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PHOTOCATALYTIC DEGRADATION OF A CATIONIC DYE "METHYLENE BLUE" USING Fe₂O₃ AND TiO₂ BENTONITE PILLARED NANOCOMPOSITE

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ABSTRACT

Bentonite pillared nanocomposite clay based on Fe, Al, Fe-Al and Ti were prepared and characterized via XRD, XRF and FTIR to be used as photocatalysts for the degradation (discoloration) of methylene blue dye (MB) using visible irradiation range 300-800 nm since MB is a dye sensitizer excitable by the visible light. In this work, the application of the advanced oxidation process (AOP), including H₂O₂ incorporation in the photoirradiated solution was applied. The optimum concentration of H₂O₂ was 0.3 mmol l⁻¹. The results show that the current pillared clays, except for the Aluminum-pillared-clay, exhibited significant photoactivities. However, insertion of Fe pillars in the spaces between the bentonite clay layers has resulted in the highest activity for discolorizing the dye solution. Impregnating Fe(NO₃)₃ in Al-pillared clay to attain the same Fe content in Fe-Al pillared clay gives, even, a high photo-activity due to distribution of Fe sites in the voids among the Al pillars in the form of isolated sites in the catalyst. First order kinetic rate constants were calculated to acquire justifiable comparisons of the photocatalytic activities for MB discoloration.

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1. INTRODUCTION

Nano-structured materials have been developed and employed as heterogeneous catalysts for various applications including the remediation of air and water [1,2]. Of these materials, clay based catalysts have also been developed [3-5]. Recently, laponite and bentonite clay-based Fe nano-composites have been used as photo-fenton catalysts for degradation of organic dyes [6] and both of them exhibited a high photocatalytic activity, long term stability, and low cost, which are good candidates for industry waste water treatment.

TiO₂ pillared clay has attracted much attention as a new type of photocatalyst, due to its strong adsorption properties which accelerate photocatalytic reactions [7–13]. This pillared clay has a structure in which parallel two dimensional silicate layers of clay are supported by nanoparticles of TiO₂ and micro- to meso-pores with large interlayer surface area are formed. The interlayer surface of TiO₂ pillared clay is generally hydrophobic [14], which is an advantage in adsorbing and enriching diluted hydrophobic organic compounds in water. Furthermore, TiO₂ pillared clays also show photocatalytic activity owing to nano-sized TiO₂ pillars. Thus, this would be one of the suitable materials for photocatalysis in water [15–23]. Zinc oxide nanoparticles deposited on silica nanoparticles showed higher photocatalytic activity for methylene blue degradation [24]. Moreover, TiO₂ fibers, carbon-doped TiO₂, TiO₂/SiO₂ and TiO₂/PDMS films have been also used for photocatalytic degradation of methylene blue [25-27].

In the present work, we prepared nanocomposed bentonite clay based Fe, Al, Fe-AL and Ti pillared bentonite clay to be used for photocatalytic discoloration of methylene blue dye.

2. EXPERIMENTAL

2.1- Materials

Bentonite clay was obtained from (Aldrich) The cation exchange capacity of the bentonite was determined to be 1.15 meq.g⁻¹, TiCl₄ and Fe(NO₃)₃ from sigma were used directly without further purification.

2.2-Synthesis of Fe₂O₃ Bentonite Nanocomposite

A solution of 0.2M ferric nitrate was prepared by dissolving the equivalent amount of the salt in deionized and distilled water. Solid sodium carbonate was added slowly to alter the pH of the solution, hydrolysis of ferric nitrate with sodium carbonate was carried out at 25°C, and an aging period of 24 h was allowed as suggested by Rightor et al [28]. The value of OH/Fe was 2.0 and the pH of this solution was 1.8. A suspension containing 1.0 g of bentonite clay in 100 ml water was added to the hydrolyzed ferric solution. This suspension and the pillaring agent were rigorously stirred at room temperature for 24h, recovered by filtration, washed repeatedly with water, and then dried in air overnight at 110°C. The filtrate was calcined at 300°C for 5h [29].

2.3- Synthesis of TiO₂ Bentonite Nanocomposite

The pillaring agent solution (partially hydrolyzed Ti-polycations) was primarily prepared by first adding TiCl₄ into a 2M HCl solution. The mixture was then diluted by slowly adding deionized water with constant stirring to reach, a final Ti concentration of 0.82 M. The final concentration of HCl was 0.11 M [30] and the pillaring solution was aged for 24h at room temperature before use. The pH of this solution was 1.1. Bentonite (2.0 g) was dispersed in 500 ml of deionized water and kept in suspension for 24 h by stirring. The filtered product was washed, dried and calcined with in a similar procedure to Fe-PILC [31]. Finally, the heated products were ground into fine powder.

2.4-Photocatalytic Decomposition of Methylene Blue Dye

The experiments were carried out in a photocatalytic oxidation reactor in the center of the cylindrical reactor, using a 50 W, tungsten-halogen lamp (400-800 nm). The decay of Methylene blue (MB) dye in aqueous medium was evaluated at different irradiation periods. Prior to starting illumination, a suspension containing 1.0 g l⁻¹ of catalyst and 0.1 g l⁻¹ of MB were stirred continuously in the dark for 15 min. The concentration of MB in solution at this point was used as the initial value for the kinetic treatment of the photodegradation processes. Cooling by water circulation at 25°C during the experiments was performed at constant stirring at given intervals of illumination, a sample of the catalysts particulate was collected, centrifuged, and then filtered through a Millipore filter (pore size 0.22 μm). The filtrates were analyzed by UV-Vis spectroscopy using a UV-VIS spectrophotometer. The spectral measurements were taken at a wavelength at 665 nm, which is the maximum absorption wavelength. A concentration-absorption calibration curve was used.

3. RESULTS AND DISCUSSION

3.1 Characterization of Metal-Bentonite Nanocomposites

3.1.1 Chemical Composition

Table 1 gives the elemental analyses of the prepared clay catalysts, determined by XRF. During the pillaring of the bentonite clay with Fe, analysis shows that 28.6% Fe has contributed to the constitution of the pillars. However, in Fe-Al-PILC, only 7.2% Fe has additionally contributed to the constitution of pillars. On the other hand, Al participation in the pillars = 23.2 - 18.7 = 4.5%, since bentonite originally contained 18.7% of aluminum. However, aluminum in the Fe-Al-PILC comprises 9.4%. In case of the Ti-PILC, as high as 43.5% of Ti has contributed to Ti pillaring.

3.1.2 Specific Surface Area

The specific surface area of the bentonite clay is 28.4 m²g⁻¹, whereas those of the prepared Fe-PILC, Fe-Al-PILC and Ti-PILC were 280, 245 and 301 m²g⁻¹,

respectively. Evidently, the combined Al-Fe pillaring has decreased the surface area than that of the Fe-PILC (Table 2).

3.1.3 XRD

The XRD pattern of the host clay shows diffraction peaks at $2\theta = 26.6$ and 19.88 , which are assigned to SiO_2 crystallite [32]. For Fe-PILC, the main diffraction peaks are at $2\theta = 33.2$ and 35.5 , assigned to Fe_2O_3 crystals. Ti-PILC shows clear peaks corresponding to anatase phase at $2\theta = 25.3$ in addition to the host clay peaks. The XRD data indicated that Ti and Fe particles are intercalated in silicate layers in the catalysts. The size particles calculated from these data for the current catalysts are listed in Table 2.

3.1.4 FTIR

The FTIR spectra of the raw Na bentonite and the prepared pillared bentonite samples in the region $2000\text{-}500\text{ cm}^{-1}$ are illustrated in Fig.1-a-c, where sharp bands at 523 and 456 cm^{-1} attributed to the vibration of the Si-O group and Si-O-Al groups due to kaolinite. The bands at 722 and 621 cm^{-1} correspond to the isolated AlO_4 tetrahedra and alternating SiO_4 and AlO_4 tetrahedra, respectively [33]. The band centered at 910 cm^{-1} related to the Al-OH group. The large and relatively broad band at 1044 cm^{-1} is characteristic of bentonite. The 1625 cm^{-1} is characteristic of pseudo layer silicates, interstratified minerals. This bentonite structure is still present in the FTIR spectra obtained for the Al-PILC (Fig.1b) and Fe-PILC (Fig.1c) after carrying out the pillaring process.

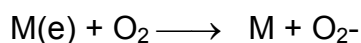
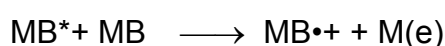
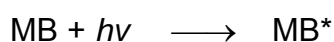
Evaluation of Metal Bentonite Nanocomposites As Photocatalysts

The evaluation of these catalysts was conducted in a batch photoreactor using a halogen lamp inserted in the center of the reactor and surrounded by a quartz cooling jacket. The model pollutant was methylene blue (MB) dye, the degradation of which was followed by UV-VIS spectroscopy, using a calibration curve obtained at a frequency obeying the Lambert-Beer law during the concentration range used.

Hydrogen peroxide was used in the present work according to advanced oxidation technology (AOT) for activating the photocatalytic degradation using the prepared Fe-PILC nanocomposite catalyst. Fig.2 depicts the MB decoloration activity of this catalyst in presence of different concentrations of H_2O_2 (between 0.1 and 0.5 mmol l^{-1}), whereby a concentration of 0.3 mmol l^{-1} gave evidently the optimum discoloration activity. Treatment of the concentration vs. discoloration in a simple first order form resulted in straight line plots of $\ln C/C_0$ vs. irradiation time (Fig. 3) and the k values accordingly calculated for each concentration are listed in Table 3. This table shows that the increase of H_2O_2 concentration from 0.1 up to 0.3 mmol l^{-1} , increases the photodiscoloration of MB to reach a maximum of 99% at 0.3 mmol l^{-1} , beyond which the color fading declines with a further increase of H_2O_2 concentration. Hence, in this work, this optimum concentration of H_2O_2 (0.3 mmol l^{-1}) was always

used. This phenomenon has been attributed [33] to the favorable role of hydrogen peroxide to continue the oxidation of the reaction products and avoiding their re-adsorption on the catalyst surface which, at higher concentration of H₂O₂, can compete with the dye for adsorption sites on the surface.

The degradation process takes place by combination of adsorption process of the dye on the surface of nano-composite clay which causes the discoloring of MB and the photo-oxidation process of the MB by oxidizing species. The sensitivity of MB dye to the visible light irradiation could be excited directly and its molecule injected electron in the conduction band of TiO₂ or Fe₂O₃ after which electrons were scavenged by oxygen adsorbed of the surface of the nano clay



Photocatalytic Degradation of MB

Irradiation of an aqueous solution containing a cationic dye (methylene blue; MB) with visible light in absence of a catalyst has been carried out for incremental periods up to 120 min, where 16.0% discoloration took place (Fig 4). The experiment was again carried out in absence of light irradiation (in dark) but in presence of the Fe-PILC to examine the behavior of adsorption of MB on the surface of this clay. It is found that during the initial 5 min, 10.0% decoloration of MB took place, (Fig.4) beyond which the desorption rate took place more slowly till at 120 min 25% discoloration was achieved. Repeating this experiment, also in dark and in presence of the same quantity of Fe-PILC, but, moreover adding 0.3 mmol l⁻¹ of H₂O₂, a more effective decoloration was achieved, such that during the initial 5 min, as high as 20.2% of MB decolorizes, and after 20 min 44.5% decolorizes. Nevertheless, at 20 min, discoloration amounted to 44.5%. Beyond 20 min, decoloration became insignificant such that it comprised 48.0% at 120 min. This experiment shows how effective has been the addition of H₂O₂, although in dark.

Fig .5 compares the photodiscoloration of MB in presence of the Fe-PILC and Ti-PILC while adding 0.3 mmol l⁻¹ of H₂O₂. The superiority of the former pillared clay catalyst is evident. Using the FePILC, MB discoloration is almost complete after 30 min irradiation, whereas 65% using the Ti-PILC. The apparent k values for this discoloration are 0.1145 and 0.0379 min⁻¹, respectively. However, on the Ti-PILC, the discoloration steps to higher rate between 60 and 80 min.

In another experiment (Fig. 6), Fe–Al-PILC has been prepared such that the pillars were composed of both Fe and Al located between the bentonite clay layers. Also an Al-PILC has been prepared then a solution of Fe in the form of Fe (NO₃)₃ was impregnated in order to fill the spaces between the Al pillars. This preparation has been performed such that Fe in both PILCs (Fe-Al-PILC and Al-Fe-imp-PILC) is of the same percentage. Using these two Fe-Al-PILCs as photocatalysts for MB photodiscoloration, it is found that the latter is more active indicating that the isolated

Fe distributed between pillars of Al gave higher photoactivity than when Fe is in the form of pillars.

Table 4 compares the discoloration rate constants, which have been calculated applying the plots in Fig.7. The activities of the current catalysts are arranged in the order:



Evidently, the light alone gives a negligible activity relative the photocatalytic values. The lower activity of the Ti-PILC compared to the Fe-PILC is attributed to the lower action of Ti than Fe in the visible light [35]. The lower activities of the Fe-Al-PILC and Fe(imp)-Al-PILC compared to that of the Fe-PILC is attributed to the lower Fe content of the former two catalysts.

CONCLUSION

Addition of 0.30 mmol l⁻¹ of H₂O₂ is the optimum quantity found to be the most efficiently accelerating the photodiscoloration of methylene blue in aqueous solution. Fe-PILC is the most active discoloration photocatalyst, compared to Fe-AL-PILC and AL-Fe(imp)-PILC catalysts. The latter catalyst is more active than the Fe-AL-PILC catalyst, since impregnated Fe particles inside the aluminum pillars is more active than that containing Al-Fe pillars. In these pillars, Fe particles are in bonded structures, whereas the impregnated Fe particles are isolated ones.

REFERENCES:

- [1] Gratzel, M. and Russel, F. H., *J. phys. chem.*, 94, (1990).
- [2] Millis, A., Peral, J. and Dmench, J., *J. Mol. Catal.* 87,67, (1994).
- [3] Zhu, H.Y. and Lu, G. Q., *Langmuir* 17,588, (2001).
- [4] Feng, J.Y., Hu, X. and P.L. Yue, *Environ. Sci. Technol*, 38,269, (2004).
- [5] Feng, J.Y., Hu, X., Yue, P.L., Zhu, H.Y. and LU, *Water Res.* 37,275, (2003).
- [6] Feng, J.Y., Hu, X., Yue, P.L., Zhu H.Y. and LU, G.Q, *Chem. Eng. Sci.* 58,679, (2003).
- [7] Kaneko, T., Fujii, M., Kodama, T. and Kitayama, Y. *J. Porous Mater.* 8,99, (2001).
- [8] Ooka, C., Akita, S., Ohashi, Y., Horiuchi, T., Suzuki, K., Komai, S., Yoshida, H. and Hattori, T., *J. Mater. Chem.* 9, 2943, (1999).
- [9] Yamanaka, S., Nishihara, T., Hattori, M. and Suzuki, Y., *Mater. Chem. Phys.* 17, 87, (1987).
- [10] Bernier, A., Admaiai, L.F. and Grange, P., *Appl. Catal.* 77, 269, (1991).
- [11] Khalfallah Boudali, L., Ghorbel, A., Tichit, D., Chiche, B., Dutartre, R. and Figueras, F., *Micropor. Mater.* 2, 525, (1994).
- [12] Yamanaka, S. and Makita, K., *J. Porous Mater.* 1,29, (1995).
- [13] Vicente, M.A., Banares-Munoz, M.A., Torenzo, R., Gandia, L.M and Gil, A., *Clay Miner.* 36, 125, (2001).
- [14] Sterte, J., *Clays Clay Miner.* 34, 658, (1986).
- [15] Kaneko, T., Fujii, M., Kodama, T. and Kitayama, Y., *J. Porous Mater.* 8, 99, (2001).

- [16] C. Ooka, H. Yoshida, M. Horio, K. Suzuki, T. Hattori, *Appl. Catal. B: Environ.* 41 (2003) 313.
- [17] Murayama, H., Shimizu, K., Tsukada, N., Shimada, A., Kodama, T. and Kitayama, Y., *Chem. Commun.* 2678, (2002).
- [18] Shimizu, K., Kaneko, T., Fujishima, T., Kodama, T., Yoshida, H. and Kitayama, Y., *Appl. Catal. A: Gen.* 225, 185, (2002).
- [19] Ooka, C., Akita, S., Ohashi, Y., Horiuchi, T., Suzuki, K., Komai, S., Yoshida, H. and Hattori, T., *J. Mater. Chem.* 9, 2943, (1999).
- [20] Yoneyama, H., Haga, S. and Yamanaka, S., *J. Phys. Chem.* 93, 4833, (1989).
- [21] Yoshida, H., Kawase, T., Miyashita, Y., Murata, C., Ooka, C. and Hattori, T., *Chem. Lett.* 715, (1999).
- [22] Ding, Z., Zhu, H.Y., Lu, G.Q. and Greenfield, P.F., *J. Colloid Interface Sci.* 209, 193, (1999).
- [23] Kaneko, T., Shimotsuma, H., Kajikawa, M., Hatamachi, T., Kodama, T. and Kitayama, Y. *J. Porous Mater.* 8, 295, (2001).
- [24] Shen, W., Li, Z., Wang, H., Liu, Y., Guo, O. and Zhang, Y., *J. Hazard. Mater.* 152, 172, (2008).
- [26] Xiao, Q., Zhang, J., Xiao, C., Si, Z. and Tan, X., accepted in *Solar Energy*, (2008).
- [27] Novotna, P., Zita, J., Krysa, J., Kalousek, V. and Rathousky, J., *Appl. Catal. B: Environ.* 79, 179, (2007).
- [28] Rightor, E.G., Tzou, M.S. and Pinnavaia, T.J., *J. Catal.* 130, 29, (1991).
- [29] Baksh, M.S., Kikkinides, E.S. and Yang, R.T., *Ind. Eng. Chem. Res.* 31, 2181, (1992).
- [30] Choe, H.J., Nam, I.S., Ham, S.W. and Hany, S.B., *Catal. Today* 68, 31, (2001).
- [31] Long, R.Q. and Yang, R.T., *J. Catal.* 186, 25, (1999).
- [32] Feng, J., Hu, X., and Yu, P.L., *Environ. Sci. Technol.*, 38, 269, (2004).
- [33] Coudurier, G., Naccache, C. and Vedrin, J.C., *J. Chem. Soc. Chem. Commun.*, 1413, (1982).
- [34] Sularez-Parra, R., Hernandez-Perez, I., Rincon, M.E., Liopez-Ayala, S. and Roldan-Ahumada, M.C., *Solar Energy Materials & Solar Cells* 76, 189, (2003).
- [35] Burrows, H.D., Ernestova, L.S., Kemp, T.J., Skurlatov, Y.I., Purmal, A.P., Yermakov, A.N., *Prog. React. Kinet.* 23, 145, (1998).

Table 1. XRF data for the prepared catalysts

Sample	Ti	Fe	Si	Al
Bentonite	0.0	5.4	69.3	18.7
Ti-PILC	34.5	2.5	51.5	12.0
Fe- PILC	0	34.0	51.5	14.5
AL- PILC	0	9.2	63.4	23.2
Fe-Al- PILC	0	12.6	50.6	28.2

Table 2. physico-chemical characteristics of prepared catalysts

Sample	Surface area m² g⁻¹	Particle size, nm Form XRD
Ti-PILC	301	27.3
Fe-PILC	280	12.2
Fe-Al-PILC	214	9.9

Table 3. Methylene blue decoloration reaction rate constants (k) at different additions of H₂O₂ using Fe-PILC catalyst

H₂O₂, mmol l⁻¹	k, min⁻¹
0.1	0.0179
0.2	0.0179
0.3	0.1145
0.4	0.0273
0.5	0.0089

Table 4. Methylene blue decoloration reaction rate constants (k) using different catalysts in presence of H₂O₂

Catalysts	k, min⁻¹
light	0.0021
Ti-PILC	0.0379
Fe- PILC	0.1145
Fe-Al- PILC	0.055
Fe (imp)-PILC	0.0841

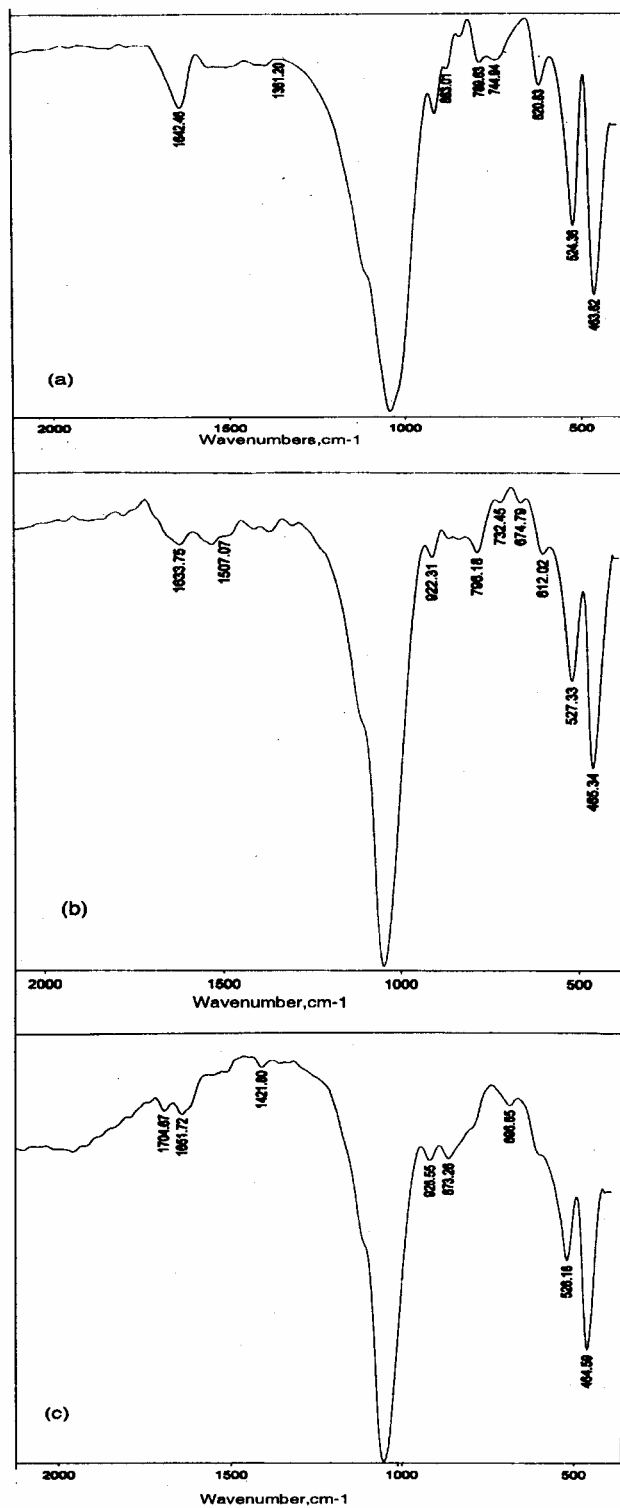
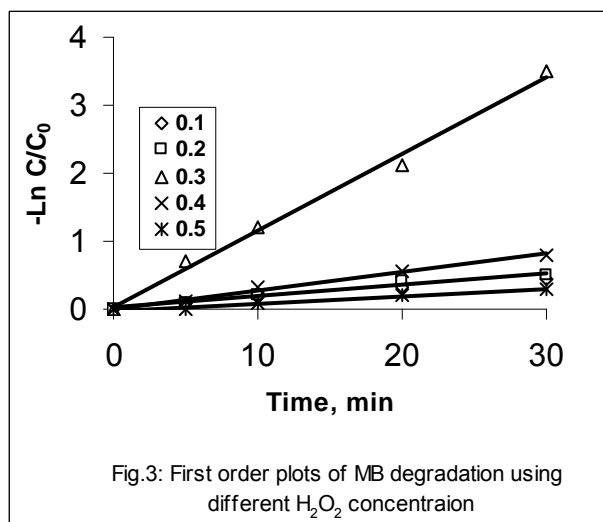
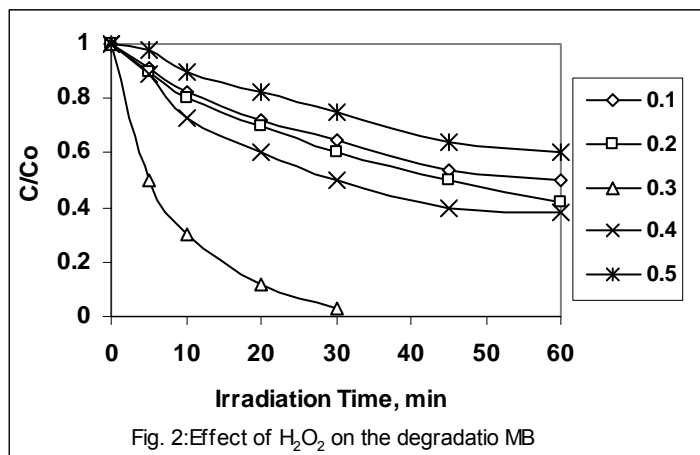
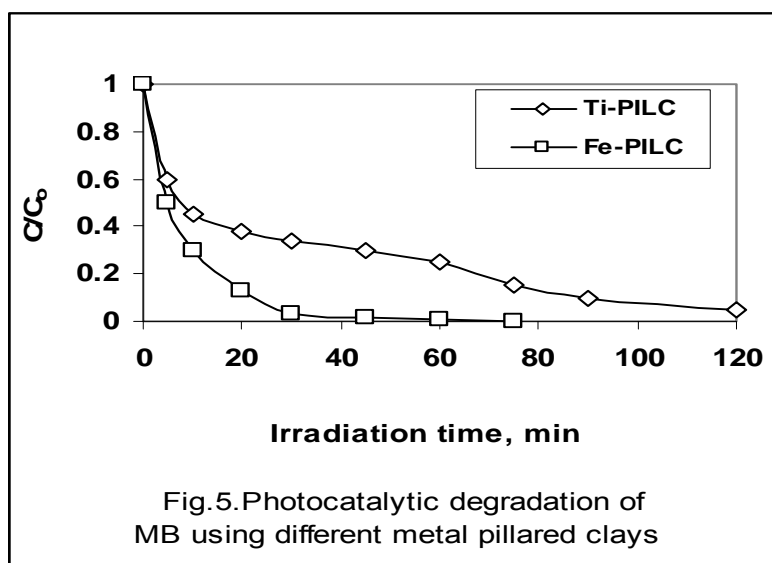
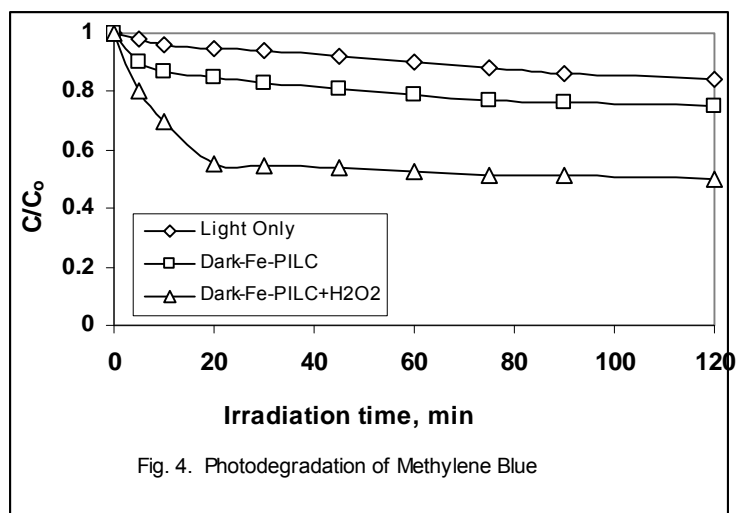


Fig.1. FTIR of the bentonite (a), Fe-PILC (b) and Fe-Al-PILC (c).





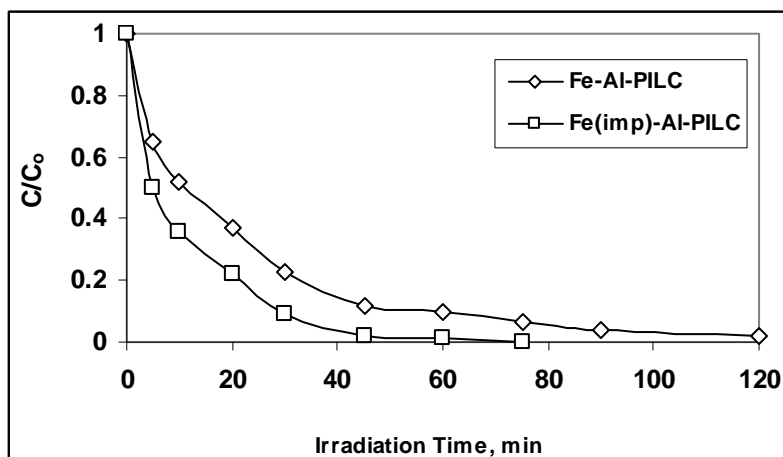


Fig.6. photocatalytic degradation of Mb using Fe-Al-PILC and Fe(imp) Al-PILC

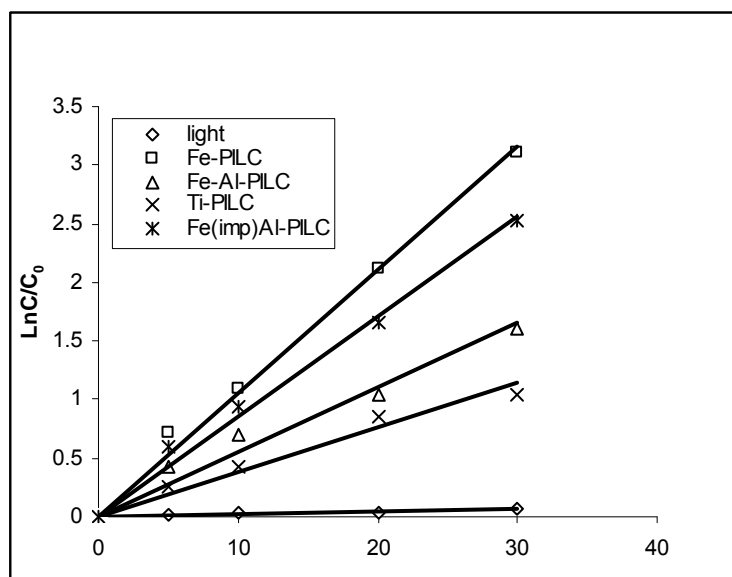


Fig.7: First order plots of MB degradation using different catalysts.