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Determination of the Efficiency of Electro-Persulfate Process in Reducing Concentration of Ciprofloxacin from Aquatic Environment by Voltammetric Measurement

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ABSTRACT

Introduction: In recent decades, the use of organic matters has been increasing as a micro-pollutant resistant to antibiotics. Antibiotic resistance is one of the effects of these micro-pollutant on humans. The purpose of this research was to determine the efficiency of electro-persulfate process in removing antibiotic ciprofloxacin from aqueous solution by voltammetric measurements.

Method: This is an experimental study that was carried out using a reactor with a volume of one liter, coupled with electrodes of iron as a cathode and anode with an area of 40 cm2. The effect of pH variables, flow intensity, persulfate concentration and concentration of antibiotic ciprofloxacin was studied. Concentration of Antibiotic ciprofloxacin was read by using an HPLC apparatus at wavelength of 275 nm. Voltammetric technique was used to ensure antibiotic degradation.

Results: The results of the experiment showed that the process under optimal conditions of the experiment includes pH equal to 3, 12 mM of persulfate concentration, 12 mA / cm2 of current density, initial concentration of antibiotic by 5 mg / L and reaction time of 10 minutes, removal efficiency of Antibiotics of ciprofloxacin by 98.51%. The electro-fenton and persulfate processes separately, the maximum removal efficiency in optimal conditions was 65.12% and 5.7%, respectively. The diagram resulting from analysis of data by the voltammetric technique has been shown to reduce the flow of desired pollutant.

Conclusion: taking into account the analysis of data, a voltammetric method showed that the electro-persulfate process can be a suitable process in the direction of the desired pollutant.

Keywords: Electro-Persulfate, Ciprofloxacin, Voltammetric.

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INTRODUCTION

The use of organic matters as micro-pollutants, including pharmaceuticals, especially antibiotics, has been rising. The sources of the entrance of antibiotics into the environment have been in humans and animals for treatment or prevention. Approximately 100 to 200 tons of antibiotics are consumed annually in the world (Bajpai SK, et al., 2012). These compounds are introduced into the wastewater purification plant as micro-pollutants through the urine and stool or directly through the disposal of the pharmaceutical industry, and subsequently, due to the inability of these installations to remove these compounds, they enter into the surface or underground water, then by entering the water purification plant and not being eliminated by existing processes, they enter the distribution network and then the drinking water system (Xu W-h, et al., 2007) . The most important effect of antibiotics is the development of antimicrobial resistance in

humans and also an effect on non-target pathogens, altering the structure of algae in aquatic resources and interfering with the photosynthesis of plants (Wei R, et al., 2011). Ciprofloxacin is a broad-spectrum antibiotic from the fluoroquinolones group that has been widely used in hospitals to treat bacterial infections (Githinji LJ, et al., 2011). This antibiotic is of high solubility and also about 25% of it is absorbed by the body, and the rest is excreted into the sewage system (Garoma T, et al., 2010). Ciprofloxacin was detected in sewage and surface water (concentration less than 1µg/L), in the hospital effluent (concentration higher than 150µg/L) and the pharmaceutical factory 30mg/l. Also, this antibiotic can be absorbed in sludge (concentration of 2.42mg/kg) (Sun S-P, et al., 2009). In certain conditions, the peripheral concentration of this antibiotic can be 5-20000 times higher than the reported amount (Vasconcelos TG, et al., 2009). The presence of these compounds in the environment as a pollutant has led to the selection of a suitable method for purifying water or sewage containing pharmaceuticals, especially antibiotics, by experts. Conventional methods for removing antibiotics and medicinal residues from water and sewage have included ozonation

(Carabineiro S, 2011), fenton and photofenton (Lin AY-C, et al., 2009), electrochemical process (Rozas O, et al., 2010), electron radiation (Kim T-H, et al., 2012), nanofiltration (Koyuncu I, et al., 2008), chemical coagulation (Choi K-J, et al., 2008), ion exchange (Choi K-J, et al., 2007) and adsorption process (Crisafully R, et al., 2008). In general, it can be said that the superficial adsorption methods due to the lack of decomposition of the pollutants, also the low efficiency and high cost of investment in the membrane process, the difficult management and maintenance of the biological process (Garoma T, et al., 2010), hydrogen peroxide and ozone due to the short duration of oxidizing factor, low solubility, high cost storage and transportation have not attracted more attention (Samadi MT, et al., 2014). But in recent years, the advanced oxidation process has been used to reduce the pollution caused by the presence of drug residual in water. The use of oxidants in advanced oxidation processes has been an effective way of eliminating pollutants (Klavarioti M, et al., 2009). Among the oxidants, the persulfate can be referred as an appropriate oxidizer because of properties like high oxidizing (V), nonselective reactivity, stability, high solubility, low cost, ease of transport due to solidity, and the safety of lateral products (Nawrocki J, et al., 2010; Khataee A, et al., 2009) . Persulfate reactions for stimulation will need for light or heat, certain metal ions as catalyzers. The equations 1 and 2 show the thermal and chemical activation (S₂ O₈ ²⁻) (20, 21):

$$S_2O_8^{2-}$$
 heat or UV \longrightarrow $SO_4^{\bullet-}$ 1
 $S_2O_8^{2-}$ + Me^{n+} \longrightarrow $SO_4^{\bullet-}$ + $Me^{(n+1)}$ + SO_4^2 2

Among the intermediate metals used for the activation of (S₂ O₈ ²⁻), the most common use is for Fe²⁺, which can be described according to Equation 3 (Lin Y-T, et al., 2011; Bennedsen LR, et al., 2012):

$$S_2O_8^{2-}+ Fe^{+2} \longrightarrow SO_4^{0-} + Fe^{3+} + SO_4^{2-} 3$$

In this study the iron anode electrode was used to produce F^{2+} . According to reaction 4 and 5, Fe^{2+} is produced as follows (Oturan N, et al., 2008):

$$0_{2}+2H^{+}+2e^{-} \longrightarrow H_{2}O_{2} \qquad 4$$
$$2+Fe^{+2} \longrightarrow Fe^{3+}+e^{-} \qquad 5$$

The aim of this study was to determine the activation of persulfate with iron produced by electrical method using an iron electrode in the removal of antibiotic ciprofloxacin by voltammetric measurement of ciprofloxacin.

METHOD OF STUDY

Antibiotic ciprofloxacin, hydrochloride, hydrogen chloride, sodium hydroxide, potassium persulfate with a purity of 99.8% were purchased from Merck and Sigma Aldrich companies. For the power required the PS-405 model of power adapter digital equipment, the pH adjustment from pH meter of model Sensoal Manufactured by Company (HACH) was used.

Pilot specifications and procedure

This research was carried out in chemical researches laboratory of Hamedan University of Medical Sciences in 2015. The used reactor was circular of plexiglass by a useful volume of one liter. 4 electrodes of iron are connected to a DC generator of electricity with dimension of $2 \times 20 \times 2 \times 200$ mm and an area of 40 cm² and a distance of 2 cm, so that 2 electrodes were as cathodes and 2 electrodes as anodes.

Samples containing desired concentrations of antibiotic ciprofloxacin (5 to 145mg/1) were prepared using a stock solution (based on solubilizing a certain amount of antibiotic in 1000 mg / l distilled water). Also, the required concentrations, $S_2O_{8^{2-}}$ (4 to (15 Mm to 4), were introduced into the reactor as a discontinuous current. Adjustment of the current density Ampere (4 to 15 mA / cm²) and pH adjustment was performed in the range (11-3). The desired persulfate values and the current intensity were chosen with similar study (Lin H, et al., 2013). After the start, the contents of the reactor were shaken by a magnetic magnet in accordance with Fig. 1. For a period of 0 to 20 minutes and in the time range of 5 minutes for being fixed, the process efficiency for removing this pollutant by the process was investigated. In each sampling, 5 cc samples were taken for reading samples and then centrifuged at 2500 rpm for 1 minute.

- 1. Direct current electric power generator
- 2. Reactor
- 3. Iron electrode
- 4. Mixer



Figure 1. Schematic form of reactor used in the process

Measurement of ciprofloxacin

In the present research, determination of antibiotic concentration of ciprofloxacin was done using a HPLC device (Germany-Wellchroml-Knauer model) equipped with UV detector (K2600-Germany-Knauer model), column of 250 × 6.4 (m μ 5-18Waters-C mm) at wavelength of 275 nm and 25% acetonitrile, 25% methanol, 50% Acetic acid and water with débit of 0.7 ml / min. Injection volume was considered to be 40 μ L in all samples and the retention time (RT) of antibiotic was determined to be 9.03 minutes. The chromatograph of HPLC-UV has been shown in Fig. 1. In this study, a cyclic voltammetry of model PGSTAT20 was used. This device has a carbon-plate glass electrode (1.8 mm in diameter) and another platinum electrode.



Figure 2. Chromatography of Ciprofloxacin

FINDINGS

Effect of PH on Process Efficiency

First, the effect of pH was investigated. As shown in Fig. 3, in the conditions of the current intensity of $8mA/cm^2$, the concentration of persulfate of 4Mm, the antibiotic concentration of 45 mg/1, the maximum removal efficiency is related to 3pH. At this pH, 10 minutes after the reaction the process efficiency is at maximum 80.66%. At the same time, with an increase of pH to 7 and 11, the efficiency of the process will be reduced to 57.45 and 35.68.



Figure 3. Effect of pH on process efficiency (current intensity 8 mA/cm², persulfate 4 Mm, antibiotic concentration 45 mg/1)

Effect of current intensity

After optimizing the determination of pH, at conditions of 3pH, the concentration of persulfate 4mM, the concentration of antibiotic 45mg/1, and the effect of changes in the current intensity in the range of 4 to 18mA/cm² were investigated. As shown in Fig. 4, with an increase in the current intensity during 10 minutes from 4 to 12mA/cm², the efficiency increases from 84% to 94%, while increasing the current intensity at the same time to 18mA/cm², the process efficiency has been reduced to 90%.



Figure 4. Effect of current intensity on process efficiency (3pH, concentration of persulfate 4mM, concentration of antibiotic 45mg/1)

Effect of Persulfate Concentration

After optimizing the pH and the current intensity the effect of the changes in the persulfate in the range of 4Mm to 15 at 3pH, the current intensity 12mA/cm², the concentration of antibiotic 45mg/1 was investigated. As shown in Fig. 5, the increase in persulfate at 10 minutes from 4Mm to 12 the increase of the process efficiency has reached from 80 to 91%. This is followed by an increase of 15 percent of the persulfate at the same time of 15Mm the process efficiency has been reduced to 85 percent.



Figure 5. Effect of persulfate concentration on process efficiency (3pH, current intensity 12mA/cm², concentration of antibiotic 45mg/1)

Effect of concentration of antibiotic ciprofloxacin

In the final stage, after the optimization of pH, current intensity and persulfate concentration, the effect of changes in the concentration of antibiotic ciprofloxacin has been investigated. As shown in Fig. 5, in the 10-minute period, with increasing concentration the process efficiency has decreased. So that the maximum process efficiency was achieved at a concentration of 5mg/l with efficiency of 98%. The process efficiency decreased to 88, 94, 96%, with increasing concentrations to 25, 45, 145.



Figure 6. Effect of concentration of antibiotic on Process Efficiency (3pH, current intensity 12mA/cm², Persulfate Concentration 12Mm)

Determining the efficiency of single process parameters in the efficiency of ciprofloxacin antibiotic removal

At this stage of the study, the effects of processes affecting the removal of pollutants were considered separately. In optimal conditions of experiment consisting of the initial concentration of antibiotic ciprofloxacin equal to 5 mg / L, pH equal to 3, current intensity 12 mA / $\rm cm^2$, persulfate concentration equal to 12mM and reaction time of 10 minutes, the process efficiency is maximal and equal to 98.51%. However, when the electrochemical process did occur in the non-presence of persulfate, 65.12% of the antibiotic ciprofloxacin and persulfate alone eliminated 5.07% of the antibiotic ciprofloxacin.



Figure 7. Determination of process efficiency of electropersulfate, electro-fenton and persulfate in the elimination of antibiotic ciprofloxacin in optimum conditions of experiment (3pH, current intensity 12mA/cm², concentration of persulfate 12Mm, concentration of antibiotic 5mg/1)

On voltammetric studies

In this stage of the study after obtaining optimal conditions to ensure that the concentration of antibiotic ciprofloxacin was reduced by electro-persulfate process, the voltammetric measurement technique was used. As shown in Fig. 7, based on the electro-active nature of antibiotics, we can observe the reduction of concentration of this material through process at different times.



Figure 8. investigating Voltammetric studies in optimal conditions of experiment (3pH, current intensity 12mA/cm², concentration of persulfate 12Mm, concentration of antibiotic 5mg/1)

DISCUSSION AND CONCLUSION

As it is known, one of the parameters influencing chemical processes, especially advanced oxidation processes, is the pH of the environment (Rastogi A, et al., 2009). The speed of chemical reactions depends on the pH of the environment and directly or indirectly affects the process. In AOPs processes, the pH changes through the production of various radicals affect the amount of oxidation. In the electrochemical process with persulfate, pH has affected the mechanism of producing Fe⁺² for activating radical of persulfate, as well as its reaction with the pollutant (Rastogi A, et al., 2009). When pH is increasing and the environment goes to become alkaline, Fe3+ is dominant in environments, while Fe2+ is the dominant species for the activation of persulfate and production of radical of persulfate. Also, at high pHs, the Fe²⁺ solubility has been reduced and iron is colloidal, which leads to a decrease in the production of persulfate radicals (Wang Q-J, et al., 2010; Masomboon N, et al., 2010). Also, according to the reaction done at high pH, the reaction proceeds to OH⁰ and the radical of hydroxyl was prevalent in the environment. Under these conditions, the oxidation potential has strongly reduced by OH, because radical persulfate stability is higher. Another reason for lowering the efficacy of high pH is the reaction between radicals of persulfate and hydroxyl, which have eliminated them in the environment (Masomboon N et al., 2010). A study by Romero et al on the efficiency of persulfate process activated with Fe2+ showed that the process efficiency in eliminating the pollutant was decreasing with the trend of increasing pH (Romero A et al., 2010). Also, Dang et al (2011) reported the highest efficiency in the removal of COD and ammonia by activated persulfate by 91% and 100% at pH equal to 4 (Deng et al., 2011).

The current intensity is the most important factor in controlling the reaction speed in electrochemical processes (Ghosh D et al., 2008). According to equations 6-7, with the increase in the current intensity the production of ferric ion in the anode, which is responsible for the activation of persulfate and the formation of persulfate radical, as well as the ferric ion reduction in the cathode surface will increase (Lin H et al., 2013; Jie Wu HZ et al., 2012).

$$Fe \longrightarrow Fe^{+2} + 2e^{-} \qquad 6$$

$$Fe^{+3} + e^{-} \longrightarrow Fe^{+2} \qquad 7$$

In this method, due to the continuous production of Fe^{*2} , in a way that after oxidation as Fe^{*3} at the cathode electrode surface, it will be restored to Fe^{*2} , thereby the amount of sludge produced will be reduced. On the other hand, the increase in production of Fe^{*2} more than optimal amount does not result in an increase in eliminating pollutant and subsequently increased efficiency. This is due to the role of Fe^{2*} as an abductor of produced persulfate radicals according to Equation 8, which has interfered with the reaction of persulfate radical with pollutants(Rodriguez Set al., 2014).

$$SO_4^{-} + Fe^{2+} \longrightarrow SO_4^{2-} + Fe^{3+}$$

In advanced oxidation processes, the type and concentration of oxidizing matter are important factors (DANESHVAR N et al., 2008). Anion persulfate has two electrons as a strong oxidant, which, through reactions in the presence of activators (Equation 3-6), produces sulfate free radical with highoxidation and reduction power. Radical of produced persulfate is one of the most powerful oxidizing agents that can decompose organic compounds resistant to carbon dioxide, water and mineral acids. This radical not only has the ability to attack organic compounds directly and degrade them according to the 9-10, but also indirectly can react with water and hydroxyl ions and produce hydroxyl radicals, which are an important factor in decomposition of Organic matter (Ta N et al., 2006).

$$SO_4^{0-+} H_2O \rightarrow HO^0$$
 9
HO⁰ + M \rightarrow Product 10

On the other hand, increasing the concentration of persulfate to more than optimal amount does not result in increased removal efficiency. This is due to Persulfate Radical, on the other hand, as a radical of radical abductor and acts as a factor in the conversion of sulfate radical to persulfate, and generally it causes to destruct the sulfate radicals (Liang C et a;, 2007).

$$S_2O_8^{2-} + SO_4^{0-} \rightarrow S_2O_8^{0-} + SO_4^2$$
 11

The results are consistent with the study of Hui Zhang et al in 2013 on the removal of bisphenol A with an electrically activated persulfate process (Lin H et al., 2013). The primary concentration of pollutants is one of the factors affecting various processes. Obviously, by increasing the concentration of pollutants, the efficiency of removal will be reduced due to the shortage of manufactured radicals and the production of intermediate products. This is consistent with most researchers' works, including the studies by(Yaha et al., 2014) and (Gad-Allah TA et al., 2011) on the removal of antibiotic ciprofloxacin; they showed that the highest efficiency of the processes was at the lowest pollutant level. Concerning the synergistic effects, it can be said that application of electrochemical method with persulfate will cause synergistic effect, so that according to figure the separate application of each of the processes will have a much lower removal efficiency in the removal of pollutants. In a research, Hui Zhang has studied the removal of Orange color 7 by using the electro / iron / persulfate process, the effectivity of persulfate parameters alone, trivalent iron ion and persulfate, electrical current (EC), electrical current and trivalent iron ion, electrical current and persulfate and persulfate and electric current and trivalent iron ion. His results show that the highest efficiency is related to the use of three parameters of persulfate, electric current and trivalent iron ion (Jie Wu HZ et al., 2012). A cyclic voltammetry involves the linear method of potential of a fixed working electrode (in a non-moving solution) using a triangular program. Therefore, the higher the concentration of the matter, the greater the amount of electrical current applied to the system and vice versa. With the changes in the intensity of the electric current and the increase and decrease of the peak, it is possible to find out the concentration of matter. Considering that each matter is oxidized or reduced at a certain potential, by decreasing the amount of the peak and eliminating it, it can be concluded that the concentration of desired matter in the solution has decreased or completely eliminated. Consequently, according to Figure 7, the decrease of oxidation potential and reduction have been shown the reduction of the initial concentration of antibiotic ciprofloxacin (Shahrokhian S et al., 2003) and making it more environmentally less dangerous compounds. Also, studies have shown that electrochemical processes are capable of converting ciprofloxacin compound into compounds of NH^{4+} , NO^{3+} , Cl⁻ and F⁻ (Yahya MS et al., 2014).

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