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Research Paper / Makale

The Effect of pH on Removal of Phosphate from Water Using Aluminum Electrodes by Electrocoagulation Method

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Abstract: In this study, the effect of wastewater pH on phosphate removal by electrocoagulation method using aluminum plate electrodes was investigated. For this purpose, experiments were carried out at initial pH values ranging from 3-10, and the effect of the initial pH of the wastewater on phosphate removal efficiency, energy consumption and reaction rate was analyzed. From the results obtained, it was determined that the initial pHs of the optimum wastewater was 3 and 4. Because at low pH, both phosphate removal efficiency is high and the energy consumption of the system is low. While 97% removal efficiency is reached in 20 minutes at pH_i=3, it increases in this period with the increase of the wastewater initial pH. These data show that the removal rate is higher at lower initial pHs. While the 1st degree reaction rate constant at pH_i=3 is k_1=0.2154 min^{-1}, this value decreases to k_1=0.071 min^{-1} at pH_i=10. At pH_i=3, the energy consumption of the system has been determined as 0.553 kWh m^{-3} in 12 minutes of contact time. In addition, in the measurements made during the trials, it was observed that the highest PO_4-P removal occurred during the period when the pH of the system was between 5-7.

Keywords: Aluminum electrode, effect of pH, electrocoagulation, phosphate removal.

Alüminyum Elektrotlar Kullanılarak Elektrokoagülasyon Yöntemi ile Sulardan Fosfat Gideriminde pH'ın Etkisi

Öz: Bu çalışmada, alüminyum plaka elektrotlar kullanılarak elektrokoagülasyon yöntemiyle sentetik olarak hazırlanmış sulardan fosfat giderimi üzerine atıksu pH'sının etkisi araştırılmıştır. Bu amaçla, 3-10 arasında değişen başlangıç pH değerlerinde deneyler yapılmış ve atıksuyun başlangıç pH'sının fosfat giderim verimliliği, enerji tüketimi ve reaksiyon hızı üzerindeki etkisi analiz edilmiştir. Elde edilen sonuçlardan optimum atıksuyun başlangıç pH'larının 3 ve 4 olduğu tespit edilmiştir. Çünkü düşük pH 'larda hem fosfat giderim verimi yüksek hem de sistemin enerji tüketimi düşüktür. pHi=3'te 20 dakikada %97 giderim verimine ulaşılırken, atıksu başlangıç pH'sının artmasıyla bu arıtım süresi de artmaktadır. Bu veriler, daha düşük başlangıç pH'larında giderim veriminin daha yüksek olduğunu göstermektedir. pHi=3'te 1. derece reaksiyon hızı sabiti k1=0.2154 dak-1 iken, pHi=10'da bu değer k1=0.071 dak-1'e düşmektedir. pHi=3'te sistemin enerji tüketimi 12 dakikalık temas süresinde 0.553 kwh m-3 olarak belirlenmiştir. Ayrıca denemeler sırasında yapılan ölçümlerde en yüksek PO4-P gideriminin sistemin pH'sının 5-7 arasında olduğu dönemde gerçekleştiği tespit edilmiştir.

Anahtar Kelimeler: Alüminyum elektrot, elektrokoagülasyon, fosfat giderimi, pH'ın etkisi.

1. Introduction

One of the parameters used in monitoring environmental water resources in industrialized countries is the phosphate concentration in the water. The most important types of phosphorus found in wastewater are orthophosphate, polyphosphate and organic phosphate [1]. The main reason for

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phosphate compounds in water is phosphate fertilizers used in rural areas. The most important environmental problem caused by phosphate in water is eutrophication [2]. This event, which causes excessive growth of algae in inland waters and coastal waters, is due to the concentration of nitrogen and phosphorus in wastewater discharge from various industries into the receiving environment [3-5].

In wastewater, phosphate exists as orthophosphate, polyphosphate and organic phosphate. The known of phosphate species is important for the determination of the removal mechanism[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]. Among these methods, adsorption and chemical precipitation are widely used for phosphate removal [15]. The most important process used in the removal of phosphate from wastewater 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 water and wastewater treatment in the recent years. Electrocoagulation is a process in which some soluble metals such as iron and aluminium 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 from chemical coagulation is the way the coagulant is given to water [16]. In electrocoagulation, flocs occur not by adding chemicals to the system, but by dissolving aluminium and iron electrodes in the reactor [17]. 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 [18]. Electrode selection is one of the most important parameters of the electrocoagulation process. Therefore, choosing the right material is very important [19]. The main reason why aluminium and iron are widely used for electrocoagulation is that they are cheap and easily available. They are also preferred because hydroxides of aluminium and iron are poorly soluble in water. The reactions occurring in water when aluminium is used as electrode are given in Equation 1-3 [20].

At the cathode;

$$3H_2O + 3e^- \rightarrow 3/2H_2(g) + 3OH^- \tag{1}$$

At the anode;

$$Al \rightarrow Al^{+3} + 3e^- \tag{2}$$

In the solution;

$$Al^{+3}_{(aq)} + 3H_2O \rightarrow Al(OH)_{3(s)} + 3H^+ \tag{3}$$

The purpose of this study is to examine the effect of the initial pH of the wastewater on phosphate removal from wastewater using aluminium electrodes and to determine the most appropriate initial pH. In the study, most appropriate wastewater pH was examined in terms of both phosphate removal efficiency, energy consumption and reaction rate.

2. Experimental Methods

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 aluminum 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 contents of the reactor were mixed with a magnetic stirrer (Heidolph MR-3004) at a constant speed of 150 rpm. During the experiments, the temperature, pH and conductivity values of the solution were measured using a multi-parameter meter (WTW Multiline P-4-F-Set-3).

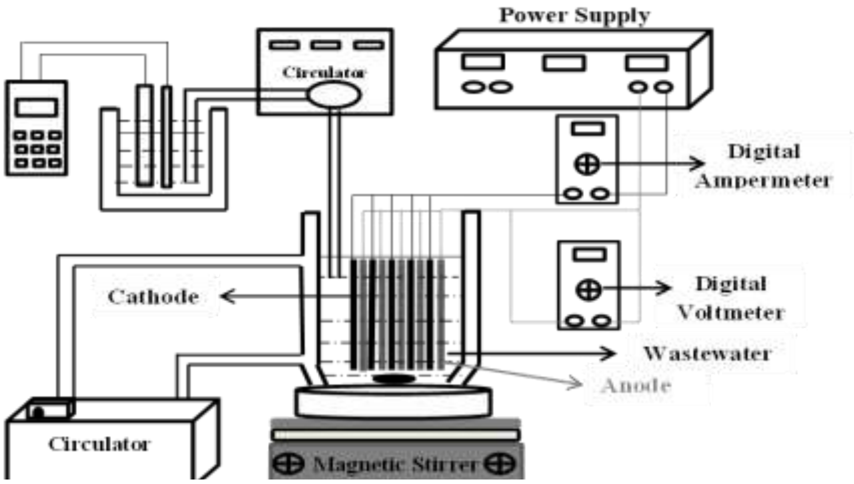

Figure 1. Schematic view of the experimental setup.

During the experiments, phosphate analyzes were performed spectrophotometrically (Shimadzu UV 160A) at 400 nm wavelength using ammonium vanadomolybdate reagent [21].

2. Results and Discussion

While examining the effect of the initial pH on phosphate removal from wastewater by electrocoagulation method, the current intensity was chosen as 0.75 A (current density 0.5 mA cm^{-2}) and the PO_4-P concentration of 100 mg L^{-1} in the reactor, and the system variables were examined at different initial pH. The change of phosphate removal efficiency vs time at different initial pH is given in Figure 2a. The change of treatment times and removal efficiencies versus pHi are also given in Figure 2b.

When Figure 2a and 2b are examined, it is seen that the highest removal efficiency and removal rate are reached at the initial pH of 3 and 4. In this case, 98.5% efficiency is reached in about 20 minutes at 100 ppm PO_4-P concentration and 0.5 mA cm^{-2} current density. these times increase with the increase of the initial pH. For example, it was determined that the highest efficiencies at pH_i = 6, 8 and 10 was reached in 40, 50 and 60 minutes, respectively. In addition, it was observed that the highest PO_4-P removal occurred during the period when the pH of the system was between 5-7 in the measurements made during the experiments [22, 23].

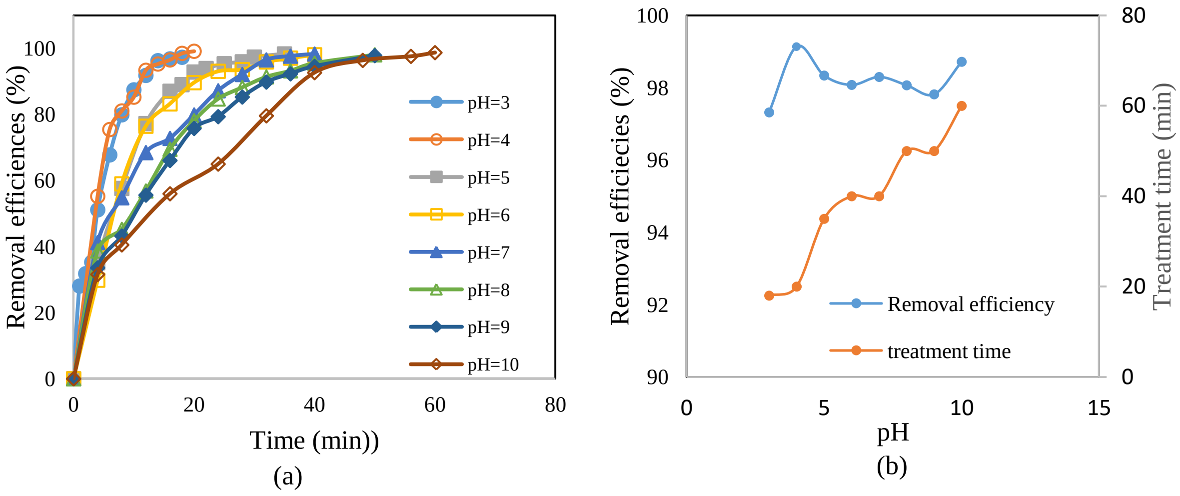

Figure 2. a) The change of phosphate removal efficiencies vs time at different wastewater initial pHs b) The change of treatment times and removal efficiencies versus pH_i

During the experiments, it was tried to determine the optimum pH by calculating the energy consumption of the system from the potential difference values measured against time. Energy consumptions in the system according to time at different initial pHs is shown in Figure 3 graphically.

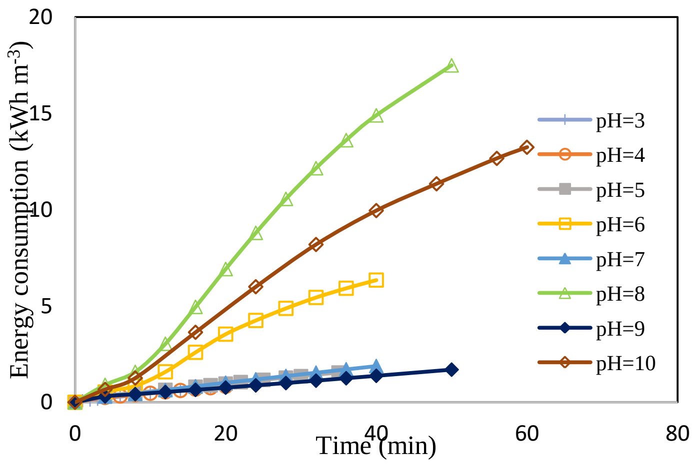

Figure 3. The change of energy consumption in the system vs time at different initial pHs.

When Figure 2 and Figure 3 are examined, it can be said that low initial pHs are more suitable for phosphate removal by electrocoagulation in terms of both reaction rate, energy consumption and removal efficiency. For 12 minutes at pHi = 4, 7 and 9, while the removal efficiencies were 93%, 68% and 33%, respectively, the energy consumption was determined as 0.540, 0.635, 0.532 kwh m^{-3}, respectively [24].

In addition, the ln (C/C_o) graph vs time plotted according to first order kinetics for different initial pH values are given in Figure 4 and the rate constants obtained from this graph are given in Table 1 [25]. As can be seen from Table 1, the highest removal rate occurs at low initial pH in the experiments to remove phosphate ions by electrocoagulation using aluminum as the electrode. The calculated correlation coefficients show that the reaction took place in accordance with the first order kinetics [26].

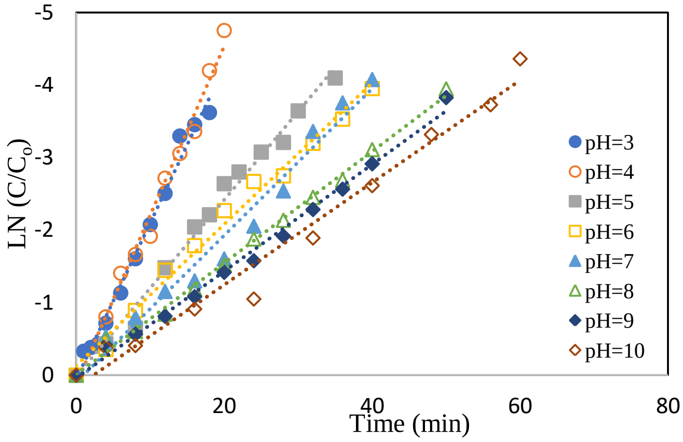

Figure 4. Showing reaction rates according to first order kinetics at different initial pHs.

Table 1. First order reaction rate constants at different initial pHs

pH	k_1 (min^{-1})	R^2
3	0.2154	0.9878
4	0.2328	0.9875
5	0.1217	0.9874
6	0.0974	0.9891
7	0.1001	0.9759
8	0.077	0.9961
9	0.0737	0.9929
10	0.0705	0.9784

When Figure 2, 3, 4. and Table 1 were examined, it was determined that the optimum initial pH was 4 in terms of both removal efficiency, energy consumption and reaction rate in the removal of phosphate ions by electrocoagulation method using aluminum electrodes. Figure 5 shows the distribution of Al species depending on the pH of the environment [27].

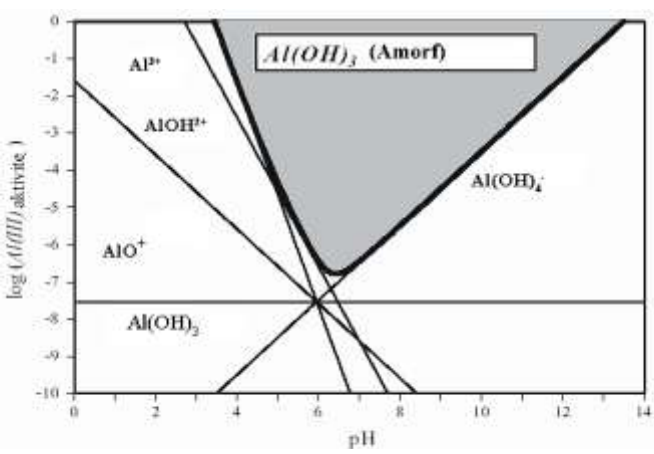

Figure 5. Activity diagram of aluminum depending on the pH of the environment.

When Figure 5 is examined, it is seen that the solubility of aluminum is very low at pH values between 6.5-7.8. In the light of this information, it is thought that it provides the fastest treatment since there is sufficient flocculant in the environment at this pH range where aluminum has the lowest solubility [28]. As a result of studies carried out at different initial pHs, the change of system pH according to time is shown in Figure 6.

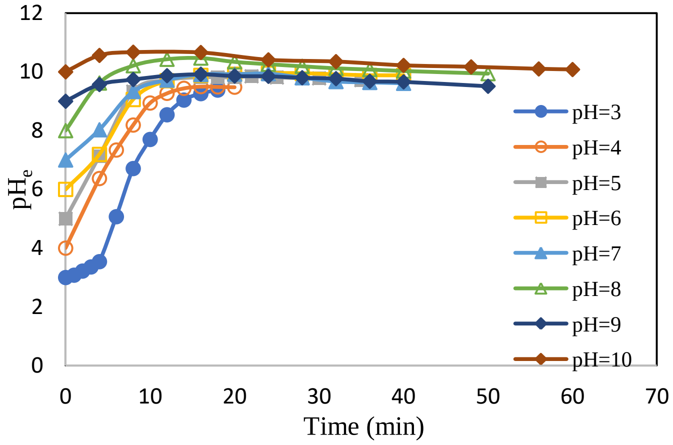

Figure 6. Change of system pH vs time at different initial pHs.

As seen in Figure 6, while the pH of the system at low pHs rises rapidly at the beginning, after a certain pH this increase decreases and even in some cases the pH remains constant. In studies carried out with aluminum electrodes, it is seen that the system pH changes little or even almost does not change if the initial pH is above 9.

In Figure 6, Regardless of the initial pH, it is seen that the pH does not rise too much above 10. Phosphate removal at low pH is initially achieved by the formation of $AlPO_4^{3-}$ with Al^{3+} ions given to the water. In this case, the pH of the wastewater rises rapidly due to the OH_- ions given to the water. Phosphate removal occurs due to coagulation with the resulting $Al(OH)_3$ flocs when the pH is above 7. In this case, since (OH^-) ions precipitate as $Al(OH)_3$, the rate of rise in pH slows down. Above this pH, due to the formation of soluble $Al(OH)_4^-$ in the environment, this compound buffers the pH of the water and prevents it from increasing further [29].

Conclusion

In studies of phosphate removal from synthetically prepared waters by electrocoagulation method, the effect of pH of wastewater on removal efficiency, energy consumption and reaction rate was investigated. In the study, pH_i = 3 and 4 were determined as the most suitable starting pHs in terms of both removal efficiency, energy consumption and reaction rate. While the phosphate removal efficiency at 100 mg L^{-1} phosphate concentration at these pHs approached 100% in approximately 12 minutes, the energy consumption of the system was obtained as 0.540 kWh m^{-3}. In addition, while the highest removal rate constants were obtained at pH=3 and 4 with 215.4 and 232.8 min^{-1}, respectively, at the studied pHs, it was observed that the removal efficiency decreased as the initial pH of the wastewater increased. As a result, it is possible to remove phosphate ions in both drinking water and wastewater with the electrocoagulation system both quickly and at low costs.

Authors' Contributions

Şİ carried out the experiments and wrote the article. ZB and SK conducted the analyses. FET performed the graphics and calculations. All authors read and approved the final manuscript.

Competing Interests

The authors declare that they have no competing interests.

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