Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2018.21736

101 (2018) 185–192
January

Investigation of the efficiency of heterogeneous Fenton-like process using modified magnetic nanoparticles with sodium alginate in removing Bisphenol A from aquatic environments: kinetic studies

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Received 21 August 2017; Accepted 24 November 2017

ABSTRACT

Bisphenol A (BPA) is one of the endocrine disrupting compounds that has significant estrogenic effects and if it is not treated, it will enter into water resources and will cause irreparable environmental problems. Thus, this study aims at determining the efficiency of heterogeneous Fenton-like process using modified magnetic nanoparticles with sodium alginate in removing BPA from aquatic environments. In this experimental research, the effects of environmental factors including pH (3–9), contact time (10–180 min), initial concentration of catalyst (0.5–20 g/L), initial concentration of hydrogen peroxide (50–300 mg/L) and the initial concentration of BPA (10–60 mg/L) were studied in removing efficiency of BPA using processes of heterogeneous Fenton-like, alginate sodium and hydrogen peroxide. Results of present study showed that during heterogeneous Fenton-like process, the highest removal efficiency (BPA) is achieved (95%) at pH 5, catalyst concentration 5 g/L, initial concentration of hydrogen peroxide 100 ppm and BPA concentration 20 ppm in 120 min in a way that the processes of sodium alginate and hydrogen peroxide had smaller removal efficiency. Also, studies of kinetic reaction revealed that removal of BPA in heterogeneous Fenton-like process followed a second-order kinetic model ($R^2 = 0.98$). Results demonstrated that heterogeneous Fenton-like process is able to remove BPA effectively from aquatic environments using modified magnetic nanoparticles with sodium alginate as a catalyst under optimal conditions and this process could be used to remove other similar compounds.

Keywords: Sodium alginate; Hydrogen peroxide; Bisphenol A; Kinetic; Heterogeneous Fenton-like process

1. Introduction

Recently, the presence of endocrine disrupting compounds (EDCs) has turned into a public concern. EDCs are compounds that can disturb the natural hormonal function. As a result, they interfere with the reproduction system of humans and animals. Therefore, these compounds have effects on humans and animals' health and their growth [1]. Phenol and phenolic compounds like Bisphenol A (BPA) or 2,2-bis (4-hydroxyphenyl) are considered as organic pollutant and EDCs [2,3].

BPA is considered as an important chemical substance in industry and is basically used in the production of epoxy resins, polycarbonate plastics and it is also used to cover the inner surface of cans used for conserving foods, and also in dental filler materials, water bottles and many other industrial products [4–6]. Increased global demand for BPA, led to increase in the production of this product from 2.8 million tons in 2002 to around 5.5 million tons in 2011 [7]. This chemical material leads to increased breast cancer, prostate cancer, reduced fertility, evolutionary sexual anomalies, changes in the function of pituitary and thyroid glands [8–10]. According to studies carried out on the concentration of BPA, its value is so high in urban and industrial sewages that it reaches

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0.15 mg/L in paper plant sewage and 0.04 mg/L in laundry wastewater and up to 0.1 mg/L in the production of chemical products [11].

There are effective methods to remove this pollutant from different sources including chemical, electrochemical, surface adsorption, oxidation and biological processes [12,13]. Other types of technology that are used in removing organic pollutants are advanced oxidation processes that are economical for their high efficiency, simplicity and low cost [14]. Zhang et al. [15] reported 85% efficiency for the removal of BPA using advanced oxidation.

Advanced oxidation is one of the most effective oxidation methods for organic pollutants in sewage treatment and Fenton process compared with other methods and it is used to treat the wastewater of different industries including aromatic amines, dyes, pesticides and surfactants [16,17]. Fenton mechanism is based on reaction between hydrogen peroxide and divalent iron ion. Eq. (1) shows Fenton reaction [18]:

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^- + HO^\bullet \quad (1)$$

This reaction is one of the major sources for the production of hydroxyl radicals where these radicals act as the first oxidizing species in the reaction [19]. During Fenton reaction, hydrogen peroxide is decomposed into hydroxyl radicals by divalent iron ions [20]. Hydroxyl radical produced has very high oxidation power (2.8 eV) and can turn many of the pollutants into mineral materials [21]. Fenton reaction consists of unique advantages including high efficiency in decomposing pollutants, safety, use of cheap and functional materials [22].

Fenton homogeneity has disadvantages such as (1) need to separate iron ions after the reaction and (2) limited range of pH (2–3), probable deactivation of some ions of iron due to reaction with materials such as phosphate anions and other intermediate compounds [23]. To overcome these disadvantages of the homogeneous Fenton process, heterogeneous Fenton-like systems have recently been developed using iron-based catalyst where iron ions are fixed on materials like clay, silica resins and active carbon [24,25]. Alginate sodium is among the polymers used along with iron ions in heterogeneous Fenton-like reaction. Use of magnetic materials such as iron nanoparticles in the beads of sodium alginate, results in easy separation of the beads from flow [26]. Sodium alginate is a non-toxic and cheap polyanionic polysaccharides that is obtained from brown seaweeds [27].

In the study carried out on removing azo dye using heterogeneous Fenton process and catalytic property of iron, it was revealed that alginate beads increase the efficiency of heterogeneous Fenton for oxidizing two types of azo dye, that is, blue Radioactive 222 and Black acid 234, in the presence of H_2O_2 and visible light [28]. Hence, considering the hazards of BPA, present study aims to determine the efficiency of heterogeneous Fenton-like process using modified magnetic nanoparticles with alginate sodium in removing BPA from aquatic environments.

2. Materials and methods

2.1. Materials

All materials required such as BPA, ammonia (25%), hydrogen peroxide, powdered active carbon, chloroferric, iron sulfate and calcium chloride were purchased from Merck (Germany) and alginate sodium powder from Sigma-Aldrich (Germany). The characteristics of BPA have been presented in Table 1. All chemicals used in this study were of analytical grade type and used without further purification.

2.2. Methods

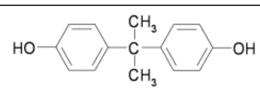
Present study was experimental where the effects of different variables in removing BPA were studied separately using heterogeneous Fenton-like, sodium alginate and hydrogen peroxide processes and one factor at a time method was used to optimize them and experiments were carried out under static conditions. To reduce error, all experiments were repeated three times at 25°C ± 3°C and the conical flask was wrapped in aluminum foil to provide dark conditions.

The BPA concentration measured according to standard method and used instruction 5530 D. Considering the BPA concentrations and considering the use of a valid reference and removing all the interferences, a spectrophotometric method was used to measure BPA.

2.3. Synthesis of magnetic nanoparticles

At first, iron oxide nanoparticles were synthesized using chemical precipitation method in order to produce the magnetic beads of sodium alginate. In this stage, 10.8 g of chloroferric with 5.6 g iron sulfate are dissolved in 300 mL distilled water and the resulting solution is put into the mixer for 15 min at 80°C then, 200 mL of ammonia (25%) is added and mixed for 15 min. Then, the resulting solution is put on a magnet for precipitation. Later, the solution is washed with distilled water until its pH reaches 7. In the end, to stabilize the nanoparticles produced, they are covered with citrate anions. To this end, 5 g of citric acid is dissolved into 10 mL of deionized water and the nanoparticles produced were added to this solution until its volume was 250 mL and the resulting solution was put into the mixer and was mixed for 90 min at 90°C [29,30]. To produce the magnetic beads of sodium alginate, 79.25 mL of iron nanoparticles covered with citrate sodium was taken and 3 g of sodium alginate powder and 0.3 g of powered active carbon were added to it. In the final stages, the suspension

Table 1
Properties and chemical structure of the Bisphenol A

Chemical structure	
Chemical formula	$C_{15}H_{16}O_2$
Molar mass	228.29 g/mol
Density	1.20 g/cm³
Melting point	158°C to 159°C
Boiling point	220°C
Solubility in water	120–300 ppm
Vapor pressure	5×10^{-6} Pa (25°C)

obtained was added dropwise to 400 mL of calcium chloride solution 0.5 m. To avoid the contact among the beads in the solution and new magnetic beads, a magnate was put under the calcium solution, then, synthesized beads were kept in calcium chloride solution to provide sufficient time for their formation [31]. In the end, the synthesized beads were transferred to a container and were kept in the oven for 24 h at 80°C to be dried [19].

2.4. Assessing the impact of variables

A batch reactor was used in this section of the study. To this end, the synthetic samples with value of 100 mL were provided and its pH was adjusted using hydroxide sodium and sulfuric acid. Parameters studied in the investigation consisted of pH (3, 5, 7 and 9), contact time (10, 30, 60, 120 and 180 min), initial concentration of catalyst (0.5, 1, 1.5, 2, 5, 10 and 20 g/L), concentration of hydrogen peroxide (50, 100, 200 and 300 mg/L) and concentration of BPA (10, 20, 40 and 60 mg/L), the concentration ranges have been selected based on previous studies [32–34]. After the reaction, the sample was taken from conical flask and the residual amount of pollutant was assessed using a spectrophotometer at wavelength of 500 nm according to standard method [35]. Also to determine the characteristics of the magnetic beads, X-ray diffraction analysis (XRD) was used in the angle range of 2θ = 5°–100°, using Rigaku X-ray diffractometer.

3. Results and discussion

3.1. Characterization of modified magnetic nanoparticles with sodium alginate

To study the structural properties of modified magnetic nanoparticles with sodium alginate, XRD experiment was conducted. According to Fig. 1, some peaks were observed at angles 2θ of 35°, 45° and 65° that were related to Fe_3O_4 crystals. In fact, this diagram confirms the presence of cubic magnetic nanoparticles in the structure of sodium alginate [16].

The beads made were quickly absorbed by magnet that is indicative of the good paramagnetic behavior of modified nanoparticles with alginate sodium (Fig. 2). Therefore, these particles are easily separated in aquatic solutions by applying a magnetic field. As it is observed in this figure, the beads formed are black and their size ranges from 0.5 to 1 mm.

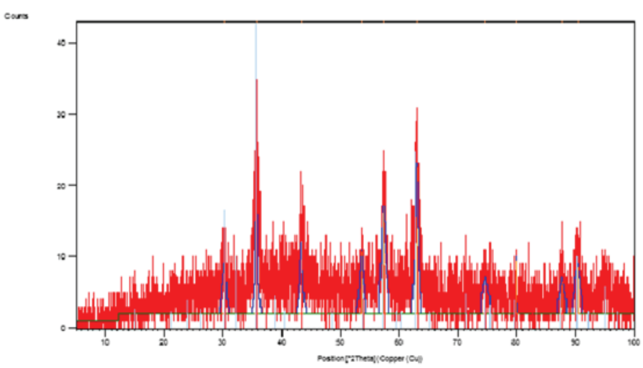


Fig. 1. XRD patterns of modified magnetic nanoparticles with alginate sodium.

To determine the surface morphology of modified magnetic nanoparticles with sodium alginate, the scanning electron microscope (SEM) was used. In Figs. 3 and 4, the images of SEM related to sodium alginate and modified magnetic nanoparticles with sodium alginate have been shown. As it is observed in Fig. 4, iron particles are on sodium alginate surface in spherical form and their size is at nanoscale.

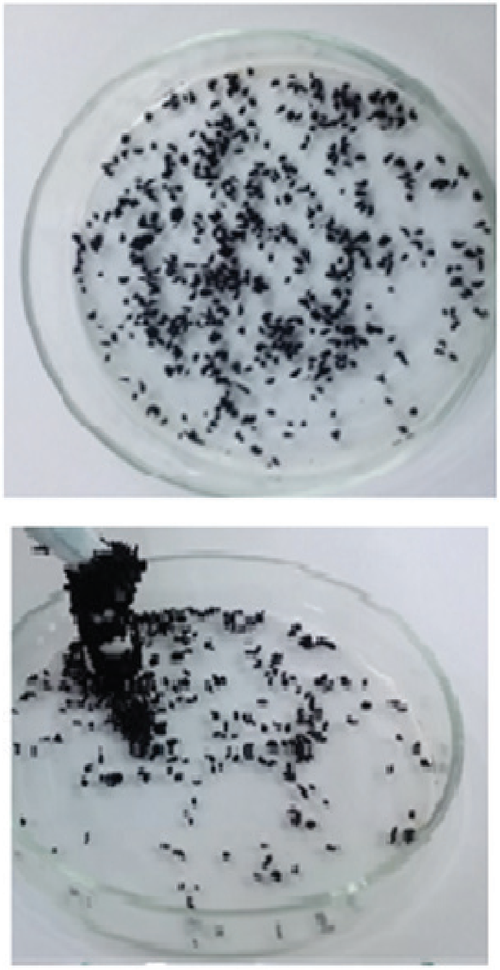


Fig. 2. Modified magnetic nanoparticles with alginate sodium and the magnetic behavior of catalyst.

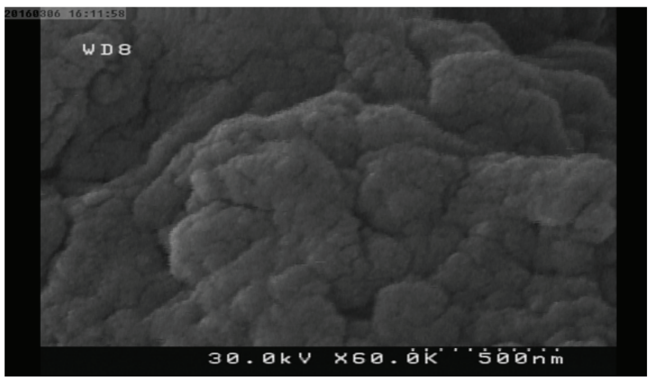


Fig. 3. SEM image of sodium alginate.

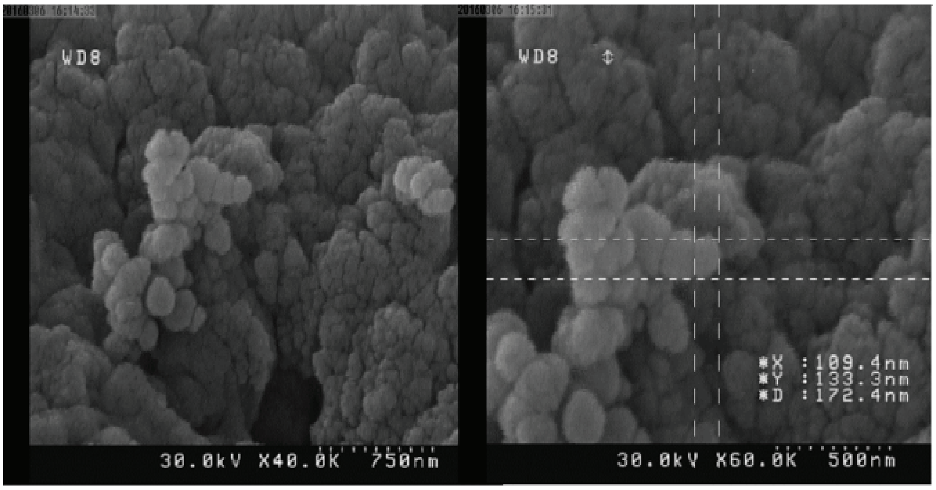


Fig. 4. SEM of modified magnetic nanoparticles using sodium alginate.

3.2. Determining the efficiency of Bisphenol A removal using modified magnetic nanoparticle with sodium alginate

3.2.1. Effect of pH

To study the effect of pH on the removal of BPA, pH was selected at (3, 5, 7 and 9) range and experiments were conducted in three modes. In the first state, only the adsorption property of modified magnetic nanoparticles with sodium alginate was tested. In another experiment, the removal of BPA was measured only by hydrogen peroxide at desired pH, and in the end, the heterogeneous Fenton-like process for BPA removal was studied. As it is seen in Fig. 5, in general, the removal of BPA by modified magnetic nanoparticle reactions with sodium alginate and hydrogen peroxide is low (25%–35%) and the amount of removal changed slightly with changing pH. While in the process of heterogeneous Fenton-like, with increasing pH, the efficiency of removal declined and the highest efficiency (79%) was achieved at acid pH and in particular at pH = 5. The rate of pH affects the oxidation of organic compounds and production of hydroxyl radicals directly and indirectly and as a result, the efficiency of the reaction and Fenton process rose at low pH. The reason for this increase is the presence of hydroxyl radicals and complexes of ferric hydroxide that were formed in large amount in the acid environment. In pH less than 4, $Fe(OH)^{2+}$ reacts slowly with hydrogen peroxide, leading to reduction in hydroxyl radicals and in consequence, decline in the efficiency of the process.

Although in alkaline pH the removal efficiency of about 55% indicates the catalytic efficiency of the magnetic beads of sodium alginate in these conditions, according to studies conducted if the iron nanoparticles are used in pure form, they are turned into Fe^{3+} at alkaline pH and are deposited in the form of $Fe(OH)_3$ and leave the catalytic cycle [28,36].

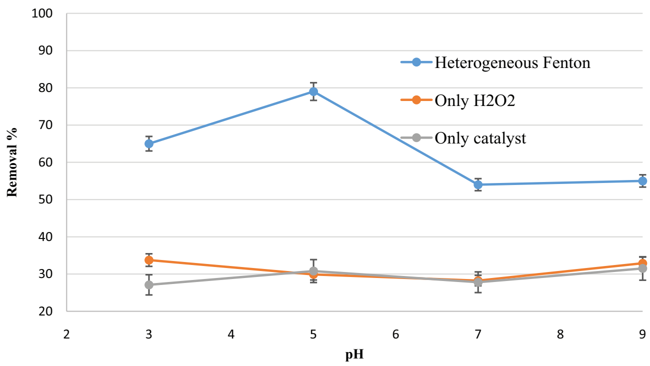


Fig. 5. Effect of pH on the removal of Bisphenol A by heterogeneous Fenton, sodium alginate and hydrogen peroxide (contact time 30 min, initial dose of catalyst 5 g/L, initial concentration of hydrogen peroxide 100 mg/L and initial concentration of Bisphenol A 20 mg/L).

3.2.2. Effect of contact time

To study the effect of mixing time on the efficiency of BPA, batch experiments were conducted according to previous method, in three states, pH = 5 and at different times. Fig. 6 shows the effect of contact time on the removal efficiency of BPA using heterogeneous Fenton-like, sodium alginate

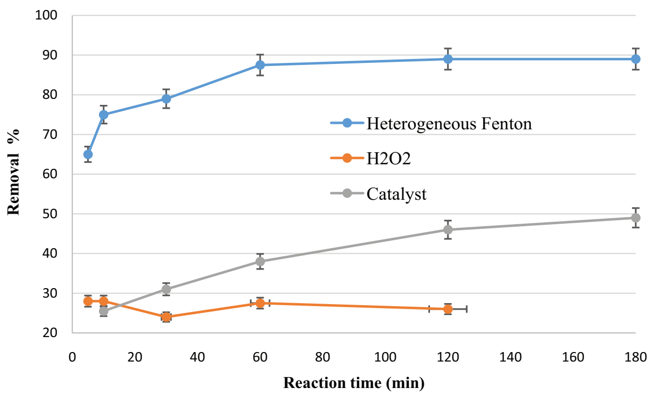


Fig. 6. Effect of reaction time on Bisphenol A removal in heterogeneous Fenton, sodium alginate and hydrogen peroxide (pH = 5, initial catalyst dose 5 g/L, initial concentration of hydrogen peroxide 100 mg/L and initial concentration of Bisphenol A 20 mg/L).

and hydrogen peroxide process. As it is observed, in alginate sodium process, with growing contact time, the removal efficiency rose and at mixing time of 180 min, efficiency was 49%. In removal efficiency by hydrogen peroxide, mixing time had no effect on removal efficiency. But in Fenton-like process, raising contact time led to increase in removal efficiency and at mixing time of 120 min, efficiency was 89% and from then on, increase in time had no effect on removal efficiency. Increase in pollutant removal efficiency with increasing contact time is due to higher contact of catalyst with BPA. Quick and high rate of oxidation in the initial stages are because of existence of numerous empty places on the surface of catalyst. Over time, these places are gradually occupied by the pollutant molecules and due to the presence of repulsive force between the molecules of BPA, the occupation of the remained empty places becomes very difficult [37,38]. Cleveland et al. [39] in studying the efficiency of heterogeneous Fenton process using Fe_3O_4/multi-walled carbon nanotube (MWCNT) for the removal of BPA, achieved the highest efficiency in contact time of 2 h and catalyst dose of 0.5–1 g/L. In the study carried out by Titouhi and Belgaied [40] into the removal of ofloxacin using heterogeneous Fenton process with modified sodium alginate beads. Increasing contact time led to increase in efficiency and maximum rate of removal in 60 min and in later studies when the Fenton process has been studied, the optimal time obtained was in the same range.

3.2.3. Effect of catalyst concentration

To study the effect of changes in the concentration of modified nanoparticles with sodium alginate on the efficiency of BPA removal, the experiment was conducted by making changes in the rates (0.5, 1, 1.5, 2, 5, 10 and 20 g/L), pH 5, contact time 120 min and in two states, that is, with hydrogen peroxide (heterogeneous Fenton-like process) and without hydrogen peroxide. Fig. 7 demonstrates the effect of the initial catalyst by heterogeneous Fenton-like process on the removal efficiency. As it is seen with increasing the catalyst concentration amount from 1 to 20 g/L, the efficiency of BPA removal rose from 37% to 77%. Also, in relation with Fenton process, by increasing catalyst concentration from 0.5 to 5 g/L, the removal efficiency grew from 60% to 92%. In the study carried out by Dong et al. [28], the removal of dye using this process and modified alginate beads with iron, it was revealed that with increasing the beads of sodium alginate, the efficiency of dye removal rose. With increasing beads, the number of active catalyst sites and the amount of ions on the surface grew, as a result conversion of H_2O_2 into $HO^•$ radicals in the solution increased and the efficiency of BPA rose in this reaction but increasing it more than optimal limit of the beads dose, did not show any increase in BPA removal.

3.2.4. Effect of initial concentration of hydrogen peroxide

The effect of hydrogen peroxide on the efficiency of removal was studied by making changes in four concretions (50, 100, 200 and 300 mg/L). As it is shown in Fig. 8, the heterogeneous Fenton-like process increasing hydrogen peroxide from 50 to 100 mg/L, led to increase in removal efficiency from 75% to 95% and then, with further increase in the amount of hydrogen peroxide, significant changes were not observed in the efficiency of the process, in contrast, it fell slightly. The reason for this decline was that hydrogen peroxide as an electron receptor leads to production of $HO^•$ radicals and peroxide as an electron receptor leads to $HO^•$ radical production according to Eq. (2) or (3) and that these radicals play an important role in Fenton process [41].

$$H_2O_2 + e^- \rightarrow HO^• + OH^- \tag{2}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^• \tag{3}$$

But with increasing the concentration of hydrogen peroxide to over optimal limit, this material is decomposed to oxygen and water (Eq. (4)) and also hydroxyl radicals react with extra hydrogen peroxide, resulting in hydroperoxyl radical production (HO_2) (Eq. (5)) that has less oxidation potential compared with the ($HO^•$) radical itself, as a result, it leads to reduction in removal efficiency. Therefore, excessive hydrogen peroxide's presence in the solution prevents from the formation of hydroxyl radicals and leads to decline in the efficiency of the process [3,4].

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{4}$$

$$HO^• + H_2O_2 \rightarrow H_2O + HO_2 \tag{5}$$

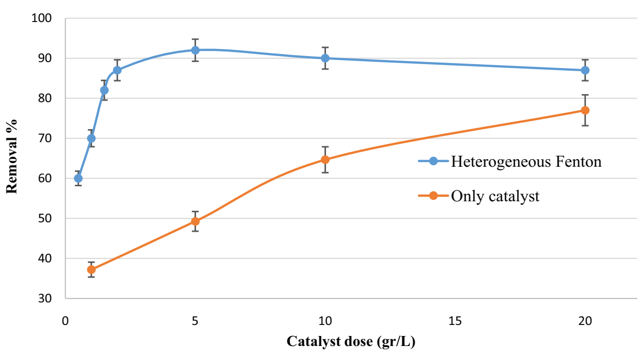


Fig. 7. Effect of initial dose of catalyst on Bisphenol A removal by heterogeneous Fenton and sodium alginate processes (contact time 120 min, pH = 5, initial concentration of hydrogen peroxide 100 mg/L and initial concentration of Bisphenol A 20 mg/L).

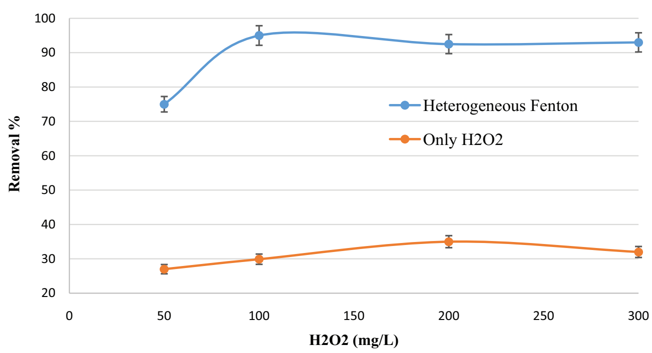


Fig. 8. Effect of hydrogen peroxide initial concentration on removal of Bisphenol A by Fenton and hydrogen peroxide processes (pH = 5, contact time 120 min, catalyst dose 5 g/L and initial concentration of Bisphenol A 20 mg/L).

3.2.5. Effect of initial concentration of Bisphenol A

Fig. 9 demonstrates the effect of initial concentration of BPA on its removal efficiency by three processes of heterogeneous Fenton-like, sodium alginate and hydrogen peroxide that in sodium alginate process with increasing the initial concentration of the pollutant from 10 to 60 mg/L, the removal efficiency declined from 78% to 73%. In heterogeneous Fenton-like process, at low concentrations of BPA, removal efficiency was relatively low. But with increasing the initial concentration of the pollutant from 10 to 20 mg/L removal efficiency rose from 82% to 95% and then with increasing the concentration of BPA, the efficiency of the process went down and reached 77.5%. Results of study carried out by Xu and Wang [42], the removal of 4-chloro-3-methyl phenol from aqueous solutions by Fenton-like process also emphasizes that at low concentrations of phenol, the efficiency of the process was relatively low and with increasing the initial concentration, indeed, the initial concentration of pollutant up to a definite amount, the efficiency rose and then declined. Indeed, the initial concentration of BPA, and the radicals produced by the process are not enough for all molecules of the pollutant and efficiency reduced and on the other hand, the number of catalyst positions where radical reactions are carried out, is limited at high concentrations of the pollutant [40].

3.3. Kinetics of heterogeneous Fenton process

In this study, first- and second-order kinetics were used to study the reaction kinetic of BPA removal in heterogeneous Fenton-like process.

First-order kinetics:

$$dc/dt = -k_1 C \quad (6)$$

Second-order kinetics:

$$dc/dt = -k_2 C^2 \quad (7)$$

In above equations, C is the concentration of BPA, k_1 and k_2 are kinetic constants of first- and second-order of the reaction and t is the contact time [23].

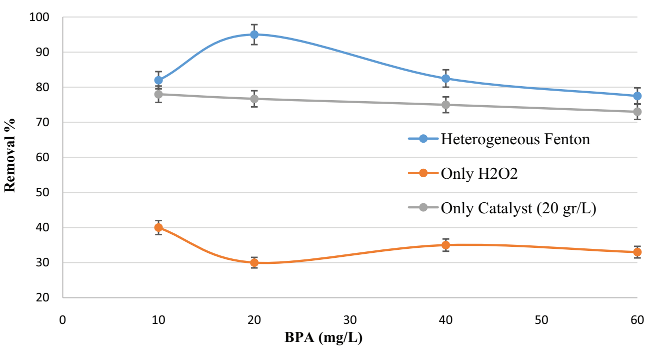


Fig. 9. Effect of initial concentration of Bisphenol A on the removal by heterogeneous Fenton, sodium alginate and hydrogen peroxide (pH = 5, contact time 120 min, catalyst dose 5 g/L and hydrogen peroxide concentration of 100 mg/L).

By integrating Eqs. (8) and (9), the first- and second-order kinetic equations will be respectively as follows:

$$C_t = C_0 e - k_1 t \quad (8)$$

$$1/C_t = 1/C_0 + k_2 t \quad (9)$$

where C_t is the concentration of BPA at t time [23].

Results of the study on removal kinetics of BPA demonstrated that the second-order kinetics had a higher regression coefficient (0.9805) compared with first-order model (0.9763) and the data are better described using this model (Fig. 10). Reaction speed for second-order kinetics for the process was equal to 2.87×10^{-4} L/mg min. Hence, result of the study shows that the concentration of hydroxyl radical and the number of active sites in the catalyst are restrictive factors for the process of heterogeneous Fenton-like oxidation [43]. In the study carried out by Karthikeyan et al. [44] to remove aniline using heterogeneous Fenton and homogeneous Fenton the results of removal kinetic study are consistent with heterogeneous Fenton process of second-order model.

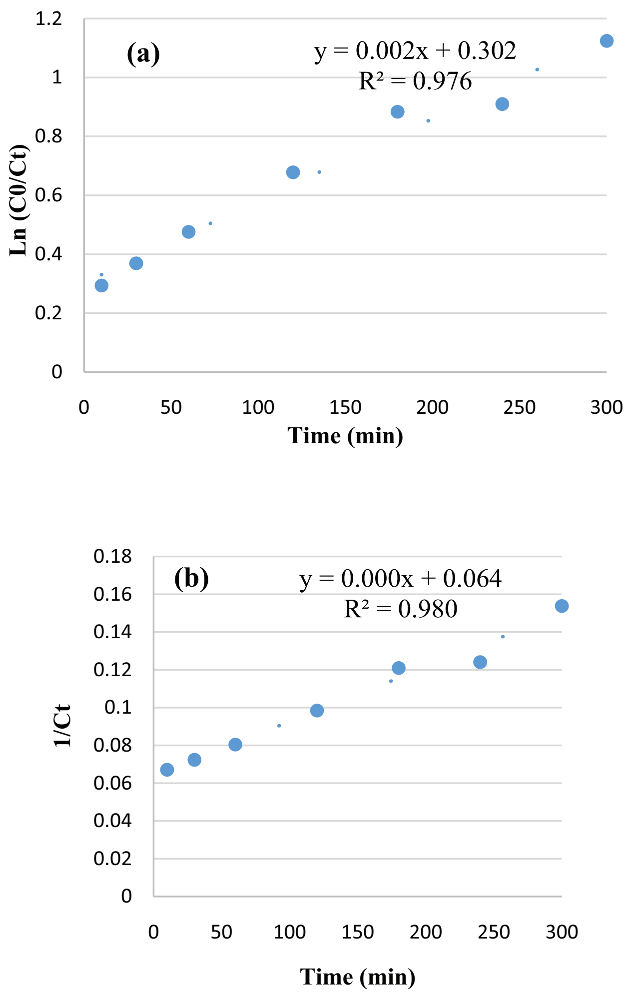


Fig. 10. (a) First-order kinetics and (b) second-order kinetics of heterogeneous Fenton (pH = 5, catalyst dose 5 g/L and initial concentration of Bisphenol 20 mg/L).

The mechanism of the heterogeneous Fenton-like reaction occurs on catalyst surface and can be presented as follows:

$$Sc - Fe^{2+} + H_2O_2 \rightarrow Sc - Fe^{3+} + OH^- + HO^\bullet \quad (10)$$

$$Sc - Fe^{3+} + H_2O_2 \rightarrow Sc - Fe^{2+} + HO_2^\bullet + H^+ \quad (11)$$

where Sc represents the catalyst's surface [16]. The results indicated that the Fe_3O_4 nanoparticles could catalyze H_2O_2 to form $HO^\bullet$ radicals which were mainly responsible for the degradation of BPA.

4. Conclusion

Results of present study showed that the highest removal of BPA was achieved 95% at concentration of 20 mg/L of the pollutant, pH = 5, time 120 min, hydrogen peroxide concentration 100 mg/L and the concentration of sodium alginate magnetic beads 5 g/L. Also, the kinetic studies of the reaction showed that decomposition of BPA in heterogeneous Fenton-like process conforms to second-order kinetic model. It should be mentioned that in the synthesis of sodium alginate magnetic beads, cheap and easily accessible materials are used and another point is the simplicity of the synthesis of this catalyst. According to laboratory results, it was revealed that heterogeneous Fenton-like process using modified magnetic nanoparticles with sodium alginate as a catalyst is able to effectively remove BPA from aqueous environments and this process could be applied in removing other similar compounds.

Acknowledgment

Authors gratefully acknowledge Experts of Chemistry Laboratories in Department of Environmental Health Engineering, Hamadan University of Medical Sciences.

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