Geochemical and Physicochemical Characteristics of Clay Materials from Congo with Photocatalytic Activity on 4-Nitrophenol in Aqueous Solutions

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ABSTRACT: This study investigated the geochemical and physicochemical characteristics of natural clay collected in the Democratic Republic of Congo. The optical properties of the sample collected in Golf (GOL) were tested in the removal of 4-nitrophenol in aqueous solution. The geochemical analysis depicted that all the samples are plotted within the shale quadrant. Furthermore, the Chemical Index of Alteration (CIA) indicated that the samples are extremely weathered. The particle size distribution ranged from 0.41 to 418.6 μm, while the pore diameters for all the samples were under 100 Å. A flake-like surface morphology was observed in all the samples. SiO₂, Al₂O₃, Fe₂O₃, K₂O, and TiO₂ were the major chemical compounds found in all the samples, while the XRD analysis showed the presence of quartz, kaolinite, magnetite, and illite. The presence of metal oxides (i.e., TiO₂ and Fe₂O₃) indicated that these natural clays can be used for photocatalytic oxidation of pollutants. The sample collected in Katuba (KAT) displayed the higher reflectance percentages for the selected wavelengths except at 200 nm. Interestingly, the GOL sample exhibited lower energy band gaps (2.68 and 3.94 eV) necessary for photocatalysis. The untreated GOL clay sample removed 99.13% of 4-nitrophenol from aqueous solution through the photodegradation process. The usage of the untreated GOL clay could be a cost-effective solution in the removal of 4-nitrophenol in wastewater.

1. INTRODUCTION

Nowadays, it is established that the knowledge on the physicochemical properties of materials is of importance, and it enables the use of materials for various applications. Information on the properties of natural clay from various geographic locations would result in their extensive usage, which could have a positive impact on the environment.

Several researchers have studied clay samples from different locations and have provided their usages, including the construction and ceramic industry,†−4 cosmetic,5−7 and removal of pollutants such as pharmaceuticals8,9 from wastewater. Globally, hazardous chemicals including nitrophenol are released into sewages, rivers, seas, and the environment. Also, the presence of those pollutants has a detrimental effect on human beings and animals. Abdollahi and Mohammadi9 reported that 4-nitrophenol can be found in effluents in the manufacturing of some pharmaceuticals. They further said that 4-nitrophenol can also be found in dyes, fungicides, and chemical used to darken leather. This shows that 4-nitrophenol is present in various wastewaters, and therefore, enters into the environment. The presence of 4-nitrophenol in contaminated water can expose the population to inhale and ingest the 4-nitrophenol contaminated water or dry soil (surface). For example, the personnel where the pesticide parathion is used can be exposed to 4-nitrophenol.10

Natural clays can also be combined with other materials for enhanced application in water treatment. Modified clay materials and clay composites have been utilized for the removal of 4-nitrophenol in effluents.11−16 Ozola et al.11 utilized modified organoclays and enhanced the removal efficiency of p-nitrophenol in solutions. El Ouardi et al.12 removed 99.5% of p-nitrophenol in the aqueous solution using montmorillonite clay.12 Moreover, Dos Santos et al.13 also used organoclay modified from montmorillonite clay to remove p-nitrophenol in aqueous solution. In their studies, the removal of p-nitrophenol between 79.12 and 75.67% at 25 °C was obtained. Each of the reported modified natural clays was collected from different geographical locations and presented varying physicochemical properties.11−16

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Furthermore, the removal of nitrophenol has been attempted by various researchers through adsorption and photodegradation using different materials, including aluminum metal–organic and reduced graphene composites (MIL–68(Al)/RG), a nanocomposite hydrous ferric oxide/aminated hyper-cross-linked polymeric adsorbent composite (HFO-802), nitric acid-activated fly ash (AFA), gold nanoparticles supported on a functionalized mesoporous carbon composite, biochars (rice straws), TiO$_2$/natural hematite-supported bentonite (TiNHB), a hybrid photocatalysis/membrane, cobalt and copper phthalocyanine, TiO$_2$, a metal-free and copper(II) porphyrins (CuPp/TiO$_2$) composite, Fe-doped TiO$_2$/SiO$_2$ nanofibrous membrane with molecular imprinted modification, zinc acetyl acetonate/zeolite (ZnO/HZSM-5) nanocomposites, copper-anchored carbon nanotubes, advanced oxidation by a UV/H$_2$O$_2$ process. It is, therefore, important to investigate the removal of toxic elements using natural clays that are readily available in rural and impoverished communities where the quality of water they consume is severely compromised.

Natural clays have been used for adsorption and photocatalytic activity removal of pollutants, such as ammonium, cadmium and 2-chlorophenol, and cationic and anionic dyes.

The characteristics of natural clay from unreported locations, such as Golf (GOL), Katuba (KAT), and Kolwezi (KOL), in the Democratic Republic of Congo warrant the need to investigate and provide scientific data based on that geographical space. Communities surrounding these mining cities consume potentially contaminated water. The usage of natural clay in the removal of pollutants in aqueous solutions will provide a cost-effective removal technique because natural clay samples can be obtained at a very low cost and in some instances free of charge.

Therefore, this study aimed to provide scientific characteristics data on the quality of clays from the Democratic Republic of Congo (DRC). This is important especially because physicochemical properties of the natural clays from the selected locations are inexistent in the open literature. In this study, the selected clay samples coded GOL, KAT, and KOL were fully characterized. In addition, the ability of untreated natural clay materials to remove 4-nitrophenol in aqueous solutions was studied through the photocatalytic process. The study also provides a starting point for more investigations on the various utilizations, i.e., wastewater treatment of the clay’s materials from the selected areas in the DRC.

2. MATERIALS AND METHODS

2.1. Materials. This study was carried out using three clay samples collected from three different locations in the Democratic Republic of the Congo (DRC), namely, Golf and Katuba (in the Haut Lomami province) and Kolwezi in the Lualaba province. The latitudes of the three locations are $-11.642190$, $-11.699710$, and $-10.711270$, respectively, for Golf, Katuba, and Kolwezi. The three samples were coded GOL, KAT, and KOL for Golf, Katuba, and Kolwezi, respectively. The clay samples were dried at 105 °C until a constant weight was obtained, and then the samples were pulverized. The 4-nitrophenol was purchased from Sigma–Aldrich, South Africa. Figure 1 depicts the selected locations in the Democratic Republic of Congo where the clay samples were collected.
were used for the chemical analysis and phase identification, respectively.

The surface morphology and chemical analysis were carried out using a JEOL JSM-IT300 (scanning electron microscopy), while a Perkin–Elmer Frontier FTIR spectrometer was used for Fourier transform infrared (FTIR) spectroscopy. The weight loss and dehydration process of the clay samples were carried out using thermal analysis (TGA). The samples were heated in the thermal range from 50 to 900 °C at a rate of 10 °C/min in a nitrogen atmosphere using a Discovery TGA 550–TA system. A Lambda 650S Perkin–Elmer UV–Vis spectrometer was utilized for the UV–visible spectrophotometric analysis. UV–Vis analyses were also used to calculate the energy band gaps of the three clay samples according to the Kubelka–Munk relationship. Furthermore, based on the photoresponse of the clay samples, a preliminary analysis was conducted on the ability of the GOL clay sample in the photodegradation of 4-nitrophenol in wastewater.

A photocatalytic testing experiment for GOL clay application in wastewater treatment was devised as previously reported.34 Briefly, the degradation experiment was performed in a solar simulator (HAL–320 Asahi Spectra, Japan). A 300 W compact xenon light with apparent power of 500 VA was used as the light source. The solar simulator radiation spectrum output wavelength ranges were set from 350 to 1100 nm, and an air mass filter (1.5 global filter) was placed in front of the lamp to eliminate most of the UV radiation. The intensity distance that was the distance from the collimator lens to the sample surface was set at 37 mm. It created an effective radiated area of 50 mm² and an irradiance of approximately 100 mW cm⁻². GOL clay (0.1 g) was mixed with the 4-nitrophenol solution (80 ppm, 100 mL) and stirred in the dark for 60 min before the light was turned on. A sample was drawn from the solution using a syringe unit fitted with a 0.45 μm pore size hydrophilic PVDF membrane. The first sample was drawn after the adsorption–desorption equilibrium was considered as the initial concentration (C₀). The solar simulator was prewarmed (30 min) for a stable irradiance output, and samples (a mixed solution of photocatalysts and 4-nitrophenol) were subsequently irradiated in a 250 mL quartz beaker. Samples were drawn from the solution at 45 min intervals, filtered, and analyzed using a UV–vis spectrometer.

Figure 2. Particle size distribution of GOL, KAT, and KOL clay samples.

Figure 3. Discrimination diagram log wt % (SiO₂/Al₂O₃) versus log wt % (Fe₂O₃/K₂O) using the Heron plot of the three clay samples.37
The experiments were undertaken for 225 min, and the solution was stirred throughout the experiment. The UV–vis photometric measurements of standards and samples were done at a maximum absorbance of 400 nm to obtain the concentration of 4-nitrophenol after the elapsed time interval \((C_t)\). A calibration curve was obtained from the standards and the percentage of 4-nitrophenol degraded was calculated after eq 1:

\[
\text{Degradation\%} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100\%
\]  

(1)

3. RESULTS AND DISCUSSION

3.1. Density, pH, and Particle Size Distribution. The three clay samples exhibited different colors, namely, red for KOL, gray for KAT, and brown for GOL.

![Figure 4. CIA values of the GOL, KOL, and KAT clay samples. Furthermore, the weathering of the samples was quantified by plotting the chemical composition of the samples in the A–CN–K ternary plot of Nesbitt and Young39 (Figure 5).](image)

![Figure 5. Ternary diagram for the clay samples from the current study with similar age samples.](image)

The density measurement of the clay samples was carried out, and the results show that the density of GOL is the lowest \(2.7089 \text{ g/cm}^3\), whereas the density values of KAT and KOL are 2.8052 and 2.8678 \text{ g/cm}^3, respectively. The values of the pH were acidic 5.80, 4.54, and 4.93, respectively, for GOL, KAT, and KOL clay samples. It has been reported that the skin pH values range from pH 4 to 7; nonetheless, the surface pH of natural skin is just below 5.35.

In the current study, the pH of the KAT and KOL clay samples is below 5, and these can be used in the cosmetic industry. These values indicate that the three clay samples contain relatively the same type of molecules and that the clays will react similarly to the hydration. It has been reported that simple factors, such as water, exchangeable cation, and pH, can drastically affect the ability of clays to oxidize phenols to oligomers. Figure 2 depicts the particle size distribution of the GOL, KAT, and KOL clay samples. The three samples have similar particle size distribution. The GOL sample has particle sizes ranging from 0.409 to 352 \(\mu\text{m}\), whereas the KAT sample has particle sizes ranging from 0.409 to 418.6 \(\mu\text{m}\). Furthermore, it was observed that the particle size of the KOL sample ranged from 0.409 to 296 \(\mu\text{m}\).

3.2. Geochemical Characteristics. The three clay samples demonstrated a consistent geochemical composition. The classification scheme has been proven reliable for discriminating clastic sedimentary rocks. The geochemical characteristics of the clay samples were classified using the Herron plot. Figure 3 depicts a plot on the SiO2/Al2O3 vs Fe2O3/K2O discrimination diagram of Herron.

All the clay samples were plotted within the shale quadrant of the discrimination diagram. This could be further seen from the particle size distribution results, showing that the particle sizes measured in the samples demonstrated that the samples are shales. The samples investigated in the current study contained a high Al2O3 concentration (ranging from 23.0 to 33.8 wt %). This enrichment suggested the presence of clay minerals include kaolinite as well as associated clay-sized phases. This was confirmed with the X-ray diffraction results of the three clay samples.

During weathering, alkaline and alkaline-earth elements are removed in siliciclastic sediments. This process necessitates the use of Al2O3 (A), CaO and Na2O (CN), and K2O (K) to evaluate the geochemical alteration of sediments. To this end, numerous chemical indices that make use of the concentrations of these elements have been proposed. The most present of these is the Chemical Index of Alteration (CIA). The CIA is defined as \([\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})] \times 100\), where CaO* is Ca exclusive of carbonates and the values are in molar proportions to emphasize mineralogical relationships.

Furthermore, this index is sensitive to chemical alteration of sediments and provides a quantitative estimation of secondary aluminous clay mineral abundance with respect to the primary feldspar. High values of CIA (ranging from c. 76 to 100) indicate intense chemical weathering occurring at the source areas, while low values (from c. 50 or less) indicate unweathered source areas. In the current study, the samples analyzed showed an average CIA value of 92, which indicated that the samples are intensely weathered sediments. Figure 4 shows the CIA values of the GOL, KOL, and KAT clay samples. Furthermore, the weathering of the samples was quantified by plotting chemical composition of the samples in the A–CN–K ternary plot of Nesbitt and Young39 (Figure 5).
It was observed on the diagram that the sample plot is in the neighborhood of the top apex, which is typical of clay minerals rich in Al₂O₃, such as kaolinite and chlorite. Furthermore, similarly, aged samples from the study of Ngueutchoua et al.⁴⁰ are plotted together with studied samples (Figure 5). It can be seen that the comparison shows a high level of consistency with similar strongly weathered samples.

3.3. BET Measurements. Figure 6 depicts the BET typical nitrogen adsorption−desorption isotherms and the pore diameters for the GOL, KAT, and KOL samples. It was observed that all the clay samples are mesoporous. The findings are interesting because they imply that these three clay samples can be used in the water treatment processes. A recent study shows the application in water for mesoporous and silica-based nanomaterials.⁴¹ Other mesoporous materials for water treatment processes have also been reported.⁴² The average surface areas of 20.9145, 37.5422, and 39.4117 m²/g were obtained for GOL, KAT, and KOL samples, respectively. On the other hand, the average pore volume of 0.088292, 0.195899, and 0.184767 cm³/g values are respectively for GOL, KAT, and KOL samples. Furthermore, the average pore size of 178.077, 208.114, and 186.727 Å were obtained for GOL, KAT, and KOL, respectively. It was further observed that the pore diameters ranging from 29.544 to 862.318 Å, 17.963 to 932.970 Å, and 20.513 to 1475.380 Å are respectively for GOL, KAT, and KOL (Figure 6). Most of the pore diameters for all the samples are under 100 Å, which could have an impact on the water absorption of the bricks, fabricated using the selected clay.

3.4. Chemical Composition and Phase Identification. The chemical composition of the three clay samples is shown in Table 1, where SiO₂ is the most abundant compound in the clay samples. The presence of Al₂O₃ of different concentrations was observed and the concentrations were 29.8861, 33.8194,
The clay could play a substantial role as a physical UV filter, whereas the KOL sample has the highest of Fe₂O₃, K₂O, and MgO. The KAT sample has the highest concentration of Al₂O₃ and TiO₂, followed by KAT with 56.5194% and KOL with 53.3235%. The GOL clay sample had 64.035% of SiO₂, which is the highest.

Furthermore, 1.5726, 2.8952, and 2.3429% of TiO₂ were found in the samples respectively for KOL, KAT, and GOL. Therefore, the UV reflection ability of the three selected clay samples is discussed in the current study. The amounts (wt %) of TiO₂ found in the samples are 1.5726, 2.8952, and 2.3429, respectively, for KOL, KAT, and GOL. The KAT clay could have higher ability to reflect UV followed by the GOL and KOL. Furthermore, the amount of TiO₂ found in the clay samples had a higher concentration compared to other clay samples from different African countries. The main chemical components (SiO₂, Al₂O₃, Fe₂O₃, K₂O, TiO₂, and MgO) in the clay samples are efficient oxide used as semiconductors or promoters in nanomaterial composites for environmental application, including wastewater treatment.

The XRD analysis was utilized to determine the mineralogical composition of the clay sample components and to confirm the XRF results. The X-ray diffractograms are presented in Figure 7 for KAT, KOL, and GOL respectively.

All the samples contained quartz. The KAT sample also contained kaolinite and anatase (TiO₂), while the KOL sample contained magnetite. In the GOL sample, it contained quartz, magnetite, kaolinite, and illite. The obtained XRD results are similar to the one found in the literature. The presence of the obtained phases is further confirmed with the FTIR analysis. It was also observed that the peaks of minor phases such as illite overlapped with those of major phases.

The XRF results were in agreement with the obtained chemical composition of the identified phases using XRD and that showed the presence of aluminum, iron, and silicon as major chemical elements. The XRD showed the presence of quartz, kaolinite, anatase, magnetite, and illite.

### 3.5. Surface Morphology and Functional Groups Analysis

The surface morphology of GOL, KAT, and KOL samples are shown in Figure 8. All the three clay samples presented similar surface morphology. A flake-like morphology was noticed in all the three clay samples and could correspond to a part where there is a presence of an amorphous material.

The FTIR analysis assists in identifying the functional groups, which are part of the minerals in the selected materials. The identified functional groups in the three clay samples using FTIR are depicted in Figure 9.

It was noticed that the FTIR spectra of all the three samples are similar. The important FTIR bands for clay materials and their assignments are in agreement with the literature. The Si–O–H stretching vibrations were observed at 681.13, 780.22, and 1006.00 cm⁻¹. On the other hand, the Al–O–H stretching was observed at 3697.8 cm⁻¹, while an Al–O–H inter-octahedral band was observed at 3621.39 cm⁻¹. Furthermore, the band observed at 1628.18 cm⁻¹ could suggest the possibility of water hydration in the clay sample (H–O–H stretching).

The density results indicated that the three clay samples could have the same response toward hydration. The functional groups could confirm those findings. The shift in the bands could be due to the presence of other chemical elements and impurities in the clay samples. The presence of the various assigned bands linked to chemical elements confirmed the phases present in the clay samples obtained using XRD.

### 3.6. Thermal Analysis

TGA results are presented in Figure 10. The first mass loss that occurred at around 100 °C is mostly due to the loss of water adsorbed at the surface of the clay samples. This was in agreement with the results reported by Madzikizela et al. The GOL sample exhibited the lowest mass loss (8.33 wt %) compared to the other two samples, namely, KAT (12.59 wt %) and KOL (12.04 wt %), implying that GOL contains fewer organic constituents. Furthermore, it has been reported that mass losses are often associated with...
the oxidation of organic constituents present in the materials. Boulingui et al. have also reported that there are major reactions involving loss of H₂O, CO₂, and/or organics in clay materials.

3.7. UV Measurements. In some part of the world, including the African continent, clays are used for cosmetic purposes. Morekhure-Mphahlele et al. indicated that some clays in the Eastern Cape in South Africa are used for their moisturizing effect. To study the potentiality of using the three clay samples as a substitute in creams such as sunblock, the clay samples were studied in regard to investigating their abilities to protect against ultraviolet radiation in the wavelength range of 200–400 nm. This could provide information if they can be used in the cosmetic industry. Furthermore, the ability of these materials to respond to UV could indicate their ability to be used as photocatalytic materials. The assumption is more likely accurate due to the presence of TiO₂ and Fe₂O₃, which could render natural clay photoresponse and is suitable for adsorption and photocatalytic activity.

Figure 8. SEM micrographs of GOL, KOL, and KAT clay samples.

Figure 9. FTIR spectra for the GOL, KAT, and KOL samples.

Figure 10. TGA thermograms of the GOL, KAT, and KOL clay.
wavelength from 200 to 280 nm covers a part of the short wave UV-C spectral range. The reflectance percentage values of the three clay samples were observed at a specific wavelength, namely, 200, 250, 300, 350, and 400 nm and are displayed in Figure 12.

Reflectance values of 19.8794, 22.8894, and 21.3048% were obtained for KOL, KAT, and GOL, respectively, at 200 nm. Furthermore, the GOL sample has 15.5583, 16.8340, 16.2544, and 20.2414% reflectance at 250, 300, 350, and 400 nm, respectively. The KAT samples have 19.0457, 23.91766, 24.9590, and 32.31063% reflectance at 250, 300, 350, and 400 nm, respectively. Reflectance values 16.5750, 18.3752, 18.6058, and 21.6219% were respectively obtained at 250, 300, 350, and 400 nm for the KOL sample. The KAT sample exhibited higher reflectance percentages for the selected wavelengths except at 200 nm. Furthermore, the lowest reflectance percentage for the GOL sample is 15.5488% obtained at 320 nm; the KAT sample has 18.9396% reflectance, which is its lowest reflectance at 256 nm. The lowest for the KOL sample is 16.2131% reflectance recorded at 260 nm wavelength. It can be said that the GOL sample has the highest reflectance percentage at all the selected wave-

Table 2. Photodegradation Percentages of 4-Nitrophenol Using the GOL Clay Sample

| sample | time (min) | photodegradation % |
|--------|------------|------------------|
| GOL    | Photolysis | 2.77             |
|        | 45         | 20.61            |
|        | 90         | 36.20            |
|        | 135        | 51.49            |
|        | 180        | 98.16            |
|        | 225        | 99.13            |

Figure 11. Ultraviolet reflectance percentage variation of the selected clay samples.

Figure 12. Variation of reflectance percentage values of the GOL, KAT, and KOL clay samples at selected wavelengths.

Figure 13. Kulbelka–Munk curves of the two calculated energy band gaps for the GOL (a), KAT (b), and KOL (c) clay samples and the comparison (d).
It has been reported that the presence of inorganic compounds, namely, titanium dioxide (TiO₂) and zinc oxide (ZnO), in sunscreen products act as physical ultraviolet filters and have the ability to block out sunlight and reflect ultraviolet light. This could be seen by the presence of the TiO₂ compound in all the selected clay samples. Moreover, the data also suggest that the three clay samples can be used in the UV photocatalysis. TiO₂ is known to be excited from UV light leading to the generation of electrons and holes at the conduction and valence bands. Consequently, oxidizing radicals are created, and these species are essential for photodegradation in wastewater treatment. It can be said that the higher reflectance percentage of UV in the GOL sample compared to the other two samples could be due to the additional presence of the ZnO compound, which was not found in the other two clay samples. Further purification of the raw clay samples can enhance the blocking ability of UV of the GOL sample, which could be used for the cosmetic application. However, it is important to treat TiO₂ with other materials to ensure application in the visible light.

### 3.8. Photocatalytic Experiment

The energy band for the three clays, namely, GOL, KAT, and KOL was measured from the Kubelka–Munk curves as depicted in Figure 13a–c. Furthermore, the compared values of the energy band gap of the three clays are shown in Figure 13d.

The results presented in Figure 13d show that GOL clay is characterized by low energy band gaps (2.68 and 3.94 eV), which is a good photocatalytic feature for semiconductors. The energy band gaps for KAT is 2.93 and 3.85 eV, whereas the KOL displayed the energy band gaps of 2.71 and 3.44 eV. The photocatalytic activity of the untreated GOL clay was tested in the degradation of 4-nitrophenol. The photodegradation percentages were calculated using eq 1, and the results are presented in Table 2. The experimental data indicated that 99.13% of 4-nitrophenol was decomposed within 225 min of irradiation, which is closely in agreement with the literature. A previous study has also reported that more than 225 min is required to achieve 98% of 4-nitrophenol decomposition under the visible light irradiation. The results are quite interesting because they confirm that GOL clay can be used as a photocatalytic material under the current conditions in the degradation of 4-nitrophenol. Furthermore, the photolysis experiment revealed that only 2.77% of 4-nitrophenol was removed from aqueous solution using the GOL clay sample, indicating that the irradiation played a crucial role in the removal of 4-nitrophenol.

Additional experimental data are depicted in Figure 14a,b for the UV spectra of the photoreduction reaction and UV spectra showing a decrease in the absorbance value at 400 nm and increment at 300 nm with time over 3 h 45 min.
disappeared rapidly at 400 nm and implies that 4-nitrophenol has been effectively removed from the reaction solution. As the reaction proceeded, a color change was observed from the solution being colorless to orange, and then gradually disappeared with a prolonged reaction time. The results suggested that expected intermediate products in the photodegradation of 4-nitrophenol could have been present as indicated by the increment of absorption at 300 nm. The discoloration of 4-nitrophenol could be ascribed to the hydroxylation of hydroxyl radicals photogenerated in the 4-nitrophenol solution.29

Based on the literature, the removal of 4-nitrophenol was attributed to the oxidation by a OH radical, which can be expressed by

$$\text{4-nitrophenol} + \cdot \text{OH} \rightarrow \text{intermediates}$$

while the discoloration or disappearance rate of 4-nitrophenol can follow eq 2:

$$\frac{dC}{dt} = k_1 C$$  \hspace{1cm} (2)

where $k_1$ represents the product of the pseudo first-order rate constant of the reaction between 4-nitrophenol and hydroxyl radicals. The pseudo first-order rate kinetic equation can be written as follows (eq 3):

$$\ln \left( \frac{C_t}{C_0} \right) = -k_1 t$$  \hspace{1cm} (3)

where $k_1$ can be referred to as a pseudo first-order rate constant; $C_t$ and $C_0$ are the concentrations at time ($t$) and time (0) in that order.29

The kinetic graph is displayed in Figure 15, and the pseudo first-order model can explain the degradation reaction better when $\ln(C_t/C_0)$ is plotted against $t$ as displayed in the inserted table in Figure 15b.

The photocatalytic results obtained in this study using untreated natural GOL clay were compared with the reported data in the literature as summarized in Table 3. It is important to note that this kind of comparison is not fully accurate due to the difference in parameters, such as the source of light, time of irradiation, the concentration of the 4-nitrophenol, and the material investigated by numerous researchers.24–27 This is demonstrated in Table 3 where some authors have reported the performance of their material based on the reaction rate

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Table 3. Comparison between the Current Results and Those in the Literature

| material/treatment procedure | light source | pollutant | removal percentage and some parameters | reference |
|-----------------------------|--------------|-----------|----------------------------------------|-----------|
| untreated natural clay (GOL) | 300 W compact xenon light | 4- nitrophenol | 99.13% (80 ppm) at 225 min | this study |
| ZnO/HZSM-5 nanocomposites | 30 W (UV-C) lamp (Philips) | 4- nitrophenol | 91% TOC (20 mgL$^{-1}$) at 90 min. | 27 |
| impinging streams photoreactor coupled with a membrane | 18 W UV-C radiation (Philips Co.) | 4- nitrophenol | 55.6% TOC and 45% COD (30 ppm) at 180 min | 23 |
| Fe-doped TiO$_2$/SiO$_2$ nanofibrous membranes | 500 W xenon lamp | 4- nitrophenol | (10 mg/L) $k$ (reaction rate constant) value of the target 4NP over nanofibrous photocatalysis are 0.00417, 0.00155, and 0.00263 for MI-Fe@TS, NI-Fe@TS, and Fe@TS | 26 |
| novel copper(II) porphyrin–TiO$_2$ photocatalysts | 350 W xenon lamp under simulated solar irradiation. | 4- nitrophenol | 4-NP could be photodegraded much rapidly to almost zero (1 x $10^{-4}$ M) at 300 min | 25 |
| bare TiO$_2$ microspheres | 350 W xenon lamp under simulated solar irradiation. | 4- nitrophenol | 35% (1 x $10^{-4}$ mol/L) at 300 min | 25 |
| TiO$_2$/Fe$_2$O$_3$-supported bentonite (TiO$_2$/natural hematite-supported bentonite (TiNHB)) | UV$_{254\text{nm}}$ irradiation (25 W, 18 mÅ) | 4- nitrophenol | 98% (20 mg/L) at 180 min. | 22 |
| UV/H$_2$O$_2$ process | A low pressure 14 W UV lamp (S2-Q-PA12, Canada R-Can Environmental Inc) | 4- nitrophenol | > 98% (25 ppm) in 12 min and 94% and TOC (25 ppm) in 106 min | 29 |
| novel Co and Cu phthalocyanine | under visible light | 4- nitrophenol | 95% for CoPc and 97% (or CuPc (0.025 M) at 1 h | 24 |

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Figure 15. Kinetic plots (a) of the concentrations (b) of the natural log of concentrations as a function for the degradation of 4-nitrophenol in aqueous solution.
constant, while others in the form of percentage removal. However, based on the closest comparison of parameters presented in this study and those reported in the literature, it can be said that untreated natural GOL clay has demonstrated superior removal ability of 4-nitrophenol through simulated solar light irradiation.

4. CONCLUSIONS

The physicochemical characterization of selected clay samples from three different locations in the Democratic Republic of Congo (DRC) was investigated. The density of the three clay samples was relatively close: 2.71 g/cm³ for GOL and 2.81 and 2.87 g/cm³ for KAT and KOL, respectively. On the other hand, the particle size distribution for all the samples is ranged in water treatment applications. It was observed that most of the pore diameters for all the clay samples are under 100 Å, in which could have an impact on the application of the three clay samples for various purposes, including wastewater treatment. The GOL clay sample showed the highest UV reflectance percentage at all the selected wavelengths, and this could be due to the presence of a ZnO compound, which was not found in the other two clay samples. The GOL clay could be coupled with other materials and find photocatalytic activity in the UV and visible light ranges. Furthermore, preliminary analysis on the photodegradation of 4-nitrophenol using the untreated GOL clay sample showed a 99.13% degradation obtained at 225 min.

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