



Preparation of zeolite nanorods by corona discharge plasma for degradation of phenazopyridine by heterogeneous sono-Fenton-like process



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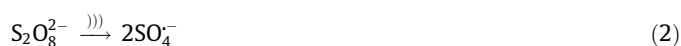
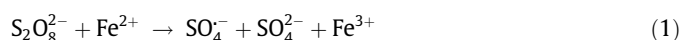
ABSTRACT

The plasma-modified clinoptilolite (PMC) nanorods were prepared from natural clinoptilolite (NC) utilizing environmentally-friendly corona discharge plasma. The PMC and NC were characterized by XRD, FT-IR, SEM, EDX, XPS and BET, which confirmed the nanocatalyst formation. The catalytic performance of the PMC in the heterogeneous sono-Fenton-like process was greater than the NC for treatment of phenazopyridine (PhP). The desired amounts were obtained for experimental parameters including initial pH (5), PMC dosage (2 g/L), K₂S₂O₈ concentration (2 mmol/L), ultrasonic power (300 W) and PhP concentration (10 mg/L). Reactive oxygen species scavengers decreased the removal efficiency of the PhP. The treatment process followed pseudo-first order kinetic and seven degradation intermediates were identified by the GC-MS technique.

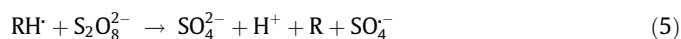
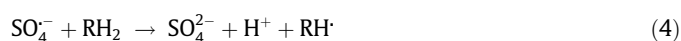
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1. Introduction

An extensive number of synthetic pharmaceuticals known as emerging contaminants (ECs) are being found in the aqueous environments, which considered as potentially hazardous materials owing to their toxicity, resistant to biodegradation and photo-transformation [1–3]. Phenazopyridine hydrochloride is an analgesic drug to reduce pain related to the urinary tract infections or irritation [4]. If the PhP or its metabolites such as *p*-aminophenol and alanine discharge into an aquatic environment, they will have a negative influence on the aquatic life owing to disastrous effects on the liver and other organs. Moreover, carcinogenic effect was detected in rats and mice due to long-term usage of this drug [4,5]. Hence, efficient degradation methods like advanced oxidation processes (AOPs) have been developed to remove drugs from water bodies [6]. Reactive oxygen species (ROS) such as hydroxyl ($\cdot\text{OH}$), hydroperoxyl ($\cdot\text{OOH}$) and sulfate ($\text{SO}_4^{\cdot-}$) radicals can be produced in various AOPs [7]. For instance, the $\text{SO}_4^{\cdot-}$ radicals are generated from $\text{S}_2\text{O}_8^{2-}$ redox decomposition using a transition metal like iron (Eq. (1)) or in the presence of ultrasonic irradiation (Eq. (2)); Moreover, $\cdot\text{OH}$ radicals can also be produced from water cleavage under sonication (Eq. (3)) [8,9].



The $\text{SO}_4^{\cdot-}$ radical has redox potential of 2.5–3.1 V and life time of 30–40 μs which is more than the $\cdot\text{OH}$ radical [10]. Moreover, inert sulfate ion produced as end product does not considered as the contaminant [11]; other main possible reactions are given in Eqs. ((4)–(7)) [10–12]:



Based on hot spot approach, after entering ultrasonic waves into a liquid phase, the cavitation phenomenon leads to generation, growth, and finally collapse of microbubbles generating localized high pressures and temperatures [8]. The ultrasonic process has been properly used for treatment of halogenated hydrocarbons

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[13], drugs [14] and dyes [15]. However, it consumes high energy owing to its low degradation rate; thus it should be combined with other treatment methods such as Fenton process [16,17]. It should be mentioned that catalyst separation and recycling from the treated water confine the usage of homogeneous Fenton process, which should be performed in acidic medium ($\text{pH} = 3$) to prevent from the precipitation of iron; hence, application of heterogeneous Fenton process is a practical way to overcome these drawbacks [18]. Natural zeolites [19], pyrite [20], magnetite [21], goethite [22], laponite [23] and pillared clays [24] with superficial solid Fe ions can be used as the heterogeneous catalysts in Fenton process.

The zeolites are considered as hydrated aluminosilicates; their porous and crystalline structure comprises of three-dimensional network of AlO_4^- and SiO_4 tetrahedral units linked by sharing of oxygen atoms [25–29]. Each anion in the zeolite structure is neutralized by an extra framework cation from group IA or IIA. Their structures contain regular channels or cages with various size (3–20 Å) occupied by the charge balancing ions and water molecules [29–31]. Clinoptilolite, which is a green catalyst and the most well-known natural zeolite, has been widely used in the AOPs owing to its low-cost and non-toxicity [27,32–35]. However, the clinoptilolite possesses low surface area, which affects the mass transfer in the reactions and hence its appropriate usage [36,37]. So, the crystal size should be decreased to nanometer scale to enhance its performance [38,39]. For instance, diverse synthetic methods have been introduced to produce nanozeolites, which generally require sophisticated equipment and toxic precursors [40–45].

Plasma, which is noticed as the fourth state of matter, consists of ions, electrons and neutral species. Recently, non-thermal plasma as an environmentally-friendly method including corona discharge, glow discharge and radio frequency plasmas, have been utilized for catalysts modification and nanostructures production [46–50]. For instance, the effectiveness and activity of Pd/HZSM-5, Pd/TiO₂, magnetite and pyrite catalysts are improved after non-thermal plasma treatment [15,51–53]. The corona discharge plasma is applied for improvement of the nickel catalytic activity in partial oxidation of methane to syngas and production of modified NaY zeolite for reduction of carbon dioxide [54]. The catalyst stability can also enhance after plasma treatments [55].

The aim of this study is to produce nano-sized clinoptilolite from the NC using the corona discharge plasma. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS) and Brunauer–Emmett–Teller (BET) were applied to characterize the NC and PMC. Then, the efficiency of the PMC catalyst for treatment of PhP in the heterogeneous sono-Fenton-like process ($\text{US}/\text{S}_2\text{O}_8^{2-}/\text{PMC}$) was determined and compared to the NC. The effect of operational parameters including the solution pH, modified catalyst dosage, $\text{S}_2\text{O}_8^{2-}$ concentration, ultrasonic power, initial PhP concentration and radical scavengers were investigated on the removal efficiency (RE%) of the PhP in a series of batch experiments. Finally, gas chromatography–mass spectrometry (GC–MS) was applied to identify the generated intermediates through the PhP degradation and the possible pathway.

2. Experimental

2.1. Chemicals

The PhP or 2,6-Pyridinediamine,3-(phenylazo) monohydrochloride as a model heterocyclic aromatic azo drug was supplied from Shahr Darou Co. (Iran); Table 1 presents its structure and characteristics. Natural clinoptilolite tuffs were provided from the Mianeh region (Kan Azar Co, Iran). Hydrochloric acid (37%), sodium

hydroxide (99%) and potassium persulfate (98%) were purchased from Merck (Germany). Ethanol (96%) was purchased from Jahan Alcohol Teb Co. (Arak, Iran). Distilled water was used in all of the experiments.

2.2. Plasma-treatment procedure

Fig. 1 shows the experimental set-up used for the corona discharge plasma modification procedure. The main body of the reactor was consisted of two stainless steel electrodes with the air gap of 4.0 cm. The voltage of 30 kV and frequency of 300 Hz with nano-rise time from a power supply were applied between the electrodes. The clinoptilolite particles were washed with distilled water and dried at 60 °C for one day. Then, the dry clinoptilolite powder (3 g) was placed in the reactor and modified by the corona plasma for 10 min. After the plasma modification procedure, the PMC particles were collected for application in the sono-Fenton-like process.

2.3. Catalysts characterization

To determine the morphology and the chemical composition of the samples, the SEM (Mira3 FEG–SEM, Tescan, Czech) coupled with EDX microanalysis (acceleration voltage of 10 kV) was used. Diameter distribution of the PMC was calculated by microstructure distance measurement software (Nahamin Pardazan Asia Co., Iran). The XRD analysis was applied on the NC and PMC with a Siemens X-ray diffractometer (D8 Advance, Bruker, Germany) with Cu K α radiation ($\lambda = 0.15406$ Å) at an accelerating voltage of 40 kV and an emission current of 30 mA to investigate their crystallographic properties. The FT-IR spectra of the samples were obtained using Tensor 27, Bruker spectrometer (Germany). The XPS measurements were performed by K-Alpha, Thermo Scientific (UK) for quantitative compositional analysis. BET analysis was done by PHS-1020 (China) instrument.

2.4. Heterogeneous sono-Fenton-like process

The treatment experiments were carried out in a 250 mL Erlenmeyer, which was placed in an ultrasonic bath (EP S3, 40 kHz, Sonica, Italy). The distance between the bottom of the reaction vessel and the sonication source was placed at 1.0 cm, in which the solution surface had the maximum turbulence. In general, 100 mL of the PhP solution with known concentration and certain dosage of the catalyst were used in all of the experiments. Then, the solution pH was adjusted by adding of NaOH (0.1 mol/L) and HCl (0.1 mol/L) and measured by the pH-meter. During the process, 3 mL of sample was withdrawn and then the suspended particles were separated from the solution by centrifuging. The drug solution absorbance was measured at its maximum wavelength ($\lambda_{\text{max}} = 430$ nm) using an UV–Vis spectrophotometer (Light-wave S2000, England) to calculate the RE%. The GC–MS analysis was performed using a method described in our previous work for identification of the generated intermediates during the process [9,56].

3. Results and discussion

3.1. Characterization and formation of the PMC

Fig. 2 shows the XRD patterns of the NC (curve (a)) and PMC (curve (b)) samples. In these spectra, the XRD peaks at 2θ values of 10.9°, 17.53°, 22.7° and 27.63° were in good agreement with the clinoptilolite data (JCPDS card 83-1260) [30,34]. Besides, biotite, feldspar and quartz phases were identified in minor quantities

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