



Modification of clinoptilolite nano-particles with iron oxide: Increased composite catalytic activity for photodegradation of cotrimaxazole in aqueous suspension



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ABSTRACT

Photocatalytic degradation of a pharmaceutical cotrimaxazole capsule in aqueous solution was studied using Iron oxide (IO) supported onto clinoptilolite nano-particles (NCP) and Hg-lamp as radiation source. The ball mill prepared NCP was ion exchanged in Ferrous chloride aqueous solution (0.3 M) for 24 h and then calcined at 450 °C for 12 h for preparation of the IO–NCP catalyst. The raw and modified samples were characterized by X-ray diffraction (XRD), Fourier transformation infrared (FT-IR), UV–vis diffuse reflectance spectroscopy (DRS) and Transmission electron microscope (TEM). Degradation extent of the pollutant was estimated by UV–vis spectroscopy and confirmed by COD and HPLC. Experimental parameters significantly affected the efficiency of the process and their optimum values were estimated as: 0.5 g L⁻¹ of the photocatalyst, 50 folds diluted of the original solution (one capsule/100 mL) and pH 4.3. The proposed catalyst retained above 60% of its initial activity after 3 sequential re-using runs.

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1. Introduction

Emerging pollutants such as pharmaceuticals in the aquatic environment have increasing concern to the ecosystem sustainability [1]. Pharmaceutically active compounds, complex organic molecules with different physicochemical and biological properties and functionalities, can reach to the aquatic environment via a variety of ways including: improper disposal by private households, hospitals and industrial units [2,3] or domestic wastewaters containing unused or human excreted drugs [1]. So these pharmaceuticals can enter into agricultural wastewater [4], ground and drinking water and hence into the food chain and finally can severely affect

human health [3,5]. Antibiotics are among the important class of pharmaceuticals, which were widely detected in sewage effluents and surface waters, usually with a concentration ranging from ng L⁻¹ to µg L⁻¹ [1,6]. Cotrimoxazole is a fixed-ratio (1:5) combination of trimethoprim and sulfamethoxazole [7]. Trimethoprim (2,4-diamino-5-(3,4,5-trimethoxybenzyl) pyrimidine) is commonly prescribed for the treatment of various infectious diseases for both human and animals [8] and is a white to cream colored, odorless and bitter compound. It works by stopping the growth of bacteria [9] and it has two sub-structural subunits, chemical moieties, 1,2,3-trimethoxybenzene (TMBz) and 2,4-diaminopyrimidine (DAP) [10].

Some of the pharmaceutical products or their metabolites are not completely removed in wastewater treatment systems by: bioremediation, physicochemical treatments including: coagulation, volatilization, adsorption, sedimentation and filtration and therefore could persist long enough to enter

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drinking water systems [11]. Recent researches have been focused on the application of advanced oxidation processes (AOPs), which are widely applied for treating pharmaceutical residues and pharmaceutical wastewaters [12]. The final goal of AOP is converting the organic pollutants into CO_2 and H_2O . In heterogeneous photocatalysis, as the most famous category of AOP methods [13], the light energy equal to or higher than the band gap energy of a semiconductor [14], generates electron-hole pairs on the catalyst surface. The photo-generated holes (h^+) can oxidize H_2O or OH^- to yield HO^\bullet and the photo-generated electrons will adsorb by O_2 to produce superoxide radical ions ($\text{O}_2^{\bullet-}$). These radicals can react with pollutant molecules and disintegrate them into CO_2 and H_2O [15].

The heterogeneous iron oxide has been used as an effective source of oxidative radicals and shows semiconductor properties with a narrow band gap about 2.0–2.3 eV [16]. In this work, for increasing the photo-reactivity of iron oxide, it was supported onto clinoptilolite nano-particles. Zeolitic support can distribute the photo-generated electrons in its framework and prevents the electron-hole recombination, leading to increase the photocatalytic efficiency [17]. Zeolites offer several distinct advantages including: high surface area, unique nanoscaled porous structure, adsorptive and ion exchange properties. Hence, they have been widely used in photocatalytic systems [18–20]. An increasing interest has been applied for using natural zeolites, especially clinoptilolite, because they are cheap, easily available and environmentally friendly [21,22]. It would be expected that supported Iron oxide onto clinoptilolite nanoparticles shows significant increase in the photocatalytic activity with respect to unsupported one in the photodegradation process of cotrimaxazole aqueous solution. In the present work, a cotrimaxazole capsule was used as pollutant to have more similarity to real wastewater samples.

2. Experimental

2.1. Reagents

Natural clinoptilolite tuffs, belong to the Semnan region in the north-east of Iran, were purchased from Afrand Touska Company (Isfahan, Iran). Cotrimaxazole (trimethoprim/sulfamethoxazole $\text{C}_{14}\text{H}_{18}\text{N}_4\text{O}_3/\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_3\text{S}$) pharmaceutical capsule (500 mg) was purchased from Chemidarou Company in Iran. Other chemicals were purchased from Merck Company. Distilled water was used throughout the experiments. The pH of solutions was appropriately adjusted with sodium hydroxide or hydrochloric acid solution.

2.2. Preparation of the nano-zeolite and catalysts

Natural clinoptilolite tuffs were mechanically pretreated, by crushing in an agate mortar and sieving in analytical sieves, for separating the 100 μm particle-size fractions. Clinoptilolite nano-particles (NCP) were prepared using a planetary ball mill (PM100; Retsch Corporation) using a dry milling method at the milling duration of 6 h, speed of 600 rpm and balls-to-powder ratio of 4. To remove water soluble and paramagnetic impurities, an aqueous suspension of nanoparticles was heated at 70 °C for 3 h under magnetic stirring. This process

was repeated 3 times. The resulting suspension was centrifuged and air dried over night.

To prepare Fe(II)-exchange NCP, 4 g of NCP was added to 100 mL Ferrous chloride (0.1 M) and the prepared suspension was shaken for 24 h. The suspension was centrifuged and the filtrate was washed and air dried for 1 day and finally calcined at 450 °C for 12 h to prepare iron oxide–nanoclinoptilolite catalyst (IO–NCP). Similar method was performed for 0.2, 0.3 and 0.5 M Ferrous chloride solutions. As we know, zeolites are hydrated aluminosilicates which can be dehydrated during thermal processing. To have precise and accurate weights of the calcinated zeolite during the experiments, it is necessary to fix the water content of the modified zeolite. For this goal, the calcinated material was stored in desiccators over a saturated sodium chloride solution for 1 week. This condition provides a constant water vapor pressure and thus modified zeolite adsorbs water molecules to reach its equilibrium water content.

2.3. Catalyst characterization

The amount of Ferrous cations in the catalysts was measured using atomic absorption spectrometer (AAS) (AAAnalyst 300, Perkin Elmer Co. USA). Infrared spectrophotometer (FT-IR, model Impact D400) and UV–vis DRS spectrophotometer (V-670, JASCO, Japan) were also used to characterize the samples. X-ray diffraction patterns (XRD) were recorded by using a diffractometer Bruker, D8ADVANCE, X-ray tube anode: Cu, wavelength: 1.5406 Å (Cu $K\alpha$ radiation). The microstructures of the NCP and Iron oxide-NCP samples were recorded using Transmission Electron Microscope (TEM S-3500 N with Absorbed Electron Detector S-6542 Hitachi Science System Ltd.). A UV–vis spectrophotometer (Model Cary 100, double beam, Australia) was used to record the absorbance of samples. HPLC analysis of samples was performed by an Agilent Technologies 1200 Series instrument with Quaternary pump, column XDB-C₁₈ ($L=15$ cm, $id=4.6$ mm and particle size=5 mm) and UV detector. The pH of point of zero charge, pH_{pzc} , for the catalyst was determined using the procedure reported in our previous works [23,24]. For this goal, the pH of a series of 25 mL 0.5 M NaCl solutions was adjusted to a value between 2 and 12 by adding HCl or NaOH solution in closed Erlenmeyer flasks. Before adjusting the pH, the solutions degassed by purging N_2 gas to remove dissolved CO_2 . The pH of these solutions was recorded as initial pHs (pH_i). Then, 0.5 g of the IO–NCP catalyst was added and the resulted suspensions were shaken for 48 h and the final pHs (pH_f) was measured. Finally, the plots of pH_f versus pH_i and also pH_i versus pH_f were constructed. In this case, plot of pH_i versus pH_f yield a linear line (can consider as bisector of the curve) which intersect other curve. The intersection of these curves considered as pH_{pzc} for the catalyst.

2.4. The catalytic activity

To prepare cotrimaxazole solution, the content of a 500 mg capsule was dissolved in sufficient water and it was shaken for 30 min and obtained solution was transferred to 100 mL volumetric flask and diluted to the mark. The obtained solution was diluted 10, 50 and 100 times

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