

DECOLOURIZATION OF METHYL ORANGE IN UV ASSISTED FENTON-LIKE REACTION USING FE-MKSF CATALYST

Nur Hidayati Abdullah¹, Nor Aida Zubir¹ and Hamizura Hassan¹
Faculty of Chemical Engineering, Universiti Teknologi MARA, Pulau Pinang Malaysia
*corresponding author: ¹hamizura179@ppinang.uitm.edu.my

ARTICLE HISTORY

ABSTRACT

Received
22 May 2017

Received in revised form
15 June 2017

Accepted
29 June 2017

In this work, two types montmorillonite clay (MKSF and MK10) were applied as catalyst support in heterogeneous UV assisted Fenton-like reaction. MKSF was chosen for the iron immobilization based on catalytic activity performance. Fe-supported montmorillonite KSF (Fe-MKSF) exhibited both increment in surface area, 175.208 m²/g and pore volume, 0.3536 cm³/g compared to the pristine MKSF as a result of incorporation of iron species onto MKSF matrix. The reactivity of Fe-MKSF was further tested on the effect of UV irradiation. Fe-MKSF exhibited 99% of methyl orange (MO) removal within 45 min of reaction under UVC illumination but it takes more than 120 min under UVA illumination. These findings proved Fe-MKSF as a promising alternative catalyst in decolourization of recalcitrant contaminant in wastewater.

Keywords: Montmorillonite clay; methyl orange; heterogeneous Fenton-like reaction UVA/UVC

1. INTRODUCTION

Pollution of water resources by azo dyes has drawn huge concern among environmental scientific researches because of its recalcitrant and stable azo structure. Numerous industries such as painting, textile, printing and plastics have extensively used azo dyes as colour pigments. In the textile industry, the dye loses to the water stream during dyeing and finishing operations with more than 700 000 tonnes discharged annually. Azo dye dominates over 50% of the total discharge (Q. Chen et al., 2010). The effluent poses a high potential threat to both ecological and human as it is carcinogenic and highly toxic (Hassan & Hameed, 2011a). Therefore, the need for proficient wastewater treatment is important to ensure safe effluent discharge into the environment.

Both physical and chemical treatments have been explored for azo dye wastewater remedies. Physical treatments such as adsorption processes also received fair consideration in the literature. However, studies reported the usage of biomass as economical adsorbents for dye wastewater remedies such as mussel shells (Haddad, 2015), sugar-extracted spent rice (Rehman, Kim, & Han, 2012), and rice husk (Zhang, Wang, Zhang, Pan, & Tao, 2016) in adsorption, only effective for certain types of dyes and ineffective in treating vast volumes of dyes-contaminated wastewater.

Advanced oxidation processes (AOPs) are innovative methods and robust alternatives in wastewater treatment. Extensive studies using AOPs in degrading various types of

contaminant including aromatic compound, volatile organic compound, halogenated hydrocarbon, pesticide as well as inorganic compound such as sulphides and nitriles (Soon & Hameed, 2011). Among the AOP's, Fenton or Fenton-like process has drawn the researchers' attention because it procure less cost as no energy required in producing hydroxyl radical. Despite of its advantage, Fenton process also faces several challenges for industrial application such as tight pH range, high iron loss that requires secondary treatment and hard for catalyst recovery after the reaction (Lan, Wang, Liu, Liu, & Qu, 2015). Fenton-like heterogeneous processes emerge as an alternative technique to overcome this limitation by the utilization heterogeneous catalysts. Heterogeneous Fenton process is widely studied by researchers since this technique proven to exhibit high proficiency in dye decolourization in wider pH range, high catalyst stability and very minimum iron loss (Rusevova, Kopinke, & Georgi, 2012).

Generally, homogeneous Fenton involved reaction of iron salts and hydrogen peroxide to produce hydroxyl radical. The highly reactive hydroxyl radical with oxidation potential of +2.8V (Khankhasaeva et al., 2015) will attack target contaminant competently and unselectively (Khataee, Salahpour, Fathinia, Seyyedi, & Vahid, 2015). While in heterogeneous Fenton, the iron species are immobilize onto the structure of catalyst support. The reaction of the heterogeneous Fenton process can be described as below:



The \equiv character represents the iron ions attach to the surface of the catalyst. Numerous type of supports have been applied as heterogeneous catalysts support in Fenton-like process. Among the supports, clay draws large attention as excellent support for iron immobilization because it is abundant, natural, and environmentally friendly (Pérez, Montes, Molina, & Moreno, 2014).

Montmorillonite is a type of clay from smectite group. It composed of one octahedral aluminate layers and sandwiched by two tetrahedral silicate layers. Iron, magnesium and aluminium ions occupies the octahedral site whereas silicon and aluminium ions occupies the tetrahedral centres (Fazaeli & Aliyan, 2007). Montmorillonite clay has intrinsic properties such as fine solid with high mesoporosity and active surface area. It is noteworthy that montmorillonite is an iron-rich catalyst and has high cation exchange capacity (CEC) value of 108.4 mequiv/100g clays (Ayodele, Auta, & Nor, 2012). These properties of montmorillonite clay make it a feasible catalyst support for waste water remedies. Previous study reported that powerful UV irradiation has potentials to degrade organic pollutant (Kusic, Koprivanac, & Srsan, 2006). However, in the case of dye decolourization, the degradation is difficult as certain type of dyes are photolysis -resistant (Riaz et al., 2012). The addition of UV light to heterogeneous Fenton-like process was reported to be very effective to speed up the dye decolourization process. The energy from the UV enhances the production of radical in heterogeneous Fenton in addition to photolysis of hydrogen peroxide (H_2O_2) itself. The photolysis of H_2O_2 can be described as follows:



In heterogeneous photo assisted Fenton-like reaction, Guo and co-workers (Guo, Lin, Zheng, Xiao, & Li, 2012) reported that more radicals such as hydroxyl and superoxide were produced due to transition electron from valance band to conducting band. As a result, heterogeneous Fenton like reaction with light irradiation degrade organic contaminant faster and more effective. Wide range of light in the spectrum are utilized in photo-assisted Fenton from visible light (Jia, Zhang, Wang, Habibi, & Zhang, 2016) to UVA (Bel Hadjltaief, Ben Zina, Galvez, & Da Costa, 2016), UVB (Petrella et al., 2014), and UVC (Riaz et al., 2012). A study of UVC assisted Fenton-like reaction in degrading acid orange 7 using laponite clay as support catalyst showed 100% dye removal in 45 min (Feng, Hu, Yue, Zhu, & Lu, 2003). Similar result has been observed in UVA irradiation where 100% decolourization of acid orange 7 was achieved in 120 min (J. Chen & Zhu, 2006). To the best of our knowledge, details study on montmorillonite clay as catalyst support combined with different energy source is not yet been explored. Hence, the use of montmorillonite clay as support in heterogeneous photo assisted Fenton-like reaction in different light spectrum seems to fill the loop in the literature domain.

The objective of this paper is to investigate the oxidative degradation of azo dye in heterogeneous photo assisted Fenton like reaction using Fe-MKSF as catalyst combined with different types of UV radiation. Methyl orange (MO), a mono azo dye, was chosen as model dye contaminant because of its widespread usage and recalcitrant behaviour (Wei et al., 2012). The effects of types of UV lights on catalytic activity of MO were discussed.

2. METHODOLOGY

2.1 Chemicals and Reagents

Azo dye, methyl orange (MO) and hydrogen peroxide, H_2O_2 (30% w/w) was purchased from Sigma Aldrich, iron precursor, iron (ii) chloride tetrahydrate, $FeCl_2 \cdot 4H_2O$ from Merck, sodium carbonate, Na_2CO_3 was purchased from QReC. For pH modification, 1M HCl and 1M NaOH had been used.

2.2 Catalytic Performance of Montmorillonite Clays as Potential Catalyst

The potential of montmorillonite KSF (MKSF) and montmorillonite K10 (MK10) clay as supports towards decolourization of MO was examined for adsorption and hydrogen peroxide (H_2O_2) activation performance. The catalytic activity was carried out using MO at concentration of 35 mg/L. The reaction was initiated by adding 6 mM hydrogen peroxide into the suspension consisting of 0.2 g/L motmorillonite clay at pH 3. The suspension was shaken at 150 rpm and sampling was taken in every 15 min time intervals. The samples were filtered using 0.2 μm syringe filters. The filtrates were immediately analyzed by a UV/Vis spectrophotometer (Perkin Elmer Lambda25 UV/VIS Spectrophotometer) at 464 nm wavelength. At the same time, in order to verify whether the adsorption was concurrently taking place during the catalysis; adsorption analysis was also been carried out via an analogous procedure in the absence of H_2O_2 . The decolourization of MO was calculated as follows:

Dye Decolourization = $\frac{C_t}{C_0}$, where C_0 (mg/L) is the initial concentration of MO at $t = 0$ and C_t (mg/L) is the concentration of MO at reaction time, (t, min).

2.3 Preparation of Fe-Clay Catalyst

The Fe-clay was synthesized by reacting solution consisting of iron precursor and dispersion of clays as described elsewhere (Feng et al., 2003). Na_2CO_3 was added slowly to vigorously stirred 0.2 M of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ solution at 1:1 molar ratio for $[\text{Na}^+]/[\text{Fe}^{2+}]$. The solution was continuously stirred until homogeneously mixed. Then, clay was added to the resultant solution. The iron precursor's/clay ratio was kept at 10 mmol of iron/g clay. The mixture was stirred for 2 h and subsequently aged at 95 °C for 5 h. The resulting precipitate was centrifugally recovered and washed several times using deionized water and dried at 60 °C overnight. The dried samples undergo calcination in air atmosphere at 350 °C for 20 h to produce the Fe-clay catalyst.

2.4 Characterization of Catalyst

The resultant catalysts will be characterized by using nitrogen sorption analysis (Micromeritic, ASAP 2020).

2.5 Catalytic Activity

The Fe-clay catalysts were tested in the both heterogeneous and UV assisted Fenton-like reactions for the oxidative degradation of MO. In brief, similar procedure and reaction conditions were employed in the heterogeneous Fenton-like reaction as previously described. For UV assisted Fenton-like reaction, the test were executed out by using a custom made photoreactor set-up equipped with 1 9W UV-C lamp (Sankyo-GPX9, λ_{max} 257.3nm) or 2 8W UV-A lamps (Sylvania Blacklite F8 W/BL350, $315 < \lambda < 380$ nm). A 200 mL beaker was placed in the center of the rig, with radiation by UV lamp as presented in Figure 2. The reaction was commenced by switching on the UV lamps after the addition of H_2O_2 into the suspension consisting of 0.2 g/L catalyst with 35 mg/L MO at pH of 3. Sampling was carried out 15 mins time intervals. The drawn-out suspension was then filtered and immediately analyzed as previously discussed.

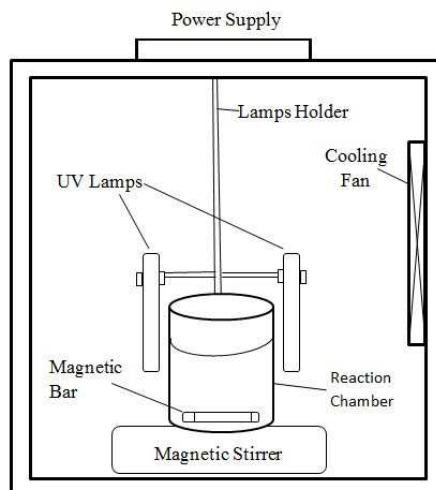


Figure 1: Schematic diagram of photoreactor

3. RESULTS AND DISCUSSION

3.1 Montmorillonite Clay as Catalyst Support

Two different type of montmorillonite clay have been chosen as potential support catalyst in heterogeneous Fenton-like reaction. The decolourization process is observed for 180 mins in incubating shaker with 150 rpm at pH 3 as Fenton reaction is at its optimum condition in acidic solution (Arshadi et al., 2016). The percentage removal of MO by catalytic and adsorption test were presented in Figure 2. The result indicated that MKSF depicted superior inherent catalytic activity of 50% compared to MK10, only 21% of colour removal. It was approximately 30% disparity between catalysis and adsorption of MO removal for MKSF whilst less 20% for MK10. As for adsorption process, less than 19% for MKSF and 13% for MK10, MO removal was achieved. Evidently, adsorption of MO onto clays did not contribute significant roles in decolourization process (Hassan & Hameed, 2011b). The difference percentage of MO removal for MKSF and its dissimilar to MK10 significantly showed that the effect of heterogeneous catalysis as both catalysis and adsorption occurs simultaneously (Zubir, Yacou, Motuzas, Zhang, & Diniz da Costa, 2014). This finding is in line with work done by Zubir et. al. (Zubir, Yacou, Zhang, & Diniz da Costa, 2014) as both adsorption and heterogeneous reaction of orange II occurs concurrently and can be described by details of Langmuir-Hinshelwood mechanism studies. Therefore, MKSF was chosen as better montmorillonite clay's support to synthesize Fe-clay catalyst.

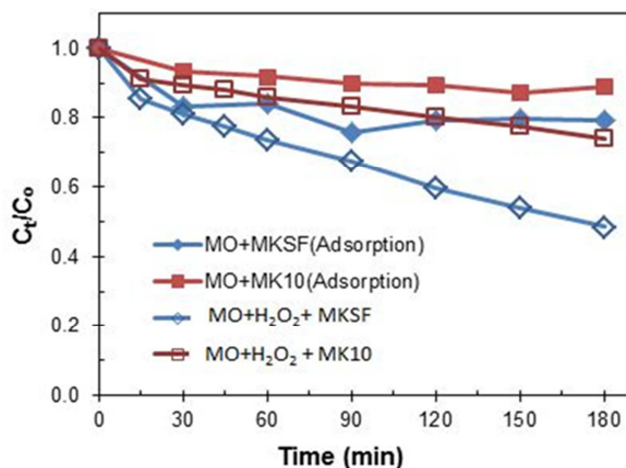


Figure 2: Decolorization of MO by MKSF and MK10 in heterogeneous Fenton-like reaction and adsorption. Reaction conditions : pH= 3, catalyst dosage= 0.2 g/L , initial concentration of MO = 35 mg/L and H₂O₂ concentration = 6 mM

3.2 Nitrogen Sorption Analysis

The textural properties of MKSF and Fe-MKSF were analyzed by nitrogen sorption analysis and the results are shown in Table 1 and Figure 3. Based on Figure 3, both MKSF and synthesized Fe-MKSF display the isotherms of type IV hysteresis loop extending from relative pressure of 0.40 to 0.98. The extended loop indicates a wide range of mesopores presences in the both samples. Prominent changes in pore volume were apparent in Fe-MKSF with more than 3 times higher compared to pristine MKSF. It is plausible owing to incorporation of iron species during synthesizing of catalyst. Moreover, the surface area of Fe-MKSF was increased up to 61% after iron immobilization onto MKSF matrix (Munoz, de Pedro, Casas, & Rodriguez, 2015). Enrichment of both surface area and pore volume of Fe-MKSF as displayed in Table 1 definitely provide high accessibility of dye pollutants towards active site during the catalysis (Zubir et al., 2015). These findings are in evidence with the enlargement of the initial pore width of MKSF upon the incorporation of active sites as presented in Figure 3b and 3c.

Table 1: The BET surface area and pore volume of MKSF and Fe-MKSF catalyst

Catalyst	Surface Area (m ² /g)	Pore volume (cm ³ /g)
MKSF	108.849	0.125
Fe-MKSF	175.208	0.3536

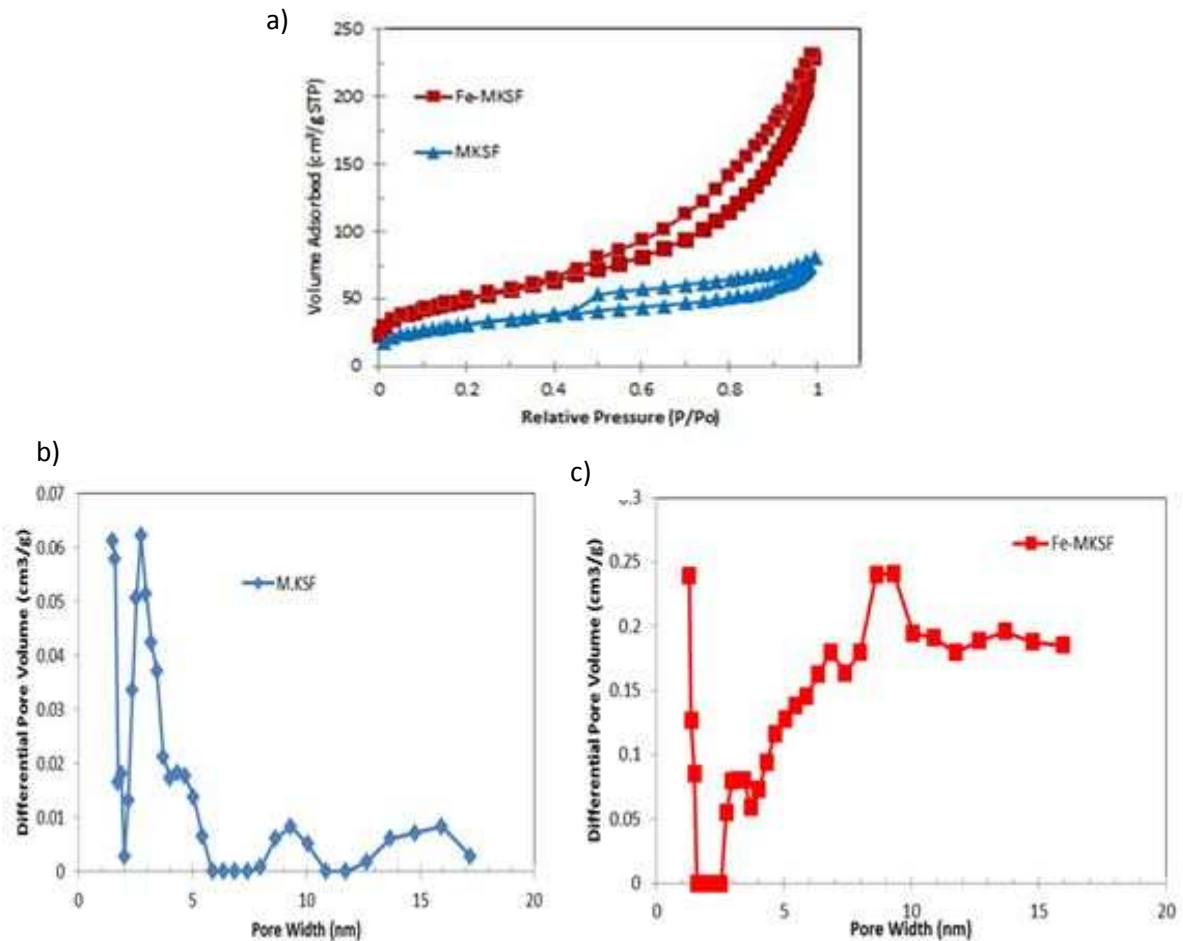


Figure 3: (a) Nitrogen adsorption-desorption of MKSF and Fe-MKSF, DTF pore size distribution for (b) MKSF and (c) Fe-MKSF

3.3 UV assisted Fenton –like Reaction

Figure 4 shows the decolourization profile of MO in heterogeneous Fenton-like reaction. Fe-MKSF exhibits a prominent decolourization profile of MO with almost 99% decolourization, achieved within 180 min reaction time. The improved catalytic activity of Fe-MKSF was suggested to be due to the well intercalation of active catalyst (Fe species) with MKSF matrix as well as the combined effect between both components.

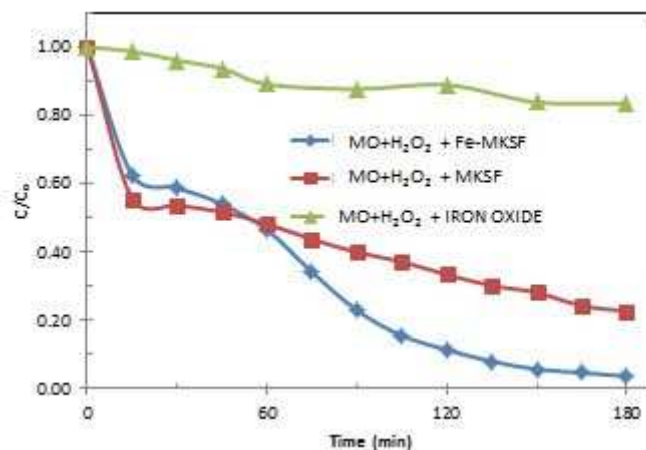


Figure 4: MO removal by heterogeneous Fenton-like reaction. Reaction conditions: pH= 3, catalyst dosage= 0.2 g/L , initial concentration of MO = 35 mg/L and H₂O₂ concentration = 12 mM

Similar catalytic performance of Fe-MKSF was observed in the UV assisted Fenton-like reaction using UVA and UVC. Upon the effective illumination of UVC (Figure 5a), MO was successfully decolorized within 45 min whilst almost complete decolourization in 120 mins for UVA radiation (Figure 5b). In contrast to the dark catalysis, the reaction took longer time to achieve the same decolourization result. Such enhanced catalytic behavior might be attributed to the synergistic effect of both components (Kerkez et al., 2014) (i.e. active catalyst and MKSF) in producing more hydroxyl radicals (HO[•]) to oxidize MO under photo assisted reaction process. The disparate reaction period of UVA and UVC can be attributed to photon of the light source respectively. UVC illuminate higher photon energy and shorter electromagnetic wavelength.

Theoretically, the mechanism of photo assisted Fenton-like reaction initiates when electron's energy is quantized, it will excite from valance band (VB) to conducting band (CB) of catalyst and moves to the surface, consequently react with oxygen and subsequently generating superoxide radicals. Meanwhile, a charged hole was produced due to electron excitement from the VB. This charged hole (h^+) react with water to form more hydroxyl radicals (Tian et al., 2013). Shorter wavelength of UVC (253.7 nm) comprises more energy in comparing with UVA ($315 < \lambda < 380$ nm), resulted in faster electron excitation in the same band gap of Fe-MKSF catalyst and thus increase the production of radicals.

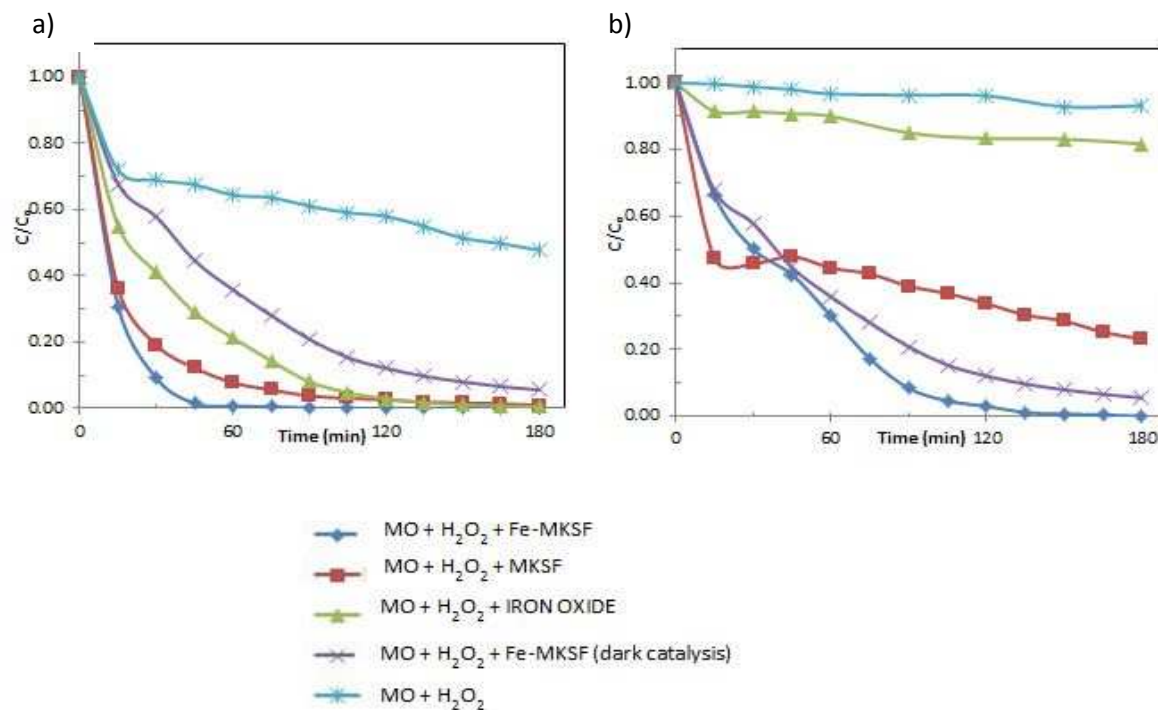


Figure 5: MO removal in (a) UV assisted Fenton-like reaction with 1 UVC, (b) 2 UVA. Reaction conditions: pH= 3, catalyst dosage= 0.2 g/L , initial concentration of MO = 35 mg/L and H₂O₂ concentration = 12 mM

4. CONCLUSION

Fe-MKSF catalyst has successfully degraded methyl orange in heterogeneous UV assisted Fenton-like reaction. Fe-MKSF showed increment in surface area and pore volume as the results of iron incorporation to the MKSF structure. Upon illumination of UVC, Fe-MKSF show superior performance by having 99% MO removal within 45 mins compared to 120 mins in UVA radiation. The exceptional performance of Fe-MKSF in UVC could be attributed to successful intercalation of Fe onto MKSF matrix and pristine photon from UVC. These findings proved Fe-MKSF as a promising alternative catalyst in rapid decolourization of recalcitrant pollutant in waste water treatment.

5. ACKNOWLEDGEMENT

The authors acknowledge the funding support under Research Acculturation Grant Scheme (RAGS/1/2014/TK05/UITM//1) from Ministry of Higher Education (MOHE), Malaysia that resulted in this article.

REFERENCES

- Arshadi, M., Abdolmaleki, M. K., Mousavinia, F., Khalafi-Nezhad, A., Firouzabadi, H., & Gil, A. (2016). Degradation of methyl orange by heterogeneous Fenton-like oxidation on a nano-organometallic compound in the presence of multi-walled carbon nanotubes. *Chemical Engineering Research and Design*, 112, 113–121.

<http://doi.org/10.1016/j.cherd.2016.05.028>

- Ayodele, O. B., Auta, H. S., & Nor, N. (2012). Artificial Neural Networks , Optimization and Kinetic Modeling of Amoxicillin Degradation in Photo-Fenton Process Using Aluminum Pillared Montmorillonite-Supported Ferrioxalate Catalyst. *Industrial & Engineering Chemistry Research*, 16311–16319.
- Bel Hadjtaief, H., Ben Zina, M., Galvez, M. E., & Da Costa, P. (2016). Photocatalytic degradation of methyl green dye in aqueous solution over natural clay-supported ZnO–TiO₂ catalysts. *Journal of Photochemistry and Photobiology A: Chemistry*, 315, 25–33. <http://doi.org/10.1016/j.jphotochem.2015.09.008>
- Chen, J., & Zhu, L. (2006). Catalytic Degradation of Orange II by UV-Fenton with Hydroxyl-Fe-pillared Bentonite in Water. *Chemosphere*, 65, 1249–1255.
- Chen, Q., Wu, P., Dang, Z., Zhu, N., Li, P., Wu, J., & Wang, X. (2010). Iron pillared vermiculite as a heterogeneous photo-Fenton catalyst for photocatalytic degradation of azo dye reactive brilliant orange X-GN. *Separation and Purification Technology*, 71(3), 315–323. <http://doi.org/10.1016/j.seppur.2009.12.017>
- Fazaeli, R., & Aliyan, H. (2007). Clay (KSF and K10) -supported heteropoly acids : Friendly , efficient , reusable and heterogeneous catalysts for high yield synthesis of 1 , 5-benzodiazepine derivatives both in solution and under solvent-free conditions. *Applied Catalysis A: General*, 331, 78–83. <http://doi.org/10.1016/j.apcata.2007.07.030>
- Feng, J., Hu, X., Yue, P. L., Zhu, H. Y., & Lu, G. Q. (2003). Degradation of Azo-dye Orange II by a Photoassisted Fenton Reaction Using a Novel Composite of Iron Oxide and Silicate Nanoparticles as a Catalyst. *Industrial & Engineering Chemistry Research*, 42(10), 2058–2066. <http://doi.org/10.1021/ie0207010>
- Guo, H., Lin, K., Zheng, Z., Xiao, F., & Li, S. (2012). Sulfanilic acid-modified P25 TiO₂ nanoparticles with improved photocatalytic degradation on Congo red under visible light. *Dyes and Pigments*, 92(3), 1278–1284. <http://doi.org/10.1016/j.dyepig.2011.09.004>
- Haddad, M. El. (2015). *Removal of Basic Fuchsin dye from water using mussel shell biomass waste as an adsorbent: Equilibrium, kinetics, and thermodynamics*. *Journal of Taibah University for Science*.
- Hassan, H., & Hameed, B. H. (2011a). Decolorization of Acid Red 1 by heterogeneous Fenton-like reaction using Fe-ball clay catalyst. In *International Conference on Environment Science and Engineering IPCBEE* (Vol. 8, pp. 232–236).
- Hassan, H., & Hameed, B. H. (2011b). Oxidative decolorization of Acid Red 1 solutions by Fe-zeolite Y type catalyst. *Desalination*, 276(1–3), 45–52. <http://doi.org/10.1016/j.desal.2011.03.018>
- Jia, Z., Zhang, W. C., Wang, W. M., Habibi, D., & Zhang, L. C. (2016). Amorphous Fe₇₈Si₉B₁₃ alloy: An efficient and reusable photo-enhanced Fenton-like catalyst in degradation of cibacron brilliant red 3B-A dye under UV-vis light. *Applied Catalysis B: Environmental*, 192, 46–56. <http://doi.org/10.1016/j.apcatb.2016.03.048>

- Kerkez, D. V., Tomašević, D. D., Kozma, G., Bečelić-Tomin, M. R., Prica, M. D., Rončević, S. D., ... Kónya, Z. (2014). Three different clay-supported nanoscale zero-valent iron materials for industrial azo dye degradation: A comparative study. *Journal of the Taiwan Institute of Chemical Engineers*, 45, 2451–2461. <http://doi.org/10.1016/j.jtice.2014.04.019>
- Khankhasaeva, S. T., Dambueva, D. V., Dashinamzhilova, E. T., Gil, A., Vicente, M. a., & Timofeeva, M. N. (2015). Fenton degradation of sulfanilamide in the presence of Al,Fe-pillared clay: Catalytic behavior and identification of the intermediates. *Journal of Hazardous Materials*, 293, 21–29. <http://doi.org/10.1016/j.jhazmat.2015.03.038>
- Khataee, A., Salahpour, F., Fathinia, M., Seyyedi, B., & Vahid, B. (2015). Iron rich laterite soil with mesoporous structure for heterogeneous Fenton-like degradation of an azo dye under visible light. *Journal of Industrial and Engineering Chemistry*, 26, 129–135. <http://doi.org/10.1016/j.jiec.2014.11.024>
- Kusic, H., Koprivanac, N., & Srsan, L. (2006). Azo dye degradation using Fenton type processes assisted by UV irradiation: A kinetic study. *Journal of Photochemistry and Photobiology A: Chemistry*, 181(2–3), 195–202. <http://doi.org/10.1016/j.jphotochem.2005.11.024>
- Lan, H., Wang, A., Liu, R., Liu, H., & Qu, J. (2015). Heterogeneous photo-Fenton degradation of acid red B over Fe₂O₃ supported on activated carbon fiber. *Journal of Hazardous Materials*, 285, 167–172. <http://doi.org/10.1016/j.jhazmat.2014.10.057>
- Munoz, M., de Pedro, Z. M., Casas, J. A., & Rodriguez, J. J. (2015). Preparation of magnetite-based catalysts and their application in heterogeneous Fenton oxidation - A review. *Applied Catalysis B: Environmental*, 176–177, 249–265. <http://doi.org/10.1016/j.apcatb.2015.04.003>
- Pérez, A., Montes, M., Molina, R., & Moreno, S. (2014). Modified clays as catalysts for the catalytic oxidation of ethanol. *Applied Clay Science*, 95, 18–24. <http://doi.org/10.1016/j.clay.2014.02.029>
- Petrella, A., Boghetich, G., Petrella, M., Mastrorilli, P., Petruzzelli, V., Petruzzelli, D., ... Via, E. (2014). Photocatalytic Degradation of Azo Dyes . Pilot Plant Investigation.
- Rehman, M. S. U., Kim, I., & Han, J. I. (2012). Adsorption of methylene blue dye from aqueous solution by sugar extracted spent rice biomass. *Carbohydrate Polymers*, 90(3), 1314–1322. <http://doi.org/10.1016/j.carbpol.2012.06.078>
- Riaz, N., Chong, F. K., Dutta, B. K., Man, Z. B., Khan, M. S., & Nurlaela, E. (2012). Photodegradation of Orange II under visible light using Cu – Ni / TiO₂: Effect of calcination temperature, 186, 108–119. <http://doi.org/10.1016/j.cej.2012.01.052>
- Rusevova, K., Kopinke, F., & Georgi, A. (2012). Nano-sized magnetic iron oxides as catalysts for heterogeneous Fenton-like reactions — Influence of Fe (II)/ Fe (III) ratio on catalytic performance. *Journal of Hazardous Materials*, 241–242, 433–440. <http://doi.org/10.1016/j.jhazmat.2012.09.068>
- Soon, A. N., & Hameed, B. H. (2011). Heterogeneous catalytic treatment of synthetic dyes in

- aqueous media using Fenton and photo-assisted Fenton process. *Desalination*, 269(1–3), 1–16. <http://doi.org/10.1016/j.desal.2010.11.002>
- Tian, S., Zhang, J., Chen, J., Kong, L., Lu, J., Ding, F., & Xiong, Y. (2013). Fe₂(MoO₄)₃ as an Effective Photo-Fenton-like Catalyst for the Degradation of Anionic and Cationic Dyes in a Wide pH Range. *Industrial & Engineering Chemistry Research*, 2.
- Wei, G., Fan, C., Zhang, L., Ye, R., Wei, T., & Tong, Z. (2012). Photo-Fenton degradation of methyl orange using H 3 PW 12 O 40 supported Fe-bentonite catalyst. *CATCOM*, 17, 184–188. <http://doi.org/10.1016/j.catcom.2011.11.003>
- Zhang, S., Wang, Z., Zhang, Y., Pan, H., & Tao, L. (2016). Adsorption of Methylene Blue on Organosolv Lignin from Rice Straw. *Procedia Environmental Sciences*, 31, 3–11. <http://doi.org/10.1016/j.proenv.2016.02.001>
- Zubir, N. A., Yacou, C., Motuzas, J., Zhang, X., & Diniz da Costa, J. C. (2014). Structural and functional investigation of graphene oxide-Fe₃O₄ nanocomposites for the heterogeneous Fenton-like reaction. *Scientific Reports*, 4, 4594. <http://doi.org/10.1038/srep04594>
- Zubir, N. A., Yacou, C., Motuzas, J., Zhang, X., Zhoa, X. S., & Diniz da Costa, J. C. (2015). The sacrificial role of graphene oxide in stabilising a Fenton-like catalyst GO-Fe₃O₄. *Chemical Communication*, (45), 9291–9293. <http://doi.org/10.1039/C5CC02292D>
- Zubir, N. A., Yacou, C., Zhang, X., & Diniz da Costa, J. C. (2014). Optimisation of graphene oxide-iron oxide nanocomposite in heterogeneous Fenton-like oxidation of Acid Orange 7. *Journal of Environmental Chemical Engineering*, 2(3), 1881–1888. <http://doi.org/10.1016/j.jece.2014.08.001>