FULL LENGTH ARTICLE

Investigation on the sonocatalytic degradation of nitrobenzene using heterogeneous nanostructured catalysts in absence and presence of surfactant

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Fenton like systems; Advanced oxidation processes (AOPs); Nanostructured oxides; Sonication; Cetyl trimethyl ammonium bromide surfactant (CTAB); Nitrobenzene

Abstract
Because of the extensive use and excessive release of various NB, economical and efficient methods for the treatment of wastewater and cleanup of petrochemical compounds are needed. This study focused on the sonocatalytic degradation of NB in aqueous solution assisted with H2O2 oxidant and nanostructured metal oxide catalysts, prepared in the absence of CTAB (series I), (Fe2O3-I, CuO-I, NiO-I, and Co3O4-I) and nanostructured metal oxide catalysts prepared in the presence of CTAB (series II), (Fe2O3-II, CuO-II, NiO-II, and Co3O4-II). The physicochemical properties of these catalysts were investigated via X-ray powder diffraction (XRD), transmission electron microscope (TEM), scanning electron microscope (SEM), and point of zero charge (PZC).

The potential degradation feasibility for NB in US/nano metal oxide (series I and or series II)/H2O2 systems was measured by GC analysis at regular time intervals. Otherwise, some operational parameters such as ultrasonic irradiation time, solution pH value, H2O2 concentration, different weights of the nano-sized catalysts, NB concentration, leaching of the nano-sized catalysts, and reaction kinetics had been examined. It was found that H2O2 oxidant can effectively assist the sonocatalytic degradation of NB in the presence of nano-sized oxides (series I) and with more efficiency in the presence of nano-sized oxides (series II), and the effect of efficiency in degradation was changed in the order of (Fe2O3 > CuO > NiO > Co3O4). Therefore, oxides prepared in micellar solution were found to upgrade the economic aspect of NB degradation.

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1. Introduction

Nitroaromatic compounds are widely used as raw materials in several industrial processes related to pesticides, explosives, colorants, and paper pulp production. Many of these substances, such as nitrobenzene and nitrophenols, are usually found in wastewaters of these industries and are considered potentially toxic [1]. The remediation of wastewaters containing these pollutants is difficult since, due to their high toxicity, they are refractory to conventional biological treatments [2,3].

Nitrobenzene (NB) is a very toxic substance and a carcinogenic pollutant [4]. It is one of the fastest-growing end use synthetic products of benzene [5] such as dyes [6], plastics,

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explosives, pharmaceuticals [7], and pesticides [8]. NB is used to produce aniline and, as an organic solvent, has been widely dispersed in water and soil, causing great environmental concern because of its toxicity, quantity of production, and difficult biodegradation, even at low concentrations [9,10]. The strong electron-withdrawing property of the nitro-group makes NB resistant to oxidation by biological treatment and conventional chemical oxidation [4,6,11]. Furthermore, NB and some of its transformation metabolites, such as nitrobenzene, hydroxylaminobenzene, and aniline; exhibit toxic and mutagenic effects on biological systems [12,13]. Therefore, exploration of effective methods for NB degradation represents an important research challenge, and various alternative treatment technologies have been developed over the last two decades in order to cost-effectively meet environmental regulatory requirements, some of which are advanced oxidation processes (AOPs).

Advanced oxidation processes (AOPs) [14] which are generally based on the generation of highly reactive species such as hydroxyl radicals (·OH), are of great interest for degradation of pollutants that are difficult to eliminate with conventional treatments. In particular, Fenton processes are useful to achieve considerable reduction in the concentrations of aromatic compounds in wastewaters and they could be applied as pretreatment stages to reduce the effluent toxicity before biological treatment [15–17]. Fenton reaction bases on the use of hydrogen peroxide combined with metal salts.

A considerable interest in the development of heterogeneous catalysts for the oxidation of wastewater streams, to overcome the problems associated with Fenton processes has been reported. From the material point of view, it is generally accepted that heterogeneous catalysts in the form of nanoparticles are considerably more efficient than those comprising micrometer sized and larger particles.

Studies on the sonolysis of a wide range of organic compounds have demonstrated that ultrasonic irradiation has potential for treatment of hazardous wastewater [18]. A literature survey reveals that, the use of ultrasounds for wastewater treatment has been a subject of much current interest, but ultrasonic irradiation alone has not been able to provide high enough rate of degradation to be applied in practice. This is particularly true for hydrophilic compounds, which are usually hard to be decomposed [19]. One of the solutions to increase the degradation efficiency of organic pollutants in water is to combine the ultrasound application with advanced oxidation processes (AOPs). One of the promising AOPs is the Fenton’s reagent treatment. Some researchers have tried to use the combined methods to improve the degradation of organic pollutants [20].

One of the main objectives of this work is to focus on the degradation of NB in the presence of Fenton-type reagent aided by ultrasonic operating at 20 kHz. Our goal is to find a new combination of sonication conditions and Fenton-type for maximum efficiency with nano-sized catalysts. In the current study, we combine sonolysis and catalysis by employing FeO\(_2\)\(_\text{O} \)\(_y\), CuO, NiO, and Co\(_x\)O\(_y\) as heterogeneous nano-sized catalysts in the absence and presence of CTAB, under different conditions (pH, irradiation time, H\(_2\)O\(_2\) concentration, solution pH value, different weights of nano-sized catalysts, NB concentration, leaching of the nano-sized catalysts, and reaction kinetics) while NB is employed as a pollutant.

2. Materials and methods

2.1. Chemicals

Nitrobenzene (99%) was obtained from Sigma–Aldrich and hydrogen peroxide (H\(_2\)O\(_2\)) (30%, w/v) was purchased from Fluka (USA). FeCl\(_3\)-6H\(_2\)O, CoCl\(_2\)-6H\(_2\)O, NiCl\(_2\)-6H\(_2\)O, CuCl\(_2\)-2H\(_2\)O, and FeSO\(_4\)-7H\(_2\)O were purchased from ADWIC (Cairo, Egypt) as precursor compounds. NaOH (96%) was supplied from ADWIC (Egyptian Chemical Reagents) and cetyl trimethyl ammonium bromide (CTAB) was supplied from Merck (Germany Chemical Reagents). All chemicals were used without further purification.

2.2. Catalysts preparation

2.2.1. Preparation of nano-sized metal oxide catalysts in absence of CTAB

Metal oxide catalysts (MO, where M = Fe, Co, Ni, Cu) were prepared starting from the corresponding metal chlorides MCl\(_x\)-yH\(_2\)O (CoCl\(_2\)-6H\(_2\)O, NiCl\(_2\)-6H\(_2\)O, CuCl\(_2\)-2H\(_2\)O), and FeSO\(_4\)-7H\(_2\)O. The metal hydroxide gel was firstly prepared by dissolving 1 mol of MCl\(_x\)-yH\(_2\)O or FeSO\(_4\)-7H\(_2\)O in deionized water and then sodium hydroxide solution (2 M) was added dropwise to form the metal hydroxide gel. The solutions were then stirred for 2 h at room temperature. During this time, the reaction mixtures form various colored gels.

The prepared colored gels were filtered, then washed with distilled water and dried. The obtained powder was then calcined in air at 450 °C for 4 h to obtain the corresponding metal oxides. The oxides obtained by this method will be designated followed by the number I, e.g. for NiO oxide will be NiO-I.

2.2.2. Preparation of nano-sized metal oxide catalysts in presence of CTAB

Metal oxide catalysts MO, (M = Fe, Co, Ni, or Cu) were prepared by the one-step co-precipitation in the presence of cetyl trimethyl ammonium bromide (CTAB), as described by [21]. Appropriate amounts of MCl\(_x\)-yH\(_2\)O (FeCl\(_3\)-6H\(_2\)O, CoCl\(_2\)-6H\(_2\)O, NiCl\(_2\)-6H\(_2\)O, CuCl\(_2\)-2H\(_2\)O) and CTAB were dissolved in distilled water (molar ratio: CTAB/(M) = 0.8), then aqueous solution of NaOH (2 M) was added dropwise until the pH arrived at ca.11, measured with pH meter (Mettler-Toledo Group). After continuous stirring for 2 h, the obtained suspension was transferred to a Teflon-sealed autoclave and hydrothermally aged at 120 °C for 48 h. After centrifugation, washing, and drying; the powder was calcined in air at 450 °C for 4 h. The oxides obtained by this method will be designated followed by the number II, e.g. CuO-II and Co\(_x\)O\(_y\)-II.

2.3. Catalysts characterization

2.3.1. Determination of PZC

Point of zero charge, PZC, for the metal oxides (FeO\(_2\)\(_y\), CuO, NiO, and Co\(_x\)O\(_y\)) was measured according to the method described by Franca et al. [22]. Several amounts of metal oxides (0.1 g, 0.3 g, 0.5 g, and 0.7 g) were added to 50 mL of
distilled water adjusted to pH of 5 or 11. The aqueous suspensions containing different amounts of the metal oxides were left to equilibrate while covered for 24 h under agitation (100 rpm) at 25 °C. The pH of each solution was then measured using a digital pH meter (Mettler-Toledo AG 8603, Switzerland). The PZC was determined as the converging pH value from the pH vs. adsorbent mass curve [23].

2.3.2. X-ray diffraction technique (XRD)
The X-ray diffraction patterns were recorded in the range 2θ = 4–80°, using Philips powder diffractometer with Cu Kα1 radiation. The instrument was operated at 40 kV and 40 mA. The spectra were recorded at scanning speed of 2° in 2θ/min. The 2θ and the relative intensity I/I₀ were deduced from the chart and the corresponding d-values were calculated from the Bragg’s equation:

\[2d \sin \theta = \lambda \rightarrow n \lambda, \quad \text{at } n = 1\]

where, \(d = \) Lattice space = \(λ/2 \sin θ\), \(θ = \) Bragg’s angle, and \(λ = \) X-ray wave length = 1.54 Å.

The average crystallite size of different catalysts was calculated from XRD spectra by using Scherrer equation which is limited to nano-scale particles:

\[D = \frac{\beta \lambda}{\beta \cos θ}\]

where, \(β = \) the shape factor = 0.9, \(β = \) the line broadening or band width at half the maximum intensity in radians, and \(D = \) the mean size of the ordered (crystalline) domains.

2.3.3. Transmission electron microscope (TEM)
Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused into an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a charge-coupled device CCD camera. TEM images were obtained by using a Jeol 2010 named DV 300W1 system operating at 130 kV. The sample was ultrasonically suspended and deposited on a carbon film supported on a copper grid.

2.3.4. Scanning electron microscope (SEM)
Scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern.

The electrons interact with the atoms that make up the sample producing signals that contain information about the sample’s surface topography, composition, and other properties such as electrical conductivity. The gold-coated catalyst was observed through the scanning electron microscope (SEM, model Jeol 5410). Power was set to 30 kV.

2.3.5. Atomic absorption spectrometry (AAS)
Atomic absorption spectrometry (AAS) is a spectroanalytical procedure for the qualitative and quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state. In analytical chemistry, the technique is used for determining the concentration of a particular element (the analyte) in a sample to be analyzed, and we have used this technique to determine the metal ions in the solution after the reaction due to leaching of the catalysts in the solution. The actual concentration of the metal ions was analyzed by an atomic absorption spectrometer (ZEEnit 700P).

2.4. Catalytic degradation of NB by heterogeneous catalysts using ultrasonic irradiation
A standard aqueous nitrobenzene was used in all the experiments with a concentration of 10 mg/L solution. A commercial sonicator, VCX-750 (Sonics and Materials, Inc.) equipped with a titanium probe (diameter 13 mm) capable of operating in continuous mode at a fixed frequency of 20 kHz with a variable electric output power up to 125 W was used for ultrasonic experiments. Experiments were carried out in a glass reaction vessel with thin and indented bottoms for uniform and more efficient energy transmission. Ultrasound power output was set at 100 W for all the experiments. The experimental procedure was as follows. The metal oxides (Fe₂O₃, CuO, NiO, and Co₃O₄) used as heterogeneous catalysts were heated at 450 °C for 1.0 h for activation and then were dispersed into 50 mL of 10 ppm NB aqueous solution followed by shaking for 15 min, these suspensions were treated by vigorous stirring to make a good dispersion of the catalysts. After the adsorption-desorption equilibrium was attained, it was filled into the reactor which was immersed in a water bath adjusted at 11 °C with the help of an external cooling device. Afterward, this reactor was placed in an ultrasound apparatus and irradiated according to the experimental requirements. Sonication was applied in continuous mode. The tip of the titanium probe was placed about 2 cm below the surface of the NB solution during sonication. During the degradation, the reactor was immersed in a water bath at 25 ± 2 °C. The reaction temperature was monitored by a thermocouple located inside the reactor (Fig. 1). Due to the heat dissipation caused during the ultrasound run, the temperature of NB aqueous solution that was initially cooled at 11 °C increased rapidly to 27 °C after 5 min, 28 °C after 1 h and remained constant. In order to study the impact of ultrasound on the system, silent experiments (without sonication) were carried out at identical conditions with an axial stirring device instead of the sonicator. Increase in reaction temperature and mixing are known to

![Figure 1](image-url)
occur during ultrasound irradiation in aqueous media. Thus, a steady state temperature (28 °C) and maximum stirring speed (500 rpm) were used in the silent experiments to offset those ultrasonic effects and highlight the impact of ultrasound in the heterogeneous system.

The degradation of NB was initiated by rapid addition of H2O2 to the reactor containing the solid catalyst and immediately turning on the ultrasonic equipment. Initial H2O2 concentration of 5 mmol/L and catalyst loading of 1 g/L were used when those conditions were required for combined systems. Synchronously, the various influencing factors such as ultrasonic irradiation time, oxidant concentration, weight of the catalysts, solution pH, and NB concentration were considered in different experiments. The general experimental conditions such as NB concentration of 10 mg/L, catalysts addition amount of 1 g/L, ultrasonic irradiation time of 30 min, systematic temperature of 25 ± 2 °C, and total volume of 50 mL were adopted. At given time intervals, 20 mL aliquots of the reaction solution were sampled, and immediately centrifuged at 14,000 rpm for 15 min with an EBA-21 centrifugal (Hettich, Germany) to remove the catalysts. The resultant solution was used for the analysis of related chemical species in it.

2.5. Solid phase microextraction (SPME)

SPME is a technique to extract organics from an aqueous matrix into a stationary phase immobilized on a fused-silica fiber. The analytes are thermally desorbed directly into the injector of a gas chromatograph [24].

2.6. Data collection and chemical analyses for Fenton and modified Fenton

The concentration of the undegraded nitrobenzene was determined by solid-phase microextraction (SPME) using 65 μm p olydimethylsiloxane/divinylbenzene (PDMS/DVB) fibers (Sigma–Aldrich, Germany) in combination with GC analysis as described in Refs. [25,26]. Briefly, the fiber was introduced through the septum of a vial containing the solution withdrawn from the reaction flask and immersed in the solution for 30 min. During this time, the solution was stirred on a magnetic stirrer using glass-coated stirring bar. Afterward, the fiber was removed and introduced into the GC injector (220 °C, 30 min, splitless injection) for desorption of analytes and GC analysis. The degradation of nitrobenzene was monitored by determining the residual concentration remaining after certain periods of reaction using HP 5890 gas chromatograph, provided with a flame ionization detector and equipped with a column (3.048 m in length and 3 mm int. diam.) packed with Benton 34 (5%); diisoderyl phthalate 5% (wt%) on chromosorb W (AW), 80–100 mesh. Alternatively, wide bore column DB1 (100% polydimethylsiloxane) gas chromatograph, was provided with a flame ionization detector and equipped with a column (30 m in length, 0.530 mm int. diam, and 3 μm film thickness), made in USA. Temperature limits: –60 to 260 °C (280 °C). The initial oven temperature (80 °C) was held for 3 min, programed at 2 °C min\(^{-1}\) to 120 °C (5 min). The injector and the detector temperatures were 250 and 275 °C, respectively. Under these conditions, the retention time for nitrobenzene was 20.2 min.

### Table 1 Characterization of catalysts in the absence of CTAB (series I).

<table>
<thead>
<tr>
<th>Characterization</th>
<th>Sample</th>
<th>Fe2O3-I</th>
<th>CuO-I</th>
<th>NiO-I</th>
<th>Co3O4-I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size nm (X-ray)</td>
<td>92</td>
<td>18.2</td>
<td>10.3</td>
<td>22.9</td>
<td></td>
</tr>
<tr>
<td>Particle size nm (TEM)</td>
<td>135</td>
<td>136</td>
<td>129</td>
<td>131</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2 Characterization of catalysts in the presence of CTAB (series II).

<table>
<thead>
<tr>
<th>Characterization</th>
<th>Sample</th>
<th>Fe2O3-II</th>
<th>CuO-II</th>
<th>NiO-II</th>
<th>Co3O4-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size nm (X-ray)</td>
<td>61.2</td>
<td>10.6</td>
<td>8.9</td>
<td>14.7</td>
<td></td>
</tr>
<tr>
<td>Particle size nm (TEM)</td>
<td>(20–60)</td>
<td>(2–10)</td>
<td>(2–10)</td>
<td>(2–10)</td>
<td></td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Investigation of some physical and structural properties of the prepared catalysts

3.1.1. X-ray diffraction (XRD)

The information concerning the crystalline phases has been obtained by using X-ray diffraction (XRD) for nanostructured metal oxide catalysts prepared in absence and presence of CTAB (series I and series II, respectively), Tables 1 and 2.

3.1.2. Transmission electron microscope (TEM)

Transmission electron microscope (TEM) is used to describe the shape and determine the size of the particles of nanostructured metal oxide catalysts prepared in absence and presence of CTAB (series I and series II, respectively), Tables 1 and 2.

From Tables 1 and 2 we can conclude the following:

1. In the presence of CTAB, there is correspondence between values of particle size measured by TEM and X-ray.
2. In absence of CTAB, the particle size determined by TEM is greater than that by X-ray implying some degree of aggregation.

3.1.3. Scanning electron microscope (SEM)

Scanning electron microscope (SEM) is used to describe the shape of the particles of nanostructured metal oxide catalysts prepared in the absence of CTAB (series I). All SEM images show that the particles are highly agglomerated (Fig. 2).

Many literatures have reported that the introduction of surfactant can control the size of nanoparticles [27,28]. CTAB as stabilization or capping agent makes the dispersion of nanoparticles in the fluid possible. Also, the TEM images of the catalysts (Fe2O3, CuO, NiO. and Co3O4) are shown to be dispersed because the surfactant molecules surrounding the...
particles make a covering layer, and prevent the aggregation of the particles.

3.2. Degradation of NB assisted with $\text{H}_2\text{O}_2$ oxidant and heterogeneous catalysts (Fenton like system)

3.2.1. Silent degradation of NB assisted with $\text{H}_2\text{O}_2$ and heterogeneous catalysts (without sonication)

Influence of stirring time with $\text{H}_2\text{O}_2$ and metal oxides ($\text{Fe}_2\text{O}_3$, CuO) on the degradation of NB is studied. The classical representation of the Fenton type reaction would rather be [29]:

$$
\text{H}_2\text{O}_2 + \text{Cu}^{2+} \rightarrow \text{Cu}^+ + \text{HO}_2^- + \text{H}^+
$$

$$
\text{H}_2\text{O}_2 + \text{Cu}^+ \rightarrow \cdot\text{OH} + \cdot\text{OH} + \text{Cu}^{2+}
$$

In order to test the role of sonication, the reaction has been carried out without ultrasound in the presence of $\text{H}_2\text{O}_2$ and $\text{Fe}_2\text{O}_3$ or CuO, and shows that the decomposition of 10 mg/L NB is 40% and 35% for $\text{Fe}_2\text{O}_3$ and CuO, respectively; after 1 h. This indicates that the flow of the solution has little effect on the decomposition rate in absence of sonication, as shown in Fig. 3.

3.2.2. Sonolysis degradation of NB assisted with $\text{H}_2\text{O}_2$ and heterogeneous catalysts

3.2.2.1. Sonolysis degradation of NB assisted with $\text{H}_2\text{O}_2$ and heterogeneous nano-sized catalysts in absence of CTAB (series I). 3.2.2.1.1. Influence of irradiation time on sonocatalytic degradation of NB assisted with $\text{H}_2\text{O}_2$ and heterogeneous nano-sized catalysts ($\text{Fe}_2\text{O}_3$-I, CuO-I, NiO-I, and Co$_3$O$_4$-I) (series I).

Fig. 4 reveals that all degradation ratios of NB in these systems increase in the presence of $\text{H}_2\text{O}_2$ and absence of CTAB with the increase of ultrasonic irradiation time, but their difference is tremendous. The full degradation is achieved in $\text{Fe}_2\text{O}_3$-I, CuO-I, NiO-I, and Co$_3$O$_4$-I after 20 min, 30 min, 30 min, and 40 min, respectively.

Ultrasonic irradiation generates benefits in heterogeneous catalytic systems by decreasing mass transfer limitations, and fragmentation of catalyst in small particles that provide a higher surface area [30–33]. Moreover, the additional generation of free radical species in ultrasound systems should enhance the overall catalytic performance [34,35]. In the combined method (ultrasound and catalyst), ultrasonic waves not only destroy the pollutant through the cavitation process but also increase the adsorption process by increasing the surface area of the catalyst.

The decomposition mechanism for hydrogen peroxide at metal surfaces (Eqs. (1)–(6)) is thought to be applicable for metal oxides as well [36]:

$$
\text{M} + \text{H}_2\text{O}_2 \rightarrow \text{M}^+ + \text{OH}^- + \cdot\text{OH}
$$

(1)

$$
\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2^-
$$

(2)

$$
\text{HO}_2^- \rightarrow \text{H}^+ + \text{O}_2
$$

(3)

$$
\text{M}^+ + \text{O}_2^- \rightarrow \text{M} + \text{O}_2
$$

(4)

$$
\text{M} + \text{HO}_2^- \rightarrow \text{M}^+ + \text{H}_2\text{O}
$$

(5)

$$
\text{M}^+ + \text{HO}_2^- \rightarrow \text{M} + \text{HO}_2
$$

(6)

Figure 2 Shows the scanning electron microscope (SEM) images of (A) $\text{Fe}_2\text{O}_3$-I, the bar represents 10 μm; (B) CuO-I, the bar represents 100 μm; (C) NiO-I, the bar represents 100 μm; and (D) Co$_3$O$_4$-I, the bar represents 50 μm.
In the concentration on sonocatalytic with the catalyst active sites. The influence of oxidant concentration on degradation ratios of NB at initial concentration of 10 mg/L, metal oxide catalysts (Fe$_2$O$_3$, CuO) amounts of 0.06 g. H$_2$O$_2$ oxidant concentration of 65 mmol/L, temperature of 25 °C, and pH 6.8 ≈ 7.0.

Figure 3 Influence of stirring time on degradation ratios of NB at initial concentration of 10 mg/L, metal oxide catalysts (Fe$_2$O$_3$, CuO) amounts of 0.06 g. H$_2$O$_2$ oxidant concentration of 65 mmol/L, temperature of 25 °C, and pH 6.8 ≈ 7.0.

Influence of sonication time on degradation ratios of NB initial concentration of 10 mg/L, metal oxide catalysts (Fe$_2$O$_3$-I, CuO-I, NiO-I, and Co$_3$O$_4$-I) amounts of 1.0 g/L, oxidant concentration of 10 mmol/L, temperature of 25 °C, pH 7.0, and a total volume of 50 mL.

The chemical forms of NB in aqueous solution and the surface properties of (Fe$_2$O$_3$-I, CuO-I, NiO-I, and Co$_3$O$_4$-I) nanoparticles both depend on the pH value of the solution. The point of zero charge (PZC) of (Fe$_2$O$_3$-I, CuO-I, NiO-I, and Co$_3$O$_4$-I) powder is about pH 9, 8.4, 8, and 8.6, respectively. Above this pH value, the surfaces of these particles are negatively charged, while below this pH value they are positively charged.

Most of nitroaromatic compounds such as NB have negative charges in a wide pH value range. Hence, when the solution pH value is below the PZC of the oxides, the NB anions should be easily adsorbed on the surfaces of (Fe$_2$O$_3$-I, CuO-I, NiO-I, and Co$_3$O$_4$-I) nanoparticles. It can be presumed that the degradation reactions mainly occurred in terms of the direct oxidation, which can be accelerated under acidic conditions. On contrary, under strongly alkaline conditions, because of the repulsion force due to the negatively charged surfaces, the NB anions in aqueous solution are mainly degraded through radical (·OH) oxidation in bulk solution; which is a slow-motion degradation process.

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Fig. 5 reveals that in case of the four oxides, a concentration of 10 mmol/L H$_2$O$_2$ is sufficient for a complete degradation of 10 mg/L NB after 30 min of sonication in presence of 1 g/L of each oxide. The existence of these heterogeneous oxides offers large numbers of active sites on the surface of nano-sized particles due to fast diffusion and high distribution ability, which can promote the decomposition of various oxidants under ultrasonic irradiation and the generation of ·OH radicals. These generated ·OH radicals can participate in the increased degradation of NB.

![Influence of oxidant concentration on degradation ratios of NB initial concentration of 10 mg/L, nano metal oxides (Fe$_2$O$_3$-I, CuO-I, NiO-I, and Co$_3$O$_4$-I) amounts of 1.0 g/L, ultrasonic irradiation time of 30 min, temperature of 25 °C, pH 7.0, and a total volume of 50 mL.](image)

Figure 5 Influence of oxidant concentration on degradation ratios of NB initial concentration of 10 mg/L, nano metal oxides (Fe$_2$O$_3$-I, CuO-I, NiO-I, and Co$_3$O$_4$-I) amounts of 1.0 g/L, ultrasonic irradiation time of 30 min, temperature of 25 °C, pH 7.0, and a total volume of 50 mL.
values of the solution from 5.0 to 11.0, with 10 min of irradiation time by ultrasonic waves, is independent on the amount of Fe$_2$O$_3$-I. However, in case of the other oxides, Figs. 8–10, the catalytic efficiency shows positive dependence on the amount of the catalyst at any of the pH values. The increase in efficiency can be partly attributed to the increased chances to produce point of contact between cavities and NB at solid particles with a consequent increase in OH production.

3.2.2.1.5. Influence of irradiation time on sonocatalytic degradation of NB assisted with H$_2$O$_2$ and different weights of heterogeneous nano-sized catalysts (Fe$_2$O$_3$-I, CuO-I, NiO-I, and Co$_3$O$_4$-I) (series I). Figs. 11–14 show that the rate of NB removal in the presence of 10 mmol/L H$_2$O$_2$ at different ultrasonic waves, for nano-sized catalysts (Fe$_2$O$_3$-I, CuO-I, NiO-I, and Co$_3$O$_4$-I) is increased with increasing the amount of catalyst. In sonicated solution, the adsorption of NB is increased by increasing the amount of catalyst due to the higher surface area at higher concentrations. Also in sonicated solution, the number of cavities and radicals is increased with increasing the amount of catalyst, leading to the higher removal rate. In the studied range of concentration, the higher waves are generated in the bulk of the solution from imploding the cavities. The shock waves also improve the mass transfer from the bulk to the surface of the catalyst. It is known that sonication of H$_2$O produces OH that may partly participate in NB degradation, besides the highly produced OH radicals due to sonication of H$_2$O$_2$ that greatly participate in NB degradation.

3.2.2.1.6. The effect of initial NB concentration. Results show that the degradation efficiency is decreased with

![Figure 6](image6.png) Influence of pH value on degradation ratios of NB initial concentration of 10 mg/L, nano metal oxides (Fe$_2$O$_3$-I, CuO-I, NiO-I, and Co$_3$O$_4$-I) amounts of 1.0 g/L, ultrasonic irradiation time of 30 min, oxidant concentration of 10 mmol/L, temperature of 25 °C, and a total volume of 50 mL.

![Figure 7](image7.png) Influence of pH on degradation ratios of NB initial concentration of 10 mg/L, nano metal oxide (Fe$_2$O$_3$-I) amounts of 1.0, 0.5, 0.25 g/L, ultrasonic irradiation time of 10 min, oxidant concentration of 10 mmol/L, temperature of 25 °C, and a total volume of 50 mL.

![Figure 8](image8.png) Influence of pH on degradation ratios of NB initial concentration of 10 mg/L, nano metal oxide (CuO-I) amounts of (1.0, 0.5, 0.25) g/L, ultrasonic irradiation time of 10 min, oxidant concentration of 10 mmol/L, temperature of 25 °C, and a total volume of 50 mL.

![Figure 9](image9.png) Influence of pH on degradation ratios of NB initial concentration of 10 mg/L, nano metal oxide (NiO-I) amounts of (1.0, 0.5, 0.25) g/L, ultrasonic irradiation time of 10 min, oxidant concentration of 10 mmol/L, temperature of 25 °C, and a total volume of 50 mL.

![Figure 10](image10.png) Influence of pH on degradation ratios of NB initial concentration of 10 mg/L, nano metal oxide (Co$_3$O$_4$-I) amounts of (1.0, 0.5, 0.25) g/L, ultrasonic irradiation time of 10 min, oxidant concentration of 10 mmol/L, temperature of 25 °C, and a total volume of 50 mL.

![Figure 11](image11.png) Influence of ultrasonic irradiation time on degradation ratios of NB initial concentration of 10 mg/L, nano metal oxide (Fe$_2$O$_3$-I) amounts of 0.25, 0.5, 1.0 g/L, oxidant concentration of 10 mmol/L, temperature of 25 °C, pH 7.0, and a total volume of 50 mL.
increasing the initial NB concentration. When the initial NB concentration is 10 mg/L (Fig. 4), the degradation efficiency reached about 100% in 30 min. When initial NB concentration is increased to 20 mg/L (Fig. 15), the degradation efficiency declined in 30 min to about 98% and 94% for nanocatalysts Fe$_2$O$_3$-I and CuO-I, respectively and 90% for both nanocatalysts NiO-I and Co$_3$O$_4$-I. This effect is increased with the formation of more intermediate species.

3.2.2.1. The effect of leaching of the heterogeneous nano-sized catalysts (Fe$_2$O$_3$-I, CuO-I, NiO-I, and Co$_3$O$_4$-I) (series I) with the irradiation time on sonocatalytic degradation of NB assisted with H$_2$O$_2$. Results in Fig. 4 show that the degradation efficiency has reached about 100% in 30 min for the first usage of the four catalysts. Under the same conditions for reusing catalysts (Fig. 16), the results show that the degradation efficiency of Fe$_2$O$_3$-I, CuO-I, and NiO-I has reached about 100%, but the degradation efficiency has declined to about 82% for Co$_3$O$_4$-I. These results indicate that the catalysts have a small leaching tendency except Co$_3$O$_4$-I. This is in good agreement with the trace amounts of soluble ionic species observed by atomic absorption spectrometry (AAS).

3.2.2.2. Sonolysis degradation of NB assisted with H$_2$O$_2$ and heterogeneous nano-sized catalysts in presence of CTAB (series II). 3.2.2.2.1. Influence of irradiation time on sonocatalytic degradation of NB assisted with H$_2$O$_2$ and heterogeneous nano-sized catalysts (Fe$_2$O$_3$-II, CuO-II, NiO-II, and Co$_3$O$_4$-II) (series II). Fig. 17 shows that all degradation ratios of NB in the system of US/H$_2$O$_2$ + nano-sized catalysts (Fe$_2$O$_3$-II, CuO-II, NiO-II, and Co$_3$O$_4$-II) modified with CTAB increased with the increase in ultrasonic irradiation time, but with some differences. Within 60 min, NB is fully degraded after 20 min in the case of CuO-II, NiO-II, and Co$_3$O$_4$-II; while in the case of Fe$_2$O$_3$-II, only 15 min is sufficient for complete degradation. Therefore, nano-metal oxides catalysts (series II) can efficiently assist the sonocatalytic degradation
of NB in the presence of H2O2, compared to nano metal oxide catalysts (series I) in which the full degradation is achieved after more ultrasonic irradiation time (Fig. 4).

3.2.2.2. Influence of H2O2 concentration on sonocatalytic degradation of NB using heterogeneous nano-sized catalysts (Fe2O3-II, CuO-II, NiO-II, and Co3O4-II) (series II). Fig. 18 reveals that in the case of the four oxides, the degradation rate for an initial NB concentration of 10 mg/L and pH 7 at different H2O2 concentrations of 10, 20, 30, 40, and 50 mmol/L is substantially completed by the addition of 10 mmol/L H2O2 to the ultrasound system within 30 min of sonication in presence of 1 g/L of each oxide. This is due to the extremely high temperatures and pressures formed in collapsing cavitation bubbles phase to the bulk-bubble, leading to the decomposition of H2O2 into ‘OH radicals and causing high degradation rate [40]. The same result (10 mmol/L H2O2) was obtained in the case of series I (Fig. 5), indicating that the amount of H2O2 is not as critical as the rate of ‘OH production due to sonication in the presence and absence of CTAB.

3.2.2.3. Influence of pH on sonocatalytic degradation of NB assisted with H2O2 and heterogeneous nano-sized catalysts (Fe2O3-II, CuO-II, NiO-II, and Co3O4-II) (series II). Fig. 19 shows that when the pH is higher than 7, the activity of the nona-sized catalysts (Fe2O3-II, CuO-II, NiO-II, and Co3O4-II) toward NB degradation is sharply decreased.

3.2.3.1. The effect of method of catalysts preparation on NB degradation with sonication. To inspect the role of preparation method, the degradation test results obtained in the presence of 1 g of series I oxide are compared with those obtained in the presence of 0.1 g of series II oxides, keeping all other variables the same. The results are presented in Figs. 20–23 which show that, for both series I and series II, Fe2O3 is still of the highest efficiency. Furthermore, the degradation rates of NB in case of the four oxides in the presence of 0.1 g of series II are comparable with the corresponding rates of 1 g of series I. These results may be attributed to the attack of active radicals on organic compounds with good distribution on the fragmented catalyst particles that leads to an increase in the accessibility of NB to the catalyst surface and thus, increases the collision probability between NB and active radicals that are produced as a result of reaction of even 5 mmol/L H2O2 with the catalyst.

The results previously indicated show that the weight of the catalyst in the nano-sized oxides has very important effects. Large numbers of active sites appear on the surface of nano-sized (Fe2O3-II, CuO-II, NiO-II, and Co3O4-II) particles, which can promote the decomposition of the oxidants under ultrasonic irradiation and generation of needed ‘OH radicals.
These generated \( \cdot \text{OH} \) radicals can participate in the degradation of NB by radical oxidation pathways.

3.2.3.2. Reaction kinetics. The calculated values of first order rate constants of NB degradation are given in Tables 3 and 4 and the plots of the linear representation of first order equation of \( \text{Fe}_2\text{O}_3 \), as an example, in presence of \( \text{H}_2\text{O}_2 \) are given in Figs. 24 and 25.

Data in Table 3 study the rate constant (min\(^{-1}\)) for series I (0.25 g, 0.5 g, 1 g) nano-sized oxides for NB degradation and show that the rate constant of 1 g has a higher value than that of 0.25 g of nano-sized oxides from series I. This indicates that the rate constant for NB degradation increases with increasing the weight of the catalyst.

From Tables 3 and 4, when comparing the rate constant of 0.1 g from series II and the rate constant of 0.25 g from series I, it has been found that the rate constant of 0.1 g of nano-sized oxides from series II is greater than that of 0.25 g of nano-sized oxides from series I. This may be due to the aggregation of series I nano-sized oxides in absence of CTAB. In this respect, aggregated particles does not completely and homogeneously disperse in the NB matrix, which cause part of these particles does not react with NB within sonication or participate in NB degradation process, leading to a decrease in the rate constant for NB degradation. This effect is compensated with increasing the weight of the catalyst.

Data in Table 4 show that the rate constant of 1 g of nano-sized oxides from series I is nearly equal to the rate constant of 0.1 g of nano-sized oxides from series II. This is explained as in

Table 3  First order rate constant (min\(^{-1}\)) for series I oxides for NB degradation 10 mg/L in the absence and in the presence of (10 mmol/L \( \text{H}_2\text{O}_2 \)) using different oxide weights.

<table>
<thead>
<tr>
<th>wt</th>
<th>( \text{Fe}_2\text{O}_3-I ) W</th>
<th>( \text{CuO-I} ) W</th>
<th>( \text{NiO-I} ) W</th>
<th>( \text{Co}_3\text{O}_4-I ) W</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 g/L</td>
<td>0.3420</td>
<td>0.1454</td>
<td>0.1505</td>
<td>0.1325</td>
</tr>
<tr>
<td>0.5 g/L</td>
<td>0.2826</td>
<td>0.1101</td>
<td>0.1103</td>
<td>0.0843</td>
</tr>
<tr>
<td>0.25 g/L</td>
<td>0.1883</td>
<td>0.0834</td>
<td>0.0793</td>
<td>0.0796</td>
</tr>
</tbody>
</table>

W i.e. with 10 mmol/L \( \text{H}_2\text{O}_2 \).
1 g of aggregated nano-sized oxides, the sonication at first acts to disperse the aggregation, and then implosion of cavitation bubbles occurs with the formation of ‘OH radicals; so a higher energy of sonication is lost in the dispersion of these particles.

In the case of 0.1 g of nano-sized oxides from series II (disaggregated particles), the sonication starts to form cavitation bubbles and then implosion takes place to form ‘OH radicals, and the reaction immediately occurs without any delay.

### 3.2.3.3. Efficient surface area of the catalyst.

As heterogeneous catalysis is a surface phenomenon, it is well documented that the overall kinetics of the oxidation process is highly dependent on the surface area that participates in the reaction [41].

It has been reported [42] that only active sites of the catalyst surface area are available for the reaction. However, it is quite difficult to estimate the amount of active sites that is present in the catalytic system, due to the catalyst deactivation processes which lead to low catalytic efficiency. When ultrasound irradiation is applied, the significant variation in the surface area occurs with the possible increase in the number of active “clean” sites and consequently, the increase in the reaction rates may be observed.

The morphology of the iron surface with/without sonication is analyzed via scanning electron microscope (SEM). It could be seen that the sonicated samples are visibly cleaned due to the continuous ultrasonic cleaning. In addition, the pitting on the surface caused by shock waves produced upon implosion is apparent [43].

### 4. Conclusions

1. Oxides of Fe, Cu, Ni, and Co prepared in the nano-size range without CTAB result in aggregated particles.
2. Addition of CTAB to the preparation recipe results in nano-sized particles lacking the aggregation drawback recorded in the absence of CTAB.
3. Heterogeneous Fenton degradation at pH 7 aided by sonication is successful in the presence of nano-sized metal oxides like Fe$_2$O$_3$, CuO, NiO, and Co$_3$O$_4$ in degrading 10 ppm NB within a time ≤30 min.
4. The order of efficiency of the tested oxides is Fe$_2$O$_3$ > CuO > NiO > Co$_3$O$_4$.
5. Sonication plays the role of dispersing the aggregating particles of used oxides.
6. The present oxides increase the chance of ‘OH formation at their surfaces which increase the rate of NB degradation.

(7) The usage of oxides which are initially disaggregated improves the efficiency of the process via decreasing the needed weight of the used oxide.

(8) The efficiency of NB degradation obtained on using 0.1 g of oxide, prepared in the presence of CTAB is the same as that obtained on using 1.0 g of oxide, prepared without CTAB.

(9) Using oxides prepared in micellar solution can upgrade the economic aspect of the process of NB degradation via AOP using sonication + H$_2$O$_2$ combination.

(10) The process of sonication + H$_2$O$_2$ + oxide combination in NB degradation shows failure at pH > 7.

### References