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Catalytic oxidation of aromatic aldehydes to carboxylic acids in mild conditions with $NaClO_2$

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Abstract

This study aimed to improve the conditions for the oxidation of benzaldehyde to benzoic acid using chlorine dioxide generated from sodium chlorite, across various pH ranges and different catalysts. The powerful oxidation capability of chlorine dioxide played a crucial role in enhancing the kinetic efficiency of the reactions. In our research, we examined various reaction conditions, including sodium dihydrogen phosphate, sodium dihydrogen phosphate together with sodium chlorite, sodium dihydrogen phosphate combined with sodium chlorite and potassium permanganate, and sodium dihydrogen phosphate with sodium chlorite and V_2O_5. Additionally, different oxidation combinations having the promoters with sodium chlorite such as sodium tripolyphosphate (STPP), 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), and formic acid were also tested. The stabilized chlorine dioxide solution was also used directly as the oxidation reagent. The role of chlorine dioxide in these combinations significantly impacted the selectivity and yield in terms of product.

Furthermore, some Mn(III) complexes (Cat.1 and Cat.2) were used as the catalysts in this study, and the findings revealed with chlorine dioxide are to be an effective oxidant for the selective oxidation of aromatic aldehydes to aromatic acids. For the catalytic applications in buffer solutions, a leveling effect was observed. When Mn(III) complexes were used, it showed a similar leveling effect in buffer solutions for pH >1, which was resulting in slow ClO_2 formation. With these findings it was found that the use of Mn(III) complexes in NaH_2PO_4+$NaClO_2$ combination provided the highest yield in the oxidation of aromatic aldehydes to acids. These results underscore the importance of chlorine dioxide as a powerful oxidant in the chemical transformation processes.

Keywords: Chlorine dioxide, catalysts, oxidation agent, aromatic aldehydes, aromatic acids

1. Introduction

Oxidation is a crucial process in organic synthesis, with various methods developed for the targeted purposes such as oxidation of alcohols to organic acids via aldehydes [1,2]. One significant yet less common transformation is the oxidation of aromatic aldehydes to aromatic acids, which holds industrial importance. Although only a limited number of methods are effective across different aldehydes [3], several reagents have been employed for this reaction in the literature [4]. Among these, sodium chlorite stands out as a selective and mild reagent for oxidizing aromatic aldehydes to acids [5,6]. Other oxidizing agents like hydrogen peroxide, sodium hypochlorite, and $KMnO_4$ can also be used, but they often produce undesirable by-products, reducing their appeal [7–9].

Chlorine dioxide (ClO_2) stands out as an effective alternative for oxidation reactions, particularly within the pH range of 3–5 with high yields. Known for its high efficiency and lack of by-products, chlorine dioxide quickly gained attention upon its discovery, and it has a broad range of applications [10–13]. However, due to its high reactivity, it cannot be stabilized in pure form but can be maintained at low concentrations in various chemicals. This stabilization allows for safer and more controlled use, especially in specific applications, minimizing unwanted side effects and explosion risks. In practice, chlorine dioxide as an oxidant is generated from sodium chlorite in the reaction media by adjusting the pH with acids and catalysts, ensuring safe handling and optimal reaction conditions.

Chlorine dioxide is an eco-friendly oxidant that does not bioaccumulate or persist in the environment. Its use in catalytic methods is expected to grow, given its non-polluting nature. These qualities make ClO_2 highly valuable for both environmental and industrial applications. Its strong oxidizing properties are particularly effective in removing colored compounds, odors, and metal ions like iron and manganese [14].

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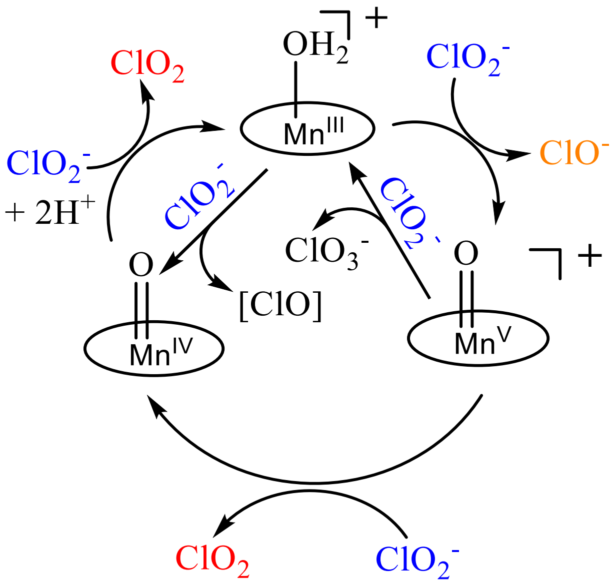


Figure 1. General mechanism for the conversion of chlorine dioxide presence Mn(III) catalyst [19]

The conversion of aldehydes to aromatic acids is crucial due to its industrial applications. Various reagents have been explored for this purpose [15], but only a few are suitable for aldehydes [16]. Sodium chlorite is uniquely effective under mild conditions for converting aldehydes to carboxylic acids [17]. It acts as a chemoselective reagent that tolerates diverse functional groups and produces environmentally friendly by-products compared to metal-based oxidants [18].

In 2014, Scott D. Hicks and colleagues investigated the reactions of chlorine dioxide using manganese catalysts in water under mild conditions. They observed that chlorine dioxide forms catalytically at a pH of around 5 and ambient temperature, some oxy-chlorine species formed were presented in Fig. 1 [19].

In 2016, Kei Ohkubo and colleagues reported in their article that chlorite, combined with a strong Lewis acid like scandium triflate, accelerates the disproportionation of ClO_2 into ClO^- and ClO_3^- [20].

Oxidation in water purification uses oxidizing agents to convert contaminants into safer compounds. Meng-Yuan Xu and colleagues review the challenges of using ClO_2, focusing on controlling disinfection by-products (DBPs) in drinking water and highlighting the efficiency of the UV/ClO_2 process in both disinfection and reusing ClO_2^- [21]. Valentin Rougé and colleagues studied in 2022 and found that chlorite oxidation by chlorine which produces chlorate (60–70%) and ClO_2 (30–40%) can be modeled as the disinfecting and purifying agent for the domestic and waste waters. The study underscores that predicting chlorite and chlorate levels can optimize ClO_2 peroxidation, and increasing ClO_2 dosage can improve the mitigation of disinfection by-products [22].

In a 2023 study, A.V. Kutchin and colleagues explored the oxidation of various alkylphenols using chlorine dioxide in water and dichloromethane. They discovered specific features of alkylphenol oxidation under different reaction conditions resulted in the formation of quinones and chlorinated products. The yields of quinones depended on the position of substituents on the aromatic ring of the starting phenols [23].

The chemoselective catalytic oxidation of 1,2-diols to α-hydroxy acids, a challenging process, has been successfully achieved. Various 1,2-diols were oxidized into their corresponding α-hydroxy acids, including optically active forms. A key finding was the CT complex formation during oxidation, significant for advancing nitroxyl-radical-catalyzed reactions, making this method a valuable tool in organic synthesis [24].

Based on this information, experiments in this study modified catalytic conditions for oxidizing aromatic aldehydes to acids using sodium chlorite. These adjustments resulted in high conversions with minimal by-products under mild conditions.

2. Experimental

2.1. Materials and methods

Sodium dihydrogen phosphate, potassium permanganate, sodium chlorite, benzaldehyde, stabilized chlorine dioxide, sodium tripolyphosphate (STPP), formic acid, HEDP (1-hydroxy ethylidine-1,1-diphosphonic acid), vanadium pentoxide, tetra hydro furan (THF), ethyl acetate, dichloromethane, acetonitrile, glacial acetic acid, urotropine, 2,4-ditertbutylphenol, cis/trans 1,2-diaminocyclohexane, potassium hydroxide, $Mn(CH_3COO)_2.4H_2O$, LiCl, $CoCl_2.6H_2O$, diethylenetriamine and water were used as the reagents in Aldrich quality.

Experiments were conducted using various glassware and glass storage containers. In addition to these common laboratory equipment and tools were also used. Melting points were determined using a Barnstead-Electrothermal 9200 and a Stuart SMP 10 melting point determination device. For pH measurements, pH papers and a pH meter (PHM 210 STANDARD pH METER, analytical KCl.Ag meterLab) were used, while magnetic and mechanical stirrers were preferred for mixing solutions. Infrared spectra were recorded on a Perkin Elmer UATR-TWO FT-IR spectrophotometer equipped with a diamond ATR. UV-visible spectra were recorded using a Hitachi U-2900 UV-visible PC spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer. Finally, TLC plates (Silica Gel 60 ADAMANT on TLC Plates) and a rotary evaporator (BÜCHI Water bath B-480) were used.

2.2. Synthesis

2.2.1. [Mn(III)(acacen)Cl] (Cat.1)

The synthesis of Mn(III) complex of bis-acetylacetone-ethylenediamine (acacen) [Mn(III)(acacen)Cl] (Cat.1) (Fig. 2) was done according to the literature procedures [25].

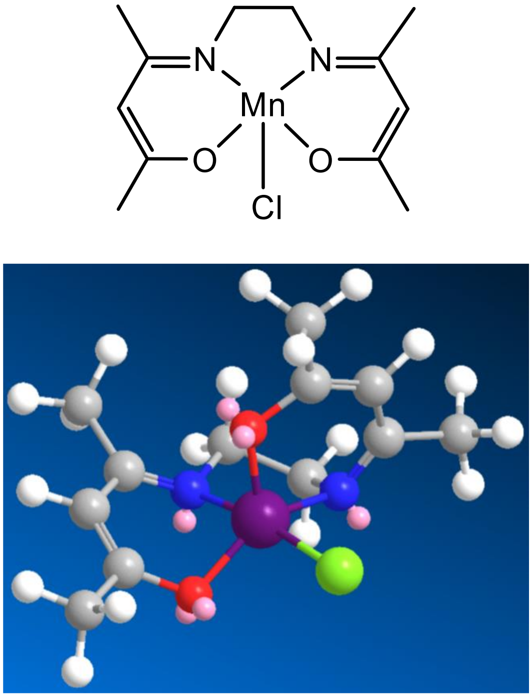


Figure 2. [Mn(III)(acacen)Cl] (Cat.1) and its calculated molecule structure using chem 3D Pro

2.2.2. 6,6′-((1E,1′E)-(cyclohexane-1,2-diylbis(azaneylylidene))bis(methaneylylidene))bis(2,4-di-tert-butylphenolate) Mn(III)Cl, [Mn(III)(SchL)Cl] (Cat.2)

A Schiff base compound, 6,6'-((1E,1'E)-(cyclohexane-1,2-diylbis(azaneylylidene))bis (methaneylylidene))bis(2,4-di-tert-butylphenol) (SchLH$_2$) was synthesized trough the literature procedure [26]. The complexation process for the Mn(III) ion was carried out as follows, as well;

SchLH$_2$ (0.2 g, 0.37 mmol), KOH (42 mg, 0.75 mmol), and Mn(OAc)$_2$·4H$_2$O (90 mg, 0.37 mmol) were mixed and heated to boiling for 4 hours in an ethanol (20 mL) solution using a 250 mL round-bottom flask equipped with a condenser. After the completion of the reaction, the mixture was cooled down to room temperature, and LiCl (42 mg, 0.75 mmol) was added. The reaction was then continued for an additional 3 hours while passing air through the mixture. The progress of the reaction was monitored by TLC (60F$_{254}$-SiO$_2$, fixed phase / THF:Hexane (3:4), mobile phase) for both steps. After the reaction was complete, the mixture was cooled to room temperature, appeared precipitate filtered, and thoroughly washed with distilled water and methanol respectively. Finally, the product (Cat.2) was dried for spectroscopic measurements and analysis in a vacuum oven at 50 °C.

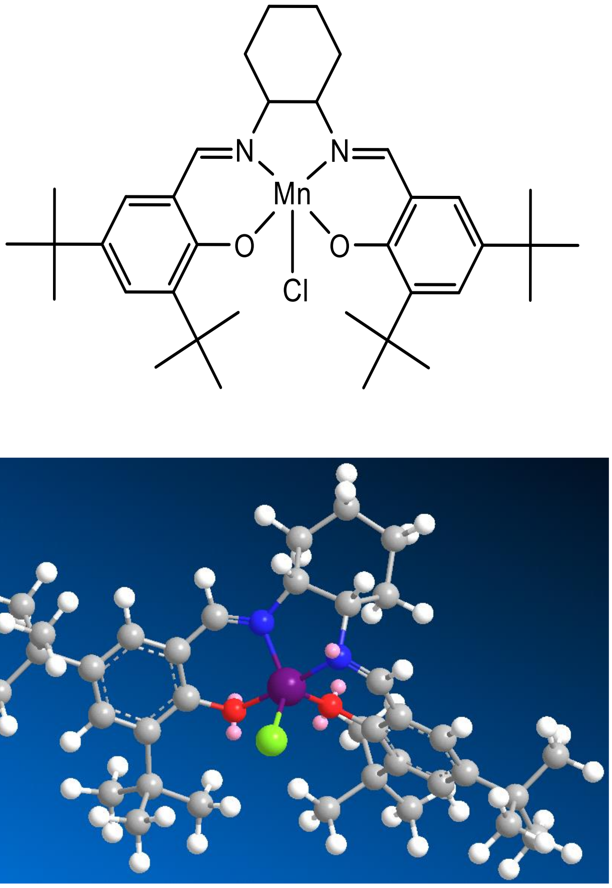


Figure 3. [Mn(III)(SchL)Cl] (Cat.2) and its calculated molecule structure using chem 3D Pro

Yield: 0.192 g, 82%; **m.p.:** 240–250 °C (decomposition).

FT-IR (PIKE Miracle TM ATR) $V_{max.}/cm^{-1}$: 3055 (Ar, C-H), 2951-2866 (Aliph., C-H), 1608 (C=N), 1535(Ar, C=C), 1458-1388 (Aliph., C-C), 1249, 1172.

UV–Vis. (CHCl$_3$-1x10^{-5} M) $\lambda_{max.}$ (nm) (log ε): 258 (4.02), 294 (4.23), 329 (4.01), 444 (3.54).

Theoretical compound, ($C_{36}H_{52}ClMnN_2O_2$) (%): C, 68.07; H, 8.25; N, 4.41; O, 5.04; Cl, 5.58; Mn, 8.65; **Found (%):** C, 68,40; H, 8,77; N, 5,16; Mn, 8.12 (ICP-OES).

2.3. Thin Layer (TLC) Chromatography System

TLC analyses were performed to examine the conversion of aromatic aldehydes to aromatic acids. All experiments progressed in various reaction conditions using different catalysts were performed and monitored using thin layer chromatography. Pre-coated silica gel plates fixed on glass were used as the stationary phase. The pre-coated plates, originally sized 20x20 cm, were cut to 2x5 cm dimensions using a diamond cutter. Application points were marked on the prepared plates with a pencil. For the mobile phase, a 1/5-THF/hexane mixture was prepared as a 25 mL stock solution and stored in a sealed bottle. 25 mL tall beakers were used as chromatography tanks. The separation power of the mobile phase was tested using benzaldehyde as the starting material and benzoic acid as the main product.

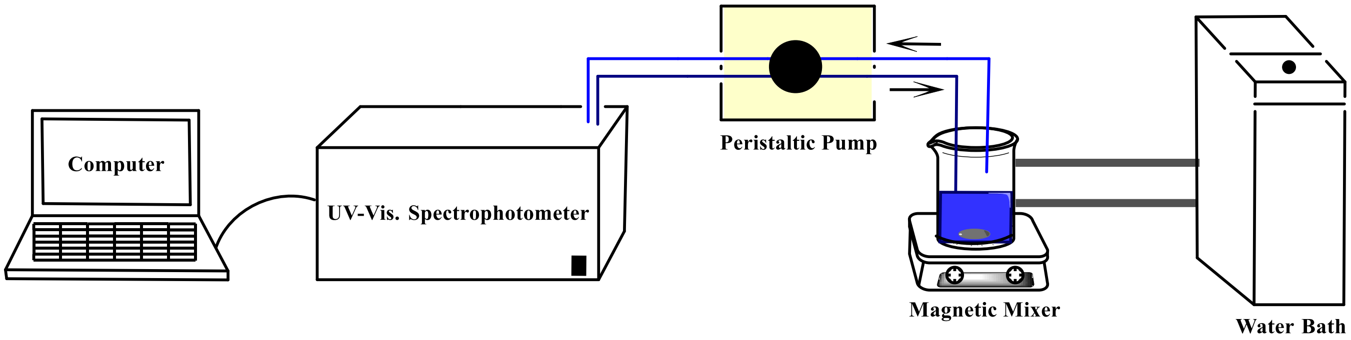


Figure 4. System for catalytic kinetic oxidation measurement of H_2O_2 [29]

2.4. Solution preparation

2.4.1. Preparation of Stabilized Chlorine Dioxide Solution

31% sodium chlorite (13.7 g) was taken and mixed with 2 g of light soda. The mixture was dissolved in 100 mL of distilled water and then diluted to a total volume of 900 ml. Separately, a solution containing 5.33 g of sodium persulfate and 2 g of sodium bisulfate dissolved in 100 ml of water was prepared and added to the mixture. The resulting solution was left to stand in a dark place for 3 days to ensure the stability [27]. The ClO_2 amount was measured as 3000 ppm by using ClO_2 strips (Bart-vation ClO_2 measurement strips 0–500 ppm range, made in USA).

2.4.2. Preparation of Buffer Solution

Buffer solutions with different pH values to be used to take catalytic measurements were created using literature sources [28].

Preparing buffers involves a series of precise steps to ensure they are suitable for their intended use. First, we calculated the required components concentrations and amounts based on the specific application and target volume. Next, we carefully weigh the components and dissolve them in an appropriate solvent. After dissolving, for adjusting the pH of the solution to the desired level we used pH meters and appropriate reagents. Once the pH was adjusted, we diluted the solution to the final desired volume. Finally, we labeled the buffer clearly to indicate its contents and any important details. And use some of it directly for experiments and stored some for future use.

2.5. Kinetic studies

The system used for catalytic kinetic oxidation measurement of H_2O_2 in the literature was modified to allow for ClO_2 measurements [29]. To prevent the evaporation and light interaction of ClO_2, the reaction vessel was specifically modified into a sealed, amber-colored reaction vessel. The schematic demonstration of the modified system is shown in Fig. 4.

The synthesized Mn(III)SchLCl complex (Cat.2) is shown in Fig. 3. Dimethyl sulfoxide (DMSO) solutions of Cat.2 were prepared. Buffers at different pH levels (pH= 1, 2, 4, 6) and their respective preparation materials are listed in Table 1. The experimental conditions were set up with 10^{-2} M sodium chlorite, 10^{-5} M metal complex, and 0.1 M buffer in a total volume of 100 ml vessel**.** The production of ClO_2 was monitored automatically using a UV-VIS Spectrophotometer at 360 nm for 90 minutes in a kinetic cuvette. Changes in the absorbance at 360 nm for the recorded spectra were attributed to variations in ClO_2 concentration.

2.6. The oxidation of benzaldehyde to benzoic acid studies

In the studies of the oxidation of benzaldehyde to benzoic acid, experiments were conducted using different reaction conditions and catalysts while considering the parameters such as pH, reaction time, and yield. The results related to the studies are provided in Table 2 as isolated benzoic acid yield percentage.

Table 2 Reaction conditions of preparation of aromatic acids from aromatic aldehydes.

Table 1. The reaction conditions of ClO_2 generation kinetic studies and results

No	Starting Material	Formation product	Complexes (10^{-5} M)	Buffer Conditions	Molarity of Buffer	Buffer pH	Time (min.)	% Formation
1	0.01 M $NaClO_2$	ClO_2	—	HCl-KCl	0.1 M	1.05	1.5 h	16.41
2	0.01 M $NaClO_2$	ClO_2	—	Citric Acid NaH_2PO_4	0.1 M	2.10	1.5 h	1.45
3	0.01 M $NaClO_2$	ClO_2	—	Citric Acid NaH_2PO_4	0.1 M	4.07	1.5 h	0.442
4	0.01 M $NaClO_2$	ClO_2	—	Citric Acid NaH_2PO_4	0.1 M	6.02	1.5 h	0.013
5	0.01 M $NaClO_2$	ClO_2	Complex Cat.2	HCl-KCl	0.1 M	1.05	1.5 h	9.29
6	0.01 M $NaClO_2$	ClO_2	Complex Cat.2	Citric Acid NaH_2PO_4	0.1 M	2.10	1.5 h	10.32
7	0.01 M $NaClO_2$	ClO_2	Complex Cat.2	Citric Acid NaH_2PO_4	0.1 M	4.07	1.5 h	5.59
8	0.01 M $NaClO_2$	ClO_2	Complex Cat.2	Citric Acid NaH_2PO_4	0.1 M	6.02	1.5 h	2.56

3. Result and discussion

In the present study, the oxidation of benzaldehyde to benzoic acid experiments were conducted considering pH, reaction time, and yield values applying different reaction conditions and catalysts. For this purpose, the study examined under mild conditions, using sodium chlorite as the oxidant and varying catalytic combinations to achieve high conversions with minimal side products (Fig. 5). As stated in the literature, the experiments were carried out in an acetonitrile-water medium [30].

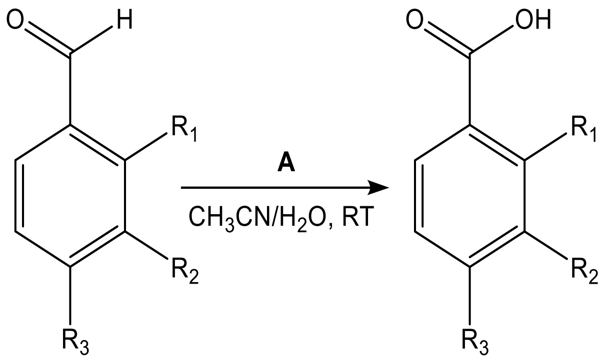


Figure 5. Reaction: preparation of aromatic acids from aromatic aldehydes, **A:** Catalysts and reaction conditions given in Table 2

The progress of the reactions was monitored by Thin Layer Chromatography (TLC). The resulting chromatogram is shown below in Fig. 6. The observed Rf values were: 2/3 for benzaldehyde and 1/3 for benzoic acid.

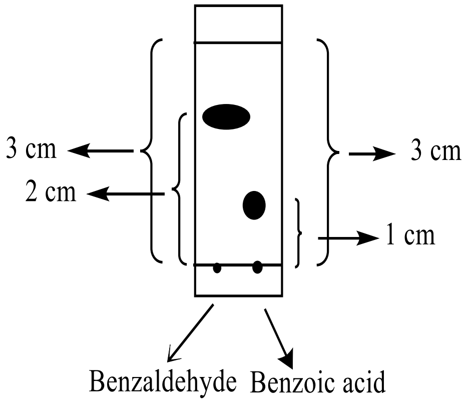


Figure 6. The TLC chromatography of benzaldehyde and benzoic acid

In the initial experiment, oxidation studies were performed using only sodium dihydrogen phosphate (NaH_2PO_4) as the basic reagent to make sure if there was any conversion without sodium chlorite. At 4.90 pH after 72 hours, benzoic acid was not obtained.

Table 2. Reaction conditions of preparation of aromatic acids from aromatic aldehydes

No	Starting Material	R_1,R_2,R_3	A	pH	Time	Yield, %
1	Benzaldehyde	$R_1,R_2,R_3 = H$	Stabilized ClO_2 solution	—	60 h	73.00
2	*m*-Tolyl Aldehyde	$R_1,R_3 = H, R_2= CH_3$	Stabilized ClO_2 solution	—	96 h	13.20
3	*p*-Tolyl Aldehyde	$R_1,R_2 = H, R_3= CH_3$	Stabilized ClO_2 solution	—	96 h	16.37
4	4-methyl Benzaldehyde	$R_1,R_2 = H, R_3= OCH_3$	Stabilized ClO_2 solution	—	96 h	3.81
5	Salicylaldehyde	$R_2,R_3 = H, R_1= OH$	Stabilized ClO_2 solution	—	96 h	—
6	4-Hydroxy Benzaldehyde	$R_1,R_2 = H, R_3= OH$	Stabilized ClO_2 solution	—	96 h	—
7	Benzaldehyde	$R_1,R_2,R_3 = H$	NaH_2PO_4	4.90	72 h	—
8	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaH_2PO_4 + NaClO_2$	6.98	48 h	33.10
9	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaH_2PO_4 + NaClO_2$	6.05	48 h	38.50
10	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaH_2PO_4 + NaClO_2$	5.65	48 h	43.10
11	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaH_2PO_4 + NaClO_2$	5.45	48 h	64.60
12	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaH_2PO_4 + NaClO_2$	5.30	48 h	78.10
13	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaClO_2$ + HEDP	4.90	60 h	58.50
14	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaClO_2$ + HEDP	3.50	60 h	75.00
15	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaClO_2$ + STPP + Formic Acid	3.50	60 h	52.00
16	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaClO_2 + KMnO_4$	11.90	48 h	—
17	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaH_2PO_4 + NaClO_2 + KMnO_4$	6.10	48 h	16.10
18	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaH_2PO_4 + NaClO_2 + KMnO_4$	5.85	48 h	28.00
19	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaH_2PO_4 + NaClO_2 + KMnO_4$	5.40	48 h	64.80
20	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaClO_2 + V_2O_5$	12.00	72 h	—
21	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaH_2PO_4 + NaClO_2 + V_2O_5$	6.40	60 h	12.70
22	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaH_2PO_4 + NaClO_2 + V_2O_5$	5.65	60 h	48.50
23	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaH_2PO_4 + NaClO_2 + V_2O_5$	5.40	60 h	67.60
24	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaH_2PO_4 + NaClO_2$ + Cat.1	11.88	60 h	2.78
25	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaH_2PO_4 + NaClO_2$ + Cat.1	6.72	60 h	77.7
26	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaClO_2$ + Cat.2	11.8	48 h	—
27	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaH_2PO_4 + NaClO_2$ + Cat.2	7.12	48 h	34.32
28	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaH_2PO_4 + NaClO_2$ + Cat.2	6.32	48 h	60.72
29	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaH_2PO_4 + NaClO_2$ + Cat.2	5.77	48 h	74.64
30	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaH_2PO_4 + NaClO_2$ + Cat.2	5.44	48 h	87.97
31	Benzaldehyde	$R_1,R_2,R_3 = H$	$NaH_2PO_4 + NaClO_2$ + Cat.2	5.40	48 h	90.08

In the subsequent studies, the combination of NaH_2PO_4 and sodium chlorite under the same conditions used to balance the oxidative strength of sodium chlorite, thereby increasing the selectivity of the reaction. To observe the catalytic difference when sodium chlorite is added, measurements were taken for 48 hours at different pH values. This allowed for a thorough analysis of how sodium chlorite affects the catalytic activity under various conditions. For this, the reaction was carried out firstly by adding NaH_2PO_4 to adjust the pH to 6.98 and using 7 mmol of $NaClO_2$ for 5 mmol of aldehyde. After the reaction for 48 hours, it was observed that pH decreased from high (basic) to low (acidic) values, the yield increased to 33.1% (Table 2). The results demonstrated that the yield of the reaction depends strictly on the pH. Specifically, at pH 6.05, the yield was 38.5%. When the pH was adjusted to 5.65, the yield increased to 43.1%. Further lowering the pH to 5.45 resulted in a yield of 64.6%, and at pH 5.30, the yield reached 78.1%. These findings indicate that a decrease in pH leads to a significant increase in reaction yield, suggesting that the catalytic activity of the system is enhanced under more acidic conditions. These results of different pH values are presented in Table 2.

However, increasing the benzoic acid yield at neutral pH is an important task in terms of industrial applications due to reducing the corrosion risks and making the facilities easier. To enhance the oxidation capacity for the catalytic purposes, the use of chlorine dioxide (ClO_2) in combination with potassium permanganate ($KMnO_4$) as a catalyst was attempted. Under the existing conditions, it was expected that it would cause $NaClO_2$ to decompose and release ClO_2 at high pH (11.9), but this did not happen, and no product was formed. Consequently, a system involving $KMnO_4$ and $NaClO_2$ was tested. By adding 5 mmol of $KMnO_4$ to the sodium chlorite and NaH_2PO_4 system and allowing the reaction to proceed for 48 hours, the pH decreased from 11.9 to 6.10. This process resulted in the formation of benzoic acid with a yield of 16.1%. Additionally, to observe the effects of lower pH values over the same period, further experiments were conducted. At pH: 5.85, the yield increased to 28%, and at pH: 5.40, the yield significantly rose to 64.8 %. These results demonstrate that lowering the pH further enhances the yield at the same level with NaH_2PO_4 + $NaClO_2$ system, and there is no catalytic impact for KMnO4, as well.

In parallel, Vanadium Pentoxide (V_2O_5) as another oxidation catalyst like $KMnO_4$ was used additionally. The catalytic effect of V_2O_5 was studied under the same conditions to measure its influence on the oxidation process. When it was used solely with $NaClO_2$ at 12.0 pH, benzoic acid was not obtained after 72 hours. At pH: 6.40, benzoic acid with a yield of 12.7% was obtained by adding 0.5 mmol of V_2O_5 to sodium dihydrogen phosphate and sodium chlorite combination after 60 hours of reaction. Also, at pH: 5.65 the yield increased to 48.5%, and at pH: 5.40 increased to 67.6% over the same period. All the experiments assessed the effect of pH but no catalytic effect for V_2O_5 on the reaction yield (Table 2).

Some other oxidation combinations were tested for the oxidation of benzaldehyde to benzoic acid, as well. Sodium chlorite was used in conjunction with Sodium Tripolyphosphate (STPP) and formic acid. The pH in the STPP/formic acid system was buffered to 3.5. At the end of a 60-hour reaction, benzoic acid was obtained with a yield of 52.0%. In another system, 1-Hydroxyethylidene-1,1-Diphosphonic Acid (HEDP) was used alongside sodium chlorite. Similarly, by adjusting the pH to 3.5 in the studies with HEDP, benzoic acid was obtained with a yield of 75.0% at the end of a 60-hour reaction. This was also tested in pH: 4.90 to see the difference of yield with this yield descend to 58.5%.

Additionally, measurements were taken by using stabilized chlorine dioxide solution directly as an oxidation reagent. In this study, 0.6 g of stabilized chlorine dioxide was added for 5 mmol of benzaldehyde. After 60 hours of reaction, benzoic acid was obtained with a yield of 73.0%.

Mn complexes are organic compounds containing transition metals and are effective catalysts in oxidative processes. We also investigated Mn complexes as catalysts, alongside using a stabilized chlorine dioxide solution as a direct oxidation reagent in various catalytic systems. In the final stage of our catalytic studies was focused on examining the catalytic effect of manganese-containing complexes in the presence of ClO_2. To this end, manganese-containing complexes were synthesized, and their catalytic effects were studied under identical conditions. The Mn(III)(acen)Cl complex (Cat.1), known for its catalytic activity, was prepared following the procedure described in the literature and used as the catalyst [25]. However, no product was obtained at the end of this Cat.1 and $NaClO_2$ combination experiment at 11.8 pH after 48 hours. Therefore, the catalytic effect of 5 mmol Cat.1 in the presence of $NaClO_2$ and NaH_2PO_4 was investigated at different pHs for the same period. As a result, benzoic acid was obtained with a yield of 34.32% at 7.12 pH, 60.72% at 6.32 pH, 74.64% at 5.77 pH, 87.97% at 5.44 pH, and 90.08% at 5.40 pH, after adding the additives to the system under the same conditions. The significant catalytic effect was observed at the same pH levels for Cat.1 when it compared with the NaH_2PO_4 + $NaClO_2$ combination applications.

Specifically, we synthesized Mn(III)SchLCl complex (Cat.2) with a fine-tuned synthesis procedure starting from 3,5-di-tert-butyl-2-hydroxybenzaldehyde as the specific Mn(III) catalyst known as "Jacobsen's Catalysts" in the literature [26]. Initially, the Schiff base was formed by reacting the aldehyde with cis/trans-1,2-diaminocyclohexane in ethanol. This was followed by the addition of a metal salt in a basic media to complete the complex formation. The progress of this reaction was monitored by Thin Layer Chromatography (TLC). The formation of the Mn(III)SchLCl complex (Cat.2), obtained from the reaction of the Schiff base ligand with $Mn(OAc)_2 \cdot 4H_2O$, is indicated by the spectroscopic analysis and elemental analysis. In the FTIR spectrum of Cat.2 the C=N band appeared at 1608 cm^{-1}, demonstrating the involvement of the imine group in the complex formation, shifted to lower wave-number when it compared with the related ligand [26]. The other signals recorded, were supported to the complex formation, as well. The elemental and ICP-OS analysis results of the prepared complex are consistent with the values theoretically calculated and given in the literature [26,31].

The catalytic effect of Cat.2 (Mn(III)SchLCl complex), in the presence of $NaClO_2$ and NaH_2PO_4 was investigated at different pHs for the same period of time. Catalytic measurements were recorded after 90 min. than adding Cat.2. UV-Vis graphs of these measurements and their comparison to buffers can be seen at Fig. 7. The recorded UV-Vis. spectra were examined, and ClO_2 generation was observes with the increase of the absorption at 360 nm by pH adjusting and catalysis which is accorded with the literature [19, 32]. In Fig. 7a, it is observed that ClO_2 formation proceeds with the effect of pH (pH:1 buffer) and therefore the catalytic effect cannot be predicted clearly. However, in the studies carried out in pH:2 buffer in Fig. 7b, it was determined that the Cat.2 catalyst added to the buffer increased the formation of ClO_2. Although increasing the pH reduces this effect, it is seen in Fig. 7c that the catalytic effect continues in the pH:4 buffer. But, when Fig. 7d is examined, it is observed that the formation of ClO_2 in the pH:6 buffer in the aqueous environment decreases to an almost non-existent level by the pH effect or the catalytic effect.

The time-dependent absorptions of generated ClO_2 at different pHs were represented at Graph 1, while the catalytic activities and the yields were presented in Table 1. To be able to clarify the catalytic mechanism, we examined the ClO_2^- to ClO_2 conversion kinetics and compared with the literature results [32]. Under HCl and KCl buffer conditions at pH 1.05, conversion was 16.41% in 90 min. In this environment, a very rapid linear conversion occurs and the formation of ClO_2 are clearly visible.

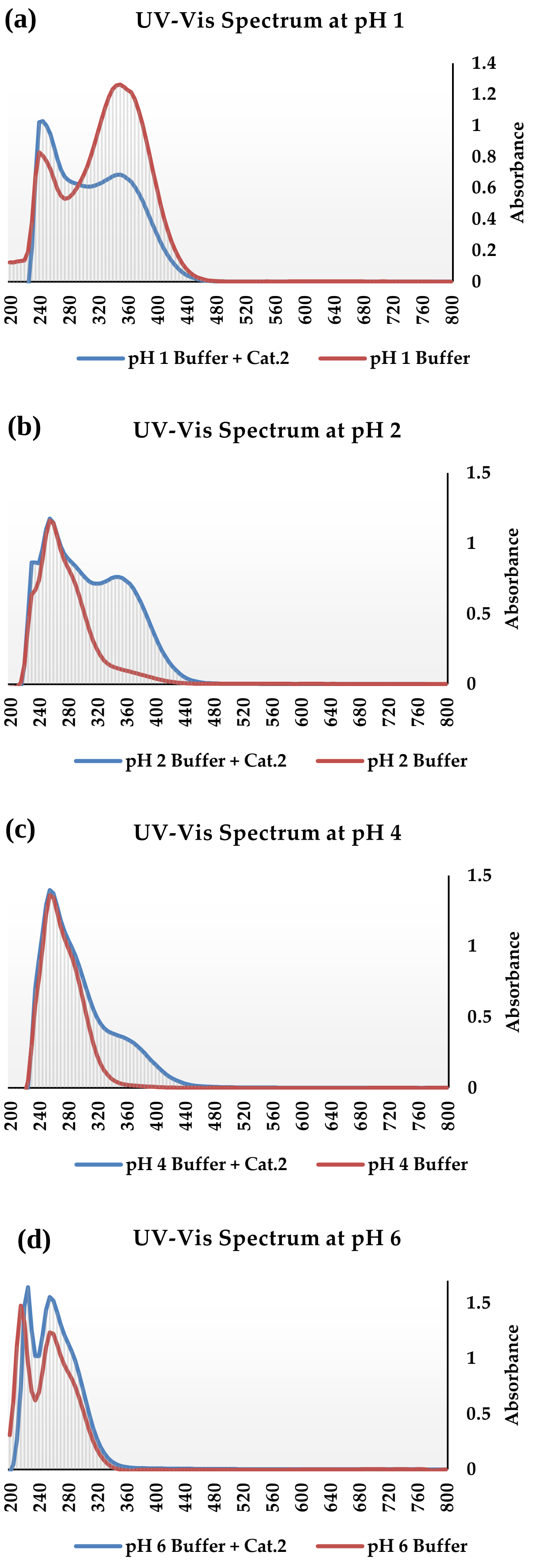
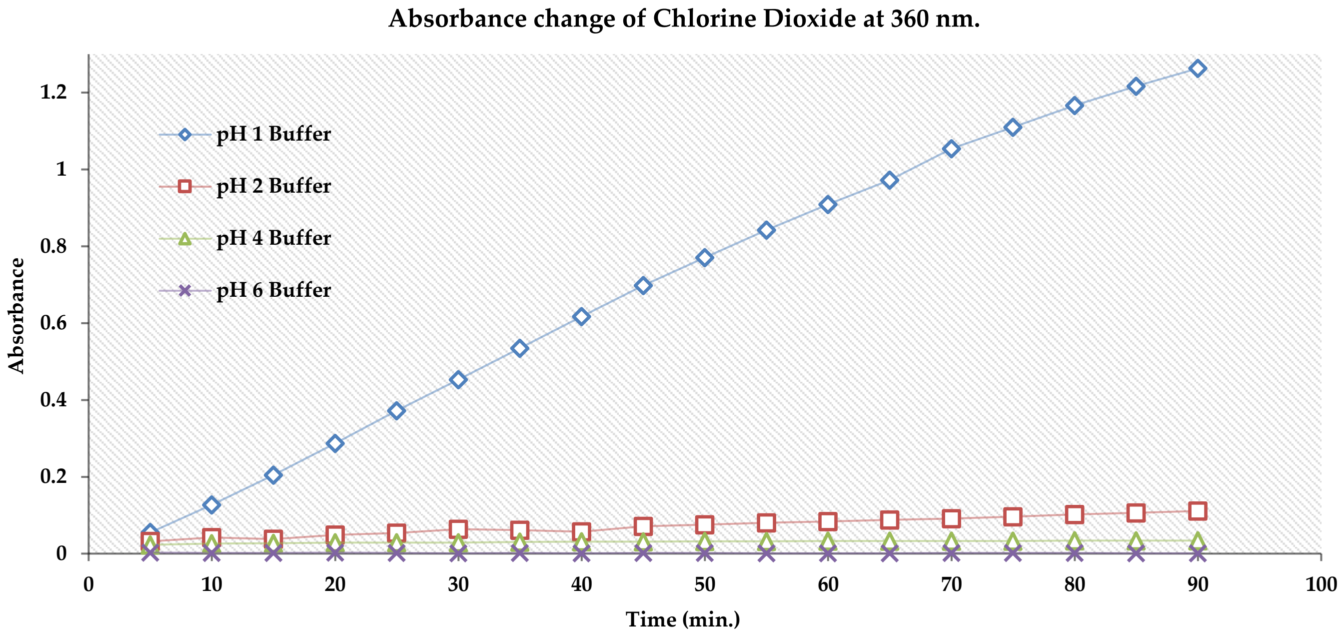


Figure 7. UV-Vis spectra of Cat.2 in buffer at: **a)**1.05 pH after 90 minutes, **b)** 2.10 pH after 90 min., **c)** 4.07 pH after 90 min., **d)** 6.02 pH after 90 min.

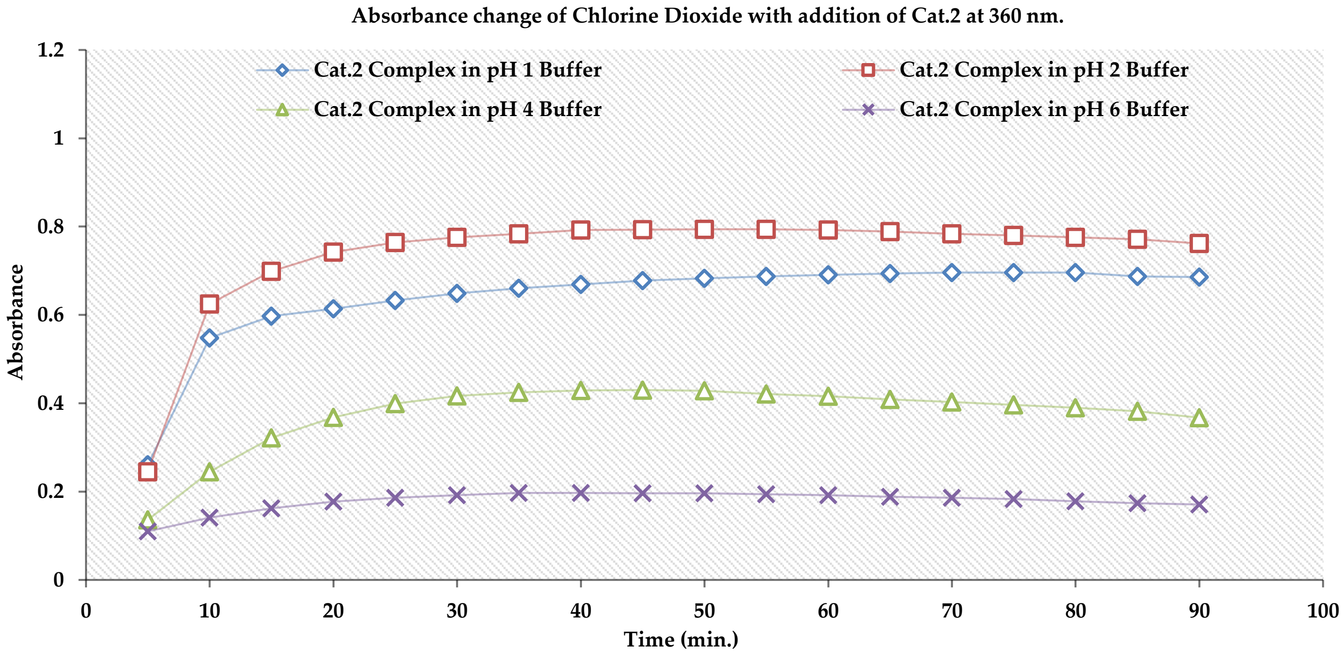


Graph 1. Absorbance change graph of Chlorine Dioxide in the specified buffers at 360 nm

To see the conversion results of citric acid and NaH_2PO_4 combination at different pH, we tested them for 90 min. at similar conditions, as well. At pH:2.10, formation was 1.45%, at pH:4.07 formation was 0.442%, and at pH:6.02 formation was measured as 0.013%, respectively. In other pH experiments, conversion results in citric acid and NaH_2PO_4 buffer showed us that there was a leveling effect here and ClO_2 formation occurred slowly. When the buffer was changed, there were large differences in ClO_2 formation between the two measurements (Graph 1). The reason why the reaction is carried out in the presence of NaH_2PO_4 is that it acts as a buffer for the ClO_2 formed during the reaction. This buffering effect helps stabilize the ClO_2 concentration, allowing for more controlled and effective catalytic reactions [19,32,33].

The time-dependent absorption of ClO_2 with Cat.2., as well as citric acid and NaH_2PO_4 with Cat.2 were presented in Table 1. Also, activities at different pHs were presented in Graph 2 respectively.

Cat.2 in HCl and KCl buffer (pH: 1.05), ClO2 formation was 9.29% in 90 minutes. under the same conditions. Although a leveling effect is observed here, the amount of ClO_2 in the environment is higher due to the catalyst effect. Since Cat.2 also buffers, a similar leveling effect can be seen even in buffer solutions where pH is close to 1. This shows us that measurements made



Graph 2. Absorbance change graph of Chlorine Dioxide in the specified buffers with addition of Cat.2 (360 nm)

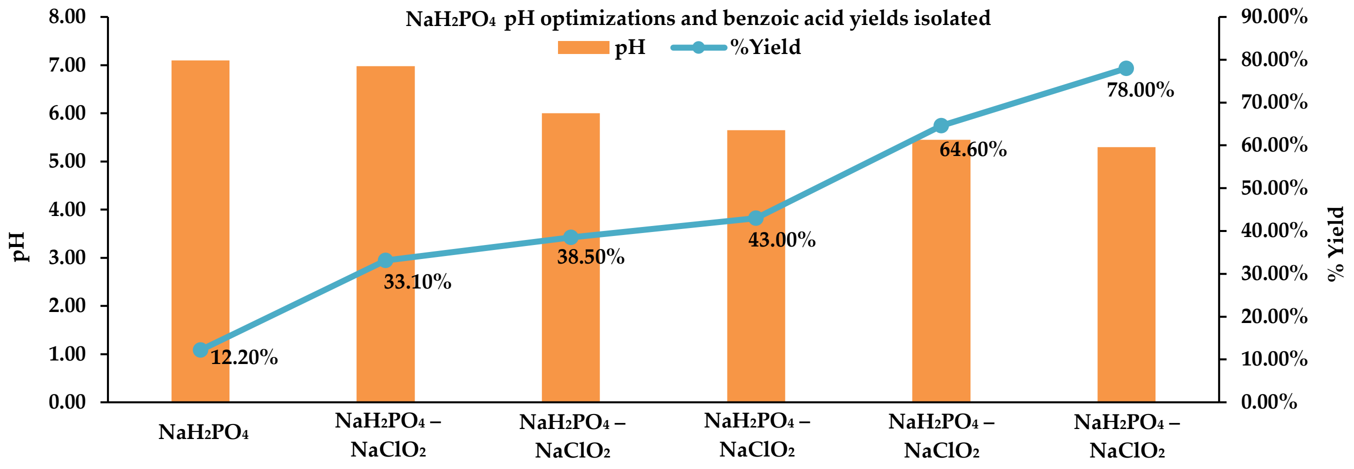


Figure 8. pH buffering with NaH_2PO_4 and benzoic acid yields isolated

with the metal complex in NaH_2PO_4 environment will give the highest conversion rate. As expected, the results of Cat.2 and NaH_2PO_4 formation in citric acid at different pH values were 10.32% at pH 2.10, 5.59% at pH 4.07 and 2.56% at pH 6.02 for 90 minutes.

The leveling effect seen here and increased by Cat.2 can be expected to make a positive contribution to the oxidative conversion of benzaldehyde to benzoic acid. When the yields of benzoic acid given in Table 2 are compared with the efficiencies obtained both in buffer solutions and when using catalyst together with buffer are quite high compared with the ClO_2 conversion efficiency. It can be interpreted that the effect of the mentioned leveling effect of ClO_2 which is increased by the ClO_2 complexes formed with the catalysts used, and in this case, high percentages of benzoic acid conversions are obtained even at pH close to neutral [34,35]. As a result, benzoic acid was obtained with the isolated yield of 2.78% at 11.82 pH, and 77.7% at 6.72 pH after 60 hours reaction.

In line with the studies, attempts were made to catalytically oxidize aromatic aldehydes including 4-methyl benzaldehyde, *m*-Tolyl Aldehyde, *p*-Tolyl Aldehyde, Salicylaldehyde, and 4-Hydroxy benzaldehyde using stabilized chlorine dioxide. The results of the conducted studies are presented in Table 2.

Table 2 shows that 31 different experiments were carried out. As a first step of the experiments, different aldehyde derivatives (benzaldehyde, *m*-tolyl aldehyde, *p*-tolyl aldehyde, 4-methoxy benzaldehyde, 2-hydroxy benzaldehyde and 4-hydroxy benzaldehyde) were reacted with stabilized ClO_2 solution. At the end of the reaction, it was observed that there was no transformation in the aldehyde derivatives containing the free –OH group. It was interpreted that the antioxidant property of the phenolic structure in these molecules prevents the radical oxidation.

In the second stage of the experiments, the oxidation conditions and yields of benzaldehyde to benzoic acid in different pH buffers and catalysts in the presence of $NaClO_2$ were investigated. In the experiment performed with only NaH_2PO_4 without $NaClO_2$ at pH 4.90, no benzoic acid could be isolated after 72 hours. However, in the combination of NaH2PO4 + $NaClO_2$, benzoic acid was obtained at increasing rates from 33.1% to 78.1% at decreasing pH values from pH: 6.90 to pH: 5.30, respectively (Fig. 8).

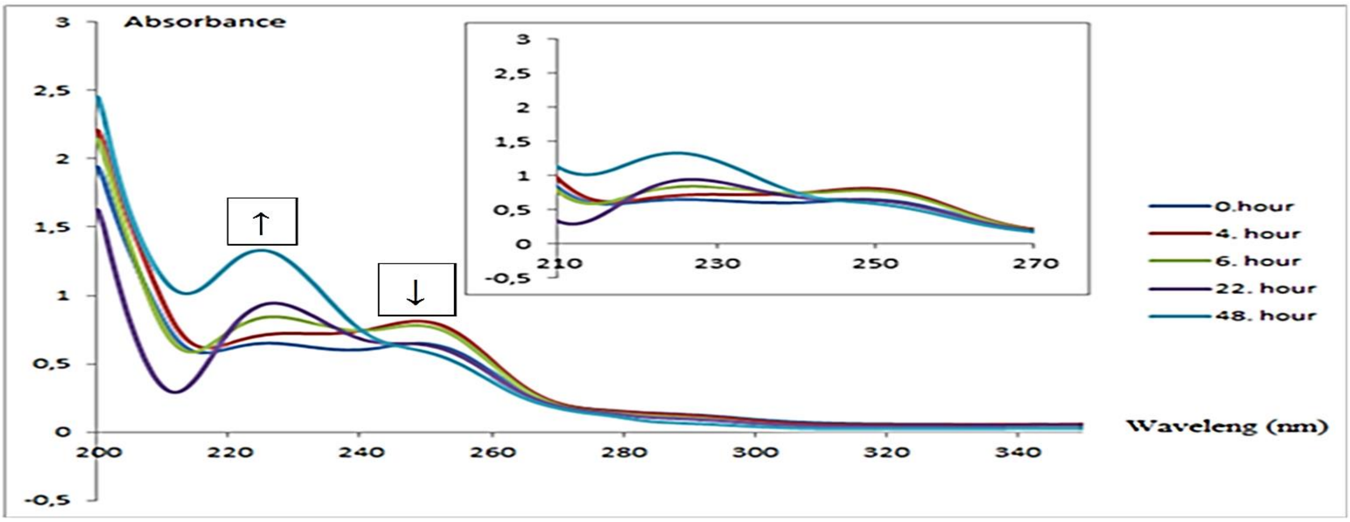


Figure 9. Absorption spectra of the conversion of benzaldehyde to product (benzoic acid)

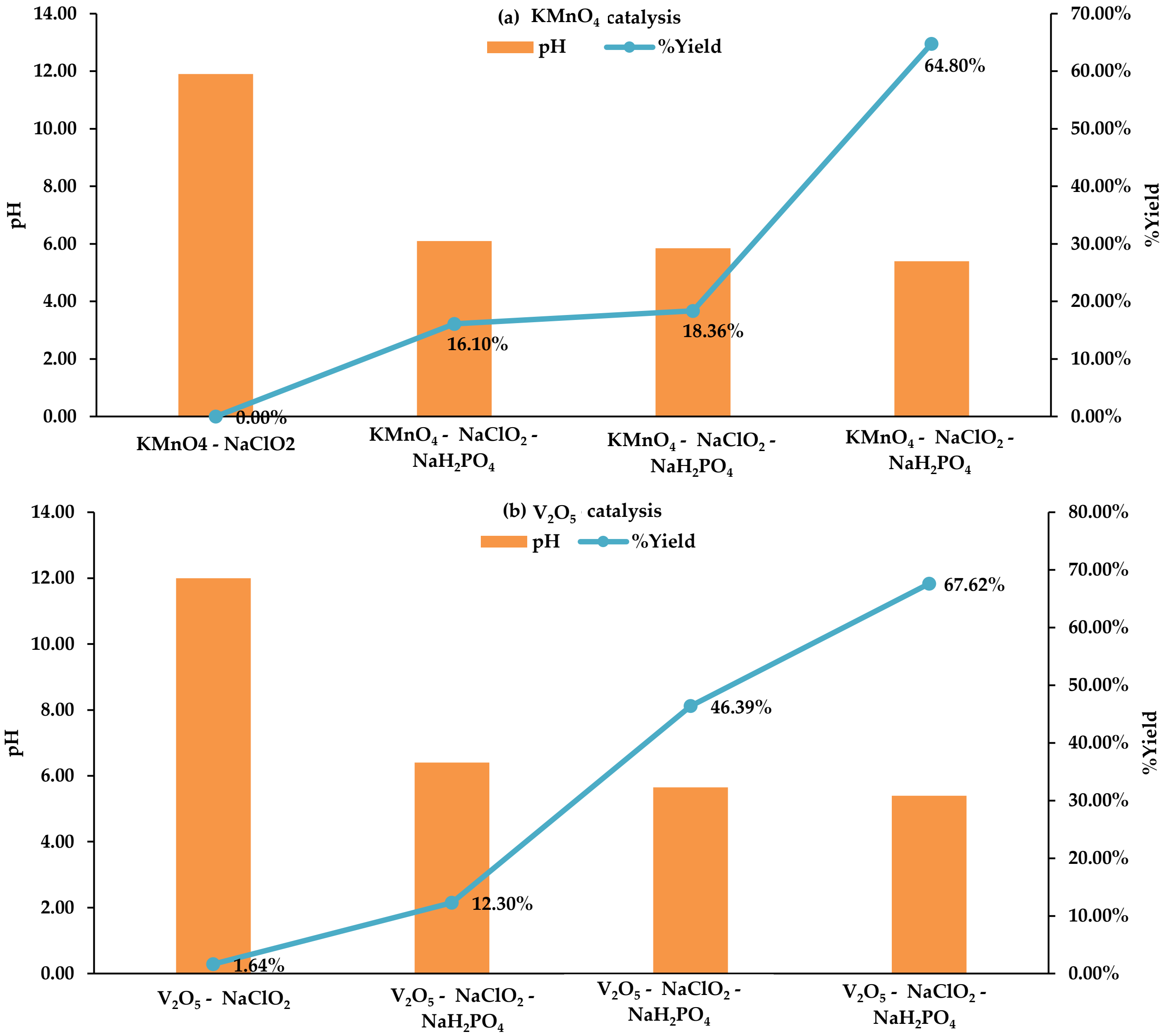


Figure 10. a) $KMnO_4$ catalysis with NaH_2PO_4+$NaClO_2$ system, **b)** V_2O_5 catalysis with NaH_2PO_4+$NaClO_2$ system

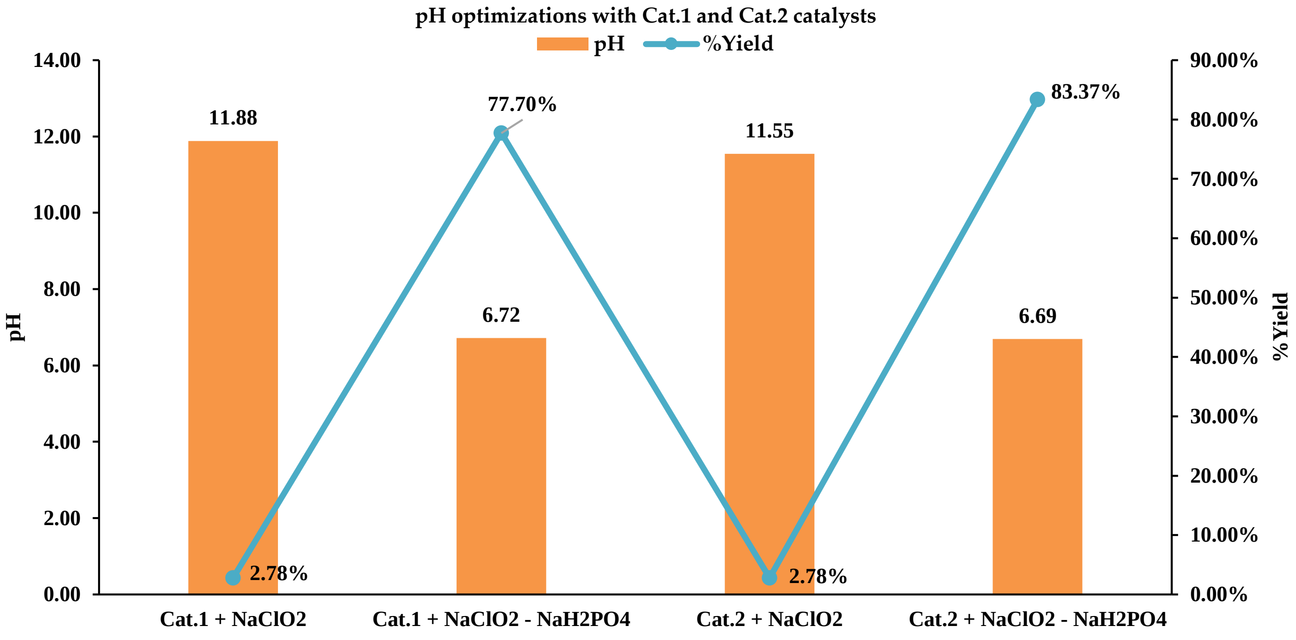
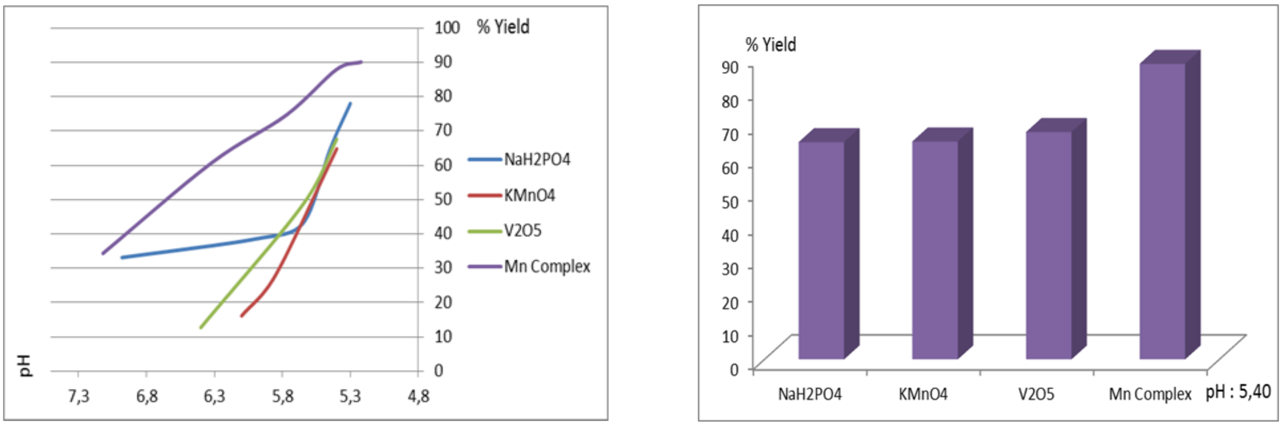


Figure 11. Catalytic conversion yields of benzoic acid at different pHs with Cat.1 and Cat.2



(a) **(b)**

Figure 12. **a)** The pH-yield variation of catalysts, **b)** The yield comparison of catalysts at pH 5.40

Although benzoic acid conversion was monitored by UV-Vis spectroscopy (Fig. 9), the isolated benzoic acid yields were presented to justify the results.

Other organic acids such as HEDP and citric acid which have been known of their application with $NaClO_2$ were also used as buffering agents [36,37].

In these applications, benzoic acid yields gradually increasing with the pH structure were obtained.

The catalytic studies were continued with $KMnO_4$ and V_2O_5 which were used with the NaH_2PO_4+$NaClO_2$ combination. While no product was obtained with $KMnO_4$ at high pH (pH: 12), in the study conducted with the V_2O_5 catalyst, 1.6% benzoic acid yield was obtained at pH: 12. However, it was observed that the other yields obtained by pH change were lower compared to the yields obtained with the combination of NaH_2PO_4+$NaClO_2$, which was assigned that the catalysts were not sufficient to stabilize the formed ClO_2 (Fig. 10a and b).

In the last step of the study, the prepared complexes ([Mn(III)(acacen)Cl] and [Mn(III)(SchL)Cl]) were used as catalysts (Cat.1 and Cat.2). For both complexes, benzoic acid formation was observed at pH values above 11.5. However, benzoic acid was obtained in very high yields of 77.7% and 83.4% at pH values close to neutral (pH: 6.72 and pH: 6.69), respectively by using Cat.1 and Cat.2 (Fig. 11).

Benzoic acid yields of the catalysts depending on pH are shown in the graph in Fig. 12a. It is seen that the benzoic acid yield in NaH_2PO_4 buffer depends entirely on the pH value and increases rapidly after pH: 5.8. For $KMnO_4$ and V_2O_5 catalysts, lower yields were obtained due to the reaction of the catalysts with ClO_2 formed at pH < 5.5, while the same effect was observed with buffer at pH > 5.5. When the graph of Cat.2, one of the prepared catalysts, was examined, the catalytic effect was clearly seen, and it was understood that the reaction was catalyzed at every pH value. The highest efficiency for Cat.2 was determined as 90% at pH: 5.40. The comparative yields of other catalysts at the same pH value are given in Fig. 12b.

4. Conclusion

Firstly, measurements were taken by using stabilized chlorine dioxide solution directly as an oxidation reagent to make sure if the substituent bearing on the benzene ring effected the rection kinetic. Free -OH group bearing benzaldehyde derivative did not give any conversion. NaH_2PO_4 was used as a buffering agent for adjusting the reaction pH to the desired value. The lower the pH, the greater the yield of benzoic acid obtained. Other oxidation combinations tested included Sodium Chlorite with Sodium Tripolyphosphate (STPP), 1-Hydroxyethylidene-1,1-Diphosphonic Acid (HEDP), and formic acid. STPP was used to modulate the oxidative capacity of sodium chlorite, phosphonic acid to enhance the effect of sodium chlorite, and formic acid to strengthen the oxidation process.

The combination of the catalyst with sodium chlorite was utilized to enhance the yield of the reaction by balancing the oxidative powers of sodium chlorite in the corresponding pH. Subsequently, the addition of $KMnO_4$ aimed to increase the oxidation capacity. Additionally, during the oxidation process, measurements were taken by adding V_2O_5 to the combination of Sodium Dihydrogen Phosphate and Sodium Chlorite as an extra catalyst. But not much improvement was observed for these applications.

Furthermore, Mn (III) complexes were also examined as catalysts (Cat.1 and Cat.2) which are organic compounds containing transition metals and are effective catalysts in oxidative processes. It was found that the use of Mn (III) complexes (Cat.1 and Cat.2) in NaH_2PO_4+$NaClO_2$ combination provided the highest yield in the oxidation of aromatic aldehydes to acids. For the catalytic application in buffer solutions, a leveling effect was observed which was resulting in slow ClO_2

formation. Mn complexes (Cat.1 and Cat.2) exhibited a similar leveling effect in buffer solutions with a pH >1. These findings proved that utilizing Mn complexes in a NaH_2PO_4 environment yields the highest conversion rates.

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References

[1] BÄCKVALL, Jan-Erling (ed.), Modern oxidation methods (2nd edition), 2011, USA, John Wiley & Sons.

[2] B.O. Lindgren, T. Nilsson, Preparation of carboxylic acids from aldehydes (including hydroxylated benzaldehydes) by oxidation with chlorite, Prep Org Chem, 4, 1973, 35.

[3] G. Tojo, M. Fernández, Oxidation of primary alcohols to carboxylic acids: A guide to current common practice (Basic Reactions in Organic Synthesis), (2007th edition), 2006, USA, Springer.

[4] A. Raach, O. Reiser, Sodium chlorite-hydrogen peroxide—A mild and selective reagent for the oxidation of aldehydes to carboxylic acids, J Prakt Chem, 342:6, 2000, 605-608.

[5] J.M. Grill, J.W. Ogle, S.A. Miller, An efficient and practical system for the catalytic oxidation of alcohols, aldehydes, and α, β-unsaturated carboxylic acids, J Org Chem, 71:25, 2006, 9291-9296.

[6] G. Pass, Practical Inorganic Chemistry: Preparations, Reactions and Instrumental Methods (2nd edition), 2013, USA, Springer Science & Business Media.

[7] G. Lunn, E.B. Sansone, Destruction of Hazardous Chemicals in the Laboratory (4th edition), 2023, USA, John Wiley & Sons.

[8] A. Asghar, A.A.A. Raman, W.M.A.W. Daud, Advanced oxidation processes for in-situ production of hydrogen peroxide/hydroxyl radical for textile wastewater treatment: A review, J Clean Prod, 87, 2015, 826–838.

[9] H.B. Ji, β-Cyclodextrin promoted oxidation of aldehydes to carboxylic acids in water, Chin Chem Lett, 20, 2009, 139–142.

[10] T. Beddoes, Davy, In A History of Chemistry (Latest edition), 1964, Palgrave, London.

[11] N. Riegels, M.J. Richards, Humphry Davy: His life, works, and contribution to anesthesiology, J Am Soc Anesthesiol, 114, 2011, 1282–1288.

[12] M. Zhao, Oxidation of primary alcohols to carboxylic acids with sodium chlorite catalyzed by TEMPO and bleach, J Org Chem, 64(7), 1999, 2564–2566.

[13] S.B. Jonnalagadda, S. Nadupalli, Chlorine dioxide for bleaching, industrial applications and water treatment, Indian Chem Eng, 56(2), 2014, 123–136.

[14] W. Gan, Y. Ge, Y. Zhong, X. Yang, The reactions of chlorine dioxide with inorganic and organic compounds in water treatment: Kinetics and mechanisms, Environ Sci Water Res Technol, 6(9), 2020, 2287–2312.

[15] A.R. Mohite, R.G. Bhat, A practical and convenient protocol for the synthesis of (E)-α, β-unsaturated acids, Org Lett, 15(17), 2013, 4564–4567.

[16] A.P. Krapcho, Uses of sodium chlorite and sodium bromate in organic synthesis: A review, Org Prep Proced Int, 38(2), 2009, 177–216.

[17] S. Erdemir, Schiff bazı ve polimerlerinin geçiş metal komplekslerinin sentezi karakterizasyonu ve oksidasyon katalizörü olarak etkilerinin incelenmesi, Doktora Tezi, Çukurova Üniversitesi, Fen Bilimleri Enstitüsü, 2007.

[18] S. Abramovici, R. Neumann, Y. Sasson, Sodium hypochlorite as oxidant in phase transfer catalytic systems: Part I. Oxidation of aromatic aldehydes, J Mol Catal, 29(3), 1985, 291–297.

[19] S.D. Hicks, Non-heme manganese catalysts for on-demand production of chlorine dioxide in water and under mild conditions, J Am Chem Soc, 136, 2014, 3680–3686.

[20] K. Ohkubo, Dihydroxylation of styrene by sodium chlorite with scandium triflate, J Phys Org Chem, 30(e3619), 2016, 5.

[21] M.Y. Xu, Y.L. Lin, T.Y. Zhang, C.Y. Hu, Y.L. Tang, J. Deng, B. Xu, Chlorine dioxide-based oxidation processes for water purification: A review, J Hazard Mater, 436, 2022, 129195.

[22] V. Rougé, Y. Lee, U. von Gunten, S. Allard, Kinetic and mechanistic understanding of chlorite oxidation during chlorination: Optimization of ClO2 pre-oxidation for disinfection byproduct control, Water Res, 220, 2022, 118515.

[23] K. Furukawa, M. Shibuya, Y. Yamamoto, Chemoselective catalytic oxidation of 1,2-diols to α-hydroxy acids controlled by TEMPO–ClO2 charge-transfer complex, Org Lett, 17(9), 2015, 2282–2285.

[24] J. Cubillos, S. Vásquez, C.M. de Correa, Salen manganese (III) complexes as catalysts for R-(+)-limonene oxidation, Appl Catal A Gen, 373(1-2), 2010, 57–65.

[25] A.V. Kutchin, I.V. Fedorova, I.V. Loginova, I.Y. Chukicheva, Features of the use of ClO2 in the oxidation of some alkylphenols, Russ Chem Bull, 72(1), 2023, 202–212.

[26] A. Westphal, A. Klinkebiel, H.M. Berends, H. Broda, P. Kurz, F. Tuczek, Electronic structure and spectroscopic properties of mononuclear manganese (III) Schiff base complexes: A systematic study on [Mn (acen) X] complexes by EPR, UV/vis, and MCD spectroscopy (X= Hal, N CS), Inorg Chem, 52(5), 2013, 2372–2387.

[27] R. Habib, Method for the production of chlorine dioxide, 1993, US5380518A.

[28] S.S. Nielsen, C. Tyl, B. P. Ismail, Preparation of reagents and buffers, Food Analysis Laboratory Manual (5th edition), 2017, 21–32.

[29] P. Sen, D. Kara Simsek, S.Z. Yildiz, Functional zinc (II) phthalocyanines bearing Schiff base complexes as oxidation catalysts for bleaching systems, Appl Organomet Chem, 29(8), 2015, 509–516.

[30] G. Kaya, Oksidasyon katalizörü olarak çeşitli koordinasyon bileşiklerinin hazırlanması, karakterizasyonu ve etkinliklerinin ölçülmesi, Doctoral Thesis, Sakarya University, Fen Bilimleri Enstitüsü, 2018.

[31] E.N. Jacobsen, W. Zhang, A.R. Muci, J.R. Ecker, L. Deng, Highly enantioselective epoxidation catalysts derived from 1,2-diaminocyclohexane, J Am Chem Soc, 113(18), 1991, 7063–7064.

[32] S.D. Hicks, S. Xiong, C. J. Bougher, G. A. Medvedev, J. Caruthers, M.M. Abu-Omar, Mechanistic study of a manganese porphyrin catalyst for on-demand production of chlorine dioxide in water, J Porphyrins Phthalocyanines, 19(01n03), 2015, 492–499.

[33] P. Barman, A. S. Faponle, A. K. Vardhaman, D. Angelone, A. M. Löhr, W.R. Browne, S.P. de Visser, Influence of ligand architecture in tuning reaction bifurcation pathways for chlorite oxidation by non-heme iron complexes, Inorg Chem, 55(20), 2016, 10170–10181.

[34] Z. Hu, H. Du, W.L. Man, C.F. Leung, H. Liang, T.C. Lau, Catalytic reactions of chlorite with a polypyridylruthenium (II) complex: Disproportionation, chlorine dioxide formation and alcohol oxidation, Chem Commun, 48(8), 2012, 1102–1104.

[35] I. Fábián, The reactions of transition metal ions with chlorine (III), Coord Chem Rev, 216, 2001, 449–472.

[36] S. Z. Yıldız, S. Dursun, The investigation of the effect of sodium chlorite and phosphonic acid catalysts on cotton bleaching process conditions, Turk J Anal Chem, 5(1), 2023, 61–69.

[37] S. Dursun, S.Z. Yıldız, Eco-friendly bleaching of cotton fabrics without heating using direct process water in the presence of sodium chlorite and phosphonate, J Nat Fibers, 20(1), 2023, 2146248.