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The effects of pH on phosphate removal from wastewater by electrocoagulation with iron plate electrodes

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Abstract

In this study, the effect of pH on phosphate removal from wastewater by electrocoagulation with iron plate electrodes has been investigated. For this aim, experiments have been carried out controlled initial pH values within the range of 3–9. Effects of initial pH have been analyzed on efficiencies of phosphate removal and energy consumptions. From obtained results, it was found that optimal initial pH is 3. Besides, experiments have been carried out controlled system pH. Effects of system variables have been analyzed on constant pH. From obtained results in these experiments, it was found that optimal system pH is 7.
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Keywords: Phosphate removal; Electrochemical treatment; Electrocoagulation; Iron electrodes

1. Introduction

As well known, nowadays eutrophication is one of the main problems nowadays encountered in the monitoring of the environmental water sources in 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 [1]. 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, membrane filtration and electrocoagulation. Adsorption and chemical precipitation among the above methods have been widely used for phosphate removal [2–12]. 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 suitable for precipitation of phosphate with calcium as apatites and hydroxyapatites.

In recent years, electrocoagulation has been successfully used 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 aluminium [13]. The difference between electrocoagulation and chemical coagulation is mainly in the way of iron ions are given to wastewater [14]. In electrocoagulation, coagulation and precipitation are not conducted by delivering chemicals – called coagulants – to the system, but via electrodes in the reactor [13]. 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

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Nomenclature

C_0	initial phosphate concentration (mg/L)
I	current (A)
pH_e	effluent pH
pH_i	initial pH
pH_s	system pH
V	applied potential (V)
W	system energy consumption (kW h/m^3)

Greek symbol

η	efficiency of phosphate removal (%)

to the charged particles via appropriate electrodes, the surface charge of particles is neutralized and several particles combine into larger and separable agglomerates [15]. 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 [16]. When iron is used as electrode material, the reactions are as follows.
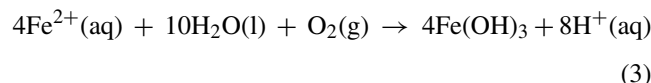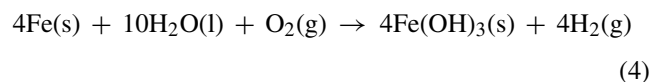
- At the cathode:

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

- At the anode:

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

- and with dissolved oxygen in solution:

$$4Fe^{2+}(aq) + 10H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3 + 8H^+(aq) \tag{3}$$

- overall reaction:

$$4Fe(s) + 10H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(s) + 4H_2(g) \tag{4}$$

Aim of this study is to investigate the effects of initial pH on phosphate removal from wastewater by electrocoagulation method using iron electrodes.

2. Experimental

The experimental setup used in uncontrolled pH conditions is schematically shown in Fig. 1a. The electrocoagulation unit consists of six pair of electrodes made of plate iron with total area of approximately 1500 cm^2 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 experimental setup is shown in Fig. 1. 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 μm (Schleicher and Schuell) before the analysis. Reactor was operated in batch and galvanostatic mode.

The experimental setup used in uncontrolled pH conditions is schematically shown in Fig. 1b. In order to provide the constant pH conditions, system has been operated in recirculation mode. In these test runs, experimental setup shown in Fig. 1a was modified by attaching a peristaltic pump, magnetic stirrer (Heidolp MR 3004 S) and tank. pH of the system was kept constant by adding acid or base to the tank.

Wastewater used in the experiments was prepared synthetically by dissolving KH$_2$PO$_4$ in distilled water. pH adjustments were conducted by concentrated HNO$_3$ and NaOH (5 M) all chemicals used in the experiments are analytic grade.

The analysis of phosphate was carried out using vanadomolybdophosphoric acid method by a double beam spectrophotometer (Shimadzu UV-160 A) according to the Standard Methods for Examination of Water and Wastewater [17].

3. Result and discussion

The effects of initial pH on phosphate removal from wastewater using iron plate electrodes by electrocoagulation was investigated using 0.75 A current, 100 mg/L PO$_4$–P concentration and phosphate removal efficiency and energy consumption was analyzed. Variation of phosphate removal efficiency versus time in different initial pH is shown in Fig. 2.

As seen in Fig. 2, while initial pH is 3, highest efficiency of phosphate removal and removal rate has been obtained. Efficiencies of phosphate removal using iron plate electrodes by electrocoagulation are 86% for pH_i 3, 71% for pH_i 6, 64% for pH_i 9 at the end of 20 min.

In the removal of phosphate removal by Fe^{3+}, optimum pH is approximately in the range of 4.5–5.5 [18]. FePO$_4$ has the minimum solubility within this pH range, but phosphate removal efficiencies reach a plateau approximately at 16 min for all pH values (see Fig. 2) at this point, it can be seen from the Fig. 5 that pH of the wastewaters equal to 10.1, 10.6 and 11.5 for the initial pH values of 3.0, 5.0 and 7.0, respectively. Solubility of the FePO$_4$ has increased with increasing pH [18] whereas phosphate removal efficiencies have slightly risen above these high pH levels. Fe(OH)$_3$ and Fe(OH)$_4$$^-$ are available this pH range (see Fig. 3a), but Fe(OH)$_4$$^-$ [18,19] is in the state of dissolved in the wastewater. Thus, it can be concluded that phosphate removal takes place formation of FePO$_4$ and Fe(OH)$_3$ although the FePO$_4$ is favored relatively low pH values.

In Fig. 2, it is seen that reaction rate and removal efficiency have decreased by increasing pH with time. It can be attributed that Fe(III) flocks are near neutral at pH 8.3 because Fe(OH)$_3$^{0} is the dominant dissolved iron species [18]. At pH 10.6 (pH of the solution treated), dominant species of dissolved iron is
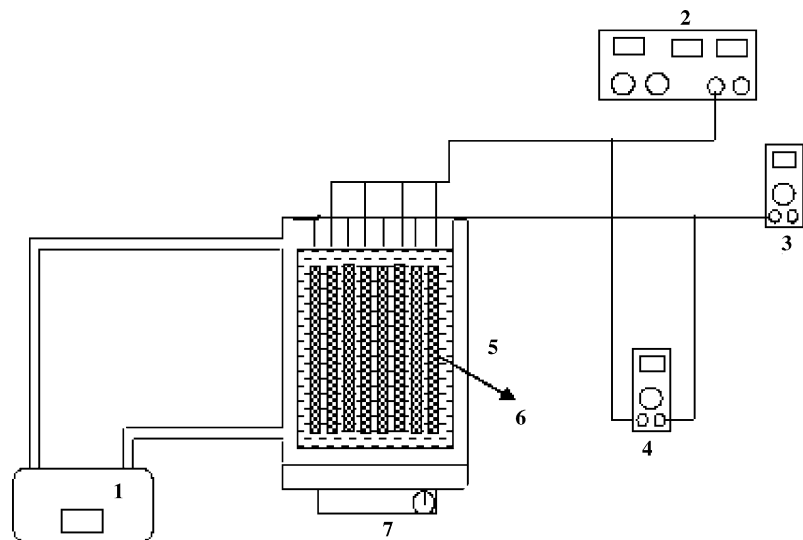
1. Water Circulator　　　　5. Electrochemical Reactor

2. Digital D.C. Power Supply　　　6. Electrodes

3. Digital Ampermeter　　　　7. Digital Magnetic Stirrer

4. Digital Voltmeter

(a)
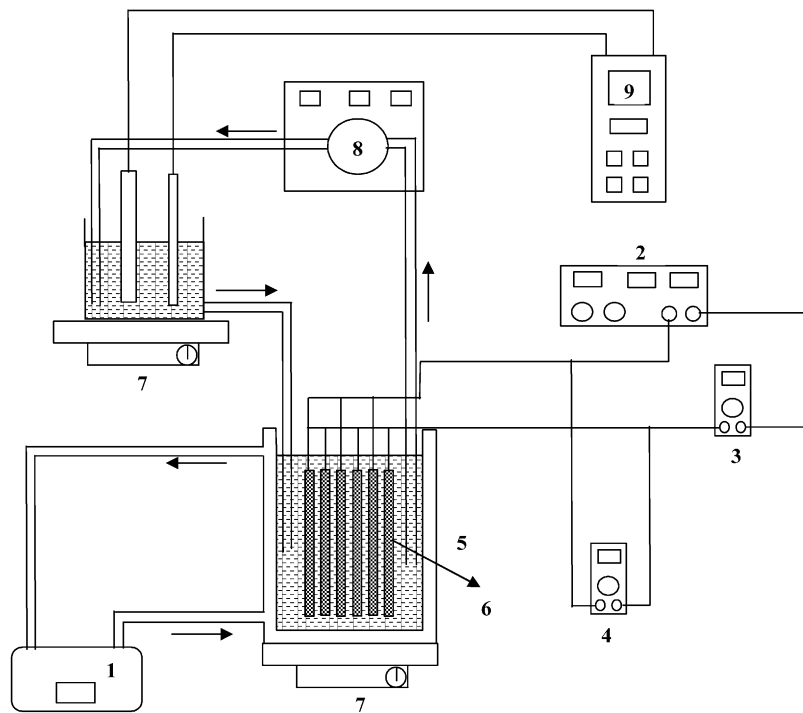
1. Water Circulator　　　　5. Electrochemical Reactor

2. Digital D.C. Power Supply　　　6. Electrodes

3. Digital Ampermeter　　　　7. Digital Magnetic Stirrer

4. Digital Voltmeter　　　　8. Recirculation Pump

9. Multiparameter

(b)

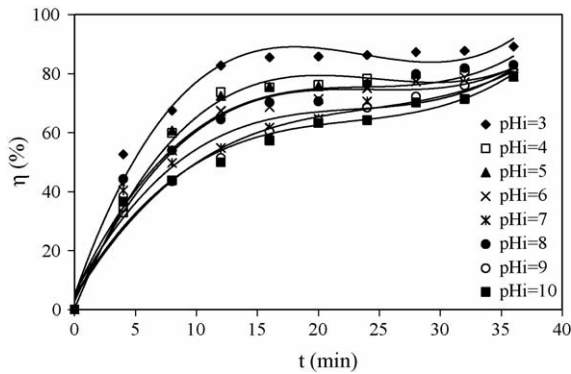Fig. 1. (a) Schematic diagram of the experimental setup; (b) schematic diagram of the modified experimental setup.

Fig. 2. Variation of phosphate removal efficiency vs. time ($C_0 = 100$ mg/L PO$_4$–P, $I = 0.75$ A, $n = 150$ rpm).
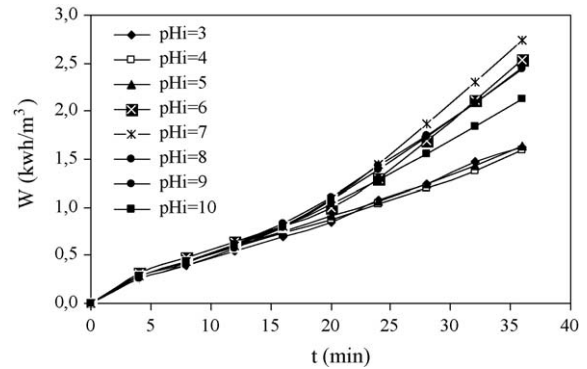
Fig. 4. Variation of system energy consumption vs. time ($C_0 = 100$ mg/L PO$_4$–P, $I = 0.75$ A, $n = 150$ rpm).

Fe(OH)$_4^-$ [20]. Activity diagrams of Fe(II) and Fe(III) according to pH is shown in Fig. 3 [21].

During experiments, system energy consumptions were determined using measured applied potential. From obtained results, variation of system energy consumptions versus time is shown in Fig. 4.

As seen in Fig. 4, system energy consumption has been affected from initial pH. For example, system energy consumptions are 0.847 kW h/m^3 for pH$_i$ 3; 0.999 kW h/m^3 for pH$_i$ 6; 1.109 kW h/m^3 for pH$_i$ 9. Studies have indicated that system energy consumptions have decreased and phosphate removal rates have increased in low initial pH using iron plate electrodes on the removal of phosphate by electrocoagulation. Energy consumption is relatively lower in low and high initial pH because there is sufficiently dissolved matter (H$^+$, OH$^-$) in solution. Besides, when wastewater's pH have risen over 10, because Fe(OH)$_4^-$ ions have formed, energy consumptions have decreased.

Furthermore, variation of system pH versus initial pH during reaction is shown in Fig. 5. While system pH has rapidly risen in low initial pH, this increase is being slower in higher initial pH, so it can be said that highest phosphate removal efficiencies are obtainable within the pH range of 5–7. Phosphate removal rate has decreased when system pH have mainly increased.

When system pH is raised above 10, phosphate removal rate is very slow. Thus, it has been considered that energy consumptions have increased and phosphate removal rates have decreased when this system have been studied above pH$_e$ 10. While this system has been designed, initial pH might be rather low.

In addition, experiments in controlled pH were built. Energy consumptions and efficiencies of phosphate removal were analyzed in this state. Drawn due to results of obtained from these experiments, variation of efficiency of phosphate removal versus time is shown in Fig. 6 and variation of energy consumption versus time is shown in Fig. 7.

As seen in Fig. 6, efficiencies of phosphate removal are 40% in pH$_s$ 3, 93% in pH$_s$ 7 and 61% in pH$_s$ 9 in the end of 20 min. Shown in Fig. 7, energy consumptions are 0.5 kW h/m^3 in pH$_s$ 3, 0.641 kW h/m^3 in pH$_s$ 7 and 0.562 kW h/m^3 in pH$_s$ 9 in the end of 20 min. As seen, highest efficiency of phosphate removal have been obtained in pH$_s$ 7 and lowest efficiency of phosphate removal have been in pH$_s$ 3. Whereas highest efficiency of phosphate removal have been obtained from pH$_i$ 3 when pH has been not fixed. To fix pH addition of acid is the cause of increase of wastewater conductivity, thus energy consumption has decreased, but system cost have increased for chemical matters have been added to system. In the low and high pH, energy consumption have decreased because Fe(III) is dissolving and there is high dissolved matter. Energy consumption is relatively higher in neutral pH.
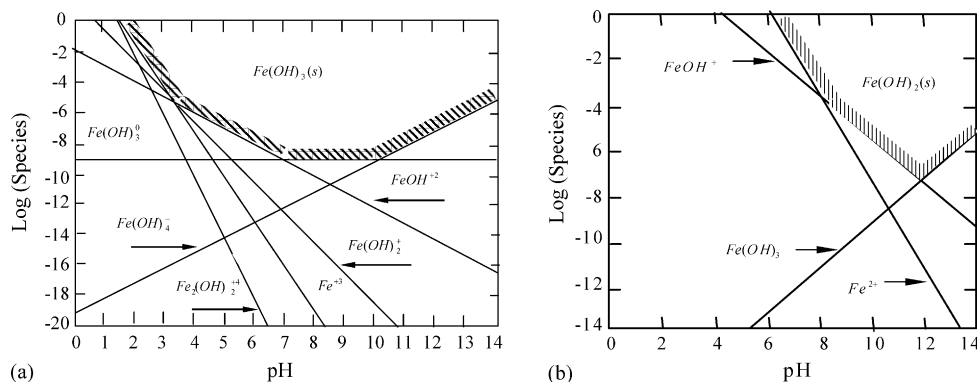

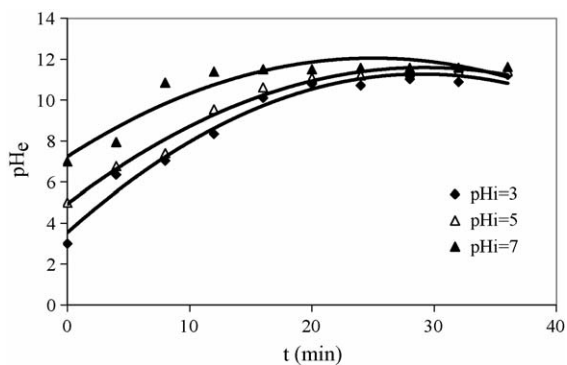Fig. 3. Activity diagrams of Fe(III) (a) and Fe(II) (b) according to pH.

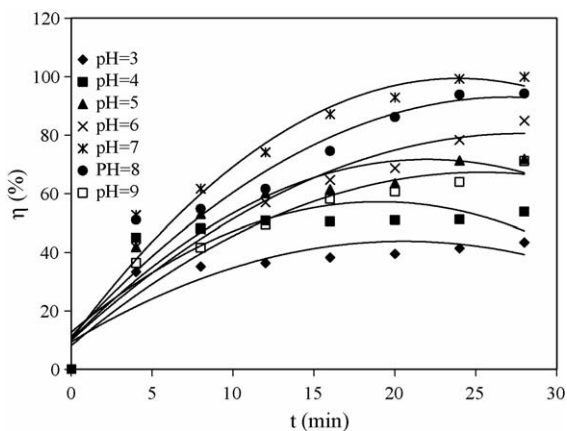Fig. 5. Variation of system pH vs. time in various initial pH.

Fig. 6. Variation of efficiency of phosphate removal vs. time in controlled pH.
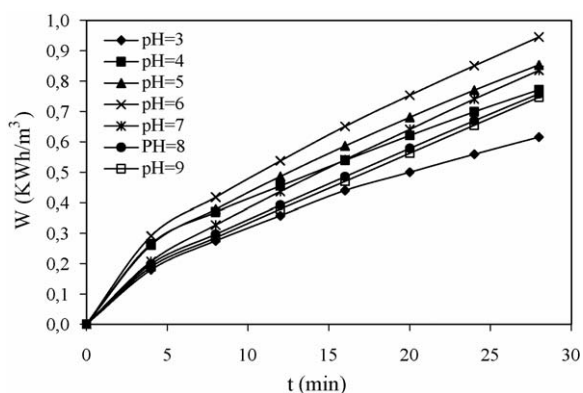

Fig. 7. Variation of energy consumption vs. time in controlled pH.

4. Conclusion

In this present work, effect of initial pH on the removal of phosphate ions from wastewaters has been investigated. Test runs were carried out controlled and uncontrolled pH conditions and ranged 3–10. Effect of initial pH on the system performance has been evaluated based on removal efficiency and energy consumption.

From obtained results in experiments, it is seen that phosphate removal from wastewater by electrocoagulation with iron plate electrodes is an effective process. Low initial pH is suitable either efficiencies of phosphate removal or system energy consumption when pH have been not controlled. But when system pH has been controlled, it was found that optimal pH is within the range of 6–7. Because solubility of $Fe(OH)_2$ is minimum in interval of this pH (see Fig. 3b).

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