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Introduction

Many pharmaceutical compounds are considered as environmental pollutants and their presence even at very low concentration (ng.L⁻¹) may adversely influence the biological system [1]. These compounds are frequently detected in wastewaters, surface and ground waters and even in the treated wastewaters because the waste treatment facilities are not equipped to remove them. As a result, many streams and rivers are exposed to entrance of pharmaceutical compounds from stimulants and antibiotics to analgesics and antihistamines compounds.

Phenylephrine hydrochloride (Figure 1S) used for nasal congestion is considered as one of the most important pharmaceutical pollutant [2]. Several methods have been used for elimination of the pollutants from aqueous solution including sono degradation [3], Fenton oxidation [4], nanofiltration [5], adsorption [6] and advance oxidation processes [7,8]. Advanced oxidation process have also been intensively used for effective degradation of many organic pollutants [9–13]. The essential requirement for the AOP process is an adequate heterogeneous photocatalyst, which is irradiated by UV, visible or sunlight radiations to produce electron–hole pairs (e⁻/h⁺). The electron–hole pairs subsequently generate highly active species such as OH radicals. The radicals then react with the pollutant molecules adsorbed on the surface of the photocatalyst [14,15].

The method is capable to destroy environmentally persistent pollutants by using photocatalysts activated by photons with energy higher or equal to the band gap energy of the photocatalyst. When the photon is absorbed by photocatalyst particle, an Electron (e⁻) from the Valence Band (VB) is transferred to the Conduction Band (CB), generating a hole (h⁺) in the VB. The e⁻ and h⁺ can recombine on the surface or in the bulk of the particles releasing the energy as heat, or migrate to the photocatalyst surface where they can react with pollutant molecules absorbed on the surface of the particle. In the presence of water molecules, electrons are transferred from water molecule to the positive holes to produce "OH radicals which are powerful oxidants and react with organic and toxic compounds. "OH radicals play an important role in initiating oxidation reactions, especially for substances that are weakly absorbed on the photocatalyst surface.
The nano-sized photocatalyst possesses many advantages over their micro-sized counterparts, including higher degradation efficiency, proper mineralization potential, and higher efficiency with visible light. However, separation of the nano-sized photocatalysts from degradation solution is usually imperfect and time consuming. The nano-sized particles also tend to aggregate to large clusters, leading to lower specific surface area and lower degradation efficiency [16]. To eliminate these drawbacks, the particles can be magnetized by the aid of Fe₃O₄. The magnetized photocatalyst can be readily removed by use of a magnetic bar put outside of degradation vessel [17].

In photocatalytic degradation, recombination of electron/hole is a common problem, which adversely influences the efficiency of the photocatalyst. The process can be quenched or eliminated by immobilizing of the photocatalyst on the surface of an adequate support or an isolator. The conducting polymers such as polypyrrole (PPy) are potential candidates to reduce the aggregation of the nano-sized particles and to lower the electron–holes recombination.

This research was focused on the preparation of a magnetic polypyrrole composite (Fe₃O₄-PPy) to use it as the support for NiO photocatalyst. The synthesized photocatalyst and the bulk NiO were then used for degradation of phenylephrine under visible light, and UV irradiations.

**Experimental**

**Materials and methods**

All chemicals, including pyrrole (C₄H₅N), iron (III) chloride (FeCl₃.6H₂O), iron (II) chloride (FeCl₂.4H₂O), hydrochloric acid (HCl), sodium hydroxide (NaOH), m-cresole, ammonium persulphate (APS), NiCl₂.6H₂O, hydrogen peroxide (H₂O₂), were purchased from Merck company (Germany).

**Characterization of the samples**

Characterization of the synthesized photocatalyst was performed by different techniques including; FTIR, TG–DTG, XRD, SEM, BET (Brunauer Emmett Teller). The FTIR spectra were prepared on Nicolet single beam Impact 400D, Perkin Elmer Spectrophotometer (USA), in the region of 4000–400 cm⁻¹. The FTIR spectra were prepared by a Cary Eclipse, FL0906M003 instrument (USA). Photoluminescence analysis (PL) was performed by the method described by Nalage [23], (Figure 2Sb). Concisely, 1.0g of Fe₃O₄@PPY and 1.0g of NiO nanoparticle were dispersed in 20mL of m-cresol solution and the mixture was stirred for 24h (Figure 2Sa), then transferred into a 250mL two-neck flask. 0.5mL of pyrrole was added and the mixture was shaken at 25°C for 8h under N₂ atmosphere. The precipitate; Ni(OH)₂ was separated by magnetic bar put outside of the vessel. It was thoroughly washed with distilled water until the filtrate become neutral. The product was dried at 60°C for 8h [19].

The magnetite composite Fe₃O₄-PPy was prepared by oxidative polymerization of pyrrole in the presence of APS solution [20]. 1.0 g of as-synthesized Fe₃O₄ nanoparticles was added into aqueous solution of APS (0.5g in 20mL of distilled water). The mixture was homogenized by sonication for 1h and then transferred into a 250mL two-neck flask. 0.5mL of pyrrole was added and the mixture was shaken at 25°C for 8h under N₂ atmosphere. The optimized amounts of materials were given in Table 1S. The black-coloured product (Fe₃O₄-PPy) was magnetically separated and thoroughly washed with deionized water and methanol and dried at 60°C for 24h (Figure 2S).

**Preparation of NiO and Fe₃O₄-PPY-NiO nanophotocatalysts**

The NiO nanoparticles were first prepared as follows.

12.0g of NiCl₂.6H₂O was dissolved in 30mL of deionized water, the pH was adjust to 11.0 by addition of 0.1M NaOH solution. The precipitate; Ni(OH)₂ was separated by filtration, dried at 100°C and calcined at 550°C for 3h [22].

The Fe₃O₄-PPy-NiO nanophotocatalyst was prepared through the method described by Nalage [23], (Figure 2Sb). Concisely, 1.0g of Fe₃O₄@PPy and 1.0g of NiO nanoparticle were dispersed in 20mL of m-cresol solution and the mixture was refluxed for 15h at room temperature under N₂ atmosphere. The magnetized photocatalyst was collected by use of a magnet bar put outside of the vessel. It was thoroughly washed with deionized water and methanol and dried at 70°C for 6h. In the same manner, several photocatalysts with different NiO content (10%–80%) was prepared [23].

**Photodegradation of the pollutant**

The degradation experiments were carried out in a light tight reactor consisting of a cylindrical Pyrex–glass cell, a medium pressure Hg lamp (60W, Philips), and a fluorescent lamp (60W) located 10cm above the degradation cell. Known Company, (Japan). The concentration of phenylephrine (PHE) was measured by high performance liquid chromatography (HPLC), Aligent Technology 1200 series, (USA) by use of an ODS Hypersil C18, 250mm×4.7 mm, 5μm (Particle Size) column and a UV detector operated at 215nm. The degradation products were identified by a GC–MS instrument, 5975C Agilent, (USA) with a Bpx 30m×0.25mm×0.25μm capillary column.

**Preparation of Fe₃O₄, Fe₃O₄-PPY composite**

Synthesis of Fe₃O₄ nanoparticles and Fe₃O₄-PPy was performed by the method described by Torki, et al., [18]. Briefly, 10.8g of FeCl₃.6H₂O, and 3.98g of FeCl₂.4H₂O were transferred into a beaker, under N₂ atmosphere, 50mL of HCl (0.5M) was added, and the mixture was shaken for proper homogenization. The pH of the solution was adjusted to 11 by drop wise addition of NaOH solution. The solid product was then separated by a magnet bar put outside of the vessel. It was thoroughly washed with distilled water until the filtrate become neutral. The product was dried at 60°C for 8h [19].
amount of photocatalyst (0.2g) was added into 25mL of phenylephrine solution. The suspension was shaken for 30min at dark and then was irradiated for 240min. The photocatalyst was magnetically separated and the PHE concentration in the remaining solution was measured by HPLC-UV at λ 215 nm. The degradation efficiency was calculated by the following equation:

\[ D(\%) = \left[ \frac{(C_0 - C)}{C_0} \right] \times 100 \] (1)

Where \( C_0 \) and \( C \) are respectively the PHE concentration before and after irradiation.

Results and Discussion
Characterization of the synthesized photocatalyst

In the SEM image of Fe3O4–PPY given in Figure 3Sa, the formation of uniform spherical–shaped particles were clearly observed. The particles were mostly aggregated forming clusters of the particles. After introduction of NiO, the molecules were homogeneously distributed on the surface of the magnetized composite and the morphology of the photocatalyst was remained unchanged. The average particles size of Fe3O4–PPY and Fe3O4–PPY–NiO was respectively 45 and 65nm. The increase in the particle size of Fe3O4–PPY–NiO was attributed to the coordination bond formed between the free electron pair of N atoms of PPY [23] and NiO molecule according to the scheme illustration given in Figure 3Sb.

In the XRD pattern the relative intensity and positions of the lines were in good agreement with the Fe3O4 reference (JCPDS #65–3107), (Figure 4Sa) and NiO reference (JCPDS# 47–1049) [24,25] (Figure 4Sb). The average particle sizes of Fe3O4 and NiO was calculated by Scherrer’s equation:

\[ D=\frac{0.94\lambda}{SSCOS\theta} \] (2)

Where \( D \) is the average size and \( S \) stands for the full–width at half–height of the peaks. The average particle size of Fe3O4 and NiO were respectively 14 and 25 nm.

The XRD pattern of Fe3O4–PPY–NiO sample, (Figure 4Sc) the presence of diffraction lines belonged to Fe3O4 structure was observed at \( \theta \) of 41.5, 50.7, 63, 67, 74, 5°, and those related to NiO were recorded at \( \theta \) of 37, 43.5, 63 and 76°.

From the EDAX analysis of Fe3O4–PPY–NiO, the presence of Fe, O, Ni, C, N atoms on the surface of the photocatalyst was detected (Figure 5S). According to the map of elements represented in Figure 6S, it was concluded that the elements were uniformly distributed on the surface of the synthesized photocatalyst. The uniform distribution of NiO on the surface of the support is very advantageous for enhanced degradation efficiency.

The surface area of the samples measured by Nadsorption–desorption isotherms indicated that after immobilization of NiO on the surface of magnetized support, the surface area was reduced from 62.2 to 34.5m^2g^{-1} (Table 1). With lower surface area, it was expected to obtain lower degradation efficiency because lower amount of the pollutant was adsorbed on the photocatalyst surface, but immobilization of NiO on the surface of the magnetized support increased the efficiency of the photocatalysts by lowering the electron–hole recombination.

In the FT-IR spectrum of Fe3O4 (Figure 7Sa), the adsorption band appeared at 470cm^{-1} was attributed to the characteristic Fe–O band and the peak at 1400cm^{-1} belonged to OH in–plane vibration of water molecules. The peaks appeared at 1600 and 3400cm^{-1} were related to water molecules adsorbed on the surface. The Fe–O band of Fe3O4–PPY, observed in Figures 7Sb,c slightly shifted to lower wave number. This reflects the effect of coordination interaction between Fe3O4 nanoparticle and polypyrrole chain [26]. In the spectra of Fe3O4–PPY (Figure 7Sb), and Fe3O4–PPY–NiO (Figure 7Sc), the characteristic absorption bands of polypyrrole were observed. The bands at 1080 and 900cm^{-1} were arisen respectively from CH in plane and CH out–of–plane vibration, indicating the successful polymerization of pyrrole [27]. The bands at 1500 and 1474cm^{-1} were respectively attributed to C–N and C–C asymmetric and symmetric ring stretching of PPY [26]. The peak at 1400cm^{-1} was attributed to the stretching band related to C=C of PPY ring. The weak bands of NH and CH stretching vibration of polypyrrole appeared respectively at 3404 and 2358cm^{-1} and the band at 3404cm^{-1} related to symmetrical stretch vibration of NH group has been buried under broad OH peak of water molecules at 3400cm^{-1} [28]. From the results, it was concluded that the polymerization was successfully performed. In Fe3O4–PPY–NiO sample, the NiO stretching and vibrating band at 626cm^{-1} was observed. The main absorption band at 1600cm^{-1} belonged to water molecules became more intense due to the adsorption of water molecules by NiO nanoparticles. The absorption band at 3400cm^{-1} related to Fe3O4 was disappeared because of adsorption of water molecules by NiO particles.

In the thermal curves (TG–DTG) of Fe3O4–PPY–NiO represented in Figures 8Sa,b, a continuous weight loss peak from 25–800°C with two distinct steps was observed. The weight loss peak appeared between 80–15°C was attributed to the elimination of water molecules and unreacted monomer [23]. The second weight loss started from 500°C and ended at 800°C was attributed to the decomposition of PPY molecules. It was reported that pure PPY decomposed around 150°C, and after combination with nanoparticles, its thermal decomposition shifted to higher temperature (600–800°C) [29,30].

From the magnetization curves of Fe3O4, Fe3O4–PPY and Fe3O4–PPY–NiO given in Figures 1a–c, it was concluded that the samples were super paramagnetic in nature and no hysteresis, neither coactivity was observed. The saturation magnetization of Fe3O4, Fe3O4–PPY and Fe3O4–PPY–NiO was respectively 80.2, 58.3, and 55.8emu\cdot g^{-1}. The significant decrease on the saturation magnetization of Fe3O4–PPY–NiO was attributed to the presence of non–magnetic materials; PPY and NiO on the structure of the composite.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Surface area (m^2g^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NiO</td>
<td>53.2</td>
</tr>
<tr>
<td>2</td>
<td>Fe3O4–PPY</td>
<td>62.2</td>
</tr>
<tr>
<td>3</td>
<td>Fe3O4–PPY–NiO</td>
<td>34.5</td>
</tr>
</tbody>
</table>
However, the magnetic property of the synthesized photocatalyst was sufficient for removal of the used photocatalyst by putting a magnet bar outside of the vessel. The magnetized particles were collected on the internal surface of the vessel within two second and immediately redistributed when the magnet bar was removed (Figure 1d).

**Optical properties of the photocatalysts**

The absorption edges of Fe₃O₄-PPY-NiO and NiO were obtained by DRS spectra (Figures 2a,b). The optical band gap (E_{gopt}) was obtained by equation 3:

\[ E_{gopt} = \frac{h \nu}{hc/e} \lambda_{edge} \]  

The constant parameter of hc/e are equal to 1240 and Eq.3 was simplified as Eq. 4

\[ E_{gopt} (eV) = \frac{1240}{\lambda_{edge} (nm)} \]  

Where h is Planck’s constant, c is the speed of light in the vacuum (3×10⁸ m/s), e is the electron charge, ℓ (nm) is the wavelength obtained from the intersection point of the horizontal and vertical parts of the absorption curve [31].

The absorption edge of NiO and Fe₃O₄-PPY-NiO were respectively at 364 and 406nm and the related band gap energy calculated by Eq. 4 was respectively 3.4 and 3.0 eV. The significant shift to lower energy, happened after immobilization of NiO on the magnetized support, was very beneficial for visible light-assisted degradation of the pollutant.

Similar observation was made by Singh who studied the degradation efficiency of TiO₂ immobilized on polyaniline catalyst support and reported higher degradation efficiency for brilliant blue [32].

The charge separation efficiency of the photocatalysts was determined by PL spectra. The samples were excited at 227 nm, and the emission peaks were recorded at 541 and 549 nm respectively for NiO and Fe₃O₄-PPY (Figures 3a,b). In Fe₃O₄-PPY-NiO sample (Figure 3c), the peaks at 541 belonged to NiO and the peak at 549 were overlapped and appeared with lower intensities indicating that after immobilization of NiO on the PPY-Fe₃O₄ support because of lower electron–hole recombination, the activity of charge carriers was decreased and the photoluminescence emission was quenched.

Similar observation was made by Akhundi, who grafted Ag₂SO₄ onto g-C₃N₄ and Fe₂O₃/Agl/Ag₂CrO₄ and reported that the photoluminescence intensity of the sample was significantly quenched [33,34].

**Photocatalyst performance**

The initial degradation experiment was performed by preparation of a suspension comprising of 25mL of PHE solution (500mg.L⁻¹) and 0.2g nanophotocatalyst. The stock solution was prepared by dissolving of 200mg of PHE in 100mL of deionized water. The calibration curve was plotted over the concentration range of 10−700mgL⁻¹. The suspension was shaken for 30min at dark until adsorption/desorption process was at equilibrium.

After equilibration, the degradation solution was irradiated for predetermined time, the photocatalyst was removed and the PHE concentration was measured in the remaining solution by HPLC-UV at 217nm. The mobile phase was a mixture of KH₂PO₄.
buffer (pH 4.7) and methanol (70:40 v/v). The flow rate was adjusted at 1.0mL/min. The retention time for PHE was found to be at 2.5 min [2]. From the chromatograms of the samples taken before and after degradation it was concluded that the intensity of PHE peak (RT 2.5min) was significantly decreased after degradation indicating the good performance of the photocatalyst for degradation of the pollutant (Figures 9Sa,b).

The statistical data of the method is given in Table 2S. the R² value of 0.9972 for calibration curve, and the acceptable RSD value indicated the the applicability of the method.

To optimize the degradation efficiency, the effect of different influencing parameters on the degradation efficiency were studied.

**Optimizing of degradation efficiency**

**Effect of initial PHE concentration:** The effect of initial PHE concentration was evaluated in the concentration range of 20–1000 mgL⁻¹ (Figure 4). At low concentration (20–50mgL⁻¹), the degradation efficiency under visible light was 85 and 60% respectively with NiO–PPY–Fe₃O₄ (S2) and NiO (S4). Even at concentration of 1000mgL⁻¹, 70% of the pollutant molecules were degraded by NiO–PPY–Fe₃O₄. This showed the high performance of the synthesized catalyst for degradation of the pollutant under visible light. The higher efficiency obtained at low concentration was attributed to the fact that the pollutant molecules were properly adsorbed on surface of the catalyst where the generated OH radicals easily reacted with them. This is very advantageous for elimination of the pollutant from the waste streams in which the pollutant concentration is usually low. However the degradation of the pollutant by UV irradiation was always higher than visible light because lower fractions of the visible light had sufficient energy to excite the photocatalyst molecules.

The degradation efficiency obtained by Fe₃O₄–PPY–NiO was much higher than the value obtained by bulk NiO. This was attributed to the enhancing effect of catalyst support through lowering the band gap energy of the photocatalyst and limiting the electron–hole recombination as discussed in section 3.2.

**Effect of photocatalyst dosage:** Degradation of PHE was studied with different photocatalysts dosage (0.001–0.35g) added to 25mL of the pollutant solution (500mgL⁻¹). By increasing of catalyst dose, more adsorption sites were supplied for the pollutant, more photocatalyst molecules (NiO) was provided, therefore, the degradation was increased through effective interaction between OH radicals and the pollutant molecules. With catalyst dose beyond 0.2g, the degradation first became constant and then was slightly decreased owing to the aggregation of the photocatalyst nanoparticles which decreased the surface area of the photocatalyst. With lower surface area lower amount of the pollutant are adsorbed and the photocatalyst molecules are not fully accessible [35]. (Figure 10S). With the same amount of the photocatalyst, the degradation efficiency obtained by Fe₃O₄–PPY–NiO was higher than that of bulk NiO. This indicated the enhancing effect of catalyst support on the efficiency of the photocatalyst.

**Effect of irradiation time:** The degradation efficiency was evaluated for irradiation time of 0 to 240min (Figure 5). By increasing of irradiation time, the degradation was initially increased until the equilibration was established within 240min.

With the increasing of irradiation time, more OH⁻ radicals were generated and at equilibrium, the generated OH radicals and pollutant molecules adsorbed on the surface of the photocatalyst were at steady state. The degradation efficiency obtained by Fe₃O₄–PPY was insignificant throughout the studied time. The activity of Fe₃O₄–PPY–NiO was higher than bulk NiO at each interval time. The degradation efficiency obtained by Fe₃O₄–PPY–NiO under UV and visible light irradiations became closer (respectively 81% and 71%). This was highly beneficial for degradation of the pollutant by visible light energy.

**Effect of pH:** The pH of the degradation solution has important influences on the degradation efficiency through changing the amount of adsorbed pollutant on the surface of photocatalyst and the quantity of the generated hydroxyl radicals ([36]. In this work, the effect of pH on the degradation efficiency was studied on pH range of 3–9 (Figure 6). The maximal degradation was obtained at pH 7. To evaluate the effect of pH on the surface charge of the photocatalyst, its pHₚzc was determined. As indicated in (Figure 6), the pHₚzc of the photocatalysts was at pH 7. At this pH, the surface of the

![Figure 4: Effect of the initial concentration of PHE.](image)

![Figure 5: Effect of irradiation time on PHE degradation.](image)
photocatalysts was neutral and the pollutant molecules were absorbed on the surface of photocatalyst by van der walls attraction forces [37]. In acidic solutions, functional groups of PHE and PPY molecules were protonated and their charge was converted to positive. Therefore, the repulsion force between the PHE molecules and the catalyst surface limited the adsorption of the pollutant.

In acidic solutions, functional groups of PHE and PPY molecules were protonated and their charge was converted to positive. Therefore, the repulsion force between the PHE molecules and the catalyst surface limited the adsorption of the pollutant. At pHs higher than pHpzc, the surface of the catalyst was negatively charged, the PHE molecules were deprotonated and their charge became negative. Hence the repulsion force was negatively charged, the PHE molecules were deprotonated and their charge became negative. Hence the repulsion force again reduced the number of adsorbed pollutant molecules. Moreover, at alkaline pHs, according to the following reactions, the OH⁻ radicals were converted to new radicals with less active species [38].

\[
\text{OH}^+ + \text{HO}_2^- + \text{H}_2\text{O} + \text{O}_2^- \quad (5)
\]
\[
\text{OH}^+ + \text{H}_2\text{O}_2 + \text{O}_2 + \text{H}^+ \quad (6)
\]

**Effect of NiO content:** To study the effect of NiO content of the photocatalyst on the degradation efficiency, the degradation experiments were conducted in the presence of photocatalysts with different NiO content (10%–80%) (Figure 7). With the catalysts containing low content of NiO, limited extent of degradation was obtained owing to the limited number of the generated OH radicals. With increasing of NiO content, the degradation efficiency was increased and the optimized efficiency was obtained with the photocatalyst containing 50% of NiO. When the NiO content exceeded to 50%, aggregation of the particle reduced the surface area of the photocatalyst resulting lower degradation efficiency.

Similar results were reported by Pourtaheri, who prepared a photocatalyst by immobilization of NiO on the surface of clinoptilolite and reported that the maximal efficiency of (80%) was obtained with the catalyst containing 13% of NiO [39].

**The effect of temperature on the degradation efficiency:** In this work, the degradation efficiency was measured at different temperatures of 25, 35, 45 and 55°C (Figure 8). The results indicated that at higher temperature, lower degradation efficiency was obtained. It was suggested that by increasing of temperature, the amount of dissolved oxygen was decreased.

The dissolved oxygen increased the generation of hydroxyl radical through Eqs. 7–10. By capturing the photo-induced electrons, \( \text{O}_2^- \) radicals were produced (Eq. 7) which then reacted with \( \text{h}^+ \) generating H\(_2\)O\(_2\) (Eqs. 8–9). H\(_2\)O\(_2\) was finally converted to OH⁻ radicals (Eq. 10).

\[
\text{O}_2^- + \text{e}^- \rightarrow \text{O}_2^- \quad (7)
\]
\[
\text{O}_2^- + \text{h}^+ \rightarrow \text{H}_2\text{O}_2 \quad (8)
\]
\[
\text{O}_2^- + \text{e}^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O}_2^- \quad (9)
\]
\[
\text{H}_2\text{O}_2 + \text{e}^- \rightarrow \text{OH}^- + \text{OH}^+ \quad (10)
\]

Similar observation was reported by Shivaraju, who studied the effect of temperature on the photocatalytic degradation efficiency organic matters [40].

**Addition of \( \text{H}_2\text{O}_2 \)**

The effect of \( \text{H}_2\text{O}_2 \) on the degradation efficiency was studied by addition of \( \text{H}_2\text{O}_2 \) solution into 25mL of degradation solution (500mgL\(^{-1}\)) (Figure 9). It was concluded that by increasing of \( \text{H}_2\text{O}_2 \) concentration, the degradation efficiency was firstly increased owing to the generation of extra OH radicals through reactions 11–12 and the maximized efficiency was obtained with 0.1M. \( \text{H}_2\text{O}_2 \) concentration.

However, by exceeding the optimum concentration, the degradation efficiency was declined because at higher concentration, \( \text{H}_2\text{O}_2 \) scavenged the hydroxyl radicals through reactions 13 and 14. The excess \( \text{H}_2\text{O}_2 \) reacts with OH⁻ radicals to form weaker HO₂⁻ radicals [41].

\[
\text{H}_2\text{O}_2 + \text{HO}^- + \text{OH}^- \quad (11)
\]
\[
\text{HO}_2^- + \text{HO}^- + \text{OH}^- \quad (12)
\]
\[
\text{H}_2\text{O}_2 + \text{OH}^- + \text{H}_2\text{O}^- \quad (13)
\]
\[
\text{HO}_2^- + \text{OH}^- + \text{H}_2\text{O}_2^- \quad (14)
\]

Tseng, et al., studied the effect of hydrogen peroxide on the photocatalytic degradation of monochochlorobenzene in the presence of TiO\(_2\) and reported that degradation efficiency in the presence of hydrogen peroxide was enhanced [41].
who studied the photodegradation of some drugs reported that addition of H2O2 increased the degradation efficiency [42,43].

**Regeneration of the photocatalyst**

One of the most important advantages of magnetized photocatalyst is the ease of separation of catalysts from the reaction solution which facilitates the regeneration of the photocatalyst. In this work, the used photocatalyst was separated from the solution by a magnet bar put outside of the degradation cell. The photocatalyst was then regenerated by heat treatment at 250°C for 6h to eliminate the degradation products deposited on the surface of the photocatalyst. The regenerated photocatalyst was reused for degradation of PHE at optimized conditions. The process was repeated for five successive regeneration steps (Figure 11S). It was concluded that the activity of the catalysts, in terms of the PHE degradation efficiency was slowly decreased in each cycle, and the decrease was more pronounced with increasing the number of reusing cycles.

However, after fifth regeneration cycle, 80% of the initial efficiency was observed for S1 sample. The decrease was explained by partial occupation of adsorption sites by degradation products, or dislocation and aggregation of NiO particles during heat treatment.

**GC-MS Analysis and identification of degradation products**

The degradation products of PHE were analyzed by full scan mode of GC-MS. Aliquots of PHE solutions after degradation and a sample containing standard PHE were prepared. The extraction of degradation products from aqueous solution was done by chloroform. It note that PHE is insoluble in chloroform but degradation products extracted. The Mass spectrum of PHE was similar to that of reference sample (Figure 12S). The GC spectra of PHE before and after degradation is displayed in Figure 13S. To identify the degradation fragments, they were separated from the solution by extraction with chloroform, and the mass spectra of the identified degradation products is represented in Figure 14S.

The MS spectrum of degradation products were concluded that the peaks appeared at retention time of 3.8, 3.9, 4.7, 4.8, 7.7 and 7.5mins beonged to the degradation products and the peak appeared at RT 11.0 was related to the remaining PHE. The identified compounds are listed in Table 3S. The main degradation products are di-sec-buthyl ether, di-sec-buthyl acetal, benzyl ether, 4- o xo-pentanoic acid and 4-chlorobenzaldehyde.

The aim of AOPs process is to mineralize the organic pollutant and to convert them into H2O and CO2. To evaluate the mineralization degree of the pollutant, the Total Organic Carbon (TOC) of the degradation solution was measured before and after irradiations. It was concluded that 85% of degraded pollutant was mineralized. Therefore, the concentration of the identified degradation products was very small.

**Conclusions**

In this work, a magnetized support was prepared by in-situ oxidative polymerization of polypyrrole in the presence of Fe3O4. The support was then employed as the catalyst support for NiO photocatalyst. The synthesized catalyst was characterized by different techniques. The SEM images showed that the particle size of Fe3O4-PPY and Fe3O4-PPY-NiO were respectively 45 and 65nm. The DRS analysis indicated that band gap energy of NiO after immobilization on the support shifted to lower energy which was benificial for visible light degradation of the pollutant. PL analysis of the photocatalysts showed that after embeding of NiO on the support, the electron–hole recombination was significantly quenched leading to higher degradation efficiency. The synthesized photocatalyst, and the bulk NiO, were used for degradation of PHE under UV and visible light irradiaions. The degradation process was kinetically fast and the equilibrium was achieved within 4h of irradiation. The used magnetized nanophotocatalyst was removed from the degradation solution by applying external magnetic field and was regenerated by heat treatment at 250°C. Most of its initial activity was remained after five regeneration cycles.

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