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Nanoparticle for degradation of BTEX in produced water; an experimental procedure

Z. Sheikholeslami *, D. Yousefi Kebria, F. Qaderi

Department of Civil Engineering, Babol Noshirvani University of Technology, P.O. Box 484, Babol, Iran

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ABSTRACT

BTEX are the most aromatic hydrocarbons in produced water. Due to hazardous effects of BTEX on environment and to human health, different methods were applied for produced water treatment. One of these methods is nanophotocatalytic process. In this paper for the first time, maghemite nanoparticles were used to remove the pollutants. Maghmite was synthesized by wet chemical method as semiconductor photocatalysis. The synthesized nanoparticles were characterized by Diffuse Reflectance Spectroscopy (DRS), X-ray diffraction analysis technique and scanning electron microscope (SEM). The impact of the main factors including pH (3–7), catalyst concentration (0–250 mg/l) and UV light intensity (0–100 W) were studied. Response surface methodology was utilized to apply and optimize the experiments and results. From the analysis of the results the equation of quadratic polynomial model was obtained. R^2 and R^2_{adj} for the model were 0.94 and 0.88 respectively, which indicate the model matches the experimental data. Outputs reveal that the best removal efficiency of BTEX (82%) was observed in 90 min at pH = 3, nanoparticle concentration = 170 mg/l, and UV light intensity = 100 W.

1. Introduction

BTEX (Benzene, Toluene, Ethyl benzene, and Xylenes) are the most aromatic hydrocarbons in produced water (PW), and can be shown in untreated PW from diverse sources. BTEX concentration in produced water worldwide is 0.068–578 mg/l [1], which is over the limitation of discharging to the environment [2]. Due to hazardous effects of BTEX on human health and environment, there exists an instantaneous need to use the technology of PW treatment [1]. Typical treatment technology, such as hydrocyclones, filtration, gas flotation, adsorption and, photocatalytic process are able to eliminate most of the hydrocarbons and other hazardous ingredients from the PW [3–5]. Recently researchers have focused on nanophotocatalytic process in wastewater treatment. Semiconductor photocatalysis is identified as a beneficial way to remove the pollutants and generation of fewer intermediate products [6,7]. Nanophotocatalytic semiconductors have two energy levels in their structure (valence bands (VB) and, conduction band (VB)) [8]. When the semiconductors exposed to the photons which, energy is equal to or greater than the band gap energy, the electrons (e^-) in the VB have been excited to the CB and the holes (h^+) were create in VB [9]. The h^+ of nanophotocatalysis separates the water molecule to create hydroxyl radical ($\dot{O}H$) and the e^- reacts with oxygen molecule to create super oxide anion [10]. The $\dot{O}H$ radicals are often considered as the main oxidizer to directly oxidize pollutants [11,12]. The most effective factors in a photocatalytic process are pH, light intensity and catalyst concentration [13]. The mechanism of photocatalytic process appears in Table 1 [11].

Newly nanoparticles have various applications in different fields [14–17]. Maghemite (γ-Fe_2O_3) is a kind of nanoparticles that use in photocatalytic process [18]. Among plentiful chemical ways for preparing of γ-Fe_2O_3, co-precipitation process (wet chemical method at room temperature) is an easy and feasible technique and has various benefits such as: high homogeneousness, low cost, unnecessary to use organic solvents and heat treatment, and high purity of maghemite [19].

According to the recent years most researchers were used maghemite nanoparticles doped with other nanoparticles to remove different pollutants like: chromium (VI) [20], pharmaceuticals [21], dye [22], cesium [23], heavy metals [24], hydrocarbons [25–28]. In this paper for the first time maghemite nanoparticles were used to eliminate the BTEX in produced water. The objectives of this work are:

(1) To synthesize of maghemite nanoparticles as semiconductor photocatalysis by co-precipitation method.
(2) To investigate the removal efficiency of BTEX, by changing the operational parameters consisting pH, catalyst concentration, and light intensity. The experiments were applied by response surface methodology.
(3) To investigate the effects of interactions and present interactive diagrams for the first time.

* Corresponding author.
E-mail addresses: z_sh.eslami@yahoo.com, z.sheikholeslami@stu.nit.ac.ir (Z. Sheikholeslami).

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Table 1
The mechanism of photocatalytic process.

Mechanism	Description of the mechanism
$Photocatalyst + h\upsilon \rightarrow e^- + h^+$	Photoexcitation
$O_{2(ads)} + e^- \rightarrow O_2^{-\cdot}$	Photoexcited e^- scavenging
$OH^- + h^+ \rightarrow \dot{O}H$	Oxidation of hydroxyls
$R-H + \dot{O}H \rightarrow \dot{R} + H_2O$	Photodegradation by $\dot{O}H$
$R + h^+ \rightarrow \dot{R}^+ \rightarrow$intermediate product	Direct photoholes
$O_2^{-\cdot} + \dot{O}H \rightarrow O\dot{H}H$	Protonation of superoxides
$\dot{O}OH + e^- \rightarrow HO_2^-$	Co-scavenging of e^-
$\dot{O}OH + H^+ \rightarrow H_2O_2$	Formation of H_2O_2

2. Materials and methods

2.1. Materials

BTEX (Benzene, Toluene, Ethylbenzene, and Xylene) was used as an indicator of PW. To synthesis of maghemite nanoparticle, the chemicals were $FeCl_3$, $FeCl_2 \cdot 4H_2O$, HCL, NH_4OH, distilled water and ethanol. Sodium hydroxide and sulfuric acid were used to regulate the pH of the solution. All chemical materials were prepared from Merck Company (Germany).

2.2. Preparation of synthetic wastewater

BTEX concentration was considered 600 mg/l that is higher than worldwide concentration. Approximately 600 mg/l of synthetic wastewater was provided by dissolving 600 mg of benzene, toluene, ethyl benzene, xylene in 1 l of distilled water and placed in an ultrasonic bath for 60 min. Then it was stirred continuously for 24 h. After stirring for 30 min, the solution is returned to the ultrasonic bath. Finally, the concentration of the solution will be 600 mg/l [29].

2.3. Maghemite nanoparticle synthesis process

Maghemite with a moderate particle size 25 nm, was prepared by using a wet chemical method. To prepare iron (III) chloride solution 1 M and iron (II) chloride Tetrahydrate solution 2 M, $FeCl_3$ and $FeCl_2 \cdot 4H_2O$ were dissolved in an HCL 2 M solution. These solutions were combined with a weight ratio of 2: 1 (iron (II): iron (III)) and placed on a magnetic stirrer. Then, for 2 h, ammonium hydroxide was added dropwise to form an iron oxide nanoparticle. The pH of the final solution was 9.5. The black sediments obtained have been washed three times with ethanol, water and were dried at 55–70 °C for 24 h [30].

2.4. The experiment of Photocatalysis

X-ray diffraction described the crystalline structure of the maghemite nanoparticles by using Cu Kα (=1.54060 Å) radiation. SEM was employed to specify the structure properties and the particle size distribution of γ-Fe_2O_3 nanoparticles. The optical absorption characteristics of the synthesized γ-Fe_2O_3 are specified through the Diffuse Reflectance Spectroscopy (DRS).

2.5. Analytical methods

The chemical oxygen demand is used as a dependent variable to evaluate the removal efficiency. The tests are performed according to the standard method 5220 C [32].

2.6. Experimental design

The Design Expert is authoritative software for the statistical simulation of various processes. It can be possible to model the desired processes statistically. For the design of the experiments and analysis of data, the Design Expert Software (version 7.1.5) was used. In this work, Response Surface Methods (RSM) have been used for optimizing the three principal independent variables (pH, catalyst concentration, and light intensity). In this method, each independent variable is defined at five levels (−α, −1, 0, +1, +α) and the number of experiments equal to $2^k + 2k + 6$ that k is the number of independent parameter. Table 2 shows the variables and their levels.

Table 2
Experimental range and levels of the independent variables.

Factors	−α(−1)	−1	0	+1	+α(+1)
pH	3	3	5	7	7
Catalyst (mg/L)	0	0	125	250	250
Light intensity (nominal UV lamp power)	0	0	50	100	100

2.7. Pilot configuration

The pilot used for the photocatalytic treatment of PW is shown in Fig. 1. The refrigerator is used to adjust the temperature (25 °C). Open cubic plexiglas 2.5 × 2.5 cm^2 and quartz plate 2.5 × 2.5 cm^2 are used to put the synthetic wastewater under UV light. The flow was mixed by magnetic stirrer and the nanoparticles were placed against light for better reflection of light. The pilot consisted of 4 UVC lamps, 25 watt (100–280 nm). The light intensity of UV lamp around each lamp at the mentioned wavelength was almost 0.62 mW·cm^2. The UV lamps were placed on a steel plate and positioned on top of the refrigerator.

3. Result and discussion

3.1. Structural nanoparticles analysis

X-ray diffraction spectroscopy was utilized to decide the phase identification of crystalline maghemite nanoparticles and the patterns are shown in Fig. 2. All the peaks of γ-Fe_2O_3 nanoparticles are in accordance with the standard structure. The results indicate good purity phases (JCPDS file, No. 04-0755).

After confirming the synthesis of the γ-Fe_2O_3 nanoparticle, the morphology and particle size were demonstrated by SEM. Fig. 3 illustrates that the average dimension of maghemite nanoparticle in this work is

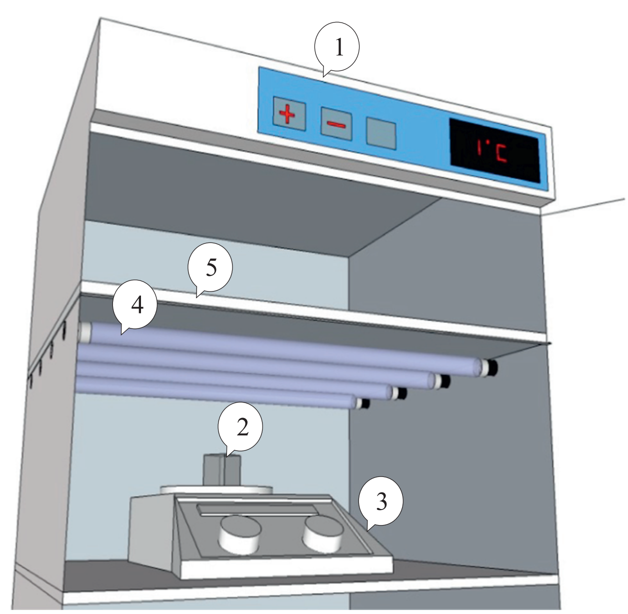

Fig. 1. Experimental set-up: (1) refrigerator, (2) open cubic plexiglas, (3) stirrer, (4) UV lamps.