

## Photocatalytic Degradation of Acid Blue 113 Over Iron Modified Vermiculite Using Solar Light

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Natural vermiculite was enriched with iron by incipient wet method, and characterized by XRD and FT-IR. The structure of vermiculite was retained after modification. The modified vermiculite was used as the catalyst for the solar light assisted degradation of acid blue 113, a very commonly used dye in textile industry. The degradation was carried out by varying amount of H<sub>2</sub>O<sub>2</sub> (15 mM - 75 mM) for 250 mL of 50 ppm dye solution. The degradation was monitored by measuring absorbance at 566 nm. The complete degradation of the dye required 240 min. The degradation was more than 90 % solar light assisted and removal of dye by adsorption was minimum (5 %). Complete mineralization of dye was evident from total organic carbon analysis. In support of total organic carbon results, the percentage chemical oxygen demand (% COD) increased with an increase in irradiation time. The optimum pH range for degradation was 2.9 to 3.5. Dissolution of iron from vermiculite was proved negligible. It was established that any textile effluent carrying acid blue 113 will be effectively mineralized using low cost naturally occurring eco-friendly vermiculite.

**Key Words:** Vermiculite, Photocatalysts, Acid blue 113, Mineralization, Solar light.

### INTRODUCTION

Chemical process industries, such as oil industries, petrochemical refining industries, dye and dye intermediate manufacturing units and textile industries are typical industries that dump toxic organic pollutants to the nearer water courses, thus making them polluted<sup>1</sup>. To treat water pollution advanced oxidation process involving light irradiated semiconducting materials such as TiO<sub>2</sub>, ZnO, CdS *etc.* as catalysts has been practiced<sup>2-4</sup>. The process involved the generation of the highly reactive radicals (OH<sup>•</sup>) to mineralize the pollutants<sup>5</sup>. In addition, the oxidation involving Fenton's reagent, Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>, has been practiced to mineralize pollutants. The Fenton's reagent also generates OH<sup>•</sup> radicals for pollutant mineralization<sup>6-10</sup>. In contrast to TiO<sub>2</sub>, Fenton's reagent carries a problem for photocatalytic degradation: Fe<sup>3+</sup> ions in it are not recovered and recycled. Since the contents of Fe<sup>3+</sup> ions in every batch process is in the range 52-80 ppm of iron, removal of sludge containing Fe<sup>3+</sup> ions at the end of the treatment is expensive and requires large amount of chemicals and man power. To overcome these disadvantages, porous materials with framework incorporated iron were also used as catalysts<sup>11-15</sup>. The use of zeolite<sup>16,17</sup> and carbon<sup>18,19</sup> to support iron catalysts were also studied. Compared to these heterogeneous catalysts, iron carrying vermiculite could be a cheap natural catalyst

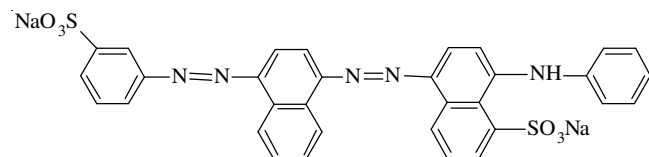
for the degradation of organic pollutants by the Fenton's procedure.

Vermiculite is a mineral resembling mica and when heated has an appearance of little worms. Gruner<sup>20</sup> examined the structure of vermiculite and showed it to be composed of mica layers separated by water molecules. Hendricks and Jefferson<sup>21</sup> pointed out that the structure is not neutral and the negative charge is balanced by interlayer ions, most commonly magnesium and sometimes calcium. The structural formula is (OH)<sub>2</sub> (Mg, Fe)<sub>3</sub> (Si<sub>4x</sub>Al<sub>x</sub>)O<sub>10</sub> (Mg, Ca)<sub>x/2</sub>. Since iron content of vermiculite is low, in the present study it was enriched with Fe<sup>3+</sup> ions and tested for the photocatalytic mineralization of acid blue 113 using solar light. The structure of acid blue 113 is shown below. It is a commonly employed dye in the textile industries of southern part of India. The effluents from textile industries are not subjected to any treatment for the removal of the dye. As advanced oxidation process has been proved to be the ultimate technique to treat textile effluents, in the present study the degradation of the dye over vermiculite was examined in solar light. The effect of H<sub>2</sub>O<sub>2</sub> was also examined on the rate of degradation. Like other porous materials this vermiculite carrying framework iron offers large surface to adsorb pollutants, which is also important in the degradation of dye as hydroxide radicals can be close enough to degrade the dye. So, vermiculite is a cheap, novel, eco-friendly high

TABLE-1  
 COMPOSITION OF VERMICULITE

Constituent	Average moisture	Loss on ignition	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Alkalies
Percentage	7.89	11.05	30.52	16.32	2.63	14.74	9.47	3.68	3.68

surface bearing photocatalyst for the mineralization of organic pollutants.



Molecular structure of acid blue 113

## EXPERIMENTAL

The vermiculite clay purchased from TAMIN (Tamil Nadu Minerals) Ltd., with surface area 3.5 m<sup>2</sup>/g and particle size 250 μm was used throughout the investigation. Iron(III)nitrate, potassium dichromate, concentrated sulphuric acid, hydrogen peroxide (30 wt %) and other chemicals used in this investigation were of analytical grade and obtained from E. Merck, India. The dye, acid blue 113, was purchased commercially from Rajasthan Chemicals and Dyeing Company, Chennai, India and used without further purification. The composition of vermiculite given by TAMIN Ltd., (Tamil Nadu Minerals) is given Table-1.

**Enrichment of vermiculite with Fe<sup>3+</sup>:** Finely pulverized vermiculite (200 mesh) was taken in a 500 mL beaker and 250 mL of deionized water and iron(III) nitrate (for 10 % iron loading) were added to it. The mixture was stirred vigorously for 24 h and filtered. The residue was dried in an oven at 70 °C for 12 h and calcined at 600 °C for 8 h in air. The obtained material was designated as Fe-vermiculite.

**Catalyst characterization:** The X-ray diffraction patterns of vermiculite and Fe-vermiculite catalysts were recorded on an X-ray diffractometer (PAN alytical X' Pert Pro) using CuK<sub>α</sub> (λ = 1.54 Å) radiation and liquid nitrogen-cooled germanium solid-state detector. The diffractograms were recorded in the 2θ range 5-80° in step of 1.2° with count time of 10 s at each point. The FT-IR spectra of the catalysts were recorded on an FT-IR Nicolet Avatar 360 using KBr pellet technique in 4000-400 cm<sup>-1</sup> region.

**Total organic carbon analyzer:** The samples withdrawn at different time intervals during the photocatalytic degradation were centrifuged, filtered and analyzed using total organic carbon analyzer to estimate the amount of total organic carbon. The inorganic carbon was removed from the sample by pouring 2 N HCl in presence of air. After removing inorganic carbon, the sample was allowed to flow through the combustion tube, which was packed with platinum catalyst at 700 °C. When the sample entered the combustion tube, total carbon in the sample was completely oxidized to carbon dioxide. The carrier gas (oxygen) flow was regulated (150 mL/min), which carried the combustion products from the combustion tube and flow through dehumidifier.

**Solar photocatalytic reactor:** The cylindrical photocatalytic reactor of 500 mL capacity was made of borosilicate glass

having a dimension of 10 × 4 cm (height × diameter) with ports at the top for sampling, gas purging and gas outlet. Solar light was used as the energy source for catalyst excitation. The experiment was performed at ambient temperature. The reaction mixture, composed of 250 mL of 50 ppm dye solution and catalyst, was taken in the reactor was stirred using a magnetic stirrer. At periodic intervals, the samples were withdrawn from the reactor and analyzed after centrifugation for degradation. The experiments under solar light were carried out between 10.00 AM and 5.00 PM during the month of March. The degradation was monitored by measuring absorbance at 566 nm in an UV-VIS spectrophotometer.

## RESULTS AND DISCUSSION

**X-ray diffraction:** The X-ray diffraction patterns of vermiculite and Fe-vermiculite are shown in Fig. 1. The X-ray diffraction pattern of vermiculite (Fig. 1A) showed peaks similar to those reported in the literature<sup>22</sup>. The material was largely crystalline but there were missing of many peaks in the spectrum, hence the crystal dimension may be in nano range. The nano size was once again confirmed by the broadening of peaks. The XRD pattern of Fe-vermiculite (Fig. 1B) also showed similar features as that of vermiculite. Hence as a result of iron impregnation there was no structural distortion in vermiculite. The spectrum revealed suppression of the peak at 11.3° (2θ) and appearance of a peak at 12.3°, but both are the characteristic peaks of vermiculite. Hence, as a result of iron loading, the plane at 12.3° (2θ) was newly constructed, but the original peak at 18.5° (2θ) destroyed. The characteristic reflections of iron oxide were not obtained, hence iron might be exclusively in the form of Fe<sup>3+</sup> intercalated between the layers.

**UV-VIS analysis:** The UV-VIS spectrum of the dye acid blue 113, is shown in Fig. 2. It showed a broad absorption band between 400 and 600 nm. The λ<sub>max</sub> occurred at 566 nm. This absorption was ascribed to n → π\* transition occurring in the azo group of the dye. This λ<sub>max</sub> was used in monitoring the progress of degradation.

**FT-IR:** The FT-IR spectrum of vermiculite is shown in Fig. 3. The intense sharp peak at 3443 cm<sup>-1</sup> was due to -OH stretching vibration of water. Presence of water was also confirmed by its bending vibration at 1636 cm<sup>-1</sup>. The peak at 1418 cm<sup>-1</sup> was assigned to carbonate vibration. The intense sharp peak at 1011 cm<sup>-1</sup> was due to asymmetric stretching vibration of silica. The peaks lying below 900 cm<sup>-1</sup> were due to metal oxide vibration.

The FT-IR spectrum of Fe-vermiculite is shown in Fig. 4. It showed similar features as that of Fig. 3. The peaks due to metal oxide vibrations were more intense than that of Fig. 3. In both the spectra the peak due to bending vibration of water was split into two peaks, hence there might be coordinated and adsorbed water on the surface of vermiculite.

The FT-IR spectrum of acid blue 113 is shown in Fig. 5. The broad intense peak at 3447 cm<sup>-1</sup> was due to -OH stretching

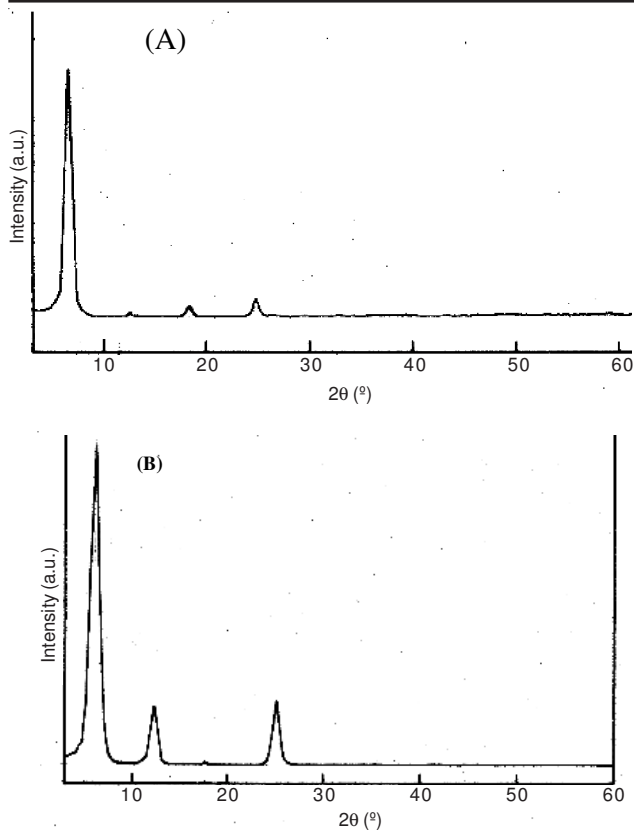


Fig. 1. XRD patterns of (A) vermiculite and (B) Fe-vermiculite

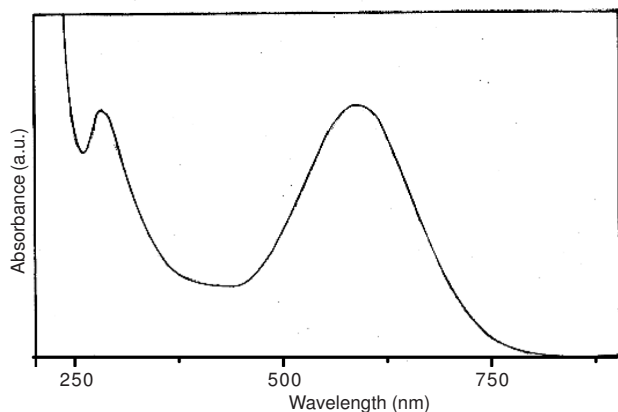


Fig. 2. UV-VIS spectrum of the dye AB113

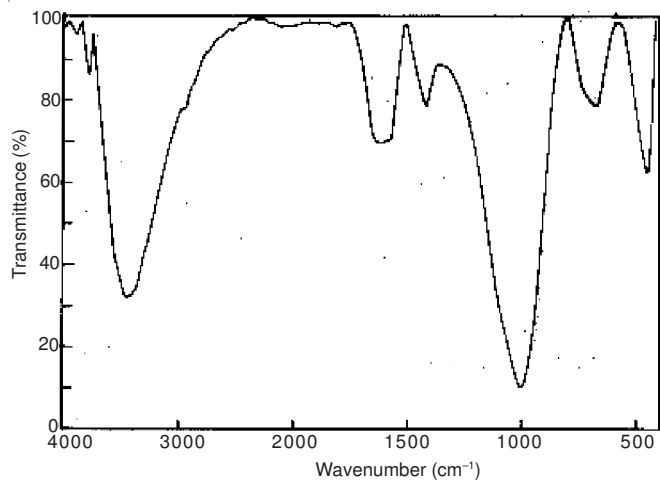


Fig. 3. FT-IR spectrum of vermiculite

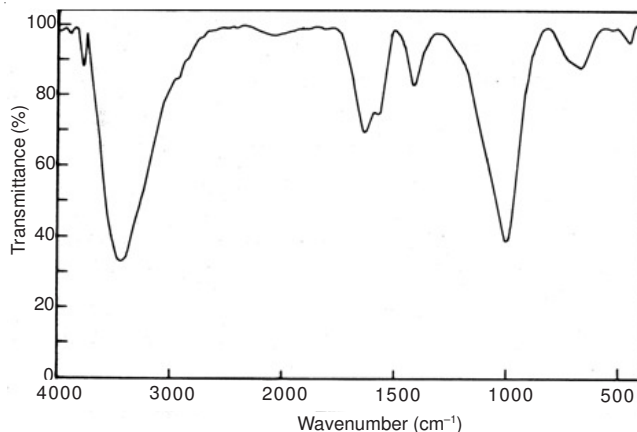


Fig. 4. FT-IR spectrum of Fe-vermiculite

vibration of water. The C-H stretching vibrations of aromatic rings and alkyl groups were not clearly resolved due to appearance of fine structures in the broad band. Presence of water was confirmed by its bending vibration, which appeared as a shoulder (*ca.* 1620  $\text{cm}^{-1}$ ) to the peak at 1569  $\text{cm}^{-1}$ . The later peak was due to N=N stretching vibration. The sulphonic acid groups gave their characteristic peaks at 1182 and 1419  $\text{cm}^{-1}$ . The peak at 1341  $\text{cm}^{-1}$  could be assigned to  $-\text{CH}_2$  bending vibration. The aromatic  $-\text{CH}$  bending vibration gave a peak below 800  $\text{cm}^{-1}$ .

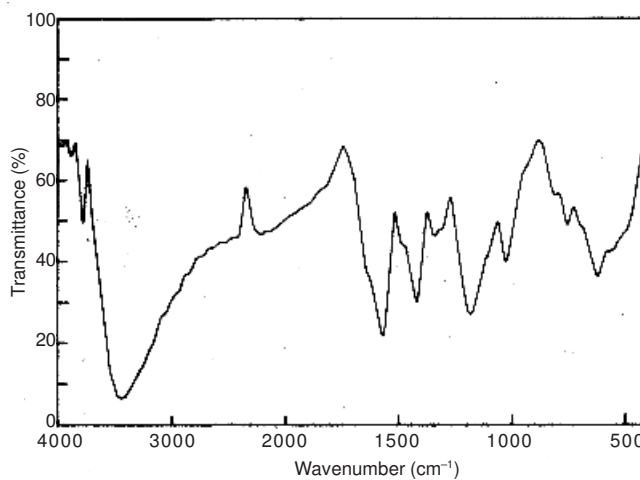
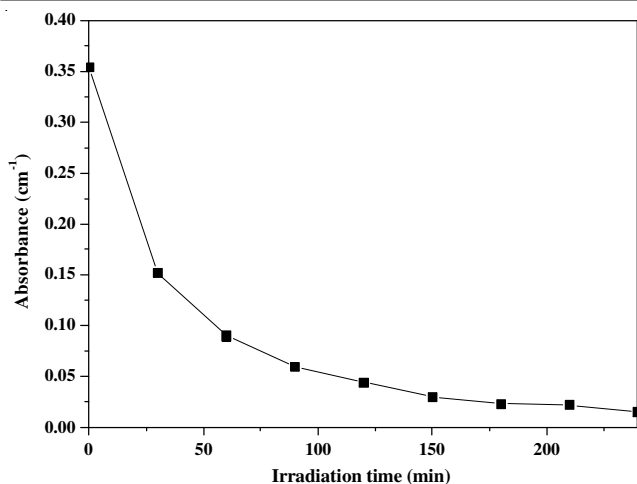


Fig. 5. FT-IR spectrum of acid blue 113 dye

**Photocatalytic degradation of acid blue 113:** The photocatalytic degradation of acid blue 113 with Fe-vermiculite was carried out in solar light between 10 AM and 5 PM the progress of degradation was monitored by measuring absorbance of aliquots of the reaction mixture at regular intervals. The plot of irradiation time *versus* absorbance is shown in Fig. 6. The absorbance decreased rapidly below 55 min and then decreased slowly. The slow decrease at high irradiation time was due to competing of degradation products for subsequent mineralization along with the parent dye. The decrease of absorbance with irradiation time was also similar to previous reports of degradation of dye<sup>23</sup>.

Fig. 6. Plot of irradiation *versus* time absorbance

#### Degradation of acid blue 113 in dark and solar light:

In order to establish that the degradation of acid blue 113 was rapid in presence of catalyst, the process was carried out with H<sub>2</sub>O<sub>2</sub>, Fe-vermiculite, Fe-vermiculite and H<sub>2</sub>O<sub>2</sub> (dark) and Fe-vermiculite and H<sub>2</sub>O<sub>2</sub> in the presence of solar light. The results of degradation are illustrated in Fig. 7. The A/A<sub>0</sub> (where A is the absorbance at time t in mins and A<sub>0</sub> is the initial absorbance) of solution collected at regular intervals in each experiment was plotted against irradiation time. The decrease in A/A<sub>0</sub> was minimum (less than 10 %) for H<sub>2</sub>O<sub>2</sub>, Fe-vermiculite, Fe-vermiculite and H<sub>2</sub>O<sub>2</sub> (dark) systems. In contrast, the decrease in A/A<sub>0</sub> was rapid with increase in time for Fe-vermiculite and H<sub>2</sub>O<sub>2</sub> in the presence of solar light system. So, this observation established that the degradation was photocatalytic.

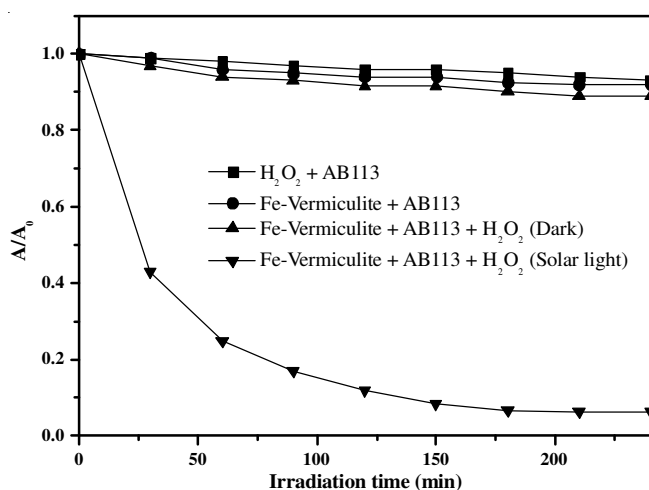


Fig. 7. Degradation of acid blue 113 in dark and solar light

**Total organic carbon analysis:** The degradation of dye was also monitored by determining total organic carbon at regular intervals of time. The results are illustrated in Fig. 8. The total organic carbon decreased gradually with increase in irradiation time. At the end of 240 min, the total organic carbon was 0.0212 mg, which corresponds to 91.3 % degradation. Actually the dye took about 240 min for complete mineralization. Hence at the end of 180 min there might be residual dye to be degraded. Since the total organic carbon decrease

was linear with respect to irradiation time, the process might not produce any fragment that resist mineralization. Hence throughout the process the fragments produced out of degradation might be susceptible to mineralization.

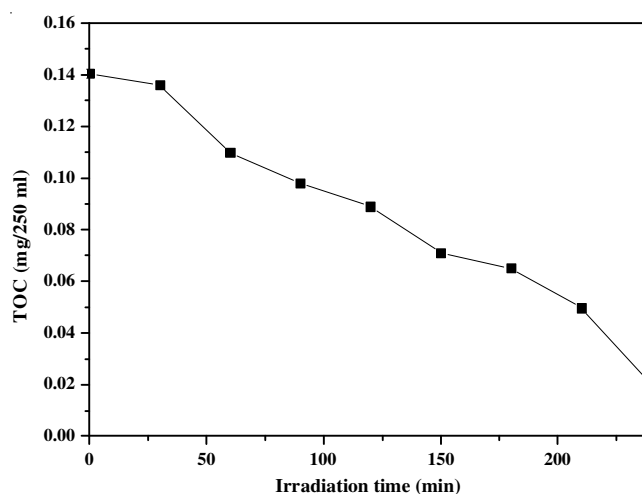
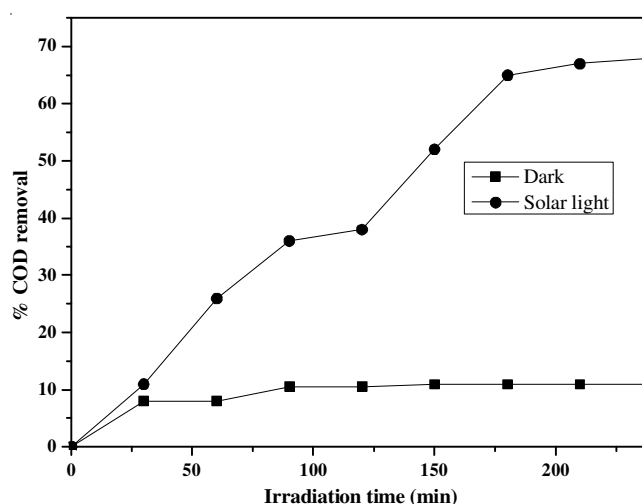


Fig. 8. Effect of irradiation time on total organic carbon (TOC)

**Chemical oxygen demand:** The plot of % chemical oxygen demand removal with irradiation time is shown in Fig. 9. The % chemical oxygen demand removal increased with increase in irradiation time. Hence the process might be free of any fragments, which could resist mineralization. Actually the dye required 240 min for complete mineralization, but chemical oxygen demand was determined for 180 min degradation gave 65 % chemical oxygen demand removal. In order to establish that the degradation was a light assisted one, it was also carried out in the absence of solar light. The total % chemical oxygen demand removal was about 9 % at the end of 180 min. This observation clearly established that the degradation as a light assisted one.

Fig. 9. Plot of irradiation time *vs.* % chemical oxygen demand (COD) removal

**Effect of pH:** The effect of pH on acid blue 113 degradation was examined at pH 2, 3, 4 and 5 and the results are illustrated in Fig. 10. At low pH values, Fe<sup>3+</sup> ions dissolves



hence, the study was carried out close to the precipitating pH of 2, 3, 4 and 5. As the degradation depends on generation of  $\text{OH}^\cdot$  radicals as shown in the following equations, the optimum pH is important.

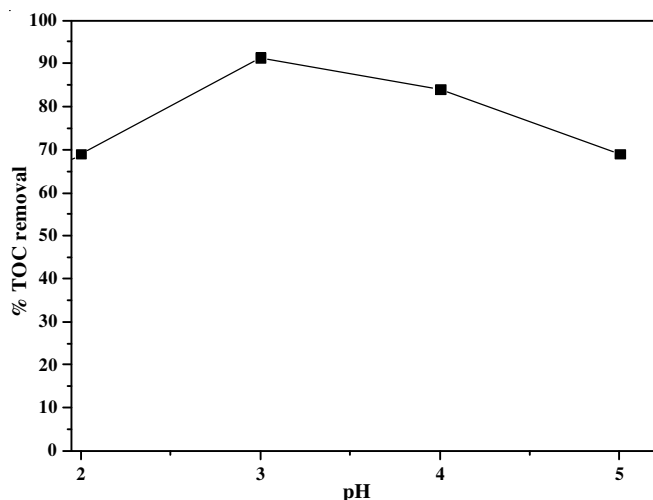
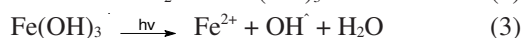
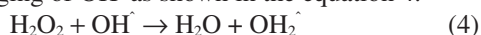


Fig. 10. Effect of pH on acid blue 113 degradation

At pH 2 the rate was less than pH 3. At pH 2, reaction 1 is favoured to form  $\text{OH}^\cdot$  radicals, but  $\text{Fe}^{3+}$  cannot be hydrolyzed to form  $\text{Fe}(\text{OH})_3$ , which is to decompose latter to form  $\text{Fe}^{2+}$ . At pH 3,  $\text{Fe}^{3+}$  can readily form  $\text{Fe}(\text{OH})_3$  precipitate, which in the presence of solar light gives  $\text{OH}^\cdot$  radicals. Hence at pH 3, both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  might be active for the degradation of dye. At pH 4, the rate of degradation was less than pH 3, as the  $\text{H}_2\text{O}_2$  might be rapidly decomposed to form molecular oxygen<sup>24</sup> without the formation of  $\text{OH}^\cdot$  radicals. The same decrease in degradation of dye was also noted at pH 5. From this study, it was confirmed that the acidic pH below 2 was not good for photocatalytic degradation of dye using vermiculite.

**Effect of initial  $[\text{H}_2\text{O}_2]$  on dye degradation:** The effect of  $[\text{H}_2\text{O}_2]$  on percentage degradation of acid blue 113 was examined with 15, 30, 45, 60 and 75 mM solution of  $\text{H}_2\text{O}_2$ . The concentration of dye was 50 mg/L (50 ppm). The rate of degradation in dark was monitored using UV-VIS spectrophotometer. The results are presented in Table-2. In dark, the degradation was very minimum, not exceeding 12 % even with 75 mM  $\text{H}_2\text{O}_2$ . Hence the degradation might depend on light. This is clearly evident from the % degradation in the presence of solar light but there was a non linear variation of % degradation. When concentration of  $\text{H}_2\text{O}_2$  was increased from 15-45 mM, the % degradation increased from 67 to 85 %. Above 45 mM, the % degradation decreased. The decrease was attributed to scavenging of  $\text{OH}^\cdot$  as shown in the equation 4.



Although  $\text{HO}_2^\cdot$  radicals were produced, their oxidation potential is much lower than that of  $\text{OH}^\cdot$  radicals<sup>25</sup> to degrade organics.

The effect of  $\text{H}_2\text{O}_2$  on % chemical oxygen demand removal was monitored with 15, 30, 45, 60 and 75 mM  $\text{H}_2\text{O}_2$  in dark and solar light. In dark the % chemical oxygen demand

removal varied from 10-11 %. Hence the process appeared to be light dependent. In support of our view, in the presence of solar light the % chemical oxygen demand removal increased from 24 to 38 %, when  $[\text{H}_2\text{O}_2]$  increased from 15 to 45 mM. When the concentration of  $\text{H}_2\text{O}_2$  was further increased, the % chemical oxygen demand removal decreased. As explained in the effect of  $[\text{H}_2\text{O}_2]$  on % degradation at 60 and 75 mM of  $\text{H}_2\text{O}_2$ , the  $\text{OH}^\cdot$  radicals were scavenged, hence % chemical oxygen demand also decreased.

TABLE-2  
EFFECT OF INITIAL  $[\text{H}_2\text{O}_2]$  ON DYE DEGRADATION

$[\text{H}_2\text{O}_2]$ (mM)	% Degradation	
	Dark	Solar light
15	5.7	65
30	6.9	72
45	8.1	85
60	10.5	74
75	12	62

**Stability and recycling of the catalyst:** For a practical implementation of a heterogeneous catalytic system, it is crucial to evaluate the stability of the catalysts. For that purpose, a sample that shows a low iron leaching, but presenting simultaneously good catalytic performance, should be selected. The dye degradation was performed in 4 consecutive runs. To recover the catalyst, the final effluent was filtered. After the first cycle and in order to check whether the leached iron was responsible for the catalytic activity, both dye and  $\text{H}_2\text{O}_2$  were added to the solution in the same concentrations. The experiment showed that under these conditions, acid blue 113 degradation was only a very small fraction of that recorded in the presence of the clay, thus demonstrating that the Fe leaching was insignificant. For subsequent cycles, the filtered clay was dried overnight between consecutive runs. The activity slightly decreased illustrating loss of iron (*ca.* 1.5 % per cycle that represents a final concentration smaller than 0.3 mg/L) but dye degradation decreased from 95.8 to 90.3 % in 4 cycles. Regarding chemical oxygen demand reduction, in the 4 cycles the final values were 57 %. Other authors reported similar results, but they attributed the loss of activity to poisoning of the active catalytic sites due to adsorbed organic species<sup>26</sup>. However, this could be avoided by submitting the catalyst to an intermediate calcination step, thus restoring its catalytic activity<sup>27</sup>. Nevertheless, catalyst deactivation may occur due to a diversity of factors, as pointed by Guo and Al-Dahhan<sup>28</sup> such as poisoning of the catalysts by compounds formed during oxidation, surface deposition, *etc.*

## Conclusion

Vermiculite was enriched with iron by incipient wet method and characterized by XRD and FT-IR studies. Its catalytic activity for the degradation of acid blue 113 was studied using solar light at pH 3. Periodic measurement of total organic carbon established complete mineralization. The result of chemical oxygen demand was also in support of it. Dissolution of vermiculite was not noticed in the degradation process. As its surface area was higher, it showed degradation activity higher than Fenton's reagent whose recovery and reusability are difficult. Hence vermiculite is a convenient

substitute to TiO<sub>2</sub>, ZnO, Fenton's reagent and CdS for the degradation of textile dyes and all other environmental organic pollutants. It is also a cheap and eco-friendly catalyst.

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