ISBN: 978-81-949998-0-5

Chapter 3

Application of Montmorillonite Clay Supported Catalysts in Effective Dye Degradation: A Brief Study

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3.1 Introduction:

Use of natural dyes has been started with the starting of human civilization. Later synthetic dyes took the place of natural dyes and with the development of variety of industries such as dye synthesis, printing, textile, paper, electroplating, pulp mill, food, paints, polymers etc., use of synthetic dye also increased, in fact they have become indispensable chemicals[1-4]. Due to their increasing applications in different industries, production of dyes is increasing to larger scale day by day and hence it is now an integral part of industrial wastewater. In fact more than 10-15% of dyes that are produced annually are lost in the wastewater during manufacturing and application processes which is a matter of great concern [5]. Unfortunately, most of them are very toxic and due to the toxicity, carcinogenicity, and mutagenicity of synthetic dyes, they create a huge threat to human health as well as for animals [6]. As dyes and their intermediates can undergo reductive processes and it results in the development of potentially carcinogenic compounds which have harmful impact towards the survival of microorganism’s aquatic life and environmental matrix etc. [7]. The ingestion of such contaminated water in the human body may also be vulnerable to a broad spectrum of immune-suppression, central nervous, respiratory, neurobehavioral disorders presage as allergy, eye (or skin) infections etc.

Hence even at very low concentration the dye containing waste water is a major source of water pollution [8]. Therefore, effective removal of toxic dyes is extremely important and already it has received a major attention and several physical, chemical, and biological methods already developed to deal with the problem. Till date different technologies such as biodegradation [9], coagulation [10], adsorption [11-12], photocatalysis [13] etc. have been used for dye degradation.

Among the developed technologies, catalysis is a very important and efficient technique and it has attracted an extensive attention from the scientific community and a large number of heterogeneous catalytic systems have been reported to be highly effective for degradation of organic dyes. In this regard a considerable number of clay based heterogeneous catalysts have been found very effective. Clays such as montmorillonite, bentonite are often employed as heterogeneous catalysts or as support for different catalytic systems and they show promising results.

3.1.1 Montmorillonite Clay in Catalysis:

Clay minerals are hydrous silicates of the phyllosilicate family (i.e., layered silicates or silicates based on a two-dimensional structure). The basic building blocks of clay are the $Si(O, OH)_4$ tetrahedra and the $M(O, OH)_6$ octahedra (where $M=Al^{3+}$, Mg^{2+}, Fe^{3+} or Fe^{2+}) [14]. Montmorillonite (MMT) is smectite clay and it is one of the most abundantly available and cheapest nature layered silicates.

In this aluminosilicate clay, a central metal octahedral layer is sandwiched in between the two tetrahedral silicate layers. Montmorillonite possess excellent dispersibility in water and also features good intercalation by other ions and easy exfoliation under minor mechanical force [15-16].

Montmorillonite (MMT) has widely been used in heterogeneous catalysis, matrix for synergistic toughening of artificial nacre [17], catalyst carriers for photo catalytic degradation etc [18]. When many metal and nanoparticles of metal compound (oxides, sulfides, etc.) are deposited on MMT with some nanoparticles intercalated into its interlayers, these MMT-based catalysts combined the functions of the nanoparticles and MMT together and exhibited synergetic effects [19]. MMT based catalysts are also considered as potential catalysts for dye degradation. In pure form, montmorillonite shows high ability to adsorb dye molecules via a cationic exchange and molecular sieve mechanism [20].

3.1.2 Basic Outline about Conjugated Organic Dye:

The two main components of organic dyes are the chromophores and auxochromes. Chromofores are delocalized electron systems with double bonds and the auxochromes are the electron-donating or electron-withdrawing substituents which intensify the colour of the chromophore by altering the overall energy of the electron systems. Usual chromophores are –C=C-, -C=N-, -C=O, -N=N-, $-NO_2$ and quinoid rings, whereas the auxochromes are $-NH_3$, -COOH, $-SO_3H$ and -OH groups [21]. Based on the chemical structure or chromophore, dyes can be distinguished into different groups. The largest class of dyes in the CI is acid dyes. Acid dyes are anionic compounds and they are usually water soluble. Acid dyes are the largest class of dyes that that are mainly applicable in dyeing nitrogen-containing fabrics like wool, polyamide, silk etc. Another type of dye known as reactive dyes have reactive groups that are capable of forming a covalent bond between a carbon atom of the dye molecule and -OH, -NH or -SH groups in fibers. Direct dyes are water soluble anionic dyes and when dyed from aqueous solution in the presence of electrolytes have high affinity for cellulose fibers. Direct dyes are relatively large molecules and they are mainly used in the dyeing of cotton, rayon, nylon and to some extent to leather and paper. They are water soluble anionic dyes and when dyed from aqueous solution in the presence of electrolytes have high affinity for cellulose fibers. These dyes are mostly azo dyes with more than one azo bond or phthalocyanine, stilbene or oxazine compounds. Basic dyes are water soluble cationic compounds and they yield colored cations in solution and that is why are called as cationic dyes. Another important class of dye is Vat dyes, which are water-insoluble dyes that are particularly and widely used for dyeing cellulose fibers. More or less all vat dyes are anthraquinones or indigoids [22]. Hence, in this article, some of the research work on montmorillonite clay supported catalyst for degradation of different organic dyes is presented. In this particular article, focus is given to the synthetic and characterization techniques of the catalysts and insights will also be given to the efficiency of the catalysts in the process of dye degradation.

3.2 Montmorillonite Clay Supported Catalyst in Dye Degradation:

3.2.1 Methylene Blue (MB) Degradation:

M.A. Mekewi and group reported copper nanoparticles supported onto montmorillonite clays for efficient degradation of methylene blue.

Copper nanoparticles were first prepared by the reduction of copper chloride ($CuCl_2.2H_2O$) using hydrazine in the aqueous cetyle trimethyl ammonium bromide (CTAB) solution and then copper nanoparticles were supported on activated Montmorillonite clay (MMT).

The native and the modified clay as well as the prepared copper nanoparticle supported catalyst were characterized using FTIR, SEM, TEM, and BET etc. This copper nanoparticles supported onto montmorillonite clay catalyst was then used for degradation of solutions containing methylene blue (MB).

Variation of pH, concentration of Methylene blue solution as well as variation of contact time influence the efficiency of the catalyst for degration of MB.

Their study shows that the degradation rate increases by increasing the reaction pH values. It is also reported that degradation efficiency of the catalyst towards of methylene blue is inversely proportional to its concentration of the solution. This is due to the reason that the degradation efficiency relates to the formation of hydroxyl radicals, increasing initial concentration of MB dye in solution lead to adsorption of high extents of heavy MB organic compounds which renders interactions between the metallic catalytic sites and the oxidant molecules (H_2O_2). Thus, the amount of generated oxidizing species could suffer marked leakage causing a great reduction in the degradation efficiency of MB dye. From the study it is also seen that copper immobilized onto acid as well as organo-treated clay exhibits complete decomposition of the MB dye molecules within 2 h [23].

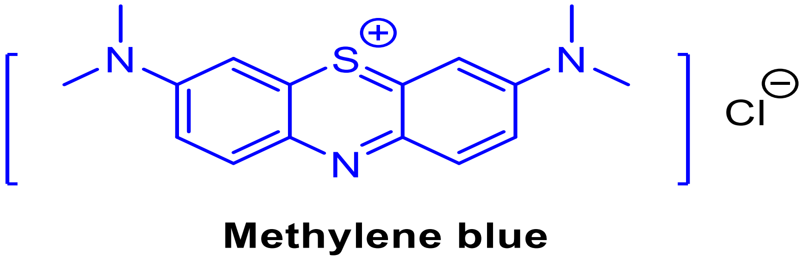


Figure 3.1. Methylene Blue

Pd supported Cu-doped Ti-pillared montmorillonite is another catalyst which also used for degradation of methylene blue dye. When investigated for methylene blue degradation, catalyst shows very proficient performance in presence of $NaBH_4$, even in room temperature. Almost complete degradation was achieved within 20 min. In order to prepare the catalyst, the purified montmorillonite was first pillared by a Ti^{4+}-pillaring solution doped with Cu^{2+}, and then the resulting solid was impregnated with a Pd^{2+} precursor, which gives the final trimetallic MTiCuPd500 catalyst. While investigating the catalytic efficiency of the prepared catalyst, Ti-pillared montmorillonite, MTi500 solid, was found to be less efficient in the degradation of the dye, in spite of having larger specific surface area and acidity than MTiCuPd500.

Hence there comes the importance of the incorporation of Cu and Pd as active phases [24]. Another catalyst ZnO/Montmorillonite was utilized for photo catalytic and photochemical degradation of methylene blue [25].

This photo catalyst was synthesized using a sol-gel intercalation method. The physicochemical properties of the material were characterized by XRD, SEM, TEM, N2 adsorption-desorption.

The adsorption of MB dye on ZnO/montmorillonite was higher than that on natural montmorillonite.

The significant improvement of MB adsorption by ZnO/ montmorillonite was related to the enhanced specific surface area from 48.6 m^2/g to 231.6 m^2/g.

The pre-intercalation process helps in the formation of uniformed porous structure in the composite material.

Table 3.1. Textural properties of ZnO/montmorillonite and raw montmorillonite [25].

Sample	Specific Surface Area (m^2/g)	Pore Volume (cc/g)	Pore Radius (Å)
Raw Montmorillonite	48.60	0.038	15.9
ZnO/ Montmorillonite	231.56	0.179	18.5

For either montmorillonite or ZnO/montmorillonite, addition of H_2O_2 increased MB degradation. H_2O_2 accelerates the reaction rate via increasing hydroxyl radical formation by its initiation with UV light in the photo oxidation.

Table 3.2. Initial rate of MB degradation in various systems [25].

Reaction Condition	Initial Rate (ppm/min)
Montmorillonite	0.578
Montmorillonite-UV	0.626
Montmorillonite-H_2O_2-UV	1.165
ZnO/montmorillonite	0.700
ZnO/montmorillonite–UV	1.744
ZnO/montmorillonite-H_2O_2-UV	2.652
ZnO-UV	2.772
ZnO-H_2O_2-UV	2.82

Yunliang Zhao reported Self-assembled gels of Fe-chitosan/montmorillonite (Fe-CS/MMTNS) nanosheets for effective degradation of methylene blue. This catalyst was prepared for degradation of methylene blue under visible light irradiation using H_2O_2 through the synergy effect of both adsorption and photo-Fenton. On this catalyst, methylene blue was degraded through demethylation and oxidation in two pathways, in one pathway, methylene blue was directly attacked by reactive radicals and gradually converted into inorganic substances and in second pathway the dye was first adsorbed by Fe-CS/MMTNS gel and then it was degraded by reactive radicals upon its desorption[26]. TiO_2 pillared montmorillonites is also used for methylene blue degradation.

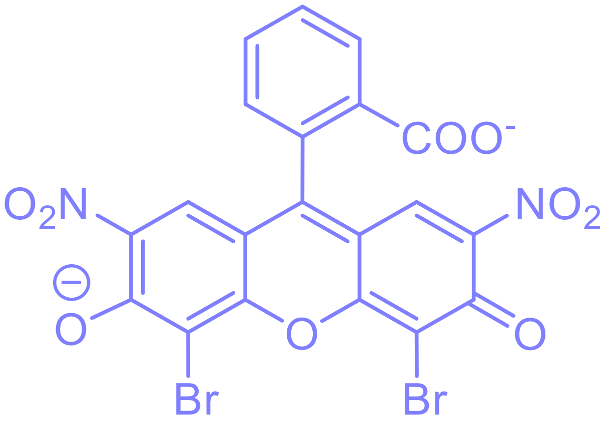
This composite shows excellent result in photocatalytic degradation of methylene blue under visible light irradiation (99% within 60 min) [27].

3.2.2 Eosin B Degradation:

Shiding Miao and group reported one kind of nano composites of zinc sulfide (ZnS) and montmorillonite (MMT) for photo catalytic degradation of eosin B.

The nano composite were prepared via a hydrothermal route. ZnS itself is a semiconductor type photo catalyst and MMT has a strong capacity to adsorb organic compounds from aqueous solutions.

Hence the prepared ZnS-MMT possesses both the adsorptive ability of MMT and the catalytic degradation ability of ZnS and combining the two ability together ZnS-MMT performs very efficiently in removing eosin B from its aqueous solution [28].

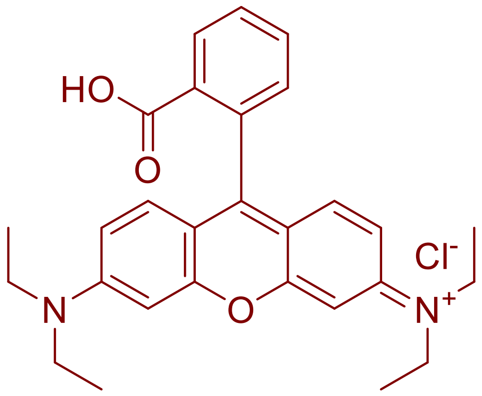


Eosin B

Figure 3.2. Eosin B

3.2.3 Rhodamine B and Rhodamine 6G Degradation:

Photocatalys Fe_2O_3 pillared montmorillonite doped TiO_2 catalyst was reported by D. A. D. N. Dewi for photocatalytic degradation of Rhodamine B under visible light irradiation. The montmorillonite clay was first intercalated using Fe_2O_3 to produce Fe_2O_3-pillared montmorillonite clay, and then it is doped with TiO_2 to get a photocatalyst material Fe_2O_3-PILC/TiO_2. The result of photodegradation at optimum condition with visible light at pH 3 using 400 mg photocatalyst was 99.84%. The study shows that rhodamine B is comparatively easily degradable in acidic pH than alkaline pH [29].

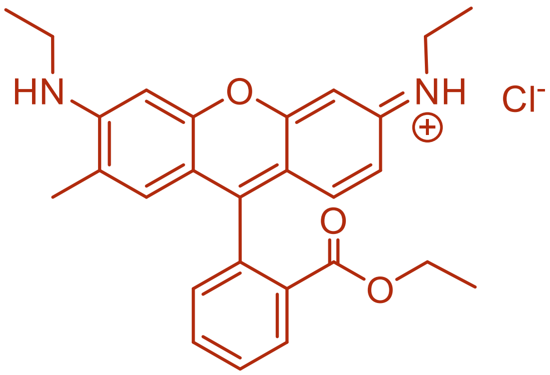


Rhodamine B

Figure 3.3. Rhodamine-B

ZnO-montmorillonite nanocomposite is reported to be a promising photoctalyst for removal of Rhodamine 6G dye from aqueous solution through degradation and adsorption.

For adsorption of Rhodamine6G from aqueous solution, efficiency of the catalyst is influenced by contact time, pH, dye concentration and adsorbent dose. The lower pH 3 favours removal of dye. With increase in contact time as well as initial dye concentration the amount of dye adsorbed by the catalyst, increases and it decreases with increase in catalyst dose [30].



Rhodamine-6G

Figure 3.4. Rhodamine-6G

3.2.4 Crystal Violet Degradation:

L. Guz et.al studied Montmorillonite (MMT) and iron modified montmorillonite (MMT-Fe) as adsorbents and heterogeneous catalysts for Fenton and photo-Fenton like oxidation of cationic dye Crystal Violet (CV). XRD, SEM, EDX, BET surface area etc. are used to characterize both Montmorillonite (MMT) and iron modified montmorillonite (MMT-Fe). MMT-Fe presents iron in the interlayer space and oxo hydroxide particles on its surface. In order to stimulate the removal of pollutants in water, CV dye was first adsorbed on MMT (or MMT-Fe), separated from the water. After that it is re-dispersed in a lower amount of water, finally where it was oxidized by Fenton or photo-Fenton process. Both the clay show high CV adsorption capacity, but MMT-Fe oxidizes faster and have a higher mineralization rate of adsorbed CV than MMT with Fe(II) or Fe(III) added externally[31].

A composite of TiO_2-montmorillonite composite (TiO_2-M), was also reported for degradation of crystal violet dye. Infact the catalytic activity of this composite was studied for five selected dyes including crystal violet. This photo catalyst was prepared by impregnating montmorillonite with $TiCl_4$ followed by calcinations at 350°C. Characterization results show that TiO_2 was efficiently formed in Na-montmorillonite (Na-M) framework, and only a crystalline, pure anatase phase was produced. Degradation of dyes by TiO_2-M under visible light irradiation is found in the order: crystal violet> methylene blue> rhodamine B > methyl orange > Congo red. It is worth noting the similarity in the orders obtained in the adsorption and photodegradation of the dyes under investigation.

These results confirm the relationship between the adsorption and the photocatalytic activity, as the photodegradation reaction of organic pollutants occurs after their adsorption on the surface. Adsorptionn effectiveness of the catalyst for different dyes reflects the higher adsorptive capacity of the cationic dyes (methylene blue, crystal violet and rhodamine B) whereas, the anionic dyes show a smaller adsorption. This is due to less attraction charges of TiO_2-M for the anionic dyes. The results of the photocatalytic activity of the catalyst for five different dyes are summarized in **Table-3.3**[32].

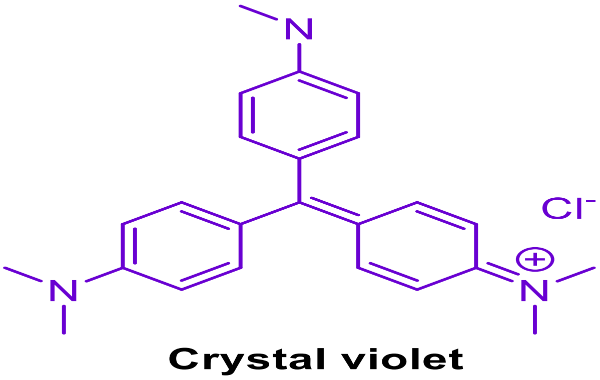


Figure 3.5. Crystal Violet

Table 3.3. Results of the catalytic efficiency (removal rate in %) of the catalyst for five different dyes [32].

	Crystal Violet	**Methylene Blue**	**RhodamineB**	**Methyl Orange**	**Congo Red**
In dark	58.8	67.6	45.0	14.9	6.2
Under UV	97.1	93.2	79.8	36.1	22.6

Recently Self-assembly montmorillonite nanosheets supported hierarchical MoS_2 was reported for degradation of methyl orange.

A simple Layered in-situ hydrothermal technique was used to hybridise MoS_2 and montmorillonite nanosheets in order to develop an efficient catalyst (MoS_2/MMT) for better MO degradation.

Different characterization results indicated that the montmorillonite nanosheets self-assemble into a cross-linked structure first, then the MoS2 nanosheets grew along the montmorillonite nanosheets surface, forming a cross-link grid construction.

When its catalytic efficiency is studied for MO degradation, it is found that MMTNS has no effect on the decomposition of MO dye, but pure MoS_2 has high decomposition efficiency towards MO. Surprisingly it is found that MoS_2/MMT hybrid displays a reasonably good 98.6% decomposition efficiency, which was much better than that of pure MoS_2. [33].

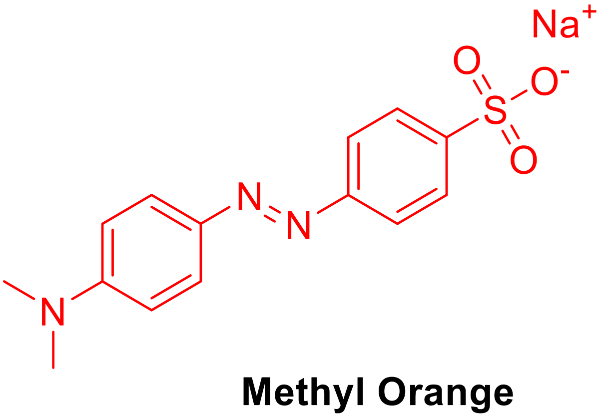


Figure 3.6. Methyl Orange

3.3 Conclusion:

In this study, some of the montmorillonite supported catalysts developed for the degration of different organic dyes have presented. These clays supported catalysts are found to be very efficient in degradation of various cationic and anionic dyes such as crystal violet, methylene blue, methyl orange dyes etc. The reported findings have also suggested that type of dyes, contact time, pH of solution etc. are some of the parameters that influence the efficiency of the catalyst for effective degradation of dyes.

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