Removal of ammonium and phosphate from slaughterhouse wastewater by electrochemical method using magnesium electrodes

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ABSTRACT

In this research, the treatability of slaughterhouse wastewater was investigated by using the electrochemical method with Mg electrodes. The influence of the variables such as initial pH (4, 5, 6, 7, 8, and 9), current density (15, 30, and 45 mA/cm^2), and reaction time (20, 25, and 30 min) on the removal efficiency of ammonium and phosphate was studied. The highest phosphate removal efficiency was reached at 100% after 20 min of electrochemical treatment with 30 mA/cm^2 of current density and initial pH 6. Meanwhile, the maximum removal percent of ammonium was approximately 52%. Thus, this method is feasible to apply for the removal of phosphate and ammonium in slaughterhouse wastewater.

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1. Introduction

As the economy is growing, people's living standards are increasing day by day. Therefore, the basic needs also increase, especially food is one of the indispensable needs. Livestock and poultry slaughter takes place every day to meet the people's demand for meat products. Meat consumption has been steadily increasing in recent decades. The slaughtering of animals and the cleaning of slaughterhouse facilities and meat processing plantsgenerates substantial amounts of slaughterhouse wastewater (Bustillo-Lecompte & Mehrvar, 2015). The composition of slaughterhouse wastewater changes greatly depending on the various industrial processes and unique water requirements (Matsumura & Mierzwa, 2008; Bustillo-Lecompte et al., 2014). Because of the presence of organic materials such as blood, fat, grease, and proteins, these wastewaters have high levels of organics such as biochemical oxygen demand (BOD) and chemical oxygen demand

(COD), nitrogen, and phosphorus (Sirianuntapiboon & Manoonpong, 2001). As a result, slaughterhouse waste water requires treatment before they can be released into the environment in a safe and sustainable manner.

Traditionally, aerobic and anaerobic methods are applied to slaughterhouse wastewater treatment. Nonetheless, biological processes necessitate long hydraulic retention times and huge reactor capacities, as well as high biomass concentration and sludge loss control (Kobya et al., 2006). In recent years, the application of an electrochemical technique to successful wastewater treatment and resource recovery has attracted interest (Hand & Cusick, 2021; Salazar-Banda et al., 2021; Escobedo et al., 2022). Compared with conventional physico-chemical processes, electrochemical has many advantages such as simple equipment, easy operation and automation, a short retention time, low sludge production and no chemical requirement.

Electrode material can play a very important role in the electrolytic degradation of ammonium and phosphate present in wastewater. In this study, magnesium electrode material was used to examine the efficiency of the electrochemical removal of ammonium and phosphate in slaughterhouse wastewater. The process was examined under different values of current density, pH, and reaction time in order to determine optimum operating conditions.

2. Materials and Methods

2.1. Materials and characterization of wastewater

The wastewater was collected from a local slaughterhouse located in Di An city, Binh Duong province, Vietnam. The samples were eliminated hair and large suspended particles. The wastewater samples were stored at 4°C before use in experiments and further studies. The characteristics of slaughterhouse wastewater are shown in Table 1. The chemicals used in this study were purchased from Xilong Scientific Co., Ltd., China with a purity of 99%. Magnesium electrodes were chosen for use as both anode and cathode. Electrodes are manufactured according to Italian technology with chemical components including Al 2.5-5.5%, Zn 2.5-3%, Mn 0.2-4%, Cn 0.01%, Si 0.01%, Fe 0.006%, Ni 0.001%, the rest is Mg.

Table 1. The characterization of slaughterhouse wastewater used in this study

Parameters	Unit	Value
pH	-	7 - 7.2
COD	mg/L	863 - 935
TSS	mg/L	328 - 384
$NH_4{}^+$	mg/L	186 - 194
$PO_4{}^{3-}$	mg/L	34 - 35
Mg^{2+}	mg/L	12 - 16
Ca^{2+}	mg/L	18 - 23

COD: Chemical oxygen demand; TSS: Total suspended solids.

2.2. Experimental setup

According to previous studies (Ahmadian et al., 2012; Ozturk & Yilmaz, 2019) , the experiments were conducted by a laboratory-scale reactor using Berker 1000 mL (Figure 1). In the studies, 800 mL of wastewater was used. The cylindrical Mg electrodes had the following parameters: diameter of 1.8 cm, length of 10.5 cm, and effective area of 66.73 cm^2. All electrodes were arranged vertically in which the distance between the electrodes was 6 cm. They were connected to terminals of a direct current power supply (ROBOT®, model: 11JA, Vietnam) which is characterized as 10 A and 12/24 V. The laboratory-scale reactor has been stirred at 120 rpm by a magnetic stirrer (Thermostat magnetic stirrer 85-2, China).

Batch mode experiments were conducted to investigate the efficiency of ammonium and phosphate removal in slaughterhouse wastewater. The influence of varied reaction conditions on ammonium and phosphate efficiency were examined by altering the initial pH samples (viz., 4, 5, 6, 7, 8, 9), current density (viz., 15, 30, 45 mA/cm^2), and reaction time (viz., 20, 25, 30 min). At the end of each treatment, the samples were left to stand for 30 min, then filtered and analyzed. All of experiments were carried out in triplicates. The removal efficiency of pollutants was calculated using the following equation:

$$\text{Removal efficiency } (\%) = [(C_0 - C_t)/C_0\ ] \times 100 \quad (1)$$

where C_0 is the initial concentration of the pollutants and C_t is the concentration of the pollutants at reaction time t.

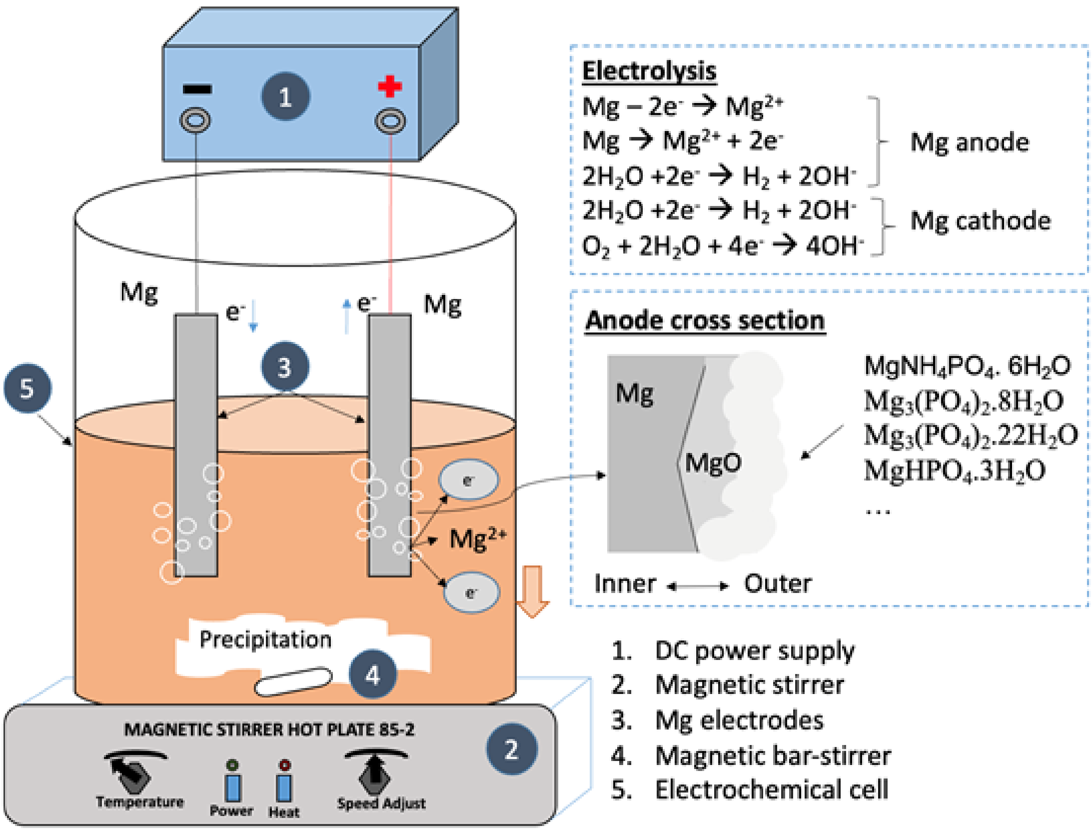

Figure 1. Electrochemical reactor schematic.

2.3. Analytical methods

The characterization of slaughterhouse wastewater including chemical oxygen demand (COD), total suspended solids (TSS), NH_4^+, PO_4^{3-}, Mg^{2+}, and Ca^{2+}+ was analyzed in accordance with standard methods for water and wastewater examination (Rice et al., 2012). The pH was measured using a pH meter (HI98107 Hanna). SPSS software was also used to analyze the data, as well as the variance test (one-way ANOVA) for mean comparisons.

3. Results and Discussion

3.1. Influence of initial pH

The effect of initial pH on the removal of ammonium and phosphate was investigated at a constant current density of 30 mA/cm^2 and reaction time of 20 min. As seen in Figure 2, the performance removal of ammonium gradually increased with the initial pH range of 4 – 6. However, it can be seen that the removal efficiency of ammonium decreased when the initial pH range of 7 – 9. The highest NH_4^+ removal efficiency (approximately 52%) is obtained when the initial pH is 6. In table 2, the results showed a significant difference in the treatment efficiency when increasing the pH value beyond 6 ($P < 0.05$). For phosphate, high PO_4^{3-} removal percent may be attained in the pH range of 4 – 8. At this pH range, the PO_4^{3-} removal completely occurred. When the pH is increased to 9, the PO_4^{3-} removal efficiency tends to slightly decrease, and the difference is statistically significant ($P < 0.05$).

Table 2. The removal efficiecy of ammonium and photphase at current density: 30 mA/cm^2, and reaction time: 20 min

Treatments	Removal efficiency (%)	
	NH_4^+	PO_4^{3-}
pH 4	$48.4^a \pm 1.4$	$100^a \pm 0.0$
pH 5	$50.2^a \pm 1.7$	$100^a \pm 0.0$
pH 6	$51.6^a \pm 1.4$	$100^a \pm 0.0$
pH 7	$37.8^b \pm 1.6$	$99.7^a \pm 0.3$
pH 8	$35.0^b \pm 2.3$	$99.5^a \pm 0.2$
pH 9	$34.6^b \pm 2.1$	$91.3^b \pm 1.4$

In the same raw, numbers with the same letter do not have a statistically significant difference; significant difference at the level of $\alpha = 0.05$.

This result is explained by the complicated reaction mechanism of ion Mg^{2+}, NH_4^+, and

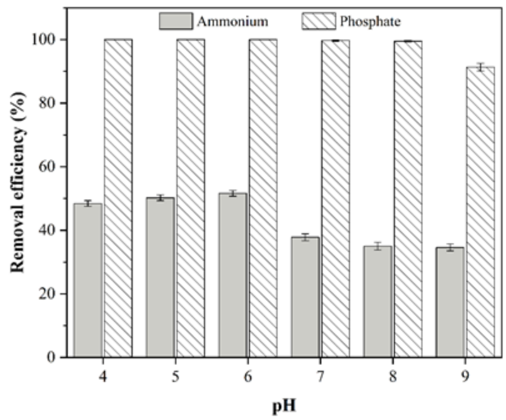

Figure 2. Influence of pH on ammonium and phosphate removal (current density: 30 mA/cm^2; reaction time: 20 min).

PO_4^{3-} in solution (Figure 1). According to the report of Carmona-Carmona et al. (2020), it is observed that from pH 5, the precipitation of solids were formed, which could correspond to $MgHPO_4.3H_2O$ (newberyite). The precipitates could correspond to $Mg_3(PO_4)_2.8H_2O$ (bobierrite) and $Mg_3(PO_4)_2.22H_2O$ (cattiite) when pH 8.5. Besides, the elimination of NH_4^+ could be related to the creation of struvite because it is feasible to stimulate the $MgNH_4PO_4.6H_2O$ formation, which is one of the most critical forms of precipitation of the dissolved phosphorus.

3.2. Influence of current density

The Figure 3 represents the effects of the current density on NH_4^+ and PO_4^{3-} removal efficiency, for magnesium electrode material, with a reaction time of 20 min and pH 6. In general, increasing current density improved processing efficiency. In the case of ammonium removal, the highest removal efficiency was obtained for the current density of 45 mA/cm^2 was approximately 52%. As can be seen in Figure 3, the experiment achieved PO_4^{3-} removal efficiency of above 95% when increased current density. At the current density of 30 mA/cm^2, the PO_4^{3-} removal efficiency was obtained approximately 100%. It is possible to argue that the rise in current density has accelerated the elimination of contaminants due to the generation of extra electrons (Ozturk & Yilmaz, 2019). Phosphate elimination was accelerated by increasing the current in wastewater as a result of increased Mg^{2+} generation to enhance precipitation. Nonetheless, the cur-

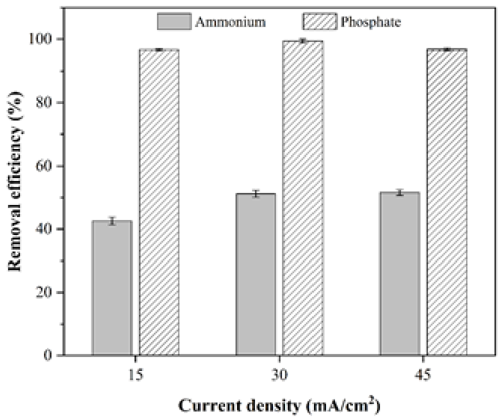

Figure 3. Influence of current density on ammonium and phosphate removal (initial pH: 6; reaction time: 20 min).

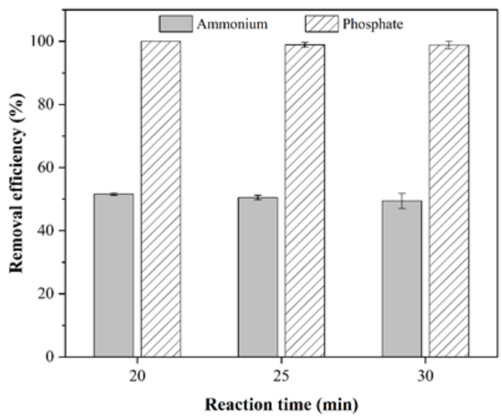

Figure 4. Influence of reaction time on ammonium and phosphate removal (initial pH: 6; current density: 30 mA/cm^2).

rent density also strongly influences the metal dissolution leading to a change in the mass of the electrodes. Therefore, in order to facilitate the removal of NH_4^+ and PO_4^{3-}, as well as reduce electrode wear, the optimal current density was selected as 30 mA/cm2. In Table 3, the results showed that the association between different current density was statistically significant ($P < 0.05$).

Table 3. The removal efficiecy of ammonium and photphase at pH 6, reaction time: 20 min

Current density	Removal efficiency (%)	
	NH_4^+	PO_4^{3-}
15 mA/cm^2	$42.6^a \pm 1.5$	$96.7^a \pm 0.3$
30 mA/cm^2	$51.2^b \pm 1.3$	$99.4^b \pm 0.8$
45 mA/cm^2	$51.6^b \pm 1.1$	$96.8^a \pm 0.5$

In the same raw, numbers with the same letter do not have a statistically significant difference; significant difference at the level of $\alpha = 0.05$.

3.3. Influence of reaction time

To investigate the effect of reaction time, the current density was set to 30 mA/cm^2 and the pH of the wastewater was adjusted to 6. The result of experiment is shown in Figure 4. In general, the removal effectiveness of NH_4^+ and PO_4^{3-} slightly decreased as the reaction time increased. In the case of ammonium removal, when reaction time was set to 20 min, the removal efficiency of NH_4^+ was approximately 52%. For phosphate, the PO_4^{3-} removal completely occurred (100%). In fact, the Mg^{2+} ion concentration increased as reaction time increased (Abdel-Shafy et al., 2020). After 20 min, however, it is obvious that removal efficiencies of both NH_4^+ and PO_4^{3-} have not significantly changed. This could be due to the discovery of dissolved metal ions and their hydroxides during the saturation stage of floc development. This result tends to be similar to the study of Luo et al. (2022). Thus, the optimum reaction time chosen was 20 min. Results of one-way ANOVA showed no difference between different reaction times ($P > 0.05$).

4. Conclusions

The current study explored the feasibility of simultaneous removing NH_4^+ and PO_4^{3-} from slaughterhouse wastewater using an electrochemical technique. The experimental results demonstrated that treating phosphate and ammonium from slaughterhouse wastewater is achievable by using magnesium as the electrodes. Moreover, the current density, reaction time, and initial pH are the key factors influencing the removal efficiency. On the other hand, when using Mg electrodes for electrolysis can form useful products in the form of fertilizers. Further research on the pilot plant size will disclose the economic feasibility of treating slaughterhouse wastewater with electrochemical method.

Conflict of interest

The authors declare no conflict of interest.

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