

MB Dye Removal by Adsorption and Photo-Degradation using Modified (Mobil Composition of Matter No 41) MCM-41

Lopamudra Mohanty, Suresh Kumar Dash*, Lizarani Biswal, Sadhana Pradhan

Article Info

Volume 82

Page Number: 2614 - 2621

Publication Issue:

January-February 2020

Abstract

Dyes in surface water are ubiquitous mostly due to textile industries, tanning, dye-stuff manufacturing, and food processing industries. These are the crucial reasons of water contamination. For the recalcitrant or non-biodegradable nature they pose a great threat to the aquatic animals and act as carcinogens and very toxic to mammals. Different methods are used to remove dyes i.e. reverse osmosis, and ultra-filtration. In this paper we have compared two methods that are low cost, efficient and have repetitiveness. Iron and cobalt doped “(MOBIL COMPOSITION. OF MATTER NO 41) MCM-41” and transitional metal doped TiO₂ – “(MOBIL. COMPOSITION OF MATTER NO. 41) MCM-41” were taken as the adsorbents and photo catalysts respectively. The characterisation with PXRD, SEM, FTIR and UV-DRS showed that the alteration are not change the structure, huge surface zone and greater pore volume of pristine “(MOBIL COMPOSITION. OF MATTER NO 41) MCM-41” This acted as a very good adsorbent in removing MB at PH = 4 and at a temperature of 308 K. The uptake was more with increment in starting fixation and absorbent position. It pursued a chemical reaction of second order and connected well to Freund-lich model. The photo catalytic degradation with transition metal incorporated TiO₂ “(MOBIL COMPOSITION. OF MATTER NO 41) MCM-41” is best fit for Pseudo-first order kinetics under visible light. Between the studied methods the dye removal was optimum upto 99% in 2 h during adsorption and 100% in 1 h during photo degradation. Therefore it is concluded that photo catalytic degradation is a more efficient method in comparison to adsorption for aqueous dye removal from surface water.

Article History

Article Received: 14 March 2019

Revised: 27 May 2019

Accepted: 16 October 2019

Publication: 18 January 2020

Keywords: Adsorption, photo catalytic degradation, (MOBIL. COMPOSITION OF MATTER NO 41) MCM.-41

I. INTRODUCTION

Currently, water pollution has become a severe global problem due to contamination of ground and water by hazardous material coming from various industrial sectors. A large amount of dye in surface water comes from many industrial and food

processing plants [1]. The presence of noxious colorants cause water toxicity and due to their non bio degradability the toxic water causes lethal diseases to human beings [2-3]. A great deal of work has been finished by utilizing physical, substance and natural strategies for expelling hued contaminants from drain

water. The most popular methods are used including adsorption, flocculation, coagulation, electrolysis, bio degradation and photo catalytic degradation. It can be modified by using transition metal or transition metal oxide, organic compound, polymer etc [4-5]. The advanced photo degradation method and adsorption method are used for the removal of dye by using various modified ("MOBIL COMPOSITION OF MATTER NO 41) MCM-4" [6-7]. *Cestari et al.* did the surface modification of amine groups on mesoporous silica gel with 3-(trimethoxysilyl) propylamine to remove yellow and red dyes [8]. Mn doped ("MOBIL COMPOSITION OF MATTER NO 41) MCM-41" to improve the adsorption efficiency for methyl blue [9]. A. V. *Borhade* synthesized ("MOBIL COMPOSITION OF MATTER NO 41) MCM-4" by hydrothermal for removal of the EG dye by photo degradation method [10]. Bi/Ti ("MOBIL COMPOSITION OF MATTER NO 41) MCM-4" for degradation of the MB [11]. Photo degradation of methyl orange by *Liu et al* [12]. Amine- and carboxylic functional groups modified ("MOBIL COMPOSITION OF MATTER NO 41) MCM-41" The photo degradation of Methyl Orange by ZnO loaded ("MOBIL COMPOSITION OF MATTER NO 41) MCM-41" [12]. TiO₂ loaded W- ("MOBIL COMPOSITION OF MATTER NO 41) MCM-41" for degradation of Methyl orange [14] TiO₂ supported on ("MOBIL COMPOSITION OF MATTER NO 41) MCM-41" for the photo degradation of the aqueous orange II [14]. Recently, a carbonaceous material shows high effectiveness. [14].

II. MATERIALS AND METHODS

Amalgam of ("MOBIL COMPOSITION OF MATTER NO 41) MCM-41"

The amalgam of ("MOBIL COMPOSITION OF MATTER NO.41) MCM-41" is generally performed by sol-gel process. It requires only four gradients, a template (surface directing agent), a silica source, mineralizing agent (to dissolve silica) and a solvent. By *Terres et al.* [08], the amalgam of MCM-41 is

prepared. 2.4g of CTAB was mixed in 120ml of DI under vigorous stirring for 30min by magnetic stirrer to obtain a homogeneous solution. 8ml of aqueous NH₃ was added to the solution after complete dissolution, continuous stirring was going on. Then after 30min 12 ml TEOS is add in mixture (to make 0.05M solution) drop wisely under vigorous stirring for 1h. The mixture was taken off and the solution was filtered. The residue was then kept in the oven for drying. After it completely dried, the obtained substance was grinded by using by mortar and pastel. To make the product porous free and to remove the surfactant, it was calcined at 550°C for 5h [06].

Amalgam of adsorbents:

Ferrum-doped (MOBIL COMPOSITION OF MATTER NO 41) MCM-41 and Co-MCM-41 :

To elude from the arrangement of oxides and hydroxides of iron, different measures of Fe doped ("MOBIL COMPOSITION OF MATTER NO 41) MCM-41" that is combined by changing the first technique in antacid medium at pH value ranges from 8.0 to 8.5. For iron adjustment 0.57 g of Fe(NO₃)₃·9H₂O salt was taken in a measuring beaker, then 50ml of water was added and stirred on a magnetic stirrer. After 30 min 2 g of unclaimed (MOBIL COMPOSITION OF MATTER NO 41) MCM-41 was added of and stirred for 2 hours. Then it was sonicated for 2 h and ageing was done for overnight and filtered and the residue was dried by hot air oven. Then that was calculated for 5 h at 500°C. The similar procedure was followed to prepare Co- ("MOBIL COMPOSITION OF MATTER NO 41) MCM-41" with 0.4gm of the Co (NO₃)₂·6H₂O.

Amalgam of TiO₂- ("MOBIL COMPOSITION OF MATTER NO 41) MCM-41"

TiO₂- ("MOBIL COMPOSITION OF MATTER NO 41) MCM-41" was amalgamate by co-precipitation technique by taking the titanium (IV) isopropoxide as titania source [19]. Titanium isopropoxide (0.45 gm) and (1.5g) Cetyl trimethyl ammonium bromide (CTAB) were collected with 30 ml distilled liquid (i.e. water). Then that mixture was stirred for 15min. 3ml

of tetraethyl orthosilicate (TEOS) can be wisely added in the above mixture and 46 ml ethanol (C_2H_5OH) was mixed with the above solution with vigorous stirring of 15min. At one time 10ml of ammonium hydroxide (NH_4OH) is further added into blend & was stimulated for 31 minutes. The mixture was filtered, washed and dried for 24h in an oven at $80^\circ C$. The final product was ground with the help of mortar and pestle, to keep away from environmental contamination it should be in air tight glass bottle. This contains 15% TiO_2 .

Amalgam of Cr/TiO_2 -("MOBIL COMPOSITION OF MATTER NO 41) MCM-41" and Mn/TiO_2 -("MOBIL COMPOSITION OF MATTER NO 41) MCM-41"

Cr/TiO_2 -("MOBIL COMPOSITION OF MATTER NO 41) MCM-41" is prepared with the help of ultrasonic-assisted "pH-adjusting" method taking Chromium trioxide (Cr_2O_3) as dopant metal and TiO_2 -("MOBIL COMPOSITION OF MATTER NO 41) MCM-41" as support material that has semiconducting property in photocatalysis. 1g of 15% TiO_2 -("MOBIL COMPOSITION OF MATTER NO 41) MCM-41" was dispersed in 1g of 1.6 M chromium-oxide (Cr_2O_3) for getting homogeneous solution [07]. An ultrasonic sensor cleaning machine is used for sonication of the mixture at the room temperature (for 1 hr.). The product was then filtered by Whatmann-40 filter paper. The residue was washed by the help of deionized liquid that is used for removing an unreacted support material, then it is dried in a hot air kiln for 1h at $110^\circ C$. Then the surfactant was removed by calcinations in a muffle furnace for 5h at $550^\circ C$ with a temperature gradient of $2^\circ C/min$. The similar procedure was followed to prepare Mn/TiO_2 -("MOBIL COMPOSITION OF MATTER NO 41) MCM-41" by taking potassium permanganate ($KMnO_4$) as manganese source [08][09].

Then the prepared samples were subjected for spectral characterisation by XRD (PERKIN-ELMER), SEM

(NOVANOSEM 450), UV-DRS (VARIEN CURY) and FTIR (SIMATZU) techniques.

METHODS

Adsorptive removal of MB by adsorbents

Methylene Blue stock mixture was set up by dissolving MB (weight- 1.0g & 99% purity) with purified liquid (1000 ml) in a volumetric flask. Then it was diluted to acquire arrangement of 100 to 400 mg/L of MB solution. 0.1N HCl and 0.1 N NH_4OH are used to change the value of PH. 0.02 g of Fe/Co-("MOBIL COMPOSITION OF MATTER NO 41) MCM-41" adsorbent with 20 mL liquid solution of MB is added for batch mode tests and was stirred for 2h at 300 K on a magnetic stirrer. The batch style trainings were done by changing many parameters, for example, temperatures, starting concentration. The adsorption isotherm was obtained at optimum conditions.

Photo deprivation of MB

By using an appropriate amount of catalyst and 100 mL of "MB solution of dye" (20 mg/L MB), the deprivation experiment of MB dye performed in a beaker. The solution is filtered in sunlight after 2 h of stirring. Then filtrate is collected and analyzed via UV-visible for pH adjustment (ELICO SL244) to detect the remaining concentration of MB dyes at absorption maxima = 556nm.

III. RESULTS AND DISCUSSION

Spectral Characterisation of adsorbents and photo catalysts

According to the Fig.1 the morphology of Fe-("MOBIL COMPOSITION OF MATTER NO 41) MCM-41" and Co-("MOBIL COMPOSITION OF MATTER NO 41) MCM-41" is uniformly distributed with the spherical particles of the metal oxides. The incorporation of Fe and Co in to the framework of hexagonal ("MOBIL COMPOSITION OF MATTER NO 41) MCM-41" can be assumed basing upon the activity of adsorbent during removal of MB dye. The agglomerated metal oxide is well

distributed uniformly on the surface of (MOBIL COMPOSITION OF MATTER NO 41) MCM-41.

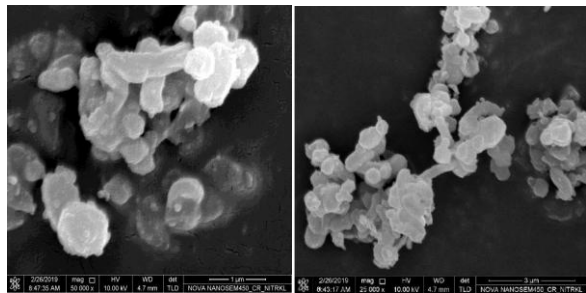


Figure -1. FESEM of Fe/Co-(“MOBIL COMPOSITION OF MATTER NO 41) MCM-41”

As showed in Fig.2 the angle of XRD pattern of Fe-(“MOBIL COMPOSITION OF MATTER NO 41) MCM-41” and Co-(MOBIL COMPOSITION OF MATTER NO 41) MCM-41 conforms either mesoporosity or long range order of silica matrix in the materials. The regions shown at 20-25° 2θ conforms subsistence of Fe₂O₃ and Co₂O₃ amorphous layers on (“MOBIL COMPOSITION OF MATTER NO 41) MCM-41”. Any other peak obtained after 30° conforms the presence of transition metal incorporations.

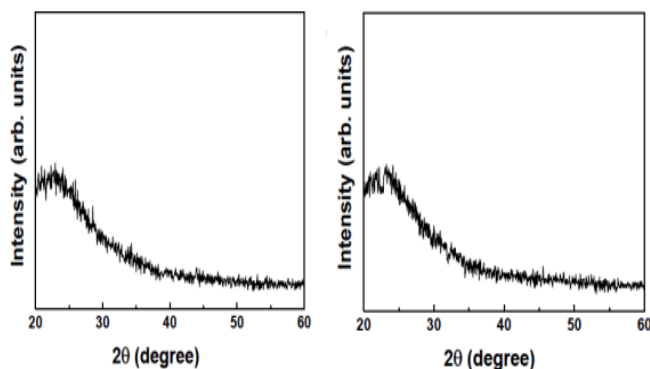


Fig-2 angle of XRD design of Fe/Co-(“MOBIL COMPOSITION OF MATTER NO 41) MCM-41”

immersion of MB in to Fe/Co-(“MOBIL COMPOSITION OF MATTER NO 41) MCM-41”

Immersion Isotherms

The Langmuir and the Freund-lich adsorption isotherms models are examined to analyse the sorption isotherm. The adsorption model of Langmuir

was often used to describe the sorption of a liquid solution as equation (1),

$$C_e/q_e = 1/Q_0.b + C_e/Q_0$$

(1)

The adsorption efficiency has been estimated by the RL dimensional balance parameter defined in equation (2),

$$RL = 1/ 1+ b.C_0,$$

(2)

Where, C_0 is primary concentration of the cobalt in solution (mg/L). 23

The Freundlich isotherm is mainly used to explain the adsorption of the organic components and inorganic components in the solution (Fig. 3). Such empirical very satisfactory can be used for non-ideal sorption involving heterogeneous sorption and expressed as an equation (3),

$$q_e = K_F . (C_e)^{1/n}$$

(3)

the logarithmic form is given as equation (4),

$$\log q_e = \log K_F + n \log C_e$$

(4)

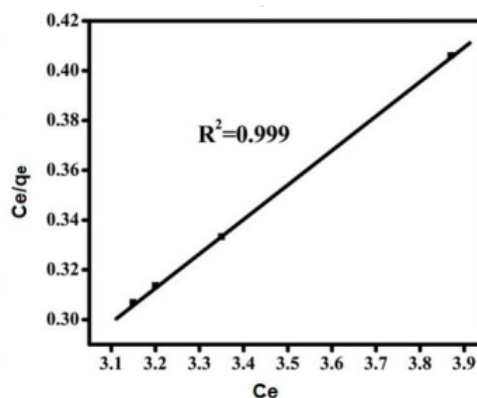


Fig.3 Adsorption isotherm of MB onto Co-(“MOBIL COMPOSITION OF MATTER NO 41) MCM-41” fitted well to Freundlich model. The Langmuir model considered presumptions like the confined adsorption, comparative energies on all the dynamic locales and the restricting response of the surface [08]. Joining of iron particles into the dividers of (“MOBIL COMPOSITION OF MATTER NO 41) MCM-41” creates negative focuses that upgrade the material performance towards cationic colors

absorption. The amalgam and portrayal of iron fused (“MOBIL COMPOSITION OF MATTER NO 41) MCM-41” (Fe-(“MOBIL COMPOSITION OF MATTER NO 41) MCM-41” and its reactant properties are already announced. The development of oxides and hydroxides of iron were restricted and stacking of iron into the structure was similarly featured [14].

pH Consequences

The adsorbent pH value plays an important role during adsorption due to change in surface charges of the adsorbate. As Fig.8. Illustrates the percentage removal of MB onto Co-(“MOBIL COMPOSITION OF MATTER NO 41) MCM-41” increased from 58% to 93% with an increase in from pH~2 to pH~10. After that the uptake remained constant with further increase in pH value. It is due the presence of positively charged H⁺ ions at lower pH that competed with cationic MB dye thus decreasing the amount of adsorption. As schemed in Fig.8 OH⁻ ions Co-(“MOBIL COMPOSITION OF MATTER NO 41) MCM-41” favored the adsorption of positively charged MB dye increasing the uptake to 93%.The optimum pH is 9.

The consequences of an agitation time on MB dye removal by Co-(“MOBIL COMPOSITION OF MATTER NO 41) MCM-41” is represented in Figure. 4. The dye removal percentage is increased by increasing an agitation time and after 20 minute's it will reach up to an equilibrium for the MB dye concentration (100 mg/l used). During agitation 75% of MB was removed after 5 min that increased to 76.2% after 20 min and almost remained same with increase in agitation time. However, the removal percentage of MB is decreasing by increasing in dye concentration ranges 20 - 100 mg/l. The percent dye removal at equilibrium decreased from 95% to 76%. Consequently, the crowdedness produced with the help of dye molecules of MB and reach up to the equilibrium state after 60 min (almost 97.33%) [11].

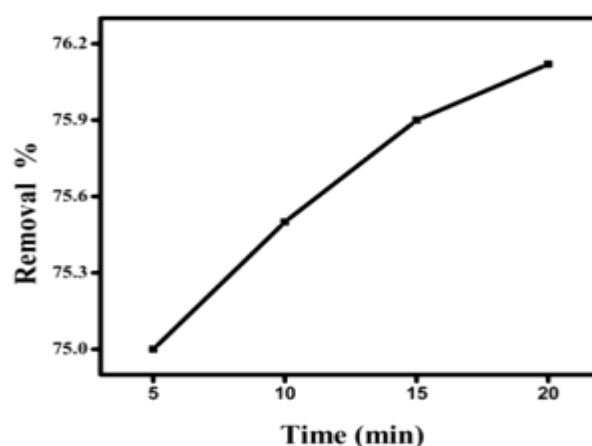


Fig.4 agitation time consequences by removal of MB through Co-(“MOBIL COMPOSITION OF MATTER NO 41) MCM-41”.

The MB elimination efficiency is affected by the solution temperature because of the surface textural features of adsorbents. The rate of the diffusion is increased by decreasing the solution viscosity via increasing temperature. [25].

Photocatalytic degradation of MB by Cr/Mn-TiO₂-(“MOBIL COMPOSITION OF MATTER NO 41) MCM-41”

Spectral Characterization of photocatalysts

From figure 5, the lower angle of XRD pattern of (“MOBIL COMPOSITION OF MATTER NO 41) MCM-41” exhibits the characteristics interferences of long range ordered mesoporous material corresponds to the d₁₀₀, d₁₁₀ and d₂₀₀ diffraction pattern by using the Cu K α radiation. The Cr modified 15%TiO₂-(“MOBIL COMPOSITION OF MATTER NO 41) MCM-41” appeared greenish fine powder. The peak for 15% TiO₂ loaded are agree with the *N. Riaz et al.* [10] and *O. Y. Khai* [11] which corresponds to the peak of $\theta_2 = 26.44^\circ$ and $\theta_2 = 28.46^\circ$. The x-ray diffraction pattern of Manganese modified 15%TiO₂-(“MOBIL COMPOSITION OF MATTER NO 41) MCM-41” become visible in Grey colour, represent a long order range mesoporous structure by using Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation .

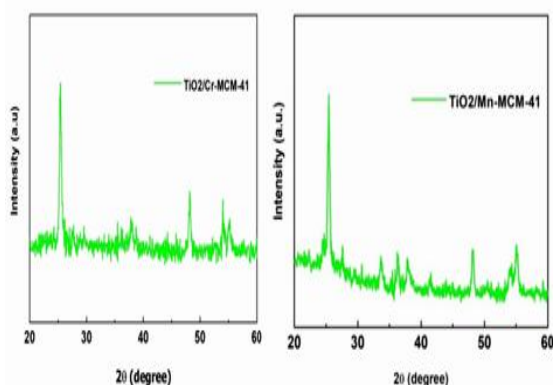


Fig- 5 Metal doped TiO₂- (“MOBIL COMPOSITION OF MATTER NO 41) MCM-41” XRD angle pattern

Similar result were obtained by *N.Riaz et al.*[24, 25] for agglomeration of Cu/TiO₂ which has spherical shaped morphology.

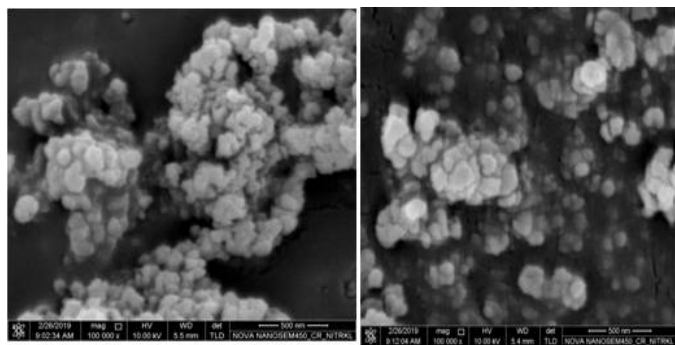


Fig 6 FESEM images of a) Cr/TiO₂-MCM-41 b) Mn/TiO₂-MCM-41

The Figure-7 represents the ultra violet-Visible DR bands Cr/Mn doped TiO₂ supported on (“MOBIL COMPOSITION OF MATTER NO 41) MCM-41” materials. The adsorption peak shift towards visible region after doping of Cr/TiO₂ into the (“MOBIL COMPOSITION OF MATTER NO 41) MCM-41”. The spectra determined at 200-700 nm indicate the presence of Chromium / TiO₂- (“MOBIL COMPOSITION OF MATTER NO 41) MCM-41”. The absorption peak ranges from 190-400 nm show the presence of TiO₂ [08]. The broad adsorption peak ranges 400-800 nm established the presence of Cr [08]. With the increase in volume of doping material, the absorption spectra is increased at visible region [09]. The band gap can be calculated by equation (5),

$$\alpha h\nu = A (h\nu - E_g)^n$$

(5) “a, A, ν , and E_g are the coefficient of absorption, frequency of light, proportionality constant, and band

gap, correspondingly”. For the direct transition the value of the n is ½ and 2 for indirect transition. The band gap of (“MOBIL COMPOSITION OF MATTER NO 41) MCM-41” is 4.5ev. After modification of (“MOBIL COMPOSITION OF MATTER NO 41) MCM-41” with TiO₂ band gap is shifted to 3.2ev [11]. Again by modification with Mn, the band gap is further reduced to 1.90ev. The presence of TiO₂ in UV-vis DRS spectrum ranges from 190-400 nm, and transition metal incorporated Mn/TiO₂ activates the catalyst under visible spectrum [10]. The bandgap of the photocatalyst can be calculated as reported earlier [11].

In sample different functional group can be known from the FTIR spectra. The FTIR spectra of Cr/Mn-TiO₂- (“MOBIL COMPOSITION OF MATTER NO 41) MCM-41” are shown below. Absorption peak at 955 cm⁻¹ represents Si-OH vibration and asymmetric of Si-O-Si group showed at 1086, 1370 cm⁻¹. A TiO₂ spectrum appears at 400 cm⁻¹ but overlaps with bending Si-O-Si group. The peak at 1620-1650 cm⁻¹ associates with the vibration of water molecule. The absorption peak at 970 cm represents Si-OH vibration and asymmetric of Si-O-Si group showed at 1050,1240 cm. TiO₂ spectra appears at 400cm but overlaps with bending Si-O-Si group. The peak at 1620-1650 cm associates with the vibration of water molecule.

Effect of pH:

The pH of solution performs a critical role in photocatalytic degradation of the dye solution. The rate of reaction and surface charge of TiO₂ varies with the any change in pH solution. Thus the surface of the titania may be positively or negatively charged according to the value of pH_{zpc} (The zero point charge is responsible for adsorption) when it is in acidic or basic medium. The degradation of methylene blue occurs in between 4 to 8 pH as shown in the above fig-9. It explains that the surface of the photocatalyst acquires a negative charge at lower pH values that supports MB adsorption. It is also views that the

charged state cannot be due to change in pH [12]. In alkaline medium, hydroxyl radical ($\bullet\text{OH}$) an oxidant can be formed.

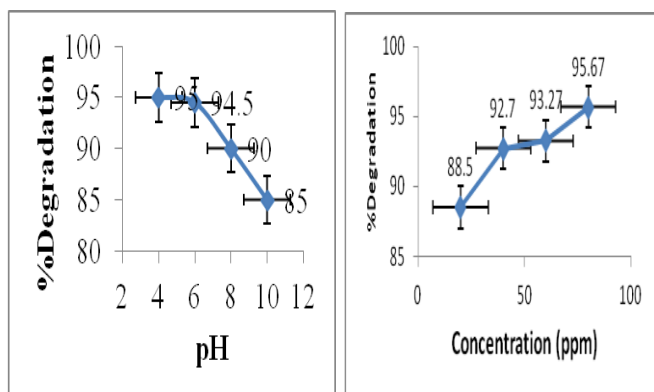


Figure 7. Consequences of pH on MB Photodegradation. Fig 10. Effect of concentration Of MB by Cr /TiO₂-("MOBIL COMPOSITION OF MATTER NO 41) MCM-41"

Effect of Concentration:

The absorption of dyes impacts a photo degradation rate. The primary concentration of the dye solution is an important parameter for the photo degradation. The percentage degradation is decreasing by increase in the quantity of dye is due to two facts. i) With an increase in the amount of dye, the adsorption of no of dye will increase on the surface of catalyst; hence active sites will be reduced. So the OH^- ion generation will be diminished. ii) On increasing the concentration of dye, the no of photons will diminished hence the dye molecule will absorb more light. But the excitation of photocatalyst by photons will diminished. So the degradation efficiency decreases [14].

Here MB exhibit the highest photodegradation rate with the increase amount of concentration. Similar response was observed by Huajing Gao et al. 2018 [13] by using CeO_2 nano particle as photocatalyst under the solar light for MB. (Methyl Orange, Rhodamine 6G) using different photocatalyst (TiO_2 , ZnO , SnO_2 , ZnS , CdS) under the UV and solar light.

Effect of Catalyst amount:

The rate of the degradation has also affected by the quantity of photocatalyst. The rate of the degradation

risers with the amount of photocatalyst dosage because with rise in number of the particles, there will be increase in adsorption of no of photons and also in the adsorption of no of the dye molecules. When the amount of catalyst is more than 0.04g, the rate of degradation will decrease due to the aggregation of molecules that helps in decreasing the quantity of active sites. So the path of irradiation will be diminished. Apart from this the quantity of active sites of photocatalyst becomes more with the increase in the dose of the catalyst which is responsible for enhancement of the OH^- particles that is the main reason for degrading dye from solution [13].

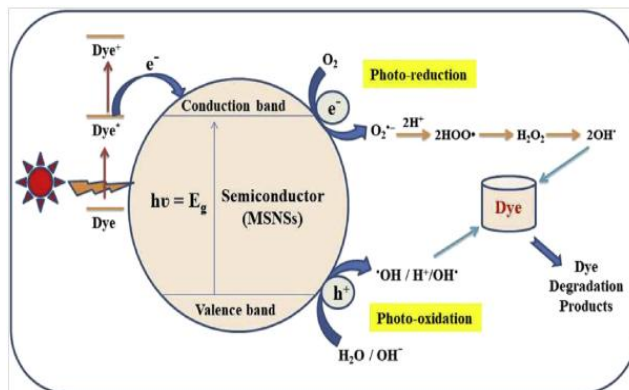


Fig.8. Proposed mechanism of photocatalytic degradation of the dye by solar light

By increasing a photo catalyst amount the dye depreciation ratio increases with increase in weight. Since it is directly proportional to the amount absorption of photo-catalyst. It is verified that optimum catalyst load increases the surface area which will depend on the first dye concentration value. The mixture becomes turbidity with the increase in higher amount of catalyst so the interpenetration of radiation decreases. At last the degradation rate decreases.

IV. CONCLUSIONS

The ubiquitous and non bio-degradability of dyes in surface water has caused a lot of concern for the availability of pure and safe water. It is an urgency to develop simple, low cost and environmentally benign methods for removal of dyes. Adsorptive removal and

photo-catalytic degradation are prominent methods for the above purpose. At optimum pH = 9, adsorption value 0.02gm, Connection period of 2 h and at a temperature of 308 K, MB was removed to 99% by Co-(“MOBIL COMPOSITION OF MATTER NO 41) MCM-41”. Likewise Cr-TiO₂-(“MOBIL COMPOSITION OF MATTER NO 41) MCM-41” could photo-degrade 100% of MB under solar light at pH=4 and catalyst dose of 0.04g in 1h. Hence transition metal incorporated TiO₂-(“MOBIL COMPOSITION OF MATTER NO 41) MCM-41” can act as a good source for removal of dyes from contaminated water.

REFERENCES

- [1]. X. Zhang, T. Zeng, S. Wang, H. Niu, X. Wang, Y. Cai, “One-pot amalgam of C18-functionalized core-shell magnetic mesoporous silica composite as efficient sorbent for organic dye”, *J. Colloid Interface Sci*, 448, 2015, pp.189–196.
- [2]. Y. Shao, B. Ren, H. Jiang, B. Zhou, L. Liping V. Ren, J. Dong, L. Liu, Z. Jing, “Dual-porosity Mn₂O₃ cubes for highly efficient dye adsorption”, *J. Hazard. Mater*, 333, 2017, pp.222–231.
- [3]. Z. Yang, H. Yang, Z. Jiang, T. Cai, H. Li, A. Li, R. Cheng, “Flocculation of both anionic and cationic dyes in aqueous solutions by the amphoteric grafting flocculant carboxymethylchitosan-graft-polyacrylamide”, *J. Hazard. Mater*, 254, 2013, pp.36–45.
- [4]. D. Bassyouni, H. Hamad, E. El-Ashtoukhy, N. Amin, M.A. El-Latif, “Comparative performance of anodic oxidation and electrocoagulation as clean processes for electrocatalytic degradation of diazo dye Acid Brown 14 in aqueous medium”, *J. Hazard. Mater*, 335, 2017, pp.178–187.
- [5]. S. Xin, N. Yang, F. Gao, J. Zhao, L. Li, C. Teng, “Three-dimensional polypyrrole-derived carbon nanotube framework for dye adsorption and electrochemical supercapacitor”, *Appl. Surf. Sci*, 414, 2017, pp.218–223.
- [6]. W. Sun, C. Zhang, J. Chen, B. Zhang, H. Zhang, Y. Zhang, L. Chen, “Accelerating biodegradation of azo dye Acid Orange 7 by using its endogenous electron donors”, *J. Hazard. Mater*, 324, 2016, pp.739–743.
- [7]. H. Yu, P. Xiao, J. Tian, F. Wang, J. Yu, “Phenylamine-Functionalized rGO/TiO₂ Photocatalysts: Spatially Separated Adsorption Sites and Tunable Photocatalytic Selectivity”, *ACS Appl. Mater. Interfaces* 8, 2016, pp.29470–29477.
- [8]. X. Zhao, Y. Tan, F. Wu, H. Niu, Z. Tang, Y. Cai, J.P. Giesy, “Cu/Cu₂O/CuO loaded on the carbon layer derived from novel precursors with amazing catalytic performance”, *Sci. Total Environ*, 571, 2016, pp.380–387.
- [9]. Y. Hao, T. Fei, W. Gu, Z. Liu, Y. Zhao, Z. An, L. Zhe, Y. Teng, “A simple post-amalgam conversion approach to Zn(OH)F and the effects of fluorine and hydroxyl on the photodegradation properties of dyewastewater”, *J. Hazard. Mater*, 333, 2017, pp.250–258.
- [10]. Q. Huang, M. Liu, L. Mao, D. Xu, G. Zeng, H. Huang, R. Jiang, F. Deng, X. Zhang, Y. Wei, “Surface functionalized SiO₂ nanoparticles with cationic polymers via the combination of mussel inspired chemistry and surface initiated atom transfer radical polymerization: Characterization and enhanced removal of organic dye”, *J. Colloid Interface Sci*, 499, 2017, pp.170–179.
- [11]. D. Wang, H. Shen, L. Guo, C. Wang, F. Fu, “Porous-BiOBr/Bi₂MoO₆ heterostructures for highly selective adsorption of methylene blue”, *ACS Omega*, 1, 2016, 566–577.
- [12]. H. Chaudhuri, S. Dash, S. Ghorai, S. Pal, A. Sarkar, “SBA-16: Application for the removal of neutral, cationic, and anionic dyes from aqueous medium”, *J. Environ. Chem. Eng.* 4, 2016, pp.157–166.
- [13]. Z. Liang, Z. Zhao, T. Sun, W. Shi, F. Cui, “Enhanced adsorption of the cationic dyes in the spherical CuO/meso-silica nano composite and impact of solution chemistry”, *J. Colloid Interface Sci.* 485, 2017, pp.192–200.
- [14]. Y.K. Ryoo, S.R. Cho, H.S. Lee, K.E. Jeon, H. Ryoo, R. Min, “Facile amalgam of monodispersed mesoporous silica nanoparticles with ultralarge pores and their application in gene delivery”, *ACS Nano*, 5, 2011, pp.3568–3576.