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Implications of COD analysis use in the peracetic acid-based wastewater treatment

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ABSTRACT

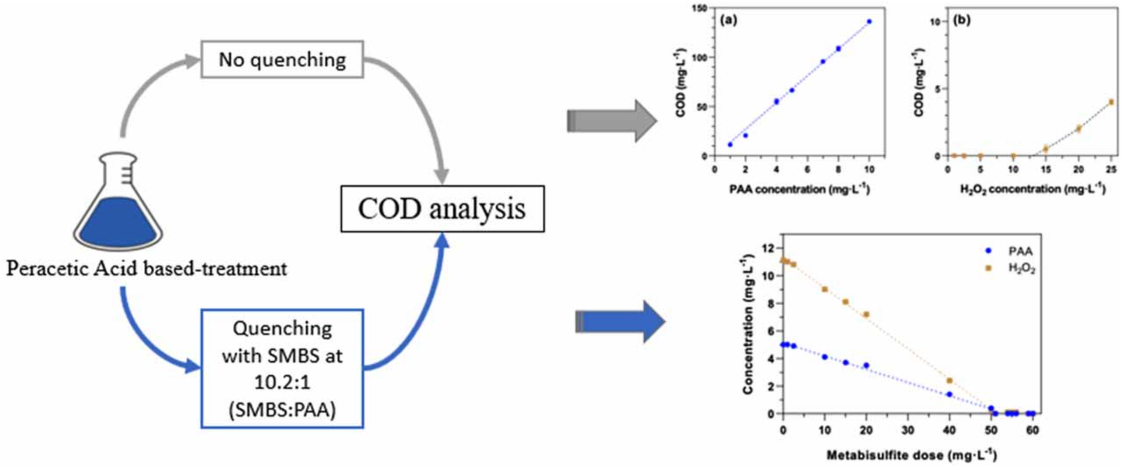
Peracetic acid (PAA) stands out as a safe and environmental-friendly oxidant and disinfectant which has been effectively used in wastewater treatment. Chemical oxygen demand (COD) is a very popular analysis in wastewater treatment; however, the interference of residual PAA on the COD measurement is still unknown. In this context, this study investigated the implications of applying the COD analysis in PAA-based treatment. Each 1 mg·L^{-1} of PAA increased the COD concentration around 13.5 mg O_2·L^{-1}. Residual PAA and hydrogen peroxide (H_2O_2) were efficiently neutralized by sodium metabisulfite (SMBS) at the optimal SMBS/PAA ratio of 10.2:1 in a wide pH range (5 to 9). The effect of PAA addition on the COD concentration was evaluated in different water matrices (potassium hydrogen phthalate and wastewater solutions). The COD results with the SMBS addition at optimal SMBS/PAA ratio were lower than the ones without it. It may happen due to the neutralization of residual H_2O_2/PAA and the complexity of the water matrices which can interfere in the COD results. This study discussed the impact of the residual H_2O_2/PAA neutralization before the COD analysis, and this investigation can be used as a practical guideline for the correct COD measurement in PAA-based treatment.

Key words: chemical oxygen demand, hydrogen peroxide, oxidant, sodium metabisulfite

HIGHLIGHTS

- Influence of peracetic acid (PAA) in COD test was analyzed.
- Sodium metabisulfite (SMBS) was efficient in quenching the PAA.
- Total neutralization by SMBS allowed a correct COD measurement.

GRAPHICAL ABSTRACT



INTRODUCTION

Disinfection is a very important process in wastewater treatment to minimize the release of pathogens into the receiving water bodies, which can endanger the public health and ecosystems (Dippong *et al.* 2017; Otter *et al.* 2020; Roșca *et al.* 2020). Chlorine is the most popular chemical disinfectant applied globally in the wastewater treatment, because of its efficiency, easy application, long-lasting effect, and low cost (El-Rehaili 1995; Quartaroli *et al.* 2018). Nevertheless, the chlorine reactions with the organic compounds present in wastewater can produce harmful disinfection byproducts (*e.g.* haloacetic acids and trihalomethanes) (Luo *et al.* 2020). As an alternative, other chemical disinfectants have also been proposed for wastewater disinfection, such as hydrogen peroxide (H_2O_2), ozone, and peracetic acid (PAA) (Collivignarelli *et al.* 2018).

PAA (peroxyacetic acid, CH_3COOOH) stands out as a safe and environmentally friendly disinfectant, which breaks down into harmless products such as H_2O_2, oxygen, water, and acetic acid (Ao *et al.* 2021; Kim & Huang 2021). In the recent years, PAA has been attracting greater interest in wastewater treatment for disinfection and oxidation of targeted compounds (Falsanisi *et al.* 2006; Appels *et al.* 2011; Amerian *et al.* 2019; Luukkonen *et al.* 2020; Freitas *et al.* 2021). According to a recent report, the global PAA market will grow to $1.3 billion by 2026, while the market fraction for wastewater treatment is expected to grow by 8% per year over that same time frame (Bettenhausen 2020). Usually, PAA is commercially available as a stabilized equilibrium mixture containing PAA (typically 5 to 15% w/w), H_2O_2, acetic acid (CH_3COOH), and water (Equation (1)) (Kitis 2004; Luukkonen *et al.* 2014).

$$CH_3COOOH + H_2O \leftrightarrow CH_3COOH + H_2O_2 \tag{1}$$

Chemical oxygen demand (COD) is a popular parameter usually applied to design wastewater systems and quantify the amount of oxygen that can be consumed by reactions with potassium dichromate under controlled conditions (APHA 2012). It has been reported that the presence of chemical oxidants can analytically interfere in the COD analysis due to the interactions with the dichromate ion ($Cr_2O_7^{2-}$). Although the reactions between H_2O_2 and $Cr_2O_7^{2-}$ are well documented (Talinli & Anderson 1992; Grampp *et al.* 2002; Lee *et al.* 2011; Wang *et al.* 2013; Luukkonen *et al.* 2014), there is no information addressing the reactions between $Cr_2O_7^{2-}$ and PAA. Then, it is fundamental to guarantee the total neutralization of oxidant species using quenching agents before the COD quantification in PAA-based treatment.

Different quenching agents of residual PAA/H_2O_2 have been reported in the literature, such as sodium thiosulfate (Luukkonen *et al.* 2014), catalase (Flores *et al.* 2014), sodium metabisulfite (SMBS) (Freitas *et al.* 2021), and sodium bisulfite (Wang *et al.* 2019). The SMBS application is usually recommended by some manufacturers of PAA solution due to its effectiveness in terms of mass ratio (Enviro Tech Chemical Services 2021). Published studies usually adopt a SMBS/PAA ratio or theorical values; however, no additional investigation is requested or reported (Enviro Tech Chemical Services 2021; Freitas *et al.* 2021). Furthermore, the pH effect in PAA neutralization by SMBS in a wide range of pH is still unknown. Thus, it is fundamental to determine the optimal neutralization conditions to measure precisely the COD concentration.

In this context, this study investigated the implications of COD use as a parameter in PAA-wastewater based treatment. The main objectives of this paper were: (1) to assess the impact of PAA and H_2O_2 concentration on the COD results; (2) to determine the optimal SMBS dose to neutralize the residual PAA and H_2O_2 in the aqueous solution; (3) to check the pH effect in the neutralization of PAA and H_2O_2 by SMBS; and (4) to evaluate the interference of PAA addition and different SMBS doses in the COD measurement using different water matrices.

MATERIALS AND METHODS

Influence of PAA/H_2O_2 dose in COD test

A commercial PAA solution (Vetec Química Fina, Brazil) was used in this study, which contained 15% PAA and 30% H_2O_2 (w/w). The COD test was performed in solutions with different PAA concentrations (1 to 10 mg $PAA \cdot L^{-1}$) prepared previously by diluting the commercial PAA solution in ultrapure water.

Considering that the commercial PAA solution has a considerable H_2O_2 concentration, the COD content was also determined in pure solution of H_2O_2 to distinguish its influence from the COD results of commercial PAA solution. Solutions with different H_2O_2 concentrations (1 to 25 mg $H_2O_2 \cdot L^{-1}$) were prepared using reagent grade ($H_2O_2 \geq 35\%$ (w/w), Sigma-Aldrich, Germany) and ultrapure water to be quantified by COD test. These H_2O_2 concentrations were selected based on the H_2O_2/PAA mass ratio (2.4:1 w/w) present in the commercial PAA solution (w/w) at the moment that this study was performed.

All the volumetric flasks were covered with aluminium foil before their use to protect the solutions from light.

Optimal sodium metabisulfite dose and pH influence

SMBS is an usual reagent applied to quench residual PAA and H_2O_2. Different SMBS concentrations (1 to 61 $mg{\cdot}L^{-1}$) were tested to optimize the SMBS dose to neutralize residual PAA/H_2O_2 in the used PAA commercial solution. In the tests, an approppriate amount of SMBS solution (5 $g{\cdot}L^{-1}$) was added to conical tubes filled with 50 mL of 5 mg $PAA{\cdot}L^{-1}$ solution and the tubes were shaken for 5 min in a static mixer (Dragon Lab, Brazil). Then, samples were collected to measure the residual concentrations of PAA and H_2O_2.

Based on the results of these tests, four mass ratios of SMBS/PAA were selected to check the possible pH influence in the neutralization. The tests were carried out at different initial pH values (5 to 9) using a solution of 5 mg $PAA{\cdot}L^{-1}$. The pH was modified using 1N HCl or 1N NaOH prior to the SMBS addition.

Oxidation experiments

To check the effect of PAA addition in terms of COD concentration in different water matrices, oxidation tests were carried out in wastewater and potassium hydrogen phthalate (KHP) solutions. KHP is often used as a standard analyte for COD analysis (Domini *et al.* 2006). Standard solutions of KHP (10, 40, and 100 $mg{\cdot}L^{-1}$) were prepared by diluting appropriate amounts of KHP (Merck, Germany, CAS-No 887-24-7) in ultrapure water.

The raw wastewater used in this study was collected at the wastewater treatment plant (WWTP) of São Carlos (São Paulo state, Brazil). Three solutions with different wastewater ratios (25, 50, and 100%) were used in the experiments. Raw wastewater samples were analyzed for total solids (TS), total fixed solids (TFS), total volatile solids (TVS), and total suspended solids (TSS). All analyses were performed in triplicate and according to APHA (2012). The collected sample of raw wastewater showed mean concentrations of 459 ± 11 mg $O_2{\cdot}L^{-1}$ of COD, 479.5 ± 17.4 $mg{\cdot}L^{-1}$ of TS, 242.8 5 ± 11.2 $mg{\cdot}L^{-1}$ of TFS, 236.8 ± 22.2 $mg{\cdot}L^{-1}$ of TVS, and 138.7 ± 37.5 $mg{\cdot}L^{-1}$ of TSS.

The characterization of the KHP and wastewater solutions used in the tests is shown in the Supplementary Material file (Table S1). The tests were performed in 500 mL glass bottles covered with aluminium foil. A solution volume of 200 mL was added into the bottles and was maintained under continuous agitation using a magnetic stirrer at 60 rpm during the period of the test. The experimental procedure was divided into two steps:

1) The PAA dose of 5 $mg{\cdot}L^{-1}$ was added to the solutions and samples were collected at the selected time (10 s, 30 min, and 60 min) to be characterized by COD and residual PAA and H_2O_2. The time of 10 s represents the completely mixed state after the PAA addition in which the oxidation effect is insignificant.
2) Based on the previous results of residual PAA/H_2O_2, the SMBS dose was calculated for two selected SMBS/PAA mass ratios (10.2:1 and 12:1) for each time analysed (30 and 60 min). Then, the tests were repeated at the same conditions as stage 1. A sample volume of 25 mL was collected and immediately mixed with the required SMBS dose.

The oxidation tests used the same PAA concentration just to standardize all the steps of this study, such that the study focused on the PAA interference in the COD tests and not on the PAA application itself. It is important to mention that the PAA concentration required for wastewater treatment needs to be optimized according to the desirable quality for the wastewater effluent (Freitas *et al.* 2021).

Analytical methods

The COD analyses were performed according to the reactor digestion method using the COD Hach Kit. In this method, the sample is digested at 150 °C for 2 hours with sulfuric acid and potassium dichromate ($K_2Cr_2O_7$). The oxidizable organic compounds react, reducing the dichromate ion ($Cr_2O_7^{2-}$) to green chromic ion (Cr^{3+}). Then, the COD content can be spectrometrically measured at 420 nm in the Hach DR 3900 spectophotometer. The method sensitivity is 3 mg $O_2{\cdot}L^{-1}$, which represents the concentration changes per 0.010 absorbance change. In this study, all COD tests were performed in triplicate.

The residual concentration of PAA and H_2O_2 was also measured using spectrometric methods. PAA concentration was determined by the N,N-diethyl-p-phenylenediamine (DPD) method using the Vacu-vials® Kit (Chemetrics, USA). H_2O_2 concentration was quantified in the presence of a phenanthroline using the Spectroquant® Hydrogen Peroxide test (Merck, Germany).

Statistical analyses

Statistical analyses were performed using GraphPad Prism software (version 6.01, USA). The significance of the results and differences among the COD results obtained in each treatment were evaluated using a two-way analysis of variance (ANOVA) analysis and Tukey test with a significance level of 0.05.

RESULTS AND DISCUSSION

COD variation with PAA concentration

The results of the COD tests with different PAA concentrations are shown in Figure 1(a). Results showed a linear trend, which was confirmed by the high determination coefficient ($R^2 = 0.999$) obtained by the linear regression analysis. The slope of the obtained linear function showed that 1 $mg{\cdot}L^{-1}$ of PAA increases the COD concentration around 13.5 $mg\ O_2{\cdot}L^{-1}$. This result is higher than the ones found in other studies. For comparison, Luukkonen *et al.* (2014) and Kitis (2004) observed an increment of 4.0 and 2.8 $mg\ O_2{\cdot}L^{-1}$ in the COD values, respectively, due to the addition of 1 $mg{\cdot}L^{-1}$ of PAA.

The theorical COD value of the PAA can be calculated assuming that all PAA reacts to acetic acid and then is completely oxidized according to Equation (2) (Luukkonen *et al.* 2014). Based on Equation (2), the addition of 1 mg of PAA represents a COD increment of 1.07 mg in the solution.

$$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O \qquad (2)$$

It can be observed that the experimental results obtained in this study and in others (Kitis 2004; Luukkonen *et al.* 2014) are higher than the theoretical COD value. The differences may happen due to the variations in the PAA solution composition used in each study. As mentioned, PAA commercial solution is not pure and contains different concentrations of PAA, acetic acid and H_2O_2, which will also have an impact on the COD results.

To check the influence of the H_2O_2 in the COD results shown in Figure 1(a), the COD tests were performed for different H_2O_2 concentrations (Figure 1(b)). As can be observed, COD values were not detected until the concentration of 15 $mg\ H_2O_2{\cdot}L^{-1}$. Hydrogen peroxide is consumed during COD analysis by potassium dichromate according to Equation (3) (Lee *et al.* 2011).

$$K_2Cr_2O_7 + 3H_2O_2 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3O_2 \qquad (3)$$

Based on Equation (3), the theoretical COD value is 0.47 mg per mg of H_2O_2. Then, it was theoretically expected that an H_2O_2 concentration of 20 $mg{\cdot}L^{-1}$ would result in a COD concentration of 9.4 $mg\ O_2{\cdot}L^{-1}$; however, the results showed a concentration of 2.0 $mg\ O_2{\cdot}L^{-1}$ (Figure 1(b)). Talinli & Anderson (1992) also observed a non-linearity of the COD × H_2O_2 curve for values below 60 $mg\ H_2O_2{\cdot}L^{-1}$. This underestimation may be a consequence of several possible reactions between the hydrogen peroxide and the standard oxidizing agent, the dichromate ion ($Cr_2O_7^{2-}$), which makes the correct determination by COD test

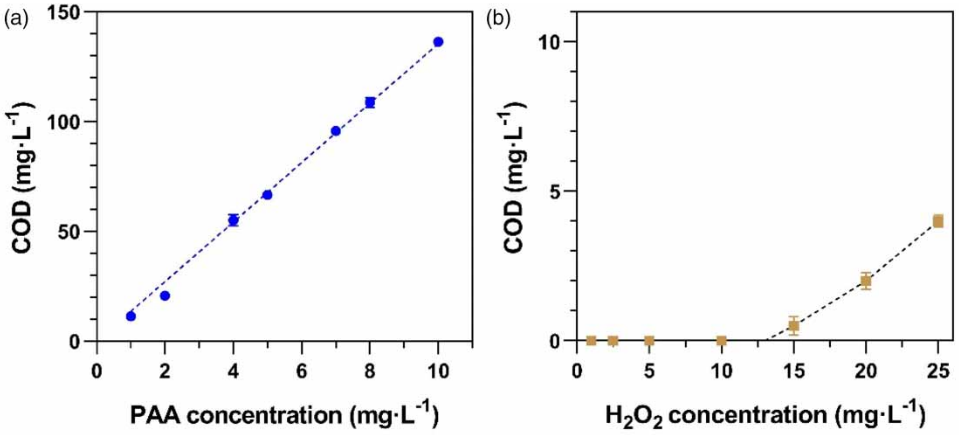


Figure 1 | COD variation with (a) PAA and (b) H_2O_2 concentration.

difficult (Talinli & Anderson 1992). For instance, in aqueous acidic medium, H_2O_2 and $Cr_2O_7^{2-}$ can form a final and relatively stable blue chromium peroxide ($(CrO(O_2)_2 \cdot H_2O)$) complex (Grampp *et al.* 2002). Thus, this reaction can affect the concentration of the dichromate ion and its availability to react with the samples, which can interfere in the final absorbance.

These results endorse the fact that the COD test should be done and analyzed carefully in PAA-based wastewater treatment, since the commercial solution contains three different chemicals (PAA, H_2O_2, and acetic acid), which react differently with the traditional COD test. It is important to mention that the PAA solution has organic compounds (*i.e.* PAA and acetic acid), which increases the organic carbon concentration and consequently, the COD concentration (De Souza *et al.* 2015). However, the presence of oxidizing agents (H_2O_2 and PAA) may also interfere analytically with the COD analysis due to the interactions with $Cr_2O_7^{2-}$. Although the reactions between H_2O_2 and $Cr_2O_7^{2-}$ are well documented (Talinli & Anderson 1992; Grampp *et al.* 2002), there is no information addressing the possible reactions between $Cr_2O_7^{2-}$ and PAA. In this context, it is essential to remove the PAA and H_2O_2 completely prior to the COD analysis to ensure the correct measurement.

Optimal SMBS dose and pH influence

Several quenching agents of residual PAA/H_2O_2 have been reported in the literature, such as sodium thiosulfate (Luukkonen *et al.* 2014), catalase (Flores *et al.* 2014), SMBS (Freitas *et al.* 2021), and sodium bisulfite (Na_2HSO_3) (Wang *et al.* 2019). The application of SMBS is usually recommended by some manufacturers of PAA solution (Enviro Tech Chemical Services 2021), because one SMBS molecule dissolves in water into two molecules of Na_2HSO_3 (Equation (4)), improving the neutralization efficiency on a per mass basis.

$$Na_2S_2O_5 + H_2O \rightarrow 2NaHSO_3 \tag{4}$$

The quench reaction of PAA and H_2O_2 is shown by the Equations (5) and (6). Based on these equations, 1 mg·L^{-1} of PAA and H_2O_2 would need 1.25 and 2.79 mg·L^{-1} of SMBS, respectively. Thus, the SMBS:PAA ratio of 7.39 is required for total neutralization of both the H_2O_2 and PAA present for every 1 mg·L^{-1} of PAA. This value was calculated considering that the H_2O_2/PAA ratio in the solution was 2.3:1 (w/w) at the moment that the study was done.

$$2NaHSO_3 + 2CH_3COOOH \rightarrow 2CH_3COOH + 2NaHSO_4 \tag{5}$$

$$2Na_2HSO_3 + 2H_2O_2 \rightarrow 2Na_2HSO_4 + 2H_2O \tag{6}$$

Different SMBS concentrations were tested to check the SMBS dose required for the total neutralization of PAA/H_2O_2 in the commercial solution used in this research (Figure 2). The decay of PAA and H_2O_2 concentration had different slopes but reached the same SMBS concentration required for total neutralization at 51 mg·L^{-1}, which gives the SMBS/PAA ratio of 10.2:1. As observed, this value is higher than the theoretical value (SMBS/PAA ratio of 7.39). Keen *et al.* (2013) also observed

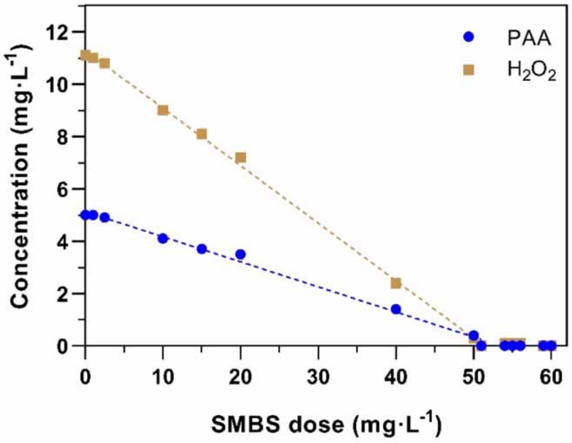


Figure 2 | Variation of PAA and H_2O_2 concentration in the solution after the addition of different sodium metabisulfite (SMBS) doses. The tests were carried out using a PAA solution of 5 mg·L^{-1} at pH 3.9.

quenching doses higher than the theoretical to neutralize the H_2O_2 by sodium thiosulfate. Additionally, a more comparative discussion is not possible because no other study investigated the PAA quench by SMBS dose in detail. Usually, the studies adopt a SMBS/PAA ratio or theoretical values; however, no additional investigation is requested or reported (Enviro Tech Chemical Services 2021; Freitas *et al.* 2021). In this context, it is fundamental to determine the optimal SMBS dose to guarantee the total neutralization before using the PAA commercial solution in tests.

A COD test was carried out after the total neutralization at the SMBS:PAA ratio of 10.2, and an average COD value of 68 ± 1 mg $O_2 \cdot L^{-1}$ was found. The difference between this result and the initial COD concentration of 67 ± 2 mg $O_2 \cdot L^{-1}$ (Figure 1, 5 mg $PAA \cdot L^{-1}$) is not significant (Tukey test, $p > 0.05$). As shown in Equation (5), after the neutralization the PAA species becomes acetic acid, which maintains the COD values as in Equation (2). Besides the insignificant difference, the SMBS application is needed because it can take some time to perform the COD analysis and during this period, the residual PAA may continue reacting with compounds of the sample, which can therefore change its quality. Furthermore, the procedure of quenching is also required before the analysis of other parameters commonly used to characterize the wastewater, such as dissolved organic carbon, faecal indicator bacteria (*E. coli* and total coliforms), sulfide, etc. (Quartaroli *et al.* 2018; Freitas *et al.* 2021).

The effect of a wide pH range in PAA neutralization by SMBS is still unknown. Based on this, three SMBS:PAA ratios were selected to be tested with different initial pH values (Table 1). These values were selected based on the pH found in different water matrices (Leite *et al.* 2019; Sacchi *et al.* 2020; Freitas *et al.* 2021). PAA is commonly used below the pK_a (pH 8.2–8.4), because the non-dissociated form (CH_3COOOH) is thought to be more efficient than the dissociated form (CH_3COOO^-) (Kitis 2004).

As evidenced from Table 1, PAA and H_2O_2 can be neutralized after the SMBS addition at the SMBS/PAA mass ratio of 10.2:1 or 12:1 for all the pH values tested. Thus, the total neutralization by SMBS was independent of pH, which implies an easy operation to eliminate the residual PAA/H_2O_2 since no pH adjustment is required. It is important to mention that the application of SMBS/PAA higher than the optimal ratio can interfere in the COD measurement because the residual SMBS and Na_2HSO_3 (after the dissolution) can also contribute to the COD increment, leading to an overestimation of the COD concentration (Wang *et al.* 2013). The interference of SMBS overdose will be discussed in the section ‘Influence of SMBS dose on COD measurement’.

Table 1 | Variation of PAA and H_2O_2 concentrations after the application of different SMBS/PAA ratios at different initial pH values. The tests were carried out using a PAA solution of 5 $mg \cdot L^{-1}$

		Concentration ($mg \cdot L^{-1}$)	
pH	**SMBS:PAA ratio**	**PAA**	**H_2O_2**
5	8	0.78	1.43
	10	0.11	0.14
	10.2	0.00	0.00
	12	0.00	0.00
6	8	0.46	3.26
	10	0.10	0.33
	10.2	0.00	0.00
	12	0.00	0.00
7	8	0.28	3.24
	10	0.10	0.33
	10.2	0.00	0.00
	12	0.00	0.00
8	8	0.25	2.79
	10	0.10	0.21
	10.2	0.00	0.00
	12	0.00	0.00
9	8	0.24	0.80
	10	0.05	0.13
	10.2	0.00	0.00
	12	0.00	0.00

Oxidation experiments

Influence of PAA addition on COD measurement

To check the effect of PAA addition in terms of COD concentration in different water matrices, oxidation tests were carried out in different solutions of KHP and wastewater (Figure 3).

As expected, the COD concentration increased significantly after the PAA addition of 5 mg·L^{-1} (Tukey test, $p > 0.05$). After 10 s (completely mixed state), the COD concentration increases, ranging from 70 to 75 mg O_2·L^{-1} for KHP solutions and from 43 to 130 mg O_2·L^{-1} for wastewater solutions when compared with the initial COD concentration. The COD values obtained in KHP experiments are close to the COD concentration added in the PAA dose (67 ± 2 mg O_2·L^{-1}, Figure 1), unlike what was observed in wastewater samples. The COD of wastewater samples may be affected by the wastewater complexity, because the PAA may be decomposed by various water matrix components (Kim & Huang 2021). In this case, PAA might have immediately reacted with some wastewater components, and when the samples were collected (10 s), the organic matter and the PAA/H_2O_2 concentration had already been changed. The PAA decay is observed mainly for wastewater after a contact time of 30 min (Figure 3(c) and 3(d)). For instance, the residual PAA reached the concentration of 4.9 and 3.2 mg·L^{-1} for a solution of 100 mg·L^{-1} KHP and 25% wastewater proportion at 30 min, respectively, which have similar initial COD concentration. Moreover, the change in the organic matrix can increase the COD results, making it more feasible to be oxidized by potassium dichromate in the COD test (El-Rehaili 1995).

No significant difference was observed between the COD results at different times (10 s, 30 min, and 60 min) in each condition in the experiments (Tukey test, $p > 0.05$). This happened possibly because the PAA and H_2O_2 reacted with the samples mostly at the moment that the PAA was added, and after that the oxidant consumption was reduced. The mentioned results can be observed by comparing the residuals at 30 and 60 min and are in agreement with previous studies (Amerian *et al.* 2019; Freitas *et al.* 2021). Also, the PAA consumed was converted in to acetic acid, which maintains the COD values as shown in Equation (2). It is important to highlight that after adding the PAA, part of the organic matter can be solubilized or degraded during the oxidation reaction (Appels *et al.* 2011), but it is very unlikely that the organic matter present in

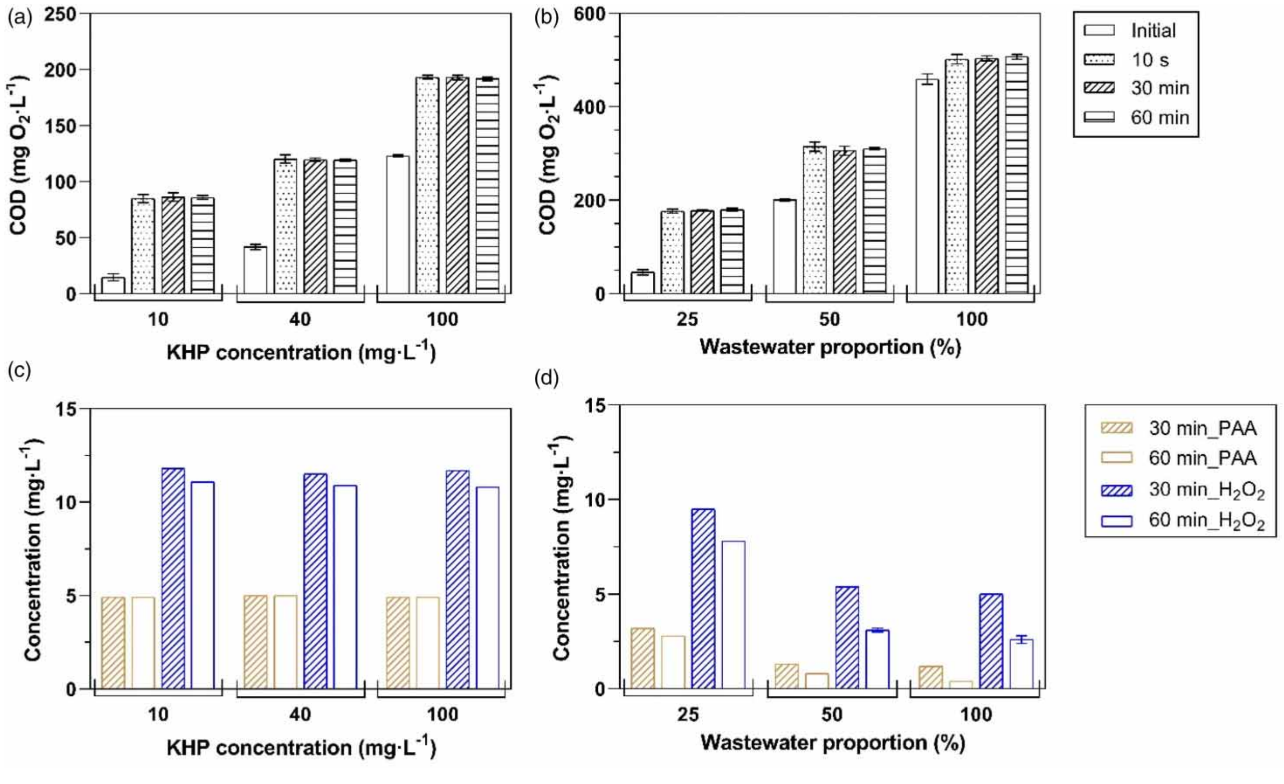


Figure 3 | COD concentration after the PAA addition at different times (initial, 10 s, 30 min, and 60 min) in (a) KHP and (b) wastewater solutions and the variation of residual PAA and H_2O_2 in the (c) KHP and (d) wastewater solutions. The tests were carried out using a PAA dose of 5 mg·L^{-1}.

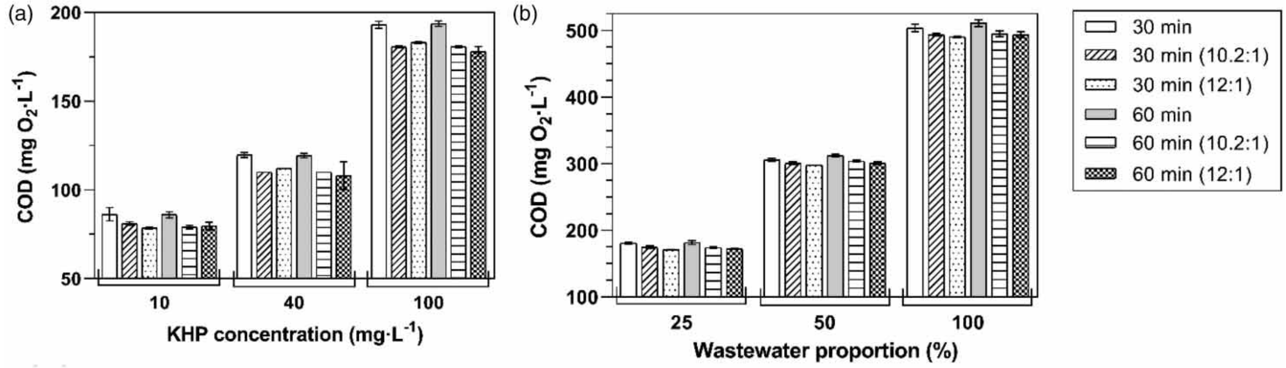


Figure 4 | COD concentration of experiments performed with and without the addition of SMBS at different contact times (30 and 60 min). The tests were carried out using a PAA dose of 5 mg·L^{-1} and two SMBS/PAA ratios (10.2:1 and 12:1).

the wastewater is completely oxidized to CO_2 (Luukkonen *et al.* 2020). Thus, it is not expected a COD decay in PAA-based wastewater treatment (De Souza *et al.* 2015).

Influence of SMBS dose on COD measurement

Based on the previous results of residual PAA/H_2O_2 (Figure 3(c) and 3(d)), the SMBS dose was calculated for two SMBS/PAA mass ratios (10.2:1 and 12:1) for each time analysed (Figure 4). Significant differences between the COD results with and without the addition of SMBS/PAA optimal ratio (10.2:1) were found (Tukey test, $p < 0.05$). Detailed information about the COD results and statistical analysis are shown in the Supplementary Material file (Tables S1 and S2). The COD results with the SMBS addition were lower than the ones without it. The percentage differences varied from 6.1% to 9.0% for KHP solutions and from 1.8% to 5.3% for wastewater solutions. This finding is different from what was previously found in the tests using the commercial PAA solution, in which the neutralization maintained the COD values as shown in Equation (2). It may happen because the oxidation dynamic in the real water matrices is rather complex and, therefore, it is difficult to accurately predict the influence of SMBS/PAA on COD, probably due to the presence of different compounds, as can be observed in Figure 4. Also, the residual H_2O_2/PAA may analytically interfere in the COD test due to the reaction with dichromate ion (Talinli & Anderson 1992; Grampp *et al.* 2002). In this context, the addition of optimal SMBS dose may allow a more precise COD measurement more precise in PAA-based wastewater treatment.

Besides the excess of quenching reagent being able to increase the COD concentration (Wang *et al.* 2013), no significant differences between the COD results using the two SMBS/PAA ratios (10.2:1 and 12:1) were found (Tukey test, $p > 0.05$). According to Equation (7), 1 mg·L^{-1}of SMBS would represent a COD increment of 0.18 mg O_2·L^{-1}. Then, the concentration in excess (1.8 mg·L^{-1} of SMBS) due to the addition of SMBS/PAA ratio of 12:1 would increase the COD results by 0.32 mg O_2·L^{-1}. This low concentration may explain why this SMBS addition did not show significant influence in the COD results. Further discussion is not possible because no other study has checked the concentration effect of quenching agents in COD analysis.

$$2NaHSO_3 + O_2 \rightarrow 2NaHSO_4 \tag{7}$$

In this context, further studies are required to check the impact of different SMBS doses in the COD measurements under different operational conditions and water matrices. This information could bring some flexibility to determine correctly the COD concentration in PAA based-treament, once the SMBS dose can be determined considering only the initial PAA concentration used in the test. It is important to mention that this simplification can only be used if the SMBS excess does not significantly increase the COD results.

CONCLUSIONS

This study investigated the interference of residual PAA in the COD measurement, which is still unknown in the literature. Each 1 mg·L^{-1} of PAA increased the COD concentration around 13.5 mg O_2·L^{-1}, while no COD values were detected below the concentration of 15 mg H_2O_2·L^{-1}. Residual concentrations of PAA and H_2O_2 were efficiently neutralized by SMBS and the optimal SMBS/PAA ratio of 10.2:1 was effective in a wide pH range (5 to 9). The effect of PAA addition in terms of COD concentration was tested in KHP and wastewater solutions. The COD results with the SMBS addition at optimal SMBS/PAA ratio were lower than the ones without it. This may happen due to the neutralization of residual H_2O_2/PAA and the complexity of the water matrices, which can interfere in the COD results. This study discussed the impact of the residual H_2O_2/PAA neutralization before the COD analysis, and this investigation can be used as a practical guideline for the correct COD measurement in PAA-based treatment.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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