Removal of phosphate from aqueous solutions by electro-coagulation

Nihal Bektaş, Hilal Akbulut, Hatice Inan, Anatoly Dimoglo*

Environmental Engineering Department, Gebze Institute of Technology, Gebze/Kocaeli, P.O. Box 141, 41400, Turkey

Abstract

The aim of this paper was to investigate the feasibility of the removal of phosphate from aqueous solution by electro-coagulation (EC). The current density (CD) between 2.5 and 10 mA cm^{-2} and duration in the limits of 5–20 min were tried for different concentrations. In order to determine optimal operating conditions, the EC process used for the phosphate removal was examined in dependence with the CD, initial concentrations and time. The results of the experimental batch processing showed high effectiveness of the EC method in removing phosphate from aqueous solutions.
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1. Introduction

As known, phosphate discharged into the surface waters accelerates eutrophication [1,2]. This can in turn disturb the balance of organisms present in the water and affect water quality, mainly through the depletion of oxygen level as the algae decay. Reduced oxygen level can have harmful effects on fish and other aquatic life, causing reductions in biodiversity. Eutrophication can also affect the recreational value of natural resources. Generally, total phosphorus concentrations in excess of 100 µg P/l provide sufficient nutrient enrichment in the lakes.

The treatment of phosphate can be achieved by several physical, chemical, and biological methods [3]. In biological treatment plant, it is necessary to transfer phosphate from liquid to the sludge phase and the removal efficiency usually does not exceed 30%, which means that remaining phosphate should be removed by another techniques [4]. The phosphate removal from wastewater by adsorption using different materials has also been explored [5,6]. Chemical precipitation is also widely used for phosphate removal [7,8]. The common precipitants used are the aluminum sulphate and ferric chloride. Chemical precipitants imply fur-

ther costs for the purchase and installation of dosing equipment and operating costs for power, disposal of additional sludge, manpower, and surely chemicals used. Moreover, during the process, an alkaline condition is necessary for precipitation by calcium and neutral to acidic environments are required if aluminum and iron are used. This not only increases the chemicals expenditure but also is detrimental to biological treatment processes. The removal of different forms of phosphorous (namely, soluble phosphorous, particulate phosphorous, and total phosphate) has been studied [9]. The results of the paper provide a basis for developing such schemes for phosphate removal, which may be adapted to particular configurations of the wastewater studied.

Electro-coagulation (EC), which is known as a reliable and mainly cost-effective wastewater treatment process [10–18], is characterized by simple and easy-to-operate equipment, short operation time, none or negligible amount of chemicals and decreased amount of sludge [19,20]. The flocs formed by EC are relatively large and contain less bound of water. They are also more stable and therefore amenable to filtration [21].

The aim of this paper was to study the feasibility of the removal of phosphate from aqueous solution by electro-coagulation. The process was examined under different values of current density (CD), pH, initial concentrations, and time, in order to determine optimal operating conditions.

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* Corresponding author. Tel.: +90-262-653-84-97x1428; fax: +90-262-653-84-90.

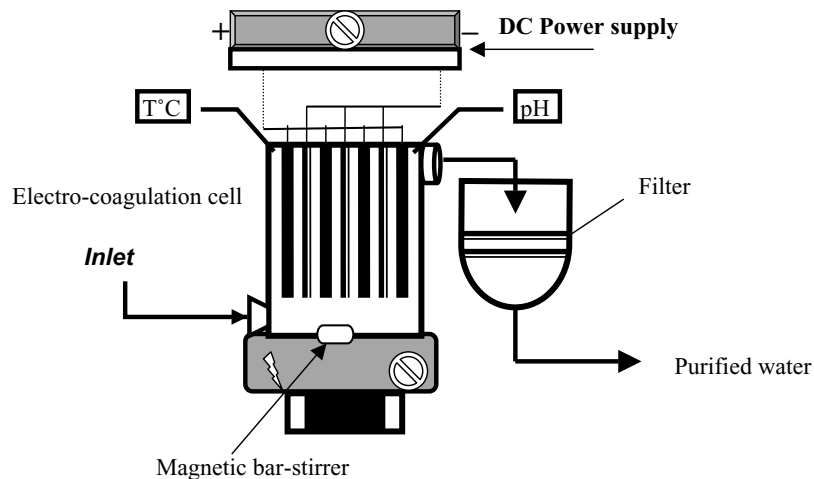*E-mail address:* dimoglo@gyte.edu.tr (A. Dimoglo).

Fig. 1. The EC reactor used in the laboratory experiments.

2. Materials and methods

2.1. Chemicals

All chemicals used were analytical grade and used without further treatment. Distilled water was used in all experiments. Stock phosphate solutions were prepared from KH_2PO_4 (Carlo Erba, 99.5%). A spectrophotometer (MERCK) was used for the analysis of phosphate in accordance with the standard methods (vanadomolybdophosphoric acid calorimetric method) [22] after separating the turbidity through the standard filter designed for a wide range of laboratory applications (MF-Millipore membrane filter, mixed cellulose ester, 0.45 μm). When necessary, pH was adjusted by using 0.1 N HCl or 0.1 N NaOH.

2.2. Experimental

A laboratory-scale reactor (15 cm × 8 cm × 8 cm, 500 ml), made of organic glass, was used in all experiments (Fig. 1). Two groups of alternating electrodes being cathodes and anodes (by eight plates of each type) were arranged vertically. Distances between any paired anode and cathode were taken equal to 3 mm.

The electrodes were made of Al and immersed, prior to the experiments, in 1% solution of HCl for 8 h. They were connected to terminals of a direct current power supply characterized by the ranges 0–5 A for current and 0–30 V for

voltage. Temperature (21–22 °C) was stable during the experiments. Synthetic phosphate solutions (their concentration varied in the range of 10 and 200 mg l^{-1}) were taken for the study. At the beginning of each run the solution of phosphate (450 ml) of the desired concentration was fed into the reactor and 50 ml of 1% solution of NaCl (as electrolyte) was added to it to increase the solution conductivity. Each run was timed starting with the DC power supply switching on.

As known, Al^{3+} ions dissolve and combine with hydroxyl ions in the water [23,24] when direct current passes through the Al anodes. They form metal hydroxides, which are partly soluble in the water under definite pH values. This step results in the colloidal particles formation with metal hydroxides as nuclei of the latter. Around a nucleus, the adsorption layer of cations and anions is being organized. Taken together, the nucleus and adsorption layer form a granule of the colloidal particle, which has a small positive charge. To compensate the charge, a diffusion layer is being formed around the granule, which makes the particle a neutral one. The main reactions that occur during the electrolysis reactions are shown in Table 1.

It is to be noted that the disengaged Al^{3+} ions form hard-to-dissolve sediment of $AlPO_4$ in the presence of PO_4^{3-} ions. The specific electrical energy consumption of the reactor for the phosphate removal is low enough (0.8–1.5 kWh m^{-3}) for the values of CD in the range of 2.5–10 mA cm^{-2}.

Table 1
Reactions at the electrodes and in the bulk solution

Anode	In bulk solution	Cathode
$4OH^- - 4e^- = 2H_2O + O_{2(g)}$ $2H_2O - 4e^- = O_{2(g)} + 4H^+$	$Cl_{2(g)} + H_2O = HOCl + H^+ + Cl^-$	$2H_3O^+ + 2e^- = H_{2(g)} + 2H_2O$ (in acid solutions)
$2Cl^- - 2e^- = Cl_{2(g)}$		
$Al_{(s)} - 3e^- = Al_{(aq)}^{3+}$	$Al_{(aq)}^{3+} + 3H_2O = Al(OH)_3 + 3H^+$ $Al_{(aq)}^{3+} + PO_4^{3-} = AlPO_4$	$2H_2O^+ + 2e^- = H_{2(g)} + 2OH^-$ (in alkaline solutions) $O_2 + 2H_2O + 4e^- = 4OH^-$

3. Results and discussion

3.1. pH, time and initial concentration's effects

Initially the percentage of phosphate removal (PPR) from the solution in dependence with its initial pH values was studied. As seen from Fig. 2, under low initial value of pH 4, the 15 min duration of the EC process gives PPR = 80%. The initial pH increase (up to 7) causes increase of PPR for the same duration. PPR achieves its maximum under pH 6.0. If pH increases, the PPR values are somewhat decreased. It is worth of noting that in the EC process pH itself changes. For low initial pH (4 and 5) 15 min processing implies pH increase up to pH_{fin} (6.0 and 6.5, respectively). If higher initial pH (7 and 8) is taken, pH_{fin} decreases (6.6 and 6.9, respectively).

In other words, if the solution accumulates enough $Al(OH)_3$ and $AlPO_4$, then pH of the solution stabilizes (pH 6.5), irregardless of the initial pH. Based on the observation, further studies were carried out under natural initial pH 6.2.

In Fig. 3, variations of the phosphate removal are shown in dependence with the EC duration and initial concentration of the solution. CD was stable in the experiments ($10 \, mA \, cm^{-2}$).

As seen from Fig. 3, first 5 min of the EC process give inconsiderable PPR (35–50%) for 200 and $100 \, mg \, l^{-1}$ of initial phosphate concentrations. Under low phosphate concentrations (10–$50 \, mg \, l^{-1}$) and EC duration equals to 5 min, the removal degree is 81–90%. The increase of the EC duration gives better results of the removal parameter. Thus, the 10 min EC process duration demonstrates the 70 and 94% phosphate removal for 200 and $100 \, mg \, l^{-1}$ solutions, respectively. The most considerable phosphate removal is reached under some optimal values of EC duration (15 min). However, further increase of the EC duration is of small influence on the degree of phosphate removal, as seen from Fig. 3. Curves in the figure become parallel and close to each other. The solution concentration also influences the
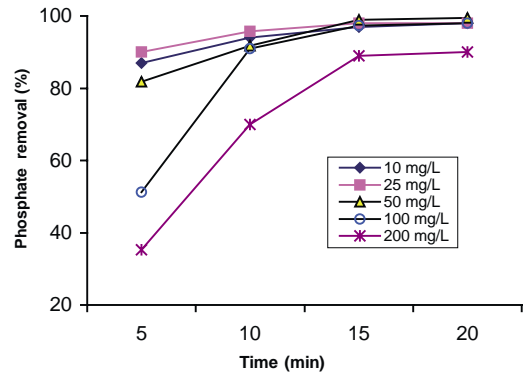

Fig. 3. Percentage of the phosphate removal vs. time and initial concentrations (pH 6.2, $CD = 10 \, mA \, cm^{-2}$, $T = 21.5 \, °C$).

time of the phosphate removal. For low concentrations (up to $50 \, mg \, l^{-1}$) the PPR is high enough. For high concentrations (100, $200 \, mg \, l^{-1}$), 5 and 10 min duration results in low PPR values. Under duration of 15 and 20 min PPR increases (for the same concentrations of the solution). It can be supposed that the amount of Al^{3+} ions generated at the first stages of the EC is not sufficient for the phosphate ions binding. When duration of the EC process increases, the Al^{3+} ions concentration increases as well and results in higher quantity of the bound phosphate.

A linear dependency exists between EC duration and charge loading, Q (see Fig. 4). By this, higher solution concentrations imply higher values of Q. As far as conductivity also depends on the initial concentration linearly, voltage increases linearly under fixed CD.

Analogous temporal dependency is observed for the electrical energy consumption, W (see Fig. 5). For low concentrations of phosphate ions (10–$100 \, mg \, l^{-1}$) W does not exceed $1 \, kWh$ per m^3 when the process duration is equal to 20 min. For the initial concentration of $200 \, mg \, l^{-1}$, the value of W does not exceed $1.5 \, kWh \, m^{-3}$ for same duration.
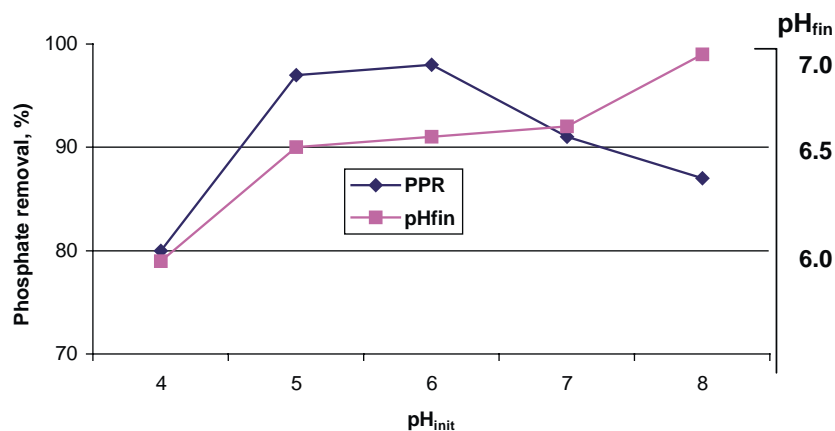

Fig. 2. Percentage of the phosphate removal vs. initial pH ($C_0 = 100 \, mg \, l^{-1}$, $CD = 10 \, mA \, cm^{-2}$, $t = 15 \, min$, $T = 21.5 \, °C$).
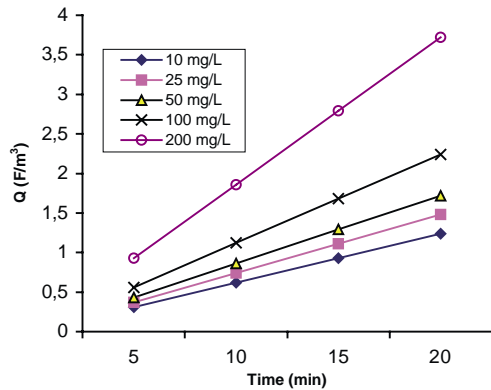
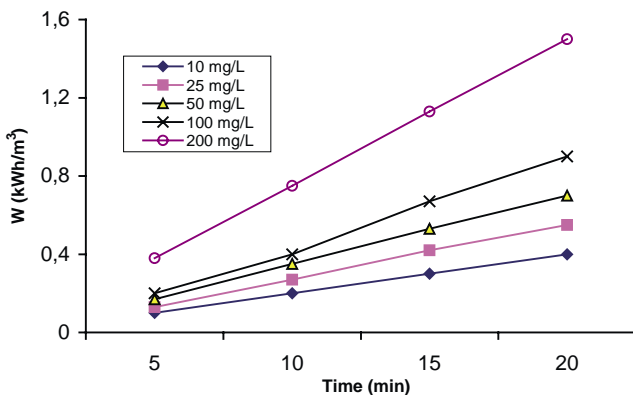Fig. 4. Charge loading (Q) vs. time and initial concentrations (pH 6.2; $CD = 10\,\text{mA cm}^{-2}$, $T = 21.5\,°C$).

Fig. 5. Electrical energy consumption (W) vs. time and initial concentrations, (pH 6.2; $CD = 10\,\text{mA cm}^{-2}$, $T = 21.5\,°C$).

3.2. Effect of current density

Previously it was shown that CD can influence the treatment efficiency of the EC process. In Fig. 6 the dependency of PPR on the CD is shown for different initial concentrations of the phosphate solution.

As seen from Fig. 6, the maximal percentage of PO_4^{3-} ions removal for low initial concentrations ($10–50\,\text{mg}\,l^{-1}$)
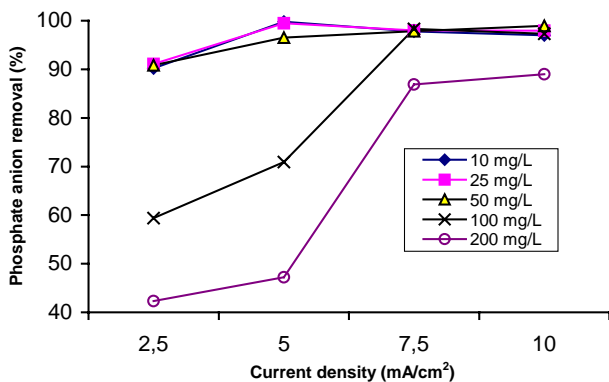

Fig. 6. Percentage of the phosphate removal in dependence on the current density and initial concentrations (pH 6.2, $t = 15\,\text{min}$, $T = 21.5\,°C$).

happens already under low CD values ($2.5\,\text{mA cm}^{-2}$). For high initial concentrations of the phosphate ($100–200\,\text{mg}\,l^{-1}$), low level of CD is not so effective for the phosphate removal. A considerable qualitative jump can be observed beginning with $CD = 7.5\,\text{mA nm}^{-2}$. Data given in Figs. 3 and 6 show that the 15 min duration and $CD = 7.5$ are considered as optimal parameters for the effective phosphate removal by means of EC (90%) under its high initial concentration ($100–200\,\text{mg}\,l^{-1}$). For low initial concentrations ($10–50\,\text{mg}\,l^{-1}$), duration is 7 min and $CD = 5\,\text{mA cm}^{-2}$.

4. Conclusions

The efficiency of the EC processes applied for the phosphate-containing aqueous solutions purification is studied in this work. The results show that the EC processes provide high and stable effects as to the contaminants removal. The results of the EC application have shown that it is capable of removing phosphate from aqueous solutions of high enough concentrations.

The EC method does not use any chemical reagents and makes the process of phosphate-containing wastewater treatment easy for regulation and automation. A constructional optimization of the EC apparatus for the phosphate treatment is offered. In our opinion, further studies can promote successive passing from laboratory-scale models to the industrial specimens possessing same level of technological characteristics.

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