Novel Resin Bound MnO$_2$ Nanocomposite for the Degradation of Crystal Violet Dye in Aqueous Medium

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Introduction

In the recent past various technologies have been developed for the removal of organic pollutants from water environment using advanced oxidation processes (AOPs). It has proved its efficiency in complete mineralization of a large number of hazardous and organic pollutants. Crystal violet (CV) is a well-known triphenyl methane dye (also known as Basic Violet 3), extensively used in textile dying and paper printing industries. Even in low concentration this dye affects aquatic life and the food web, and acts as a mutagen and a mitotic poison. Nanoparticles in recent days have shown their efficiency as catalyst due to their high surface energy, and thus have successful applications in many homogeneous and heterogeneous catalysis reactions. The large surface-to-volume ratios and special binding sites of the fine particles create the driving force in developing newer methodologies for industrial applications. Here we demonstrate the application of Resin-bound MnO$_2$ nanoparticles for CV dye degradation in aqueous media.

Experimental

Preparation of resin-bound MnO$_2$-nanocatalyst
The MnO$_2$-resin was prepared[1] using anion-exchange resin having cross-linked polystyrene containing quaternary ammonium groups as the integral part and chloride as the anion part with ion-exchange capacity 3.5mmol g^{-1}. In the primary stage, Cl$^-$ ions of the anion-exchange resin (represented as [R$^+$Cl$^-$]), was exchanged with MnO$_4^-$ ions. This results in the formation of resin-bound permanganate moiety [R$^+$MnO$_4^-$]. After that, the resin-bound permanganate moiety [R$^+$MnO$_4^-$] was washed several times with distilled water. The resin-bound permanganate moiety [R$^+$MnO$_4^-$] was photo irradiated using a tungsten lamp in dilute NaOH solution. This led to the formation of resin bound MnO$_2$ nanoparticles, which was used as a catalyst for CV degradation. TEM images showed that the particles had rod shape. The particles were characterized from XRD, SEM, FTIR studies, and found to be α- MnO$_2$.

Degradation of CV using MnO$_2$-nanocatalyst in water medium
The degradation of CV was carried out in aqueous media in presence of air and under stirring conditions. The degradation was monitored spectrophotometrically at λ_{max} = 590 nm.

Results and Discussion

Degradation of CV in aqueous solution was investigated in presence of resin bound MnO$_2$ nano-catalyst (designated as MnO$_2$-resin) under aerobic condition. The time dependent absorption spectra of CV were shown in Fig. 1. The degradation of dye with and without stirring was also compared. The kinetic studies with varying CV initial concentrations 2 ppm, 5 ppm, 10 ppm, and 20 ppm using MnO$_2$-resin (at a dose of 5g/l) showed that the degradation was

92%, 83%, 63%, 54%, respectively at 120 min of reaction (Fig. 2). The effect of catalyst dose and temperature was also evaluated. The degradation of CV followed the first-order kinetics both under stirred and unstirred condition.
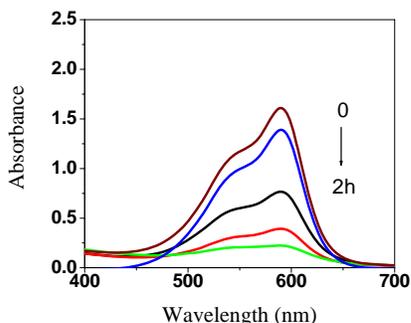

Fig. 1 Time dependent absorption spectra of CV (at 30 min interval) while degrading in presence MnO_2-resin under aerobic condition. [CV]: 5 ppm; [MnO_2-resin]: 5g/l.
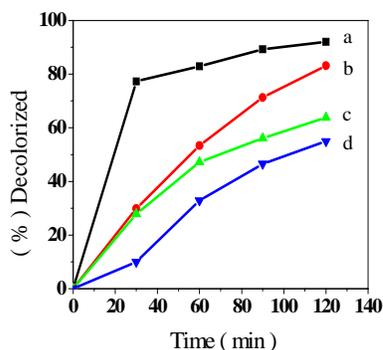

Fig. 2 Kinetic plot for the degradation of CV by MnO_2-resin at varying initial CV concentrations. [CV]: (a) 2 ppm, (b) 5 ppm, (c) 10 ppm, and (d) 20 ppm.

Effects of different parameters like pH, presence of different ions were studied. The degradation process was influenced by pH of the medium (Fig. 3). Among different ions tested (Cl^-, NO_3^-, SO_4^{-2}, $H_2PO_4^-$, Fe^{+2}, Ca^{+2}) $H_2PO_4^-$ and Ca^{+2} showed maximum interference on CV degradation.

The column study was conducted with MnO_2-resin as the catalyst to find out its suitability for continuous mode of operation. The column with 0.9-cm diameter and having bed depths of 8 cm could treat 11.25 liter of CV bearing water (concentration 20 ppm). The breakthrough occurred at 15h. The adsorption bed was exhausted within 48h. The corresponding volumes of wastewater treated at breakthrough point (corresponding to $C/C_o=0.1$) was 2.34 liter and at exhaust point (corresponding to $C/C_o=0.92$) 10 liter.
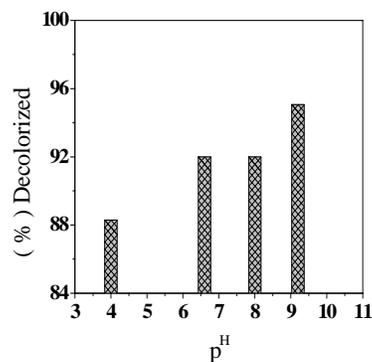

Fig. 3 Effect of initial pH on the degradation of CV.

Conclusion

The resin bound MnO_2 nanocatalyst has been used as an effective catalyst for CV dye degradation in aqueous medium under aerobic condition. The degradation depends on various operating parameters, like the adsorbent dose, the contact time, the initial dye concentration, the stirring condition, presence of interfering ions and the pH of the medium. Among all interfering ions tested, phosphate and calcium ion showed maximum interference. It was noticed that oxygen is a prerequisite for CV degradation. At lower pH the degradation efficiency is slightly less. Thus pH control may be necessary to improve the percentage of degradation. Column operation showed that the catalyst might be useful for degrading CV bearing wastewater in continuous mode.

References
1. Jana, S.; Praharaj, S.; Panigrahi, S.; Basu, S.; Pande, S.; Chang, C.; Pal, T. *Org. Lett.* **2007**, *9*, 2191-2193.