Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 136 (2015) 423–428

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Comparison of adsorption and photo-Fenton processes for phenol and paracetamol removing from aqueous solutions: Single and binary systems

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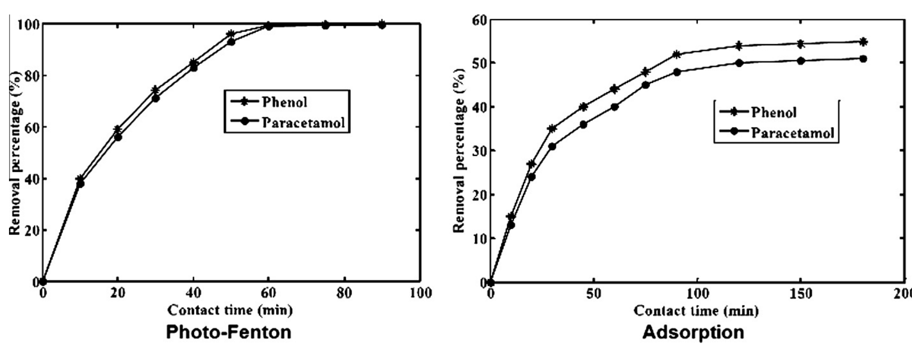
HIGHLIGHTS

- The adsorption and photo-Fenton processes was studied.
- The phenol and paracetamol removing was investigated in a binary system.
- The NaX nanozeolite and cobalt ferrite nanoparticles were synthesized.
- The complete elimination of phenol and paracetamol was found during processes.
- The alternative method was found to be adsorption process at lower concentrations.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 6 July 2014
Received in revised form 6 September 2014
Accepted 18 September 2014
Available online 7 October 2014

Keywords:
Adsorption
Photo-Fenton
Phenol
Paracetamol
NaX nanozeolites
Cobalt ferrite nanoparticles

ABSTRACT

In the present study, adsorption and photo-Fenton processes have been compared for the removal of phenol and paracetamol from aqueous solutions in a single and binary systems. NaX nanozeolites and cobalt ferrite nanoparticles were used during adsorption and photo-Fenton processes, respectively. Both nanoparticles were synthesized using microwave heating method. The synthesized nanoparticles were characterized using powder X-ray diffraction (XRD) and scanning electronic microscopy (SEM) analysis. Based on results, more than 99% removing percentages of phenol and paracetamol were obtained during photo-Fenton process at initial concentrations of 10, 20, 50, 100 and 200 mg/L of phenol and paracetamol. Moreover, the complete removing of phenol and paracetamol was only achieved at lower initial concentrations than 10 mg/L for phenol and paracetamol during adsorption process. The results showed a significant dependence of the phenol and paracetamol removing on the initial concentrations of phenol and paracetamol for selection of process. The photo-Fenton process could be considered an alternative method in higher initial concentrations of phenol and paracetamol. However, the adsorption process due to economical issue was preferred for phenol and paracetamol removing at lower initial concentrations. The kinetic data of photo-Fenton and adsorption processes were well described using first-order and pseudo-second-order kinetic models. The results of phenol and paracetamol removing in a binary system confirmed the obtained results of single removing of phenol and paracetamol in selection of process.

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http://dx.doi.org/10.1016/j.saa.2014.09.052
1386-1425/

Introduction

The pharmaceutical residues in the water is one of important serious environmental pollutants [1,2]. Paracetamol [(N-acetyl-4-amino phenol), ATP] is commonly used as analgesic and anti-inflammatory agents for human and animals [3,4]. A very low concentration of paracetamol is commonly detected in the surface water includes rivers, drinking water, and groundwater [4]. The presence of trace pharmaceuticals in drinking water has toxic effect for human and animal health [1]. On the other hand, Phenol is one of hazardous material and is highly toxic to humans and environment at very low concentrations. Phenol is an important industrial raw material frequently used in the manufacture of pharmaceutical compounds such as diclofenac, amoxicillin and paracetamol. The permissible limit of phenol is less than 0.5 mg/L in USEPA list [5]. Therefore, the removal of phenol and paracetamol in a binary system is inevitable. Several methods are developed for the removal of phenolic compounds from industry wastes in past few years [5–7]. These techniques were including advanced oxidation processes (AOPs), membrane filtration, biological treatment, photocatalytic degradation and adsorption processes [7]. Among all, AOPs have been extensively used for the treatment of phenol and pharmaceutical wastes [8,9]. Various AOP techniques such as Fenton, photo-Fenton, ozone oxidation, son-photo-Fenton and photo-catalytic oxidation are widely used for the removal of organic compounds of pharmaceutical wastes [10]. Photo-Fenton process due to its higher efficiency was found to be an efficient process compared to other AOP techniques [11]. However, photo-Fenton process is associated with problems such as high energy consumption [12]. Among mentioned techniques, adsorption process due to its simplicity, moderate operational conditions and economical feasibility, could be considered as an effective method for treatment of pharmaceutical wastes [13]. Although, the efficiency of adsorption process was lower than that of photo-Fenton process. For this, photo-Fenton and adsorption processes compared together as effective methods for the treatment of phenol and paracetamol at different initial concentrations. In recent years, various types of adsorbents such as activated carbon [14], zeolites [15], and mesoporous silica [13] have been used for the removal of phenolic wastes. Among all, zeolites due to the ion exchange properties and their hydrophilic affinities as well as higher surface area have been widely used for the treatment of pharmaceutical compounds [12,15]. Furthermore, nanozeolites due to higher surface area and ion exchange properties have a higher potential for treatment of pharmaceutical wastes in compared with microzeolites [16]. In photo-Fenton process, degradation of organic compounds from wastewater is based on the generation of reactive free hydroxyl radicals ($^{\cdot}OH$) [17]. To accelerate the degradation rate of organic compounds, spinel-structured ferrite nanoparticles are widely used as catalyst in AOP processes [18–20]. For this, we synthesized the cobalt ferrite nanoparticles and the potential of synthesized nanoparticles was investigated for the removal of phenol and paracetamol during photo-Fenton process.

In the present study, the synthesized cobalt ferrite nanoparticles were used in photo-Fenton process for the removal of phenol and paracetamol from aqueous systems. Furthermore, the potential of synthesized NaX nanozeolites was tested for phenol and paracetamol sorption during adsorption process in a bath mode. Both cobalt ferrite and NaX nanoparticles were synthesized using microwave heating method. The effect of initial concentrations of phenol and paracetamol was investigated for phenol and paracetamol removal during mentioned techniques in a single and binary systems. Finally, the kinetic data of photo-Fenton and sorption processes were analyzed by first-order and pseudo-second-order kinetic models.

Experimental

Materials

$FeSO_4{\cdot}7H_2O$, $CoCl_2{\cdot}6H_2O$, Fumed silica (7 nm) and $NaAlO_2$ were purchased from Sigma–Aldrich (Sigma Aldrich, USA). NaOH and Ethanol were obtained from Merck (Merck, Darmstadt, Germany). Phenol from (analytical grade; Fluka) was used. Paracetamol ($C_8H_9NO_2$) was provided from *Jalinous* pharmaceutical company of Iran. The microwave equipment used in this study was a commercial microwave oven (CE1110 C, Sumsung, Korea) with 900 W output power at wavelength of 2.45 GHz. The oven was equipped with an electronic system in order to control the temperature, accurately.

Synthesis of cobalt ferrite nanoparticles

The cobalt ferrite nanoparticles were synthesized using microwave heating method. For synthesis of nanoparticles, firstly, 0.56 g of $FeSO_4{\cdot}7H_2O$ and 0.24 g of $FeCl_3{\cdot}6H_2O$ were dissolved in 20 mL of de-ionized water by intensive stirring to obtain the homogeneous solution. Then, NaOH was added to the solution and the stirring was continued at room temperature for 1 h. then, the homogenous solution was applied into the microwave at temperature of 160 °C for 10 min. Then, the solid products was collected by magnetic filtration and washed by de-ionized water and ethanol. Finally, the samples were dried in a vacuum oven at 100 °C for 6 h.

Synthesis of NaX nanozeolites

The NaX nanozeolites were synthesized according to the method described previously [21]. Briefly, aluminosilicate gel was prepared in a 250 mL polypropylene bottle by mixing freshly prepared aluminate and silicate solutions together in the molar ratios of 5.5 Na_2O:1.0 Al_2O_3:4.0 SiO_2:190 H_2O. Then, microwave heating proceeded at 90 °C for 3 h. Finally, the prepared powder was washed with the de-ionized water until the pH value reached below 8, and dried at room temperature for 24 h.

Photo-Fenton process

The performance of the synthesized catalysts was evaluated in the photo-Fenton process of phenol and paracetamol degradation. The experiments were carried out under 4 UV lamps (15 W, λ_{max} = 365 nm) in a 500-mL Pyrex-glass cell wrapped in aluminum foil. The effect of initial concentrations of phenol and paracetamol and contact time on degradation of phenol and paracetamol were evaluated at optimum conditions of photo-Fenton process including catalyst dosage of 0.2 g/L, pH of 3, hydrogen peroxide concentration of 50 mmol/L, and temperature of 45 °C.

Adsorption process

The performance of the synthesized NaX nanozeolites was evaluated in the adsorption process of phenol and paracetamol in a bath mode. The effect of initial concentrations of phenol and paracetamol and contact time were investigated at optimum conditions of adsorption process including adsorbent dosage of 0.2 g/L, pH of 4, and temperature of 45 °C on the phenol and paracetamol sorption.

Characterization of synthesized nanoparticles

The powder's X-ray diffraction (XRD) patterns were recorded at 25 °C on a Philips instrument (X'pert diffractometer using Cu Kα