were collected from the four-descended level sampling ports. Electronic probes and meters for in-situ data logging of pH, dissolved oxygen and temperature (TPS, Australia) were connected to the reactor. The operating temperature for the ASP system was kept at room temperature of 25^{o}C during the experiments. The detailed picture of the ASP and experimental setup are shown in Fig. 4.

Figure 4: A laboratory-designed Annular Slurry Photoreactor System

3.3 An Adsorption - Photocatalysis Hybrid System

The Adsorption-Photocatalysis hybrid treatment process used in this study involved a consecutive treatment series of our development 1) formulated clay-FBR system and 2) TiO_2-K-ASP system.

Chemical removal by the clay mixture in the FBR was operated in a continuous operation mode. Two and a half litres of the studied solution was initially pumped into the reactor, where regulated air of 1 L min^{-1} was supplied constantly through the air sparger to generate fine bubbles. Then, the optimal amount of the clay-lime mixture was added into the reactor, allowing the removal interaction to take place, before the suspension was transferred continuously to the sand column, where the samples were collected from the column at pre-determined time intervals and analysed for residual concentration. The influent was continually fed to the reactor to maintain a constant volume, with addition of the clay mixture every 2 h over the experimental period.

The treated solution from the FBR was subsequently transferred to the reservoir for pH adjustment and to ensure sufficient volume of the solution for the operation of the TiO_2-K-ASP system. Thereafter, 3 L of the solution was pumped into the ASP. Constant aeration at 7 L min^{-1} was supplied to facilitate the homogeneous fluid hydrodynamic performance and also the photocatalytic reaction. The TiO_2-K catalyst was then added into the solution. The TiO_2-K suspension was kept in the dark and homogenised for 0.5 h to ensure constant dispersion and mixing prior to the UV light being turned on to initiate the photochemical reaction. This ASP system was operated in a batch operation mode, in which the samples were collected at pre-determined time intervals through elevated sampling ports. The samples were then centrifuged (Eppendorf Centrifuge 5415R, Germany) at 16.1 rcf for 20 minutes. The supernatants were then filtered using Millex VX filter (Millipore 0.45 um) to ensure the solutions were free from TiO_2-K particles before measuring the residual concentration.

4. Analytical Procedure

4.1 Monochromatic Spectroscopy Measurement of Congo Red and Aromatic Compound Concentration

The residual concentration of Congo red (CR) was determined colorimetrically using a monochromatic spectroscopy method. In this study, the correlation of the CR and its intense characteristics peak at 496.5 nm using a UV-visible spectrophotometer (model γ, Helios, UK) was developed [6]. A calibration curve was plotted between absorbance and concentration of the dye solution to obtain an absorbance-concentration profile (Fig. 5). The percentage removal and the adsorption of the dye were calculated from the concentration changes. A similar analytical protocol was carried out to determine the aromatic organic compound content at the wavelength 254 nm.

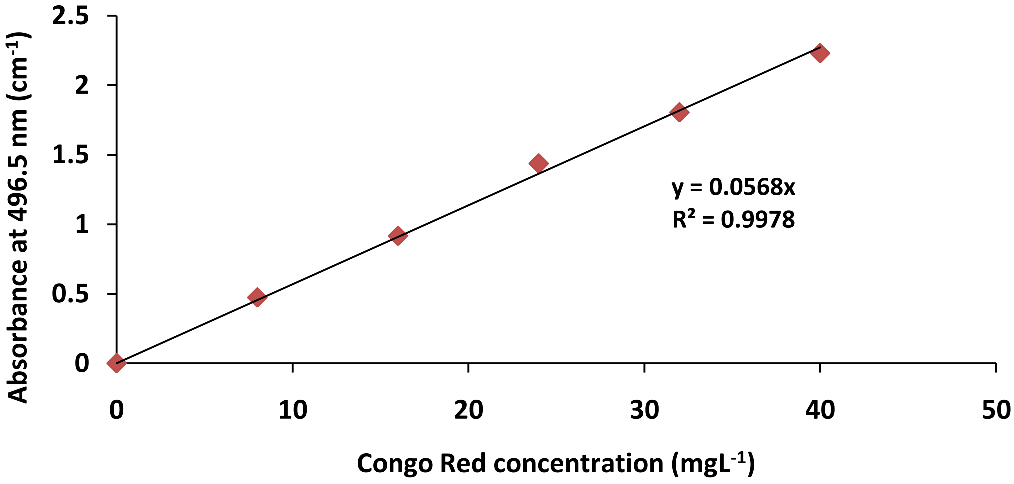

Figure 5: A calibration curve of an absorbance-concentration profile

4.2 Chemical Oxygen Demand (COD)

The residual organic contaminants were measured in term of COD. COD is the total amount of oxygen consumed (mg) per litre of the sample. The COD measurement was obtained through the open flux method using the test kits provided by Hach Lange GmbH (Germany) under two concentration ranges, i.e. high range COD, 0-1500 mg L^{-1} and low range COD, 0-150 mg L^{-1}, containing potassium dichromate oxidising agent ($K_2Cr_2O_7$). Two millilitres of sample was added into the reagent kit and subsequently heated at 150 °C for 2 h in a digestion reactor DRB 200 (Hach Lange GmbH, Germany) [7]. The oxidisable organic compounds present in the sample solution react with the $K_2Cr_2O_7$ causing reduction of the dichromate ion to green chromic ion. Based on this method, the total oxidisable organic compounds were correlated to the spectroscopic measurement (spectrophotometer DR/4000, Hach Lange GmbH, Germany) of the amount of Cr^{3+} formed at the wavelength of 620 nm.

4.3 High Performance Size Exclusion Chromatography Analysis

To investigate changes in the molecular weight distribution profile of the wastewater samples during photocatalysis, the samples were analysed using a coupling method of High Performance Size Exclusion Chromatography (HPSEC) and UV detection as shown in Fig 6 [8]. Sample injection and separation were conducted with a Waters 2690 Alliance system with a temperature-controlled oven (30 °C) and a Shodex KW802.5 glycol functionalized silica gel column [9]. Elution was monitored with a Waters 996 photodiode array detector (260 nm). Samples were filtered through a 0.22 μm membrane filter prior to analysis and 100 μL sample was injected. The mobile phase was 0.02 M phosphate buffer at pH 6.8 adjusted to an ionic strength of 0.1 M with sodium chloride. The system was operated at isocratic conditions with an eluent flow rate of 1.0 mL min^{-1}. Polystyrene sulfonate standards (Polysciences, USA) with molecular weight (MW) 4.6, 8, 18, and 35 kDa were used to calibrate the retention time response to apparent molecular weight.

Figure 6: High performance size exclusion chromatography system

4.4 Inorganic Ion Measurement

4.4.1 Phosphate

In order to determine phosphates, a vanadium molybdate spectrometry method (spectrophotometer DR/4000, Hach Lange GmbH, Germany) was applied [10]. The reagents kits (Total Phosphorous, 0-100 mg L^{-1} PO_4^{3-}) were obtained from Hach Lange GmbH, Germany.

The reaction commenced when the orthophosphate in the sample reacted with molybdate in an acid medium to produce a phosphomolybdate complex. With further reaction with vanadium, yellow vanadomolybdophosphoric acid was formed, in which the intensity of the yellowish appearance was proportional to the phosphate concentration in the collected samples. To hydrolyse the condensed inorganic forms of phosphorous, the samples were pre-treated under acidic and high temperature conditions (30 minutes, 105 °C) using a DRB 200 digester. The final PO_4^{3-} concentration was determined based on the yellow colour correlation given as the total phosphorous concentration, and therefore a subsequent conversion to PO_4^{3-} using their corresponding molecular weight was carried out.

4.4.2 Nitrate

The nitrate concentration was determined based on a persulfate digestion method. The testing kits were provided by Hach Lange GmbH (Germany), which comprises of DR/4000 spectrophotometer and reagent tubes (Total Nitrogen 0-25 mg L^{-1}) [11].

Within this method, all forms of nitrogen are converted into nitrate through an alkaline persulfate digesting reagent and thermal treatment at 105 °C for 30 minutes using DRB 200 reactor. Thereafter, sodium metabisulfite was added to the digested samples in order to eliminate any interference from halogen oxides during the measurement. The reaction of nitrate with chromotropic acid under acidic conditions results in a yellow complex formation. The final NO_3^- concentration was determined by measuring the yellow complex at the maximum absorbance characteristic at 410 nm.

5. Error Analyses

In this work, the removal efficiency of the materials was also evaluated via the isotherm and kinetic models, where the correlation of the experimental data to the studied model was determined using the linear correlation coefficient (R^2). However, due to the inherent bias resulting from linearization of the isotherm model, the non-linear regression Chi-square (X^2) test was also employed as a criterion to verify the fitting quality. This statistical analysis is based on the sum of the squares of the differences between the experimental and model calculated data, of which each squared difference was divided by the corresponding data obtained by calculating from models. More this discussion and calculation details of the error analyses are given in Chapter 4.

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CHAPTER 4

ADSORPTION AND EVALUATION OF KINETIC ISOTHERM STUDIES OF NATURAL CLAY MATERIALS

SUB-CHAPTER 4.1

KINETIC STUDY AND EQUILIBRIUM ISOTHERM ANALYSIS OF CONGO RED ADSORPTION BY CLAY MATERIALS.

V. Vimonses [a], S. Lei [c], B. Jin [a,b,d], C. Chow [d], C. Saint [b,d]

[a] School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

[b] School of Earth and Environmental Sciences, The University of Adelaide, Adelaide, SA 5005, Australia

[c] School of Resource and Environment Engineering, Wuhan University of Technology, Wuhan 430070, China

[d] Australian Water Quality Centre, SA Water Corporation, Bolivar 5108, Australia

Chemical Engineering Journal 2009; 148: 354-364.

STATEMENT OF AUTHORSHIP

KINETIC STUDY AND EQUILIBRIUM ISOTHERM ANALYSIS OF CONGO RED ADSORPTION BY CLAY MATERIALS.

Chemical Engineering Journal 2009; 148: 354-364.

Vimonses, V. (Candidate)

Performed experiment design; analysis of samples; interpreted data; manuscript evaluation; wrote manuscript.

Signed……………………………………………………………*Date*………………

Lei, S.

Performed experiment design; interpreted data.

I give consent for V. Vimonses to present this paper for examination towards the Doctor of Philosophy

Signed……………………………………………………………*Date*………………

Jin, B.

Supervision of manuscript preparation; manuscript evaluation; acted as corresponding author.

I give consent for V. Vimonses to present this paper for examination towards the Doctor of Philosophy

Signed……………………………………………………………*Date*………………

Chow, C. W. K.

Supervision of manuscript preparation; manuscript evaluation

I give consent for V. Vimonses to present this paper for examination towards the Doctor of Philosophy

Signed…………………………………………………………………*Date*………………

Saint, C.

Supervision of manuscript preparation; manuscript evaluation

I give consent for V. Vimonses to present this paper for examination towards the Doctor of Philosophy

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Vimonses, V., Lei, S., Jin, B., Chow, C.W.K. & Saint, C. (2009) Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay materials.
Chemical Engineering Journal, v. 148 (2-3), pp. 354-364

SUB-CHAPTER 4.2

ADSORPTION OF CONGO RED BY THREE AUSTRALIAN KAOLINS

V. Vimonses [a], S. Lei [c], B. Jin [a,b,d], C. Chow [d], C. Saint [b,d]

[a] School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

[b] School of Earth and Environmental Sciences, The University of Adelaide, Adelaide, SA 5005, Australia

[c] School of Resource and Environment Engineering, Wuhan University of Technology, Wuhan 430070, China

[d] Australian Water Quality Centre, SA Water Corporation, Bolivar 5108, Australia

Applied Clay Science 2009; 43: 465-472.

STATEMENT OF AUTHORSHIP

ADSORPTION OF CONGO RED BY THREE AUSTRALIAN KAOLINS.

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Vimonses, V. (Candidate)

Performed experiment design; analysis of samples; interpreted data; manuscript evaluation; wrote manuscript.

Signed……………………………………………………………*Date*………………

Lei, S.

Performed experiment design; interpreted data.

I give consent for V. Vimonses to present this paper for examination towards the Doctor of Philosophy

Signed……………………………………………………………*Date*………………

Jin, B.

Supervision of manuscript preparation; manuscript evaluation; acted as corresponding author.

I give consent for V. Vimonses to present this paper for examination towards the Doctor of Philosophy

Signed……………………………………………………………*Date*………………

Chow, C. W. K.

Supervision of manuscript preparation; manuscript evaluation

I give consent for V. Vimonses to present this paper for examination towards the Doctor of Philosophy

Signed……………………………………………………………*Date*………………

Saint, C.

Supervision of manuscript preparation; manuscript evaluation

I give consent for V. Vimonses to present this paper for examination towards the Doctor of Philosophy

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Vimonses, V., Lei, S., Jin, B., Chow, C.W.K. & Saint, C. (2009) Adsorption of congo red by three Australian kaolins.
Applied Clay Science, v. 43 (3-4), pp. 465-472

Brief Summary for Chapter 4

Key research findings in Chapter 4 are summarised as follow:

- Sodium bentonite, kaolin and zeolite possess variation in their clay mineral structures, and hence this results in differences in their physiochemical properties, i.e. cation-exchange capacity, swelling properties and adsorption behaviours etc.

- Sodium bentonite performed the best among natural clays with a removal capacity of 19.9 mg g^{-1}, followed by kaolin (5.6 mg g^{-1}) and zeolite (4.3 mg g^{-1}), respectively. However, the adsorption of the CR can vary depending upon the operating conditions, i.e. initial dye concentration, adsorbent loading, pH and temperature etc.

- Two common adsorption isotherms, i.e. the Freundlich and Langmuir models were employed to describe the adsorptive characteristics of the clay minerals. The Freundlich isotherm was found to best describe the adsorptive interaction for sodium bentonite and zeolite; whereas the Langmuir model was well-fitted to all kaolins.

- The adsorptive kinetic studies revealed that the adsorption of all natural clays followed the pseudo-second order kinetic models, indicating the adsorption mechanism was dependent on the adsorbate and adsorbent interaction. Further investigation on the intra-particle mass transport rate revealed that there are two or three adsorption stages taking place, where intra-particle diffusion rate is the rate-controlling step.

- Dye adsorption by the natural clay was a pH dependent process, in which the pH of dye solution can significantly affect the surface charge of the adsorbent and the degree of ionisation and speciation of the adsorbate. Bentonite gave the most stable adsorption over the studied pH range compared to kaolin and zeolite. Acidic pH condition was found to enhance the dye removal due to electrostatic attraction, but more than 90% dye removal was still obtained at neutral pH.

Thermodynamic studies indicated that adsorption of all clays was stable over an extensive range of temperatures. The adsorption is an exothermic reaction and can take place spontaneously in nature.

- The thermal structural stability of kaolin provides a potential for the clay to be reused. The repetitive thermal regeneration of the used-adsorbent demonstrated comparable dye removal efficiencies even after the 5th cycle runs.

CHAPTER 5

SYNTHESIS AND ADSORPTIVE EVALUATION OF THE CALCINED CLAY MIXTURES AND ITS INSIGHT KINETICS AND REMOVAL MECHANISMS

SUB-CHAPTER 5.1

ENHANCING REMOVAL EFFICIENCY OF ANIONIC DYE BY COMBINATION AND CALCINATION OF CLAY MATERIALS AND CALCIUM HYDROXIDE

V. Vimonses [a,b], B. Jin [a,b,c], C. Chow [c], C. Saint [b,c]

[a] School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

[b] School of Earth and Environmental Sciences, The University of Adelaide, Adelaide, SA 5005, Australia

[c] Australian Water Quality Centre, SA Water Corporation, Bolivar 5108, Australia

Journal of Hazardous Materials 2009; 171: 941-947.

STATEMENT OF AUTHORSHIP

ENHANCING REMOVAL EFFICIENCY OF ANIONIC DYE BY COMBINATION AND CALCINATION OF CLAY MATERIALS AND CALCIUM HYDROXIDE

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Vimonses, V. (Candidate)

Performed experiment design; analysis of samples; interpreted data; manuscript evaluation; wrote manuscript.

Signed……………………………………………………………*Date*………………

Jin, B.

Supervision of manuscript preparation; manuscript evaluation; acted as corresponding author.

I give consent for V. Vimonses to present this paper for examination towards the Doctor of Philosophy

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Chow, C. W. K.

Supervision of manuscript preparation; manuscript evaluation

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Saint, C.

Supervision of manuscript preparation; manuscript evaluation

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SUB-CHAPTER 5.2

INSIGHT INTO REMOVAL KINETIC AND MECHANISMS OF ANIONIC DYE BY CALCINED CLAY MATERIALS AND LIME

V. Vimonses [a,b], B. Jin [a,b,c], C. Chow [c]

[a] School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

[b] School of Earth and Environmental Sciences, The University of Adelaide, Adelaide, SA 5005, Australia

[c] Australian Water Quality Centre, SA Water Corporation, 250 Victoria Square, Adelaide SA 5100, Australia

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Vimonses, V. (Candidate)

Performed experiment design; analysis of samples; interpreted data; manuscript evaluation; wrote manuscript.

Signed……………………………………………………………*Date*………………

Jin, B.

Supervision of manuscript preparation; manuscript evaluation; acted as corresponding author.

I give consent for V. Vimonses to present this paper for examination towards the Doctor of Philosophy

Signed……………………………………………………………*Date*………………

Chow, C. W. K.

Supervision of manuscript preparation; manuscript evaluation

I give consent for V. Vimonses to present this paper for examination towards the Doctor of Philosophy

Signed……………………………………………………………*Date*………………

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Brief Summary for Chapter 5

Key research findings in Chapter 5 are summarised as follows:

- A feasible physically modified approach of combination and calcination of the natural clays with addition of lime was developed to enhance removal capacity of the anionic dye congo red (CR) from wastewater effluent.

- The compositions of clay-lime mixtures were selected in accordance with their physical and chemical properties. The optimally formulated mixture was found to be in the range of 65-70% of lime, 10-15% for sodium bentonite and kaolin, and 5-10% zeolite. Subsequent investigation on the calcination conditions was also performed with respect to different temperatures and treatment periods. The obtained results showed that the highest removal capability can be achieved under thermal treatment at 300 °C for 1.5 h.

- The clay-lime mixture demonstrated substantial enhancement in their decolourisation efficiency, in comparison to the individual clays. The removal capacity of this adsorbent mixture was greater than 575 mg g^{-1}. This was accounted to 10-20 times higher removal capacity than the natural bentonite, kaolin and zeolite, which were used along as the major clay-lime mixture components.

- The removal mechanisms of the clay-lime mixture towards the CR dye was suggested as a combination of adsorption-precipitation process, in which the rapid removal was predominated by precipitation of calcium ions and dye molecules, especially at high concentration of dye. It was estimated that this precipitation process accounted for over 70% of the total removal of CR.

- A predominant removal mechanism of the dye can be varied depending upon the mixture of pH suspension, i.e. adsorption/coagulation at acidic pH and precipitation at basic condition.

- The effect of solution pH was found to be insignificant for the dye removal as a result of strong alkalinity of the clay-lime mixture. This removal character provides a significant advantage over other low-cost adsorbents, in which their applications are mostly limited by the pH of the solution.

- The recycling study showed an enhancement of dye removal efficiency as the number of recovery cycles increased, even after the fifth run. It was proposed that the repetitive heat treatment during the recycle process likely promotes the decomposition of small foreign molecules attached subterraneously inside the micropores, providing more available active sites. The result indicated the potential for regeneration of the material.

CHAPTER 6

DEVELOPMENT OF A PILOT FLUIDISED BED REACTOR SYSTEM WITH A FORMULATED CLAY-LIME MIXTURE FOR CONTINUOUS REMOVAL OF CHEMICAL POLLUTANTS FROM WASTEWATER

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V. Vimonses [a, b], B. Jin [a,b,c], C.W.K. Chow [c], C. Saint [b,c]

[a] School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

[b]School of Earth and Environmental Sciences, The University of Adelaide, Adelaide, SA 5005, Australia

[c]Australian Water Quality Centre, SA Water Corporation, 250 Victoria Square, Adelaide, SA 5100, Australia

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DEVELOPMENT OF A PILOT FLUIDISED BED REACTOR SYSTEM WITH A FORMULATED CLAY-LIME MIXTURE FOR CONTINUOUS REMOVAL OF CHEMICAL POLLUTANTS FROM WASTEWATER

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Vimonses, V. (Candidate)

Performed experiment design; analysis of samples; interpreted data; manuscript evaluation; wrote manuscript.

Signed……………………………………………………………*Date*………………

Jin, B.

Supervision of manuscript preparation; manuscript evaluation; acted as corresponding author.

I give consent for V. Vimonses to present this paper for examination towards the Doctor of Philosophy

Signed……………………………………………………………*Date*………………

Chow, C. W. K.

Supervision of manuscript preparation; manuscript evaluation

I give consent for V. Vimonses to present this paper for examination towards the Doctor of Philosophy

Signed……………………………………………………………*Date*………………

Saint, C.

Supervision of manuscript preparation; manuscript evaluation

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CHAPTER 7

SYNTHESIS AND CHARACTERISATION OF NOVEL TITANIA IMPREGNATED KAOLINITE AND ITS PHYSICAL PROPERTIES AND PHOTOOXIDATION ABILITY

SUB-CHAPTER 7.1

SYNTHESIS AND CHARACTERISATION OF NOVEL TITANIA IMPREGNATED KAOLINITE NANO-PHOTOCATALYST

M.N. Chong [a], V. Vimonses [a], S. Lei [c], B. Jin [a,b,d], C. Chow [d], C. Saint [b,d]

[a] School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

[b] School of Earth and Environmental Sciences, The University of Adelaide, Adelaide, SA 5005, Australia

[c] School of Resource and Environment Engineering, Wuhan University of Technology, Wuhan 430070, China

[d] Australian Water Quality Centre, SA Water Corporation, Bolivar 5110, Australia

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Chong, M.N.

Performed experiment design; analysis of samples; interpreted data; manuscript evaluation; wrote manuscript.

I give consent for V. Vimonses to present this paper for examination towards the Doctor of Philosophy

Signed…………………………………………………………*Date*………………

Vimonses, V. (Candidate)

Performed experiment design; analysis of samples; interpreted data; manuscript evaluation.

Signed…………………………………………………………*Date*………………

Lei, S.

Performed experiment design; interpreted data.

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Jin, B.

Manuscript evaluation; acted as corresponding author.

I give consent for V. Vimonses to present this paper for examination towards the Doctor of Philosophy

Signed…………………………………………………………………*Date*………………

Chow, C.

Manuscript evaluation.

I give consent for V. Vimonses to present this paper for examination towards the Doctor of Philosophy

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Synthesis and characterisation of novel titania impregnated kaolinite nano-photocatalyst.
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SUB-CHAPTER 7.2

EVALUATION OF THE PHYSICAL PROPERTIES AND PHOTODEGRADATION ABILITY OF TITANIA NANOCRYSTALLINE IMPREGNATED ONTO MODIFIED KAOLIN

V. Vimonses [a, b], M. N. Chong [a, b], B. Jin [a,b,c]

[a] School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

[b] School of Earth and Environmental Sciences, The University of Adelaide, Adelaide, SA 5005, Australia

[c] Australian Water Quality Centre, SA Water Corporation, Bolivar 5108, Australia

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EVALUATION OF THE PHYSICAL PROPERTIES AND PHOTODEGRADATION ABILITY OF TITANIA NANOCRYSTALLINE IMPREGNATED ONTO MODIFIED KAOLIN

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Performed experiment design, analysis of samples; interpreted data; manuscript evaluation; wrote manuscript.

Signed……………………………………………………………*Date*………………

Chong, M. N.

Performed experiment design; interpreted data; manuscript evaluation.

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Signed……………………………………………………………*Date*………………

Jin, B.

Manuscript evaluation; acted as corresponding author.

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Brief Summary for Chapter 7

Key research findings in Chapter 7 are summarised as follow:

- A reproducible two step sol-gel method was developed for synthesising a novel titania impregnated kaolin (TiO_2-K) nanophotocatalyst. The nitric acid concentration showed a profound effect on the titania sol formation and the photocatalytic activity of the catalysts. The optimal nitric acid concentration range of 0.25–0.30 M can contribute to the formation of transparent titanium sol with consistent viscosity after aging for 13–16 h.

- A series of acid-alkali-thermal treatments was further developed to modify the functional surface of the kaolin as a catalyst substrate. The modification was found to promote the delaminated structure of the clays, resulting in significant increase in their specific surface area available for subsequent TiO_2 immobilisation. In addition, the heterocoagulation between the negative surface charges of the modified kaolin and the positively charged TiO_2 sol can be highly augmented during the course of synthesis as a result of electrostatic interaction.

- The thickness of the titania crystalline layer on the core kaolin was manipulated through the clay loading during the heterocoagulation. An excess amount of clay led to an over agglomerated and inconsistently coated layer of TiO_2 particles on the catalyst surface, which in turn reduced the available photocatalytic active sites. In this study, the 10% (w/v) of the kaolin was selected as the optimal loading enabling a constant titania coating thickness of 7 nm to be produced. Homogeneous distribution of the TiO_2 nanocrystals on the clay surface enhances the photo-oxidation performance of the light photon activation process.

- The final stage thermal treatment of the prepared TiO_2-K catalysts demonstrated different physical characteristics upon elevated temperature. The optimal calcination temperature was found to be at 600 ºC, which was capable of transforming amorphous-to-crystalline TiO_2 whilst suppressing the formation of the rutile TiO_2 phase. The resultant TiO_2-K catalysts possess lower surface area than the prior treated sample due to the rupture of Ti-O bonds.

- The thermal treated TiO_2-K catalyst demonstrated high photostability as a result of chemical bonding between the titania nanocrystal and the siliceous side of the kaolin substrate.

- Repetitive thermal regeneration of the catalysts caused the melding of the original microporous anatase TiO_2 into a macroporous structure without any significant phase transformation to rutile. The structure transition was accompanied by a slight reduction in specific surface area and increase in the average nanocrystal sizes. However, the photoactivity of the recycled TiO_2-K catalysts remained relatively constant after six thermal regenerative cycles.

- The separation of the TiO_2-K particle by means of gravitational sedimentation was estimated based on Kynch's theory, where the single particle terminal velocity was found to be 5.28×10^{-3} ms^{-1}. This result indicated self-separation capability of the catalysts after photocatalytic reaction.

CHAPTER 8

AN ADSORPTION-PHOTOCATALYSIS HYBRID PROCESS USING MULTI-FUNCTIONAL-NANOPOROUS MATERIALS FOR WASTEWATER RECLAMANTION

CHAPTER 8

AN ADSORPTION-PHOTOCATALYSIS HYBRID PROCESS USING MULTI-FUNCTIONAL-NANOPOROUS MATERIALS FOR WASTEWATER RECLAMATION

V. Vimonses [a, b], B. Jin [a,b,c], C.W.K. Chow [c], C. Saint [b,c]

[a] School of Chemical Engineering, The University of Adelaide, Adelaide, SA 5005, Australia

[b]School of Earth and Environmental Sciences, The University of Adelaide, Adelaide, SA 5005, Australia

[c]Australian Water Quality Centre, SA Water Corporation, 250 Victoria Square, Adelaide, SA 5100, Australia

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STATEMENT OF AUTHORSHIP

AN ADSORPTION-PHOTOCATALYSIS HYBRID PROCESS USING MULTI-FUNCTIONAL-NANOPOROUS MATERIALS FOR WASTEWATER RECLAMATION

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Vimonses, V. (Candidate)

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Saint, C.

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CHAPTER 9

CONCLUSIONS AND FUTURE DIRECTION

1. Conclusions

The utilisation of natural clay minerals has been widely investigated for various environmental remediation facets according to their economical viability, abundant availability, non-toxicity, sorption properties and potential for ion exchange for charged pollutants [1] . The meso-, micro-, and nano-porosity in conjunction with high structural stability of the clay minerals provides them with unique properties to be employed via different physiochemical reactions, i.e. adsorption of contaminants, coagulation (as a coagulation aid), catalytic application etc. However, in many cases, the removal efficiency of the natural clays appeared less effective than the commonly used commercially available options such as activated carbon, due to its significant higher active surface area and non-selective adsorption capability. As a result, attention has been paid to surface modification of the natural clay, where their surface functionality can be altered to suit desired exploitation purposes and to improve their overall removal performance.

In this present study, three Australian clay minerals, sodium bentonite, kaolin and zeolite have been tailored to suit the wastewater treatment application for potential reclamation. The inherent adsorption properties of these selective clay minerals were initially examined against several key removal parameters, i.e. the adsorption isotherms and kinetics, to evaluate removal behaviour. Based on obtained information, two modifying approaches were adopted to synthesise novel clay based functional materials as: 1) alternative low-cost adsorbents; and 2) titania impregnated kaolin (TiO_2-K) catalysts for photocatalytic application. The adsorbent preparation protocols used were focused on combinations of different clays with lime under optimised treatment conditions. The resultant adsorbent mixtures demonstrated significant improvement in their removal efficiency toward recalcitrant compounds with the potential for extended recovery. The subsequent preparation of immobilised titanium dioxide onto the kaolin clay was carried out to promote self-separation of the catalyst after reaction. The TiO_2-K catalysts exhibited adsorption augmentation of the dyes onto the particle surface, where the photooxidation reaction was induced and took place. Both novel materials were then evaluated for feasibility of use in large-scale operation using a lab-designed

Fluidised Bed Reactor (FBR) and Annular Slurry Photoreactor (ASP) to facilitate applications of the adsorbent mixture and TiO_2-K catalyst, respectively. An improvement of treated wastewater quality was finally achieved via the integration of these two processes. The adsorption-photocatalysis hybrid system revealed a positive synergetic effect within the process, where substantial reduction of nutrients and COD was observed. The results demonstrated a potential employment of this hybrid system for wastewater treatment.

Major outcomes of this project are highlighted in detail in the following section.

2. Major Achievements

2.1 Evaluation of the adsorption capabilities of Australian natural clays

Five Australian natural clays, namely sodium bentonite, kaolins (Q38, K15GR, Ceram) and zeolite, were selected as representative clay minerals to investigate their adsorption capacity. This is due to the fact that these clays possess unique physiochemical properties that can result in different adsorptive characters. The natural clays were subjected to various characterisation analyses, i.e. surface image (SEM), elemental compositions (XRD), surface area (BET), thermal structural stability (DTA-TG) etc. to obtain the basic physical information. Thereafter, the adsorption capacity of each clay was evaluated using the recalcitrant anionic dye congo red and maximum removal efficiency was estimated. Adsorption isotherms and kinetic studies revealed that the removal mechanisms of these clays were varied from one to the other. The adsorption capacity was influenced by solution pH, of which the dye adsorption was more favourable under acidic conditions. The adsorption of bentonite and zeolite were best described by the Freundlich model, where multilayer adsorption could take place. This was contrary to the three kaolins, where the adsorption of dye on the clay surface was governed by the monolayer Langmuir adsorption model. It was found that the adsorption of all clays followed the pseudo-second order kinetic model, indicating the adsorption mechanism was mainly dependent on the adsorbate and adsorbent interaction.

The obtained results demonstrated that sodium bentonite had the highest removal efficiency, followed by the kaolins and zeolite. Kaolins, in contrast, possess higher thermally structural stability than the others, indicating their potential in reuse of the clay and regeneration. The information from this study provided comprehensive understanding of the adsorption behaviour of these clays and their functional characteristics for further utilisation.

2.2 Development of a clay-lime mixture as an alternative low-cost adsorbents

An innovative clay-lime mixture was successfully developed as an alternative low-cost adsorbent for wastewater treatment processes. Different natural clays and lime composition was optimised according to their individual physiochemical characters. In this present work, a thermal treatment was selected as an economical modification method to develop desirable properties and prevent undesirable properties from developing in the clay minerals for suitable applications. The optimum calcination condition for preparation of the clay-lime mixture was 300ºC for 1.5 h. This clay-lime mixture demonstrated superior removal efficiency with rapid reaction towards the anionic dye owning to integration of an adsorption/precipitation mechanism. The obtained results showed that more than 80% of 150 mg L^{-1} of the dye can be decolourised within the first 5 min of reaction. Comprehensive removal kinetic studies of the mixture were also provided. This information can facilitate the optimisation of operating conditions and enable the prediction of the removal performance of the clays, especially in the practical wastewater treatment process. Recyclability and the material lifespan studies indicated that the clay-lime mixture possesses a recovery potential, where the comparable removal efficiency can be maintained even after the 5th recycle run.

2.3 Development of a fluidised bed system with clay-lime mixture for continuous adsorption of wastewater pollutants

In this work, a mini pilot-scale fluidised bed reactor (FBR) was developed to accompany the continuous operating scheme. This was to examine the feasibility of application of the alternative clay-lime mixture adsorbent for wastewater treatment.

Several parameters that could influence operational conditions of the contaminant removal performance by the FBR systems using the clay-lime mixture were examined, i.e. material loading, influent flow rate, aeration rate, kinetic reaction time, and re-addition period of the mixture etc. The FBR reactor was designed to accommodate the effective removal while economical operation should still be achievable. The results obtained revealed that the FBR system required less adsorbent loading (8 gL^{-1}) of the clay-lime mixture compared to the small batch system (1 gL^{-1}). Due to the light particle nature of the mixture, a minimum aeration rate of 1 $Lmin^{-1}$ was sufficient to maintain a homogeneous suspended condition inside the reactor. This developed FBR system was tested against anionic dye and oxyanions present in the wastewater stream. An excellent removal of anionic dye and PO_4^{3-} was observed despite experiments being performed under co-existing conditions. The potential reaction time of the FBR system under continuous operation was determined by the suspension pH. Under this optimal operating condition, 100%, 20-40% and 10-15% removal of PO_4^{3-}, NO_3^-, and COD, respectively from the primary wastewater effluent can be attained.

2.4 Development of a novel titanium dioxide impregnated kaolin photocatalyst via a reproducible synthesis method

A novel titanium dioxide impregnated kaolin (TiO_2-K) nanophotocatalyst was developed via a reproducible modified two-step sol-gel approach. In this study, kaolin was used as a core substrate for titania deposition in order to facilitate post-separation and catalyst recovery by means of sedimentation. Pre-surface modification of the thermally stable kaolin was initially performed. The modification was preceded through a series of acidic-alkali-thermal treatments prior to undergoing the catalyst preparation procedure. This was to eliminate inherent impurities and to promote a delamination of the clay and to increase its specific surface area available for titania deposition. The sol-gel preparation was carried out under optimised conditions. Nitric acid concentration in the range of 0.25–0.30 M contributed to the formation of a transparent titanium sol with consistent viscosity after aging for 13–16 h. The following heterocoagulation of titania sol and the modified kaolin occurred due to electrostatic interaction between the positively charged TiO_2 sol and negatively charged kaolin particles. In this case, a 10% (w/v) of the kaolin was selected as the optimal loading enabling a homogeneous titania coating thickness of 7 nm. Further calcination of the TiO_2-K particles at 600°C was found to effectively transform amorphous-to-crystalline TiO_2 as a photoactive titania phase. The resultant TiO_2-K photocatalysts demonstrated superior adsorption of the pollutants on the catalyst surface which also enhanced the photo-oxidation performance. The chemical Ti-O-Si bonding between titania crystal and kaolin contributed to a significant increase in structural stability and photostability of the catalysts. This was evidenced by the comparable photo-degradation efficiency after 6 cycles of thermal re-generation. The self-separation by gravitational settling should enable practical application of this TiO_2-K catalyst in the wastewater industry.

2.5 Development of an Adsorption-Photocatalysis Hybrid System for Wastewater Reclamation

The ultimate aim of this project was to develop an adsorption-photocatalysis hybrid system for wastewater reclamation purposes. This hybrid system was to combine the well established conventional adsorption with photo-oxidation via highly active hydroxyl radicals in order to enhance elimination of recalcitrant compounds present in wastewater effluent. The initial adsorption was carried out using a fluidised bed system with clay-lime mixture under the selected optimum conditions. Thereafter, the effluent was transferred to the annular slurry photoreactor for pursuing photocatalytic reaction as a final polishing stage. The hybrid system was evaluated against both primary and secondary biological municipal effluents. Adsorption by the clay-lime mixture revealed excellent performance in removal of anionic compounds via either adsorption or precipitation reactions. The complete removal of PO_4^{3-}, for instance, was observed within the first hour of contact time. This preliminary treatment stage also enabled removal of suspended solids present in the raw effluent by in-house sand bed filtration as part of the FBR system, making the effluent suitable for the subsequent photo-degradation process. The remaining dissolved organic compounds from the FBR system were later oxidised or mineralised to simple compounds by the photocatalytic process using the synthesised TiO_2-K catalysts. The results showed a synergetic effect of this integration process over their individual treatment. The pH adjustment to neutral conditions prior to photodegradation resulted in an increase in removal efficiency by 30% and 10% for COD and NO_3^-, respectively. A study of molecular weight distribution profile of the organic contaminants under photocatalysed conditions was also investigated to accommodate the oxidation process. Although the complete elimination of the COD may not be applicable within the experimental period of 5 h, especially in the presence of macro organic molecules in the effluents that are very difficult to breakdown, the results revealed that the substantial organic pollutants were removed or photocatalysed to smaller compounds. This allows the compounds to be biodegradable providing the possibility to implement this hybrid system to operate as a pre-or sequential treatment to the conventional biological treatment. This present work provides the foundation for the development of the adsorption-photocatalysis hybrid process as an alternative treatment process for wastewater reclamation.

3. Perspective Benefits of the Adsorption-Photocatalaysis Hybrid System for Water and Wastewater Treatment

The recovery of treated wastewater is considered as a sustainable practice to better manage Australian water resources. The treated wastewater, as one of the largest portions of alternative water resources, can be recycled for a number of applications i.e. farm irrigation, local household benefits etc. However, the use of recycled wastewater is still limited by its potential risk associated with its chemical and biological contaminants. In general, the removal of chemical organic contaminants from wastewater is responsible by the biological degradation as a secondary treatment, while the biological decontamination is generally accomplished by disinfection as the essential tertiary or final treatment stage for inactivation and destruction of waterborne pathogens potentially present in the treated effluent.

Chlorination is the most common disinfection practice for wastewater treatment around the world since it is technically simple and inexpensive to implement. Chlorine can effectively inactivate a wide range of pathogens with its long lasting residual effects. Yet, this chemical disinfection has proved to generate secondary hazardous effects due to its associated reactions with recalcitrant/non-biodegradable effluent organic matters (EfOM) remaining in the effluent, to form potentially carcinogenic disinfection by-products (DBPs) such as halogenated compounds i.e. trihalomethanes (THM), haloacetic acids (HAA), and total organic halides (TOX) [2]. Also, the high nitrogen organic content of the effluent can promote a formation of more toxic-carcinogenic N-DBPs during chlorine disinfection. In addition to this, prior to discharge of recycled wastewater, removal of chlorine residuals after chlorination is often required as a final step to prevent complications with downstream environmental issues. Dechlorination can be accomplished by using reducing agents i.e. sulfur dioxide or activated carbon adsorption [3], resulting in an additional operating cost.

To eliminate the potential risks and limitations of chlorine disinfection associated with the DBP formation, a number of mitigation strategies have been developed. This includes the physical removal of organic precursor materials to reduce potential DBP formation, or by switching to alternative disinfection procedures, including ozonation or UV irradiation, to maintain the disinfection goals. However, these alternative disinfectants are still facing challenging limitations of different DPB species formation as well as their incapability in inactivating certain pathogenic microorganisms [4]. UV irradiation, for instance, is known as a safe physical disinfection widely implemented in water and wastewater treatments. It efficiently eliminates enteric bacteria, without producing DBPs at the UV doses generally used in wastewater disinfection [5]. Nevertheless, the downside of this technology is laid on a lack of a bacteriostatic effect and a possibility of repairing UV-damaged DNA resulting in further bacterial regeneration [6]. Ozonatation, on the other hand, is more prevalent to chlorination in removal of viruses and bacteria, and has been widely used, particularly in Europe, to meet discharge requirements for coliform and virus inactivation since the 1970s [7]. Also, this strong oxidant recently demonstrated an ability to oxidise emerging pollutants such as endocrine disrupting chemicals (EDCs) and pharmaceuticals in wastewater effluents [8]. However, the formation of alternative bromated DPBs and short life time of ozone residuals, allowing the potential for microbial regrowth, make this disinfection technique less attractive to wastewater reclamation.

In this present work, the integration of adsorption with photocatalysis was investigated as alternative advanced wastewater treatment to replace conventional chlorine disinfection. This study is conceptually beneficial to wastewater reclamation industries since it can reduce the DBP formation by substantially reducing the EfOMs via adsorption and photo-degradation of recalcitrant compounds. The combination of adsorption and photocatalysis under optimum conditions can increase overall treatment efficiencies compared to the efficiency of each individual stage. As discussed in Chapter 6 and 8, the initial adsorption by formulated clay-lime mixture using the fluidised bed system was found to significantly enhance the removal of suspended solids, phosphorous and nitrogen from the effluent. The high alkalinity pH of the clay-lime mixture would improve the reduction of microbial content in the effluent. Moreover, due to the use of low-cost clay materials, this treatment process would provide more economical wise than the commercial adsorbents i.e. activated carbons which are expensive and difficult to be regenerated.

Following the preliminary adsorption, the subsequent photocatalysis treatment is employed to facilitate the polishing step for the reclaimed wastewater. The strong hydroxyl radicals generated by photocatalytic reaction enable oxidation/mineralisation of EfOMs, resulting in a reduction of DBP precursors as evidenced in a number of studies [4]. In addition to the elimination of recalcitrant compounds, photocatalysis as a final stage treatment was reported to effectively disinfect faecal contamination present in wastewater effluents [9-10], without additional chlorine required. Therefore, the formation of DBPs can be eliminated or minimised in this case.

Based on operational point of views, this hybrid treatment permits an ease of implementation, of which the system does not require stringently controlled condition. The removal process can be preceded practically at ambient temperature. With the buffering capacity of the clay-lime mixture, the hybrid system is capable of handling a range of the effluents under different pH conditions.

Although the adsorption-photocatalysis integration process can potentially bring about several advantages to water industries, there are still a number of challenges needed to be further investigated. These technical limitations and potential solutions will be discussed in the following section.

4. Future Direction

4.1 Modification of the adsorbent mixture

Based on this study, it is suggested that the concept of clay adsorbent mixture can be extended into a number of applications. By modifying the mineral components, the adsorbent mixture can be altered to suit removal of particular contaminants. Further investigation on using the developed clay-lime adsorbent for removal of other pollutants such as heavy metals, nutrients, organic and inorganic compounds would be of interest. This is based on the fact that clay particles, as important component of the mixtures, have large surface area to mass ratios and possess variations in their structures and functional properties. Such unique features enable them to be effectively interacted with a range of pollutant components as mentioned in Chapter 2. A successful application towards these hazardous/toxic contaminants will enable the mixture of adsorbents to be employed in other water and wastewater treatment practices, i.e. industrial wastewater, mining, stormwater harvesting etc.

4.2 Development of TiO_2/K nanophotocatalyst synthesis procedure

In order to promote the photocatalysis application in wastewater industries, development of the catalyst with high photo-efficiency is one of the major concerns. A number of studies reported that doping ions onto the TiO_2/K photocatalysts, for example, could extend utilisation of light energy to the visible component of the solar spectrum, therefore resulting in a reduction of energy input required to initiate photo-reaction. Further investigation of the solar utilising TiO_2/K catalyst preparation is considered worthy of further investigation.

In addition to this, developing a catalyst preparation method that can yield higher production rates would also be in great demand. To date, the TiO_2/K nanophotocatalyst preparation was carried out on a laboratory scale, to ensure that attentive control of synthetic conditions can be achieved. It is anticipated that by accelerating the TiO_2/K catalyst generation process with high production yield, the large-scale operation of photocatalysis water treatment technology can be realised in the near future.

4.3 Applications of Adsorption-Photocatalysis hybrid system

In this present study, the adsorption – photocatalysis hybrid system revealed a high removal efficiency towards phosphate nutrients and recalcitrant compounds present in wastewater. However, by implementing this hybrid system as a standalone process to replace either secondary or tertiary wastewater treatment systems, there are some technical challenges that need to be overcome. The presence of high organic concentrations can prolong the adsorption and photo-degradation processes to some extent. A development of sequential treatment that can incorporate this hybrid system into the conventional wastewater treatment process can be one of the alternative solutions as discussed in Chapter 8. Moreover, extending applications of this integrated process into potable water systems should also be considered. The adsorption-photocatalysis treatment system can potentially improve the treated water quality by degrading the remaining organic residuals, resulting in higher drinking water quality with low disinfection by-product formation potential. Also, lower contaminant levels of water samples would enable the system to perform better under shorter retention times and lower energy requirements.

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