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Adsorption Studies on Removal of Malachite Green Dye by French Green Clay-MnO2 Nanocomposite

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Abstract

The contamination of water bodies with artificial dyes causes serious health and ecological concerns. The discharge of dyes into water systems from various industries, including textiles, paper, and others, causes significant ecological disturbances and poses health risks to humans. This study deals with the development of eco-friendly Nano composite made with French green clay and MnO2 and to examine the potential of composite for Malachite green (MG) removal. The composite's adsorptive capabilities are improved by the addition of MnO_2, while the French green clay serves as a stable matrix. The various material characterization technique was employed for both French green clay and of the Nano composite sample before and after adsorption of MG dye. X-ray diffarction (XRD), scanning electron microscopy (SEM), and Fourier Transform Infrared (FT-IR) analysis were all employed to characterize the crystalline nature, surface morphology and functional groups of the nanocomposite thoroughly. The operational parameters such as effect of time and adsorbent dosage were investigated. According to the results, French green clay-MnO2nanocomposite act as an effective and environmentally friendly adsorbent for MG dye removal.

Keywords: French green clay-MnO2 nanocomposite, Dye removal, FT-IR, SEM and XRD techniques.

1. Introduction

The enormous industrialization of the current century has presented substantial environmental issues, notably in the management of wastewater that contains hazardous contaminants. Specifically, man-made dyes utilised in leather, textile, paper, and cosmetic sectors pose significant challenges because of their intricate chemical compositions, which are resistant to biodegradation and persist in the environment for prolonged period of time (Younis et al.2021). These pigments not only provide colour to bodies of water but also obstruct the passage of sunlight, therefore disturbing aquatic ecosystems and causing a decrease in oxygen levels in the drinking water (Saad and Atia, 2014). Furthermore, numerous dyes have poisonous, mutagenic, or carcinogenic properties, so presenting significant hazards to both human health and the atmosphere (Gupta and Suhas, 2009). The textile industry generates significant quantities of chemicals that are exceedingly hazardous, and these chemicals are subsequently released at various phases of the processing lifecycle (Kishor et al.2021). Moreover, it is widely

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recognized that textile dyes, if not adequately processed, pose substantial eco-toxicological risks to living species (Lou et al.2021). Malachite green (MG) is one of the synthetic dye belonging to the triphenylmethane class of dyes. It is highly soluble in water and is primarily used in aquaculture, textile, and paper industries but it can be very harmful to health and the environment. It has been found to cause cancer, damage organs like the liver and kidneys. It also harms the immune system and damage cells by casing oxidative stress. It kills small fish and other aquatic animals in the water bodies (Srivastava et al.2004).

Adsorption is widely acknowledged as a very efficient and versatile technique for eliminating dyes, offering advantages such as low operational costs, simplicity, and immense efficacy (Mudhoo et al.2020). The evolution of novel adsorbents with enhanced surface properties and adsorption capacities is crucial for improving the effectiveness of this technique. Currently, the substitution of artificial adsorbents with unconventional and economically viable materials has emerged as a focused area of study and development (Eletta et al. 2018). The principal benefit of adsorption in the context of wastewater treatment is in its comparatively economical nature and robust efficacy in removing contaminants. Adsorbents effectively capture deleterious elements by means of intermolecular forces acting on the surface of the adsorbent material. Thus, additional treatment procedures are used to achieve thorough cleansing of water resources (Pan et al.2020).

Nanocomposites, which integrate the distinctive characteristics of nanoparticles with traditional materials, are a highly promising category of adsorbents. The incorporation of metal oxides into clay matrices has shown significant potential for improving the adsorption of pollutants from water (Joshi et al.2020). French green clay, a natural substance composed primarily of iron oxides and trace minerals, has been studied for its soft, fine texture, and relatively high surface area, making it a potential substance for adsorption applications. Nevertheless, the adsorption capability of the material could be further improved by its combination with manganese dioxide (MnO_2), a metal oxide renowned for its exceptional adsorption and oxidative characteristics. The extensive application of MnO_2 in the elimination of organic pollutants and heavy metals can be attributed to its capacity to engage in redox reactions and establish robust surface complexes with contaminants (Anujam et al. 2023). This research presents the environmentally feasible production of French green clay-MnO_2 nanocomposite specifically developed to function as an extremely efficient adsorbent for the removal of hazardous dyes such as MG.

2. Methods

2.1 Preparation of French green clay- MnO2 Nanocomposite

The French green clay was rinsed with double distilled water to eradicate dirt and other impurities. Then, 15 g of French green clay was dispersed in 75 ml of ethanol for 3 hours at ambient temperature to get a homogeneous suspension. Then, 15 g of MnO_2 was mixed with 75 mL of ethanol. Following that, the diluted MnO_2 was progressively disseminated into the clay suspension and agitated continuously for 7 hours at room temperature. Eventually, a 10mL volume of ethanol was combined with 1mL of distilled water and then gradually poured into the clay-MnO2 matrix. Furthermore, the stirring process was carried out at ambient temperature for an additional period of six hours. Following centrifugation, the final suspension was repeatedly rinsed with double distilled water. Following a 24-hour drying period in a vacuum oven set at 90°C, the cleaned product was then cooled to room temperature. The desiccated composite was subsequently pulverized to a fine powder using a crusher or stone. The homogenous particle size was achieved by sieving the fine powder. The final product, which was designated as French green clay-MnO2nanocomposite, was stored in a sealed tight container for future use.

3. Result and Discussion

3.1 Adsorption Studies for the Removal of Dyes

3.1.1 Effect of Contact Time

The dye solution of appropriate concentration was agitated with 0.5g/L of French green clay-MnO2 nanocomposites at 30 C for various intervals of time in a magnetic stirrer. The percentage of adsorption shows an increasing trend on increase of contact time and reached equilibrium after 60 min.

S.No	Time (min)	Optical density	% dye degradation
1	0	0.998	–
2	10	0.180	81.96
3	20	0.157	84.27
4	30	0.145	85.47
5	40	0.116	88.38
6	50	0.114	88.58
7	60	0.005	99.53

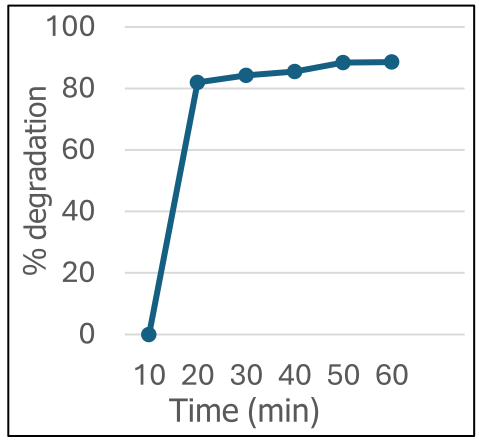


Fig 3.1: Effect of contact time on % dye degradation

At the beginning adsorption rate is faster as the dye ions are adsorbed by the exterior surface of the French green clay-MnO2 nancomposite. When the adsorption of the exterior surfaces reaches saturation, the ions exerted onto the pores of the adsorbent and are adsorbed by the interior surface of the particle. This phenomenon relatively takes long contact time.

3.1.2 Effect of Adsorbent Dose

Dye solution of appropriate concentration was agitated with variable amount of French green clay-MnO2 nanocomposites (0.2 to 1.0 g/L) for 45 minutes at room temperature (30C). It shows that percentage removal of Malachite green increases with increase in French green clay-MnO2 nanocomposite.

Adsorbent Dosage (g)	Optical Density	% Dye Degradation
0.2	0.593	44.84
0.4	0.382	60.62
0.6	0.115	88.58
0.8	0.005	99.53
1.0	0.004	99.61

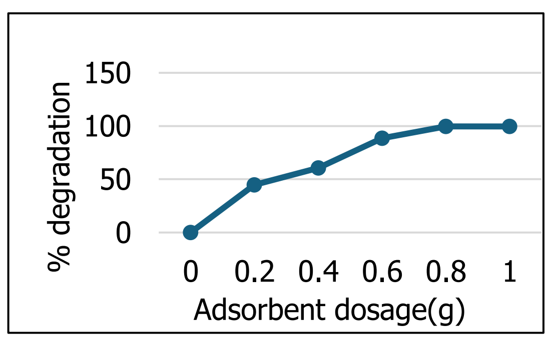


Fig 3.2: Effect of Adsorbent Concentration

3.2 Characterization

3.2.1 French green clay and Nanocomposite

The various material characterization technique was employed both French green clay and Nanocomposite sample for the confirmation of French green clay-MnO2 nanocomposite.

X-Ray Diffraction (XRD) Analysis

The crystallographic phase of French green clay and French green clay-MnO2 nanocomposites was identified using X-ray diffraction analysis. Fig (3.2.1a) and (3.2.1b) show XRD examinations of French green clay and French green clay-MnO2 nanocomposite, which demonstrate crystalline structures and variations in diffractions patterns after adding MnO2.

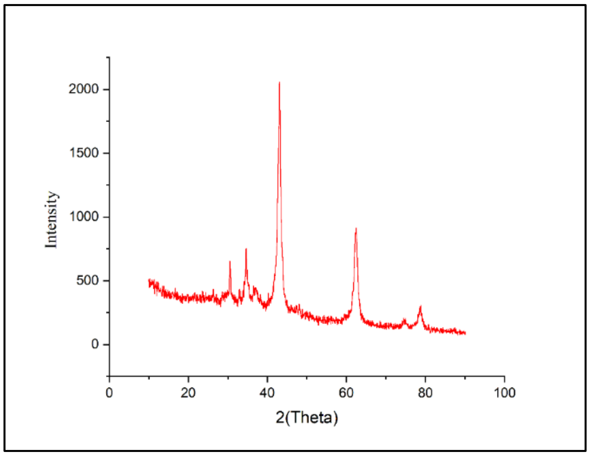


Fig3.2.1 a: XRD analysis of French clay

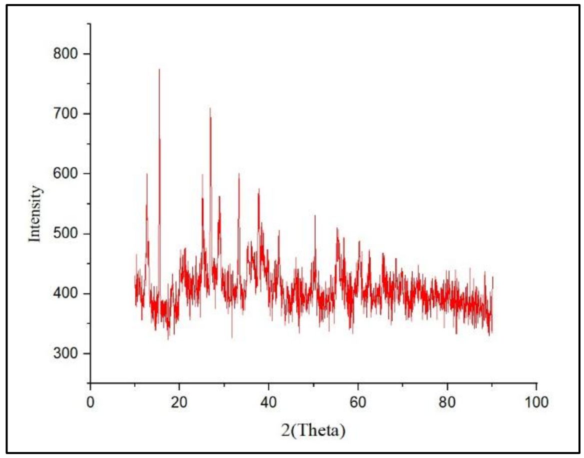
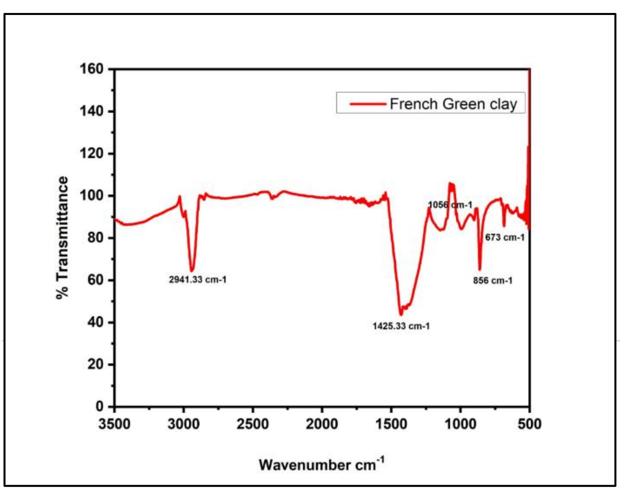


Fig 3.2.1 b: XRD analysis of nanocomposite

The XRD configuration of the French green clay exhibits distinct peaks and indicates belonging to the tetragonal structure. The existence of these distinct peaks verifies the integrity and crystalline structure of the French green clay. Significant alterations were observed in the XRD pattern of the resulting nanocomposite after the integration of MnO2 nanoparticles into the French green clay matrix. Several new peaks associated with MnO2 were detected in the XRD pattern, providing confirmation of the effective amalgamation of MnO2 into the clay matrix. The widening of these peaks indicates the presence of MnO2 nanoparticles with fine crystalline dimensions, a characteristic feature of nanocomposites and beneficial for improving the adsorption surface area.

Fourier Transform Infrared (FT-IR) Analysis

The FT-IR spectra of French green clay and French green clay-MnO2 nanocomposites were examined to determine the existence of particular functional groups. The FT-IR spectra of French green clay and French green clay-MnO2 nanocomposite are shown in fig (3.2.2 a) and (3.2.2 b), which show the unique functional groups and changes in the chemical structure after MnO2 is added.



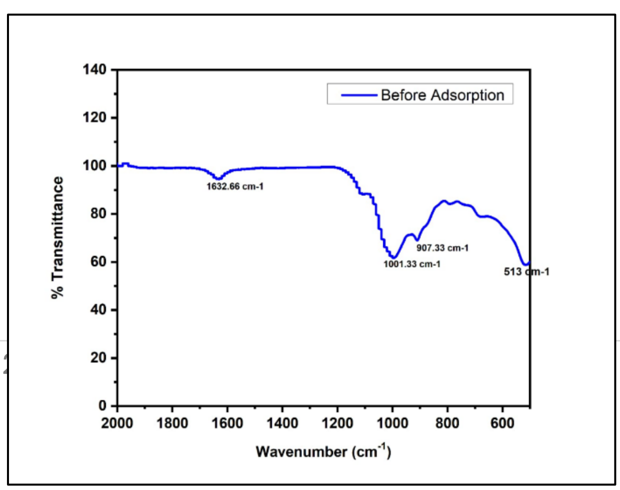
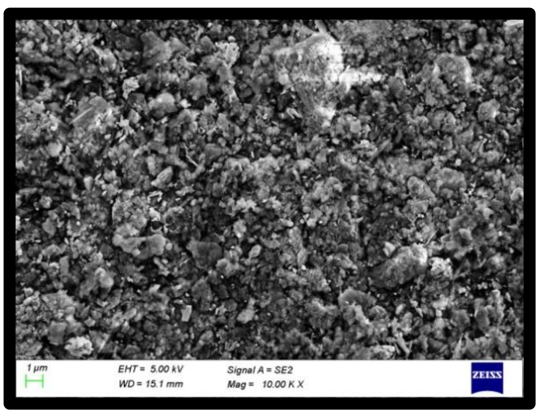


Fig 3.2.2 a: FT-IR analysis of French clay **Fig 3.2.2 b**: FT-IR analysis of nanocomposite

The adsorption band in French green clay which is situated between 3500 cm-1 and 3000 cm-1, is a result of the -OH stretching vibration of the water molecule. This band was relocated to 2000 cm-1 to 1400 cm-1 in the French green clay-MnO2 nanocomposite. Appearance of new bands around 500-600 cm-1, corresponding to Mn-O vibrations, confirm the presence of manganese oxide nanoparticles. Slight modifications in Si-O and Al-OH bands also occur due to surface modification and structural interaction with MnO2. The interaction between MnO2 nanoparticles and the clay matrix is evident from changes in hydroxyl and silicate vibration regions, as well as the appearance of Mn-O bands.

Scanning Electron Microscope (SEM)

SEM illustrations of the samples using French green clay and the SEM images of French green clay-MnO2 nanocomposites are shown in Fig (3.2.3a) and (3.2.3b), respectively, which illustrate the surface morphology and structural changes after MnO2 incorporation.



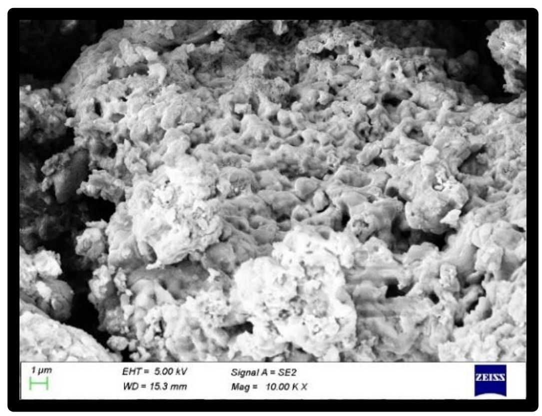


Fig 3.2.3 a: SEM image of French clay **Fig3.2.3 b:** SEM image of nanocomposite

The surface alterations are observed in the French green clay-MnO2 nanocomposite in comparison to French green clay. French green clay was composed with a variation of irregular sizes and shapes of flakes, as well as damaged margins. This structure was compact and dense, suggesting a high level of crystallinity in the particles. This is a characteristic of natural clay materials, as the surface appeared to be flat with some minor porosity. The nanocomposite surface appeared to be more porous and uncovered, which allowed for a greater degree of dye adsorption. The French green-MnO_2 nanocomposite exhibited substantial alterations in surface morphology when contrasted with the purified stishovite clay, as evidenced by the SEM images.

The surface was more heterogeneous and had a significant increase in surface roughness as a consequence of the incorporation of MnO_2 nanoparticles. Small, uniformly distributed concentrations of MnO_2 nanoparticles were observed on the surface of the French green clay particles. These nanoparticles contributed to a more porous and irregular surface, which is advantageous for improving the composite's adsorption capacity. An increase in surface area is indicated by the alteration in surface morphology, which is characterized by the formation of nanostructures.

3.2.2 Before and After adsorption of the Dye

The French green clay-MnO2 nanocomposite was characterized before and after adsorption of the Malachite green dye.

X-Ray Diffraction (XRD) Analysis

Fig (3.2.4 a) and (3.2.4 b) shows the XRD analysis of the nanocomposite before and after adsorption of Malachite green dye. The basal reflection of nanocomposite is slightly shifted to different angles, suggesting intercalation of dye molecules into the interlayer spaces of the nanocomposite. A reduction in intensity or broadening of the MnO2 peaks occurred, due to surface coverage or slight amorphization caused by dye degradation.

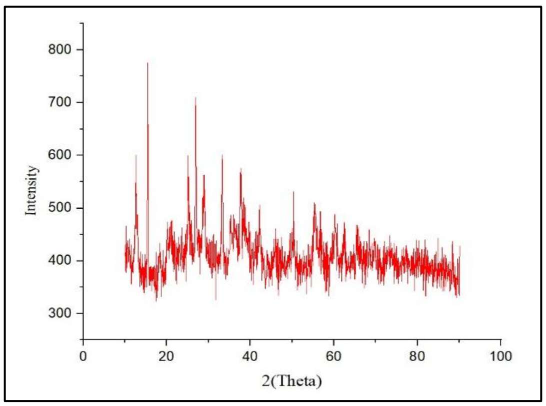


Fig 3.2.4 a: XRD analysis Before Adsorption

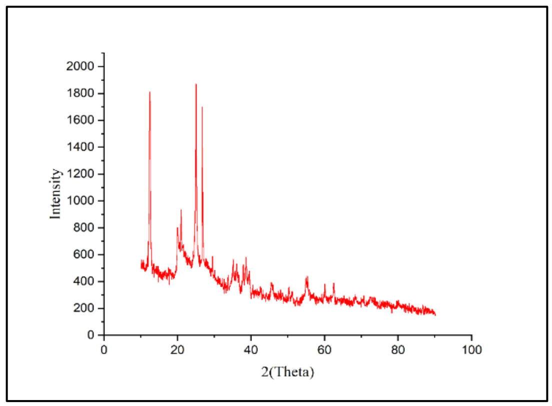


Fig 3.2.4 b: XRD analysis After Adsorption

Fourier Transform Infrared (FT-IR) Analysis

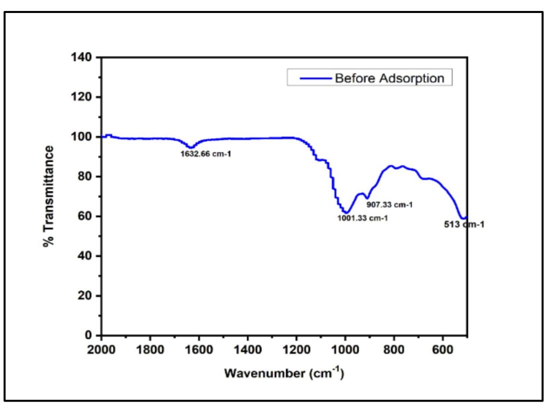


Fig 3.2.5 a: FT-IR analysis Before Adsorption

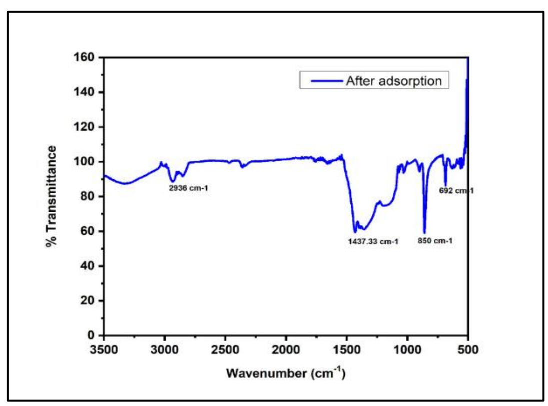


Fig 3.2.5 b: FT-IR analysis After Adsorption

The Fig (3.2.5 a) and (3.2.5 b), FT-IR spectrum of prepared French green clay-MnO2 nanocomposite shows all the major bands of French green clay-MnO2. The bands before 16301/cm were due to O-H stretching of hydroxyl groups. The peak presented at 1630 cm-1 is attributed to Si-O stretching from the clay layers. The peak 910 cm-1 is attributed to Al-OH bending. Dye adsorbed French green clay-MnO2 nanocomposite gives different spectrum compared with un-adsorbed French green clay-MnO2 nanocomposite. New peaks at 1600 cm-1 correspond to C=C stretching of the aromatic rings from Malachite green. The peak 1480 cm-1 indicates C-N stretching vibrations from the dye's amine group. The peak 1350 cm-1 indicates Methyl bending vibrations from the dimethyl-amino group of Malachite green.

Scanning Electron Microscope (SEM)

The French green clay-MnO2 nanocomposite is analysed by SEM, before and after adsorption of Malachite green dye. The French green clay-MnO2 nanocomposite has heterogenous surface, micro-pores and meso-pores as seen from its surface micrographs. The aggregates of dye molecules are visible on the surface as amorphous or thin film-like layers. The flake structure after adsorption of the Malachite green dye appear on French green clay-MnO2 nanocomposites. Fig (3.2.6 a) and (3.2.6 b) indicate the surface morphology of nanocomposite before and after adsorption of the dye.

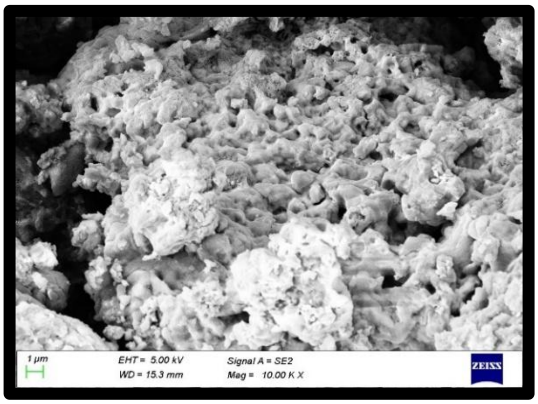


Fig 3.2.6 a: SEM image before adsorption

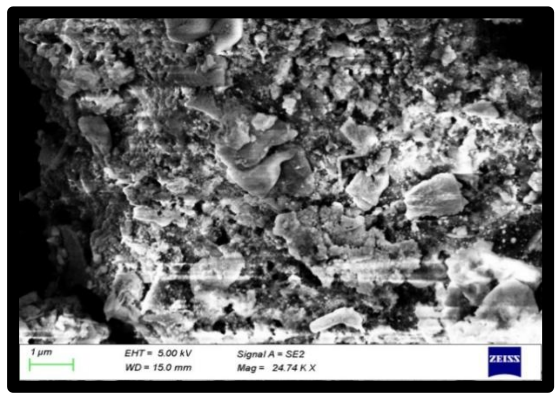


Fig 3.2.6 b: SEM image after adsorption

4. Conclusion

The subsequent inferences were arrived based on the experimental studies:

➤ The rate of adsorption increases with increases in contact time and reaches a limiting value. Percentage of dye degradation increases with increase in time.

➤ The rate of adsorption also increases with increase in adsorbent dosage.

➤ SEM images shows that adsorption is happening in the surface of the adsorbent and the images also demonstrated a substantial alteration in surface morphology and the formation of nanoscale MnO2 particles, which improved the composite's porosity and surface area.

➤The effective integration of MnO2 into the French green clay matrix was confirmed by FT-IR spectra and the nanocomposite shows different spectrum of FT-IR, before and after adsorption of the dye.

➤The crystalline nature of the French green clay and the incorporated MnO2 nanoparticles was verified by the XRD analysis. It also confirms the adsorption of Dye by the nanocomposite.

➤ The research findings revealed that the French green clay-MnO2 nanocomposite has the potential to be an environmentally friendly and efficient material for environmental remediation. It effectively removes dyes from aqueous solution.

➤ At a short period of time, adsorption happens. This shows that adsorption is an efficient process for the removal of dyes from aqueous solution.

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