

Ammonia and COD Removal from Landfill Leachate Using MAP Precipitation Method

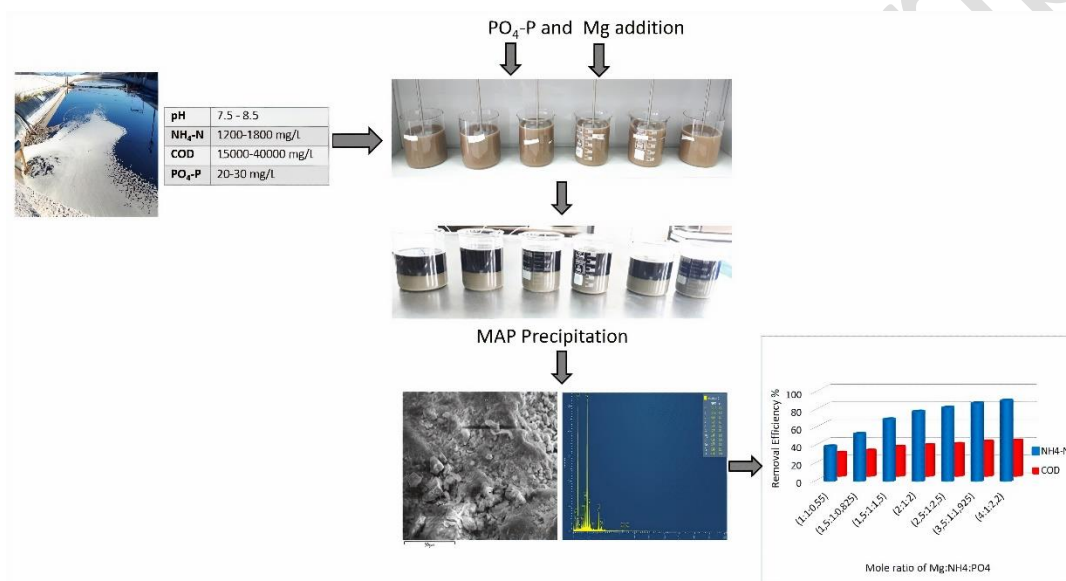
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GRAPHICAL ABSTRACT



Abstract: Most of the major cities in our country are opposed to the problem of water pollution due to the uncontrolled leachate resulting from the decomposition of solid wastes in irregular landfills. The waste waters that have high nitrogen content such as leachate cause various problems like eutrophication. In this study; the preliminary treatment of leachate which formed on the landfill site storing solid wastes of Samsun Metropolitan Municipality by MAP (Magnesium ammonium phosphate) precipitation was examined. For this purpose, optimization of the parameters that affecting the MAP precipitation was performed and the conditions for optimum removal efficiency were investigated. As a result of MAP precipitation, various mole ratios were tested with the aim of providing the best ammonia removal efficiency. The maximum ammonia removal was found to be 90.63% at pH 9.5 and at Mg:NH₄:PO₄ ratio of 4: 1: 2.2. At this conditions the ammonia concentration was decreased from 1792 mg/L to 168 mg/L. The linear regression analysis, widely used and very efficient method to describe the relationships between independent variables and the dependent variable, were performed by using these data.

Key words MAP precipitation, leachate, ammonia removal

INTRODUCTION

Sanitary landfills are widely used due to 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 causes the greatest environmental impact as it contains high amounts of organic compounds, inorganic ions and ammonia nitrogen (NH₃-N). Discharge of this wastewater to the receiving environment without proper purification can cause serious pollution in both groundwater aquifers and surface waters.

Therefore, the organic compounds and ammonia nitrogen should be removed from the leachate before the leachate is discharged to the receiving 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 reusable. 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].

Among the alternative processes, the precipitation of MAP (magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$) has been shown to be a promising method for the removal of ammonia nitrogen due to its high rate of reaction and removal ratio [9,10].

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].

Due to high toxicity in landfill leachate, nitrogen and phosphorus removal by MAP precipitation seems to be more advantageous than biological methods. In the MAP precipitation, magnesium and phosphorus are added at the molar concentration equivalent to ammonia, depending on the composition of the wastewater. $MgNH_4PO_4 \cdot 6H_2O$ precipitate is formed and ammonia is removed [11,12].

In this study, ammonia removal from leachate using MAP precipitation method was experimentally investigated and the principles of application of the process were described. At the same time, the linear regression analysis was made for these experiments using Minitab 16.

MATERIAL AND METHOD

Material

Experimental study was carried out on samples of landfill leachate taken from Samsun Metropolitan Municipality Sanitary Landfill.

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

Table 1: Characterization of the landfill leachate used in this study.

Parameters	Unit	Range
pH	-	7.5-8.5
NH_4 -N	mg/L	1200-1800
COD	mg/L	15000-40000
PO_4 -P	mg/L	20-30

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

Analysis

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

The concentrations of NH_4 and COD in leachate were measured according Standard Methods [13].

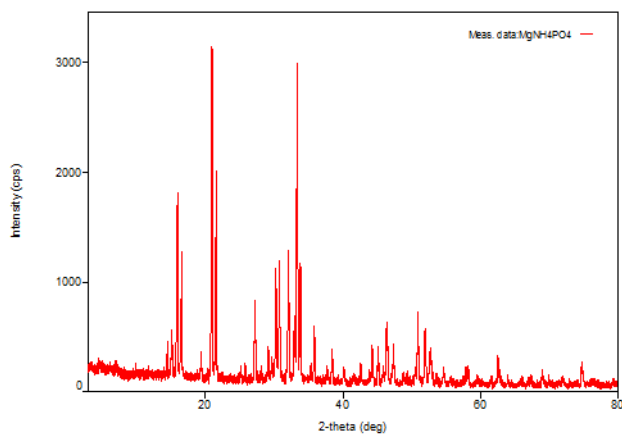


Figure 1: XRD of the MAP precipitates

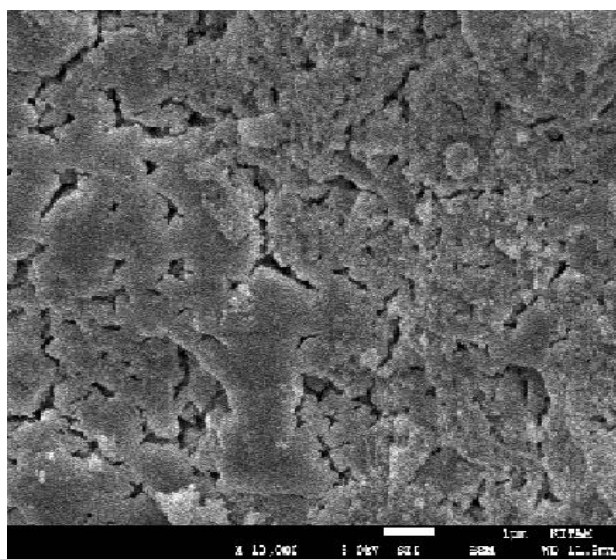


Figure 2: SEM micrograph of the MAP precipitates

Experimental Study

The MAP precipitation experiments were carried out on a Velp brand JLT6 model jar test system and, Kjeltec System 1002 Distilling Unit Tecator brand Kjeldahl nitrogen detection device was used for the ammonia nitrogen determination. The experiments were carried out at pH 9.5 and at room temperature.

9 different mixing times have been tested between 2 minutes and 120 minutes with the aim of determining the optimum mixing time in the MAP precipitation process. $\text{NH}_4\text{-N}$ and COD analyses were carried out on the samples after stirring at 150 rpm and settling 30 min.

Various mole ratios ($\text{Mg}:\text{NH}_4:\text{PO}_4$) have been tested for the purpose of achieving the best ammonia and COD removal efficiency by MAP precipitation.

For this purpose, the efficiency of ammonia and COD removal was determined by keeping the others fixed and increasing the Mg ratio 4 times. The other components were then kept constant and the $\text{PO}_4\text{-P}$ ratios were increased up to 2.2 times, after which the ratio of both Mg and $\text{PO}_4\text{-P}$ was increased by keeping the $\text{NH}_4\text{-N}$ ratio constant. As a result of the experiments ammonia and COD removal efficiencies were determined.

The Regression Model

To estimate relationship that relates between dependent variable (y) and independent variables (x), the regression model can be used. Also, the regression model can be determined the mathematical relationship between the dependent and independent variables as a linear, nonlinear, exponential etc. models [14-15]. The most used and the simplest of the regression models is the linear regression method. The general linear regression formula can be given as follows,

$$y_i = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \dots + \beta_n x_n$$

In this formula x_i is the independent variable and y_i is the dependent or response variable, β_i is coefficients [16].

The linear regression analysis was made for Ammonia and COD removal data by using Minitab 16 in this study.

RESULTS AND DISCUSSION

Determination of MAP Precipitation Conditions

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

In the first step of the MAP precipitation experiments, the Mg ratios were increased and the other components were kept constant.

At the Mg:NH₄:PO₄ ratio of 1: 1: 0.55, 44.83% ammonia removal was achieved at and COD removal remained at 14.08%. When the Mg ratio is increased to 4 times, the ammonia and COD removal efficiencies are increased, the increase after the 2.5 times Mg ratio is not significant. This indicates the saturation of the leachate to the Mg source.

For ammonia with the highest Mg ratio (4: 1: 0.55), 63.79% removal was obtained, while for COD, 37.56% removal was obtained. The experimental results of MAP precipitation, in which the Mg ratio are increased and the other components are kept constant, are presented in Figure 3 and Figure 4.

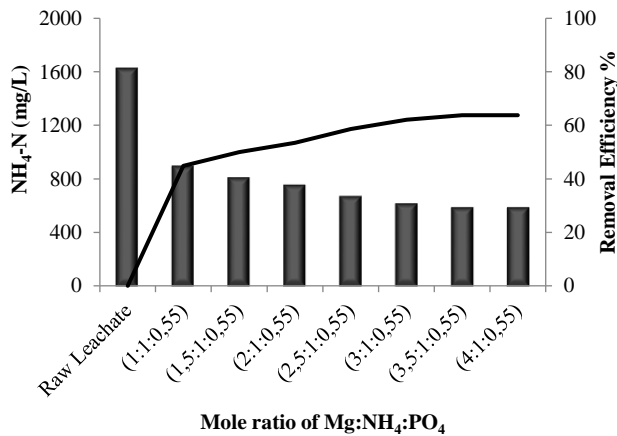


Figure 3: Ammonia removal efficiencies for the MAP precipitation experiment in which the Mg ratios were increased

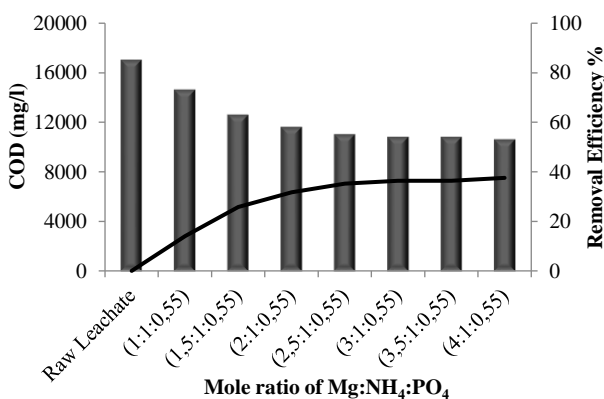


Figure 4: COD removal efficiencies for the MAP precipitation experiment in which the Mg ratios were increased

In the second step of the MAP precipitation experiments, PO₄-P ratio was increased and other components were kept constant.

At the Mg:NH₄:PO₄ ratio of 1: 1: 0.55, the ammonia removal was 37.5% and the COD removal was 27.60%.

When PO₄-P ratio was increased up to 2.2 times, a continuous increase in ammonia and COD removal efficiency was observed. This shows that PO₄-P in the leachate is low and that the leachate is not saturated. The higher PO₄-P concentrations were not tested in order to avoid higher PO₄-P concentration in the effluent.

The best ammonia and COD removal efficiency was achieved at Mg:NH₄:PO₄ ratio of 1: 1: 2.2. Ammonia was removed by 81.25% COD by 35.21%.

Figure 5 and Figure 6 show the results of MAP precipitation experiments in which PO₄-P ratio is increased and other components are kept constant.

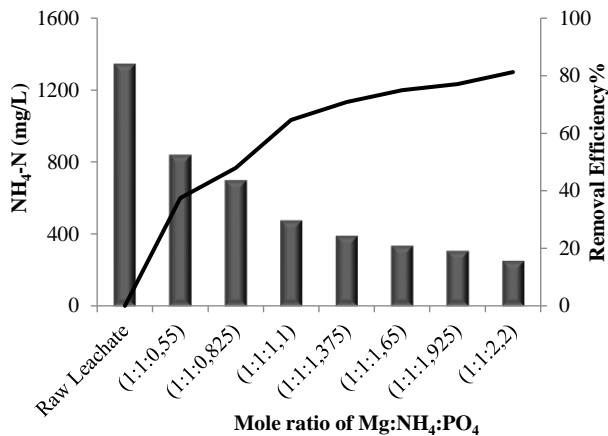


Figure 5: Ammonia removal efficiencies for the MAP precipitation experiment in which the PO₄-P ratios were increased

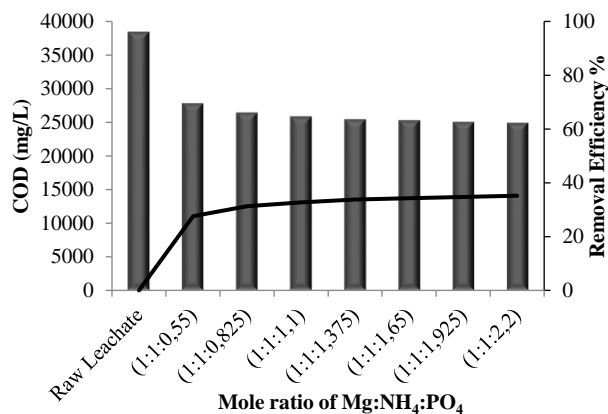


Figure 6: COD removal efficiencies for the MAP precipitation experiment in which the PO₄-Pratios were increased

In the third step of the MAP precipitation experiments, both Mg and PO₄-P ratios are increased and ammonia concentration is kept constant.

At the Mg:NH₄:PO₄ ratio of 1: 1: 0.55, 39.06% ammonia removal and 26.08% COD removal were obtained. When both Mg and PO₄-P ratios were increased, a steady increase in the removal efficiency was observed.

The highest ammonia and COD removal efficiencies were achieved at Mg:NH₄:PO₄ ratio of 4: 1: 2.2. At this condition ammonia removal was 90.63% and COD removal was 39.64%.

Figure 7 and Figure 8 show the results of MAP precipitation experiments in which both Mg and PO₄-P ratios are increased and ammonia concentration is kept constant.

The Regression Analysis

The Analysis of Variance (ANOVA) is made to determine the dependent variable significant effects on the independent variable. The ANOVA results for ammonia and COD removal experiments were given in Table 2-3.

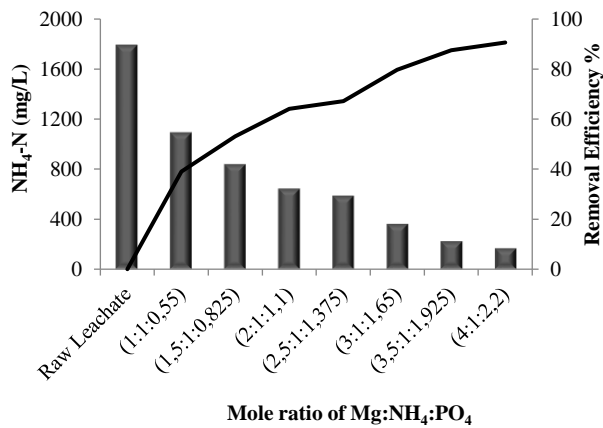


Figure 7: Ammonia removal efficiencies for the experiment of MAP precipitation, in which both Mg and PO₄-P ratios were increased

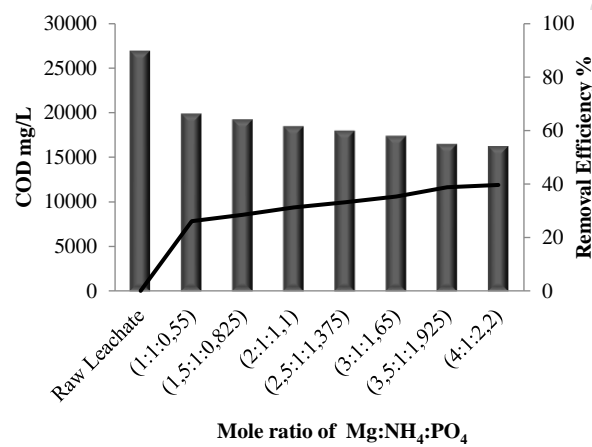


Figure 8: COD removal efficiencies for the experiment of MAP precipitation, in which both Mg and PO₄-P ratios were increased

Table 2: The results of ANOVA for ammonia removal.

Source	Adj SS	Adj MS	F-Value	P-Value
Regression	7744.87	3872.43	189.03	0.000
Mg	917.85	917.85	44.80	0.000
PO ₄	6165.23	6165.23	300.95	0.000
Model Summary	S	R-sq	R-sq(adj)	R-sq(pred)
	4.52614	91.53%	91.04%	89.90%

Table 3: The results of ANOVA for COD removal

Source	Adj SS	Adj MS	F-Value	P-Value
Regression	181.82	90.910	12.46	0.000
Mg	159.32	159.317	21.83	0.000
PO ₄	102.75	102.748	14.08	0.001
Model Summary	S	R-sq	R-sq(adj)	R-sq(pred)
	2.70158	56.73%	52.18%	46.27%

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

$$\text{Ammonia removal} = 29.97 + 4.889 \cdot \text{Mg} + 21.53 \cdot \text{PO}_4$$

$$\text{COD Removal} = 22.56 + 3.399 \cdot \text{Mg} + 4.14 \cdot \text{PO}_4$$

Finally, the Residual Plots for Ammonia and COD Removal were obtained (Fig. 9-10).

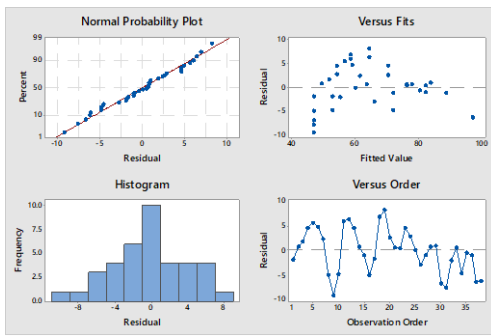


Figure 9: The Residual Plots for Ammonia Removal

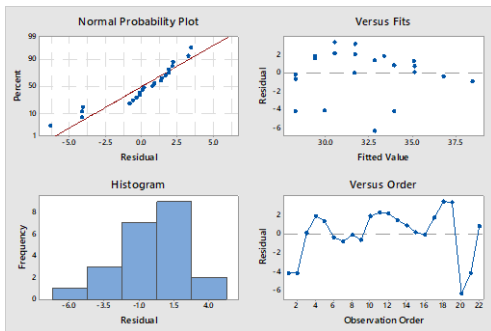


Figure 10: The Residual Plots for COD Removal

CONCLUSION

MAP precipitation as a pre-treatment process was used to achieve high ammonia removal from raw leachate collected from sanitary landfill. The removal of ammonia at Mg:NH₄:PO₄ ratio of 1: 1: 0.55 varied between 37-44%. The best ammonia removal efficiency ratio was achieved by 90.63% at Mg:NH₄:PO₄ ratio of 4: 1: 2.2 . No significant removal of COD was observed during MAP precipitation. For this reason, a biological process should be applied to remove COD. In the experiments, the highest COD removal efficiency was 39.64%.

When applying the MAP precipitation method, attention should be paid to the TDS and PO₄-P parameters that can remain in the effluent at high concentrations due to the use of chemicals.

It was seen that the different levels of Mg and PO₄ have significant effects on the ammonia and COD removal from the results of statistical analysis. The experiments of Ammonia removal have been described with the linear regression models. The data was very close to the fitted regression line in ammonia removal (91.53%). On the contrary to the data was not close to the fitted regression line in COD removal (56.73%). In this case, it can be said that the linear regression model is not suitable for the COD removal data.

ACKNOWLEDGMENT

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