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Optimization of the combined adsorption/photo-Fenton method for the simultaneous removal of phenol and paracetamol in a binary system

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ABSTRACT

The coupling of adsorption and photo-Fenton processes has been studied for the simultaneous removal of phenol and paracetamol from aqueous systems. Photo-Fenton process exhibited the complete elimination of phenol and paracetamol during 1 h. For mineralization of contact time, the adsorption process was combined to the photo-Fenton process. The both NaX nanozeolites and cobalt ferrite nanoparticles were synthesized by microwave heating method and were used through the adsorption and photo-Fenton processes, respectively. The nanoparticles were characterized by XRD and SEM analysis. The Box–Behnken design was applied to evaluate the effect of key parameters including pH (3–4), phenol initial concentration (20–100 mg L^{-1}), paracetamol initial concentration (20–100 mg L^{-1}) and NaX to cobalt ferrite nanoparticles ratio (0.5–1.5) on the simultaneous removal of phenol and paracetamol at contact time of 30 min. By optimization of parameters, the removal percentages of phenol and paracetamol were found to be 99.95% and 99.80%, respectively. The results demonstrate that the coupling of adsorption and photo-Fenton processes is an alternative method to eliminate the phenolic compounds from wastewaters.

1. Introduction

Phenol is an important industrial raw material frequently used in the manufacture of pharmaceutical compounds such as paracetamol [1]. Therefore, the presence of phenol in paracetamol waste is inevitable. Several technologies including advanced oxidation processes (AOPs) [2], membrane filtration [3], biological treatment [4], photocatalytic degradation [5] and adsorption [6] have been used for the treatment of pharmaceutical pollutants from aqueous systems. Among all, AOPs have been extensively used for the treatment of pharmaceutical wastes [7–9]. Various AOP techniques such as Fenton [10], photo-Fenton [11], ozone oxidation [12], son-photo-Fenton [13] and photo-catalytic oxidation [14] are widely used for the removal of organic compounds of pharmaceutical wastes. Photo-Fenton process due to its higher efficiency and economical feasibility was found to be an efficient process compared to other AOP techniques [11,15]. However, photo-Fenton process is associated with problems such as excessive time requirements, and high energy consumption. On the other hand, although, the adsorption process due to its simplicity, moderate operational conditions and economical feasibility, could be considered as an effective method for treatment of pharmaceutical wastes [6,16], the removal efficiency of pharmaceutical compounds by adsorption technique is lower than other techniques [16]. Therefore, combination of mentioned technologies such as photo-Fenton and adsorption processes could be considered as an effective method for the treatment of pharmaceutical wastes.

In recent years, various types of adsorbents such as activated carbon [17], zeolites [18], and mesoporous silica [19] have been used for the removal of pharmaceutical 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 treatment of pharmaceutical compounds [18,20].

Furthermore, nanozeolites due to higher surface area and ion exchange properties have a higher potential for treatment of pharmaceutical wastes in compared with microzeolites. In the present work, NaX nanozeolites were synthesized by microwave method and were used for the adsorption of phenol and paracetamol.

In photo-Fenton process, degradation of organic compounds from wastewater is based on the generation of reactive free hydroxyl radicals (·OH). To accelerate the degradation rate of organic

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compounds, spinel-structured ferrite nanoparticles are widely used as catalyst in AOP processes [21–23]. For this, we synthesized the cobalt ferrite nanoparticles and the potential of synthesized nanoparticles is investigated for degradation of phenol and paracetamol during photo-Fenton process.

Different parameters affect on the simultaneous removal of phenol and paracetamol during adsorption/photo-Fenton process. Therefore, statistical experimental design methods could be used to evaluate the effects of variables on the treatment of phenol and paracetamol wastes. In recent researches, the factor space Central-Composite Design (CCD) and Box–Behnken Design (BBD) are commonly selected as experimental design techniques [24,25].

In the present study, the response surface methodology based on Box–Benkhen design (BBD) was used to evaluate the parameters of coupled adsorption and photo-Fenton processes including pH (3–4), phenol initial concentrations (20–100 mg L^{-1}), paracetamol initial concentrations (20–100 mg L^{-1}) and NaX to cobalt ferrite nanoparticles ratio (0.5–1.5) on the simultaneous removing of phenol and paracetamol from aqueous systems.

2. Experimental

2.1. 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, ethanol and phenol were obtained from Merck (Merck, Darmstadt, Germany). 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.

2.2. 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 $CoCl_2{\cdot}6H_2O$ were dissolved in 20 mL of deionized 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. After that, 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.

2.3. Synthesis of NaX nanozeolites

The NaX nanozeolites were synthesized according to the method described previously [26]. 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 deionized water until the pH value reached below 8, and dried at room temperature for 24 h.

2.4. 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 contact time on degradation of phenol and paracetamol was evaluated at optimum conditions of photo-Fenton process including catalyst dosage of 0.2 g L^{-1}, pH of 3, hydrogen peroxide concentration of 50 mmol L^{-1}, and temperature of 45 °C.

2.5. Adsorption process

The performance of the synthesized NaX nanozeolite was evaluated on the phenol and paracetamol sorption in a bath mode. The effect of contact time on adsorption of phenol and paracetamol was investigated at adsorbent dosage of 0.2 g L^{-1}, pH of 4, and

Table 1
The experimental design and results.

Run number	pH (X_1)	Phenol concentration (ppm) (X_2)	Paracetamol concentration (ppm) (X_3)	Zeolite/ ferrite (X_4)	Phenol removal (%)	Fitted value by model	Paracetamol removal (%)	Fitted value by model
1	3.0	20	60	1.0	94.0	93.6	91.0	90.4
2	4.0	20	60	1.0	93.0	92.7	92.0	91.5
3	3.0	100	60	1.0	79.0	78.9	80.0	80.2
4	4.0	100	60	1.0	78.0	78.1	82.0	81.3
5	3.5	60	20	0.5	88.5	87.8	90.0	89.7
6	3.5	60	100	0.5	79.5	79.4	76.0	75.6
7	3.5	60	20	1.5	92.0	92.1	95.0	94.1
8	3.5	60	100	1.5	83.0	83.6	80.0	79.9
9	3.0	60	60	0.5	86.0	85.9	85.0	84.8
10	4.0	60	60	0.5	85.0	84.9	86.0	85.9
11	3.0	60	60	1.5	90.0	90.1	89.2	89.1
12	4.0	60	60	1.5	89.5	89.2	90.0	90.3
13	3.5	20	20	1.0	98.0	98.1	97.0	98.0
14	3.5	100	20	1.0	79.0	78.4	83.0	82.4
15	3.5	20	100	1.0	84.5	84.6	77.8	78.5
16	3.5	100	100	1.0	75.5	74.9	74.5	73.6
17	3.0	60	20	1.0	90.0	90.4	91.0	91.3
18	4.0	60	20	1.0	89.0	89.5	92.0	92.5
19	3.0	60	100	1.0	82.0	81.9	77.0	77.2
20	4.0	60	100	1.0	81.0	81.0	78.0	78.3
21	3.5	20	60	0.5	90.5	91.1	89.0	88.7
22	3.5	100	60	0.5	75.5	76.4	77.5	78.5
23	3.5	20	60	1.5	95.5	95.3	93.5	93.1
24	3.5	100	60	1.5	80.5	80.6	82.0	82.9
25	3.5	60	60	1.0	88.0	87.5	87.0	87.5