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Research Article

Phenol and Polyphenol Removals in Olive Mill Effluent with Nano-Zno-Magnetite Composite via Photo Catalysis

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1. Abstract

Olive mill wastewater (OMW) contains high concentration of organic matter, acidic pH values, suspended solids and high content of phenols and polyphenols which are toxic substances. The aim of this study is the removals of total phenol and two polyphenos namely tyro sol and hydroxytyrosol in the OMW by Nano-ZnO-Magnetite composite via photo catalytic degradation. For photo catalytic degradation under UV, with the optimum concentration of Nano-ZnO-Magnetite (3 mg per liter), maximum 75% total phenol yield, 80% and 51% tyro sol and hydroxytyrosol removals was obtained at a irradiation time of 30 minute and at a UV power of 300 W.

2. Keywords

Olive mill effluent; Nano-znO-magnetite composite; Phenol; Tyrosol; Hydroxytyrosol; Photo catalysis

3. Introduction

Most researchers concentrated their studies on TiO_2 as photo catalyst compared to the other metal oxides for the degradation of environmental pollutants [1]. ZnO is better because it absorbs large fraction of the solar spectrum and more light quanta than TiO_2 [2]. Researchers have highlighted the performance of ZnO on degradation of some organic compounds [3]. In addition, ZnO has more functions than TiO_2 [4]. Recently, researchers have pointed out that ZnO can also be used in the acidic or alkaline conditions through proper treatment [5]. Furthermore the optimum pH reported for ZnO process is close to neutral value, whereas the optimum pH for TiO_2 mostly lies in acidic region. Hence the ZnO process is more economical for the treatment of industrial effluents. ZnO has been reported to be more efficient than TiO_2 in some processes such as the advanced oxidation of pulp mill bleaching wastewater [6], the photo oxidation of phenol [7] and photocatalysed oxidation 2-phenyl phenol [8]. In particular, ZnO has attracted much attention with respect to the degradation of various pollutants due to its high photosensitivity, stability and wide band gap. While TiO_2 is widely employed as a photo catalyst, ZnO is a suitable alternative to TiO_2 as it has a similar band gap energy (3.2 eV) [9], with larger quantum efficiency. Higher photo catalytic degradation efficiencies of contaminant dyes have been reported.

Therefore, the aim of this study is the removals of total phenol, and two polyphenols (tyro sol and hydroxytyrosol) in the OMW via photo catalytic processes at increasing 3 mg/L Nano-ZnO-Magnetite concentration at increasing irradiation times (30 min, 60 min, 90 min, 180 min and 240 min) and at pH 4.

4. Materials and Methods

4.1. Synthesis of Nano-ZnO-Magnetite Composite under laboratory conditions

Nanoparticle is produced under laboratory conditions and immobilization method is used for this purpose. The magnetite sample was ground and sieved to 200-mesh size, then is washed with demineralized water for 3–4 times. The slurry of magnetite was prepared in water and it was stirred for 1 h, kept overnight, filtered under vacuum and the resultant solid cake was exposed to slow evaporation till the completely dry material was obtained. 10 g of magnetite was added to a solution containing 2g zinc acetate dihydrate dissolved in 250 ml of N, N-dimethylformamide and the mixture was sonicated for about 3 h in order to obtain homogeneous suspension. To this solution, 100 ml of 0.1 MNaOH/H_2O solutions was added with constant stirring for 1 h. The Nano composite powder was obtained after successive centrifugation

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and dispersions in alcohol and the solid mass was dried at 75 ◦C under vacuum incubator for 4 h. Then it is calcinated at 200 ◦C for 2–3 h in a Muffle furnace. The dried Nano-ZnO-Magnetite Nano composite was then is used for photo catalytic experimentations.

4.2. Analytical Methods

A HPLC Degasser (Agilent 1100), a HPLC Pump (Agilent 1100), a HPLC Auto-Sampler (Agilent 1100), a HPLC Column Oven (Agilent 1100) and a HPLC Diode-Array-Detector (DAD) (Agilent 1100) were used for phenol and 2 polypenol measurements namely tyro sol and hydroxytyrosol determined in the OMW. About 10 mg of a standard of phenolic acids (phenol, tyro sol and hydroxytyrosol) was weighed accurately and they were dissolved into volumetric flasks containing 10 mL 1:1 MeOH/distilled water to obtain stock solutions. For calibration curves, the stock solution was diluted with 1:4 MeOH/distilled water to obtain the concentration sequence. The linear range and the equations of linear regression were obtained through such a sequence of 50 mg/L, 20mg/L, 10 and 5 mg/L. Mean areas generated from the standard solutions were plotted against concentration to establish calibration equations. R^2 values of calibration graphs of caffeic acid, was found as 0.99.

4.3. Photo catalytic reactor and operational conditions

Photo catalytic degradation experiments were carried out in self-designed quartz glass reactors. The dimensions of the reactors were 38 and 3.5 cm and the costant power of the UV lamps was 300 W. The experiments were performed at room temperature and the pH of the reaction mixture was 4. Photo catalytic experiments were carried out with a known quantity of Nano-ZnO-Magnetite (3 mg/l) composite at different irradiations times (30 min, 60 min, 90 min, 180 min and 240 min).

4.4. X-ray diffraction (XRD) Analysis

XRD measurements were carried out with the RIGAKU D-Max 2200 PC. X-ray diffraction were used for the identification of crystalline materials and their structure. Each crystalline solid has its unique characteristic X-ray powder pattern and can be used for the characterization of crystalline properties of materials. Preliminarily, the material was characterized; X-ray crystallography may be used to determine the atom distribution in the crystalline structure and the distance between atoms and angles [10].

4.5. Fourier transform infrared (FT-IR)

FTIR spectra were determined using an Perkin Elmer System with a Spectrum of BX. Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. FTIR spectrometer catch resolution with high spectrum data. This advantage of the spectrometer cause determining the intensity of wavelengths [11].

5. Results and Discussion

5.1. X-ray diffraction (XRD) Analysis Results

XRD was used to verify the chemical composition and the crystal structure of Nano-ZnO-Magnetite Nano composite [12]. **Figure 1** represents the XRD pattern of Nano-ZnO-Magnetite core/shell. Considering this figure, it is shown that after coating, we have enhancement in peak intensity which is caused by overlapping of Fe_3O_4peaks [13] .No peaks corresponding to the impurities are detected, indicating thatFe_3O_4–ZnO heterostructure were formed during the photo degradation process [14].

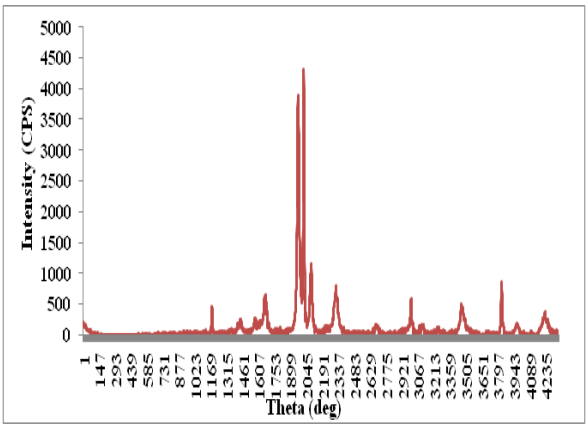

Figure 1: XRD patterns of Nano-ZnO-Magnetite.

5.2. FT-IR Analysis results

Figure 2 shows the FT-IR spectra of Nano-ZnO-Magnetite. A the absorptions at 1395.25/cm and 1591.29/cm are special peaks of the COO-Fe bond. This bond appeared via the hydroxide groups on the outer layer of the magnetite [15]. These peaks reveal that Fe_3O_4has been successfully immobilized onto the surface of ZnO. Combining the XRD results, it can be concluded that ZnO had been coated on the Fe_3O_4, successfully. Therefore, crystal form of Nano-ZnO-Magnetit composite converts the amorphous shape. As a result, the peak number in the Nano-ZnO-Magnetit composite decreases in the amorphous shape.

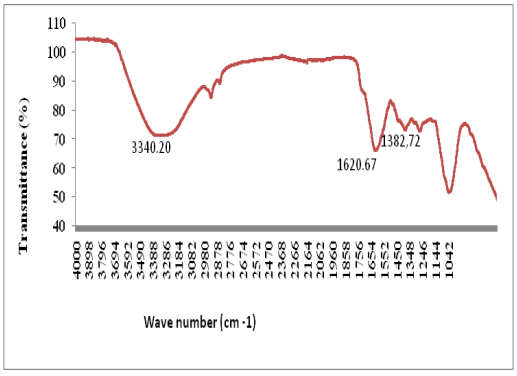

Figure 2: FTIR spectrum of Fe3O4, ZnO, Nano-ZnO-Magnetite and Nano-ZnO-Magnetite .

5.3. Effect of İrradiation times on the Removals of phenol in the OMW

Figure3shows the effect of different UV irradiation times (30 min., 60 min., 90 min., 180 min. and 240 min) on photo degradation of phenol at a pH of 4.60 at a temperature of 20 ^{0}C after at a 3 g/L concentration of Nano-ZnO-Magnetite Nano composite with an UV lamp with a power of 300 W. From Figure 3 it can be seen that as the irradiation time were increased from 30 min, to 60 min, to 90 min, and to 180 min, the phenol yield increased from 57%, to 63%, to 65%, to 77%, and stabilized to 77%. Further increase of adsorption time to 240 min did not increase the phenol yield. The optimum irradiation time can be considered as 180 min for the maximum removal efficiency of phenol (77%). The percentage of degradation of phenol was 65.5% under UV light after 150 min irradiation time. The phenol degradation was only52% when pure ZnO was used, which is lower than that in the presence of either Fe_3O_4-ZnO.

5.4. Polyphenol analysis Results

According to the results of chromatograms in HPLC analysis, 112.6 mg/L concentration of hydroxytyrosol and 172.7 mg/L concentration of tyro sol was identified in raw OMW illustrated in Figure 4. In a study investigated byManouchehr et al., (2014), polyphenols were analyzed in the olive oil mill effluents. 115.9 mg/L and 50.3 mg/L concentration of hydroxytyrosol and tyro sol were found, respectively, and these data are consistent with our The results showed that hydroxytyrosol and tyro sol were most abundant phenolic compounds in OMW (**Figure 4**). Hydroxytyrosol and caffeic acid show a powerful antioxidant activities [16] Hydroxytyrosol inhibits human LDL oxidation, inhibits platelet aggregation and exhibits anti-inflammatory and anticancer properties [17]. Tyro sol showed similar concentrations with hydroxytyrosol in the OMW (Figure 4). Samuel et al. (2008) reported that hydroxtytrosolis very effective in preserving cellular anti-oxidant defenses [18].

By using 3 g/L Nano-ZnO-Magnetite Nano composite with 30 min irradiation time at pH 4 and a temperature of ±20 ^{0}C with an UV power of 300 W during photo oxidation. The removal efficiencies of tyro sol and hydroxytyrosol were obtained as 80% and 51%, respectively. Their concentrations decreased from 172.7 mg/L to 34.8 mg/L for tyro sol and from 112.6 mg/L to 55.2 mg/L for hydroxytyrosol, respectively, after treatment with 3 g/L Nano-ZnO-Magnetite Nano composite under 300 W UV irradiation after 30 min irradiation time (**Figure 5, Table 1**).

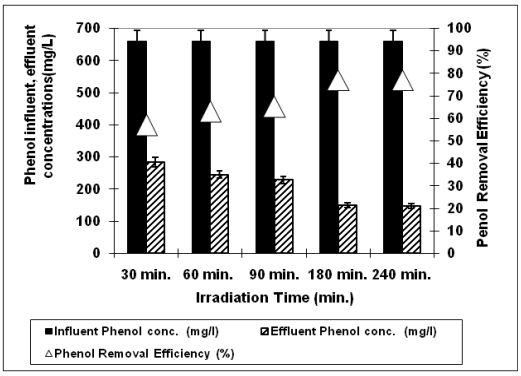

Figure 3: The effect of Irradiation time on phenol yield (Influent Conc.: 660 mg/L, T: ±20 ^{0}C, pH: 4.00, Nano-ZnO-Magnetite concentration: 3g/L, UV power: 300 W).

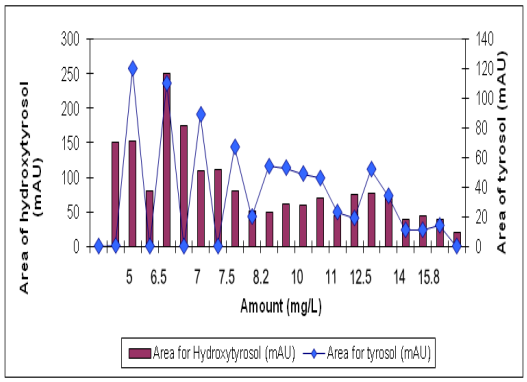

Figure 4: The concentration of tyrosol and hydroxytyrosol found in raw OMW.

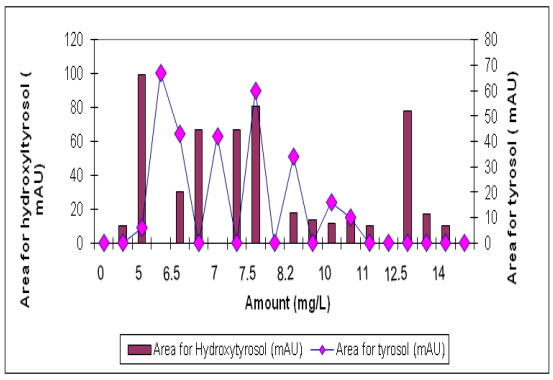

Figure 5: The concentration of tyrosol and hydroxytyrosol found in treated OMW with UV photo oxidation.

Table 1: Removal Efficiencies of polyphenols (tyro sol and hydroxytyrosol) in OMW.

Polyphenols	Raw OMW (mg/L)	Treatment of OMW with UV photooxidation (mg/L)	Removal Efficiency (%)
Tyrosol	172.7	34.8	80
Hydorxytyrosol	112.6	55.2	51

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