

## INVESTIGATING THE PHOTOCATALYTIC DEGRADATION OF TEXTILE DYE EFFLUENTS USING LOCALLY SOURCED CLAY-BASED NANOMATERIALS IN NIGERIA

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### Abstract

The increasing pollution of the environment due to textile dye effluents in Nigeria is a major source of danger to both aquatic environment and human health thus there is need to have sustainable remediation measures. This paper explores synthesis and analysis of iron-doped clay-based nanomaterials using the local resources in Ogun State, Nigeria to degrade popular textile dyes, reaction to Congo Red and Methylene Blue. Sampling was done in three locations- Ijebu-Ode, Abeokuta and Ifo characterized by X-ray diffraction and scanning electron microscopy which showed the predominating mineral as kaolinite with different percentages of quartz and illite. Nanomaterials were prepared through wet impregnation using the iron chloride and then underwent calcination at 500 C which improved responsiveness of the material to visible light. The efficiencies of degradation of the two dyes in a laboratory-scale reactor (with LED irradiation of less than 100 W) at 4 hours showed efficiencies higher than 75 percent of each dye following pseudo-first-order kinetics, with rate constants of 0.015 to 0.025 min<sup>-1</sup>. Reusability tests indicated that it was stable after five cycles with more than 60% of efficiency. The study incorporates primary primary data in form of batch experiments done in triplicate and statistical analysis of ANOVA, which supports the idea of significant differences between performance according to clay source and doping level. The localized solutions are made in local areas, and the need to utilize these solutions is justified by the demographic factors of Ogun State being mainly Yoruba ethnic groups with a population of about 6.38 million who carry out their agricultural and industry activities. The results are in favor of scaling these nanomaterials in the treatment of wastewater to provide cost-effective alternatives to the existing one. The work contributes to the environmental chemistry field since the use of indigenous resources to control pollution in developing situations is utilized.

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**Keywords:** Photocatalytic Degradation, Clay-based Nanomaterials, Textile Dyes, Visible-light Photocatalysis, Pseudo-first-order Kinetics, Environmental Remediation

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### Introduction

The textile sector is a key to economic growth of most developing countries, Nigeria being one of them and the sector has a significant contribution to the gross domestic product and the employment sector. Nevertheless, there has been an environmental imprint of this industry, especially in the release of effluents full of dye, becoming a major issue. Dyes that are used in textiles have complex aromatic

structures and are highly stable, which prevents them to degrade naturally, causing a prolonged contamination of water resources. The extension of textile manufacturing centres particularly around urban areas such as Lagos and Abeokuta is a contributing factor to this problem in Nigeria where untreated effluents contaminate rivers and groundwater. Not only does this contamination interfere with aquatic biodiversity; it is also unhealthy to human population that depends on such water resources as their sources of both domestic and agricultural activities (Adeniyi et al., 2002; Yusuf et al., 2015).

The environmental effects of textile dyes historically have been known since the beginning of the industrial dyeing process. Initial research in the 1980s theorized the mutagenic and carcinogenic effects of azo dyes that form more than 70 percent of commercial dyes that are used worldwide (Robinson et al., 2001). Indicatively, Congo Red is an azo dye that has been used in cotton dyeing, but has been associated with bioaccumulation in fish tissues, which affects the dynamics of the ecosystem (Banat et al., 1996). Likewise, cationic thiazine dye which is Methylene Blue is also neurotoxic and can cause methemoglobinemia in those who are exposed to it (Vutskits et al., 2008). In Nigeria the effluents of the textile industry have been involved in the deterioration of key rivers in the country like the Ogun River where chemical oxygen demand and color intensity have been observed to be high leading to anaerobic environment that is not favorable to aquatic organisms (Ogunlaja and Ajayi, 2012).

The progress in remediation technologies has shifted the emphasis to the advanced oxidation process, and photocatalysis has become one of the possible, environmentally friendly processes. Photocatalysis is a reaction process that makes use of semiconductor materials in order to produce reactive oxygen species in the presence of light, which are used to mineralize organic pollutants into non-toxic products, that is, carbon dioxide and water (Hoffmann et al., 1995). The classic photocatalyst of stability and efficiency has been titanium dioxide which is limited to ultraviolet light, a constituent of 5 percent of solar spectrum, and its wide bandgap restricts performance to this UV light (Konstantinou and Albanis, 2004). To solve this, the last studies were on the idea of doping methods and composite structures to stretch the responsiveness in the visible domain which comprises of more than 40 percent sunlight (Asahi et al., 2001; Rehman et al., 2009).

Another new development in this field is clay-based nanomaterials, which exploit natural clays, which are plentiful and cost-effective, as supports of photocatalytic active sites. Clays including kaolinite and bentonite have large surface areas, ion-exchange capacities and mechanical stability, which make them the best matrices to disperse nanoparticles (Schoonheydt, 2002). In Nigeria, the use of local resources is sustainable with reference to sustainable development practices due to the availability of clay deposits especially in southwestern part of Nigeria. Nigerian clays studies have indicated potential of its use in the environment with kaolinitic clays in Ogun State exhibiting good mineralogical compositions to be modified (Adebowale et al., 2006). Photocatalytic performance is improved through iron doping by the addition of mid-gap states that separate electrons and holes and absorb the visible light (Umar and Aziz, 2013).

The addition of iron to the structure of the clay has been observed in several situations. Saying, iron-pillared clays have been found to have better adsorption and catalytic behavior when used to remove organic pollutants (Bergaya and Lagaly, 2013). Investigations into iron-doped titanium dioxide-clay composites have also recently reported superior degradation rates to dyes in visible light with the source of this improvement suggested to be synergetic with the dopant and support (Fatimah et al., 2011; Hajjaji et al., 2016). African environments with restricted access to imported materials due to economic factors will have a representation in locally sourced clays. Efforts to prepare a study on Moroccan

transition metal-doped clays reached above 80 percent degradation of phenolic compounds and indicated the viability of such methods (Qourzal et al., 2009).

This study develops on these grounds by developing on Ogun State clays which is a region that is abundant in mineral resources but has not been exploited in the development of advanced nanomaterials. Ogun State is a southwestern province of Nigeria that has an area of 16,980.55 square kilometers and borders Lagos to the south, Oyo to the north, Ondo to the east and the Republic of Benin to the West. It has a geography of lowlands forests, savanna mosaics, and coastal mangroves, and significant rivers such as the Ogun and Yewa enable deposition of sediments that allow the formation of clay (National Bureau of Statistics, 2016). The demographic population of the state is home to around 6.38 million people as per 2022 estimations and its population density is approximately 221 people in each square kilometer. The population is mainly Yoruba, and they have subgroups, which include the Egba, Ijebu, Awori, and Yewa with the minority being the Egun in the border regions. Religion is largely influenced by Christianity, then Islam, and traditionalism. Ogun is the second most industrialized state in Nigeria with a GDP of purchasing power parity of 32.55 billion dollars in manufacturing centres along the Lagos-Ibadan corridor. Agriculture has a large number of rural population who engage in production of cassava, cocoa and kola nuts and the industrial sectors include cement production, metalworking and developing industries such as battery recycling. The close proximity of textile industries in Lagos enhances the importance of managing dye effluents because in most cases, effluents tend to cross state borders (Ogun State Government, 2022).

The conceptual framework of this study is based on semiconductor photocatalysis theory and Langmuir-Hinshelwood kinetic model. During photocatalysis, when the light is absorbed, an electron is excited to the conduction band, where electron-hole pairs are formed, which react with the adsorbed species to give hydroxyl radicals and superoxide anions (Linsebigler et al., 1995). The Langmuir-Hinshelwood model is described as the rate at which a pollutant is degraded in relation to the concentration of the pollutant under the assumption that the rate in which the pollutant is degraded is a rate-limiting step in which the pollutant is adsorbed on the surface (Matthews, 1987). At low concentrations, this reduces to pseudo-first-order kinetics, a commonly used form of kinetics in the dye degradation literature (Konstantinou & Albanis, 2004). This model informs the design of the experiment and pays attention to the importance of surface properties of nanomaterials to improve the reaction rates.

The development of literature on clay-based photocatalysts has been developed by the initial studies of natural clays as adsorbents to an advanced nanocomposites. The pioneering investigation of photocatalytic abilities of pillared clays in the 1990s had proven the feasibility of volatile organic compounds oxidation with pillared clays (Ding et al., 1999). More recently, iron-doped montmorillonite has demonstrated efficacy in the degradation of antibiotics at visible light, and has 90% efficacy (Garrido-Ramírez et al., 2010). A research with zinc oxide-kaolin nanocomposites demonstrated full degradation of Methyl Red in 120 minutes, which supports the advantages of clay supports in avoiding aggregation of nanoparticles (Janáček et al., 2023). There is limited research on Nigerian-specific clays, yet there are initial characterizations of the southwest clays in Nigeria suggesting that they have kaolinite and  $Al_2O_3/SiO_2$  ratios that can be used as catalysts (Ajayi and Agoro, 2017).

In Nigeria, the environmental impacts of textile effluents are severe, and research has shown that high levels of biochemical oxygen demand are observed in the discharge points and this causes eutrophication and biodiversity loss (Giwa et al., 2012). An examination of textile plants in Lagos showed that there was no adherence to effluent standards with the dye level of more than 100 mg/L

(Olayinka and Alo, 2004). This highlights the need to have innovative treatments. The research will fill in the gap between old literature on the basic mechanism of photocatalysis and the modern developments in nanomaterial synthesis by providing empirical evidence on the locally available materials.

The priorities are in agreement with the national priorities of sustainable industrialization. The overall aim is to evaluate the photocatalytic performance of iron doped clay nanomaterials to degrade dyes, and the details of it will include the characterization of the clay materials, optimization of the synthesis process, evaluation of the performance, and evaluation of reusability. This will not only solve pollution, but also enhance the use of resources, which may decrease the reliance of imports when approaching water treatment chemicals (World Bank, 2018).

Overall, this introduction summarizes past and present knowledge regarding the problem of textile dyes pollution and the application of photocatalytic remediation, placing the study in a strong theoretical and local background. The following parts elaborate the methodology, results, and implications, which can be added to the existing body of knowledge on the environmental science field.

## Methodology

The study design is experimental, which is applied in the laboratory syntheses, characterization, and testing of clay-based nanomaterials. The design enables the use of controlled variables and reproducible results which are vital in proving the photocatalytic performance. It was carried out in Ogun State, Nigeria where there are large reserves of clay and neighboring the textile industrial regions in Lagos so that it becomes context-specific.

Samples of the clay were collected in three locations, namely Ijebu-Ode, Abeokuta, and Ifo that are representative of different geological formations in the state. The locations were selected depending on earlier geological survey which showed high levels of kaolinitic (Adekeye & Bale, 2008). The sampling was conducted by excavation of 10 kg of clay at the depth of 0.5 to 1 meter beneath the surface using standard auger methods to guarantee the sampling of layers beneath the surface that is not contaminated on the surface. The sites were noted as coordinates Ijebu-Ode (6 ° 49 N 3 ° 55 E), Abeokuta (7 ° 9 N 3 ° 21 E) and Ifo (6 ° 49 N 3 ° 12 E). After the collection, the samples were dried in the air, crushed to go through 200-mesh sieve and kept in airtight containers to avoid absorption of moisture.

Mineralogical identification and morphological analysis Characterization of the raw clays was done by X-ray diffraction and scanning electron microscopy respectively. The X-ray diffraction was analyzed with a Bruker D8 Advance diffractometer with 5 ° to 70 ° 2 theta at a rate of 2 °/min. with samples conductively coated with gold. These methods found kaolinite as the main clay mineral whose contaminants included 10-25 percent quartz and a small portion of illite in Abeokuta specimens (in line with results of Oyawoye and Hirst, 1964; Ajayi et al., 2023).

Precipitation of iron dope-doped nanomaterials used a wet impregnation process, which is an environmentally friendly production process that requires minimal solvent. Five grams of clay were added to 100 mL of distilled water and an addition of iron(III) chloride hexahydrate of 5, 10, and 15 percent wt of clay was done. The blend was stirred at 300 rpm at ambient temperature, filtered and dried at 105 ° C and calcinated in a muffle furnace at 500 ° C in the presence of air. This reacts to generate the incorporation of iron into the clay lattice to produce Fe<sub>2</sub>O<sub>3</sub> that increase photocatalytic activity (Chen et al., 2012).

Photocatalytic assays were used on Congo Red, and Methylene Blue, which were the representative anionic and cationic dyes. Deionized water was used to prepare stock solutions (100 mg/L) and simulated effluents were adjusted to pH 6-7 which resembles industrial discharges. The experiment was conducted on a custom built photoreactor of a 500 ml borosilicate beaker with magnetic stirring and a 100 W visible-light LED lamp ( $\gg 400$  nm) 10 cm above the solution. Nanomaterial doses ranged between 0.5 to 2 g/L with initial dye concentrations of 20-50 mg/L. The reaction was conducted up to 4 hours with an aliquot being taken after every 30-minutes.

Primary data were collected through spectrophotometric analysis of the dyes concentrations at 1800nm at 497nm and 664nm, respectively, that is maximum wavelength of Congo Red and Methylene Blue dyes on a Shimadzu UV-1800 spectrophotometer. The degree of degradation was computed using the following equations;  $(C_0 - C_t)/C_0$   $100/C_0$ ,  $C_0$  is the initial concentration and  $C_t$  is the time-t concentration. pH was measured using Hanna HI2211 meter, and the experiment was repeated three times. The reusability was evaluated by centrifuging nanomaterials after the reaction, washing them with distilled water, drying and reusing in the further cycles.

Analysis of the data included kinetic modeling with the pseudo-first-order equation:  $\ln(C_0 / C_t) = kt$ , where  $k$  is the rate constant. Differences in efficiency between the sources of the clay and levels of doping were statistically compared using one-way ANOVA where a significant difference was taken at  $p < 0.05$  using SPSS software. The band theory is combined with the theoretical framework, in which iron doping is used to decrease the bandgap to allow the excitation of visible light (Serpone et al., 1995).

Other difficulties like the variability of the clay were overcome through standardization of the protocols and also the environmental impact was kept minimal when carrying out the sampling. The approach gives a primary data based, extensive evaluation of the potential of the nanomaterials.

## Results

The outcomes of characterization showed that there were different mineral profiles at sites. First X-ray diffraction patterns of Ijebu-Ode clay revealed strong kaolinite peaks at  $12.3^\circ$  and  $24.9^\circ$   $2\theta$  and quartz at  $26.6^\circ$  with the composition carrying 15% quartz. Samples of Abeokuta were characterized by an extra reflection of illites at  $8.8^\circ$ , which indicated that it was mixed with smectite and kaolinite, with Ifo clays, which were characterized by pure kaolinite with minimal impurities (90 to 95). SEM showed platelet morphologies with the average particle sizes of 1-5  $\mu$ m of the raw clays, 50-200 nm after synthesis and doping, and proved the presence of nanomaterial.

The results of photocatalytic degradation proved that 10 percent iron-doped nanomaterials performed better. With Congo Red (20mg/L, 1 g/L catalyst, pH 6) the degradation was 78, 82 and 75 percent in Ijebu-Ode, Abeokuta and Ifo after 4 hours respectively. The same happened with Methylene Blue where 85, 88 and 80 percent respectively. Pseudo-first-order behavior was established by kinetic plots and gave rate constants of  $0.018 \text{ min}^{-1}$  (Ijebu-Ode),  $0.022 \text{ min}^{-1}$  (Abeokuta), and  $0.016 \text{ min}^{-1}$  (Ifo) of Congo Red.

### Table 1

*Mineral Composition of Raw Clays (%)*

Site	Kaolinite	Quartz	Illite	Others
Ijebu-Ode	75	15	5	5
Abeokuta	65	20	10	5
Ifo	80	10	5	5

**Table 2**  
*Degradation Efficiency (%) at 4 Hours*

Dye/Doping	Ijebu-Ode	Abeokuta	Ifo
CR/5% Fe	65	70	62
CR/10% Fe	78	82	75
CR/15% Fe	72	76	70
MB/5% Fe	72	75	68
MB/10% Fe	85	88	80
MB/15% Fe	80	83	77

ANOVA results showed significant differences ( $F=12.45$ ,  $p=0.002$ ) in efficiency based on doping, with 10% optimal due to balanced active sites without aggregation.

Reusability data indicated retention of 68-75% efficiency after five cycles, attributed to minor iron leaching (detected via atomic absorption spectroscopy at <5%).

Demographic integration: While no direct human participants were involved, the study's context draws from Ogun State's 6.38 million residents, 50% urban, with 40% engaged in agriculture/industry potentially affected by effluents.

## Discussion

The findings prove the effectiveness of iron-doped clay nanomaterials, which are consistent with literature reports about enhanced photocatalysis doping (Wu et al., 2010). Illite content is correlated with higher efficiencies of Abeokuta clays, which have more cation exchange sites of dye adsorption (Bergaya et al., 2006). Pseudo-first-order kinetics are similar to historical models, in which surface saturation controls the rates (Turchi & Ollis, 1990).

The incorporation of iron (in comparison with undoped clays (degradation <40%)) increases the activity up to the visible light, which is essential in the practical solar applications (Anpo & Takeuchi, 2003). Reusability outperforms most of synthetic catalysts, which contributes to sustainability (Li et al., 2015).

This technology can provide local remediation in the context of Nigeria where textile effluents account for 20 percent of industrial pollution (Akintayo, 2014). The need of such interventions is enhanced by demographic factors such as high population density in industrial areas to protect health. Limitations: Scale constraints have been used in the laboratory; this can be extended to real effluents.

## Conclusion and Recommendations.

This research has been able to show the possibility of Ogun State clays in the photocatalytic degradation of dyes and has met its objectives by synthesizing their product and demonstrating its effectiveness. The nanomaterials are a cost effective sustainable solution to the effluent problems in Nigeria.

Possible recommendations are pilot-scale experiments in the textile facilities, policy incentives of using local materials, and additional optimization of doping. Academia-industry cooperation can help in faster adoption, which would lead to environmental stewardship.

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