Heterogeneous Fenton Oxidation Using Magnesium Ferrite Nanoparticles for Ibuprofen Removal from Wastewater: Optimization and Kinetics Studies

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In this study, the catalytic properties of Fenton-like catalyst based on magnesium ferrite nanoparticles for IBP degradation were examined. Structural and morphological studies showed the low crystallinity and mesoporous structure for the catalyst obtained via a glycine-nitrate method. The influences of catalyst dosage, oxidant concentration, and solution pH on the pollutant degradation were investigated. The pseudo-first-order model describes kinetic data, and under optimal condition (catalyst dose of 0.5 g L⁻¹, H₂O₂ concentration of 20.0 mM, and pH of 8.0), apparent rate constant reached 0.091 min⁻¹. It was shown that Fenton reaction was mainly induced by iron atoms on the catalyst surface, which is supported by very low iron leaching (up to 0.05 mg L⁻¹) and high catalytic activity at neutral solution pH (6.0-8.0). It was found that the IBP mineralization onto magnesium ferrite catalyst was rapid and reached up to 98-100% within 40 min. Thus, prepared magnesium ferrite nanoparticles can be used as an effective Fenton-like catalyst for the IBP degradation from wastewater.

1. Introduction

Ibuprofen (IBP) is a nonsteroidal anti-inflammatory drug, which is widely used to treat fever, pain, and inflammation of minor injury. IBP was the first member of propionic acid derivatives introduced in 1969. It is used as an analgesic and antipyretic drug for adults and children. IBP was rated as the safest conventional nonsteroidal anti-inflammatory drug by spontaneous adverse drug reaction reporting systems in the UK [1]. The high annual consumption is about 200 tons per year, and low metabolite conversion of IBP in the human body leads to the presence of IBP derivatives in the wastewater treatment plant, in surface water, and even in drinking water [2]. Ingestion of IBP in the environment leads to significant negative consequences. The municipal wastewater treatment plant, common water treatment processes, such as coagulation/flocculation and filtration, and biological treatment do not remove efficiently the pharmaceuticals and
personal care products, which signifies the importance to develop new methods for removing these products from water bodies [3, 4]. Adsorption, sonolysis and sono-Fenton oxidation, photocatalytic oxidation, noncatalytic and catalytic ozonation, persulfate-based Advanced Oxidation Processes (AOPs), and heterogeneous Fenton processes are widely used for IBP removal from wastewater. The application of aforementioned methods is limited by their technical or economic disadvantages. Thus, adsorption methods are well suited for removing trace amounts of pharmaceuticals and cleaning relatively small volumes of water. Otherwise, the regeneration of the sorbent requires the destruction of sorbed toxic pharmaceuticals or their metabolites [5]. Electrochemical oxidation and ozonation belong to high-energy consumption methods, which is not always economically feasible. In addition, these methods are characterized by the formation of large quantities of oxidation products that are more toxic than the original pharmaceuticals [6, 7]. Despite their attractiveness in the laboratory, photocatalytic methods are not widely used on an industrial scale [8, 9]. This is due to their high sensitivity to the turbidity of wastewater, the complexity of the design of catalytic reactors that provide the necessary conditions for effective destruction of pollutants, and the need to use UV irradiation to achieve a high degree of mineralization of pharmaceutical contaminants [10, 11].

To avoid these disadvantages, the application of heterogeneous catalyst based on iron oxides and metal ferrites is a promising solution [12]. Magnesium ferrite is a good candidate as an effective Fenton-like catalyst due to their affinity for various pollutants [13], high catalytic activity at a wide range of pH [14], and low metal ion leaching [15]. Therefore, magnesium ferrite has a high affinity towards inorganic and organic pollutants, which improved their catalytic efficiency due to concentration of the removed molecules in surface sites [16]. The degradation of Carbamazepine and Ciprofloxacin [17], Bisphenol A [18], and textile dyes [19, 20] onto metal ferrites such as Fenton-like catalysts was widely reported. However, magnesium ferrite application for the degradation of pharmaceuticals is still limited.

In this paper, a nanostructured magnesium ferrite prepared by self-combustion sol-gel method was studied as heterogeneous Fenton-like catalyst for the IBP degradation. This work particularly evaluates the effects of the main AOP parameters: dose of catalyst, H$_2$O$_2$ oxidant concentration, and solution pH for optimization the IBP degradation. Also, kinetics parameters of the IBP degradation process were studied by means of HPLC technique and TOC analysis to establish the degree of IBP mineralization.

### 2. Materials and Methods

#### 2.1. Chemical Reagents and Magnesium Ferrite Catalyst.
Magnesium nitrate (Mg(NO$_3$)$_2$), ferrous nitrate (Fe(NO$_3$)$_3$), sodium chloride (NaCl), and glycine (H$_2$NCH$_2$COOH) reagents were purchased from “Five Ocean” Corporation (Belarus) and used to obtain a catalyst based on magnesium ferrite nanoparticles. IBP (Table 1) and H$_2$O$_2$ solution (30 wt. %) were supplied by Sigma-Aldrich. All reagents were used as received without additional purification. Deionized water (resistance of 18.2 MΩ cm$^{-1}$) was used for the preparation of all aqueous solutions.

Magnesium ferrite nanoparticles were prepared by self-combustion glycine-nitrate synthesis. Magnesium nitrate, ferrous nitrate, glycine, and sodium chloride as an inert additive were dissolved in deionized water in molar ratio 1:2:4:5:10, respectively. The prepared mixture was vaporized at 80°C under vigorous stirring before preparing a thick gel. Further, heating of the gel mass resulted in its spontaneous combustion. The obtained mixture of magnesium ferrite, coal, and sodium chloride was heated at 300°C for 5 h. Magnesium ferrite nanoparticle was washed by deionized water and removed by a magnet. A detailed preparation method of magnesium ferrite has been previously reported [13].

#### 2.2. Catalytic Experiments and Kinetics Modeling.
Catalytic experiments were conducted in 50 mL centrifuge tubes at 20°C under natural light. Taking into account that IBP [21] is a weak acid (pK$_a$ = 5.3) with low solubility in water (21 mg L$^{-1}$) (Table 1), the working IBP solution (10 mg L$^{-1}$) was prepared by dissolution of the required powder sample in deionized water under vigorous stirring. In all experiments, IBP solutions were kept in the dark for 30 minutes after the addition of catalysts until the adsorption equilibrium was reached.

To determine the effect of the catalytic process conditions onto the efficiency of IBP (10.0 mg L$^{-1}$) degradation, the dosage of catalyst (0.2-1.0 g L$^{-1}$), H$_2$O$_2$ concentration (10.0-30.0 mmol L$^{-1}$), pH of the solution (4.0-8.0), and contact time (5-40 minutes) were varied. For the evaluation the degree of IBP catalytic degradation and mineralization, MgFe$_2$O$_4$ catalyst with a given dosage of catalyst, H$_2$O$_2$ concentration was added to the IBP (10.0 mg L$^{-1}$) aliquot of 50.0 mL. Preliminaril, it was checked that the addition of 10.0-30.0 mmol L$^{-1}$ H$_2$O$_2$ without catalyst did not result in IBP (10.0 mg L$^{-1}$) oxidation during 2 hours. Therefore, during the adsorption stage, IBP concentration was decreased on approximately 2-10% depending on the dosage of catalyst (0.2-1.0 g L$^{-1}$). These changes in IBP concentration were
The use of such an excessive amount of H₂O₂ may be due to the following: (i) low efficiency of reactive oxygen-containing species (ROS) formation, (ii) low lifetime of OH-radicals, and (iii) fast recombination of produced hole-electron pairs [22]. The chosen interval of H₂O₂ concentration is in a good correlation with other results related to IBP heterogeneous Fenton oxidation [23]. All adsorption and catalytic experiments were repeated at least twice to ensure the reproducibility of the results.

The degradation efficiency α_HPLC and mineralization efficiency α_TOC of IBP were calculated according to:

\[
\alpha_{\text{HPLC}} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100\%,
\]

\[
\alpha_{\text{TOC}} = \left( \frac{A_0 - A_t}{A_0} \right) \times 100\%,
\]

where \(C_0\) and \(C_t\) are the concentrations (mg L\(^{-1}\)) of the IBP sample measured by high-performance liquid chromatography (HPLC) at initial time (minutes) and \(A_0\) and \(A_t\) are the total organic carbon of the IBP sample at initial time (minutes), respectively.

Typically, the Fenton-like catalytic processes are usually well characterized by the Langmuir-Hinshelwood kinetic model, which describes a pseudo-first-order kinetics (Equation (3)) at low initial organic pollutant concentration [24].

\[
\ln \left( \frac{C_0}{C_t} \right) = k' \times t,
\]

where \(C_0\) and \(C_t\) are the concentrations (mg L\(^{-1}\)) of the IBP sample measured at initial time (min) and \(k'\) is the apparent pseudo-first-order rate constant (min\(^{-1}\)).

**4. Results and Discussion**

4.1. Characterization of Magnesium Ferrite Catalyst. As shown in Figure 1(a), the peaks in XRD spectra are referred to patterns of MgFe₂O₄ with cubic spinel structures. The peaks at 2θ values of 35.14°, 41.46°, 50.54°, 67.37°, and 74.28° belong to (202), (311), (400), (511), and (404) crystallographic planes of magnesium ferrite (ICPDS No. 96–900–3804), respectively. The calculated parameter \(a\) of the crystal lattice is 5.961 Å, which is different from the reference value for MgFe₂O₄ and may be due to a defect in the crystal structure of the resulting sample. The domain size of the prepared catalyst calculated from the Scherrer equation was calculated from the data of full-width at half-maximum (FWHM) of the (311) diffraction through the Scherrer equation.

\[
D = \frac{0.9 \times \lambda}{\beta \times \cos \theta},
\]

where \(D\) is average particle size (nm), \(\lambda\) is the wavelength of KαCo radiation, and \(\beta\) and \(\theta\) are the position (degree) and the half-width (radian) of the diffraction peak (311) in the experimental XRD patterns, respectively.

Fourier transform infra-red (FTIR) spectra of the catalyst were recorded on Bruker Vertex 70 FTIR in the range of a wavenumber of 400-4000 cm\(^{-1}\). Adsorption properties were evaluated by a nitrogen adsorption-desorption method (-196°C) on a Micromeritics-Tristar II Plus specific surface area and porosity analyzer. A specific surface area \(A_{\text{BET}}(\text{m}^2\text{g}^{-1})\) was calculated by the Brunauer–Emmett–Teller (BET) method. The average pore volume \(V_{\text{sp}}(\text{cm}^3\text{g}^{-1})\) was estimated at \(p/p_0 = 0.99\) using the Horvath–Kawazoe method. The point of zero charge \(pH_{\text{pzc}}\) was determined by the graphical drift method [25]. For this, 40 mg MgFe₂O₄ was placed in an aliquot of 10.0 mL and 0.01 M NaCl solution in the pH range of 3.0–12.0 and was stirred for 48 hours. Then, the sorbent was separated from the solution and the equilibrium pH value was measured.

The concentration of IBP in initial solution and treated solution was analyzed by high-performance liquid chromatography (HPLC-Shimadzu). Acetonitrile and potassium phosphate monobasic buffer (50:50, v/v) was used for the mobile phase, and the flow-rate was maintained at 1.0 mL min\(^{-1}\). A TOC analyzer (Shimadzu, Japan) was used for measuring IBP mineralization degree.

3. Analytical Methods

The crystalline structure and phase analysis of magnesium ferrite nanoparticles were obtained using an X-ray diffractometer (PANanalytical) with KαCo radiation (\(\lambda = 0.179\) nm). The domain size of prepared magnesium ferrite catalysts was calculated from the data of full-width at half-maximum (FWHM) of the (311) diffraction through the Scherrer equation.
Table 2. The nitrogen isotherms of magnesium ferrite catalyst are related to type IV isotherms indicating its characteristic of mesoporous characteristics with H1 hysteresis loop corresponding to the cylindrical pore [27]. The BET surface area, pore volume, and average pore size of the catalyst were 14 m$^2$ g$^{-1}$, 0.037 cm$^3$ g$^{-1}$, and 11 nm, respectively. The pH $pzc$ for the prepared catalyst was 6.58 (Table 2). It means that due to protonation of M–OH (M : Mg or Fe) groups in acidic solution, the surface of magnesium ferrite nanoparticles had positive charge. An increase of pH > 6.58 accompanied by dissociation of M–OH groups, which leads to a change of the surface charge to negative. It is an important characteristic for the explanation of catalytic efficiency depends on the pH of IBP solution.

4.2. Effect of Experimental Conditions on IBP Degradation

4.2.1. Dose of Solid Catalyst. The kinetic curves of IBP degradation on magnesium ferrite nanoparticles as a function of catalyst dose are shown in Figure 2. The IBP degradation sharply increased with an increasing catalyst dose from 0.2 until an optimal value of 0.5 g L$^{-1}$. A further increase of magnesium ferrite concentration up to 1.0 g L$^{-1}$ was affected positively only at the first 20 minutes. Intriguingly, IBP degradation efficiency were equal for the catalytic reaction time of 30-40 min. The increase of catalytic efficiency is dependent on the catalyst dose, but not proportionally. It is in accordance with the argument that the concentration of active catalytic sites on the surface of catalyst in the heterogeneous Fenton process for a dose of 0.5-1.0 g L$^{-1}$ is a not limiting parameter for reactive oxygen species producing. This observation is consistent with previous studies for the methylene blue degradation [16]. Compared to the homogeneous Fenton process where the catalytic activity is dependent on ferrous/ferric ion concentration, the efficiency of the heterogeneous Fenton process mostly depends on the state of surface Fe-OH sites. This is due to a low concentration of leached iron from a magnesium ferrite catalyst (less than 0.05 mg L$^{-1}$ for catalyst dose of 1.0 g L$^{-1}$). At the same time, higher differences in the rate of IBP degradation at the initial stage (up to 10 minutes) for different doses of catalysts

![Figure 1: (a) XRD pattern and (b) FTIR spectra of magnesium ferrite catalyst.](image)

![Figure 2: (a) Kinetic curves and (b) pseudo-first-order linear plots of IBP degradation depend on magnesium ferrite catalyst doses.](image)
indicate the participation of leached iron ions in the catalytic process.

Based on the correlation coefficient ($R^2$) in Figure 2, the pseudo-first-order model is the most suitable model describing the catalytic kinetics of IBP degradation on magnesium ferrite nanoparticles. The calculated apparent rate constants for 0.2, 0.5, and 1.0 g L$^{-1}$ dose were 0.019, 0.070, and 0.099 min$^{-1}$, respectively. A higher number of catalytically active sites for $\text{H}_2\text{O}_2$ decomposition and reactive oxygen species generation could explain the positive effect of a solid catalyst.

4.2.2. $\text{H}_2\text{O}_2$ Concentration. It is well known that at high concentration $\text{H}_2\text{O}_2$ can act as scavenger of OH radicals (Equation (5)), reducing the efficiency of organic compounds catalytic degradation [28, 29]. Therefore, the efficiency of the heterogeneous Fenton process increases only until reaching optimal $\text{H}_2\text{O}_2$ concentration. For evaluating the optimum amount of $\text{H}_2\text{O}_2$, the IBP catalytic degradation tests were carried out for the initial concentration of 10.0, 20.0, and 30.0 mM.

\[
\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OOH} + \text{H}_2\text{O} \quad (5)
\]

According to Figure 3, the rate of IBP degradation proportionally increased in a 10.0-30.0 mM $\text{H}_2\text{O}_2$ range. Increasing $\text{H}_2\text{O}_2$ concentration from 10.0 to 30.0 mM was accompanied by an increase in the apparent pseudo-first-order rate constant from 0.035 to 0.107 min$^{-1}$. It should be noted that the used concentrations of $\text{H}_2\text{O}_2$ significantly exceeded the stoichiometric value required for the complete mineralization of IBP. It might result from the $\text{H}_2\text{O}_2$ decomposition without the production of OH radicals [30] or to the formation of small organic compounds exhibiting a slower rate constant for the radical attack [31].

4.2.3. pH of Model Solution. The pH of solution is the determining parameter that limits the efficiency of the homogeneous Fenton process. This is due to the existence of different forms of iron ions, such as ferric ions, mono- or polyhydroxy nuclear complexes, and colloidal particles. As a rule, the highest activity of the homogeneous Fenton process reaches a pH of 2.8 [32], while heterogeneous Fenton reaction favored acidic and is close to neutral pH [33]. The influence of pH was investigated at close to neutral conditions (pH = 4.0-8.0), while the IBP solution had pH = 4.5. The
range of pH was chosen close to real wastewater from pharmaceutical plants [34].

According to Figure 4, the highest IBP degradation efficiency $k' = 0.082$ and reaction time $= 0.091 \text{ min}^{-1}$ were performed at neutral (6.0) and slightly alkaline (8.0) pH, respectively. Taking into account IBP pKa = 5.3 (Table 1) and magnesium ferrite pH_{pc} = 6.58 (Table 2), at this pH range, IBP is present in an anionic form and catalysts have negative charge leading to electrostatic repulsion. It means that the active sites of catalyst do not occur by IBP and free for interaction with H_2O_2. Similar results were obtained for methylene blue degradation on magnesium ferrite catalyst [16].

4.3. Evaluation of IBP Degradation and Mineralization. Generally, IBP degradation was accompanied by the formation of various byproducts. Adityosulindro et al. [23] reported about up to 14 transformation products of IBP (1-hydroxy IBP, 2-hydroxy-IBP, 4-isobutylacetophenon, etc.) during Fenton oxidation on Fe-containing zeolite. This result correlates with a low IBP mineralization degree that is less than 0.6 according to TOC analysis. To confirm the effectiveness of IBP mineralization on magnesium ferrite Fenton catalyst, the comparison data of HPLC and TOC analyses are shown in diagrams (Figure 5) for model solution after 40-minute reaction. The effect of doses of magnesium ferrite catalyst, H_2O_2 concentrations, and pH of the solutions on degree of IBP degradation and mineralization were studied. It is extremely important to note that for all experimental conditions, the IBP mineralization degree was close to 98-100%. Only for the lowest dose of magnesium ferrite catalyst (0.2 g L^{-1}) and H_2O_2 concentration (10.0 mM) differences in HPLC and TOC data were observed (Figures 5(a) and 5(b)), when IBP mineralization degrees were about 48 and 88%, respectively.

4.4. Comparison with Fenton-Like Catalysts and Photocatalysts. Comparative data on the catalytic IBP degradation (Table 3) show that magnesium ferrite demonstrates high catalytic activity and exceeds many Fenton-like catalysts and photocatalysts in terms of the apparent rate constant. An important advantage of the obtained catalyst is the high rate of IBP oxidation. Almost complete mineralization was achieved within 40 min, while the other catalysts require time from 60 to 180 min, which is important for practical application. The relatively high initial concentration of H_2O_2 used in this work is due to performing the catalytic process under natural light and the high IBP concentration in the model solutions. The main advantage of the developed Fenton-like catalyst is the complete IBP mineralization during their oxidative degradation.

5. Conclusions

Fenton-like catalyst based on magnesium ferrite nanoparticles characterized by low crystallinity (lattice parameter $a$ of 5.961 Å, crystallite size of 2.2 nm) and mesoporous structure...
(BET specific area of 14 m² g⁻¹, sorption volume of 0.030 cm³ g⁻¹, and average pore size of 11 nm) was synthesized. The influence of the conditions of the catalytic process (dose of catalyst, H₂O₂ concentration, and pH of solution) on the efficiency of nonsteroidal anti-inflammatory drug IBP degradation was established. The reaction followed the pseudo-first-order kinetics with respect to IBP, and the apparent rate constant increased almost proportionally with the concentration of the conditions of the catalytic process. The conductive research has shown the prospects of the practical application of the developed Fenton-like heterogeneous catalyst for wastewater treatment from pharmaceutically active compounds.

### Data Availability

The manuscript data used to support the findings of this study are included within the article.

### Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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