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Solvent free mechanochemical synthesis of MnO₂ for the efficient degradation of Rhodamine-B

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ABSTRACT:

MnO₂ nanorods were synthesized by mechanochemical processing with subsequent heat treatment and their photocatalytic activity was studied on the decolourization of aqueous solution of Rhodamine B at different pH levels. A solid state redox reaction $2\text{KMnO}_4 + \text{MnCl}_2 \rightarrow 3\text{MnO}_2 + 2\text{KCl} + \text{O}_2$ was activated during mechanical milling. Excess KCl salt was added in the starting powder mixture to prevent agglomeration of MnO₂ nanoparticles. The milling resulted in the production of amorphous MnO₂ nanoparticles with a high surface area of 204 m² g⁻¹. Crystalline MnO₂ nanorods of diameters about 15 nm - 20 nm were produced by heating the as-milled powder at 350°C for 1 hour in air. Amorphous MnO₂ nanoparticles showed higher degradation rate of Rhodamine B than crystalline MnO₂ nanorods under simulated sunlight. The degradation rate was higher under acidic conditions. This work demonstrates the potential for cost effective, green and scalable synthesis of MnO₂ nanocatalysts for environmental applications.

Keywords: Mechanochemical processing, Manganese dioxide, Dye degradation, Photo catalyst

1. Introduction

In recent years, organic pollutants in water have significantly increased due to intensified industrial activities. In particular, industries such as the textile, paper and cosmetic sectors release large amounts of dye effluents, which have become one of the major causes of water contamination [1]. The effluents often contain toxic and noxious dyestuffs, engendering adverse effects on aquatic life, human health and environment [2]. In the past, significant amounts of research have been conducted on developing technologies for eliminating these pollutants [3-6]. Photocatalytic reaction is one of the promising ways to remove the pollutants by utilization of sunlight, an abundant and clean energy source [7].

The photocatalytic degradation of various dyes has been investigated by using a wide variety of photocatalysts such as TiO_2 [8], ZnO [9], WO_3 [10] and bismuth compounds [6, 11-13]. Among them, manganese dioxide is of significant practical interest due to its considerable redox activity, low cost and earth-abundant composition [14]. A number of efforts have been made for the development of various morphologies of MnO_2 to enhance the catalytic performance [15-17]. Yin *et al.* reported a simple hydrothermal synthesis of MnO_2 nanorods and studied their performance on the degradation of congo red, eosin red and methyl orange under UV-light irradiation [18]. Dang's group investigated the decolourization of methylene blue and methyl orange with a MnO_2 -coated diatomite composite prepared using a wet-chemical method [19]. Combariza's group reported the removal of indigo carmine dye by a bio-nano composite produced by in situ synthesis of nanostructured MnO_2 onto natural figue fibers [20]. Fathy et al. prepared a $\gamma\text{-MnO}_2/\text{MWCNT}$ nanocomposite catalyst using a co-precipitation approach and evaluated the oxidative degradation of RB19 dye [21]. Cui et al. employed refluxing process to synthesize manganese oxides with different crystal types (α -

MnO₂, β-MnO₂, and δ-MnO₂) and reported decolourization of Rhodamine-B (RhB) dye at various pH levels [22].

Mechanochemical processing (MCP) is a unique bottom-up approach to synthesise a variety of nanomaterials [23-25]. It is a scalable technique utilising mechanical energy to trigger chemical reactions in a ball mill. Previously, a report by Liu et al. demonstrated the mechanochemical synthesis of MnO₂ using KMnO₄ and Mn(CH₃COO)₂ and employed H₂SO₄ to remove K⁺ to study the charge-discharge properties of MnO₂ supercapacitor [26]. However, the use of H₂SO₄ during synthesis is a considerable drawback for environment. Moreover, the particle size of resulting MnO₂ was not reported. Another report by Yang et al. demonstrated the synthesis of MnO_x via a redox reaction between Mn⁷⁺ and Mn²⁺ in a ball mill [27]. However, the end product consisted of highly agglomerated particles.

In this work, MnO₂ nanorods were synthesized via a low cost, solvent free and scalable mechanochemical route for the first time and their photocatalytic activities to degrade dyes were investigated. A mixture of KMnO₄ and MnCl₂ was milled to initiate a solid state redox reaction $2\text{KMnO}_4 + \text{MnCl}_2 \rightarrow 3\text{MnO}_2 + 2\text{KCl} + \text{O}_2$. Excess KCl was introduced in the starting powder mixture to control the particle size of MnO₂ in the product phase. As-prepared MnO₂ showed high photo-degradation efficiency towards RhB dye under the illumination of simulated sunlight at low pH. This work demonstrates a solvent free and economic fabrication method to produce MnO₂ nanoparticles with exceptional catalytic performance.

2. Experimental Procedure

2.1. Preparation of MnO₂ nanoparticles

All chemicals were used without further purification. Stoichiometric amounts of KMnO₄ (analytical grade, Univar) and MnCl₂ (99.9%, Sigma Aldrich) powders were mixed in the molar ratio of 2 : 1. KCl (Analar NORMAPUR, VWR) powder was added to this mixture as an inert diluent to ensure that the volume fraction of MnO₂ is 10% in the product phase in order to limit the agglomeration of MnO₂ [28]. All three chemicals were sealed in a steel vial with hardened steel balls of 9.2 mm in diameter. The ball to powder ratio of 10:1 was used for all milling operations. The mixture was milled for 4 hours in a SPEX 8000M mill (Spex, USA). The as-milled powder was heated at 350° C for 1 hour in air to crystallize amorphous MnO₂. The powder was washed thrice to remove KCl, with Millipore Milli-Q ultrapure water (18 MΩ cm) using an ultrasonic bath and a centrifuge. The remaining black powder was collected and dried in an oven at 50°C for 9 hours.

The composition of the powder was examined at room temperature using a D₂ Phaser X-ray diffraction system (XRD, Bruker, USA) with Cu-K α radiation. The average crystallite sizes were estimated from the diffraction peak using the Scherrer equation [29]. The nanostructure and surface morphology of the powder was investigated using a CM 300 transmission electron microscope (TEM, FEI, USA) at 300 kV and a Ultra Plus field-emission scanning electron microscope (FESEM, Zeiss, Germany) at 3 kV. The specific surface area of nanopowders was measured by the Brunauer-Emmett-Teller (BET) N₂-gas adsorption method using a TriStar 3020 (Micromeritics, USA). Prior to BET measurements, the powders were degassed at 150 °C for 24 hours. UV-vis absorption spectra were collected using a Varian Cary 60 spectrometer (Agilent, USA). Optical band gap energies were estimated by converting UV-Vis absorption spectra into Tauc plots [30].

2.2. Photocatalytic degradation of Rhodamine B

Photocatalytic degradation of RhB dye was studied to evaluate the photocatalytic activity of MnO_2 samples. A small amount of MnO_2 (8 mg) was dispersed in 50 ml of an aqueous RhB solution with a concentration of $0.0096 \text{ mg ml}^{-1}$. The pH of the solution was adjusted with HCl. A low-density polyethylene film (>85% transparent to UVA and UVB) was tightly wrapped to seal the mouth of the silica beaker for preventing the evaporation of water. Subsequently, the suspension was irradiated with simulated sunlight using a Suntest CPS+ instrument (Atlas, USA) equipped with a 1,500 W xenon lamp and a daylight reduced IR filter. The irradiation intensity was 65 W m^{-2} over the wavelength range of 300–800 nm. The aliquots (4 ml) were collected at various irradiation times and immediately centrifuged at 12,000 rpm for 10 min to remove catalyst nanoparticles from the RhB solution. The Optical absorption of the RhB solution was measured using a Cary 60 spectrophotometer (Agilent, USA) to observe the photocatalytic degradation of RhB. The degradation of RhB was also investigated without light irradiation otherwise under the same conditions for both amorphous and crystalline samples.

3. Result and Discussions

3.1. MnO_2 nanoparticles

Figure 1(a) shows the XRD pattern of the powder milled for 4 hours. The pattern predominantly consists of peaks corresponding to KCl (JCPDS card No 73-0380) due to the presence of excess KCl in the powder mixture. Figure 1(b) represents the XRD pattern of the

powder after washing to remove KCl. The lack of well-defined sharp peaks, except two broad peaks near 13° and 37° , can be attributed to the amorphous-like nature of the powder. Figure 1(c) represents the XRD pattern of the powder after heat treatment at 350°C for 1 hour in air and subsequently washed, where the diffraction peaks can be indexed to $\alpha\text{-MnO}_2$ (JCPDS card No 72-1982).

Figures 2 (a) and (c) show a typical SEM and TEM images of MnO_2 samples without heat treatment. The sample consisted of irregular-shaped particles and few needle-like structures of less than 10 nm in diameter. The inset in Figure 2(c) is a selected area electron diffraction pattern, showing rings with only few spots. The result indicates poor crystalline nature of the MnO_2 , consistent with the XRD data (Fig. 1b). The few spots on the diffraction rings may stem from the needle-like structure visible in the SEM image. The needle-like structure was not observed in TEM images, possibly due to the scarcity of the structure. Figures 2 (b) and (d) show the respective SEM and TEM images of crystalline MnO_2 that was obtained after heat treatment. The sample consisted of only nanorods of about 15 nm - 20 nm in diameter with varying lengths. The inset in Figure 2(d) shows lattice fringes running parallel to the surface of a nanorod along the length direction. The lattice spacing between adjacent planes was ~ 0.7 nm corresponding with the distance between two (110) crystal planes of $\alpha\text{-MnO}_2$. The average crystallite size estimated using the diffraction peak corresponding to (110) crystal plane at 13° was 16 nm. This value is in good agreement with the observed diameter of nanorods. The BET surface areas of the amorphous and crystalline MnO_2 powders were $204\text{ m}^2\text{ g}^{-1}$ and $76\text{ m}^2\text{ g}^{-1}$, respectively.

Figure 3 shows the Tauc plot in the form of $(\alpha h\nu)^2$ versus $h\nu$ for (a) amorphous and (b) crystalline MnO_2 , where h is the Planck's constant, ν is the photon's frequency, and α is the

absorption coefficient. The Tauc plot was made from the optical absorption spectra shown in Figure S1. The intercept of the straight line with the x-axis (energy axis) suggests an optical band gap of 2.54 eV and 2.33 eV for amorphous and crystalline MnO₂, respectively.

3.2. Dye degradation

Figures 4 (a) and (b) show the dye degradation rates at different pH levels upon light irradiation for amorphous and crystalline MnO₂, respectively. The original optical absorption spectra of RhB dye solutions are shown in Figure S2. In the y-axis of Figure 4, C is the absorbance value of RhB at each irradiation time at the wavelength of 554 nm and C₀ is the absorbance value at the same wavelength before the irradiation. At pH 7, only 4 % of the dye was decolorized within 120 min by the crystalline sample. On the other hand, the amorphous sample degraded nearly 28 % of the dye within the same exposure time. For the crystalline sample, lowering the pH to 5 resulted in the degradation efficiency exceeding 47% in 120 min of irradiation. At this pH level, the amorphous sample degraded the dye almost completely in 34 min. At pH 3, the absorption peaks corresponding to the dye diminished in 30 min and 49 min with the amorphous and crystalline MnO₂, respectively.

Figures 4 (c) and (d) show the dye degradation rates at different pH levels in the dark without light irradiation, for amorphous and crystalline MnO₂, respectively. The original optical absorption spectra of RhB dye solutions are shown in Figure S3. The changes in peak shape and peak position at 450 – 600 nm indicate the removal of RhB by redox-mediated degradation, not by adsorption alone. At pH 7, after 120 min of mixing time, only 2% of RhB was degraded by the crystalline sample. In contrast, 26% of the dye was degraded by the amorphous sample. Further lowering the pH to 5 resulted in 40% degradation of the dye by

crystalline sample. At this pH, the amorphous sample degraded almost entire dye in just 60 min. At pH 3, the amorphous sample degraded 95% of the dye in 48 min, which is a significantly higher degradation rate than that of the crystalline MnO_2 which could only degrade 73% of the dye in 120 min.

Upon the irradiation of simulated sunlight, the dye degradation in the presence of crystalline and amorphous MnO_2 showed linear relationships between $\ln(C/C_0)$ and irradiation time, indicating pseudo-first order kinetic models for the degradation process. This is a typical characteristic of photocatalytic reactions [31]. Under the dark condition, the dye removal proceeded quickly in the short time span after the mixing of MnO_2 into the dye solution and then afterwards followed pseudo first order kinetics throughout the degradation process (Figure S3). Similar behaviours in the initial stage of mixing MnO_2 with dye solutions were reported previously [32, 33]. One possible explanation for this behaviour is the high rate of adsorption of dye molecules on the surface of MnO_2 nanoparticles after mixing [34, 35]. This phenomenon was more pronounced for amorphous samples than crystalline samples (Figure 4), due mainly to the higher specific surface area of the amorphous samples.

The pseudo first order degradation rate constant (k , min^{-1}) at each pH value was calculated by fitting the data in Figure 4 with the following equation [36];

$$\ln(C/C_0) = -k \cdot t \quad (1),$$

where t (min) is the irradiation time under light or mixing time under the dark condition. Due to the fast adsorption of the dye during the initial stage of mixing, $\ln(C/C_0)$ values are fitted only to the data points with $t > \sim 10$ min. Figure 5 depicts the rate constants in the presence of amorphous and crystalline MnO_2 as a function of pH. In order to elucidate the effect of crystallinity, the rate constants in Figure 5 are normalised with the specific surface areas of

the samples. For both amorphous and crystalline MnO_2 , the photocatalytic activity was higher under lower pH conditions. This can be attributed to that fact that, in aqueous solution under pH less than 7, Mn^{4+} can change to Mn^{2+} to form strongly oxidizing hydroxyl radicals with help from H^+ ions [19].

As evidenced in Figure 5, light irradiation accelerated the degradation rate for both amorphous and crystalline MnO_2 , due to the photo-induced free radicals generated by the photocatalytic activity of MnO_2 . Under pH 3 condition, light illumination enhanced the dye-degradation ability significantly more for crystalline samples than for amorphous samples. This difference can be attributed to the fact that amorphous samples have a higher number of defects that act as recombination sites for photo-generated charges to suppress photocatalysis[37].

It is interesting to note that, under the dark condition, amorphous MnO_2 showed much higher ability to decompose RhB than crystalline MnO_2 . Even under pH 5 condition, where crystalline MnO_2 showed almost no degradation activity, amorphous MnO_2 exhibited strong ability to decompose RhB. The outstanding activity of amorphous MnO_2 was also reported by Iyer et al. on the selective photo-oxidation of 2-propanol, destruction of toxic organic compounds and water-oxidation [38]. They attributed the high activity to the ease of lattice oxygen mobility and excess surface oxygen in the amorphous structure. Robinson et al. compared the photo-oxidation of water by various manganese oxides with different crystal structures and argued that weaker and flexible Mn-O bonds are more catalytically reactive whereas stronger and rigid Mn-O bonds such as in crystalline MnO_2 do not foster the high oxidation potential for O_2 formation [39]. One can hypothesise that, amorphous MnO_2 is more reactive than crystalline MnO_2 due to the higher number of defects such as dangling

bonds and oxygen vacancy sites [40] as well as weaker Mn-O bonds on the surface. However, one should not dismiss the possibility of reductive dissolution reaction to decompose RhB [22].

Nonetheless, only few reports have been published on the catalysis of amorphous MnO_2 to date and further efforts are required to gain a full understanding of its mechanism [38].

4. Conclusion

Dry mechanochemical synthesis is of great importance for producing a variety of nanostructures without using hazardous organic solvents. MnO_2 nanorods were successfully synthesized using a mechanochemical solid-state displacement reaction for the first time. During the ball milling of a $2\text{KMnO}_4 + \text{MnCl}_2 + \text{KCl}$ starting powder mixture, amorphous MnO_2 nanoparticles were formed. After subsequent calcination at 350°C for 1 hour in air, the amorphous MnO_2 was transformed into crystalline MnO_2 nanorods with diameters of less than 20 nm. Both amorphous and crystalline phases exhibited the ability to degrade dye pollutants at low pH under the dark condition. Irradiation of simulated sunlight accelerated the decomposition reaction for both amorphous and crystalline samples. Amorphous MnO_2 showed higher activities than crystalline MnO_2 under the dark conditions, possibly due to the presence of high energy dangling bonds on the surface. Amorphous MnO_2 could effectively degrade the dye even without exposure to light under near-neutral pH conditions, which is a potential advantage over other photocatalysts in the large-scale treatment of industrial effluents in a simple, economical and eco-friendly way.

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List of Figures

Figure 1: XRD patterns of (a) as-milled powder milled for 4 hours, (b) after subsequent washing and drying, and (c) powder milled for 4 hours followed by heat treatment at 350°C, washing and drying.

Figure 2: FESEM micrograph of (a) amorphous MnO_2 and (b) crystalline MnO_2 ; TEM micrograph of (c) amorphous MnO_2 and (d) crystalline MnO_2 . The inset in image (c) shows a selected area electron diffraction pattern of the same area. The inset in image (d) shows lattice fringes running parallel to the surface of a nanorod along the length direction.

Figure 3: Tauc plot of (a) amorphous MnO_2 and (b) crystalline MnO_2 nanowires.

Figure 4: Pseudo-first order kinetic models for the degradation process at various pH values for (a) amorphous MnO_2 , (b) crystalline MnO_2 upon irradiation of light, and (c) amorphous MnO_2 and (d) crystalline MnO_2 without light irradiation.

Figure 5: Dye-degradation rate constant (K) normalised with specific surface area (SSA) at various pH levels for amorphous and crystalline MnO_2 with and without light irradiation.