

Full Length Research Paper

Electrocoagulation process for removal of adenosine-5'-monophosphate and sodium hexamethaphosphate from the synthetic wastewater

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As well known, eutrophication is one of the main problems encountered in surface water. This phenomenon is caused by the excess phosphate level in the effluent of wastewater treatment plant. Thus, to control of eutrophication, removal of phosphorus is required. The aim of this study was to determine the efficiency of electrocoagulation (EC) process to phosphorus removal from the synthetic wastewater. This study was an experimental work which has been carried out by steel electrodes at constant current density of 1.15 mA/cm^2 on synthetic wastewater. The effect of reaction time and initial phosphate concentration is also studied. The results showed that the maximum removal efficiency of 98.72 and 100% was achieved for adenosine-5'-monophosphate (AMP) and sodium hexamethaphosphate (SHMP), respectively. In conclusion, electrochemical process is very efficient for removal of phosphate from the synthetic wastewater.

Key words: Electrocoagulation process, phosphorus removal, nutrient removal.

INTRODUCTION

Phosphorus is one of basic nutrients alive and it is present in water environment in smaller quantities than nitrogen and it is necessary for all kind of living phytoplankton organisms, so, its concentration is of crucial importance in water quality protection (Sedlak, 1991; Rybicki, 1997). As is well known, eutrophication is one of the main problems encountered nowadays in the monitoring of environmental water sources in industrialized countries. This phenomenon, which is responsible for the dramatic growth of algae occurring in drinking water, is caused by the excess phosphate concentration in the effluents from municipal or industrial plants discharged to the environment (Irdemez et al., 2006 a, b; Nouri et al., 2010; Wei et al., 2011).

Therefore, most of the recent nutrient removal studies have focused on the removal of phosphorus. In the environment, the usual forms of phosphorus found in solutions include orthophosphate, polyphosphate and organic phosphate (Shin et al., 2007; Akbal and Kuleyin 2010;

Lacasa et al., 2011; Lee et al., 2011). Nevertheless, the principal phosphorus compounds in wastewater are generally orthophosphate forms together with smaller amounts of organic phosphate. The concentration of phosphorus in raw municipal wastewater is about 8 to 10 mg/L PO_4^{3-} . The main sources of phosphorus in municipal wastewater are domestic wastewater, usage of detergents in the house, commercial and industrial consumptions and human excreta (Crites and Tchobanoglous, 1998, 1999; Hammer, 2008).

Therefore, phosphate content of effluents or streams that are discharged directly to the environment is regulated by the national and international effluent standard. For example, in the US, India and Iran discharge limits of phosphate are 0.5 to 1, 5 and 6 mg/L as P, respectively. To meet water quality standards, further treatment of wastewater is required (Vasudevan et al., 2009; Behbahani et al., 2011). Phosphate removal techniques fall into three main categories: physical, chemical and biological (Ozacar and Sengiel, 2003; Golder et al., 2006; Bayramoglu et al., 2007). Biological methods are cost-effective and produce less sludge than physical or chemical methods, but they have disadvantages such as longer treatment time and lower

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phosphorous removal efficiency (Kim et al., 2010).

Chemical treatment is widely used for phosphate removal. The common chemicals used for treatments are aluminum sulfate and ferric chloride. At present, chemical treatments are not used due to disadvantages like high costs of maintenance, further cost for buying and installation of dosing equipments, problems of sludge handling and its disposal and neutralization of the effluent (Vasudevan et al., 2009; Behbahani et al., 2011).

Physical methods have proven to be either too expensive, as in the case of electro dialysis and reverse osmosis, or inefficient, removing only 10% of the total phosphate (Irdemez et al., 2006a). In a biological treatment plant, it is necessary to transfer phosphate from the liquid to the sludge phase, and the removal efficiency usually does not exceed 30%, which means that the remaining phosphate should be removed by other techniques. In this framework, electrochemical methods offer a good opportunity to prevent and remedy pollution problems due to the discharge of industrial and sewage effluents (Bektas et al., 2004; Golder et al., 2006). The electrochemical technologies have attracted a great deal of attention, because of their versatility, which makes the treatment of liquids, gases and solids possible and environmental compatibility (Ugurlu et al., 2008).

In fact, the main reagent is the electron which is a "clean reagent". As a consequence, the electrochemical methods and several applications, such as metal ion removal and recovery, electro dialysis, electrodeionisation and especially, destruction of toxic and non-biodegradable organics by direct or indirect anodic oxidation (Panizza et al., 2000).

Electrochemical methods such as electrocoagulation, electrolysis and electroflocculation have been successfully applied in the purification of wastewater from dye production, alcohol production, olive oil production, tanneries, textiles, wastewater containing cyanides, heavy metal, phenols, Cr- EDTA, landfill leachate and domestic sewage (Vlyssides et al., 2000, 2009).

Recently, electrocoagulation (EC) process have received considerable attention for treatment of wastewater, since it is an emerging water treatment technology that has been applied successfully to treat various pollutants, including arsenic (Balasubramanian et al., 2009), indium (Chou et al., 2009), poly vinyl alcohol (Chou et al., 2010), hardness (Hasson et al., 2010) and chemical mechanical polishing (Drouiche et al., 2008; Lee et al., 2011). The advantages which the EC has over conventional technologies include high removal efficiency, compact treatment facility and possibility of complete automation, simple and easily operated equipment, short operation time, no addition of chemicals and low sludge production (Koby et al., 2010, 2011). Although the most common type of phosphorous used in activated sludge effluent is orthophosphate, other forms of phosphorous have until now not been considered for the special removal of organic phosphorus and

polyphosphates. Therefore, this research was done to examine the electrochemical efficiency of organic phosphorus and polyphosphate in the removal of synthetic wastewater.

MATERIALS AND METHODS

This research is an experimental study which has been done in bench scale on the synthetic wastewater samples with the different calculating concentrations of 2, 4, 8, 16, 24 and 32 mg/L-p in the shape of organic phosphorus and polyphosphate in the water and wastewater chemistry laboratory of the Faculty Health in Kashan Medical Sciences University during 2011. In each run, 2000 ml from the synthetic wastewater with distinct concentration was placed in electrolytic cell equipped with magnetic stirrer and EC process was applied on it by steel electrodes. Two digital multimeter as amperemeter and voltmeter were used to measure the current passing through the circuit and the applied potential, respectively.

Eight steel electrodes with dimension of $2.5 \times 0.02 \times 15$ cm (width \times thickness \times length) were applied in the role of anode and cathode. Electrodes were connected to a digital direct current (DC) power supply in monopolar mode. Chloridric acid was used for cleaning electrodes before the start of experiments. The electrode pair was immersed on synthetic wastewater containing phosphorus to a depth of 13 cm, and distance between anode and cathode maintained a constant of 2 cm during electrolysis. The EC unit has been stirred at 300 rpm by a magnetic stirrer (Hiedolp MR 3004 S). All the experiments were carried out under potentiostatic conditions at room temperature ($25 \pm 1.8^\circ\text{C}$).

The direct current power source was operated with constant density of 1.15 mA/cm^2 and EC test run lasted 60 min in all experiments and one sample was taken at any 10 min. Previous studies on EC process showed that optimum current density for phosphorus removal is 1.15 mA/cm^2 (Mesdaghinia, 2003). Hence, this study was carried out in this current density. The experiments were repeated 5 times for any different initial concentrations of each of the synthetic wastewaters. Then, the phosphorus in raw and treated samples was turn into the orthophosphate with per sulfate digestion method and the formed orthophosphate was metered by stannous chloride method as phosphorus. The absorbance in this method was metered by spectrophotometer in 690 nm wavelength (Clesceri et al., 1999). The system has been operated in uncontrolled pH with initial pH of 7 to 7.5. After EC process, the pH of the solution was measured with a pH meter. The effects of solution conductivity on the removal rate of phosphorus were not the subject of this study, so, all experiments were carried out in uncontrolled condition of conductivity. Initial conductivity of synthetic wastewater were between 3450 to 4877 $\mu\text{s/cm}$. Reduction for total phosphorus in less than 1 mg/L-P (standard limit) was spotted on the removal of phosphorus. Figure 1 shows a schematic diagram of the EC system in this study.

The synthetic wastewater preparation

For the preparation of the synthetic wastewater, potable water was used with distinct amount of adenosine-5'-monophosphate (AMP) in the role of a compound containing phosphorus in the shape of organic phosphorus and sodium hexamethaphosphate (SHMP) in the role of a compound containing phosphorus in the shape of polyphosphate. The characteristic of the used water as supporting electrolyte is as shown in Table 1. The standard reference materials used in this experiment was in form Merck with purity of at least 99%.

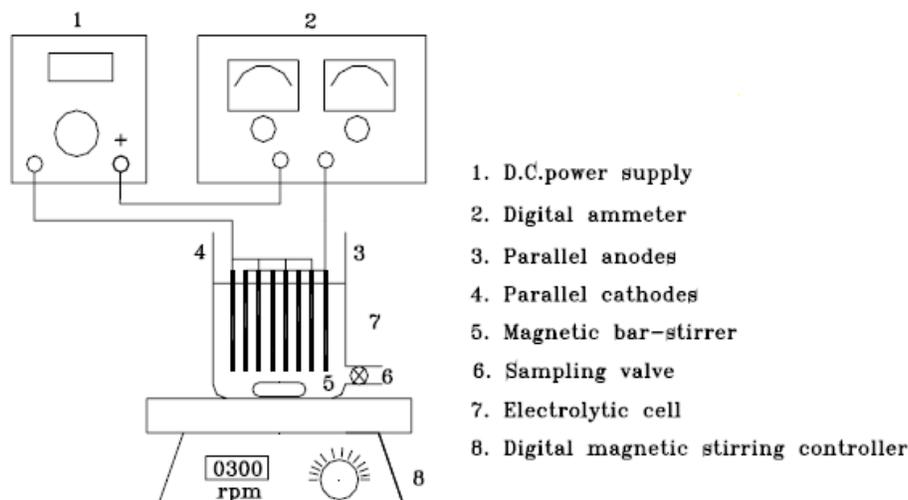


Figure 1. Schematic of the experimental system of electrochemical process in this research.

Table 1. Chemical quality of used water in preparing of the synthetic wastewater.

Parameter	Amount
EC	2070 $\mu\text{s}/\text{cm}$
pH	7.2
TDS	1242 mg/L
Temperature	25°C
Total hardness	516 as CaCO_3
Calcium hardness	318 as CaCO_3
Magnesium hardness	197.79 as CaCO_3
Sulphate	340 mg/L- SO_4^{2-}
Chloride	448 mg/L- Cl^-
Sodium	260 mg/L- Na^+
Potassium	2 mg/L- K^+
Phosphate	0.049 mg/L- PO_4^{3-}

RESULTS

Initially, the residual concentration of AMP after EC process independence with its initial concentrations and various reaction times was studied. The results of this stage of the study in constant current density of 1.15 mA/cm^2 are as shown in Table 2. As shown in Table 2 at initial concentration of 2 mg/L after 20 min reaction time, the residual concentration of AMP reaches less than 1 mg/L and similar results were obtained at the initial concentration of 32 mg/L at 50 min reaction time.

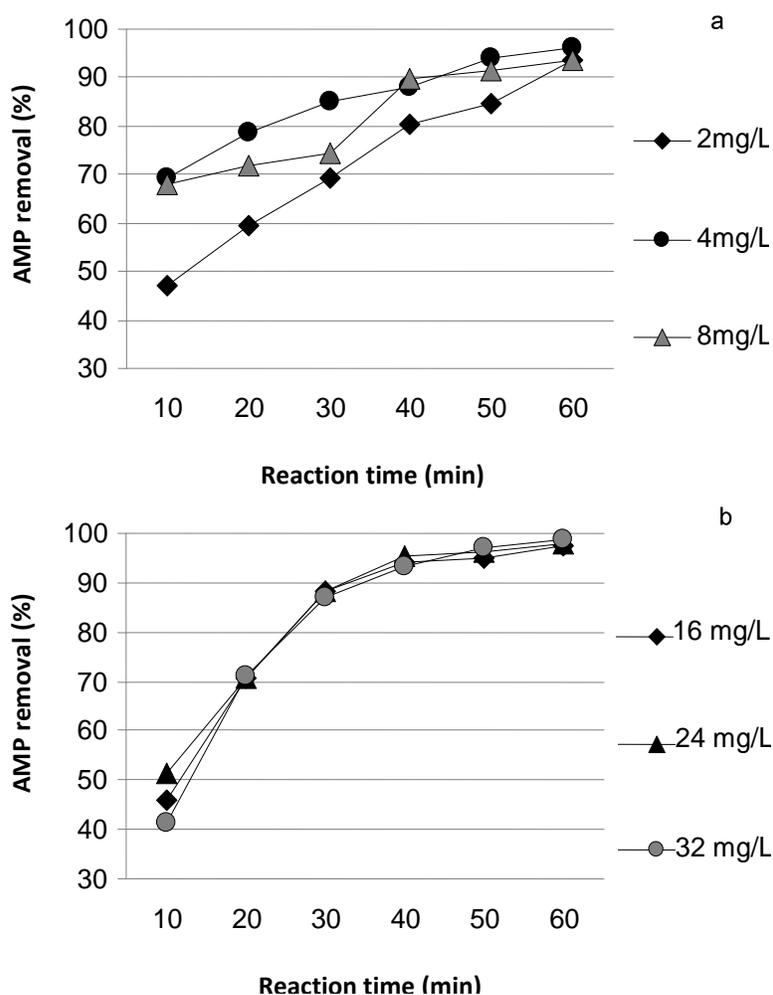
Figure 2 summarized the efficiency of EC process for AMP removal under the different reaction time and initial concentration. As can be observed, the removal of AMP varied in range 46.99 to 98.72% in reaction time 10 to 60 min and for initial concentrations of 2 to 32 mg/L AMP. Sharp increase removal efficiency was clearly observed

initially and removal efficiency increases with increasing reaction time at constant current density. The results of EC process under the different operating condition on the residual concentration of SHMP were presented as shown in Table 3. As shown in this table for initial concentration of 2 mg/L after 50 min reaction time, the residual concentration of SHMP reached zero, and also, the residual concentration of SHMP is reduced to less than 1 mg/L (reuse standard) for all initial concentrations at 30 min reaction time.

In Figure 3, variations of SHMP removal are independence with EC duration and initial concentrations of SHMP at constant current density. As illustrated in this figure, it can be seen that the removal efficiency of SHMP was increased with increasing reaction time. The minimum removal efficiency of SHMP was less than 90% for initial concentration of 2 mg/L and above 90% for

Table 2. The residual concentrations of AMP at different reaction times and various initial concentrations using EC process.

Time (min)	Concentration (mg/L)					
	2	4	8	16	24	32
0	2.08±0.11	4.08±0.12	8.04±0.18	15.85±0.23	23.92±0.36	31.91±0.51
10	1.1±0.04	1.26±0.06	2.58±0.17	8.56±0.13	11.64±0.61	18.6±0.41
20	0.84±0.02	0.87±0.04	2.28±0.11	4.66±0.19	7.04±0.25	9.20±0.5
30	0.64±0.03	0.61±0.04	2.07±0.08	1.87±0.13	2.79±0.16	4.12±0.56
40	0.41±0.03	0.48±0.13	0.84±0.01	0.93±0.06	1.08±0.04	2.17±0.15
50	0.32±0.02	0.25±0.01	0.69±0.02	0.78±0.05	0.9±0.44	0.92±0.04
60	0.13±0.01	0.16±0.01	0.53±0.04	0.38±0.02	0.47±0.02	0.41±0.07

**Figure 2.** Variation of AMP removal efficiency versus time using EC process at various initial concentrations (a and b).

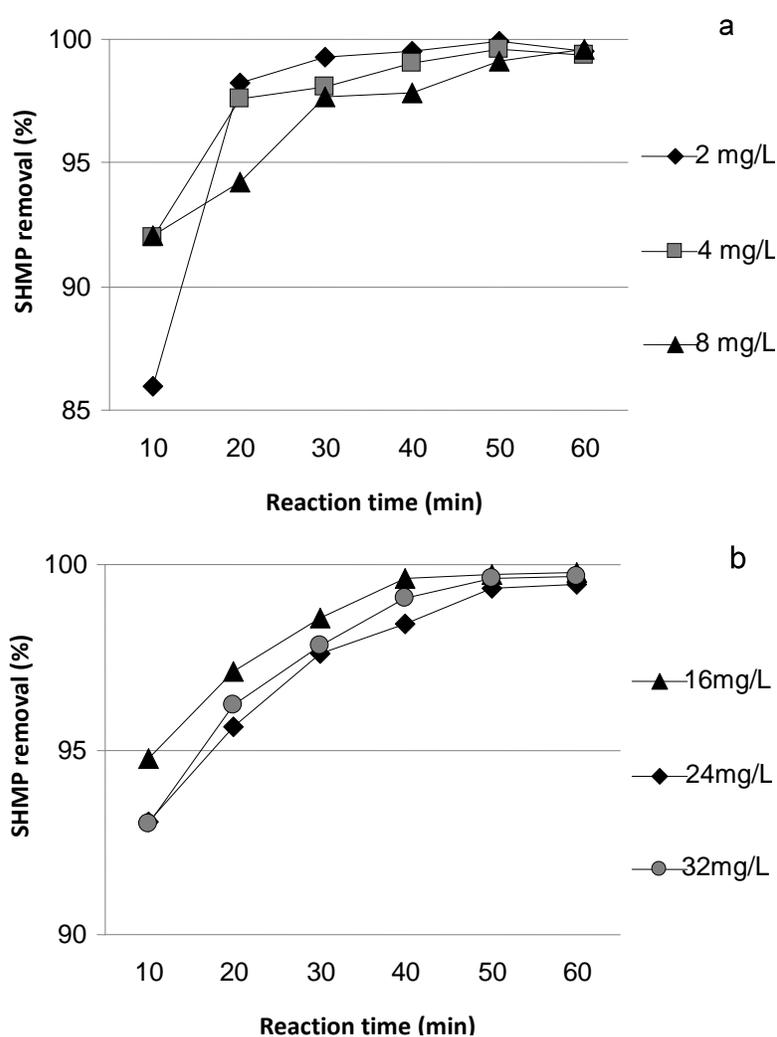
other initial concentrations. The maximum removal efficiencies are 100, 99.76, 99.63, 99.81, 99.45 and 99.66% for initial concentrations of 2, 4, 8, 16, 24 and 32 mg/L, respectively.

The variation of PH during EC process was not recorded

step by step, because this study was done in an uncontrolled pH condition. Therefore, the results showed that pH vary during the EC process from the neutral (initial pH = 7 to 7.5) towards alkaline condition (PH = 8.2 to 9 in treated samples).

Table 3. The residual concentrations of SHMP at different reaction times and various initial concentrations using EC process.

Time (min)	Concentration (mg/L)					
	2	4	8	16	24	32
0	1.98±0.12	0.25±4.23	8.13±0.09	0.25±16.01	23.86±0.4	32.2±0.72
10	0.28±0.04	0.34±0.02	0.65±0.02	0.84±0.03	1.66±0.16	2.26±0.07
20	0.04±0.01	0.1±00	0.47±0.14	0.46±0.05	1.04±0.19	1.22±0.22
30	0.01±00	0.08±0.01	0.19±0.03	0.23±0.05	0.58±0.05	0.7±0.02
40	0.01±00	0.04±0.02	0.18±0.05	0.06±0.01	0.38±0.11	0.29±0.03
50	00±00	0.02±0.01	0.07±0.01	0.04±0.01	0.15±0.02	0.12±00
60	00±00	0.01±0.01	0.04±0.01	0.03±0.02	0.13±0.01	0.11±0.02

**Figure 3.** Variation of SHMP removal efficiency versus time using EC process at various initial concentrations (a and b).

DISCUSSION

Experiments were carried out to remove AMP and

sodium SHMP from the synthetic wastewater using tap water. Two operating parameters that were studied in details include initial concentration of phosphate and

reaction time. Electrochemical process was carried out for 10 to 60 min reaction time for AMP and SHMP initial concentration of 2 to 32 mg/L at constant current density of 1.15 mA/cm². The results showed that the minimum and maximum removal efficiency were 41.52 and 98.72% for AMP and 85.82 and 100% for SHMP, as shown in Figures 2 to 3. It can be seen that the removal efficiency of AMP and SHMP was increased with increase in the reaction time, and the maximum removal efficiency of 98.72% for AMP was obtained for 50 min and for SHMP at 50 to 60 min reaction time. These results are comparable with results obtained by other researchers (Mesdaghinia et al., 2003).

Although, the effects of pH on AMP and SHMP removal were not the subject of this study, but the results showed that the solution pH increases from neutral range (7 to 7.5) to alkaline range (8.2 to 9) during EC process, thus, creating favorable condition for formation of ferric hydroxide flocks. This is compatible with other studies findings (Lacasa et al., 2011; Mesdaghinia et al., 2003).

In addition, the concentration of AMP in synthetic wastewater decreased to 1 mg/L (effluent standard to discharge into receiving water to prevent eutrophication) after 50 min in all initial concentrations of AMP (Mesdaghinia et al., 2003). Thus, the optimum reaction time to efficient removal of AMP by EC process at constant current density of 1.15 mA/cm² are 50 min. Regarding to SHMP in reaction time of 30 min, the residual concentration decreased to 1 mg/L in all initial concentrations of 2 to 32 mg/L. It was found out that the optimal reaction time for removal of SHMP was 30 min. The difference observed between the optimal reaction time is probably due to the formation of larger and more than flock more increase of pH for SHMP. The reaction time observed for SHMP was in agreement with the results of other study found in literature (Lacasa et al., 2011). Statistical analysis of variance (ANOVA and repeated measurement) was performed to determine the correlation between removal degree and the process parameters.

These analyses showed that a significant correlation ($P < 0.05$) exists between removal efficiency of AMP and SHMP, and reaction time does not exist between initial concentration and removal efficiency ($P > 0.05$). Removal efficiency increase with increasing reaction time from 10 to 60 min for removal, for initial concentration of 2 mg/L AMP and reaction time of 10 min, the removal efficiency was 46.99% and reached 93.73% at 60 min reaction time (Figure 2).

There was no significant change in the removal efficiency of AMP and SHMP at initial concentration of 2 to 32 mg/L. These results disagree with the results presented in the literature which is probably due to different operating condition of electrodes material, constant current density and initial concentrations (Bektas et al., 2004; Irdemez et al., 2006c; Vasudevan et al., 2009). The results showed that the maximum removal

efficiency of AMP (98.72%) and SHMP (100%) was achieved at 60 and 50 min reaction time, respectively. It can be concluded that the AMP and SHMP can be decreased to 1 mg/L from the synthetic wastewater by using EC process.

Conclusion

The electrochemical removal of AMP and SHMP from synthetic wastewater was investigated in a bench scale EC process. The results showed that the maximum removal efficiency of 98.72 and 100 % was achieved for AMP and SHMP, respectively. It was concluded that EC process is very efficient for the removal of phosphate from the synthetic wastewater.

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