www.czasopisma.pan.pl PAN POLSKA AKADEMIA NAUK www.journals.pan.pl

Archives of Environmental Protection
Vol. 50 no. 3 pp. 54–64

PL ISSN 2083-4772
DOI:10.24425/aep.2024.151686

Enhancing photocatalytic performance of kaolin clay: an overview of treatment strategies and applications

Samor Boonphan[1], Suriyong Prachakiew[1], Khuruwan Klinbumrung[2],
Chananbhorn Thongrote[2], Arrak Klinbumrung[3,4]*

[1]Faculty of Science and Agricultural Technology, Rajamangala University of Technology Lanna, Chiang Rai, Thailand.
[2]Scientific Instrument and Product Standard Quality Inspection Center, University of Phayao, Phayao, Thailand
[3]Unit of Excellence on Advanced Nanomaterials, University of Phayao, Phayao, Thailand
[4]School of Science, University of Phayao, Phayao, Thailand

* Corresponding author's e-mail: arrak.kl@up.ac.th

Keywords: Kaolin clay, Photocatalytic, Surface modification, Water treatment

Abstract: The objective of this study is to enhance the photocatalytic capabilities of kaolin clay to improve its efficiency in environmental remediation. Various techniques were employed to modify kaolin clay, including heat treatment, acid modification, and material integration. These methods aimed to reduce its bandgap and improve its selective adsorption properties, thereby enabling better visible light activation and pollutant removal. The study discovered that modified kaolin-derived nanomaterials exhibit remarkable potential in breaking down pollutants, disinfecting, capturing heavy metals, and eliminating airborne contaminants. These advanced materials have been successfully used in water filtration, air purification, and the development of self-cleaning surfaces. The modifications increased surface area, adsorption capacity, and overall catalytic performance. Unmodified kaolin, with its broad bandgap, has limitations that hinder its ability to be driven by visible light for photocatalytic purposes and to selectively absorb specific pollutants, including heavy metals. The novelty of this research lies in the systematic exploration and optimization of diverse modification strategies for kaolin clay, showcasing its versatility in photocatalytic applications. The tailored modifications of kaolin to address specific environmental needs have the potential to be a cost-effective and eco-friendly solution for sustainable environmental restoration.

Introduction

Photocatalysis is a process that harnesses semiconductor-based photocatalysts to drive chemical reactions utilizing solar energy (Goodarzi et al. 2023; Xiao et al. 2023). This method offers advantages, including high efficiency, eco-friendliness, and cost-effectiveness (Yu & Jang, 2023). The photocatalysis technique has gained significant attention due to its efficiency and cost-effectiveness in multiple fields while remaining eco-friendly. Through sunlight irradiation, photocatalysis can enable reactions that can produce clean energy, treat water, clean the environment, and even convert CO_2 into valuable hydrocarbon products that reduce carbon emissions (Wang & Yu, 2023). Although photocatalysis has excellent potential in various applications, researchers face challenges in making it more efficient. One of the significant limitations is its reliance on a light source to function, which makes its use problematic in low-light or dark environments. To overcome these limitations, current research primarily focuses on developing new materials and exploring innovative ways to integrate photocatalysis with other technologies. By focusing on the scientific principles of photocatalysis and continuously striving to enhance its effectiveness, researchers aspire to unleash its full potential as a versatile tool for air and water purification, self-cleaning surfaces, and anti-fogging applications (Panda et al. 2023; Wang & Yu, 2023). Interdisciplinary collaboration has led to advancements in photocatalysis, proving it to be a valuable technology for generating sustainable energy and restoring the environment.

Kaolin clay, also known as china clay, is a naturally occurring mineral composed of hydrated aluminum silicate ($Al_2Si_2O_5(OH)_4$) (Ayalew, 2023). Recent studies have shown that kaolin clay possesses unique properties. While kaolin itself does not have intrinsic photocatalytic properties, when metal oxides with photocatalytic properties are supported by kaolin, the overall efficiency and stability of the photocatalytic process are enhanced. This is because dispersing metal oxides on kaolin improves the overall surface area and dispersion of the active photocatalyst. Consequently, integrating metal oxides into kaolin can overcome the limitations of pure metal oxide photocatalysts (Chuaicham et al. 2023; Hu et al. 2023; Ma et al. 2023). The effectiveness of modified kaolin clay in

Table 1. The chemical composition of kaolin clay obtained in Malaysia (Yahaya et al. 2017).

Chemical composition	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**CaO**	**K_2O**	**TiO_2**	**P_2O_5**
Weight (%)	57.633	37.766	0.860	0.596	0.346	1.801	0.605	0.311

adsorption processes is improved, particularly in the removing of heavy metals from contaminated environments.

Integrating nanomaterials into kaolin clay has enhanced its photocatalytic performance, leading to heightened efficacy in decomposing pollutants and expediting disinfection procedures via photocatalysis (Hu et al. 2023). This method has showcased remarkable efficiency and selectivity in addressing specific contaminants in the ecosystem (Chen et al. 2023). The effort has focused on exploring various modification methods to address these challenges.

This analysis provides an overview of the different strategies used to improve the photocatalytic effectiveness of kaolin and its applications in sustainable methodologies and environmental remediation. Various modifications have been employed to address limitations in photocatalytic performance, adsorption selectivity, and cation exchange properties. Methods to improve the adsorption and photocatalytic properties of kaolin include heat treatment, acid modification, metal modification, inorganic salt modification, and organic modification. Additionally, combining kaolinite with various nanomaterials has shown promising results in enhancing its photocatalytic efficiency. Kaolin-based materials possess the potential to address environmental issues and promote sustainable practices by efficiently breaking down pollutants and improving water treatment processes. This report contributes to a more environmentally friendly and sustainable world by utilizing the unique qualities of kaolinite and employing advanced treatment techniques.

Properties of Kaolin Clay as a Photocatalyst

Chemical composition and structure

Kaolin clay has unique properties and is composed of various oxides, including silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3), magnesium oxide (MgO), calcium oxide (CaO), potassium oxide (K_2O), titanium dioxide (TiO_2), and phosphorus pentoxide (P_2O_5). According to an XRF study on the chemical composition of Malaysia kaolin, as shown in Table 1, the primary phases, SiO_2 and Al_2O_3, constitute 57.633 wt% and 37.766 wt%, respectively, while all other oxides comprise less than 2 wt% (Yahaya et al. 2017). The composition of materials in kaolin can vary depending on their geological origin, resulting in differences in component quantities and impurities.

Kaolin is a type of dioctahedral sheet silicate with a complex crystal structure. This structure is characterized by infinite two-dimensional layers of corner-shared SiO_4 tetrahedra and edge-connected $Al_2O_2(OH)_4$ octahedra. The layers are stacked through hydrogen bonding between the hydroxyl groups on the alumina sheet and the oxygen atoms on the silica sheet, giving kaolin its characteristic plate-like shape, as depicted in Fig.1. Its triclinic nature is indicated by specific lattice parameters: a = 5.056 Å, b = 9.122 Å, c = 7.250 Å, $\alpha = 88.72°$, $\beta = 104.18°$, $\gamma = 90.25°$.

The integrity of the crystal structure is crucial in applications such as zeolite synthesis from metakaolin. SiO_2, an inorganic compound, can be utilized in waste management, significantly contributing to environmental sustainability. The cost-effective silica derived from a silicate extract obtained from palm frond ash serves as an efficient adsorbent for copper ions, with a maximum capacity of 20 mg/g. This indicates that the synthesized silica ash-based adsorbent can effectively remove Cu(II) ions from aqueous solutions (Al-Qadri & Alsaiari, 2023). Mechanochemical techniques enhance the structural transformation to silica-rich phases (Tanwongwan et al. 2020). Innovations in calcination methods aim to preserve the shape of kaolin crystals by ensuring even heating and preventing damage during the dehydroxylation process, emphasizing the importance of maintaining the physical strength and stability of the structure (San Nicolas et al. 2013). Morphological and chemical analyses of kaolin deposits indicate variations in crystal properties across different layers, suggesting the influence of depositional environments (Varajão et al. 2001). Additionally, the production of hydrated kaolinites with different basal spacings (10 and 8.4 Å) illustrates the flexibility of kaolin's atomic arrangement in accommodating water molecules in various configurations (Belmokhtar et al. 2017). Layer stackings and interlayer displacements in kaolinite structures are extensively studied to understand the theoretical and actual arrangements, offering valuable insights into the diverse structural modifications and deformation mechanisms within the material (Zvyagin & Drits, 1996). As a hydrated aluminum silicate, kaolin's structure and connection with other minerals are defined by its chemical composition and empirical

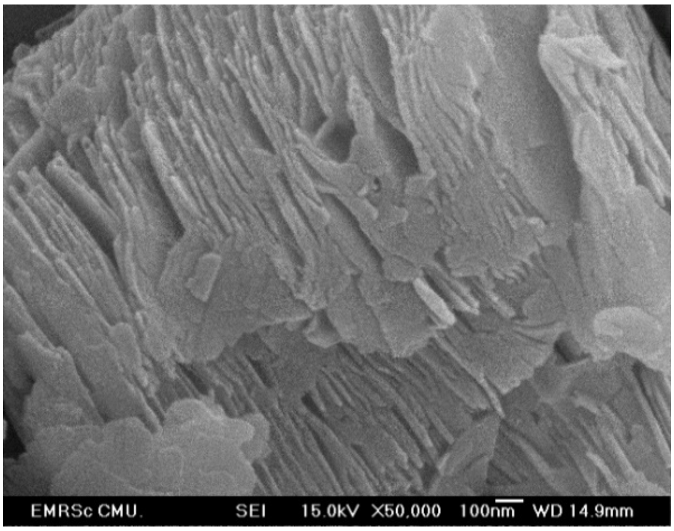

Figure 1. The stacked layer of alumina and silica in the kaolin clay structure.

Table 2. Influence of surface area and treatment process in kaolin composites on photocatalytic efficiency.

Composites	Treatment process	Surface area (m^2/g)	Photocatalytic Efficiency (%)	Ref.
TiO_2/kaolin	Sol-gel method with calcination temperature of 300°C.	106.19	92.4% (more than pure TiO_2 1.42 times)	Li et al., 2020
Kaolin/$CaCO_3$/TiO_2	The composite was prepared in a 1:1:1 ratio and heated at 1000°C for 1 h.	15.342 (kaolin = 14.629, $CaCO_3$ = 5.912, TiO_2 = 8.321)	82.62 % (operated in pH3 for 6h, using Reactive Black 5 as dye)	Tharakeswari et al., 2022
TiO_2 Nanoparticles/kaolin	TiO_2 with intrinsic point defect decorates on kaolin surface	-	About 100 % for 2 h reaction time (higher than pristine TiO_2 32.1 %)	Hu et al., 2023
ZnO/kaolin	50 wt% ZnO / kaolin mixture calcined at 600°C	-	95% (photodegradation of A07 dye, exposing to UV irradiadtion)	Mamulová Kutláková et al., 2015
ZnO/kaolin	Treatment surface by citric acid	-	Cr(VI) photocatalytic removal of 88% for composite and 98 % for acid treatment	Shirzad-Siboni et al., 2014

formula. The crystal structure of kaolin plays a crucial role in industry, where it is highly valued for its unique qualities and is essential across various sectors. The material can be modified to meet different needs and is studied extensively. The adaptability underscores the significance of its crystal structure and its potential to revolutionize different fields.

Influence of surface area, treatment, and porosity on the photocatalytic activity

The surface area, including surface treatment and porosity of kaolin clay, significantly impacts the photocatalytic activity (Vagvolgyi et al. 2021). Kaolin clay is generally considered to have a low level of purity, but its surface can be modified to enhance photocatalytic properties through various methods such as intercalation, exfoliation, mechanochemical activation, acid treatment, and thermal treatment (Hu et al. 2023). These surface modification techniques can improve the natural properties of kaolin-based materials, thereby increasing their photocatalytic activity (Ma et al. 2023). Intercalation produces delaminated and exfoliated structures from double-layered minerals, while mechanochemical activation and thermal treatment reduce the coordination of octahedral Al atoms (Abdo et al. 2022). Acid treatment alters the surface's acid-base properties and mineral composition (Shirzad-Siboni et al. 2014)(Alkhabbas et al. 2023). Hydrochloric acid treatment of kaolin removes Fe_2O_3 compounds (Eze et al. 2012). These findings confirm the enhancement of the performance of kaolin-based photocatalysts by applying and combining various methods.

Additionally, using kaolin clay as a carrier for photocatalytic nanomaterials can overcome the limitations of pure photocatalysts, including poor activity, narrow spectral responses, and limited electron transport. Combining kaolin clay with nanomaterials enhances photocatalytic efficiency and broadens the applications for pollutant degradation, disinfection, and heavy metal adsorption in environmental decontamination. Therefore, optimizing the surface properties of kaolin clay can lead to the development of efficient photocatalysts for a wide range of environmental applications.

Interestingly, the high specific surface area of kaolin clay provides a larger contact area for the photocatalytic reaction, allowing more reactants to come into contact with the catalyst and enhancing the overall efficiency of the process (Tharakeswari et al. 2022). The porosity of kaolin clay facilitates the diffusion of reactants and products within the material, improving the photocatalytic reaction and overall performance of the catalyst (Hu et al. 2023). The effect contributes to the synergistic adsorption and catalysis in composites such as TiO_2/kaolinite, leading to superior photocatalytic degradation performance (Li et al. 2020). ZnO-incorporated kaolin exhibits superior photodegradation than ZnO (Mamulová Kutláková et al. 2015). Combining these properties in kaolin clay-based photocatalysts leads to improved photocatalytic degradation of organic pollutants in wastewater. The large specific surface area and suppressed recombination rate of photogenerated carriers in clay-based photocatalysts contribute to their high photocatalytic activity, making them promising candidates for low-cost, visible-induced environmental treatment (Chuaicham et al. 2023). As presented in Table 2, the influence of metal oxide dopants on the surface area and treatment process in kaolin composites leads to better efficiency in photocatalysis.

Effect of Kaolin's energy bandgap on its light absorption

Kaolin clay has a large energy bandgap, approximately 4.52 eV (Xia et al. 2009). The capacity of a material is significantly affected by the reduction in its energy bandgap (E_g). A material with a smaller E_g can absorb light across a broader spectrum range, which is crucial for light-driven processes such as photocatalysis. Research reveals that doping with metals or creating nanocomposites can decrease the E_g of kaolin clay, thereby enhancing its ability to absorb visible light for various applications. Nanocomposites of synthesized oxide/kaolin and graphene restrict the recombination of electron-hole pairs generated during photosynthesis (Rajan et al. 2022).

The UV-visible absorbance of treated kaolin is measured to determine its energy bandgap (E_g) The Wood and Tauc equation (eq.1) was employed using the absorption data to calculate the energy bandgap (E_g). The equation illustrates the relationship between the absorption coefficient (α) and the photonic energy (hν), as follows (Burns, 1985).

$$\alpha h\nu = (h\nu - E_g)^n \tag{1}$$

Where h, ν, Eg, and n represent the Planck constant ($4.1357 * 10^{-15}$ eV•s), photon frequency, energy bandgap, and an integer linked to the electron transition mechanism (n = 1/2 for the direct transition, n = 2 for indirect transition, n = 3/2 for direct forbidden, and n = 3 for indirect forbidden transitions). As depicted in Fig.2, the estimation of Eg value can be determined by identifying the linear portion where $\alpha h\nu^n = 0$.

The development of hybrid clay nanocomposites doped with Zn and Cu salts from kaolinite clay and *Carica papaya* seeds significantly reduced the E_g of kaolinite, lowering it from between 4.9 and 8.2 eV to as low as 1.5 eV for Cu/Zn hybrid clay nanocomposites, thereby enhancing their photocatalytic activity under solar light irradiation (Zhang et al. 2013). The synthesis of black TiO_2/kaolinite composites narrows the E_g and increases the specific surface area, further enhancing photocatalytic performance (Ma et al. 2023). Additionally, incorporating Fe_2O_3 into TiO_2/kaolinite composites shifts the absorption edge towards visible light, improving both light absorption and photocatalytic activity (Aritonang et al. 2022).

These modifications improve the light absorption properties of kaolin clay and its photocatalytic efficiency in applications such as water disinfection and pollutant degradation. The optical and electrical characteristics of kaolinite/polystyrene composites also indicate that the optical energy gap varies with kaolinite grain size, suggesting that physical modifications can influence the material's light absorption properties (Kareem et al. 2022). Modification methods used for Egyptian kaolinite in paper coatings, such as chemical bleaching and calcination, can impact the structure and light absorption characteristics (Lindberg & Snyder, 1972). The E_g of kaolin clay can be influenced by factors such as the presence of point defects, oxygen vacancies, and modifications to other materials (Sofi'i et al. 2022). These changes can significantly impact the clay's properties, including its electrical conductivity, mechanical strength, and surface reactivity. Point defects and vacancies affect the clay's adsorption and catalytic properties, resulting in various industrial applications. As a photocatalyst, these factors contribute to kaolin clay's improved absorption and utilization of light. Enhanced methods are achieved through various modifications, including metal doping, nanocomposite creation, and physical alterations (El-Sherbiny et al. 2015; Fourdrin et al. 2009; Lindberg & Snyder, 1972; Sbeih & Zihlif, 2009; Ugwuja al. 2019).

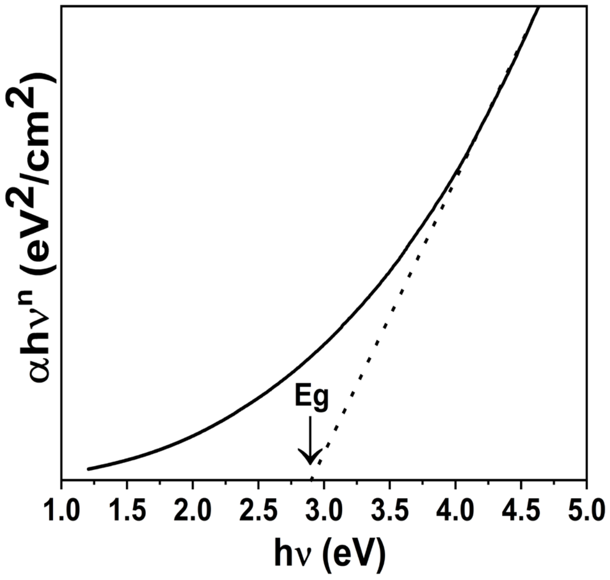

Figure 2. The demonstration of E_g value approximation along the Wood and Tauc equation.

Challenges in using raw kaolin for photocatalysis

Using raw kaolin in photocatalysis presents challenges due to its low effectiveness and limited light absorption capabilities. Raw kaolin has insufficient surface hydroxyl activity and cation exchange capacity, resulting in poor adsorption selectivity and heavy metal desorption, which significantly impact its photocatalytic efficiency (Hu et al. 2023). Additionally, kaolinite with its layered silicate structure exhibits inadequate activities, limited electron transport, and narrow spectral responses, further restricting its application in environmental decontamination (Chen et al. 2023).

Recent studies have shown that reducing the dimensionality of kaolinite to two-dimensional nanostructured layers can significantly improve its photocatalytic performance. This approach effectively reduces the E_g of kaolinite, enhancing its activity as a photocatalyst under visible light (Abdo et al. 2022). Thermal and acid treatments have also been tested as modifications to kaolin clay for removing cationic dyes from water systems, with modified kaolin showing significantly higher adsorption efficiency (Erasto et al. 2023). These findings suggest that such modifications, including changes in composition, increased surface area, and other targeted alterations, can greatly enhance the effectiveness of kaolin in catalytic process. The research highlights a beneficial technique to promote progress and stimulate innovation within the field (Rajan et al. 2022). .

Treatment Strategies to Enhance Photocatalytic Activity

Calcination

Improving the photocatalytic efficiency of kaolin through calcination requires various strategic approaches that exploit the intrinsic properties of kaolin and the effects of calcination. Intercalation and exfoliation techniques are essential to this process, which aims to transform the kaolin structure in order to optimize its performance as a photocatalyst (Abdo et al. 2022). By introducing chemical substances into the layers of kaolin, researchers have successfully decreased the E_g of kaolin, enhancing the generation of charge carriers and improving its photocatalytic performance under visible light.

Calcination plays a critical role in transforming kaolin into a more photoactive state. For example, the treatment of kaolin/ZnO nanocomposites through calcination at 600°C results in the transformation of kaolinite to metakaolinite phase, leading to a notable enhancement in the photodegradation efficiency of the composites (Ma et al. 2023). The thermal treatment not only stimulates the creation of ZnO crystals but also improves the connection between the kaolin framework and ZnO nanoparticles, ensuring the prolonged efficacy of the photocatalyst (Huang et al. 2020). Moreover, incorporating TiO_2 and ZnO into kaolin using various synthesis techniques, such as sol-gel and hydrothermal methods, combined with calcination at suitable temperatures, has effectively improved the breakdown of organic contaminants via photocatalysis (Kutláková et al. 2015). These modifications enhance the adsorption capacity of kaolin-based photocatalysts and increase the production of active radicals responsible for degrading pollutants (El-Sheikh et al. 2020).

Doping with Metals or Metal Oxides

Metal or metal oxide doping has been shown to significantly enhance the photocatalytic performance of kaolin-based photocatalysts for environmental remediation purposes. Adding titanium dioxide (TiO_2) to kaolin has been a primary objective to improve the photocatalytic effectiveness (Ma et al. 2023). For example, the hydrothermal method has been employed to produce highly active composites of TiO_2 and acid-activated kaolinite, resulting in the notable elimination of contaminants in wastewater. Similarly, the sol-gel method has been employed to produce TiO_2-kaolinite nanocomposite photocatalysts, where the efficacy of photocatalysis is directly proportional to the quantity of TiO_2 present in the nanocomposite (Abdo et al. 2022). Moreover, modifying kaolin's surface properties has been studied to further enhance its photocatalytic capabilities. These techniques have created kaolinite with modified E_g and reduced charge carrier recombination, thereby improving its photocatalytic performance (Vagvolgyi et al. 2021). As previously reported, ternary composites such as kaolin/CeO_2/g-C_3N_4 were formed using sol-gel and hydrothermal procedures, followed by calcination. This composite produces a synergistic effect that enhances photocatalytic efficiency. Establishing a three-dimensional "sandwich" formation through this method improves photo-induced charge separation and increases the specific surface area - both crucial elements for effective photocatalysis (Xu et al. 2018).

Furthermore, integrating TiO_2 nanoparticles onto kaolinite surfaces has resulted in composites with a decreased E_g and an elevated specific surface area, leading to enhanced photocatalytic pollutant removal (Hu et al. 2023). The emerging wetness impregnation method has also been employed in producing kaolin-anatase titania nanoparticle composites, which manifest improved photocatalytic efficiency because of the accelerated generation of reactive radicals (Kamaluddin et al. 2021). To further increase the photocatalytic performance of metal-organic frameworks (MOFs), recent reports have explored integrating MOFs with metal oxides or constructing MOFs-based core-shell structures. These approaches promote charge separation and facilitate charge transfer between components, advancing the potential applications of MOFs in various fields. Such advancements have enabled important processes such as water splitting, CO_2 reduction, and pollutant degradation (Zhang et al. 2022).

The integration of metals or metal oxides into kaolin has a significant impact on its photocatalytic performance. The employment of doping techniques leads to the formation of heterojunctions, which enhance charge separation (Hoai et al. 2022; Zhang et al. 2022). Metal doping induces additional energy levels within the bandgap, thereby improving light absorption and the separation of charge carriers. Efficient interface engineering is essential for enhancing charge separation efficiency and improving overall photocatalytic reaction efficiency. By applying these innovative techniques, kaolin-based photocatalysts can be significantly improved for environmental cleanup applications, such as pollutant degradation and sterilization.

Surface Modification

Various surface modification methods have been employed to improve the photocatalytic efficiency of kaolin. These methods include hydrothermal synthesis, intercalation, exfoliation, mechanochemical activation, and integration of nanocomposites. This approach demonstrates significant potential for environmental remediation, especially in wastewater treatment. For instance, the hydrothermal process was employed to fabricate a black TiO_2/kaolinite mixture, which exhibited superior pollutant eliminating elimination through photocatalysis. This enhanced performance was attributed to the decreased E_g and expanded specific surface area of the mixture (Abdo et al. 2022). Intercalation and exfoliation techniques have been applied to modify the composition of kaolin, resulting in the generation of two-dimensional nanostructured layers that operate in the visible light region, thereby improving photocatalytic performance (Ding et al. 2012). Mechanochemical methods, involving dry grinding and thermal processing, have decreased the coordination of octahedral aluminum atoms in kaolin, resulting in intrinsic photochemical reactivity (Chen et al. 2023). Additionally, surface modifications through acid treatment, metal modification, and organic modification have been utilized to enhance kaolin's adsorption capabilities and photocatalytic efficiency (Hu et al. 2023). Another strategy for modifying the surface of kaolin involves introducing compound modifiers into the kaolin slurry before ball milling. This method increases the dispersibility, usability, and photocatalytic properties of the kaolin (Rajan et al. 2022).

Surface modification methods have been identified as effective strategies for enhancing the photochemical reactivity of doping minerals in a kaolinite structure. These methods significantly alter the surface chemistry and pollutant attraction capacity of the minerals by modifying their composition, structure, impurities, and arrangement (Vagvolgyi et al. 2021). Enhancing the adsorption of organic pollutants and increasing the degradation rate have been achieved by attaching organosilanes to TiO_2 and fixing TiO_2 onto bentonite clay (Roques-Carmes et al. 2020). Additionally, a composite material with 0D/2D dimensions of TiO_2/kaolinite was synthesized using a mild sol-gel approach combined with nitrogen induction.

The processed material has exhibited superior efficacy in degrading pollutants through adsorption-photocatalytic mechanisms, particularly for compounds like ciprofloxacin. This outstanding performance is attributed to the generation of oxygen vacancies and the enhanced light absorption attributes of the composite material (Li et al. 2018). In particular, mechanochemical processes, which include homogenization and ultrasonication followed by the introduction of polycations, have notably impacted the surface characteristics of kaolin, influencing the efficiency of flocculation in kaolin suspensions (Bhatti et al. 2023). The combination of highly efficient photocatalytic materials, such as TiO_2/acid-activated kaolinite, through a hydrothermal technique, has demonstrated promising results in wastewater remediation. Studies on reactive radicals have identified holes as the primary oxidizing agents (Ma et al. 2023). Besides, kaolinite/TiO_2 composites prepared using sol-gel techniques have also yielded positive results. Acid treatment and exfoliation are crucial in enhancing the distribution and quantity of TiO_2 grains in these composites, improving their photocatalytic performance (Xu et al. 2018).

An example of kaolin infused with aminated chitosan showed excellent efficiency in adsorbing anionic Congo red dye, indicating the promising capabilities of these combinations in remediating contaminated water sources (Mei et al. 2023). The development of geopolymers from coal fly ash and biomass ash utilizing specific activators has shown more effective metal sorption capabilities compared to coal ash-based geopolymers (Sitarz-Palczak et al. 2019). Additionally, a hybrid hydrogel composed of sodium alginate, chitosan, and kaolin effectively removes heavy metal ions from polluted water through adsorption, demonstrating the potential of these materials to eliminate harmful pollutants (Rekik et al. 2023). Combining kaolin with chitosan-based adsorbents has significantly improved their adsorption effectiveness. For instance, a study combining kaolin with chitosan beads resulted in material with a remarkable ability to capture chromium ions (Abou Alsoaud et al. 2022).

Mechanisms of Enhanced Photocatalytic Activity

The enhanced photocatalytic efficacy of composites incorporating kaolin can be attributed to various mechanisms, including the generation of reactive oxygen species (ROS). Recent research has revealed the presence of other materials integrated into kaolin as the composite (Rajan et al. 2022; Sun, Li, et al. 2018; Sun, Yuan, et al. 2018; Zhang et al. 2011). Incorporating transition metal oxides such as MnO_2 and CuO onto kaolin surfaces creates strong composite structures characterized by high durability, numerous edges, distinct corners, and interconnected pathways. These features facilitate the rapid transport and dispersion of substances, enhancing oxygen absorption and activation, thereby increasing oxygen mobility and reactivity during CO oxidation (Liu et al. 2022). The introduction of environmentally persistent free radicals (EPFRs) onto the surfaces of anatase-coated mineral powders has been shown to boost hydroxyl radicals (*OH) production. This enhancement occurs when photo-induced holes and water molecules participate in the oxidation process, aided by the intrinsic electric field and increased water adsorption caused by the existence of EPFRs. (Liu et al. 2021). Using silica nanomaterial surfaces to break down substances through photocatalysis has been observed through certain modifications, such as introducing amino groups or decorating the surfaces with silver nanoparticles. This process leverages photo-excitable surface defects and plasmon effects, effectively functioning under white and monochromatic light (Romolini et al. 2021). The photocatalytic degradation of dyes under UV light is more efficient when using composite nanoparticles made of kaolin-anatase titania. The finding is due to the elevated generation of *OH radicals on the surface of the composite, which enhances the process (Kamaluddin et al. 2021). Incorporating graphene carboxyl into TiO_2/kaolin composites has demonstrated effectiveness in immobilizing TiO_2, expanding the the absorption range of visible light, and preventing the recombination of electron-hole pairs generated during photosynthesis. These enhancements lead to higher levels of hydroxyl radicals (Rajan et al. 2022). These findings illustrate the diverse methods for increasing ROS generation across different applications. It is crucial to evaluate the advantages of these methods for potential utilization in environmental cleanup and energy generation. By exploring these approaches, there is significant potential to improve the efficiency and efficacy of natural kaolin-derived materials in producing ROS, with potential impacts across various disciplines.

In addition to the increased production of ROS, the improved efficiency of kaolin-derived photocatalysts can be attributed to enhanced mechanisms for separating charges, including intercalation to lower E_g and the creation of heterojunctions to facilitate faster transfer of charge carriers (Wang et al. 2022). Establishing heterojunctions has been acknowledged as a highly efficient method in advancing and manufacturing composite photocatalysts. This method enhances the photocatalytic performance by facilitating the separation and movement of photo-induced charges (Lin et al. 2023). The significance of heterojunctions in improving photocatalytic efficiency has been extensively documented. By developing heterojunction Fe_2O_3-TiO_2/kaolinite composites, the photocatalytic activity can be enhanced by enlarging the surface area and facilitating charge separation. These composites establish a heterostructure that effectively reduces the recombination of photogenerated hole and electron charge pairs (Zhang et al. 2023). Similarly, incorporating CeO_2 and $g\text{-}C_3N_4$ into kaolin forms a ternary composite presenting a unique "sandwich" structure. This configuration boosts the efficacy of segregating light-induced charges, resulting in a remarkable enhancement in the photocatalytic capability of the mixture (Huang et al. 2020). The efficiency of separating photogenerated charges can also be enhanced by combining photo-responsive, natural iron-rich kaolinite with CdS composite photocatalyst. This composite is achieved by utilizing the high oxygen adsorption capability of kaolinite nanosheets. (Jiang et al. 2018).

Additionally, research has shown that including TiO_2 nanoparticles in kaolin enhances photocatalytic performance by reducing the energy barrier for photocatalytic degradation. This finding highlights the significance of the material's composition and structure in promoting charge separation and photocatalytic efficiency (Kamaluddin et al. 2021). The formation of a heterostructured photocatalyst with increased electron transfer and separation emphasizes the substantial importance of heterojunctions in photocatalytic applications.

The mechanism of photoactivation can be understood through a similar process. For example, the fusion of TiO_2 and graphene carboxyl has been explained, broadening the absorption spectrum of TiO_2 to include visible light and facilitating the successful decomposition of contaminants through photocatalysis (Rajan et al. 2022). The following equations, as presented in eqs.2-8, summarize the chemical reactions involved in a photocatalytic process using TiO_2/kaolin-graphene carboxyl composites.

$$TiO_2/\text{kaolin - graphene carboxyl} + h\nu \rightarrow TiO_2/\text{kaolin - graphene carboxyl}\ (e^- + h^+) \quad (2)$$

$$e^- + O_2 \rightarrow {}^{*}O_2 \quad (3)$$

$$h^+ + \text{kaolin - graphene carboxyl} \rightarrow {}^{*}OH \quad (4)$$

$$h^+ + H_2O \rightarrow {}^{*}OH \quad (5)$$

$$h^+ + \text{pollutant} \rightarrow \text{Oxidation products} \quad (6)$$

$$e^- + \text{pollutant} \rightarrow \text{Reduction products} \quad (7)$$

$${}^{*}OH/{}^{*}O^{2-}/h^+ + \text{pollutant} \rightarrow CO_2 + H_2O + \text{other intermediates} \quad (8)$$

The subsequent reactions outline the mechanism of material activation by light (hν), leading to the generation of electron-hole pairs (e^- and h^+). The electrons (e^-) then interact with oxygen (O_2), producing superoxide anions (*O^2). Simultaneously, the holes (h^+) react with kaolin-graphene carboxyl to produce hydroxyl radicals (*OH), as well as with water (H_2O) to generate additional hydroxyl radicals (*OH). Subsequently, the electrons (e^-) and holes (h^+) react with pollutants, resulting in oxidation and reduction products, respectively. Both superoxide anions and hydroxyl radicals are instrumental in the degradation process, converting pollutants into less harmful oxidation products. The composite material generates more active sites and enhances charge separation, thereby increasing photocatalytic efficiency.

Potentials of Enhanced Kaolin Clay in Environmental Remediation

Water Treatment

Enhanced kaolin clay shows great potential for various water treatment applications, surpassing its traditional role of breaking down organic pollutants. TiO_2/acid-activated kaolin composites have proven effective and versatile in environmental rehabilitation procedures, demonstrating their value and practicality. These composites are particularly useful in purifying wastewater from mineral processing activities, underscoring the importance of innovative materials in addressing specific challenges within the environmental engineering. Additionally, these materials have exhibited significant photocatalytic activity in removing harmful compounds such as sodium ethyl xanthate, indicating their potential in treating industrial wastes (Ma et al. 2023).

Kaolin has also been used to improve the health of common carp infected with *Pseudomonas aeruginosa*, showing potential for water treatment applications in aquaculture (Al-Rudainy et al. 2023). The combination of kaolin clay, biopolymers, and surfactants has led to the development of water-based drilling fluids, which are crucial in the oil and gas industry. These fluids have enhanced rheological characteristics and filtration control capabilities, improving the efficiency of drilling operations (Omary et al. 2023). Moreover, the effectiveness of kaolin in removing water pollutants through adsorption has been enhanced through modification (Liang et al. 2023). This composite material has demonstrated exceptional catalytic performance and durability in eliminating dye. Similarly, other composite materials have shown outstanding catalytic performance and resilience in dye removal (Asmare et al. 2022). Kaolin-based nanomaterials have been used in various water treatment applications, including the photocatalytic breakdown of contaminants, disinfection, and heavy metal adsorption, effectively targeting a wide range of water pollutants.

Kaolin clay has been studied as a potential alternative material for evaluating sprayer cleanout and agitation systems. Research has demonstrated its effectiveness in ensuring the proper functioning of water treatment equipment (Román et al. 2023). The use of modified kaolin clay for the removal of cationic dyes from water systems has shown promise in treating dye-polluted water (Erasto et al. 2023). Additionally, zeolite derived from kaolin has been found to activate inorganic peroxides for decomposing organic contaminants in water, providing a targeted and efficient approach to water treatment (Serna-Galvis et al. 2023). A combination of kaolin clay, graphene oxide, and polyethylene glycol has proven effective in adsorbing veterinary antibiotics from water, addressing the issue of pharmaceutical contaminants in aquatic environments (Akpotu et al. 2022). The surface area of kaolin can be enhanced by altering its thermal properties and activating it with acid, thus improving its ability to absorb and retain substances, particularly synthetic organic dyes (Bondarieva et al. 2022).

Furthermore, using kaolin to produce ceramic membranes for filtration can enhance mechanical, thermal, and chemical properties. These improvements are achieved by adjusting the kaolin loading concentration and the sintering temperature (Usman et al. 2020). After treatment with concentrated sulfuric acid, activated kaolin clay has proven to be a cost-effective adsorbent for removing fluoride from groundwater. The effectiveness of this adsorbent is influenced by experimental factors such as temperature, pH, and the quantity of adsorbent used (Ayalew, 2020). Additionally, the potential of kaolin clay to produce aluminum sulfate through acid leaching offers an economical option for water treatment coagulation (Kuranga et al. 2018). Using kaolin clay in creating ceramic membranes for treating textile wastewater has demonstrated exceptional separation capabilities, highlighting the potential of kaolin in advanced water treatment technologies (Bousbih et al. 2021). As indicated in the literature, kaolin clay presents an efficient and cost-effective solution for water treatment with significant environmental benefits.

Air Purification

The enhanced adsorption efficiency of kaolin clay makes it an attractive option for air purification, a crucial aspect of environmental remediation. Recent research has demonstrated the effectiveness of mechanochemical techniques in modifying the properties of kaolin. These modifications lead to a significant increase in surface area, a reduction in particle size, and improvements in dispersion and adsorption capabilities. These key features play a crucial role in ensuring the successful removal of air contaminants, highlighting the importance of kaolin as a promising substance in air quality control (Liang al. 2023). Developing composite membranes using kaolin and chitosan is both environmentally friendly and cost-effective. These membranes demonstrate enhanced strength and can withstand acidic conditions, making them suitable for air filtration applications (Rekik et al. 2023). Furthermore, modifying kaolin with Cetyl Trimethyl Ammonium Bromide (CTAB) increases the adsorption of Cr(VI) from aqueous solutions and improves its capacity to adsorb air pollutants. The modified kaolin significantly removes Cr(VI) from liquid solutions, achieving a removal efficiency of 99% at adsorption equilibrium (Chen et al. 2023). The CTAB modification has been found to enhance kaolin's ability to adsorb Cr(VI), suggesting the potential for improving the adsorption of air pollutants. Regarding gaseous Hg adsorption, kaolin's effectiveness as an adsorbent provides promising results, particularly when combined with $CuCl_2$. These findings highlight the potential for energy-neutral environmental remediation strategies (Belachew & Hinsene, 2020).

Challenges and Future Directions

Future research on kaolin-based materials for photocatalytic treatment presents intriguing challenges and opportunities. The key challenges include optimizing kaolin's photocatalytic activity, stability, and ability to degrade pollutants under different environmental conditions. In order to address these challenges, it would be valuable to investigate new methods for modifying the surface properties of kaolin to improve light absorption and facilitate efficient charge separation. Additionally, exploring the potential for performance enhancement through the use of other photocatalysts or additives could be beneficial. Recent research has also focused on refining kaolin applications in agriculture and soil stabilization (Bahniuk et al. 2022; Mohd Yunus et al. 2019). Expanding the range of these applications could significantly improve the effectiveness and efficiency of kaolin-based treatments in diverse sectors.

The research on kaolin-based treatments addresses challenges and improves effectiveness through various strategic approaches. Recent reports suggest that bioflocculants can serve as eco-friendly alternatives to synthetic polymers (Bahniuk et al. 2022). This research investigates kaolin's impact on aquaculture and optimizes mechanochemical treatments. Additionally, various studies have introduced new methods for treating and optimizing kaolin for multiple applications, including removing contaminants and impurities in wastewater and producing water treatment coagulants (Taheri, 2023).

Another important consideration is addressing the challenges of reusability and scalability of kaolin-based photocatalysts for practical applications. It is essential to study the mechanisms of pollutant adsorption and degradation on kaolin surfaces, and the effects of variables such as contact time, adsorption capacity, pH, and dosage (Gad et al. 2022; Kuranga et al. 2018; Zakaria Djibrine et al. 2018). The results of this study can provide valuable guidance for future research aimed at unlocking the full potential of kaolin-based materials in photocatalytic treatment.

Conclusions

This report presents an overview of techniques for improving the photocatalytic efficiency of kaolin clay through integrating metal oxides, nanomaterials, and structural modifications. These methods have significantly enhanced kaolin's surface area, adsorption capacity, and catalytic performance, proving to be effective in the degradation of pollutants. The various modification strategies illustrate the versatility of kaolin for photocatalytic applications. Promising prospects are anticipated, with advancements in material science expected to optimize these materials further. Future research efforts should focus on refining synthesis processes, exploring synergistic multi-component effects, and scaling up production for industrial use. Interdisciplinary collaboration is vital in finding practical solutions to environmental challenges. Suggestions include investigating the extended-term durability and reusability of modified kaolin, evaluating the environmental impact of modification techniques, and examining the use of kaolin-based composites in advanced treatments. This research highlights the economical and environmentally friendly potential of kaolin-based photocatalysis for sustainable environmental cleanup.

Acknowledgments

The authors thank the Unit of Excellence on Advanced Nanomaterials, the School of Science, and the Scientific Instrument and Product Standard Quality Inspection Center (SIPQC) at the University of Phayao for their general support. Additionally, we extend our gratitude to the Faculty of Science and Agricultural Technology, Rajamangala University of Technology Lanna, Chiang Rai, Thailand, for their partial assistance. This research project was made possible by the Thailand Science Research and Innovation Fund and the University of Phayao (FF67).

Data Availability

The data will be made available on request.

Statements and Declarations

Competing Interests

The authors declare no financial or non-financial interests related to the work submitted for publication.

References

Abdo, S. M., El-Hout, S. I., Shawky, A., Rashed, M. N. & El-Sheikh, S. M. (2022). Visible-light-driven photodegradation of organic pollutants by simply exfoliated kaolinite nanolayers with enhanced activity and recyclability. *Environmental Research*, 214, 113960. DOI:10.1016/j.envres.2022.113960

Abou Alsoaud, M. M., Taher, M. A., Hamed, A. M., Elnouby, M. S. & Omer, A. M. (2022). Reusable kaolin impregnated aminated chitosan composite beads for efficient removal of Congo red dye: Isotherms, kinetics and thermodynamics studies. *Scientific Reports*, 12(1), 12972. DOI:10.1038/s41598-022-17305-w

Akpotu, S. O., Lawal, I. A., Diagboya, P. N., Mtunzi, F. M. & Ofomaja, A. E. (2022). Engineered geomedia kaolin clay-reduced graphene oxide–polymer composite for the remediation of olaquindox from water. *ACS omega*, 7(38), pp. 34054-34065. DOI:10.1021/acsomega.2c03253

Al-Qadri, F. A. & Alsaiari, R. (2023). Silica ash from waste palm fronds used as an eco-friendly, sustainable adsorbent for the Removal of cupper (II). *Archives of Environmental Protection*, 49(2). https://DOI 10.24425/aep.2023.145894

Al-Rudainy, A. J., Mustafa, S., Ashor, A. & Bader, M. (2023). Role of Kaolin on Hemtological, Biochemical and Survival Rate of Cyprinus Carpio Challenged with Pesuydomonas Aeruginosa. *Iraqi Journal of Agricultural Sciences*, 54(2), pp. 472-477. DOI:10.36103/ijas.v54i2.1723

Alkhabbas, M., Odeh, F., Alzughoul, K., Afaneh, R. & Alahmad, W. (2023). Jordanian Kaolinite with TiO$_2$ for Improving Solar Light Harvesting Used in Dye Removal. *Molecules*, 28(3), 989. DOI:10.3390/molecules28030989

Aritonang, A. B., Selpiana, H., Wibowo, M. A. & Adhitiawarman, A. (2022). Photocatalytic Degradation of Methylene Blue using Fe$_2$O$_3$-TiO$_2$/Kaolinite under Visible Light Illumination. *JKPK (Jurnal Kimia dan Pendidikan Kimia),* 7(3), pp. 277-286. DOI:10.20961/jkpk.v7i3.66567

Asmare, Z. G., Aragaw, B. A., Atlabachew, M. & Wubieneh, T. A. (2022). Kaolin-Supported Silver Nanoparticles as an Effective Catalyst for the Removal of Methylene Blue Dye from Aqueous Solutions. *ACS omega*, 8(1), pp. 480-491. DOI:10.1021/acsomega.2c05265

Ayalew, A. A. (2020). Development of kaolin clay as a cost-effective technology for defluoridation of groundwater. *International Journal of Chemical Engineering*, 1-10. DOI:10.1155/2020/8820727

Ayalew, A. A. (2023). Physiochemical Characterization of Ethiopian Mined Kaolin Clay through Beneficiation Process. Advances in Materials Science and Engineering, DOI:10.1155/2023/9104807

Bahniuk, M. S., Alidina, F., Tan, X. & Unsworth, L. D. (2022). The last 25 years of research on bioflocculants for kaolin flocculation with recent trends and technical challenges for the future. *Frontiers in Bioengineering and Biotechnology*, 10, 1048755. DOI:10.3389/fbioe.2022.1048755

Belachew, N. & Hinsene, H. (2020). Preparation of cationic surfactant-modified kaolin for enhanced adsorption of hexavalent chromium from aqueous solution. *Applied Water Science*, 10(1), pp. 1-8. DOI:10.1007/s13201-019-1121-7

Belmokhtar, N., Ammari, M. & Brigui, J. (2017). Comparison of the microstructure and the compressive strength of two geopolymers derived from Metakaolin and an industrial sludge. *Construction and Building Materials*, 146, pp. 621-629. DOI:10.1016/j.conbuildmat.2017.04.127

Bhatti, Q. A., Baloch, M. K., Schwarz, S. & Ishaq, M. (2023). Impact of mechanochemical treatment on surface chemistry and flocculation of kaolinite dispersion. *Asia-Pacific Journal of Chemical Engineering*, 18(3), e2886. DOI:10.1002/apj.2886

Bondarieva, A., Yaichenia, I., Zahorodniuk, N., Tobilko, V. & Pavlenko, V. (2022). Water purification from cationic organic dyes using kaolin-based ceramic materials. *Technology audit and production reserves*, 2(3/64), pp. 10-16. https://doi:10.15587/2706-5448.2022.254584.

Bousbih, S., Errais, E., Darragi, F., Duplay, J., Trabelsi-Ayadi, M., Daramola, M. O. & Ben Amar, R. (2021). Treatment of textile wastewater using monolayered ultrafiltation ceramic membrane fabricated from natural kaolin clay. *Environmental Technology*, 42(21), pp. 3348-3359. DOI:10.1080/09593330.2020.1729242

Burns, G. (1985). Solid State Physics Academic Press Inc. New York.

Chen, M., Yang, T., Han, J., Zhang, Y., Zhao, L., Zhao, J., Li, R., Huang, Y., Gu, Z. & Wu, J. (2023). The application of mineral kaolinite for environment decontamination: A review. *Catalysts*, 13(1), 123. DOI:10.3390/catal13010123

Chuaicham, C., Trakulmututa, J., Shu, K., Shenoy, S., Srikhaow, A., Zhang, L., Mohan, S., Sekar, K. & Sasaki, K. (2023). Recent clay-based photocatalysts for wastewater treatment. *Separations*, 10(2), 77. DOI:10.3390/separations10020077

Ding, S. L., Zhang, L. L., Xu, B. H. & Liu, Q. F. (2012). Review and prospect of surface modification of kaolin. *Advanced Materials Research*, 430, pp. 1382-1385. DOI:10.4028/www.scientific.net/AMR.430-432.1382

El-Sheikh, S., Shawky, A., Abdo, S. M., Rashed, M. N. & El-Dosoqy, T. I. (2020). Preparation and characterisation of nanokaolinite photocatalyst for removal of P-nitrophenol under UV irradiation. *International Journal of Nanomanufacturing*, 16(3), pp. 232-242. DOI:10.1504/IJNM.2020.108042

El-Sherbiny, S., Morsy, F. A., Hassan, M. S. & Mohamed, H. F. (2015). Enhancing Egyptian kaolinite via calcination and dealumination for application in paper coating. *Journal of Coatings Technology and Research*, 12, pp. 739-749. DOI:10.1007/s11998-015-9672-5

Erasto, L., Hellar-Kihampa, H., Mgani, Q. A. & Lugwisha, E. H. J. (2023). Comparative analysis of cationic dye adsorption efficiency of thermally and chemically treated Tanzanian kaolin. *Environmental Earth Sciences*, 82(4), 101. DOI:10.1007/s12665-023-10782-w

Eze, K., Nwadiogbu, J., Nwankwere, E., Appl, A. & Res, S. (2012). Effect of acid treatments on the physicochemical properties of kaolin clay. *Archives of Applied Science Research*, 4(2), pp. 792-794.

Fourdrin, C., Balan, E., Allard, T., Boukari, C. & Calas, G. (2009). Induced modifications of kaolinite under ionizing radiation: an infrared spectroscopic study. *Physics and Chemistry of Minerals,* 36, pp. 291-299. DOI:10.1007/s00269-008-0277-8

Gad, A., Al-Mur, B. A., Alsiary, W. A. & Abd El Bakey, S. M. (2022). Optimization of carboniferous Egyptian kaolin treatment for pharmaceutical applications. *Sustainability*, 14(4), 2388. DOI:10.3390/su14042388

Goodarzi, N., Ashrafi-Peyman, Z., Khani, E. & Moshfegh, A. Z. (2023). Recent progress on semiconductor heterogeneous photocatalysts in clean energy production and environmental remediation. *Catalysts*, 13(7), 1102. DOI:10.3390/catal13071102

Hoai, P. T. T., Huong, N. T. M., Huong, P. T. & Viet, N. M. (2022). Improved the light adsorption and separation of charge carriers to boost photocatalytic conversion of CO$_2$ by using silver doped ZnO photocatalyst. *Catalysts,* 12(10), 1194. DOI:10.3390/catal12101194

Hu, P., Zhang, Y. & Cheng, G. (2023). *Molecular Catalysis*, 547, 113312. DOI:10.1016/j.mcat.2023.113312

Huang, Z., Li, L., Li, Z., Li, H. & Wu, J. (2020). Synthesis of novel kaolin-supported g-C$_3$N$_4$/CeO$_2$ composites with enhanced photocatalytic removal of ciprofloxacin. *Materials*, 13(17), 3811. DOI:10.3390/ma13173811

Jiang, D., Liu, Z., Fu, L., Jing, H. & Yang, H. (2018). Efficient nanoclay-based composite photocatalyst: the role of nanoclay in photogenerated charge separation. *The Journal of Physical Chemistry C,* 122(45), pp. 25900-25908. DOI:10.1021/acs.jpcc.8b08663

Kamaluddin, M. R., Zamri, N. I. I., Kusrini, E., Prihandini, W. W., Mahadi, A. H. & Usman, A. (2021). Photocatalytic activity of kaolin–titania composites to degrade methylene blue under UV light irradiation; kinetics, mechanism and thermodynamics. *Reaction Kinetics, Mechanisms and Catalysis*, 133(1), pp. 517-529. DOI:10.1007/s11144-021-01986-x

Kareem, R. A., Alqadoori, M. A. I. & Ismail, M. M. (2022). Enhancement mechanical, thermal and dielectrical characteristics of polystyrene reinforcement by glass fiber and additive kaolin. *Materials Science Forum*, 1077, pp. 79-86. DOI:10.4028/p-qiok7y

Kuranga, I., Alafara, A., Halimah, F., Fausat, A., Mercy, O. & Tripathy, B. (2018). Production and characterization of water treatment coagulant from locally sourced kaolin clays. *Journal of Applied Sciences and Environmental Management*, 22(1), pp. 103-109. DOI:10.4314/jasem.v22i1.19

Kutláková, K. M., Tokarský, J. & Peikertová, P. (2015). Functional and eco-friendly nanocomposite kaolinite/ZnO with high photocatalytic activity. *Applied Catalysis B: Environmental*, 162, pp. 392-400. DOI:10.1016/j.apcatb.2014.07.018

Li, C., Sun, Z., Song, A., Dong, X., Zheng, S. & Dionysiou, D. D. (2018). Flowing nitrogen atmosphere induced rich oxygen vacancies overspread the surface of TiO_2/kaolinite composite for enhanced photocatalytic activity within broad radiation spectrum. *Applied Catalysis B: Environmental*, 236, pp. 76-87. DOI:10.1016/j.apcatb.2018.04.083

Li, C., Zhu, N., Dong, X., Zhang, X., Chen, T., Zheng, S. & Sun, Z. (2020). Tuning and controlling photocatalytic performance of TiO_2/kaolinite composite towards ciprofloxacin: Role of 0D/2D structural assembly. *Advanced Powder Technology*, 31(3), pp. 1241-1252. DOI:10.1016/j.apt.2020.01.007

Liang, X., Li, Q. & Fang, Y. (2023). Preparation and characterization of modified kaolin by a mechanochemical method. *Materials*, 16(8), 3099. DOI:10.3390/ma16083099

Lin, M., Chen, H., Zhang, Z. & Wang, X. (2023). Engineering interface structures for heterojunction photocatalysts. *Physical Chemistry Chemical Physics*, 25(6), pp. 4388-4407. DOI:10.1039/D2CP05281D

Lindberg, J. D. & Snyder, D. G. (1972). Diffuse reflectance spectra of several clay minerals. American Mineralogist: *Journal of Earth and Planetary Materials*, 57(3-4_Part_1), pp. 485-493.

Liu, J., Dong, G., Jing, J., Zhang, S., Huang, Y. & Ho, W. (2021). Photocatalytic reactive oxygen species generation activity of TiO_2 improved by the modification of persistent free radicals. *Environmental Science: Nano*, 8(12), pp. 3846-3854. DOI:10.1039/D1EN00832C

Liu, Q., Wang, S., Han, F., Lv, S., Yan, Z., Xi, Y. & Ouyang, J. (2022). Biomimetic tremelliform ultrathin MnO_2/CuO nanosheets on kaolinite driving superior catalytic oxidation: an example of CO. *ACS Applied Materials & Interfaces*, 14(39), pp. 44345-44357. DOI:10.1021/acsami.2c11640

Ma, R., Zhao, S., Jiang, X., Qi, Y., Zhao, T., Liu, Z., Han, C. & Shen, Y. (2023). Modification and regulation of acid-activated kaolinite with TiO_2 nanoparticles and their enhanced photocatalytic activity to sodium ethyl xanthate. *Environmental Technology Reviews*, 12(1), pp. 272-285. DOI:10.1080/21622515.2023.2202827

Mamulová Kutláková, K., Tokarský, J. & Peikertová, P. (2015). Functional and eco-friendly nanocomposite kaolinite/ZnO with high photocatalytic activity. *Applied Catalysis B: Environmental*, 162, pp. 392-400. DOI:DOI:10.1016/j.apcatb.2014.07.018

Mei, X., Li, S., Chen, Y., Huang, X., Cao, Y., Guro, V. P. & Li, Y. (2023). Silica–chitosan composite aerogels for thermal insulation and adsorption. *Crystals*, 13(5), 755. DOI:10.3390/cryst13050755

Mohd Yunus, N. Z., Ayub, A., Wahid, M. A., Mohd Satar, M. K. I., Abudllah, R. A., Yaacob, H., Hassan, S. A. & Hezmi, M. A. (2019). *Strength behaviour of kaolin treated by demolished concrete materials*. IOP Conference Series: Earth and Environmental Science, 220, 012001. DOI 10.1088/1755-1315/220/1/012001

Omary, P. M., Ricky, E. X., Kasimu, N. A., Madirisha, M. M., Kilulya, K. F. & Lugwisha, E. H. (2023). Potential of Kaolin Clay on Formulation of Water Based Drilling Mud Reinforced with Biopolymer, Surfactant, and Limestone. *Tanzania Journal of Science*, 49(1), pp. 218-229. https://DOI:10.4314/tjs.v49i1.19

Panda, T., Roy, N., Dutta, S. & Maity, T. (2023). Implementations of Photocatalysis: A Futuristic Approach. *International Journal of Chemical and Environmental Sciences*, 4(3), pp. 48-61. DOI:10.15864/ijcaes.4305

Rajan, M. S., Yoon, M. & Thomas, J. (2022). Kaolin-graphene carboxyl incorporated TiO_2 as efficient visible light active photocatalyst for the degradation of cefuroxime sodium. *Photochemical & Photobiological Sciences*, 21(4), pp. 509-528. DOI:10.1007/s43630-022-00179-2

Rekik, S. B., Gassara, S., Bouaziz, J., Baklouti, S. & Deratani, A. (2023). Performance Enhancement of Kaolin/Chitosan Composite-Based Membranes by Cross-Linking with Sodium Tripolyphosphate: Preparation and Characterization. *Membranes*, 13(2), 229. DOI:10.3390/membranes13020229

Román, C., Jeon, H., Zhu, H. & Ozkan, E. (2023). Evaluating Kaolin Clay as a Potential Substance for ISO Sprayer Cleaning System Tests. *Applied Engineering in Agriculture*, 39(3), pp. 347-358. https://doi: 10.13031/aea.15466

Romolini, G., Gambucci, M., Ricciarelli, D., Tarpani, L., Zampini, G. & Latterini, L. (2021). Photocatalytic activity of silica and silica-silver nanocolloids based on photo-induced formation of reactive oxygen species. *Photochemical & Photobiological Sciences,* 20(9), pp. 1161-1172. DOI:10.1007/s43630-021-00089-9

Roques-Carmes, T., Alem, H., Hamieh, T., Toufaily, J., Frochot, C. & Villiéras, F. (2020). 3 - *Different strategies of surface modification to improve the photocatalysis properties: pollutant adsorption, visible activation, and catalyst recovery*. [In] C. Mustansar Hussain & A. K. Mishra (Eds.), Handbook of Smart Photocatalytic Materials (pp. 39-57). Elsevier. DOI:10.1016/B978-0-12-819049-4.00007-6

San Nicolas, R., Cyr, M. & Escadeillas, G. (2013). Characteristics and applications of flash metakaolins. *Applied Clay Science*, 83, pp. 253-262. DOI:10.1016/j.clay.2013.08.036

Sbeih, S. A. & Zihlif, A. M. (2009). Optical and electrical properties of kaolinite/polystyrene composite. *Journal of Physics D: Applied Physics*, 42(14), 145405. https://DOI 10.1088/0022-3727/42/14/145405

Serna-Galvis, E. A., Martínez-Mena, Y. L., Arboleda-Echavarría, J., Hoyos-Ayala, D. A., Echavarría-Isaza, A. & Torres-Palma, R. A. (2023). Zeolite 4A activates peroxymonosulfate toward the production of singlet oxygen for the selective degradation of organic pollutants. *Chemical Engineering Research and Design*, 193, pp. 121-131. DOI:10.1016/j.cherd.2023.03.015

Shirzad-Siboni, M., Farrokhi, M., Darvishi Cheshmeh Soltani, R., Khataee, A. & Tajassosi, S. (2014). Photocatalytic Reduction of Hexavalent Chromium over ZnO Nanorods Immobilized on Kaolin. *Industrial & Engineering Chemistry Research*, 53(3), pp. 1079-1087. DOI:10.1021/ie4032583

Sitarz-Palczak, E., Kalembkiewicz, J. & Galas, D. (2019). Comparative study on the characteristics of coal fly ash and biomass ash geopolymers. *Archives of Environmental Protection*, 45(1), pp. 126-135. DOI 10.24425/aep.2019.126427

Sofi'i, Y. K., Sudarman, S. & Suprianto, H. (2022). *Application of molecular dynamic energy of kaolin clay as photocatalysts*. AIP Conference Proceedings, 2453(1), 020014. DOI:10.1063/5.0094250

Sun, Z., Li, C., Du, X., Zheng, S. & Wang, G. (2018). Facile synthesis of two clay minerals supported graphitic carbon nitride composites as highly efficient visible-light-driven photocatalysts. *Journal of colloid and interface science*, 511, pp. 268-276. DOI:10.1016/j.jcis.2017.10.005

Sun, Z., Yuan, F., Li, X., Li, C., Xu, J. & Wang, B. (2018). Fabrication of novel cyanuric acid modified g-C_3N_4/kaolinite composite with enhanced visible light-driven photocatalytic activity. *Minerals*, 8(10), 437. DOI:10.3390/min8100437

Taheri, B. (2023). Iron removal from kaolin by oxalic acid using a novel pre-agitating and high-pressure washing technique. Clay Minerals, 58(2), pp. 224-233. DOI:10.1180/clm.2023.11

Tanwongwan, W., Wongkitikun, T., Onpecht, K., Srilai, S., Assabumrungrat, S., Chollacoop, N. & Eiad-ua, A. (2020). *Structure development of Thailand's kaolin by mechanochemical technique*. AIP Conference Proceedings, 2279(1), 060001. DOI:10.1063/5.0025045

Tharakeswari, S., Saravanan, D., Agrawal, A. K. & Jassal, M. (2022). Kaolin-Calcium Carbonate-Titanium Dioxide (KCT) Composites for Decolourisation of Reactive Dye Effluent. *Journal of the Chemical Society of Pakistan*, 44(6). DOI:10.52568/001188/jcsp/44.06.2022

Ugwuja, C. G., Adelowo, O. O., Ogunlaja, A., Omorogie, M. O., Olukanni, O. D., Ikhimiukor, O. O., Iermak, I., Kolawole, G. A., Guenter, C. & Taubert, A. (2019). Visible-light- mediated photodynamic water disinfection@ bimetallic-doped hybrid clay nanocomposites. *ACS Applied Materials & Interfaces*, 11(28), pp. 25483-25494. DOI:10.1021/acsami.9b01212

Usman, J., Hafiz, M., Othman, D., Ismail, A., Rahman, M., Jaafar, J. & Abdullahi, T. (2020). Comparative study of Malaysian and Nigerian kaolin-based ceramic hollow fiber membranes for filtration application. *Malaysian J Anal Sci*, 16(2), pp. 78-82. DOI:10.11113/mjfas.v16n2.1484

Vagvolgyi, V., Zsirka, B., Győrfi, K., Horváth, E. & Kristóf, J. (2021). *Different Methods for Preparation of Active Sites in Kaolinite Surface and their Usability in Photocatalytic Processes*, [in] Proceedings of the 2nd International Electronic Conference on Mineral Science, 1–15 March 2021, MDPI: Basel, Switzerland, DOI:10.3390/iecms2021-09357

Varajão, A. F. D. C., Gilkes, R. J. & Hart, R. D. (2001). The relationships between kaolinite crystal properties and the origin of materials for a Brazilian kaolin deposit. *Clays and Clay Minerals*, 49(1), pp. 44-59. DOI:10.1346/CCMN.2001.0490104

Wang, L. & Yu, J. (2023). Principles of photocatalysis. In Interface science and technology (Vol. 35, pp. 1-52). Elsevier. DOI:10.1016/B978-0-443-18786-5.00002-0

Wang, T., Xu, L., Cui, J., Wu, J., Li, Z., Wu, Y., Tian, B. & Tian, Y. (2022). Enhanced Charge Separation for Efficient Photocatalytic H_2 Production by Long-Lived Trap-State-Induced Interfacial Charge Transfer. *Nano Letters*, 22(16), 6664-6670. DOI:10.1021/acs.nanolett.2c02005 Burns, G. (1985). Solid State Physics Academic Press Inc. *New York*.

Xiao, Y., Tian, X., Chen, Y., Xiao, X., Chen, T. & Wang, Y. (2023). Recent Advances in Carbon Nitride-Based S-scheme Photocatalysts for Solar Energy Conversion. *Materials*, 16(10), 3745. DOI:10.3390/ma16103745

Xu, H., Sun, S., Jiang, S., Wang, H., Zhang, R. & Liu, Q. (2018). Effect of pretreatment on microstructure and photocatalytic activity of kaolinite/TiO_2 composite. *Journal of sol-gel science and technology,* 87, pp. 676-684. DOI:10.1007/s10971-018-4760-5

Yahaya, S., Jikan, S. S., Badarulzaman, N. A. & Adamu, A. D. (2017). Chemical composition and particle size analysis of kaolin. Traektoriâ Nauki, Volume 3, Number 10, 2017, pp. 1001-1004(4) DOI:10.22178/pos.27-1

Yu, J. M. & Jang, J.-W. (2023). Organic Semiconductor-Based Photoelectrochemical Cells for Efficient Solar-to-Chemical Conversion. *Catalysts,* 13(5), 814. DOI:10.3390/catal13050814

Zakaria Djibrine, B., Zheng, H., Wang, M., Liu, S., Tang, X., Khan, S., Jimenéz, A. N. & Feng, L. (2018). An effective flocculation method to the kaolin wastewater treatment by a cationic polyacrylamide (CPAM): Preparation, characterization, and flocculation performance. *International Journal of Polymer Science*, pp. 1-12. DOI:10.1155/2018/5294251

Zhang, B., Wang, D., Cao, J., Zhao, C., Pan, J., Liu, D., Liu, S., Zeng, Z., Chen, T. & Liu, G. (2023). Efficient doping induced by charge transfer at the hetero-interface to enhance photocatalytic performance. *ACS Applied Materials & Interfaces*, 15(10), pp. 12924-12935. DOI:10.1021/acsami.2c19209

Zhang, C., Xie, C., Gao, Y., Tao, X., Ding, C., Fan, F. & Jiang, H. L. (2022). Charge separation by creating band bending in metal–organic frameworks for improved photocatalytic hydrogen evolution. *Angewandte Chemie*, 134(28), e202204108. DOI:10.1002/ange.202204108

Zhang, Q., Shan, A., Wang, D., Jian, L., Cheng, L., Ma, H. & Li, J. (2013). A new acidic Ti sol impregnated kaolin photocatalyst: synthesis, characterization and visible light photocatalytic performance. *Journal of sol-gel science and technology*, 65, pp. 204-211. DOI:10.1007/s10971-012-2925-1

Zhang, Y., Gan, H. & Zhang, G. (2011). A novel mixed-phase TiO2/kaolinite composites and their photocatalytic activity for degradation of organic contaminants. *Chemical Engineering Journal*, 172(2-3), pp. 936-943. DOI:10.1016/j.cej.2011.07.005

Zvyagin, B. & Drits, V. (1996). Interrelated features of structure and stacking of kaolin mineral layers. *Clays and Clay Minerals*, 44, pp. 297-303. DOI: 10.1346/CCMN.1996.0440301