MnFe$_2$O$_4$ nanoparticles as new catalyst for oxidative degradation of phenol by peroxydisulfate

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ABSTRACT

Manganese ferrite nanopowder was prepared by thermal decomposition at 400°C of the gel synthesized from manganese and iron nitrates and polyvinyl alcohol. X-ray diffractometry evidenced that manganese ferrite was formed as single crystalline phase at this temperature. Scanning electron microscope images evidenced the formation of very fine spherical particles ($d < 11$ nm) of manganese ferrite, with specific surface area of 147 m$^2$/g.

The powder obtained at 400°C was used as a catalyst for the oxidative degradation of phenol in aqueous solutions, in the presence of potassium peroxydisulfate as oxidant. High phenol removal efficiencies above 90% were reached at: pH 3–3.5, phenol initial concentration around 50 mg/L, peroxydisulfate:phenol mass ratio 10:1, and catalyst dose 3 g/L. Total organic carbon measurements showed that the degradation of phenol goes, under these conditions, to mineralization in an extent of 60%.

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Introduction

In the last few years, nanoscale spinel ferrites have drawn a major attention because of their technological applications in magnetic recording, catalysts and ferrofluids. Nanoparticles of such magnetic materials have different characteristics in comparison with the bulk material, due to their small size and the effect of magnetic interactions between particles (Ahmed et al., 2011). Superparamagnetic spinel ferrites MFe$_2$O$_4$ (M = Mn, Fe, Co, Ni) are currently considered among the most successful magnetic nanoparticles for medical applications such as contrast enhancement in magnetic resonance imaging (MRI), magnetically guided drug delivery, and hyperthermia cancer therapy (Vamvakidis et al., 2013).

One of the magnetic ferrites applications extensively studied in the last decades is the removal of heavy metals from water bodies due to the abundant surface hydroxyl groups and magnetic properties, allowing their magnetic separation (Guan et al., 2013; Yao et al., 2014). The possibility to use magnetic materials to remove very toxic organic pollutants e.g., phenol and its derivatives or organic dyes, has received a great attention in the last decades (Saputra et al., 2013a; Yao et al., 2014).

Phenol is an important pollutant in wastewater that can cause considerable damage and threat to the ecosystem and to the human health even at low concentrations. Phenol is a pollutant with high toxicity and poor biodegradability. It is also difficult to be degraded using primary and secondary treatment processes, needing a tertiary treatment of waste-water. These tertiary treatments can include advanced oxidation processes (AOPs) such as chemical oxidation, catalytic oxidation, thermal oxidation, wet air oxidation, etc. (Chen et al., 2014; Muhammad et al., 2012).

Advanced oxidation processes (AOPs) are the most promising method for degradation of organic pollutants in wastewater.
AOPs are based on generation of reactive species, such as hydroxyl radicals (HO·) or sulfate radicals (SO4·) that have a high standard oxidation potential and react non-selectively (Govindan et al., 2014; Litter and Quici, 2010; Yao et al., 2014). In certain conditions, the AOPs can completely mineralize the contaminants to harmless products such as CO2, H2O and mineral acids (Muhammad et al., 2012).

Heterogeneous catalytic oxidation systems have attracted much interest due to some advantages among which may be mentioned: operation at room temperature and normal pressure with high-energy efficiency and easy recovery and reuse of the catalysts (Muhammad et al., 2012).

Due to their physical and chemical properties, manganese oxides (MnO, MnO2, Mn2O3 and Mn3O4) have been studied as potential catalysts (Saputra et al., 2013a; Wang et al., 2015; Zhang et al., 2011). It was established that the reactivity of catalysts decreases in the order Mn2O3 > MnO > Mn3O4 > MnO2; this sequence of catalytic activity was correlated with oxygen mobility on the catalysts and with the capacity of manganese to form various oxidation states (Mn2+/Mn3+ or Mn3+/Mn4+) (Saputra et al., 2013b). This suggests that manganese ferrite, where Mn (II) is present, might act as an active catalyst. More, its magnetic properties allow the facile magnetic separation of this catalyst from solutions. Nanosized manganese ferrite was reported to be a very good catalyst for hydrogen peroxide decomposition (Valdés-Solís et al., 2007). It was also reported that MnFe2O4 presents high activity in activating PMS to produce sulfate radicals for degradation of organic dyes and could be separated with a magnet without any loss (Yao et al., 2014).

In this paper, we report a study regarding the use of manganese ferrite nanopowder as catalyst for the oxidative degradation of phenol, in the presence of peroxysulfate anion as oxidant. Manganese ferrite was obtained by thermal decomposition of the precursor formed by the interaction of metal nitrates and polyvinyl alcohol (PVA). The influence of several parameters (pH of the solutions, initial concentration of the pollutant, catalyst dose, and oxidant:phenol ratio) on the efficiency of catalytic oxidation of phenol was studied. The kinetic of the process was also studied.

1. Materials and methods

1.1. Materials

The reagents used in synthesis and catalysis experiments were of analytical grade (Merck, Germany) and were used without further purification: Mn(NO3)2·4H2O, Fe(NO3)3·9H2O, polyvinyl alcohol (PVA) (M = 60,000 g/mol), phenol C6H5–OH, potassium peroxysulfate K2S2O8, nitric acid HNO3, sodium hydroxide NaOH, and potassium iodide KI.

1.2. Synthesis of manganese ferrite

The procedure for catalyst synthesis was described elsewhere (Stoia et al., 2015). Manganese(II) and iron(III) nitrates were dissolved in 4% PVA aqueous solution, in a molar ratio NO3−:PVA(monomer) of 1:1. The obtained sol was heated up to 100°C until became a gel, then the temperature was gradually raised to 180°C until the emission of nitrogen oxides stopped. A voluminous, porous (sponge like) solid product was obtained. After grinding, a fine fluffy powder was obtained, which was subjected to annealing at 400°C for 6 hr.

1.3. Characterization techniques

The phase composition of the nanopowder was determined by X-ray diffractometry (XRD), using a Rigaku Ultima IV diffractometer (Cu Kα radiation). Crystallite size was calculated using the whole pattern profile fitting method (WPPF). The instrument influence was subtracted using the diffraction pattern of a Si standard recorded in the same conditions as the pattern of the sample. Fourier-transform infrared (FT-IR) spectra were recorded using a Prestige-21 spectrometer (Shimadzu, Japan) in the range 400–4000 cm−1, in KBr pellets, with a resolution of 4 cm−1. Specific surface area of the powder (SBET) was measured by BET (Brunauer-Emmett-Teller) nitrogen gas adsorption technique using an ASAP 2020 instrument (Micromeritics, USA). The pore size distribution was calculated from the desorption branch using the Barret-Joyner-Hallenda (BJH) method. The morphology of the nanopowder was investigated by scanning electron microscopy (SEM), using a Quanta FEG 250 microscope (FEI, USA) (operating at 30 kV and a working distance of 7 mm). The behavior in external magnetic field of the obtained manganese ferrite powder was studied using an installation equipped with a data acquisition system (Mihalca and Ercuta, 2003).

For the determination of point of zero charge (pHpzc), the batch equilibration technique was employed. The experiments were carried out using 25 mL of 0.01 mol/L NaCl solutions with pH values ranging from 2 to 12 adjusted with 0.1 mol/L NaOH or HNO3 solutions. 50 mg of manganese ferrite powder was then added into each of the flasks. The suspensions were allowed to equilibrate for 24 hr at 25°C and then the powder was magnetically separated from the aqueous phase. The pH values of final solutions were measured using a MultiMeter MM41 (CRISON, Spain) fitted with a glass electrode, which was calibrated using various buffer solutions. The values of the final pH (pHfin) were plotted against the values of the corresponding initial pH (pHin).

1.4. Catalysis experiments

The synthesized nanopowder was investigated as a potential catalyst for the oxidative degradation of phenol from synthetic solutions. The catalysis experiments were performed at a temperature of 25°C, in an automatic shaker with a shaking speed of 200 r/min. The concentration of phenol was determined by means of spectrophotometry using a Lambda 25 spectrometer (Perkin-Elmer, USA).

The synthetic solutions were obtained by the dissolution of the necessary phenol mass and oxidation agent mass into distilled water, for the desired concentrations. 25.0 mL of the solution was added on a certain mass of the catalyst and the suspensions were shaken for different times. Finally, the catalyst was separated from the aqueous solution using a magnet. The absorbance of the residual phenol was measured at the wavelength of maximum absorbance (270 nm).
The efficiency of catalytic oxidative degradation of phenol (\(\eta\) (%)) was calculated using Eq. (1):

\[
\eta = \frac{(C_{ph,i} - C_{ph,f})}{C_{ph,i}} \times 100\%
\]

where, \(C_{ph,i}\) (mg/L) is the initial concentration of phenol and \(C_{ph,f}\) (mg/L) is the final concentration of phenol in the solution, after the separation of the catalyst.

Several parameters (pH, catalyst dose, phenol concentration, oxidant: phenol ratio) were varied in order to see their influence on catalytic phenol degradation process in the presence of S\(_2\)O\(_8\)^{2–} anion as oxidant and MnFe\(_2\)O\(_4\) as catalyst. In order to assess the stability of the catalyst, the concentrations of leached manganese and iron were measured using a SpectrAA 280 FS atomic absorption spectrometer (VARIAN, USA).

Total organic carbon in the phenol synthetic solutions, after the heterogeneously catalyzed oxidative degradation was estimated using a TOC analyzer (Shimadzu, Japan). After catalyst separation, the residual oxidant was quenched by addition of solid KI.

### 2. Results and discussion

#### 2.1. Catalyst characterization

The XRD pattern and FT-IR spectrum of the powder annealed at 400°C are shown in Fig. 1.

It can be seen that cubic MnFe\(_2\)O\(_4\) (International Centre for Diffraction Data ICDD file no. 04-016-1572) is present in the powder as single crystalline phase. The average size of the crystallites calculated using WPPF method was of 6.1 nm.

Several IR absorption bands were reported in the literature for manganese ferrite. Thus, Goodarz Naseri et al. report that absorption bands of Mn–O and Fe–O bonds appeared at 404, 502, and 556 cm\(^{-1}\), respectively, for pure spinel manganese ferrite that was calcined at 873 K (Goodarz Naseri et al., 2011), while Yang et al. (2010) report for the manganese ferrite an absorption band around 566 cm\(^{-1}\). Han et al. (2011) reported for manganese ferrite powder adsorption bands at 420 and 574 cm\(^{-1}\). Other authors (Chakraborty et al., 2013) reported the characteristic peaks of MnFe\(_2\)O\(_4\) at wave numbers 576 and 670 cm\(^{-1}\) assigned to Fe–O and Mn–O stretching vibrations.

FT-IR spectrum of our manganese ferrite powder annealed at 400°C exhibits a large band in the range 400–750 cm\(^{-1}\), with maxima at 638 and 571 cm\(^{-1}\), and a shoulder at 486 cm\(^{-1}\) (Fig. 1b). The same phenomenon was reported in literature (Ma et al., 2003) for magnetite (Fe\(_3\)O\(_4\)) — the splitting of the band located around 570 cm\(^{-1}\) into two peaks, at 624 cm\(^{-1}\) and 582 cm\(^{-1}\). This was explained by the effect of finite size of nanoparticles – the breaking of a large number of bonds for surface atoms, resulting in the rearrangement of electrons on the particle surface – leading to the split of the energy levels of the quantized Fe\(_3\)O\(_4\) nanoparticles. Taking into account the small size of our MnFe\(_2\)O\(_4\) nanoparticles, a similar explanation can be accepted. Another possible explanation for the multiple bands present in the FT-IR spectrum of manganese ferrite is the variable cation distribution in octahedral and tetrahedral sites inside the crystalline network. MnFe\(_2\)O\(_4\) has a mixed spinel structure, with an inversion degree that depends on the synthesis route (Gabai and Ata-Allah, 2004).

The morphology of the powder was studied by SEM microscopy. Fig. 2 presents the obtained SEM image, which evidences fine spherical particles with diameters up to ~11 nm. The average value is around 7 nm, which is consistent with the average size of the crystallites calculated from XRD data. This proves that the manganese ferrite particles are single crystals.

Magnetic measurements performed on MnFe\(_2\)O\(_4\) annealed at 400°C showed that the powder exhibits a superparamagnetic behavior, which confirms the fine nature of manganese ferrite nanoparticles. Due to the small size of ferrite nanoparticles (Yang et al., 2010), at a field of 5 kOe a value of saturation magnetization of only 16 emu/g was reached. Although this value of saturation magnetization might be considered low, it is high enough to ensure the possibility of magnetic separation of the powder from a suspension, by using a normal magnet.

In order to have a complete characterization of the catalyst, we performed N\(_2\) adsorption–desorption experiments on
MnFe₂O₄ powder. Fig. 3 presents the N₂ adsorption–desorption isotherm (Fig. 3a) and the pore size distribution (Fig. 3b) of the analyzed powder. The adsorption–desorption isotherm exhibits a type IV isotherm with an H₄ type hysteresis loop, characteristic to mesoporous materials with disordered pores (Naumov, 2009; Yang et al., 2013). The pore size distribution evidences the existence of mesopores with a relatively narrow pore-size distribution around 5 nm, and a smaller fraction around 10 nm. The value of BET specific surface area was found to be 147 m²/g, characteristic to nanosized powders (Nalbandian et al., 2008). This high specific surface area recommends the use of our manganese ferrite powder as catalyst.

To evidence the nature of the charge generated in aqueous solutions on the surface of the synthesized nanoparticles, we studied the acid–base properties of MnFe₂O₄ powder. The point of zero charge (pHpzc) reveals the characteristics of the surface charge generated on MnFe₂O₄ in aqueous media. Fig. 4 shows the plot of final pH (pHfin) versus initial pH (pHin), which allows the determination of the point of zero charge (pHpzc), as the ordinate of the plateau (Negrea et al., 2010). This plateau corresponds to the pH range where buffering of the MnFe₂O₄ surface occurs, which means that for any pHin value in this range, the value of pHfin is about the same and represents the pHpzc. From the plot shown in Fig. 4, it results that manganese ferrite nanopowder has buffering capacity in the pHin range 4–10 and a pHpzc around 6.4. For pH values under 6.4, the surface of the catalyst will be positively charged due to protons adsorbed on –OH groups found on the oxides surface in aqueous media (Eq. (2)), favoring the adsorption of anionic species. For pH values above 6.4, the surface will be negatively charged due to dissociation of –OH groups (Eq. (2)) and adsorption of OH⁻ ions from solution, and therefore the adsorption of cationic species will be favored.

\[
\text{Cat}^- + \text{OH}^+ \rightleftharpoons \text{Cat}^- \text{OH} \rightleftharpoons \text{Cat}^- \text{O}^- \\
pH < \text{pHpzc} \quad \text{pH} \sim \text{pHpzc} \quad \text{pH} > \text{pHpzc}
\]  (2)

The buffering property of the catalyst in a wide pH range represents an advantage in view of wastewater treatment: one can treat wastewater with pHin between 4 and 10, and the pH of the treated water will reach a final value of 6–7, suitable for discharge.
2.2. Catalysis experiments

MnFe₂O₄ nanopowder obtained at 400°C was used as catalyst for the oxidative degradation of phenol from aqueous solutions in the presence of peroxydisulfate as oxidizing agent. We chose peroxydisulfate because sulfate radical SO₄⁻ is a strong oxidant with the redox potential of 2.5–3.1 V vs. NHE, and it is somewhat stronger than HO⁻ (1.89–2.72 V vs. NHE) (Olmaz-Hanci and Arslan-Alaton, 2013; Wang et al., 2015). This radical is usually generated from peroxides such as peroxymonosulfate (PMS) and peroxydisulfate (PDS) by UV, heat, transition metals, quinones, or electrochemical activation (Govindan et al., 2014; Guan et al., 2013). Furthermore, the tests done with H₂O₂ revealed the high catalytic activity of our powder, hydrogen peroxide being decomposed almost instantly. Considering these, we chose PDS anion as oxidant, knowing (from the literature) that it is more difficult to activate than PMS (Guan et al., 2013).

There are no studies reported in the literature for the degradation of phenol with peroxydisulfate in the presence of manganese ferrite. A comparison of peroxydisulfate, peroxymonosulfate and hydrogen peroxides as oxidants was reported for the degradation of atrazine in the presence of copper monosulfate and hydrogen peroxides as oxidants was reported (Govindan et al., 2014; Guan et al., 2013). Furthermore, the mechanism proposed for the degradation of phenol by peroxydisulfate in the presence of manganese ferrite:

\[
\text{Mn}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Mn}^{3+} + \text{SO}_4^{2-} + \text{SO}_4^{2-} \quad (3)
\]

To explain the dependence of phenol degradation efficiency on the pH value, one must take into account the processes occurring on the catalyst surface: the adsorption of oxidant S₂O₈⁻, phenol adsorption, activation of SO₄⁻ radicals, and their action on phenol.

The oxidant S₂O₈⁻ represents the anion of the strong acid H₂S₂O₈, which is completely ionized in aqueous solution, and therefore the anionic species S₂O₈⁻ is the single one in the whole pH range 0–14. The activation of SO₄⁻ radicals takes place after peroxydisulfate anions adsorption on the catalyst surface. Negatively charged anions are adsorbed better at pH < pHₚzc, when the catalyst surface is positively charged, by Coulombic attractions (physisorption) (Deliyanni and Matis, 2005; Negrea et al., 2013), Eq. (5):

\[
\text{Cat-OH}^+ + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Cat-OH}^+ \ldots \text{S}_2\text{O}_8^{2-} \quad (5)
\]

Peroxydisulfate anions adsorption is more intense as the positive surface charge increases, i.e., with decreasing pH. This explains the increase of phenol degradation efficiency when the pH value decreases from 6 to 3. At pH values around pHₚzc, although the surface is not charged, phenol degradation efficiency is still high (86.6% at pHₚzc ~ 7). Probably in this pH range, another type of mechanism predominates — specific adsorption (ligand exchange) (Deliyanni and Matis, 2005; Negrea et al., 2013). The adsorption can be physisorption Eq. (6) and/or chemisorption Eq. (7):

\[
\text{Cat-OH}^+ + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Cat}^+ \ldots \text{S}_2\text{O}_8^{2-} + \text{OH}^{-} \quad (6)
\]

\[
\text{Cat-OH}^+ + \text{S}_2\text{O}_8^{2-} \rightarrow \text{CatS}_2\text{O}_8^{2-} + \text{OH}^{-} \quad (7)
\]

As the pH increases to higher values, surface negative charge increases and S₂O₈⁻ adsorption decreases due to electrostatic repulsion; therefore, phenol degradation efficiency decreases.

Fig. 5 shows that maximum phenol degradation efficiency was reached at pH 3. The efficiency decreased at pH 2, although we would have expected it to increase due to higher positive charge of the catalyst surface and more intense S₂O₈⁻ adsorption. This decrease can be explained by the activation of another redox couple in this more acidic medium (Sukhotina, 1981):

\[
\text{S}_2\text{O}_8^{2-} + 2e^- + 2H^+ = 2\text{HSO}_4^- \quad E^0 = 2.123 \text{ V} \quad (8)
\]

As some of the oxidant S₂O₈⁻ participates in process (8), the yield of activation of SO₄⁻ radicals in process (3) decreases, and therefore the efficiency of phenol degradation decreased at pH 2.

![Fig. 5](Image)  
**Fig. 5** – Effect of initial pH on phenol removal efficiency.  
**Conditions:** Cₚₕᵢ = 54.08 mg/L, Cₗₒₓ = 0.5002 g/L, catalyst dose 3 g/L, contact time 6 hr.
Adsorption tests performed before catalysis experiments showed that phenol adsorption on manganese ferrite powder (at pH 3.5 and pH 7) was insignificant.

For pH values below \( pK_a = 9.98 \) (Harvey, 2000), the neutral species \( \text{C}_6\text{H}_5\text{OH} \) is dominant. This species does not adsorb on the surface of the catalyst, but it approaches to the surface to interact with \( \text{SO}_4^{2-} \) radicals; this process is not influenced by the charge of the catalyst surface. For pH values above \( pK_a \), phenolate anionic species \( \text{C}_6\text{H}_5\text{O}^- \) is dominant. This species is electrostatically repulsed by negatively charged surface of the catalyst, and phenol degradation efficiency decreases significantly, approaching zero.

Catalyst stability as a function of pH value was also investigated. The results presented in Fig. 6 show that the catalyst stability was lower at pH 2 where manganese was leached in higher proportion (~8%) than iron (~0.03%). As the pH increased, both iron and manganese leaching significantly decreased.

2.2.2. Influence of catalyst dose on phenol removal efficiency
To establish the optimal catalyst dose, we used a synthetic solution with an initial phenol concentration \( C_{\text{ph},i} = 52.8 \text{ mg/L} \), \( \text{pH}_{\text{in}} = 3.5 \), for an initial oxidant concentration \( C_{\text{ox}} = 0.5010 \text{ g/L} \). The contact time was 6 hr, at 200 r/min. From Fig. 7 it results that the optimal catalyst dose is 3 g/L which ensures an ~91% phenol removal efficiency. The use of a higher catalyst dose, does not lead to a significant increase of removal efficiency.

2.2.3. Influence of oxidant concentration on phenol removal efficiency
The optimal oxidant concentration \( C_{\text{ox}} \) was established employing solutions having the same initial phenol concentration \( C_{\text{ph},i} = 53.12 \text{ mg/L} \), for a catalyst dose of 3 g/L, \( \text{pH}_{\text{in}} = 3.5 \), with different oxidant concentrations \( C_{\text{ox}} = 12.5, 25.0, 50.0, 100, 500, 1000, 2000, \) and \( 3000 \text{ mg/L} \); the contact time was 6 hr at 200 r/min. The dependence of phenol removal efficiency on the oxidant: phenol mass ratio is shown in Fig. 8.

According to the results, phenol removal efficiencies higher than 90% were obtained for oxidant: phenol mass ratios within the range 2–20. The highest value (92%) was reached at an oxidant: phenol ratio of 10 \( (C_{\text{ox}} = 0.504 \text{ g/L}) \). The further decrease of phenol removal efficiency might be explained by the fact that, at high concentrations of peroxydisulfate (starting with 1 g/L), the absorbance of residual peroxydisulfate at 270 nm becomes significant and overlaps with residual phenol absorbance. This leads to a higher value of final absorbance and apparently to a higher concentration of residual phenol.

2.2.4. Kinetics of phenol catalytic oxidation with \( \text{S}_2\text{O}_8^{2-} \)
To understand the kinetics of catalytic oxidation of phenol with peroxydisulfate anions in the presence of manganese ferrite as catalyst, we employed a catalyst dose of 3 g/L, for two initial phenol concentrations \( C_{\text{ph},i(1)} = 55.5 \text{ mg/L} \) and \( C_{\text{ph},i(2)} = 104 \text{ mg/L} \) at \( \text{pH}_{\text{in}} = 3.5 \), and in case of the second
concentration at a $\text{pH}_{\text{in}} = 5.5$ also, for different contact times, at 200 r/min. The obtained results are shown in Fig. 9a. The dependence of phenol removal efficiency on the contact time is similar for the two initial phenol concentrations; for the higher initial concentration, the final removal efficiency is slightly smaller. The effect of initial pH is more significant; thus, the increase of $\text{pH}_{\text{in}}$ from 3.5 to 5.5 leads to significant smaller phenol removal efficiency (78% instead of 87%).

To estimate the kinetic rates of phenol degradation, experimental data were fitted using the pseudo first order and the pseudo second order kinetic models. The best results were obtained for the pseudo first order kinetic model, given by Eq. (9) (Saputra et al., 2013b):

$$\ln \frac{C_{\text{ph},t}}{C_{\text{ph},i}} = kt$$  \hspace{1cm} (9)

where, $k$ (hr$^{-1}$) is the apparent first order rate constant of phenol removal, $C_{\text{ph},t}$ (mg/L) is the concentration of phenol at time ($t$) and $C_{\text{ph},i}$ (mg/L) is the initial phenol concentration. Using this model to draw plots of $\ln(C_{\text{ph},i}/C_{\text{ph},t})$ as a function of time produced a straight line for the two different phenol concentrations and different $\text{pH}_{\text{in}}$ values as shown in Fig. 9b.

Based on regression coefficients $R^2$ (Table 1), one can conclude that phenol oxidation by peroxydisulfate anion in the presence of manganese ferrite as catalyst follows a pseudo first order kinetics, in agreement with the data reported in literature for the oxidative degradation of phenol with peroxy-monosulfate in the presence of Mn$_3$O$_4$ (Saputra et al., 2013a).

Measurements of total organic carbon (TOC) (conditions: $C_{\text{ph},i} = 52.8$ mg/L, catalyst dose 3 g/L, $C_{\text{ox}} = 0.5010$ g/L, pH$_{\text{in}} = 3.5$) showed that phenol was mineralized by peroxydisulfate anion in the presence of manganese ferrite up to 60% after 6 hr contact time, leading to a decrease of the TOC value from 41 mg/L to 16 mg/L.

2.2.5. Reuse of catalyst

The possibility to reuse the manganese ferrite catalyst was investigated by successive batch experiments. In each cycle, the working conditions were the same: initial concentration of phenol 104.7 mg/L, catalyst dose 3 g/L, concentration of oxidant 0.5002 g/L, contact time 6 hr, and initial pH 3.5. After 4 cycles of repeated use, phenol removal efficiency decreased from ~95% to ~32% (Fig. 10).

In the XRD pattern recorded for the catalyst after 4 cycles (Fig. 1a), the diffraction peaks of MnFe$_2$O$_4$ are still present, but they are wider and the intensity diminished to about half of the initial one. This shows that the processes that took place during catalysis, especially manganese leaching (Fig. 6) affected the superficial structure of the catalyst particles, leading to the decrease of MnFe$_2$O$_4$ crystallite size. However, there are no new peaks indicating the formation of other crystalline phases.

On the other hand, the FT-IR spectrum of the recovered used catalyst has changed in comparison with the one of the initial manganese ferrite powder (Fig. 1b). Thus, the band located at 638 cm$^{-1}$ appears as a very weak shoulder of the wide band located around 570 cm$^{-1}$, with a shoulder at 460 cm$^{-1}$. This change might be explained by the superficial oxidation of Mn(II) to Mn(III) followed by leaching; this spectrum is similar to that recorded for the manganese ferrite powder annealed at 700°C, when MnFe$_2$O$_4$ goes to Mn$_{0.176}$Fe$_{1.824}$O$_3$ (Stoia et al., 2015). These processes, which damage the superficial structure of the catalyst, might explain the decrease of phenol removal efficiency in the case of the reused catalyst.

The obtained results evidence a good catalytic activity of the synthesized manganese ferrite nanopowder.

### Table 1 – Results of the kinetic study.

<table>
<thead>
<tr>
<th>Initial phenol concentration (mg/L)</th>
<th>Initial pH</th>
<th>Pseudo-first order</th>
<th>$R^2$</th>
<th>$k$ (hr$^{-1}$)</th>
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<td>55.5</td>
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3. Conclusions

Magnetic MnFe$_2$O$_4$ nanopowder was obtained by a facile synthesis method based on the redox reaction between the manganese (II) and iron (III) nitrates and polyvinyl alcohol,
followed by thermal decomposition at 400°C. The powder consisted of fine spherical ferrite nanoparticles, with diameters between 5 and 11 nm, leading to a superparamagnetic behavior and a high specific surface area of 147 m²/g. The magnetic manganese ferrite powder was used as catalyst for the oxidative degradation of phenol in aqueous solutions, in the presence of peroxydisulfate anion as oxidant.

The synthesized MnFe₂O₄ nanopowder exhibited high catalytic activity, leading to a maximum removal efficiency of ~95% for an initial phenol concentration of 50 mg/L, peroxydisulfate concentration 0.5 g/L, catalyst dose 3 g/L and pH 3.5. Total organic carbon measurements evidenced that under these conditions, phenol oxidation goes in an extent of 60% to CO₂.

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