Sigma J Eng Nat Sci, Vol. 40, No. 1, pp. 118–131, March, 2022

Sigma Journal of Engineering and Natural Sciences
Web page info: https://sigma.yildiz.edu.tr
DOI: 10.14744/sigma.2022.00010

Research Article

Waste sludge disintegration and bound water reduction by chemical oxidation: A comparative study

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ARTICLE INFO

Article history
Received: 18 January 2021
Accepted: 01 March 2021

Key words:
Waste sludge; Disintegration, bound water; Hyrogen peroxide; Hypochlorite; Persulfate

ABSTRACT

Waste sludge disintegration and bound water reduction was investigated by comparative chemical oxidation using calcium hypochlorite, hydrogen peroxide, peroxymonusulfate and peroxydisulfate in the study. Response surface methodology (RSM) with Box-Benhken Design (BBD) was used to determine operating parameters namely initial pH (2–10), oxidant dosage (5–85 mg/g TSS), and Fe^{2+} to oxidant ratio (0.2-2) and disintegration time (20–100 min). According to ANOVA results, determination coefficient (R^2) was found 93.2%, 76.3%, 84% and 84.8% for each oxidant, respectively. Under the optimum operating conditions, disintegration degree in terms of chemical oxygen demand (DD_{COD}) was calculated 11.09%, 5.23%, 10.75%, and 5.34%, respectively. Furthermore, bound water reduction (BWR) of waste sludge increased after the disintegration process, and 33.52%, 24.56%, 44.63% and 32.80% BWR values were obtained under the same operating conditions. Results show that the higher DD_{COD} and BWR values were achieved by calcium hypochlorite and peroxymonosulfate treatment.

Cite this article as: Sarı Erkan H. Waste sludge disintegration and bound water reduction by chemical oxidation: A comparative study. Sigma J Eng Nat Sci 2022;40(1):118–131.

INTRODUCTION

As a result of the widespread use of the activated sludge process, excessive activated sludge production is inevitable in wastewater treatment plants (WWTP) [1]. Since the activated sludge contains high amounts of water (exceeding 95%), the transfer, storage and disposal of sludge is quite difficult, and the cost of sludge treatment is highly dependent on the volume and water content of the sludge produced [2]. In biological wastewater treatment plants, approximately 35-60% of the total cost consists of sludge treatment and disposal. Waste sludge, which contains high concentrations of solid and organic matter, is heterogeneous and colloidal complex and it is considered as a renewable energy source for energy recovery [3]. Endocrine disrupting compounds, bis (2-ethylhexyl) phthalate, tetracycline, phenol, heavy metals and pathogen present in the sludge cause serious environmental risks and the elimination of odor emitted

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This paper was recommended for publication in revised form by Regional Editor Azmi Seyhun Kıpçak

Published by Yıldız Technical University Press, İstanbul, Turkey

from sludge is very important to maintain air quality [4-8]. Therefore, carrying out the necessary processes and analyzes in sludge disposal is an urgent obligation.

Advanced oxidation processes, physical treatment, biological treatment and pyrogenic decomposition methods such as sludge dewatering, sludge minimization, thermal drying, anaerobic digestion, removal of pollutants and pelletizing for fuel preparation are used to reduce sludge volume, to recover and to reduce associated risks. Among these methods, advanced oxidation processes (AOPs) have high performance and are widely applied in sludge treatment. Different oxidants such as hydrogen peroxide (H_2O_2), persulfate, hypochlorite, permanganate and ozone are used for this purpose [9–10]. Disintegration and dewatering of sludge can be achieved at shorter reaction times and at higher degree of disintegration when applied the AOPs as a pretreatment of sludge [11].

H_2O_2 is one of the widely used oxidants in advanced oxidation treatment, and it is based on the conversion of H_2O_2 to high oxidative hydroxyl radical ($OH^{\bullet}$) after activations such as metal conversion, microwave, ultrasound, electrolysis and light radiation [9]. $OH^{\bullet}$, which is produced with the use of H_2O_2 in the sludge disintegration and dewatering in the advanced oxidation processes, leads to the destruction of sludge flocs and cell membranes. Thus, water between sludge cellular tissues and intracellular is released and this contributes to the improvement of the dewatering of the sludge. Extracellular polymeric substances (EPS) and certain recalcitrant organic components are converted to dissolved organics or carbon dioxide and water in the process, thereby improving sludge minimization [12]. The H_2O_2-based advanced oxidation process shows high performance also in the removal of contaminants in the sludge and refractory organic contaminants in the sludge can be effectively degraded by oxidative $OH^{\bullet}$ [9, 13–14].

As is known, Fenton oxidation is one of the most effective advanced oxidation methods that increase sludge disintegration and dewaterability and it activates the production of $OH^{\bullet}$ under acidic conditions and in the presence of iron ions as catalyst [15]. Fenton process is closely related to pH value and requires strong acidic conditions. This is one of the drawbacks of the Fenton process in sludge disintegration and dewatering [16]. Recently, advanced oxidation processes based on $OH^{\bullet}$ using hypochlorite salt ($Ca(OCl)_2$) as oxidants attract great attention. When compared to the traditional Fenton process, the hypochlorite salt can catalyze Fe^{2+} over a wide pH range and produce $OH^{\bullet}$ [16–17]. However, there are few studies in sludge treatment on the use of Fe^{2+} activated hypochlorite treatment which is widely used in wastewater treatment [18]. Similar to H_2O_2 oxidation, $OH^{\bullet}$, which is generated by the hypochlorite salt, ensures the trapped water in the bacterial cell and the bound-water in the extracellular polymeric substances (EPS) to be released as well as cell destruction, sludge minimization and disintegration. After the oxidation process, re-coagulation is realized with Fe^{3+} and Ca^{2+} ions and dewaterability of sludge is increased, sludge minimization is provided [16–17]. Sulfate radical ($SO_4^{-\bullet}$) based technologies are also becoming increasingly important in both academic and industrial platforms. Peroxymonosulphate (PMS) and peroxydisulphate (PDS) are precursors of sulfate radical and they are both effectively used in the degradation of persistent organic pollutants [19–21]. Although peroxymonosulfate and peroxydisulfate are both strong oxidant matters, their direct reactions with many pollutants are slow [21–22]. When they are activated, they produce a highly reactive $SO_4^{-\bullet}$ and it has a higher oxidation potential (2.5–3.1 V) which allows operation at wider pH ranges compared to $OH^{\bullet}$ [23]. Activated peroxymonosulfate or peroxydisulfate oxidation is much more effective than peroxymonosulfate or peroxydisulfate alone in improving the disintegration and dewatering of sludge. Iron is the most widely used transition metal and it is widely used due to its high activation efficiency, relatively less toxicity, low cost and being eco-friendly structure. For production of $SO_4^{-\bullet}$, peroxymonosulfate and peroxydisulfate react with Fe^{2+} and is being activated. Activation can also be achieved with zero-valent Fe (Fe^0) or heterogeneous activation of Fe^{2+} and Fe^0 [24–26]. Peroxymonosulfate and peroxydisulfate activation can also be achieved by heat, by providing alkali conditions and by electrolysis [20-22, 27]. Oxidation with $SO_4^{-\bullet}$, which is produced by using peroxydisulfate in sludge treatment has been intensely investigated for the last decade [28–31]. Recently, activated peroxymonosulfate oxidation in sludge dewatering and disintegration has been investigated [23, 32–34].

The main purpose of this study is to investigate of disintegration and bound water reduction of waste activated sludge by using several oxidants such as hydrogen peroxide, calcium hypochlorite, peroxymonosulfate and peroxydisulfate. In the study, optimum operating parameters affecting sludge disintegration such as initial pH, oxidant dose, Fe^{2+}/oxidant ratio and treatment time were determined by using Box-Behnken experimental design (BBD).

MATERIAL AND METHODS

PHYSICO-CHEMICAL CHARACTERISTIC OF WASTE SLUDGE

Waste sludge was taken from the end of the aeration tank of a wastewater treatment plant (WWTP) in Istanbul, Turkey. Following the sampling, the sludge was transferred to the laboratory and stored at 4°C. The main properties of sludge are shown in Table 1. All the analysis performed according to Standard Methods (2005) [35].

EXPERIMENTAL PROCEDURE

A serious of batch experiments was carried out in order to determine the effect of oxidants type for the

Table 1. Physico-chemical properties of raw waste activated sludge

Parameter	Mean value	SD	Method or equipment
Mixed liquor suspended solids (MLSS)	9130	26.45	SM 2540 D [35]
Mixed liquor volatile suspended solids (MLVSS)	6696.7	40.41	SM 2540-E [35]
pH	6.9	0.017	WTW MultiLine P4 SenTix 41
Conductivity, (μS/cm)	942	20	Eutech Instruments Con510
sCOD (mg/L)	45.7	1.6	SM 5520 C Close reflux titrimetric method [35]
Total COD (mg/L)	3982.4	25.4	SM 5520 C Close reflux titrimetric method[35]

Table 2. Experimental design matrix and levels of the sludge conditioning parameters for hydroxyl and sulfate radical oxidation

Factors	Ranges and level		
	–1	0	1
X_1: Initial pH of waste sludge	2	6 (only 3 for H_2O_2)	10 (only 4 for H_2O_2)
X_2: Oxidant dosage (mg/g TSS)	5	45	85
X_3: Fe^{2+}/oxidant dosage	0.2	1.1	2
X_4: Conditioning time (min)	20	60	100

disintegration of sludge. Calcium hypochlorite ($Ca(OCl)_2$), hydrogen peroxide (H_2O_2), potassium peroxymonosulfate ($2KHSO_5*KHSO_4*K_2SO_4$) and sodium peroxydisulfate ($Na_2S_2O_8$) were chosen as oxidants. All chemicals used in this study were of analytical-reagent grade.

Optimization and confirmation experiments were conducted in Erlenmeyer flasks by adding 150 mL of sludge. The chemical reactions were started swiftly after adjusting the pH value (between 2 and 10) with 6 N H_2SO_4 and 6 N NaOH, then added desired amount of $FeSO_4.7H_2O$ and oxidants for each batch test. After that Erlenmeyer flasks were shaken with a WISD- WIS-20 orbital shaker at 250 rpm and 30°C throughout desired reaction time (20-100 min). At the end of the pretreatment process, a 30 mL treated sludge sample was withdrawn and centrifuged at 3000 rpm throughout 30 min. The COD analyses of supernatant of sludge samples was measured after filtration by round filter with a 0.45 μm pore size according to Standard Methods [35].

RSM DESIGN

Initial pH (X_1), oxidant dosage (X_2), ferrous iron to oxidant ratio (X_3) and conditioning time (X_4) were optimized by Box-Behnken Design. The experiment sets were created by Design Expert software (trial version 7.0.0). The ranges and levels of the four factors are listed in Table 2. The response variables were distintegration degree of WAS (Y_1, Y_3, Y_5, Y_7) and reduction of bound water of WAS (Y_2, Y_4, Y_6, Y_8) in the study. The experimental design for optimization is presented in Table 3. Response function is given in the Equation (1) [36].

$$\begin{aligned} Y = {} & \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{11} X_1^2 \\ & + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{44} X_4^2 + \beta_{12} X_1 X_2 \\ & + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 \\ & + \beta_{34} X_3 X_4 \end{aligned} \tag{1}$$

where, β_0, β_1, β_2, β_3 and β_4 are the regression coefficients for linear terms, $\beta_{11,}$ $\beta_{22,}$ β_{33} and β_{44} are quadratic terms, and $\beta_{12,}$ $\beta_{13,}$ $\beta_{14,}$ $\beta_{23,}$ $\beta_{24 \text{ and }}$ β_{34} are interaction terms respectively. $X_{1,}$ $X_{2,}$ X_3 and X_4 are the coded independent variables in the generalized.

DETERMINATION OF WASTE SLUDGE DISINTEGRATION

The distintegration degree of pre-treated sludge was determined by soluble COD (sCOD) concentration [23, 37–39]. DD_{COD} values of pre-treated sludge were calculated with Eq. (2).

$$DD_{COD} = \frac{(sCOD - s0COD)}{(TCOD - s0COD)} \tag{2}$$

where, sCOD and s_0COD are released COD concentrations for pre-treated and raw sludge (mg/L), respectively. $_T$COD is the total releasable COD concentration in the raw sludge (mg/L) and it was determined by an alkaline hydrolysis procedure. In the procedure, 0.5 M NaOH was added in raw sludge sample and then mixed with at room temperature throughout 24 hours. After the procedure, a 30 mL sludge sample was withdrawn and centrifuged at 3000 rpm throughout 30 min and filtered using round filter with a pore size of 0.45 µm.

DETERMINATION OF WASTE SLUDGE BOUND WATER

Bound water content of treated and raw sludge samples was determined by centrifugation method [34], [40]. Bound water is defined as the sum of internal water, interstitial water and surface water. Internal water may be water in bacterial cells and it physically and/or chemically bound in the sludge, whereas interstitial water may be water trapped in voids and capillaries between and inside flocs. On the other hand, surface water may be found adsorbed or adhered onto the wet sludge [40]. According to this method, 35 mL of sludge sample was centrifuged at 3000 rpm throughout 10 min, then the supernatant of sludge was discarded and centrifuge tube was weighted. Then, water content in the centrifuge tube was dried in an oven at 105°C overnight and weighted again. Bound water of raw and pretreated sludge were calculated the weight of before and after the treatment.

$$BWR = \left(\frac{1 - BW_{treated}}{BW_{raw}} \right) \times 100 \tag{3}$$

where, $BW_{treated}$ and BW_{raw} are bound water for treated sludge and raw sludge.

RESULTS AND DISCUSSION

EVALUATION OF MULTIVARIATE OPTIMIZATION IN TERMS OF DISINTEGRATION DEGREE AND BOUND WATER REDUCTION

The results of batch experiments based on the BBD design for all oxidant are presented in Table 3. Analysis of Variance (ANOVA) was conducted for the response variables of DD_{COD} and BWR, and Table 4-7 show the ANOVA results for each oxidant. According to ANOVA results, the predicted data were found in a good agreement with the corresponding terms. For $Ca(OCl)_2$ treatment, the determination coefficient (R^2), adjusted R^2 (Adj. R^2), F-value and the p-value of DD_{COD} were found 93.2%, 91.7%, 62.89 and <0.0001, respectively. These parameters in Table 4 show the high significance of model for $Ca(OCl)_2$ treatment. For H_2O_2 treatment, these model terms were determined as 76.3%, 72.4%, 19.35 and <0.0001 respectively (Table 5). Generally, a good fit of the model should have a rate of R^2 higher than 80% [41], therefore, therefore, lower quadratic equations' accuracy for the operating variables may be observed for H_2O_2 treatment. As can be seen from Table 6, the R^2, Adj. R^2, F-value and p-value of DD_{COD} for peroxymonosulfate treatment were 84%, 79.7%, 19.30 and <0.0001, respectively. These model parameters of DD_{COD} were also found 84.8%, 82.2%, 33.41 and <0.0001 for peroxydisulfate treatment, respectively (Table 7). The model terms are significant and highly significant when the p-value of the model is lower than 0.05 and 0.0001, respectively. According to p-values of the models for all oxidant, the regression models were highly significant. The model's quality of the fitness also follows model F-value. Large F-value shows a high significance of the corresponding term. According to Table 4-7, highest R^2 and largest F-value were obtained by $Ca(OCl)_2$ treatment although all model p-value was found lower 0.0001. Therefore, it can be said that $Ca(OCl)_2$ treatment represented a high quality of fitness in terms of DD_{COD} compared the other treatments.

As seen from Table 4, linear parameter (initial pH (X_1) and oxidant dosage (X_2)) were found highly significant (p-value <0.0001), whereas, Fe2+/oxidant ratio was found significant (p-value: 0.0152) for $Ca(OCl)_2$ treatment. Furthermore, interaction term between X_1 and X_3 was significant (p-value: 0.0256), and quadratic terms of initial pH (X_1) were found highly significant (p-value <0.0001). The obtained results show that the initial pH has great influences on DD_{COD} in $Ca(OCl)_2$ treatment. On the other hand, only linear and quadratic terms of H_2O_2 dosage (X_2, X_2^2) were found highly significant, interaction term between X_2 and X_3 was also found significant in H_2O_2 treatment. In peroxymonosulfate treatment, oxidant dosage (X_2), quadratic term of X_2 and Fe^{2+}/oxidant ratio (X_3) were found highly significant, whereas interaction term of X_1 and X_3, and quadratic term of X_3 were found significant on DD_{COD}. In terms of peroxydisulfate treatment, initial pH (X_1) and oxidant dosage (X_2) have a highly significant effect, whereas Fe^{2+}/oxidant ratio (X_3) and quadratic term of pH has significant effect on DD_{COD}.

Approximate functions (Eq. (4-7)) for DD_{COD} for each treatment were yielded through the obtained results. As it can be known, positive and negative sign of the coefficients in Eq. (4-7) indicates the effects of independent variables on DD_{COD}. Positive coefficients reveal that decrease the value of independent parameters can enhance DD_{COD}, while negative coefficients indicate that increase the value of operating variables can improve DD_{COD} in each treatment.

$$\begin{aligned} Y_1 &= +4.71992 - 1.71517 X_1 + 0.089815 X_2 \\ &\quad + 2.42814 X_3 - 0.28437 X_1 X_3 + 0.13333 X_1^2 \end{aligned} \tag{4}$$

$$\begin{aligned} Y_3 &= -1.88280 + 0.22664 X_2 + 2.44296 X_3 \\ &\quad - 0.043435 X_2 X_3 - 1.43485E-003 X_2^2 \end{aligned} \tag{5}$$

Table 3. Experimental conditions and responses in the study

Run	X_1	X_1	X_2	X_3	X_4	$Ca(OCl)_2$		H_2O_2		Peroxmono sulfate		Peroxydisulfate	
	Initial pH for $Ca(OCl)_2$, PMS and PDS	Initial pH for H_2O_2	Oxidant dosage	Fe^{2+}/oxidant ratio	Conditioning time	Y_1;DD_{COD}, %	Y_2;BWR,%	Y_3;DD_{COD}, %	Y_4;BWR,%	Y_5; DD_{COD}, %	Y_6; BWR,%	Y_7; DD_{COD}, %	Y_8; BWR,%
1	2	2	85	1.1	60	9.66	38.4	6.79	23.01	9.69	44.68	6.30	28.69
2	6	3	45	0.2	20	3.11	20.6	5.70	23.92	9.38	36.99	1.57	8.13
3	6	3	45	1.1	60	3.74	20.7	5.42	6.19	4.025	14.82	2.97	16.43
4	6	3	85	1.1	100	8.92	16.6	4.55	2.35	6.19	21.89	3.29	10.00
5	6	3	5	1.1	100	0.38	15.6	1.25	23.17	0.24	14.72	0.31	12.00
6	6	3	45	2	100	5.67	21.2	4.83	4.79	4.27	10.74	4.23	10.670
7	2	2	45	0.2	60	7.17	35.1	6.16	34.42	9.97	48.75	5.49	29.91
8	2	2	45	1.1	20	8.01	36.7	6.93	26.29	7.63	38.04	5.91	24.74
9	2	2	45	1.1	100	8.15	35.7	7.77	24.84	8.89	36.98	5.945	37.12
10	6	3	85	0.2	60	7.45	20.5	6.79	23.08	11.58	49.045	4.35	23.36
11	6	3	85	2	60	9.66	25.5	6.26	9.32	6.37	21.61	5.95	17.39
12	6	3	5	0.2	60	0.0083	10.7	0.18	16.82	2.80	19.09	2.03	14.91
13	10	4	45	1.1	20	4.23	17.3	5.77	13.24	5.00	10.33	1.15	10.90
14	6	3	5	1.1	20	0.21	9.1	0.49	21.94	0.91	15.78	0.49	16.69
15	6	3	45	1.1	60	3.71	20.3	5.42	13.68	3.99	13.93	3.08	17.54
16	6	3	45	1.1	60	3.39	20.7	5.49	9.59	4.09	14.07	3.12	16.73
17	6	3	45	2	20	5.46	22.2	5.21	2.81	4.16	10.67	3.97	19.71
18	10	4	45	0.2	60	6.12	17.1	4.58	11.40	19.63	27.61	1.89	10.18
19	10	4	5	1.1	60	1.19	2.5	1.02	12.51	5.18	12.03	0.41	6.51
20	6	3	45	1.1	60	3.64	20.2	5.28	20.09	4.55	18.65	2.97	17.64
21	10	4	45	2	60	3.85	18.9	6.12	17.24	4.97	14.96	3.11	13.54
22	6	3	45	1.1	60	3.60	20.8	5.42	11.97	4.02	16.90	3.04	19.22
23	10	4	45	1.1	100	4.16	21.4	7.66	17.38	4.51	12.32	2.62	12.00
24	6	3	85	1.1	20	7.59	23.4	4.93	5.62	6.93	29.97	3.60	15.69
25	10	4	85	1.1	60	7.35	23.9	4.51	8.66	8.22	12.66	3.60	13.97
26	2	2	5	1.1	60	5.46	32.2	1.12	39.35	5.67	36.90	4.93	39.62
27	6	3	45	0.2	100	2.24	17.7	6.47	22.72	8.96	38.79	0.59	15.44
28	2	2	45	2	60	8.99	33.2	6.82	32.79	6.37	34.75	6.30	36.23
29	6	3	5	2	60	0.28	8.3	5.91	28.50	0.49	14.99	0.56	16.95

$$Y_5 = +10.82126 - 1.76204 X_1 + 0.070218 X_2 - 5.77980 X_3 - 0.76805 X_1 X_3 + 0.21603 X_1^2 + 3.21935 X_3^2 \quad (6)$$

$$Y_7 = +5.75619 - 1.40518 X_1 + 0.038239 X_2 + 0.75833 X_3 + 0.078757 X_1^2 \quad (7)$$

The 3D response surface and contour graphs of the models for DD_{COD} are shown in Figure 1. In Figure 1a-g, one process variable kept at the center level and the other two varying within the experimental intervals. Figure 1a-b presents the effects of the initial pH and Fe^{2+}/oxidant ratio on the response of DD_{COD} for $Ca(ClO)_2$. It can be said that DD_{COD} value increased with an increase of Fe^{2+}/oxidant ratio. Lower pH value and higher Fe^{2+}/oxidant ratio is suitable to obtain maximum DD_{COD} in $Ca(ClO)_2$ treatment. For H_2O_2 treatment, oxidant dosage and Fe^{2+}/oxidant ratio were effect on DD_{COD} and maximum DD_{COD} can be found in higher oxidant dosage and Fe^{2+}/oxidant ratio (Figure

Table 4. ANOVA results of DD_{COD} and BWR for $Ca(ClO)_2$

Response 1: DD_{COD}

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	231.33	5	46.27	62.89	< 0.0001
X_1-Initial pH	35.17	1	35.17	47.81	< 0.0001
X_2-Oxidant dosage	154.88	1	154.88	210.52	< 0.0001
X_3-Fe^{2+}/Oxidant	43651,00	1	5.07	6.89	0.0152
X_1X_3	43556,00	1	4.19	5.70	0.0256
X_{12}	32.01	1	32.01	43.51	< 0.0001
Residual	16.92	23	0.74		
Lack of Fit	16.85	19	0.89	47.31	0.0010
Pure Error	0.075	4	0.019		
Cor Total	248.25	28			
R^2	0.9318				
Adj R^2	0.9170				

Response 2: Bound water reduction

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	1878.69	4	469.67	48.94	< 0.0001
X_1-Initial pH	1012.11	1	1012.11	105.47	< 0.0001
X_2-Oxidant dosage	406.17	1	406.17	42.33	< 0.0001
X_1X_2	57.09	1	57.09	34820,00	0.0225
X_{12}	403.32	1	403.32	42.03	< 0.0001
Residual	230.31	24	6.90		
Pure Error	0.28	4	0.071		
Cor Total	2109.00	28			
R^2	0.8908				
Adj R^2	0.8726				

Table 5. ANOVA results of DD_{COD} and BWR for H_2O_2

Response 3: DD_{COD}

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	96.64	4	24.16	19.35	< 0.0001
X_2-Oxidant	47.47	1	47.47	38.02	< 0.0001
X_3-Fe^{2+} /Oxidant	2,32	1	2,32	1,86	0.1857
X_2X_3	9,78	1	9,78	7,83	0.0100
X_{22}	37.08	1	37.08	29.69	< 0.0001
Residual	29.97	24	1,25		
Pure Error	0.023	4	5.851E-003		
Cor Total	126.61	28			
R^2	0.7633				
Adj R^2	0.7239				

Response 4: Bound water reduction

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	1619.43	3	539.81	13.13	< 0.0001
X_1-Initial pH	238.13	1	238.13	28976,00	0.0238
X_2-Oxidant	411.21	1	411.21	10.00	0.0041
X_{12}	370.55	1	370.55	9,01	0.0060
Residual	1028.07	25	41.12		
Pure Error	107.38	4	26.84		
Cor Total	2647.49	28			
R^2	0.6117				
Adj R^2	0.5651				

Table 6. ANOVA of DD_{COD} and BWR for PMS

Response 5: DD_{COD}

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	345.96	6	57.66	19.30	< 0.0001
X_1-Initial pH	0.041	1	0.041	0.014	0.9080
X_2-Oxidant	94.67	1	94.67	31.68	< 0.0001
X_3-Fe^{2+} /Oxidant	106.21	1	106.21	35.55	< 0.0001
X_1X_3	30.58	1	30.58	10.23	0.0041
X_{12}	82.46	1	82.46	27.60	< 0.0001
X_{32}	46.93	1	46.93	15.71	0.0007
Residual	65.73	22	2.99		
Pure Error	0.22	4	0.055		
Cor Total	411.69	28			
R^2	0.8403				
Adj R^2	0.7968				

Response 6: Bound water reduction

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	4030.60	6	671.77	38.58	< 0.0001
X_1-Initial pH	1879.66	1	1879.66	107.95	< 0.0001
X_2-Oxidant	366.85	1	366.85	21.07	0.0001
X_3-Fe^{2+} /Oxidant	1055.68	1	1055.68	60.63	< 0.0001
X_2X_3	136.31	1	136.31	7.83	0.0105
X_{12}	348.71	1	348.71	20.03	0.0002
X_{32}	324.60	1	324.60	18.64	0.0003
Residual	383.08	22	17.41		
Pure Error	16.71	4	4.18		
R^2	0.9132				
Adj R^2	0.8895				

Table 7. ANOVA of DD_{COD} and BWR for PDS

Response 6: DD_{COD}

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	85.48	4	21.37	33.41	< 0.0001
X_1-Initial pH	40.64	1	40.64	63.54	< 0.0001
X_2-Oxidant	28.07	1	28.07	43.89	< 0.0001
X_3-Fe_{2+} /Oxidant	5.59	1	5.59	8.74	0.0069
X_{12}	11.17	1	11.17	17.46	0.0003
Residual	15.35	24	0.64		
Pure Error	0.016	4	4.108E-003		
Cor Total	100.83	28			
R^2	0.8477				
Adj R^2	0.8224				

Response 5:Bound water reduction

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	1887.31	8	235.91	23.01	< 0.0001
X_1-Initial pH	1391.67	1	1391.67	135.74	< 0.0001
X_2-Oxidant	0.48	1	0.48	0.047	0.8303
X_3-Fe_{2+} /Oxidant	13.19	1	13.19	1.29	0.2701
X4-Disintegration time	0.16	1	0.16	0.016	0.9011
X_1X_2	84.57	1	84.57	8.25	0.0094
X_3X_4	66.59	1	66.59	6.49	0.0191
X_{12}	227.00	1	227.00	22.14	0.0001
X_{42}	64.26	1	64.26	6.27	0.0211
Residual	205.05	20	10.25		
Lack of Fit	200.35	16	12.52	10.65	0.0170
Pure Error	4.70	4	1.18		
Cor Total	2092.36	28			
R^2	0.9020				
Adj R^2	0.8628				

1c-d). For peroxymonosulfate treatment, DD_{COD} value was gradually increased with increasing initial pH and with decreasing Fe^{2+}/oxidant ratio (Figure 1e-f). On the other hand, higher oxidant dosage and lower initial pH led to increase DD_{COD} value for peroxydisulfate treatment (Figure 1g-h).

Statistical results of bound water reduction are presented in Table 4-7. As seen from ANOVA results, R^2 values for BWR were found 89.1%, 61.2%, 91.3% and 90.2% for $Ca(OCl)_2$, H_2O_2, peroxymonosulfate and peroxydisulfate, respectively. Adj. R^2 values were also found as 87.3%, 56%, 88.9% and 86.3%, respectively. F values of the models were determined 48.94, 13.13, 38.58 and 23.01, respectively and p-values of each model for BWR were found <0.0001. According to the ANOVA results, initial pH has a highly significant effect on BWR for each treatment (Table 4-7). On the other hand, the dosage of $Ca(OCl)_2$ and peroxymonosulfate were found highly significant effect on BWR, whereas H_2O_2 dosage was found significant effect on BWR in H_2O_2 treatment. Peroxydisulfate dosage has not a significant effect on BWR in peroxydisulfate treatment. Quadratic terms of initial pH (X_1^2) have a highly significant effect on BWR for $Ca(OCl)_2$, peroxydisulfate treatmnets, and significant effect for H_2O_2 and peroxymonosulfate treatments. Furthermore, interactive term between initial pH and oxidant dosage has significant effect on BWR in $Ca(OCl)_2$ and peroxydisulfate treatments. Fe^{2+}/oxidant ratio was found highly significant effect on BWR in peroxymonosulfate treatment.

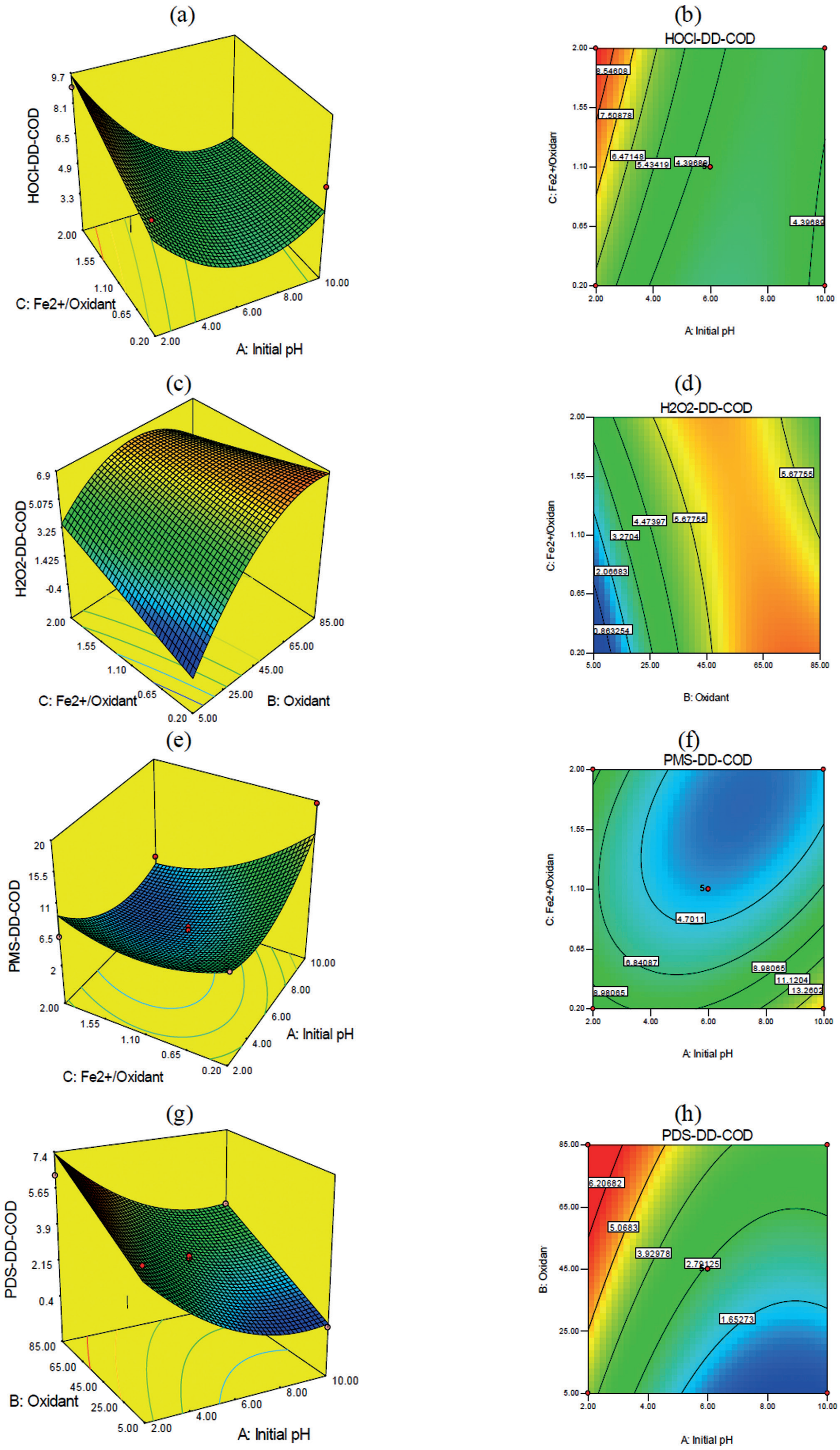

Figure 1. 3D response surface graphs and contour graphs for DD_{COD} in all treatments.

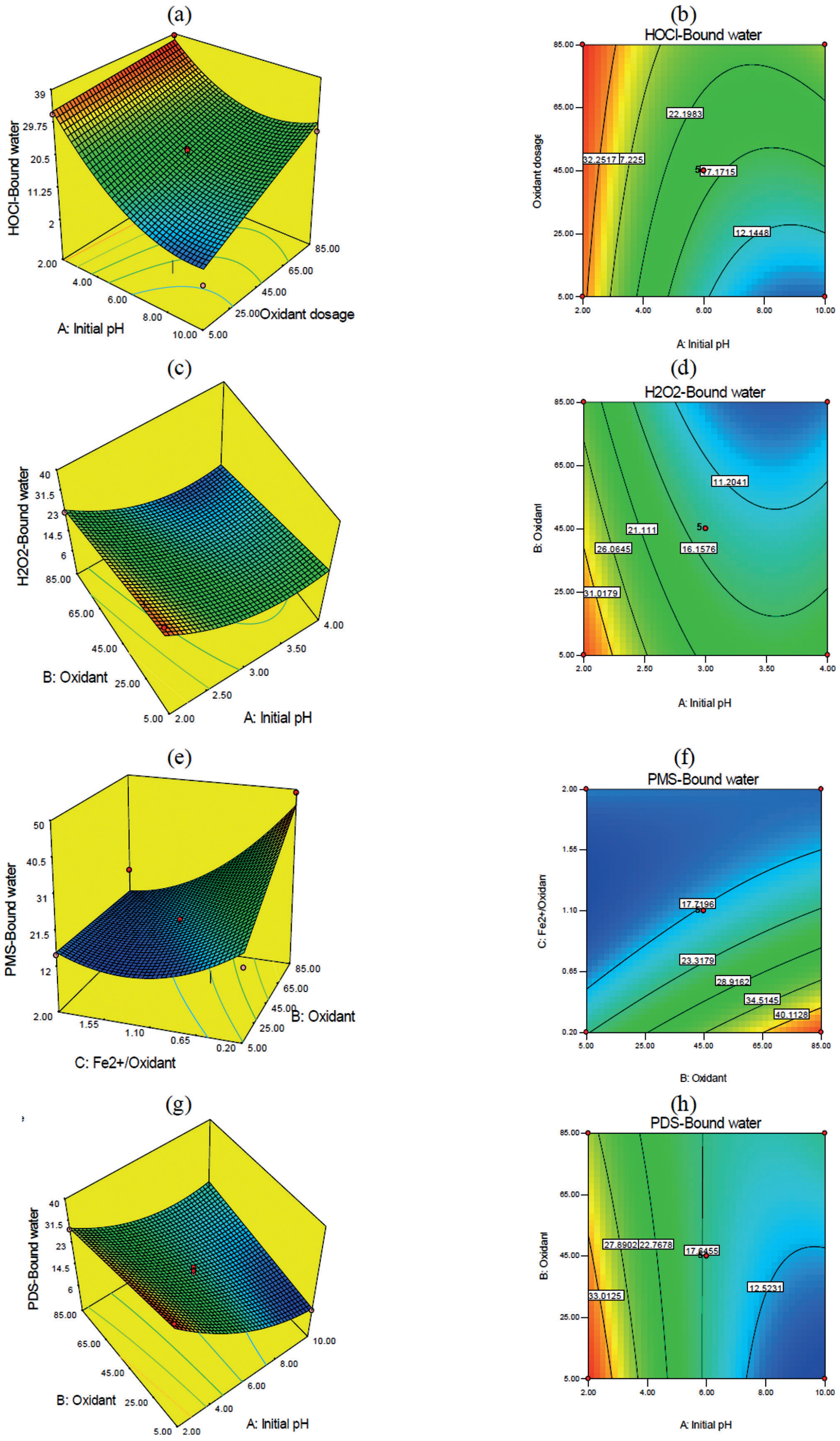

Figure 2. 3D response surface graphs and contour graphs for BWR in all treatments.

Table 8. Optimum operating conditions and confirmation experiments results

Factor	**$Ca(OCl)_2$**	**H_2O_2**	**Peroxymonosulfate**	**Peroxydisulfate**
Initial pH of sludge (mA/cm^2)	2	2.85	2	2.01
Oxidant dosage (mg/gTSS)	85	75.93	85	40.09
Fe^{2+}/Oxidant dosage	1.34	0.2	0.2	2.0
Conditioning time (min)	59.41	44.21	50.13	47.40
DD_{COD} Model prediction results (%)	11.94	6.88	12.79	6.29
BWR Model prediction results (%)	37.28	40.71	48.30	36.21
DD_{COD} Model Experimental results (%)	11.09	5.23	10.75	5.34
BWR Experimental results (%)	33.52	24.56	44.63	32.80

Approximate functions for BWR ratio were yielded through the ANOVA results by excluding the actual factors with a p-value greater than 0.05 (Eq. (8-11)).

$$\begin{aligned} Y_2 &= +49.12537 - 9.03745X_1 + 3.77606E-003X_2 \\ &\quad + 0.023612X_1X_2 + 0.47325\,X_1^2 \end{aligned} \tag{8}$$

$$\begin{aligned} Y_4 &= +111.47577 - 51.90204X_1 - 0.14635X_2 \\ &\quad + 7.25785\,X_1^2 \end{aligned} \tag{9}$$

$$\begin{aligned} Y_6 &= +60.33466 - 8.45985X_1 + 0.31660X_2 \\ &\quad - 21.75079X_3 - 0.16216X_2X_3 + 0.44425\,X_1^2 \\ &\quad + 8.46647\,X_3^2 \end{aligned} \tag{10}$$

$$\begin{aligned} Y_8 &= +38.02262 - 8.28666X_1 - 0.16741X_2 \\ &\quad + 7.96512\,X_3 + 0.35642X_4 + 0.028737X_1X_2 \\ &\quad - 0.11334X_3X_4 + 0.35843\,X_1^2 - 1.90705E \\ &\quad - 003\,X_4^2 \end{aligned} \tag{11}$$

The 3D response surface graphs and contour graphs in Figure 2a-d and Figure 3a-d show the effects of the operating conditions on the bound water reduction in all pretreatments with oxidants. As seen from the Figure 2a-b, BWR increased with an increase of oxidant dosage and it increased with a decrease of initial pH for $Ca(OCl)_2$ treatment. In H_2O_2 treatment, BWR increased with a decrease of both oxidant dosage and initial pH (Figure 2c-d). In terms of peroxymonosulfate treatment, lower pH and Fe^{2+}/oxidant ratio and higher oxidant dosage led to higher BWR (Figure 2e-f). As seen from Figure 2g-h, lower initial pH and oxidant dosage enhanced BWR in peroxydisulfate treatment.

Optimum operating conditions derived from the multivariate optimization to of DD_{COD} and BWR for all treatments are presented in Table 8. As can be seen from the Table 8, model prediction results of DD_{COD} were 11.94%, 6.88%, 12.80% and 6.30% for $Ca(OCl)_2$, H_2O_2, peroxymonosulfate and peroxydisulfate treatment, respectively. Confirmation experiments for all treatments were performed under the optimum operating conditions to confirm the accuracy of models. DD_{COD} values were found 11.09%, 5.23%, 10.75%, and 5.34%, confirming the models' reliability. According to these results, it was found $Ca(OCl)_2$ and peroxymonosulfate treatment the most effective process in terms of sludge disintegration. On the other hand, Model prediction results of BWR were 37.28%, 40.71%, 48.30% and 36.21% under the same operating conditions, respectively. BWR ratios were found 33.52%, 24.56%, 44.63% and 32.80% by confirmation experiments, respectively.

Disintegration of waste sludge using H_2O_2 has been widely researched by several authors [43-46]. Excess activated sludge disintegration using H_2O_2 was investigated by Kim et al. [42] and they found that sludge solubilization increased from 1.6% to 54.7% at 1.6 M H_2O_2 dosage regardless of sludge initial pH. Waste sludge disintegration by Fenton oxidation was also investigated by Erden and Filibeli [43] and 25.2% DD_{COD} was obtained at 60 g H_2O_2/kg TS of dosage and 4 g Fe^{2+}/kg TS. Şahinkaya et al. [44] also investigated sludge disintegration using H_2O_2 and they found 20% DD_{COD} at pH 3, 40 g/kg TS H_2O_2 dosage, 4 g Fe^{2+}/kg TS and 60 min reaction time. Feki et al. [45] also researched waste sludge disintegration by chemical treatment and they found 19.2% COD solubilization at 1.8 g/L H_2O_2 dosage, 3 of pH and 60 min oxidation time. Similar disintegration degree (19.3%) was also obtained by Yildiz and Cömert [47] at pH 2, 10 mg/g H_2O_2 dosage, 4 mg/g Fe^{2+} and 60 min retention time. Ferrentino et al. [46] also investigated waste sludge solubilization and dewaterability by H_2O_2 treatment and they found 3.2% DD_{COD} value at pH 2, 6 g/L H_2O_2 dosage, 0.8 Fe^{2+}/H_2O_2 ratio and 60 min oxidation time. Sludge disintegration by hypochlorite (ClO^-) treatment was investigated by Ye et al. [48] and they obtained 11.8% DD_{COD} value at 0.8% ClO^-/sludge (v/v).

Peroxymonosulfate treatment of waste sludge has been widely investigated similar to hydrogen peroxide treatment

[23, 28–34, 39]. Ren et al. [23] investigated sludge disintegration using peroxymonosulfate and they obtained 22.9% DD_{COD} value at 72 mg/g SS peroxymonosulfate dosage. Niu et al. [39] also investigated sludge disintegration by peroxymonosulfate treatment and they found 29.7% DD_{COD} value at 25 mg/g SS peroxymonosulfate dosage and the peroxymonosulfate treatment effectively destructs waste activated sludge particles and enhanced disintegration degree.

CONCLUSION

In this study, chemical disintegration process was investigated in order to enhance waste sludge disintegration degree and bound water reduction using calcium hypochlorite, hydrogen peroxide, peroxymonosulfate and peroxydisulfate. RSM using BBD optimization was applied to optimize initial pH, oxidant dosage, Fe^{2+}/oxidant ratio and disintegration time in the aim to get the highest DD_{COD} and BWR percentage. The results of the confirmation experiments show that the DD_{COD} values for each oxidant were found 11.09%, 5.23%, 10.75%, and 5.34% under the optimized conditions, respectively. On the other hand, 33.52%, 24.56%, 44.63% and 32.80% BWR percentages were obtained, respectively. $Ca(OCl)_2$ and peroxymonosulfate treatments show higher model accuracy according to ANOVA results. The results of this sthudy also show that the $Ca(OCl)_2$ and peroxymonosulfate treatment can be applied successfully in waste sludge pre-treatment compared to hydrogen peroxide and peroxydisulfate.

ACKNOWLEDGEMENTS

This work was supported by the Scientific Research Projects Council of YildizTechnical University, Project Number of FBA-2019-3469. The authors would like to thank for this support.

AUTHORSHIP CONTRIBUTIONS

Authors equally contributed to this work.

DATA AVAILABILITY STATEMENT

The authors confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

ETHICS

There are no ethical issues with the publication of this manuscript.

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