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Oxidative decolourisation of Congo red using water washed sea nodule leached reside

S. Padhi[1], Rita Das[2] and N. Das[1]*

[1]P. G. Department of Chemistry, Utkal University, Bhubaneswar 751 004, Odisha
[2]Department of Chemistry, R.D. Women's University, Bhubaneswar 751 022, Odisha
Corresponding Author : e-mail: dasnn64@rediffmail.com

Abstract

The catalytic efficiency of leached Sea nodule residue, generated from reduction-roasting ammoniacal leaching process, for oxidative degradation of Congo red under varying experimental was studied. The extent of decolourisation was decreased with increase of pH but increased in presence of H_2O_2. CR decolourisation occurred in two consecutive steps with first step was faster than the later. Formation of a surface precursor complex between WSNR and CR at a rate limiting step followed by electron transfer from CR to active metal centre of WSNR and release of product(s) was proposed for the decolourisation process.

Keywords: Sea nodule, Leached residue, Organic dyes, Oxidative decolourisation, Congo red

Introduction

Synthetic dyes are widely used as one of the colouring agents in the textiles, paper, plastics, leather, food and cosmetic industries. Due to their extensive use and substantial loss (*ca.* 10-15 %) during the manufacturing and dying processes, the effluents containing dyes are highly coloured and are considered as potential source of water pollution [1,2]. These effluents produce adverse effects on the environment due to their non-biodegradability, toxicity, potential carcinogenic and mutagenic nature. Out of more than 10,000 various types of dyes are available in the world, azo dyes (–N=N–) constitute about 20–40% of the total dyes used for colouring [1,2].

Several methods like chemical coagulation/flocculation, chemical and photocatalytic degradation, adsorption and biological degradation are now available to remove the excess dyes from the wastewaters. Due to high solubility of dyes in water each of the above method has its own advantages and disadvantages. Among them, the adsorption and chemical coagulation are two common techniques used most widely for treatment of these wastewaters although they generate secondary wastes which require further

treatment proper or disposal. In recent years extensive research has been dedicated to develop alternative processes for complete degradation of dyes in to environmentally compatible products using suitable catalytic/photocatalytic systems [3-5]. A number of manganese based synthetic/naturally occurring materials have also been used for oxidative/photocatalytic degradation of a variety of dyes [6-8].

Although manganese nodules or manganese oxides have been extensively used for studying their adsorptive properties and catalytic activities for adsorptive removal of various cationic anionic pollutants and degradation of organic substrates [9-12], the use of leached residue is scanty [13-15]. After the selective extraction of strategic metals like Cu, Co and Ni along with some Mn and Fe of manganese nodules about 70% residue is left behind as wastes for disposal. Due to increasingly stringent disposal rules it has become imperative to develop methods for proper utilization of such a huge quantity of leached residues. These leached residues containing oxides/oxyhydroxides of Fe, Mn, Al and Si showed reasonable high porosity and surface area which is favourable for adsorption of different cationic and anionic species [13-15]. Moreover, Fe and Mn in these residues are present in variable oxidation states. In view of above characteristics, one can envisage the use of leached residues as an effective oxidation catalyst for a variety of organic contaminants [16]. The present study aims to assess the catalytic activity of leached residue taking Congo red as a model dye.

Materials and Methods

The collection of leached sea nodule residue (SNR), its washing with water to generate water washed sea nodule residue (WSNR) and their characterizations have been reported earlier [16]. Congo red (BDH) and H_2O_2 (Merck) were used in the catalytic experiments. All other chemicals used were of AR grade.

The oxidative decolourisation of CR was carried by batch technique following the decolourisation at 25±0.5°C under static air and starring conditions. Based on some preliminary experiments, the different parameters affecting the decolourisation were varied. Weighed amounts of catalyst (0.6-3.0 g/L) were added into the reaction flasks containing 100-500 mL of dye solution at varying concentrations (10-100 mg/L) and pHs (previously adjusted at desired pH in between 3-10 using 0.1 M HCl or NaOH) to initiate the reaction. The pH of the reacting solutions was not maintained during the course of reaction by addition inorganic or organic buffer in order to avoid any interference from the added buffer. At pre-determined intervals 10 mL aliquots were withdrawn, centrifuged and measured the absorbance by a UV–Vis spectrophotometer (Systronics 2201) at 660 nm ($ë_{max}$) to determine the residual CR concentration.

The kinetics of oxidative decolourisation were determined from separately run experimental data using WSNR (0.8 g/L) with an initial CR concentration of 30 mg/L and pH ~ 3.0. The rate constants were calculated from the plots of $\ln(C_t/C_0)$ versus time where C_0 and C_t represent the initial CR concentration and concentration at time 't', respectively.

Results and discussion

Characterizations of Leached residue

The chemical analyses shows that WSNR mainly contains Mn, Fe, Si and Al. Mn(IV) remains one of the major constituents (~45%) of total manganese present in WSNR. The BET surface areas of WSNR is found 66.7 m^2/g which is less than the parent sea nodule (130 m^2/g) due to loss of porosity. The pH_{pzc} of WSNR is found to be 6.5. The XRD of WSNR mainly shows the characteristic peaks of manganese carbonate and silicates.

Decolourisation of Congo red

General observations

The time course UV-visible spectra of Congo red (29.9 mg/L) in presence of WSNR (0.4 g/L) and H_2O_2 (0.02 M) is shown in Fig 1. It is seen that although the absorbance is progressively decreased with time; the decrease is fast at the beginning and then shows a slow decrease. At lower concentration, the absorbance of residual Congo red is very small indicating complete decolourisation by WSNR (0.4 g/L). The intensities of all the peaks are reduced with a shift towards lower wavelength for peaks at 350 and 500 nm. On the other hand, the intensity of peak at ~245 nm is reduced progressively without any shift in the position. The disappearance of peaks with time without any appearance of new peaks indicates that there is no formation of other products during the reaction and the Congo red is completely mineralized at the end of reaction.

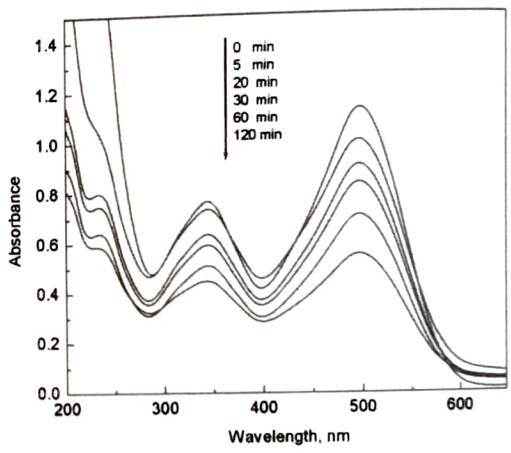
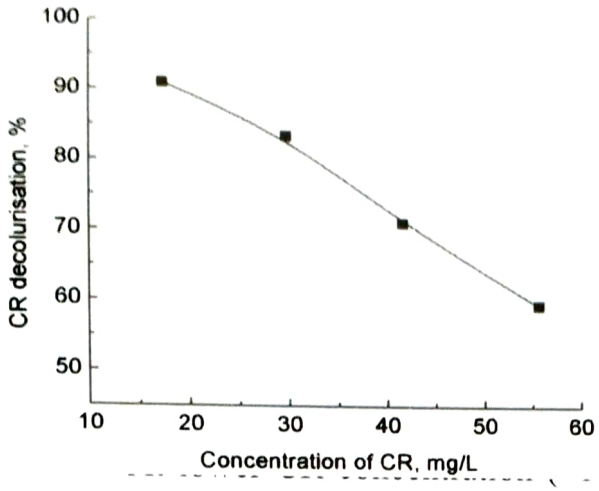


Fig. 1: Repetitive UV-visible spectra of Congo red with time (CR = 30 mg/L, pH ~ 8.4, WSNR = 0.4 g/L)

Effect of initial Congo red concentration

The effect of initial CR concentrations (10 mg/L to 100 mg/L) on decolourisation by WSNR (0.5 g/L) at initial pH 5.0 is shown in Fig. 2.



mg/L) the decolourisation percentage reached 93% within 30 min and the colour is almost completely disappeared within 180 min. However at higher CR concentration (56 mg/L) the decolourisation percentage is reached to ~ 59.1 % in 180 min. It is well established that oxidative degradation of organic matter by Mn-oxides occurs on the surface of the catalyst. The organic compounds are adsorbed on the surface of Mn oxides to form surface precursor complex, electron transfer takes place within the surface complex from organic compound to the surface bound $Mn^{III/IV}$, followed by release of oxidation products and soluble Mn^{II}.

Fig. 2 shows that at a fixed loading of the nodules, CR decolourisation decreases with increasing initial CR concentration, indicating reactive surface sites are saturated or blocked with CR at first round, and do not provide active site further for formation of precursor complex and thus percentage of decolourisation is decreased at higher CR concentration. These experimental findings suggest that surface reactivity and number of absorption sites are two crucial factors for oxidative decolourisation of CR.

Effect of WSNR loading

The effect of amount of WSNR on decolourisation of Congo red is shown in Fig. 3. It is seen that with increase of catalyst amount, the percentage of decolourisation increases. However, complete decolourisation is not achieved even at the highest amount of catalyst (1.6 g/L) when the concentration of Congo red is 30 mg/L.

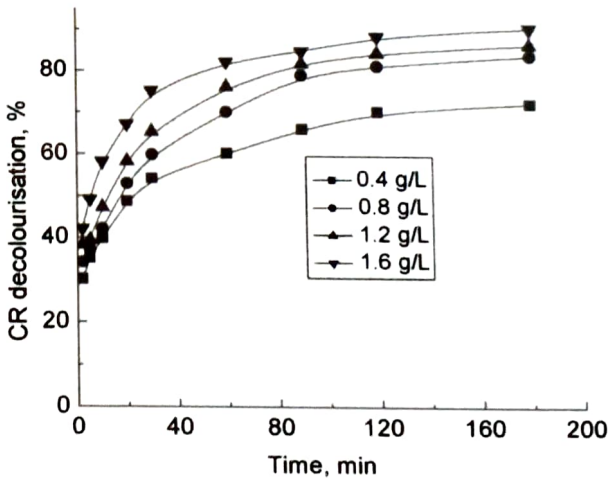


Fig. 3: Effect of amount of WSNR on decolourisation of Congo red

Effect of initial pH of CR solution on decolourisation

The decolourisation efficiency of WSNR at various pH with or without H_2O_2 presence is shown in Fig. 4.

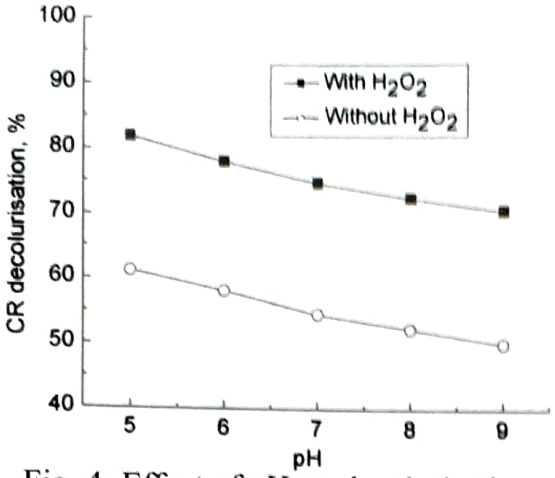


Fig. 4: Effect of pH on decolurisation of Congo red

As seen in the figure, the decolourisation efficiency decreases with increase of pH both in absence and presence of H_2O_2. For example, in the presence of H_2O_2, the percentage of decolourisation decreases from 81.9% to 70.1% with increase of pH from 5 to 9. A similar trend is also observed in the case of without H_2O_2. The oxidation of organic dyes on WSNR 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 WSNR plays vital role in the formation of surface complex. The pH at zero point charge (pH_{zpc}) of WSNR is 6.5. At pH lower than the pH_{pzc} (6.5) the surface of the leached residue is positively charged due to protonation, which favours the adsorption of anionic dye (CR) and in turn facilitates the formation of surface precursor complex due to electrostatic attraction. On the other hand at higher suspension pH (> 6.5), the surface is negatively charged due to deprotonation and hinders surface complex formation. Due to favourable surface complex formation and improve reduction potential of Mn(hydr)oxide/Mn^{2+} couple, decolourisation activity is jigher at lower pH. In contrast, the increase of solution pH would decrease oxidizing power of Mn (hydr)oxides and favours the adsorption of Mn(II) on the particles, there by resulting in decreasing surface sorption sites. Hence, further adsorption and oxidation of dye compound on the catalyst particle are greatly inhibited.

4.2.5 Effect of H_2O_2 concentration on decolourisation

Hydrogen peroxide alone or conjunction is used for oxidation and degradation/ decolourisation of many harmful organic compounds including dyes. Addition of small amount catalyst to a system containing H_2O_2 may lead to generation of free radicals like OH with reasonably high reduction potential (2.3 eV) that facilitates faster degradation. Also the presence of manganese based mineral/ materials significantly enhances the decomposition of H_2O_2 [16]. As such it is believed that WSNR in presence of H_2O_2 may further accelerate the oxidative decolourisation of CR.

The effect of H_2O_2 concentration on decolourisation of Congo red is shown

in Fig. 5. As evident from the figure, the percentage of CR decolourisation increases with addition of H_2O_2 up to 0.02M and thereafter decreases on further increase of H_2O_2 concentration.

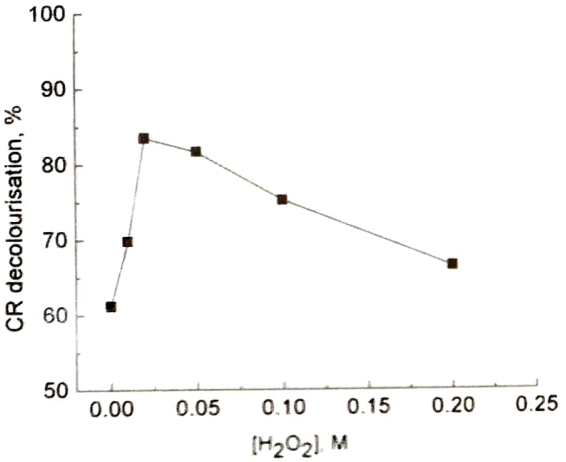


Fig. 5: Effect of H_2O_2 concentration on decolurisation of Congo red

The enhance activity in presence of H_2O_2 is primarily due to the formation of free radical species (e.g. HO, HOO or O_2^{-}) during the process which leads to faster oxidative decolourisation of CR. The marginal effect of $[H_2O_2]$ beyond 0.02M is presumably due to well known free radical scavenging effect via the reaction of free radicals with excess H_2O_2.

Kinetics of Congo red decolourisation

From the plots of percentage of CR decolourisation versus time (Fig. 3), it is very much clear that the decolourisation is fast at the beginning followed by a slow step decolourisation process. In other words, the decolourisation of CR takes place in a two step process. In the typical run with initial CR concentration of 30 mg/L, pH ~ 3.0 and WSNR (0.8/L), the derived rate constants for first and second stage decolourisation are found to be 1.8×10^{-2} and 0.81×10^{-3} min^{-1}. In fact several other studies also reported a two step process for dye degradation using Mn based oxides as catalyst [16,17].

Conclusions

Leached residue generated from manganese nodule after extraction of metal values through reduction-roasting ammoniacal leaching process contains mainly the oxides of Mn, Fe, Si and Al along with $MnCO_3$. Water washed sea nodules residue (WSNR) is found effective towards decolourisation of Congo red (CR). The extent of decolourisation is dependent on several factors and found to decrease with increase of pH values and initial CR concentration. The activity of WSNR is enhanced in presence of H_2O_2 at lower concentrations. The formation of a surface complex between WSNR and CR at a rate limiting step followed by electron transfer from CR to active metal centre of WSNR and release of products is most likely operative during the decolourisation process.

References

[1]. Beydilli, M.I., Pavlostathis, S.G. and Tincher, W.C. (2010). Biological decolorization of the azo dye reactive red 2 under various oxidation-reduction conditions. ***Water Environmental Research,*** 72: 698–705.

[2]. Zollinger, H. (1991). Color Chemistry, 2nd Edn. VCH Publishers, NY.

[3]. Daneshvar, N., Salari, D. and Khataee, A.R. (2004). Photocatalytic degradation of azo dye acid red 14 in wateron ZnO as an alternative catalyst to TiO_2. ***Journal of Photochemical and Photobiology A,*** 162: 317-322.

[4]. Du, W., Xu, Y. and Wang, Y. (2008). Photoinduced Degradation of Orange II on Different Iron (Hydr)oxides in Aqueous Suspension: Rate Enhancement on Addition of Hydrogen Peroxide, Silver Nitrate, and Sodium Fluoride. ***Langmuir,*** 24: 175-181.

[5]. Giri, S.K. and Das, N. N. (2013). Iron oxide/titania photocatalyst derived from $TiO_2.nH_2O$ coated ferric hydr(oxide) precursors: Characterisations and visible light activity. ***Powder Technology,*** 239: 193-198.

[6]. Chen, J.Q., Wang, D., Zhu, M.X. and Gao, C.J. (2006). Study on degradation of methyl orange using pelagite as photocatalyst. ***Journal of Hazardous Materials,*** 138: 182-186.

[7]. Ge, J. and Qu, J. (2003). Degradation of azo dye acid red B on manganese dioxide in the absence and presence of ultrasonic irradiation. ***Journal of Hazardous Materials,*** 100 (2003), pp. 197-207.

[8]. Gemeay, R.G., El-Sharkawy, I.A., Mansour, I.A. and Zaki, A.B. (2008). Catalytic activity of polyaniline/MnO_2 composites towards the oxidative decolorization of organic dyes. ***Applied Catalysis B,*** 80: 106-115.

[9]. Maity, S., Chakravarty, S., Bhattacharjee, S. and Roy, B.C. (2005). A study on arsenic adsorption on polymetallic sea nodule in aqueous medium. ***Water Research,*** 37: 3954.

[10].Parida, K.M., Satapathy, P.K. and Das, N.N. (1995). Studies on Indian Ocean Manganese Nodules. I. Physico-chemical characteristics and catalytic activity of ferromanganese nodules. ***Journal of Colloid Interface Science,*** 173: 112.

[11]. Gemeay, A.H., El-Sharkawy, R.G., Mansour, I.A. and Zaki, A.B. (2008). Catalytic activity of polyaniline/MnO_2 composites towards the oxidative decolorization of organic dyes. ***Applied Catalysis B,*** 80: 106-115.

[12].Zhang, W., Yang, Z., Wang, X., Zhang, Y., Wen, X. and Yang, S. (2006). Large-scale synthesis of â-MnO_2 nanorods and their rapid and efficient catalytic oxidation of methylene blue dye. **Catalysis Communication,** 7: 408-412.

[13].Agrawal, A., Sahu, K.K. and Pandey, B.D. (2006). Kinetic and isotherm studies of cadmium adsorption on manganese nodule residue. ***Journal of Hazardous Materials,*** B137: 915-924.

[14]. Das, N.N. and Jana, R.K. (2006). Adsorption of some bivalent heavy metal ions from aqueous solutions by manganese nodule leached residues. ***Journal of Colloid Interface Science,*** 293: 253-262.

[15]. Behera, R.K., Satapathy, P.K., Randhawa, N. S. and Das, N.N. (2010). Adsorptive removal of Phosphate using leached sea nodule residue generated by reduction-roasting ammoniacal leaching process. ***Adsorption Science Technology,*** 28: 611-627.

[16]. Satapathy, P.K., Randhawa, N.S. and Das, N.N. (2012). Oxidative decolourisation of methylene blue by leached sea nodule residues generated by reduction-roasting ammoniacal leaching process. ***Environmental Technology,*** 33: 515-522.

[17]. Zhu, M.X., Wang, W. and Zhou, L.Y. (2008). Oxidative decolourisation of methylene blue using pelagite. ***Journal of Hazardous Materials,*** 150: 37- 45.