# The influence of ozonation and sedimentation on water treatment plant sludge: evaluation of clarified water and thickened sludge

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# ABSTRACT

It is fundamental to develop techniques that promote the improvement of the treatment and reduction of the sludge mass of water treatment plants (WTPs). Reports of the use and influence of ozone ( $O_3$ ) for this waste have not yet been found, aiming at its treatment. Ozone is a strong oxidant, that promotes mineralization through the decomposition of the organic matter into carbon dioxide and water. Hence, the main goal of this work was to investigate the effect of  $O_3$  on WTP sludges. Ozonation essays were carried out in a batch, at the end of the control time, the WTP sludge was transferred to the sedimentation column. The effects of ozone and sedimentation were assessed on the characteristics of thickened sludge and clarified water. The treatment with the highest ozone dosage (1.1 g $O_3$  (g TS)<sup>-1</sup>) yielded the most considerable alterations both in the thickened sludge and the clarified water, resulting in superior indices of total solids (39.1 g L<sup>-1</sup>), total fixed solids (28.9 g L<sup>-1</sup>), total carbon removal (13%), and aluminum solubilization (88.6 mg L<sup>-1</sup>), as well as lower particle sizes (42.6 µm) and pH (3.6). Results showed that the sludge settling periods only alter the solids content of the thickened sludge, while the ozonation influenced all parameters evaluated.

Keywords: Sludge; Ozone; Treatment; Sedimentation; Mineralization; Aluminum solubilization

# 1. Introduction

Due to urbanization and population growth in the last centuries, the demand for potable water escalated proportionately. This required the expansion of the treatment and distribution system [1]. Concurrently, the degradation of water resources occurs at a brisk pace. Such factors significantly contribute to the rise in sludge generation by water treatment plants (WTPs), made evident by the increase in suspended solids in raw water, more considerable use of chemical products in the clarification process, and the expansion of potable water production. WTP sludge encompasses the waste produced during water treatment [2–5], originated in the coagulation/flocculation process, and retained in the decantation (flotation) and filtration units. The properties of the sludges typically depend on the quality of the raw water, treatment method applied, and chemical products used, along with their dosages [3,4,6–8].

In developed countries, most of the WTP sludge is discarded in landfills [3,7,9], the destination of 57% of all United Kingdom WTPs sludges [7]. In developing countries, the sludge is generally released in water bodies, downstream of the water catchment source [4,9,10]. The

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inadequate disposal of sludges may be a risk for both human health and the environment [10–12], notably due to their potentially toxic constituents, among which are metals that may be bioaccumulated and biomagnified in the organism [13,14]. Hence, such residues are recognized as a pollution problem [15].

The stimulation for the change in this frame is the growing concern with environmental quality. WTP sludge disposal needs to receive ever-more-stringent control [16]. Restrictive legislation regarding the treatment and elimination of sludge and their related costs encourage the development of strategies to reduce the excessive production of waste [17]. In this sense, sludge ozonation presents as an alternative, enabling the decrease of the volume of sludge with aluminum solubilization and organic matter mineralization.

Ozone is a strong oxidant [18], with the capacity to oxidize a series of inorganic and organic compounds, promoting effective treatment for an array of pollutants such as humic acids [19–24]. During ozonation, oxidation may occur through a direct reaction (molecular ozone –  $O_3$ ), indirect reaction (hydroxyl radical – OH), or both simultaneously [20,25,26].

There is a lack of literature studies considering water treatment sludge that aim pretreatment with ozone injection, so it is of utmost importance to understand the alterations caused by this oxidant on WTP sludges. The sludge ozonation from sewage treatment plants (STPs) is a promising technique that has been gaining more and more interest [27,28], and is used primarily to reduce the excess of sludge with solubilization and recirculation [29–33] or as a pretreatment before anaerobic digestion [34,35]. Studies report that ozonation of STP sludge also resulted in the improvement of sludge sedimentation and dehydration [17,29,36], the gradual lowering of the pH, and solubilization of metals [22,33], reduction of the proportion of the total solids that are volatile (VTS (TS)<sup>-1</sup>) [22], and the mineralization of organic matter [17,19,29,33].

The effective reduction of the sludge mass through ozonation occurs with the decomposition of the organic matter into carbon dioxide ( $CO_2$ ) and water, promoting mineralization [17,33]. The curtailment of the sludge mass is considered a promising development strategy [36]. In comparison with other oxidative pretreatment processes, ozonation has the potential to meet the requirements of sustainable sludge management, it is one of the most promising methods for its treatment [28,36]. The ozonation costs are relatively modest when compared to other sludge treatment methods [36].

Ozone causes alterations in the characteristics and properties of sludges. Hence, in search for new alternatives that improve the treatment of WTP sludges, ozone presents features that may promote benefits for this treatment. However, reports of the use and influence of ozone for this waste have not yet been found. Thus, the main goal of this work was to assess the effect of injecting ozone, after sedimentation, in WTP sludges, evaluating the alterations in the clarified water and thickened sludge.

# 2. Methodology

# 2.1. WTP under study and sludge characterization

The sludge used in this study stems from the WTP of São Gabriel, in Southern Brazil (Fig. 1). The nominal operation capacity of the WTP is 137 L s<sup>-1</sup>, possibly reaching operation with a throughput of 220 L s<sup>-1</sup>. The coagulant used for water treatment is polyaluminum chloride (PAC).



Fig. 1. Location of the São Gabriel water treatment plant.

Sludge sampling occurred after the cleaning of the decanters, in the waste-receiving tank. After their gathering, the sludge samples were referred to the laboratory and kept under refrigeration at ~4°C  $\pm$  1°C.

For the characterization of sludge, the physicochemical parameters analysis followed the procedures in the Standard Methods for the examination of water and wastewater [37]. The determination of oxides was carried out in a sequential X-ray fluorescence spectrometer (XRF) by wavelength, Bruker S8 Tiger model.

In the microstructural characterization of the sludge, the evaluation and identification of the crystalline structure of the sample were carried out through X-ray diffraction (XRD) with an X-ray diffractometer (Rigaku, Miniflex 300). The identification of the functional groups of the sludge was performed by means of an infrared spectrophotometer with Fourier transform infrared (FT-IR) (Shimadzu, IR Prestige 21), in the range of 4,500–500 cm<sup>-1</sup>. The morphological characterization of the sludge surface was carried out by scanning electron microscopy (SEM) analysis using an SEM (Tescan, VEGA-3G).

# 2.2. Sludge ozonation

Ozonation essays were carried out in batch, in a 150 mL reactor with a continuous ozone injection. The experiments took place at an environmental temperature of 19.3°C  $\pm$  1.6°C. The ozone generator used was by Tholz-TH50<sup>®</sup>, attached to an air compressor, with a maximum production capacity of 3 g O<sub>3</sub> h<sup>-1</sup>, but the calibration performed in the laboratory-measured that the average ozone production reached was of 0.536  $\pm$  0.033 g O<sub>3</sub> h<sup>-1</sup>. The airflow and pressure were kept at fixed values in the O<sub>3</sub> generator.

At the end of the control time (0, 44, 150, 256, and 300 min), the generator was shut off, supplying different ozone doses in the WTP sludge. The ozone gas that did not react was collected using two potassium iodide traps (2% KI) connected in series. Then, the exhaust gas was discharged into the atmosphere. The dose of ozone consumed in the reaction (g  $O_3$  (g TS)<sup>-1</sup>) was calculated from the input and output ozone mass, as per the methodology indicated in the Methods for the examination of water and wastewater [37], method 4500- $O_3$ , which followed the procedures described by Rakness et al. [38].

# 2.3. Experimental design

After the ozonation, the WTP sludge was transferred to the sedimentation column for the thickening for different periods and control (0.5, 3.9, 12.25, 20.6, and 24 h). The effects of ozone injection and sedimentation were evaluated on the characteristics of the clarified water and densified sludge using a rotational central composite design (RCCD), shown in Table 2.

#### 2.4. Evaluated responses

At the end of the treatment, the clarified water, after settling, was sampled with the aid of a pipette. The responses evaluated were, in the clarified water, the pH and total aluminum, and, in the thickened sludge, the total solids (TS), total fixed solids (TFS), particle size (PS), and total carbon content (C).

The physicochemical parameters of pH and series of solids (TS and TFS) were determined following the procedures described in the Standard Methods [37]. The total aluminum solubilized in the clarified liquid as well as in the raw sludge was determined by graphite furnace atomic absorption spectrometry.

Particle size distribution of the sludge was determined using laser diffraction on a Mastersizer 3000E (Malvern Instruments, UK), through the dispersion of the sample in water. The average size ( $d_{50}$ ) was used to indicate the particle size, which is defined as the diameter equivalent in volume to 50% of the particles.

Sludge aliquots were dried in a laboratory kiln at 60°C, subsequently determining the total carbon content (C) in a CHNS autoanalyzer of model FlashEA 1112 (Thermo Finnigan, Milan, Italy).

# 3. Results and discussion

# 3.1. Sludge characterization

Table 1 presents the characterization of physicochemical parameters and the quantification of oxides of the raw sludge from the WTP in São Gabriel.

Results demonstrated that the sludge is constituted primarily of inorganic solids, with low TVS  $(TS)^{-1}$  ratio (0.27) and a predomination of SiO<sub>2</sub>, AlO<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> in the WTP sludge. The characteristics of the sludge under study are typical of sludges from other WTPs [1,4,39,40].

The mineralogical content of the sludge is shown in the X-ray diffractogram of Fig. 2, the dominance of the amorphous phase was observed. The predominant diffraction peaks are characteristic of the crystalline phases

Table 1

Characterization of physicochemical parameters and composition of oxides of the sludge from the WTP of São Gabriel through XRF

Parameter/element analyzed	Result		
рН	$6.17\pm0.030$		
Turbidity, NTU	$1,239.17 \pm 10.9$		
Total aluminum (Al), mg L⁻¹	1,533.4		
Total solids (TS), g L <sup>-1</sup>	$10.41\pm0.13$		
Total fixed solids (TFS), g $L^{-1}$	$7.60\pm0.19$		
Total volatile solids (TVS), g L <sup>-1</sup>	$2.82\pm0.16$		
TVS·TS <sup>-1</sup> ratio	0.27		
$d_{_{50}}$ Particle size (PS), $\mu m$	$55.5 \pm 1.13$		
Total carbon content (C), %	$8.44\pm0.02$		
SiO <sub>2</sub> , mg g <sup>-1</sup>	336.93		
$Al_{2}O_{3'}$ mg g <sup>-1</sup>	268.0		
$Fe_2O_{3'}$ mg g <sup>-1</sup>	75.55		
$K_2O$ , mg g <sup>-1</sup>	8.15		
$\text{TiO}_{2'}$ mg g <sup>-1</sup>	6.53		
MgO, mg g <sup>-1</sup>	5.95		



Fig. 2. X-Ray diffractogram of WTP sludge.

referring to kaolinite  $(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)$  and quartz  $(SiO_2)$ . The diffractogram of sludge from WTPs carried out by other authors also demonstrated the predominance of these minerals [5,41–43].

The FT-IR analysis for the WTP sludge is shown in Fig. 3. It can be seen that between the 1,100 and 1,000 cm<sup>-1</sup> transmittances, peaks were observed, which were attributed to referring Si–O–Si vibrations kaolinite [44,45]. The transmittance in the 3,345 cm<sup>-1</sup> band suggests the O–H stretch, consistent with the presence of kaolinite [45]. The characteristic vibrations of Si–O–Si and Si–O–Al are obtained in the ranges of 500–750 cm<sup>-1</sup> for clay materials, in the range of 916 cm<sup>-1</sup> the characteristic band is of Al–Al–OH connections [46].

Figs. 4a and b show the morphological characteristics of the sludge obtained by SEM, it is shown that the sludge



Fig. 3. FT-IR spectrum of WTP sludge.

has an irregular shape, characterized by presenting small agglomerates consisting of mesopores. Other authors have also identified an irregular profile and presence of pores in WTP sludges [41,43,46,47]. The morphological characterization of the sludge carried out by SEM also made it possible to identify the structure of lamellar plates, attributed to the presence of kaolin.

# 3.2. Responses evaluated in the rotational central composite design

Table 2 presents the results obtained in the eleven essays of the RCCD regarding ozone injection and sedimentation time of the WTP sludge. For the clarified water, the pH of the sample varied between 6.8 (essay 5) and 3.6 (essays 2 and



Fig. 4. SEM image of the sludge at 2,000× magnification (a) and 5,000× magnification (b).

Table 2

Matrix of the RCCD (actual and encoded values) with results expressed relative to the characteristics of the clarified water and the thickened sludge after ozonation and sedimentation

Essay	Ozone (g O <sub>3</sub> (g TS) <sup>-1</sup> )	Sedimentation (h)	TS (g L <sup>-1</sup> )	TFS (g L <sup>-1</sup> )	d <sub>50</sub> PS (μm)	C removal (%)	рН	Al (mg L <sup>-1</sup> )
1	0.15 (-1)	3.92 (-1)	27.97	20.56	52.2	4.8	5.2	0.567
2	0.91 (+1)	3.92 (-1)	33.28	24.05	43.2	12.3	3.6	43.52
3	0.15 (-1)	20.58 (+1)	32.61	23.26	51.2	0.3	5.0	1.25
4	0.91 (+1)	20.58 (+1)	38.78	28.21	43.2	12.5	3.8	41.63
5	0 (-1.41)	12.25 (0)	32.04	22.26	60.5	3.0	6.8	4.56
6	1.1 (+1.41)	12.25 (0)	39.15	28.90	42.6	13.0	3.6	88.6
7	0.54 (0)	0.5 (-1.41)	17.99	12.98	44.9	6.3	4.1	32.40
8	0.54 (0)	24 (+1.41)	36.50	27.20	45.5	4.3	3.8	38.38
9	0.54 (0)	12.25 (0)	37.43	27.20	47.5	4.6	3.8	30.63
10	0.54 (0)	12.25 (0)	37.35	27.64	47.2	4.4	3.8	29.94
11	0.54 (0)	12.25 (0)	37.23	27.55	49.1	4.1	4.1	34.55

6). Among these treatments which resulted in the lowest pH values, essay 6 presented more significant aluminum solubilization, with 88.6 mg  $L^{-1}$ , representing 5.8% of the total aluminum of the raw sludge, which showed a concentration of 1,533.4 mg  $L^{-1}$ .

Regarding the solids content (Table 2), the treatments resulted in sludge with TS concentrations from 17.99 to 39.15 g L<sup>-1</sup> and TFS contents from 12.98 to 28.9 g L<sup>-1</sup> (essays 7 and 6). The particle sizes ( $d_{50}$ ) observed in the treatments differed from 60.5 to 42.6 µm, resulting from essays 5 and 6. Ozonation alters the characteristics of sludges, causing the dispersion of the particles [22].

Ozone acts mechanically as an oxidizer, resulting in the breakdown of the sludge particle, the intensity of the break depends on the dose and duration of the ozone application [17,22,28,36]. For WTP sludges, ozone causes the particle to break, with the release of the binding water. With the decrease of the particle size, a greater compaction of the solids is possible with the sedimentation time.

For the thickened sludge, the results shown in Table 2 demonstrate that there was a decrease in C, with removal percentages from 0.3 to 13% (treatments 3 and 6). Sludge reduction is a promising strategy which reduces the disposal cost and solves the problem of secondary pollution of sludges [36].  $O_3$  promotes mineralization of organic matter which occurs as a function of the applied dose and the type of sludge [17], therefore, this study is of fundamental importance to understand the dynamics of ozone application to reduce the WTPs sludge mass.

Degradation/mineralization caused by ozone in an aqueous medium occurs mainly through the hydroxyl anion (OH<sup>-</sup>). The reaction route is quite complex and can be influenced by several factors and by the nature/concentration of chemical species present, such as metals. The reactions of ozone with organic compounds in water can show the flow-chart sequence in Fig. 5 [19].

Additionally, comparing the treatments carried out, essay 6 from Table 2 (with the highest dosage of ozone: +1.41) resulted in more considerable alterations both in the clarified water as in the thickened sludge, presenting the highest



Radicals

Fig. 5. Mechanisms of direct and indirect decomposition of ozone in aqueous media (OM = organic matter;  $OM_{ox}$  = oxidized organic matter).

Source: Adapted from Mahmoud and Freire [19].

indices of TS, TFS, C removal, and Al solubilization, as well as the lowest PS and pH.

#### 3.3. Effects of ozone injection and sedimentation on WTP sludge

The data in Table 2 were used to calculate the effect of the linear (L) and quadratic (Q) variables and the interactions on the responses obtained for clarified water and

densified sludge. The results were expressed in a Pareto graph, as presented in Fig. 6.

The linear ozone dosage and the linear and quadratic sedimentation times were statistically significant (p < 0.05) in the interval studied for the concentrations of TS and TFS. For TS and TFS, the ozone and the linear sedimentation presented positive effects, while the quadratic sedimentation had an adverse impact (Figs. 6a and b). This demonstrates that the more considerable sedimentation and ozone injection time increases the solids content, propitiating greater sedimentation ability of the sludge, concurrently with the reduction of the volatile

material. In a study conducted by Park et al. [29] the ozone treatment also increased the sedimentation capacity of the STP sludge.

The mineralization of the sludge, besides being recommended due to the increase in the TFS, was also pointed out because of the more considerable C removal. The C removal was statistically significant (p < 0.05) for the linear and quadratic terms of the ozone dosage, both with positive effects, as indicated in Fig. 6d.

For the PS of the thickened sludge and the Al concentration in the clarified water, only the linear ozone dosage was statistically significant (p < 0.05), with an adverse effect



Fig. 6. Pareto graph expressing the effect of ozone injection and sedimentation time in WTP sludge regarding the TS (a), TFS (b),  $d_{50}$  PS (c), C removal (d), pH (e), and recovered Al (f).

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for the PS and a positive effect for the Al, as one may observe in Figs. 6c and f. This demonstrates that the higher the ozone dosage in the sludge is, the smaller the PS, entailing the breakage of the particles and release of the Al into the clarified water. The rupture of the flake causes the discharge of metals and interstitial water imprisoned within the sludge particle.

The release of metals into the clarified water is also associated with the lowering of the sludge's pH [22,29,33,48,49]. The pH was statistically significant (p < 0.05) for the linear and quadratic terms of the ozone dosage with adverse and positive effects, respectively (Fig. 6e), indicating that the injection of ozone leads to the reduction of the pH.

Results in Table 2 were used to estimate the effects of the independent variables of the RCCD (ozone and sedimentation) on the parameters evaluated. The effects are related to the terms of a linear and/or quadratic model, which are presented in Eqs. (1)–(6), considering a 95% confidence level (p < 0.05).

 $TS = 36.931 + 5.392 \cdot O + 9.087 \cdot S - 9.004 \cdot S^2$ (1)

 $TFS = 26.859 + 4.464 \cdot O + 6.748 \cdot S - 6.430 \cdot S^2$ (2)

 $PS = 47.918 - 10.591 \cdot O \tag{3}$ 

$$C = 4.995 + 8.475 \cdot O + 3,673 \cdot O^2 \tag{4}$$

 $pH = 3,881 - 1,833 \cdot O + 1,229 \cdot O^2 \tag{5}$ 

$$AI = 31,453 + 50,594 \cdot O \tag{6}$$

where TS is the total solids concentration (g L<sup>-1</sup>), TFS is the TFS concentration (g L<sup>-1</sup>), PS is the  $d_{50}$  particle size (µm), C is the carbon content removal (%), pH is the potential hydrogen, Al is the total aluminum concentration (mgL<sup>-1</sup>), O is the encoded ozone dosage, and S is the encoded sedimentation time.

The described models were validated statistically through the analysis of variance (ANOVA), shown in Table 3. The regression coefficients ( $R^2$ ) were of 0.8963, 0.8735, 0.8068, 0.8916, 0.9388, and 0.8284 for TS, TFS, PS, C, pH, and Al, respectively, showing that the models were significant. The high values for the determination coefficient indicate a fine adjustment of the experimental data, allowing the use of the models to predict the behavior of the densified sludge and the clarified water, that is, forecast the behavior of the raw sludge after ozonation and sedimentation.

Only the linear term of the ozone dosages was significant (p < 0.05) in the range evaluated for all the parameters studied, demonstrating that ozone injection alters the characteristics of WTP sludges. In a study by Zhang et al. [36], ozonation also entailed alterations in the assessed sludge.

In order to elucidate better the influence of the ozone dosage and sedimentation time on the characteristics of the thickened sludge and clarified water, the validated model was graphically shown in Figs. 7 and 8.

Figs. 7a and 8b show that the TS and TFS presented the same behavior in response to the sedimentation times and ozone dosages, with higher concentrations for the sedimentation times varying from 12.25 to 20.58 and ozone dosages over  $0.91 \text{ g O}_3 \text{ (g TS)}^{-1}$ .

The more considerable sedimentation ability of the sludge after the ozonation may have occurred due to the release of water and reduction in particle size. Ozone leads

Table 3

ANOVA for the characteristics of the densified sludge and the clarified water after ozonation and sedimentation

Parameter	Variation source	Sum of squares	Degrees of freedom	Mean square	F-test	$R^2$
	Regression	346.69	3	115.56		
TS	Residues	40.10	7	5.73	$20.17^{a}$	0.8963
	Total	386.79	10	38.68		
	Regression	193.79	3	64.60		
TFS	Residues	28.06	7	4.01	$16.12^{b}$	0.8735
	Total	221.85	10	22.18		
	Regression	223.68	1	223.68		
PS	Residues	53.57	9	5.95	37.58 <sup>c</sup>	0.8068
	Total	277.26	10	27.73		
	Regression	163.88	2	81.94		
С	Residues	19.92	8	2.49	$32.90^{d}$	0.8916
	Total	183.80	10	18.38		
	Regression	9.01	2	4.51		
рН	Residues	0.59	8	0.07	61.33 <sup>e</sup>	0.9388
	Total	9.60	10	0.96		
	Regression	5,104.23	1	5,104.23		
Al	Residues	1,057.00	9	117.44	43.46 <sup>f</sup>	0.8284
	Total	6,161.23	10	616.12		

 ${}^{a,b}F_{0.05,3,7} = 4.35; {}^{c,f}F_{0.05,1,9} = 5.12; {}^{d,e}F_{0.05,2,8} = 4.46.$ 



Fig. 7. Contour graph expressing the influence of the injection of ozone and the sedimentation time in WTP sludge regarding the TS (a), TFS (b), and  $d_{50}$  PS (c).

to the alteration of the sludge's structure, releasing water retained in the particle structure [22,29,36,50], which may entail a better dehydration of the sludge [50].

The sludge PS was changed by the ozone, with a gradual reduction with the increase of the dosage, resulting in a smaller value for the dosage of 1.1 g  $O_3$  (g TS)<sup>-1</sup> (Fig. 7c). In studies conducted by several authors, the injection of ozone in STP sludges also propitiated a slight reduction of the PS [22,29,36,51]. Park et al. [29] reported that the average size of the sludge particles under study was 70 µm, and, after the ozone injection of 0.5 g  $O_3$  (g TS)<sup>-1</sup>, the size was reduced to around 40 µm.

One of the main impacts of the ozone action on the WTP sludge observed was the average decrease in PS, caused by the breaking and forming of finer particles. Smaller diameters of sludge particles difficult dehydration [52], so, for better dehydration results, ozonation should be used as a pre-treatment.

The results obtained with this work indicate that ozonation followed by flocculation can be used as a pre-treatment for dewatering sludge from WTPs. Conventional sludge dehydration only removes free water [53]. Other pre-treatments such as oxidation release the bound water but are unable to achieve an ideal dehydration performance. Thus, the combined use of pre-treatments with flocculation shows the potential for the efficient dehydration of WTP sludges [54].

The highest rate of mineralization of the sludge occurred with lower ozone doses (between 0.15 and 0.54 g  $O_3$  (g TS)<sup>-1</sup>), but there was a gradual increase in the removal of C with the rise in the ozone dosage, as one may observe in Fig. 8a. The most considerable C removal reached was of 13% for a dose of 1.1 g  $O_3$  (g TS)<sup>-1</sup>. The sludge ozonation process propitiates the mineralization, reducing the organic matter that decomposes into carbon dioxide and water, consequently reducing the sludge mass [17,19,29,33].

In a study conducted the mineralization index reached for the sludge investigated was of a mean value of  $13\% \pm 3\%$ of the initial total chemical oxygen demand (COD), representing half of the total sludge reductions [17]. Lee et al. [55] reported that a dosage of 0.05 g O<sub>3</sub> g<sup>-1</sup> of total suspended solids (TSS) yielded 8% of mineralization of the raw sludge. In turn, in a study carried out by Park et al. [29] the reduction of the sludge mass through mineralization went from 5% to 20% when the applied ozone dosage increased from 0 to 0.5 g O<sub>3</sub> (g TS)<sup>-1</sup> in the treatment process of the studied sludge. According to the authors, the injection of ozone into the sludge entailed the reduction of both the mass and the volume of sludge.

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Fig. 8. Contour graph expressing the influence of the injection of ozone and the sedimentation time in WTP sludge regarding the C removal (a), pH (b), and recovered Al (c).

Figs. 8b and c represent the effect of ozone on the clarified water, with the increase of the dosage resulting in the reduction of the pH and the rise in aluminum solubilization. With a dosage of  $1.1 \text{ g O}_3 \text{ (g TS)}^{-1}$ , the pH of the clarified water was 3.6, and the solubilized aluminum was 88.56 mg L<sup>-1</sup>. The solubilization of aluminum to the clarified water resulted in a decrease of the metal in the densified sludge.

Several authors reported that the injection of  $O_3$  in sludge reduces the pH and propitiates the solubilization of metals in the clarified liquid [22,29,33,48,49]. In a study with STP sludge, it was made evident that the addition of ozone reduced the pH of the sludge from 7 to 5, which resulted in the dissolution of metals [48]. Park et al. [29] also reported that the injection of ozone entailed the gradual lowering of the pH, implicating in the reduction of metals in the sludge.

# 4. Conclusions

With the increase of the sedimentation time and ozone dosage, the thickened sludge presented higher TS and TFS content, which may aid the dehydration of the sludge. The injection of  $O_3$  also led to the lowering of the pH, thus solubilizing aluminum, as well as to the reduction of the particle size and the mineralization of organic matter. Considering

the mineralization of 13% of the total C and the solubilization of 5.8% of the total Al of the raw sludge with a dosage of 1.1 g  $O_3$  (g TS)<sup>-1</sup>, we may state that the maximum effective reduction of the sludge mass was of 18.8%.  $O_3$  contributes effectively to the reduction of mass and to the thickening of WTP sludge, but in order to have a real understanding of the viability of ozonation, pilot scale studies are essential.

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