Research Paper:

Investigation of Electro-coagulation Process for Phosphate and Nitrate Removal From Sugarcane Wastewaters

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How to cite this paper Ebadi E, Asareh A, Jalilzadeh Yengejeh R, Hedayat N. Investigation of Electro-coagulation Process for Phosphate and Nitrate Removal From Sugarcane Wastewaters. Iranian Journal of Toxicology. 2021; 15(1):19-26. http://dx.doi.org/10.32598/ijt.15.1.483.4

http://dx.doi.org/10.32598/ijt.15.1.483.4

Article info:
Received: 10 Jan 2020
Accepted: 28 Oct 2020
Online Published: 01 Jan 2021

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ABSTRACT

Background: Highly-concentrated phosphate and nitrate anions from sugarcane wastewater are often discharged into public waters without standardized treatments. This study assessed the effects of electrical coagulation, initial pH and reaction time in the removal of phosphate and nitrate pollutants.

Methods: We used aluminum electrodes to remove the pollutants at Hakhim Farabi Agricultural and Industrial complex, Khuzestan Province, Iran. A septic tank was used for collecting water samples followed by measuring the pH, and the concentrations of phosphate and nitrate in the samples. The pH was set at 5, 7, 9 or 11. Six aluminum electrodes were placed perpendicular to the water flow and were connected to power in a single-polar method. They were used to assess the effects of pH changes, electrical power at 10 and 30 volts and the water retention time at 15, 30, 45 or 60 min. on the efficiency of the pollutants' removal.

Results: The results indicated that under equal retention time and varying pH values, as voltage increased from 10 to 30, the phosphate and nitrate removal increased progressively. It was further demonstrated that the maximum phosphate removal efficiency was achieved at pH7, while it declined at higher pH levels. The highest possible nitrate removal efficiency was achieved under alkaline pH levels. The overall results showed that at every pH and voltage, the percentage of phosphate and nitrate removal increased over time.

Conclusion: This study demonstrated that electro-coagulation process is an appropriate and efficient method to remove phosphate and nitrate pollutants from sugarcane wastewaters.

Keywords: Electro-coagulation, Phosphate and nitrate anions, Sugarcane wastewater, Environmental protection

Introduction

The growing global population, improved hygiene and health standards, and the industrial and economical development across many nations call for renewable water resources. As the demands for water resources by agricultural, industrial, and domestic sectors increase, there will be a corresponding rise in the volume of wastewaters, the major sources of pollution in the environment [1, 2]. The post-modern era is associated with the accumulation of hazardous industrial materials and wastewater effluents, causing major concerns by the global community [3, 4].

Rivers and other renewable water resources are vulnerable to the increasing rate of global pollution [5, 6]. Wastewater discharges as surface run-offs are the potential pollution sources for aquifers, the underground layers of water-bearing permeable rocks [7, 8].

Recent developments in the agricultural and industrial sectors in Khuzestan Province, Iran, and the associated pollutions call for adopting urgent wastewater treatment measures to mitigate its adverse effect on the environment. The sugarcane wastewater effluents from the plants in Khuzestan contain high levels of phosphate and nitrate. These anions are among the pollutants, the entry of which into the water bodies causes harmful effects on the environment [3, 9, 10]. This renders the pre-treatment and removal of phosphate and nitrate from wastewater bodies an inevitable and crucial issue.

Electro-coagulation is an emerging wastewater treatment technique. It is the process that produces coagulated materials onsite, using electrical current in aluminum or iron electrodes to produce metal anions in the anode and hydrogen gas in the cathode [11-13]. The significant difference between electrical and chemical coagulation is in the method of producing sediments. Chemical coagulation involves adding coagulating materials to wastewaters, causing the production of sediment from pollutants. In electrical coagulation; however, the separation or precipitation process occurs in the presence of metals and metal hydroxides. Based on the latter technique, the colloid matters in water or wastewater are separated by positive electrical charges, resulting in the production of Al^{+3} and Fe^{+3} [13-16]. If aluminum electrodes are used, the chemical reactions Equations 1 - 3 occur in anode, cathode and solution, respectively [17, 18].

1. $AL \rightarrow AL^{+3}) + 3e^{-}$

2. $3H_2O + 3e^{-} \rightarrow \frac{3}{2}H_2 + 3OH^{-}$

3. $AL^{+3} + 3H_2O \rightarrow AL(OH_3 + 3H^{+}$

The generated Al^{+3} and OH- ions in the anode are ultimately shaped in a solid form as $Al(OH)_3$ [19, 20] . Electro-coagulation technique is in fact a combination of oxidation, precipitation and coagulation. Through oxidation in the anode, the sediments are produced and the pollutants become unstable and precipitate. This method has several features, including the applicability to treating various polluted wastewaters, economic and feasible utilization, environmentally friendly, low retention time, easy operation and no need for adding coagulants. In addition, this method produces minimal sludge, the treated water is clear, colorless and without bad odor [14, 16, 21]. The aim of this study was to investigate the effects of specific operational conditions, such as voltage, pH and the retention time for the elimination of phosphate and nitrate contaminants from Hakhim Farabi Agricultural and Industrial farmlands.

Materials and Methods

The research was conducted in Hakim Farabi Agricultural and Industrial Sugarcane Farms, 35 kilometers south of Ahvaz, in the Shadegan region (longitude 30°54 to 31°3 E and latitude 48°31 to 48°39 N). The area under cultivation amounts to 120 square kilometers, producing 170,000 tons of refined sugar annually. In addition, it is planned to produce sugar, molas and bagas for medicinal purposes. The industrial wastewater treatment has been developed over a 25000 m^2 of land with a capacity of 50 m^3 per hour in wastewater treatment. The operation is based on active aerobic and anaerobic sludge processing. The compositions of the spring wastewater processed by this operation are shown in Table 1.

Hakim Farabi Agricultural and Industrial Sugarcane Farmlands were selected as the typical sample-taking sites, where the wastewaters are discharged into septic tanks at the treatment plant. Samples were taken from three different points (1/3, 1/2 and 2/3 along the tanks). They were taken at a depth of one meter and kept in a polyethylene container at pH<2 and 4°C. The samples were then transported to the water quality control laboratory, stationed at the above mentioned Farabi farms to perform analyses on the physical and chemical constituents of the samples.

The elimination process of phosphate and nitrate contaminants was carried out by electro-coagulation method, with their pH levels adjusted at 5, 7, 9 or 11. Some of the wastewater samples were filtered for refinement, using Whatman paper No. 41. The phosphate and nitrate contents of the wastewater samples were determined on a spectrophotometer (Hach, 5000; Loveland, CO, USA). The pH was measured by a pH meter (Lab Metrohm, 827, Switzerland).

Electrical coagulation process: The electrical coagulation process involved feeding the reservoir of PS 3020 Taiwanese model to convert the alternative current to DC. Six perforated aluminum electrodes (15×3cm, 2mm thick) with an effective area of 45 cm2 each and 3cm apart were placed in a rectangular tank (19×9×18 cm). The tank was made of reinforced glass, totally resistant against acidic corrosion. The six electrodes (3 anodes & 3 cathodes) were placed perpendicular to the direction of the electrical current and were connected to power. The system was started out while adjusting a transformer between 10 and 30 volts with the

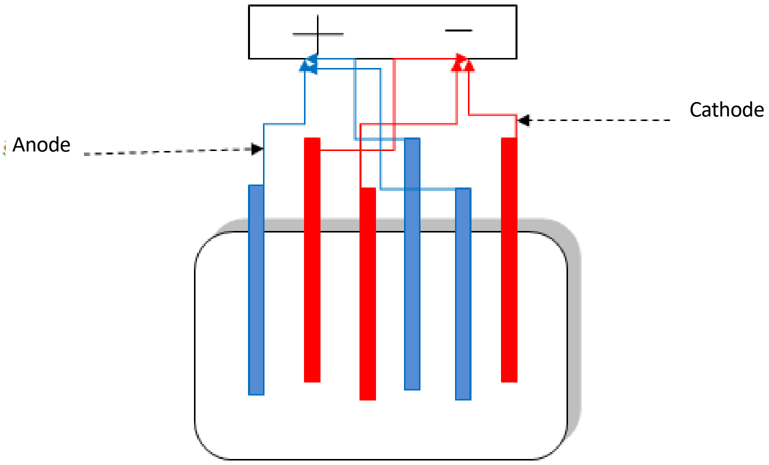

Figure 1. Schematic diagram of the electro-coagulation system

rotation time of 15, 30, 45 or 60 minutes. The aluminum plates were positioned in the wastewater samples.

The transformer was switched off at the end of the predetermined rotation times and observing the effects of anode and cathode plates. Each sample was then poured into the laboratory container and filtered on a Whatman paper No. 41. The methodology used to measure nitrate and phosphate contents of the processed samples, was identical to those applied to the control samples but without adjusting the pH or turning on the electrical current. The data obtained from each sample were systematically analyzed and compared to the control samples. The electrodes were initially washed under tap water and wiped with hydrochloric acid at the beginning of each experiment to remove the impurities, and dried before immersing them into the wastewater samples.

The schematic configuration of the electro-coagulation system is illustrated in Figure 1. The efficiency of phosphate and nitrate removal was calculated by Equation 4:

4. $\text{Parameter reduction} = (C0 - C1) / C0 \times 100$

Where C1 and C0 represent the rates of phosphate and nitrate before and after the electro-coagulation experiments.

Results

The results indicated that at identical reaction time of electrolysis, increasing the voltage from 10V to 30V increased the efficiency of phosphate and nitrate removal. Considering the similarity of the results at different pH values, the

Table 1. Wastewater specifications from the sugarcane production plant

Row	Parameter	Unit	Max.	Min.	Mean±SD
1	Color	-	Grey		
2	pH		11.50	6	8.75±2.75
3	Temp	C0	55	35	45±10
4	Concentration		9.97	0.2	4.885±5.085
5	COD	mg/ L	7000	6000	6500±500
6	BOD	mg/ L	3500	3000	3250±250
7	TDS	mg/ L	3000	1000	2000±1000
8	TSS	mg/ L	400	300	350±50
9	EC	µs/Cm	4000	1000	2500±1500
10	Turbidity	NTU	400	200	300±100

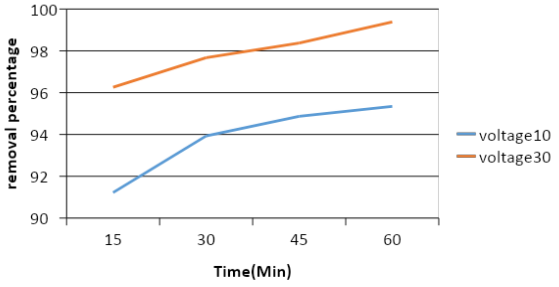

Figure 2. Effect of differential electrical potential on the efficiency of phosphate removal at pH7

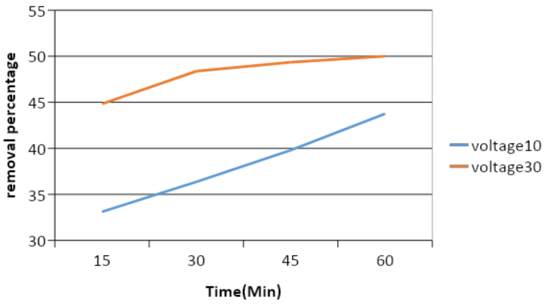

Figure 3. Effect of differential electrical potential on the efficiency of nitrate removal at pH7

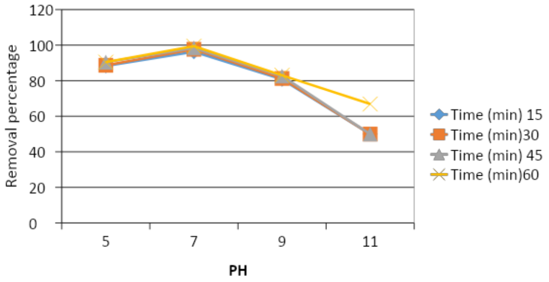

Figure 4. Effect of pH on efficiency of phosphate removal at 30 volts

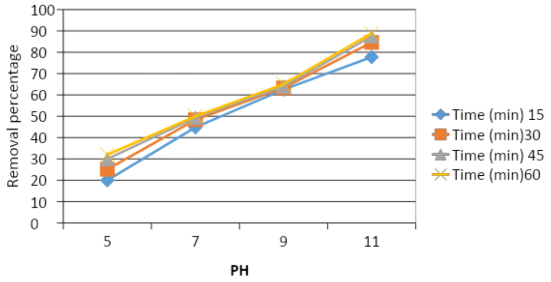

Figure 5. Effect of pH on the efficiency of nitrate removal at 30 volts

data for the experiments conducted at pH7 are shown in Figures 2 and 3.

The effect of different pH values on the phosphate removal efficiency at 30 volt is shown in Figure 4, indicating that the highest phosphate removal was achieved at pH7. The effect of pH on the nitrate removal at 30 volt is presented in Figure 5. It shows the highest nitrate removal was achieved at alkaline pH levels. Further, increases in pH values increased the percent removal of the nitrate contaminant.

The effect of the reaction time on the phosphate removal efficiency at different pH values at 30 volts is shown in Figure 6. It reveals that the rates of phosphate removal increased at different pH values with increasing the reaction time. The highest percentage of phosphate removal (99.38%) was achieved at pH7 and a reaction time of 60 minutes. The lowest percent of phosphate removal (50%) was achieved at pH11 and a reaction time of 15 minutes.

The effects of reaction time on the percent removal of nitrate at 30 volts and varying pH values are shown in Figure 7. It was found that an increase in the reaction time increased the percentage of removed nitrate. The highest percentage (88.9 %) of nitrate removal was achieved at pH11 and a reaction time of 60 minutes. The lowest percentage (20%) of nitrate removal was achieved at pH5 and a reaction time of 15 minutes.

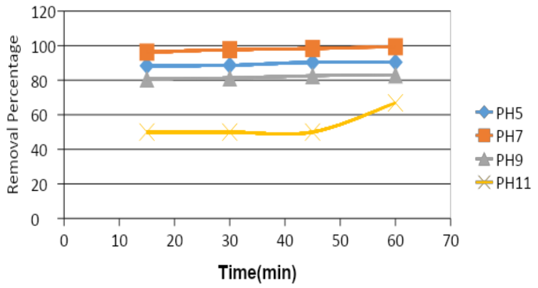

Figure 6. Effect of retention time on the efficiency of phosphate removal at various pH values

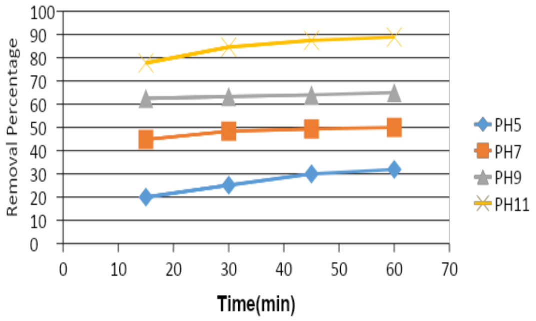

Figure 7. Effect of retention time on efficiency of nitrate removal at various pH values

Discussion

As reflected in Figures 2 and 3, the results demonstrated that at equal reaction time and different pH values, the percent removal of phosphate and nitrate increased as the voltage current increased from 10 to 30. According to previous studies [22, 23], the time needed to achieve a similar percentage of removal of these pollutants decreased as the voltage increased and vice versa. The reason is that increases in the current voltage caused increases in electrodes releasing anions, resulting in greater sediment formed due to the pollutant removal [22, 23]. Further, decreases in the bubble size and increases in the rate of bubble formations occurred at higher voltages. Thus, increasing the voltage increased the sludge formation and the pollutant removal [24].

Based on the findings reported by a previous study [25], it was confirmed that the highest percent removal of the parameters was achieved at a reaction time of 60 minutes and electrical potentials of 60-98.8V. These authors studied the effect of reaction time at 15, 30, 45 or 60 minutes and voltage 10, 20, 30, 40, 50 or 60V in the removal of water pollutants, using an electro-coagulation method.

Based on the results of this study, one may conclude that pH is the main and effective factor in the electro-coagulation process. As seen in Figure 4, the best efficiency for phosphate removal was achieved at neutral pH. However, the removal efficiency of phosphate decreased as the pH increased. It has been suggested that the phosphate removal efficiency in electro-coagulation process depends on the initial pH [26]. Also, it has been reported that aluminum is influenced by pH and chemical substances in the reaction, and can be released in different forms [27]. Further, these authors stated that at pH7, aluminum is produced in the form of polymer Al13O4 (OH)24+7 and the release of $Al(OH)_3$ increases the formation of coagulate and the removal efficiency of phosphate [28]. The findings of the latter study showed that at pH 2-4, $Al(OH)^{+2}$ and Al^{+3} were the prominent material, but at pH values greater than 10, aluminum hydroxide will be substituted with some forms of $Al(OH)^{-4}$. It is worth noting that the ability of $Al(OH)^{+2}$ and $Al(OH)^{-4}$ is less than that of $Al(OH)_3$ in floc form. Flocs are the fine particles in a solution, which either float to the surface or precipitate. The highest phosphate removal efficiency was achieved at pH7 [29].

As reflected in Figure 5, it is evident that at both 10V and 30V, the most nitrate removal efficiency was achieved at alkaline pH. Evidently, rises in the pH values increases the rate of nitrate removal. As suggested by another study [23], increases in pH values raise the nitrate removal efficiency that could be attributed to the increased reaction between the metal and hydroxide ions in the solution. According to another study [30], the effects of initial NO_3-concentration, initial pH, applied voltage, and NaCl concentration on the nitrate removal efficiency reached 100% after 100 min [30]. In that study, more than 80% of the nitrate removal was achieved at 60 min and pH7 [30].

Based on the data presented in Figures 6 and 7, it is clear that at the selected pH values (5, 7, 9, 11) and voltages (10V & 30V), increasing the reaction time increases the percent removal of phosphate and nitrate by the electro-coagulation method. Based on the Faraday law (WA = (I×T×M) / (N/F), where, WA is the reduced anode weight in grams, I is the voltage, T is the utilization time in seconds, M is the molecular mass of the anode, N is the electron values released from the anode, and F is the Faraday coefficient. The produced coagulant amount is directly related to the reaction time; i.e. as the time increases, more coagulates are formed, leading to greater removal efficiency [31]. Another study has suggested that the non-gaseous materials, such as nitrite ammonium (NH_4NO_2) and nitrate ammonium (NH_4NO_3), increase the nitrate removal efficiency in the solution [32]. Finally, a study has reported that the reduction in the replaced chloride ions in the absorption sites results in nitrate reduction in the solution. Hence, the reasons for reduction in nitrate removal efficiency when the reaction time exceeds 66 minutes [33].

Conclusion

This study concluded that the treatment of sugarcane wastewater to remove phosphate and nitrate by electro-coagulation process is one of the environmentally friendly methods. We found that the highest removal efficiency was achieved at alkaline pH for nitrogen and neutral pH for phosphorus, at 30 volts. Also, the removal efficiency improved over longer reaction times. The present study demonstrated that the electro-coagulation process can be used to treat wastewaters from sugarcane and similar industries. Wastewaters produced by food industries contain contaminants, and if not treated before being discharged into environmental waters and soils, they are hazardous to humans. Therefore, application of new methods in the treatment of industrial wastewaters is essential, considering their low costs and high efficiency. We suggest future studies investigate the removal efficiency of other contaminants and their economic impact compared to those achieved by other methods.

Ethical Considerations

Compliance with ethical guidelines

This article does not contain any studies with human participants or animals.

Funding

This article was extracted from the MSc. thesis of the first author, Department of Environmental Engineering, Ahvaz Branch, Islamic Azad University.

Author's contributions

All authors contributed in preparing this article.

Conflict of interest

The authors declared no conflict of interests.

Acknowledgements

The authors appreciate the Islamic Azad University of Ahvaz for providing financial and instrumental support to conduct this work.

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