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Removal of ammonia and COD from leachate by MAP precipitation method and contribution of natural materials

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ABSTRACT

The objective of this study was to examine the preliminary treatment of landfill leachate by magnesium ammonium phosphate (MAP) precipitation. For this purpose, the optimum conditions for ammonia and chemical oxygen demand (COD) removal have been investigated. In MAP precipitation, experiments, various stoichiometric ratios were tried to provide the best ammonia removal efficiency. The maximum ammonia removal was found to be 80% at pH 9.5 and Mg:NH_4:PO_4 molar ratio of 1:1:2.5. As a result of the study, the feasibility of the MAP process was evaluated and the application principles of the process were defined. Then, the contribution of natural materials to the MAP precipitation was examined. For this purpose, zeolite, sepiolite and diatomite were added to the system at a dose of 2 g/L. Ammonia and COD removal was increased by about 10%, while no significant difference was observed between natural materials. Experimental data were also evaluated by statistical methods and the regression equations of ammonia and COD removal were obtained using Minitab 16 statistical software.

Keywords: MAP precipitation; Leachate; Ammonia removal

1. Introduction

Sanitary landfills are widely used due to the low cost and effectiveness of municipal solid waste disposal in Turkey as well as in other developing countries [1,2]. One of the biggest environmental risks of sanitary landfills is leachate [3,4].

Landfill leachate is one of the wastewater types that cause the greatest environmental impact as it contains high amounts of organic matter, inorganic ion, and ammonia nitrogen (NH_4–N). Discharge of this wastewater to the receiving environment without suitable treatment can cause serious pollution in both groundwater aquifers and surface waters. Therefore, the organic matter and ammonia nitrogen must be removed from the leachate before the leachate is discharged to the natural waters [5,6].

Due to the complex composition and the high pollutant content, many physical-chemical and biological treatment methods have been applied to treat the landfill leachate. Among these methods, biological processes are considered to be cost-effective and usable. However, due to the high concentration of ammonia nitrogen and the lack of sufficient electron donors in the leachate, the performance of the conventional activated sludge process used to treat the landfill leachate was not satisfactory [7,8].

In recent years, magnesium ammonium phosphate (MAP) precipitation has been successfully applied to industrial wastewaters as well as municipal landfill leachate for the removal of nitrogen in the form of ammonia. [9–12]. Leachates contain low concentrations of magnesium and phosphorus, so it is necessary to add these compounds

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externally. However, for stabilized leachates characterized by high ammonium concentrations and very low BOD/COD (chemical oxygen demand) ratios, the MAP process can potentially compete even with the cheapest method available. Due to its high effectiveness, reaction rate, simplicity, and environmental sustainability, the precipitation of ammonium by MAP formation is a valid alternative for the removal of high ammonium concentrations from leachate [10].

MAP is a white insoluble crystalline compound that can occur naturally when the concentrations of Mg, NH_4, PO_4 in solution are higher than the solubility limits [10]. The basic chemical reaction to form MAP has been expressed in Eq. (1) [10–14].

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 \times 6H_2O \downarrow \quad (1)$$

In this study using MAP precipitation method, ammonia removal from leachate was experimentally investigated and the application principles of the process were described. In addition, the effects of natural materials on the process were examined. Additionally, the linear regression analysis was applied to experimental data using Minitab 16.

2. Material and method

2.1. Material

All experiments were carried out on a laboratory scale and experimental studies were performed on the landfill leachate samples taken from Samsun Metropolitan Municipality Solid Waste Landfill. Samsun Solid Waste Landfill is approximately 10 km from the city center. The site consists of three lots and the total area is 18.5 hectares. On-site waste storage operation has been carried out from May of 2008. At the moment, 780 t of waste is stored in the field per day.

The characterization of the raw leachate used in the experimental study is given in Table 1. Ammonia, pH, COD, and PO_4–P analysis were carried out for each sample taken during the study and the average values are given in Table 1.

In the MAP precipitation process, $MgSO_4·7H_2O$ was used as the magnesium source, K_2HPO_4 was used as the phosphate source, and 6N NaOH was used to increase the pH.

2.2. Analysis

The collected MAP precipitates were washed with distilled water three times, dried in an oven at 40°C for 48 h, and then analyzed by X-ray diffraction (XRD, Rigaku, Smartlab) and scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDX, JEOL JSM-7001F). The results of XRD and SEM-EDX are given in Figs. 1 and 2.

The XRD graph shows that the precipitate is close to the MAP standard pattern [15]. According to SEM analysis, MAP crystal is amorphous, rough surface and irregular in size. In the EDX analysis, while the composition of the precipitate has a high percentage of O, Mg, Si, P, Al elements, a low percentage of trace elements such as Fe, Ca, Cl, Na are found (Fig. 2).

The concentrations of NH_4 and COD were measured according to Standard Methods [16].

2.3. Experimental study

The MAP precipitation experiments were carried out on a Velp JLT6 model jar test system. Ammonia nitrogen was determined by Kjeltec System 1002 Distilling Unit Tecator Kjeldahl nitrogen detection device. The experiments were carried out at room temperature.

The effect of initial pH value on the removal of ammonia and COD was examined at three different initial pH values.

Different mixing times have been tried between 2 min and 120 min to determine the optimum mixing time in the MAP precipitation process. NH_4–N, and COD analysis were carried out on the samples taken after 30 min residence time after stirring at 150 rpm.

Various stoichiometric ($Mg:NH_4:PO_4$) ratios have been tried to achieve the best ammonia and COD removal efficiency as a result of MAP precipitation.

For this purpose, the efficiency of ammonia and COD removal was determined by keeping the NH_4 and PO_4 doses

Table 1
Characterization of the landfill leachate used in this study

Parameters	Average
pH	8.5
NH_4–N, mg/L	1,800
COD, mg/L	21,300
PO_4–P, mg/L	27
Cl^-, mg/L	3,315
NO_3, mg/L	3,217
SO_4, mg/L	4,264
NO_2, mg/L	127
Ca, mg/L	406
Na, mg/L	1,118
EC, µS/cm	28,600

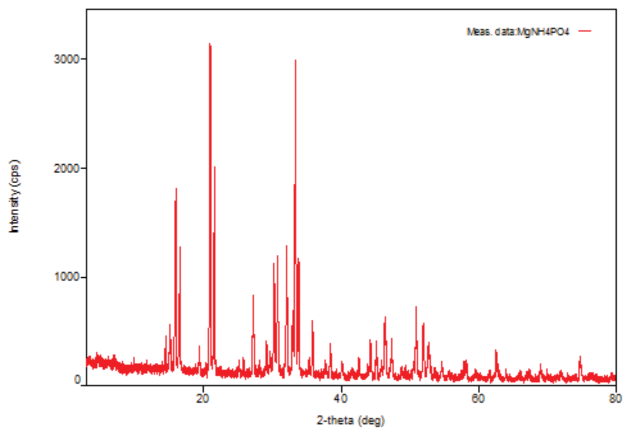

Fig. 1. XRD graph of leachate using MAP precipitation method under optimum conditions.

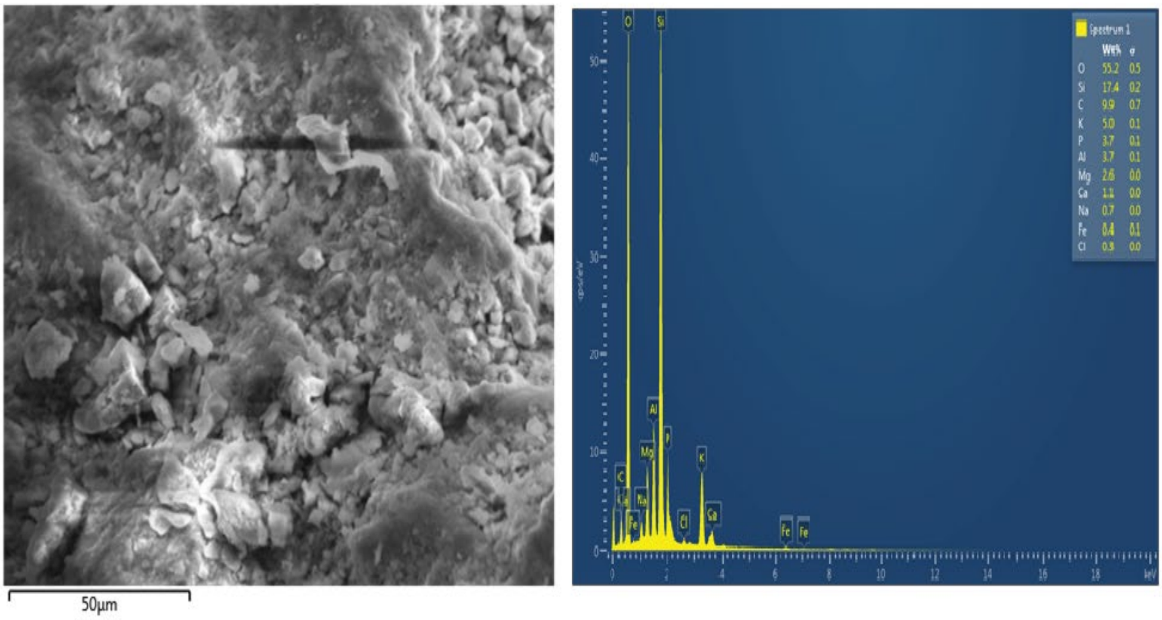

Fig. 2. SEM image and EDX graph taken under optimum conditions using MAP precipitation method in leachate.

fixed and increasing the Mg ratio 3 times. Then Mg and NH_4 doses were held constant and the PO_4 ratios were increased up to 2.5 times, after which the ratio of both Mg and PO_4 was increased by keeping the NH_4 dose constant. As a result of the experiments, ammonia and COD removal efficiencies were measured.

2.4. Regression model

The regression model is a statistical procedure that allows a researcher to estimate a relationship that relates two or more variables [17]. Regression analysis is a statistical technique used to determine mathematical relationships between depending on variable y and independent variables x [18]. The relationship can be described as a different mathematical formula as a linear curvilinear exponent. The linear regression analysis is the most used and the simplest method. The formula of the linear regression analysis can be written as follows,

$$y_i = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \varepsilon_i \tag{2}$$

where x_i is the independent variable and y_i is the dependent or response variable, β_i is coefficients, ε_i is the noise of model [19].

In this study, 38 and 22 experimental data were realized to determine ammonia and COD removal respectively. The linear regression analysis was made using Minitab 16.

3. Results and discussion

3.1. Determination of MAP precipitation conditions

When the results obtained from the leachate characterization study are compared with the literature data, it can be said that the measured concentrations of pollutant parameters are in the range of values given in the literature.

3.1.1. Effects of initial pH

According to the literature, the range of pH, which is one of the significant factors of MAP precipitation is between pH 8–10 [20]. Experimental studies were carried out using natural pH (8.6), pH 9.0 and pH 9.5 values to find the optimum pH value. When the results of the experiment were examined, an increase in removal efficiency was observed with increasing pH (Fig. 3). This is because ammonia behaves as a moderately strong base between pH 9 and 10 and provides an increase in ammonia removal efficiencies [21]. NH_4–N removal efficiency at natural pH was 28.9%, and COD removal was 10.52%. NH_4–N removal efficiency at pH 9.5 was 59.85% and COD removal was 16.73%. According to these results, the best removal efficiencies were obtained at pH 9.5.

3.1.2. Effects of stirring time

An optimum time was required for the reaction of ammonia, magnesium and phosphate ions. In the experimental study, NH_4–N and COD removal efficiencies were examined between 2–120 min at Mg:NH_4:PO_4 molar ratio of 1:1:1 and pH 9.5.

According to the data obtained, NH_4-N removal efficiencies were between 54% and 58% and did not change much during the stirring time of 2–20 min. After 30 min, the ammonia removal efficiency reached 62% and remained unchanged at about 64% for up to 120 min. Therefore, it was concluded that the mixing time did not have a significant effect on ammonia removal efficiency. COD removal efficiency increased by only 3% between 2 min and 120 min (Fig. 4).

Considering that increasing the mixing time did not affect NH_4–N and COD removal efficiencies significantly and the cost of the process increases with increasing time, it was concluded that the optimum time is 2 min.

Öztürk [22] performed MAP precipitation at different times between 1–180 min and observed that there was no significant increase in NH_4–N removal efficiency, and 1 min was selected as the optimum mixing time. This result also supports the results of our study.

3.2. Effects of $Mg:NH_4:PO_4$ ratios

PO_4–P, Mg, and NH_4–N were three basic ions to form MAP precipitate and to affect the crystallization of struvite. An appropriate $Mg:NH_4:PO_4$ molar ratio is important for NH_4–N removal [23].

3.2.1. Effect of increasing molar ratios of Mg

In this study, the $Mg:NH_4:PO_4$ molar ratios from 1:1:1 to 3:1:1 were investigated. At the stoichiometric ratio of MAP precipitation (1:1:1), ammonia removal was achieved as 56% and COD remained at 28%. When the Mg ratio was increased to 3 times, the ammonia and COD removal efficiencies were increased, but it was observed that the increase after the Mg ratio of 2.5 times was not significant. This indicates the saturation of the leachate to the Mg.

For ammonia at the highest Mg ratio (3:1:1) 70% removed was obtained, while for COD, 32% removed was obtained. The MAP precipitation experiment results, in which the Mg ratio was increased and the other constituents are kept constant, are presented in Fig. 5.

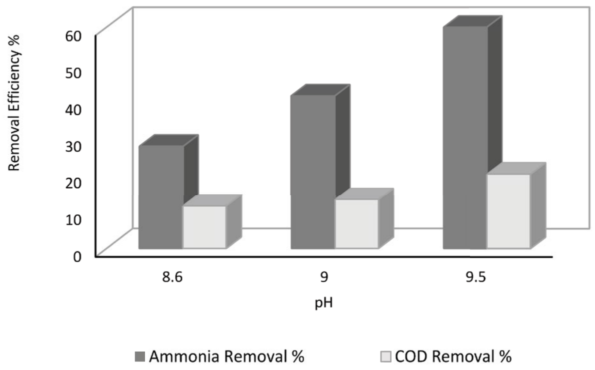

Fig. 3. Effect of initial pH on removal efficiency ($Mg:NH_4:PO_4$ molar ratio of 1:1:1).

3.2.2. Effect of increasing molar ratios of PO_4–P

The PO_4 molar ratio from 0.55 to 2.5 was studied by keeping NH_4 and Mg molar ratio constant. According to the MAP precipitation results, the ammonia removal was 40% and the COD removal was 24% at $Mg:NH_4:PO_4$ ratio of 1:1:0.55. When we increase PO_4 ratio up to 2.5 times, a continuous increase in ammonia and COD removal efficiency was observed. This shows that PO_4 in the leachate was low and that the leachate is not saturated. Higher PO_4–P has not been tried to avoid high PO_4 concentrations in effluent.

The best ammonia and COD removal efficiency was achieved for 1:1:2.5-mole ratios. Ammonia was removed by 80%, COD by 35%. It is clear from these results that the concentration of PO_4 was the rate limiting factor in the MAP precipitation reaction. This result was also consistent with the study of Zhang et al. [9].

Fig. 6 shows the results of MAP precipitation experiments in which PO_4 ratios are increased and other constituents are kept constant.

3.2.3. Effect of increasing both the Mg and PO_4 molar ratios

In this part of the study, the effects of Mg and PO_4 ions on NH_4–N, and COD removal were investigated in MAP precipitation process. At the stoichiometric ratio of MAP precipitation (1:1:1), 55% for ammonia and 28% for COD removal were obtained. When we increase both Mg and PO_4 ratios, a steady increase in removal efficiency was observed. In this condition, the highest ammonia and COD removal

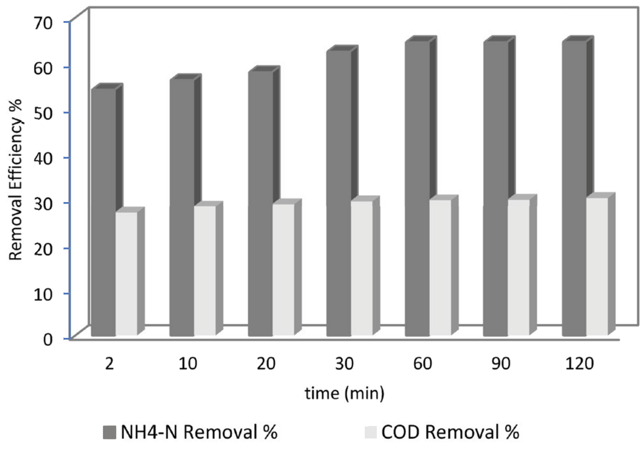

Fig. 4. Effect of stirring time on ammonia and COD removal efficiency.

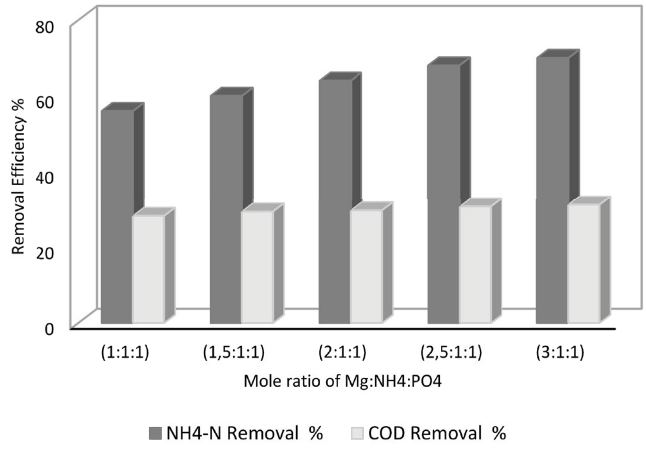

Fig. 5. Ammonia and COD removal efficiencies at different molar ratio of Mg.

efficiencies were achieved, with 83% for ammonia and 37% for COD at the Mg:NH_4:PO_4 ratio of 2.5:1:2.5.

Fig. 7 shows the results of MAP precipitation experiments in which both Mg and PO_4 ratios are increased and ammonia concentration is kept constant.

3.3. Effects of natural materials on the removal of NH_4–N from leachate by MAP precipitation method

In this part of the study, zeolite, sepiolite, and diatomite were added to the MAP precipitation process and their effects on NH_4–N, and COD removal were investigated at Mg:NH_4:PO_4 molar ratio of 1:1:1, a natural material dosage of 2 g/L. As can be seen from Fig. 8, the addition of natural materials increased the removal efficiency of NH_4–N and COD by about 10%. Thus, the addition of zeolite, sepiolite and diatomite did not affect the removal significantly.

It is thought that the additional 10% removal observed in NH_4–N, and COD was caused by adsorption. In order to investigate the contribution of adsorption, the natural material-leachate interaction study was carried out for 2 min. The results showed a 16%–17% NH_4–N and a 17%–19% COD removal by each material. When the MAP precipitation and adsorption processes were used together, the total NH_4–N and COD removal efficiencies were found to be 66% and 38%, respectively. To determine the influence of the amount of natural material added to the MAP process the material dose was increased from 2 to 4 g/L, but no significant increase (≤4%–5%) in the removal efficiencies was observed.

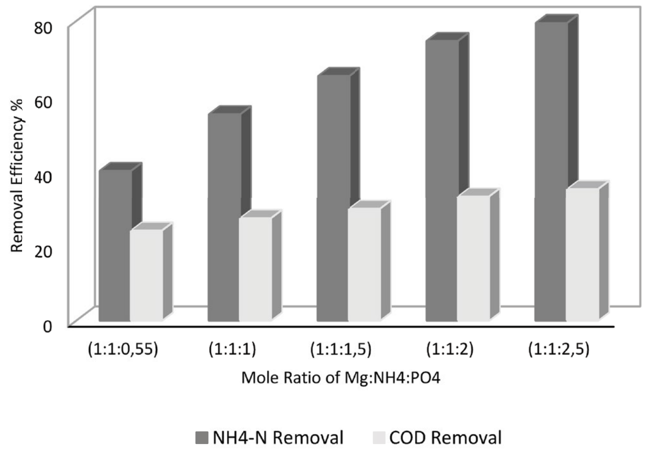

Fig. 6. Ammonia and COD removal efficiencies at different molar ratio of PO_4.

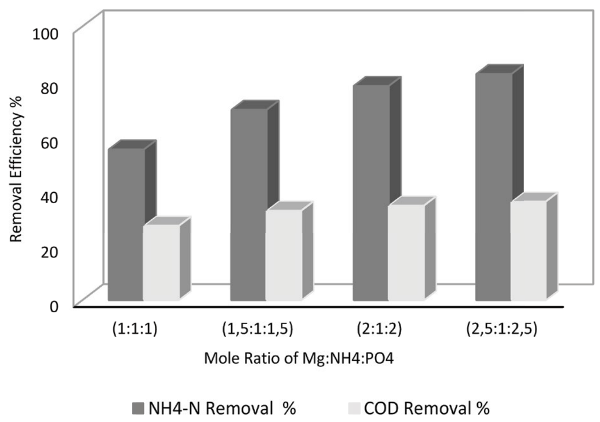

Fig. 7. Ammonia and COD removal efficiencies at different molar ratio of Mg and PO_4.

3.4. Regression analysis

Firstly the analysis of variance (ANOVA) results was obtained for ammonia and COD removal from experimental results (Tables 2 and 3).

Then, the linear regression equations of ammonia and COD removal were calculated from these results.

$$\text{Ammonia Removal \%} = 33.59 + 0.0966 \times \text{Time (min)} + 6.47 \times \text{Mg} + 15.63 \times PO_4 \tag{3}$$

$$\text{COD Removal \%} = 21.484 + 0.02454 \times \text{Time (min)} + 1.622 \times \text{Mg} + 4.769 \times PO_4 \tag{4}$$

For the statistical analyses, the residuals of data must be normally and independently distributed with the same variance [24]. This assumption was checked by the residuals plot given in Figs. 9 and 10. Here, it can be seen that a) the residuals of data are normally and independently distributed (Normal probability plot), b) the mean of residuals is equal to zero and there are no outliers in the data (histogram), c)

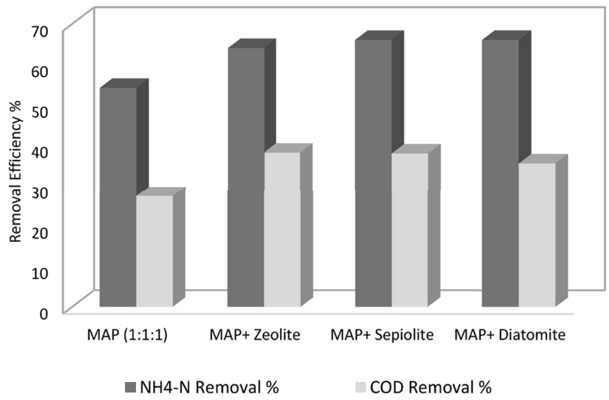

Fig. 8. Effect of adding natural materials to MAP precipitation process on ammonia and COD removal.

Table 2
Results of ANOVA for ammonia removal

Source	Adj SS	Adj MS	*F*-Value	*P*-Value
Regression	1,811.88	603.96	55.61	0.000
Time (min)	176.12	176.12	16.22	0.001
Mg	297.98	297.98	27.44	0.000
PO_4	1,293.94	1,293.94	119.14	0.000
Model summary	*S*	*R*-sq	*R*-sq (adj)	*R*-sq (pred)
	3.2956	90.75%	89.12%	82.32%

Table 3
Results of ANOVA for COD removal

Source	Adj SS	Adj MS	*F*-Value	*P*-Value
Regression	156.597	52.199	66.63	0.000
Time (min)	11.366	11.366	14.51	0.001
Mg	18.712	18.712	23.89	0.000
PO_4	120.473	120.473	153.79	0.000
Model summary	S	*R*-sq	*R*-sq (adj)	*R*-sq (pred)
	0.8851	92.16%	90.78%	86.90%

the variance is constant because the distribution of the residuals is random (versus fit), and d) there is no systematic effect on the data (versus order plot).

4. Conclusion

MAP precipitation as a pre-treatment process was used to achieve ammonia and COD removal from raw leachate collected from sanitary landfills. The ammonia removal efficiency obtained at the stoichiometric ratio of 1:1:1 was 55%. The highest ammonia removal efficiency was 83% at

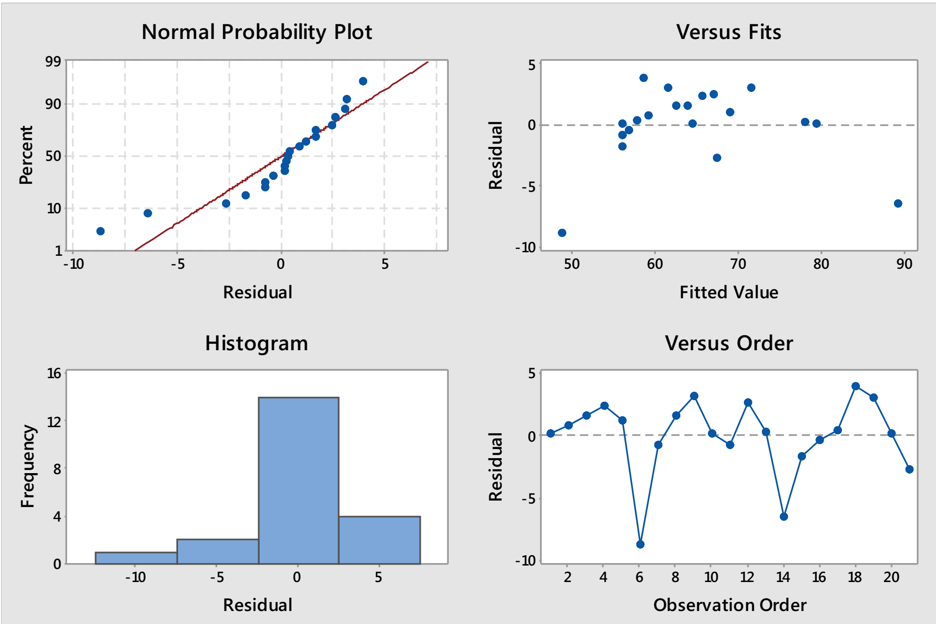

Fig. 9. Residual plots for ammonia removal.

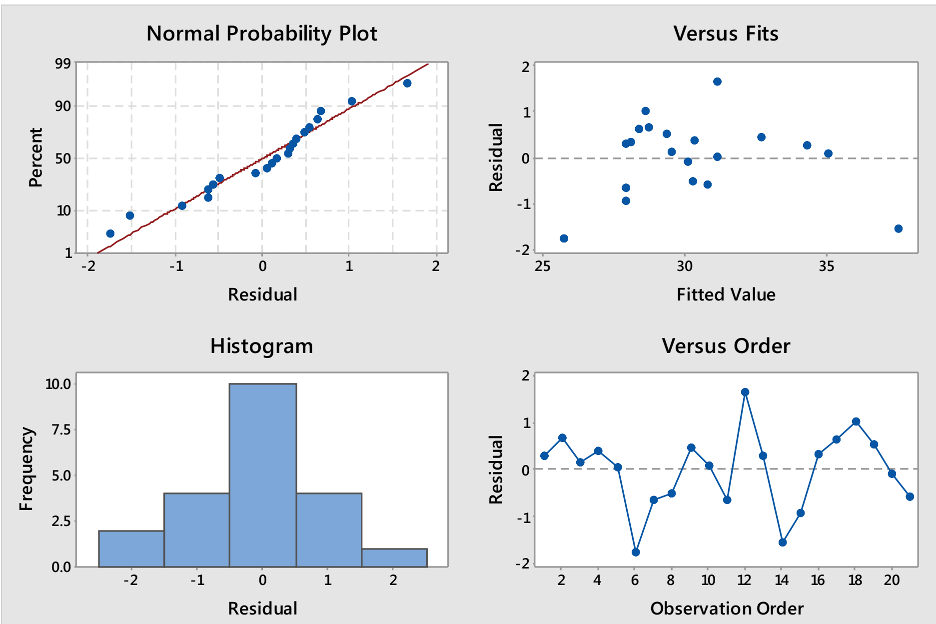

Fig. 10. Residual plots for COD removal.

the molar ratio of 2.5:1:2.5. No significant COD removal was observed by increasing molar ratios. For this reason, the biological process has to be applied to remove COD following the MAP precipitation process. The highest COD removal efficiency was achieved as 37% for optimum conditions.

Natural materials such as zeolite, sepiolite, and diatomite were added to the MAP precipitation process and their effects on NH_4–N, and COD removal were investigated. Natural materials increased the removal efficiency of NH_4–N and COD by only about 10%. Although the addition of natural materials did not seem to contribute much to ammonia and COD removals, the presence of these materials with the fertilizer formed by MAP precipitation will improve the soil structure and plant fertilization.

According to the results of the statistical analysis, the different levels of time, Mg and PO_4 dosages were found to have significant effects on ammonia and COD removal. In this study, the values of *R*-Sq were determined as 89.12% and 90.78% of the total variations were explained by the model for ammonia removal and COD removal. These regression models are considered very successful because of the values of *R*-Sq.

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