Effective oxidative decolourization of azo dyes over Indian Ocean manganese nodules

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The degradation of cationic dyes such as methylene blue is studied using Indian Ocean manganese nodules. Effect of various parameters, such as catalyst loading, dye concentration, initial pH of the solution, effect of various electrolytes and effect of heat treatment of manganese nodules on the decolourization of methylene blue is investigated. The extent of decolourization decreases with increase in pH and increases in the presence of NaCl. Anions like CO\textsubscript{3}\textsuperscript{2-}, PO\textsubscript{4}\textsuperscript{3-}, Cl\textsuperscript{-} inhibit decolourization, whereas SO\textsubscript{4}\textsuperscript{2-} and NO\textsubscript{3}\textsuperscript{-} accelerate the decolourization rate of methylene blue to a remarkable extent. The rate of dye degradation is dramatically reduced with increase in calcination temperature.

Keywords: Manganese nodules, Degradation, Dye degradation, Decolourization, Methylene blue

The naturally occurring marine manganese nodules contain primarily Mn and Fe oxide minerals\textsuperscript{1}. Manganese nodules and its leached residues were found effective adsorbent for a number of anionic and cationic pollutants such as Zn\textsuperscript{2+}, Pb\textsuperscript{2+}, Ni\textsuperscript{2+}, phosphate, selenite, hexavalent chromium, etc. and can be used in water treatment\textsuperscript{2-7}. The characteristics of manganese nodules, namely large surface area, high reduction potential and high surface reactivity, enthused many researchers to evaluate possible application of manganese nodules as an effective oxidant of inorganic compounds, degradation of organic contaminants in water treatment and oxidative decolourization of methylene blue\textsuperscript{8} and methyl orange\textsuperscript{9}.

The removal of toxic pollutants mainly residual dyes from waste water is an important and widely studied research area. Of the various polluntant dyes, methylene blue (MB) is considered a particularly hazardous pollutant due to its toxicity even at low concentration, and non biodegradability. MB is being used as colouring agent in chemical, textile, pulp and paper, printing, cosmetics, leather and food industries\textsuperscript{10, 11}. The various effective techniques for removal of MB from wastewater are reverse osmosis, biological degradation, chemical oxidation, precipitation, electrodialysis, adsorption, etc\textsuperscript{12, 13}. In recent years extensive research has been dedicated towards developing alternative processes for complete degradation of dyes using suitable catalytic/photocatalytic systems. These include UV/H\textsubscript{2}O\textsubscript{2}, UV/O\textsubscript{3} or UV/Fenton’s reagent and TiO\textsubscript{2}-based materials\textsuperscript{14-18}. A number of manganese based synthetic or naturally occurring materials have also been used for oxidative/photo catalytic degradation of a variety of dyes including methylene blue\textsuperscript{8, 9, 19-22}. In the present investigation, we had studied the oxidative decolourization of methylene blue using a variety of Indian ocean manganese nodules by varying different parameters like initial dye concentration, catalyst dose and pH. The effect of heat treatment and electrolyte on decolourization is also studied. The decolourization activity of Indian ocean manganese nodules has been correlated with its physico-chemical properties.

Materials and Methods

Preparation and characterization of Mn nodules

Manganese nodules collected from different stations of the central Indian Ocean basin were crushed and sieved to powdered form. The powdered samples were dried at 110 °C for 8 h and were designated as MN-1, MN-2, MN-3, MN-4, MN-5 and MN-6, based on the location from where the sample was collected. To study the effect of heat treatment on Mn nodule towards decolourization of methylene
blue, MN-4 was heated at different temperatures (110-900 °C) and designated as MN-110,MN-200, MN-300, MN-400, MN-500 and MN-900.

The material was characterized by chemical analysis, crystal structure, surface area, surface available oxygen, surface hydroxyl groups etc. The details on surface and textural characterization have been reported elsewhere. The analysis, crystal structure, surface area, surface hydroxyl groups etc. The details on surface and textural characterization have been reported elsewhere. Details on surface and textural characterization have been reported elsewhere.

Oxidative decolorization of dyes

Decolorization of organic dyes was conducted using a batch technique in a constant temperature water bath at (25±1.0) °C. In a typical experiment, a certain amount of sea nodule (0.6-3.0 g L⁻¹) was dispersed into the reaction flask containing 500 mL of MB (10-100 mg L⁻¹) solution to initiate the reaction. The pH (3–10) of the solution was previously adjusted to the desired value by addition of dil. NaOH/HCl. An accurately weighed amount of the nodule was added to 500 mL stirred dye solution taken in a 3-necked round-bottomed flask equipped with a magnetic stirrer. The dye concentration was kept in the range 10-100 mg/L and pH ranging from 3.10–10.0. The pH of the suspension was not controlled as the reaction proceeds. At specific time intervals, 10 mL of suspension was filtered through 0.22 µ syringe and the absorbance was measured on a Varian 1E CARY UV/visible spectrophotometer at characteristic wavelengths of 665 nm to determine the residual MB concentration. The influence of pH of suspension, dye concentration, loading and particle size of manganese nodule, effect of NaCl concentration, different electrolytes and heat treatment on decolourization efficiency was studied. The results are presented in Table 1. As the nodules possess a complex matrix, a correlation between the decolourization efficiency and any single physicochemical parameter (e.g. surface area, surface hydroxyl group, metal oxide content, surface acidity), is extremely difficult. However, it is quite evident from Table 1 that the samples with higher surface area, surface hydroxyl group and surface acidity have higher decolourization efficiency (MN-2, MN-4) than those with lower values (e.g. MN-3, MN-6). Although sample (MN-3) has surface area comparable with that of MN-2 and MN-4 and possesses the highest manganese content, it shows the lowest efficiency in decolourization reaction. Higher iron oxide content in MN-2 and MN-4 may be partly responsible for decolourization (the main adsorbing oxide) as it plays the role of an adsorbent, which is prerequisite for oxidative degradation process. Taking into

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn (%)</th>
<th>Fe (%)</th>
<th>Al₂O₃ (%)</th>
<th>SiO₂ (%)</th>
<th>Surface OH (meq/g)</th>
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<th>Surface area (m²/g)</th>
<th>Decolourization (%)</th>
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<tr>
<td>MN-1</td>
<td>24.91</td>
<td>8.23</td>
<td>4.53</td>
<td>19.19</td>
<td>0.354</td>
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The feasibility of consecutive use of Mn nodules was assessed by treating MB on Mn nodules by consecutive batch technique. Initially, 500 mL of MB (50 mg/L, pH: 3.0) solution was taken in a three necked round bottom flask and thermostated at 25 °C and stirred before the addition of Mn nodule (3.0 g/L). Same sampling procedure was adopted as earlier. When colour of the dye is discharged to almost 95%, requisite amount of fresh concentrated MB solution was added to obtain dye concentration at the initial stage, followed by rapid pH adjustment to about 3.0 using HNO₃ solution. A third round addition was also made when the color of MB was again decreased to about 95% and pH adjustment was followed.

Results and Discussion

Effect of using different Mn nodules

Methylene blue decolourization by various manganese nodule samples under identical conditions of pH, temperature (25 °C), methylene blue concentration (100 ppm), nodule concentration (1 g/L) were studied. The various physicochemical characteristics and decolourization efficiency data of the manganese nodules are presented in Table 1. As the nodules possess a complex matrix, a correlation between the decolourization efficiency and any single physicochemical parameter (e.g. surface area, surface hydroxyl group, metal oxide content, surface acidity), is extremely difficult. However, it is quite evident from Table 1 that the samples with higher surface area, surface hydroxyl group and surface acidity have higher decolourization efficiency (MN-2, MN-4) than those with lower values (e.g. MN-3, MN-6). Although sample (MN-3) has surface area comparable with that of MN-2 and MN-4 and possesses the highest manganese content, it shows the lowest efficiency in decolourization reaction. Higher iron oxide content in MN-2 and MN-4 may be partly responsible for decolourization (the main adsorbing oxide) as it plays the role of an adsorbent, which is prerequisite for oxidative degradation process. Taking into

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consideration of all the parameters, it is evident from the Table 1 that decolourization of dye on the nodule surface is the combined effect of surface area, surface hydroxyl group, surface acidity and iron content.

**Effect of initial concentration of MB**

The effect of initial methylene blue concentration (10–100 mg/L) on decolourization by manganese nodule was studied (Fig. 1) taking nodule loading 0.6 g/L at initial pH 3.0. At lower concentration (10 mg/L) the decolourization percentage reached 93% within 10 min and colour almost completely disappeared after 45 min. However, at higher methylene blue concentration (100 mg/L) the decolourization was ~ 40% in 3 h.

It is well established that oxidative degradation of organic matter by manganese occurs on the surface of the catalyst\(^{21,24}\) and not in the aqueous phase. The organic compounds adsorbed on the surface form surface precursor complex and then electron transfer takes place from organic compound to the surface bound Mn(III), (IV), followed by release of oxidation product as soluble Mn(II). Petrie et al.\(^{25}\) reported that methylene blue decolourization by Mn nodule is a surface phenomenon. Figure 2 shows that at a fixed loading of the nodules, decolourization decreased with increasing initial concentration. This indicates that reactive surface sites were saturated and did not provide active site for further formation of precursor complex. Thus, percentage of decolourization decreased at higher methylene blue concentration. The experimental findings suggest that surface reactivity and number of adsorption sites are two crucial factors for oxidative decolourization of methylene blue.

**Effect of catalyst loading**

Studies on MB decolourization with varying amounts of manganese nodule (0.6–4 g L\(^{-1}\)) indicate that the extent of MB decolourization decreased with the decrease in catalyst amount (Fig. 2). At higher Mn nodule loading (4 g/L), decolourization increased rapidly approaching 95% within 10 min, and was completely decolorized in 60 min. The decolourization rate decreased substantially at 0.6 g/L of sample.

As discussed earlier, methylene blue decolourization is a surface oxidation process; greater efficiency is shown by higher Mn nodule loading due to larger number of active sites available for formation of precursor complex and subsequent decolourization.

The solubility of manganese oxide [Mn(III), (IV)] is low in acidic solution. In contrast, in the presence of MB, concentration of Mn is enhanced and gradually increases with time. This may be attributed to reduction of Mn(III) and Mn(IV) species by organic reductant (MB) to form soluble Mn(II) species in solution\(^{24}\). The total concentration of Mn(II) released into the solution is equal to Mn(II) present in solution and Mn(II) adsorbed on nodule\(^{26}\).

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Fig. 1 – Effect of initial concentration of MB on its decolourization by Indian Ocean Mn nodules. [Initial pH: 3.0; nodule loading: 0.6 g/L. [MB]: 1, 10 ppm; 2, 30 ppm; 3, 50 ppm; 4, 100 ppm].

Fig. 2 – Effect of manganese nodule loading on decolourization of MB. [Initial conc. of methylene blue: 100 mg/L; initial pH: 3.0. Mn loading: 1, 0.6 g L\(^{-1}\); 2, 1 g L\(^{-1}\); 3, 2 g L\(^{-1}\); 4, 3 g L\(^{-1}\); 5, 4 g L\(^{-1}\)].
Comparison with water washed sea nodule residue

Figure 3 shows the decolourization efficiency of air dried (110 °C) manganese nodule and water washed manganese nodule leached residue (WMNLR). Decrease in rate of decolourization of methylene blue on WMNLR is due to decrease in manganese content, other major metallic components and surface potential. Water washed manganese nodule leached residue was obtained after the extraction of valuable metal components like Ni, Cu and part of manganese from sea bed manganese nodule. This causes a dramatic reduction in its surface active sites as well as oxidizing components like manganese(IV) and (III) contents, which plays a major role in decolourization.

Effect of initial pH of MB solution

The decolourization of methylene blue in the pH range 3-10 was evaluated and the results obtained are presented in Fig. 4. It is evident that the MB decolourization by Indian Ocean manganese nodules decreases progressively with increase in pH up to 10. The oxidation of organic dye on manganese nodule suspension appears to be a heterogeneous reaction, which involves the diffusion of dye compound onto the catalyst surface to form surface precursor complex between the reactants, followed by electron transfer and products release\(^{27}\). The surface charge of Mn nodule plays a vital role in the formation of the surface complex. The pH at zero point charge (pH\(_{zpc}\)) of manganese nodule was determined to be 4.5 by Parida et al.\(^{28}\). At pH lower than the pH\(_{zpc}\) (4.5), the surface of the nodule is positively charged due to protonation, which does not favor cationic dye (methylene blue as model dye) adsorption and hinders the formation of surface precursor complex due to electrostatic repulsion. On the other hand, at higher suspension pH (>4.5) the surface is negatively charged due to deprotonation and favors surface complex formation. Though lower pH inhibits the surface complex formation, it would improve reduction potential of Mn(hydro) oxide/Mn\(^{2+}\) couple. In contrast, the increase in suspension pH would decrease oxidizing power of Mn (hydro) oxides and favor the adsorption of Mn(II) on the particles, thereby resulting in decreasing surface sorption sites. Hence, further adsorption and oxidation of dye compound on the catalyst particle are greatly inhibited\(^{29}\). The present study indicates that lower pH of the suspension suppressed MB adsorption on the nodule but increased reduction potential of Mn(hydro) oxide/Mn\(^{2+}\) couple and enhanced decolourization of methylene blue. The small change in methylene blue decolourization at higher pH is probably due to compensation of the two factors.

Effect of added electrolytes

Decolourization of methylene blue was carried out in the presence of varying concentrations of NaCl (0.02-0.2 mol L\(^{-1}\)) (Fig. 5). The pH of the suspension at the end of the reaction in each run was measured and was found to be slightly higher than the pH initially adjusted. Although there is a progressive increase in the percentage of decolourisation, the salt effect is more significant at lower concentration (0.02 mol L\(^{-1}\) NaCl), presumably because of the following two factors. In the presence of NaCl, there is a possible decrease in the thickness of the electrical double layer formed between Mn nodule and water\(^{21}\). As a consequence, there is close approach between the dye molecule and Mn nodule surface, which

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**Fig. 3** – The comparative plots of MB decolourization by (1) Mn nodule and (2) WMNLR.

**Fig. 4** – Effect of initial pH of suspension on decolourization of MB. [Initial conc. of methylene blue: 30 mg/L; nodule loading: 0.6 g/L. [pH: 1, 3.1; 2, 4.42; 3, 6.74; 4, 8.0; 5, 10.0].]
facilitates the formation of a surface complex. Also, the solubility of the MB is believed to decrease upon addition of NaCl owing to the common ion effect, which favours the exclusion of dye molecules from the solution phase to the particle surface. The second factor for the increase of MB decolourization may be the increase in surface potential of the solid catalyst in the presence of added electrolyte. The rate enhancement of dye degradation in the presence of electrolyte has also been reported in an earlier study.

Effect of other anions on the decolourization of methylene blue by manganese nodule was illustrated in Fig. 6. A series of experiments were performed using different electrolytes, i.e., NaCl, NaNO₃, Na₂HPO₄, Na₂SO₄ and Na₂CO₃. For this, 0.02 mol L⁻¹ of each of the electrolyte was added to MB solution maintained at initial pH 3.0 and temperature of 25±2 °C. The suspension pH of each run was measured at the end of the experiment and it was found that the pH value changed in the order Na₂CO₃ (pH 10.5) > Na₂HPO₄ (pH 8.1) > NaCl (pH 5.75) > NaNO₃ (pH 5.3) > Na₂SO₄ (pH 5.03). Carbonate, phosphate and chloride ion inhibited the decolourization reaction of the dye, whereas the presence of nitrate and sulfate ion accelerated the rate of decolourization. Among all the anions, carbonate inhibited the decolourization process to the maximum extent. In contrast, presence of SO₄²⁻ ion leads to a remarkable increase in decolourization of methylene blue on manganese nodule surface. The inhibition by inorganic salts for the degradation of methylene blue at acidic pH is in the order: carbonate > phosphate > chloride > nitrate > sulfate.

A perfectly linear correlation was observed between inhibition effects of the electrolytes and final pH of the suspension. The inhibition by inorganic salts increases with increasing suspension pH of methylene blue solution. The highest inhibition exhibited by Na₂CO₃ is due to its alteration of suspension pH from acidic (pH 3.0) to basic (pH 10.5). Hence, alkaline medium is unfavorable for oxidative degradation of methylene blue. In contrast, Na₂SO₄ favors the decolourization of methylene blue by decreasing suspension pH to 5.03. Further, due to high mobility of sulfate ion, it can compress the electrical double layer between manganese nodules and water interface and make the catalyst surface available for dye molecules to approach each other more closely, leading to enhancement in rate of decolourization.

Consecutive use of catalyst

Decolourization of the methylene blue was studied in consecutive batch system. It is found that in the first cycle, 97% decolourization of dye was achieved within 10 min for 50 mg/L of methylene blue at initial suspension pH 3.0 and Mn nodule loading 0.6 g/L. In the second cycle, requisite amount of concentrated methylene blue solution was added and pH was maintained immediately with the help of concentrated acid solution. More than 85% of decolourization was achieved in the next 45 min, which is longer period than the first cycle. A considerable decrease in decolourisation (about 60%) was observed in the third cycle in 300 min. From the above observations it was concluded that in the consecutive use, the decolourization efficiency of Mn-nodule was decreased markedly. The inhibition in dye decolourization is,
probably due to the accumulation of Mn^{2+} on the surface of catalyst and the formation of some possible organic intermediates. Therefore, it is necessary to remove the oxidized product from the system to retain the efficiency of the catalytic material for satisfactory reuse towards decolourization of methylene blue.

**Effect of heat treatment**

The decolourization of methylene blue on manganese nodules samples activated at different temperatures is given in Fig. 7. The rates of disappearance of methylene blue followed the order: MN-110>MN-200>MN-400>MN-500>MN-900. The percentage of disappearance of dye decreased with increasing activation temperature, which is due to the absence of active component MnO_{2}, which is transformed to Mn_{3}O_{4} at higher activation temperature\(^{30}\). In other words, decolourization efficiency of activated manganese nodules can be correlated with Mn(IV) content which decreases slowly for samples MN-100 to MN-400 and then reduces dramatically beyond 500 °C, which is also indicated from O/Mn ratio (Table 2). The activated catalyst sample (MN-900) showed least catalytic activity in dye decolourization. This is probably due to the lowest O/Mn ratio, lowest surface area, minimum N_{2} pore volume, surface oxygen and lowest surface acidity. Parida et al.\(^{30}\) have reported that the catalytic activity of Mn nodule for H_{2}O_{2} decomposition and CO oxidation increases with increase in activation temperature from 110–400 °C and then decreases with further increase in activation temperature. Also, MN-900 exhibited least activity. This shows that the factors which are responsible for H_{2}O_{2} decomposition and CO oxidation may not contribute wholly towards dye decolourization activity. However, surface acidity and Mn(IV) content in the Mn nodule samples are contributing factors towards decolourization.

**Conclusions**

The present study shows that dye decolourization rate was significantly increased with increase in catalyst loading. The extent of decolourization was decreased with increase in pH but increased in the presence of NaCl. Anions like CO_{3}^{2-}, PO_{4}^{3-}, Cl\(^{-}\) inhibit decolourization, whereas SO_{4}^{2-} and NO_{3}^{-} accelerate the decolourization rate of MB to a remarkable extent. Consecutive reuse of manganese nodule sample for dye decolourization showed a marginal decreasing tendency in the catalytic activity. The rate of dye degradation dramatically reduced with increasing calcination temperature. Manganese nodules dried at 110 °C show high mineralization and are promising material for decolourization of methylene blue in the concentration range (10–50 mg/L).

**Acknowledgement**

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**References**