rGO/MnO₂ nanowires for ultrasonic-combined Fenton assisted efficient degradation of Reactive Black 5
Martha Ramesh, Martha Purnachander Rao, F. Rossignol and H. S. Nagaraja

ABSTRACT

Reduced graphene oxide (rGO) coated manganese dioxide (MnO₂) nanowires (NWs) were prepared by the hydrothermal method. Raman spectra confirmed the presence of rGO and the Brunauer–Emmett–Teller surface area of rGO/MnO₂ NWs was found to be 59.1 m² g⁻¹. The physico-chemical properties of prepared catalysts for the degradation of Reactive Black 5 (RBS) dye were investigated. 84% of RB5 dye in hydrogen peroxide solution was successfully degraded using rGO/MnO₂ NWs, while only 63% was successfully degraded with pristine α-MnO₂ NWs in 60 min owing to the smaller crystallite size and large surface area. Further, the ultrasonic-combined Fenton process significantly enhanced the degradation rate to 95% of RBS by the catalyst rGO/MnO₂ NWs due to synergistic effects. The decomposition products identified using gas chromatography-mass spectrometry revealed a higher production rate of fragments in the ultrasonic-combined Fenton process. Therefore, rGO/MnO₂ NWs with the ultrasonic-combined Fenton process is an efficient catalyst for the degradation of RB5, and may be used for environmental protection.

Key words | catalysis, MnO₂ NWs, nanowires, rGO, RBS, ultrasonic-combined Fenton

INTRODUCTION

Large amounts of synthetic/reactive dyes including Reactive Blue, Reactive Red and Reactive Yellow, are used in industry for dying and colouring materials. Reactive Black 5 (RBS) dye is much used in textile colouring due to its special features such as solubility, high shade of the colour and easy attachment to fibre (Vijayaraghavan et al. 2013). During the colouring/dying process, a significant proportion of dyes are released into the environment which affects aquatic life, drinking water and the health of human beings (Gupta et al. 2012; Karatas et al. 2012). Hence the removal of organic pollutants from waste water is a major environmental challenge. In this regard, a wide variety of methods, such as biological, physical and chemical methods have been developed to remove RB5 molecules from waste water (Siboni et al. 2011; Kalkan et al. 2014; Sadeghi et al. 2014; Amin et al. 2015). All of these approaches have some drawbacks, such as formation of by-products, slow reaction rate for the degradation of RB5 molecules, the need for dissolved oxygen and long retention time, low efficiency, and some of them are very expensive. Therefore, development of a suitable catalyst and a simple, efficient and environmentally friendly method is essential. 

Metal oxides (Poulilos & Tsachpinis, 1999; Aguedach et al. 2008; Kansal et al. 2009; Chong et al. 2015) have applications as catalysts for the degradation of RB5 owing to their structural and optical properties which play a crucial role in the catalytic activity. Among these, MnO₂ draws much attention due to its relatively low crystallite size and large surface area (Kumar et al. 2014). In particular, MnO₂ has revealed a superior catalytic activity and adsorption capability for dye degradation and heavy metal ion removal from wastewater. For instance, single crystalline β-MnO₂ nanowires (NWs) fabricated by a simple hydrothermal method showed a maximum degradation rate of 95% for methylene blue in the presence of hydrogen peroxide (Zhang et al. 2015). Up to now, many methods like redox-precipitation (Wu et al. 2013), microwave irradiation (Ai et al. 2008), and vapor–liquid–solid (Li et al. 2005) have been proposed to synthesize nanocrystalline MnO₂. However, these methods suffer from drawbacks such as agglomeration, stability, heat control, pressure issues, requirement of high
temperatures, low reaction rate and production of secondary nanostructures. Recently, a graphene/MnO₂ nanocomposite has proved to have superior electrode performance in super capacitor applications, using graphene oxide and manganese sulphate as the precursors (Feng et al. 2015).

The Fenton reaction suffers from the drawback of the constant loss of the catalyst (Zhang et al. 2006; Harichandan & Prasad 2016). In this regard, ultra-sonication can be used as a support, during which the propagation of the sound wave through the Fenton reaction causes extremely high temperatures and pressures in a microscopic region of the sonicated liquid, thereby resulting in chemical excitation, resulting in the initiation or enhancement of the catalytic activity in the solution through the formation of new, relatively stable chemical species that can diffuse further into the solution to create chemical effects. Hence, an ultrasonic-combined Fenton reaction in an aqueous solution not only enhances the amount of free radicals, but also alters the reactor conditions favouring a good interaction of the created free radicals with the organic effluents for efficient removal (Namkung et al. 2008; Song et al. 2009). Recently it has been used in the improvement of degradation of several reactive dyes, such as Rhodamine B (Chen et al. 2016), Reactive Blue 181 (Basturk & Karatas 2014) and Reactive Blue 49 (Siddique et al. 2014), but the use of an ultrasonic-assisted Fenton reaction for the decoloration of RB5 dye using reduced graphene oxide (rGO)/MnO₂ NWs has not yet been reported.

Herein, we report the synthesis and physico-chemical properties of rGO coated MnO₂ NWs for enhanced catalytic decoloration of RB5 dye with an ultrasonic-combined Fenton process. Further, both rGO coating and ultrasonication of the NWs reveal an increase in decoloration of RB5 by 30%. Also, a higher production rate of organic fragments in the ultrasonic-combined Fenton process is witnessed.

MATERIALS AND METHODS

Graphite powder and RB5 dye were purchased from Sigma-Aldrich and used as received. Manganese sulfate, potassium permanganate, sodium nitrate, sodium hydroxide, sulfuric acid (98%), hydrogen chloride, and hydrogen peroxide (30%) from Merck were used to produce the NWs. All reagents were of analytical grade. The crystalline phases of the products were identified using powder X-ray diffraction (Rigaku miniflex 600, Japan) using CuKα radiation (λ = 1.5406 Å). Scanning electron microscopy (JEOL/JSMM6580LA, Japan) was employed to observe the morphologies and sizes of the NWs. The Raman spectra was registered in the spectral range of 400-2,000 cm⁻¹ using a Raman spectrometer LabRam HR800 (Horiba Jobin Yvon Inc. USA). The specific surface area of the prepared samples was estimated using the Brunauer–Emmett–Teller (BET) method from the nitrogen adsorption–desorption isotherms obtained using a BELSORP Mini II instrument (BEL Japan Co., Ltd).

The concentration of the RB5 dye after degradation was recorded using a UV-Vis spectrometer (ocean optics USB4000-UV-VIS, India). All reactions were conducted with stirring, using a magnetic stirrer (Remi MLH Plus, India) at 700 rpm and centrifugation was carried out using a centrifuge (Remi, R-8C, India). The aqueous solutions were sonicated using a Le-120UPP (20 KHz, 120 W, Leela Electronics Company, India) sonicator. To evaluate the bio-products, gas chromatography-mass spectrometry (GC-MS) was used (GCMS-QP 2010 Plus Shimadzu mass spectrometer). An HP-5 ms column with dimensions of 0.25 μm, 30 m x 0.25 mm (i.d.) was used. The temperature was ramped as follows: 36 °C for 1 min, 5 °C min⁻¹ up to 300 °C and hold time 10 min. The temperature of the inlet, source and transfer line was 250, 230 and 280 °C, respectively. The analyses were done using splitless (0.7 min) injection.

Synthesis of rGO

A modified Hummer’s method was used to prepare rGO (Sreejesh et al. 2015). To prepare graphene oxide, 0.5 g of sodium nitrate, 1 g of graphite flakes and 23 mL of concentrated sulfuric acid, were stirred on a magnetic stirrer at room temperature to form a homogeneous solution. 3 mg of potassium permanganate was added to the above solution within 1 h to avoid the rise of temperature of the mixture and the suspension was continuously stirred at 35 °C for 12 h. Finally, the solution was oxidized by adding 5 mL 30% hydrogen peroxide to the above suspension. To remove the organic residues and other metal ions in the mixture as a result of reduction of potassium permanganate, the brown solid product was centrifuged at 2,000 rpm for 30 min at each time by soaking with deionized water and 5% hydrogen chloride for several times, then dried at 60 °C in a vacuum oven for 12 h. The obtained product was dispersed using ethanol and calcined at 150 °C for 4 h to reduce GO into rGO.

Synthesis of MnO₂ NWs and rGO/MnO₂ NWs

In a typical synthesis, the manganese sulfate was annealed at 500 °C for 3 h to eliminate water content, resulting in the
formation of anhydrous manganese sulfate. 0.2 M of anhydrous manganese sulfate and 0.63 M of potassium permanganate was taken separately in 30 mL of distilled water. Then the mixture was stirred in a magnetic stirrer at ambient conditions to form the uniform suspension. MnO₂ was obtained from the oxidation of anhydrous manganese sulfate by potassium permanganate using the reaction,

$$2\text{KMnO}_4 + 3\text{MnSO}_4 + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + \text{K}_2\text{SO}_4 + 2\text{H}_2\text{SO}_4$$

(1)

After 1 h, the viscous liquid was transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at 150 °C for 24 h, then cooled down to room temperature. The resulting block solid suspension was washed with distilled water, filtered and dried at 60 °C. In order to transform Mn²⁺ into MnO₂, additional potassium permanganate was added slowly into the system following the stoichiometric reaction equation (Peng et al. 2013),

$$2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 4\text{H}^+$$

(2)

rGO-MnO₂ NWs were prepared using the same method as described above by adding 0.025 g of rGO to the above solution.

RESULTS AND DISCUSSION

MnO₂ NWs and rGO/MnO₂ NWs were characterized by X-ray diffraction as shown in Figure 1(a). All the diffraction peaks of MnO₂ NWs were indexed and matched well with the body-centered tetragonal phase, with lattice constants a = b = 9.7847 Å and c = 2.8630 Å, which agrees with standard JCPDS No. 44–0141 (Zhong 2016). The appearance of the broad diffraction peak positioned at 23.7° corresponds to the (002) plane, indicating the presence of an rGO on the surface of rGO/MnO₂ NWs. The interlayer spacing of rGO is 0.37 nm, slightly larger than that of graphite, which resulted from the small amount of residual oxygen-containing functional groups or other structural defects (Fu et al. 2013). These two samples have apparent variations in the intensity and broadening of the diffraction peaks. As seen in Figure 1(a), with the coating of the rGO, the intensity of MnO₂ NWs peak decreases and peak broadening increases. In the case of bare MnO₂ NWs, the crystallites are larger in size, resulting in a narrow diffraction peak. However, the smaller crystallites of rGO/MnO₂ NWs account for the observed peak broadening. From the diffraction using the high intensity peak (211), the crystallite size of MnO₂ and rGO/MnO₂ was estimated using Scherrer’s equation (Zang & Tang 2015),

$$D = \frac{K\lambda}{\beta \cos \theta}$$

(3)

where D is the mean size of the crystallite (nm), K is the shape factor equal to around 0.9, λ is the X-ray wavelength, 0.154 nm of CuKα radiation, β is the line widening at half intensity of the peak (radians), and θ is the angle of the diffraction peak (degrees). The measured crystallite size of the MnO₂ NWs was in the range 14–23 nm. Further, from

Figure 1 | (a) X-ray diffraction and (b) Raman spectra of α-MnO₂ NWs and rGO/MnO₂ NWs.
Table 1, it can be observed that the average crystallite size of MnO2 NWs decreases with the coating of the rGO. Using the above crystallite values, the dislocation density (δ), which reveals the amount of defects in a unit volume of MnO2 and rGO/MnO2 NWs, was estimated using Williamson and Smallman’s formula (Williamson & Smallman 1956),

\[
\delta = \frac{1}{D^2}
\]

Evidently, rGO/MnO2 NWs consist of more dislocations due to heterogeneous nucleation, as well as interfaces between the MnO2 lattice and rGO nanosheets (Abdolhosseinizadeh et al. 2013). The dislocation density is 1.96 \times 10^{15} \text{ m}^{-2} and 4.63 \times 10^{15} \text{ m}^{-2} for the NWs of MnO2 and rGO/MnO2, respectively. The results are summarized in Table 1.

To gain more structural information, the Raman spectra of MnO2 and rGO/MnO2 NWs are shown in Figure 1(b). Three core peaks at 506 cm\(^{-1}\), 565 cm\(^{-1}\), and 648 cm\(^{-1}\) are identified for the MnO2 NWs. The Raman band at 648 cm\(^{-1}\) is due to the symmetric v\(_2\) (Mn–O) stretching vibration of MnO\(_6\) groups, and the band at 565 cm\(^{-1}\) is attributed to the v\(_3\) (Mn–O) stretching vibration in the basal plane of MnO2 sheets (Li et al. 2012). The low-frequency Raman band at 506 cm\(^{-1}\) refers to an external vibration that is due to the translational motion of the MnO\(_6\) octahedra, thus revealing good crystallinity of the \(\alpha\)-MnO\(_2\). The rGO is characterized using the Raman spectrum by two specific peaks, G band at 1,599.4 cm\(^{-1}\) which is a characteristic of sp\(^2\)-hybridized C–C bonds in a two-dimensional hexagonal lattice, and D band at 1,345.8 cm\(^{-1}\) corresponding to the defects in the graphene structure. As shown in Figure 1(b), the I\(_D\)/I\(_G\) ratio is reduced slightly from 0.99 for rGO to 0.97 for rGO/MnO2 NWs, due to the presence of defects during hydrothermal reduction. In addition, the characteristic band observed at 572.2 cm\(^{-1}\) in rGO/MnO2 NWs belongs to A\(_\delta\) spectroscopic species originating from breathing vibrations of MnO\(_6\) octahedral, suggesting the successful integration of MnO2 into rGO (Yao et al. 2013).

Figure 2(a) shows scanning electron microscopy (SEM) images of MnO2 NWs. The NWs shown in Figure 2(a) are small and attached to each other at the top of the view. From Figure 2(B-b), it is clear that the MnO2 NWs grew on the surface of the GO sheets that acted as substrates for the nucleation of MnO2 NWs, indicating that this is a heterogeneous nucleation. Furthermore, when there are more nucleation sites, it is expected to have more MnO2 NWs with relatively thinner diameters, which is evident from the SEM images shown in Figure 2(a) compared to Figure 2(B-a), thus resulting in a higher surface area. The average surface area, from BET analysis, calculated for rGO/MnO2 NWs is about 59.1 m\(^2\) g\(^{-1}\), whereas for pristine MnO2 NW it is about 37.7 m\(^2\) g\(^{-1}\). The increased surface area of NWs is due to the presence of rGO nanosheets in the rGO/MnO2. The graphene nanosheets were predominantly in the form of a few layers, with some single layer containing a number of pores. Therefore, the presence of rGO nanosheets in rGO/MnO2 NWs cause more pore volume of around 0.032 cm\(^3\) g\(^{-1}\) using BET analysis. By comparison for bare MnO2 NWs the pore volume is 0.020 cm\(^3\) g\(^{-1}\), leading to a greater surface area of rGO/MnO2 NWs (Samejima et al. 1977, pp. 7–27). Evidently, the BET surface area of the rGO/MnO2 NWs was found to be more than that of the bare MnO2 NWs. This indicated that the MnO2 NWs on the surface of rGO, as shown in both parts of Figure 2(b), possess an enhanced surface area.

The morphology of the rGO sheet is shown in the inset of Figure 2(B-a), revealing a crumpled structure after exfoliation (Kakaei & Hasanpour 2014). Therefore, from Raman and scanning electron microscopy studies, it is evident that MnO2 NWs are wrapped with rGO sheets, which prevents the agglomeration of MnO2 NWs. Figure 2(B-b) shows the rippled morphology of the rGO sheets, bundling MnO2 NWs at lower magnification.

**Catalysis: the Fenton and ultrasonic-combined Fenton process**

The catalytic activity of the products was performed in a 250 mL borosil glass beaker. Initially, the reactants consisted of a 10 \(\mu\)M RB5 compound with 100 mL H\(_2\)O and pH was set at 5 using sulfuric acid or a sodium hydroxide solution. Subsequently, a 20 mg catalyst MnO2 or rGO/MnO2 was added to the solution. After mixing 6 mL of 30 wt% hydrogen peroxide solutions, O\(_2\) bubbles were produced simultaneously. The resulting suspension was stirred on a magnetic stirrer for 30 min to attain the adsorption/desorption equilibrium between dye RB5 and suspended solid particles. In addition, an rGO/MnO2 stock solution was
dispersed with probe sonication using an ultrasonic power of 120 W and a frequency of 20 ± 2 kHz. The tip of the probe was 6 cm in length, and 1 cm in diameter. pH was again tuned to a desired value at a reaction temperature of 40 ± 2 °C. The ultrasonication facilitates a direct contact of the reaction matrix with the mechanical vibrations without significant loss of energy. Ultrasonic-combined Fenton experiments were carried out in a 50 mL polypropylene beaker at a regular time interval from 0 to 60 min. The samples designated as MnO₂, rGO/MnO₂, and US/rGO/MnO₂ were used for catalysis. After achieving the complete adsorption/desorption equilibrium state, the analytical samples (5 mL) were extracted from the solution at the regular time intervals. Subsequently, the catalyst was separated from the solution by centrifugation at 2,000 rpm for 10 min and the remaining solution was analyzed by an ultraviolet visible spectrophotometer to measure the absorbance of the dye solution.

To study the catalytic oxidation ability of the above α-MnO₂ NWs, the decomposition of RB5 with the assistance of hydrogen peroxide was preferred as a probe reaction. A blank cuvette filled with ultrapure water was used prior to each measurement.

Figure 2 shows the plot of absorption vs wavelength of RB5 based on the ultraviolet visible absorption spectra as a function of the catalytic reaction period for the various catalysts. A spectrum analysis was performed in the wavelength range from 400 to 700 nm. The intensity of the absorption at the highest peak is directly proportional to the concentration of RB5 in the solution, and is used to determine the percentage of dye removed from the solution over the course of the experiment. From the spectrum, the percentage of dye remaining in the suspension at different reaction times (0–60 min) was determined by measuring the maximum absorbance value at λ_{max} = 596 nm.

The optical spectra of the RB5 solution based on the absorbance vs wavelength along with the decolorization rate at different reaction periods is shown in Figure 3(a)–3(c).

The intensity of the maximum absorption peak of the RB5 reduced gradually with time. It can also be noted that the maximum wavelength of absorption was changed from 600 nm to 596 nm, 590.5 nm, and 582.5 nm after reaction durations of 10 min, 20 min, and 60 min, respectively. The blue shifts of the absorption wavelength revealed the catalytic decay of the RB5 (Weng et al. 2013). Eventually, the unique absorption peak became wide and weak in intensity, indicating the decolorization of RB5.

Figure 3(a)–3(c) show the absorption curves of RB5 solution. The plot at t = 0 is the initial dye solution (100 mL, 20 mg L⁻¹) after stirring magnetically for 30 min to achieve
adsorption/desorption equilibrium. Initially, a huge amount of dye is removed because of the larger generation of hydroxyl radicals accompanied by the fast disintegration of hydrogen peroxide. The concentration of dye in all samples decreases with increasing reaction time until the almost complete degradation of the dye.

Figure 3(d) shows the estimation of the degradation rate of RB5 by plotting decolorization (%) vs reaction time (t) for the three different catalysts. The color removal efficiency was estimated using the following expression,

\[
\text{Decolorization} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]  

(5)

where \(C_0\) refers to the initial dye concentration, and \(C_t\) is the concentration of dye at time \(t\) (Chen et al. 2015). It may be noted that the use of US/rGO/MnO\(_2\) as a catalyst resulted in the decolorization rate of 40% in only 20 min and as high as 95% in 60 min. In the same period, the highest effectiveness for dye elimination is 63% and 84% for MnO\(_2\), and rGO/MnO\(_2\), respectively.

We suggest the Fenton mechanism for the degradation of RB5. Briefly, the Fenton process uses the mixture of manganese ions and hydrogen peroxide to decay the pollutants via production of hydroxyl radicals in a catalytic process. Initially, hydrogen peroxide molecules could be adsorbed on the surface of rGO/MnO\(_2\) NWs (Equation (6) in the Fenton reaction), then disintegrated into free radical species, such as HO\(^-\), O\(_2\)\(^{\bullet}\) or HOO\(^-\) radical species, (Equations (7)–(10)). The generated free radical species (HO\(^-\), O\(_2\)\(^{\bullet}\)) have the high oxidative capability to break the adsorbed dye molecules. Likewise, more RB5 molecules could transfer from the suspension to the MnO\(_2\) surface and later be decayed into carbon dioxide, water and other small components, (Equation (11)). The obtained small components from the dye decomposition leave the catalyst surface by desorption, which results in recovery of a catalyst. Further, the hydrogen peroxide molecules in the Fenton
reaction are mostly consumed in oxidizing the dye molecules and producing oxygen molecules with an assistance of free radical species (Equation (12)).

\[
\text{rGO/} + \text{Mn(IV)} + \text{H}_2\text{O}_2 \leftrightarrow \text{rGO/} + \text{Mn(IV)}^*\text{H}_2\text{O}_2
\]

(6)

\[
\text{rGO/} + \text{Mn(IV)}^*\text{H}_2\text{O}_2 \rightarrow \text{rGO/} + \text{Mn(II)} + \text{HO}_2^- + \text{H}^+
\]

(7)

\[
\text{rGO/} + \text{Mn(II)} + \text{H}_2\text{O}_2 \rightarrow \text{rGO/} + \text{Mn(IV)} + \text{HO}^* + \text{OH}^-
\]

(8)

\[
\text{HO}_2^- \leftrightarrow \text{H}^+ + \text{O}_2^-
\]

(9)

\[
\text{rGO/} + \text{MnO}_2\cdot\text{H}_2\text{O} \leftrightarrow \text{HOO}^- + \text{H}^+
\]

(10)

\[
\text{HO}^*(\text{O}_2^-) + \text{dye(adsorbed)} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \ldots
\]

(11)

\[
2\text{HO}^* + 2\text{H}^* \rightarrow \text{O}_2 + 2\text{H}_2\text{O}
\]

(12)

The enhanced performance of rGO/MnO$_2$ towards the degradation of RB5 could be ascribed to the synergistic effect between MnO$_2$ and rGO in the presence of hydrogen peroxide. Graphene with 2D layers of sp$^2$-bonded structures can provide strong chemical and mechanical interactions, as well as increased electron transport between MnO$_2$ NWs and the rGO matrix (Qu et al. 2014). The RB5 molecules are easily adsorbed to the surfaces of GO through π-π conjugation based on its giant π-conjugation frame and two-dimensional planar configuration until the adsorption-desorption equilibrium. This accounts for the high concentration of hydroxyl radicals on the surface of rGO/MnO$_2$ NWs compared to bare MnO$_2$. Also, the structural and morphological properties of rGO/MnO$_2$ NWs reveal the superior catalytic activity.

Firstly, based on the XRD results, the average crystallite size of rGO/MnO$_2$ NWs is smaller with more dislocation density compared to the α-MnO$_2$ NWs. As a result of the lower particle size, the surface area increases, resulting in the adsorption of more H$_2$O$_2$ and dye molecules onto the surface of rGO/MnO$_2$. It is also evident from the BET data that the rGO/MnO$_2$ NWs reveals a higher surface area than the pristine MnO$_2$ NWs. This promotes the amount of reactive ‘OH and O$_2^-$ free primitives attacking the dye molecules, leading to an enhancement in the degradation of RB5 molecules (Videla et al. 2015). Meanwhile, increased surface defects such as dislocations in the nanocomposite, as given in Table 1, play a crucial role in increasing the internal surface area of the catalyst, enhancing species diffusivity and chemical reactivity.

Secondly, it is evident from scanning electron microscopy analysis, that MnO$_2$ NWs are wrapped with rGO, which prevents the aggregation of MnO$_2$ NWs as well as serving as electron transfer channels to generate free radicals ‘OH, HOO’, or O$_2$, which cause disintegration of RB5 molecules. As a result, the MnO$_2$/rGO NWs shows enhanced catalytic performance for degradation of RB5 dye.

To improve the degradation of RB5 further, we used ultrasonic treatment, where small size particles of rGO/MnO$_2$ catalyst were produced. In the ultrasonic-combined Fenton process, the collapse of the cavitation bubbles results in an extremely high temperature and pressure. These high-energy phenomena cause decomposition of organic effluents in aqueous solutions. The heat from the cavity collapse splits water molecules into abundantly reactive hydrogen and hydroxyl radicals (Equation (13)). The hydrogen radicals combine to create molecular hydrogen (H$_2$) and hydroxyl radicals combine to create hydrogen peroxide (Equations (14) and (15)). Meanwhile, hydrogen peroxide and O$_2$ molecules from the aqueous solution cause formation of oxide and other radicals (Equations (16 and 17)), where |) indicates the ultrasound. rGO/Mn-OOH$_2^+$ degenerate into Mn$_2^{2+}$ and ‘OH (Equation (18)) due to a synergistic effect between Fenton’s reagent and ultrasound. The separated Mn(II) ions can react ultimately with hydrogen peroxide to create hydroxyl radicals, leading to a cyclic process (Bagal & Gogate 2014). Therefore, the synergy of ultrasound and Fenton’s process together increases the reaction rate of Mn$_2^{2+}$ isolation from Mn-OOH$_2^{2+}$ and accelerates the hydroxyl radical formation due to the reaction between Mn$^9$/H$_2$O, Mn$^{2+}$/H$_2$O$_2$ or Mn$^{3+}$/H$_2$O, as shown in Equations (19)-(22). The generated hydroxyl radicals can react with RB5 molecules evolving carbon dioxide and water (Equation (23)).

\[
\text{H}_2\text{O} + )\text{)} \leftrightarrow \text{•OH} + \text{H}^+
\]

(13)

\[
2\text{H}^* \rightarrow \text{H}_2
\]

(14)

\[
\text{OH}^* + \text{OH}^* \rightarrow \text{H}_2\text{O}_2
\]

(15)

\[
\text{H}_2\text{O}_2 + )\text{)} \rightarrow 2\text{•OH}
\]

(16)
O₂ + ))) → 2O*  
(17)

rGO/Mn-OOH₂ + ))) → Mn₂⁺ + HOO*  
(18)

Mn²⁺ + H₂O₂ + ))) → Mn³⁺ + OH⁻ + OH⁻  
(19)

Mn³⁺ + H₂O + ))) → Mn₂⁺ + OH⁻ + H⁺  
(20)

Mn⁰ + 2H₂O + ))) → Mn²⁺ + H₂ + 2OH⁻  
(21)

2Mn⁰ + O₂ + 2H₂O + ))) → 2Mn₂⁺ + 2H₂ + 4OH⁻  
(22)

Dye + HO* → [Dye-OH adduct]⁺ → Oxidized dye + CO₂ + H₂O  
(23)

efficiency of RB5 in the present work is relatively more than the reported values, as shown in Table 2. rGO/MnO₂ NWs catalyst exhibits better performance in terms of low dosage and short reaction time and efficiency.

The decomposition yield formed at the end of the reaction for 60 min was examined by GC–MS and identified with mass spectra data for various catalysts (20 mg L⁻¹ each) of RB5/MnO₂ (Figure 4(a)), RB5/rGO/MnO₂ (Figure 4(b)) and US/RB5/rGO/MnO₂ (Figure 4(c)).

It is evident from Figure 4 that the intensity of the corresponding peaks increases consistently from RB5/MnO₂, RB5/rGO/MnO₂, to US/RB5/rGO/MnO₂, indicating the higher decomposition rate of the dye by the ultrasonic-combined Fenton process. Particularly, the selected peaks at m/z ratio value 78, 106, 143, 198 and 300 match very well with the organic by-products as given in Table 3.

As seen in Figure 3(d), after 60 min, the degradation efficiency in Fenton’s process is 84.5%. However, during the same period, the ultrasonic-combined Fenton process results in about 95% decolorization. The results clearly indicate the significant enhancement in the ultrasonic-combined Fenton process compared with Fenton’s alone could be due to the synergistic effects. The maximum color removal

Table 2 | Reported values for decolorization of RB5 using MnO₂ and GO

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>Catalyst dose (mg)</th>
<th>RB5 dye concentration</th>
<th>Degradation (%)</th>
<th>Time (min)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-MnO₂</td>
<td>Fenton</td>
<td>20</td>
<td>1 × 10⁻⁵ M</td>
<td>38</td>
<td>60</td>
<td>Ramesh et al. (2016)</td>
</tr>
<tr>
<td>Mn-alginate</td>
<td>Fenton</td>
<td>6,000</td>
<td>air flow 1 L/min</td>
<td>98</td>
<td>100</td>
<td>Fernández de Dios et al. (2015)</td>
</tr>
<tr>
<td>MnP</td>
<td>Biodegradation</td>
<td>20</td>
<td>25 mg/L</td>
<td>80</td>
<td>90</td>
<td>Mahmoudian et al. (2014)</td>
</tr>
<tr>
<td>GO</td>
<td>Fenton</td>
<td>300</td>
<td>1 × 10⁻⁵ M</td>
<td>57–75</td>
<td>5 h</td>
<td>Cheng et al. (2012)</td>
</tr>
<tr>
<td>Magnetic GO</td>
<td>Fenton</td>
<td>20</td>
<td>20 mL</td>
<td>62</td>
<td>60</td>
<td>Ali et al. (2014)</td>
</tr>
<tr>
<td>rGO</td>
<td>Photo catalytic</td>
<td>30</td>
<td>10 mg/L</td>
<td>26</td>
<td>60</td>
<td>Wong et al. (2015)</td>
</tr>
<tr>
<td>GO NPs</td>
<td>Fenton</td>
<td>1,000</td>
<td>1 × 10⁻⁵ M</td>
<td>80</td>
<td>2 h</td>
<td>Kyzas et al. (2014)</td>
</tr>
<tr>
<td>Fe alginate</td>
<td>Fenton</td>
<td>500</td>
<td>2.68 mM</td>
<td>85</td>
<td>60</td>
<td>Iglesias et al. (2015)</td>
</tr>
<tr>
<td>FO</td>
<td>Fenton</td>
<td>100</td>
<td>100 mg⁻¹</td>
<td>68</td>
<td>120</td>
<td>Merić et al. (2004)</td>
</tr>
<tr>
<td>Fe</td>
<td>Fenton</td>
<td>300</td>
<td>50 mg⁻¹</td>
<td>63</td>
<td>120</td>
<td>Rahmani et al. (2010)</td>
</tr>
<tr>
<td>FeSO₄</td>
<td>Fenton</td>
<td>250</td>
<td>50 mg⁻¹</td>
<td>63</td>
<td>20</td>
<td>Lucas &amp; Peres (2006)</td>
</tr>
<tr>
<td>NiO/Al₂O₃</td>
<td>Fenton</td>
<td>200</td>
<td>100 mg⁻¹</td>
<td>53</td>
<td>250</td>
<td>Bradu et al. (2010)</td>
</tr>
<tr>
<td>CuO/Al₂O₃/phosphate</td>
<td>Fenton</td>
<td>200</td>
<td>100 mg⁻¹</td>
<td>37.5</td>
<td>250</td>
<td>–</td>
</tr>
<tr>
<td>β-MnO₂</td>
<td>Fenton</td>
<td>160</td>
<td>40 mg⁻¹</td>
<td>56</td>
<td>40</td>
<td>Yu et al. (2014)</td>
</tr>
<tr>
<td>α-MnO₂</td>
<td>Fenton</td>
<td>20</td>
<td>1 × 10⁻⁵ M</td>
<td>63</td>
<td>60</td>
<td>Present work</td>
</tr>
<tr>
<td>rGO/α-MnO₂</td>
<td>Fenton</td>
<td>20</td>
<td>1 × 10⁻⁵ M</td>
<td>84</td>
<td>60</td>
<td>Present work</td>
</tr>
<tr>
<td>rGO/α-MnO₂</td>
<td>Sono-Fenton</td>
<td>20</td>
<td>1 × 10⁻⁵ M</td>
<td>95</td>
<td>60</td>
<td>Present work</td>
</tr>
</tbody>
</table>
Effect of operational parameters

In order to determine the effect of other parameters on the decoloration of the pollutant, experiments were performed at constant pH = 5 for 60 min, using the ultrasonic-combined Fenton catalysis, with different concentrations of dye, rGO/MnO₂, and H₂O₂.

Effect of dye concentration

The concentration of dye is one of the main parameters in an ultrasonic-combined Fenton reaction. The decomposition of the dye was studied by varying the initial concentration range from 10 to 20 μM at pH = 5, with 20 mg catalyst rGO/MnO₂ NWs loading. The results are shown in Figure 5(a). As the concentration of the dye increases, the molecules bond strongly to the catalyst surface which then reduces the efficiency of the catalytic reaction due to the decline in OH⁻ and OH₂⁻ concentrations, leading to saturation and a lower degradation rate. Also, the existence of a large amount of adsorbed dye decreases the probability of direct contact with the hydroxyl radicals, resulting in an inhibitive effect on the dye degradation (Tayeb & Hussein 2018).

Effect of catalyst amount

The amount of catalyst in the ultrasonic-combined Fenton reaction is another factor taken into consideration. Generally it is observed that the percentage degradation increases when increasing the amount of catalyst, while keeping other factors fixed. As the catalyst amount increases, a larger quantity of dye is adsorbed on the surface of the rGO/MnO₂ NWs. This increases the probability of a reaction between dye molecules and oxidizing species, thus causing an enhancement in the degradation percentage.
Table 3 | Possible degradation products of RB5 after catalytic reaction as determined using GC-MS

<table>
<thead>
<tr>
<th>Name of the intermediate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4-ethylsulfonyl)phenyl)diazene</td>
</tr>
<tr>
<td>Naphthalene</td>
</tr>
<tr>
<td>Benzene</td>
</tr>
<tr>
<td>Sodium 5-aminonaphthalene-1,6-disulfinate</td>
</tr>
<tr>
<td>Sodium 5-aminonaphthalene-1-sulfinate</td>
</tr>
<tr>
<td>Naphthalen-1-amine</td>
</tr>
<tr>
<td>Phenyl diazene</td>
</tr>
<tr>
<td>Sodium 1-[(4-sulfamoylphenyl)amino] ethanesulfonate</td>
</tr>
</tbody>
</table>
Figure 5(b) shows the effect of catalyst amount on the dye decolorization percentage.

Effect of $\text{H}_2\text{O}_2$ dosage

The ultrasonic-combined Fenton degradation of RB5 is also affected by the concentration of hydrogen peroxide in the solution. To determine the optimal dosage of the $\text{H}_2\text{O}_2$, 3–9 mL was mixed in the 100 mL dye solution. The degradation increased considerably when increasing the initial $\text{H}_2\text{O}_2$ concentration from 3 to 6 mL as shown in Figure 5(c). This is attributed to an increase in the adsorption and interfacial reactions, which in turn increases the number of hydroxyl radicals. As the concentration of $\text{H}_2\text{O}_2$ is further increased from 6 to 9 mL, the solution becomes turbid and blocks the Fenton reaction, and therefore the percentage degradation of the dye decreased (Alaton & Balcioglu 2001). However, $\text{H}_2\text{O}_2$ itself acts as an effective $\text{OH}^-$ scavenger at concentrations that are specific for the pollutant, according to the empirical equation

$$\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O}.$$ 

Thus, the presence of excess $\text{H}_2\text{O}_2$ can lower the treatment efficiency of the Fenton reaction.

The cyclic life of the prepared MnO$_2$ NWs, rGO/MnO$_2$ NWs was also studied using the degradation of the RB5 as shown in Figure 6. In order to check the reusability of MnO$_2$ NWs, they were filtered, washed with deionized water and dried in air at 60°C for 4 h, and reused in the number of cycles from the 1st to Vth cycle. The degradation efficiency reduces slightly from 84.5% to 81.2% for GO/MnO$_2$ NWs, whereas, the degradation efficiency largely reduced from 63.1% to 55.5% in the case of pristine MnO$_2$ NWs, because some amount of catalyst is lost during centrifugation, washing and filtration. The wrapping of MnO$_2$ NWs with rGO sheets reduces the contact of NWs during centrifugation, as well as their solubility in water. This is attributed to the lower mass loss of the rGO/MnO$_2$ NWs compared with the pristine MnO$_2$ NWs. Therefore, rGO/MnO$_2$ NWs have cyclic stability and can be reprocessed without substantial reduction in catalytic performance for degradation of the RB5 in water.

**CONCLUSIONS**

MnO$_2$ NWs and rGO/MnO$_2$ NWs were synthesized by a simple hydrothermal method, and catalytic performance was tested using RB5 as a model pollutant. rGO/MnO$_2$
NWs reveal superior catalytic performance towards the decomposition of the RB5, because the large surface area of sp²-bonded rGO structure provides good electron transfer channels and interface dislocations. Besides, as has been shown by X-ray diffraction and scanning electron microscopy studies, the structural and morphological properties of NWs, such as defect density and agglomeration, are well correlated with the catalytic performance. The rGO coating of MnO₂ NWs results in 20% enhancement in catalytic activity compared to pristine MnO₂ NWs towards degradation of RB5 dye with hydrogen peroxide based on the Fenton catalysis. The application of a coupled ultrasonic-combined Fenton process using an rGO/MnO₂ catalyst, further enhances the degradation rate of RB5 by 30% due to synergic effects. Additionally, the as-grown rGO/MnO₂ retained its catalytic stability for several cycles due to the wrapping of NWs with rGO. The various intermediate byproducts formed during the catalytic reaction were successfully detected with higher production rates in the ultrasonic-combined Fenton reaction compared to the Fenton reaction. Therefore, rGO/MnO₂ NWs exhibit good catalytic activity and can be used for environmental protection.

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