Environment Protection Engineering

Vol. 40 2014 No. 1
DOI: 10.5277/epe140110

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OPTIMIZATION OF PROCESS PARAMETERS FOR COMPOSTING OF PULP/PAPER MILL SLUDGE WITH HAZELNUT KERNEL USING A STATISTICAL METHOD

An effective way to remove ammonium from compost using hazelnut kernels (HK) has been presented. The role of experimental factors on the removal of ammonium was examined by using the full factor experimental design (FFED). The experimental factors and their related levels were selected as time of 1–6 weeks, moisture of 50–70%, and HK amendment ratio of 5–25. The results were then evaluated by the ANOVA test to examine importance of the process variables (inputs) and their levels. A regression model taking into account main significant and interaction effects was suggested. According to the optimization algorithm, time of 5 weeks, moisture of 50%, and HK amendment ratio of 25 with the removal capacity of 60% were selected as optimum levels. The proposed analyzing procedure is simple to implement and cost-effective.

1. INTRODUCTION

Sludge management is an important economic and environmental issue in many pulps and paper mills [1]. Pulps and paper mills, together with increased production, generate a considerable amount of sludge which should be disposed of in an environmentally safe manner [2]. Sludge is produced as a result of primary and secondary/tertiary wastewater treatment of pulp/paper mill [3]. Primary treatment generally consists of screening, sedimentation, neutralization, and flotation/hydrocycloning. The main purpose of primary treatment in pulp/paper mill is to remove suspended and floating solids. Secondary and tertiary treatment systems such as activated sludge, aerated lagoons, anaerobic fermentation and adsorption are used to reduce organic content, toxicity and color of wastewater. Although sludge characterization mainly

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depends on the type of paper being produced and the source of cellulose fibres (wood or recycled paper), sludge typically includes fibres, fines and fillers lost which vary from 3–4% for pulp mills to 15–30% for the waste paper mills [4].

In Turkey, approximately 60 000 tons of pulp/paper mill sludge is produced annually, originated from primary and secondary wastewater treatment processes. At present, landfilling is the main disposal method for pulp/paper mill sludge. The estimated 36 000 tons, a total weight of pulp/paper mill sludge produced in Turkey, is disposed in sanitary landfills, while 16 500 tons/year is disposed at open dumping areas. Unfortunately, landfilling sites have not been properly operated by the poor regulation and caused many environmental problems resulting in surface and groundwater pollution, soil contamination. In addition to these, one of the largest concerns is the production of landfill gas in landfills. Dewatering followed by incineration is applied for about 170 tons/year pulp/paper mill sludge. The incineration of treatment sludge produces significant amounts of dioxin, furan and fly ash which contain toxic metals such as copper, zinc, cadmium and lead. Regulations related to incineration in Turkey have strict criteria for gas emissions. Moreover, capital and operating costs have limited the use of this method. 3200 tons/year of pulp/paper mill sludge is used for production of ceramic and cement in industries. On the other hand, 20 tons/year of pulp/paper mill sludge is used for agriculture. However, this application has caused in soil unfavorable effects due to the pathogens and heavy metals contents of treatment sludges. Recently, a search for a low--cost, easily applicable and environmentally acceptable is greatly needed.

Composting is a biological decomposition process of organic materials under controlled aerobic conditions. Composting may be economically and environmentally favorable methods as compared to alternative solid waste disposal methods [5]. Composting provides the volume reduction of wastes, removal of phytotoxicity and of pathogens. The ultimate goal of composting is to produce a humus-like product called “compost” that can be used for soil improvement and plant growth [6]. Composting of pulp and paper mill sludge reduces mass, odour and nitrogen immobilization, removes toxic organic compounds and pathogenic microorganisms and produces a marketable material [7]. A major limitation of composting process are N losses by ammonia volatilization. The loss of N reduces the value of compost as a fertilizer [8]. High levels of ammonia concentrations are undesirable because it may be toxic to the microbial population. On the other hand, ammonia could threaten surface and/or groundwater quality and cause odour problem [9]. Several factors affect the composting process such as oxygen, temperature, moisture, nutrients and pH [10]. To enhance the biodegradation rate of organic matter and improve the quality of the final compost, several amendments are added. The most widely used amendments in composting are pruning waste and wood chips [11]. Turkey is an internationally important hazelnut producer with the production of 530 000 tons in 2009, representing 75% of the total world market [12].

The objective of this work was to investigate composting of pulp/paper mill sludge with hazelnut kernels. Optimization of process parameters such as time (weeks), moisture content, and amendment ratio was examined using statistical method. The suggested experimental procedure is based on full factorial design, which takes into account all main and interaction effects on the response.

2. MATERIALS AND METHODS

Collection and preparation of samples. Pulp and paper mill sludge (containing 70% of primary sludge and 30% of secondary one) was obtained from wastewater treatment plant of Olmuksa Pulp/Paper Industry in the Black Sea region (Çorum, Turkey). The composition of sludge is given in Table 1.

Table 1

Characteristics of pulp/paper mill sludge

Parameter	Value
pH	7.02±0.1
Moisture content, %	70.6±0.2
Ash, %	9.6±0.2
Volatile matter, %	52.21±0.4
Total N, %	1.04±0.6
NH_4^--N, mg/dm^3	57.5±4.2
NO_3^--N, mg/dm^3	26.4±2.3
Total C, %	44.4±0.4
C/N	42.7±0.3

Hazelnut kernels were used as a bulking agent. The kernels were provided from the farm located in the Black Sea region (Samsun, Turkey). Table 2 shows the main characteristics of hazelnut kernel composted.

Table 2

Physical and chemical properties of hazelnut kernel

Parameter	Value
Phsicochemical analysis	
moisture content, %	5.61±0.2
bulk density, g/cm^3	0.21±0.1
surface area, m2/g	3.85±0.4
Ultimate analysis	
carbon, %	51.5±4.2
oxygen, %	46.4±2.3
hydrogen, %	5.2±0.4
nitrogen, %	0.2±0.1
ash, %	2.1±0.2

Composting process. Composting of pulp and paper mill sludge was performed in in-vessel prototype composters which were constructed of the volume of 25 dm^3 from a closed-ended tank. The air flow rates used in the systems were 0.8 $m^3/(min \cdot m^3)$. A temperature sensor for check and control purpose was placed at the center of the reactor. During the processes, the composters worked under the same conditions [13]. 27 composters were used simultaneously by mixing approximately 20 dm^3 of sludge with hazelnut kernel in three different volumetric ratios as bulking agent:sludge. The selected ratios were as follows:

- r1: 5% of hazelnut kernel + 95% pulp/paper mill sludge
- r2: 10% of hazelnut kernel + 90% of pulp/paper mill sludge
- r3: 25% of hazelnut kernel + 75% of pulp/paper mill sludge

The initial moisture content of sludge was approximately 70%. In the experiments, 50%, 60% and 70% of moisture content levels of sludge were selected. To reach 50% and 60% levels, sludge was dried in the open air. Once the moisture content levels were reached, hazelnut kernels were well mixed at the selected ratios. The composting experiments have been carried out for 6 weeks, from the 1st of June 2011 to the 13th of July, 2011. The compost was mixed manually every other to seven days throughout the composting reaction. At the end of 1, 3 and 6 weeks, sampling was carried out. The content of NH_4^+-N for each sample was determined by the steam distillation Kjeltec method [14].

3. RESULTS AND DISCUSSIONS

The effects of time, moisture, and HK amendment ratio are discussed in detail by using the experimental design. Experimental design is a practical balance to multivariate data analysis. It generates "prearranged" data tables that contain an important amount of prearranged variation. This fundamental arrangement will then be used as a basis for the multivariate modeling, which will guarantee stable and robust designs. More generally, experimental study is a procedure that response variable is observed and analyzed by changing input variables [15]. As a result, experimental designs are playing an important role for product and process development in engineering.

FFED is used in the experimental study to define and understand the ammonium removal system with hazelnut kernels. Figure 1 shows the proposed the ammonium removal system. The input parameters are time, moisture, and HK amendment ratio, while the output parameter is ammonium removal in per cents. The 'process block' contains FFED experimental design followed by optimization. Table 3 shows the FFED and min/max ammonium removal data.

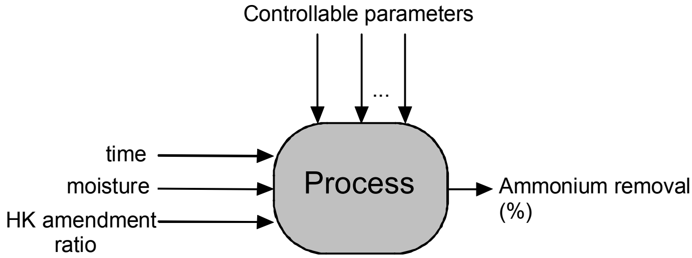

Fig. 1. System of ammonium removal with hazelnut kernel

Table 3

FFED with the response variable

Parameter	Levels for time			Levels for moisture			Levels for amendment ratio			Ammonium removal [%]
Coded	–1	0	1	–1	0	1	–1	0	1	2.47
Uncoded	1	3	6	50	60	70	5	10	25	64.78

As can be seen from Table 3, 3^3 FFED is employed for ammonium removal. Unlike fractional factor experimental designs such as response surface modeling, Taguchi designs, D-optimal designs, etc., main and interaction effects can be calculated accurately since all the experimental combinations are done randomly. Randomization is often employed to eliminate bias using only their expert decision. In a randomized experimental design, experimental runs are randomly assigned to an experimental group. Homogeneous treatment groups are reliably generated using randomization. Furthermore, the effects of the uncontrolled factors are also reduced.

A total of 27 experiments are performed for a 3^3 FFED and duplicated to increase the reliability of ammonium removal system. Then average values were taken into account. Table 4 shows the whole experimental design with repetitions and associated standard deviations.

The results of all runs were analyzed and a second degree polynomial equation was proposed to correlate the removal of ammonium with hazelnut kernels with three independent parameters. Equation (1) gives the general regression equation including main and interactions effects:

$$R = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_{ii}^2 + \beta_{ij} X_i X_j \quad (1)$$

where, β_0 is the constant term, β_i is the slope or linear effect of the input factor X_i, β_{ii} is the quadratic effect of input factor X_i, and β_{ij} is the linear by linear interaction effect between the input factor X_i and X_j [16–20].

ANOVA test was employed to optimize the process parameters. Using ANOVA test, the type of regression equation was decided. Table 5 shows the ANOVA results [21].

Table 4

FFED with repetitions and associated standard deviations

Time [week]	Moisture [%]	HK amendment ratio	Repetition1	Repetition2	Average	STD[1]
3	60	10:100	22.17	22.76	22.47	0.4148
6	60	10:100	26.24	26.18	26.21	0.0432
1	50	25:100	13.65	14.98	14.32	0.9413
6	60	25:100	43.23	41.67	42.45	1.1025
6	60	5:100	15.27	13.88	14.57	0.9791
1	60	5:100	5.20	6.34	5.77	0.8009
6	70	10:100	20.89	18.41	19.65	1.7503
6	50	25:100	64.19	65.38	64.78	0.8394
1	60	10:100	8.42	7.10	7.76	0.9341
3	50	25:100	48.89	46.12	47.50	1.9564
1	70	10:100	5.30	3.23	4.26	1.4600
3	70	10:100	11.52	11.26	11.39	0.1773
3	50	10:100	32.05	30.77	31.37	0.9524
1	50	5:100	5.13	7.47	6.30	1.6513
1	60	25:100	13.40	13.45	13.43	0.0377
6	70	25:100	29.14	30.34	29.74	0.8503
1	50	10:100	6.89	7.93	7.41	0.7340
6	70	5:100	13.75	12.81	13.28	0.6634
6	50	5:100	35.85	36.47	36.16	0.4390
3	70	5:100	7.68	5.94	6.81	1.2276
1	70	25:100	9.71	10.88	10.30	0.8253
6	50	10:100	46.19	48.32	47.26	1.5067
3	60	5:100	15.76	16.55	16.16	0.5585
3	70	25:100	22.91	24.09	23.50	0.8348
3	60	25:100	33.68	33.23	33.45	0.3135
1	70	5:100	2.04	2.89	2.47	0.6063
3	50	5:100	24.66	24.55	24.60	0.0834

[1]STD – standard deviation.

Table 5

Analysis of variance for the ammonium removal system

Source	DF	Seq. SS.	Adj. SS.	Adj MS.	*F*	*P*	Remarks
Regression	9	6219.40	6219.397	691.044	93.75	0.000	Significant
Linear	3	5466.93	831.480	277.160	37.60	0.000	
Square	3	211.65	211.654	70.551	9.57	0.001	
Interaction	3	540.82	540.816	180.272	24.46	0.000	
Residual error	17	125.32	125.315	7.371			
Total	26	6344.71					

DF – degrees of freedom, Seq. SS –sequential sum of squares, Adj. SS – the adjusted sum of squares, Adj. MS – the adjusted mean square.

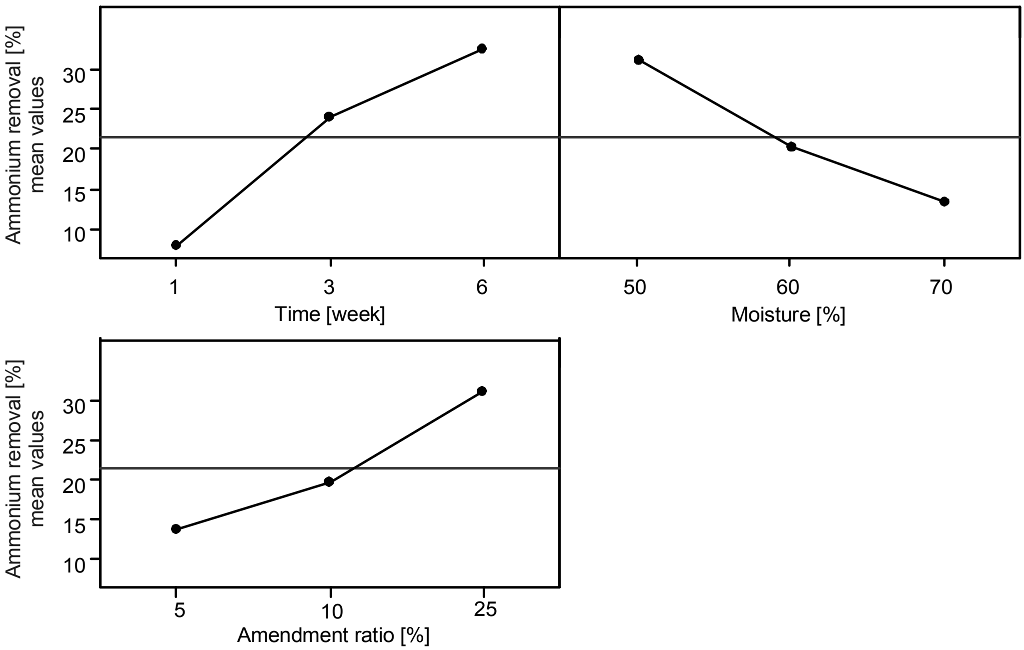

Fig. 2. Main effects for ammonium removal system

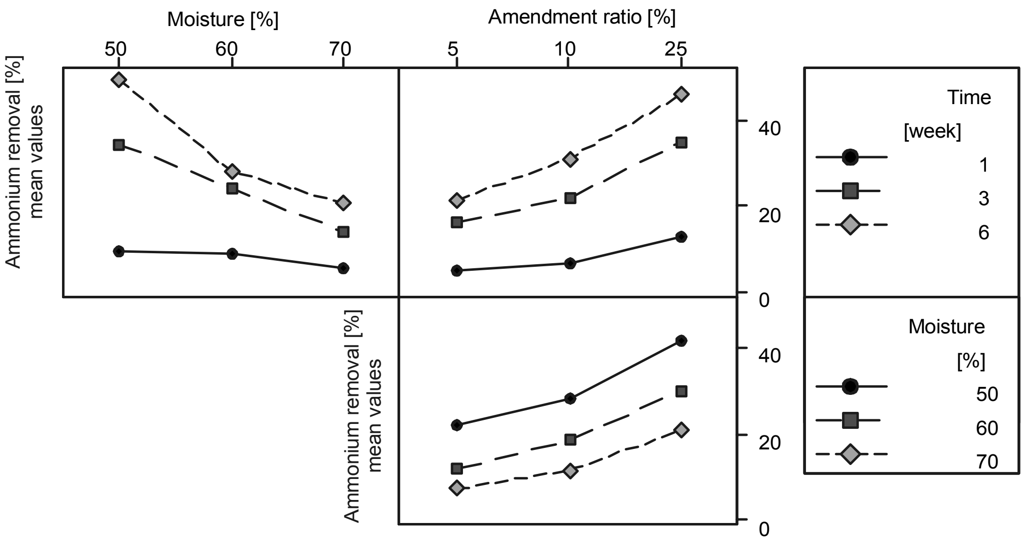

Fig. 3. Interaction effects for ammonium removal system

It can easily be concluded from Table 5 that interaction effects are significant with the probability of 0.000. If an upper level relationship (interaction effects) is found significant in ANOVA table that simply means that all lower level relations (main effects) are also significant. Main and interaction effects prove this statement (Figs. 2 and 3). As can be seen from Fig. 2, time and HK amendment ratio have positive effects on the removal system, while moisture has negative effect. Regarding to Fig. 3, middle and high levels (0 and 1) of the analyzed factors have great importance for the removal system, and interaction effects are observed within those levels. The interaction effects among time–moisture, time–HK amendment ratio, and moisture–HK amendment ratio can easily be seen (Fig. 3). The effect of time–moisture has less impact on the response variable rather than the effects of time–HK amendment ratio and moisture–HK amendment ratio have.

Adjusted R^2 was calculated as 96.98% which means that the selected levels of the input variables for ammonium removal system present high correlation between the inputs and response variable. The final regression equation with interaction effects is as follows:

$$\begin{aligned} R = {} & 41.94 + \text{time}\times 23.53 - \text{moisture}\times 1.86 + \text{ratio}\times 1.96 \\ & -\text{time}\times\text{time}\times 0.94 + \text{moisture}\times\text{moisture}\times 0.016 \\ & -\text{ratio}\times\text{ratio}\times 0.011 + \text{time}\times\text{ratio}\times 0.11 - \text{moisture}\times\text{ratio}\times 0.019 \end{aligned} \tag{2}$$

The time factor has the largest positive effect on ammonium removal with hazelnut kernel. The HK amendment ratio factor also has positive effect, while moisture has negative effect (Eq. (2)). This assumption has been analyzed in Figs. 4 and 5. In Figure 4, time dependences of ammonium removal are shown at various HK amendments ratios and constant moisture value of 50%. Similarly, in Fig. 5, time dependences of ammonium removal are shown at various moisture values and constant HK amendments ratio of 5. As is seen in Fig. 5, the effect of moisture on the removal of ammonium is not of major importance comparing to the effect of HK amendment ratio.

Gaussian probability density function shown in Fig. 6 was applied to the residuals to check the normality and confirmed the above findings.

Two important parameters have also been calculated from the probability density function. The skewness value was found to be –0.3893, which means that it is between ±1.96 (for 95% confidence interval), and the curve presents a Gaussian shape. Moreover, the kurtosis value was found to be 2.6895, which means that the value is very close to 3, presenting a Gaussian shape.

The experimental design using FFED can economically satisfy the needs of problem solving and product/process design optimization projects. By learning and applying this technique, engineers, scientists, and researchers can significantly reduce the time required for experimental investigations. For this purpose, the process variables are optimized to maximize the response variable. Table 6 gives the optimization results.

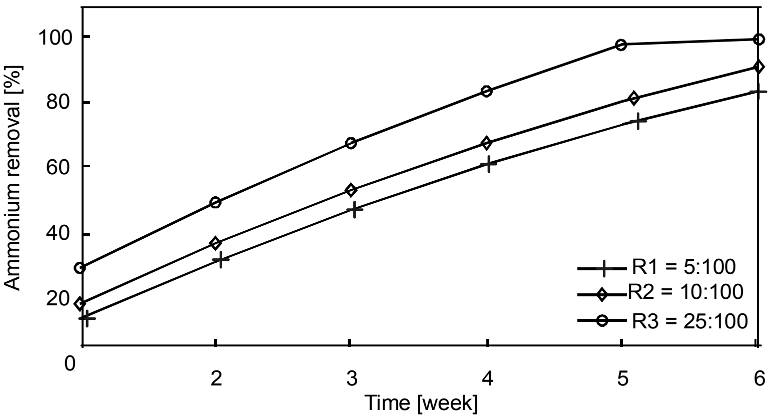

Fig. 4. Time dependences of ammonium removal at the constant moisture value of 50%; R1, R2, and R3 – HK amendment ratio)

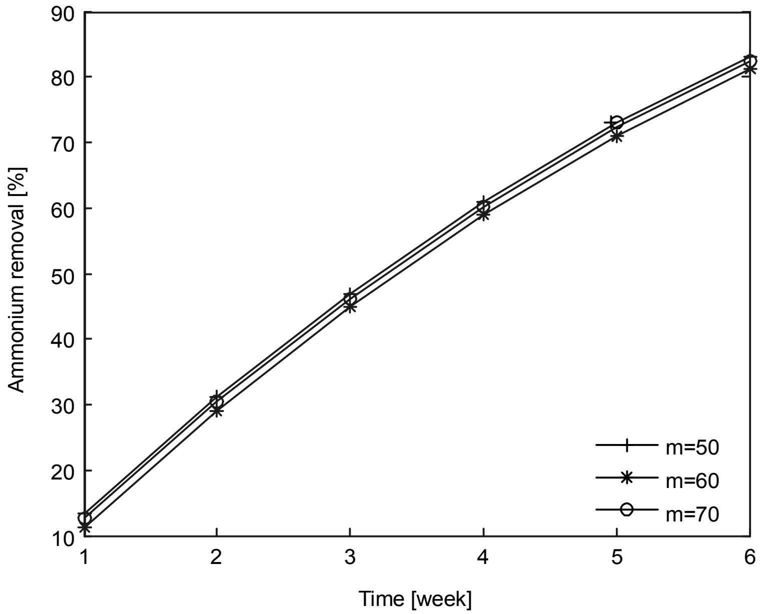

Fig. 5. Time dependences of ammonium removal at the constant ratio of 5; *m* – moisture, %

Table 6

Optimized process variables

Time [week]	Moisture content [%]	HK amendment ratio	Ammonium removal [%]
5	50	25:100	60

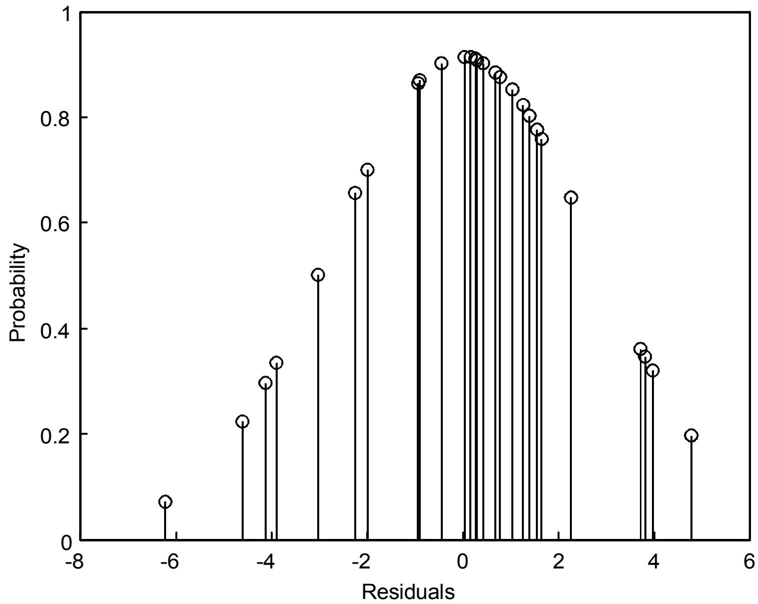

Fig. 6. Gaussian probability density function of the residuals

According to the optimization results, maturity parameters of pulp/paper mill sludge compost treated with hazelnut kernel are presented in Table 7. Their values were found to lie in the optimum ranges. As a result, the final compost is accepted as "mature".

Table 7

Characteristics of pulp/paper mill sludge compost

Parameter	Value	Optimum value	Reference
pH	6.96	5.5–8.0	[21]
Moisture content, %	50.0	50–60	[22]
Conductivity, mS/cm	0.77	<2	[23]
NH_4^+-N, mg/kg	47.5	<500	[24]
NH_4^+-N/NO_3^--N	0.66	<3	[24]
C/N	11.5	<20	[25]

4. CONCLUSION

Composting of pulp and paper mill sludge is an effective way of sludge regeneration since it reduces mass, odour and nitrogen immobilization, removes toxic organic compounds and pathogenic microorganisms and produces marketable materials. However, ammonia volatilization limits composting process due to the odour, N-losses and other environmental problems. After optimizing all the input variables studied in this work, it was found that hazelnut kernel is an effective sorbent to remove ammonium and can be used for composting purposes. The calculated removal of ammonium was 60% after optimization for the time of 5 weeks, moisture of 50% and amendment ratio of 25%. The proposed experimental design (FFED) was found cost-effective and easy to implement. The main and interaction effects of the analyzed factors were obtained accurately by FFED. In future work, various low-cost sorbents will be used for composting of sludges.

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