Transdisciplinary Insights in Life Sciences

ISSN: 2584-2161(Online)
Journal Homepage: www.panainool.com

RESEARCH ARTICLE

Photocatalytic activity of metal oxide/kaolinite nanocomoposites under UV light irradiation

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ARTICLE HISTROY

Received 16 November 2023
Revised 17 November 2023
Accepted 20 November 2023

Keywords

Kaolinite
Titanium dioxide,
Methylene blue
Solvothermal
Photocatalysis

ABSTRACT

Wastewater treatment, especially for industrial pollutants, may harm the environment. Many nations face a technological issue with textile, paper pulp, and other industries' colored wastewater disposal. Textile wastewater pollution is a major source of environmental pollution that taints and colors aquatic systems. The current study involved the investigation of the photocatalytic properties of TiO_2/kaolinite nanocomposites by utilizing the solvothermal technique. The synthesized nanocomposites underwent additional characterization by the utilization of various analytical techniques, including X-ray diffraction, scanning electron microscopy with energy dispersive X-ray spectroscopy, atomic force microscopy, transmission electron microscopy and ultraviolet-visible absorption spectroscopy. The X-ray diffraction analysis indicates that during the creation of nanocomposites, the presence of the anatase phase of TiO_2 was detected in the TiO_2/kaolinite composite. The scanning electron microscopy investigation revealed the presence of spherical morphology in the TiO_2/kaolinite nanocomposites. The UV-Vis absorption margins exhibit a blue shift towards lower wavelengths, potentially attributed to the nanosize effect. The study assessed the photocatalytic performance of TiO_2/Kaolinite nanocomposites by measuring the degradation of methylene blue dyes under UV light exposure. The results indicated that the application of swift heavy ion irradiation led to a notable improvement in the photocatalytic efficacy of the synthesized TiO_2/Kaolinite nanocomposites in terms of degrading MB dyes.

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Introduction

According to the definition given in the context of chemistry, nanoscale materials are structures with a size between 1 and 100 nm. In recent years, these materials have helped to accelerate the

development of nanoscience and nanotechnology (Joudeh & Linke, 2022). As of right now, titanium dioxide (TiO_2) nanoparticles are minuscule fragments of the inorganic molecule. Usually ranging in size from 1 to 100 nanometers, they possess distinct characteristics when contrasted with titanium dioxide in bulk (Khan et al., 2022). TiO_2 nanoparticles are highly reactive and valuable in a range of applications because of their small size and enormous surface area relative to their volume (Musial et al., 2020). TiO_2 nanoparticles usually appear in paints, coatings, ceramics, and sunscreens and cosmetics (Irshad et al., 2021). Additionally, they have potential uses in the biomedical, catalysis, water treatment, and self-cleaning surfaces (Waghmode et al., 2019).

Materials that consist of a mixture of clay particles and titanium dioxide (TiO_2) nanoparticles are known as clay nanocomposites. Typically, layered silicate minerals like illite, montmorillonite, and kaolinite form the clay particles (Serwicka, 2021). The application of clays including montmorillonite, rectorite, and kaolinite in the treatment of waste water has garnered significant interest in recent years (Chuaicham et al., 2023). Naturally occurring materials have the ability to absorb organic compounds either on their external surfaces or within their interlaminar regions through processes of contact or replacement (Isa et al., 2022). In addition, these structures possess layered arrangements, extensive surface areas, and notable capacities for cation exchange. According to reports, TiO_2 particle dispersion into layered clays can enhance catalytic performance because the architectures of these composites can stabilise TiO_2 crystals, making them accessible to a variety of molecules (Chuaicham et al., 2023; Hamidi & Aslani, 2019). TiO_2 nanoparticles can be intercalated into the layers of the clay mineral or dispersed in a clay solution to create these nanocomposites. The ability of TiO_2/clay nanocomposites to enhance the individual component's qualities is one of its key advantages (Chuaicham et al., 2023). While the TiO_2 nanoparticles can improve the optical, catalytic activity, electrical property, and photocatalytic characteristics of the clay, the clay particles can improve the TiO_2's mechanical strength and thermal stability (Dharma et al., 2022). Researchers have already looked into the antibacterial, structural, and morphological properties of Kaolinite/TiO_2 nanocomposites (R. Li et al., 2020; Xie et al., 2022). It is the goal of this study to use the solvothermal method to make metal oxide/clay nanocomposites, which will then be used to get rid of the methylene blue dye.

Materials and method

Preparation of TiO_2/Kaolinite Nanocomposites

1% w/w clay-water dispersion was agitated for two hours. 70% w/w TiO_2 content was reached by adding a small amount of TiO_2 solvent to the mixture. This was done over the course of a day. After that, the mixture was spun at 3,800 rpm for ten minutes. Three times of centrifugation were done after ultrapure water was used to clean the dry phase. The finished clay-TiO_2 mix was mixed in a solution of 1:1 water to ethanol. It was then heated at 180 °C for five hours in an autoclave to treat it hydrothermally. The item was spun at 3,800 rpm for another 15 minutes and then dried

in a 60 °C oven for 3 hours (Undabeytia et al., 2021).

Instrumental Characterizations

For X-ray diffraction (XRD) measurements, a Philips diffractometer made by the "X" company was used with radiation that was monochromatized Cu K± (λ=1.54060 Å). Scherrer's analysis of X-ray diffraction (XRD) is a widely employed method for the assessment of crystallite size. All absorbance measurements in the range of 200 nm to 800 nm were conducted using a Jascow-500 double-beam UV-Vis spectrophotometer equipped with quart cells with an optical path length of 1 mm. The scanning electron microscopy (SEM) image was acquired using the HITACHI-S-3400H model. The transmission electron microscopy (TEM) investigation was conducted using a Philips CM-200 electron microscope, which operated at a voltage of 200 KV and had a resolution of 2.4 Å. Atomic force microscopy (AFM) provides exceptional precision in the determination of particle sizes, operating by physically scanning materials at a sub-micron scale with a probe tip of atomic dimensions.

Photocatalytic activity of Nanocomposites

Methylene blue dye solutions are prepared and introduced into a UV multilamp photoreactor tube. The dye solution was supplemented with the necessary quantity (20 mg) of produced material. To achieve adsorption-desorption equilibrium, the dye solutions were dark-conditioned for thirty minutes prior to irradiation. It was then stored for 30 minutes within the UV multilamp photoreactor. Prior to the UV-visible absorption tests, the collected liquid underwent centrifugation and filtration. The following formula was used to predict the dye's rate of degradation,

$$Removal\ percentage\ (\%\ R) = [C_i - C_f / C_i] \times 100 \quad \text{----------(1)}$$

Where, C_i and C_f is the initial and final dye concentration in ppm at a given time.

Results and Discussion

XRD analysis of TiO_2/Kaolinite Nanocomposites

Fig. 1 displays the XRD pattern of the TiO_2/Kaolinite nanocomposites made using a solvothermal technique. The (101), (004), (200), (105) and (204) planes are given to the sharper and stronger diffraction peaks in Figure 1. These peaks are found at 25.5°, 37.8°, 47.9°, 53.59°, and 62.36°. The X-ray diffraction pattern exhibited a high degree of concordance with the JCPDS file 21-1272, indicating that all the peaks observed can be attributed to the presence of anatase phases of titanium dioxide (Baltabayeva et al., 2021; Damkale et al., 2021). The high purity of the nanocomposite samples is indicated by the absence of any further impurity peaks. The resulting products exhibit high crystallinity, as seen by the strong and crisp diffraction peaks. This finding confirms that clay/metal oxide development is occurring. The dimensions of nanocomposites were determined using the Debye-Scherrer formula. The size of the crystals was determined to be 81.61 nm.

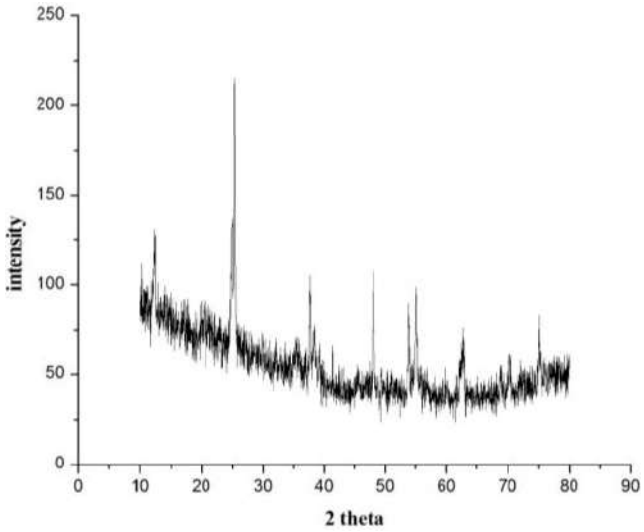

Fig.1. XRD pattern of TiO_2/Kaolinite nanocomposites

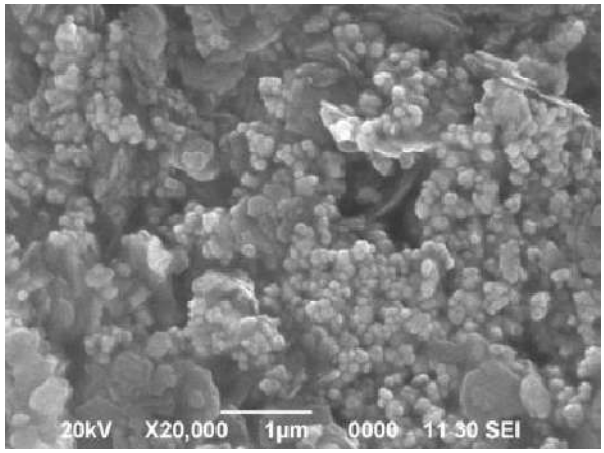

Fig.2. SEM image of TiO_2/Kaolinite nanocomposites

SEM with EDAX analysis of TiO_2/Kaolinite Nanocomposites

The morphological surface of TiO_2/Kaolinite nanocomposites was examined using SEM. The nanocomposites in Fig. 2 SEM picture have an agglomeration nanocomposites shape and are generally spherical and spongy. The sample under investigation's SEM picture demonstrated a matrix made up of sub-micron TiO_2 particles adhered to the clay matrix's surface and micro-sized kaolinite particles with a layered structure. The SEM images of the proven matrix, which included sub-micron TiO_2 particles adhered to the clay matrix's surface and microsized kaolinite particles with a layered structure, were reported by (Samuvel Raj et al., 2023). Musial et al., (2020) also reported the similar observation. An EDAX spectrum of the material is shown in Fig.2a. These studies using EDAX show that the sample has the right amounts of Ti, O, Al, and Si in prepared sample was recorded in elemental composition analysis.

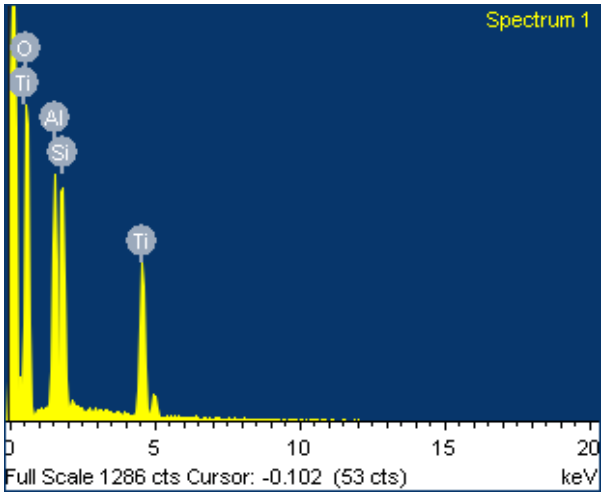

Fig.2.a. EDAX image of TiO2/Kaolinite nanocomposites

AFM analysis of TiO_2/Kaolinite Nanocomposites

An essential tool for any study on nanoscale phenomena is AFM. The figure shows the AFM picture of metal oxide/clay nanocomposites that were created using a solvothermal process (Fig.3). For this sample, the micrograph at 5 µm × 5 µm shows a consistent distribution of cone-shaped grains covering the nanocomposites surface. The particle's homogeneous dispersion and nanometer-sized size have been noted. Using AFM

investigation, the surface roughness, heights, and RMS average value were ascertained. The XRD result and the metal oxide/clay nanocomposites are in good agreement. The very uniform distribution of spherically shaped particles was observed by (Asamoah et al., 2020; Joudeh & Linke, 2022). The statistical roughness analysis (CSPM) showed that the surface skewness was -0.0806, the surface kurtosis was 2.47, the average roughness was 0.422 nm, and the root mean square roughness was 0.513 nm.

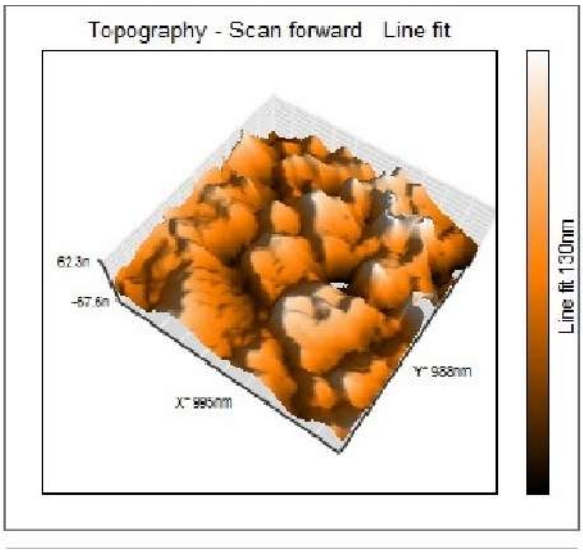

Fig.3. AFM image of TiO_2/Kaolinite nanocomposites

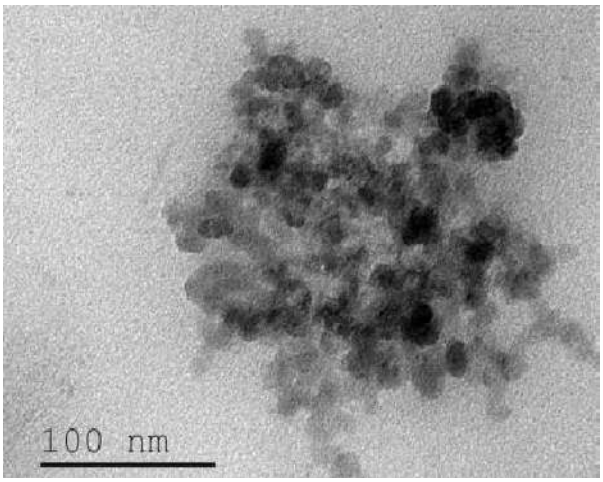

Fig.4. TEM image of TiO_2/Kaolinite nanocomposites

TEM analysis of TiO_2/Kaolinite Nanocomposites

Confirmation of the particle size, growth pattern, and crystallite distribution was achieved using transmission electron spectroscopy investigation. A representative TEM picture of the TiO_2/Kaolinite nanocomposites is shown in Fig. 4. The particles' comparatively homogeneous particle size distribution is evident. Based on the TEM picture, the nanocomposites' average size is approximately 50 nm.

UV-Vis Absorption Spectroscopy

Figure 5 displays the UV-Vis absorption spectrum of TiO_2/Kaolinite nanocomposites. The absorption characterisation of nanoparticles is a valuable tool. The wavelength range for the UV-Vis spectral study was 200–800 nm. Using the following formula (Agustina et al., 2021), we can find the optical band gap (Eg) with the use of absorption spectroscopy.

$$\alpha = (h\nu - Eg)/2h\nu \quad \text{..... (2)}$$

In this context, the symbol $h\nu$ represents the energy of a photon, while α and n are constants. In the case of a direct energy gap, the value of n is 2, while for an indirect energy gap, the value of n is ½.

TiO_2/Kaolinite nanocomposites exhibit a blue shift in the absorption edge and a corresponding band gap of 3.3 eV, as illustrated in Figure 5.a. The produced TiO_2/Kaolinite nanocomposites have band gap energy of 3.3 eV, which is higher than the 3.2 eV value of the bulk TiO_2. This makes sense because it has been discovered that the semiconductor's band gap depends on particle size

(Almatroudi, 2020). Comparing these nanocomposites to bulk TiO_2, they exhibit blue shift, or increased energy. The structural flaws in nanomaterials and the influence of nanosize may be the source of the blue shift (D. Li et al., 2020).

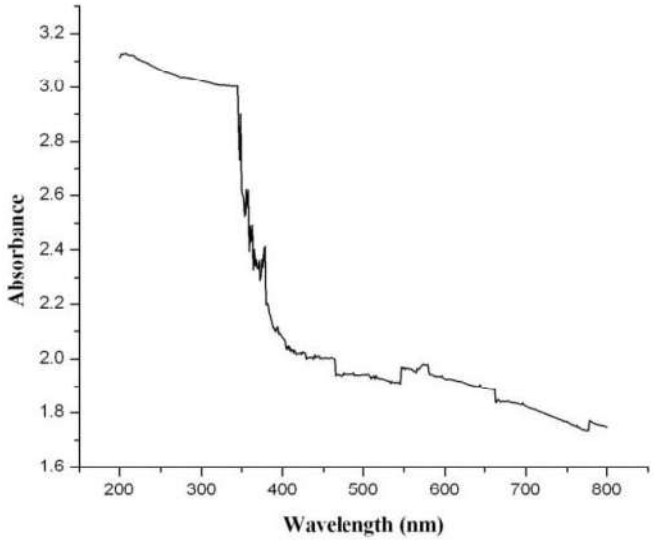

Fig.5. UV-Vis absorption spectrum of TiO_2/Kaolinite nanocomposites

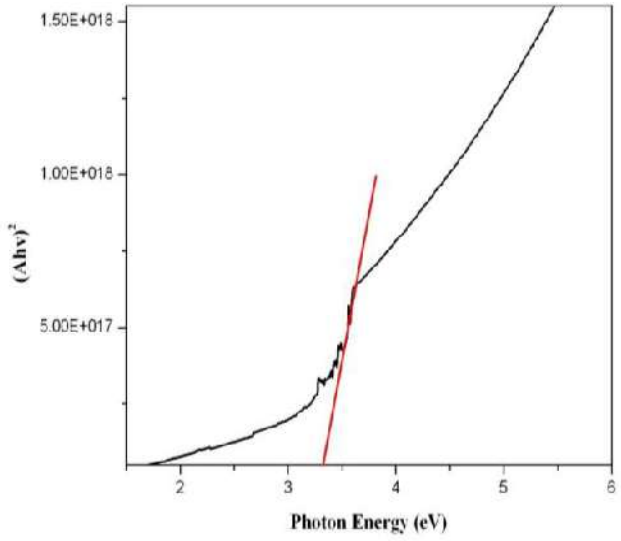

Fig.5.a. Band gap energy of TiO_2/Kaolinite nanocomposites

Photocatalytic activity of TiO_2/Kaolinite Nanocomposites

Effect of contact time

Figure 6 illustrates the way time variation affects MB dyes. The percentage of dye removed also rises with time. Based on the experimental findings, it can be observed that the photocatalytic degradation of MB dye exhibits a tendency to adhere to pseudo-first-order kinetics, with the following equation providing the rate expression:

$$\ln (C_o/C_t) = kt \quad \text{.....} \quad (3)$$

Where, C_o = initial concentration of the dye

C_t = final concentration of the dye in various time interval.

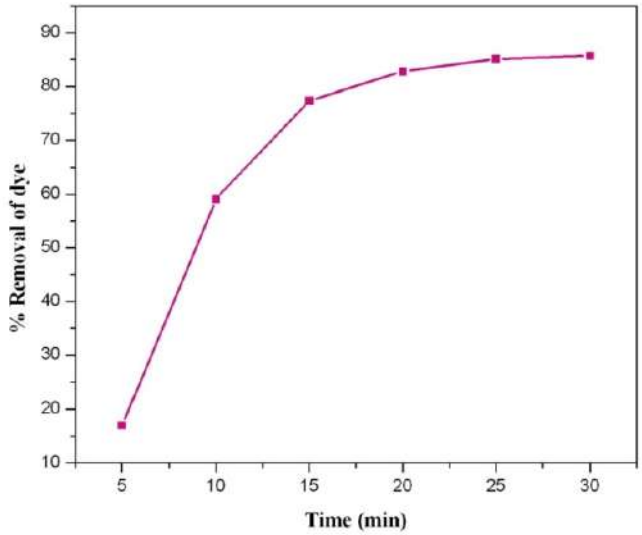

Fig.6. Effect of Contact time

Effect of pH

The pH levels of waste water from the textile industry typically vary greatly. Moreover, pH influences the production of hydroxyl radicals .For MB dye, the pH ranges from 3 to 11. TiO_2 has a

zero point charge of 6.25. Increases in MB dye pH from 3 to 11 resulted in better percentage elimination (under fundamental conditions). The catalyst's surface will become negatively charged in this state. Therefore, the catalyst readily attracted the MB dye. The illustration appears in Fig.7.

Effect of Dose Variation

Catalyst concentrations ranged from 12 mg to 20 mg. Figure 8 shows that as the amount of photocatalyst climbed, the efficiency seemed to go up. This is likely because there were more active sites for the photocatalytic reaction on the surface. When the photocatalyst is overdosed, however, the number of active sites on its surface may stay about the same. This is because more light is scattered, less light can pass through, and the surface area is lost because of solids sticking together at high concentrations.

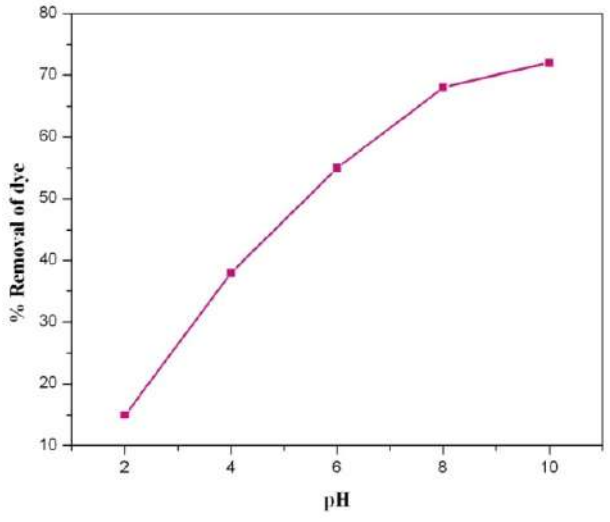

Fig.7. Effect of pH on MB dye

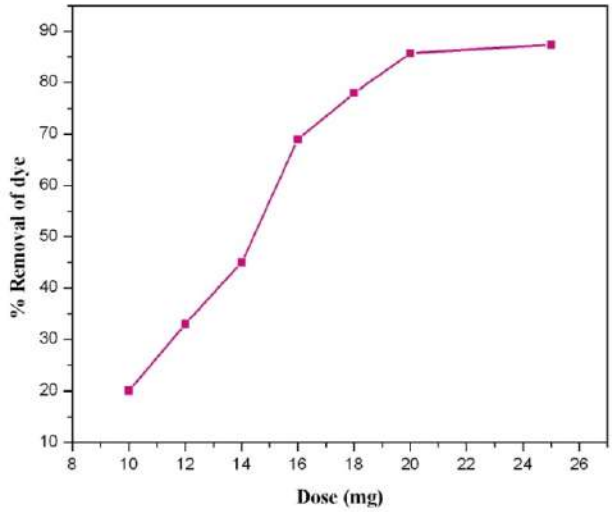

Fig.8. Effect of different dose concentrations of photocatalytic reaction

Effect of concentration of dyes

Under UV light systems, methylene blue was photocatalytically decolored at varying starting concentrations ranging from 10 ppm to 50 ppm. The percentage of elimination reduced as dye molecule concentrations increased. Because of the surface of the photocatalyst absorbs a greater quantity of dye molecules. As a result, the photon entry channel will be shortened. The methylene blue dyes' breakdown, as depicted in fig. 9.

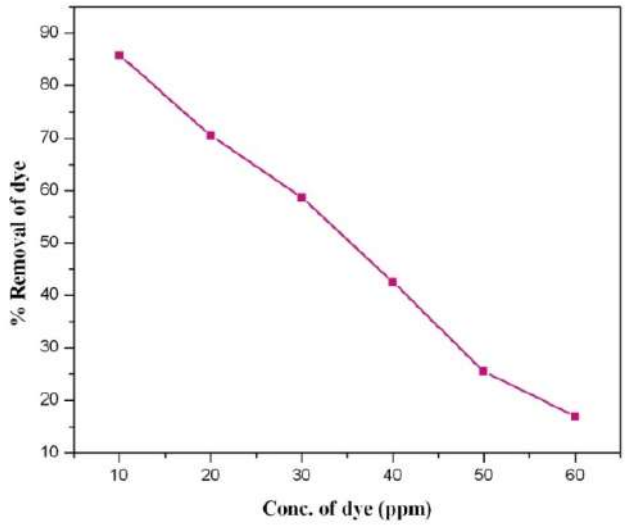

Fig.9. Effect of Initial Concentration of dye

Conclusion

Overall, the synthesis of titanium dioxide/kaolinite nanocomposites has been effectively achieved by the solvothermal approach. The produced nanocomposites underwent characterization using a range of analytical techniques, including X-ray diffraction, scanning electron microscopy with energy-dispersive X-ray spectroscopy, atomic force microscopy, transmission electron microscopy, and ultraviolet-visible absorption spectroscopy. The X-ray diffraction analysis indicated the existence of the anatase crystalline phase of titanium dioxide (TiO_2). The samples were subjected to characterization in terms of their size and morphology by the utilization of scanning and transmission electron microscopy techniques, respectively. The composite material exhibits band gap energy of 3.3 eV, surpassing the bulk TiO2's value of 3.2 eV. The nanocomposites exhibit a blue shift, indicating a higher energy state in comparison to the bulk TiO_2. The data obtained from the decolorization reactions of the metal oxide/clay nanocomposite demonstrated a good fit with the pseudo-first-order kinetic model. The investigation indicates that the materials obtained possess significant utility in the field of water treatment.

Acknowledgement

The authors' thankful to the Department of Chemistry, Merit Arts and Science College Idaikal, Tamil Nadu, for providing necessary facilities for carried out of this work.

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