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The effect of supporting electrolyte type and concentration on the phosphate removal from water by electrocoagulation method using iron electrodes

Elektrokoagülasyon yöntemi ile demir elektrotlar kullanılarak sulardan fosfat giderimi üzerine destek elektrolit türü ve konsantrasyonunun etkisi

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Abstract

In this study, the effect of the type and concentration of the supporting electrolyte given to the water to increase the conductivity in the electrocoagulation process on the phosphate removal from synthetically prepared waters was investigated. In addition, experiments were carried out without electrolyte and the results were compared. The effect of support electrolyte type and concentration on phosphate removal efficiency, energy consumption and reaction rate was analyzed. Experiments have shown that electrolyte use has no significant effect on phosphate removal efficiency. However, it has been found that the addition of electrolyte reduces energy consumption and increases the removal rate. From the results obtained, it was determined that NaCl as the most suitable electrolyte type and 5 mM electrolyte was sufficient as the optimum dose. Under these conditions, for 100 mg L^{-1} PO_4-P at 0.5 mA cm^{-2} current density, the phosphate removal efficiency was 96.98%, the energy consumption was 1.13 kWh m^{-3} and the first order reaction rate constant was 0.0593 min^{-1}.

Keywords: Electrocoagulation, Phosphate removal, Supporting electrolyte, Iron electrode

Özet

Bu çalışmada elektrokoagülasyon prosesi kullanılarak atıksuyun iletkenliğini artırmak için suya verilen destek elektrolitin türü ve konsantrasyonunun sulardan fosfat giderimine etkisi araştırılmıştır. Ayrıca elektrolitsiz deneyler yapılmış ve sonuçlar karşılaştırılmıştır. Destek elektrolit tipi ve konsantrasyonunun fosfat giderme verimliliği, enerji tüketimi ve reaksiyon hızı üzerindeki etkisi analiz edilmiştir. Deneyler, elektrolit kullanımının fosfat giderme verimliliği üzerinde önemli bir etkisi olmadığını göstermiştir. Ancak elektrolit ilavesinin enerji tüketimini azalttığı ve uzaklaştırma oranını arttırdığı bulunmuştur. Elde edilen sonuçlardan en uygun elektrolit türü olarak NaCl ve optimum doz olarak 5 mM elektrolitin yeterli olduğu belirlenmiştir. Bu koşullar altında, 0.5 mA cm^{-2} akım yoğunluğunda 100 mg L^{-1} PO_4-P için fosfat giderme verimi %96.98, enerji tüketimi 1.13 kWh m^{-3} ve birinci dereceden reaksiyon hızı sabiti 0.0593 dk^{-1} olarak elde edilmiştir.

Anahtar Kelimeler: Elektrokoagülasyon, Fosfat giderme, Destek elektrolit, Demir elektrot

1 Introduction

One of the parameters used in monitoring environmental water resources in industrialized countries is amount of phosphate in the natural waters. One of the main causes of eutrophication, which is one of the environmental problems occurring in aquatic environments, is phosphorus released into the environment without treatment [1]. Eutrophication, which means excessive growth of algae in aquatic environments, is caused by the concentration of nitrogen and phosphorus in wastewater released from various industries to the receiving environment [2-5]. The main source of phosphorus in wastewater is agricultural, industrial and domestic uses [6].

Phosphorus removal techniques include adsorption [7], chemical precipitation [8], ion exchange [9], electrodialysis [10], membrane filtration [11], electrocoagulation [12] and biological phosphate removal [13, 14]. The most important process used in the phosphate removal from wastewaters is to convert the soluble phosphate compounds into an insoluble solid phase and separate them from water by solid-liquid separation methods such as precipitation and filtration. The most widely used chemical method in wastewater treatment and phosphate removal is precipitation of phosphate in the form of Al^{3+}, Ca^{2+} and Fe^{3+} compounds.

Electrochemical treatment methods and especially electrocoagulation process have begun to be widely used in domestic and industrial wastewaters treatment todays. Electrocoagulation is a process in which some soluble metals such as iron and aluminum are used as anodes and this anode material dissolves into water by electric current. The dissolved anode material performs the treatment by forming metal hydroxides that are insoluble in water. The most important difference that distinguishes electrocoagulation

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from chemical coagulation is the way the coagulant is given to water [15]. In electrocoagulation, flocs occur not by adding chemicals to the system, but by dissolving aluminum and iron electrodes in the reactor [16]. Electrocoagulation is based on the principle that undissolved suspended solids and emulsions in water are unstable by changing their electrical charges. In this way, the surface charge of the particles is neutralized and colloids come together to form flocs that can collapse [17]. Electrode selection is one of the most important parameters of the electrocoagulation process. Therefore, choosing the right material is very important [18]. The main reason why aluminum and iron are widely used for electrocoagulation is that they are cheap and easily available. They are also preferred because hydroxides of aluminum and iron are poorly soluble in water. In the case of using iron as anode, two different mechanisms occur in the formation of Fe(OH)n, depending on the environment pH, with the condition that n = 2 or 3 [12].

First mechanism;

The cathode reactions;

$$8H^{+} + H_2O + 8e^{-} \rightarrow 4H_{2(g)} \qquad (1)$$

The anode reactions;

$$4Fe_{(s)} \rightarrow 4Fe^{2+}{}_{(aq)} + 8e^{-} \qquad (2)$$

In solution;

$$4Fe^{2+}{}_{(aq)} + 10H_2O_{(g)} + O_{2(g)} \rightarrow 8H^{+}{}_{(aq)} + 4Fe(OH)_3 \qquad (3)$$

Finally, total reaction can be summarized as;

$$4Fe_{(s)} + 2H_2O_{(g)} + O_{2(g)} \rightarrow 4H_{2(g)} + 4Fe(OH)_{3(s)} \qquad (4)$$

Second mechanism

The cathode reactions

$$Fe_{(s)} \rightarrow 2e^{-} + Fe^{2+}{}_{(aq)} \qquad (5)$$

The anode reactions;

$$2H_2O_{(g)} + 2e^{-} \rightarrow 2OH^{-}{}_{(aq)} + H_{2(g)} \qquad (6)$$

Finally, total reaction can be summarized as;

$$Fe_{(s)} + 2H_2O_{(g)} \rightarrow 4Fe(OH)_{2(s)} + H_{2\,(g)} \qquad (7)$$

In this study, the effect of the type of supporting electrolyte added to the system in order to increase the conductivity of the wastewater in the electrocoagulation process in the removal of phosphate compounds in high concentrations in wastewater was examined and the most appropriate electrolyte dosage was tried to be determined. In the study, the suitable electrolyte type was examined in terms of both phosphate removal efficiency, energy consumption and reaction rate.

2 Material and method

Phosphate solutions used in the experiments were synthetically prepared from solid KH_2PO_4 with analytical purity. pH adjustments were made using 5M HNO_3 and NaOH. Electrocoagulation experiments were carried out in the setup shown in Figure 1. The reactor used in the experiments is made of plexiglass material, its volume (100x110x100) is 1100 ml and has a cooling jacket. In the experiments, 850 ml phosphate solution was used. In the experiments, 6 anodes and 6 cathode Fe electrodes of 100x75x3 mm were used. The dimensions of the submerged part of these electrodes are 80x75x3 mm and they are placed at 5 cm intervals.

The experiments were conducted in batch mode. The potential difference applied to the cell and the current flowing through the cell were obtained by using a digitally controlled direct current source (Shenzhen-Mastech HY3005-3) and these parameters were measured with the help of two digital multimeters (Brymen-201). The wastewater in the electrocoagulation reactor was mixed at a constant speed of 150 rpm using a Heidolph MR-3004 brand magnetic stirrer. During the experiments, the temperature, pH and conductivity values of the solution were measured using a WTW Multiline P-4-F-Set-3 multi-parameter device.

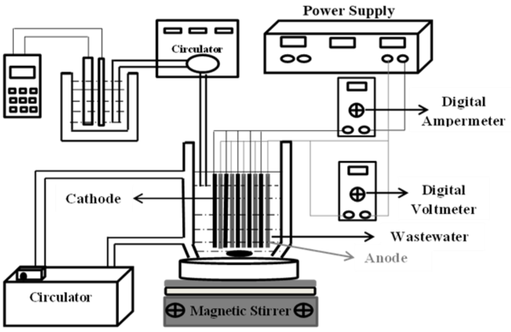

Figure 1. Schematic view of the experimental system used in the study

During the experiments, phosphate analyzes were performed spectrophotometrically (Shimadzu UV 160A) at 400 nm wavelength using ammonium vanadomolybdate reagent.

3 Results and discussion

3.1 The effect of supporting electrolyte type on system variables

Studies examining the effect of supporting electrolyte type on phosphate removal from wastewater by electrocoagulation method, I=0.75 A (CD=0.5 mA cm^{-2}), initial pH value of wastewater was chosen as pHi=3 and supporting electrolyte concentration CSE=5 mM [19].

Na_2SO_4, $NaNO_3$, NaCl and KCl salts, which are abundant and have high water solubility, were used as support electrolytes and the effects of these electrolytes on phosphate removal efficiency, energy consumption and reaction rate were investigated. The variation of phosphate removal efficiency and energy consumption of the system versus time for different types of supporting electrolytes are given in Figure 2 and Figure 3, respectively.

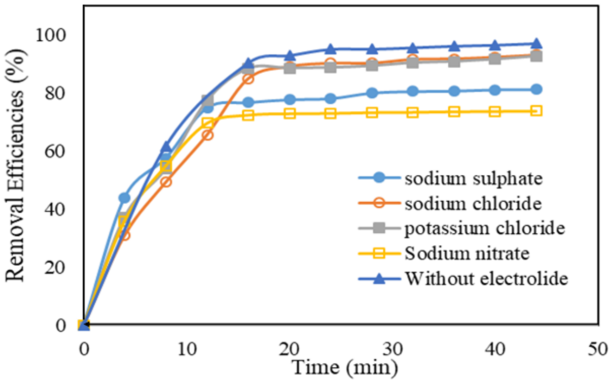

Figure 2. The change of removal efficiencies vs time for PO_4-P ions in different types of supporting electrolyte

When Figure 2 is examined, it is seen that relatively higher removal efficiency is obtained in experiments without using any electrolyte. This is thought to be due to the competition between PO_4^{3-} ions in the environment and Cl^-, NO_3^- and SO_4^{2-} ions added to the water. It has been determined that this decrease in the removal efficiency is less in CI^- ions because of the oxidation of chlorine in water to CI_2 and other forms. Reactions of chlorine in water are shown Equaiton (8), (9) and (10) [20]. In studies, NaCl and KCI showed almost the same effect in terms of phosphate removal efficiency. The highest removal efficiencies were obtained with NaCl and KCl, while the lowest removal efficiency was obtained with $NaNO_3$ [21]. In addition, a decrease in efficiency is observed as a result of forming a complex with Fe^{3+} in the presence of SO_4^{2-} ions and affecting the current efficiency by adhering to the electrode surface [22]. At the end of the reaction period of 20 minutes, the phosphate removal efficiencies of the system for Na_2SO_4, $NaNO_3$, NaCI and KCI were found to be 78%, 73.2%, 93.03% and 92.58%, respectively.

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{8}$$

$$Cl_2 + H_2O \rightleftarrows HOCI + H^+ + Cl^- \tag{9}$$

$$HOCI \rightleftarrows H^+ + OCl^- \tag{10}$$

As can be understood from these equations, the reactions that occur in the presence of CI^- ions in the environment are equilibrium reactions and change according to the pH of the wastewater. At low pHs, the HOCI molecule is dominant, while at high pH, the OCI^- molecule is dominant. Since the oxidation power of HOCI is much higher than that of OCI- ion, it is desirable that the pH of the wastewater be low in order for the oxidation to occur in the water to occur faster and more effectively.

As seen in Figure 3, the highest energy consumption occurs when electrolyte is not used. NaCl and KCI showed the same effect in energy consumption as in efficiency. However, the lowest energy consumption was obtained when Na_2SO_4 was used [23]. Because while other electrolytes give water two ions, one positive and one negative, sodium sulphate gives 3 ions, 2 positive and negative. At the end of the reaction period of 20 minutes, the energy consumptions of the system for without electrolyte, Na_2SO_4, $NaNO_3$, NaCI and KCI were found to be 0.815, 0.443, 0.624, 0.520 and 0.500 kwh m^{-3}, respectively. Electronegativity is a relative concept that varies from compound to compound. Since the electronegativity value of SO_4^{2-} ion is higher than other anions, it increases the conductivity at a higher rate. For this reason, the Na_2SO_4 compound provides a lower energy consumption.

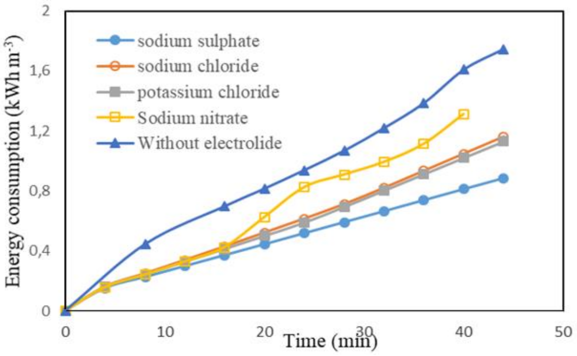

Figure 3. The change of energy consumptions vs time for PO_4-P ions in different types of support electrolyte

Although the most suitable supporting electrolyte in terms of power consumption is sodium sulphate, considering the removal efficiency, it is seen that NaCI and KCI are the most suitable electrolytes. $NaNO_3$ is not preferred due to both the lowest removal efficiency and the highest energy consumption. The rate constants calculated according to first and second order reaction kinetics for different support electrolyte types are shown in Table 1.

When Table 1 is examined, it is seen that the reaction proceeds according to the 2nd degree when the electrolyte is not used. The highest removal rate was achieved when no electrolyte was used. In both reaction degrees, the lowest R^2 values were obtained in Na_2SO_4 and $NaNO_3$ electrolytes. In terms of reaction rate, it is seen that the most suitable electrolytes are KCI and NaCl.

3.2 The effect of supporting electrolyte concentration on system variables

While examining the effect of supporting electrolyte concentration on phosphate removal from wastewater by electrocoagulation method, current intensity was chosen as 0.75 A (current density 0.5 mA cm-2) and initial pH of 3. The experiments were performed at 2.5 mM, 5 mM, 7.5 mM and 10 mM electrolyte concentrations using NaCl and KCl which gave similar results with other types of support electrolyte. The change of phosphate removal efficiency for different KCI and NaCl concentrations is given in Figure 4, and the change of the energy consumption of the system is given in Figure 5

Table 1. Reaction rate constants for different types of support electrolyte according to first and second order reaction kinetics

Supporting electrolyte type	k_1 (min^{-1})	R^2	k_2 (L mg-1 min^{-1})	R^2
Without electrolyte	0.0764	0.8562	0.0073	0.9785
Na_2SO_4	0.0305	0.7071	0.0008	0.8192
$NaNO_3$	0.0250	0.5932	0.0005	0.6761
NaCI	0.0619	0.8547	0.0031	0.9468
KCI	0.0557	0.7985	0.0025	0.9234

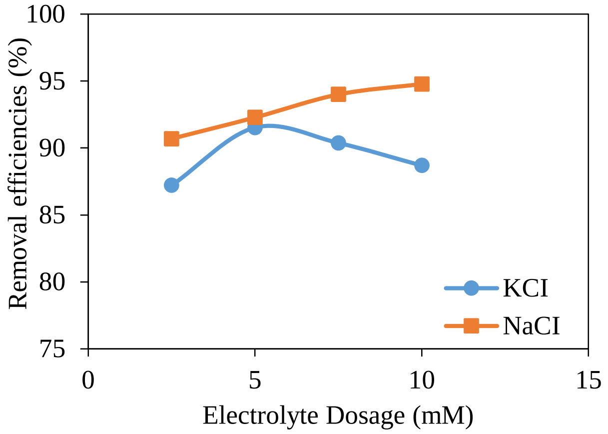

Figure 4. The change of phosphate removal efficiencies vs different supporting electrolyte concentrations

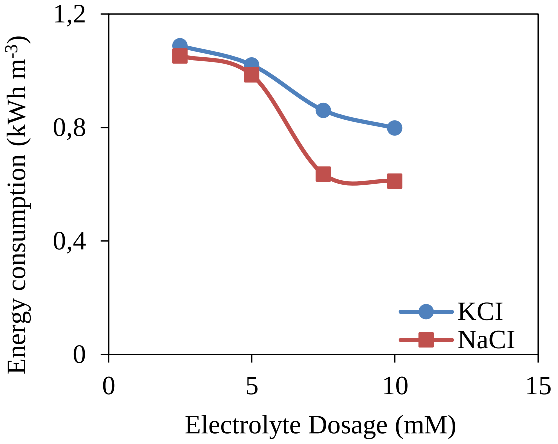

Figure 5. The change of energy consumptions vs different supporting electrolyte concentrations

When KCI and NaCI are compared, it can be said that NaCI is a little more suitable in terms of phosphate removal efficiency. As the NaCI concentration increases, the phosphate removal efficiency increases, even if only a small amount. However, this increase is not high enough when the cost of the chemicals used is considered. Therefore, an electrolyte concentration at which both energy and chemical substance consumption will be low must be applied.

Figure 5 show that NaCI reduces energy consumption a little more compared to KCI. The increase in the electrolyte concentration does not affect the efficiency, but significantly reduces the energy consumption. At the end of the 40-minute reaction time, the energy consumption of the system 2.5 mM, 5 mM, 7.5 mM and 10 mM KCI are 1.088, 1.021, 0.8611 and 0.798 kwh m^{-3}, respectively. This values for NaCI were determined as 1.052, 0.986, 0.6364 and 0.6117 kW m^{-3}. As the conductivity of the wastewater increases with the addition of electrolyte, its electrical resistance decreases, which causes a decrease in the potential difference applied to the system at constant current density. The reduction of this potential difference means that the energy consumption of the system is reduced.

The rate constants calculated according to the second order reaction kinetics are also given in Table 2. According to the data in Table 2, it is seen that NaCI is a more suitable electrolyte in terms of reaction rate.

Table 2. Second order reaction rate constants at different KCl and NaCl concentrations

C_{SE}	KCI		NaCI	
(mM)	k_2 (L mg^{-1}min^{-1})	R^2	k_2 (L mg^{-1}min^{-1})	R^2
0	0.002	0.91	0.002	0.91
2.5	0.0018	0.91	0.0032	0.79
5	0.0024	0.88	0.0708	0.76
7.5	0.0014	0.91	0.0791	0.63
10	0.0021	0.93	0.1417	0.90

4 Results

While examining the effect of electrolyte type and concentration in studies of removing phosphate ions by electrocoagulation, Na_2SO_4, NaCl, $NaNO_3$ and KCl were used as electrolytes. Studies with iron electrodes have shown that the use of electrolyte does not affect the phosphate removal efficiency much. However, since the use of supporting electrolyte increases the conductivity of the wastewater, the energy consumption of the system is greatly reduced. When the electrolyte is not used, while the energy consumption of the system to achieve 90% efficiency is 1.626 kWh m^{-3}, when 5 mM NaCl and 5 mM KCI was used, these values are determined as 0.614 and 0.692 kWh m^{-3}, respectively.

In studies of removal of phosphate ions from wastewater by electrocoagulation method, it is seen that the most suitable electrolyte type is NaCl and KCl when both disposal efficiency, energy consumption and reaction rate are taken into consideration. Although Na_2SO_4 is more suitable in terms of energy consumption, it reduces phosphate removal efficiency. $NaNO_3$, on the other hand, is not considered suitable in terms of both energy consumption and removal efficiency. The optimum electrolyte concentration was determined as 5 mM. Although the use of more electrolyte reduces the energy consumption of the system, it is not considered appropriate in terms of removal efficiency and total cost.

Conflicts of interest

No conflict of interest was declared by the authors.

Similarity rate (iThenticate): %18

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