



Research article

Modeling sustainable photocatalytic degradation of acidic dyes using Jordanian nano-Kaolin–TiO₂ and solar energy: Synergetic mechanistic insights

Waed Alahmad^{a,*}, Fekhra Hedhili^{b,c}, S.M. Al-Shomar^b, Hissah Saedoon Albaqawi^b, Nwuyyer A. Al-Shammari^b, Selma Abdelrahman^b

^a Department of Chemistry, Faculty of Science, Applied Science Private University, P. O. Box 166, Amman, 11931, Jordan

^b Department of Physics, College of Science, University of Ha'il, P.O. Box 2440, Ha'il, Saudi Arabia

^c Department of Physics, Faculty of Science, Al Manar University, 1060, Tunis, Tunisia

ARTICLE INFO

Keywords:

Jordanian kaolin
Sol-gel synthesis
Solar energy
Cost reduction
Water purification

ABSTRACT

The abstract highlights the global issue of environmental contamination caused by organic compounds and the exploration of various methods for its resolution. One such approach involves the utilization of titanium dioxide (TiO₂) as a photocatalyst in conjunction with natural adsorption materials like kaolin. The study employed a modeling-based approach to investigate the sustainable photocatalytic degradation of acidic dyes using a Jordanian nano-kaolin–TiO₂ composite material and solar energy. Mechanistic insights were gained through the identification of the dominant reactive oxygen species (ROS) involved in the degradation process, as well as the synergetic effect between adsorption and photocatalysis. The Jordanian nano-kaolin–TiO₂ composite was synthesized using the sol-gel method and characterized. The nanocomposite photocatalyst exhibited particle sizes ranging from 27 to 41 nm, with the TiO₂ nanoparticles well-dispersed within the kaolin matrix. The efficacy of this nanocomposite in removing Congo-red dye was investigated under various conditions, including pH, initial dye concentration, and photocatalyst amount. The optimal conditions for dye removal were found to be at pH 5, with an initial dye concentration of 20 ppm, and using 0.1 g of photocatalyst, resulting in a 95 % removal efficiency. The mechanistic insights gained from this study indicate that the hydroxyl radicals (•OH) generated during the photocatalytic process play a dominant role in the degradation of the acidic dye. Furthermore, the synergetic effect between the adsorption of the dye molecules onto the photocatalyst surface and the subsequent photocatalytic degradation by the ROS was found to enhance the overall removal efficiency. These findings contribute to the fundamental understanding of the photodegradation mechanisms and guide the development of more efficient photocatalytic systems for the treatment of acidic dye-containing wastewater. The use of solar power during the purification procedure also leads to cost reduction and strengthens sustainability efforts.

* Corresponding author.

E-mail address: w.alahmad@asu.edu.jo (W. Alahmad).

<https://doi.org/10.1016/j.heliyon.2024.e36978>

Received 19 January 2024; Received in revised form 24 August 2024; Accepted 26 August 2024

Available online 28 August 2024

2405-8440/© 2024 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC license (<http://creativecommons.org/licenses/by-nc/4.0/>).

1. Introduction

Kaoline, a clay variety rich in kaolinite minerals, exhibits a chemical constitution predominantly defined by $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. Notably, it manifests sheets of silicates, wherein alternate silicate strata are composed of tetrahedral silica sheets and octahedral alumina sheets. The linkage between these layers involves an oxygen atom bridging a silica sheet to an octahedral alumina sheet. The widespread application of kaoline as an adsorbent in water treatment derives from its economic viability, abundant availability, and considerable surface area [1,2]. In contemporary discourse, there has been a notable surge in interest regarding the utilization of modified kaoline incorporated with metal oxides. This heightened attention is motivated by the augmented adsorption capacities and photocatalytic attributes exhibited by such formulations in the mitigation of a broad spectrum of pollutants. Notably, these pollutants encompass heavy metals, organic dyes, and pharmaceutical compounds [2,3].

Various auxiliary materials are utilized in conjunction with TiO_2 to enhance the indispensable photocatalytic capabilities necessary for water treatment [4,5]. Silica emerges as a prominent auxiliary due to its substantial surface area, stability, and compatibility with TiO_2 . Furthermore, activated charcoal, zeolites (crystalline aluminosilicates) [6], clays (including montmorillonite, bentonite, and kaoline), polymeric materials such as polyethylene glycol (PEG) and polyvinyl alcohol (PVA), and carbon-based materials such as graphene, carbon nanotubes (CNTs), and carbon nanofibers (CNFs) are employed [7,8]. These auxiliary materials collectively augment photocatalytic activities by providing augmented surface area, enhanced dispersion, improved adsorption capacity, and efficient charge transfer, all of which are pivotal for effective water treatment applications [9–11].

Jordan possesses ample reservoirs of kaoline, presenting a spectrum of distinctive attributes that can confer advantages to diverse industries [12,13]. Recent inquiries have systematically explored the utilization of Jordanian kaoline in distinct environmental applications. Awwad et al. (2020) have investigated its effectiveness in removing heavy metals from water [14], while the work of Mohammadhosseini et al. (2022) has scrutinized its photocatalytic ability in degrading organic pollutants under both UV and visible light exposure [15]. Furthermore, Ibbini et al. (2018) have demonstrated the suitability of Jordanian kaoline in antimicrobial removal applications [16]. These comprehensive studies collectively underscore the versatile applications of Jordanian kaoline across various environmental domains and affirm its potential as a sustainable solution for environmental remediation, as articulated by Chen et al. (2023) [11].

Various methodologies have been employed to incorporate metal oxides into kaolinite, with the aim of augmenting its efficacy in water treatment. These methodologies encompass co-precipitation [17], sol-gel [18], impregnation [19], and hydrothermal techniques [20]. The literature suggests that the introduction of metal oxides enhances the adsorption capacity of kaolinite, particularly concerning pollutants such as heavy metals and dyes [11].

A comprehensive understanding of the synthesis methodology plays a pivotal role in optimizing the efficacy of kaoline- TiO_2 composites photocatalysts for water treatment applications. Hydrothermal synthesis is commonly associated with the generation of composites featuring expanded surface areas, contrasting with co-precipitation and sol-gel techniques which tend to yield more crystalline structures [21,22]. Additionally, co-precipitation and sol-gel methods typically result in kaoline- TiO_2 composites characterized by heightened crystallinity levels, potentially enhancing charge carrier mobility and overall photocatalytic efficiency [23, 24]. Furthermore, the long-term stability and durability of kaoline- TiO_2 composites are contingent upon various factors such as crystal phase, defect density, and resistance to aggregation. Notably, hydrothermally synthesized composites often demonstrate superior stability and durability when compared to counterparts synthesized through alternative methods [21,22,24,25].

Several metal oxides, including TiO_2 [26,27], Fe_2O_3 [28], and ZrO_2 [29], have been employed in conjunction with kaoline for water treatment applications. Each metal oxide exhibits distinct properties that contribute to the removal of pollutants from water. Notably, titanium dioxide emerges as a prominent metal oxide photocatalyst in the modification process. When combined with kaoline, it displays significant promise for degrading organic contaminants in water, owing to its exceptional photocatalytic efficiency [14, 30–32].

Moreover, the synergy of adsorption and photocatalytic attributes is evident in studies such as Barbosa et al.'s (2015) investigation [18]. The uniform dispersion of TiO_2 across the kaoline surface not only enhances effective adsorption but also accelerates dye degradation. Similarly, iron oxide (Fe_2O_3) has proven capable of enhancing the adsorption efficiency of kaoline for heavy metal ions, attributed to its expansive surface area and strong affinity for these ions [33,34].

These findings spotlight the potential of composite materials combining kaoline and metal oxides as a robust and sustainable approach for water treatment and environmental remediation. Kaoline- TiO_2 composites are reputed for their lack of effectiveness as either adsorbents or photo-degradation catalysts, due to their low photostability, high cost, inferior degradation efficiency, and high toxicity.

The study's hypothesis suggests that synthesizing a Kaoline- TiO_2 nanocomposite using Jordanian kaoline as a decontaminant will enhance the removal efficiency of Congo-red dye compared to pure TiO_2 . It anticipates that incorporating kaoline will improve product properties such as surface area and porosity, resulting in a more effective photocatalyst for water purification. The well-spread TiO_2 nanoparticles within the kaoline matrix are expected to offer heightened active sites for adsorption and photocatalytic degradation of organic pollutants. Consequently, under optimal conditions, the nanocomposite is projected to exhibit superior dye removal efficiency, making it a promising water purifier solution, particularly for regions with limited freshwater resources like Jordan. Moreover, the utilization of solar energy during the purification process is expected to decrease expenses and boost system sustainability. This hypothesis forms the basis of the study, suggesting that the Kaolin- TiO_2 nanocomposite will outperform pure TiO_2 and address environmental contamination caused by organic compounds through synergistic effects with kaolin as a natural adsorption material.

The primary objective of this study is to investigate the synergistic effect between adsorption and photocatalysis using Jordanian nano-kaolin- TiO_2 composites for the sustainable degradation of Congo-red dye. By systematically varying parameters such as pH,

initial dye concentration, and nanocomposite dosage, the influence of these factors on the removal efficiency was evaluated. Furthermore, the mechanistic insights gained through the identification of the dominant reactive oxygen species (ROS) involved in the degradation process were crucial for understanding the underlying photocatalytic degradation pathways. The examination of scavenger effects on the nanocomposite provided valuable information about the relative importance of hydroxyl radicals ($\bullet\text{OH}$), superoxide radicals ($\bullet\text{O}_2^-$), and holes (h^+) in the degradation mechanism. Monitoring the removal efficiency across multiple recycling cycles also allowed for the assessment of the reusability and sustainability of the nanocomposite material. These comprehensive investigations, focusing on the synergistic effect and the mechanistic aspects, collectively contribute to advancing the potential application of this approach in wastewater treatment, specifically in Olive oil presses in Jordan, where the availability of naturally sourced materials like Jordanian kaolin can be leveraged for cost-effective and sustainable water purification solutions.

2. Materials and methods

2.1. Chemicals and reagents

All reagents are chemically pure and used without further purification. Titanium tetra isopropoxide (TTIP), ethanol, Congo red dye [acidic dye] ($\text{C}_{32}\text{H}_{22}\text{N}_6\text{Na}_2\text{O}_6\text{S}_2$), Tertbuta-nol (TBA), Na_2EDTA , sodium hydroxide (NaOH), Hydrochloric acid (HCl). The Jordanian kaolin employed in this study was sourced from the Mahis and Hiswa localities, pre-treated; washed and calcined at $500\text{ }^\circ\text{C}$ for 5 h.

2.2. Synthesis

During this experimentation, two solutions were employed: Solution A, consisting of 1 % kaolin in distilled water (pre-treated), and Solution B, comprising 10 % TiO_2 in ethanol. The addition of Solution B to Solution A was executed gradually under robust stirring conditions at $75\text{ }^\circ\text{C}$ overnight. Subsequently, the combined solution was allowed to stand at room temperature for a duration of 7 days for the aging process until complete drying occurred. The ensuing powder underwent annealing at $500\text{ }^\circ\text{C}$ for 5 h. The resultant powder, characterized by a weight-to-weight percentage ratio of 1:10 %, was utilized in subsequent photocatalytic experiments.

2.3. Characterization of Kaolin– TiO_2

The chemical compositions of the kaolin– TiO_2 nanocomposites were assessed through X-ray fluorescence (XRF) spectrometry. The structural characteristics were investigated via powdered X-ray diffraction (PXRD) using a 7000 Shimadzu 2 kW model X-ray spectrophotometer instrument with nickel-filtered copper radiation ($\text{CuK}\alpha$) at $\lambda = 1.5456\text{ \AA}$. The 2θ range was scanned from 2° to 60° with a step size of 0.02° , and the instrument was based in Kyoto, Japan. The microstructures of the specimens were scrutinized using a scanning electron microscope (SEM) from Hitachi High-Tech, Tokyo, Japan. Specific surface areas were determined by employing a Nova 2200 gas sorption analyzer from Quantachrome Co., Syosset, NY, USA. The assessment of degradation percentage was conducted using the PEAK Instruments C-7000UV Spectrometer.

2.4. Experimental design for photocatalytic degradation

The experiment utilized 200 ml of distilled water, incorporating various parameters to achieve optimal conditions. These factors encompassed the initial concentration of Congo-red dye, a specified dosage of Kaolin– TiO_2 , and a range of pH values.

Dye concentrations were set at 5, 10, 15, 20, and 25 ppm, while Kaolin– TiO_2 dosages varied at 0.1, 0.25, 0.50, 0.75, and 1 g. pH levels of 3, 5, 7, and 10 were considered.

At pH 3, the wavelength (λ max.) was 550 nm, and for pHs 5, 7, and 10, it was 497 nm. Sunlight energy parameters averaged over the experiment days included $45.6\text{ }\mu\text{T}$, 96852 lux, 15 EV, with temperatures ranging between 30 and $37\text{ }^\circ\text{C}$ during the August experiments.

Before starting the photodegradation process, samples underwent equilibrium in darkness with continuous stirring for approximately 1 h. Subsequently, 10 ml aliquots were extracted every 45 min, filtered using syringe glass filters, and absorption was measured with a UV–Vis spectrophotometer.

To assess the impact of the synthesized material without solar radiation interference, a dark experiment was conducted under identical conditions as previously described. Photodegradation percentage was calculated using the equation:

$$\text{Degradation \%} = \frac{C_0 - C_t}{C_0} \times 100\%$$

Where C_0 represent the initial concentration after equilibrium time, and C_t denotes the concentration after 225 min (final reading). Control groups encompass the assessment of degradation percentages for Congo red under two distinct conditions: firstly, in the absence of Kaolin– TiO_2 , and secondly, with Kaolin alone.

2.5. Kaolin– TiO_2 reusability

To investigate the efficacy of reutilizing the synthesized material, the optimal parameters were selected for successive degradation,

employing the same dosage for up to five iterations. The optimized conditions included a 20-ppm dye concentration, 0.1 g of Kaolin-TiO₂, and a pH of 5. Following the conditions, absorption measurements were taken after 225 min. Subsequently, the Kaolin-TiO₂ material was filtered, rinsed with distilled water, dried at 100 °C, and subjected to reuse in subsequent experiments.

2.6. Scavenger investigation

The examination of the primary precursor in the photodegradation process involved the utilization of tert-butanol (TBA) as a hydroxyl radical scavenger and EDTA disodium as a hole scavenger. A solution with a 20 ppm dye concentration, pH 5, and a dosage of 0.1 g was prepared, incorporating 200 mmol of scavengers.

3. Results and discussion

3.1. Characterization of Kaolin-TiO₂

Kaolin-TiO₂ nanocomposites were subjected to characterization using various techniques, including SEM, XRD, XRF, and BET, to elucidate their physicochemical properties. The SEM images (Fig. 1) provide insight into the nature of the synthesized material, depicting particle size both before initial use in Fig. 1 (a) and after undergoing five recycling cycles in Fig. 1 (b). The particle size exhibited a range between 41 and 27 nm. Notably, the Kaolin-TiO₂ powder displayed increased aggregation after the recycling process.

Kaolin has an infinitely repeated structure, including a silica tetrahedral sheet and a gibbsite sheet. Its particles are flaky and often white, with a hexagonal outline. Fig. 1 showed that the nanocomposite had a spherical shape of size between 27 and 41 nm, in which the kaolin had a sheet-like texture. From the two images, the originally smooth kaolinite plates are covered with TiO₂ nanoparticles. The nanocomposite after the photo experiment becomes more aggregated, which makes the filtration process more challenging. In a study by Wongso et al. (2019), the surface morphology of hybrid kaolin/TiO₂ composites was studied using SEM displaying spherical nanoparticles with a diameter mostly in the range of 14–20 nm [35]. In addition, they found that kaolin shows a sheet-like texture. The results revealed that the kaolinite-TiO₂ composites had a more uniform and homogeneous distribution than pure TiO₂. Consequently, Azeez et al. (2022) found that SEM micrographs of TiO₂-Kaolinite show a clear change in surface morphology due to the appearance of spongy discrete particles that differ from pure TiO₂ and kaolinite. They also found that the SEM micrographs of TiO₂-kaolinite and TiO₂ after degradation revealed that the dye molecules had degraded on both the TiO₂-AKC and TiO₂ surfaces, as was found in this study [36].

Henych and Štengl (2013) demonstrated that extensively crystallized TiO₂ was evenly distributed across the entire surface of the kaolin substrate, confirming exceptional uniformity and homogeneity [37]. Li et al. (2018) examined the impact of the form of kaolinite clay on the effectiveness of TiO₂ nanoparticles. They observed that TiO₂ nanoparticles adhered to one-dimensional nanorods and two-dimensional nanoflakes exhibited superior dispersion and smaller grain size due to close interactions and strong interfacial contacts, highlighting the significance of morphology in achieving uniformity and homogeneity [17](Li et al., 2018b)

The XRD pattern (Fig. 2) shows the kaolin, TiO₂ and kaolin-TiO₂ before photocatalytic experiment and after 5 reuse times, the pattern shows the crystallin form of titanium dioxide (anatase phase), which is characterized by peaks appearing at 2θ values of 25.3°, 38.2°, 48.0°, 54.0, and 55.0° [35,38]. The characteristic peaks for kaolin are 12° and 26°, which are characteristic peaks for kaolinite minerals in kaolin (Wongso et al., 2019; Azeez et al., 2022a). The characteristic peaks for TiO₂ 2θ = 25° are found in the synthesized

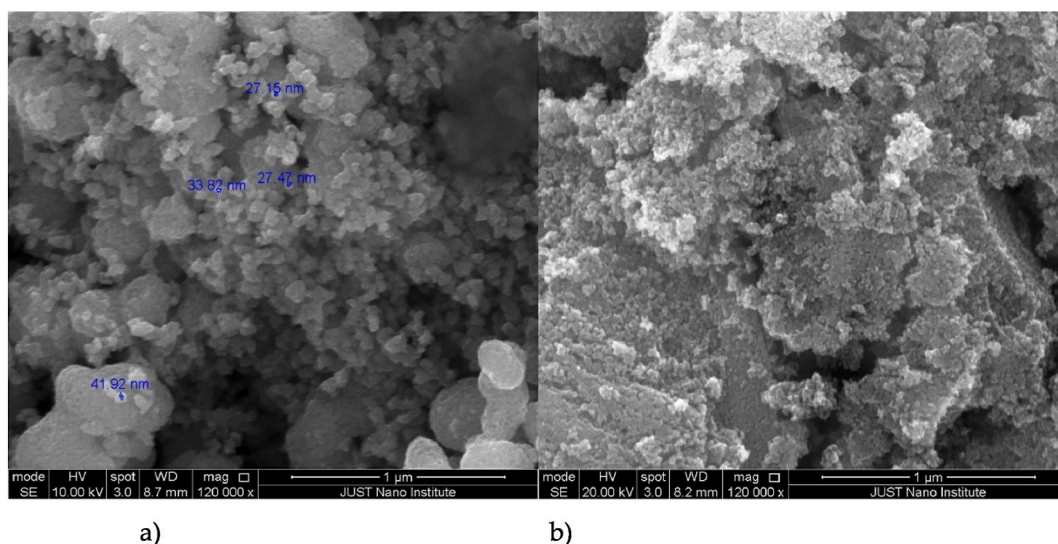


Fig. 1. SEM images of Kaolin-TiO₂: a) before initial use and b) after undergoing five recycling cycles.

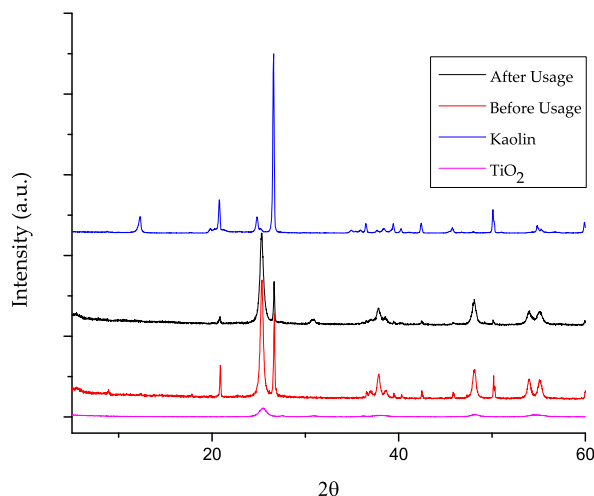


Fig. 2. XRD pattern for Kaolin, TiO₂, Kaolin-TiO₂ before initial use and after undergoing five recycling cycles.

sample (before) and in the after-used sample but with less intensity, also the $2\theta = 26^\circ$ peak related to the kaolin is found in both the before- and after-used samples [35,36].

Mustapha et al. (2020) prepared kaolin-TiO₂ nanocomposites using a hydrothermal approach and subjected them to XRD analysis for characterization. The obtained XRD patterns validated the existence of both anatase and rutile phases of TiO₂, suggesting the successful synthesis of the nanocomposite. Additionally, the authors noted a shift in peak positions, indicating alterations in the crystal structure attributed to the inclusion of kaolin [39].

Table 1 displays the XRF outcomes, revealing variations in the percentages of SiO₂, Al₂O₃, and TiO₂ between the Kaolin-TiO₂ Pre-treatment and the sample after photocatalytic procedures. Notably, there was an increase in the percentage of TiO₂ post-treatment. According to the XRF analysis reported by Yahaya et al. (2017), the predominant constituents of kaolin clay include approximately 58.73 % SiO₂, 24.35 % Al₂O₃, 5.36 % K₂O, and incidental impurities such as Fe₂O₃ (2.06 %) [40].

The observed reduction of around 50 % in SiO₂ and Al₂O₃, as indicated by both SEM images and experimental data, signifies the physical characteristics of TiO₂ nanoparticles experiencing pronounced aggregation. This reduction underscores the necessity of incorporating kaolin to address the aggregation issue in TiO₂ nano particles.

3.1.1. Determination of the specific surface areas

The BET method was employed to determine the specific surface area of the nanocomposites, revealing an augmentation post the introduction of TiO₂ and kaolin-TiO₂. Initially measured at 25.8 m²/g, it exhibited a decrease to 34.9 m²/g after five usages (Figs. 3 and 4). Wongso et al. (2019) highlighted that the loading of TiO₂ on kaolin supports results in higher surface areas for hybrid kaolin/TiO₂ composites [35]. With a moderate range of surface areas (22–35 m² g⁻¹), kaolin exhibits exceptional adsorption capabilities toward the methylene blue dye, fostering enhanced interaction between TiO₂ nanoparticles and methylene blue and, consequently, improved photocatalytic performance [35]. It's noteworthy that the specific surface area of composites can vary based on factors like synthesis method, TiO₂ loading, and calcination temperature [11].

The integration of SEM, XRD, XRF, and BET analyses alongside performance data enables a comprehensive evaluation of the uniformity and homogeneity of kaolin-modified TiO₂ nanocomposites, providing valuable insights into their adsorption and photocatalytic capabilities for water purification applications. Enhanced uniformity and homogeneity often result in increased adsorption capacity due to the augmentation of active sites for pollutant binding [17,37,41]. Additionally, regarding photocatalytic activity, the uniform distribution of TiO₂ nanoparticles ensures efficient light absorption and charge separation, consequently leading to improved degradation efficiency [17,37,41].

3.2. Photodegradation

Figs. 5–7 depict the degradation percentage against time (minutes), showcasing variations in pH and dosage. The overall duration of the experiment was 225 min, revealing that the optimal degradation occurred at pH 5. It was observed that an escalation in the

Table 1
XRF results for Kaolin-TiO₂, Pre-treatment, and post photocatalytic procedures.

%	SiO ₂	Al ₂ O ₃	TiO ₂
Before usage	18.7	5.03	75.6
Post usage	11.1	3.82	84.1

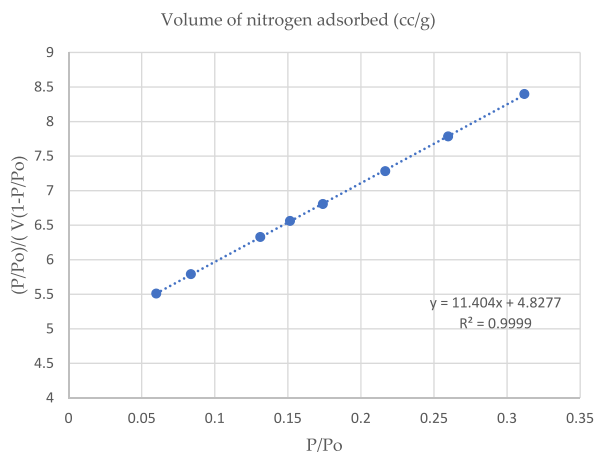


Fig. 3. Linear BET plot for the initial sample, represented by $(P/P_o)/(V(1-P/P_o))$ vs. P/P_o .

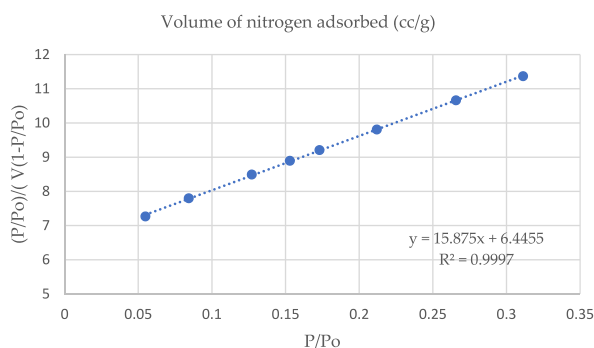


Fig. 4. Linear BET plot for after usage sample, represented by $(P/P_o)/(V(1-P/P_o))$ vs. P/P_o .

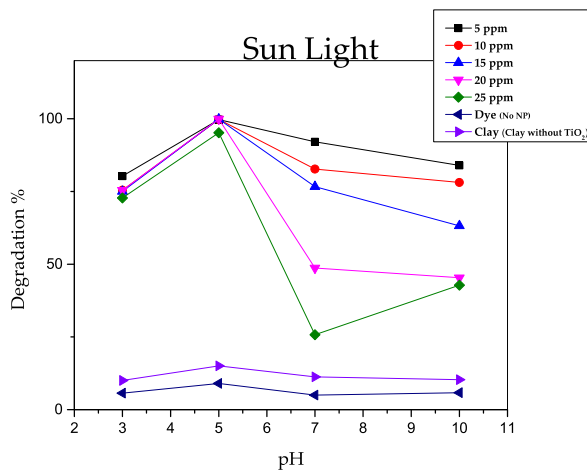


Fig. 5. The degradation percentage (under sunlight) in relation to pH for various initial concentrations (5, 10, 15, 20, and 25 ppm) of the organic dye, both in the absence of kaolin–TiO₂, and with a 15-ppm initial concentration of the organic dye combined with kaolin without treatment.

dosage of kaolin–TiO₂ from 0.1 g to 0.5 g led to an increase in the percentage of degradation; however, beyond 0.5 g, the dosage exhibited diminishing returns in enhancing degradation. Consequently, the optimized condition was determined to be 0.1 g.

Conducting the same experimental procedure without exposure to sunlight (Dark) (refer to Fig. 5), the highest removal percentage reached approximately 45 % at pH 5. Consistently, under sunlight, pH 5 demonstrated the highest removal percentage. Moreover, the removal percentage exhibited an upward trend with increasing dosage.

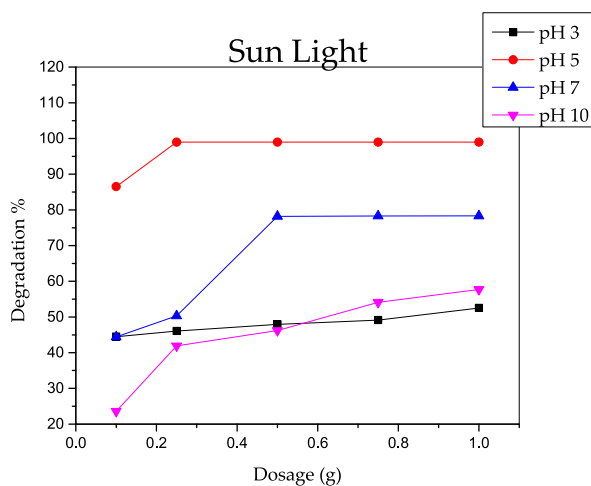


Fig. 6. The degradation percentage in correlation with the varying mass (dosage) of kaolin-TiO₂ at pH levels of 3, 5, 7, and 10, with an initial dye concentration of 20 ppm.

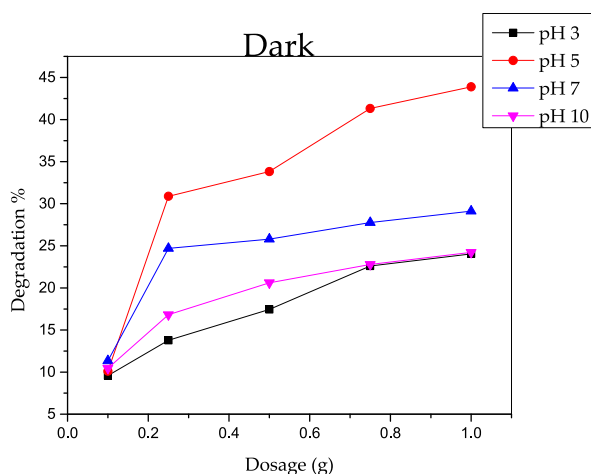


Fig. 7. Percentage degradation in relation to the dosage of Kaolin-TiO₂ at pH levels ranging from 3 to 10 in the absence of sunlight irradiation, with an initial dye concentration of 20 ppm.

Congo Red is widely used as a reliable representative substance in studies of photocatalysis because of its perceptibility, chemical structure that closely resembles industrial pollutants, comprehensively understood rate of decomposition, and the uniformity it offers for comparative analysis [42].

The optimum photocatalytic degradation efficiency for Congo Red, an acidic dye, was observed at pH 5, with similar degradation percentages at pH 3 and pH 10. These results indicate electrostatic repulsion in both highly acidic and basic environments. In aqueous settings, the negative surface charge of kaolin is generally influenced by the pH-dependent deprotonation/protonation of the surface [11,27]. Li et al. conducted a study on the photodegradation of anionic dyes on TiO₂ nanoparticles assembled on kaolin with varying surface charges, they found that the adsorption capacity of the nanocomposites for anionic dyes was influenced by the kaolin surface charge, which, in turn, was affected by pH [17].

The quantity of kaolin-TiO₂ has a direct proportional impact on the degradation percentage, with an increase in the amount leading to an increase in active sites. Comparing removal in darkness to sunlight irradiation, the approximately 45 % removal in the dark suggests a substantial adsorption capacity of kaolin-TiO₂, thereby enhancing photodegradation. The synergistic effect becomes pivotal in studying natural adsorbates with the addition of metal oxides as catalysts for degradation [17].

The introduction of TiO₂ into the kaolin composite goes beyond just enhancing the active surface area; it creates a synergistic (both adsorption and photodegradation) [43–45] effect leveraging the distinctive qualities of both materials. This collaboration enhances the overall efficiency of the photocatalytic process. The Kaolin's porous structure and surface functional groups contribute to a substantial adsorption capacity [45–47]. This unique property enables Kaolin to effectively adsorb pollutants from water. These pollutants concentrated at the catalyst surface, resulting an overall efficiency of the photocatalytic process.

Optimizing the phase composition of nanocomposites is critical, as the anatase phase of TiO_2 offers superior photocatalytic activity compared to rutile. Maintaining predominantly anatase phases enhances photocatalytic efficiency [41,48]. Moreover, nanocomposites with high surface areas demonstrate heightened photocatalytic activity, facilitated by increased availability of active sites for reactants and photogenerated charges. Control over calcination conditions, including temperature and time, directly impacts nanocomposite surface area. Ensuring well-dispersed TiO_2 nanoparticles within the kaolin matrix is essential for maximizing photocatalytic activity [41,48].

The results show that the kaolin- TiO_2 nanocomposite exhibits the best dye removal efficiency at pH 5, both in dark conditions and under sunlight irradiation. At pH 5, the removal efficiency reached 45 % in the dark and 99 % under photodegradation.

The synergistic effect of the kaolin- TiO_2 nanocomposite is more effective for the overall degradation process of acidic dyes compared to basic dyes. This is due to two main factors.

1. Adsorption Capacity: Kaolin and other clay minerals generally have a higher adsorption capacity for cationic (basic) dyes compared to anionic (acidic) dyes. However, the modification of kaolin with TiO_2 enhances the adsorption of anionic/acidic dyes on the nanocomposite surface. The negatively charged surface of the kaolin- TiO_2 nanocomposite provides better electrostatic attraction for the adsorption of acidic dye molecules [38,49,50].
2. Photocatalytic Activity: The kaolin- TiO_2 nanocomposites exhibit higher photocatalytic activity towards the degradation of acidic dyes compared to basic dyes. The photogenerated electron-hole pairs in TiO_2 can more effectively oxidize the adsorbed acidic dye molecules through the generation of reactive oxygen species. Acidic dyes are more susceptible to photodegradation by the oxidizing radicals produced on the nanocomposite surface[51–53].

The synergistic effect of the adsorption of acidic dyes on the nanocomposite, which brings them in close proximity to the photocatalytically active TiO_2 , enhances the overall degradation efficiency. The improved adsorption capacity and higher photocatalytic activity towards acidic dyes make these kaolin- TiO_2 nanocomposites a suitable choice for the treatment of acidic dye-containing wastewater[51,54–57].

3.3. Scavenger

In the photocatalytic degradation process, a series of photogenerated active species is suspected to be involved in the photocatalytic reaction. To further evaluate the roles of these active species during the photodegradation of CR dye, different scavengers were introduced to quench the relevant active species, including holes (h^+), hydroxyl radicals ($\bullet OH$), and superoxide radicals ($\bullet O_2^-$). As shown in Table 2, the photocatalytic degradation of CR over the kaolin- TiO_2 composite was affected by the addition of different scavengers. The sequence of the photocatalytic degradation efficiency of CR in descending order was:

1. Tert-butyl alcohol (TBA) - a scavenger for hydroxyl radicals ($\bullet OH$)
2. Sodium ethylenediaminetetraacetate (Na_2EDTA) - a scavenger for superoxide radicals ($\bullet O_2^-$)

This indicates that both superoxide radicals ($\bullet O_2^-$) and hydroxyl radicals ($\bullet OH$) are active species contributing to the photocatalytic activity of the composite catalyst. The sequence of the contributions of the ROS to the photocatalytic activity is: $\bullet O_2^- > \bullet OH$. The results suggest that the superoxide radicals ($\bullet O_2^-$) play a more dominant role in the photocatalytic degradation of CR dye compared to the hydroxyl radicals ($\bullet OH$) when using the kaolin- TiO_2 composite as the photocatalyst. These active species trapping experiments provide valuable insights into the relative importance of different ROS in the photocatalytic degradation mechanism. This information can guide the optimization of the photocatalytic system and the development of more efficient strategies for the removal of organic pollutants like CR dye.

Two scavengers, Tert-butanol (TBA) and disodium EDTA, were employed in the study. Under optimized conditions (pH = 5, 20 ppm, and 0.1 g dosage), there was a substantial reduction in the removal percentage, dropping from 82 % to 25 % for TBA and to 30 % for Na_2EDTA . In the realm of heterogeneous photocatalysis, the use of radical scavengers serves the purpose of unraveling degradation mechanisms and enhancing degradation efficiency [58–60].

Tert-butyl alcohol (TBA) and ethylenediaminetetraacetic acid (EDTA) have no significant roles in the degradation of dye compounds through the process of photodegradation. These compounds function as scavengers, effectively controlling the presence of radical species and exerting a significant influence on the overall efficiency of the degradation process[61–64].

Radical scavengers used in photocatalytic degradation are categorized based on their functions as radicals, electron donors, and hole scavengers [65]. Radicals bind to radicals formed during photocatalytic degradation, impeding their interaction with the target pollutant. Examples include oxalate, methanol, azide, tert-butanol, para-benzoquinone, and tris(hydroxymethyl)aminomethane [65].

Table 2
Scavengers percentage removal under optimized conditions.

	% Removal
Optimized conditions	82.9
Tert-butanol (TBA)	25.8
Na_2EDTA	30.4

Electron donors contribute electrons to the photocatalyst, potentially enhancing photocatalytic efficiency; examples include oxygen and hydroxyl groups. Hole scavengers react with holes formed during photocatalytic degradation, preventing them from reacting with target pollutants. Examples of hole scavengers are tert-butyl alcohol (TBA), isopropanol (IPA), and disodium EDTA.

Table 2 illustrates the decrease in percentage removal after the addition of Na₂EDTA and TBA, both of which halved the removal percentage. This suggests that the photodegradation mechanism involves the formation of holes and radicals. The general mechanism of photodegradation involves the photocatalyst, stimulated by a light source, enhancing the formation of electron-holes. These electron-holes then react with water to form $\bullet O_2^-$ and $\bullet OH$, which subsequently react with the pollutant, resulting in the removal of the pollutant and leaving behind less toxic byproducts [65,66].

The photocatalytic degradation of acidic dyes involves both direct and indirect mechanisms.

- Direct Degradation Mechanism

In the direct degradation mechanism, the dye molecules can undergo photolysis upon direct absorption of light energy. This leads to the excitation of the dye molecules, causing them to break down and degrade without the involvement of any intermediates or reactive species [5,67,68].

- Indirect Degradation Mechanism

The indirect degradation mechanism involves the generation of reactive oxygen species (ROS) on the surface of the photocatalyst. When the photocatalyst is irradiated with light energy, electron-hole pairs are generated. The conduction band electrons can react with dissolved oxygen to form superoxide radicals ($\bullet O_2^-$), which then undergo further reactions to produce other ROS like hydroxyl radicals ($\bullet OH$) and hydrogen peroxide (H₂O₂) [68–70].

These highly reactive ROS, particularly the hydroxyl radicals, can then non-selectively degrade the adsorbed dye molecules through oxidation reactions. The dye molecules can also undergo photosensitization, providing additional electrons to the photocatalyst and generating more radicals like ($\bullet O_2^-$ [5,68,70,71].

The indirect mechanism involving the generation and utilization of ROS is generally considered more prevalent and influential in the overall photocatalytic degradation of acidic dyes compared to the direct photolysis pathway [53,72].

3.4. Reuse of Kaolin–TiO₂: Five recycles

The SEM analysis of Kaolin–TiO₂ (refer to Fig. 1) reveals an increased aggregation tendency, whereas the XRD results (Fig. 2) indicate a reduction in the intensity of the crystalline pattern of TiO₂. Additionally, the XRF data (Table 1) demonstrate a decrease in the percentage of SiO₂ and Al₂O₃, accompanied by an increase in the percentage of TiO₂. The degradation percentage against time (Fig. 8) showcases a commendable removal percentage even after undergoing five reuse cycles. However, a notable transformation of kaolin–TiO₂ into a very fine powder poses challenges in the filtration process. Despite the efficient performance after five reuses, the fine powder texture necessitates a solution. To address this concern, a prospective approach involves applying a coating on the beads and columns during advanced work.

Kaolin plays a crucial role in enhancing the photocatalytic activity of TiO₂ in the degradation of water pollutants; Kaolin improves the dispersion of TiO₂, thereby increasing the available surface area for photocatalysis [73]. The adsorption of O₂ by kaolin enhances photocatalysis efficiency [73]. Kaolin facilitates the formation of anatase and inhibits its transformation to rutile, thereby enhancing the photocatalytic activity of TiO₂ [74]. Kaolinite induces a shift in the absorption edge of TiO₂ to lower energy levels, improving photocatalysis efficiency and the type-II energy band alignment of TiO₂. This improvement enhances the separation and transfer of photogenerated electron–hole pairs, thereby boosting the overall efficiency of photocatalysis [1,74,75].

The integration of Kaolin into the TiO₂ composite engenders a synergistic enhancement of the photocatalytic process across multiple dimensions. The addition of Kaolin contributes to an expanded active surface area, thereby facilitating both photocatalytic degradation and the adsorption of organic pollutants [76,77]. Furthermore, the refinement of TiO₂ nanoparticle crystal within the composite results in improved catalytic properties and heightened stability [78,79]. Lastly, the presence of Kaolin aids in the effective separation of the photocatalyst from the reaction mixture, streamlining the process of recovery and catalyst reuse [77].

Congo red, an azo dye aggregate in water and organic solutions due to hydrophobic interactions, the occurrence of π – π stacking helps its absorption onto the surface of the TiO₂/kaolin composite, the existence of active sites on the composite surface, resulting from specific functional groups or modifications in pore size [51,80–82].

To enhance the photocatalytic performance, improvements in charge carrier dynamics (including separation, recombination, and lifetime) within the TiO₂/kaolin system are achieved. The treatment with acid enhances the distribution and loading of TiO₂ crystal grains into nano-sized particles [70,74,83], while the concentrated presence of negatively charged hydroxyl groups on the kaolin surface contributes to the enhanced behavior of charge carriers [68,70].

Aggregation of composites can be achieved by employing low concentrations of kaolin particles, which induce electrostatic repulsion and hinder aggregation [84]. Moreover, lower concentrations of kaolin particles may facilitate better dispersion within the TiO₂ matrix [84]. Treating kaolin with acids introduces additional functional groups and alters surface properties, enhancing compatibility with TiO₂ nanoparticles [85]. Additionally, the kaolinite matrix can influence the crystal structure of TiO₂ nanoparticles, potentially enhancing catalytic performance and reducing aggregation [86].

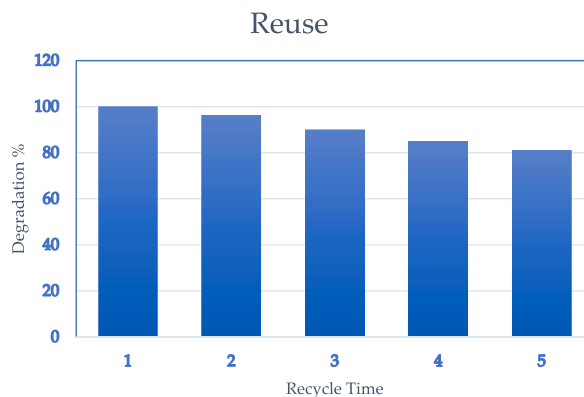


Fig. 8. Degradation % vs. five recycling times, at the optimized conditions; pH 5, with an initial dye concentration of 20 ppm, and using 0.1 g.

Higher calcination temperatures generally result in increased surface areas for both kaolin and TiO₂ components, leading to larger specific surface areas in the final nanocomposites [87]. Longer calcination durations facilitate greater conversion of kaolinite to metakaolin, which typically possesses a higher surface area compared to the original kaolinite. Moreover, extended calcination times support the growth and stabilization of TiO₂ crystals, further enhancing the overall surface area of the nanocomposites [48].

4. Conclusions

This study introduces a novel approach by utilizing Jordanian kaolin as a natural adsorption material, distinguishing it from previous research employing different types of kaolin. Through the sol-gel method, a Kaolin-TiO₂ nanocomposite with a specific weight ratio was synthesized, followed by comprehensive characterization via SEM, XRD, XRF, and BET analysis, providing detailed insights into its structural and morphological properties. The nanocomposite's efficacy in removing Congo-red dye under various conditions was investigated, showcasing its performance and versatility in water purification applications. Optimal removal conditions were determined, highlighting the practical applicability and effectiveness of the Kaolin-TiO₂ nanocomposite. Moreover, the emphasis on utilizing solar energy during the purification process underscores its sustainability and cost-effectiveness, particularly in regions with limited freshwater resources like Jordan. This study's unique combination of utilizing Jordanian kaolin, detailed synthesis and characterization processes, optimization of removal conditions, and emphasis on solar energy utilization contributes significantly to advancements in water purification technologies.

The application of kaolin-TiO₂ composites in photodegradation for water treatment has garnered considerable attention due to their amplified photocatalytic activity. The collaborative interaction between kaolin and TiO₂ nanoparticles enhances photocatalysis efficiency, proving instrumental in the efficient degradation of diverse water pollutants under sunlight or UV light. Kaolin's multifaceted impact includes improving TiO₂ dispersion, expanding photocatalytic surface area, promoting O₂ adsorption, inhibiting anatase transformation into rutile, and refining photocatalysis efficiency by inducing a shift in TiO₂'s absorption edge towards lower energy levels.

In Jordan, a nation with limited water reserves and economic challenges, exploring cost-effective purification solutions using regionally available materials assumes heightened significance. The demonstrated efficiency and reusability of kaolin with titanium oxide present a promising avenue for water treatment. The study's societal impact lies in the material's capacity to effectively eliminate impurities, catering to the urgent need for clean drinking water, while the emphasis on utilizing solar power brings about economic advantages by decreasing operational costs and fostering sustainability.

The study's focus on tackling global environmental pollution through inventive measures aligns with endeavors to conserve the environment. By efficiently eliminating impurities, the nanocomposite aids in purifying water sources, positively impacting public health outcomes. Additionally, the endorsement of sustainable water treatment techniques demonstrates dedication to societal obligations and the preservation of natural resources for future generations.

Ethical approval

This manuscript reports studies which do not involve human participants, human data or human tissue and animals.

Data availability statement

All data utilized in this article are included within the manuscript.

CRediT authorship contribution statement

Waed Alahmad: Writing – review & editing, Writing – original draft, Methodology, Conceptualization. **Fekhra Hedhili:** Writing –

review & editing, Writing – original draft, Supervision, Resources, Project administration, Investigation, Funding acquisition, Conceptualization. **S.M. Al-Shomar**: Software, Formal analysis. **Hissah Saedoon Albaqawi**: Software, Formal analysis. **Nwuyeri A. Al-Shammari**: Software, Formal analysis. **Selma Abdelrahman**: Software, Formal analysis.

Declaration of competing interest

The authors declare no conflicts of interest.

This research has been funded by Scientific Research Deanship at University of Hail-Saudi Arabia through project number RG-23 199.

Acknowledgment

This research has been funded by the Scientific Research Deanship at the University of Hail-Saudi Arabia through project number RG-23 199. The authors thank University of Hail - Saudi Arabia for financial support of this project.

References

- [1] D. Ewis, M.M. Ba-Abbad, A. Benamor, M.H. El-Naas, Adsorption of organic water pollutants by clays and clay minerals composites: a comprehensive review, *Appl. Clay Sci.* 229 (2022) 106686, <https://doi.org/10.1016/j.clay.2022.106686>.
- [2] A. Mishra, A. Mehta, S. Basu, Clay supported TiO₂ nanoparticles for photocatalytic degradation of environmental pollutants: a review, *J. Environ. Chem. Eng.* 6 (2018) 6088–6107, <https://doi.org/10.1016/j.jece.2018.09.029>.
- [3] G. Ren, H. Han, Y. Wang, S. Liu, J. Zhao, X. Meng, Z. Li, Recent advances of photocatalytic application in water treatment: a review, *Nanomaterials* 11 (2021), <https://doi.org/10.3390/nano11071804>.
- [4] M.A. Al-Nuaim, A.A. Alwasiti, Z.Y. Shnain, The photocatalytic process in the treatment of polluted water, *Chem. Pap.* 77 (2023) 677–701, <https://doi.org/10.1007/s11696-022-02468-7>.
- [5] A. Haleem, A. Shafiq, S.Q. Chen, M. Nazar, A comprehensive review on adsorption, photocatalytic and chemical degradation of dyes and nitro-compounds over different kinds of porous and composite materials, *Molecules* 28 (2023), <https://doi.org/10.3390/molecules28031081>.
- [6] D.A.H. Hanaor, C.C. Sorrell, Sand supported mixed-phase tio₂ photocatalysts for water decontamination applications, *Adv. Eng. Mater.* 16 (2014) 248–254, <https://doi.org/10.1002/adem.201300259>.
- [7] H. Yang, B. Yang, W. Chen, J. Yang, Preparation and photocatalytic activities of TiO₂-based composite catalysts, *Catalysts* 12 (2022), <https://doi.org/10.3390/catal12101263>.
- [8] E.D.H. Kong, J.H.F. Chau, C.W. Lai, C.S. Khe, G. Sharma, A. Kumar, S. Siengchin, M.R. Sanjay, GO/TiO₂-Related nanocomposites as photocatalysts for pollutant removal in wastewater treatment, *Nanomaterials* 12 (2022), <https://doi.org/10.3390/nano12193536>.
- [9] J. Feng, X. Ran, L. Wang, B. Xiao, L. Lei, J. Zhu, Z. Liu, X. Xi, G. Feng, Z. Dai, R. Li, The synergistic effect of adsorption-photocatalysis for removal of organic pollutants on mesoporous Cu₂V₂O₇/Cu₃V₂O₈/g-C₃N₄ heterojunction, *Int. J. Mol. Sci.* 23 (2022), <https://doi.org/10.3390/ijms232214264>.
- [10] C. Li, L. Sun, J. Niu, A.A. Reka, P. Feng, H. Garcia, Core-shell Bi-containing spheres and TiO₂ nanoparticles co-loaded on kaolinite as an efficient photocatalyst for methyl orange degradation, *Catal. Commun.* 175 (2023), <https://doi.org/10.1016/j.catcom.2023.106609>.
- [11] M. Chen, T. Yang, J. Han, Y. Zhang, L. Zhao, J. Zhao, R. Li, Y. Huang, Z. Gu, J. Wu, The application of mineral kaolinite for environment decontamination: a review, *Catalysts* 13 (2023), <https://doi.org/10.3390/catal13010123>.
- [12] H.N. Khoury, Review of clays and clay minerals in Jordan, *Arabian J. Geosci.* 12 (2019), <https://doi.org/10.1007/s12517-019-4882-2>.
- [13] M. Gougazeh, J.C. Buhl, Synthesis and characterization of zeolite A by hydrothermal transformation of natural Jordanian kaolin, *Journal of the Association of Arab Universities for Basic and Applied Sciences* 15 (2014) 35–42, <https://doi.org/10.1016/j.jaubas.2013.03.007>.
- [14] A.M. Awwad, M.W. Amer, M.M. Al-aqarbeh, TiO₂-kaolinite nanocomposite prepared from the Jordanian Kaolin clay: adsorption and thermodynamics of Pb(II) and Cd(II) ions in aqueous solution, *Chem. Int.* 6 (2020) 168–178, <https://doi.org/10.5281/zenodo.3597558>.
- [15] S. Mohammadhosseini, T.J. Al-Musawi, R.M. Romero Parra, M. Qutob, M.A. Gatea, F. Ganji, D. Balarak, UV and visible light induced photodegradation of reactive red 198 dye and textile factory wastewater on Fe₂O₃/bentonite/TiO₂ nanocomposite, *Minerals* 12 (2022) 1417, <https://doi.org/10.3390/min12111417>.
- [16] J.H. Ibbini, M.I. Al-Qinna, K.Y. Mashal, J. Abuidhail, K.H. Alzoubi, M.M. Masadeh, Are clay minerals in Jordanian soils antibacterial? *Jordan Journal of Earth and Environmental Sciences* 9 (2018).
- [17] X. Li, K. Peng, H. Chen, Z. Wang, TiO₂ nanoparticles assembled on kaolinites with different morphologies for efficient photocatalytic performance, *Sci. Rep.* 8 (2018), <https://doi.org/10.1038/s41598-018-29563-8>.
- [18] L.V. Barbosa, L. Marçal, E.J. Nassar, P.S. Calefi, M.A. Vicente, R. Trujillano, V. Rives, A. Gil, S.A. Korili, K.J. Ciuffi, E.H. De Faria, Kaolinite-titanium oxide nanocomposites prepared via sol-gel as heterogeneous photocatalysts for dyes degradation, *Catal. Today* 246 (2015) 133–142, <https://doi.org/10.1016/j.cattod.2014.09.019>.
- [19] B. Hakimi, M. Ghorbanpour, A. Feizi, ZnO/bentonite nanocomposites prepared with solid-state ion exchange as photocatalysts, *J. Ultrafine Grained Nanostruct. Mater.* 51 (2018) 139–146, <https://doi.org/10.22059/JUFGNSM.2018.02.05>.
- [20] B.L. Zhu, C.L. Qi, Y.H. Zhang, T. Bisson, Z. Xu, Y.J. Fan, Z.X. Sun, Synthesis, characterization and acid-base properties of kaolinite and metal (Fe, Mn, Co) doped kaolinite, *Appl. Clay Sci.* 179 (2019) 105138, <https://doi.org/10.1016/j.clay.2019.105138>.
- [21] L. Clarizia, G. Vitiello, R. Bericac Vadell, J. Sá, R. Marotta, I. Di Somma, R. Andreozzi, G. Luciani, Effect of synthesis method on reaction mechanism for hydrogen evolution over Cu_xO_y/TiO₂ photocatalysts: a kinetic analysis, *Int. J. Mol. Sci.* 24 (2023), <https://doi.org/10.3390/ijms24032004>.
- [22] A.Y. Raya-Tapia, F. Ung-Medina, G.C. Mondragón-Rodríguez, E.M. Rivera-Muñoz, J. Apolinar-Cortés, F.J. Méndez, R. Huirache-Acuña, Photocatalytic evaluation of TiO_x films produced by cathodic arc-PVD with silver addition by UVC photo-reduction method, *INORGA* 10 (2022), <https://doi.org/10.3390/inorganics10100148>.
- [23] C. Ferreira, N. Villota, J.I. Lombrana, M.J. Rivero, V. Zúñiga, J.M. Rituerto, Analysis of a hybrid suspended-supported photocatalytic reactor for the treatment of wastewater containing benzothiazole and aniline, *Water (Switzerland)* 11 (2019), <https://doi.org/10.3390/w11020337>.
- [24] J.L.A. Do Nascimento, L. Chantelle, I.M.G. Dos Santos, A.L.M. de Oliveira, M.C.F. Alves, The influence of synthesis methods and experimental conditions on the photocatalytic properties of SnO₂: a review, *Catalysts* 12 (2022), <https://doi.org/10.3390/catal12040428>.
- [25] J. Mullis, R.F. Mählmann, M. Wolf, Fluid inclusion microthermometry to calibrate vitrinite reflectance (between 50 and 270 °C), illite Kübler-Index data and the diagenesis/anchizone boundary in the external part of the Central Alps, *Appl. Clay Sci.* 143 (2017) 307–319, <https://doi.org/10.1016/j.clay.2017.03.023>.
- [26] K. Dědková, K. Matejová, J. Lang, P. Peikertová, K.M. Kutlaková, L. Neuwirthová, K. Frydryšek, J. Kukutschová, Antibacterial activity of kaolinite/nanoTiO₂ composites in relation to irradiation time, *J. Photochem. Photobiol., B* 135 (2014) 17–22, <https://doi.org/10.1016/j.jphotobiol.2014.04.004>.
- [27] F.I. El-Dossoki, T.M. Atwee, A.M. Hamada, A.A. El-Bindary, Photocatalytic degradation of remazol red b and rhodamine b dyes using tio₂ nanomaterial: estimation of the effective operating parameters, *Desalination Water Treat.* 233 (2021) 319–330, <https://doi.org/10.5004/dwt.2021.27519>.

- [28] U. Kasimayan, A. Nadarajan, C.M. Singaravelu, G.T. Pan, J. Kandasamy, T.C.K. Yang, J.H. Lin, In-situ DRIFT investigation of photocatalytic reduction and oxidation properties of SiO₂@ α -Fe₂O₃ core-shell decorated RGO nanocomposite, *Sci. Rep.* 10 (2020) 1–14, <https://doi.org/10.1038/s41598-020-59037-9>.
- [29] M.R. Abukhadra, A. Helmy, M.F. Sharaf, M.A. El-Meligy, A.T. Ahmed Soliman, Instantaneous oxidation of levofloxacin as toxic pharmaceutical residuals in water using clay nanotubes decorated by ZnO (ZnO/KNTs) as a novel photocatalyst under visible light source, *J. Environ. Manag.* 271 (2020) 111019, <https://doi.org/10.1016/j.jenvman.2020.111019>.
- [30] M. Reli, K. Kočí, V. Matějka, P. Kovář, L. Obalová, Effect of calcination temperature and calcination time on the kaolinite/tio₂ composite for photocatalytic reduction of CO₂, *GeoScience Engineering* 58 (2014) 10–22, <https://doi.org/10.2478/v10205-011-0022-2>.
- [31] D. Kibanova, J. Cervini-Silva, H. Destaillets, Efficiency of clay - TiO₂ nanocomposites on the photocatalytic elimination of a model hydrophobic air pollutant, *Environ. Sci. Technol.* 43 (2009) 1500–1506, <https://doi.org/10.1021/es803032t>.
- [32] H.A. Kiwaan, T.M. Atwee, E.A. Azab, A.A. El-Bindary, Photocatalytic degradation of organic dyes in the presence of nanostructured titanium dioxide, *J. Mol. Struct.* 1200 (2020), <https://doi.org/10.1016/j.molstruc.2019.127115>.
- [33] T.M. Al-Momani, H.N. Khoury, Processing and treatment of Hiswa clay deposits, South Jordan using hydrocyclone separation and high intensity wet magnetic separation, *Dirasat, Pure Sciences* 37 (2010) 36–47.
- [34] D. Alvarez-Bustos, F. Sanchez-Minero, V. Santes, I.C. Romero-Ibarra, J.A. de los Reyes Heredia, R. Rios-Escobedo, F. Tzompantzi-Morales, C.E. Santolalla-Vargas, Synthesis and evaluation of FeS_x/TiO₂ for the photocatalytic degradation of phenol under visible-light region, *Catalysts* 12 (2022), <https://doi.org/10.3390/catal12050457>.
- [35] V. Wongso, C.J. Chen, A. Razzaq, N.A. Kamal, N.S. Sambudi, Hybrid kaolin/TiO₂ composite: effect of urea addition towards an efficient photocatalyst for dye abatement under visible light irradiation, *Appl. Clay Sci.* 180 (2019) 105158, <https://doi.org/10.1016/j.clay.2019.105158>.
- [36] S.O. Azeez, I.O. Saheed, F.A. Adekola, S.S. Salau, PREPARATION OF TiO₂-ACTIVATED KAOLINITE COMPOSITE FOR PHOTOCATALYTIC DEGRADATION OF RHODAMINE B DYE, *Bull. Chem. Soc. Ethiop.* 36 (2022) 13–24, <https://doi.org/10.4314/bcse.v36i1.2>.
- [37] J. Henych, V. Štengl, Feasible synthesis of TiO₂ deposited on kaolin for photocatalytic applications, *Clay Clay Miner.* 61 (2013) 165–176, <https://doi.org/10.1346/CCMN.2013.0610301>.
- [38] S.O. Azeez, I.O. Saheed, F.A. Adekola, S.S. Salau, PREPARATION OF TiO₂-ACTIVATED KAOLINITE COMPOSITE FOR PHOTOCATALYTIC DEGRADATION OF RHODAMINE B DYE, *Bull. Chem. Soc. Ethiop.* 36 (2022) 13–24, <https://doi.org/10.4314/bcse.v36i1.2>.
- [39] S. Mustapha, J.O. Tijani, M.M. Ndamitso, S.A. Abdulkareem, D.T. Shuaib, A.K. Mohammed, A. Sumaila, The role of kaolin and kaolin/ZnO nanoadsorbents in adsorption studies for tannery wastewater treatment, *Sci. Rep.* 10 (2020), <https://doi.org/10.1038/s41598-020-69808-z>.
- [40] S. Yahaya, S. Salwah Jikan, N. Azam Badarulzaman, A. Dahiru Adamu, C. Author, Chemical composition and particle size analysis of kaolin, *Traektoriā Nauki = Path of Science* 3 (2017), <https://doi.org/10.22178/pos.27-1>, 2017.
- [41] P. Mariselvi, P. Parvathiraj, T. Anantha Kumar, S. Photocatalysis, A. Kumar, Photocatalytic Activity of Metal Oxide/kaolinite Nanocomposites under UV Light Irradiation, 2023.
- [42] N. Siddique, M.I. Din, R. Khalid, Z. Hussain, A comprehensive review on the photocatalysis of Congo red dye for wastewater treatment, *Rev. Chem. Eng.* 0 (2023), <https://doi.org/10.1515/revce-2022-0076>.
- [43] J. Fito, M. Abewaa, A. Mengistu, K. Angassa, A.D. Ambaye, W. Moyo, T. Nkambule, Adsorption of methylene blue from textile industrial wastewater using activated carbon developed from Rumex abyssinicus plant, *Sci. Rep.* 13 (2023), <https://doi.org/10.1038/s41598-023-32341-w>.
- [44] Y. Sheng, Z. Wei, H. Miao, W. Yao, H. Li, Y. Zhu, Enhanced organic pollutant photodegradation via adsorption/photocatalysis synergy using a 3D g-C₃N₄/TiO₂ free-separation photocatalyst, *Chem. Eng. J.* 370 (2019) 287–294, <https://doi.org/10.1016/j.cej.2019.03.197>.
- [45] H. Huo, X. Hu, H. Wang, J. Li, G. Xie, X. Tan, Q. Jin, D. Zhou, C. Li, G. Qiu, Y. Liu, Synergy of photocatalysis and adsorption for simultaneous removal of hexavalent chromium and methylene blue by g-C₃N₄/BiFeO₃/carbon nanotubes ternary composites, *Int. J. Environ. Res. Publ. Health* 16 (2019), <https://doi.org/10.3390/ijerph16173219>.
- [46] S.M. Lin, Y.L. Yu, Z.J. Zhang, C.Y. Zhang, M.F. Zhong, L.M. Wang, S.X. Lu, W. Xu, N. Li, X. Huang, The synergistic mechanisms of citric acid and oxalic acid on the rapid dissolution of kaolinite, *Appl. Clay Sci.* 196 (2020), <https://doi.org/10.1016/j.clay.2020.105756>.
- [47] W. Liu, T. He, Y. Wang, G. Ning, Z. Xu, X. Chen, X. Hu, Y. Wu, Y. Zhao, Synergistic adsorption-photocatalytic degradation effect and norfloxacin mechanism of ZnO/ZnS@BC under UV-light irradiation, *Sci. Rep.* 10 (2020) 1–12, <https://doi.org/10.1038/s41598-020-68517-x>.
- [48] Z. Khaled, A. Mohsen, A.M. Soltan, M. Kohail, Optimization of kaolin into Metakaolin: calcination Conditions, mix design and curing temperature to develop alkali activated binder, *Ain Shams Eng. J.* 14 (2023), <https://doi.org/10.1016/j.asej.2023.102142>.
- [49] K. Dziejwińska, J. Matusik, A. Trenczek-Zajac, G. Cempura, TiO₂-loaded nanotubular kaolin group minerals: the effect of mineral support on photodegradation of dyes as model pollutants, *Appl. Clay Sci.* 245 (2023), <https://doi.org/10.1016/j.clay.2023.107123>.
- [50] Y. Hai, X. Li, H. Wu, S. Zhao, W. Deligeer, S. Asuha, Modification of acid-activated kaolinite with TiO₂ and its use for the removal of azo dyes, *Appl. Clay Sci.* 114 (2015) 558–567, <https://doi.org/10.1016/j.clay.2015.07.010>.
- [51] N.P. Lata, MdS. Hussain, Md Abdulla-Al-Mamun, T.U. Rashid, S.Md Shamsuddin, Fabrication and synergistically enhanced photocatalytic activity of ternary kaolinite, TiO₂, and Al₂O₃ (K65T30A5) nanocomposite for visible-light-induced degradation of methylene blue and remazol red dye, *Heliyon* 10 (2024) e29255, <https://doi.org/10.1016/j.heliyon.2024.e29255>.
- [52] W. Hajjaji, S. Andrejkovićová, R.C. Pullar, D.M. Tobaldi, A. Lopez-Galindo, F. Jammousi, F. Rocha, J.A. Labrincha, Effective removal of anionic and cationic dyes by kaolinite and TiO₂/kaolinite composites, *Clay Miner.* 51 (2016) 19–27, <https://doi.org/10.1180/claymin.2016.051.1.02>.
- [53] I. Groeneveld, M. Kanelli, F. Ariese, M.R. van Bommel, Parameters that affect the photodegradation of dyes and pigments in solution and on substrate – an overview, *Dyes Pigments* 210 (2023), <https://doi.org/10.1016/j.dyepig.2022.110999>.
- [54] W. Liu, T. He, Y. Wang, G. Ning, Z. Xu, X. Chen, X. Hu, Y. Wu, Y. Zhao, Synergistic adsorption-photocatalytic degradation effect and norfloxacin mechanism of ZnO/ZnS@BC under UV-light irradiation, *Sci. Rep.* 10 (2020), <https://doi.org/10.1038/s41598-020-68517-x>.
- [55] J. Feng, X. Ran, L. Wang, B. Xiao, L. Lei, J. Zhu, Z. Liu, X. Xi, G. Feng, Z. Dai, R. Li, The synergistic effect of adsorption-photocatalysis for removal of organic pollutants on mesoporous Cu₂V₂O₇/Cu₃V₂O₈/g-C₃N₄ heterojunction, *Int. J. Mol. Sci.* 23 (2022), <https://doi.org/10.3390/ijms232214264>.
- [56] J. Chen, Y. Xiong, M. Duan, X. Li, J. Li, S. Fang, S. Qin, R. Zhang, Insight into the synergistic effect of adsorption-photocatalysis for the removal of organic dye pollutants by Cr-doped ZnO, *Langmuir* 36 (2020) 520–533, <https://doi.org/10.1021/acs.langmuir.9b02879>.
- [57] Y. Yu, K. Wu, W. Xu, D. Chen, J. Fang, X. Zhu, J. Fang, X. Sun, Y. Liang, X. Hu, R. Li, Z. Fang, Adsorption-photocatalysis synergistic removal of contaminants under antibiotic and Cr(VI) coexistence environment using non-metal g-C₃N₄ based nanomaterial obtained by supramolecular self-assembly method, *J. Hazard Mater.* 404 (2021), <https://doi.org/10.1016/j.jhazmat.2020.124171>.
- [58] J. Schneider, D.W. Bahnemann, Undesired role of sacrificial reagents in photocatalysis, *J. Phys. Chem. Lett.* 4 (2013) 3479–3483, <https://doi.org/10.1021/jz4018199>.
- [59] G. Ren, H. Han, Y. Wang, S. Liu, J. Zhao, X. Meng, Z. Li, Recent advances of photocatalytic application in water treatment: a review, *Nanomaterials* 11 (2021), <https://doi.org/10.3390/nano11071804>.
- [60] M. Pavel, C. Anastasescu, R.N. State, A. Vasile, F. Papa, I. Balint, Photocatalytic degradation of organic and inorganic pollutants to harmless end products: assessment of practical application potential for water and air cleaning, *Catalysts* 13 (2023), <https://doi.org/10.3390/catal13020380>.
- [61] H. Gu, H. Zhang, X. Zhang, Y. Guo, L. Yang, H. Wu, N. Mao, Photocatalytic properties of core-shell structured wool-tio₂ hybrid composite powders, *Catalysts* 11 (2021) 1–23, <https://doi.org/10.3390/catal11010012>.
- [62] X. Li, D. Wu, Q. Luo, J. An, R. Yin, D. Wang, Advanced cyclized polyacrylonitrile (CPAN)/CdS nanocomposites for highly efficient visible-light photocatalysis, *J. Mater. Sci.* 52 (2017) 736–748, <https://doi.org/10.1007/s10853-016-0367-9>.
- [63] D. Zhang, F. Dai, P. Zhang, Z. An, Y. Zhao, L. Chen, The photodegradation of methylene blue in water with PVDF/GO/ZnO composite membrane, *Mater. Sci. Eng. C* 96 (2019) 684–692, <https://doi.org/10.1016/j.msec.2018.11.049>.
- [64] L. Duan, B. Wang, K. Heck, S. Guo, C.A. Clark, J. Arredondo, M. Wang, T.P. Senfille, P. Westerhoff, X. Wen, Y. Song, M.S. Wong, Efficient photocatalytic PFOA degradation over boron nitride, *Environ. Sci. Technol. Lett.* 7 (2020) 613–619, <https://doi.org/10.1021/acs.estlett.0c00434>.

- [65] J.T. Schneider, D.S. Firak, R.R. Ribeiro, P. Peralta-Zamora, Use of scavenger agents in heterogeneous photocatalysis: truths, half-truths, and misinterpretations, *Phys. Chem. Chem. Phys.* 22 (2020) 15723–15733, <https://doi.org/10.1039/d0cp02411b>.
- [66] A. Raza, R. Rehman, M. Batool, Recent review of titania-clay-based composites emerging as advanced adsorbents and photocatalysts for degradation of dyes over the last decade, *Adsorpt. Sci. Technol.* 2022 (2022), <https://doi.org/10.1155/2022/3823008>.
- [67] A. Ajmal, I. Majeed, R.N. Malik, H. Idriss, M.A. Nadeem, Principles and mechanisms of photocatalytic dye degradation on TiO₂ based photocatalysts: a comparative overview, *RSC Adv.* 4 (2014) 37003–37026, <https://doi.org/10.1039/c4ra06658h>.
- [68] A. Haleem, M. Ullah, S. ur Rehman, A. Shah, M. Farooq, T. Saeed, I. Ullah, H. Li, In-depth photocatalytic degradation mechanism of the extensively used dyes malachite green, methylene blue, Congo red, and rhodamine B via covalent organic framework-based photocatalysts, *Water (Switzerland)* 16 (2024), <https://doi.org/10.3390/w16111588>.
- [69] S. Modi, V.K. Yadav, D. Ali, N. Choudhary, S. Alarifi, D.K. Sahoo, A. Patel, M.H. Fulekar, Photocatalytic degradation of methylene blue from aqueous solutions by using nano-ZnO/kaolin-clay-based nanocomposite, *Water (Switzerland)* 15 (2023), <https://doi.org/10.3390/w15223915>.
- [70] M.F. Lanjwani, M. Tuzen, M.Y. Khuhawar, T.A. Saleh, Trends in photocatalytic degradation of organic dye pollutants using nanoparticles: a review, *Inorg. Chem. Commun.* 159 (2024), <https://doi.org/10.1016/j.inoche.2023.111613>.
- [71] T. Gul, I. Khan, B. Ahmad, S. Ahmad, A.A. Alsaiani, M. Almeahmadi, O. Abdulaziz, A. Alsharif, I. Khan, K. Saeed, Efficient photodegradation of methyl red dye by kaolin clay supported zinc oxide nanoparticles with their antibacterial and antioxidant activities, *Heliyon* 9 (2023) e36978, <https://doi.org/10.1016/j.heliyon.2023.e16738>.
- [72] N. Padmavathy, B.N. Murthy, K.H. Hemakumar, Direct sunlight driven photocatalytic degradation of hazardous organic dyes using TiO₂-NiO nanocomposite p-n junction, in: *J Phys Conf Ser*, IOP Publishing Ltd, 2021, <https://doi.org/10.1088/1742-6596/2070/1/012044>.
- [73] A. Wu, D. Wang, C. Wei, X. Zhang, Z. Liu, P. Feng, X. Ou, Y. Qiang, H. Garcia, J. Niu, A comparative photocatalytic study of TiO₂ loaded on three natural clays with different morphologies, *Appl. Clay Sci.* 183 (2019) 1–12, <https://doi.org/10.1016/j.clay.2019.105352>.
- [74] Y. Xie, J. Wang, F. Ren, H. Shuai, G. Du, Nonmetallic mineral as the carrier of TiO₂ photocatalyst: a review, *Frontiers in Catalysis* 2 (2022), <https://doi.org/10.3389/fgc.2022.806316>.
- [75] P. Pourhakkak, A. Taghizadeh, M. Taghizadeh, M. Ghaedi, S. Haghdoust, Fundamentals of adsorption technology, *Interface Science and Technology* 33 (2021) 1–70, <https://doi.org/10.1016/B978-0-12-818805-7.00001-1>.
- [76] Y. Zhang, H. Gan, G. Zhang, A novel mixed-phase TiO₂/kaolinite composites and their photocatalytic activity for degradation of organic contaminants, *Chem. Eng. J.* 172 (2011) 936–943, <https://doi.org/10.1016/j.cej.2011.07.005>.
- [77] L. Morjène, F. Aloulou, M. Tasbihi, M. Schwarze, R. Schomäcker, M. Seffen, New composite material based on Kaolinite, cement, TiO₂ for efficient removal of phenol by photocatalysis, *Environ. Sci. Pollut. Control Ser.* 28 (2021) 35991–36003, <https://doi.org/10.1007/s11356-021-13150-y>.
- [78] X. Li, K. Peng, H. Chen, Z. Wang, TiO₂ nanoparticles assembled on kaolinites with different morphologies for efficient photocatalytic performance, *Sci. Rep.* 8 (2018), <https://doi.org/10.1038/s41598-018-29563-8>.
- [79] K. Kočí, V. Matějka, P. Kovář, Z. Lacný, L. Obalová, Comparison of the pure TiO₂ and kaolinite/TiO₂ composite as catalyst for CO₂ photocatalytic reduction, *Catal. Today* 161 (2011) 105–109, <https://doi.org/10.1016/j.cattod.2010.08.026>.
- [80] J.A. Mbey, F. Thomas, A. Razafitianamaharavo, C. Caillet, F. Villières, A comparative study of some kaolinites surface properties, *Appl. Clay Sci.* 172 (2019) 135–145, <https://doi.org/10.1016/j.clay.2019.03.005>.
- [81] M.K. David, U.C. Okoro, K.G. Akpomie, C. Okey, H.O. Oluwasola, Thermal and hydrothermal alkaline modification of kaolin for the adsorptive removal of lead (II) ions from aqueous solution, *SN Appl. Sci.* 2 (2020), <https://doi.org/10.1007/s42452-020-2621-7>.
- [82] Y. Daniel Reta, T.D. Desissa, Composites of CoFe₂O₄/Graphene oxide/Kaolinite for adsorption of lead ion from aqueous solution, *Front Mater* 10 (2023), <https://doi.org/10.3389/fmats.2023.1277467>.
- [83] F. Sieland, J. Schneider, D.W. Bahnemann, Photocatalytic activity and charge carrier dynamics of TiO₂ powders with a binary particle size distribution, *Phys. Chem. Chem. Phys.* 20 (2018) 8119–8132, <https://doi.org/10.1039/c8cp00398j>.
- [84] V. Gupta, M.A. Hampton, J.R. Stokes, A.V. Nguyen, J.D. Miller, Particle interactions in kaolinite suspensions and corresponding aggregate structures, *J. Colloid Interface Sci.* 359 (2011) 95–103, <https://doi.org/10.1016/j.jcis.2011.03.043>.
- [85] M. Raji, A.E.K. Qaiss, R. Bouhfid, Effects of bleaching and functionalization of kaolinite on the mechanical and thermal properties of polyamide 6 nanocomposites, *RSC Adv.* 10 (2020) 4916–4926, <https://doi.org/10.1039/c9ra10579d>.
- [86] Y. Hai, X. Li, H. Wu, S. Zhao, W. Deligeer, S. Asuha, Modification of acid-activated kaolinite with TiO₂ and its use for the removal of azo dyes, *Appl. Clay Sci.* 114 (2015) 558–567, <https://doi.org/10.1016/j.clay.2015.07.010>.
- [87] K. Kočí, V. Matějka, P. Kovář, Z. Lacný, L. Obalová, Comparison of the pure TiO₂ and kaolinite/TiO₂ composite as catalyst for CO₂ photocatalytic reduction, *Catal. Today* 161 (2011) 105–109, <https://doi.org/10.1016/j.cattod.2010.08.026>.