Oxidative decolourization of Rhodamine-B using sea nodule residue

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The characterization of sea nodule leached residue catalyst has been done by various physicochemical methods, such as XRD, FT-IR and surface area measurement. The oxidative decolourization of Rhodamine-B (Rh-B) by sea nodule residues is studied in batch technique. The extent of decolourization increases with increase in catalyst dose while decreases with the increase in initial pH of the solution and dye concentration. More than 93% of 5 mg/L Rh-B is decolourized within 1 h with a catalyst dose 0.5 gm/L at pH ~ 3.

Keywords: Decolourization, Rhodamine-B, Sea nodule residue

Experimental Procedure

Sea nodule residues (SNR), generated after reduction roast-ammoniacal leaching process was collected from Pilot plant operated at Hindustan Zinc Limited, Udaipur, India. The parent Indian Ocean manganese nodule (SN), which generates the residue after leaching process, was also collected for comparison of activity. The samples were air dried for several days, mixed thoroughly and kept in airtight bottles for characterization and further use. In order to remove loosely associated metal ions/anions, the leached residue was washed with distilled water. In a typical lot 50 g of the leached residue was dispersed in 500 mL distilled water (solid : liquid ratio = 1 : 10) and stirred for 2 h at room temperature. The content was filtered, washed with distilled water for further removal of sulphate and then air dried to get the washed sea nodule residue (WSNR). These samples were used for oxidative decolourization of Rhodamine-B.

Characterization of samples

Chemical analyses for major and minor constituents in different samples were done as
described earlier by conventional wet chemical methods and by atomic absorption spectrometer (Avanta, GBC), respectively. Particle size of SNR and WSNR was determined using Malvern SA-CP3 particle size analyzer. The XRD patterns of samples were recorded on a Siemen’s D 500 X-ray diffractometer using CuKα (λ = 1.5418) radiations. FTIR spectra of different samples in KBr pellets were recorded using a ThermoNicolet 870 FT-IR in absorption mode averaging 32 scans and at a resolution of 4cm⁻¹. Surface areas of the samples were determined by N₂/BET method using a Quantasorb (Quantachrome, Novawin). All pH measurements were carried out by a Toshniwal CL 54 pH meter using a combined glass electrode.

Chemicals
Stock solutions of Rhodamine-B were prepared in distilled water. Working solutions were prepared by suitable dilution of stock with distilled water.

Oxidative decolourization of Rhodamine-B
Decolourization of Rh-B was conducted in batches at constant temperature (25° ± 1.0°C) using a water bath. An accurately weighed quantity of residue was added to a 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 while the initial pH values were adjusted in the range 3 – 10. At specific time intervals, aliquots of 10 mL suspension were withdrawn and centrifuged to separate the catalyst particles and the concentration of residual dye was measured at 554 nm using UV/Visible spectrophotometer. Residual content of the dye was calculated using the following formula:

Residual content (n), % = (Ct/C₀) × 100

where Cₜ is the dye concentration at time t; and C₀, the initial concentration of the dye under study. The influence of pH of suspension, dye concentration and loading of the residue, on decolourization of Rh-B was studied.

Results and Discussion
Characterization of leached residue
Particle size analyses show that the leached residue contains very fine particles with mean particle diameter of 17.8 µm. The BET surface areas of SN, SNR and WSNR are found to be 130, 60.9 and 66.7 m²g⁻¹ respectively. Decrease in surface area of SNR is presumably due to the loss in porosity of SN and formation of manganese carbonate and silicate on roasting of SN with coal. Marginally higher surface area of WSNR is presumably due to the increased number of accessible pores on washing of adsorbed species from SNR. The average pore diameter, however, practically remains same (~ 40 Å) in all three samples.

The XRD of air-dried SN, SNR and WSNR are given in Fig. 1. It is seen that SN is mostly amorphous in nature with a few low intensity peaks corresponding mainly to quartz todorokite. After reduction roasting followed by leaching, the XRD peaks due to todorokite disappear because of its consumption in the formation of metal, especially Mn silicates. In addition, formation of MnCO₃ is also evident from the appearance of its characteristic peaks in SNR. On washing with distilled water, no change in the characteristic peak positions is observed from that of SNR. On calcinations the intensity of characteristic peaks of MnCO₃ decreases due to its decomposition and almost disappears at around 500°C.

FTIR spectra of air-dried SN, SNR and WSNR (untreated and heat treated) revealed that broad absorption band at ~3445 cm⁻¹ and moderately intense band at ~1650 cm⁻¹ are attributed to O-H stretching and bending modes of vibrations. On washing the SNR with distilled water, the position of majority bands remain same, except the disappearance of absorption band at 1072 cm⁻¹, presumably due to loss of small amount of loosely bound NH₃ or sulphate on washing. The sulphate is most likely generated from the impurities of coal during reduction roasting with sea nodules.

Oxidative decolourization of Rhodamine-B
Effect of dye concentration
The effect of initial Rhodamine-B concentration on decolourization by SNR has been studied (Fig. 2) taking nodule loading of 0.5 g/L at initial pH 3.0. The concentration of Rhodamine-B ranges from 5 to 30 mg/L. At the concentration (5 mg/L) the decolourization percentage reaches to 93% within 1 h. However, the percentage of decolourization decreases by increasing concentration of Rhodamine-B.

It is well established that oxidative degradation of organic matter by Mn-oxides occurs on the surface of the catalyst, not in the aqueous phase. The organic compounds are adsorbed on the surface to form the
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). Figure 2 shows that at a fixed loading of the sea nodule residues, decolourization decreases with increasing initial concentration. This indicates that reactive surface sites are saturated and do not provide active sites for further formation of precursor complex. Thus, percentage of decolourization decreases at higher Rhodamine-B concentration. The experimental findings suggest that surface reactivity and number of absorption sites are two crucial factors for oxidative decolourization of Rhodamine-B.

Catalyst loading

The effect of catalyst loading on decolourization of Rhodamine-B by SNR is also studied (Fig. 3) taking Rhodamine-B concentration 10 mg/L at initial pH 3.0. The catalyst loading varies from 0.2g/L to 1.0 g/L. At the catalyst loading of 0.2g/L the decolourization percentage is less. However, by increasing catalyst loading the decolourization percentage increases and
The decolourization of Rhodamine-B at various pH (3.0-10.0) as a function of reaction time is shown in Fig. 4. The decolourization rate of dye compound decreases with increasing pH. At pH 3, 65% of decolourization takes place within 1 h whereas this value decreases slightly for higher pH. This decrease in activity with increase in pH may be described as follows.

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. The surface charge of sea nodule residue plays a vital role in the formation of surface complex. The zero point charge (pH\text{pzc}) of washed sea nodule residue (WSNR) is determined to be 6.5. At lower pH than the pH\text{pzc} (6.5) the surface of the residue is positively charged due to protonation, which does not favour cationic dye (Rhodamine-B as model dye) adsorption and hinders the formation of surface precursor complex due to electrostatic repulsion. On the other hand, at higher suspension pH (>6.5) the surface is negatively charged due to deprotonation, favors surface complex formation. Though lower pH inhibits the surface complex formation, it improves reduction potential of Mn (hydro) oxide/Mn$^{2+}$ couple. In contrast, the increase in suspension pH decreases oxidizing power of Mn (hydro) oxides and favors the adsorption of Mn (II) on the SNR surfaces, resulting in decreasing surface sorption sites. Hence, further adsorption and oxidation of dye compound on the catalyst particle are greatly inhibited. Present study indicates that lower pH of the suspension suppressed Rhodamine-B adsorption on the SNR but increases reduction potential of Mn (hydro) oxide/Mn$^{2+}$ couple and enhances decolourization of Rhodamine-B.

**Conclusion**

Sea nodule residue exhibit good catalytic activity for oxidative decolourization of Rhodamine-B. The decolourization activity decreases with the increase in pH and initial Rh-B concentration, however the decolourization percentage of Rh-B increases with increase in the catalyst dose. More than 93% decolourisation of Rh-B with initial concentration 5 mg/L is achieved within 1 h at pH 3.0 and catalyst dose 0.5 g/L.

**References**