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Anaerobic Treatability Studies of Metal Industry Wastewater in Batch Reactor

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Abstract: With the rapid growth of the world population and the acceleration of urbanization and industrialization, the metal industry and the production of metal structures and building parts started to grow and develop rapidly. With these developments, the effects of the production of metal structures and components on the environment have increased. If the wastewater originating from the metal industry is discharged into water environments without proper treatment, it causes the accumulation feature in the environment and living creatures due to their toxic properties and various health problems, resulting in the death of aquatic organisms, their water quality being reduced and being unusable as drinking, using and irrigation water. It is known that organic matter and heavy metal concentrations in metal industry wastewater are high. Therefore, wastewater from the metal industry needs to undergo a suitable and adequate treatment. In this study, optimization of anaerobic treatment of metal industry wastewater was investigated by applying statistical based experimental design in different conditions. In full factorial experiments (i) 9 different experiments based on different initial wastewater concentrations (0.5%, 1%, 2%), (ii) cosubstrate type (glucose, propionic acid, acetic acid-butyric acid-propionic acid-ABP) variables mechanism has been established. The experiments were carried out in Oxitop C bottles in a 200 ml working volume with mixing. The necessary basal medium was added for the development of anaerobic microorganisms and the pH was adjusted to 7 ± 0.2. Trials were carried out at 35°C for 30 days. At the end of the process, COD removals were determined according to the input and output COD (chemical oxygen demand) values of the trials. As a result, the highest COD removal was found to be 97% in the diluted wastewater concentration of 0.5%, when glucose is used as a cosubstrate.

Keywords: Anaerobic Treatability, Metal İndustry, Wastewater, Batch Reactor

1. Introduction

Today, industrialization has gained importance with the rapid increase of the population. The wastes and wastewater generated by the developing industry are dangerous for the environment and people. In addition, considering the vision of developing countries, the construction of wastewater treatment facilities is increasing in order to prevent environmental pollution.

The main industrial sources of pollution in wastewater are metal and metal plating industries [4,15]. It is observed that the wastes generated by the raw materials used in the metal industry are generally highly toxic and harmful to the environment and people [15,11]. Industrial wastewater such as the metal plating industry contains organic compounds, degreasing solvents, oil-grease, various harmful heavy metals such as chromium, nickel, copper, zinc, cyanide, as well as toxic substances, including some anions and cations [4,1,17]. These wastewaters are very dangerous when discharged into surface waters without any treatment [1,14]. Physical, chemical and biological processes such as adsorption, biosorption, precipitation, ion exchange, reverse osmosis, filtration and membrane separation are used to treat metal industry wastewater [4].

Metal industry wastewater is very suitable for biological treatment as it is wastewater with high organic matter content. Biological treatment can be done in two ways, aerobic and anaerobic treatment. Anaerobic treatment is preferred over aerobic treatment due to its advantages such as low energy use, low amount of waste sludge formation and lower operating costs [9,7].

Anaerobic treatment is defined as the transformation of organic materials into end products such as CH_4, CO_2, NH_3 and H_2S by microbiologically degredation with acid and methane bacteria in an oxygen-free environment [8]. Anaerobic treatment consists of three main stages: hydrolysis of high molecular weight solid and dissolved organic substances, acid production and methane production [16].

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Increasing energy requirements brought the current treatment systems to be examined in terms of investment and operating costs. As a result, there has been an increasing interest in anaerobic treatment technologies in recent years, due to its advantages such as both its applicability to various wastewaters and energy saving [13].

In this study, it was aimed to observe anaerobic treatability of metal industry wastewater in batch reactor studies. The optimization of anaerobic treatment of metal industry wastewater was statistical studied using a full factorial experimental design.

2. Materials and methods

2.1. Metal industry wastewater

In this study, the anaerobic treatment of the wastewater from the factory producing metal suspended ceilings belonging to ASPEN Yapı ve Zemin A.Ş., operating in Eskişehir, Turkey was studied in batch reactors.

Metal industry wastewater from the facility was stored at -20 ° C during research. In the preliminary studies, in the wastewater was concluded that contains high amounts of organic matter, chromium, nickel, copper, zinc, cyanide, as well as a high proportion of oil-grease. COD value of the wastewater sample coming from the facility is 650000 mg / ml^{-1} and pH 7.9.

2.2. Inoculum (Anaerobic Sludge)

Anaerobic sludge used in the batch reactor and to be used in the future studies was provided from the Anaerobic Treatment Unit of Eskişehir Wastewater Treatment Plant. Before use anaerobic sludge important properties in terms of treatment were determined such as pH, suspended solids (SS) and total solids (TS).

2.3. Basal medium

The composition of the basal medium used in the experiments is as follows (Concentrations of the Components are given as mg L^{-1}): NH_4Cl (1200), $MgSO_4$.7H2O (400), KCl (400), $Na_2S.9H_2O$ (300), $CaCl_2.2H_2O$ (50), $(NH_4)_2HPO_4$ (80), $FeCl_2.4H_2O$ (40), $CoCl_2.6H_2O$ (10), KI (10.0), $MnCl_2.4H_2O$ (0.5), $CuCl_2.2H_2O$ (0.5), $ZnCl_2$ (0.5), $AlCl_3.6H_2O$ (0.5), $NaMoO_4.2H_2O$ (0.5), H_3BO_3 (0.5), $NiCl_2.6H_2O$ (0.5), $NaWO_4.2H_2O$ (0.5), Na_2SeO_3 (0.5), ve cysteine (10.0). This basal medium contains all the micro and macronutrients necessary for an optimum anaerobic microbial growth (7).

2.4. Batch reactor studies

Optimization of anaerobic treatment of metal industry wastewater was studied by applying statistical based experimental design in batch studies. Factor designs are largely used in experiments involving several factors where it is necessary to examine the combined effect of factors on a response [6]. Batch studies were carried out with BMP (biochemical methane potential) analysis system with 200 ml volume in Oxitop C bottles with mixing [2,3]. In Full factorial tests, 9 different experimental setups were set up using different initial concentrations of wastewater (0.5%, 1%, 2%) and different cosubstrates (a-glucose, b-propionic acid c-acetic acid, a mixture of essential fatty acids containing propionic acid and butyric acid) [2,3]. In all studies, a mineral medium containing substances necessary for the growth of anaerobic microorganisms were also used. pH stability was achieved by adding $NaHCO_3$ and removal of dissolved oxygen was provided by $Na_2S.9H_2O$. The pH was adjusted to 7 ± 0.1. Experiments were carried out at 35 ° C for 30 days. At the end of the period, COD and oil-grease removal rates and total biogas amount were determined. Experiments were performed with two repetitions. Statistical analysis and interpretations were carried out using the SPSS 18 (PASW Statistics) program.

2.5. Analytical methods

COD, TS, SS, VSS, ioil/grease, inorganic matters were determined by standard methods [5]. The toxicity level was also measured with a Microtox analyzer (Microtox® Model 500 analyser).

3. Results and discussion

3.1. Properties of metal industry wastewater

The analysis and results of the wastewater sample obtained from the factory producing metal suspended ceilings in Eskişehir Organized Industrial Zone according to the parameters in the Environment and Water Quality Control Regulation (Environmental Legislation Volume 2, 1999) are given in Table 1.

Table 1. Properties of Metal Industry Wastewater

Parameter	Result
Oil / Grease (mg l^{-1})	797.580
COD (mg l^{-1})	650.000
pH	7.9
Pb (mg.l^{-1})	31.8
Ag (mg.l^{-1})	140.8
Cr (mg.l^{-1})	123.2
NH_4-N (mg.l^{-1})	139.2
S^{-2} (mg.l^{-1})	177.4
Al (mg.l^{-1})	72.5
Fe (mg.l^{-1})	330.5
Zn (mg.l^{-1})	150.4
F^- (mg.l^{-1})	142.8
Cu (mg.l^{-1})	601
Ni (mg.l^{-1})	208
CN^- (mg.l^{-1})	34.6

3.2. Inoculum features

Some properties of anaerobic sludge used in batch reactor studies are given in Table 2.

Table 2. Properties of anaerobic sludge used in batch studies

Parameter	Anaerobic Sludge
pH	7.8
TS ($g.l^{-1}$)	27.6
SS ($g.l^{-1}$)	20.7
VSS ($g.l^{-1}$)	12.3

3.3. Batch reactor studies

Batch reactor test setups were prepared using metal industry wastewater and different cosubstrate types and average COD removal rates obtained from each test result are given in Table 3.

Table 3. Batch reactor COD removal results

Wastewater Concentration			Cosubstrat Type		
Experiments	**Real (Starting COD mg/l)**	**Code**	**Real**	**Code**	**COD Removal (%)**
1	% 0.5 (7480 $mg.l^{-1}$)	-1	Glucose	-1	97.22
2	% 0.5 (7480 $mg.l^{-1}$)	-1	Propionic Acid	0	86.66
3	% 0.5 (7480 $mg.l^{-1}$)	-1	ABP	1	89.84
4	% 1 (10690 $mg.l^{-1}$)	0	Glucose	-1	95.12
5	% 1 (10690 $mg.l^{-1}$	0	Propionic Acid	0	69.13
6	% 1 (10690 $mg.l^{-1}$)	0	ABP	1	81.26
7	% 2 (13680 $mg.l^{-1}$)	1	Glucose	-1	90.14
8	% 2 (13680 $mg.l^{-1}$)	1	Propionic Acid	0	74.62
9	% 2 (13680 $mg.l^{-1}$)	1	ABP	1	75.14

Factors, levels and codes are included in relation to the experimental designs. The experimental setups given in Table 3 were carried out in two replicates for each level.

3.4. Factor analysis

In line with the results in Table 3, variance analyzes, factors alone and dual interaction analyzes were performed. Experimental design results were calculated with SPSS 18 (PASW Statistics) software. Table 4 shows the analysis of variance for COD removal.

Table 4. Variance analysis for COD removal

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	1537.879[a]	8	192.235	2089.509	.000
Intercept	127832.534	1	127832.534	1389484.064	.000
Concentration	438.065	2	219.033	2380.791	.000
Cosubstrate	958.901	2	479.451	5211.421	.000
Concentration *Cosubstrate	140.912	4	35.228	382.913	.000
Error	.828	9	.092		
Total	129371.241	18			
Corrected Total	1538.707	17			

a. R Squared = ,999 (Adjusted R Squared = ,999)

In Table 4, it is seen that the cosubstrate types and concentration ratios used in the study show a statistically significant difference in COD removal. (sig <0.05)

The statistical relationship between the cosubstrate types used and the COD removal is given in Table 5 in the homogeneous subset table.

Table 5. Relationship between cosubstrate variety and COD

Cosubstrate	N	Subset		
		1	2	3
Propionic acid	6	76,6400		
ABP	6		82,0700	
Glucose	6			94,1067
Sig.		1,000	1,000	1,000

Accordingly, it is seen that the best COD removal is when glucose is used as cosubstrate. In the batch reactor, using ABP instead of propionic acid as a cosubstrate type increases COD removal by 5.43%, while the use of glucose increases COD removal by 17.46%. Using glucose instead of ABP increases the COD removal by 12%.

According to the statistical data, the comparison of cosubstrates in COD removal is given in Table 6.

Table 6. Cosubstrate effect on COD removal

(I) Cosubstrate	(J) Cosubstrate	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
Glucose	Propionic asid	17.4667*	.17512	.000	16.9777	17.9556
	ABP	12.0367*	.17512	.000	11.5477	12.5256
Propionic asid	Glucose	-17.4667*	.17512	.000	-17.9556	-16.9777
	ABP	-5.4300*	.17512	.000	-5.9189	-4.9411
ABP	Glucose	-12.0367*	.17512	.000	-12.5256	-11.5477
	Propionic asid	5.4300*	.17512	.000	4.9411	5.9189

When Table 6 is examined, glucose use increases COD removal by 17.4667% compared to propionic acid and provides 12.0367% more COD removal than ABP. When propionic acid is used as cosubstrate instead of glucose, COD removal decreases by 17.4667%, while using it instead of ABP decreases COD removal by 5.43%. If ABP is preferred to glucose and propionic acid, COD removal decreases by 12.0367%, while COD removal increases by 5.43%, respectively.

The statistical relationship between wastewater concentration rates and COD removal is given in the subset in Table 7.

Table 7. Statistical relationship between wastewater concentration rates and COD removal

Concentration	N	Subset		
		1	2	3
%2	6	80.0000		
%1	6		81.6317	
%0,5	6			91.1850
Sig.		1.000	1.000	1.000

According to this table, it is seen that the COD removal is higher in the waste water that we dilute % 0,5. The statistical evaluation shows that the COD removal of the waste water diluted % 0,5 in the batch reactor is 11.18% and 9.55%, respectively, compared to the waste water diluted % 2 and % 1. These values are statistically significant.

The relationship between waste water concentration rates and COD removal according to the statistical data of batch reactor studies is given in Table 8.

Table 8. The effect of wastewater concentration rates on COD removal

(I) Concentration	(J) Concentration	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
%0.5	%1	9.5533*	.17512	.000	9.0644	10.0423
	%2	11.1850*	.17512	.000	10.6961	11.6739
%1	%0,5	-9.5533*	.17512	.000	-10.0423	-9.0644
	%2	1.6317*	.17512	.000	1.1427	2.1206
%2	%0,5	-11.1850*	.17512	.000	-11.6739	-10.6961
	%1	-1.6317*	.17512	.000	-2.1206	-1.1427

When the COD removal rate obtained from the waste water diluted % 1 with the waste water diluted % 0,5 is examined, it is found that the COD removal increased by 9.5533% compared to the waste water diluted % 1; It is seen that it increases 11.1850% compared to % 2 diluted waste water. When we look at the COD removal obtained in the waste water diluted % 0,5 with the waste water diluted 100 times, it is seen that the COD removal decreased by 9.5533% and the COD removal increased by 1.6317% compared to the % 2 diluted waste water. Looking at the COD removal obtained in the % 2 diluted waste water, it is seen that the removal is reduced by 11.1850% and 1.6317%, respectively, compared to the COD removal obtained in % 0,5 and % 1 diluted waste water. These values are statistically significant.

The profile graph of waste water concentration and cosubstrate interaction is given in Figure 1.

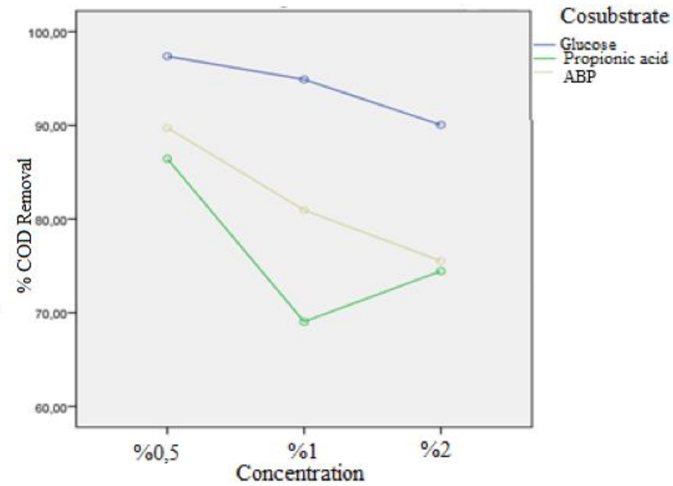

Figure 1. Profile graph of wastewater concentration and cosubstrate interaction in COD removal

When Figure 1 is examined, COD removal is maximized when % 0,5 diluted waste water concentration and glucose are used as cosubstrate.

3.5. Toxicity Results

The toxicity analysis of the metal industry wastewater and the treated wastewater were performed. According to the toxicity analysis of the treated wastewater, it was determined to be nontoxic. The result is shown in Table 9.

Table. 9. Toxicity results

	5 minutes results (% Concentration)	15 minutes results (% Concentration)
Influent wastewater	1.2	0.6
Effluent wastewater	Nontoxic	Nontoxic

4. Conclusion

Biologically treatability of metal industry wastewater under anaerobic conditions was ensured. However, it has a significant effect on anaerobic treatment of metal industry wastewater in its parameters such as alkalinity, pH, and basal medium.

According to the results of the batch reactor studies, when the glucose cosubstrate of the treatment at 0.5% diluted wastewater concentration is used, the COD removal efficiency is 97%. With this study, suitable optimization conditions were determined for future continuous reactor studies by using factorial design.

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