Facile bile salt-induced synthesis of porous MnO_2 nanoflowers: applications in dye removal and oxidation

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Abstract

MnO_2 is an important functional oxide with wide applications such as in the oxidation of benzylic and allylic alcohols, as an electrode material for supercapacitors, in dyes removal *etc.* Herein, we demonstrate a simple, bile-salt induced synthesis of porous MnO_2 at neutral pH from potassium permanganate. By tuning the reaction conditions we obtained porous $\delta\text{-MnO}_2$ with high surface area which adsorbed cationic organic dyes with high efficiency. Because of its high reactivity, we also observed higher yields in standard oxidation reactions as compared to commercial MnO_2 . The outstanding dye adsorption and oxidation abilities coupled with the simple method of preparation can make this material useful for practical applications such as for wastewater treatment.

Graphic abstract

Keywords Porous · Nanoflowers · Adsorption · Cationic dyes · Oxidation · High surface area · Adsorption isotherm · Adsorption kinetics

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1 Introduction

Manganese dioxide (MnO_2) is a well-known transition metal oxide used as a dye adsorbent [1], as an oxidant for allylic and benzylic alcohols [2–5], in pseudocapacitors [6], in ozone decomposition [7], etc. MnO_2 exhibits structural flexibility and exists in various polymorphic forms such as α , β , γ (possessing chain-like tunnel-type), δ (layered type) and λ (spinel-type) [1], based on the interlinking configuration of the MnO_6 octahedra. Out of all these forms, the δ form which has a layered type structure (birnessite), is known as one of the most reactive polymorphs [8]. The natural source of MnO_2 is the mineral *pyrolusite*, is a poor adsorbent as well as a poor oxidizing reagent [9]. Freshly prepared ‘active’ MnO_2 is typically non-stoichiometric (generally MnO_x , $1.93 < x < 2$), with a negative surface charge due to the presence of lower valent Mn species, probably Mn(III) and Mn(II) [10]. This material is effective for the removal of cationic dyes and has also been used for other applications [1–4, 6, 7].

The activity of MnO_2 is directly related to its effective surface area. MnO_2 prepared by many reported methods has low surface area [1, 11, 12], and therefore poor adsorption and oxidation ability. There are numerous methods for the preparation of MnO_2 such as self-reacting microemulsion [13], precipitation [14], hydrothermal [15], room temperature solid-state reaction [16], sonochemical [17], using rotar static reactor [18], etc. Among all these, hydrothermal method is widely used because of its simplicity and reliability to tune the size and morphology of the material. MnO_2 nanoparticles are usually prepared by using KMnO_4 as a precursor and inorganic compounds such as HCl [19], $\text{K}_2\text{S}_2\text{O}_4$ [20], Mn^{2+} , KBH_4 [21], etc. as reducing agents. However the hydrothermal method is sometimes problematic because of the use of excess acid or base which is not environmentally benign [22]. Some organic compounds such as formamide [23], fumaric acid [24], aniline [25], glucose [1], etc. have also been used as reducing agents.

Recently, MnO_2 have been prepared by reduction of KMnO_4 with $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ via a hydrothermal method and used for catalytic oxidation of HCHO [26], ozone decomposition [27], etc.

Wang and coworkers prepared α - MnO_2 nanorods using KMnO_4 under acidic conditions without any Mn^{2+} precursor via a hydrothermal method [28]. Saito and coworkers prepared nanoporous MnO_2 by solution plasma method using KMnO_4 and three different sugars (glucose - G, fructose - F, and sucrose - S) as inducers and observed porous MnO_2 (G- MnO_2 , F- MnO_2 , S- MnO_2), which were used for the removal of cationic organic dye (methylene blue). BET surface area of F- MnO_2 was higher which showed the highest dye removal efficiency [1].

Moreover, other organic compounds such as oleic acid [29], and ascorbic acid [30] have also been used as the inducers and reducing agent for the preparation of MnO_2 .

Shao et al. synthesized reduced graphene oxide/ MnO_2 composite that showed higher removal efficiency of methylene blue than that of bare MnO_2 [31]. In 2017 Jana et al. prepared MnO_2 on the surface of aluminosilicate clay nanotubes and used the resulting material for the degradation of organic dyes by irradiation with sunlight (60 min) or UV (120 min). They observed higher rates of degradation with sunlight than UV, and a control experiment showed negligible degradation under dark condition [32]. Furthermore, He et al. recently prepared MnO_2 nanosheets on montmorillonite via the hydrothermal method and used the product to efficiently remove methylene blue from an aqueous system. Montmorillonite and carbonaceous materials are often used to coat MnO_2 as they can improve the adsorption capacity and redox ability for organic pollutants [33].

In this work, we present a one-step hydrothermal synthesis of nanoflower shaped porous MnO_2 with high surface area using KMnO_4 and a bio-surfactant, sodium cholate (NaCh , a bile salt) (Fig. 1). The resulting MnO_2 was used directly (without coating on carbonaceous or silicate mineral) for highly efficient adsorption of cationic organic dyes - methylene blue (MB) and rhodamine 6G (Rh6G) under conditions just within 30 min of contact with the dye.

Oxidation reactions with MnO_2 are simple to perform but the reproducible preparation of activated MnO_2 with high activity can be difficult and time-consuming [34]. The MnO_2 prepared by us was further utilized for the oxidation of a few benzylic alcohols. Our studies showed that the

Fig. 1 Schematic representation for the preparation of MnO_2

MnO₂ prepared by our method is superior to commercial MnO₂, and MnO₂ prepared by many other methods.

2 Experimental section

2.1 Materials

Potassium permanganate (KMnO₄, 99.0%, Ranbaxy Fine Chemical Ltd., India), sodium cholate (NaCh, Sigma Aldrich, ≥99%), methylene blue (MB, 96%, Fischer Scientific), rhodamine 6G (Rh6G, 95%, Sigma Aldrich), methyl orange (MO, Fluka) cinnamyl alcohol (Sigma Aldrich), 9-anthracenemethanol (9-AC, Fluka), biphenyl-4-carboxaldehyde (BPA, Sigma Aldrich), 2-iodobenzylalcohol (Fluka), 2-hydroxybenzylalcohols (Sigma Aldrich), manganese (IV) oxide [MnO₂ (SA); Sigma Aldrich, activated, ~85%, <10 μm], manganese (IV) oxide [MnO₂ (TB); Thomas Baker, tech. 85%], 4-methyl-5-imidazolemethanol hydrochloride (Sigma Aldrich) and benzhydrol (SRL) were used as received.

2.2 Preparation of MnO₂

MnO₂ was prepared using KMnO₄ and NaCh via high temperature for 2 h (HT-2-MnO₂), 8 h (HT-8-MnO₂), 16 h (HT-16-MnO₂) and by room temperature (23 °C) method for 9 h (RT-9-MnO₂). For high temperature method, a mixture of aqueous KMnO₄ (79 mg, 0.5 mmol in 5 mL) and NaCh (86.1 mg, 0.2 mmol in 5 mL) was stirred at 120 °C in a sealed glass tube for 2 h, 8 h, 16 h respectively for HT-2-MnO₂, HT-8-MnO₂, HT-16-MnO₂. For RT-9-MnO₂ preparation, a mixture prepared as above was stirred in a 25 mL round bottomed flask at room temperature for 9 h. The precipitate obtained in all cases was separated by centrifugation, washed with water (3 × 10 mL) and dried in vacuum at 80 °C.

2.3 Characterization

Structural features of the MnO₂ were characterized by X-ray powder diffraction (PXRD) using Bruker ADVANCE X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å, and a NaI dynamic scintillation detector. XRD pattern was collected in the range of 2θ = 5–90°. Morphology of the material was observed using a scanning electron microscope (FEI Sirion XL30 FEG SEM), transmission electron microscopy and EDX (JEOL 2100F TEM). For TEM imaging, a small amount of the solid powder was dispersed in water and then the suspension was drop-cast on the carbon-coated grids followed by high vacuum drying. Absorption spectra of aqueous solutions of MB and Rh6G were recorded on a Shimadzu UV-3600 spectrophotometer at room temperature using

quartz cuvettes of 10 mm path length. The nitrogen adsorption/desorption isotherms were measured with BELSORP MAX at 77 K to analyse the physical properties of the adsorbents. The specific surface area was determined by the Brunauer-Emmet-Teller (BET) method and pore size was determined by Barrett-Joyner-Halenda (BJH) plot. Thermogravimetric analysis (TGA) was done using a METTLER thermogravimetric analyser in the range of 32 °C to 1000 °C in N₂ with a heating rate of 10 °C/min. Zeta potential measurements were done on a Zetasizer Nano ZS.

3 Results and discussion

Sodium cholate is a facially amphiphilic bio-surfactant with a steroidal backbone having three hydroxyl groups on its concave side and three methyl groups on its convex side. Out of these three hydroxyl groups, the 7-hydroxyl group of this molecule is prone to oxidation by aqueous KMnO₄, which reduces the KMnO₄ to MnO₂ [35]. Upon reduction of KMnO₄ with NaCh, a brownish-black precipitate was obtained which was washed with water and dried to furnish MnO₂ powder. Completion of the reaction was confirmed visually (purple to colourless), and by monitoring the absorbance spectra of the supernatant from the reaction mixture also (Fig. S1). It was observed that at room temperature it required 9 h for the completion of the reaction (RT-9-MnO₂), whereas at 120 °C it required only 2 h (HT-2-MnO₂). However, we optimized the reaction time to 16 h (HT-16-MnO₂), as the measured surface area was significantly higher when reaction time was 16 h at 120 °C. The rate of reduction of KMnO₄ with NaCh was systematically studied. The room temperature method was used for this study because of the slow kinetics of reaction during RT-9-MnO₂ preparation. From the collected data, the kinetics for KMnO₄ reduction by NaCh was observed to be first order with respect to KMnO₄ (Fig. S2).

Furthermore, the fate of sodium cholate to sodium 7-ketocholate was confirmed by HRMS and ¹H NMR (Figs. S3 and S4). PXRD pattern of the all synthesised MnO₂ are shown in Fig. 2, four peaks at around 2θ = 12.4°, 24.9°, 37° and 66° indexed as (001), (002), (−111), (020) correspond to the sodium birnessite-type MnO₂ with C_{2/m} space group (Table S1) [36]. Observed broadening of the peaks might be due to the amorphous nature of the material [37]. It has a layered structure made up of edge-shared MnO₆ octahedra having Na⁺/K⁺ and H₂O molecules inserted into the interlayer regions [36].

The morphology of the HT-16-MnO₂ was analysed by FE-SEM and TEM. SEM images (Fig. 3a, b) showed agglomerated spherical particles of 60–90 nm in diameter. From TEM, a 'nanoflower' type morphology of 90–100 nm was observed (Fig. 3c). HRTEM (Fig. 3d)

Fig. 2 XRD patterns of the synthesized MnO_2

showed lattice fringe spacing of 0.24 nm which corresponded to the (-111) lattice plane of birnessite MnO_2 [38].

However the resolved lattices indices from HRTEM (Fig. 3d) and lattice rings from SAED pattern (Fig. 3d inset) indicated the polycrystalline nature of the material. Furthermore, the negative surface charge was confirmed by zeta potential measurement of HT-16- MnO_2 powder dispersed in water (Fig. S6). To find out the thermal stability of HT-16- MnO_2 , thermogravimetric analysis (TGA) was done (Fig. 4).

Upon heating from 32 to 200 °C, a weight loss of nearly 15% was observed due to the evaporation of surface water, and water present in the lattice of the nanostructured material. Further, weight loss of less than 1% upon heating from 200 to 340 °C is probably due to the loss of the residual organic content. Above 340 °C, weight loss observed is attributed to the phase transformation from MnO_2 to Mn_2O_3 or Mn_3O_4 [39].

For an adsorbent, surface area and porosity are very important properties for applications. A higher surface area provides more vacant sites for the adsorbates and will have higher catalytic efficiency. Surface area and porosity of the material were examined by N_2 adsorption/desorption isotherm analysis. The specific surface area of the material was determined by the BET method whereas

Fig. 3 (a, b) FE-SEM image of HT-16- MnO_2 at 500 nm scale and 200 nm scale. (c) TEM image of HT-16- MnO_2 at 200 nm scale and (d) HRTEM image along with the corresponding SAED pattern of the HT-16- MnO_2

Fig. 4 TGA plot of the HT-16-MnO₂

the BJH method was used for the determination of pore size distribution. BJH plot (Fig. 5b) revealed the highest dV_p/dr_p peak at $r_p = 1.6$ nm in the distribution range of 1.2–8 nm which confirmed the porous structure consisting of mesopores having mean pore radius, $r_p = 2.5$ –3.6 nm (mean pore diameter, $D_p = 5.1$ –7.2 nm) in HT-16-MnO₂, HT-8-MnO₂ and HT-2-MnO₂. However, for MnO₂ prepared by high temperature method (HT-2-MnO₂, HT-8-MnO₂ and HT-16-MnO₂), the capillary condensation takes place at the very low relative pressure (p/p_0) region indicated the microporosity nature of the material. Additionally the peaks at around 1.6 nm suggested the greater population of micropores compared to mesopores but predominantly mesoporous nature was observed for RT-9-MnO₂. The surface area of the HT-16-MnO₂ determined by BET method was found to be 279.5 m² g⁻¹. This high surface area is in accordance with the highly porous nature of the material. In case of HT-2-MnO₂ and HT-8-MnO₂ the measured surface area were 112 m² g⁻¹ and 242 m² g⁻¹ with the mean pore diameter of 7.2 nm and 5.1 nm, respectively (Table 1).

Table 1 Values obtained from the porosity experiments

Sample	BET surface area (m ² g ⁻¹)	Mean pore diameter (nm)	Total pore volume (cm ³ g ⁻¹)
RT-9-MnO ₂	42	5.9	0.062
HT-2-MnO ₂	112	7.2	0.202
HT-8-MnO ₂	242	5.1	0.258
HT-16-MnO ₂	279.5	5.5	0.386

However, MnO₂ prepared at room temperature (RT-9-MnO₂) showed significantly lesser surface area of 42 m² g⁻¹ with a mean pore diameter of 5.9 nm. The much lower surface area for this sample might be due to agglomeration of material observed in the TEM imaging (Fig. S7). In brief, the surface area of MnO₂ was in the order HT-16-MnO₂ > HT-8-MnO₂ > HT-2-MnO₂ > RT-9-MnO₂.

4 Applications

4.1 Dye adsorption: experimental

Methylene Blue (MB) adsorption: MB solutions (4 mL of 10 mg/L, 31.3 μM) were stirred with 2.4 mg of HT-16-MnO₂ and commercial MnO₂ such as MnO₂ (TB) and MnO₂ (SA) in three separate test tubes (15 × 125 mm) for 30 min at room temperature. The solutions were filtered through a 0.2 μm nylon membrane and absorption spectra were recorded. In a separate experiment, 4 mL aqueous solutions of various concentrations of MB (20–210 mg/L) were individually stirred with 2.4 mg of HT-16-MnO₂ for 30 min and the filtrates obtained were used for quantifying the adsorption of MB by HT-16-MnO₂ by absorption spectra.

Rhodamine 6G (Rh6G) adsorption: Rh6G (4 mL of 6 mg/L, 12.5 μM) solutions were separately stirred with the three samples of MnO₂ as described above. Additionally,

Fig. 5 (a) N₂ adsorption/desorption isotherms and (b) pore size distribution plot of the HT-16-MnO₂ (black), HT-8-MnO₂ (red), HT-2-MnO₂ (blue) and RT-9-MnO₂ (green)

aqueous solutions of Rh6G (4 mL) of various concentrations (30 to 120 mg/L in increments of 30 mg/mL) were individually stirred with 2.4 mg of HT-16-MnO₂ for 30 min as described above for MB.

The dyes removal efficiency (%) was calculated as described in the Eq. (1)

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

The adsorption capacity (q_e) in μg per mg of HT-16-MnO₂ was calculated by the expression in Eq. (2)

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentration of the dye (in mg/L) respectively. V is the volume of the solution in litre and W is the weight of the HT-16-MnO₂ used in g.

4.2 Methylene blue adsorption

The characteristic absorption peak at 664 nm (Fig. S8a) was used to estimate the concentration of MB. Figure 6a shows that the removal efficiency for MnO₂ (TB), MnO₂ (SA) and

HT-16-MnO₂ of 7%, 70%, and $\geq 99\%$ respectively. We conclude that the higher removal efficiency by HT-16-MnO₂ is primarily due to its porous nature and high surface area. At lower initial concentration of MB dye ($C_0 = 10, 20, 30, 60$ and 90 mg/L), complete removal of dye was observed after stirring for 30 min with HT-16-MnO₂.

Furthermore, removal efficiency of MB solution (4 mL) at higher concentrations was performed by stirring 2.4 mg of HT-16-MnO₂, with 120, 150, 180, 210 mg/L of aqueous MB solutions (4 mL). Removal efficiency increased with initial concentration of dye (C_0) used till 120 mg/L after which removal efficiency remain constant. From the data (Fig. 6b), it was estimated that 1 mg of HT-16-MnO₂ could efficiently remove $194 \pm 15 \mu\text{g}$ of MB from aqueous solution (nearly 19% w/w). A comparison of dye adsorption capacity of the HT-16-MnO₂ with reported methods are shown in the Table S2.

4.3 Rhodamine 6G adsorption

Rh6G shows a characteristic absorption peak at 526 nm (Fig. S8b), which decreases upon adsorption by MnO₂. Changes in this absorbance peak was used to estimate the concentration of Rh6G dye. Figure 7a shows removal

Fig. 6 (a) Removal efficiency (in μg) of MB (4 mL, 10 mg/L) by HT-16-MnO₂ and its comparison with MnO₂ purchased from Thomas Baker [MnO₂ (TB)] and Sigma Aldrich [MnO₂ (SA)] (2.4 mg each) (b) MB removal efficiency at various concentrations of MB (4 mL) by HT-16-MnO₂ (2.4 mg)

Fig. 7 (a) Removal of Rh6G (4 mL of 6 mg/L) by HT-16-MnO₂ (2.4 mg) and comparison with commercial MnO₂ such as MnO₂ (TB) and MnO₂ (SA) (b) Rh6G removal efficiency at various concentration of Rh6G (4 mL) by HT-16-MnO₂ (2.4 mg)

efficiency for MnO_2 (TB), MnO_2 (SA) and HT-16- MnO_2 of 3%, 25%, and $\geq 99\%$ respectively.

Furthermore, removal efficiency of Rh6G solution (4 mL) at various concentrations was performed by stirring 2.4 mg of HT-16- MnO_2 , with 20, 30, 60, 90 and 120 mg/L of aqueous Rh6G solutions (4 mL). There was increase in removal efficiency of Rh6G with increase in dye Rh6G concentration that achieved saturation at comparatively less concentration of Rh6G (60 mg/L) to that of MB (120 mg/L). From the data (Fig. 7b), it was estimated that 1 mg of HT-16- MnO_2 could efficiently remove 94 ± 25 μg of Rh6G from aqueous solution (nearly 10.6% w/w).

4.4 Selectivity of dye adsorption by MnO_2

Due to the negative charged surface of HT-16- MnO_2 , it was initially tested for adsorption of cationic dyes only. To confirm its selectivity towards cationic dyes, methyl orange (MO, an anionic dye) was tested (Fig. S9a) showed negligible (0–8%) adsorption of MO (10 mg/L, 10 mL) by 6 mg of MnO_2 (HT-16- MnO_2 , MnO_2 (TB), MnO_2 (SA)). Further, an experiment with a mixture of anionic (MO) and cationic dye (MB) was carried out and selective adsorption of cationic dye from the aqueous solution was observed (Fig. S9c). Furthermore, to check the selectivity towards a

mixture of cationic dyes, a mixture of two cationic dyes, Rh6G and MB was chosen. Equal concentrations (202 μM , 6 mL) of both the dyes in water were stirred with HT-16- MnO_2 (1.8 mg).

It was observed that (Fig. 8) 1.8 mg of HT-16- MnO_2 adsorbed 158 μg (55 μM) out of 580 μg of Rh6G and 225 μg (117 μM) out of 388 μg of MB. Our earlier results showed that 1.8 mg of HT-16- MnO_2 could remove 169 μg of Rh6G and 349 μg of MB when treated with these dye solutions independently. However, when both dyes were present, a (total) higher removal efficiency was observed which is possibly due to specific adsorption of the two different dyes in the porous network of a specific size.

4.5 Adsorption isotherm

Langmuir and Freundlich model were used to describe the relationship between the amount of dye adsorbed per unit weight of the adsorbent (q_e , $\mu\text{g}/\text{mg}$) and the concentration of these dyes in bulk solution at equilibrium (C_e , mg/L). The adsorption isotherms of MB and Rh6G by HT-16- MnO_2 along with fitted models are shown in Fig. 9 and the calculated isotherm parameters are summarized in Table 2. The Langmuir and Freundlich

Fig. 8 (a) Absorption spectra before and after treatment with HT-16- MnO_2 (1.8 mg) of mixed MB and Rh6G dye (405 μM of Rh6G, 3 mL, 582 μg + 405 μM of MB, 3 mL, 388 μg) (b) Bar graph showing the concentration of total dye in the solution in terms of μg and its adsorption

Fig. 9 Langmuir (black) and Freundlich (green) adsorption isotherms curves of (a) MB (10–210 mg/L) and (b) Rh6G (10–120 mg/L) by HT-16- MnO_2 for 30 mins

Table 2 Isotherm parameters for the adsorption of MB and Rh6G on HT-16-MnO₂

	$q_{\max}$ (μg/mg)	Langmuir Isotherm		Freundlich Isotherm		
		K_L (L/mg)	R^2	K_f	n	R^2
MB	198.51	4.54	0.949	105.69	6.27	0.766
Rh6G	93.87	1.03	0.980	47.57	5.34	0.949

adsorption isotherm models in its non-linear form are expressed in Eqs. (3) and (4) respectively.

$$q_e = \frac{q_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (3)$$

where q_e is the equilibrium adsorption capacity of adsorbent in μg/mg and $q_{\max}$ is the maximum adsorption capacity by adsorbent, C_e is the dye concentration in mg/L at equilibrium and K_L is the Langmuir adsorption equilibrium constant.

$$q_e = K_f \cdot C_e^{1/n} \quad (4)$$

where K_f is the Freundlich isotherm constant associated with the index of adsorption capacity and n is the adsorption intensity of the adsorbent.

Comparing the value of R^2 in Table 2, it can be concluded that Langmuir model describe the adsorption data for both MB and Rh6G on HT-16-MnO₂ that justify the monolayer adsorption on the homogenous adsorbent surface. Monolayer adsorption capacity obtained from Langmuir isotherm for MB (198.51 μg/mg, 19.8% w/w) and Rh6G (93.87 μg/mg, 9.4% w/w) on HT-16-MnO₂ is in well agreement with the calculated adsorption capacity. The essential feature of the Langmuir isotherm is expressed by a dimensionless quantity, R_L (separation factor), shown in Eq. (5) [40].

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

where C_0 is the maximum initial concentration of dyes. R_L values dictates the nature of adsorption, if $0 < R_L < 1$, the adsorption process is favourable, $R_L > 1$ indicates the unfavourable adsorption and R_L being equal to 0 indicates the irreversible adsorption nature, on the hand value equal to unity indicates the linear adsorption process. For MB and Rh6G adsorption the calculate R_L values 0.0010 and 0.0080 respectively indicated the favourable adsorption.

4.6 Adsorption kinetics

Rate of dyes adsorption on HT-16-MnO₂ was determined by increase in the dye adsorption capacity with over a period of 25–30 min (Fig. 10). An equilibrium for the adsorption of for both the dyes was attained within 20 min

used. This suggested the high affinity of HT-16-MnO₂ for the adsorption of MB and Rh6G. The observed rapid adsorption in the initial stage is essentially due to the large number of unoccupied vacant sites on the surface of adsorbent. The adsorption kinetic data was analysed by linear form of Lagergren's kinetic model (pseudo-first order), using Ho's kinetic model (pseudo second order) and intraparticle diffusion model. A poor fit as observed by the low correlation coefficient (R^2) for both pseudo-first order and intraparticle diffusion model explain the invalidity of these models to explain the rate of adsorption for this system (Fig. S10, Table S3). However, the high correlation coefficient observed for pseudo-second order kinetic model indicates the best model to describe the adsorption kinetics of MB and Rh6G on HT-16-MnO₂ (Fig. 10, Table 3). The linear form of the pseudo-second order kinetic model is expressed by the Eq. (6)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where k_2 is the pseudo-second-order rate constant (mg μg⁻¹ min⁻¹), q_e and q_t are the dye adsorption capacity at equilibrium and at time (t). Upon plotting t/q_t versus t yield a straight line with a slope $1/q_e$ and intercept $1/k_2 q_e^2$ from which q_e and k_2 was calculated. From these initial adsorption rate V_0 (μg mg⁻¹ min⁻¹) was calculation by the Eq. (7)

$$V_0 = k_2 q_e^2 \quad (7)$$

4.7 Oxidation reaction by prepared HT-16-MnO₂

MnO₂ has been widely used for the oxidation of allylic and benzylic alcohols [3, 4]. We explored the application of high surface area HT-16-MnO₂ for the oxidation of benzylic and allylic alcohols. In general, to a 5 mL of round-bottom flask, 0.2 mmol of the benzylic or allylic alcohol was stirred with 0.3 mmol (30.7 mg.) of HT-16-MnO₂ in an argon atmosphere using an appropriate solvent (3 mL). Reaction progress was monitored by thin-layer chromatography. After completion of the reaction, the reaction mixture was filtered through a nylon membrane to remove the HT-16-MnO₂ and the filtrate was evaporated to dryness. The dried filtrate was either subjected for ¹H NMR

Fig. 10 Adsorption kinetics of MB (a) and Rh6G (c) on HT-16-MnO₂. Linear pseudo-second order kinetics model for MB (b) and Rh6G (d) adsorption on HT-16-MnO₂

Table 3 Rate constants and correlation coefficients of pseudo-second order kinetic model

Dyes	q_e (μg mg ⁻¹)	k_2 (mg μg ⁻¹ min ⁻¹)	V_0 (μg mg ⁻¹ min ⁻¹)	R^2
MB	204.9	5.2×10^{-3}	218.32	0.9999
Rh6G	94.34	2.9×10^{-2}	258.99	0.9996

Table 4 Optimization of reaction conditions

Entry	Solvent	Temperature (°C)	Time (h)	Conversion ratio
1	acetonitrile	55	4	55
2	chloroform	55	4	29
3	1,4-dioxane	55	4	20
4	toluene	55	4	86
5	toluene	105	2	≥98

^aConversion ratio calculated based on ¹H NMR. (SI Eq. 3)

Fig. 11 General scheme for the oxidation of alcohols by MnO₂

to find out the ratio of substrate and product in the crude mixture or was purified (if impure) using column chromatography and isolated yield of the product was calculated. Calculation of NMR conversion for benzhydrol is described in solvent optimization section in supporting information (SI). Oxidation of benzhydrol was done in toluene, acetonitrile, chloroform and 1,4-dioxane to optimize the solvent for the reaction by keeping the other reaction conditions same (1.5 equivalent HT-16-MnO₂, 55 °C, 4 h) in all cases. The conversion^a was found to be highest (86%) in toluene (Table 4, entry 4), whereas acetonitrile, chloroform, and

1,4-dioxane showed 55%, 29%, 20% of conversion respectively (Table 4, entry 1–3) (Fig. 11).

Further, the optimum reaction temperature was studied for oxidation reaction of benzhydrol with 1.5 equivalent of HT-16-MnO₂ in toluene at 55 °C and 105 °C. Reaction at lower temperature (55 °C) furnished (Table 2, entry 4) 86% of conversion when stirred for four hours but at a higher temperature (105 °C) nearly complete conversion (≥98%) was observed after two hours of reaction (Table 5, entry 5). Substrate scope was explored with various benzylic alcohols (Table 5, entry 3a–7a) and an allylic alcohol (Table 5, 8a) at 105 °C in toluene. Good to moderate yield were obtained in all cases. Oxidation reaction in case of

Table 5 Oxidation reactions of alcohols with 1.5 eq. of HT-16-MnO₂

Substrate	Solvent, Temperature	Time	Product	Yield/NMR ^a conversion
3a	Toluene, 105 °C	6 h	3b	91%
4a	Toluene, 105 °C	7 h	4b	83%
5a	1,4-dioxane 90 °C	16 h	5b	98% ^a
6a	C ₆ D ₆ 90 °C	7 h	6b	>99% ^a
7a	C ₆ D ₆ 90 °C	24 h	7b	80% ^a
8a	Toluene, 105 °C	13 h	8b	91%

^aConversion ratio calculated based on ¹H NMR (SI, solvent optimization, Eq. (2))

2-iodobenzylalcohol was also compared with commercial MnO₂ (SA) and conversion ratio found to be 90–92%, indicating the higher efficiency of oxidation reaction as compared to commercial MnO₂ (Figs. S12, S13, and S14).

5 Conclusion

In conclusion, we have described a simple approach for the synthesis of highly porous nanoflower shaped birnessite type MnO₂. This variety of MnO₂ has unusually high surface area and was highly efficient for the removal of cationic organic dyes. Since the MnO₂ was also found to be a

convenient and efficient reagent for the oxidation of various benzylic and allylic alcohols, this can be used for many related oxidation reactions. We are currently exploring other applications of our large surface-area HT-16-MnO₂ and these results will be reported elsewhere.

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