

Rapid adsorption of malachite green dye using eco-friendly Fe (III) - montmorillonite: Effective clay mineral for dye effluents containing

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Abstract

Herein we reported the malachite green dye removal by Fe(III)–Mt through adsorption process under ambient conditions. The amount of MG dye removal by Fe(III)–Montmorillonite(Fe(III)–Mt) was estimated from its optical density at $\lambda_{\max} = 617$ nm using UV-Vis spectrophotometer. The MG dye removal was found to be rapid at basic pH and increased further with temperature up to 50°C. At pH 7 & 8, a complete reduction (100%) was observed within 5 min and 7 min, whereas at pH 4 & 5, it took 10 min & 15 min respectively. The time taken for complete reduction at 0°C, RT (30°C) and 50°C were 10, 7 and 5 min respectively. The removal followed by adsorption of dye molecules on the spent clay mineral was evident from FESEM/EDX analysis. More importantly, Fe(III)–Mt could be separated and retrieved easily after the reaction by centrifugation from the degraded MG dye solution. The experimental results of MG dye removal from Fe(III)–Mt follows the pseudo first order kinetics. We believe that Fe(III)–Mt could be the efficient and suitable material to augment the real filed applications. This study provides a new avenue to gain in-depth insight to the applications of Fe(III)–Mt as an effective clay mineral for remediation of dye effluents. Overall Fe(III)–Mt bears the capability for environmental remediation in relation to the dye pollution. Copyright © 2016 VBRI Press.

Keywords: Fe(III)–montmorillonite, malachite green, remediation, adsorption.

Introduction

Dye effluents which are released from textile dye industries, which impair the environment and human beings continuously through contamination of water reservoirs, soil etc. Dyes can be classified into three types such as cationic, anionic and nonionic dyes. Cationic dyes are basic dyes, while anionic dyes include direct, acid and reactive dyes [1]. There are plenty of synthetic dyes used in pharmaceutical, textile, cosmetics, paper and pulp industries. Among these dyes some of them have highly intense color that pollutes the water bodies in the environment. Moreover, many of them are not degradable under normal environmental conditions, while these show mutagenic and carcinogenic behavior towards the human beings as well as environment [2].

Malachite green (MG) is a cationic triphenylmethane dye as shown in Fig. 1(a). It is widely used as colouring agent, food additive, medical disinfectant, fungicide, parasiticide and disinfectant agent in aquaculture industries. It is also used for wool, dyeing silk, jute, leather, ceramics, cotton and also a biological staining agent [3]. Even though used extensively worldwide, it exhibits carcinogenic and mutagenic properties were noticed against mammalian

cells, aquatic life and many other. For instance, it affects the human health especially the immune system and reproductive system in a short period [4]. In order to reduce the damage caused by these noxious dyes to human beings as well as environment many methods were proposed and implemented to remove dye effluents from waste water. Such as biological treatment, degradation, incineration, sedimentation and gravity separation that have been adopted for water treatment. Furthermore, different techniques such as filtration, centrifugation, micro- and ultra filtration, crystallization, precipitation, coagulation, oxidation, solvent extraction, evaporation, distillation, reverse osmosis, ion exchange, electro dialysis, electrolysis and adsorption [5, 6]. Among all of these methods adsorption is considered as a most efficient technique for the removal of noxious dyes from polluted aquatic source, since it is ease of operation, non-destructive, and easy to adopt quickly in short manner as compared with reported methods [7]. On contrary the remaining methods have some limitations such as requires more treatment time, production of sludge after the reaction and involves the generation of toxic volatile compounds [8].

Solis-Casados, *et al.* reported the application of TiO₂ modified thin films with (Ni_x: TiO₂) using sol gel technique for the degradation of MG dye, but the degradation process requires high activation energy from UV light [9]. Ju *et al.* investigated the microwave-assisted photo catalytic degradation of MG in aqueous TiO₂ suspensions, but only 85 % removal efficiency was observed [10]. Oolong tea extract was used for synthesis of iron based nanoparticles which is employed for the degradation of MG dye has been explored. However, OT-FeNP showed only 75.5% removal efficiency towards MG dye [11]. Bioremoval of MG dye using marine trichoderma hypocreia lixii is also carried out at different conditions like different pH, temperature, yeast extract and incubation period. However only 89% degradation was observed at optimal conditions of temperature 30 °C, pH of 5.8, yeast extracts 5.81 mg while dye was completely degraded after 10 days of incubation [12].

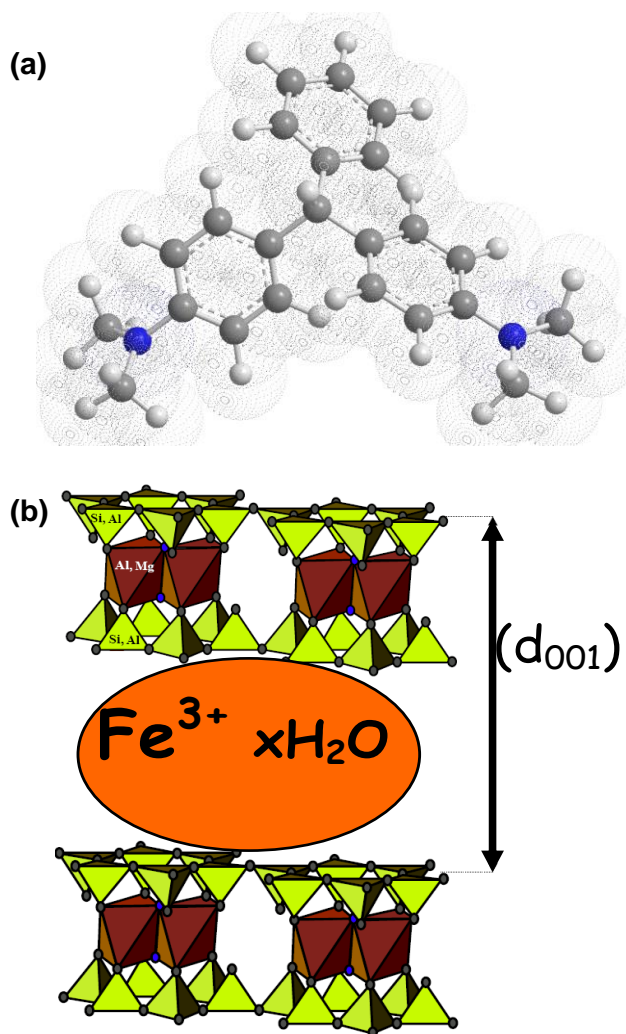


Fig. 1. (a) Chemical structure of MG dye and (b) Schematic representation of Fe(III)-Mt clay mineral.

Removal of toxic dye (MG) using polyaniline-functionalized magnetic nanoparticles from wastewater is also being reported in literature. At pH 3 – 5, there will be 85 % decoloration, while at pH 6 – 9 only 90 % decoloration was observed. Furthermore 97% decoloration

was observed at 25 °C, but if the temperature was increased more than 30 °C, gradually decoloration was decreased [13]. Similarly, Fe nanoparticles (Fe NPs) are used for degradation of MG dye. The removal efficiency of MG (reaction time 60 min) was 79.56%, 82.47%, and 48.34% at pH 3, 6 and 9, respectively. Further at different temperatures, the rate of degradation was 83.46 %, 80.24 % and 78.94% at 318, 308 and 298 K [14]. However, in the above cases 100% removal efficiency was not observed in case of pH and temperature. Moreover, these heterogeneous reductants/adsorbents are used for degradation and adsorption processes but these consist of some limitations such as there will be a slow degradation, time consumption is more, effective only in lower pH as well as in the presence of light irradiation. Nevertheless, these are not suitable for real system applications. Also, these adsorbents/ reductants cannot be produced on a large scale for real system applications.

Clay minerals are important class of materials which are readily available in nature. These are used as very good adsorbents for toxic elements such as arsenic [15, 16], decoloration agents, ion exchangers, molecular sieves and catalysts [17]. Clays, modified clays and zeolites are a few significant examples which are used for water treatment. Smectite clay minerals such as montmorillonite and nontronite have a layered structure being suitable for adsorption of cationic synthetic dyes [18, 19]. Montmorillonite (Mt) is a 2:1 dioctahedral smectite group clay mineral having a layered structure, Fig. 1(b). The octahedral alumina sheet is sandwiched between tetrahedral silicate sheets. The negative charge is created on the clay mineral due to the isomorphous substitution in the octahedral sites (by Mg, Fe and Ti) and tetrahedral sites (by Al, Fe). Such a permanent negative layer charge is balanced by exchangeable cations like Ca, Na, etc. at the interlayer. Thus, the cation exchange capacity (CEC) of clay mineral depends on the net elemental composition that varies with the geographical availability in the environment.

The properties and uses of this clay mineral can be modified not only by altering the structural Fe(II)/Fe(III) ratio [20], but also by replacing the interlayer cations with variety of inorganic and organic cations [15, 16]. There are only a few reports on natural [21, 22] or modified clay minerals [23–25] for Cr(VI) reduction. From the literature survey we found that the few modified clay minerals such as Polyacrylic acid-nanoclay nanocomposites [26] and Organoclay [27] are used for MG dye adsorption process. Moreover, clays and their modified forms have received widespread attention for their use as adsorbents of metal ions from aqueous medium, because they are readily available and much cheaper than activated carbon, zeolites and membranes [28].

Moreover, the main advantage of using these Fe clay minerals are non-toxic, easy to prepare, stored for long time, suitable for heterogeneous system, easily recoverable and relatively very cheap material in these days. Furthermore, the availability as well as the amount and/or access of structural Fe(III) for redox reactions are very limited. Hence it is important to make use of Fe(III)-Mt, i.e., the redox sensitive Fe(III) ions placed in the interlayer of clay mineral for the removal of dyes in aqueous medium.

In the preceding work, the main objective is to study the performance of Fe(III)-Mt with MG dye via adsorption at different pH and temperature. Adsorption of MG dye on Fe(III)-Mt revealed that follows pseudo first order kinetics. Furthermore a detailed studies on surface morphology of Fe(III)-Mt before and after treat with MG dye in aqueous solution. Fe(III)-Mt could be separated and retrieved easily after the reaction by centrifugation from the degraded MG dye solution.

The novelty observed from the present investigation is that experimental results showed that the Fe(III)-Mt clay mineral exhibited much higher MG adsorption efficiency in aqueous solution under ambient conditions. For instance the results we obtained from present investigations are good when comparison with other reported adsorbents/reductants in literature. Owing to this, we concluded that Fe(III)-Mt is used as lost cost attractive adsorbent for adsorption of MG dye from aqueous solution. Moreover it is feasible for significantly improving the removal of dyes from wastewater in future.

Experimental

Materials

Kunipia F montmorillonite (Kunimine Industries Co. Ltd., Japan) was used for whole experiments which contained >98% of Na-montmorillonite and the only impurity was quartz. The composition of raw montmorillonite clay mineral is given as $(\text{Na}_{0.431}\text{K}_{0.002}\text{Ca}_{0.002}) (\text{Al}_{1.56}\text{Mg}_{0.305}\text{Fe}_{0.099}\text{Ti}_{0.007})^{\text{oct}} (\text{Si}_{3.949}\text{Al}_{0.051})^{\text{tet}} \text{O}_{10} (\text{OH})_2 \text{nH}_2\text{O}$ with a CEC of about 1.2 meq/g [23]. The dye with a labelled purity of more than 99% was obtained from s. d. fine-chem limited, India and used as such. pH measurements were done with a pH meter (model 355, Systronics, Ahmedabad, India). Double distilled water was used throughout in this study. The reaction mixture was withdrawn periodically by using a syringe tube and then centrifuges (REMI, R-8C BL BENCH TOP CENTRIFUGE) to separate the suspended clay particles. The percentage of dye removal from aqueous medium was estimated from its optical density at $\lambda_{\text{max}} = 617 \text{ nm}$ using UV-Vis spectrophotometer (UV-160A, Shimadzu Corporation, Japan).

The X-ray diffraction pattern (XRD) of the samples were recorded using D2 phaser XRD (Bruker AXS GmbH, Germany) with Ni-filtered $\text{Cu K}\alpha$ radiation, $\lambda = 1.5417 \text{ nm}$. Infrared spectrum of the samples was recorded by KBr pellet method using IR analyzer (FT-IR8600PC, Shimadzu Corporation, Japan). The micrographs of freshly prepared Fe(III)-Mt was recorded using field emission scanning electron microscope (Quanta 3D FEG, FEI Company, USA) along with energy dispersive X-ray (EDX) analysis for elemental composition.

Methods

Fe(III)-Mt preparation

The raw clay mineral (10 g in 1L) was stirred with 0.4 M FeCl_3 solution up to 24 h in terms of solid to liquid ratio to convert the clay into Fe(III)-Mt. This process was repeated thrice to get the complete conversion of clay to Fe(III)-Mt. After cation exchange, the clay mineral was washed with

distilled water by centrifugation and then followed by filtration using $0.2 \mu\text{m}$ filter, until no chloride was detected while washings by AgNO_3 test. Later, solid sample was dried at room temp ($\text{RT} \sim 25^\circ\text{C}$), ground to powder form and stored in a vacuum desiccator.

In order to estimate the interlayer iron, Fe(III)-Mt was subjected for cation exchange with 0.05 M H_2SO_4 for about 24 h. The ratio of ferrous to ferric ions ($\text{Fe}^{2+}/\text{Fe}_{\text{total}}$ where $\text{Fe}_{\text{total}} = \text{Fe}^{2+} + \text{Fe}^{3+}$) released was determined by 1,10 phenanthroline method [29] using UV-Vis spectrophotometer ($\lambda_{\text{max}} = 510 \text{ nm}$).

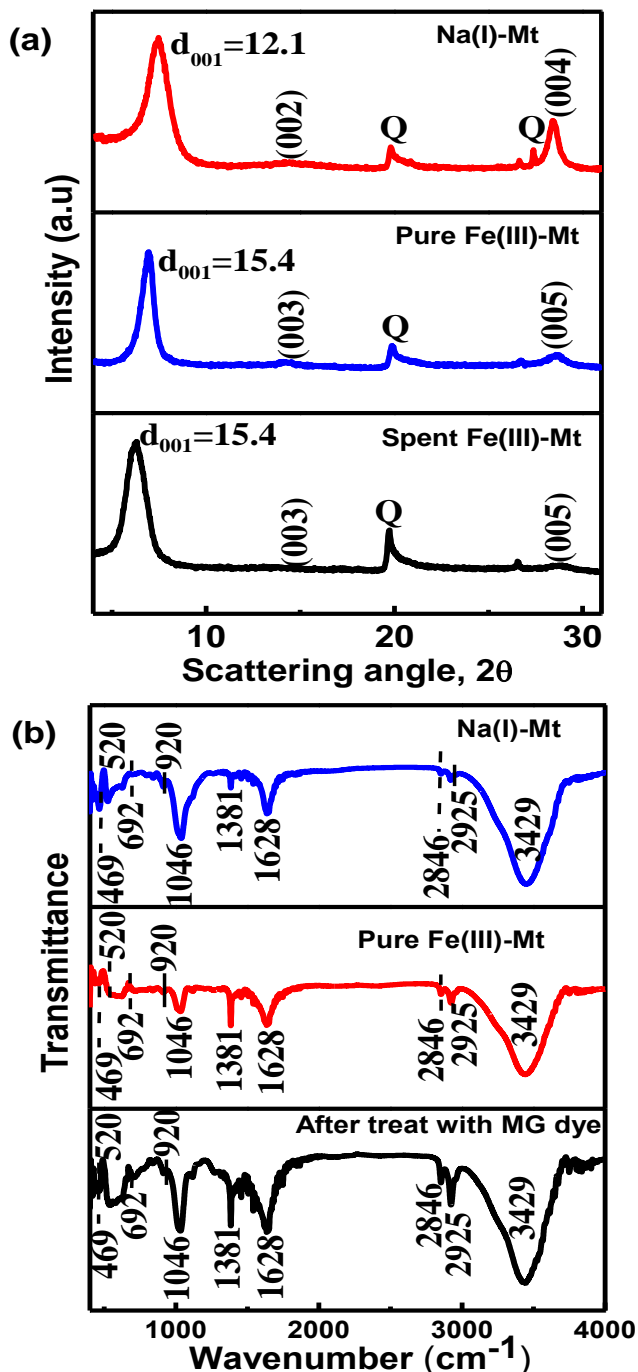


Fig. 2. (a) Powder XRD patterns of Fe(III)-Mt in comparison with Na(I)-, Fe(III)- & spent Fe(III)-Mt at relative humidity 40% and (b) FT-IR spectra of freshly prepared Fe(III)-Mt compared with Na(I)-Mt as well as spent Fe(III)-Mt.

Removal of MG dye by Fe(III)-Mt from aqueous solution

In a typical stoichiometric case, freshly prepared Fe(III)-Mt (0.05 g) was added to MG dye solution (0.05 mM, 100 mL) and stirred magnetically. The reaction was also carried out at different pH 4 – 8 (adjusted with dil. HCl and NaOH) and temperature (0, 30 & 50 °C). The reaction mixture was withdrawn periodically by using a syringe tube and then centrifuges (REMI, R-8C BL BENCH TOP CENTRIFUGE) to separate the suspended clay particles. The decrease in the dye concentration was estimated from its optical density. The decrease in the dye concentration due to reaction between Fe(III)-Mt and MG dye was expressed in terms of % reduction as a function of time. The spent Fe(III)-Mt was separated by centrifugation, washed thoroughly with water and vacuum dried at room temperature for further characterization using XRD, FT-IR and FESEM/EDAX analysis.

Results and discussion

Formation of Fe(III)-Mt

The concentration of iron has been obtained from 0.5 g of Fe(III)-Mt using different reagents (100 mL) viz., 0.05 M H₂SO₄, 0.5 M (NH₄)₂C₂O₄, 1 M NaCl, 0.05 M Na₂EDTA. The total Fe(III) ions extracted was about 1.18 meq/g. In addition, the XRD, FT-IR and FESEM/EDAX results confirmed the formation of Fe(III)-Mt.

The XRD patterns of Fe(III)-Mt in comparison with Ca(II)-Mt, Na(I)-Mt and spent Fe(III)-Mt at relative humidity (RH) 40% are shown in Fig. 2(a). The basal spacing, *d*₀₀₁, values are as follows: Fe(III)-Mt, 15.3 Å; Ca(II)-Mt, 14.9 Å and Na-Mt, 12.1 Å. It is clear that the divalent cation exchanged clay minerals showed higher *d*₀₀₁ value due to larger layer of hydration when compared to monovalent cation exchanged clay mineral.

FT-IR spectra of freshly prepared Fe(III)-Mt, Na(I)-Mt and spent Fe(III)-Mt as shown in Fig. 2(b). The FT-IR spectra of freshly prepared Fe(II)-Mt is similar to that of Na(I)-Mt. The basic structure of clay mineral has not undergone any significant change. For instance, the bending vibration bands at ~ 520 cm⁻¹ for Si-O-Al, and 920 cm⁻¹ for Al₂OH are intact. However, stretching vibrations of Si-O group ~ 1046 cm⁻¹ are slightly broadened. The vibration bands at 1628 cm⁻¹ corresponds to adsorbed water and 3429 cm⁻¹ for water present at the interlayer. However, XRD and FT-IR spectral values are in good agreement with the previously reported values [30, 31].

Removal of malachite green dye by Fe(III)-Mt

Effect of amount of Fe(III)-Mt on MG dye removal from aqueous solution

In order to determine the stoichiometric amount of Fe(III)-Mt, it was added to MG dye solution (MG solution 0.05 mM, pH 6) by varying the amount of Fe(III)-Mt from 0.01 g to 0.05 g. The concentration of MG dye removal was estimated from its optical density at λ_{max} = 617 nm using UV-Vis spectrophotometer. The effect of amount Fe(III)-Mt on the rate of adsorption of MG solution is depicted in Fig. 3. From the Fig. 3, it was observed that the required amount of Fe(III)-Mt for 100% dye removal was 0.05 g. It

was observed that the rate increases with increase in Fe(III)-Mt from 0.01 to 0.05 g.

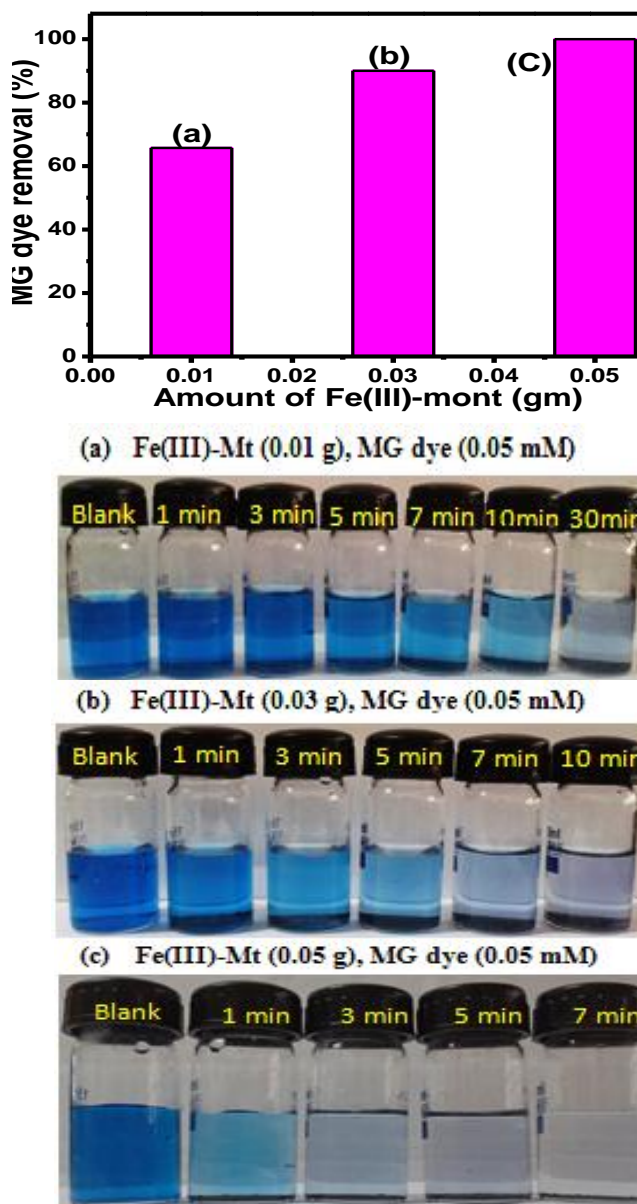


Fig. 3. Effect of amount Fe(III)-Mt on the rate of adsorption of MG dye solution; (a) Fe(III)-Mt (0.01 g), MG dye (0.05 mM) (b) Fe(III)-Mt (0.03 g), MG dye (0.05 mM) (c) Fe(III)-Mt (0.05 g), MG dye (0.05 mM).

Effect of pH on MG dye removal from aqueous solution by Fe(III)-Mt

Fig. 4(a) shows the % reduction of MG dye by Fe(III)-Mt in stoichiometric amounts at different pH as a function of time. In general, the dye removal by Fe(III)-Mt is very rapid process. In each case, we saw a two-stage removal of MG dye by Fe(III)-Mt: A rapid first stage followed by a slow second stage. A complete removal occurred in about 10 & 15 min at pH 5 and 4, whereas in basic medium complete reduction was observed at pH 6 in 7 min and at pH 8 it took 5 min when stoichiometric amount of Fe(III)-Mt was present. From the literature survey, it was reported that the dye adsorption in acidic medium takes more time when compared to basic medium [32].

It is well-known that the pH has a significant effect on the adsorption of dye. Rajabi *et al.* have demonstrated the preparation of pure ZnS QDs doped with Fe³⁺ and their application for photodecolorization of MG dye. The effect of initial pH of sample solutions on the decolorization efficiency of MG was studied in the range of 4 – 10. The experimental results revealed that the maximum decolorization efficiency i.e 80% – 90% was obtained at pH 6 – 8 whereas it was 60 – 70% efficiency at pH 4 – 6 at the irradiation time of 90 min [33]. Huang *et al.* have demonstrated the application of Fe NPs for the degradation of MG dye. However, the removal efficiency was high at pH 3 – 6 (82.47%) while at pH 9, only 48.34% degradation was observed within a period of 60 min [14]. Furthermore, nano silver impregnated TiO₂ was used as photo catalyst for the degradation of MG dye. Meanwhile, there was 90% degradation at pH 6 – 8 and only 80 – 85% degradation at pH 4 – 5, respectively. But the main drawback was that the maximum removal was obtained at a dose of 1 g/L, under the irradiation of two 15-W UV lamps for 4h [34].

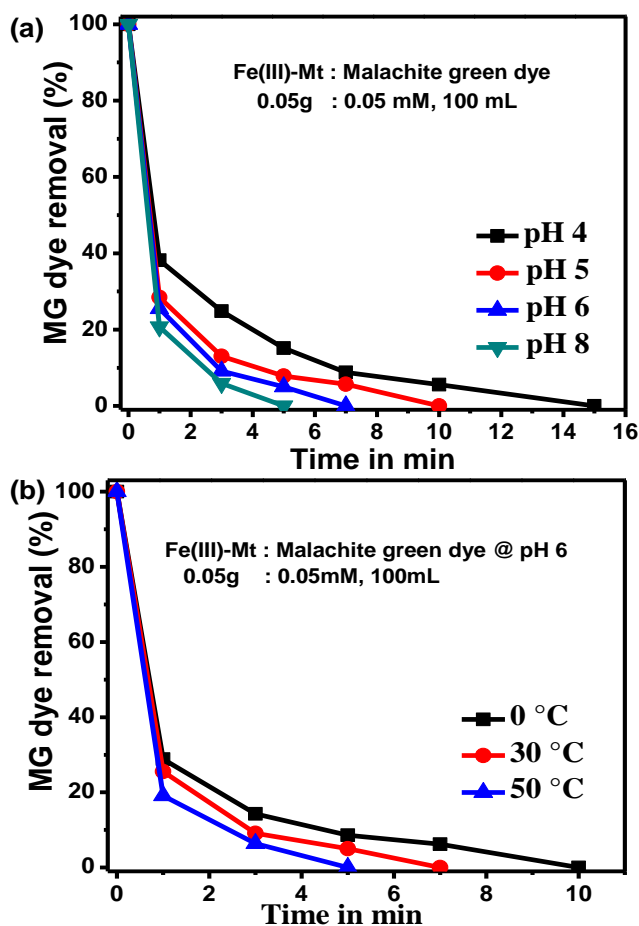


Fig. 4. Removal of MG dye by Fe(III)-Mt at pH 6: (a) Stoichiometric amount of Fe(III)-Mt at different pH and (b) Stoichiometric amount of Fe(III)-Mt at different temperature.

Although these heterogeneous reductants/adsorbents are used for degradation and adsorption processes, there will be an incomplete reduction and more time consumption. Moreover, these are effective only in the presence of co-catalysts, sunlight irradiation and/or presence of UV lamps. However, in the present study we could achieve the

efficient removal of MG dye solution both in acidic as well as basic pH.

Effect of temperature on MG dye removal from aqueous solution by Fe(III)-Mt

The reduction of MG dye by Fe(III)-Mt was carried out in different temperatures (0 – 50 °C) at pH 6 in Fig. 4(b). In general, the dye removal increased with temperature up to 50 °C. The time taken for complete reduction at 0 °C, 30 °C & 50 °C are 10, 7 and 5 min respectively. Mohammadi *et al* have shown the temperature dependant adsorption of MG by superparamagnetic sodium alginate coated Fe₃O₄ nanoparticles (Alg-Fe₃O₄). The adsorption experiments were carried out at four different temperatures including 0, 25, 50 and 75 °C to determine the effect of temperature on adsorption process. The adsorption capacity increases with increasing of the temperature [32].

The usage of Fe NPs for the degradation of MG dye was investigated by Huang *et al.* The degradation rate of MG dye by Fe NPs was 83.46 %, 80.24 % and 78.94 % at 318, 308 and 298 K, respectively [14]. Polyaniline-functionalized magnetic nanoparticles are used for the removal of toxic MG dye through adsorption process. The experimental results are studied at different temperatures in the range 20 – 70 °C, while at 20 – 40 °C and 40 – 60 °C about 93% & 85% was observed respectively [13]. Organo clay was used for the adsorption of MG dye. The results indicate that increasing the temperature leads to an increase in the adsorption of dye [27]. However, in the present study, we see the 100 % removal of MG dye from Fe(III)-Mt in all the temperatures ranging from 0 – 50 °C.

Surface interaction between MG dye and Fe(III)-Mt through adsorption process

The amount of MG dye removal by Fe(III)-Mt was estimated from its optical density at $\lambda_{\max} = 617$ nm using UV-Vis spectrophotometer. The UV-Visible spectra of the MG solution (0.05 mM) used here showed an absorption maximum at 617 nm, which is the characteristic of MG monomers. Moreover, MG dye-Fe(III)-Mt clay mineral interaction is extremely sensitive for probing the surface properties of smectites in aqueous solutions. Nevertheless, there is a gradual decrease in UV-visible absorbance spectra with increasing the amount of Fe(III)-Mt. Moreover, the adsorption capacity of Fe(III)-Mt was good (100% removal of dye via adsorption within 7 min) than that observed with other reductants/clay minerals reported in literature. The experimental results show that MG dye molecule cannot replace all of the interlayer iron species (Fe³⁺). This is presumably due to high affinity of Fe(III) ions for the clay surface. The electrostatic interactions will thus be the primary driving force for the adsorption between the adsorbent (Fe(III)-Mt) and a cationic adsorbate (MG). The Fe(III) ions are effectively interact with MG dye molecules, thereby, MG adsorption is occurs very rapidly. Hence the adsorption may occur by electrostatic attraction between Fe(III)-Mt and MG dye. Thus, in particular, adsorption of MG dye could not be directly related to the layer charge of clay mineral and also oxidation of Fe(III) ions present in Fe(III)-Mt cannot be changed upon MG dye adsorption.

Factors like pH and temperature influences on the adsorption behavior of ionic adsorbates, particularly when the interactions between dye–Mt or ion-exchange type. It also influences the dye structure determining its interaction probabilities with Fe(III)–Mt. However, MG dye removal by Fe(III)–Mt in acidic medium takes more time when compared to basic medium. Furthermore, increasing the temperature leads to an increase in the adsorption of dye on Fe(III)–Mt.

The effect of amount Fe(III)–Mt on the rate of adsorption of MG solution is depicted in **Fig. 3**. From the **Fig. 3**, it was observed that the required amount of Fe(III)–Mt for 100% dye removal was 0.05 g. It was observed that the rate increases with increase in Fe(III)–Mt from 0.01 to 0.05 g. From these results, we can have observed that extent of removal of MG dye increased when more and more Fe(III)–Mt clay mineral was used. Moreover, from the surface studies, it was clearly observed that if it is increase in amount of Fe(III)–Mt, then increase in the number of available adsorption sites on the surface of the clay mineral. This enhances the rapid removal of MG dye molecules from aqueous solution through adsorption within a short span of time.

If MG dye was interacted with other clay mineral like Na(I)–Mt, then MG dye molecules are replaced by Na⁺ ions through absorption. Furthermore, MG cations replace Na⁺ ions very easily than Fe³⁺ ions. As such, there is negligible UV-visible absorbance and not suitable for removal of MG dye molecules from aqueous solution via adsorption. Therefore, Fe(III)–Mt clay mineral can be efficiently utilized as an adsorbent for the removal of toxic dyes from aqueous solution under ambient conditions.

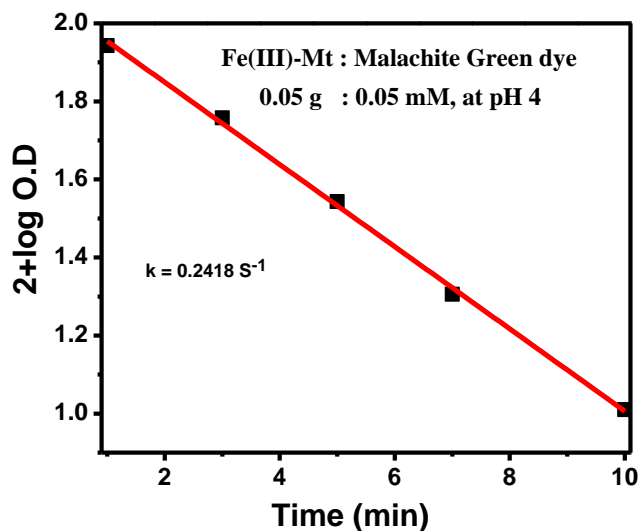


Fig. 5. Rapid removal of MG dye from Fe(III)–Mt follows the pseudo first order reaction.

Kinetics

Rapid removal of MG dye from aqueous solution was observed at $\lambda_{\max} = 617$ nm. From the UV-Vis spectra it was observed that the absorbance of MG dye solution decreases with increasing time intervals which indicates that the dye was adsorbed completely on the surface of Fe(III)–Mt. From the **Fig. 5**, it was obtained that a plot of $2 + \log$ O.D. with time was linear and MG dye adsorption from Fe(III)–

Mt follows the pseudo first order kinetics. The rate constant was determined using following expression $k = 2.303 \times \text{Slope}$. By using this expression rate constant can be easily calculated. Huang *et al.* has reported the importance of Iron-based nanoparticles (OT-FeNP) which are synthesized from oolong tea extracts used for degradation of malachite green dye. The experimental results indicated that the adsorption of MG dye was found to follow the pseudo first order kinetics [11].

Examination of spent or oxidized Fe(III)–Mt

As revealed by FTIR spectra here **Fig. 2(b)** the spent clay mineral is intact in all respects when compared to pure Fe(III)–Mt. Also, there is no indication about the presence of additional Fe–dye phase probably due to their small fraction. From the XRD analysis, we cannot observe any significant peak in the spent Fe(III)–Mt clay mineral. Moreover, in spent Fe(III)–Mt, basal spacing d_{001} was almost same due to small amount of MG dye adsorbed on the surface area and very difficult to show a significant peak using XRD analysis.

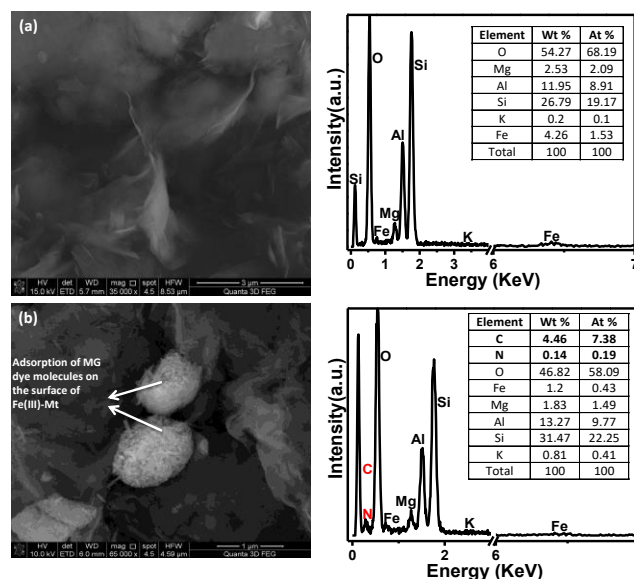


Fig. 6. FE–SEM with EDX of (a) fresh Fe(III)–Mt and (b) After treat with MG dye/spent Fe(III)–Mt.

Fig. 6 represents the morphological images of Fe(III)–Mt before and after treating with MG dye solution. In order to understand the removal of dye and its adsorption on the clay mineral, it is important to examine the spent or oxidized Fe(III)–Mt for FESEM/EDAX analysis. Accordingly, the Fe(III)–Mt was analyzed by FESEM/EDX spectra to observe any morphological changes upon dye reduction. In **Fig. 6(b)** shows an appreciable change in the microstructure of Fe(III)–Mt, i.e., Small white spots (indicated in **Fig.**) are observed on the surface of clay mineral. Moreover, EDAX analysis confirmed the adsorption of MG dye on the surface of spent Fe(III)–Mt as shown in **Fig. 6(b)**. From the surface morphology studies, we strongly recommended that Fe(III)–Mt clay mineral can be efficiently utilized as an adsorbent for the removal of toxic dyes from aqueous solutions.

Recovery of Spent Fe(III)-Mt from degraded MG dye solution

After the MG dye adsorption, the spent Fe(III)-Mt settled down at the bottom within 15 min. Then the dispersed spent Fe(III)-Mt was removed using centrifugation process. Fe(III)-Mt was completely recovered (100%) from degraded MG dye solution as shown in **Fig. 7(a)**. At the end, we got a clear solution which is free from spent Fe(III)-Mt clay mineral.

Fig. 7(b) shows the photograph of a dry clay mineral before and after treating with MG dye in aqueous solution. From this figure we can observe a lot of changes in the spent clay mineral Fe(III)-Mt and it is confirmed that MG dye was completely adsorbed on the Fe(III)-Mt, moreover dye was adsorbed rapidly (100%) within 5 min through adsorption process.

From the literature survey the major disadvantage of physical methods are the dyes molecules will be transferred to another phase rather than destroyed. Additionally, biological degradation of organic contaminants suffers from low degradation efficiency, high cost and rigorous degradation conditions. Furthermore, the disposal of chemicals containing sludge at the end of degradation also entails complicated post treatment processes [35]. Therefore, it is indispensable and emergent to explore the new reductant/adsorbant for the dye removal which could

be completely separated from the degraded solution easily. Accordingly, we have successfully achieved the complete (100%) separation of spent Fe(III)-Mt from the degraded MG dye solution by centrifugation.

Comparison with other adsorbents/reductants

Activated carbons are widely used for adsorption process for the removal of organic and inorganic pollutants from aqueous effluents. But commercially available activated carbons are expensive and difficult to handle [36]. Eskizeybek *et al.* has reported the applications of PANI/ZnO nanocomposites as photo catalyst for the degradation of (MB or MG) with 99% efficiency after 5 h. But degradation was observed only under natural sunlight [37]. Furthermore different types of natural and synthetic polymers like Graphite oxide with magnetic chitosan, *N*-benzyl-*O*-carboxymethylchitosan magnetic nanoparticles [38], γ -Fe₂O₃/crosslinked chitosan [39] and TiO₂/poly[acrylamide-co-(acrylic acid)] [40] have been modified with magnetic nanoparticles to remove dyes from wastewater. However, synthesis of these magnetic systems which involve the multistep synthetic route and was not convenient for use in routine removal processes [13]. From the above drawbacks we believe that Fe(III)-Mt has remarkable adsorption capacities towards cationic dyes. Hence on this basis, we could conclude that, Fe(III)-Mt is

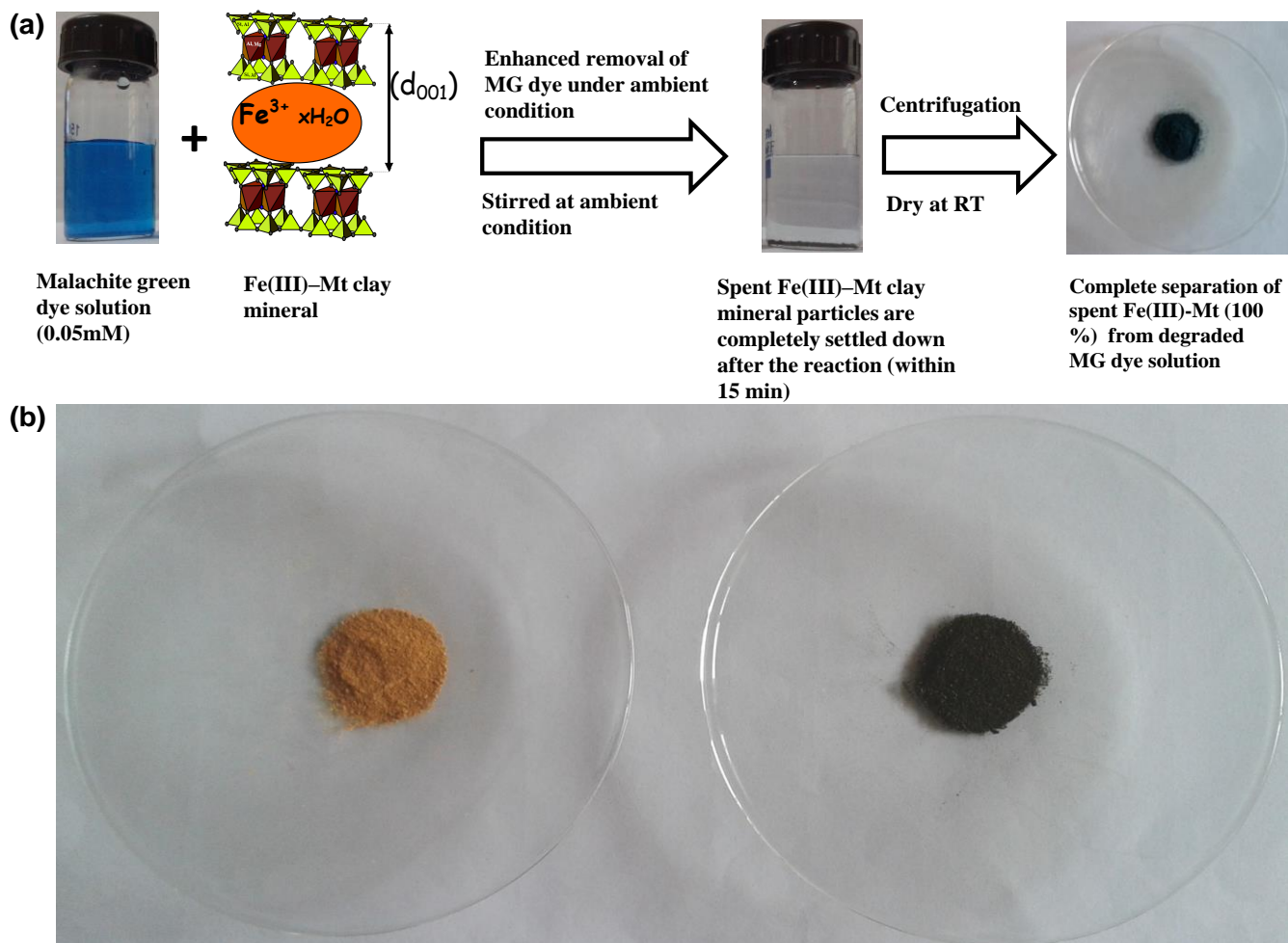


Fig. 7. (a) Complete separation (100%) of spent Fe(III)-Mt from the degraded MG dye solution through centrifugation and (b) Photographs showing the color of Fe(III)-Mt before (a) and after (b) interacting with 0.05 mM MG dye solution at pH 7. (The spent clay mineral was washed thoroughly).

economical, efficient and effective adsorbent as compared with reported reductant/adsorbents.

Conclusion

We have achieved an efficient and concise method for MG dye removal by Fe(III)–Mt through adsorption process under ambient conditions. The concentration of MG dye removal was estimated from its optical density at $\lambda_{\text{max}} = 617$ nm using UV-Vis spectrophotometer. The decrease in MG dye concentration due to reaction between Fe(III)–Mt was expressed here in terms of % reduction as a function of time. The MG dye removal was rapid at basic pH and increases with temperature up to 50 °C. A complete reduction (100%) occurred in about 5 min at pH 8 & 7 min at pH 6, while at pH 4 & 5 in about 10 min and 15 min respectively. The time taken for complete reduction at 0 °C, RT (30 °C), and 50 °C are 10, 7 and 5 min respectively. The adsorption of MG dye was confirmed from FESEM with EDX analysis. More importantly, Fe(III)–Mt could be recovered and retrieved easily after the reaction by centrifugation from the degraded MG dye solution. The efficiency of Fe(III)–Mt clay mineral in removing the dye effluent even at high concentration, under varied conditions of pH and temperature has been greatly acknowledged in the current study. Moreover the amount required for the adsorption of dye is very low, hence making their application economical. Henceforth this work paves way for environmental remediation of noxious dyes in large scale processes. In future perspective, we believe that Fe(III)–Mt could be the efficient and suitable material to augment the real filed applications, which leads to prompt waste water treatment.

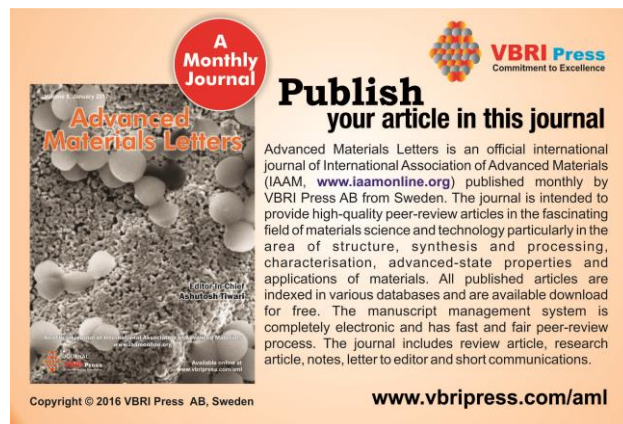
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