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The Effects of Supporting Electrolyte type and Concentration on the Phosphate Removal from Wastewater By Electrocoagulation With Aluminum Plate Electrodes

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ABSTRACT: In this study, The effects of type and concentration of electrolyte on phosphate removal from wastewater by electrocoagulation with aluminum plate electrodes have been investigated.

Effect of supporting electrolyte type was investigated using $NaCI$, KCI, $NaNO_3$ and Na_2SO_4. Although Na_2SO_4 is optimal supporting electrolyte according to energy consumption, it is obtained higher removal efficiencies using $NaCI$ and KCI. It is determined optimal supporting electrolyte dosage using $NaCI$. Consequently, it can be said that optimal electrolyte type is $NaCI$ and optimal concentration is 5 mM.

Keywords: Phosphate removal, electrochemical treatment, electrocoagulation, aluminum electrode, supporting electrolyte

Alüminyum Elektrotlar Kullanılarak Elektrokoagülasyon Yöntemiyle Atıksulardan Fosfat Giderimine Destek Elektrolit Tipi Ve Konsantrasyonunun Etkisi

ÖZET: Bu çalışmada alüminyum elektrotlar kullanılarak elektrokoagülasyon yöntemiyle atıksulardan fosfat iyonlarının giderilmesinde kullanılan destek elektrolit türü ve konsantrasyonunun etkisi çalışılmıştır.

Destek elektrolit tipi araştırılırken $NaCI$, KCI, $NaNO_3$ and Na_2SO_4 kullanılmıştır. Enerji tüketimi açısından Na_2SO_4 en uygun destek elektrolit olarak görünmesine rağmen $NaCI$ ve KCI ile elde edilen giderme verimleri daha yüksektir. En uygun destek elektrolit $NACI$ ve en uygun destek elektrolit konsantrasyonu 5 mM olarak tespit edilmiştir.

Anahtar kelimeler: Fosfat giderimi, elektrokimyasal arıtım, elektrokoagülasyon, alüminyum elektrot, destek elektrolit

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INTRODUCTION

As well known, eutrophication is one of the main problems nowadays encountered in the monitoring of the environmental water sources the industrialized countries. This phenomenon, that is responsible for the dramatic growth of algae occurring in internal and coastal waters, is caused by the excess phosphorus concentration in the effluents from municipal or industrial plants discharged in the environment(Sommariva et al.,1996). The usual forms of phosphorus found in solutions include orthophosphate, polyphosphate and organic phosphate. The principal phosphorus compounds in wastewater are generally orthophosphate forms together with smaller amounts of organic phosphate. In the countryside, where agriculture and animal husbandry are the main industries, wastes from these activities will contribute to the accumulation of P in soil and water bodies. These phosphorus compounds, dissolved in surface or ground waters, are responsible for the eutrophication in closed water systems, especially in lakes and enclosed bays where the water is almost stagnant. Phosphorus removal techniques are chemical treatments like adsorption, chemical precipitation, ion exchange, electrodialysis, hybrid systems containing fly-ash adsorption and membrane filtration and electrocoagulation. Adsorption and chemical precipitation among the above methods have been widely used for phosphate removal(Uğurlu and Salman, 1998; Agyei et al., 2003; Hequet et al., 2001; Ayala et al., 1998; Rao et al., 2002; Lin et al., 2001; Kao et al., 2000; Batabyal et al., 1995; Koumanova et al., 1997; Gupta and Tores, 1998; İrdemez et al., 2004). The removal of phosphate from aqueous streams consists of the conversion of soluble phosphate to an insoluble solid phase. This solid phase can be separated from water by means of sedimentation or filtration. In wastewater applications, the most common and successful methods to precipitate phosphate involve the dissolved cations Al^{3+}, Ca^{2+}, Fe^{3+} and to a lesser extent of Fe^{2+}. It was found that when iron and aluminum are present in the water, $FePO_4$ and $AlPO_4$ forms in the low pH range (<6.5) and at higher pH range (>6.5) iron and aluminum increasingly convert to oxides and hydroxides. A higher pH is more ideal for precipitation of phosphate with calcium as apatites and hydroxyapatites.

In recent years, electrocoagulation has been successfully tested to treat wastewater. Electrocoagulation is a process consisting of creating metallic hydroxide flocks within the wastewater by electrodissolution of soluble anodes, usually made of iron or aluminum. The difference between electrocoagulation and chemical coagulation is mainly in the way of aluminum ions are delivered(Donini et al., 1994). In electrocoagulation, coagulation and precipitation are not conducted by delivering chemicals -called coagulants- to the system, but via electrodes in the reactor(Koparal and Öğütveren, 2002a). Electrocoagulation is based on the fact that the stability of colloids, suspensions and emulsions is influenced by electric charges. Therefore, if additional electrical charges are supplied to the charged particles via appropriate electrodes, the surface charge of particles is neutralized and several particles combine into larger and separable agglomerates[(Koparal and Öğütveren, 1997a). Electrode assembly is the heart of the treatment facility. Therefore, the appropriate selection of its materials is very important. The most common electrode materials for electrocoagulation are aluminum and iron. They are cheap, readily available, and proven effective(Chen et al., 2000a). When aluminum is used as electrode material, the reactions are as follows.

At the cathode:

$$3H_2O + 3e^- \rightarrow {}^3\!/_2 H_2(g) + 3OH^- \qquad (1)$$

At the anode:

$$Al \rightarrow Al^{+3} + 3e^- \qquad (2)$$

In the solution:

$$Al^{+3}(aq) + 3H_2O \rightarrow Al(OH)_3 + 3H^+(aq) \quad (3)$$

Aim of this study is investigate the effects of initial pH and supporting electrolyte type and dosage on the treatability of the phosphate containing wastewater by electrocoagulation method.

MATERIAL AND METHOD

The experimental setup is schematically shown in Fig. 1. The electrocoagulation unit consists of six pair of electrodes made of plate aluminum with total area of approximately 1500 cm² and the gap between the electrodes is 5 mm. Electrodes were connected to a digital dc power supply (Shenzen-Mastech HY 3005-3) in monopolar mode. Two digital multimeters (Brymen Bm 201) as ampermeter and voltmeter were used to measure the current passing through the circuit and the applied potential respectively. The EC unit has been stirred at

150 rpm by a magnetic stirrer.(Heidolp MR 3004 S). The thermostat electrocoagulator is made of plexiglass with the volume of 850 mL. During the experiments, temperature, conductivity and pH of the wastewaters were measured by a multi-parameter (WTW Multiline P-4 F-Set-3). Treated wastewater was collected over a desired period of time from the reactor and collected samples were filtered by the cellulose acetate membrane filter with the pore diameter of 0.45 μ (Schleicher and Schuell) before the analysis. Reactor was operated in batch and galvanostatic mode.

The analysis of phosphate was carried out using the yellow vanadomolybdophosphoric acid method by a double beam spectrophotometer (Shimadzu UV-160 A) according to the Standard Methods for Examination of Water and Wastewater(APHA, 1985).

Wastewater used in the experiments was prepared synthetically by dissolving KH_2PO_4 in distilled water. pH adjustments were conducted by concentrated HNO_3 and NaOH (5 M) all chemicals used in the experiments are analytic grade.

RESULT AND DISCUSSION

Effects of supporting electrolyte type on the phosphate removal by electrocoagulation was investigated for 0,75 A (0,5 mA/cm^2), pHi=3, C_{SE}= 5 mM. Na_2SO_4, $NaNO_3$, NaCI and KCI were used as supporting electrolyte and effects of these electrolytes on system parameters were analyzed.

Variation of phosphate removal efficiency vs. time for different supporting electrolyte types using aluminum electrolyte is shown in figure 2. Variation of energy consumption vs. time is shown figure 3.

As seen in figure 2, supporting electrolyte has effected scarcely on phosphate removal efficiency. Besides, it can be said that phosphate removal efficiency has decreased using Na_2SO_4 and $NaNO_3$. Cause of this can be that sulphate and nitrate ions have produced competitive adsorption with phosphate ions into $Al(OH)_3$ flocks. When used NaCI and KCI as electrolyte, CI^- ions have transformed into HOCI in wastewater. These reactions are as follows(Eilbeck and Mattock, 1987);

$$2CI^- \rightarrow CI_2^- + 2e^- \quad \text{(Anodic reaction)} \quad (4)$$

$$CI_2^- + H_2O \rightarrow HOCI + H^+ CI^- \quad (5)$$

$$HOCI \rightarrow H^+ + OCI^- \quad (6)$$

Distribution of both hypochlorite and hypochlorous acid is affected by the pH (Yıldız et al., 2007).

As seen in figure 5, because solution conductivity has increased by increasing electrolyte concentration, system energy consumption has decreased. But electrolyte concentration has increased excessively, phosphate removal efficiency has decreased. In experiments used NaCI, it is obtained that optimal electrolyte concentration is 5 mM.

CONCLUSIONS

The effects of initial pH on phosphate removal from wastewater by electrocoagulation were studied

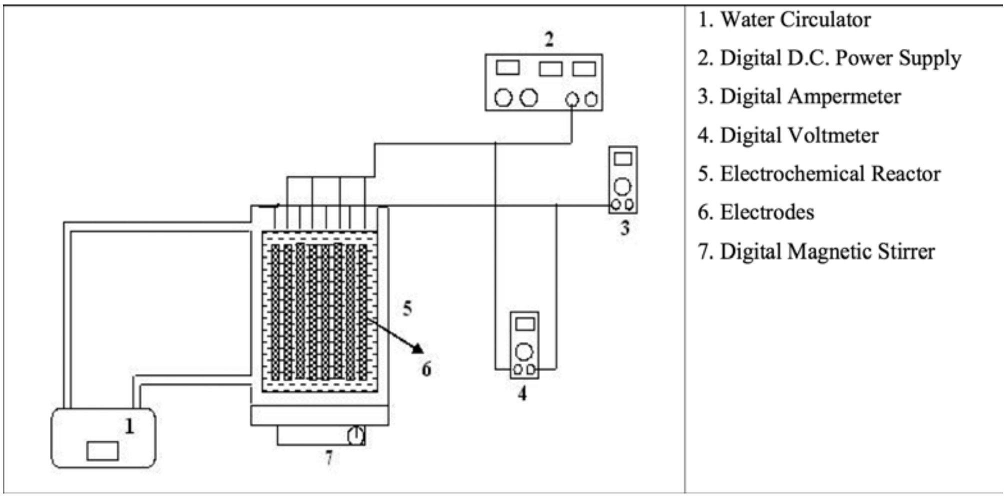

Figure 1. Schematic diagram of the experimental setup.

in pH_i interval of 3-10. Obtained results have indicated that initial pH is important parameter on the removal of phosphate by electrocoagulation. This study that aluminum electrodes were used have obtained as 100% of efficiency of phosphate removal in the almost initial pHs. But system energy consumption and removal rate have changed mainly. Studies have indicated that system energy consumptions have decreased and phosphate removal rates have increased in low initial pHs on the removal of phosphate by electrocoagulation. Therefore it could be said that pHi= 3 and 4 are suitable on the phosphate removal by electrocoagulation.

In experiments, it is found that system energy consumption has decreased using supported electrolyte. Phosphate removal efficiencies are higher using NaCI and KCI than $NaNO_3$ and Na_2SO_4. In experiments used NaCI, it is obtained that optimal electrolyte concentration is 5 mM.

In conclusion, electrocoagulation is suitable process for phosphate removal. But system parameters can be optimized for waters including phosphate

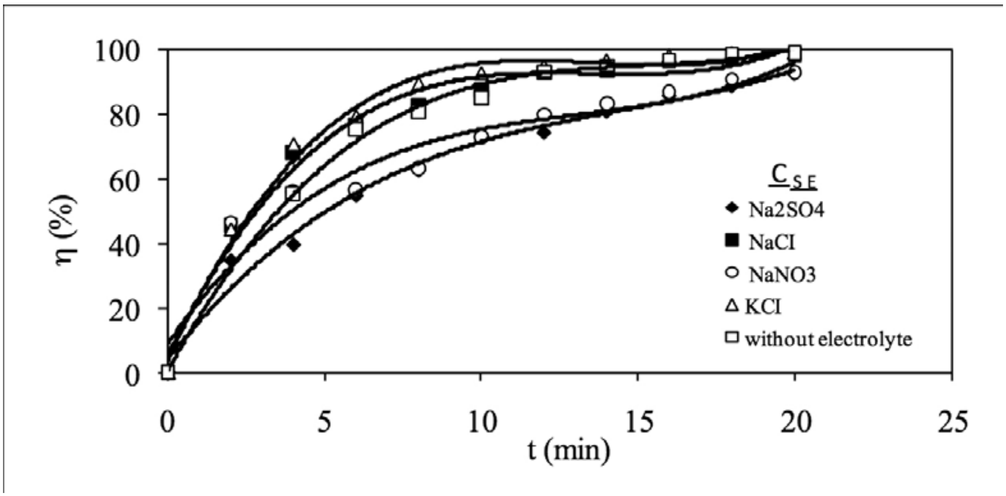

Figure 2. Variation of phosphate removal efficiency vs. time using different supporting electrolyte type (CSE= 5 mM).

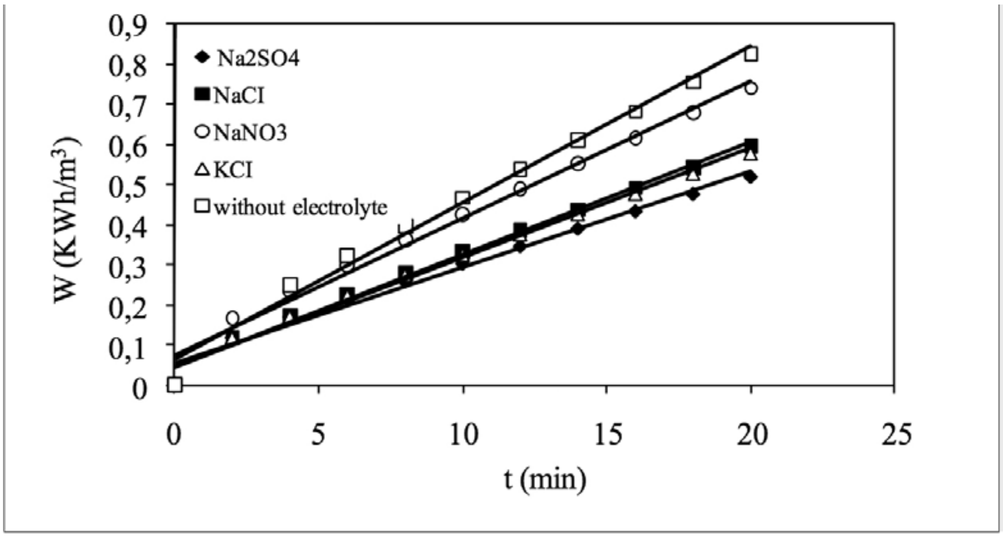

Figure 3. Variation of system energy consumption vs. time using different supporting electrolyte type(CSE= 5 mM).

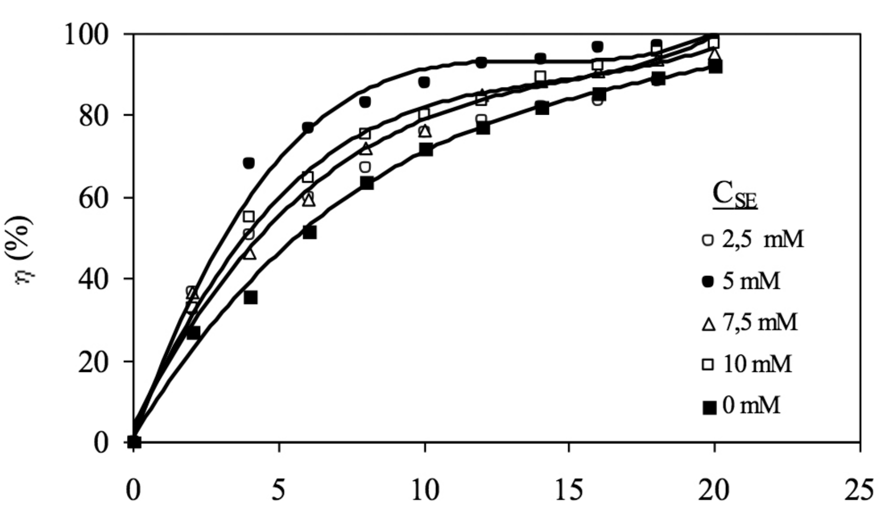

Figure 4. Variation of phosphate removal efficiencies vs time using different NaCI concentration (Co= 100 mg/L PO4-P, I= 0,75 A, pHi= 4, n= 150 rpm)

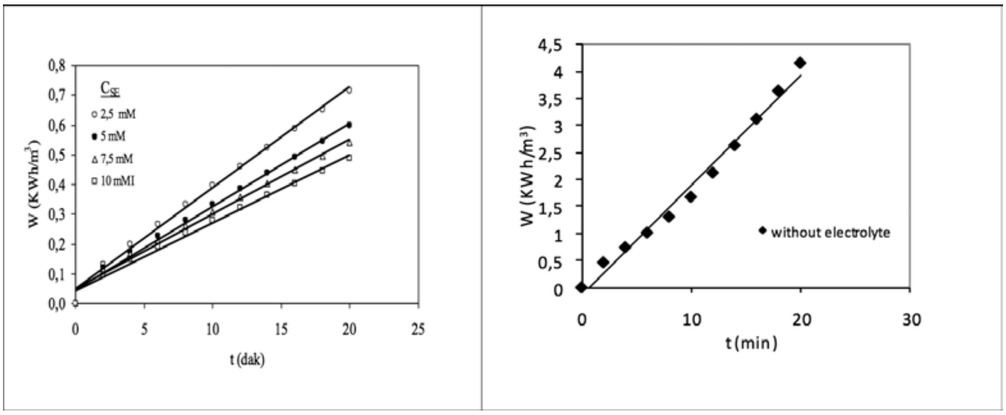

Figure 5. Variation of energy consumption vs time using different NaCI concentration (Co= 100 mg/L PO4-P, I= 0,75 A, pHi= 4, n= 150 rpm)

NOMENCLATURE

C_o	İnitial phosphate concentration	(mg/L)
I	Current density	(amper)
V	Potential	(volt)
pH_i	Initial pH	
W	System energy consumption	Kw-h/m³
h	Efficiency of phosphate removal	(%)
C_{SE}	Supporting electrolyte concentration	mM

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