Degradation of rhodamine B with manganese dioxide nanorods
V. Sabna, Santosh G. Thampi and S. Chandrakaran

ABSTRACT
This is an investigation on oxidative degradation of rhodamine B (RhB) by manganese dioxide (MnO₂) nanorods synthesized by redox co-precipitation method. Field emission scanning electron microscopy of MnO₂ nanorods at an electron voltage of 10 kV revealed a rod-like morphology for the synthesized nanoparticles. Fourier transform infrared spectra exhibited characteristic peaks of MnO₂. Surface area of MnO₂ nanorods was 277 m²/g. Effect of various parameters like initial concentration and pH of RhB solution, time of contact between MnO₂ nanorods and RhB, dosage of MnO₂, and stirring speed on decolouration of RhB was evaluated in batch experiments. Rapid decolouration in the initial period of the reaction was observed due to the adsorption of RhB molecules onto the surface of MnO₂ nanorods followed by oxidative degradation. Percentage decolouration decreased with increase in initial concentration and increased with increase in dosage, speed of stirring the mixture and with increase in pH up to pH 7. Near complete decolouration was achieved at a dose of 0.5 g/L of MnO₂ nanorods from 20 mg/L RhB solution within 3 min. Observations fitted best to the pseudo second order kinetic model. This study could pave the way for development of cost-effective, nontoxic nanostructures for treatment of wastewaters containing RhB.

Key words | decolouration, manganese dioxide nanorods, rhodamine B

INTRODUCTION
Our Earth has been under the threat of contamination ever since the industrial revolution and with advancement in technologies and materials, the threat has assumed alarming proportions. At the start of industrial development, the nature of contaminants being discharged was such that the problem remained within the assimilative capacity of nature. However, as the contaminants being discharged became more complex, things started moving out of the natural assimilative capacity of the ecosystem. One of the industries that release toxic pollutants into the environment is the textile industry; it ranks top in the list of heavily polluting industries. The effluents from these industries contain a large amount of dye which is unused in the dyeing process (Mohan et al. 2007). Water contamination with textile dyes has several adverse effects. It reduces penetration of light through water. Dyes may be persistent in nature, mutagenic, carcinogenic, micro-toxic and may cause severe damage such as dysfunction of the kidneys, reproductive system, liver, brain and the central nervous system (Kadirvelu 2005; Dinçer et al. 2007). Rhodamine B is a cationic dye, having commercial and industrial applications. It causes skin irritation, sarcoma, digestive tract irritation, neurotoxicity and reproductive toxicity. Therefore, it is essential to remove rhodamine B from the wastewater generated by industries that use
rhodamine B before discharging it to any water body. Several methods are available for the removal of dyes from effluents, such as coagulation, chemical oxidation, photocatalysis, irradiation, electrochemical destruction, ozonation, microbial degradation, membrane separation and ion exchange (Mahir et al. 2014). However, these processes are limited by sludge generation, high usage of energy, generation of dissolved oxygen, longer retention time, release of aromatic compounds, formation of by-products, high operational costs and operational difficulties (Mahir et al. 2014). Nanomaterials have been found to have wide applications as catalysts (Pradhan et al. 2013; Grunes et al. 2013; Astruc et al. 2013) for the degradation of different types of pollutants in water and wastewater. Particles in the nanometer size range have very large surface area, thereby offering many binding sites to the reacting species. Manganese dioxide, a transitional metal oxide in different shapes such as nanosheets (Saha & Pal 2014), α-MnO₂, β-MnO₂ and γ-MnO₂ (Cui et al. 2015), in combination with activated carbon (Asfaram et al. 2015), multiwalled carbon nanotubes (Sabna et al. 2016), graphene oxide (Liu et al. 2010), etc. can be used for the treatment of wastewater containing different types of pollutants. Oxidative degradation process takes place at the surface of MnO₂ after adsorption of the pollutant molecules (Stone & Morgan 1984; Li et al. 2008). The decolouration of methylene blue (Zhu et al. 2010) and malachite green (Saha & Pal 2014), oxidation of N-oxides (Zhang & Huang 2005) and polybrominated diphenyl ethers (Ahn et al. 2006), and formation of heavy metals (viz., As(III) and Cr(III)) (Fendorf & Zasoski 1992; Feng et al. 2006; Apte et al. 2006) to their higher oxidation states have also been studied by different types of MnO₂ nanomaterials. Some nanostructured MnO₂ materials have also been applied for Fenton-like catalytic degradation of rhodamine B, congo red, ethylene blue and methylene blue (Sui et al. 2009; Cao et al. 2010).

In this study, MnO₂ nanorods synthesized by redox co-precipitation method have been used for the oxidative degradation of rhodamine B. The effect of operating parameters such as the time of contact between the MnO₂ nanorods and the dye molecules, initial concentration of the dye in the aqueous solutions, pH of the aqueous solutions containing the dyes, dosage of MnO₂ nanorods, and speed of stirring the mixture of the dye and the MnO₂ nanorods was evaluated. Kinetic analysis of the oxidative degradation of these dyes using MnO₂ nanorods was performed by first order, second order, pseudo first order and pseudo second order kinetic models, and the results are reported in this paper.

MATERIALS AND METHODS

Materials

Manganese sulphate monohydrate (MnSO₄·H₂O), potassium permanganate (KMnO₄) and hydrogen peroxide (H₂O₂) procured from Merck were used for the synthesis of manganese dioxide (MnO₂) nanorods. Potassium nitrate (KNO₃), hydrochloric acid (HCl) and sodium hydroxide (NaOH) used for the determination of pHₚ₇₃C were also purchased from Merck. The dye, rhodamine B (C₂₈H₃₁ClN₂O₃, λₘₐₓ = 550 nm), was purchased from Sisco Research Laboratories Pvt. Ltd. Distilled water was used for the synthesis of MnO₂ nanorods and to prepare rhodamine B solutions of different concentrations.

Synthesis of MnO₂ nanorods

Manganese dioxide (MnO₂) nanorods were prepared by scaling down the redox co-precipitation method described in the literature (Parida et al. 1988; Gohari et al. 2014) and drying under ambient temperature. MnSO₄ solution was prepared by dissolving 30 g of MnSO₄·H₂O in 250 mL distilled water. To this, KMnO₄ solution of pH 12.5 prepared by dissolving 20 g of KMnO₄ in 250 mL distilled water was added drop by drop under vigorous stirring. The dark brown mixture, formed as the addition of KMnO₄ was completed, was kept undisturbed overnight under ambient conditions in open air. The brown precipitate thus obtained was washed thoroughly until a clear supernatant with neutral pH was obtained. The mass was separated through centrifugation and dried in ambient air instead of drying in an oven at a higher temperature as in Parida’s method (Parida et al. 1988).
Characterization of MnO₂ nanorods

Field emission scanning electron microscope (FESEM-HITACHI SU 6600, Dublin) with variable pressure field emission was used for the analysis of surface features of the MnO₂ nanorods. The sample of synthesized MnO₂ was sputter coated with gold for 40 s for inducing electrical conductivity with a sputtering unit. An electron voltage of 10 kV was applied during FESEM imaging of MnO₂ nanorods and 5 kV for commercial MnO₂. It is an important parameter for a material which acts as a catalyst or adsorbent; it is also important if the process involved in the removal of dye molecules is a function of surface area. The pHₚₑₗₚₑₗ of MnO₂ nanorods was determined following the literature (Oliveira et al. 2014). 0.005 g MnO₂ nanorods were taken into five 50 mL Erlenmeyer flasks, each containing 10 mL of 0.03 M KNO₃ solution used as an electrolyte. The pH of the mixture of 0.03 M KNO₃ solutions and MnO₂ nanorods was adjusted to a range varying from 2.5 to 11.5 using dilute aqueous HCl and NaOH solutions (pH_initial). All the flasks were then shaken in an orbital shaker for 24 h at 250 rpm and then kept undisturbed for 1 h, after which the final pH of all the solutions was measured. A graph was plotted between pH_initial (on X axis) and pH_final (on Y axis) of the 0.03 M KNO₃ solutions and MnO₂ nanorods in 0.03 M KNO₃ solution. pHₚₑₗₚₑₗ of the material is the value of pH corresponding to the point of intersection of the curves of pH_initial and pH_final of the 0.03 M KNO₃ solutions and initial (pH_initial) and final pH (pH_final) of the mixture of MnO₂ nanorods in 0.03 M KNO₃ solution. Brunauer–Emmett–Teller (BET) surface area (m²/g), pore volume (cm³/g) and pore size (nm) were determined using 3000MMD/BSMR/0101-BET (Tristar USA). Chemical bonds in the MnO₂ nanorods were identified from the Fourier transform infrared (FTIR) spectra of MnO₂ nanorods obtained from the FTIR spectrophotometer (FT/IR-4100 A, JASCO, Germany).

Batch oxidation experiments

All the oxidative degradation experiments in batch mode were performed with 10 mL (working volume) of rhodamine B solution. A range of initial concentration of rhodamine B from 20 to 85 mg/L was fixed for evaluating the influence of time of contact between the nanorods and dye molecules on percentage decolouration. The concentration of the dye in the solution was measured after specific time intervals until equilibrium was reached during the degradation process using UV/VIS spectrophotometer (Lambda 35, Perkin Elmer) at a wavelength of 550 nm. The effect of dosage of MnO₂ nanorods on the degradation of rhodamine B was studied at dosages ranging from 0.5 to 2.0 g/L. Further, the effect of pH of the rhodamine B solution was evaluated under different pH values ranging from 3 to 8. Percentage degradation of the dye as percentage decolouration (%R) and the amount of dye degraded per unit quantity of the nanorods qₑ (mg/g) at equilibrium were obtained using Equations (1) and (2), respectively.

\[
\% R = \frac{C_i - C_t}{C_i} \times 100 \tag{1}
\]

\[
q_e \text{ (mg/g)} = \frac{C_i - C_e}{m} v \tag{2}
\]

where \( C_i \) (mg/L), \( C_t \) (mg/L) and \( C_e \) (mg/L) are the initial concentration of the dye, concentration of the dye at time \( t \) and the concentration at equilibrium, respectively, \( m \) (g) is the mass of MnO₂ nanorods and \( v (L) \) is the volume of the rhodamine B solution. Oxidative degradation of textile wastewaters may be affected by the presence of low molecular weight organic acids such as oxalic acids, citric acid, maleic acid, etc. These constituents compete for adsorption sites on the surface of the nanorods. The effect of low molecular weight acids was evaluated with oxalic acid and citric acid at two concentrations, 250 mg/L and 500 mg/L. Reusability of MnO₂ nanorods was investigated to determine how long (in terms of cycles of use) these nanorods can be used without reduction in their performance with respect to degradation of rhodamine B. Each cycle consisted of a reaction with 10 mL of 5 mg/L rhodamine B solution with 0.5 g/L of the nanorods for 1 min. The same MnO₂ nanorods were used in all cycles, after washing at the end of each cycle. The amount of dye degraded by the MnO₂ nanorods was compared with that by commercial MnO₂.

The rate of oxidative degradation of rhodamine B with MnO₂ nanorods was analysed using various kinetic models such as first order, second order, pseudo first order and
pseudo second order kinetic models. The linear equations of these models, presented in Table 1, were used, and different parameters of these models were determined.

The terms \( C_0 \) and \( C_t \) in the equations are concentrations of CV at time, \( t = 0 \) and \( t = t \), respectively. \( q_t \) (mg/g) and \( q_e \) (mg/g) are amount of the dye at time \( t \) and at equilibrium, respectively, and \( k_1 \) (min \(^{-1}\)) and \( k_2 \) (g/mg·min) are the rate constants in the respective kinetic model equations. Linear equations of each of the models were plotted and the parameters of the models were determined. Non-linear equations of the models were used for determining the quantity of dye degraded per unit quantity of the MnO\(_2\) nanorods by each of the models.

**RESULTS AND DISCUSSION**

**Surface area analysis**

Nitrogen adsorption–desorption isotherms on MnO\(_2\) nanorods and commercial MnO\(_2\) are presented in Figure 1(a) and 1(b), respectively. Surface area of the MnO\(_2\) nanorods and commercial MnO\(_2\) analysed using a BET surface area analyser shows that the prepared MnO\(_2\) nanorods had very much higher surface area than the commercial MnO\(_2\). This is evident from the degradation activity of the MnO\(_2\) nanorods also. Results of the surface area analysis are presented in Table 2.

**SEM analysis**

FESEM micrographs of the synthesized MnO\(_2\) nanorods and commercial MnO\(_2\) are presented in Figure 2(a) and 2(b), respectively. The morphology of synthesized MnO\(_2\) was similar to rod-like structures with a thickness of 20 nm and length more than 750 nm. However, the commercial MnO\(_2\) consisted of particles of different sizes and structure, as seen in Figure 2(b). Since synthesized MnO\(_2\) was found to have structures with a high aspect ratio, it has a larger surface area when compared with commercial MnO\(_2\).

**Determination of pH\(_{PZC}\)**

pH\(_{PZC}\) of the MnO\(_2\) nanorods was determined from the graph plotted between the pH\(_{\text{initial}}\) and pH\(_{\text{final}}\) of KNO\(_3\) and a mixture of MnO\(_2\) nanorods in KNO\(_3\) and MnO\(_2\) nanorods (Figure 3), where the pH\(_{PZC}\) is given by the point where the two curves intersect each other. The pH\(_{PZC}\) of MnO\(_2\) is observed to be 3.9. Thus, it is expected that the surface will have a net positive charge below pH 3.9, and a net negative charge above pH 3.9.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Linear equations of kinetic models</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Kinetic model</strong></td>
<td><strong>Linear model</strong></td>
</tr>
<tr>
<td>First order</td>
<td>( \ln \frac{C_t}{C_0} = k_1 t )</td>
</tr>
<tr>
<td>Second order</td>
<td>( \frac{1}{C_t} = \frac{1}{C_0} + k_2 t )</td>
</tr>
<tr>
<td>Pseudo first order (PFOM)</td>
<td>( \ln (q_e - q_t) = \ln q_e - k_1 t )</td>
</tr>
<tr>
<td>Pseudo second order (PSOM)</td>
<td>( \frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e} )</td>
</tr>
</tbody>
</table>
FTIR analysis

FTIR spectroscopy is a technique used for the determination of characteristic bonds in molecules. FTIR spectral data were used to obtain information on bands present in MnO$_2$ nanorods. Important bands obtained in the FTIR spectra and the corresponding chemical bonds are presented in Figure 4.

Batch oxidative degradation experiments

Effect of contact time

Batch adsorption experiments were performed to evaluate the performance of MnO$_2$ nanorods in the oxidative degradation of rhodamine B from aqueous solutions. Percentage decolouration increased rapidly in the first 5 min of the reaction between the dye molecules and MnO$_2$ nanorods. However, percentage decolouration decreases with time as more and more of the nanorods are being utilized. Equilibrium was reached within approximately 20 min. Complete decolouration was observed with 20 mg/L rhodamine B solution of dosage 0.5 g/L within 3 min. At higher initial concentrations, a longer time of contact is required to attain equilibrium. Rapid increase in percentage decolouration in the initial period of the reaction was observed due to the adsorption of rhodamine B molecules onto the surface of the MnO$_2$ nanorods followed by oxidative degradation of these dye molecules on the surface of the MnO$_2$ nanorods. The time required for attaining maximum decolouration increased as the concentration of the dye in the solution was increased. The effect of time of contact between the MnO$_2$ nanorods and rhodamine B dye molecules on degradation of rhodamine B is presented in Figure 5(a).

Effect of initial concentration of rhodamine B solution

The initial concentration of rhodamine B solution affects the degradation of dye molecules by the MnO$_2$ nanorods and also the time required for attaining equilibrium. Percentage decolouration decreased from 100% for 20 mg/L dye solution to 60% for 85 mg/L dye solution for an adsorbent dosage of 0.5 g/L. For solutions with initial concentration 20 mg/L, the number of nanorods compared with the number of dye molecules was high, and not all the nanorods were utilized by the dye molecules, and so equilibrium was reached within 3 min. In all the other cases, the maximum number of dye molecules was degraded; however, the percentage of decolouration decreased with increase in the initial concentration of rhodamine B solution. The amount of rhodamine B degraded at equilibrium increased from 30 mg/g to 107 mg/g when the concentration of rhodamine B was increased from 20 to 75 mg/L for 0.5 g/L dosage of MnO$_2$ nanorods.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface area (m$^2$/g)</th>
<th>Pore diameter (nm)</th>
<th>Pore volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO$_2$ nanorods</td>
<td>277.87</td>
<td>5.379</td>
<td>0.374</td>
</tr>
<tr>
<td>Commercial MnO$_2$</td>
<td>6.96</td>
<td>8.145</td>
<td>0.015</td>
</tr>
</tbody>
</table>

Table 2 BET surface area measurements of MnO$_2$ nanorods and commercial MnO$_2$
This is because the ratio of nanorods to dye molecules in the 75 mg/L solution was low compared with that for 20 mg/L rhodamine B solution. Even after the initial concentration was increased to 85 mg/L, the amount of rhodamine B degraded at equilibrium remained the same (107 mg/g) because for initial concentration 75 mg/L and above, the nanorods are exhausted of the capacity to degrade the dye molecules. The results are presented in Figure 5(b).

Effect of pH of rhodamine B solution

The pH of the rhodamine B solution significantly affects degradation of the rhodamine B molecules by the MnO₂ nanorods. The H⁺ ions present in a highly acidic rhodamine B solution can compete for the adsorption sites on the MnO₂ nanorods. The effect of pH of the rhodamine B solution on its decolouration was investigated to determine the range of pH in which the MnO₂ nanorods can effectively degrade the dye and the change in percentage degradation of rhodamine B with pH. The study was conducted with rhodamine B solution of concentration 50 mg/L and dosage of MnO₂ nanorods 0.5 g/L. The results are presented in Figure 5(c).

Degradation of rhodamine B by MnO₂ nanorods was found to be significantly influenced by the pH of the rhodamine B solution. As the pHₚZC of MnO₂ nanorods was found to be 3.9, the MnO₂ nanorods have positive charge on their surface below this pH, causing repulsion between the particles and the cationic dye molecules. For this reason, the effect of pH was examined above the pHₚZC (i.e., >3.9) of the MnO₂ nanorods, when the surface of the MnO₂ nanorods would be negatively charged. Percentage decolouration increased with increase in pH from 4.7 to 7 due to a lower number of H⁺ ions as the pH increases, and hence there is a possibility of increased electrostatic interaction between MnO₂ and the rhodamine B molecules, thereby making the process of adsorption and further degradation of rhodamine B more favourable. Percentage degradation decreased with increase in pH from 7 to 9.4 because at higher pH MnO₂ nanorods can interact with hydroxyl ions to form manganese hydrous oxides (oxo-metal chelation) (Subramanian et al. 2005). Percentage degradation of the dye increased from 92% to 97% with increase in pH up to 7. In the acidic pH range, excess H⁺ ions compete with the cationic rhodamine B dye molecules for electrostatic attraction to the MnO₂ nanorods and so the percentage degradation of the dye decreases.

Effect of dosage of MnO₂ nanorods

The amount of nanorods added per unit volume of the dye solution is called dosage (g/L). It is an important factor in determining the cost of operation of treatment systems. Percentage degradation of rhodamine B increased with increase in the dosage of MnO₂ nanorods due to enhancement in the number of MnO₂ nanorods available for the oxidation of the dye molecules. The amount of rhodamine B dye degraded per unit weight of MnO₂ nanorods qₑ expressed in mg/g, decreased with increase in the dosage. This may be due to the
aggregation of nanorods and decrease in the surface area for the adsorption of rhodamine B dye molecules on MnO₂ nanorods and for further degradation of the same. The results are presented in Figure 5(d).

Effect of low molecular weight acids in rhodamine B solution

Results of the investigation on the effect of oxalic acid and citric acid at two concentrations, 250 mg/L and 500 mg/L, on the percentage degradation are presented in Figure 6(a). It is observed that there was about a 30% decrease in the percentage degradation of the rhodamine B with oxalic acid in it from that observed in the case of the rhodamine B solution without oxalic acid. However, in the case of degradation of rhodamine B solution in the presence of citric acid in aqueous solutions, the percentage degradation of rhodamine B was almost equal to or higher than the percentage degradation of rhodamine B in the absence of it.

Reuse of MnO₂ nanorods

Reusability of any material for several cycles of treatment is important as far as the cost of treatment is concerned. The material should be reusable until it is exhausted of all its utility. Results of evaluation of the reusability of the MnO₂ nanorods in terms of percentage degradation of rhodamine B molecules after each cycle of oxidative degradation are presented in Figure 6(a). These results indicate that the material could be used up to six cycles without much reduction in the percentage degradation of rhodamine B molecules.

Comparison with commercial MnO₂

The percentage decolouration obtained by using MnO₂ nanorods was compared with that obtained for commercially available MnO₂. The results presented in Figure 6(c) indicate that MnO₂ nanorods exhibited higher efficiency in
terms of degradation of the dye (about 33% more removal) when compared with commercial MnO₂.

Mechanism of degradation

The reactivity of MnO₂ depends on the conditions during the preparation and the degree of hydration. The hydroxyl radicals present on the surface of MnO₂ nanorods are responsible for the degradation of dye molecules. Here, the

Table 3 | Coefficient of determination ($R^2$) of the kinetic models

<table>
<thead>
<tr>
<th>Initial concentration (mg/L)</th>
<th>First order model</th>
<th>Second order model</th>
<th>Pseudo first order model</th>
<th>Pseudo second order model</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.324</td>
<td>0.940</td>
<td>0.906</td>
<td>1</td>
</tr>
<tr>
<td>30</td>
<td>0.620</td>
<td>0.846</td>
<td>0.737</td>
<td>0.999</td>
</tr>
<tr>
<td>50</td>
<td>0.525</td>
<td>0.744</td>
<td>0.850</td>
<td>0.999</td>
</tr>
<tr>
<td>75</td>
<td>0.000</td>
<td>0.000</td>
<td>0.839</td>
<td>1</td>
</tr>
<tr>
<td>85</td>
<td>0.000</td>
<td>0.000</td>
<td>0.503</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Table 4 | Parameters of kinetic models of oxidative degradation of rhodamine B

<table>
<thead>
<tr>
<th>Initial concentration (mg/L)</th>
<th>$q_e$ Exp (mg/g)</th>
<th>$q_e$ cal. (mg/g)</th>
<th>$k_1$ (min⁻¹)</th>
<th>$R^2$</th>
<th>$q_e$ cal. (mg/g)</th>
<th>$k_2$ (g/mg·min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>43</td>
<td>19.95</td>
<td>1.93</td>
<td>0.906</td>
<td>43.6</td>
<td>1.75</td>
<td>1</td>
</tr>
<tr>
<td>30</td>
<td>63</td>
<td>19.27</td>
<td>0.31</td>
<td>0.737</td>
<td>66.0</td>
<td>0.08</td>
<td>0.999</td>
</tr>
<tr>
<td>50</td>
<td>92</td>
<td>32.96</td>
<td>0.12</td>
<td>0.850</td>
<td>99.4</td>
<td>0.03</td>
<td>0.999</td>
</tr>
<tr>
<td>75</td>
<td>107</td>
<td>47.09</td>
<td>0.22</td>
<td>0.839</td>
<td>110.0</td>
<td>0.08</td>
<td>1</td>
</tr>
<tr>
<td>85</td>
<td>107.5</td>
<td>47.31</td>
<td>0.03</td>
<td>0.503</td>
<td>110.5</td>
<td>0.02</td>
<td>0.999</td>
</tr>
</tbody>
</table>
Figure 7 | Linear plot of (a) first order, (b) second order, (c) pseudo first order and (d) pseudo second order kinetic models. Comparison of $q_t$ obtained from pseudo first order and pseudo second order kinetic models with the experimental data on the degradation of rhodamine B solution with initial concentration of (e) 20 mg/L, (f) 30 mg/L, (g) 50 mg/L and (h) 75 mg/L (dosage of MnO$_2$ nanorods = 0.5 g/L).
percentage decolouration of rhodamine B (concentration = 20 mg/L) during the oxidative degradation of MnO2 nanorods treated with hydrogen peroxide decreased from 99 to 79. This may be due to the scavenging effect of hydrogen peroxide, which can scavenge the hydroxyl ions on the MnO2 nanorods. The results are presented in Figure 6(d).

**Kinetic analysis**

Oxidative degradation processes of rhodamine B by MnO2 nanorods were kinetically modelled using first order, second order, pseudo first order (PFOM) and pseudo second order (PSOM) kinetic models. Coefficients of determination of each of the kinetic models plotted with their linear model equations are presented in Table 3. The parameters of the pseudo first order and pseudo second order kinetic models, such as amount of dye degraded per unit weight of the nanorods at equilibrium ($q_e$), rate constants, $k_1$ (pseudo first order kinetic model) and $k_2$ (pseudo first order kinetic model) and coefficient of determination ($R^2$) of the modelled values of $q_e$ with pseudo first order and pseudo second order kinetic equations, are calculated from the linear plots and presented in Table 4. Parameters of the linear model equations are presented in Table 4.

The coefficient of determination for the pseudo second order model was relatively high and close to 1. The parameters of the first order, second order, pseudo first order and pseudo second order kinetic models, such as $q_t$ (mg/g), $q_e$ (mg/g), $k_1$ (min$^{-1}$) and $k_2$ (g/mg·min), were obtained by plotting the linear equations of these models (Figure 7(a)–7(d) for rhodamine B solution with initial concentration 50 mg/L). By using these parameters, the amount of dye degraded per unit weight of MnO2 nanorods, $q_t$ (mg/g), was estimated for each of the models.

**CONCLUSION**

Manganese dioxide (MnO2) nanorods were prepared via the Parida method with a slight modification in the drying process. The rod-like shape of the synthesized MnO2 could be observed from the FESEM micrographs. FTIR spectra indicated the formation of characteristic chemical bonds in the MnO2 nanorods. pH$_{PZC}$ of the material was found to be 3.9. Evaluation of the oxidative degradation characteristics of MnO2 nanorods as a function of various process variables indicated that the percentage degradation of rhodamine B increased with increase in reaction time, dosage of MnO2 nanorods and speed of stirring during the process. Percentage degradation increased with increase in the initial concentration of rhodamine B solution. pH of rhodamine B solution showed a positive effect on the percentage degradation of rhodamine B molecules up to pH 7, and it exhibited a decrease in the alkaline pH range. About 100% decolouration was achieved at 0.5 g/L dosage of MnO2 nanorods from 20 mg/L rhodamine B solution in 3 min. Kinetic analysis of the oxidative degradation of rhodamine B with the MnO2 nanorods indicated that the rate of reaction followed the pseudo second order kinetic model. Since the experimental data best suited the pseudo second order kinetic model and did not fit the first order kinetic model well, it may be concluded that the degradation process started with the adsorption of rhodamine B (which usually follows the pseudo second order kinetic model) onto the surface of the MnO2 nanorods and was followed by oxidative degradation at the surface of the nanorods.

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**REFERENCES**


Apte, A. D., Tare, V. & Bose, P. 2006 Extent of oxidation of Cr(III) to Cr(VI) under various conditions pertaining to natural environment. J. Hazard. Mater. 128, 164–174.


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