



VIALE EXPULSION OF CONTAMINATIONS FROM DAIRY WASTEWATER INVOLVING OZONATION AND HYDROGEN PEROXIDE PRETREATMENT TECHNIQUES IN SEQUENTIAL BIO REACTOR (SBR): KINETICS AND OPTIMIZATION STUDIES USING RSM

S. Rajan^[a], Sathish Sundararaman^[a], V. Balaji^[b], Narendrakumar Gopakumaran^[c]

Article History: Received: 03.12.2022

Revised: 15.01.2023

Accepted: 20.02.2023

Abstract: Background: This paper depicts the treatment of dairy profluent prior to going into the sequencing batch reactor (SBR). **Materials and method:** It incorporates treating the dairy effluent with ozone and hydrogen peroxide by fluctuating the flow and amount. Ozone was delivered by utilizing an ozone generator at the most extreme rate of 15g/hr. The performance of the ozone, H₂O₂, and the mix of ozone and H₂O₂ on dairy wastewater was explored. The investigation performed for each cycle by fluctuating the ozone time, pH, stream rate, amount of H₂O₂. **Results and Discussion:** The outcomes show that the mix of ozone and hydrogen peroxide was viewed as more effective for the evacuation of toxins. The streamlined treatment condition for the above interaction was at a response season of 5 min of ozone at the pH of 10, and how much H₂O₂ was 10ml/l. **Conclusion:** To resolve the issue of waste sludge removal during the SBR cycle, a basic investigation of elemental analysis was performed to all the more likely comprehend its qualities and the chance of reusing of sludge.

Keywords: Hydrogen peroxide; sequencing batch reactor; Ozone generator; dairy profluent; RSM.

[a]. Department of Chemical Engineering, Sathyabama Institute of Science and Technology, Chennai – 600119, Tamil Nadu, India.;

[b]. Department of Research and Development, RANITEC Pvt Ltd, Ranipet, (Tamil Nadu) India.;

[c]. Department of Biotechnology, Sathyabama Institute of Science and Technology, Chennai -600 119 Tamil Nadu, India.

DOI: 10.48047/ecb/2023.12.2.023

INTRODUCTION

The use of milk and milk products is increasing day by day in society which leads to an increase in the discharge of wastewater from the dairy industry^[1]. The dairy wastewater from the processing units is characterized by large amounts of suspended solids, organic materials, salts, fats, oil and grease. The pollutant loads coming from the effluent depend on the production method, quantity of processed milk, by-products, and washing mechanism^[2]. It contains a high amount of organics, ammonia nitrogen, and a considerable number of pathogens and toxic substances of a specific structure. In the dairy industry variety of milk products are manufactured like butter, milk, cheese, yogurt, ice cream, and milk powder through the various process^[3]. They generate about 0.2L-10L of wastewater per litre of processed milk and these have always high chemical oxygen demand^[4]. The discharge of these types of effluent to water bodies without treatment will

create various human health effects like malaria, dengue, yellow fever, lung cancer, and kidney failure^[5]. The discharging of these effluents into the river will also affect the environment due to the presence of high phosphates and nitrogen compounds. So before discharging it is necessary to treat these effluents not only for the environment but also for reuse^[6]. The traditional methods for treating this effluent are insufficient due to the ineffective removal of polycyclic organic substances because of their complex molecular structure and stable chemical properties^[7]. Supporting this revealed that the treatment of effluent with ozone is one of the promising eco-friendly green technologies. Ozone is a bluish gas with a pungent- smelling and is an extremely reactive and unstable allotrope of oxygen. The ozone can be generated by using electric corona discharge, ultraviolet radiation, thermal and chemical electrolytic process. At higher pH values the effect of ozone is better for pollutant removal when compared to lower pH values. Generally, the pH ranges lower than 10.3 and higher than 7.8 will consider for ozone treatment. The advantages of using ozone for the treatment of dairy effluent are low electricity consumption for ozone generation, it can quickly auto decomposes to nontoxic products and also ozone can be generated onsite without transportation and storage^[8]. However, the efficiency of ozone can be affected by temperature, pH, and relative humidity. The present work was carried out for treating the dairy wastewater before introducing it to the biological process. The treatment of dairy effluent by ozone, hydrogen peroxide, and a combination of ozone and hydrogen peroxide were investigated to find the

removal efficiencies of BOD, COD, TKN, TP, TSS, Chlorides, and Sulphates of each process. The study was conducted by varying the time interval of ozone to 5mins and 10mins at the pH of 5.57, 9, and 10 respectively. For the treatment of effluent with hydrogen peroxide, the concentration is varied from 1ml/l to 20ml/l. After the optimization of ozone and hydrogen peroxide, the combination of both takes place to increase the removal efficiencies of the pollutants^[9].

MATERIALS AND METHOD

Collection and Preservation of Dairy wastewater

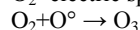
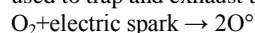
The dairy wastewater for the analysis work was collected from the Ambattur dairy milk processing unit. The samples were collected at the one common point where all these products effluents were met. The collected samples were properly labelled indicating the sample site, time of collection, location, and other records. The sealed samples were stored in the refrigerator at 4°C.

Characterization of Dairy wastewater

The effluent collected from the dairy industry was analyzed for pH, BOD, COD, TKN, Phosphates, TSS, Sulphates, Oil&Grease, and Chlorides as per American Public Health Association (APHA) standards.

Experimental Setup for ozone production

The experimental setup consists of an oxygen producer, ozone generator, fume hood, oxygen tube to the ozone generator, and the ozone tube to the sample. Commercial grade oxygen from oxygen producers was used for ozone production. In this study, the oxygen flow rate was kept at 3L/min. Ozone is prepared by an ozone generator by passing an electrical discharge through oxygen^[10]. Then the ozone generator released the ozone through the ozone tube. The ozone was produced at the rate of 15g/hr. At the end of the ozone tube, a porous diffuser was connected. The diffuser was dipped in the effluent to get the ozone for the sample. Fume hoods were used to trap and exhaust the ozone gas from the diffuser.



Optimization of Ozone pre-treatment of dairy effluent

The optimization of ozone is done by varying the pH of collected dairy effluent to 9 and 10 at the ozone time of 5mins and 10mins for each pH. In addition to that, the ozonation was done for the sample pH of 5.57 at 5mins and 10mins. The collected effluent has to be well mixed before checking the pH. The pH of the sample was changed by using a 1N NaOH solution. At pH = 9 the ozone was passed into the sample by utilizing an ozone generator for 5mins and 10mins. The ozone is generated at the rate of 15g/hr. For 5mins the amount of ozone passed into the sample is 1.25g and for 10mins the amount of ozone is 2.5g. Similarly, at pH = 10 and 5.5, the ozone is passed for 5mins and 10mins respectively. The collected ozonized samples were analyzed for pH, BOD, COD, TKN, Phosphates, TSS and Chlorides.

Optimization of Hydrogen peroxide pre-treatment of dairy effluent

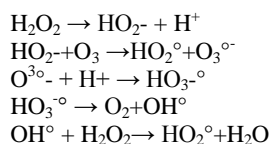
The optimization of hydrogen peroxide is done at the sample pH of the collected dairy effluent. The pH of the collected effluent is in acidic condition. After the addition of hydrogen peroxide, the foam-like white precipitate will form at the top of the effluent. In this study, a small amount of hydrogen peroxide is to be added to the effluent by varying the concentration. The collected effluent was well mixed and about 1 ml/l of H₂O₂ was added and stirred continuously for about 10-15 mins. Likewise, the concentration was varied from 2 ml/l to 20 ml/l at same pH. The treated samples were analyzed for pH, BOD, COD, TKN, phosphates, TSS, sulphates, oil & grease, and chlorides.

SBR system of Operation

The SBR was operated with a cycle time of 10 h, settling time of 1h, decanting time and idle time of 1h, respectively. The reaction time was 8 h for instantaneous filling, but reaction time was changed accordingly with the length of fill and phases. Settling, decanting and idle time were maintained constant throughout study. In the study, samples were collected from the reactor at interval of 15 min for tR up to 1.0 h, and after that at 1.0 h interval. Samples collected were then analyzed for COD and TKN removal.

Combined pre-treatment O₃/H₂O₂ for pre-treatment

The ozonation combined with H₂O₂ is an efficient system for the degradation of pollutants in dairy effluent. The O₃/H₂O₂ process commonly known as peroxone AOP involves a radical chain mechanism based on the ozone decomposition initiated by the hydroperoxide anion HO₂⁻. The synergistic effect of O₃ with H₂O₂ promotes the production of OH• radicals^[11].



O₃ likely reacts with excess HO₂²⁻ formed and generates OH•. The excess H₂O₂ leads to OH• scavenging and formation of hydroperoxide ion^[12]. Neither a hydrogen peroxide concentration that is too low is desirable because H₂O₂ competes successfully for hydroxyl radicals and decomposes without oxidizing the pollutants.

RESULTS

Description of the study sample:

Characteristics and Emission load analysis of dairy wastewater

The collected dairy wastewater sample has been tested for pH, BOD, COD, TP, TKN, TSS, Chloride, Sulphate, Oil & Grease, and Electrical Conductivity for finding its initial characteristics. The organic matter present in the dairy effluent will be normally high. The discharge of untreated effluent into the water bodies will create more environmental problems and also affect human health. So, it requires treatment before discharging. The BOD and COD of the analyzed dairy effluent

were 1975 mg/l and 3727mg/l. Mostly dairy wastewater contains a high concentration of nitrogen and phosphorous because of milk solids, detergents, sanitizers, milk wastes, and cleaning water. The use of sanitizers, detergents, or some kind of cleaning agent for the cleaning of machinery or equipment leads to an increase in the concentration of chlorides and sulphates. In this sample, the amount of chloride and sulphate present were in the range of 240 mg/l and 72 mg/l respectively.

SBR Performance

Soluble COD and TKN removal efficiencies were in the range of 85–95% during the reported period. Effluent soluble COD was always less than 195 mg/L. According to the studies, this limit is related to the generation of COD-residual fractions. Soluble BOD5 in the effluent were less than 195 mg/L, and effluent TKN was always less than regulatory standards. From these results, it can be concluded that the SBR performance was acceptable in the studied period.

Effect of ozonation Pre-treatment

The pre-treatment of dairy wastewater is required to reduce the concentration of pollutant load before introducing it into the biological process [13]. This work consists of passing the ozone at different pH of the effluent. At each pH level, different doses of ozone are injected by varying the time. Ozone is used for pre-treatment work to reduce the pollutant load and also it is capable of reducing the pathogens present in the wastewater. This experiment is carried out by varying the pH of the effluent. At each pH, the concentration of ozone dosage varied between 5mins and 10mins. The flow of the ozone to the sample is 15g/hr. The first set of the study was conducted for dairy effluent with ozone of 5mins and 10mins at sample pH. The collected ozonized samples were analysed for BOD, COD, TKN and TSS.

Effect of H₂O₂ in dairy effluent

The pre-treatment of dairy wastewater with hydrogen peroxide will help us to oxidize both organic and inorganic pollutants which contribute to COD and BOD [14]. It is used to remove the toxic compounds present in the wastewater. H₂O₂ is a strong two-electron oxidant having a standard reduction potential of 1.32V at pH=7. The use of H₂O₂ has the advantage that the decomposition of organic compounds is harmless. It will decompose in water and oxygen. The treatment of wastewater with hydrogen peroxide alone is an effective one for low concentrations of organic or inorganic compounds but it is not effective for high concentrations of pollutants. In this study, the 30% hydrogen peroxide was injected into wastewater at varying quantities of 1 ml/l, 2 ml/l, 3 ml/l, 5 ml/l, 10 ml/l, and 20 ml/l. The first set of samples was prepared by adding 1 ml/l of hydrogen peroxide to the sample. After the injection, the samples were analyzed for BOD, COD, TKN, TSS (Figure 1). In this study, we found that 10 ml/l of hydrogen peroxide in the sample gave a better removal efficiency of the above pollutants, and also we found

that increase in hydrogen peroxide above 10 ml/l decreased the removal efficiency of pollutants. So, further study was conducted to increase the percentage removal efficiency by combining the ozone and hydrogen peroxide in their better doses.

Effect of combination of ozone and hydrogen peroxide in dairy effluent

Many authors suggested that the treatment of effluent with sole ozone and hydrogen peroxide leads to low pollutant removal efficiency and high cost [15] [16]. Some of the compounds present in the effluent cannot be removed by the biological process for that purpose the use of a combination of ozone and hydrogen peroxide will effectively remove the non-degradable compounds present in the effluent. These processes are referred to as the Advanced Oxidation Process (AOP) and also suggested that the combination of ozone and hydrogen peroxide was found to be the most efficient method for the removal of pollutants in cheese whey wastewater. For instance, reported that maximum COD removable is achieved under the combination of ozone and hydrogen peroxide in pharmaceutical wastewater (Figure 2). The combination of ozone and hydrogen peroxide in dairy effluent takes place to improve the reduction capability in wastewater. It is the kind of advanced oxidation for effluent treatment. The radicals that are generated during the process are used for the degradation of organic and inorganic pollutants in the dairy effluent. This process improves the oxidation capacity of the treatment. The above studies indicated that the pH of 10 at ozone for 5mins produces the best results and 10ml/l of hydrogen peroxide concentration produces better results than others. The raw effluent was ozonated at the pH of 10 for 5mins followed by 10ml/l of hydrogen peroxide. After the injection of hydrogen peroxide, it has to be stirred for 10-15 min. The collected samples were analyzed for BOD, COD, TKN, Phosphates, TSS, Sulphates, Oil & Grease, and Chlorides. The percent removal efficiency was tabulated in Table 1.

Table 1: Treatment of dairy effluent with a combination of ozone and hydrogen peroxide (Ozone for 5 mins at pH 10 with hydrogen peroxide (10 ml/l))

Parameters	Sample Value	Final value	Percentage Removal (%)
pH@ 29.2oC	7.7	8.5	-
BOD(mg/l)	1975.3	125	93.6
COD(mg/l)	3727	195	94.8
Total Kjeldahl Nitrogen (mg/l)	26.56	8.49	68.0
Total Suspended Solids (mg/l)	930.2	230	75.2
Total Phosphates (mg/l)	52.27	11.3	78.4
Electrical conductivity (ms/ppt)	1.613	1.938	-

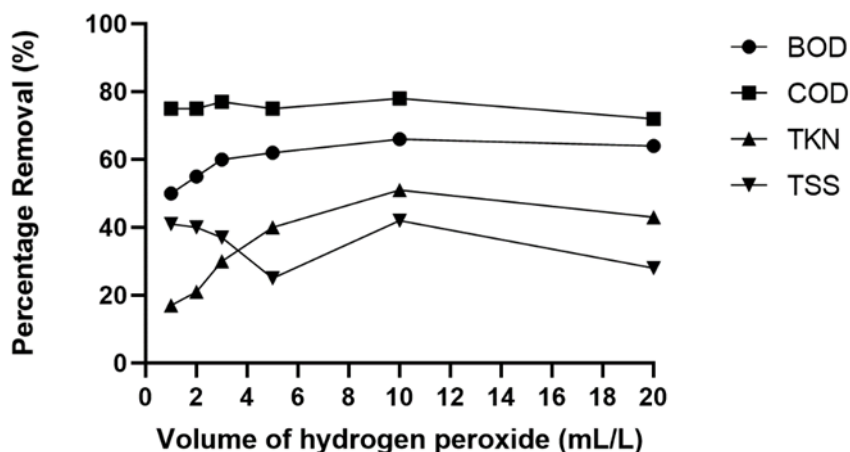


Figure 1: Effect of hydrogen peroxide at different concentrations.

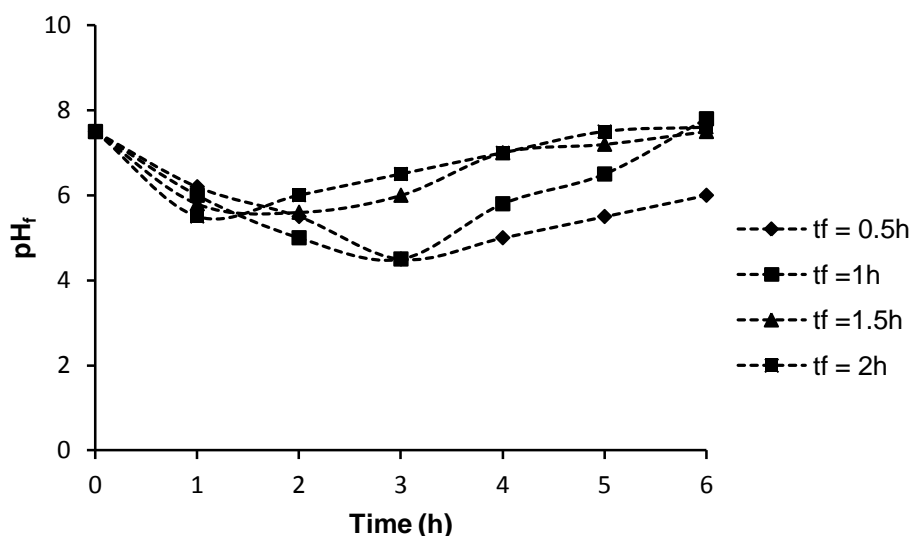


Figure 3. Effect of filling time on final pH

During the fill phase, aerated and mixed fill method was followed at to get higher COD removal efficiency, nitrification. Change in pH with time at various filling time was also set up during the SBR cycle (Figure 3). It may be seen that pH decreases and attains a minimum value then increases up to a maximum and becomes nearly constant. This trend was observed at all filling time.

As filling time increased from 0.5 to 2 h, minimum attained pH values were found to be nearly 4, while, rate of decrease in pH is higher at filling time of 2h. Nitrogen removal takes place via nitrification and denitrification, which, causes decrease and increase in pH, respectively. During the denitrification process, pH increases from pH 4 to 7.5 due to use of H⁺ ions and stripping of CO₂ [17]. Thereafter, pH becomes nearly constant showing denitrification process completed.

Central Composite Design

A second order polynomial quadratic equation was to predict the optimum value and subsequently to elucidate the interaction between the variables [18]. The quadratic equation model for predicting the optimal point is expressed according to equation

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i$$

where Y is the predicted response, X_1, X_2, X_3, X_4 are independent variables, b_0 is the offset term, $\beta_1, \beta_2, \beta_3, \beta_4$ are coefficient of linear effects, $\beta_{11}, \beta_{22}, \beta_{33}, \beta_{44}$ are coefficient of squared effects and $\beta_{12}, \beta_{13}, \beta_{14}, \beta_{23}, \beta_{24}, \beta_{34}$ are coefficient of interaction terms. The regression equation contains four linear term, four quadratic term and six cross-interactions. The empirical mathematical model was tested with the ANOVA with 5% level of significance [19]. The ANOVA was used for checking the significance of the second-order models. The statistical significance of the second-order model equation is determined by F-value. In general, the calculated F-value should be greater than the tabulated F-value to reject the null hypothesis, where all the regression coefficients are zero.

Table 2: Coded Value of physical parameters

Code	Parameter	Low Range	Mean	High Range
A	Ozone dosage	30	55	80
B	COD concentration	250	1875	3500
C	Ozone time	5	7.5	10
D	H ₂ O ₂ concentration	5	12.5	20

Table 3 Design table for removal of COD, TKN, Phosphate by SBR

Run	A	B	C	D	COD removal	TKN removal	Phosphate removal
1	55	1875	7.5	12.5	86	86	76
2	55	1875	7.5	-2.5	63	76	52
3	30	250	5	5	56	75	51
4	55	1875	7.5	27.5	76	73	49
5	55	1875	7.5	12.5	88	84	74
6	80	3500	5	20	57	73	52
7	30	3500	10	20	62	74	52
8	55	1875	7.5	12.5	85	87	75
9	80	250	5	20	52	76	51
10	55	375	7.5	12.5	57	74	52
11	105	187	7.5	12.5	50	80	47

12	80	250	5	5	51	74	52
13	30	3500	5	20	68	74	53
14	55	1875	7.5	12.5	82	84	77
15	80	250	10	20	58	71	51
16	80	3500	10	20	51	75	50
17	55	1875	7.5	12.5	87	83	77
18	80	250	10	5	55	74	55
19	55	1875	7.5	12.5	86	86	74
20	55	5125	7.5	12.5	48	73	51
21	30	250	5	20	62	77	50
22	55	1875	12.5	12.5	56	75	48
23	30	3500	10	5	58	75	48
24	80	3500	10	5	49	72	50
25	55	1875	2.5	12.5	56	74	51
26	5	1875	7.5	12.5	63	80	51
27	30	250	10	20	66	74	52
28	30	250	10	5	61	72	51
29	30	3500	5	5	59	73	51
30	80	3500	5	5	50	74	52

A:Ozone dosage

B:COD concentration

C:Ozonation time

D: H₂O₂ concentration

Table 4 ANOVA for Response Surface Quadratic Model for COD removal

Source	Sum of Squares	Mean Square	F Value	p-value Prob > F
Model	4757.45	339.817	72.38724	< 0.0001
A-Ozone dosage	376.0417	376.047	80.10355	< 0.0001
B-COD concentration	26.04167	26.0417	5.547337	0.0325
C-Ozonation time	1.04166	1.04166	0.221893	0.6444
D- H ₂ O ₂ concentration	165.375	165.375	35.2278	< 0.0001
AB	7.5625	7.5625	1.61097	0.2237
AC	0.0625	0.0625	0.01331	0.9097
AD	7.5625	7.5625	1.61097	0.2237
BC	68.0625	68.0625	14.4985	0.0017
BD	3.0625	3.0625	0.65237	0.4319
CD	5.0625	5.0625	1.07840	0.3155

A ²	1555.74	1555.74	331.405	< 0.0001
B ²	1996.33	1996.33	425.25	< 0.0001
C ²	1607.81	1607.81	342.492	< 0.0001
D ²	502.741	502.741	107.098	< 0.0001
Residual	70.4166	4.69444		
Lack of Fit	49.0833	4.90833	1.15039	0.4658
Pure Error	21.3333	4.26666	Std. Dev.	2.16666 6667
Cor Total	4827.87		R²	0.98541 4538
Mean	63.2666		Adj. R²	0.97180 144
Adeq Precision	24.8302		Pred R²	0.93507 6915

Table 5 ANOVA for Response Surface Quadratic Model for TKN removal

Source	Sum of Squares	Mean Square	F Value	Source
Model	597.616	42.6869	12.4129	< 0.0001
A-Ozone dosage	1.04166	1.04166	0.30290	0.5902
B-COD concentration	1.04166	1.04166	0.30290	0.5902
C-Ozone time	2.04166	2.04166	0.5937	0.4530
D- H ₂ O ₂ concentration	0.04166	0.04166	0.01211	0.9138
AB	0.0625	0.0625	0.01817	0.8946
AC	0.0625	0.0625	0.01817	0.8946
AD	0.5625	0.5625	0.16357	0.6916
BC	10.5625	10.5625	3.07148	0.1001
BD	0.0625	0.0625	0.01817	0.8946
CD	0.5625	0.5625	0.16357	0.6916
A ²	64.3125	64.3125	18.7015	0.0006
B ²	273.241	273.241	79.4562	< 0.0001
C ²	231.669	231.669	67.3675	< 0.0001
D ²	231.669	231.669	67.36759	< 0.0001
Residual	51.5833	3.43888		
Lack of Fit	39.5833	3.95833	1.649306	0.3025
Pure Error	12	2.4	Std. Dev.	1.854424
Cor Total	649.2		R²	0.920543
Mean	76.6		Adj. R²	0.846384
Adeq Precision	9.945784		Pred R²	0.922181

Table 6 ANOVA for Response Surface Quadratic Model for Phosphate removal

Source	Sum of Squares	Mean Square	F Value	Source
Model	2942.417	210.176	88.184	< 0.0001
A-Ozone dosage	0.375	0.375	0.15737	0.6972
B-COD concentration	2.041667	2.04167	0.85667	0.3693
C-Ozone time	3.375	3.375	1.41604	0.2525
D- H ₂ O ₂ concentration	1.041667	1.04167	0.43703	0.5186
AB	1.5625	1.5625	0.65559	0.4308
AC	0.0625	0.0625	0.02622	0.8735
AD	7.5625	7.5625	3.17307	0.0951
BC	10.5625	10.5625	4.43181	0.0525
BD	7.5625	7.5625	3.17307	0.0951
CD	0.0625	0.0625	0.02622	0.8735
A ²	1133.003	1133.00	475.3	< 0.0001
B ²	923.3601	923.301	387.423	< 0.0001
C ²	1089.36	1089.36	457.072	< 0.0001
D ²	1004.646	1004.66	421.597	< 0.0001
Residual	35.75	2.38333		
Lack of Fit	26.25	2.625	1.38159	0.3791
Pure Error	9.5	1.9	Std. Dev.	1.5438
Cor Total	2978.167		R²	0.98799
Mean	55.83333		Adj R²	0.97679
Adeq Precision	24.65721		Pred R²	0.94463

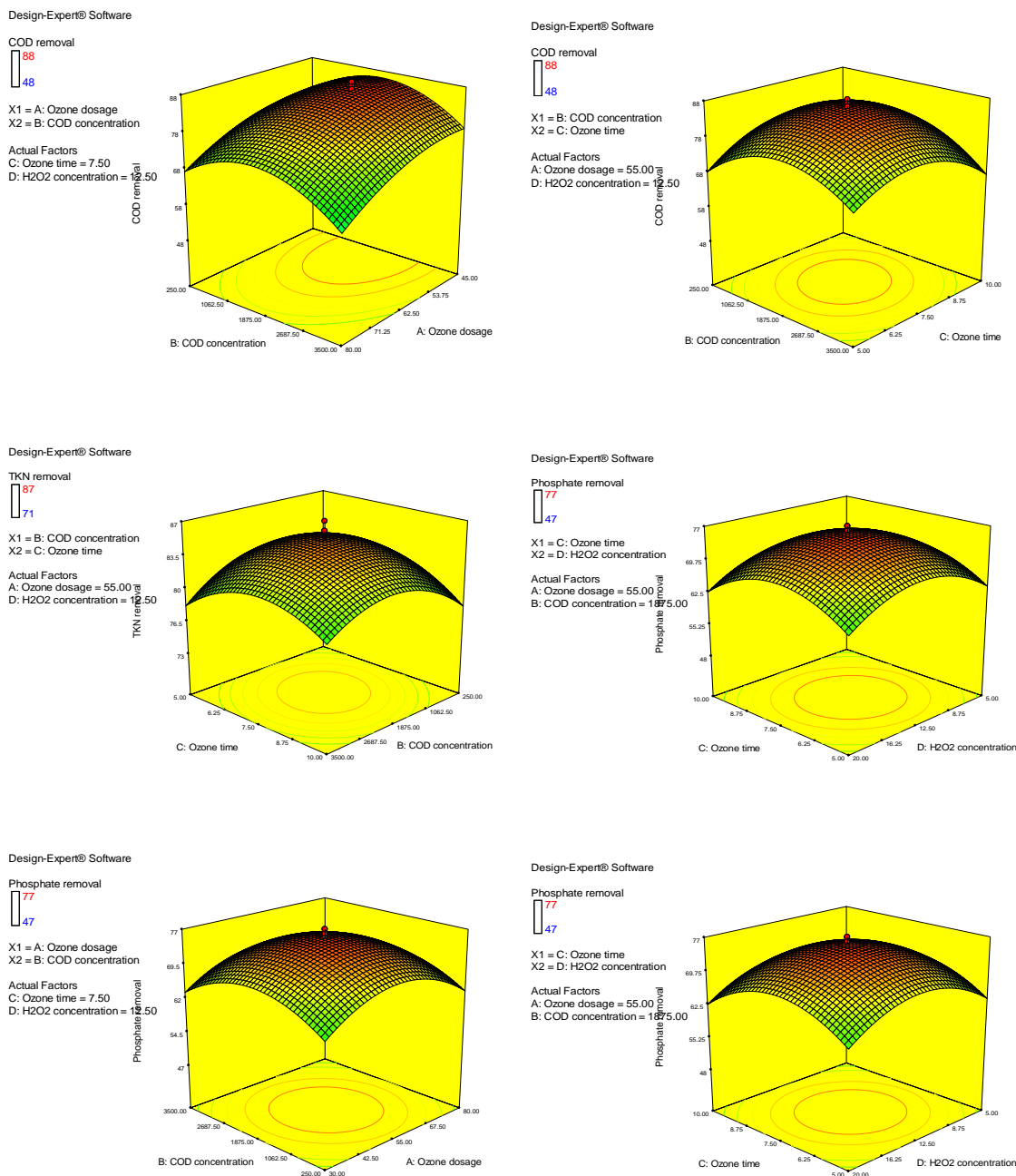


Figure 4 Interaction effects of process parameters on CR removal by electro coagulation process

The regression equation contains four linear term (A, B, C, D), four square term (A^2 , B^2 , C^2 , D^2), and six cross-interactions (AB, AC, AD, BC, BD, CD) terms plus 1 block term. The empirical mathematical model was tested with the ANOVA with 5% level of significance. The ANOVA was used for checking the significance of the second-order models. The statistical significance of the second-order model equation was determined by F-value (Table 2). In general, the calculated F-value should be

greater than the tabulated F-value to reject the null hypothesis, where all the regression coefficients are zero.

COD removal = $50.998.94 - 0.2072A + 0.0158B + 1.73C - 2.612D - 2.10 \times 10^{-5}AB - 0.001AC - 0.0037AD - 0.0005BC + 4 \times 10^{-5}BD - 0.03CD$

Sludge Settling = $0.021A^2 - 2.96 \times 10^{-6}B^2 - 0.225C^2 - 0.0761D^2 + 1.67A - 0.278A - 0.0038B + 0.6667C + 1.423D + 0.5200 \times 10^{-5}AB - 0.001AC - 0.00251A^2 - 5 \times 10^{-6}BD - 0.01CD - 0.00251A^2 - 1 \times 10^{-6}B^2 - 0.465C^2 - 0.0561D^2$

The settling characteristics of the SBR mixture of liquid-solid suspensions were quantified using the sludge volume index (SVI) = $41.67A - 0.278A - 0.0038B + 0.6667C + 1.423D + 0.5200 \times 10^{-5}AB - 0.001AC - 0.00251A^2 - 5 \times 10^{-6}BD - 0.01CD - 0.00251A^2 - 1 \times 10^{-6}B^2 - 0.465C^2 - 0.0561D^2$ was found to be 100 to 150 mL/g.

Phosphate removal = $75.74 - 0.125A - 0.28B - 0.375C - 0.208D - 0.315AB - 0.0625AC + 0.16875AD - 0.225BC + 0.6875BD - 0.0625CD - 6.421A^2 - 5.8B^2 - 0.561D^2$

Elemental Analysis of Sludge
The element distribution in sludge was studied using EDX analysis. Figure 5 shows that the presence 86% carbon, 9.13% oxygen, 1.58% calcium, and 1.36% iron in sludge. Other elements such as chlorides, sulphur, were observed in trace amount.

Multiple regression analysis was carried out considering full quadratic model equation on the responses to evaluate the adequacy of fit and results are reported in Table 4, 5, 6. The coefficient of determination (R²- values) for the model equation are R² = 0.92 to 0.98, adjusted R²=0.85 to 0.97

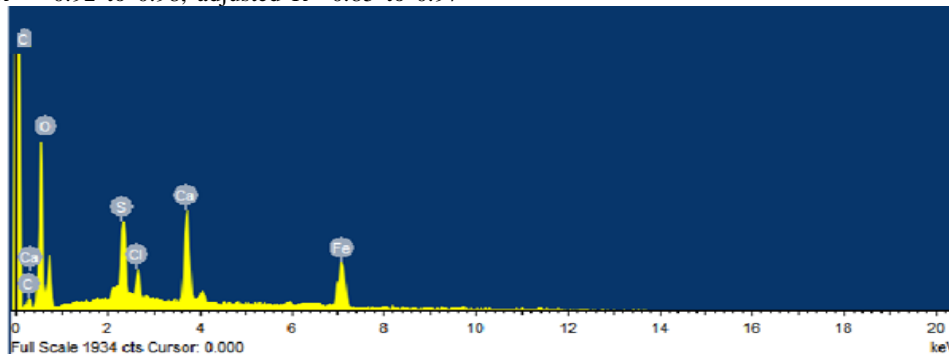


Figure 5. Effect of filling time on final p

Kinetic Studies

Kinetic studies was performed for COD removal.

$$\ln C = K_0 t + A \quad (2)$$

Where C is the substrate concentration expressed as COD (mg/L); Ko is the kinetic constant; t is the time (h).

The empirical Monod equation is

$$\mu = \mu_{\max} S / (K_s + S) \quad (3)$$

μ is the overall growth rate, μ_{\max} axis the specific rates of metabolic consumption, S is the growth substrate concentration and K_s is the substrate concentration corresponding to one half of the μ_{\max}

$$Y = dX/dS \quad (4)$$

The yield coefficient (Y), generally referred to as the substrate-to-biomass yield, converts between cell growth rate dX/dt and substrate utilisation rate dS/dt.

$$(-dS)/dt = V_{\max} XS / (K_S + S) \quad (5)$$

The material balance for the reactor

$$QS_0 - QS + V_s dS/dt = 0 \quad (6)$$

$$Xt / (S_0 - S) = K_s / kS + 1/k \quad (7)$$

where X is MLSS (mg/l); t is the reaction time (h); S₀ is initial substrate concentration expressed as COD (mg/l); k is the maximum rate of substrate utilization per unit mass of microorganisms, (h⁻¹). Using the Eq. (7), a graph (Xt)/(S₀-S) vs 1/S was plotted^[21] and kinetic parameters k and K_s were calculated from the slope and intercept. The value of k was found to be 10 h⁻¹ (Figure 6), whereas K_s was found to be 45.85 mg/L. The k value affects the volume of reactor. Greater the value of k, smaller will be the size of the reactor. The k studied was found to be very high, indicating that a small size reactor is enough for the treatment of dairy effluent.

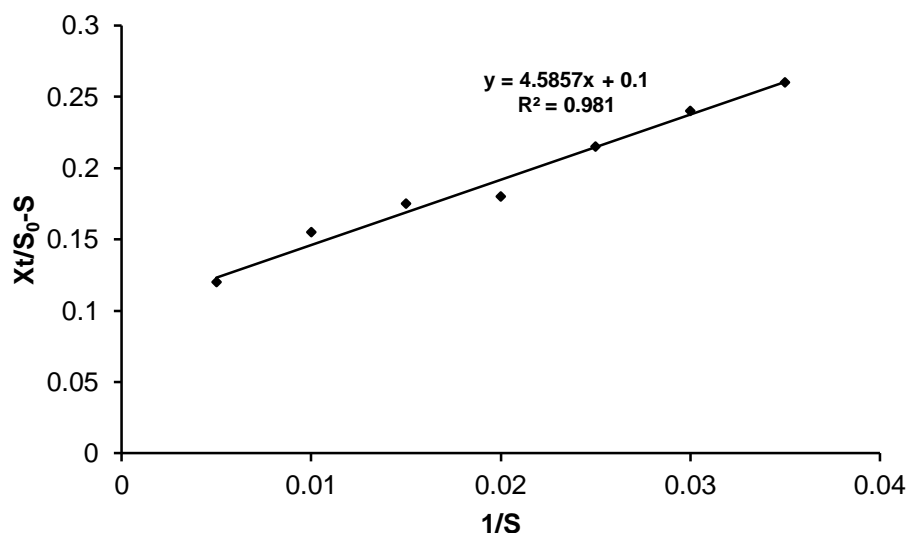


Figure 6: Kinetic studies for evaluation k and Ks

Thermo-gravimetric investigation of EM nano adsorbent

To work with the influence of heat for SBR sludge, the thermo-gravimetric examination [22] was preceded as displayed in the Error! Reference source not found. From the 7, weight reduction zones were noticed. In the primary

zone, 25°C to 100°C, about 8.3% of reduction was seen which demonstrates the existence of water and solvent. In zone 2, from 100°C to 500°C, upto 13.6 % of reduction was seen which showing the presence of organic substance. In zone 3, from 500°C to 700°C upto 20.8% of weight reduction was noticed. Above 700°C, it was observed that change in the weight reduction was not significant.

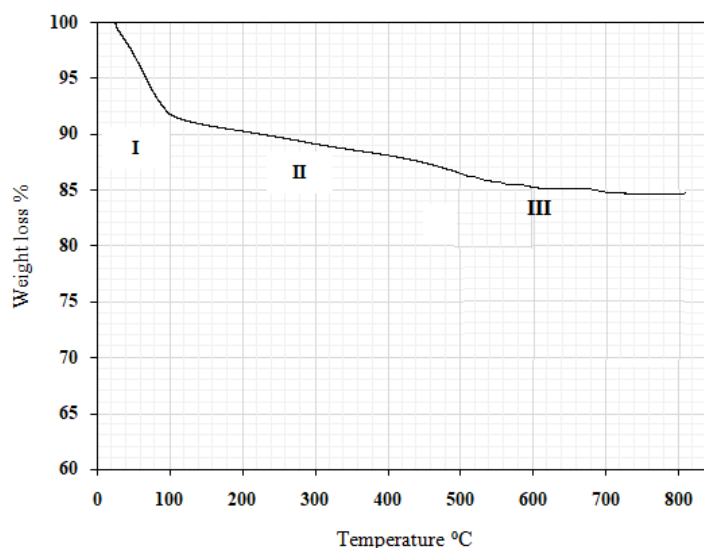


Figure 7: TGA of waste sludge from SBR

CONCLUSION

The dairy effluent from the effluent treatment plant contains a high pollution load when compared to other effluents from the food industry. So, there is a need to treat this effluent before discharging it into the water bodies. The traditional treatment methods are insufficient due to the ineffective removal of polycyclic organic substances because of their complex

molecular structure and stable chemical properties. The effluent is pre-treated before introducing it into the biological process to get high pollutant removal efficiency. This includes treating the effluent with ozone, hydrogen peroxide, and a combination of ozone and hydrogen peroxide by varying the flow and quantity. The initial characteristics of dairy wastewater are done by using APHA methods. The conditions optimized for the above process were at a reaction time of 5mins of ozone at the pH of 10, and the amount of H₂O₂ was

10ml/l. The experimental analysis was carried out and found that the combination of ozone and hydrogen peroxide gave a better removal efficiency of pollutants than the sole ozone and hydrogen peroxide. The maximum percentage removal of COD, BOD, TKN, TP, TSS, was obtained. The above-optimized condition was used to get more removal efficiency of pollutants before introducing them into the biological process like Sequencing Batch Reactor. The kinetic constant k was found to be $10h^{-1}$, whereas K_s was found to be 45.85 mg/L. The sludge analysis was performed and found to be maximum carbon sludge. So the excess sludge produced during the SBR operation can be dried and used for the production of fuel-briquette.

REFERENCES

- i. Khalaf, A.H., Ibrahim, W.A., Fayed, M., Eloffy, M.G., 2021. Comparison between the performance of activated sludge and sequence batch reactor systems for dairy wastewater treatment under different operating conditions. *Alexandria Engineering Journal*. 60. pp.1433-45. <https://doi.org/10.1016/j.aej.2020.10.062>
- ii. Coelho, M.M., Morais, N.W., Pereira, E.L., Leitão, R.C., dos Santos, A.B., 2020. Potential assessment and kinetic modeling of carboxylic acids production using dairy wastewater as substrate. *Biochemical Engineering Journal*, 156, pp.107502. <https://doi.org/10.1016/j.bej.2020.107502>
- iii. Chavez, A.M., Gimeno, O., Rey, A., Pliego, G., Oropesa, A.L., Alvarez, P.M., Beltran, F.J., 2019 Treatment of highly polluted industrial wastewater by means of sequential aerobic biological oxidation-ozone based AOPs. *Chemical Engineering Journal*, 361, pp.89-98. <https://doi.org/10.1016/j.cej.2018.12.064>
- iv. Suresh, R., Rajoo, B., Chenniappan, M., Palanichamy, M., 2021. Experimental analysis on the synergistic effect of combined use of ozone and UV radiation for the treatment of dairy industry wastewater. *Environmental Engineering Research*. 26. pp.375-380. <https://doi.org/10.4491/eer.2020.375>
- v. Xing, Z.P., Sun, D.Z., Yu, X.J., Zou, J.L., Zhou, W., 2014. Treatment of antibiotic fermentation- based pharmaceutical wastewater using anaerobic and aerobic moving bed biofilm reactors combined with ozone/hydrogen peroxide process. *Environmental Progress & Sustainable Energy*. 33. pp.170-7. <https://doi.org/10.1002/ep.11775>
- vi. Li, J., Song, W., Yu, Z., Li, Q., (2020) Preparation of the Mn-Fe-Ce/ γ -Al₂O₃ ternary catalyst and its catalytic performance in ozone treatment of dairy farming wastewater. *Arabian Journal of Chemistry*. 13. pp.3724-34. <https://doi.org/10.1016/j.arabjc.2020.01.006>
- vii. Kaewsuk, J., Thorasampan, W., Thanuttamavong, M., Seo, G.T., 2010. Kinetic development and evaluation of membrane sequencing batch reactor (MSBR) with mixed cultures photosynthetic bacteria for dairy wastewater treatment. *Journal of Environmental Management*, 91. pp.1161-8. <https://doi.org/10.1016/j.jenvman.2010.01.012>
- viii. Patil, S., Bourke, P., 2012. Ozone processing of fluid foods. In *Novel thermal and non-thermal technologies for fluid foods* pp. 225-261. Academic Press. <https://doi.org/10.1016/b978-0-12-381470-8.00009-8>
- ix. Mulla, R.K., Sutar, A.S., Ranveer, A.C., 2015. Study of various technologies available for treatment of dairy wastewater-A Review. *Int. J. Res. Appl. Sci. Eng. Technol.* 3. pp.432-5.
- x. Perna, V., Castelló, E., Wenzel, J., Zampol, C., Lima, D.F., Borzacconi, L., Varesche, M.B., Zaiat, M., Etchebehere, C., 2013. Hydrogen production in an upflow anaerobic packed bed reactor used to treat cheese whey. *International Journal of Hydrogen Energy*. 38. pp.54-62. <https://doi.org/10.1016/j.ijhydene.2012.10.022>
- xi. Kaur, N., 2021. Different treatment techniques of dairy wastewater. *Groundwater for Sustainable Development* 14:100640. <https://doi.org/10.1016/j.gsd.2021.100640>
- xii. Sinha, S., Srivastava, A., Mehrotra, T., Singh, R., 2019. A review on the dairy industry waste water characteristics, its impact on environment and treatment possibilities. *Emerging issues in ecology and environmental science*. 20. pp.73-84. https://doi.org/10.1007/978-3-319-99398-0_6
- xiii. Singh, M., Srivastava, R.K., 2011. Sequencing batch reactor technology for biological wastewater treatment: a review. *Asia-pacific journal of chemical engineering*. 6. pp3-13. <https://doi.org/10.1002/apj.490>
- xiv. Loures, C.C., Izário Filho, H.J., Samanamud, G.R., Souza, A.L., Salazar, R.F., Peixoto, A.L., Guimarães, O.L., 2013. Performance evaluation of photofenton and fenton processes for dairy effluent treatment. *International Review of Chemical Engineering (IRECHE)* 5. pp.280-8.
- xv. Heidari, M.R., Malakootian, M., Boczkaj, G., Sun, X., Tao, Y., Sonawane, S.H., Mehdizadeh, H., 2021. Evaluation and start-up of an electro-Fenton-sequencing batch reactor for dairy wastewater treatment. *Water Resources and Industry*, 25. pp.100149. <https://doi.org/10.1016/j.wri.2021.100149>
- xvi. Varga, L., Szigeti, J., 2016. Use of ozone in the dairy industry: A review. *International Journal of Dairy Technology*. 69. pp.157-68. <https://doi.org/10.1111/1471-0307.12302>
- xvii. Davarnejad, R., Nikseresht, M., 2016. Dairy wastewater treatment using an electrochemical method: Experimental and statistical study. *Journal of Electroanalytical Chemistry*, 775. pp.364-73. <https://doi.org/10.1016/j.jelechem.2016.06.016>
- xviii. Dos Santos Pereira, M., Borges, A.C., Heleno, F.F., Faroni, L.R., da Silva, J.C., 2018. Experimental design optimization of dairy wastewater ozonation treatment. *Water, Air, & Soil Pollution*, 3, pp.1-1. <https://doi.org/10.1007/s11270-018-3737-x>

- xix. Kaya, Y., Gönder, Z.B., Vergili, I., Ongen, A., 2019. Application of experimental design method for advanced treatment of dairy wastewater by ozonation. *Environmental Progress & Sustainable Energy*. 38(3). pp.e13025. <https://doi.org/10.1002/ep.13025>
- xx. Jawad, A., Chen, Z., Yin, G., 2016. Bicarbonate activation of hydrogen peroxide: A new emerging technology for wastewater treatment. *Chinese Journal of Catalysis*, 37. pp.810-25. [https://doi.org/10.1016/S1872-2067\(15\)61100-7](https://doi.org/10.1016/S1872-2067(15)61100-7)
- xxi. Mehrotra, R., Trivedi, A., Mazumdar, S.K., 2016. Study on characterisation of Indian dairy wastewater. *Int J Eng Appl Sci Technol.*, 1. pp.77-88.
- xxii. Shete, B.S., Shinkar, N.P., 2013. Dairy industry wastewater sources, characteristics & its effects on environment. *International Journal of Current Engineering and Technology*. 3. pp.1611-5.