

Rapid Removal of Hazardous Rose Bengal Dye Using Fe(III) – Montmorillonite as an Effective Adsorbent in Aqueous Solution

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Abstract

Rose bengal (RB) is xanthene dye, that extensively used in dyeing, printing industries and also as an insecticide. It has severe toxic effects on the human health. Although there are many studies on adsorption/photodegradation of rose bengal using different reductants, it is of interest to explore the environmentally benign Fe(III)–montmorillonite (Fe(III)–Mt). Fe(III)–Mt was interacted with rose bengal (RB) solution at different pH (5–10), temperature (0–40°C) and solid-to-liquid ratio. The concentration of RB removal was estimated from its absorbance at $\lambda_{\text{max}} = 545 \text{ nm}$ using UV-Vis spectrophotometer. In general, the dye removal was rapid in acidic pH and increases with temperature up to 50°C. A complete reduction through adsorption occurred within 3 min at pH 5 and 6. The time taken for complete adsorption at 0°C, 30°C and 40°C are 7 min, 5 min and 3 min respectively. The adsorption followed by immobilization of dye on the spent clay mineral was evident from FT-IR and FESEM/ EDX analysis. This adsorption process can be easily scaled-up for real system applications.

Keywords: Rose bengal; Fe(III)–montmorillonite; Adsorption

Introduction

Dyes which are discharged from textile industries are major cause for environmental contamination. Most of the dyes are made to be chemically stable and highly persistent in environment. The wastewater released from textile industries contains highly colored pigments causes serious impact not only on aquatic life but also human beings by producing carcinogenic effects [1]. Among different types of dyes, xanthene dyes are most widely used and these are characterized by presence of xanthenes nucleus with aromatic groups as chromophore [2]. Rose bengal is an important xanthene dye widely used in textile and photochemical industries whose molecular structure as shown in Figure 1a. It has severe toxic effects on the human health especially on corneal epithelium [3]. This dye is very dangerous when it comes to contact with skin and causes itchiness, irritation, reddening and blistering. It also affects to eyes like inflammation, eye redness, itching etc. [4].

There are several, physical and chemical methods have been studied to remove the organic dyes such as rose bengal, methylene blue etc. from the wastewater. Physical techniques like photo degradation, coagulation, flocculation, reverse osmosis, adsorption on the activated carbon, ion exchange method and ultra-filtration [5], have been used to reduce the toxic effects of dye effluents. Furthermore various chemical methods like photosensitized oxidation, adsorption, photo-fenton's reactions are also employed for removal of dyes [6–11]. In contrast these are fairly effective only in removing pollutants, but main drawbacks involved in these techniques are transform dyes in solution into solid forms, the secondary waste produced has to be either treated again or dumped as such [12].

Ti/TiO₂ mesh electrode process was used for the catalytic oxidation of rose bengal in aqueous medium. Here Ti/TiO₂ efficiency was completely depending on the UV light irradiation/lamp and the accumulation of adsorbate residue on the electrode surface may reduce the efficiency of photo oxidation [13]. Moreover some additives like sulphites are also used for the decoloration of rose bengal by UV/H₂O₂ using response surface method [12]. Low cost activated carbon was used for adsorption of different dyes such as rose bengal, congo red, malachite green, rhodamine B in aqueous medium. In case of rose bengal adsorption, there will be only 80% dye was adsorbed for 60

min and adsorption efficiency is less in basic medium [14]. Graphene/polyaniline nanocomposites are used for degradation of rose bengal, there will be only 56% degradation was observed in 3 h [5]. Magnetic cobalt oxide nanowires are used for the reduction of rose bengal, methylene blue and rhodamine B dyes in the presence of NaBH₄. In case of rose Bengal, reduction was completely depend upon the combination of both CoO nanoparticles and NaBH₄. Moreover reduction was completed at 130 min [15]. Degradation of rose bengal and methylene blue dyes by –Fe₂O₃ nanoparticles are also being reported in literature. In case of rose bengal, γ -Fe₂O₃ nanoparticles are effective only in the presence of visible light while complete degradation was observed in 210 min [1]. Although these heterogeneous reductants/adsorbents are used for degradation and adsorption process, there will be a slow degradation and time consumption is more. These are effective only in the presence of light irradiation, lower pH and not suitable for real system applications. Moreover these adsorbents/ reductants cannot be produced in large amounts for real system applications such as water and soil treatments. Therefore, it is imperious to look for effective reductant cum adsorbent for rose bengal in the wide range of pH and temperature. Accordingly, we have explored the use of Fe-based clay mineral for adsorption and immobilization of rose bengal in aqueous solution.

Clays are important class of materials which are readily available in nature. These are used as very good adsorbents, decoloration agents, ion exchangers, molecular sieves, catalysts [16]. Clay minerals plays a pivotal role as supports sensitizers, because of their having large surface

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area and easy adsorption of cationic sensitizers [17]. The most-used clays as nano-adsorbents are montmorillonite/smectite group and kaolinite group clays [18]. 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, as shown in Figure 1b. 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, which varies with the geographical availability in the environment [19]. Clay and clay minerals exhibit the characteristic property called cation exchange capacity (CEC). It is defined as the capacity of soil to hold cations such as Al^{3+} , Ca^{2+} , Mg^{2+} , Mn^{2+} , Zn^{2+} , Cu^{2+} , Fe^{3+} , Na^+ , K^+ , and H^+ and which is described as the quantity of positively charged ions held by the negative charge that present on the surface layer of clay minerals.

It can be expressed as milliequivalent (meq) of positive charge per 100 g of soil. A meq is the number of ions which total a specific quantity of electrical charges. Moreover higher the CEC, increase in the negative charge. As a consequence, there will be more number of cations can be held. 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 [21,22]. 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 development of new method which involves heterogeneous reaction suitable for large-scale synthesis. Fe-pillared montmorillonite and/or Fe(III) incorporated clay minerals are extensively used in heterogeneous catalytic systems and have proved to be advantages from both economic and environmental point of view [4,23].

There are few reports on natural [24,25] or modified clay minerals [26,27] for Cr(VI) reduction. The availability as well as the amount and/or access of Fe(III) ions for dye degradation 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 to augment the real field applications. Recently, Manjanna et al. has reported the preparation details and basic properties of Fe(III)–Mt, i.e., the redox sensitive Fe(III) ions placed in the interlayer of clay mineral [28]. Hence, it is possible to make use of such an important redox sensitive clay mineral for the degradation of rose bengal.

Thus in the present study, we have demonstrated the application of Fe(III)–Mt as an effective adsorbent for rose bengal in aqueous solution

followed by its immobilization. The reduction reaction was carried out at different pH and temperature by varying the amount of Fe(III)–Mt. To the best of our knowledge, there is no previous literature report concerning the use of Fe(III)–Mt for the removal of the rose Bengal from aqueous solution.

Materials and Methods

Materials

Kunipia F mont was purchased from Kunimine Industries Co. Ltd., Japan was used for whole experiments which contain >98% of Na-montmorillonite and only the impurity was quartz. The composition of raw montmorillonite clay mineral is given as $(\text{Na}_{0.431}\text{K}_{0.002}\text{Ca}_{0.002})(\text{Al}_{1.56}\text{Mg}_{0.305}\text{Fe}_{0.099}\text{Ti}_{0.007})^{\text{oct}}(\text{Si}_{3.949}\text{Al}_{0.051})^{\text{tet}}\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ with a CEC of about 1.2 meq/g [28]. The dye with a labeled purity of more than 99% was obtained from s. d. fine-chem limited, India and used as such. Double distilled water was used throughout this study. The percentage of dye removal from aqueous medium was estimated from its absorbance at $\lambda_{\text{max}} = 545 \text{ nm}$ 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 hrs at room temperature ($\text{RT} \approx 30^\circ\text{C}$) 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 into 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 ($\text{RT} \sim 25^\circ\text{C}$), ground to powder form and stored in a vacuum desiccator.

For comparison, Na(I)– and Ca(II)–Mt were also prepared by the conventional cation exchange method with 1 M solutions of NaCl and CaCl_2 , respectively. In order to estimate the interlayer iron, Fe(III)–Mt was subjected for cation exchange with 0.05 mol/L 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 [4,29] using UV-Vis spectrophotometer ($\lambda_{\text{max}} = 510 \text{ nm}$).

Removal of rose bengal by Fe(III)–Mt from aqueous solution

In a typical stoichiometric case, freshly prepared Fe(III)–Mt (2.85 g) was added to rose bengal solution (0.025 mM, 100 ml) and kept stirred magnetically. The reactions were carried out at different pH (5 – 10), solid-to-liquid ratio and different temperature (0, 30 and 40°C). The reaction mixtures was withdrawn periodically by using syringe tube and then centrifuge (REMI, R-8C BL BENCH TOP CENTRIFUGE) to separate the suspended clay particles. The decrease in the dye concentration was estimated from its absorbance. The decrease in the dye concentration, due to reaction between Fe(III)–Mt and rose bengal 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/EDX analysis.

The X-ray diffraction pattern (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,

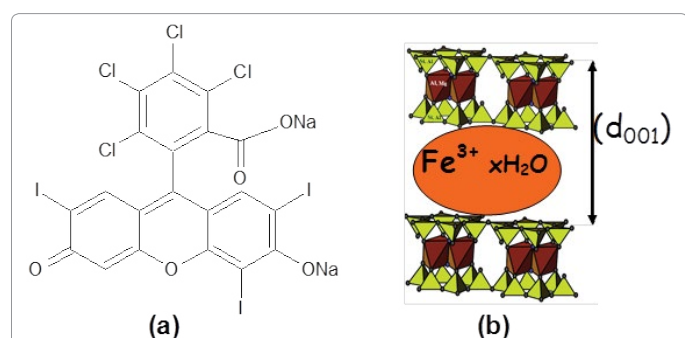


Figure 1: (a) Chemical structure of rose bengal dye (b) Schematic representation of Fe(III)–Mt clay mineral.

Netherlands) along with energy dispersive X-ray (EDX) analysis for approximate elemental composition.

Results and Discussion

Formation of Fe(III)–Mt

The concentration of iron obtained from 0.5 g of Fe(III)–Mt using different reagents (100 ml) viz., 0.05 mol/L H_2SO_4 , 0.5 mol/L $(\text{NH})_4\text{C}_2\text{O}_4$, 1 mol/L NaCl, 0.05 mol/L Na_2EDTA . The total Fe(III) ions extracted was about 1.18 meq/g. In addition, the XRD and FT-IR results are confirm 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% is shown in Figure 2. The basal spacing, d_{001} , are as follows: Fe(III)–Mt, 15.4 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} 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 [30,31]. In spent Fe(III)–Mt, basal spacing d_{001} was almost same due to small amount of rose bengal adsorbed on the surface area and very difficult to show a significant peak using XRD analysis.

As shown in Figure 3 the FT-IR spectra of freshly prepared Fe(III)–Mt is similar to that of Na(I)–Mt. The basic structure of clay mineral has not undergone any 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} corresponding to adsorbed water, and 3429 cm^{-1} for water present at the interlayer. In case of spent Fe(III)–Mt clay mineral, it has undergone some slight changes. When stoichiometric amount of Fe(III)–Mt treated with rose bengal solution, anionic rose bengal does not exchange on clays but it can be bound to the surface OH groups using the procedures for silica gel [17]. In

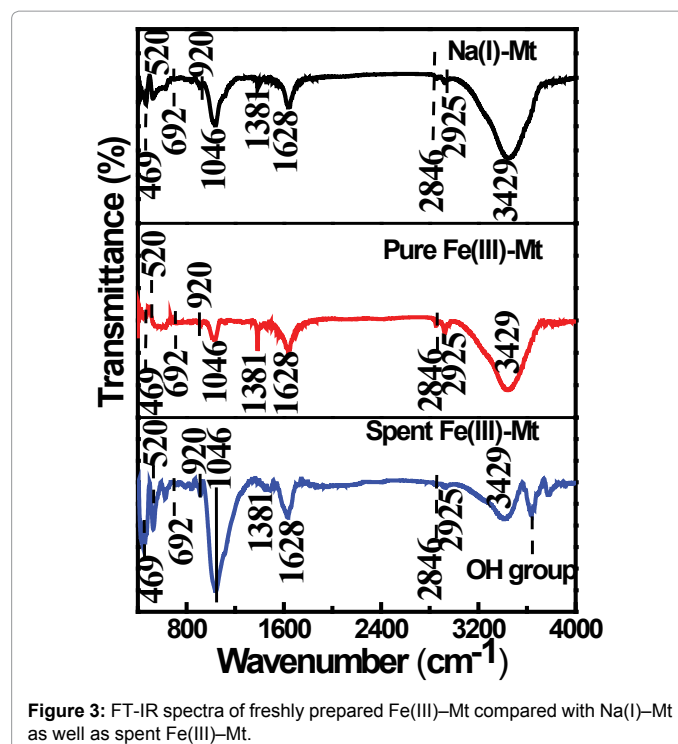


Figure 3: FT-IR spectra of freshly prepared Fe(III)–Mt compared with Na(I)–Mt as well as spent Fe(III)–Mt.

Figure 3, clearly shows the OH groups present in spent Fe(III)–Mt as strong sharp peaks in the range $3600\text{--}3700\text{ cm}^{-1}$.

Rose Bengal dye adsorption using Fe(III)–Mt

Effect of amount of Fe(III)–Mt on RB dye removal in aqueous solution: In order to determine the stoichiometric amount of Fe(III)–Mt, it was added to RB dye solution (RB solution 0.025 mM, pH 6) by varying the amount of Fe(III)–Mt from 0.5 g to 3.0 g. The concentration of RB dye removal was estimated from its absorbance at $\lambda_{\text{max}} = 545\text{ nm}$ using UV-Vis spectrophotometer. The effect of amount Fe(III)–Mt on the rate of adsorption of RB dye solution is depicted in Figure 4. From the Figure 4, it was observed that the required amount of Fe(III)–Mt for 100% dye removal was 2.85 g. It was observed that the rate increases with increase in Fe(III)–Mt from 1.0 g to 2.85 g.

Effect of pH and amount of Fe(III)–Mt on rose bengal removal from an aqueous solution: In Figure 5a-c shows the % removal of dye at different pH as a function of time for different solid-to-liquid ratio viz., (a) Fe(III)–Mt is in stoichiometric amount (2.85 g), (b) Fe(III)–Mt stoichiometrically less (2.80 g) and (c) Fe(III)–Mt stoichiometrically very less (2.50 g). In general, the dye adsorption by Fe(III)–Mt is very rapid process. At pH 5, we see one stage complete reduction. At pH 6, 8 and 10 by Fe(III)–Mt, a rapid first stage followed by a slow second stage reduction can be shown in spectra. A complete reduction occurred in about 3 min at pH 5 and 6, when stoichiometric amount of Fe(III)–Mt was present. At neutral pH and above, the adsorption was relatively slow. For instance, at pH 8 and 10 about 90% reduction within 15 min and thereafter gradual reduction occurred.

It is well-known that the pH has a significant effect on the dye removal/adsorption process. For instance, Gupta et al. have reported the adsorption of hazardous rose bengal by bottom ash under acidic pH is very faster than neutral pH and slower at alkaline pH [32]. Photo catalytic decolorization of rose bengal by $\text{UV}/\text{H}_2\text{O}_2$ was reported, at pH 2 – 4 there was 75% decolorization, whereas pH 8 – 10, only 60%

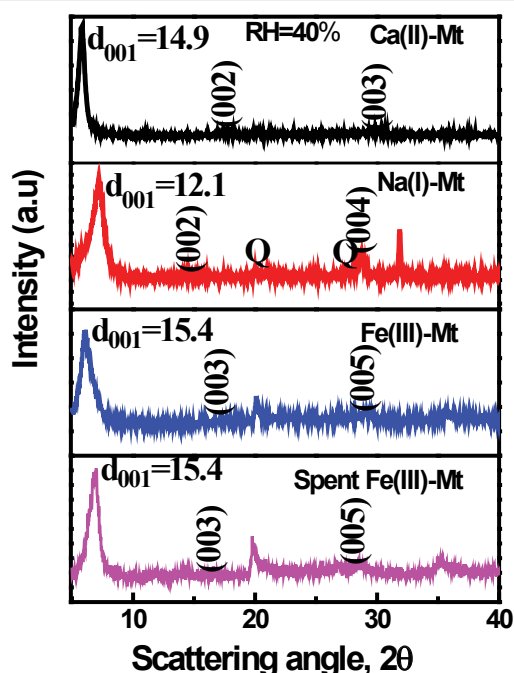
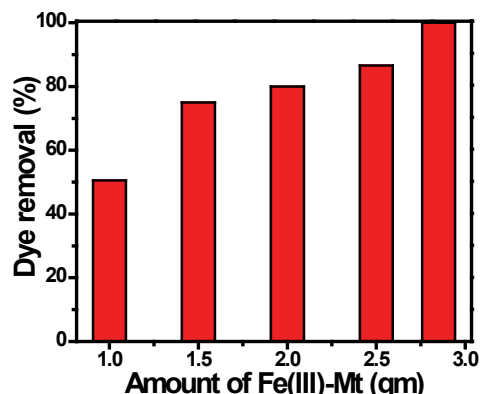
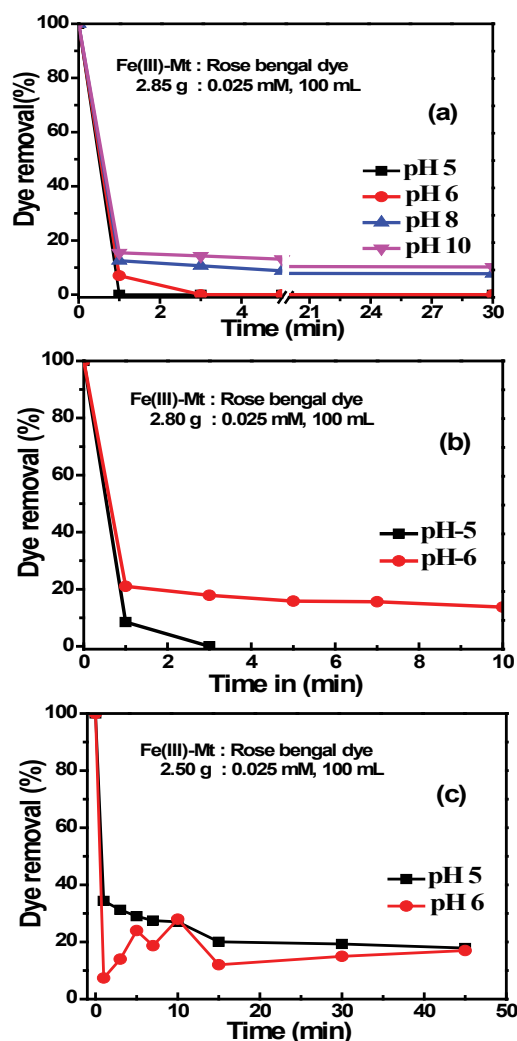


Figure 2: Powder XRD patterns of Fe(III)–Mt in comparison with Ca(II)–, Na(I)– & spent Fe(III)–Mt at relative humidity 40%.



(a) Fe(III)-Mt (1.0 g), RB dye (0.025 mM) (b) Fe(III)-Mt (1.5 g), RB dye (0.025 mM) (c) Fe(III)-Mt (2.0 g), MG dye (0.025 mM) (d) Fe(III)-Mt (2.5 g), RB dye (0.025 mM) (e) Fe(III)-Mt (2.85 g), RB dye (0.025 mM)

Figure 4: Effect of amount Fe(III)-Mt on the rate of adsorption of RB dye solution.



(a) Fe(III)-Mt is in stoichiometric amount (2.85 g) at different pH (b) Fe(III)-Mt stoichiometrically less (2.80 g) at pH 5 & 6 (c) Fe(III)-Mt stoichiometrically very less (2.50 g) at pH 5 & 6

Figure 5: Removal of rose bengal dye.

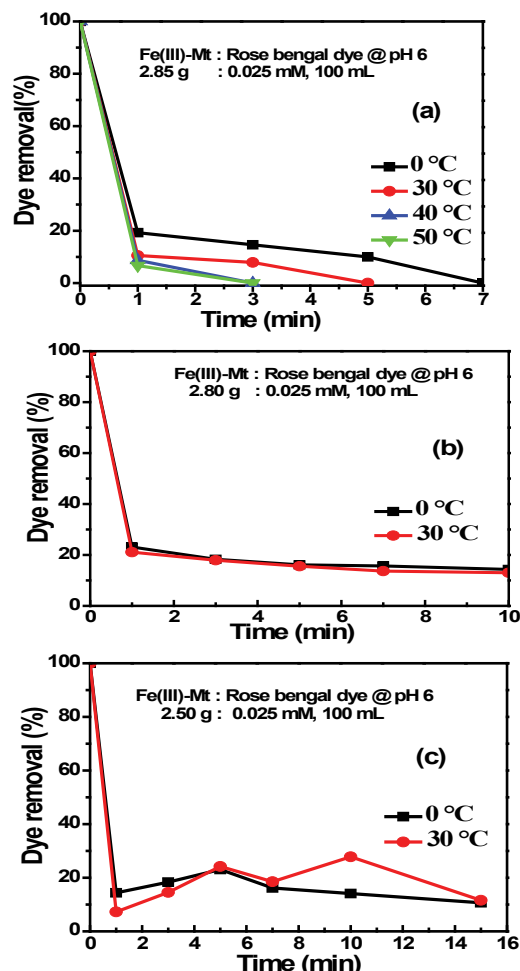
was observed [12]. Zinc oxide by coating with some natural pigments like chlorophyll and anthocyanin are used as a photocatalyst for the photobleaching of rose bengal. In contrast photocatalytic degradation of rose bengal was maximum at pH 5 and the rate of photodegradation was decreased as the pH increases more than 5 (6 – 8) [33]. There are some reports on extraction and determination of rose bengal in aqueous medium by use dispersive liquid-liquid micro extraction (DLLME) coupled to UV-Vis spectrophotometry method. There is a 65% extraction recovery at pH 2 – 4, while at pH 5 – 6, only 50% and gradually decreases to 20% at pH 7 – 10 [34]. Kaur and Singhal have reported the ZnO nanoparticles are also used as photocatalysts for the degradation of rose bengal. At pH 3 – 5, there is an increase in rate of dye degradation, but above pH 5 (pH 6 – 10); gradually there is a decrease in dye degradation [2]. Furthermore ZnO@ZnS core – shell nanoparticles were used as a photocatalyst to decompose rose bengal at different pH values. In contrast ZnO@ZnS core – shell nanoparticles shows very good adsorption efficiency at pH 4 whereas at pH 7 shows low adsorption. Moreover ZnO NPs are well performed at pH 7 but less effective at pH 4 [35]. However, in the present study we observed the efficient adsorption at acidic medium as well as basic medium. Using FT-IR and FESEM with EDAX analysis, we have shown that the rose bengal was bound on the surface of Fe(III)-Mt.

Effect of temperature on RB dye removal using Fe(III)-Mt: The adsorption of rose bengal by Fe(III)-Mt was carried out in different temperatures (0 – 50°C) at pH 6 in Figure 6a-c. In general, the dye adsorption increased with temperature up to 50°C. The time taken for complete adsorption at 0°C, 30°C, 40°C and 50°C are 7, 5, 3 and 3 min respectively. However when Fe(III)-Mt (Figure 6b) was stoichiometrically less, At 30°C and 0°C there will be a 78% and 75% removal at 1 min followed by 85% at 5 min respectively. But complete removal is not possible in both the cases due to the insufficient amount of Fe(III)-Mt for adsorption of RB dye in aqueous solution.

When Fe(III)-Mt (Figure 6c) was stoichiometrically very less, At 30°C there will be 97% reduction at 1 min, but continuous zig-zag variation in reduction was observed from 3 min to 20 min with 95% efficiency after 20 min. Whereas at 0°C also followed the same, only 90% removal was achieved. In both the cases complete removal is not attained due to the insufficient amount of Fe(III)-Mt. Salam et al. [32] have shown that temperature dependent on removal of rose bengal by MWCNTS/chitin/magnetite (MCM) nanocomposites in the range of 10 – 40°C at pH 8 with a reaction time of 40 min. The results revealed that removal of dye was observed at 10 – 50°C and there will be an 85% and 100% removal at 10 – 40°C and 50°C respectively. Batch and bulk removal of rose bengal by adsorption using bottom ash shows the maximum adsorption at temperatures 30 – 50°C was established at around 90 minutes [32]. If the temperature increases, dye adsorption also increases. Furthermore activated carbon was used for removal of acidic and basic dyes through adsorption in aqueous medium. At 30°C from pH 4 – 6 there will be 75%, whereas at pH 6 – 8 only 70% adsorption was observed for overall 60 min. From the equilibrium constant values it was noted that, as the temperature increases adsorption also increases [14]. However, in the present study, we observed the efficient removal of dye from Fe(III)-Mt in all the temperatures from 0 – 50°C.

Examination of spent Fe(III)-Mt

Figure 7 represents the images of Fe(III)-Mt before and after treat with rose bengal dye solution. In order to understand the RB dye removal and it's adsorption on the clay mineral, it is important to examine the spent or oxidized Fe(III)-Mt. Accordingly, the Fe(III)-Mt



(a) Fe(III)-Mt is in stoichiometric amount (2.85 g) at different temperature (b) Fe(III)-Mt stoichiometrically less (2.80 g) at 0 °C and RT (c) Fe(III)-Mt stoichiometrically very less (2.50 g) at 0 °C and 30 °C.

Figure 6: Removal of rose bengal dye at pH 6.

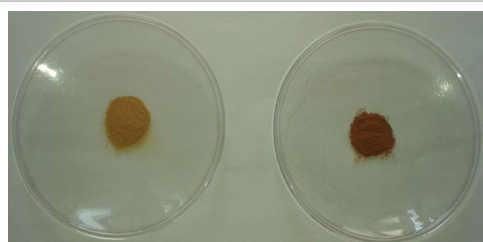


Figure 7: Photographs of Fe(III)-Mt before and after treat with rose Bengal dye solution.

was analyzed by FESEM/EDX spectra to observe any morphological changes upon dye adsorption. In Figure 8, there is an appreciable change in the microstructure of Fe(III)-Mt can be shown. Small white spots are observed on the surface of clay mineral as shown in Figure 8b (clearly visible in Figure). However, EDX confirmed the immobilized dye present in the spent Fe(III)-Mt. However we cannot observed any significant peaks regarding clay-dye interaction in XRD analysis of spent Fe(III)-Mt.

In order to quantitative estimation of iron in the spent clay mineral, Fe(III)-Mt was done with different reagents viz., 0.05 mol/L H_2SO_4 , 0.5

mol/L $(NH_4)_2C_2O_4$, 1 mol/L NaCl, 0.05 mol/L Na_2EDTA . In each case, a known amount (0.2 g) of the spent clay mineral was dispersed in 50 ml of reagents for 24 h. The ratio of ferrous to ferric ions (Fe^{2+}/Fe_{total} where $Fe_{total} = Fe^{2+} + Fe^{3+}$) released was determined by 1, 10-phenanthroline method [4,29] using UV-Vis spectrophotometer (λ_{max} 510 nm) as shown in Table 1.

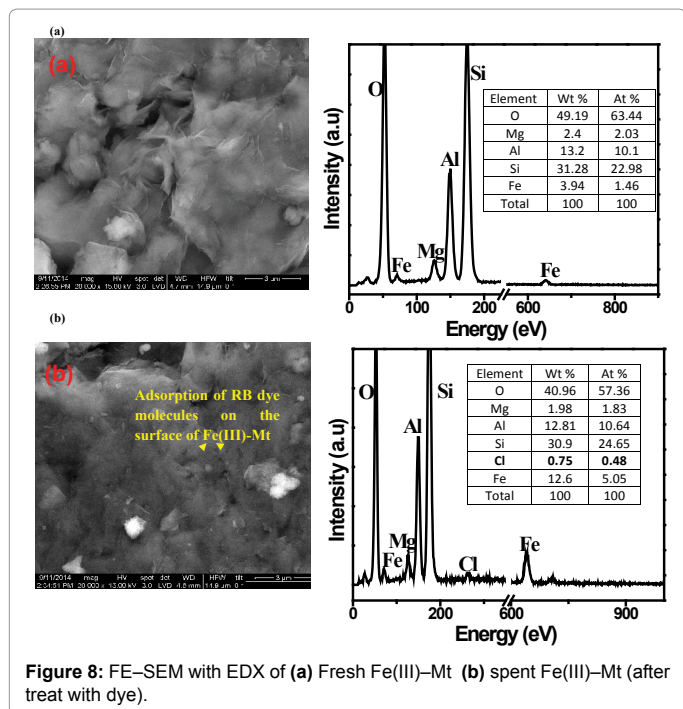
A total of 0.1 ml of the aqueous sample was taken in the 50 ml volumetric flask containing 5 ml of dil. HCl. A total of 5 ml of 10% hydroxyl ammine hydrochloride was added to this and we waited for about 5 min to reduce all Fe(III) to Fe(II). Then 2.5 ml of (acetic acid-sodium acetate) buffer was added followed by 0.5 ml of 50% ammonia solution. To this mixture, 5 ml of 0.25% of 1, 10-phenanthroline solution was added and diluted to 50 ml with distilled water. The optical absorbance was recorded for this solution at 510 nm. A similar procedure was followed for obtaining calibration plot using standard iron solution. From the slope, we could determine the concentration of the dissolved iron as Fe^{2+} and referred as $Fe_{total} = Fe^{2+} + Fe^{3+}$. To know the Fe^{2+} alone in the dissolved iron, the hydroxyl ammine hydrochloride was not added during the estimation to prevent the reduction of $Fe^{3+} \rightarrow Fe^{2+}$. Thus, the Fe^{2+}/Fe_{total} ratio could be determined in this study [4].

Comparison with other adsorbents/reductants

Although some Fe-containing clay minerals like ferrous saponite are found in the natural environment [25], the availability of Fe (III) ions is very limited. CuO-ZnO composites are used as nanophotocatalyst for the degradation of textile dyes under visible light [36,37]. Graphene oxide/sodium alginate/polyacrylamide (GO/SA/PAM) nanocomposite hydrogel [38] and FeS_2 thin films [39] are employed for the adsorption and degradation of dyes. But these are restricted to the laboratory purpose, while these are not able to prepare in large amounts and not suitable for field applications. Bottom ash is used as adsorbent for removal of hazardous dye rose bengal in bulk process. After adsorption process, discarding of bottom ash to outside or environment is a major problem. Because it is highly unsuitable for agricultural purpose and also makes the agricultural land barren and also leads to infertility [32]. Pt-graphene/ TiO_2 nanocomposites [40] and CdS nanospheres [41] are used for the photodegradation of organic dye molecules, while these have shown very good efficiency in the presence of visible light irradiation, but in the absence of visible light there will be a negligible performance in photo degradation process. On the other hand, few reduction processes developed seemed to be restricted only for laboratory use [42] and not for real system applications. Hence it is essential to propose a suitable material which acts as both 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 for remediation of dyes from aqueous solution.

Conclusion

We have achieved an efficient and concise method for RB dye removal by Fe(III)-Mt through adsorption process. Experimental studies clearly revealed the removal of RB dye from aqueous solution can be achieved rapidly through adsorption process at solid-liquid ratio, different pH and temperature. The removal of rose bengal concentration was estimated from its absorbance at $\lambda_{max} = 545$ nm using UV-Vis spectrophotometer. The decrease in rose bengal concentration, due to reaction between Fe(III)-Mt was expressed here in terms of % reduction as a function of time. In general, dye removal by Fe(III)-Mt is a rapid process, especially under stoichiometric conditions. For instance, a complete removal occurred within 3 min at pH 5 and 6; at basic pH reduction was relatively slow. The dye removal increased with different temperature 0 – 50 °C. The time taken for complete adsorption at 0 °C, 30 °C, 40 °C and 50 °C are 7 min, 5 min, 3 min and 3



Extraction reagents	Fe(II) ions present in (mM)	Fe(III) ions present in (mM)
0.05 M H ₂ SO ₄	1.07	1.26
0.50 M (NH ₄) ₂ C ₂ O ₄	2.64	1.86
1.00 M NaCl	1.47	1.56
0.05 M Na ₂ EDTA	2.64	1.03

Table 1: Amount of ferrous and ferric ions released from spent or oxidized Fe(III)–Mt in different reagents.

min respectively. The adsorption of RB dye was confirmed from FT-IR and FESEM/EDX analysis. This method provided a facile and reliable access for remediation of wide variety of dyes from aqueous solution under ambient conditions.

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References

- Dutta AK, Maji SK, Adhikary B (2014) γ -Fe₂O₃ nanoparticles: An easily recoverable effective photo-catalyst for the degradation of rose bengal and methylene blue dyes in the waste-water treatment plant. *Mater Res Bull* 49: 28-34.
- Kaur J, Singhal S (2014) Heterogeneous photocatalytic degradation of rose bengal: Effect of operational parameters. *Physica B* 450: 49-53.
- Tabery HM (1998) Toxic effect of rose bengal dye on the living human corneal epithelium. *Acta Ophthalmol Scand* 76: 142-145.
- Vinoda BM, Manjanna J (2014) Dissolution of iron in salicylic acid and cation exchange between Fe(II)-salicylate and Na-montmorillonite to form Fe(II)-montmorillonite. *Appl Clay Sci* 97: 78-83.
- Ameen S, Akhtar MS, Kim YS, Yang OB, Shin HS (2010) Synthesis and characterization of novel poly(1-naphthylamine)/zinc oxide nanocomposites: Application in catalytic degradation of methylene blue dye. *Colloid Polym Sci* 288: 1633-1638.
- Kuo WS, Ho PH (2001) Solar photocatalytic decolorization of methylene blue in water. *Chemosphere* 45: 77-83.
- Lv X, Xu Y, Lv K, Zhang G (2005) Photo-assisted degradation of anionic and cationic dyes over iron(III)-loaded resin in the presence of hydrogen peroxide. *J Photochem Photobiol A* 173: 121-127.
- López C, Moreira MT, Feijoo G, Lema JM (2004) Dye decolorization by manganese peroxidase in an enzymatic membrane bioreactor. *Biotechnol Prog* 20: 74-81.
- Salker V, Gokakakar SD (2009) Solar assisted photo-catalytic degradation of amido black 10bover cobalt, nickel and zinc metalloporphyrins. *Int J Phys Sci* 4: 377-384.
- Lall R, Mutharasan R, Shah YT, Dhurjati P (2003) Decolorization of the dye, Reactive Blue 19, using ozonation, ultrasound, and ultrasound-enhanced ozonation. *Water Environ Res* 75: 171-179.
- Lorimer JP, Mason TJ, Plattes M, Phull SS, Walton DJ (2001) Degradation of dye effluent. *Pure Appl Chem* 73: 1957-1968.
- Rauf MA, Marzouki N, Körbahti BK (2008) Photolytic decolorization of Rose Bengal by UV/H₂O₂ and data optimization using response surface method. *J Hazard Mater* 159: 602-609.
- Li XZ, Liu HL, Yue PT (2000) Photoelectrocatalytic Oxidation of Rose bengal in Aqueous Solution Using a Ti/TiO₂ Mesh Electrode. *Environ Sci Technol* 34: 4401-4406.
- Arivoli S, Sundaravadevelu M and Elango KP (2008) Removal of basic and acidic dyes from aqueous solution by adsorption on a low cost activated carbon: kinetic and thermodynamic study. *J Chem Techn* 15: 130-139.
- Kundu S, Mukadam MD, Yusuf SM, Jayachandran M (2013) Formation of shape-selective magnetic cobalt oxide nanowires: environmental application in catalysis studies. *Cryst Eng Comm* 15: 482-449.
- Klopprogge JT (1998) Synthesis of smectites and porous pillared clay catalysts: a review. *J Porous Mat* 5: 5-41.
- Cenens J, Schoonheydt RA (1988) Tryptophan photo-oxidation by clay-adsorbed sensitizers. *Clay Miner* 23: 205-212.
- Liu P, Zhang L (2007) Adsorption of dyes from aqueous solutions or suspensions with clay nano-adsorbents. *Sep Purif Technol* 58: 32-39.
- Vinuth M, Bhojya Naik HS, Chandra sekhar K, Vinoda BM (2015) Environmental remediation of hexavalent chromium in aqueous solution using Fe(II)-montmorillonite as reductant. *Proced Earth Planet Sci* 11: 275-283
- Stucki JW (2006) Iron redox processes in smectites. Chapter 8 In, Bergaya F, Theng BKG, Lagaly G (eds) *Handbook of Clay Science*, Elsevier, Amsterdam, pp 429-482.
- Grygar T, Hradil D, Bezdecka P, Dousova B, Capek L, et al. (2007) Fe(III)-modified montmorillonite and bentonite: synthesis, chemical and UV-Vis spectral characterization, arsenic sorption and catalysis of oxidative dehydrogenation of propane. *Clays Clay Miner* 2: 165-176.
- Luengo C, Puccia V, Avena M (2011) Arsenate adsorption and desorption kinetics on a Fe(III)-modified montmorillonite. *J Hazard Mater* 186: 1713-1719.
- Bigi, F, Conforti, ML, Sarotori G (2000) Trialkylamine controlled phenol-formaldehyde reaction over clay catalysts: selective and environmentally benign synthesis of salicylic aldehydes. *Tetrahedron* 56: 2709-2712.
- Brigatti, MF, Lugli C, Cibin G, Marcelli A, Giuli G, et al. (2000) Reduction and sorption of chromium by Fe(II)-bearing phyllosilicates: chemical treatments and x-ray absorption spectroscopy (XAS) studies. *Clays Clay Miner* 2: 272-281.
- Parthasarathy G, Choudary BM, Sreedhar B, Kunwar AC, Srinivasan R (2003) Ferrous saponite from the Deccan Trap, India, and its application in adsorption and reduction of hexavalent chromium. *Am Mineral* 88: 1983-1988.
- Shi LN, Zhang X, Chen ZL (2011) Removal of chromium (VI) from wastewater using bentonite-supported nanoscale zero-valent iron. *Water Res* 45: 886-892.
- Wu P, Li S, Ju L, Zhu N, Wu J, et al. (2012) Mechanism of the reduction of hexavalent chromium by organo-montmorillonite supported iron nanoparticles. *J Hazard Mater* 219-220: 283-288.
- Manjanna J, Kozai T, Sato S (2009) Fe (III)-montmorillonite: Basic properties and diffusion of tracers revent to alteration of bentonite in deep geological disposal. *Appl Clay Sci* 43: 208-217.
- Basset J, Denny RC, Jeffery GH, Mendham J (1978) *Vogel's Textbook of Quantitative 399 Inorganic Analysis*. (4th edn) ELBS/Longman, London.
- Manjanna J, Kozaki T, Kozai N, Sato S (2007) A new method for Fe(II)-montmorillonite preparation using Fe(II)-nitrotriacetate complex. *J Nucl Sci Technol* 44: 929-932.

31. Kozai N, Adachi Y, Kawamura S, Inada K, Kozai T, et al. (2001) Characterization of Fe(II)-Mt: A stimulant of buffer materials accommodating over pack corrosion product. *J Nucl Sci Technol* 38: 1141-1143.
32. Gupta VK, Mittal A, Jhare D, Mittal J (2012) Batch and bulk removal of hazardous colouring agent rose bengal by adsorption techniques using bottom ash as adsorbent. *RSC Advances* 2: 8381-8389.
33. Benjamin S, Vaya D, Punjabi PB, Ameta SC (2011) Enhancing photocatalytic activity of zinc oxide by coating with some natural pigments. *Arabian J Chem* 4: 205-209.
34. Kakhki RM, Nejati-Yazdinejad M, Kakeh F (2013) Extraction and determination of Rose Bengal in water samples by dispersive liquid-liquid micro extraction coupled to UV-Vis spectrophotometry. *Arabian J Chem*.
35. Sadollahkhani A, Kazeminezhad I, Lu J, Nur O, Hultman L, et al. (2014) Synthesis, structural characterization and photocatalytic application of ZnO@ZnS core - shell nanoparticles. *RSC Adv* 4: 36940-36950.
36. Salam MA, El-Shishtawy RM, Obaid AY (2014) Synthesis of magnetic multi-walled carbon nanotubes/magnetite/chitin magnetic nanocomposite for the removal of Rose bengal from real and model solution. *J Ind Eng Chem* 20: 3559-3567.
37. Sathishkumar P, Sweena R, Wu JJ, Anandan S (2011) Synthesis of CuO-ZnO nanophotocatalyst for visible light assisted degradation of a textile dye in aqueous solution. *Chem Eng J* 171: 136-140.
38. Fan J, Shi Z, Lian M, Li H, Yin J (2013) Mechanically strong graphene oxide/sodium alginate/polyacrylamide nanocomposite hydrogel with improved dye adsorption capacity. *J Mater Chem A* 1: 7433-7443.
39. Bhar SK, Jana S, Mondal A, Mukherjee N (2013) Photocatalytic degradation of organic dye on porous iron sulfide film surface. *J Colloid Interface Sci* 393: 286-290.
40. Ullah K, Zhu L, Meng Z-D, Ye S, Sun Q, et al. (2013) A facile and fast synthesis of novel composite Pt-graphene/TiO₂ with enhanced photocatalytic activity under UV/Visible light. *Chem Eng J* 231: 76-83.
41. Yu Z, Yin B, Qu F, Wu X (2014) Synthesis of self-assembled CdS nanospheres and their photocatalytic activities by photodegradation of organic dye molecules. *Chem Eng J* 258: 203-209.
42. Yurkow EJ, Hong J, Min S, Wang S (2002) Photochemical reduction of hexavalent chromium in glycerol-containing solutions. *Environ Pollut* 117: 1-3.