





Research paper

Synthesizing Fe_3O_4 , Mn_3O_4 and Mn_3O_4/Fe_3O_4 nanocatalysts using the sol-gel method as new precursors for the degradation of phenol by catalytic ozonation

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HIGHLIGHTS

GRAPHICAL ABSTRACT

- New supramolecules of Fe(II), Fe(III) and Mn(II) with ligand LH₂, [pyda.H₂]²⁺[pydc]²⁻, (pyda = 2,6 -pyridinediamine and pydc.H₂ = 2,6 -pyridinedicarboxylic acid) were prepared.
- The supramolecules were used for the preparation of nanocatalysts Fe₃O₄, Mn₃O₄ and Mn₃O₄/Fe₃O₄.
- The nanocatalysts were applied for degradation of phenol by ozonation.
- The combined usage of O_3 and $Mn_3O_4,\,Mn_3O_4/Fe_3O_4,\,Fe_3O_4$ nanocatalysts leads to a conspicuous $Mn_3O_4 > Mn_3O_4/Fe_3O_4 > Fe_3O_4$ for degradation and mineralization of phenol.

ARTICLE INFO

Article history:

Received 13 August 2022 Revised 11 November 2022 Accepted 19 November 2022

Keywords:

Mn₃O₄/Fe₃O₄ nanocomposite Sol-gel method Synthesis Catalytic ozonation Phenol degradation



ABSTRACT

Ozone has received much attention in wastewater treatment as an impressive oxidation agent. In this work, three new metal complexes, [pyda.H][Fe(pydc)(pydc.H)].H₂O, (I); [pyda.H][Fe(pydc)₂].H₂O, (II); and [pyda.H₂]₅[Mn(pydc.H)₂].[pydc]₅.8H₂O, (III), where $[pyda.H]^+ = 2,6$ -diaminopyridinium and $[pydc]^{2-} = 2,6$ -pyridinedicarboxylate, have been synthesized by the ultrasonic-assisted synthesis method and then characterized by field emission scanning electron microscope (FE-SEM), Fourier-transform infrared (FT-IR) spectroscopy, thermogravimetric (TGA), and elemental analyses. According to the SEM image, the morphology of compound III was a nanorod. Compounds I, II, and III were then used as precursors for the preparation of Fe₃O₄, Mn₃O₄, and Mn₃O₄/ Fe_3O_4 using the sol-gel and impregnation methods, respectively. Characterization of the synthesized nano-catalysts was carried out by FE-SEM, X-ray powder diffraction (XRD), and energy diffraction X-ray (EDX), the vibrating sample magnetometer (VSM) was replaced by magnetic studies. The VSM result showed that Fe_3O_4 and Mn_3O_4/Fe_3O_4 were superparamagnetic and ferromagnetic compounds, respectively. The Mn₃O₄, Mn_3O_4/Fe_3O_4 , and Fe_3O_4 nanocatalysts were applied for the decomposition of phenol in an aqueous solution by catalytic ozonation. Phenol degradation efficiency was obtained as 97.26, 97.74, and 88.62 %, respectively.

1. Introduction

Ozone has been used as an oxidant in wastewater treatment for many years. However, the refractory pollutants are usually not entirely oxidized, and only minor mineralization is achieved using ozonation alone. New advanced oxidation methods have been investigated to provide ozonation process efficiency, generating more active oxidant agents such as free hydroxyl radicals [1]. A combination of ozone and homogeneous or heterogeneous catalysts produces free hydroxyl radicals. Catalytic ozonation is an effective route to decompose ozone into reactive radicals to oxidize pollutants. Heterogeneous catalytic ozonation has been shown to be more efficient for degrading pollutants in water and wastewater. Heterogeneous catalysts used in the ozonation process include metal oxide, metal oxide on supports, or metal oxide composites such as γ-Al₂O₃ [2], Co₃O₄/MnO₂ [3], ZnFe₂O₄/ZnNCN [4], activated carbon (AC) [5,6], CuO/CeO₂ [7], Ce-loaded activated carbon (Ce-AC) [8], ZSM-5 zeolites [9], CeO₂ [10], Fe loaded MCM-41 (Fe/MCM-41) [11], cobalt-doped Fe₃O₄ [12], and Co-Mn-Al layered double hydroxides [13]. Catalytic activities might be increased by reducing the size of the catalysts to nanometer levels. An increasing number of researchers have recently focused on nanocatalysts that could potentially be used in heterogeneous catalytic ozonation. Compared with common nanocatalysts, nanocatalysts are used for their excellent activity, greater selectivity, and high stability. Several kinds of nanocatalysts have recently been used for pollutant degradation, such as modified bentonite as an adsorbent material [14], TiO₂:Mg^{2+/} zeolite composite [15], ZnO nanobundles [16-18], iron oxide nanoparticles (IOnPs) [19], Pt/CNTs (carbon nanotubes) [20], Ni nanoparticles on TiO₂ [21], CeO₂ nanostructured [22,23], NiO nanoparticles [24], carbon nanotube-supported manganese oxides (MnOx/MWCNT) [25], multi-walled carbon nanotube (MWCNT) [26], and NiO-CuO nanoparticles [27]. Nanocatalysts' main limitation for wastewater treatment is separating them from the water after the treatment.

Magnetic Fe_3O_4 nanoparticles can be prepared by different methods such as electrochemical [28], hydrothermal [29], thermal decomposition of $Fe_3(CO)_{12}$ in diethyleneglycol diethyl ether with oleic acid as a stabilizer [30], and thermal decomposition of Fe-urea complex ([Fe(CON₂H₄)₆](NO₃)₃) [31]. Mn_3O_4 nanoparticles can be prepared by using the thermal decomposition route of [bis(2-hydroxymanganese(II)] naphthaldehydato) complex in the presence of oleylamine [32], the solvothermal method in the presence of poly(vinyl-pyrrolidone)/ stearic acid (PVP/SA) [33], the precipitation method using Mn(CH₃COO)₂·4H₂O and NaOH as precursors at a low temperature of 30 °C [34], the oxidationprecipitation method at a low temperature (60 °C) [35], a novel dispersion-precipitation method [36], a simple sonochemical method by the reaction of Mn(CH₃COO)₂ precursors with NaOH [37], or thermal decomposition of a [bis(salicylidiminato)manganese(II)] complex [38].

In recent years, the preparation of metal oxides from supramolecular compounds as a precursor has been widely studied. For example, ZrO_2 from an isophthalic acid-zirconium(IV) nanocomposite [39], Y_2O_3 from a salicylic acid-Y(III) complex [40], La_2O_3 from [pyda.H]₂[La₂(pydc)₄(H₂O)₄].2H₂O [41], ZnO from [ZnI₂(C₃H₅NO₂S)]n [42], and PbO from [PbBr₂(C₉H₁₅N₅O)]_n [43].

In this paper, nanocatalysts Fe₃O₄, Mn₃O₄, and Mn₃O₄/Fe₃O₄ were prepared by co-precipitation, thermal decomposition, and impregnation methods, respectively, from Fe(II), Fe(III), and Mn(II) supramolecules. The compounds, [pyda.H] [Fe(pydc)(pydc.H)].H₂O, [pyda.H][Fe(pydc)₂]. H₂O, and [pyda.H₂]₅[Mn(pydc.H)₂].[pydc]₅.8H₂O were synthesized by the reaction of ferrous chloride tetrahydrate (FeCl₂.4H₂O), ferric chloride hexahydrate (FeCl₃.6H₂O), and the ligand LH₂, [(pydc)(pyda.H₂)] in 2-Butanol and the reaction of manganese (II) acetate tetrahydrate (Mn(CH₃COO)₂.4H₂O) and ligand LH₂, $[pyda.H_2]^{2+}[pydc]^{2-}$, (pyda = 2,6 - pyridinediamine, and $pydc.H_2 = 2,6$ - pyridinedicarboxylic acid) in methanol by the sonochemical method. Also, we reported the application of nanocatalysts for phenol degradation under the ozonation process. The aim of this research was to investigate the maximum degradation of only phenol without the intervention of other wastewater impurities; therefore, only phenol was used as a stock solution.

2. Materials and methods

All reagents and solvents for preparation and analysis were used as received without further purification. The 2,6-pyridinediamine = [pyda] and 2,6-pyridinedicarboxylic acid = $[pydc.H_2]$ were supplied

by Sigma-Aldrich. The $FeCl_3.6H_2O$, $FeCl_2.4H_2O$, $Mn(CH_3COO)_2.4H_2O$, methanol, and 2-butanol are available from the Merck Company.

2.1. Synthesis of Fe(II), Fe(III), and Mn(II) complexes

All the metal complexes were prepared by the reaction of metal salts with LH₂ ligand in 1:2 mole ratios. For example, compound I was obtained in a 2:1 mole ratio of LH₂ and FeCl₂.4H₂O, respectively. To prepare the nanosized compound I, ferrous chloride tetrahydrate (0.099 g, 0.5 mmol) was first dissolved in 2-butanol (20 ml and LH₂ (0.276 g, 1 mmol) was dissolved in 2-butanol, next solution ferrous chloride tetrahydrate was added dropwise to solution LH₂ in a Pyrex beaker under stirring for 15 min, then placed in a vessel of a high-density ultrasonic probe operating at frequency of 20 KHz with 70 % power output of 600 W at 90 min. It should be noted that methanol was used as a solvent in compound III. A precipitate was obtained and separated by centrifugation (4000 rpm, 15 min), washed with 2-butanol (two times) and acetone to remove residual impurities, and air dried. Compounds I, II, and III (Fe(II), Fe(III), and Mn(II) complexes), obtained a light green (0.27 g, yield: 69 %), brown (0.39 g, yield: 71 %) and pink (0.25 g, yield: 67 %) color, respectively. Afterward, the melting or decomposition point (°C), elemental analytical, and FT-IR results were obtained for compounds I, II, and III, as well as the estimated chemical formulas of [pyda.H][Fe(pydc)] (pydc.H)].H₂O, [pyda.H][Fe(pydc)₂].H₂O, and [pyda. H₂]₅[Mn(pydc.H)₂].[pydc]₅.8H₂O, respectively. The results obtained for compound I: dec.p. > 300 °C. Ana Calc. (%) for C₁₉N₅O₉H₁₇Fe: C, 43.073; H, 3.1; N, 15 Fe, 10.05 found (%): C, 43.083; H, 3.03; N, 15.01; Fe, 10.05. FT-IR (selected bands; cm⁻¹): 3398(m), 3333(m), 3216(m), 1683(s), 1579(s), 1475(w), 1378(m), 1352(m), 1189(s), 916(m), 760(s), 734(s), 683(s).

Compound II: dec.p. > 300 °C. Ana Calc. (%) for $C_{19}N_5O_9H_{16}Fe: C, 42.64; H, 3.02; N, 15.56 Fe, 10.45$ found (%): C, 42.48; H, 3.03; N, 15.66; Fe, 10.45. FT-IR (selected bands; cm⁻¹): 3372(m), 3325(m), 3198(m), 1676(s), 1616(s), 1583(s), 1481(w), 1381(s), 1356(s), 1196(s), 927(m), 744(s), 699(s), 678(s).

Compound III: dec.p. > 300 °C. Ana Calc. (%) for $C_{74}N_{22}O_{36}H_{84}Mn$: C, 46.6; H, 4.41; N, 15.94 Mn, 2.9 found (%): C, 45.33; H, 3.41; N, 16.37; Mn, 2.9. FT-IR (selected bands; cm⁻¹): 3463(m), 3372(m), 3307(m),

3177(m), 1670(s), 1605(s), 1566(s), 1488(w), 1423(s), 1371(s), 1280(s), 1085(s), 968(m), 774(s), 709(s), 669(s).

To prepare the manganese oxide nanoparticles, the calcination of compound III (0.2 g) was carried out at 400 °C at a heating rate of 5 °C.min⁻¹ in air. After cooling, a brown precipitate was obtained. All the organic components were evaporated, and Mn_3O_4 nanoparticles were produced. The obtained brown precipitate was separated by centrifugation (4000 rpm, 15 min) and washed with distilled water (two times) and acetone under stirring and heating at 40 °C to remove residual impurities and then air dried (0.042 g, yield: 21%). FT-IR (selected bands; cm⁻¹): 3435(m), 1580(m), 1392(m), 1108(m), 611(S), 494(s).

2.2. Synthesis of magnetic Fe_3O_4 nanoparticles by the ultrasonic-assisted sol-gel method

The Fe_3O_4 nanoparticles were obtained in the 1:2 molar ratio of compounds I and II, respectively. To prepare the Fe_3O_4 nanoparticles, compound I (0.515 g, 1 mmol) and II (1.024 g, 2 mmol) were dissolved in 10 ml of distilled water separately and placed in a vessel of a high-density ultrasonic probe operating at 20 kHz with 70 % power output of 600 W for 20 min. An aqueous solution containing NaOH (2.8 g, 50 mmol) was prepared separately. Then 10 ml of NaOH solution was added dropwise into the mixture solutions of compounds I and II. A black suspension was obtained in this stage, confirming the synthesis of Fe₃O₄ nanoparticles. Then the suspension was stirred and dried at 70 °C for 4 h. A black precipitate was obtained and washed three times with distilled water and acetone to remove residual impurities, separated by centrifugation (4000 rpm, 15 min), and air dried (0.65 g, yield: 42 %). FT-IR (selected bands; cm⁻¹): 3454(w), 1557(m), 565(s).

2.3. Synthesis of Mn_3O_4/Fe_3O_4 nanocomposites

The Mn_3O_4/Fe_3O_4 nanocomposite was prepared by dispersing Fe_3O_4 nanoparticles (0.0056 g, 0.1 mmol) in 100 ml of distilled water placed under ultrasonic waves at 20 kHz with 70 % power output of 600 W for 15 min, then 10 ml of aqueous solution compound **III** (11.466 g, 6 mmol) and 1 M NaOH were added dropwise to the Fe_3O_4 nanoparticles suspension. The brown suspension was placed under ultrasonic waves at 20 kHz with 70 % power output of 600 W for 90 min. The brown suspension was dried, then washed with acetone (7.915 g, yield: 69 %). FT-IR (selected bands; cm^{-1}): 3435(m), 2136(m), 1840(m), 1604(m), 1403(m), 1084(m), 942(m), 612 (s), 506(s).

2.4. Apparatus

A multiwavelength ultrasonic generator (Sonicator-4000; Misonix, USA), equipped with a titanium transducer/transducer and oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum output power of 600 W, was used for ultrasonic irradiation. The ultrasonic generator automatically adjusts the power level. Melting points were measured with a Thermo Scientific 9200 apparatus and are uncorrected. Fouriertransform infrared (FT-IR) spectra were recorded on a Philips PU 9624 spectrophotometer in KBr pellets. Elemental analyses (carbon, hydrogen, and nitrogen) were performed using a CHNO-S Costech ECS41010 analyzer. A Varian ASS-240 atomic absorption was used to determine the percentage of Fe(II), Fe(III), and Mn(II). X-Ray powder diffraction (XRD) measurements were performed using an INEL Equinox 3000 diffractometer with monochromated Cu K_{α} ($\lambda = 1.5418$ Å) radiation at room temperature from $2\theta = 10^{\circ}-100^{\circ}$. The crystallite sizes of selected samples were estimated using the Scherrer formula. Field emission Scanning electron microscopy (Fe-SEM) images were obtained on a Tescan Mirall equipped with an energy dispersive X-ray (EDX) microanalysis with gold coating. Thermogravimetric analysis-differential thermal analysis (TGA-DTA) was carried out using a simultaneous thermal analyzer STA503 with a heating rate of 10.0 °C.min⁻¹ in flowing Ar gas. The magnetic measurement was carried out on a vibrating sample magnetometer (VSM).

2.5. Catalytic ozonation experiments

Degradation of phenol using nanocatalysts and ozone was carried out in a semi-batch stirred reactor. The ozone, generated by an Ozomax OZO 1VTTL laboratory ozone generator, was produced from the air and the rate of ozone was 2.210 g.h⁻¹. Fig. 1 shows the ozonation apparatus. The simulated wastewater was a phenol solution with an initial concentration of 100 mg.L⁻¹. The solution pH was adjusted to 10 with NaOH (0.01 M). 0.1 % catalyst was mixed in a flask under stirring at 200 rpm at room temperature (23 \pm 2 °C). Then ozone was bubbled into the flask with continuous stirring. After 60 min, samples (10.0 ml) were taken from the reactor, an aliquot of 0.1 N Na₂S₂O₃ was added to the sample for phenol analysis to quench the residual ozone in the reaction solution and the clear solutions after separation were used for analytical determination. The control experiments of single ozonation (without catalyst) were also carried out under the same conditions.

2.7. Analysis

The ozone in the on-gas stream of the reactor was measured by the iodometric method using 2 % potassium iodide for ozone trapping and sodium thiosulfate as a titrant. The ozone dose was considered constant at 1.533 g.h^{-1} throughout the experiment.

The concentration of aqueous ozone was determined by the iodometric method [44]. The concentration of phenol in the solution was determined by highperformance liquid chromatography (HPLC, Kenaver) with a reverse phase of 5 μ m in a 4.6 mm × 250 mm C18 waters column (Perfectsil target ODS-3) at room temperature. The flow rate of the mobile phase, which



Fig. 1. Schematic diagram of the ozonation device.

was a mixture of 20 % acetonitrile (Merck HPLC Grade) and 80 % water (distilled and deionized), was 1.0 ml.min⁻¹. The wavelength of the UV-vis detector (K-2600) used was 270 nm. The mineralization degree of phenol was measured by a total organic carbon (TOC) analyzer (Shimadzu, TOC-VCSH) based on carbon dioxide infrared absorption. Manganese and iron ions were determined by Inductively Coupled Plasma (ICP) spectrometry (Varian, 710-ES). The pH values of the solutions were recorded by a pH analyzer (Orion, 420 A).

3. Results and discussion

3.1. Characterization of metal complexes and nanocatalysts

The reaction of LH₂ ligand with FeCl₂.4H₂O and FeCl₃.6H₂O in 2-Butanol, and Mn(CH₃COO)₂.4H₂O in methanol using the ultrasonic method at ambient temperature and atmospheric pressure leads to the formation of Fe(II), Fe(III), and Mn(II) supramolecular compounds, [pyda.H][Fe(pydc) (pydc.H)].H₂O, [pyda.H][Fe(pydc)₂].H₂O, and [pyda. H_2 [[Mn(pydc.H)₂].[pydc]₅.8H₂O; compounds I, II, and III, respectively. Fig. 2 gives an overview of the synthesis method. The elemental analysis of the supramolecules is consistent with the chemical formulas

of $C_{19}N_5O_9H_{17}Fe$, [Fe(II)LH₂]; $C_{19}N_5O_9H_{16}Fe$, [Fe(III) LH₂]; and C₇₄N₂₂O₃₆H₈₄Mn, [Mn(LH₂)], respectively. Fig. 3 shows the FT-IR spectra of compounds I and II, Fe₃O₄ nanoparticles, and LH₂. The absorption bands at 3333 and 3325 cm⁻¹ in Fig. 3 are attributed to the stretching vibration of the O-H bond and the bending vibration of H-O-H from water molecules observed in compounds I and II, respectively. It can be seen that all the vibrations assigned to the aromatic ring, including =C-H at 2980 and 3085 cm⁻¹, 3216 cm⁻¹, 3198 cm⁻¹, and aromatic C=C stretching vibrations at 1591 and 1656 cm⁻¹, 1579 and 1605 cm⁻¹, 1583 and 1616 cm⁻¹ observed in LH₂, compounds I and II supramolecules, respectively, do not appear in Fe₃O₄ indicating that there is no impurity of precursor in the as-prepared product [45]. Also, the stretching C=O vibration of LH₂ shifted to low frequency (1695, 1683, and 1676 cm⁻¹ observed in LH₂, compounds I and II, respectively) in the formation of compounds I and II indicate the coordination of carbonyl group to the metal atoms. Comparing the infrared spectra of the nanoparticles with LH₂ in compounds I and II, we can see that the organic molecules have indeed become a part of the nanoparticles. The FT-IR of the Fe₃O₄ nanoparticles shows intense adsorption. The vibration band characteristics of Fe₃O₄ are located at 565 cm⁻¹ [46], and bands at 3459 and 1556 cm⁻¹ can be assigned to the H₂O used in the individuation step.



Fig. 2. Schematic representation of the synthetic methods for compounds [pyda.H][Fe(pydc)(pydc.H)].H₂O (**I**), [pyda.H][Fe(pydc)₂].H₂O (**II**), and [pyda.H₂]₅[Mn(pydc.H)₂].[pydc]₅.8H₂O (**III**).



Fig. 3. FT-IR spectra of LH_2 , [pyda.H][Fe(pydc)(pydc.H)].H₂O (I), and [pyda.H][Fe(pydc)₂].H₂O (II) coordination compounds and Fe₃O₄.

Fig. 4 shows the infrared spectra of the crystalline and powder forms of compound III and Mn_3O_4 nanoparticles. The absorption bands at 3307 and 3310 cm⁻¹ in Fig. 4 are attributed to the bending vibration of H–O–H from water molecules and the stretching vibration of the O–H bond observed in powder and crystalline forms of compound III, respectively. All the vibrations assigned



Fig. 4. FT-IR spectra of crystalline powder forms of [pyda. $H_2]_5$ [Mn(pydc.H)₂].[pydc]₅.8H₂O (III) and Mn₃O₄.

to the aromatic ring, including =C-H bands at 2980 and 3085, 3177, 3178 cm⁻¹, and aromatic C=C stretching vibrations at 1591 and 1656, 1566 and 1606, 1558 and 1646 cm⁻¹ observed in LH_2 , powder, and crystalline forms of compound III, respectively, do not appear in Mn_3O_4 shows that there are no impurities from the raw material in the finished product. Also, the formation of powder and crystalline forms of compound III by the stretching C=O vibration bands of LH₂ shifting to a lower frequency (1695, 1670, 1663 cm⁻¹ observed in LH₂, and powder and crystalline forms of compound III, respectively) indicates the coordination of carbonyl group to the metal atoms [47]. Comparing the infrared spectra of the nanoparticles with LH₂, powder, and crystalline forms of compound III shows that the organic molecules have actually become a part of the nanoparticles. The FT-IR spectrum of the Mn₃O₄ nanoparticles shows intense adsorption. The vibration band characteristics of Mn₃O₄ are located at 611 and 494 cm⁻¹ [32], and bands at 3435, 1580, and 1392 cm⁻¹ can be assigned to the H₂O used in the isolation step.

The FT-IR spectra of the Mn_3O_4/Fe_3O_4 nanocomposites shows in Fig. 5 the intense adsorption. The vibration band characteristics of Mn_3O_4/Fe_3O_4 are located at 612 and 506 cm⁻¹ [32,48] and peaks at 3435 cm⁻¹ can be assigned to the H₂O used in the separation step.

The XRD diffraction pattern of the sample Fe_3O_4 , Mn_3O_4 nanoparticles, and Mn_3O_4/Fe_3O_4 nano-composites are shown in Fig. 6. The samples were obtained using the co-precipitation method for compounds I and II



Fig. 5. FT-IR spectra of $[pyda.H_2]_5[Mn(pydc.H)_2].[pydc]_5.8H_2O$ (III) and Fe₃O₄ and Mn₃O₄/Fe₃O₄ nanocomposites

as precursors, (Fig. 6(a)), thermal decomposition for compound III at 400 °C (Fig. 69b)), and the impregnation method for compound III as a precursor (Fig. 6(c) and 6(d), respectively. Calculating the particle size using the Scherer's formula, $D = 0.9\lambda / \beta .\cos\theta$, considering the clear broadening of the peaks, show that the particles sizes are in the range of nano dimensions. Here D is the average grain size, λ is the X-ray wavelength (1.5418) Å), and β and θ as diffraction angle or half width of a peak has been observed [49], are ~ 20, 55, 96 nm for Fe₃O₄, Mn₃O₄, and Mn₃O₄/Fe₃O₄, respectively. These sizes are in agreement with the values obtained from the SEM images (Fig. 7). According to the XRD diffraction pattern, we concluded that Fe₃O₄, Mn₃O₄, and Mn₃O₄/ Fe_3O_4 were obtained in high purity; the pattern matches that of Fe₃O₄ with a cubic structure (lattice parameters a = 8.393 Å), and the pattern matches that of Mn₃O₄ with a tetragonal structure (space lattice parameters a= 5.765 Å, c = 9.442 Å) [37,50]. The sharp diffraction peaks indicate that well-crystallized Fe₃O₄, Mn₃O₄, and Mn₃O₄/Fe₃O₄ nanostructures can be prepared using this synthetic procedure.

Fig. 7 shows the SEM images of I, II, and III supramolecules, and Fe_3O_4 , Mn_3O_4 , and Mn_3O_4 / Fe_3O_4 nanocomposites. The morphology of I, II, and III supramolecules, Fe_3O_4 , Mn_3O_4 , and Mn_3O_4 / Fe₃O₄ nanocomposites, according to the SEM images, show nanohexagonal, cloud, nanorod, nanospherical, mixed nanohexagonal, and spherical-hexagonal morphologies, respectively. The SEM images of 7(a), 7(b), and 7(c) show that Fe(II), Fe(III), and Mn(II) complexes have different morphologies, although the ligands and the synthetic protocols are the same. Magnetic oxides of iron and manganese are obtained by calcining these complexes; Fig. 7(d), 7(e), and 7(f) images show that magnetic iron oxide has a spherical morphology, while manganese oxide has a hexagonal shape. The Mn_3O_4/Fe_3O_4 nanocomposites have a mixed morphology of spherical-hexagonal.

The size distribution histogram of compounds I, II, III, Fe₃O₄, Mn₃O₄, and Mn₃O₄/Fe₃O₄ nanocomposites (Fig. 8) shows particle sizes of about 40-60 nm, 4-5 μ m, 80-120 nm, 30-40 nm, 40-60 nm, and 80-90 nm, respectively, with relatively uniform distribution. These data are approximate and based on the numbers obtained from SEM images.

The ligand LH₂, [(pydc)(pyda.H₂)] has been used to control the morphology and particle sizes. In the article by Ranjbar *et al.* (2019), the obtained nanostructures have a spherical morphology with an average particle size of 10 to 20 nm [51]. However, in the present article, the nanoparticles of Mn_3O_4 have a hexagonal



Fig. 6. HXRD pattern of the (a) Fe₃O₄ nanoparticles, (b) Mn₃O₄ nanoparticles, (c) and (d) Mn₃O₄/Fe₃O₄ nanocomposites.



Yew field: 2:67 µm Det: InBeam SOC rm

Fig. 7. The SEM images of (a) $[pyda.H][Fe(pydc)(pydc.H)].H_2O$ (I), (b) $[pyda.H][Fe(pydc)_2].H_2O$ (II), (c) $[pyda.H_2]_5[Mn(pydc.H)_2].$ $[pydc]_5.8H_2O$ (III), (d) Fe_3O_4 , (e) Mn_3O_4 , and (f) Mn_3O_4/Fe_3O_4 .



Fig. 8. Size distribution of (a) $[pyda.H][Fe(pydc)(pydc.H)].H_2O$ (**I**), (b) $[pyda.H][Fe(pydc)_2].H_2O$ (**II**), (c) $[pyda.H_2]_5[Mn(pydc.H)_2].$ $[pydc]_5.8H_2O$ (**III**), (d) Fe_3O_4 , (e) Mn_3O_4 , and (f) Mn_3O_4/Fe_3O_4 .

morphology with a medium particle size of 40 to 60 nm due to the template effect resulting from the formation of the complex.

The EDX analysis of Fe_3O_4 , Mn_3O_4 nanoparticles, and Mn_3O_4/Fe_3O_4 nanocomposites (Fig. 9) shows the presence of iron and oxygen, manganese and oxygen, iron, and manganese and oxygen as the only elementary component, respectively. These results are consistent with the elemental analysis of the products. Fig. 9 shows (a) the percentage weight of Fe (63.57 %) and O (36.43 %), (b) the percentage weight of Mn (72.81 %) and O (27.19 %), and (c) the percentage weight of Fe (2.9 %) and O (51.23 %) which confirms the formulas of Mn₃O₄, Fe₃O₄, and Fe₃O₄ to Mn₃O₄, respectively.

Thermogravimetric (TG) and differential thermal analysis (DTA) of compound **III** was carried out from 10 to 600 °C in an ambient atmosphere (Fig. 10). As



Fig. 9. EDX spectrum of $Fe_3O_4,\ Mn_3O_4$ nanoparticles and $Mn_3O_4/$ $Fe_3O_4.$

all three complexes had similar constituents, it was sufficient to investigate the thermal behavior of one of them; therefore, thermal analysis was taken only from the manganese complex as an example. The decomposition of the compound started at 25 °C and ended at 628 °C. In this temperature range, the removal of the water and LH₂ ligand was as follows: between 25-266 °C a mass loss of 3.1 % may be ascribed to the removal of H_2O_2 , between 266-303 °C a mass loss of 43.1 % may be ascribed to the removal of [pydc]²⁻, between 440-512 °C a mass loss of 23.4 % may be ascribed to the removal of [pyda.H₂]²⁺, and between 512-628 °C a mass loss of 6.7 % may be ascribed to the removal of $[pydc.H]^{-}$. At temperatures higher than 628 °C, residual compounds (probably Mn₃O₄) stop losing weight and grow in size, as shown in SEM characterization images. Based on TG/DTA analysis, production of Mn₃O₄ probably occurs after 500 °C. As thermal decomposition takes place during 4 h at 400 °C, the Mn₃O₄ nanoparticles grew, and the particle sizes increased. The TG curve exhibits four distinct decomposition stages between 25 to 628 °C with a mass loss of about 80.3 %. The results can confirm the suggested chemical formula based on the calculation of the molecular weight of compound III.

3.2. Magnetic properties of Mn_3O_4 / Fe_3O_4 nanocomposites

Fig. 11 shows the magnetic hysteresis curves of the Fe_3O_4 nanoparticles and Mn_3O_4/Fe_3O_4 nanocomposites taken by a VSM. It reveals that two loops due to the Fe_3O_4 and Mn_3O_4/Fe_3O_4 exhibit a superparamagnetic

and ferromagnetic behavior similar to the previously published results [52]. The measured saturation magnetization of the Mn_3O_4/Fe_3O_4 nanoparticles was 6.74 emu.g⁻¹, which was less than that of Fe₃O₄ nanoparticles (63.37 emu.g⁻¹). The significant difference in the magnetic properties of Fe₃O₄ and Mn_3O_4/Fe_3O_4 could be attributed to the Mn_3O_4 coating layer, which decreases the magnetic.

3.3. Catalytic activity

Ozonation experiments with and without catalysts were carried out to test the influence of nanosized Fe_3O_4 , Mn_3O_4 , and Mn_3O_4/Fe_3O_4 on the phenol decomposition and TOC removal in solutions.

Table 1 shows the results of phenol degradation under ozonation (with and without catalysts). As can be seen, the presence of nanoparticles as catalysts leads to a higher degradation rate of phenol. The reaction time was considered constant at 30 min in all cases. Table 1 shows the TOC removal during single and catalytic ozonation. As can be seen, the presence of a catalyst accelerates the TOC removal rate remarkably. Each experiment was repeated three times, and their average was calculated.

Under the experimental conditions investigated, 81.45 % of the phenol was degraded under ozonation at 60 min with a mineralization efficiency of only 3.54 %. The addition of Mn_3O_4 , Mn_3O_4/Fe_3O_4 , and Fe_3O_4 significantly promoted the degradation efficiency of phenol in ozone. Applying 1.0 g.L⁻¹ of Mn_3O_4 , Mn_3O_4/Fe_3O_4 , and Fe_3O_4 catalysts under ozonation can degrade phenol about 97.26, 97.74, and 88.62 %, respectively.



Fig. 10. TG / DTA diagrams of $[pyda.H_2]_5[Mn(pydc.H)_2]$. $[pydc]_5.8H_2O$ (III) coordination compound.



Fig. 11. Magnetic hysteresis curves of Fe_3O_4 and Mn_3O_4/Fe_3O_4 at room temperature.

Nanocatalysts	phenol concentration (ppm)	TOC removal (%)
Ozone	18.549	3.54
Fe ₃ O ₄	11.38	3.57
Mn ₃ O ₄	2.26	24.46
Mn ₃ O ₄ /Fe ₃ O ₄	2.736	17.06

 Table 1. Degradation of phenol and TOC removal under single ozonation and catalytic ozonation.

Conditions: Initial phenol concentration 100 mg.L⁻¹; ozone concentration 1.533 g.h⁻¹; initial pH of solution 10; temperature 23 °C.

In comparison with similar catalysts reported by Muhammad *et al.* (2022), at a lower reaction temperature (23 °C), the degredation of phenol is high (97.74 %) [53]. The TOC analysis showed that 24.46, 17.06, and 3.57 % of phenol was eliminated during ozonation with Mn_3O_4 , Mn_3O_4 /Fe₃O₄, and Fe₃O₄, respectively.

According to the results, the oxidation properties of Mn_3O_4 ($E_h^{298} = 1.824$ V) are higher than both Fe₃O₄ and Mn_3O_4 /Fe₃O₄ catalysts.

After the ozonation process, the manganese and iron ions concentrations were measured by ICP spectrometry. The ICP analysis showed that the Fe and Mn ions concentration was 5.39 and 4.46 ppb. Therefore, it can be concluded that the catalysts are stable during the ozonation process and can be used several times. Furthermore, since the used catalyst has magnetic properties and is easily separated from the reaction vessel by a magnet and reversibly oxidizes phenol, it seems that it can be recovered in unlimited quantities. Therefore, it has not been investigated in this research.

Many research works have been done based on the decomposition of phenol under the effect of ozone alone. This research investigated the simultaneous effect of oxidation under ozone and catalyst and showed that the degradation efficiency increased to about 98 %.

3.4. Mechanism of phenol degradation in the catalytic ozonation process

After achieving an efficient degradation of phenol from wastewater in the catalytic ozonation process, an experiment has been done to specify the mechanism of phenol degradation. Two mechanisms are generally considered to work in the heterogeneous catalytic ozonation process of organic pollutants: a direct reaction with ozone and an indirect reaction with the generated reactive radicals. Both mechanisms can occur in both the bulk solution and catalyst surfaces [54]. It is known that in the catalytic ozonation process, the catalyst can speed up the ozone decomposition and, thereby, the formation of reactive radicals, mainly HO[•] [1]. To determine whether HO[•] is involved in the catalytic ozonation process, phenol degradation was considered using the properties of metal oxides, acidity and basicity [1]. Ozone decomposition proceeds through the following five step chain reaction [1]:

$$O_{3} + H_{2}O \rightarrow 2HO^{\bullet} + O_{2} \qquad K_{2} = 1.1 \times 10^{-4} \text{ M}^{-1}.\text{S}^{-1}$$

$$O_{3} + OH^{-} \rightarrow O_{2}^{\bullet} + HO_{2}^{\bullet} \qquad K_{2} = 70 \text{ M}^{-1}.\text{S}^{-1}$$

$$O_{3} + HO^{\bullet} \rightarrow O_{2} + HO_{2}^{\bullet} \leftrightarrow O_{2}^{\bullet} + H^{+}$$

$$O_{3} + HO_{2}^{\bullet} \leftrightarrow 2O_{2} + HO^{\bullet} \qquad K_{2} = 1.6 \times 10^{9} \text{ M}^{-1}.\text{S}^{-1}$$

$$2HO_{2}^{\bullet} \rightarrow O_{2} + H_{2}O_{2}$$

The pH value of the solution plays a critical role in the performance of the catalytic ozonation process and ozone decomposition. The pH points of zero charge (pH_{pzc}) for nanocatalyst manganese dioxide [53] and Fe₃O₄[12] are 2.8 - 4.5 and 6.4, respectively. Therefore, it is assumed that the pHpzc nanocomposite Mn₃O₄/Fe₃O₄ is undervalued at 10. The surface charge nanocatalysts Mn₃O₄, Fe₃O₄, and Mn₃O₄/Fe₃O₄ are negative due to pHpzc (pH_{pzc} < pH). The hydroxide ions on the surface are known to be an initiator of a chain reaction involving ozone decomposition, leading to hydroxyl radicals' formation. Therefore according to the suggested mechanism, the ozone molecule forms a ring with the hydroxyl group hydroxyl radical for phenol degradation in the catalytic ozonation process as follows:

$$O_3 + M-OH \rightarrow M-OH-O_3$$

M-OH-O₃ \rightarrow M-OH(O') + O₂

$$M-OH(O^{\bullet}) + O_3 \rightarrow M-OH + OH^{\bullet} + O_2$$

4. Conclusions

Metal complexes I, II, and III have been synthesized by the sonochemical method. The nanocatalysts Fe_3O_4 , Mn_3O_4 , and Mn_3O_4/Fe_3O_4 were prepared using the solgel method. The compounds were characterized by SEM, XRD, EDX, and VSM. According to the SEM images, the nanocatalyst particles were homogeneous and well-separated. This study shows that metal complexes may be suitable precursors for the preparation of nanocatalysts with remarkable morphologies. The nanocatalysts of Fe₃O₄, Mn₃O₄, and Mn₃O₄/Fe₃O₄ were applied for phenol degradation by ozonation. The proposed mechanism for phenol by Fe₃O₄, Mn₃O₄, and Mn₃O₄/Fe₃O₄ under ozonation can be the hydroxyl radical type. The combined use of O₃ and Mn₃O₄, Mn₃O₄ > Mn₃O₄/Fe₃O₄, and Fe₃O₄ nanocatalysts reveal the Mn₃O₄ > Mn₃O₄ / Fe₃O₄ > Fe₃O₄ trend for degradation and mineralization of phenol.

Acknowledgment

The authors acknowledge the support rendered by the Iranian Research Organization for Science and Technology (IROST), the Iran Nanotechnology Initiative Council (INIC), and the Central Research Laboratory, as well as the Vice Chancellor of Research and Technology, Mazandaran University of Medical Sciences.

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