

EFFICIENT PHOTOCATALYTIC ACTIVITY AND DEFLUORIDATION STUDIES OF METAL OXIDE/CLAY NANOCOMPOSITES

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ABSTRACT

In this work, we report the efficient photocatalytic activity and removal of fluoride from wastewater using metal oxide/clay nanocomposites. The nanocomposites were characterized by using XRD, SEM with EDAX, AFM, TEM, and UV-Vis absorption spectroscopy. The structural properties of nanocomposites have been characterized by X-Ray Diffraction (XRD) analysis. The surface morphology of the nanocomposites was analyzed by SEM and AFM analysis. Absorption spectra have been obtained using UV-Vis spectroscopy to find the optical band gap. In addition, photocatalytic degradation of methylene blue in an aqueous solution was performed using metal oxide/clay nanocomposites under the illumination of UV light.

Keywords: Nanocomposites, Methylene Blue, Band gap, Metal oxide, Clay.

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INTRODUCTION

The new nanomaterials are a variety of exciting applications and are also used widely in various fields including electronics, energy storage, biosensors, and biomedicine.¹Nanotechnology is one of the most dynamic research areas because of its unique physicochemical characteristics such as catalytic activity, optical, electronic, magnetic properties, and biomedical uses. A number of methods are available for the preparation of pure and doped metal oxide nanomaterials, like hydrothermal, hydrolysis, sol-gel, vapor condensation, spray pyrolysis, and organic precursor flame decomposition, metal oxide chemical vapor deposition, coprecipitation, microemulsion². At present, nano semiconducting materials play an important role in predicting new features and potential applications in a variety of industries.³Industrial activities contaminate water reservoirs with hazardous chemicals, like heavy metals (Pb^{2+} , Cd^{2+})⁴ dyes⁵, fluoride, and so forth.⁶Fluorine is one of the 14 necessary elements of the human body. Fluoride has a positive effect to humans in a certain concentration, but excess fluoride intake is harmful to humans and aquatic organisms.⁷ Therefore, the removal of fluoride ions from polluted water is extremely important to the environment and human health protection. Now a day, great attention has been paid to the treatment of high fluoride water and researchers have conducted various investigations to develop effective ways to get rid of fluoride from polluted water. The most usual treatment methods for fluoride polluted water include chemical precipitation, flocculation precipitation, electro-coagulation, membrane separation, adsorption, and ion exchange.⁸⁻¹⁷ Among them, adsorption is a relatively convenient and cost-effective way that will remove fluoride from polluted water.¹⁸⁻¹⁹ Colour is taken into account because the first pollutant to be identified in wastewater and it is mostly caused by the effluents discharged from dyeing industries like paper, rubber, leather, cosmetics, textile, pharmaceuticals, plastics, and food industries.²⁰ When these colored effluents enter rivers or any surface water system they upset biological activity. Groundwater systems also are suffering from these pollutants due to leaching from the soil. Hence, the removal of dyes from wastewater is important to stop continuous environmental pollution. Our research

work is to synthesize metal oxide/clay nanocomposites via the solvothermal method. The nanocomposites were used to remove the dye and to remove fluoride. In our previous work, we have reported the synthesis, characterization, and antibacterial activity of titanium dioxide/illite nanocomposites.²¹

EXPERIMENTAL

Synthesis of Metal Oxide/Clay Nanocomposites

Illite-water dispersion (1% w/w) was stirred for two hours. An aliquot of titanium dioxide sol was added to the above solution, to get a final TiO₂ content of 70% w/w. The obtained mixture was stirred for twenty-four hours. The resulting dispersion was centrifuged at 3,800 rpm for ten minutes. The solid phase was washed with double distilled water followed by triplicate centrifugation. The resultant Titanium dioxide/Illite composite was dispersed in 1:1 water: ethanol solution, prior to hydrothermal treatment in an autoclave at 180°C for 5 hours. The product was centrifuged once again at 3,800 for 15 minutes and oven-dried at 60°C for 3 hours.²²

RESULTS AND DISCUSSION

XRD Analysis of TiO₂/Illite Nanocomposites

The X-ray diffraction of the nanocomposites was obtained by the solvothermal method, which is shown in Fig.-1. The XRD spectra suggested that the crystalline nature with 2θ peaks lying at 2θ=25.25° (101), 2θ=37.8° (004), 2θ=47.9° (200), 2θ=53.59° (105) and 2θ=62.36° (204). The preferred orientation like the plane (101) is observed. All the diffraction peaks in the XRD spectra have been indexed as anatase phases of TiO₂ and the diffraction data were in good agreement with JCPDS files 21-1272.²³

$$D = 0.94\lambda / \beta \cos\theta$$

The synthesized nanocomposite size was calculated by the Debye Scherrer equation and the value of 81 nm was observed. No characteristic peaks are detected for the rutile phase, brookite phase, or any impurities. The XRD pattern of the TiO₂ annealed at 500°C shows the diffraction pattern characteristic of the anatase crystalline phase. A major peak corresponding to 101 reflections of the anatase phase of TiO₂ was apparent at the angle of 29.45°. The XRD results are in coincide with other papers dedicated to TiO₂ reported by Karen *et al.*²⁴

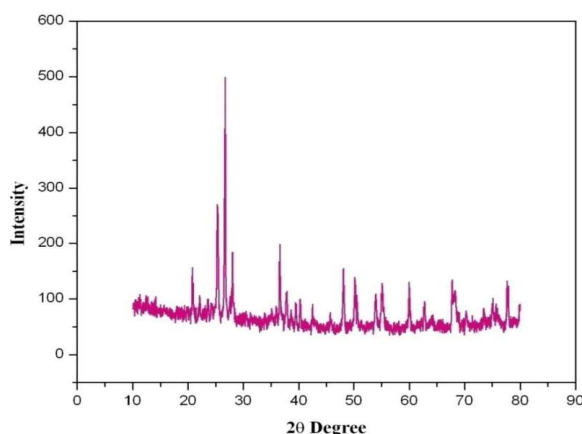


Fig.-1: XRD pattern of TiO₂/Illite Nanocomposites

SEM With EDAX Analysis of TiO₂/Illite Nanocomposites

The scanning electron microscopy was discussing the surface morphology of synthesized nanocomposites. The SEM image of the nanocomposites has a spherical shape and is well dispersed as shown in Fig.-2.a. The SEM image of the synthesized nanocomposites was proved matrix consisting of micro-sized illite particles having a layered structure with a sub-micron particle of TiO₂ attached on the surface of the clay matrix. The synthesized nanoparticles have a spherical shape with good dispersion. Less agglomeration of nanoparticles also appeared this might be due to aggregation of primary TiO₂ particles at high calcination temperature which is important to accelerate the crystal growth of titanium dioxide was reported by Sajaet *al.*²⁵ The chemical element composition of the as-grown TiO₂/Illite

nanocomposites was researched by X-ray energy dispersive spectroscopy and its spectrum is shown in Fig.-2b. It showed that the samples primarily contain Ti, O, K, Fe, Si, and Al. The result of EDAX also indicates the presence of TiO₂/Illite nanocomposites. In another case, Vijayalakshmi *et al*²⁶ investigated the SEM images of the nanoparticles prepared via sol-gel and hydrothermal. The SEM image has Clear nanostructures that can be seen having a grain size of ~ 30 nm. The synthesized crystallite size observed from TEM, in this case, is ~ 8 nm. This showed that one grain in sol-gel-derived nanoparticles is approximately equal to three crystallites. So it is clear that the nanoparticles seen by the SEM image contain a variety of crystallites that are seen by the TEM image.

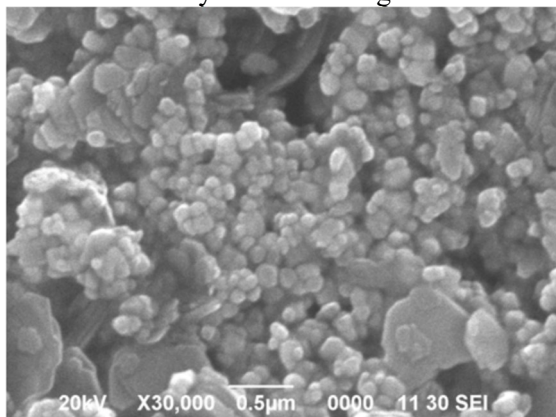


Fig.-2a: SEM image of TiO₂/Illite Nanocomposites

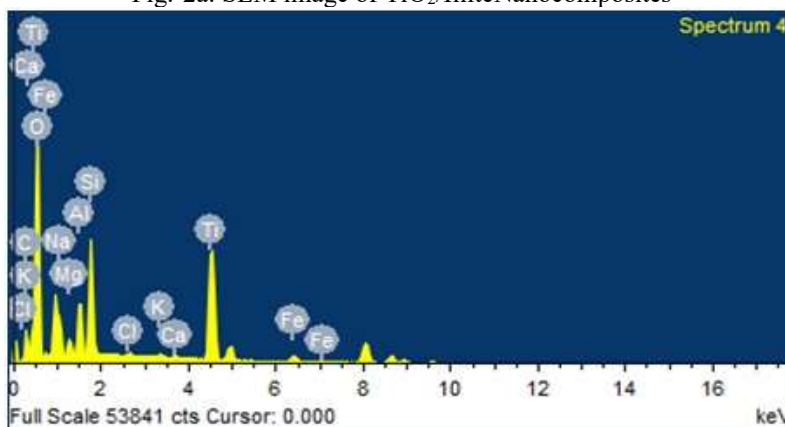


Fig.-2b: EDAX Image of TiO₂/Illite Nanocomposites

AFM Analysis of TiO₂/Illite Nanocomposites

Atomic force microscopy is a basic technique and inevitable for all nanomaterials research. The AFM image of TiO₂/Illite nanocomposites was synthesized by a simple method and the resulting image is given in Fig.-3.a and 3.b. The nanocomposites are as-observed under AFM 3D and AFM 2D images. The micrograph at 3.45 µm × 3.45 µm exhibits granular microstructures which are composed of irregular particles that can be seen in this sample. The surface roughness of the nanomaterials, RMS average value, and heights were determined by AFM analysis. The surface roughness was found to be in the range of 1.95 µm to 2.25 µm. The average crystallite size of the material was 80 nm, which has good agreement with the XRD results. AFM observation revealed the granular microstructures.

TEM Analysis of TiO₂/Illite Nanocomposites

The transmission electron microscopy image of the synthesized metal oxide/Illite nanocomposites is shown in the below Fig.-4. Clear spherical and non-homogeneous structures can be seen in the TEM image. The average particle size of the nanomaterials was estimated from the TEM image to be about 82 nm, which is in good agreement with the calculated value. Vijayalakshmi and coworker²⁶ explained the TEM image of the sol-gel-derived nanoparticles is a clear spherical shape and non-homogeneous

structures having a diameter of ~ 9 nm. This image clearly showed that the TiO_2 nanoparticles are highly crystalline in nature. TEM image and selected area diffraction pattern of the hydrothermal derived nanoparticles respectively.

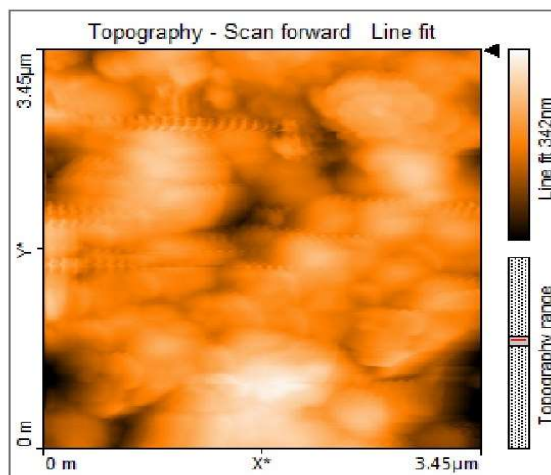


Fig.-3a: 2D AFM Image of $\text{TiO}_2/\text{Illite}$ Nanocomposites

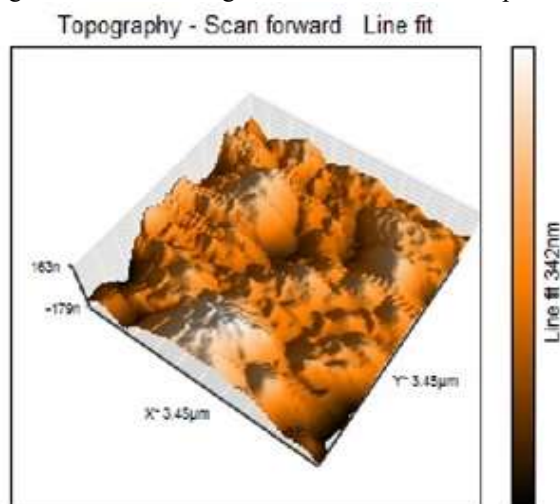


Fig.-3b: 3D AFM Image of $\text{TiO}_2/\text{Illite}$ Nanocomposites

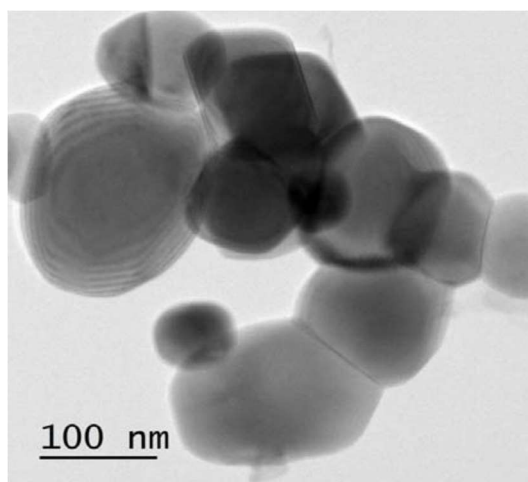


Fig.-4: TEM Image of $\text{TiO}_2/\text{Illite}$ Nanocomposites

UV-vis Absorption Spectroscopy

The absorption edge was shifted towards the lower wavelength for the nanocomposites. This clearly indicates the increase in the band gap energy of TiO₂/Illite nanocomposites. The UV absorption spectrum for composites is given in Fig.-5a. Plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) TiO₂/illite nanocomposites are shown in Fig.-5b. The band gap energy is estimated from the intercept of the tangents of the plot is 3.5eV. This showed that the blue shifted when compared with the bulk TiO₂ (3.2 eV). The blue shift could be caused by the nanosize effect and structural defect of nanomaterial. A similar result was investigated by Vijayalakshmi *et al.*²⁶

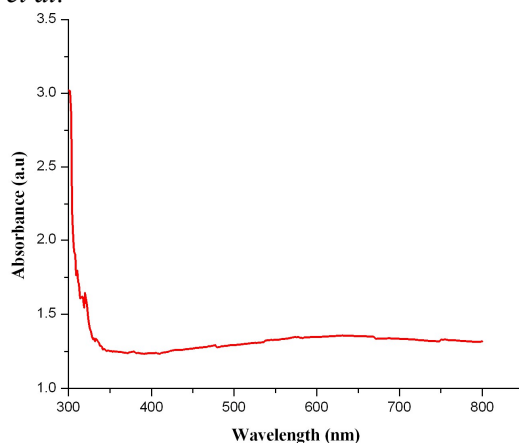


Fig.-5a: UV-vis Absorption Spectrum of TiO₂/Illite Nanocomposites

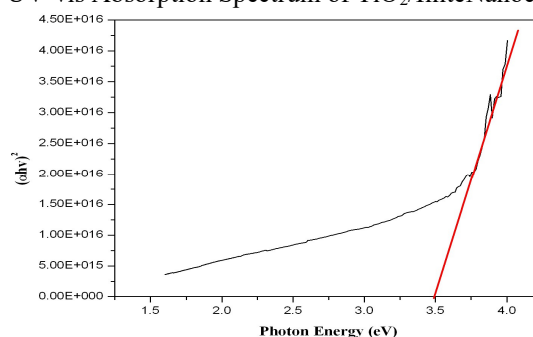


Fig.-5b: Band Gap Energy of TiO₂/Illite Nanocomposites

Photocatalytic Activity of MB dye:

The photocatalytic activity of the metal-oxide/clay nanocomposites was evaluated by photodegradation of an aqueous Methylene Blue (MB) textile dye. The experiment was administered in a cylindrical double-walled hollow photoreactor with a water circulation facility. A 20W UV lamp [wave length of 365 nm] was placed inside the reactor. The catalytic experiments were executed out with 100 mL solution of MB [5×10^{-5} M] and 20 mg of the catalyst under constant stirring. About 3 ml of the solution was withdrawn at predetermined time intervals from the reaction mixture, centrifuged, and therefore the decrease in absorbance value to be measured. A control experiment was executed under identical experimental conditions using commercial MB without catalyst.

$$\% \text{ Decolourization} = [(C_0 - C) \div C_0] \times 100$$

Where,

C_0 is the initial concentration of dye solution and

C is the concentration of dye solution after photocatalytic degradation.

Effect of Contact time

The contact time is necessary to reach equilibrium depends on the initial dye concentration. The effects of contact time on the decoloration of MB dye at 30 min are illustrated in Fig.-6. This indicates that the dye decoloration increase with the increase in contact time. This may be due to an increase in irradiation time

dye molecules and catalysts have enough time to require part in the photocatalytic degradation process and hence the percentage of degradation increases.²⁷ Harinee Subramanian et al. discussed the photocatalytic activity of green synthesized zinc oxide nanoparticles under sunlight irradiation effectively MB dye degradation 96% within 60 min.²⁸ The results of experiments showed that the photocatalytic degradation of methylene blue dye obeys apparently pseudo-first-order kinetics and the rate expression is given by the below equation.

$$\ln(C_0/C_t) = kt$$

Where,

C_0 = initial concentration of dye solution

C_t = final concentration of the dye solution in a various time intervals.

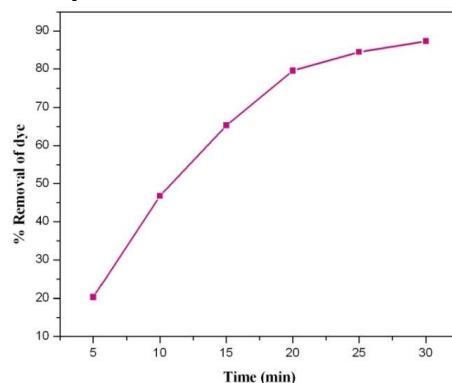


Fig.-6: Effect of Contact time

Effect of Dosage

The study discussed that increase in catalyst loading from 10 mg to 26 mg increased dye removal efficiency (Fig.-7). An increase in adsorbent dose provided an increase in pores available for the adsorption and also the surface area got increased. Hence, the Dosage of the catalyst was enhanced by increasing the percentage of degradation.²⁹ The removal of dye was increased as the adsorbent dose increased and maximum adsorption was observed in UV light irradiation. A similar result was reported by Reza Ansari *et al.*³⁰ Many reports suggested that the quantity of catalyst plays a major role in the degradation of organic compounds or dyes in photocatalytic degradation. To avoid the utilization of excess catalyst, it's necessary to find the optimum loading for the efficient removal of dye or organic compound. So it's necessary to optimize the quantity of catalyst to get the highest photocatalytic activity. The obtained result demonstrated that the increase in percentage decolorization and degradation of MB dye was lowest in the case of 0.10 g/L catalyst and it was increased up to 0.26 g/L sharply from 33% to 86% and 87%, respectively, in 30 min. This has been explained on the basis of the fact that as the catalyst load increases, the turbidity of the solution increases, resulting in a decrease in UV light penetration and photoactivated volume.

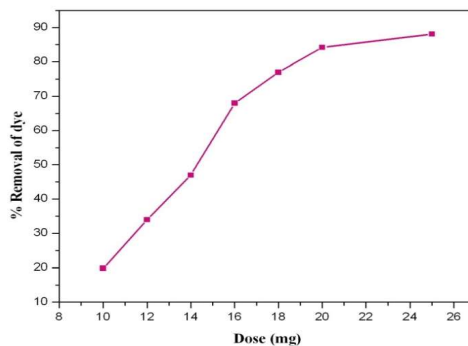


Fig.-7: Effect of Dosage

Effect of Initial Concentration of Dye

The Effect of the Initial Dye Concentration the influence of the initial concentration of the dye solution on photocatalytic degradation may be a significant aspect of the study. The initial concentrations of

methylene blue dye were selected within the range of 10-60 ppm and it had been revealed that the percentage of photodegradation decreased as the initial concentration of the dye solution increased, as shown in Fig.-8. One possible explanation of such circumstances is that as substances are adsorbed on the surface of TiO_2 ; therefore, the generation of hydroxyl radicals is reduced since there are only fewer active sites within the system causing little adsorption of hydroxyl ions, which successively leads to the decrease in the generation of hydroxyl radicals. Further, because the concentration of a dye solution increases, the photons get intercepted before they might reach the catalyst surface, hence the absorption of photons by the catalyst decreases, and consequently, the degradation percentage is reduced.³¹ When the concentration of dye molecules increases, the percentage removal was decreased. This is due to the more number of dye molecules adsorbed on the surface of the photocatalyst. Therefore the photon entering pathways are getting to be reduced. The degradation trend of methylene blue is shown in Fig.-8. Similar trends were given by Devi *et al.*³²

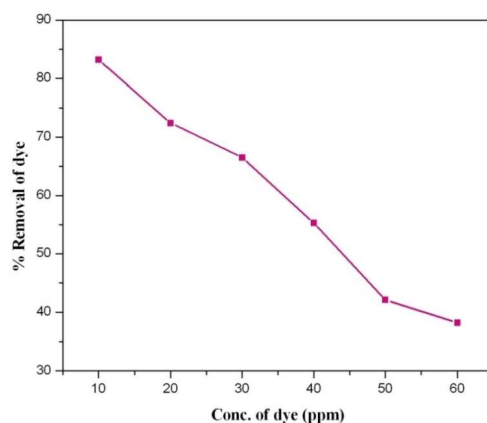
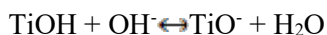
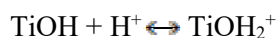


Fig.-8: Effect of Initial Concentration of dye

Effect of pH

According to the literature survey, the pH of the solution is by far the major factor influencing the rate of the photocatalytic process, because of its multiple roles:

(i) The ionization state of the titanium dioxide surface according to the following reactions:



(ii) Thus, the titanium dioxide surface is positively charged in an acidic medium, whereas it is negatively charged under an alkaline medium. For these reasons, the experiments were executed to find the optimal pH of the reaction mixture for degradation of MB (5×10^{-5} M). The examined range of pH was from 2.0 to 9.82. In all these experiments, the pH was adjusted by the addition of appropriate amounts of acid and base. The catalyst weight was 1.2 g/L. The initial pH of the solution is 6.5. It is evident from the results that when the pH of the solution is decreased from 6.5 to 2.0, the percentage of degradation and decolorization decreased as well; this may be due to the acidic solution retraining the adsorption of dye. In contrast, when the pH of the solution is increased from 6.5 to 9.82, it is observed that up to pH 8.84 of the solution there was an increase in the percentage of degradation and decolorization; this is often because in the alkaline medium the surface area of photocatalyst possesses much negative charge (changing the acidic degree of the catalytic surface), which is beneficial to MB adsorption on the photocatalyst (Fig.-9). Further increase in pH resulted in a decrease in the percentage of degradation and decolorization. This might be due to the higher adsorption of MB dye on the surface of the catalyst taking place when the pH of the solution is above 8.84, which leads to inhibition of light penetration. The results showed that the pH value of the solution was the key factor for dye degradation.

Defluorination Studies

Defluorination experiments were followed by the batch equilibration method in duplicate. In the typical case, 0.1 g of the adsorbent was added to 100 mL of NaF solution with an initial concentration of 3 mg/L.

The contents are shaken thoroughly employing a thermostated shaker rotating at a speed of 200 rpm. By keeping the weight of sorbent as 0.1g and volume of solution as 100 mL at neutral pH. The solution was then filtered and the residual fluoride concentration and the percentage of fluoride adsorption were also calculated.

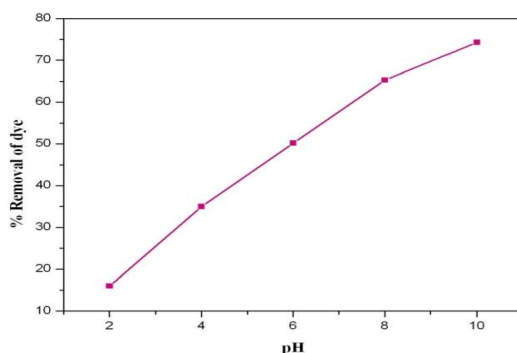


Fig.-9: Effect of pH

Instrumental Studies - XRD and SEM with EDAX Analysis

The XRD patterns of the TiO_2 /Illite nanocomposites samples before and after fluoride sorption were presented in Fig. 10a and 10b. The results indicated that there is no major change in the crystal structure after fluoride adsorption at this low concentration level. Similar results were reported by Diaz-Nava *et al.*³³ SEM was used to examine the structure of the sorbent. Figure-11a and 12a show the SEM micrographs of TiO_2 /Illite before and after fluoride sorption. There were apparent differences between the nanocomposites with many cavities before sorption and no such cavities are observed after sorption, it indicated the fluoride sorption on TiO_2 /Illite nanocomposites. The EDAX spectrum of TiO_2 /Illite nanocomposites is given in Fig. 11b which shows the presence of elements in it. An emergence of fluoride peak in the EDAX spectra of fluoride-treated TiO_2 /Illite nanocomposites confirmed the fluoride sorption onto TiO_2 /Illite nanocomposites which are shown in Fig.-12b. A similar result was reported by Viswanathan *et al.*³⁴ and Rajan *et al.*³⁵

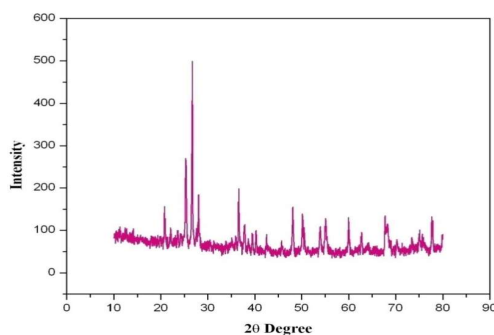


Fig.-10a: XRD Pattern of TiO_2 /Illite Nanocomposites

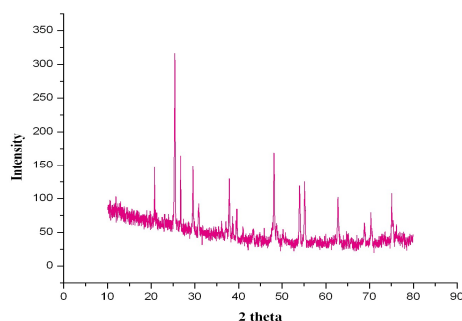


Fig.-10b: XRD Pattern of Fluoride Treated TiO_2 /Illite Nanocomposites

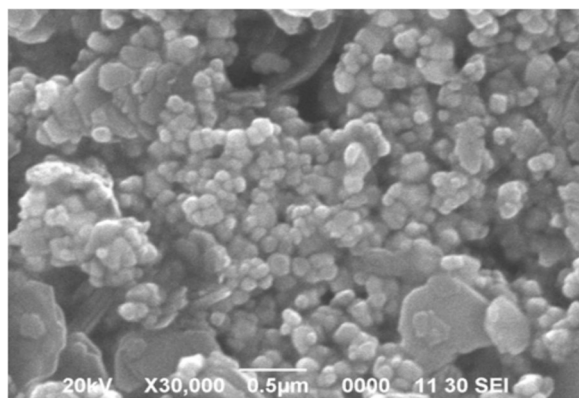


Fig.-11a: SEM Image of TiO₂/Illite Nanocomposites

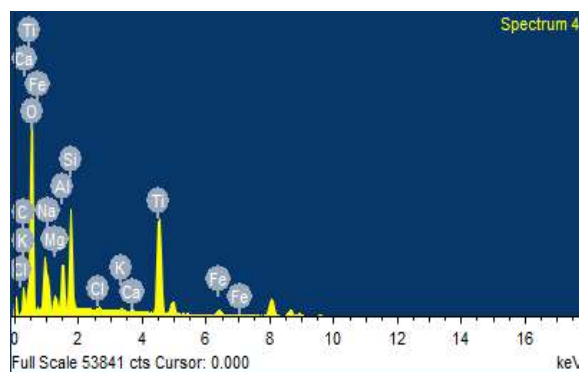


Fig.-11b: EDAX Image of TiO₂/Illite Nanocomposites

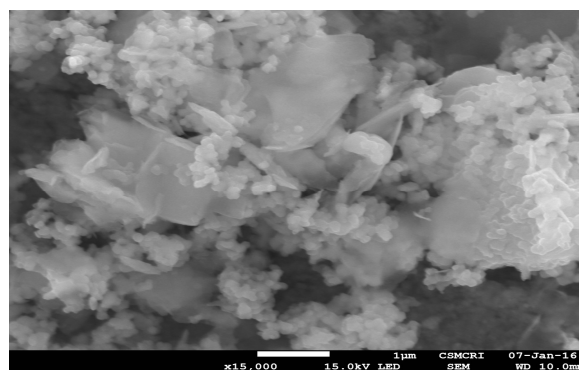


Fig-12a: SEM Image of Fluoride Treated TiO₂/Illite Nanocomposites

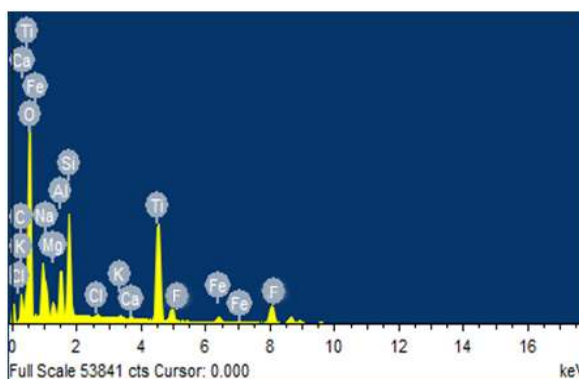
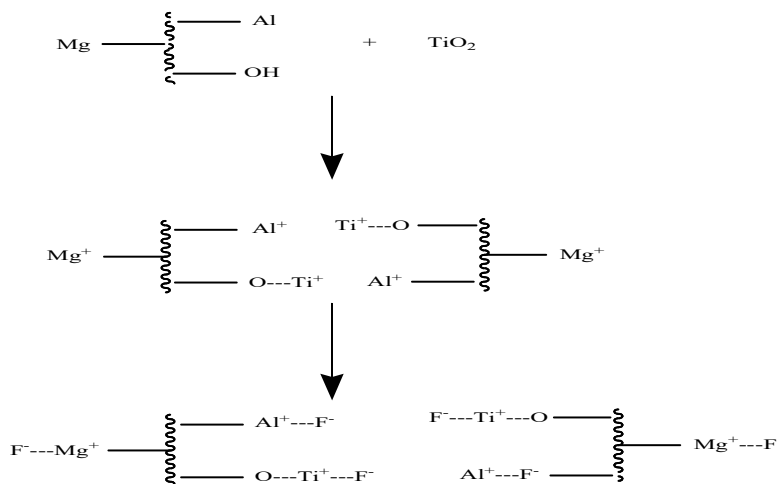


Fig.-12b: EDAX Image of Fluoride Treated TiO₂/Illite Nanocomposites

Mechanism



CONCLUSION

In conclusion, the Titanium dioxide/Illite nanocomposites have been successfully synthesized by using the solvothermal method. The synthesized nanocomposites were characterized through various analytical tools like XRD, SEM with EDAX, TEM, and UV-Vis absorption spectrum. The XRD result revealed the presence of the anatase phase of TiO₂. The synthesized Titanium dioxide/Illite Nano composites size and morphology of the sample were characterized by using TEM and SEM. SEM revealed the spherical shape and was well dispersed on the clay surface. AFM analysis shows exhibits granular microstructures which are composed of irregular particles can be seen in this sample. TEM image showed that the particles are clear spherical and nonhomogenous structures. The average size of the nanomaterials estimated from the TEM image is about 82 nm. The band gap energy of this nanocomposite is 3.5 eV, which is larger than the value of 3.2 eV for bulk TiO₂. The results showed that the decolorization reactions data were fitted by the pseudo first-order kinetic model. Based on the analysis, the resulting materials are very useful in water treatment. The fluoride adsorption by the nanocomposites was interpreted in terms of the results of X-ray diffraction and SEM with EDAX analysis. The EDAX spectrum of TiO₂/Clay nanocomposites shows the presence of elements in it. An emergence of fluoride peak in the EDAX spectra of fluoride-treated TiO₂/Clay nanocomposites confirmed the fluoride sorption onto TiO₂/Clay nanocomposites.

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