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Environmentally benign Fe(III)–montmorillonite for rapid adsorption of methylene blue dye in aqueous medium under ambient conditions

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Abstract

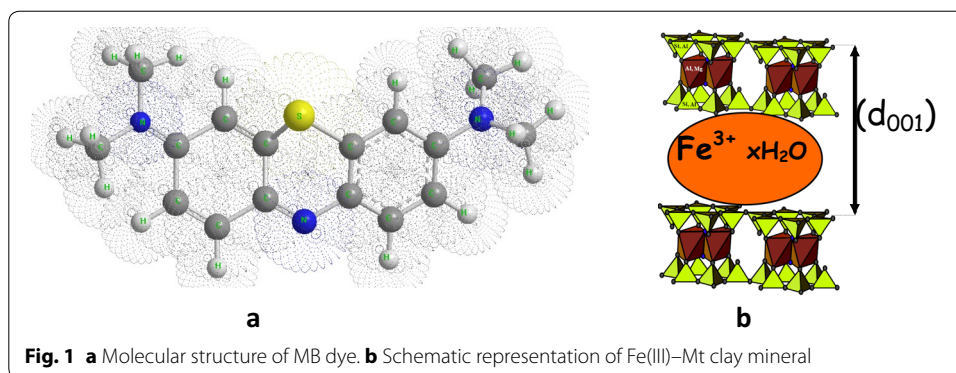
Herein we have explored the highly efficient and environmentally benign clay mineral, Fe(III)–montmorillonite [Fe(III)–Mt], for adsorption of methylene blue (MB) dye from aqueous solution under ambient conditions. The Fe(III)–Mt was interacted with MB dye solution at different pH, temperature and solid-to-liquid ratio. The concentration of MB dye removal was estimated from its optical density at $\lambda_{\max} = 665$ nm using UV–Vis spectrophotometer. The MB dye removal was rapid at basic pH and increases with temperature up to 40 °C. A complete reduction (100%) was occurred in about 7 min at pH 7 and 10 while at pH 3 in about 10 min. The time taken for complete reduction at 0, 30 and 40 °C are 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 MB dye solution. The experimental results of MB dye removal from Fe(III)–Mt follows the pseudo first order kinetics. This study reveals that Fe(III)–Mt has the potential to be used as reductant/adsorbant to remove cationic pollutants effectively and rapidly from drinking water and large scale of industrial wastewater.

Keywords: Fe(III)–montmorillonite, Methylene blue, Remediation, Adsorption

Introduction

The main difficulties associated with the treatment of textile wastewater are the removal of dye effluents which possess complex aromatic structures make them more stable and hence it is difficult to remove the effluents discharged into water reservoirs. Moreover these effluents causes water pollution in large scale become serious environmental issue in recent years (Mahlambi et al. 2015).

Methylene blue (MB) is a cationic thiazine dyes whose molecular structure as shown in Fig. 1a. This is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3S$, while it appears as a solid, odorless and dark green powder that gives a blue colour when dissolved in water. It is used in wide variety of applications such as colouring paper, temporary hair colourant, dyeing cottons, wools and coating for paper stock (Yao et al. 2010). Furthermore, it is used in cosmetics, food, leather, plastic, paper,



textile and pharmaceutical industries (Vinothkannan et al. 2015). Although MB dye is not extremely hazardous, it can cause various toxic effects such as eye burns, irritation to skin and the gastro-intestinal tract (He et al. 2013). Acute exposure to MB could cause difficulty in breathing, nausea, vomiting, profuse sweating and mental confusion (Rafatullah et al. 2010). Therefore, it is essential to treat the MB dyestuffs wastewater before being released into water reservoirs and the environment.

Existing strategies like coagulation, chemical oxidation, adsorption, electrochemical and biological degradation focus on the removal and degradation of organic contaminants from effluents (Dutta et al. 2001; Shannon et al. 2008; Schwarzenbach et al. 2006; Zhang et al. 2012). Moreover, many research groups have been developed various methods like active carbon adsorption, dissolved air flotation, biochemical, chemical and microorganisms mediated reductions to degrade the MB dye. However these techniques are considered to be ineffective due to the phase transfer of pollutants, difficulty in removal of microorganisms from the degraded dye molecules and extreme resistive character of the dyes to microorganisms (Vinothkannan et al. 2015). These methods are still persisting as a major challenge in large scale field applications. Lv et al. (2012) synthesized the ZnO-reduced graphene oxide (RGO)-carbon nanotube (CNT) composites via microwave-assisted reaction and investigated their photocatalytic performance in MB dye degradation process. As a consequence, ZnO-RGO showed 88% degradation efficiency under increased light absorption.

He et al. was investigated the batch adsorption of MB dye onto nanocrystalline cellulose (NCC) at different pH and temperature and found that carbon monolith (CM) showed 94% desorption efficiency of MB dye within 10 min (He et al. 2013). Furthermore, it has been inferred that polyacrylamide grafted xanthan gum and its nanosilica composite (h-XG/SiO₂) through a sol-gel method as adsorbents to remove both MB and MV dyes (methyl violet) from aqueous solution, the results showed 99.4% removal efficiency (Ghorai et al. 2014). Fe₃O₄@Polydopamine-Ag core-shell microspheres were used as an adsorbent for removal of MB dye, but these microspheres showed excellent reduction capabilities on MB dye only in the presence of NaBH₄ (Xie et al. 2014). PrPO₄ nanorods-reduced graphene oxide composites in comparison with bare PrPO₄ nanorods are used as photocatalysts for degradation of MB dye and showed good photocatalytic activity only in the presence of simulated sunlight irradiation (Lv et al. 2014). Although these heterogeneous reductants/adsorbents are used for the degradation and adsorption

processes, there will be an incomplete reduction and time consumption is more. These are effective only in the presence of co-catalysts and sunlight irradiation. As a consequence, a keen focus has been given on the utilization of various clay minerals such as silica, alumina, and zeolites which selectively adsorb the toxic pollutants present in the water through adsorption/degradation process.

Clays are important class of materials that are readily available in nature. These are used as very good adsorbents, decolouration agents, ion exchangers, molecular sieves, catalysts (Kloprogge 1998). More importantly, clay minerals have attracted significant attention for diversified applications including pollutants removal/remediation, because of their high specific surface area, adsorption capacity and excellent adsorption behavior towards cationic sensitizers. These play a pivotal role as it supports various sensitizers because of their large surface area and easy adsorption of cationic sensitizers (Cenens and Schoonheydt 1988). The most used clays as nano-adsorbents are montmorillonite/smectite group and kaolinite group clays (Liu and Zhang 2007). Cu(II)-exchanged montmorillonite (Ma et al. 2004) and TiO₂ pillared montmorillonites (Chen et al. 2014) are successfully employed for the adsorption and degradation of MB dye.

Montmorillonite (Mt) is 2:1 dioctahedral smectite group clay mineral having required qualities such as low diffusion, high absorption capacity, low hydraulic conductivity and layered structure. The octahedral alumina sheet is sandwiched between tetrahedral silicate sheets. The negative charge is created on the clay mineral due to the isomorphic 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 Ca²⁺, Na⁺ etc. at the interlayer. i.e., the redox sensitive Fe(III) ions are placed in the interlayer of clay mineral becomes Fe(III)-Mt as shown in Fig. 1b. Thus, the cation exchange capacity (CEC) of clay mineral depends on the net elemental composition that varies with the geographical availability in the environment (Stucki 2006). The properties and uses of this clay mineral can be modified not only by altering the structural Fe(II)/Fe(III) ratio (Grygar et al. 2007), but also by replacing the interlayer cations with a variety of inorganic and organic cations (Leungo et al. 2011; Bigi et al. 2000). Environmentally benign and redox sensitive metal ions like ferrous and ferric ions in the interlayer of smectite clay mineral can impart many technological important properties. It is obvious that the development of new method which involves heterogeneous reaction would be suitable for large-scale synthesis. Fe-pillared montmorillonite or Fe(III) incorporated clay minerals has been extensively used in heterogeneous catalytic systems and were proved to be advantageous in both economic and environmental point of view (Vinoda and Manjanna 2014; Brigatti et al. 2000).

There are only a few reports on natural (Parthasarathy et al. 2003; Shi et al. 2011) and modified clay minerals (Manjanna et al. 2009; Wu et al. 2012; Vinuth et al. 2015) for Cr(VI) reduction. The availability as well as the amount or access of Fe(III) ions for dye degradation was very limited. Hence it is important to make use of Fe(III)-Mt, i.e., the redox sensitive Fe(III) ions are placed in the interlayer of clay mineral to augment the real field applications. Recently, Manjanna et al. (2009) has reported the preparation of Fe(III)-Mt and explained the basic properties along with stability. Hence, it is possible to make use of such an important redox sensitive clay mineral for the adsorption of MB dye.

The main objective of the present study is the application of Fe(III)–Mt as an effective reductant for MB dye removal in aqueous solution. The reduction reaction was carried out at different pH and temperature by varying the amount of Fe(III)–Mt. However, to till date, the use of Fe clay minerals as a reductant/adsorbent for the adsorption of dyes was limited. Hence facile and reliable preparation of Fe(III)–Mt clay mineral is having excellent adsorption and degradation properties make a suitable reductant for removal of MB dye from aqueous solution.

Methods

Materials

Kunipia F montmorillonite was used for whole experiments which contain >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 (Manjanna et al. 2009). The dye with a labelled purity of more than 99% was obtained from s. d. fine-chem limited, India and used as such. Double distilled water was used throughout in this study. The percentage of dye removal from aqueous solution was estimated from its optical density at $\lambda_{\text{max}} = 665 \text{ nm}$ using UV–Vis spectrophotometer.

Fe(III)–Mt preparation

The raw clay mineral (10 g in 1 L) 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 μm filter, until no chloride was detected while washings by AgNO_3 test. Later, solid sample was dried at room temp (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 (Brigatti et al. 2000) using UV–Vis spectrophotometer ($\lambda_{\text{max}} = 510 \text{ nm}$).

The X-ray diffraction patterns (XRD) of the samples were recorded using D2 phaser XRD (Bruker AXS GmbH, Germany) with Ni-filtered Cu K_α 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 and spent Fe(III)–Mt was recorded using field emission scanning electron microscope (Nova NanoSEM 600, FEI Company, Netherlands) along with energy dispersive X-ray (EDX) analysis for approximate elemental composition.

Removal of MB dye by Fe(III)–Mt from aqueous solution

In a typical stoichiometric case, freshly prepared Fe(III)–Mt (0.03 g) was added to MB dye solution (0.025 mM, 100 mL) and stirred magnetically. The reaction was also carried out at different solid-to-liquid ratio, pH 3–10 (adjusted with dil. HCl and NaOH) and temperature 0, 30 and 40 $^\circ\text{C}$. 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 MB 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 X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and field emission scanning electron microscope with energy dispersive X-ray analysis (FESEM/EDXA) techniques.

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, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and Field emission scanning electron microscope with energy dispersive X-ray analysis (FESEM/EDXA) results confirmed the formation of Fe(III)-Mt.

The X-ray diffraction (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. 2a. 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. These values are in good agreement with the previously reported values (Manjanna et al. 2007; Kozai et al. 2001). In spent Fe(III)-Mt, basal spacing d_{001} value

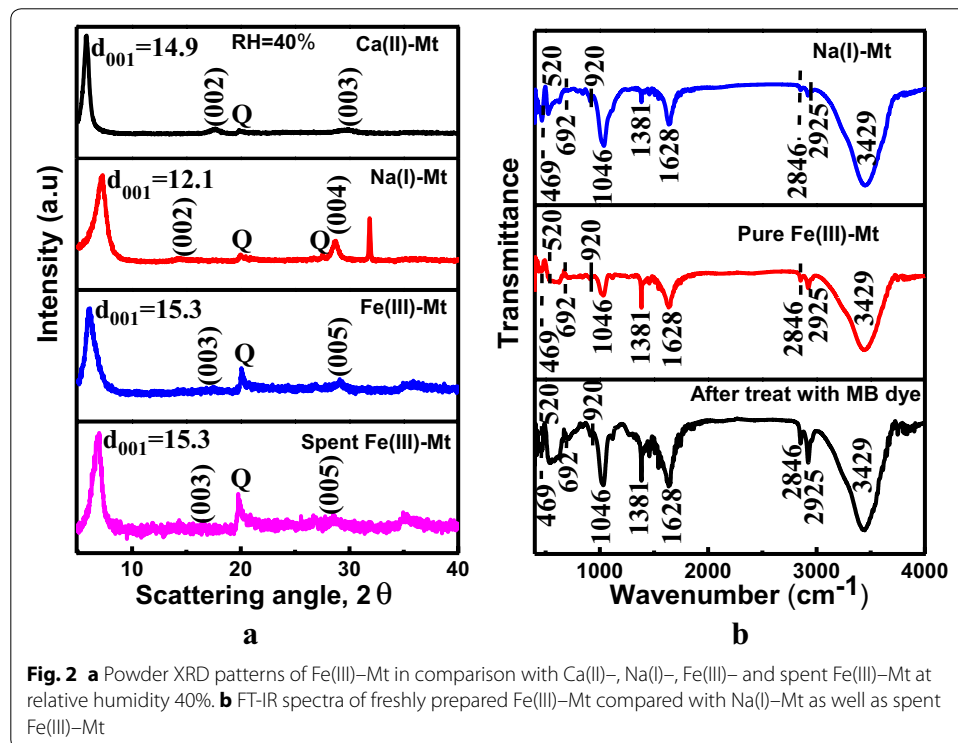


Fig. 2 **a** Powder XRD patterns of Fe(III)-Mt in comparison with Ca(II)-, Na(I)-, Fe(III)- and spent Fe(III)-Mt at relative humidity 40%. **b** FT-IR spectra of freshly prepared Fe(III)-Mt compared with Na(I)-Mt as well as spent Fe(III)-Mt

was almost same due to small amount of MB dye adsorbed on the surface area and hence it didn't show a significant peak using XRD analysis.

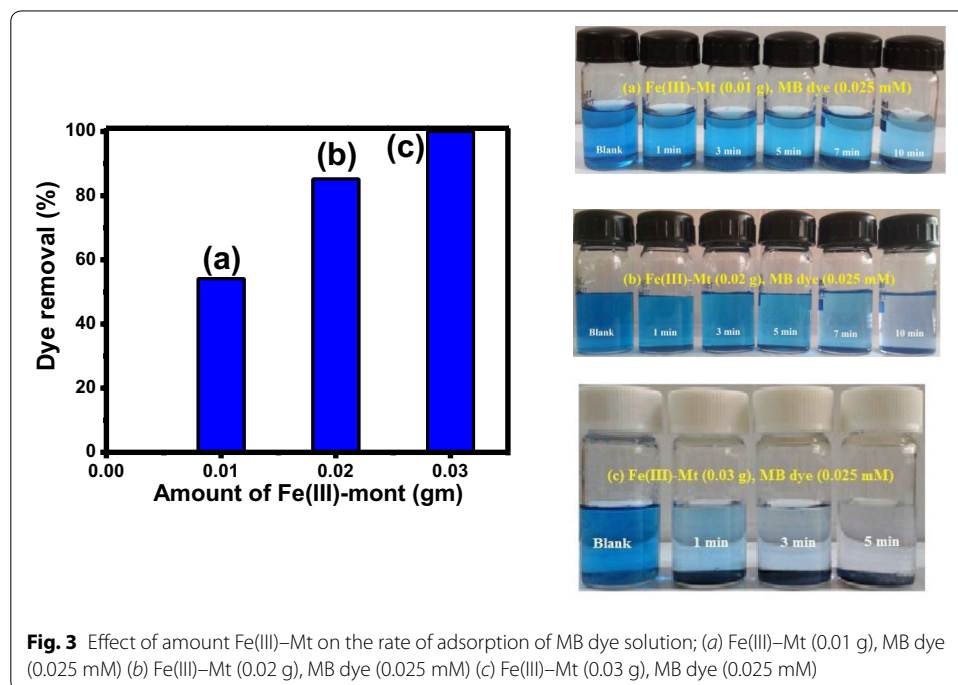
As shown in Fig. 2b, the Fourier transform infrared (FT-IR) spectra of freshly prepared Fe(II)-Mt is similar to that of Na(I)-Mt. The basic structure of clay mineral has not undergone any significant changes. For instance, the bending vibration bands at $\sim 520\text{ cm}^{-1}$ for Si-O-Al, and 920 cm^{-1} for Al_2OH are intact. However stretching vibrations of Si-O group $\sim 1046\text{ cm}^{-1}$ are slightly broadened. The vibration bands at 1628 cm^{-1} corresponds to adsorbed water and 3429 cm^{-1} for water present at the inter-layer. As revealed by Fourier transform infrared (FT-IR) spectra the spent clay mineral is intact in all respects when compared with pure Fe(III)-Mt.

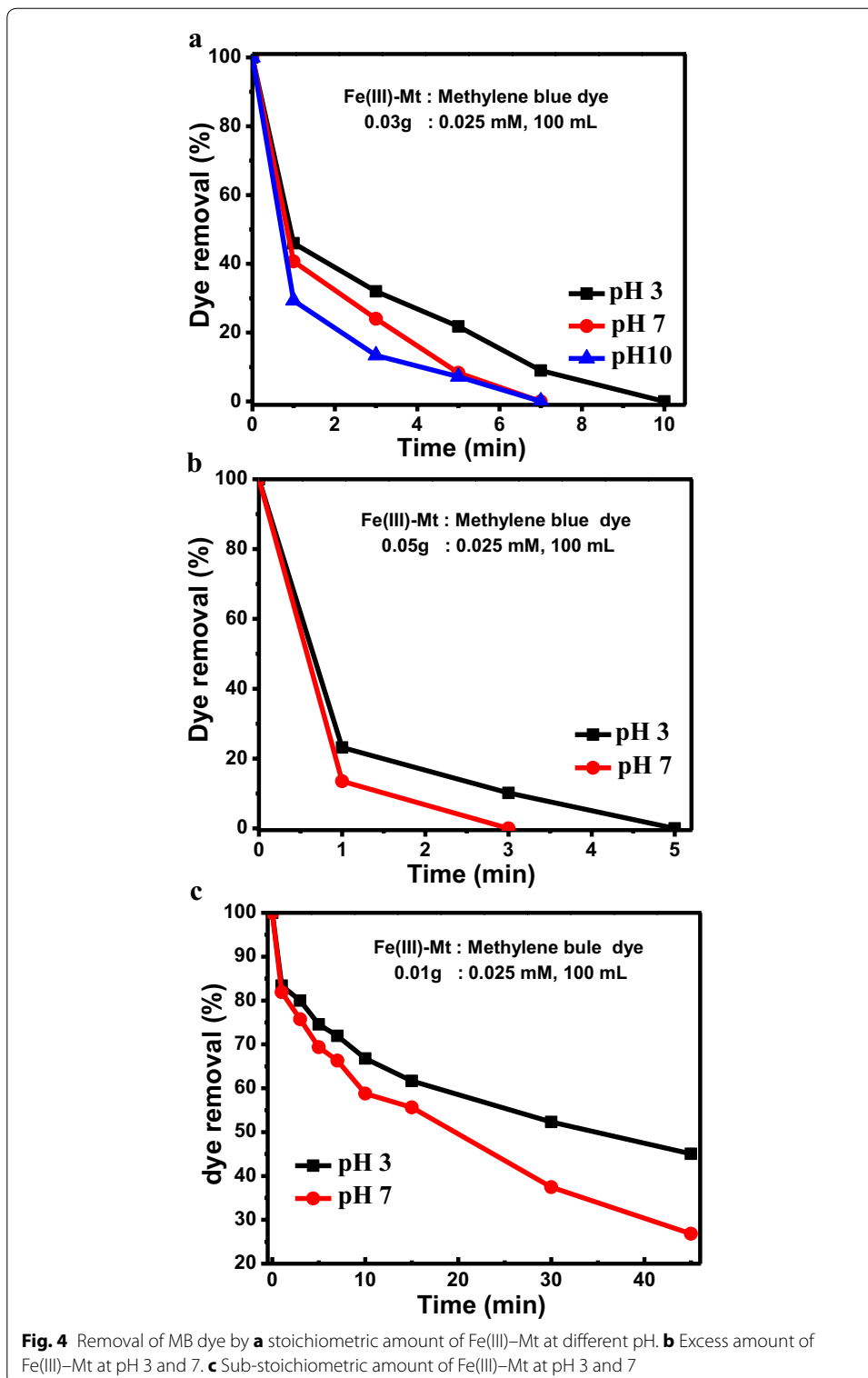
Effect of amount of Fe(III)-Mt on MB dye removal from aqueous solution

In order to determine the stoichiometric amount of Fe(III)-Mt, it was added to MB dye solution (MB solution 0.025 mM, pH 7) by varying the amount of Fe(III)-Mt from 0.01 to 0.03 g. The concentration of MB dye removal was estimated from its optical density at $\lambda_{\text{max}} = 665\text{ nm}$ using UV-Vis spectrophotometer. The effect of amount Fe(III)-Mt on the rate of adsorption of MB 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 0.03 g. It was observed that the rate increases with increase in Fe(III)-Mt from 0.01 to 0.03 g.

Effect of stoichiometry on MB dye removal from an aqueous solution

Figure 4a-c shows the % removal of MB dye at different pH as a function of time for different solid-to-liquid ratio viz., (a) Fe(III)-Mt and MB dye are in stoichiometric amounts (0.03 g, 0.025 mM), (b) Fe(III)-Mt is stoichiometrically excess (0.05 g, 0.025 mM) and (c) Fe(III)-Mt is stoichiometrically less (0.01 g, 0.025 mM). In general, the dye removal





by Fe(III)-Mt is very rapid process. In each case, we saw a two-stage removal of MB dye by Fe(III)-Mt: a rapid first stage followed by a slow second stage. A complete removal occurred in about 10 min at pH 3 whereas at pH 7 and 10 about 93% removal

within 5 min and thereafter 100% reduction occurred within 7 min when stoichiometric amount of Fe(III)–Mt was present. From the literature, it was reported that the dye adsorption in acidic solution takes more time when compare to basic solution (Sohrabnezhad et al. 2009).

As shown in Fig. 4c, when stoichiometrically less amount of Fe(III)–Mt (0.01 g, 0.025 mM) was added, we observed a slow reduction around 35–40% removal at pH 3 and pH 7 at 10 min. Reduction was faster and there after the removal efficiency gradually increased from 35 to 60% at pH 3 and 40–75% at pH 7 within 45 min. In both the cases (pH 3 and 7) complete removal was not attained due to the insufficient amount of Fe(III)–Mt.

It is well-known that the pH has a significant effect on the adsorption of dye. For instance, He et al. (2013) have demonstrated the application of powdered porous carbon monolith and nanocrystalline cellulose with high surface areas for the adsorption and desorption of MB dye. However the sorption capacity was high at basic pH (7–10) when compare to acidic pH (2–5). A similar observation was made by Ghorai et al. (2014) for the removal of MB and methyl violet (MV) dyes from aqueous solution using a nanocomposite of hydrolyzed polyacrylamide grafted xanthan gum and incorporated nano-silica. Meanwhile there was 65% adsorption of MB by h-XG/SiO₂²⁻ nanocomposite at pH 2–4 whereas it was 80% at pH 4–6 and >95% at pH 7–10. Furthermore, Sohrabnezhad et al. (2009) has investigated the photocatalytic degradation of MB dye in aqueous solution using CoS/nanoAl-MCM-41 as a photocatalyst under visible light. The maximum degradation efficiency was observed in alkaline pH 8–10 (>95%) whereas in acidic pH 2–5 only 60% degradation was observed with in a period of 30 min.

Although these heterogeneous reductants/adsorbents are used for degradation and adsorption process, there will be an incomplete reduction and time consumption is more. These are effective only in the presence of co-catalysts and sunlight irradiation. However, in the present study we see the efficient removal of MB dye solution both in acidic as well as basic pH.

Effect of temperature on MB dye removal from an aqueous solution

The reduction of MB dye by Fe(III)–Mt was carried out in different temperatures (0–40 °C) at pH 7 in Fig. 5a–c). In general, the % dye removal increased with temperature up to 40 °C. The time taken for complete reduction at 0, 30 and 40 °C are 10, 7 and 5 min respectively. Moreover when there was an excess of amount of Fe(III)–Mt (Fig. 5b), it took just 5 min, 3 min for the complete reduction of MB at 0 and 30 °C respectively. However, when Fe(III)–Mt (Fig. 5c) was stoichiometrically less, the MB dye reduction was only 45 and 52% at 30 and 0 °C even after 1 h. In both the cases complete adsorption is not attained due to the insufficient amount of Fe(III)–Mt.

He et al. (2013) have shown the temperature dependant adsorption and desorption of MB dye on porous carbon monoliths (CM) and nanocrystalline cellulose at 25 and 60 °C. The adsorption capacity of CM slightly increased with the increase of temperature up to 60 °C. Chitosan/Fe-hydroxyapatite nanocomposite beads are used for removal of lead(II) ions and MB dye from aqueous solution. The results indicate that increasing the temperature leads to an increase in the adsorption of both metal and dyes (Samaneh et al. 2014). The usage of carbon nanotubes for the adsorption of MB dye from aqueous

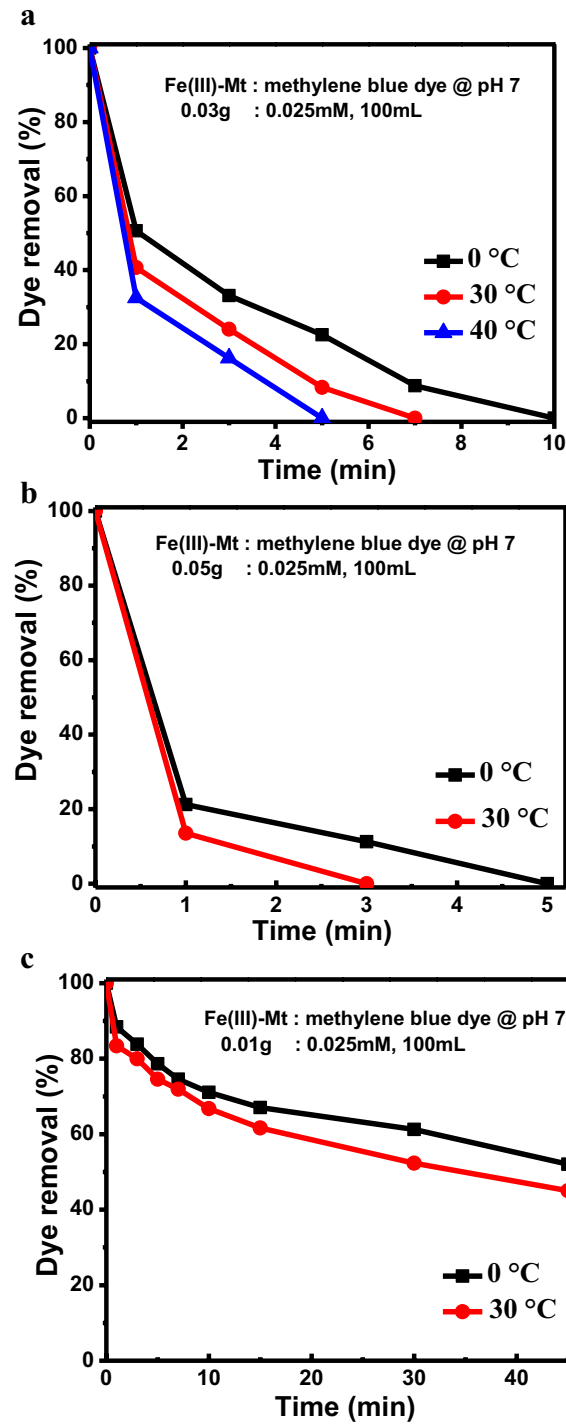


Fig. 5 Removal of MB dye by at pH 7 by **a** stoichiometric amount of Fe(III)-Mt at different temperature. **b** Excess amount of Fe(III)-Mt at 0 and 30 °C. **c** Sub-stoichiometric amount of Fe(III)-Mt at 0 and 30 °C

solution was investigated by Yao et al. (2010). The experimental results have shown that the adsorption capacity increased with increasing temperature (273–333 K), but the removal of MB dye through adsorption on CNTs was found to be rapid at the initial

period and then it became slow and stagnate with the increase in contact time. However, in the present study, we see the 100% removal of MB dye from Fe(III)–Mt in all the temperatures ranging from 0 to 50 °C.

Kinetics

Rapid adsorption of MB dye was observed at $\lambda_{max} = 665$ nm. From the UV–Vis spectra it was observed that the absorbance of MB dye solution decreases with increasing time intervals which indicates that the dye is degraded rapidly due to the effect of Fe(III)–Mt. From the Fig. 6, it was obtained that plot of $2 + \log$ O.D. with time was linear and MB dye removal 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.

Wang et al. (2014) reported the degradation of MB dye by ferrocene via heterogeneous fenton reaction. The experimental results indicated that the degradation of MB dye was found to follow the pseudo first order kinetics. Similarly, Ni/Ti layered double hydroxide is used as a photocatalyst for degradation of aqueous MB dye under visible light condition. The catalytic activity was found to be good under visible light condition and degradation reaction follows pseudo first order kinetics (Chowdhury and Bhattacharyya 2015).

Examination of spent or oxidized Fe(III)–Mt

In order to understand the removal and immobilization MB dye on the Fe(III)–Mt clay mineral, it is important to examine the spent or oxidized Fe(III)–Mt. As revealed by Fourier transform infrared (FT-IR) spectra Fig. 2a, the spent clay mineral is intact in all aspects 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 X-ray diffraction (XRD) analysis, we couldn't observe any significant peak in the spent Fe(III)–Mt clay mineral. Moreover, in spent Fe(III)–Mt, basal spacing d_{001} value was almost the same due to small amount of MB dye adsorbed on the surface and it didn't show a significant peak from XRD analysis.

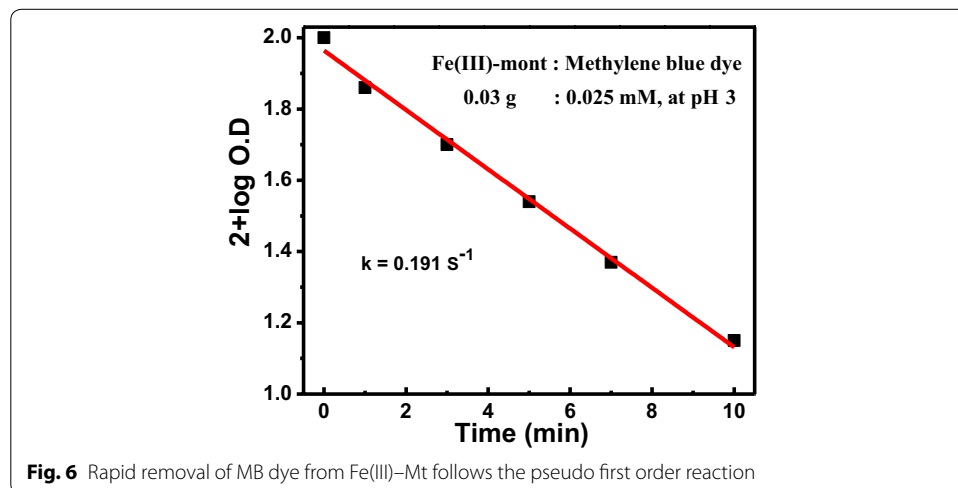
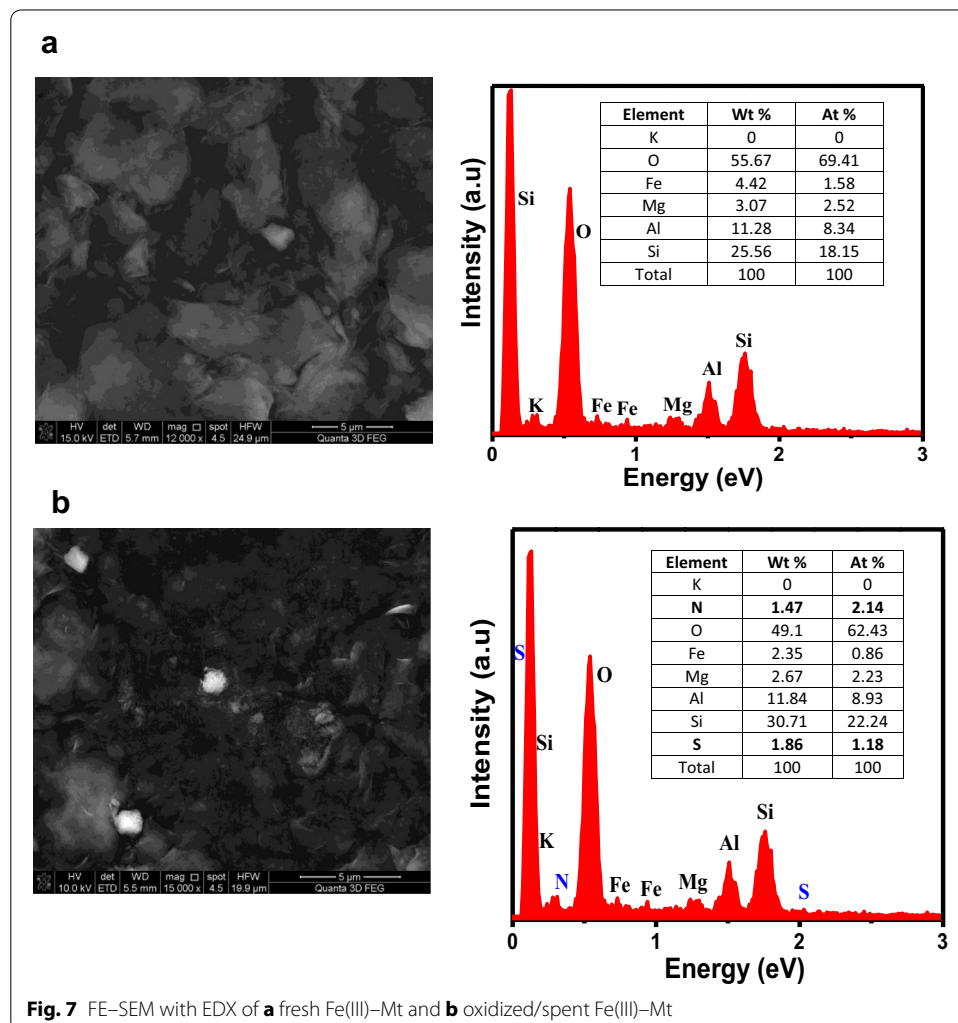


Figure 7 represents the morphological images of Fe(III)-Mt before and after treating with MB dye solution. In order to understand the reduction and its adsorption on the clay mineral, it is important to examine the spent or oxidized Fe(III)-Mt for Field emission scanning electron microscope with energy dispersive X-ray (FESEM/EDXA) analysis. Accordingly, the Fe(III)-Mt was analyzed by FESEM/EDX spectra to observe any morphological changes upon dye adsorption. In Fig. 7b shows an appreciable change in the microstructure of Fe(III)-Mt. Moreover Energy dispersive X-ray (EDXA) analysis confirmed the adsorption of MB dye on the surface of spent Fe(III)-Mt as shown in Fig. 7b.

Figure 8 shows the photograph of a dry clay mineral before and after treating with MB dye in aqueous solution. From this figure we can observe a lot of changes in the spent clay mineral Fe(III)-Mt and confirmed that MB dye was completely adsorbed on the Fe(III)-Mt, moreover dye was removed rapidly (100%) within 5 min through adsorption process.



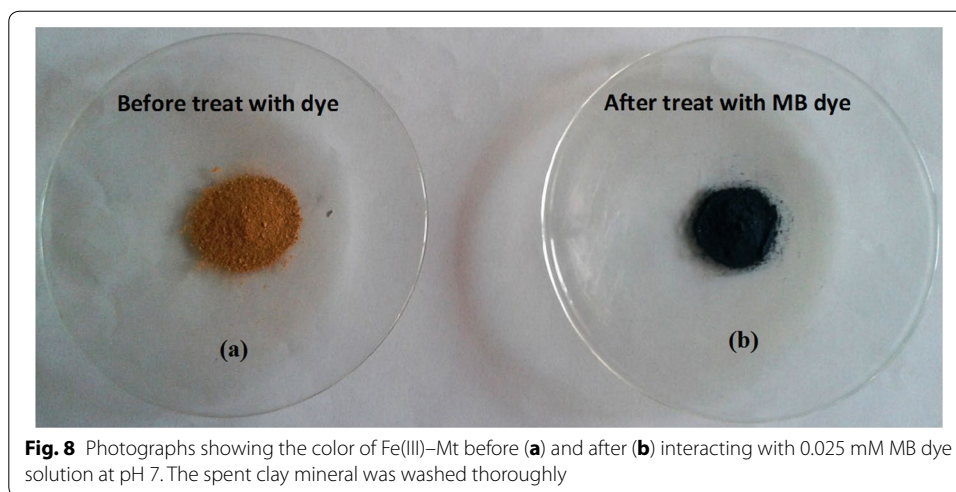


Fig. 8 Photographs showing the color of Fe(III)-Mt before (a) and after (b) interacting with 0.025 mM MB dye solution at pH 7. The spent clay mineral was washed thoroughly

Separation of spent Fe(III)-Mt from degraded MB dye solution

After the 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 MB dye solution as shown in Fig. 8a. At the end, we got a clear solution which is free from spent Fe(III)-Mt clay mineral.

The major disadvantage of physical methods is that the dye 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 (Mao et al. 2014).

Graphite powder and carbon nanotubes have been used for the removal of organic dyes from aqueous wastewater; however these adsorbents usually suffer from difficulties in the separation and regeneration processes. Furthermore activated carbon was used in the removal of dyes and pigments, but the main disadvantage is activated carbon regeneration which typically involves drying at elevated temperature (He et al. 2013). Therefore, it is indispensable and emergent to explore the new reductant/adsorbent 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 MB dye solution by centrifugation. From the experimental results, it was shown that the separation of Fe(III)-Mt from aqueous solution could be efficient, facile and reliable. Nevertheless, Fe(III)-Mt was a suitable reductant for the adsorption of dye molecules from aqueous solution with high efficiency, low cost and environmental friendliness.

Comparison with other adsorbents/reductants

Zhang et al. has described the application of porous Co_3O_4 nanorods-reduced graphene (PCNG) oxide hybrid materials for the catalytic oxidation of MB dye. PCNG showed 97% degradation after 25 min in the presence of H_2O_2 . However there was no degradation without PCNG or H_2O_2 (Zhang et al. 2013). Furthermore, Fe doped ZnS

nanoparticles (Chauhan et al. 2013) and ferrite bismuth nanoparticles (Soltani and Entezari 2013) exhibited good photocatalytic activity of MB dye but only under visible light irradiation. CoFe₂O₄/activated carbon nanocomposites have shown 99% MB adsorption in 50 min (Xu et al. 2014). Au-tipped CdSe nanorod clusters are also used as photo catalysts for MB reduction via multiple electron reduction under aerobic conditions (Li et al. 2014). The main drawbacks of afore mentioned are: the reductants/adsorbents have shown incomplete reduction, time consumption is more, effectiveness only in presence of co-catalyst or additives and rapid reduction was only under visible light irradiation conditions.

More importantly, a number of nanoparticles such as Au, Ag, Pd and Pt have been extensively used for the degradation of dyes. However, these metal nanoparticles exhibit certain limitations including limited availability, high cost and generation of ill effects such as skin allergy, eye irritation etc. Hence metal nanoparticles have considerably faded its importance for dye degradation processes (Vinothkannan et al. 2015). Hence it is essential to propose a suitable material which acts both as reductant and adsorbent for field applications, especially to treat water and soil. We believe that Fe(III)–Mt could be the efficient, facile and reliable reductant/adsorbent for the remediation of dyes from aqueous solution.

Conclusion

In this work, we have reported Fe(III)–Mt as an effective reductant cum adsorbent for removal of MB dye solution from aqueous solution through adsorption process under ambient conditions. The removal of MB dye from aqueous solution can be achieved rapidly through adsorption process by Fe(III)–Mt at solid–liquid ratio, different pH and temperature. The removal of MB dye concentration was estimated from its optical density at $\lambda_{\text{max}} = 665 \text{ nm}$ using UV–Vis spectrophotometer. The decrease in MB dye concentration due to reaction between Fe(III)–Mt was expressed here in terms of % reduction as a function of time. In general the dye removal by Fe(III)–Mt is a rapid process, especially under stoichiometric conditions. The dye removal was rapid at basic pH and increases with temperature up to 40 °C. A complete reduction (100%) occurred in about 7 min at pH 7 and 10, while at pH 3, in about 10 min. The time taken for complete reduction at 0, 30 and 40 °C are 10, 7 and 5 min respectively. The experimental results of MB dye removal from Fe(III)–Mt followed the pseudo first order kinetics. The adsorption of the degraded MB dye on spent clay mineral was confirmed from FESEM/EDAX analysis. More importantly, Fe(III)–Mt could be separated and retrieved easily after the reaction by centrifugation from the degraded MB dye solution. The enhanced removal efficiency makes Fe(III)–Mt clay mineral a promising adsorbent/reductant for environmental remediation of cationic pollutants and could be applied in the purification of drinking water and large scale of industrial wastewater.

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Authors' contributions

H.S. Bhojya naik sir guided this work very carefully with good suggestions, M.M. Mahadevaswamy helped during XRD analysis, M.C. Prabhakara gives fruitful ideas regarding adsorption and importance of clay minerals.

Competing interests

The authors declare that they have no competing interests.

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