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# Phase tunable nickel doped $\text{Mn}_3\text{O}_4$ nanoparticle synthesis by chemical precipitation: kinetic study on dye degradation

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Nickel (Ni) doped  $\text{Mn}_3\text{O}_4$  nanoparticles (NPs) were synthesized by a quick and facile chemical precipitation technique to investigate their performance in the degradation of methylene blue (MB) in the absence of light. XRD, FESEM, TEM, AAS, XPS, and FT-IR were used for the investigation of the structural, surface morphological, and elemental composition of Ni doped  $\text{Mn}_3\text{O}_4$  NPs. XRD confirms the formation of a tetragonal phase structure of pure  $\text{Mn}_3\text{O}_4$  and 1% and 3% Ni doped  $\text{Mn}_3\text{O}_4$  NPs. However, mixed phases were found in the case of 5 to 10% Ni doped  $\text{Mn}_3\text{O}_4$  NPs. Well-defined spherical-shaped morphology was presented through FESEM. Particle sizes decreased linearly (58.50 to 23.68 nm) upon increasing the doping concentration from 0% (pure  $\text{Mn}_3\text{O}_4$ ) to 7% respectively, and then increased (48.62 nm) in the case of 10% doping concentration. TEM further confirmed spherical shaped 32 nm nanoparticles for 7% Ni doped  $\text{Mn}_3\text{O}_4$ . The elemental composition and oxidation state of the prepared NPs were confirmed by using XPS spectra. Mixed valence  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$  states were found in pure  $\text{Mn}_3\text{O}_4$  and 1% and 3% Ni doped  $\text{Mn}_3\text{O}_4$  NPs in the ratio of  $2\text{MnO}-\text{MnO}_2$ . In addition, three different oxidation states  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ , and  $\text{Mn}^{4+}$  were found in 5 to 10% Ni doped  $\text{Mn}_3\text{O}_4$  NPs. Moreover, as a dopant Ni exists as  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$  states in all Ni doped  $\text{Mn}_3\text{O}_4$  NPs. The synthesized NPs were then applied as potent oxidants for the degradation of MB at pH 3. With the increase of doping concentration to 7%, the degree of degradation was increased to 79% in the first 10 min and finally, it became about 98%. The degradation of MB follows the pseudo-first-order linear kinetics with a degradation rate of  $0.0342 \text{ min}^{-1}$ .

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## Introduction

The current intense scientific interest in nanoparticle research is concentrated on metals with remarkable viability to synthesize a broad variety of oxide compounds.<sup>1</sup> Manganese oxides have attracted a lot of interest in recent years due to their physical and chemical characteristics and their prospective uses in solar energy conversion,<sup>2</sup> ion exchange,<sup>3</sup> heterogeneous catalysts,<sup>4</sup> molecular adsorption,<sup>5</sup> electrochemical materials,<sup>6</sup> *etc.* Manganese oxides form several phases like  $\text{MnO}$ ,  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$ , and  $\text{Mn}_3\text{O}_4$ . Among them,  $\text{Mn}_3\text{O}_4$  (hausmannite, trimanganese tetraoxide) is one of the most stable mixed oxides at high temperatures and has a spinel structure.<sup>7,8</sup> Due to the presence of various oxidation states of manganese in  $\text{Mn}_3\text{O}_4$ , it

can be used as an effective catalyst for the oxidation of methane and carbon monoxide<sup>9</sup> and the selective reduction of nitrobenzene.<sup>10</sup> Additionally, it is a useful compound for reducing nitrogen oxides ( $\text{NO}_x$ ) and volatile organic compound (VOC) emissions from various origins and mitigating air pollution.<sup>11</sup> Because of its various applications, scientists are trying to enhance their activity. Many researchers have already synthesized  $\text{Mn}_3\text{O}_4$  nanoparticles by using various methods including thermal decomposition,<sup>12</sup> ultrasonic bath,<sup>13</sup> sol-gel,<sup>14</sup> co-precipitation,<sup>15</sup> microwave irradiation,<sup>16</sup> surfactant assisted,<sup>17</sup> oxidation,<sup>18</sup> and physical evaporation.<sup>19</sup> Most of these procedures involve several steps or call for a high vacuum system, a longer reaction time, and oxygen protection.<sup>20</sup> Thus, it is crucial to develop a low-cost, affordable synthetic approach. Chemical precipitation is an easy, inexpensive, and non-toxic approach compared to previously reported methods.<sup>21</sup> Keeping this fact in mind, in this study,  $\text{Mn}_3\text{O}_4$  and Ni doped  $\text{Mn}_3\text{O}_4$  nanoparticles with varying doping concentrations were synthesized for the first time using a simple chemical precipitation technique. The fundamental advantage of this technique is that it produces final particles in nanometer dimension with limited size distribution. Nowadays, doping is a promising technique for altering nanomaterials to improve their electrical,

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optical, and catalytic properties.<sup>22</sup> Doping of transition metal in Mn-oxide NPs is one of the efficient methods to produce deformed Mn(III) species, which is a crucial structural feature to increase catalytic activity.<sup>23</sup> Since Ni exhibits the highest activity as a dopant of Mn-oxide NPs, in this study Ni doped Mn<sub>3</sub>O<sub>4</sub> NPs are synthesized with varying concentrations of dopants.

During the dyeing process, about 15% of the world's total dye production is wasted and discharged in textile effluents.<sup>24</sup> Even at low concentrations, dyes pose a serious threat to aquatic life and human health because they include poisonous and harmful chemical components.<sup>25</sup> Photosynthesis in aquatic plants is impeded by dyes in water, which reduce light transmission. In addition, several of the dyes are said to be very carcinogenic and have poor biodegradability.<sup>26</sup> Methylene blue (MB) is a well-known, highly carcinogenic thiazine pollutant that has been produced and utilized in numerous industries for a variety of reasons. When ingested, it becomes a major risk to human health and has been known to cause damage to the nervous system and eyes.<sup>27</sup> Therefore, researchers are very concerned with finding a quick and efficient way to remove dye and organic contaminants from industrial effluents.<sup>28</sup> Because of their high reduction potential, manganese oxides are powerful oxidants that can easily oxidize a variety of inorganic substances including Cr(III),<sup>29</sup> Sb(III),<sup>30</sup> Co(III),<sup>31</sup> Se(IV),<sup>32</sup> and organic compounds such as catechol, quinines, substituted phenols, aromatic amines, pesticides, and explosives (e.g. TNT).<sup>33–38</sup> Many researchers studied the degradation of MB using Mn<sub>3</sub>O<sub>4</sub>, however the rate of degradation was slow and took a long time.<sup>39,40</sup> In order to overcome these limitations, Ni doped Mn<sub>3</sub>O<sub>4</sub> and Mn<sub>3</sub>O<sub>4</sub> NPs for MB degradation were prepared. However, various methods such as adsorption,<sup>41</sup> biodegradation,<sup>42</sup> chlorination, and ozonation<sup>43</sup> have been used to remove dyes. In the present study, advanced oxidation technology<sup>44</sup> has been used for comparing the oxidative degradation of MB by newly prepared different concentrations of Ni doped Mn<sub>3</sub>O<sub>4</sub> and Mn<sub>3</sub>O<sub>4</sub> nanoparticles. The primary aim of this work was to synthesize Ni doped Mn<sub>3</sub>O<sub>4</sub> and Mn<sub>3</sub>O<sub>4</sub> nanoparticles using a facile chemical precipitation technique for dye (MB) removal from textile effluents. The outcome of this research work will introduce a new dimension in nanoparticle synthesis and find a potential application for the degradation of dyes present in colored aqueous effluents from textile industries.

## Experimental

### Materials

All chemicals and solvents were purchased and utilized as obtained without further purification. Manganese(II) acetate tetrahydrate (MAct), nickel acetate tetrahydrate (NAct), sodium hydroxide (NaOH), methylene blue, and ethanol were purchased from Sigma-Aldrich Co. Germany.

### Preparation of precursor solutions

36.7635 g of MAct salt was dissolved in 500 mL de-ionized (DI) water for the preparation of 300 mM MAct solution. Similarly, 300 mM of NAct solution was prepared by dissolving 7.4652 g

NAct salt in 100 mL DI water. Furthermore, a 300 mM NaOH solution was prepared for precipitation by dissolving 12 g pellets in 1000 mL DI water. For better dissolution, all solutions were kept on continuous magnetic stirring at 450 rpm at room temperature.

### Synthesis of nanoparticles

The NPs were prepared by a simple inexpensive chemical precipitation technique.<sup>8</sup> For Mn<sub>3</sub>O<sub>4</sub> nanoparticle synthesis, 100 mL of freshly prepared MAct solution was taken in a glass beaker. Then NaOH was added at a rate of 6 drops per minute to the precursor solution with continuous magnetic stirring at 450 rpm for allowing precipitation at room temperature. After complete precipitation, the precipitate (ppt) was filtered with Whatman filter paper. The ppt was rinsed with DI water. The rinse was repeated about 5 times to completely remove NaOH. There was no need to put any control over the pH of the solution in this process. Then the ppt was dried in an oven at 90 °C temperature for 24 h. The dried ppt was then weighed and ground into fine powder using a ball miller (Pulverisette 23, FRITSCH, Germany) at 50 Hz for 5 min with 20 balls. Then the powder was taken into quartz crucibles and calcined at 500 °C for 2 h inside a programmable muffle furnace and then slowly cooled down to room temperature. Samples were stored in a vial and kept in a desiccator.

For 1, 3, 5, 7, and 10% Ni doped Mn<sub>3</sub>O<sub>4</sub> NP synthesis, 1, 3, 5, 7, and 10 mL NAct solution was taken in a separate glass beaker respectively. Then the volume of each beaker was made to 100 mL by adding the corresponding amount of MAct solution. Other processes were similar to those of Mn<sub>3</sub>O<sub>4</sub> NPs. Finally, the NPs were used for different types of characterization.

### Characterization

The obtained products were characterized by various characterization techniques. X-ray diffraction (XRD) (EMMA; GBC Scientific Equipment, Australia) patterns were recorded using Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm) at 35.5 kV and 28 mA, scanning range of 10–70°, at 5° per minute. HighScore software was used to determine the crystallographic data. Surface morphology of the NPs was determined by applying field emission scanning electron microscopy (FESEM); (JSM-7610F, JEOL, Japan) with accelerating voltage: 15 kV, magnification: 1 000 00 $\times$  and transmission electron microscopy (TEM); (JEM 2100plus, JEOL, Japan). The compositional study of the prepared nanoparticles was carried out by X-ray photoelectron spectroscopy (XPS), (K-alpha, Thermo Fisher Scientific, USA) and atomic absorption spectroscopy (AAS); (AA-7000, Shimadzu, Japan). A study using Fourier transform-infrared spectroscopy (FT-IR) (Frontier, PerkinElmer, UK) was carried out on KBr pellets to characterize distinct surface functionalities in the samples. A UV-vis spectrophotometer (Cintra 2020; GBC Scientific Equipment, Australia) was used to observe the degradation of MB spectroscopically.

### Analytical method

First of all, a 500 mL volumetric flask containing 25 mg of MB was filled up to the mark with deionized water (DI) to prepare



a 50 ppm MB solution. A glass beaker was then filled with 100 mL of a produced 50 ppm MB dye solution for the decolorization experiment. The pH of the dye solution was kept at 3. After that, 10 mg of  $\text{Mn}_3\text{O}_4$  NPs were added to the dye solution with stirring at room temperature in the absence of light. The NPs were left behind as the precipitate after centrifuging 5 mL of the mixed solution for 10 min at the specified time interval. After that, the progress of decolorization was assessed using a UV-vis spectrophotometer. Similarly, MB degradation capacity was measured by using Ni doped  $\text{Mn}_3\text{O}_4$  nanoparticles keeping the constant amounts of nanoparticles and dye concentration.

## Results and discussion

### Characterization of $\text{Mn}_3\text{O}_4$ and Ni doped $\text{Mn}_3\text{O}_4$ nanoparticles

**X-ray diffraction (XRD) analysis.** The phase and purity of the synthesized  $\text{Mn}_3\text{O}_4$  and Ni doped  $\text{Mn}_3\text{O}_4$  nanoparticles were identified by XRD studies. Fig. 1 depicts their obtained diffraction patterns. The diffraction peak positions of  $\text{Mn}_3\text{O}_4$ , 1%, and 3% Ni doped  $\text{Mn}_3\text{O}_4$  were obtained at  $2\theta$  values of  $18.1^\circ$ ,  $29^\circ$ ,  $31.2^\circ$ ,  $32.4^\circ$ ,  $36.2^\circ$ ,  $38.2^\circ$ ,  $44.5^\circ$ ,  $50.9^\circ$ ,  $54^\circ$ ,  $56.1^\circ$ ,  $58.7^\circ$ ,  $60^\circ$ , and  $64.8^\circ$  corresponding to crystal planes (101), (112), (200), (103), (211), (004), (220), (105), (312), (303), (321), (224) and (400) respectively. All the reflections are perfectly coinciding with the reported tetragonal structure of  $\text{Mn}_3\text{O}_4$

nanoparticles (JCPDS card no. 024-0734).<sup>8</sup> For 1% and 3% Ni doped  $\text{Mn}_3\text{O}_4$  nanoparticles, a single phase indicates that Ni is effectively doped into the  $\text{Mn}_3\text{O}_4$  lattice. However, in the case of 5%, 7%, and 10% Ni doped  $\text{Mn}_3\text{O}_4$  mixed phases are found. The tetragonal phase structure of  $\text{Mn}_3\text{O}_4$  (JCPDS card no. 024-0734) and the spinel phase structure of  $\text{NiMn}_2\text{O}_4$  (JCPDS card no. 71-0852) are formed. The diffraction peaks at  $2\theta = 30.1^\circ$ ,  $36^\circ$ ,  $43^\circ$ ,  $57.1^\circ$ , and  $62.8^\circ$  correspond to the (220), (311), (400), (511), and (440) planes of  $\text{NiMn}_2\text{O}_4$ . The above results are in good agreement with the recent study.<sup>23</sup> However, due to the very broad and low intensity of diffraction peaks, the prepared nanoparticle size should be very small.<sup>45</sup> The average crystallite size of prepared  $\text{Mn}_3\text{O}_4$  and Ni doped  $\text{Mn}_3\text{O}_4$  NPs was calculated using the Debye-Scherrer equation<sup>46</sup> as follows

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

where  $k$  is the shape factor (0.94),  $\lambda$  is the X-ray wavelength ( $1.5418 \text{ \AA}$ ),  $\beta$  is the full width at half maxima (FWHM) of the corresponding diffraction line and  $\theta$  is the diffraction angle. The average crystallite size, FWHM, peak position, and microstrain calculated for the plane (211) of each sample are shown in Table 1.

It is found that without 1%, the most intense diffraction peak of doped nanoparticles is shifted. As doping concentrations increase from 0% (pure  $\text{Mn}_3\text{O}_4$ ) to 7%, the FWHM of the prominent peaks rises respectively, which can be attributed to a reduction in crystallite size. However, in the case of 10% doping concentration, the opposite phenomena are found. Therefore, the broadening and shifting of the diffraction peak with Ni doping strongly suggest that Ni ions have effectively supplanted the Mn ions within the  $\text{Mn}_3\text{O}_4$  lattice. The reason for the reduced sizes of the Ni doped  $\text{Mn}_3\text{O}_4$  NPs (from 1 to 7%) is thought to be either oxygen desorption or the fact that Ni, which is injected, settles within the  $\text{Mn}_3\text{O}_4$  lattice and so forms bonds with the unstable oxygen atoms of  $\text{Mn}_3\text{O}_4$ . This suggests that Ni doping can reduce the nucleation rate of  $\text{Mn}_3\text{O}_4$  and in turn, can subsequently influence the size of the particles.<sup>47</sup> Microstrain values indicate that with increasing the concentration of dopants, the internal stress is increased. But in the case of 10% doping concentration, the crystallite size suddenly increases which means that it experiences lower internal stress due to the formation of mixed phases.<sup>48,49</sup>

**Fourier-transform infrared spectroscopy (FT-IR) analysis.** The FT-IR spectra depicted in Fig. 2 supplied crucial characteristic information for the identification of  $\text{Mn}_3\text{O}_4$  and Ni

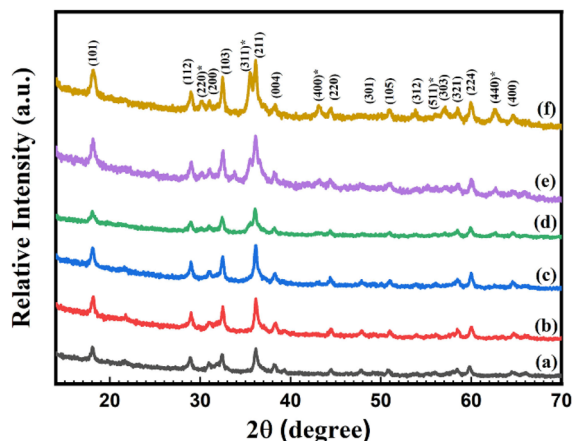


Fig. 1 X-ray diffraction (XRD) patterns of synthesized (a) pure  $\text{Mn}_3\text{O}_4$ , (b) 1% Ni doped  $\text{Mn}_3\text{O}_4$ , (c) 3% Ni doped  $\text{Mn}_3\text{O}_4$ , (d) 5% Ni doped  $\text{Mn}_3\text{O}_4$ , (e) 7% Ni doped  $\text{Mn}_3\text{O}_4$  and (f) 10% Ni doped  $\text{Mn}_3\text{O}_4$  NPs.

Table 1 Peak position, FWHM, crystallite sizes, and microstrain of prepared nanoparticles

Nanoparticles	Peak position $2\theta$ ( $^\circ$ )	FWHM, $\beta$ ( $^\circ$ )	Crystallite size (nm)	Microstrain ( $\epsilon$ ) $\times 10^{-3}$
Pure $\text{Mn}_3\text{O}_4$	36.16	0.2509	34.81	3.35
1% Ni doped $\text{Mn}_3\text{O}_4$	36.16	0.2598	33.62	3.47
3% Ni doped $\text{Mn}_3\text{O}_4$	36.12	0.2705	32.29	3.62
5% Ni doped $\text{Mn}_3\text{O}_4$	36.06	0.3788	23.05	5.08
7% Ni doped $\text{Mn}_3\text{O}_4$	36.12	0.5087	17.17	6.81
10% Ni doped $\text{Mn}_3\text{O}_4$	36.14	0.2181	40.05	2.92



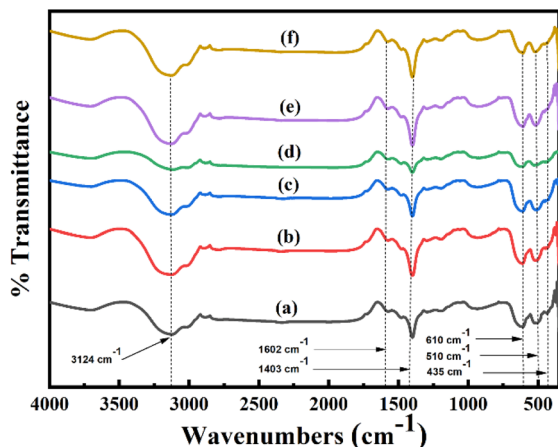


Fig. 2 FT-IR spectra of synthesized (a) pure  $\text{Mn}_3\text{O}_4$ , (b) 1% Ni doped  $\text{Mn}_3\text{O}_4$ , (c) 3% Ni doped  $\text{Mn}_3\text{O}_4$ , (d) 5% Ni doped  $\text{Mn}_3\text{O}_4$ , (e) 7% Ni doped  $\text{Mn}_3\text{O}_4$  and (f) 10% Ni doped  $\text{Mn}_3\text{O}_4$  NPs.

doped  $\text{Mn}_3\text{O}_4$  NPs at various doping levels. The characteristic peaks at  $435\text{ cm}^{-1}$ ,  $510\text{ cm}^{-1}$  and  $610\text{ cm}^{-1}$  could be linked with the stretching vibrations of Mn–O and Ni–O bonds. Moreover, the broad band near  $3124\text{ cm}^{-1}$  shows O–H stretching and the low intense band located at  $1602\text{ cm}^{-1}$  shows the bending vibration of O–H groups in the adsorbed water molecules. Additionally, the band located at  $1403\text{ cm}^{-1}$  matches the coordination bond of Mn by O–H. However, the FT-IR spectra of the prepared NPs show a notable resemblance with the previous results.<sup>8,22</sup>

**X-ray photoelectron spectroscopy (XPS) analysis.** XPS spectra as shown in Fig. 3 were used to further evaluate the elemental composition and oxidation state of the prepared nanoparticles. The XPS of Mn 2p of  $\text{Mn}_3\text{O}_4$  and 7% Ni doped  $\text{Mn}_3\text{O}_4$  NPs are shown in Fig. 3a and b respectively. In addition, binding energies of Ni 2p of 7% Ni doped  $\text{Mn}_3\text{O}_4$  are shown in Fig. 3c. Due to spin-orbit splitting Mn, the 2p peak generates two possible states as  $2p_{3/2}$  and  $2p_{1/2}$ . The deconvoluted spectrum of Mn 2p (Fig. 3a) resulted in four peaks. Among these, two peaks at  $640.5\text{ eV}$  (Mn  $2p_{3/2}$ ) and  $652.1\text{ eV}$  (Mn  $2p_{1/2}$ ) correspond to the  $\text{Mn}^{2+}$  state, while the other two peaks at  $642.5\text{ eV}$  (Mn  $2p_{3/2}$ ) and  $654.1\text{ eV}$  (Mn  $2p_{1/2}$ ) are attributed to the  $\text{Mn}^{4+}$  state. As the peak ratio of  $\text{Mn}^{2+}$  is almost two times greater than that of  $\text{Mn}^{4+}$ , the composition of the oxide would be  $2\text{MnO}\cdot\text{MnO}_2$ . These results agree well with the values reported in the literature.<sup>50</sup> The above results are similar for 1% and 3% Ni doped  $\text{Mn}_3\text{O}_4$  also. However, in the case of 5 to 10% Ni doped  $\text{Mn}_3\text{O}_4$  NPs, three types of oxidation states are found due to the change of phase. The deconvoluted spectrum (Fig. 3b) of Mn 2p of 7% Ni doped  $\text{Mn}_3\text{O}_4$  shows six peaks. Among these, two peaks at  $640.8$  and  $652.4\text{ eV}$  are associated with the  $\text{Mn}^{2+}$  state, while the other two peaks at  $644.4$  and  $654.6\text{ eV}$  are associated with the  $\text{Mn}^{3+}$  state. Again, the  $\text{Mn}^{4+}$  state is responsible for two broad peaks at  $642.1$  and  $653.6\text{ eV}$ . There are four peaks visible in the Ni 2p spectrum (Fig. 3c) of 7% Ni doped  $\text{Mn}_3\text{O}_4$  NPs after deconvolution. Two peaks at  $854.2$  and  $872\text{ eV}$  correspond to the  $\text{Ni}^{2+}$  state while the other two peaks at  $859.9$  and  $878.3\text{ eV}$  are attributed to the  $\text{Ni}^{3+}$  state.<sup>51</sup>

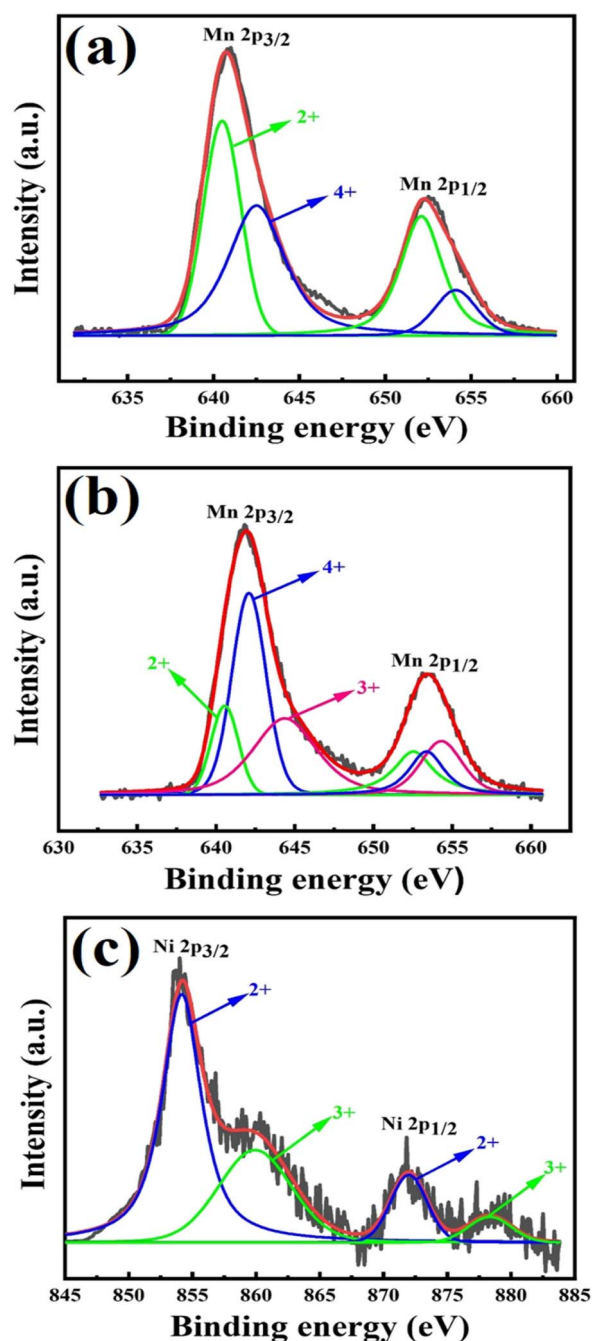


Fig. 3 XPS spectra of (a) Mn 2p of pure  $\text{Mn}_3\text{O}_4$ , (b) Mn 2p of 7% Ni doped  $\text{Mn}_3\text{O}_4$  and (c) Ni 2p of 7% Ni doped  $\text{Mn}_3\text{O}_4$  NPs.

**Field emission scanning electron microscopy (FESEM) analysis.** The surface morphology and particle size of the synthesized nanoparticles were investigated based on FESEM images shown in Fig. 4a–f. Grains with smaller sizes are distributed randomly for all cases. It can also be seen that NPs are well defined as spherical-shaped particles with the size decreasing from  $58.5\text{ nm}$  to  $23.68\text{ nm}$  with increasing doping concentration up to 7% and then increasing to  $48.62\text{ nm}$  in the case of 10% doping concentration. The estimated values from the XRD pattern and these measurements are in good agreement.



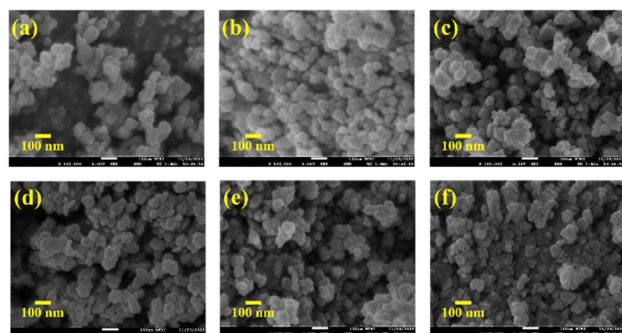


Fig. 4 FESEM images of (a) pure  $\text{Mn}_3\text{O}_4$ , (b) 1% Ni doped  $\text{Mn}_3\text{O}_4$ , (c) 3% Ni doped  $\text{Mn}_3\text{O}_4$ , (d) 5% Ni doped  $\text{Mn}_3\text{O}_4$ , (e) 7% Ni doped  $\text{Mn}_3\text{O}_4$  and (f) 10% Ni doped  $\text{Mn}_3\text{O}_4$  NPs.

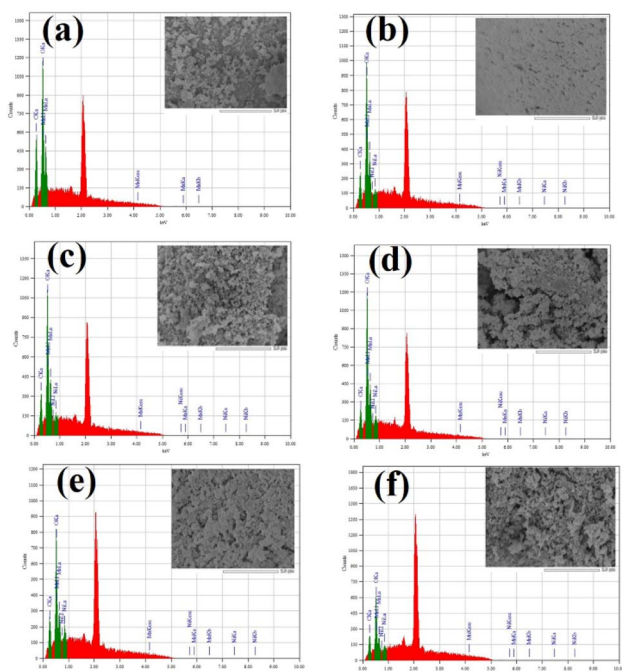


Fig. 5 EDS mapping of synthesized (a) pure  $\text{Mn}_3\text{O}_4$ , (b) 1% Ni doped  $\text{Mn}_3\text{O}_4$ , (c) 3% Ni doped  $\text{Mn}_3\text{O}_4$ , (d) 5% Ni doped  $\text{Mn}_3\text{O}_4$ , (e) 7% Ni doped  $\text{Mn}_3\text{O}_4$  and (f) 10% Ni doped  $\text{Mn}_3\text{O}_4$  NPs.

The EDS analysis was also carried out for the elemental composition of the prepared NPs which is shown in Fig. 5a–f. In the case of pure  $\text{Mn}_3\text{O}_4$  NPs, only Mn and O atomic percent

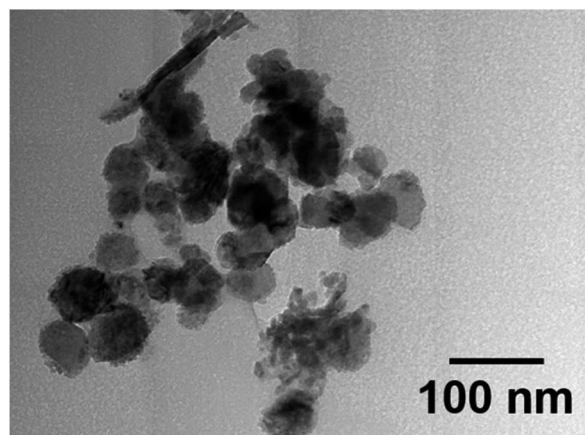


Fig. 6 TEM image of 7% Ni doped  $\text{Mn}_3\text{O}_4$  NPs.

values were found (Fig. 5a). On the other hand, Ni doped  $\text{Mn}_3\text{O}_4$  NPs showed elemental peaks of Mn, Ni and O (Fig. 5b–f). The average values of atomic percent of constituent atoms with standard deviation are presented in Table 2. The Ni atomic percent increased with increasing Ni doping percent, though the atomic percent of Ni does not directly delineate the original doping percent, but rather illustrates the increasing trend.

The elemental peak of carbon was found in each EDS spectrum because carbon tape was used for attaching the sample during FESEM and EDS analysis.

**Transmission electron microscopy (TEM) analysis.** The 7% Ni doped  $\text{Mn}_3\text{O}_4$  NPs were analysed using TEM to visualize the actual particle size and shape (Fig. 6). The result showed spherical shaped particles with size distribution. The average particle size was determined to be approximately 32 nm.

**Atomic absorption spectroscopy (AAS) analysis.** All the samples were further analysed using AAS to confirm the weight percent of Mn and Ni present in the samples. 0.03 g of each sample was dissolved in concentrated  $\text{HNO}_3$  acid by heating at 200 °C for 2 h and then stock solution and 100 and 1000 times dilution solutions were prepared using DI water. Finally the dilution solutions were characterized using AAS for Mn and Ni elements, each sample at least three times. The results are tabulated in Table 3.

**Effect of particle size of pure  $\text{Mn}_3\text{O}_4$  and Ni doped  $\text{Mn}_3\text{O}_4$  NPs on MB degradation.** Effect of particle size of pure  $\text{Mn}_3\text{O}_4$  and Ni doped  $\text{Mn}_3\text{O}_4$  NPs on MB degradation was also examined. The following equation<sup>44</sup> was employed to determine the rate of MB degradation at various reaction times:

Table 2 Elemental composition of prepared NPs obtained by EDS analysis

Nanoparticles	Atomic percent (%)			
	Mn	Ni	O	C
Pure $\text{Mn}_3\text{O}_4$	37.31 ± 0.79	Not detected	39.40 ± 2.22	23.29 ± 2.54
1% Ni doped $\text{Mn}_3\text{O}_4$	41.06 ± 0.58	0.88 ± 0.04	44.12 ± 0.57	13.94 ± 0.04
3% Ni doped $\text{Mn}_3\text{O}_4$	40.79 ± 0.26	2.41 ± 0.38	42.91 ± 0.19	13.89 ± 0.60
5% Ni doped $\text{Mn}_3\text{O}_4$	40.78 ± 0.10	4.43 ± 0.28	44.42 ± 0.07	10.37 ± 0.25
7% Ni doped $\text{Mn}_3\text{O}_4$	37.65 ± 1.05	6.63 ± 0.11	40.55 ± 0.35	15.17 ± 0.63
10% Ni doped $\text{Mn}_3\text{O}_4$	35.86 ± 1.16	8.97 ± 0.45	41.53 ± 0.18	13.63 ± 1.44



**Table 3** Elemental composition of prepared NPs obtained by AAS analysis

Nanoparticles	Atomic percent (%)	
	Mn	Ni
Pure Mn <sub>3</sub> O <sub>4</sub>	28.492 ± 0.008	Not detected
1% Ni doped Mn <sub>3</sub> O <sub>4</sub>	28.575 ± 0.033	0.600 ± 0.002
3% Ni doped Mn <sub>3</sub> O <sub>4</sub>	28.658 ± 0.017	1.879 ± 0.003
5% Ni doped Mn <sub>3</sub> O <sub>4</sub>	27.450 ± 0.050	3.758 ± 0.003
7% Ni doped Mn <sub>3</sub> O <sub>4</sub>	25.925 ± 0.008	4.626 ± 0.007
10% Ni doped Mn <sub>3</sub> O <sub>4</sub>	26.017 ± 0.050	5.232 ± 0.012

$$\text{Degree of degradation (\%)} = \frac{A_0 - A}{A_0} \times 100$$

where  $A_0$  is the initial absorbance and  $A$  is the absorbance at time  $t$  of MB. Fig. 7 displays the degradation of 50 ppm MB solution using pure Mn<sub>3</sub>O<sub>4</sub> and Ni doped Mn<sub>3</sub>O<sub>4</sub> NPs at pH 3. It is noted that pure Mn<sub>3</sub>O<sub>4</sub>, 1, 3, 5, 7, and 10% Ni doped Mn<sub>3</sub>O<sub>4</sub> removed 59, 61, 68, 69, 79, and 69% of MB after the first 10 min respectively. Hence, it is clear that the MB degradation efficiency increases with doping concentration up to 7% due to the decreasing of particle sizes. Additionally, when the particle size decreased, both the total number of active sites on the surface and the particular surface area of the NPs rose, which might significantly boost the efficiency of MB decolorization.<sup>38</sup> But in the case of 10% doping concentration, MB degradation percentage decreased because of increasing particle size. Finally, for pure Mn<sub>3</sub>O<sub>4</sub> NPs, about 95% and for Ni doped Mn<sub>3</sub>O<sub>4</sub> NPs about 98% of MB were degraded. When compared to the scientific literature, these outcomes are comparatively superior to those of zinc oxide (60%), nano cadmium sulfide (29%), zinc sulfide (27%), Mn<sub>3</sub>O<sub>4</sub>/Fe<sub>2</sub>O<sub>3</sub> (85%), Mn<sub>3</sub>O<sub>4</sub>/Fe<sub>3</sub>O<sub>4</sub> nanocomposites (93%), zinc sulfide/cadmium sulfide composites (85%), hollow

cadmium sulfide nanospheres (87%), commercial anatase (73%), cadmium sulfide –6, 8, 18 (96%) and photolysis only (21%); and lower than that of graphene–zinc oxide (100%).<sup>39,40,44,52–55</sup> Theoretically, at pH < 4.5, protonation causes the surface of Mn<sub>3</sub>O<sub>4</sub> to become positively charged. As pH decreases, the positive charge of Mn<sub>3</sub>O<sub>4</sub> increases, which inhibits the adsorption of the cationic dye MB and the creation of the surface precursor due to electrostatic repulsion. As a result, MB was decolorized by Mn<sub>3</sub>O<sub>4</sub> following a surface mechanism, *i.e.*, the interaction of MB with surface-bound Mn(II, III) to produce a surface precursor complex, where electron transport takes place.<sup>38,44</sup>

**Kinetic study.** Kinetic data could be used to determine the oxidative breakdown of MB. The degradation process of MB followed the pseudo-first-order linear kinetics and the findings are presented in Fig. 8. By drawing a graph between the variables  $\ln(C_0/C)$  and time ( $t$ ) of the following equation,<sup>44</sup> the findings of a kinetic analysis of all prepared samples were determined.

$$\ln\left(\frac{C_0}{C}\right) = kt$$

where  $C_0$  is the initial concentration at  $t = 0$  and  $C$  shows the concentration at time  $t$ , whereas the slope of the graph shows the rate constant ( $k$ ). The linear kinetics were evidently being followed by all samples, and 7% Ni doped Mn<sub>3</sub>O<sub>4</sub> NPs exhibited the best performance.

These results showed the higher values of rate constants in comparison to recent studies.<sup>38,44,52,56</sup> Furthermore, the larger value of  $k$  indicates that the NPs are more appropriate for the decolorization of MB. Rate constants,  $r^2$  values, and degree of degradation (%) of all NPs are given in Table 4.

MB degradation percentage is compared with previously reported values using similar types of doped metal oxide NPs, and the results are tabulated in Table 5.

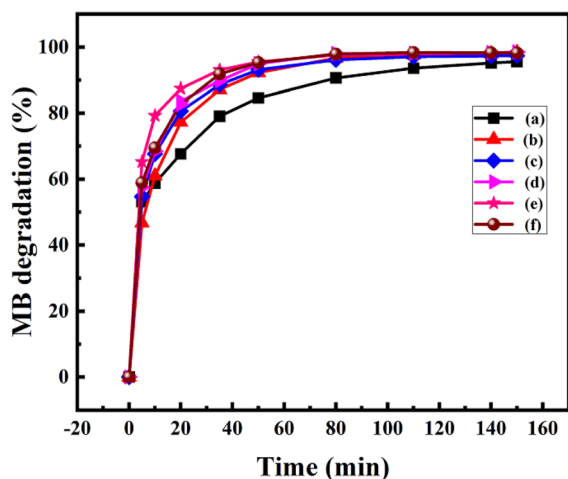


Fig. 7 Effect of particle sizes of (a) pure Mn<sub>3</sub>O<sub>4</sub>, (b) 1% Ni doped Mn<sub>3</sub>O<sub>4</sub>, (c) 3% Ni doped Mn<sub>3</sub>O<sub>4</sub>, (d) 5% Ni doped Mn<sub>3</sub>O<sub>4</sub>, (e) 7% Ni doped Mn<sub>3</sub>O<sub>4</sub> and (f) 10% Ni doped Mn<sub>3</sub>O<sub>4</sub> NPs on MB degradation at pH 3.0.

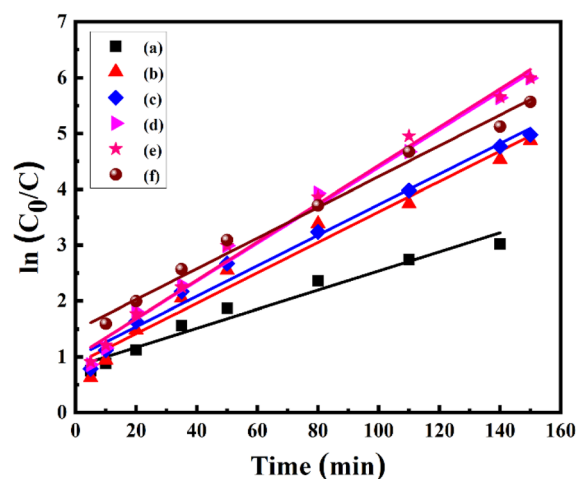


Fig. 8 Pseudo-first-order kinetic model for the degradation of MB using 50 ppm of each (a) pure Mn<sub>3</sub>O<sub>4</sub>, (b) 1% Ni doped Mn<sub>3</sub>O<sub>4</sub>, (c) 3% Ni doped Mn<sub>3</sub>O<sub>4</sub>, (d) 5% Ni doped Mn<sub>3</sub>O<sub>4</sub>, (e) 7% Ni doped Mn<sub>3</sub>O<sub>4</sub> and (f) 10% Ni doped Mn<sub>3</sub>O<sub>4</sub> NPs at pH 3.0.



Table 4 Rate constants and degree of degradation of prepared nanoparticles

Nanoparticles	MB concentration (ppm)	Degree of degradation (%)	$r^2$	Rate constants ( $\text{min}^{-1}$ )
Pure $\text{Mn}_3\text{O}_4$	50	95	0.968	0.0171
1% Ni doped $\text{Mn}_3\text{O}_4$		98	0.973	0.0272
3% Ni doped $\text{Mn}_3\text{O}_4$		98	0.983	0.0273
5% Ni doped $\text{Mn}_3\text{O}_4$		98	0.989	0.0339
7% Ni doped $\text{Mn}_3\text{O}_4$		<b>98</b>	<b>0.990</b>	<b>0.0342</b>
10% Ni doped $\text{Mn}_3\text{O}_4$		98	0.989	0.0275

Table 5 Comparison of MB degradation performance

Materials	MB degradation percentage	References
Pure $\text{Mn}_3\text{O}_4$	80%	44
Te-doped $\text{Mn}_3\text{O}_4$	82%	57
Peroxy monosulfate/ $\text{Mn}_3\text{O}_4$	86.71%	28
$\text{Mn}_3\text{O}_4/\text{Fe}_3\text{O}_4$ nanocomposites	93%	52
$\text{Mn}_3\text{O}_4/\text{ZnO}$	94.59%	58
Samarium-doped $\text{Mn}_3\text{O}_4$	95.4%	59
<b>Ni doped <math>\text{Mn}_3\text{O}_4</math> NPs</b>	<b>98%</b>	<b>This work</b>

## Conclusions

Ni doped  $\text{Mn}_3\text{O}_4$  NPs with different Ni percentages were successfully synthesized through a simple chemical precipitation technique. The particle size observed using FESEM was reduced from 58.50 to 23.68 nm when dopants were incorporated into the  $\text{Mn}_3\text{O}_4$  matrix from 0% to 7% respectively. However, in the case of 10% doping concentration, the particle size was increased to 48.62 nm. Further TEM analysis confirmed spherical shaped NPs with an average size of 32 nm for 7% Ni doped  $\text{Mn}_3\text{O}_4$ . The composition of the elements in the prepared NPs was confirmed by the XPS data. Pure  $\text{Mn}_3\text{O}_4$ , 1% and 3% Ni doped  $\text{Mn}_3\text{O}_4$  NPs were shown to have  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$  states and 5 to 10% of Ni doped  $\text{Mn}_3\text{O}_4$  NPs contained three different oxidation states, including  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ , and  $\text{Mn}^{4+}$ . Furthermore, all doping NPs contain nickel as a dopant in the  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$  states. By changing the percentage of dopants, the phase of the prepared NPs can be easily tuned. The Ni-doping process leads to the change of phases of NPs which increased the decolorization rate. But the excess incorporation of dopants (10%) increased the crystallite size and decreased the degradation rate of MB. The kinetic study confirmed that all synthesized products followed the pseudo-first-order linear kinetics, and 7% Ni doped  $\text{Mn}_3\text{O}_4$  showed a higher degradation rate of  $0.0342 \text{ min}^{-1}$  among all samples. It showed an excellent degradation rate because of the lower size and higher surface area of particles. A major advantage of the Ni doped  $\text{Mn}_3\text{O}_4$  NPs was found to be the rapid degradation of dye compared to  $\text{Mn}_3\text{O}_4$ . Due to the high degradation rate, Ni doped  $\text{Mn}_3\text{O}_4$  NPs will create a new dimension for the purification of dye polluted wastewater in the world.

## Author contributions

Conceptualization: MH; methodology: JU, MH; experimental: JU, RA; data curation: JU, RA; formal analysis: MRH, RA, JU;

writing the main manuscript: JU, MH; reviewing the manuscript: SA, AAS, MSJ; all authors have read and agreed to the published version of the manuscript.

## Conflicts of interest

The authors declare that they have no conflict of interest.

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