Pilot scale degradation study of 16 selected volatile organic compounds by hydroxyl and sulfate radical based Advanced Oxidation Processes

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Abstract

The studies of effective technologies for complete degradation of the volatile organic compounds (VOCs), are very important due to the high biotoxicity of the VOCs which makes the biological technologies ineffective. It also increases the risk of VOCs emission instead of their treatment when using open air biological technologies. In the present study, different types of Advanced Oxidation Processes (AOPs) were investigated for the degradation of several VOCs in a model pilot scale effluent, simulating effluents from bitumen production. The goal of this paper is to reach effective VOCs and wastewater degradation to make the bitumen production a cleaner process. O_3, H_2O_2, O_3/H_2O_2 (the so called peroxone), persulfate (PS) and peroxymonosulfate (PMS) were processes chosen for this work. Heat activation enhanced the total VOCs degradation in PS and PMS technologies, which achieved higher effectiveness than H_2O_2. Peroxone process at 40 ºC achieved the highest efficiency of all processes studied needing only 60 min to completely degrade all compounds without any oxidation by-products. Sulfur containing VOCs (VSCs) were completely degraded in a shorter treatment time and nitrogen containing VOCs (VNCs) needed more time of treatment in all technologies studied. The preference of the hydroxyl and sulfate radicals for degradation of oxygen containing VOCs (O-VOCs) had different behavior depending on the group of compounds and should be considered in future research for combined radical processes.

Keywords: VOCs degradation; wastewater treatment; hydroxyl radicals; sulfate radicals; GC-MS; AOPs

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1. Introduction

Volatile Organic Compounds (VOCs) represent a group of compounds that are known to need special precautions when choosing a targeted treatment. They are widely present in several types of industrial facilities, as raw materials or as by-products or as waste (Kim and Hong, 2002). Due to their carcinogenic nature, some VOCs are considered to be harmful to human health, other animals, plants and microorganisms present in the environment (Cheng and Hsieh, 2013; Ren et al., 2018). The discharge limits of each of the VOCs may depend on the country and have been decreasing in the last years (Boczkaj et al., 2010; Ojala et al., 2011). There are several types of VOCs, including oxygen containing volatile organic compounds (O-VOCs), sulfur containing VOCs (VSCs) and nitrogen containing VOCs (VNCs) (Boczkaj et al., 2014). VOCs origin depends on the type of industrial facility, which can be pharmaceutical (Li et al., 2014), dyes (Ning et al., 2015), cellulose (Rigol et al., 2002) or petroleum refinery (Cheng and Hsieh, 2013; Stepnowski et al., 2002). These types of industries are investing significantly in the last years in researching and developing strategies to treat their wastewater (WW). The idea all along is to reuse part of the WW generated with the anticipation of environmental sustainability and control over fresh water shortage. Elimination of VOCs from industrial effluents could be one of the big steps contributing to the aforementioned desire of WW reuse. To effectively degrade VOCs, there is a need to choose an appropriate technology to avoid their emission to the atmosphere. Some of the VOCs have complex structures, like aromatics and poly-aromatics, which are not degraded by the biological approach. Some studies already attempted the combination of Advanced Oxidation Processes (AOPs) and biological technologies to reach effective treatment of heavy polluted effluents and, therefore, reaching cleaner production (Bahri et al., 2018). Effluents like spent caustic (Hariz et al., 2013; Oh and

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Shin, 2013), petroleum & refinery (Saien and Nejati, 2007; Saien and Shahrezaei, 2012), bitumen (Autelitano and Giuliani, 2018; Ventura et al., 2015), post oxidative effluents from bitumen production (Boczkaj et al., 2010, 2014) are examples of caustic effluents that need special precaution when treated.

Degradation of VOCs has widely been studied by different types of remediation technologies with the investigation of all parameters affecting the technology efficiency. Nevertheless, studies are focused on a model WW containing one compound, and the effect of a second pollutant present in the model WW. To fully analyze the effectiveness of studied processes, the research should include studies using a model WW containing several VOCs for evaluation of the total effect of treatment using scenario that simulates as much real effluents as possible. Some studies have used the above approach by preparing a model WW containing several types of VOCs (Goel et al., 2004; Shen and Ku, 1999; Wols et al., 2013). Previous studies on the treatment of effluents from bitumen production by hydroxyl radical based advanced oxidation processes (H-AOPs) and sulfate radical based AOPs (S-AOPs) revealed partial decrease of the chemical oxygen demand (COD), around 45%. The particular groups of compounds responsible for the low COD reduction have been reported to be saturated hydrocarbons (Boczkaj et al., 2017; Fernandes et al., 2018). Thus, the model WW was prepared to understand if the selected conditions on the real effluents studies are effective for the certain groups of compounds. In addition, it is important to understand if their degradation behavior is the same as the VOCs present in the real effluents and if they can produce harmful by-products which can be one of the hypothesis of the partial COD reduction in previous work (Boczkaj et al., 2017). Thus, the processes and operational parameters studied in this work were the same as previous papers mentioned above.

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AOPs were first reported by Glaze, who stated that AOPs are capable for generation of highly reactive species named hydroxyl radicals ($HO^{\bullet}$) (Glaze and Kangt, 1989). $HO^{\bullet}$, possesses a high oxidation potential ($E° = 2.7$ V), is capable of oxidizing the majority of the organic compounds (Litter, 2005; Shahidi et al., 2015; Ali et al., 2018). In some cases, the compounds can be fully mineralized to CO_2 and H_2O. In the recent decades, new technologies inside the AOPs technology had emerged, based on the use of persulfate (PS) and peroxymonosulfate (PMS) as oxidants, the so called S-AOPs (Khan et al., 2013; 2014; 2017). Usually PMS is available either pure or as a triple salt ($2KHSO_5.KHSO_4.K_2SO_4$) called Oxone (Sharma et al., 2015). These processes are known to generate sulfate radicals ($SO_4^{\bullet -}$) with high oxidation potential ($E^o = 2.6$ V) similar to $HO^{\bullet}$ (Ghanbari et al., 2016; Matzek and Carter, 2016). These technologies possess a wider working pH range than classic AOPs (i.e., H-AOPs) and can be more effective for treatment of caustic effluents (Boczkaj and Fernandes, 2017).

The goal of this paper is to simulate a strong alkaline model WW, containing several VOCs, to check their degradation behavior using the same AOP technologies used in previous studies with real effluents (Boczkaj et al., 2017; Fernandes et al., 2018). Also the study of the by-products of oxidation will help understand if there are any toxic and harmful by-products produced during oxidation of the model WW. This model effluent should simulate as much as possible the caustic effluents from refinery industries, namely, post oxidative effluents. These effluents are produced by absorption or scrubbing processes used in treatment of gas streams (Boczkaj et al., 2016; Hariz et al., 2013; Sipma et al., 2004). To the best of our knowledge, no studies were made in such specific field of research. This research is focused on comparison of results for alkaline model WW with previous study (Boczkaj et al., 2017). The specific treatment methods that were studied in the present work were O_3, H_2O_2, O_3/H_2O_2, PS and PMS

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processes. The effect of the dose of oxidant and the temperature are parameters under study.

2. Experimental

2.1 Materials

Hydrogen peroxide (30%), sodium persulfate ($Na_2S_2O_8$), potassium peroxymonosulfate ($KHSO_5$) and sodium hydroxide were purchased from POCH (Poland). VOCs such as toluene, 2-ethyl-1-hexanol, phenol, were purchased from POCH (Poland), benzene, o-xylene, ethylbenzene, nitrobenzene, 2-nitrophenol, 2-nitrotoluene from Merck (Poland), 2-ethylthiophene, dibutyl sulfide, di-tert-butyldisulfide, 2,6-dimethylphenol, 4-methylbenzyldehyde and naphthalene from Sigma Aldrich (Poland) and 4-ethylphenol was purchased from Acros organics (a POCH product).

2.2 Apparatus

To conduct the experiments, an acid resistant steel closed cylindrical reactor was used, which can treat up to 15 dm^3 of effluent. The details about the reactor are fully described in our previous work (Boczkaj et al., 2017). A semi-batch mode was used where the oxidant was added in a continuous mode during whole time of treatment. The model WW was pumped into the reactor by Euralca, model UGD 100/120-03, Italy membrane (PTFE) pump. H_2O_2, $KHSO_5$ and $Na_2S_2O_8$ solutions were fed to the reactor using a Hitachi LaChrom HPLC Pump model L-7110. Ozone was fed by a Tytan 32 Ozone generator that is able to produce up to 70 mg O_3/L of oxygen. Dried air was used to produce ozone.

VOCs identification and quantification was performed by gas chromatography-mass spectrometry. The detailed description of the methods is described in our previous

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paper (Boczkaj et al., 2016). COD determination was done using a HACH COD reactor and a HACH DR/2010 spectrophotometer.

2.3 Procedure

2.3.1. Model WW

In order to simulate caustic effluents containing several VOCs, usually present in petroleum & refinery effluents, a model WW was prepared with the VOCs listed in section 2.1 with a concentration around 10 ± 2 mg/L. The model WW has an initial pH of 10.5 and a measured COD between 390-490 mg O_2/L.

2.3.2. Effluent treatment

To conduct all experiments performed, the model WW was prepared as followed; Firstly, 5 dm^3 of deionized water at a pH of 10.5 (the pH of the deionized water was corrected with 0.1 M NaOH) was pumped to the reactor and heated until the desired temperature. Afterwards a known volume of primary solution was added by the special injection port, present in the reactor using a 2 mL gas tight syringe. The final concentration of each compound in the model WW was 10 ± 2 ppm. The initial pH was 10.5 in all procedures and no pH adjustment was performed during the treatment time. The volume of model WW treated was 5 dm^3. The stirring was established at 200 rotations per minute (rpm). Regarding the oxidants used (H_2O_2, $Na_2S_2O_8$, $KHSO_5$ and Ozone), their dose and treatment time are presented in Table 1. The pH of collected samples was measured by non-bleeding pH strips.

2.3.3. Process control

Every sample was taken with the purpose of analyzing the volatile organic compounds concentration, COD, and pH. COD was measured using the Polish standard test method PN-ISO 15705:2005, based on the dichromate method by HACH.

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Regarding the VOCs monitoring, the sample preparation was done by dispersive liquid-liquid micro-extraction (DLLME) and analyzed by gas chromatography-mass spectrometry (GC-MS). Details of the procedure were fully described elsewhere (Boczkaj et al., 2016).

3. Results and discussion

The degradation efficiency of several VOCs in the basic pH water matrix was studied using H-AOPs (i.e., O_3, H_2O_2 and O_3/H_2O_2) and S-AOPs (i.e., $Na_2S_2O_8$ and $KHSO_5$). Comparison between H-AOPs and S-AOPs was possible in terms of VOCs degradation. The temperature and dose of oxidant were the parameters studied regarding the effectiveness of VOCs degradation.

3.1. Degradation efficiency of H-AOPs

The degradation of VOCs by H-AOPs under different studied conditions has been shown in Figures 1S to 5S of supporting information (SI). To investigate the relative susceptibility of VOCs and the time required for their complete removal, the obtained results were carefully interpreted in detail.

Several VOCs such as VNCs, naphthalene and 4-methylbenzaldehyde were found to be persistent to sole-H_2O_2 process (Figure 1S and Table 2). Their degradation starts after 120 min of treatment time and after benzene, toluene, ethylbenzene and o-xylene (BTEX) and phenol were degraded above 50%. Interestingly, 2-nitrophenol and 2-ethyltiophene revealed to be the by-products of other VOCs compounds as seen from their increasing concentration with treatment time. An interesting behavior was observed – when the concentration of toluene and benzene decreased, a corresponding increase in the concentration of 2-nitrophenol and 2-ethyltiophene was noted. There is evidence that 2-nitrophenol can be formed from phenol rings by reaction with nitrite

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ions (Patnaik and Khoury, 2004). The Figure 1S and Table 2 results indicate that phenol degradation enables this pathway of 2-nitrophenol formation from phenolic compounds. In addition, it is proved that nitrite ions can be formed from N_2 in the presence of H_2O_2. Even though this reaction occurs at a very low efficiency, only small amount of nitrite is needed to trigger the reaction (Gekhman et al., 2003; Vione et al., 2001) and in this study there is an excess of N_2 which enables production of the nitrite ions. Furthermore, phenol can also be produced as an oxidation by-product of compounds containing benzene ring (Berndt and Böge, 2006), which can enhance the formation of 2-nitrophenol. A possible explanation for 2-ethylthiophene formation can be related with the oxidation and cyclization of sulfides and disulfides. These groups of compounds can be oxidized to sulfoxides by oxidation (Sato et al., 2001). The sulfoxides can produce thiophenes afterwards. Previous studies showed the cyclization of sulfoxides to thiophenes (Brown and Espenson, 1996; Wright et al., 1992). Furthermore, other VSCs such as di-tert-butyl disulfide and dibutyl sulfide were degraded fast after 15 min of treatment. Similar results were obtained in the degradation of dibutyl sulfide solely in a water matrix by H_2O_2 at pH 12 but with a much higher dose of H_2O_2 applied (Popiel et al., 2009). After 120 min of treatment, most of the O-VOCs reached higher degradation efficiencies.

It is clear that sole use of H_2O_2, was less efficient comparing with O_3, and O_3/H_2O_2 for all VOCs studied. Fortunately, higher H_2O_2 dose had a positive effect on the degradation of VOCs that were more persistent to degradation. This can be related with the increase of the oxidant amount in the water matrix or even the local decrease of pH in the bulk of effluents during treatment which favors the efficiency of H_2O_2. The decrease of the pH during treatment is related with the addition of H_2O_2 and with the degradation of the pollutants present in the water matrix to more acidic compounds like

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carboxylic acids. Under basic conditions, H_2O_2 reacts with HO^- to form perhydroxyl ions (HO_2^-) (reaction 1) which has significantly lower oxidation potential than $HO^\bullet$ (Spalek et al., 1982). H_2O_2 can only produce $HO^\bullet$ by the activation of ultraviolet light (reaction 2) or in combination with ozone (reaction 3) or even by a catalyst like iron, the so called Fenton related AOPs (Shah et al., 2018b) .

$$H_2O_2 + OH^- \leftrightarrow HO_2^- + H_2O \quad (1)$$

$$H_2O_2 + h\nu \rightarrow 2HO^\bullet \quad (2)$$

$$H_2O_2 + O_3 \rightarrow HO^\bullet + HO_2^\bullet + O_2 \quad (3)$$

Furthermore, the oxidation potential of H_2O_2 is significantly lower than that of O_3 which also influences the overall efficiency of the treatment. These reasons can explain the relatively low effectiveness of H_2O_2 at these conditions. Both O_3 and O_3/H_2O_2 processes have high effectiveness at the parameters studied obtaining around 100% degradation of all VOCs studied. The generation of $HO^\bullet$ using O_3 at basic pH may explain such increase in the overall degradation efficiency of VOCs.

Figure 2S presents the degradation of the VOCs in the presence of O_3 with a dose of 35 g. It clearly shows that BTEX, phenol and VSCs reach almost complete degradation in the first 15 min of treatment. 2-nitrophenol was completely degraded in the first 30 min of oxidation. Afterwards, the oxidant molecules reacted mainly with di-tert-butyl disulfide, naphthalene and phenolic compounds until their almost complete oxidation at 120 min of treatment. 4-methylbenzaldehyde was degraded 66% in the first 15 min of treatment but remains constant until 120 min and afterwards is degraded completely at 181 min of treatment. Interestingly, 2,6-dimethylphenol and 2-nitrophenol which were found to be completely degraded at 120 min of treatment reappeared at 181 min with an increase of 15 and 8%, respectively. The reappearance of 2-nitrophenol could possibly be linked with the degradation of the nitrobenzene by $HO^\bullet$ from 80 to 94% from 120 min to the end of the treatment. The “attack” of $HO^\bullet$ on the benzene ring

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can led to the addition of the HO group to the ring and hence, to the formation of 2-nitrophenol from nitrobenzene. Another hypothesis can be related with other compounds (formed during the treatment of this model effluents, not detected by the method used) that include 2-nitrophenol in their degradation pathway. With respect to the formation of 2,6-dimethylphenol, the oxidation of 4-methylbenzaldehyde, nitrobenzene or 2-nitrotoluene cannot explain its increase, since their degradation, according to their chemical structure, is not favoring a formation of 2,6-dimethylphenol. A possible hypothesis is that some compounds, not detected by the methods used, can actually include this compound in their degradation pathways. Figure 3S describes the VOCs degradation using O_3 with a dose of 70 g. Once again, the BTEX, phenol, 2-ethyltiophene and 2-nitrophenol were degraded with effectiveness at 15 min of treatment. The most interesting behavior in this process was the degradation of 4-mehtylbenzyldehyde and 2,6-dimethylphenol. These compounds only started to degrade significantly after 120 min of treatment, when all other compounds were oxidized more than 80%. One possible explanation for the persistency of the oxidation of 4-methylbenzaldehyde can be related with the fact that this compound can be a by-product of nitrobenzene and phenolic compounds (Sun et al., 1995; Zheng et al., 1993). VNCs had a slow degradation rate after 30 min of treatment. Similar results were obtained in a recent work by Gągol et al. (2018) with similar compounds under basic pH using same dose of O_3 aided by hydrodynamic or acoustic cavitation. Gągol et al. (2018) found slightly higher degradation efficiency for 4-ehtylphenol and di-tert-butyl disulfide and lower for phenol. In the present case, the process is simpler and less expensive than ultrasonic technology and achieved similar results, making it more effective. Overall, VNCs and 4-methylbenzyldehyde were more persistent to degradation with O_3. The $HO^{\bullet}$ are more likely to attack compounds with high electron density such as double

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bonds and aromatic rings (Chen et al., 2014). Thus, the degradation efficiency of aromatic compounds is higher than non-aromatic or simple bond compounds. In addition, electron donor groups such as NH_2 and OCH_3, could accelerate the degradation rate of aromatic compounds (Chen et al., 2014), which can explain the higher degradation efficiency of BTEX and phenolic compounds. Furthermore, sulfur atom increases the reaction rate with $HO^{\bullet}$ due to the electron donating properties (Kwok and Atkinson, 1995). This is proved in this work where the VSCs are degraded with the highest efficiency. However, the presence of NO_x groups on aromatic and linear compounds, decreases the degradation efficiency of the VNCs in general (Chen et al., 2014). The higher degradation efficiency of these compounds by O_3 comparing with H_2O_2 can be related with the reaction mechanism. Ozone is able to transform the organic compounds due to its high oxidation potential (E^0 = 2.07 V) (Chandrasekara Pillai et al., 2009; Esplugas et al., 2002; Kusic et al., 2006). When present in alkaline medium, O_3 directly reacts with HO^- to generate $HO^{\bullet}$ (reaction 4) (Alaton et al., 2002; Poyatos et al., 2010; Katsoyiannis et al., 2011).

$$O_3 + OH^- \rightarrow O_3^{\bullet -} + HO^{\bullet} \qquad (4)$$

Thus, a higher amount of free reactive species is available to degrade the VOCs, namely $HO^{\bullet}$ (more reactive species than H_2O_2 and O_3). Figures 2S and 3S reveal that increase of the dose significantly affected the rate of VOCs degradation, namely 4-methylbenzyldehyde and 2,6-dimethylphenol. These two compounds had lower degradation rate in the first 120 min of treatment with a higher applied dose of O_3. Moreover, these compounds, especially 4-methylbenzyldehyde can be a by-product of oxidation of phenolic compounds. By comparing with H_2O_2, a lower dose of O_3 was needed to achieve similar VOCs degradation efficiency. This can be related with the oxidation potential of O_3 and with the presence of $HO^{\bullet}$ which can degrade the VOCs

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faster. These results are similar to the use of O_3 in the treatment of phenol solely in a water matrix at basic pH (Esplugas et al., 2002).

O_3/H_2O_2 process was found to be more effective than O_3 and H_2O_2 (Figures 4S and 5S). The combination of O_3 and H_2O_2 allow indirect and direct oxidation of organic compounds (Alaton et al., 2002; Ameta et al., 2013). H_2O_2 will promote the degradation of O_3 by electron transfer or alternatively the O_3 will activate the H_2O_2 which generates $HO^{\bullet}$ and $HO_2^{\bullet}$ (reaction 5) (Alsheyab and Muñoz, 2006; Safarzadeh-Amiri, 2001; Wu et al., 2007).

$$H_2O_2 + O_3 \rightarrow HO^{\bullet} + HO_2^{\bullet} + O_2 \qquad (5)$$

Figure 4S describes the VOCs degradation using O_3/H_2O_2 with a dose of 98 g (O_3 = 48.5 g and H_2O_2 = 49.5 g). All VOCs were degraded very quickly in just only 15 min of treatment except 2-nitrophenol which took 60 min for its complete removal. Once again, BTEX, phenol, 2-ethylthiophene and dibutyl sulfide were the first compounds to be degraded after 15 min of treatment. Other studies also reported the effective degradation of dibutyl sulfide and phenol by O_3/H_2O_2 at basic pH in a one compound model WW (Esplugas et al., 2002; Popiel et al., 2009). When O_3/H_2O_2 dose was increased from 98 (O_3 48.5 g and H_2O_2 49.5 g) to 189 g (O_3 61.5 g and H_2O_2 127.5 g) at 40 ºC, the degradation efficiency for all the studied compounds increased significantly as revealed from comparing the residues concentration at 15 min of treatment in Figures 4S and 5S. VNCs and 4-methylbenzyldehyde were found to be relatively more persistent to degradation in the peroxone processes.

Figure 1 depicts an insight into the relative susceptibility of the tested VOCs towards O_3, H_2O_2 and O_3/H_2O_2 processes and a better comparison of the studied oxidation processes. It can be seen that VNCs were more persistent to degradation in all processes studied due to the presence of the NO_2 group which decreases the degradation

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efficiency. This difference was more significant and relevant in the H_2O_2 processes. The BTEX, phenol and VSCs were the fastest degraded compounds by these technologies. 2-nitrophenol was easy to degrade only in the O_3 related processes. 4-mehtylbenzyldehyde, 2-nitrotoluene and nitrobenzene were compounds that reveal persistency to degradation and are the last compounds to degrade by all the studied technologies. InO_3/H_2O_2 process, complete degradation of all VOCs was reached at 60 min of treatment. Thus, it was possible to stop the process at that time, decreasing the dose of oxidant needed from 189 to 36 g (Figure 5S) and from 98 to 24 g at 40 ºC (Figure 4S), i.e., 4 and 5.2 times decrease in oxidant dose, respectively. In addition, they are lower than O_3 and H_2O_2 processes, making it more effective and less costly in terms of chemicals. Comparable results were obtained in a similar work, using the same compounds at basic pH, but using peroxone alone and aided with hydrodynamic or acoustic cavitation (Gągol et al., 2018). At 30 min of oxidation, all compounds with one exception (in this work 2-nitrophenol and in ultrasonic technology nitrobenzene) were completely degraded. In summary, the O_3/H_2O_2 process is more effective to degrade VOCs of effluent at basic pH with a dose of 23.5 g (H_2O_2 = 11.9 g and O_3 = 11.6 g) at 40 ºC. These processes and its operational conditions are able to treat the VOCs in a relatively short time, degrading the most problematic compounds to treat in these type of effluents, making the biological treatment stage easier – with lower pollution load and less toxic to activated sludge compounds.

3.2. S-AOPs: performance of PS and PMS technologies

Persulfate (PS) and peroxymonosulfate (PMS) are popular alternative to the classic oxidants used in the advanced oxidation technologies. Both PS and PMS have the potential to generate $SO_4^{\bullet-}$ through their activation by UV light (reaction 6), heat (reaction 7) or a catalyst (Sayed et al., 2018). $SO_4^{\bullet-}$ have an oxidation potential (E^o) of

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2.6 V (Devi et al., 2016; Ghauch et al., 2012; Liu et al., 2013; Wacławek et al., 2017), making them highly reactive species.

$$S_2O_8^{2-}/HSO_5^- + h\nu \rightarrow 2SO_4^{\bullet-} \quad (6)$$

$$S_2O_8^{2-}/HSO_5^- + \Delta \rightarrow 2SO_4^{\bullet-} \quad (7)$$

$$S_2O_8^{2-}/HSO_5^- + 2e^- \rightarrow 2SO_4^{\bullet-} \quad (8)$$

The persulfate anion ($S_2O_8^{2-}$) and peroxymonosulfate anion (HSO_5^-) are strong oxidants, with E^0 of 2.01 and 1.85 V, respectively. These can be used for degradation of wide range of organic contaminants (Liang et al., 2011; Long et al., 2014; Oh et al., 2011; Rehman et al., 2018; Shah et al., 2018a). Sulfate radicals in aqueous medium and at basic medium can generate $HO^{\bullet}$ (reactions 9 and 10) (Boczkaj and Fernandes, 2017).

$$SO_4^{\bullet-} + H_2O \rightarrow HO^{\bullet} + HSO_4^- \quad (9)$$

$$SO_4^{\bullet-} + OH^- \rightarrow HO^{\bullet} + SO_4^{2-} \quad (10)$$

Alternatively, PS and PMS can be activated by the use of a base (e.g., NaOH) (reaction 11) (Furman et al., 2010; Qi et al., 2016).

$$2S_2O_8^{2-} + 2H_2O \xrightarrow{OH^-} 2SO_4^{2-} + SO_4^{\bullet-} + O_2^{\bullet-} + 4H^+ \quad (11)$$

Figure 2 and Table 3 reveal that increasing the oxidant dose and temperature in PS and PMS processes significantly increase the degradation efficiency of the studied VOCs. The difference is more significant when the temperature was increased from 40 to 60 ºC. The activation of $S_2O_8^{2-}$ and HSO_5^- to $SO_4^{\bullet-}$ by heat is the main factor for such increase. The increase of the oxidant dose from 218 to 436 g while keeping the temperature constant led to a small increase in the VOCs degradation. Comparing both processes under the same conditions, PS revealed to be more effective than PMS technology, due to the higher oxidation potential of PS than PMS. Comparing with H_2O_2, S-AOPs degraded the VOCs with higher effectiveness. On the other hand, by comparing with O_3 related processes, S-AOPs achieved lower degradation efficiencies.

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PS and PMS processes were also studied for the degradation profile of each compound during oxidation time. For PS process at 40 ºC with a dose of 436 g, Figure 6S reveals that, as demonstrated in classic AOPs, VNCs, namely 2-nitrotoluene and nitrobenzene were persistent to degradation. 2-nitrotoluene reached 20% degradation after 30 min and it remains at the same level until the end of the treatment. Nitrobenzene achieved 45% of degradation after 30 min and remains the same until 120 min of treatment, only after this time it was degraded further up to 67% of degradation. VSCs and 2-nitrophenol were degraded faster after 30 min of treatment. On the opposite trend of the H-AOP, BTEX and phenol started to be effectively degraded at the moment when the VSCs and the other O-VOCs were almost totally degraded. When the oxidant dose was kept constant and the temperature increased from 40 to 60 ºC, positive effect on removal efficiency was observed (Figure 7S). 2-nitrotoluene and nitrobenzene were degraded efficiently, especially after 60 min of treatment. Again, BTEX started to degrade when ca. 95% degradation was achieved for VSCs and other O-VOCs. When the temperature was kept constant at 60 ºC and the oxidant dose decreased a half to 218 g, the degradation rate was similar for VSCs and O-VOCs, with differences only in three compounds (Figure 8S). Figure 8S shows that 4-mehtylbenzyldehyde had a slower degradation rate comparing with the Figure 7S because of two possible reasons. First, it indicates that the lower dose of oxidant still performs effective degradation for the most VOCs with exemption of compounds more persistent to degradation by this type of processes. Second, such behavior can also be related to the fact that 4-mehtylbenzyldehyde can be a by-product of oxidation of phenolic compounds such as 4-ethylphenol or nitrophenols (Sun et al., 1995; Zheng et al., 1993). Lower dose of oxidant could possibly be effective in degrading the target compounds but the degradation of produced by-products could be slower due to the lower concentration of

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reactive radicals. In the cases of 2-nitrotoluene and nitrobenzene, they were removed only 65 and 76%, respectively, and their degradation occurred mainly in the first 60 min. During further treatment, the degradation rate started to be lowering until the end of the treatment. The same phenomenon was observed at 40 ºC (Figure 6S) with the same compounds but at lower degradation (21 and 66% respectively). This effect can probably be related to radical scavenging by the by-products of oxidation of the other VOCs. In addition, the cations present in the water matrix and residual sulfate formation, due to the salt addition (PS and PMS) can also affect the oxidation by scavenging the radical species (Boczkaj and Fernandes, 2017; Huang et al., 2005). This can be a negative outcome of the usage of S-AOPs.

Figures 9S and 10S report the degradation profile of the VOCs for the PMS processes at a fixed dose of 114 g at 40 and 60 ºC, respectively. 2-nitrotoluene and nitrobenzene were degraded below 10%, proving to be very persistent to oxidation by PMS process. VSCs were once more the easiest to degrade, with effective degradation after 60 min of treatment. The only exception was 2-ethyltiophene in the process at 40 ºC, with only 10% of degradation. O-VOCs had a small increase in their degradation when the temperature was increased from 40 to 60 ºC. When the oxidant was decreased from 114 to 70 g while keeping the temperature constant at 60ºC, some positive results were observed (Figure 11S). VSCs and 2-nitrophenol achieved almost complete degradation after 15 min of treatment. After 15 min of treatment, all other compounds started to be significantly degraded. The most interesting behavior was the degradation of 2-nitrotoluene and nitrobenzene up to 80% after 120 treatment. One reason for such significant difference can be related with the decrease of the PMS concentration. Too high amount of PMS present in the water matrix can have a detrimental effect on its own activation to sulfate radicals or in the yield of the radicals formation. PMS can

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react with himself or even with the $SO_4^{\bullet-}$ producing sulfate ions or less reactive radical species. Thus, decreasing the amount of PMS from 114 to 70 g was beneficial to the overall degradation of VOCs.

The activation of PS and PMS by heat had a positive effect in the VOCs degradation which could help in decreasing the amount of oxidant used for the same degree of VOCs degradation. Comparing PS and PMS technologies, PS revealed to be more effective in VOCs degradation than PMS, probably due to a higher efficiency of the activation of PS than PMS. In addition, the oxidation potential of PS is higher than PMS which could also influences the results.

Furthermore, the activation of PMS by heat had a positive effect making possible to decrease the amount of oxidant used by half and at the same time achieving higher removal efficiencies. Overall, these results proved that VSCs were the first to degrade and achieved total degradation in both PS and PMS processes. VNCs were more persistent to degradation by both technologies. In case of the specific compounds, VSCs and 2-nitrophenol were the compounds to degrade first and 2-nitrotoluene and nitrobenzene where more persistent and needed more time to reach high degradation values. PS process with a dose of 436 g at 60 ºC and PMS process with a dose of 70 g at the same temperature reached higher percentage of degradation of the VOCs, with 98.6% and 95.6% of total-VOCs degradation, respectively. Taking this data into account and the dose used of each oxidant, it can be concluded that in fact PMS process needs less amount of oxidant, being more effective than PS process.

Nevertheless, to decide which process is more effective, a study of the by-products of oxidation was performed to check if any by-products of oxidation are present and if they can be toxic and more harmful to biological approaches than the initial VOCs.

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3.3. Identification of by-products

Since the ultimate goal of water treatment technologies is to reduce water toxicity, it is crucial to identify the by-products of the target VOCs to understand if there is a risk of harmful and persistent by-products formation. In addition, it can be helpful to understand some pathways of degradation of the compounds when present in multiple artificial WW. Keeping this desirable goal in mind, the final sample from each process studied was submitted to additional GC-MS analysis in SCAN mode to identify and quantify all VOCs present in the end of the process. Figures 12S to 16S show the chromatograms of the initial and final sample of the H-AOPs and Figures 17S to 24S are the chromatograms from the S-AOPs. The peaks marked as IS, represent the internal standards. In respect to the H_2O_2 process, Figure 12S reveals the absence of any by-products formed during the treatment. Only the 2-nitrophenol peak had an increase after treatment as already discussed. Figure 13S shows the chromatogram of the O_3 process with a dose of 35 g. It is possible to verify that the compounds studied were almost completely degraded with exception of dibutyl sulfide and 4-methylbenzaldehyde whose degradation was insignificant. No harmful VOCs were detected, suggesting a good and efficient VOCs treatment option. The chromatogram of the O_3 process with a dose of 70 g is presented as Figure 14S. This Figure revealed an effective degradation of all compounds in the model WW due to a "clean" chromatogram of the sample after treatment. Regarding the O_3/H_2O_2 process, Figures 15S and 16S show almost completely clean chromatograms except the presence of dibutyl sulfide peak, which was under the limit of detection (LOD). These processes revealed to be very effective due to the lack of harmful by-products formation. Since no harmful or non-biodegradable by-products were detected, the obtained results proved that the risk of emission of compounds is eliminated in one single and simple stage. It is proved that O_3/H_2O_2

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process could effectively degrade the VOCs with no toxic by-products formation. As a result, O_3/H_2O_2 process with a dose of 24 g at 40 ºC continues to be the best choice.

Regarding the S-AOPs, only one by-product was identified after treatments. It is acetophenone and it is identified in all processes with exception of PS at 60 ºC with a dose of 436 g and in PMS process at 60 ºC with a dose of 114 g. Nevertheless, the peak is very small. The acetophenone can be produced from the oxidation of ethylbenzene or 4-ethylphenol. The formation of acetophenone from ethylbenzene oxidation has already been reported (Ghiaci et al., 2010). The only big peak on the chromatograms represents the IS added to the samples prior the extraction step and the minor peaks represent the compounds that were not bellow LOD, like nitrobenzene, 2-nitrotoluene, 4-methylbenzaldehyde, 2-ethyl-1-hexanol and ethylbenzene. With this data, we can conclude that PMS process with a dose of 70 g at 60 ºC is a better approach, with no harmful and toxic by-products, having a clean chromatogram after treatment, than PS process with a dose of 436 g at 60 ºC. The significant difference between doses of oxidants used led to the conclusion that the PMS process is the most suitable approach using S-AOPs when treating VOCs.

3.4. Comparison between classic H-AOPs and S-AOPs

The trend is equal in H-AOPs and S-AOPs in terms of total VNCs, VSCs and O-VOCs degradation. The VSCs were the easiest to be degraded whereas VNCs were the most persistent. Regarding the total VOCs degradation, the H_2O_2 technology was the poorest as expected due to the fact that alone H_2O_2 does not produce high reactive radicals under basic pH conditions. PS and PMS revealed to be more effective than H_2O_2. PS and PMS are not only more stable in aqueous solutions but also have weaker O-O bonds than H_2O_2 which make them easier to dissociate and generate reactive species (Ike et al., 2018). Comparing PS and PMS with O_3 and O_3/H_2O_2, O_3 related

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processes were more effective and achieved total degradation of all compounds. In terms of specific compounds, $HO^{\bullet}$ are able to react first with BTEX, phenol and VSCs compounds and are less effective in the degradation of 2-nitrotoluene, nitrobenzene and 4-methylbenzaldehyde in accordance with reactivity effect of the electrons donating and withdrawing groups, respectively. As far as $SO_4^{\bullet-}$ is concerned, it reacts first with the other O-VOCs, like non-aromatics, 2-nitrophenol and VSCs and afterwards with phenol and BTEX. Like $HO^{\bullet}$, $SO_4^{\bullet-}$ has lower reactivity with 2-nitrotoluene, nitrobenzene and 4-mehtylbenzyldehyde. The degradation of all VOCs was slower with S-AOPs. The reaction mechanism can explain the different reactivity of $HO^{\bullet}$ and $SO_4^{\bullet-}$ towards studied VOCs. $HO^{\bullet}$ reacts mainly by addition to the multiple C-C, C-N and C-S bonds and by H-abstraction, even though it can react by electron transfer mechanism (von Sonntag, 2005). $HO^{\bullet}$ prefers to react by addition to the aromatic rings. In case of $SO_4^{\bullet-}$, it rather prefers to react by electron transfer and its H-abstraction reaction is much slower than that of $HO^{\bullet}$ (Neta et al., 1988). Comparing the best processes of H-AOPs and S-AOPs, it is possible to check several disadvantages of PMS process comparing with O_3/H_2O_2. Firstly, PMS process takes more time to reach similar degradation than O_3/H_2O_2. Secondly, not all VOCs were degraded by PMS process as did by O_3/H_2O_2. Thirdly, the temperature needed for the PMS and PS process requires extra heating of the effluents making the process more expensive. Finally, the residual sulfate generated from the oxidation can have a negative impact on biological technologies, but this hypothesis needs to be proved properly. Thus, S-AOPs are less effective and suitable to be a good option for treatment of such type of effluents. Summing up, O_3/H_2O_2 is actually the best choice to perform an effective removal of all VOCs studied. The absence of VOCs in treated effluent is an important factor in relation to biological stage

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of treatment. Biological processes are conducted in open air reservoirs and thus could cause the emission of VOCs, present in the effluent, into the atmosphere.

3.5. Economic evaluation

Selection of a proper treatment technology for specific type of real effluents is not based only on the effectiveness of the technology but also depends on its cost, when taking the decision to apply in the real case scenario. To check either these technologies are viable to implement in a real case scenario, a basic economic evaluation was performed. A similar methodology was followed as performed by Gagol and co-workers (Gągol et al., 2018). The prices of the oxidants used in this work were assumed to perform the calculations. H_2O_2 had a cost of 8.2 American dollars per liter ($/L), $Na_2S_2O_8$ was purchased by 40.74 $/L and $KHSO_5$ by 56.58 $/L. In Poland, the price of electricity to industrial customers is around 0.11 $/kWh (3600 kJ). Furthermore, the power of the ozone generator and pump, responsible to introduce the oxidants into the reactor during treatment time was also included in the cost calculation. Ozone generator and oxidant pump have working powers of 450 and 80 W, respectively. To determine the cost of treatment, it was assumed that the treatment time used in this work was enough to obtain an effective degradation, i.e., higher than 95% of the studied VOCs. Table 4 represents the cost of each technology studied. The cost of treatment was assumed to be a combined value of the chemical and energy costs. The cost calculations clearly show that H-AOPs are much cheaper than S-AOPs, mainly due to the price of oxidants. The difference is around two orders of magnitude giving a clear idea that S-AOPs are not economically viable to implement in an industrial facility. Among the H-AOPs, peroxone revealed to be the cheapest, comparing to H_2O_2 and O_3. Also, it is interesting to see that O_3 process is slightly cheaper than H_2O_2 treatment. The treatment cost obtained in this work for the H-AOPs are lower than the ones obtained in a similar

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study at the same operational conditions (Gągol et al., 2018). Taking into account that the cost evaluation was performed using large laboratory scale data, a cost of treatment per liter between 3 and 6 cents of American dollars is cheap and viable. To conclude this section, implementation of such technologies is feasible for real WW effluents due to their cheapness (3 to 6 cents of American dollars are needed for treatment of 1 L effluent) and simplicity (only a stirred tank and an ozone generator are needed).

4. Conclusions

The study of oxidation of several VOCs in simulated caustic effluents from bitumen production using O_3, O_3/H_2O_2, H_2O_2, $Na_2S_2O_8$ and $KHSO_5$ was performed with attempt for effective VOCs degradation, eliminating the most problematic compounds from this type of effluents. This is a huge step to reach a good quality of treated effluent for possible water re-utilization and to improve the aspect of "cleaner technologies" of bitumen production. Comparison between H- and S-AOPs, i.e., the behavior of hydroxyl and sulfate radicals in degradation of several VOCs was studied.

The peroxone (O_3/H_2O_2) process with a dose of 23.5 g (H_2O_2: 11.9 g and O_3:11.6 g) at 40 ºC was the most efficient technology to degrade the model WW. S-AOPs were more efficient than H_2O_2 especially at 60 ºC. Further increase of temperature was not studied due to the impractical value of such conditions related to energy costs of effluent heating. VSCs achieved higher degradation in a shortest treatment time and VNCs were the most persistent compounds to degradation in all technologies studied. The BTEX degradation time and efficiency differs in H-AOPs and S-AOPs. This can be related with a different oxidation mechanism of $HO^{\bullet}$ and $SO_4^{\bullet-}$ ($HO^{\bullet}$ reacts mainly via addition and $SO_4^{\bullet-}$ via electron transfer).

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The study of by-products revealed that no toxic, complex and non-biodegradable by-products were identified after treatment. The cost evaluation revealed that H-AOPs are two orders of magnitude cheaper than S-AOPs. Peroxone revealed to be the cheaper technology with a cost of treatment between 0.03 and 0.04 $/L of model effluent treated. Classical H-AOPs can be described as cheap and easy technologies to implement for VOCs degradation. The compounds studied in this research are also present in different types of industrial, especially refinery origin, effluents. Thus the obtained data are also useful to other branches of wastewater treatment.

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Table 1 – Operational parameters of each process studied

Process	t (min)	Amount Oxidant (g)	T (ºC)
H_2O_2	182	31	40
H_2O_2	181.5	62	40
O_3	220	35	40
O_3	356	69	40
O_3/H_2O_2	250	98 (O_3: 48.5; H_2O_2: 49.5)	40
O_3/H_2O_2	317	189 (O_3: 61.5, H_2O_2: 127.5)	40
PS	182	218	40
PS	182	436	40
PS	182	218	60
PS	182	436	60
PMS	139	114	40
PMS	139	114	60
PMS	182	70	40
PMS	182	70	60

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Table 2 – Effectiveness of degradation of each model compound using classic AOPs, i.e., H_2O_2, O_3 and O_3/H_2O_2.

Compound	primary conc. (mg/L)	Classic AOPs					
		H_2O_2 31 g	H_2O_2 62 g	O_3 35 g	O_3 69 g	O_3/H_2O_2 98 g (O_3 = 48.5; H_2O_2 = 49.5)	O_3/H2O2 189 g (O_3 = 61.5; H_2O_2 = 127.5)
Benzene	8.87	80.0%	96.5%	99.3%	99.5%	100%	100%
Toluene	8.73	76.4%	95.1%	99.7%	99.9%	100%	>99.9%
o-xylene	10.05	70.4%	94.3%	>99.9%	>99.9%	>99.9%	>99.9%
2-ethylthiophene	8.64	56.1%	94.2%	>99.8%	>99.8%	>99.9%	>99.8%
Ethylbenzene	9.45	63.7%	92.6%	>99.9%	>99.9%	>99.9%	>99.9%
2-ethyl-1-hexanol	9.35	49.1%	99.9%	>99.9%	>99.9%	>99.9%	>99.9%
Phenol	9.37	72.5%	98.7%	99.4%	99.6%	>99.9%	>99.9%
Dibutyl sulfide	10.92	>99.7%	>99.8%	>99.7%	>99.7%	>99.7%	>99.8%
4-methylbenzaldehyde	9.98	-89.2%	67.4%	100%	95.2%	100%	100%
Nitrobenzene	9.70	9.4%	61.2%	94.2%	99.8%	>99.8%	>99.8%
4-ethylphenol	9.69	42.8%	>99.8%	>99.9%	>99.8%	>99.9%	>99.9%
2-Nitrotoluene	10.13	11.7%	73.8%	98.2%	>99.9%	>99.9%	>99.8%
Naphthalene	9.77	60.8%	85.5%	99.3%	99.3%	>99.9%	100%
di-tert-butyldisulfide	11.90	-45.1%	>99.0%	>98.6%	>98.8%	>98.5%	>99.0%
2-nitrophenol	9.78	-444.7%	-121.6%	92.8%	>99.8%	>99.8%	>99.8%
2.6-dimethylphenol	9.18	44.7%	>99.8%	84.6%	>99.8%	>99.8%	>99.8%
Total O-VOCs	94.44	47.1%	91.4%	98.3%	99.3%	100%	100%
Total VSCs	31.46	36.4%	98.7%	100%	100%	100%	100%
Total VNCs	29.61	-139.1%	-2.2%	95.1%	99.9%	100%	100%
Total VOCS	155.51	10.7%	74.7%	98.0%	99.6%	100.0%	100.0%

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Table 3 - Effectiveness of degradation of each model compound using S-AOPs, i.e., $Na_2S_2O_8$ and $KHSO_5$.

Compound	primary conc. (mg/L)	Sulfate related AOPs							
		$Na_2S_2O_8$ 218 g 40 ºC	$Na_2S_2O_8$ 436 g 40 ºC	$Na_2S_2O_8$ 218 g 60 ºC	$Na_2S_2O_8$ 436 g 60 ºC	$KHSO_5$ 114 g 40 ºC	$KHSO_5$ 114 g 60 ºC	$KHSO_5$ 70 g 40 ºC	$KHSO_5$ 70 g 60 ºC
Benzene	11.24	91.0%	95.6%	97.4%	98.8%	76.2%	85.0%	47.0%	93.2%
Toluene	9.60	82.1%	85.4%	90.4%	94.7%	76.4%	89.7%	18.0%	82.4%
o-xylene	10.01	88.5%	92.7%	96.0%	97.4%	85.2%	85.5%	-13.5%	87.3%
2-ethylthiophene	10.04	95.5%	99.9%	99.9%	99.9%	10.8%	99.9%	93.3%	99.8%
Ethylbenzene	12.01	91.2%	92.2%	94.9%	96.9%	85.0%	81.2%	29.2%	91.5%
2-Ethyl-1-hexanol	13.57	56.6%	98.5%	99.2%	100%	55.4%	79.9%	0.4%	96.7%
Phenol	8.46	98.0%	96.0%	99.9%	99.9%	99.9%	99.9%	99.9%	99.9%
Dibutyl sulfide	15.35	60.0%	99.8%	99.8%	99.7%	99.8%	99.8%	95.4%	99.8%
4-methylbenzaldehyde	13.52	3.4%	100%	98.6%	100%	80.1%	100%	73.9%	97.4%
Nitrobenzene	8.87	-12.3%	65.9%	65.0%	99.8%	11.9%	1.3%	0.2%	83.7%
4-ethylphenol	10.00	98.9%	99.9%	99.8%	99.9%	99.9%	99.9%	99.9%	99.9%
2-nitrotoluene	7.81	-26.2%	21.2%	76.4%	87.4%	12.7%	1.6%	1.9%	77.5%
Naphthalene	11.21	37.1%	100%	100%	100%	96.9%	100%	33.2%	99.9%
di-tert-butyldisulfide	15.29	99.0%	99.1%	99.0%	98.8%	99.2%	98.4%	98.0%	98.5%
2-nitrophenol	11.40	99.9%	99.8%	99.8%	99.9%	99.9%	99.9%	99.8%	99.8%

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2.6-dimethylphenol	6.22	99.7%	99.7%	99.6%	99.7%	99.7%	99.7%	85.9%	99.7%
Total O-VOCs	105.84	70.6%	96.3%	97.7%	98.7%	83.9%	90.6%	56.8%	95.7%
Total VSCs	40.68	83.5%	100%	100%	100%	79.9%	100%	96.2%	100%
Total VNCs	28.08	33.0%	67.7%	82.4%	96.8%	49.4%	46.9%	44.5%	88.6%
Total VOCS	174.60	67.2%	92.9%	95.7%	98.6%	77.2%	84.8%	64.8%	95.6%

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Table 4 – Summary of the treatment cost calculations for the AOPs studied. $ represents American dollars.

AOP	Treatment time (min)	Oxidant amount (g)	T (ºC)	Treatment time for effective VOCs degradation (min)	Oxidant amount for effective VOCs degradation(g)	Chemical cost ($)	Energy demand (kJ)	Energy cost ($)	Total cost ($)	Treatment cost ($/L)
H_2O_2	181.5	31	40	181.5	31.11	0.05	871.2	0.03	0.07	0.01
H_2O_2	181.5	62	40	181.5	62.23	0.09	871.2	0.03	0.12	0.02
O_3	220.2	35	40	120	18.9	-	3240	0.10	0.10	0.02
O_3	357.6	70	40	357.6	69.38	-	9655.2	0.30	0.30	0.06
O_3/H_2O_2	250.1	O_3 48.5 H_2O_2 49.5	40	30	O_3 5.82 H_2O_2 5.93	0.01	954	0.03	0.04	0.01
O_3/H_2O_2	317.1	O_3 61.5 H_2O_2 127.5	40	30	O_3 5.82 H_2O_2 12.05	0.02	954	0.03	0.05	0.01
$Na_2S_2O_8$ -	181.5	218	40	181.5	217.79	8.87	871.2	0.03	8.90	1.78
$Na_2S_2O_8$ -	181.5	436	40	181.5	435.59	17.75	871.2	0.03	17.77	3.55
$Na_2S_2O_8$ -	181.5	218	60	120	144	5.87	576	0.02	5.88	1.18
$Na_2S_2O_8$ -	181.5	436	60	120	288	11.73	576	0.02	11.75	2.35
$KHSO_5$	138.7	114	40	138.7	114.3	6.47	665.76	0.02	6.49	1.30
$KHSO_5$	138.7	114	60	138.7	114.3	6.47	665.76	0.02	6.49	1.30
$KHSO_5$	181.5	70	40	181.5	69.67	3.94	871.2	0.03	3.97	0.79
$KHSO_5$	181.5	70	60	120	46.08	2.61	576	0.02	2.62	0.52

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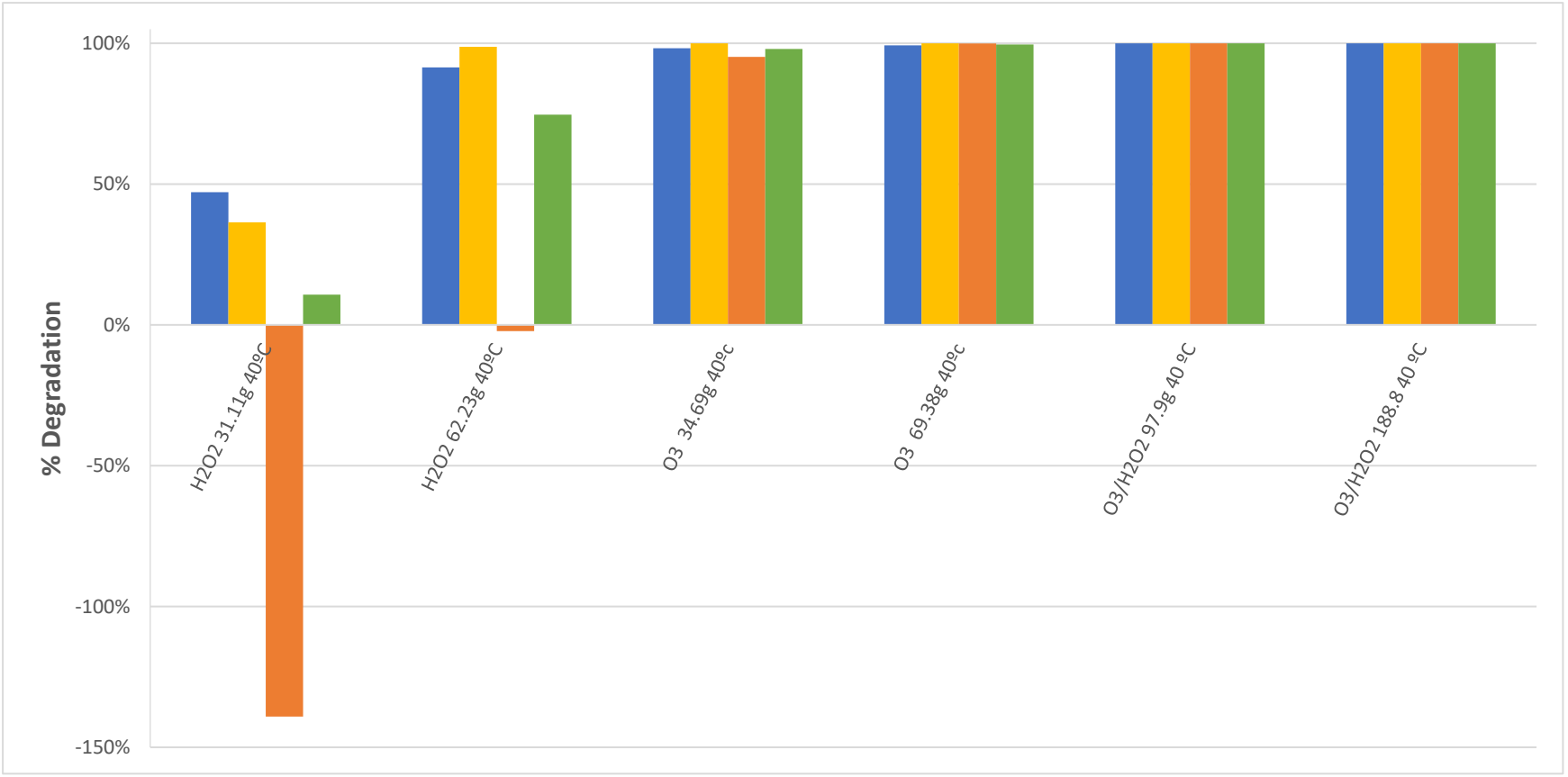

Figure 1 – total O-VOCs, VSCs, VNCs and total VOCs degradation for the classic AOPs. Blue bars, total O-VOCs; yellow bars total VSCs, orange bars, VNCs, green bars, total VOCs.

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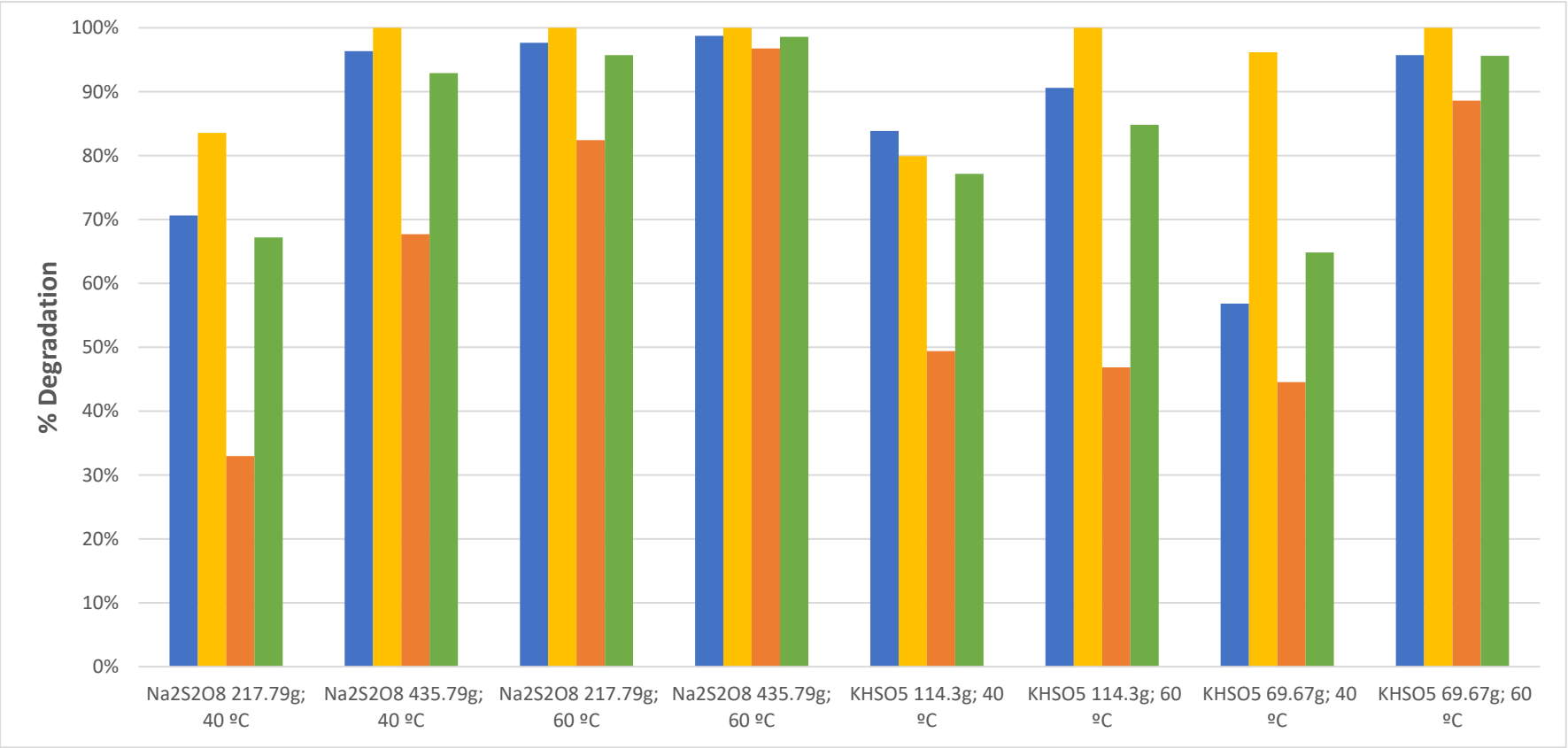

Figure 2 – total O-VOCs, VSCs, VNCs and total VOCs degradation for the S-AOPs. Blue bars, total O-VOCs; yellow bars total VSCs, orange bars, VNCs, green bars, total VOCs.

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Pilot scale degradation study of 16 selected volatile organic compounds by hydroxyl and sulfate radical based Advanced Oxidation Processes

Supporting Information

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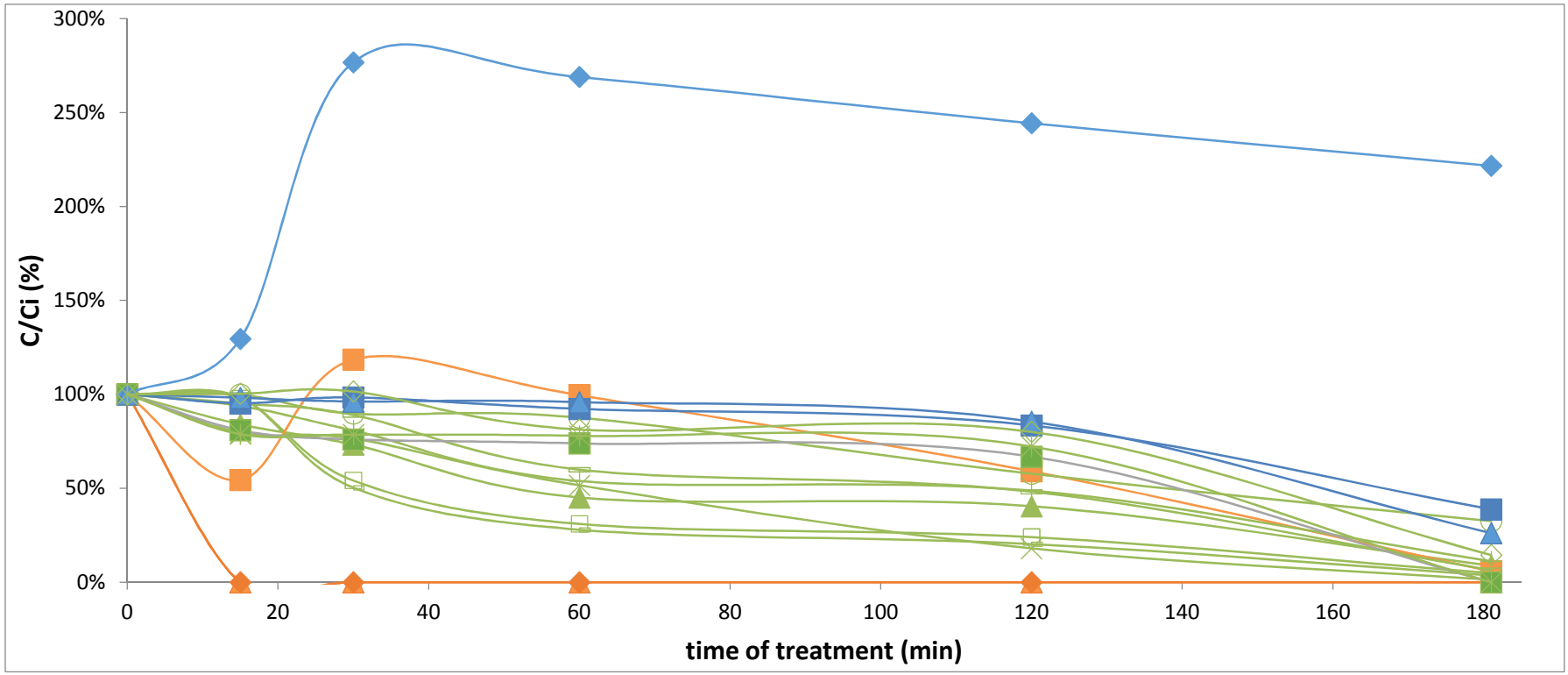

Figure 1S – VOCs degradation profile during the oxidation for H_2O_2 process at 40 ºC with a dose of 62 g. Green empty squares, toluene; green plus, ethylbenzene; empty green circles, 4-methylbenzaldehyde; green dots, benzene; green traces, 2-ethyl-1-hexanol; solid green triangles, o-xylene; green crosses, phenol; solid green squares, 4-ethylphenol; green star, 2,6-dimethylphenol; empty green diamonds, naphthalene; solid blue diamonds, 2-nitrophenol; solid blue triangles, 2-nitrotoluene; solid blue squares, nitrobenzene; solid orange diamonds, di-tert-butyl disulfide; solid orange squares, 2-ethylthiophene; solid orange triangles, dibutyl sulfide.

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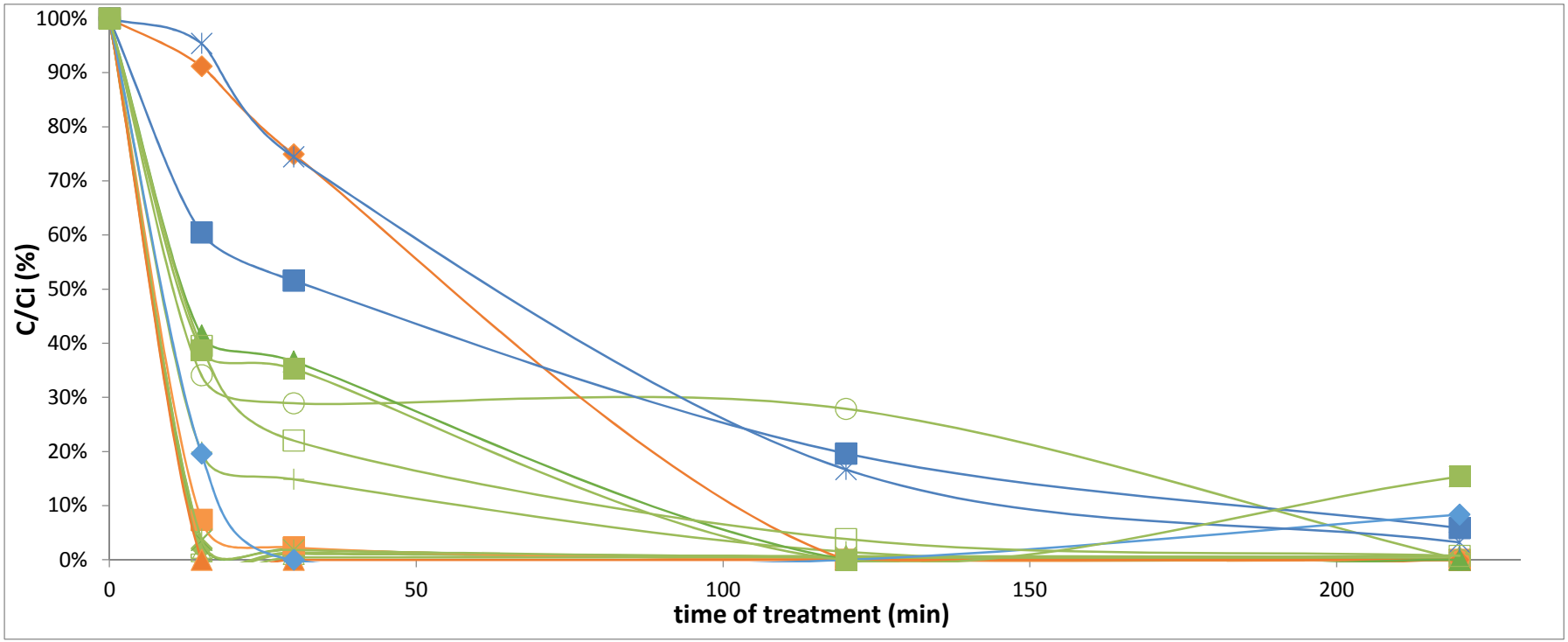

Figure 2S- VOCs degradation profile during the oxidation time for O_3process at 40 ºC with a dose of 35 g. Solid green diamonds, toluene; green stars, ethylbenzene; empty green circles, 4-methylbenzaldehyde; empty green triangles, benzene; green plus, 2-ethyl-1-hexanol; green crosses, o-xylene; green traces, phenol; solid green squares, 2,6-dimethylphenol; solid green triangles – 4-ethylphenol; empty green squares, naphthalene; solid blue diamonds, 2-nitrophenol; blue stars, 2-nitrotoluene; solid blue squares, nitrobenzene; solid orange diamonds, di-tert-butyl disulfide; solid orange squares, 2-ethylthiophene; solid orange triangles, dibutyl sulfide.

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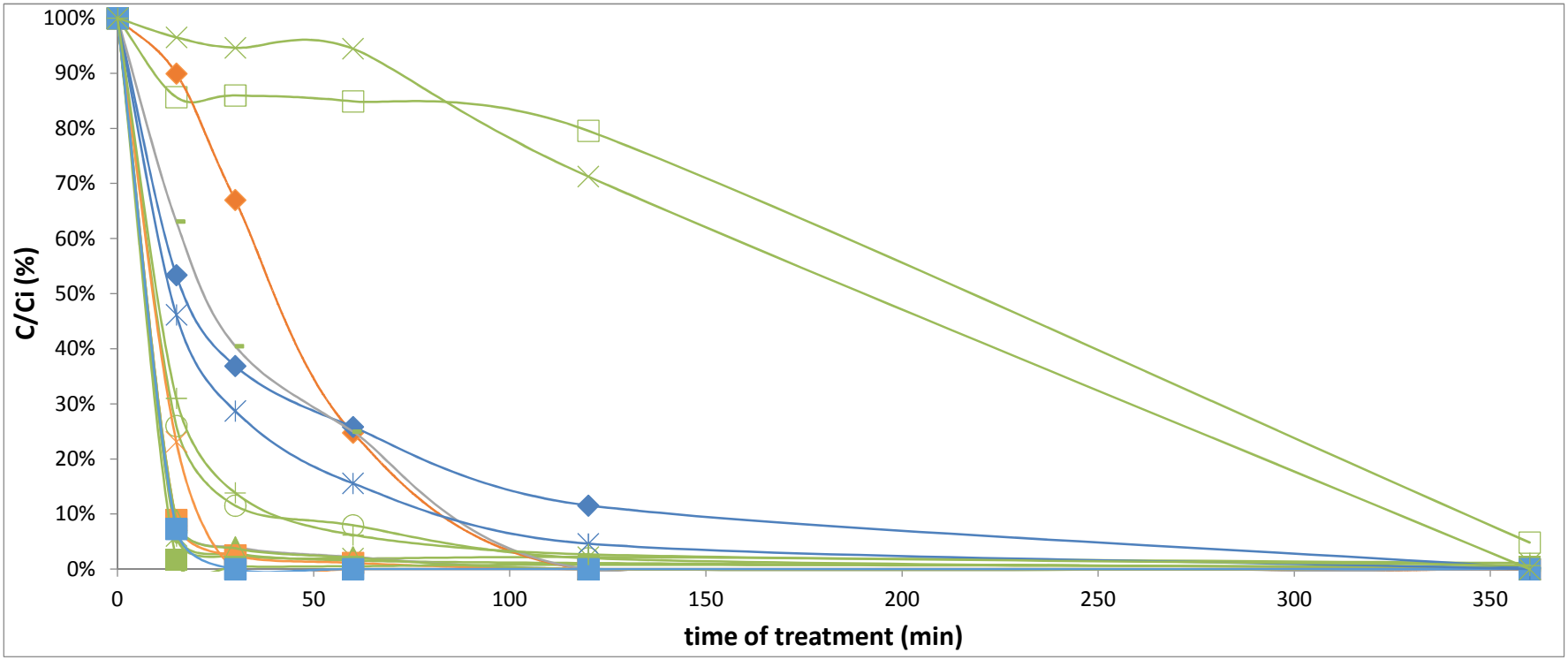

Figure 3S - VOCs degradation profile during the oxidation time for O_3 process at 40 ºC with a dose of 70 g. Solid green diamonds, toluene; empty green triangles, ethylbenzene; empty green squares, 4-methylbenzaldehyde; green stars, benzene; empty green circles, 2-ethyl-1-hexanol; solid green triangles, o-xylene; solid green squares, phenol; green crosses, 2,6-dimethylphenol; green dots – 4-ethylphenol; green pluses, naphthalene; solid blue squares, 2-nitrophenol; blue stars, 2-nitrotoluene; solid blue diamonds, nitrobenzene; solid orange diamonds, di-tert-butyl disulfide; solid orange squares, 2-ethylthiophene; orange crosses, dibutyl sulfide.

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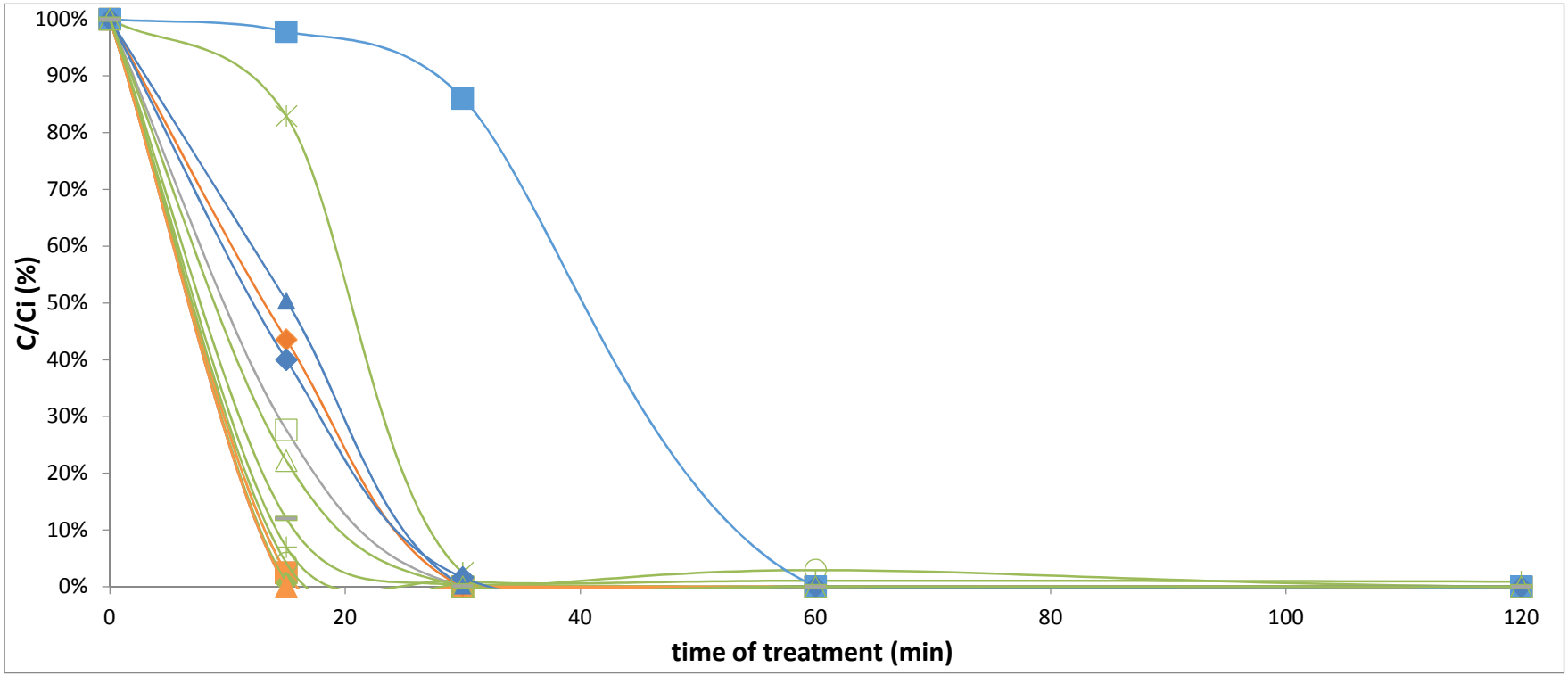

Figure 4S - - VOCs degradation profile during the oxidation time for O_3/H_2O_2 process at 40 ºC with a dose of 98 g (O_3 = 48.5, H_2O_2 = 49.5). Solid green squares, toluene; empty green circles, ethylbenzene; green stars, 4-methylbenzaldehyde; solid green triangles, benzene; green plus, 2-ethyl-1-hexanol; green crosses, o-xylene; solid green diamonds, phenol; empty green triangles, 2,6-dimethylphenol; empty green squares – 4-ethylphenol; green traces, naphthalene; solid blue squares, 2-nitrophenol; solid blue diamonds, 2-nitrotoluene; solid blue triangles, nitrobenzene; solid orange diamonds, di-tert-butyl disulfide; solid orange squares, 2-ethylthiophene; solid orange triangles, dibutyl sulfide.

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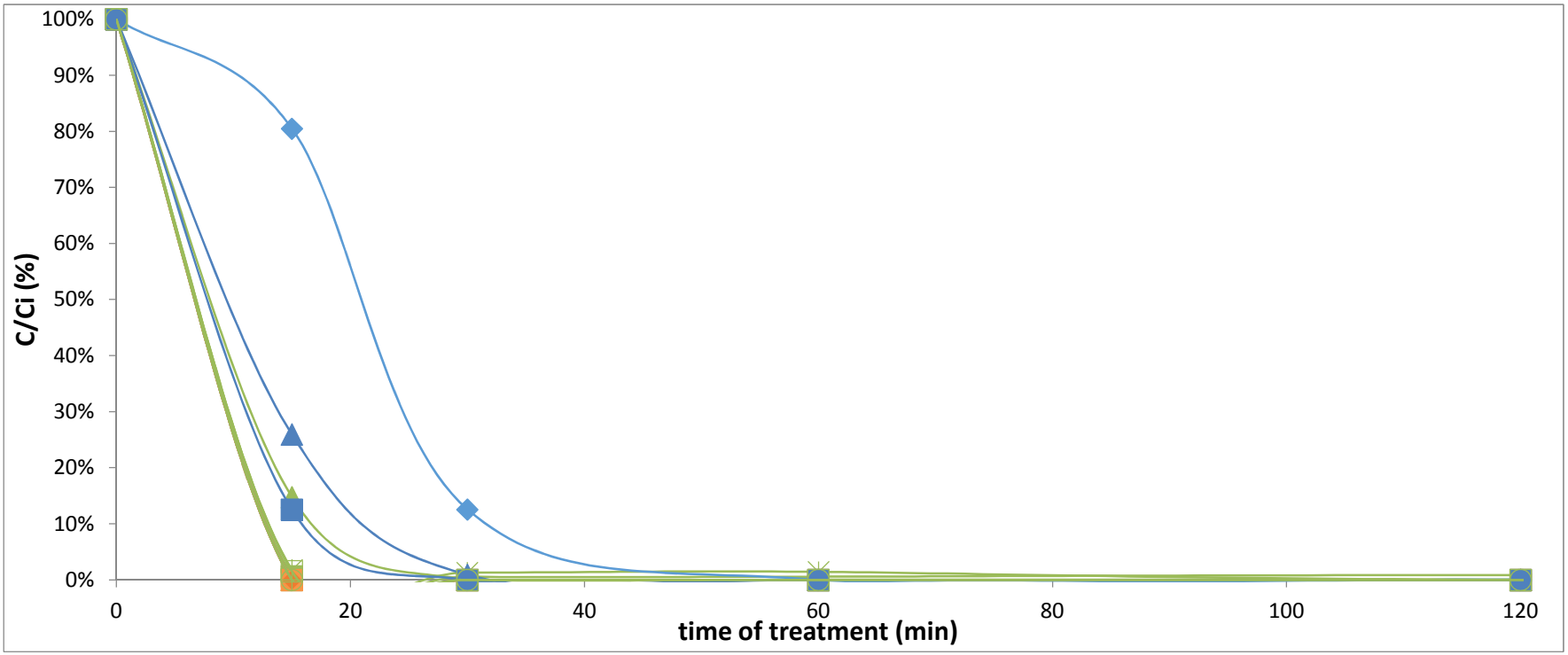

Figure 5S - VOCs degradation profile during the oxidation time for O_3/H_2O_2 process at 40 ºC with a dose of 189 g (O_3 = 61.5, H_2O_2 = 127.5). Solid green squares, toluene; solid green diamonds, ethylbenzene; solid green triangles, 4-methylbenzaldehyde; green crosses, benzene; green stars, 2-ethyl-1-hexanol; empty green triangles, o-xylene; green traces, phenol; empty green circles, 2,6-dimethylphenol; green pluses – 4-ethylphenol; empty green squares, naphthalene; solid blue diamond's 2-nitrophenol; solid blue squares, 2-nitrotoluene; solid blue triangles; solid orange diamonds, di-tert-butyl disulfide; solid orange triangles, 2-ethylthiophene; solid orange squares, dibutyl sulfide.

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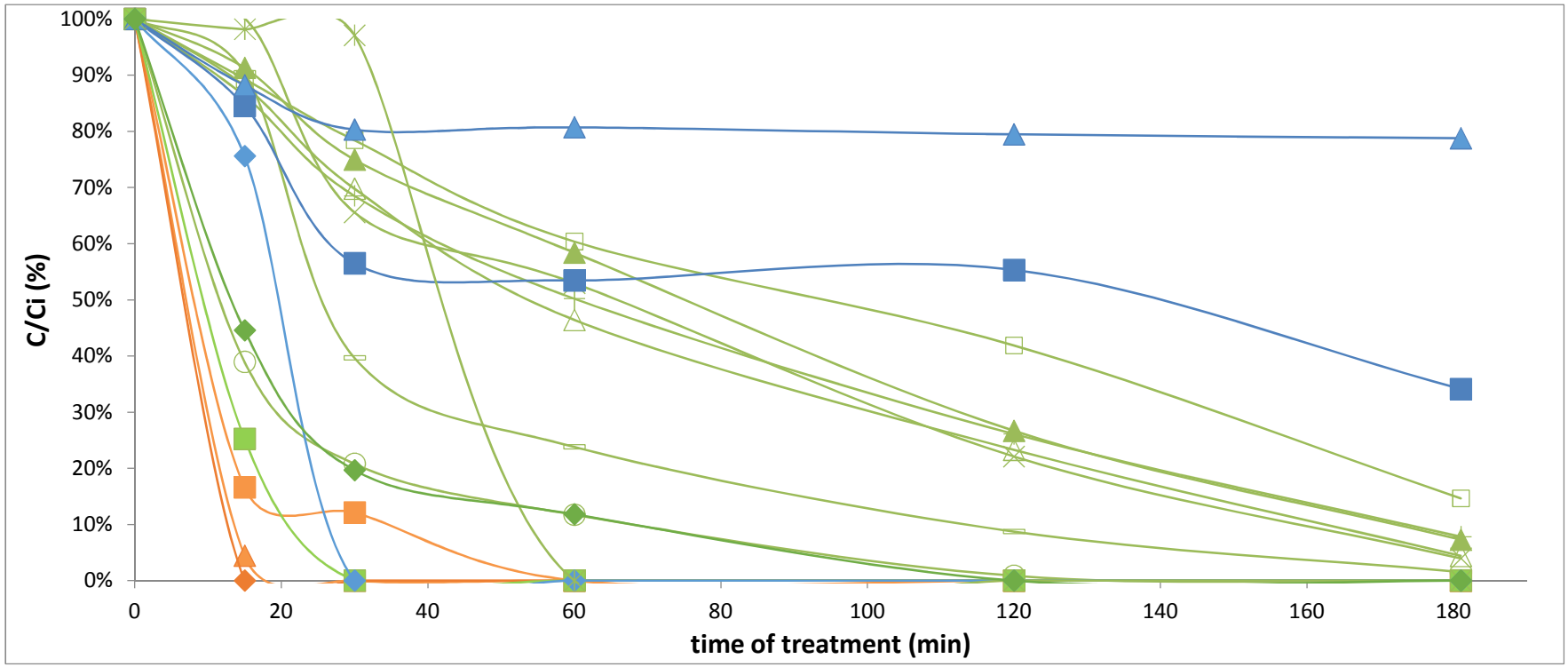

Figure 6S - VOCs degradation profile during the oxidation time for $Na_2S_2O_8$ process at 40 ºC with a dose of 436 g. Empty green squares, toluene; green pluses, ethylbenzene; empty green circles, 4-methylbenzaldehyde; empty green triangles, benzene; green traces, 2-ethyl-1-hexanol; solid green triangles, o-xylene; green crosses, phenol; green stars, 2,6-dimethylphenol; solid green squares, 4-ethylphenol; solid green diamonds, naphthalene; solid blue diamonds 2-nitrophenol; solid blue triangles, 2-nitrotoluene; solid blue squares, nitrobenzene; solid orange diamonds, di-tert-butyl disulfide; solid orange squares, 2-ethylthiophene; solid orange triangles, dibutyl sulfide.

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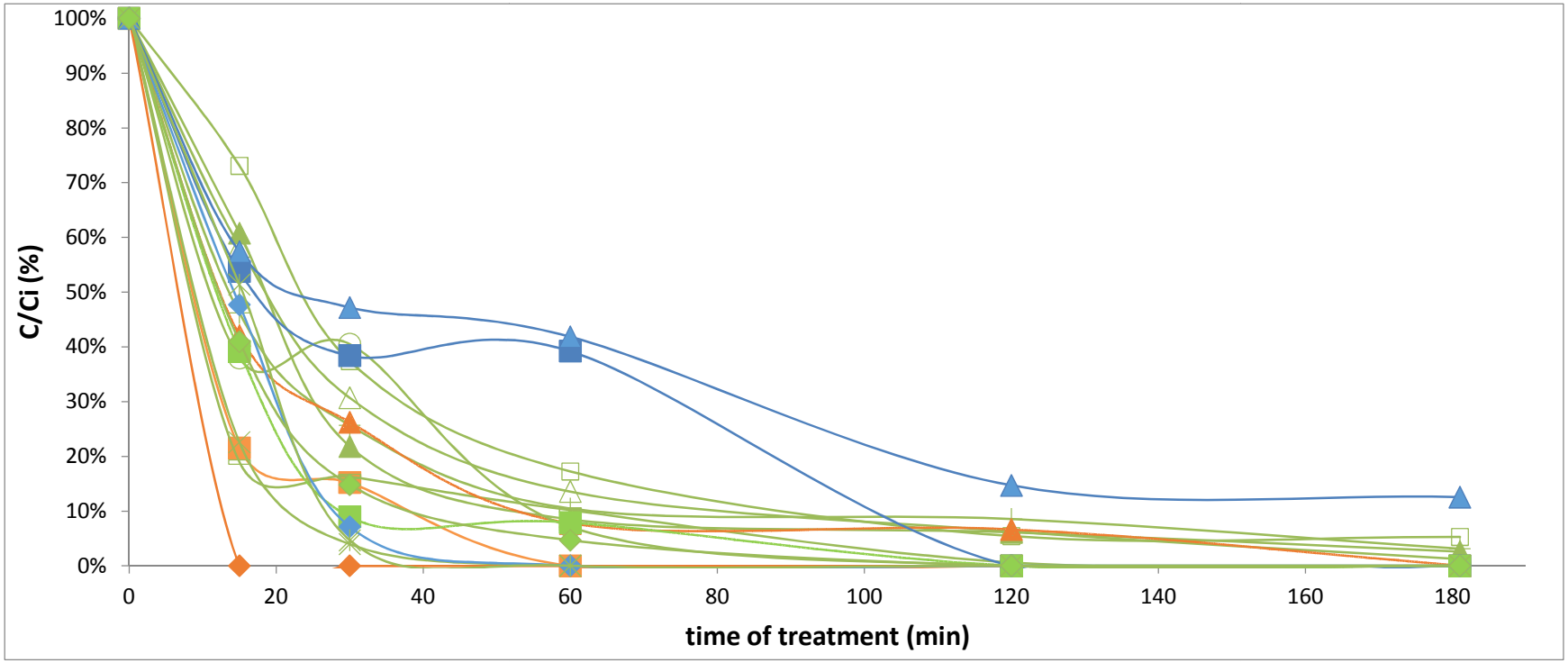

Figure 7S - VOCs degradation profile during the oxidation time for Na_2SO_8 process at 60 ºC with a dose of 436 g. Empty green squares, toluene; green pluses, ethylbenzene; empty green circles, 4-methylbenzaldehyde; empty green triangles, benzene; green traces, 2-ethyl-1-hexanol; solid green triangles, o-xylene; green crosses, phenol; green stars, 2,6-dimethylphenol; solid green squares, 4-ethylphenol; solid green diamonds, naphthalene; solid blue diamonds 2-nitrophenol; solid blue triangles, 2-nitrotoluene; solid blue squares, nitrobenzene; solid orange diamonds, di-tert-butyl disulfide; solid orange squares, 2-ethylthiophene; solid orange triangles, dibutyl sulfide.

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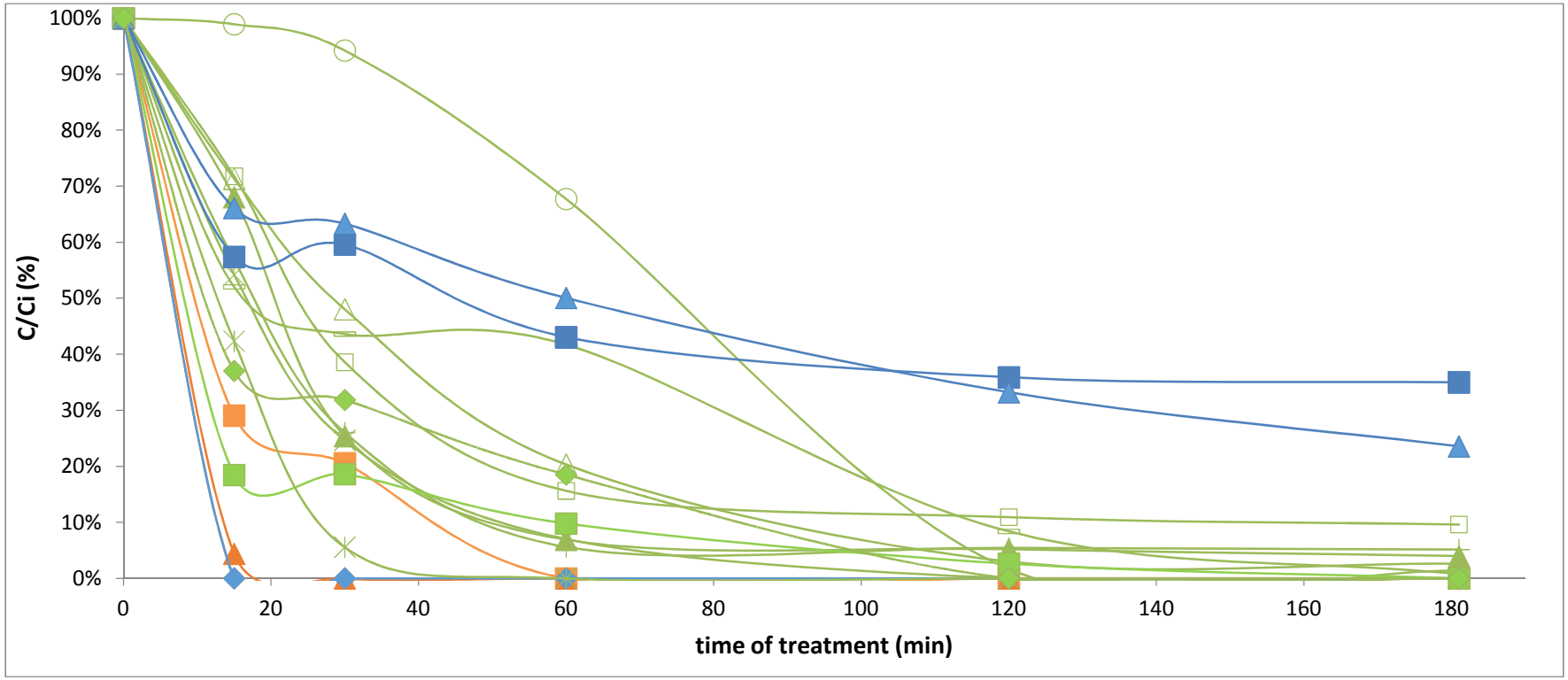

Figure 8S - VOCs degradation profile during the oxidation time for Na_2SO_8 process at 60 ºC with a dose of 218 g. Empty green squares, toluene; green pluses, ethylbenzene; empty green circles, 4-methylbenzaldehyde; empty green triangles, benzene; green traces, 2-ethyl-1-hexanol; solid green triangles, o-xylene; green crosses, phenol; green stars, 2,6-dimethylphenol; solid green squares, 4-ethylphenol; solid green diamonds, naphthalene; solid blue diamonds 2-nitrophenol; solid blue triangles, 2-nitrotoluene; solid blue squares, nitrobenzene; solid orange diamonds, di-tert-butyl disulfide; solid orange squares, 2-ethylthiophene; solid orange triangles, dibutyl sulfide.

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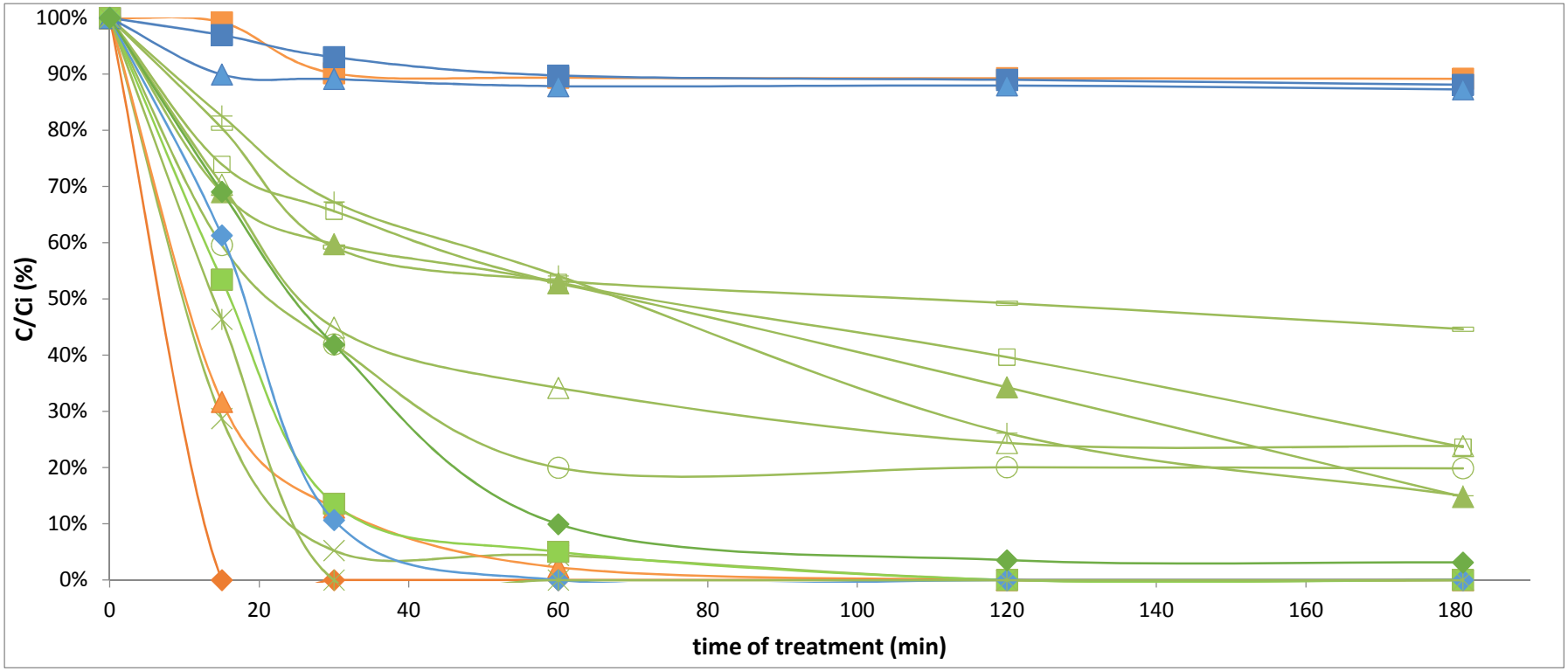

Figure 9S - VOCs degradation profile during the oxidation time for $KHSO_5$ process at 40 ºC with a dose of 114. g. Empty green squares, toluene; green pluses, ethylbenzene; empty green circles, 4-methylbenzaldehyde; empty green triangles, benzene; green traces, 2-ethyl-1-hexanol; solid green triangles, o-xylene; green crosses, phenol; green stars, 2,6-dimethylphenol; solid green squares, 4-ethylphenol; solid green diamonds, naphthalene; solid blue diamonds 2-nitrophenol; solid blue triangles, 2-nitrotoluene; solid blue squares, nitrobenzene; solid orange diamonds, di-tert-butyl disulfide; solid orange squares, 2-ethylthiophene; solid orange triangles, dibutyl sulfide.

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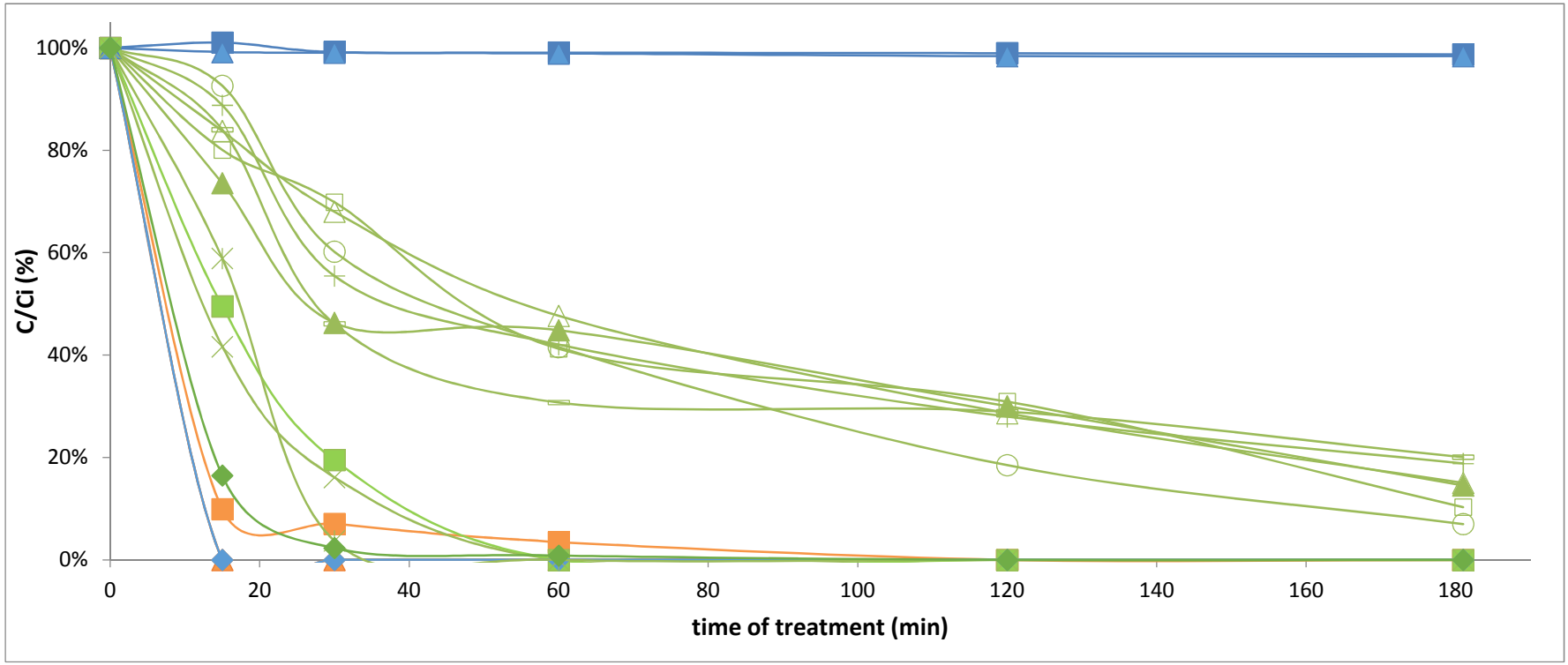

Figure 10S - VOCs degradation profile during the oxidation time for $KHSO_5$ process at 60 ºC with a dose of 114 g. Empty green squares, toluene; green pluses, ethylbenzene; empty green circles, 4-methylbenzaldehyde; empty green triangles, benzene; green traces, 2-ethyl-1-hexanol; solid green triangles, o-xylene; green crosses, phenol; green stars, 2,6-dimethylphenol; solid green squares, 4-ethylphenol; solid green diamonds, naphthalene; solid blue diamonds 2-nitrophenol; solid blue triangles, 2-nitrotoluene; solid blue squares, nitrobenzene; solid orange diamonds, di-tert-butyl disulfide; solid orange squares, 2-ethylthiophene; solid orange triangles, dibutyl sulfide.

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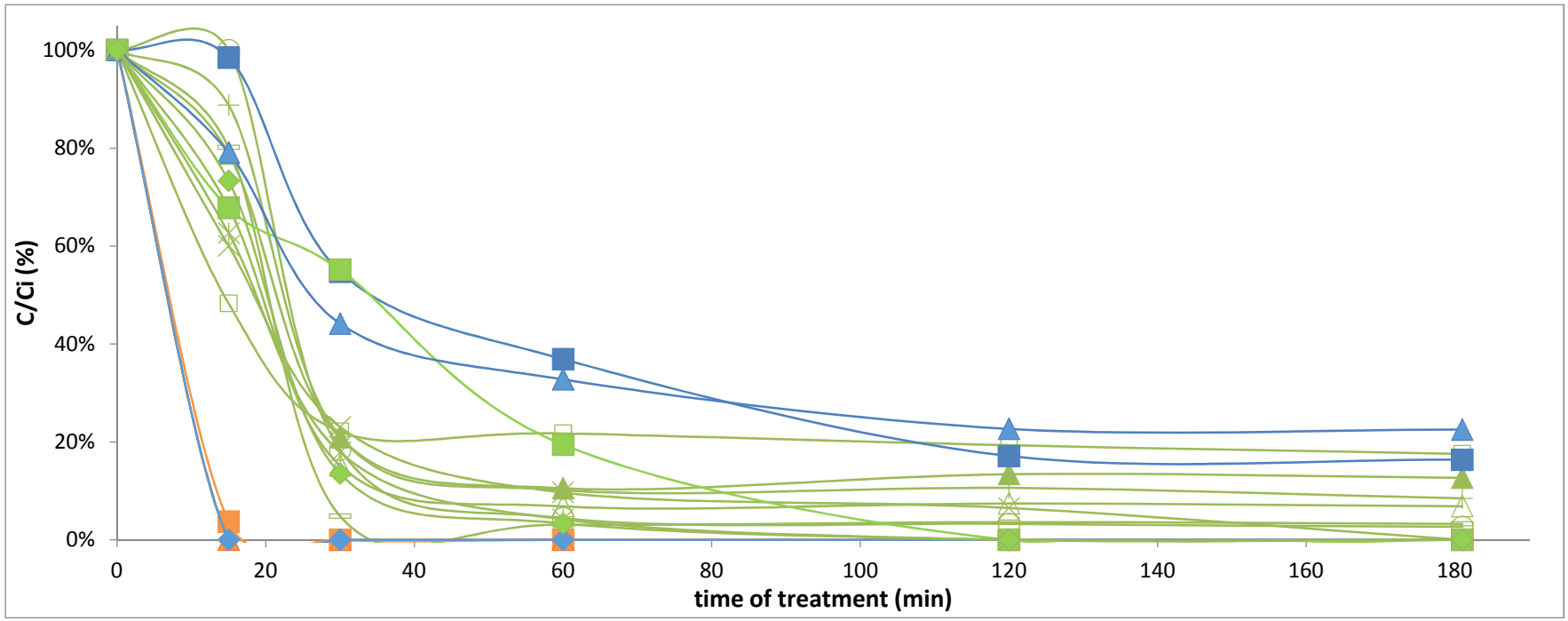

Figure 11S - VOCs degradation profile during the oxidation time for $KHSO_5$ process at 60 ºC with a dose of 70 g. Empty green squares, toluene; green pluses, ethylbenzene; empty green circles, 4-methylbenzaldehyde; empty green triangles, benzene; green traces, 2-ethyl-1-hexanol; solid green triangles, o-xylene; green crosses, phenol; green stars, 2,6-dimethylphenol; solid green squares, 4-ethylphenol; solid green diamonds, naphthalene; solid blue diamonds 2-nitrophenol; solid blue triangles, 2-nitrotoluene; solid blue squares, nitrobenzene; solid orange diamonds, di-tert-butyl disulfide; solid orange squares, 2-ethylthiophene; solid orange triangles, dibutyl sulfide

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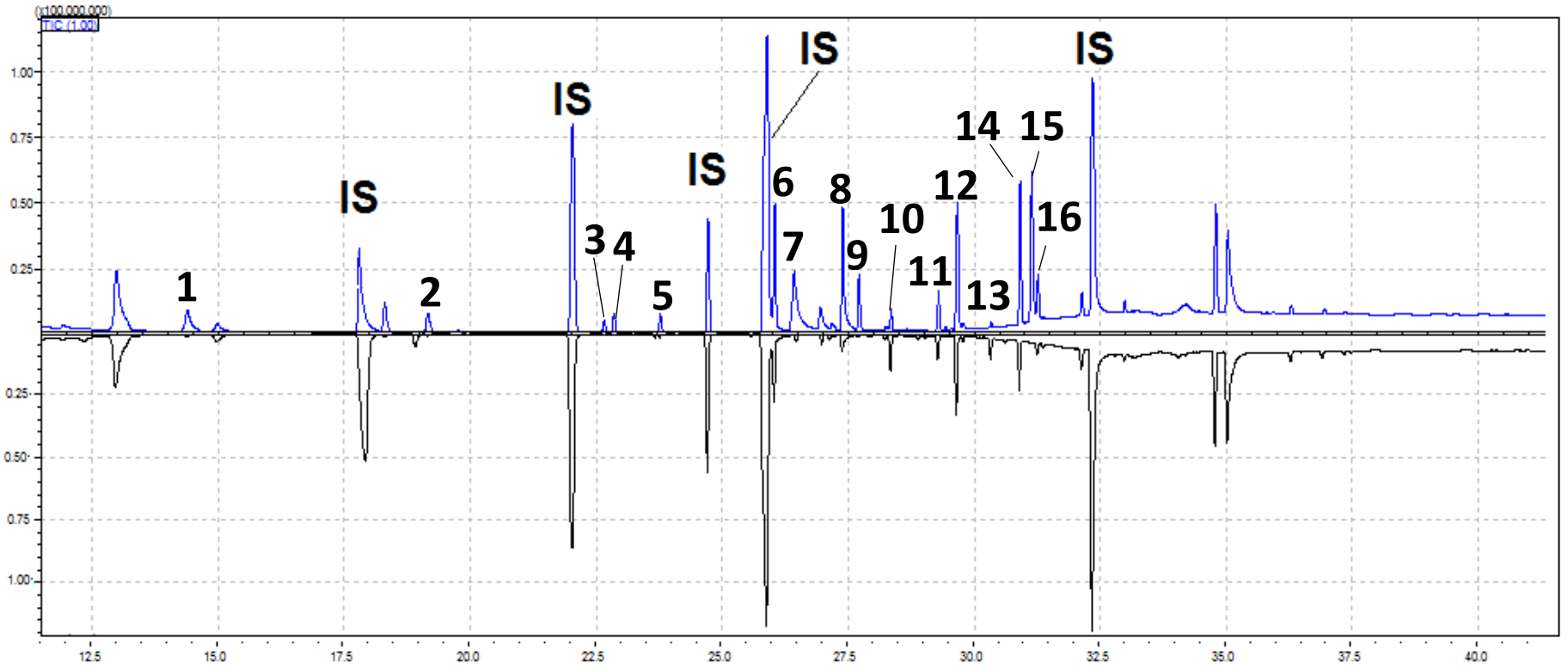

Figure 12S – Chromatogram of the H_2O_2 process at 40 ºC with an oxidant dose of 62.23 g. Blue line represent the initial sample and the black represents the final sample, after treatment. IS – internal standards; 1 –benzene; 2 – toluene; 3 – ethylbenzene; 4 – ethylthiophene; 5 – o-xylene; 6 – 2-methylcyclohexanone; 7 – 2,4,6 colidine; 8– 2-ethyl-1-hexanol; 9 – phenol; 10 – dibutyl sulfide; 11 – 4-methylbenzaldehyde; 12 – nitrobenzene + 2,6-dimethylphenol; 13 – 2-nitrophenol; 14 – 2-nitrotoluene; 15 – 4-ethylphenol; 16 – naphthalene.

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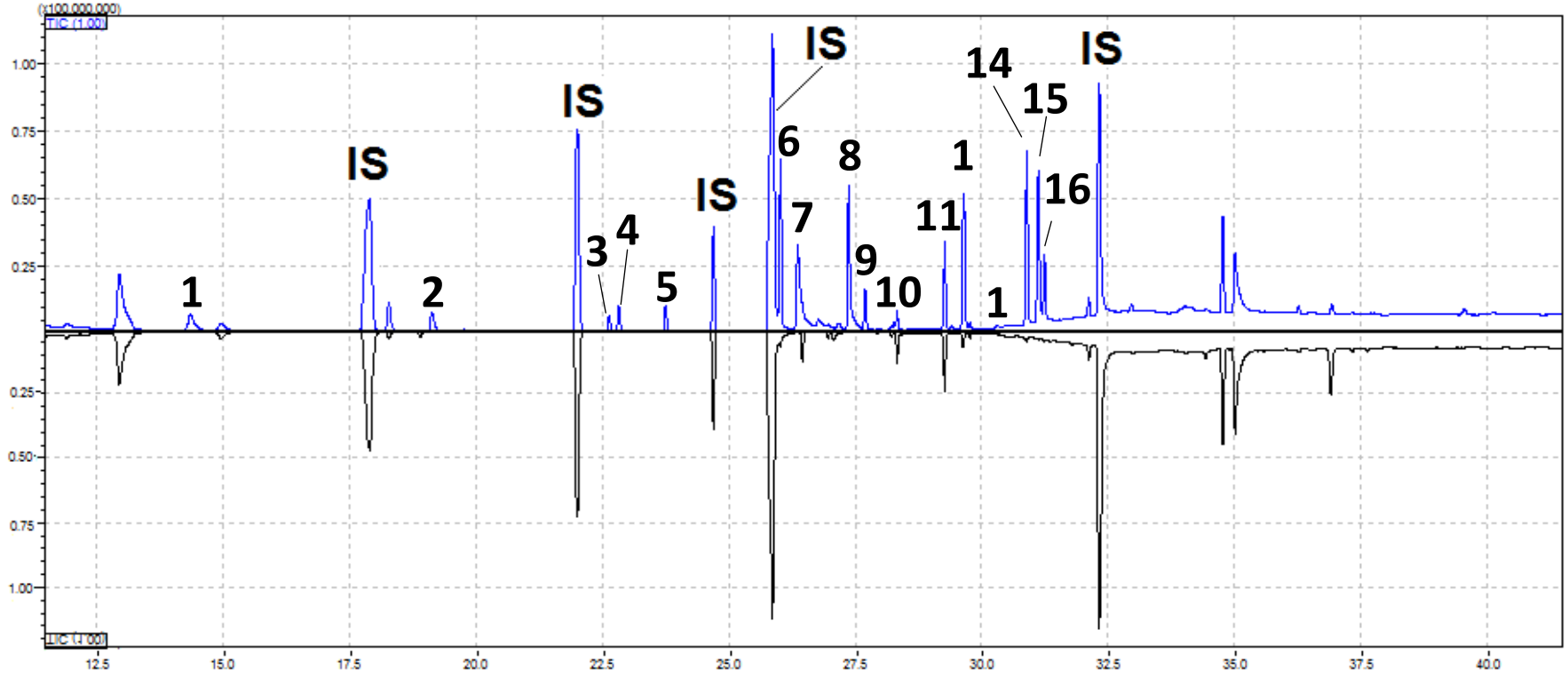

Figure 13S – Chromatogram of the O_3process at 40 ºC with an oxidant dose of 34.69 g. Blue line represent the initial sample and the black represents the final sample, after treatment. IS – internal standards; 1 – benzene; 2 – toluene; 3 – ethylbenzene; 4 – ethylthiophene; 5 – o-xylene; 6 – 2-methylcyclohexanone; 7 – 2,4,6 colidine; 8 – 2-ethyl-1-hexanol; 9 – phenol; 10 – dibutyl sulfide; 11 – 4-methylbenzaldehyde; 12 – nitrobenzene + 2,6-dimethylphenol; 13 – 2-nitrophenol; 14 – 2-nitrotoluene; 15 – 4-ethylphenol; 16 – naphthalene.

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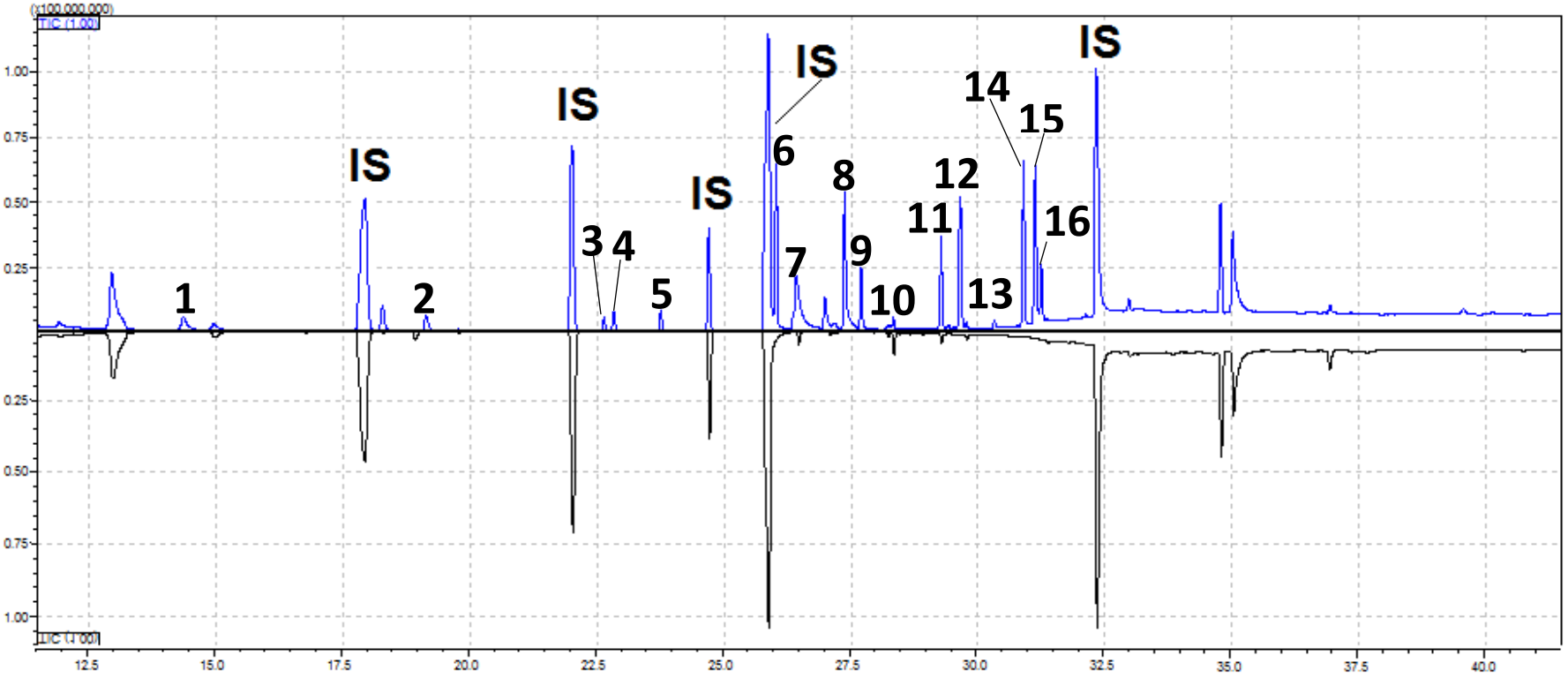

Figure 14S – Chromatogram of O_3 process at 40 ºC with an oxidant dose of 69.38 g. Blue line represent the initial sample and the black represents the final sample, after treatment. IS – internal standards; 1 – benzene; 2 – toluene; 3 – ethylbenzene; 4 – ethylthiophene; 5 – o-xylene; 6 – 2-methylcyclohexanone; 7 – 2,4,6 colidine; 8 – 2-ethyl-1-hexanol; 9 – phenol; 10 – dibutyl sulfide; 11 – 4-methylbenzaldehyde; 12 – nitrobenzene + 2,6-dimethylphenol; 13 – 2-nitrophenol; 14 – 2-nitrotoluene; 15 – 4-ethylphenol; 16 – naphthalene.

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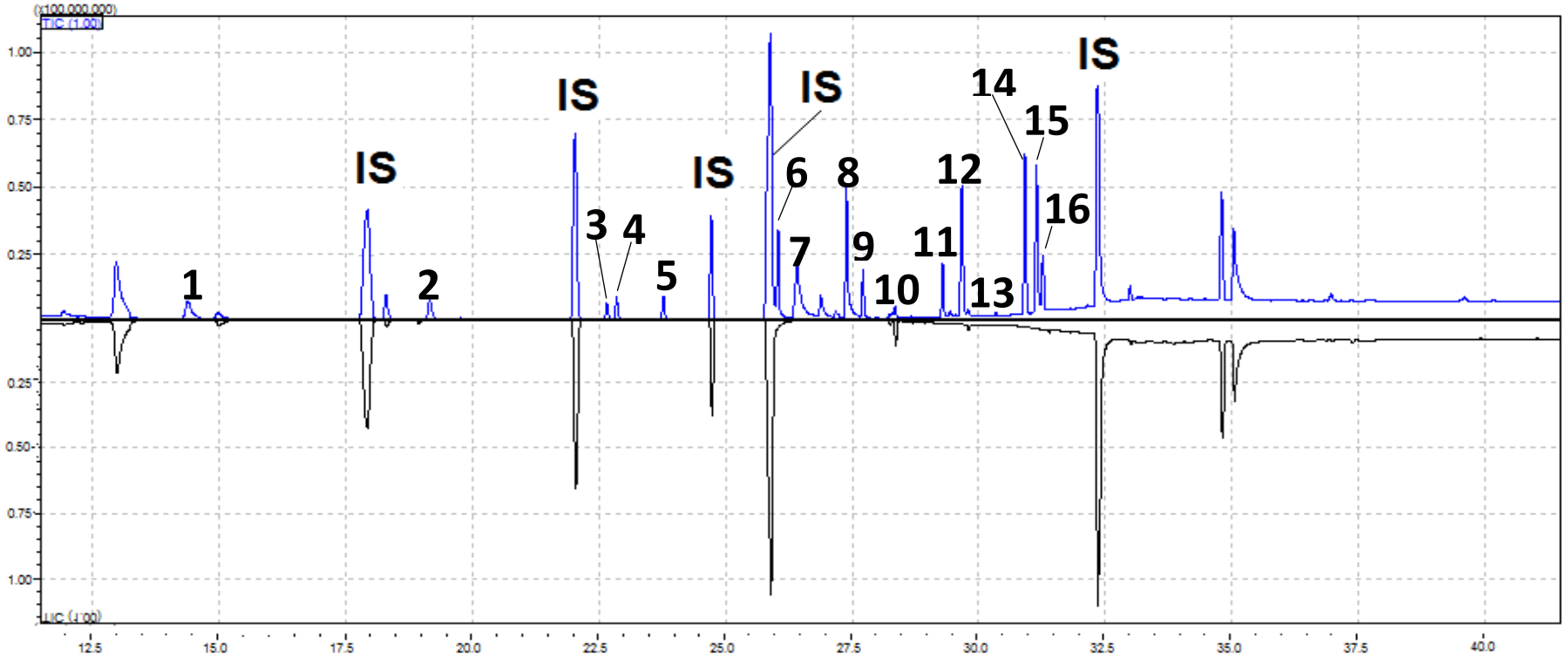

Figure 15S – Chromatogram of O_3/H_2O_2 process at 40 ºC with an oxidant dose of 97.9 g. Blue line represent the initial sample and the black represents the final sample, after treatment. IS – internal standards; 1 – benzene; 2 – toluene; 3 – ethylbenzene; 4 – ethylthiophene; 5 – o-xylene; 6 – 2-methylcyclohexanone; 7 – 2,4,6 colidine; 8 – 2-ethyl-1-hexanol; 9 – phenol; 10 – dibutyl sulfide; 11 – 4-methylbenzaldehyde; 12 – nitrobenzene + 2,6-dimethylphenol; 13 – 2-nitrophenol; 14 – 2-nitrotoluene; 15 – 4-ethylphenol; 16 – naphthalene.

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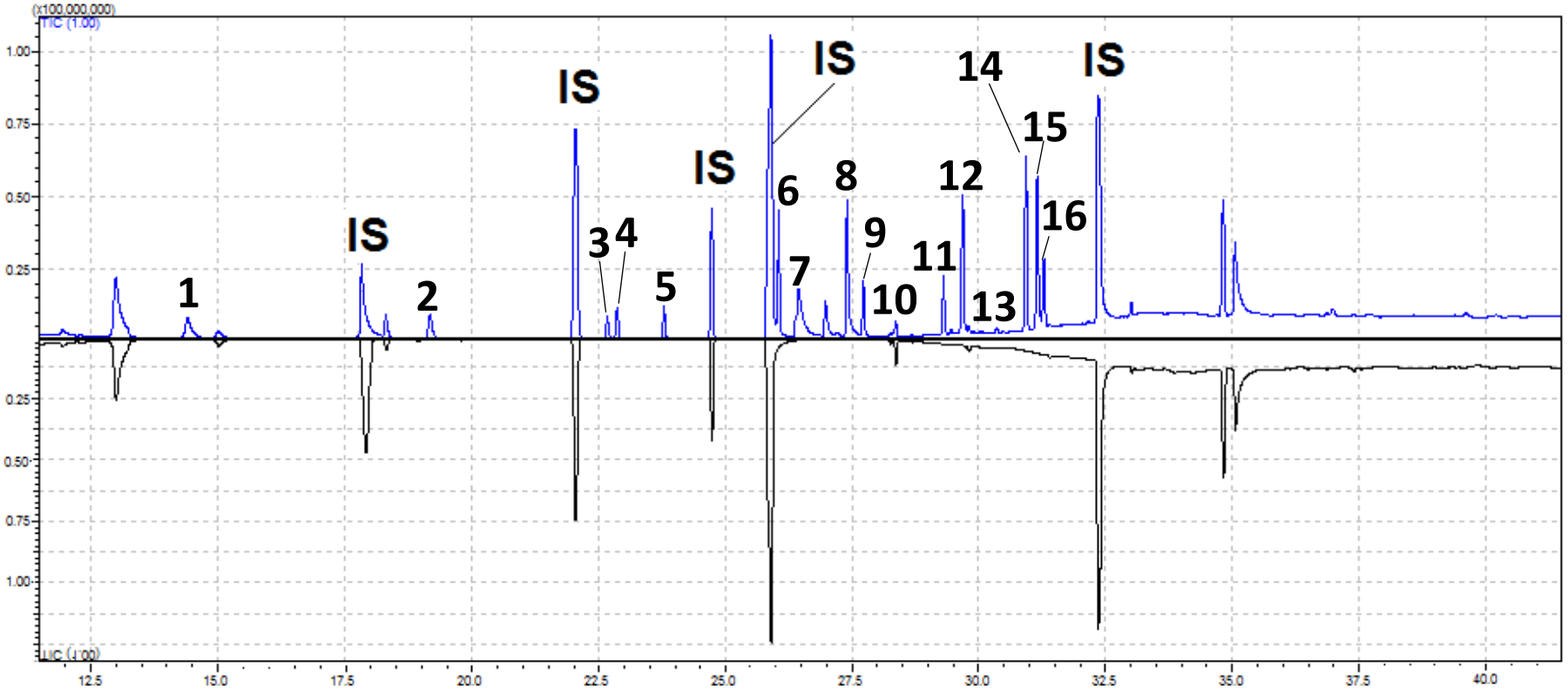

Figure 16S – Chromatogram of O_3/H_2O_2 process at 40 ºC with an oxidant dose of 188.8 g. Blue line represent the initial sample and the black represents the final sample, after treatment. IS – internal standards; 1 – benzene; 2 – toluene; 3 – ethylbenzene; 4 – ethylthiophene; 5 – o-xylene; 6 – 2-methylcyclohexanone; 7 – 2,4,6 colidine; 8 – 2-ethyl-1-hexanol; 9 – phenol; 10 – dibutyl sulfide; 11 – 4-methylbenzaldehyde; 12 – nitrobenzene + 2,6-dimethylphenol; 13 – 2-nitrophenol; 14 – 2-nitrotoluene; 15 – 4-ethylphenol; 16 – naphthalene.

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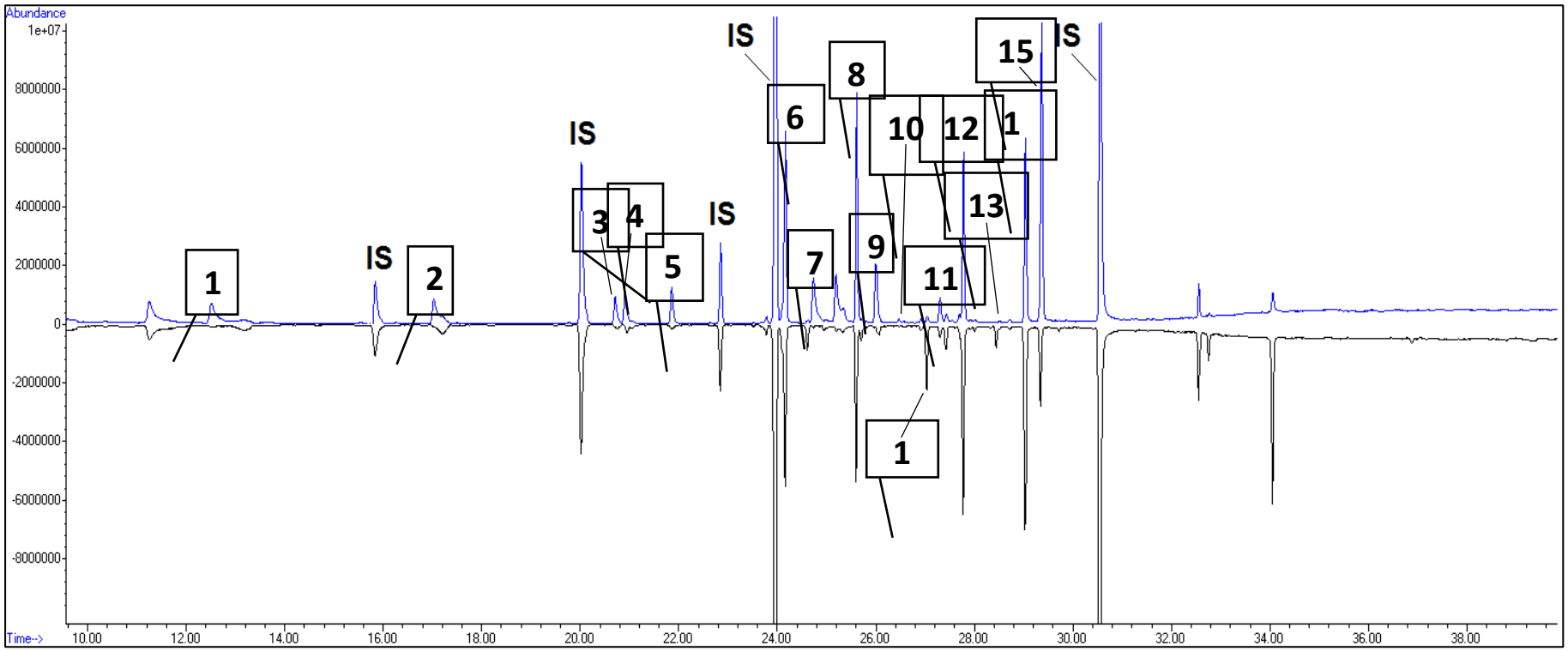

Figure 17S – Chromatogram of Na_2SO_4 process at 40 ºC with an oxidant dose of 217.79 g. Blue line represent the initial sample and the black represents the final sample, after treatment. IS – internal standards; 1 – benzene; 2 – toluene; 3 – ethylbenzene; 4 – 2-ethylthiophene; 5 – o-xylene; 6 – 2-methylcyclohexanone; 7 – 2,4,6 colidine; 8 – 2-ethyl-1-hexanol; 9 – phenol; 10 – dibutyl sulfide; 11 – 4-methylbenzaldehyde; 12 – nitrobenzene + 2,6-dimethylphenol; 13 – 2-nitrphenol; 14 – 2-nitrotoluene; 15 – 4-ethylphenol + naphthalene; 16 – acetophenone.

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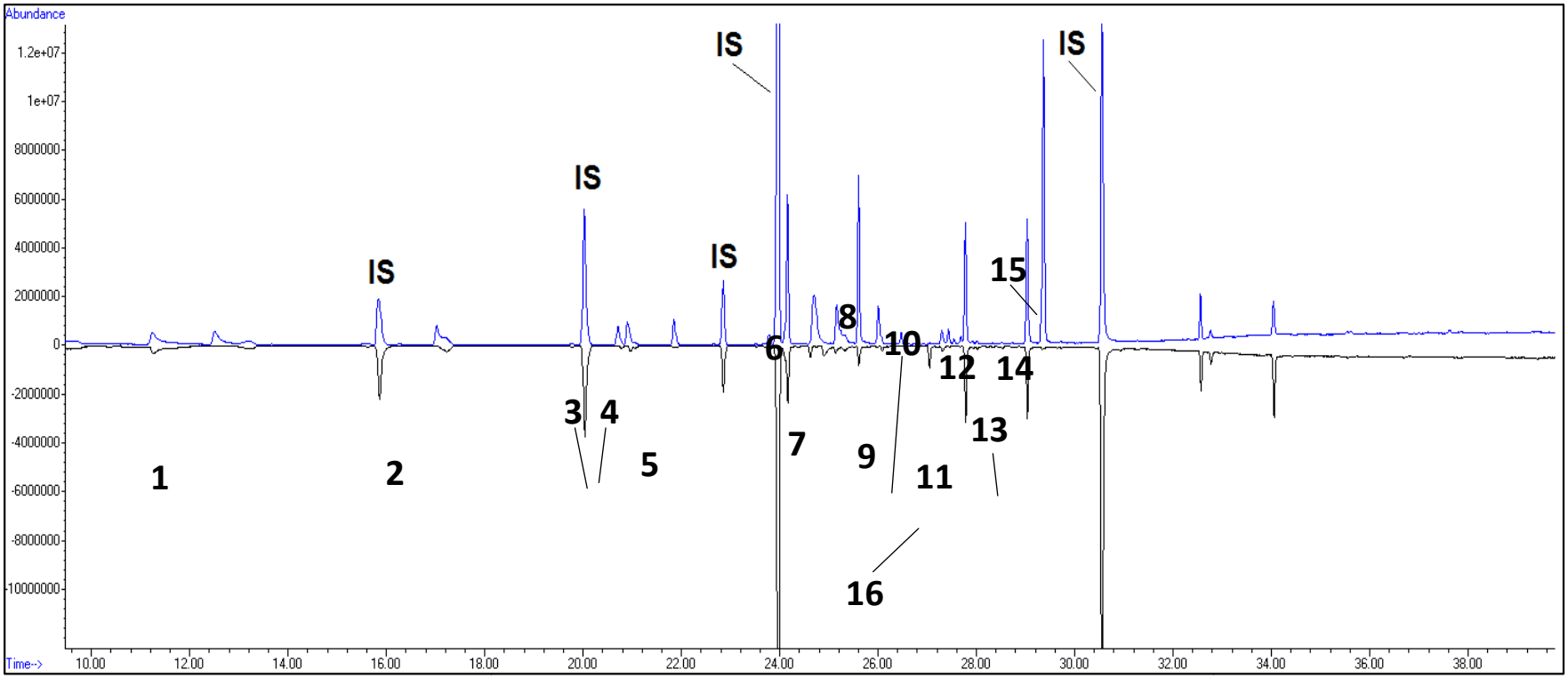

Figure 18S – Chromatogram of Na_2SO_4 process at 40 ºC with an oxidant dose of 435.39 g. Blue line represent the initial sample and the black represents the final sample, after treatment. IS – internal standards; 1 – benzene; 2 – toluene; 3 – ethylbenzene; 4 – 2-ethylthiophene; 5 – o-xylene; 6 – 2-methylcyclohexanone; 7 – 2,4,6 colidine; 8 – 2-ethyl-1-hexanol; 9 – phenol; 10 – dibutyl sulfide; 11 – 4-methylbenzaldehyde; 12 – nitrobenzene + 2,6-dimethylphenol; 13 – 2-nitrphenol; 14 – 2-nitrotoluene; 15 – 4-ethylphenol + naphthalene; 16 – acetophenone

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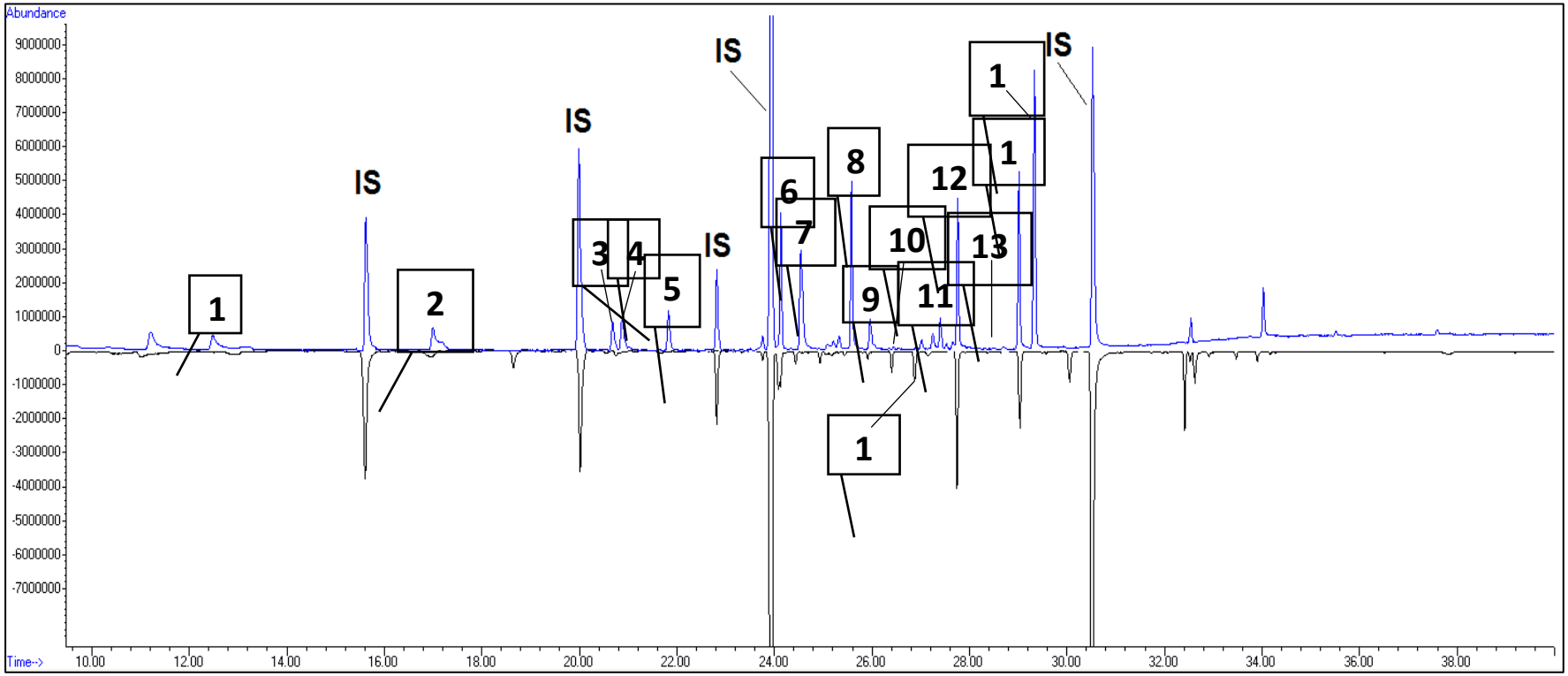

Figure 19S – Chromatogram of Na_2SO_4 process at 60 ºC with an oxidant dose of 217.79 g. Blue line represent the initial sample and the black represents the final sample, after treatment. IS – internal standards; 1 – benzene; 2 – toluene; 3 – ethylbenzene; 4 – 2-ethylthiophene; 5 – o-xylene; 6 – 2-methylcyclohexanone; 7 – 2,4,6 colidine; 8 – 2-ethyl-1-hexanol; 9 – phenol; 10 – dibutyl sulfide; 11 – 4-methylbenzaldehyde; 12 – nitrobenzene + 2,6-dimethylphenol; 13 – 2-nitrphenol; 14 – 2-nitrotoluene; 15 – 4-ethylphenol + naphthalene; 16 – acetophenone.

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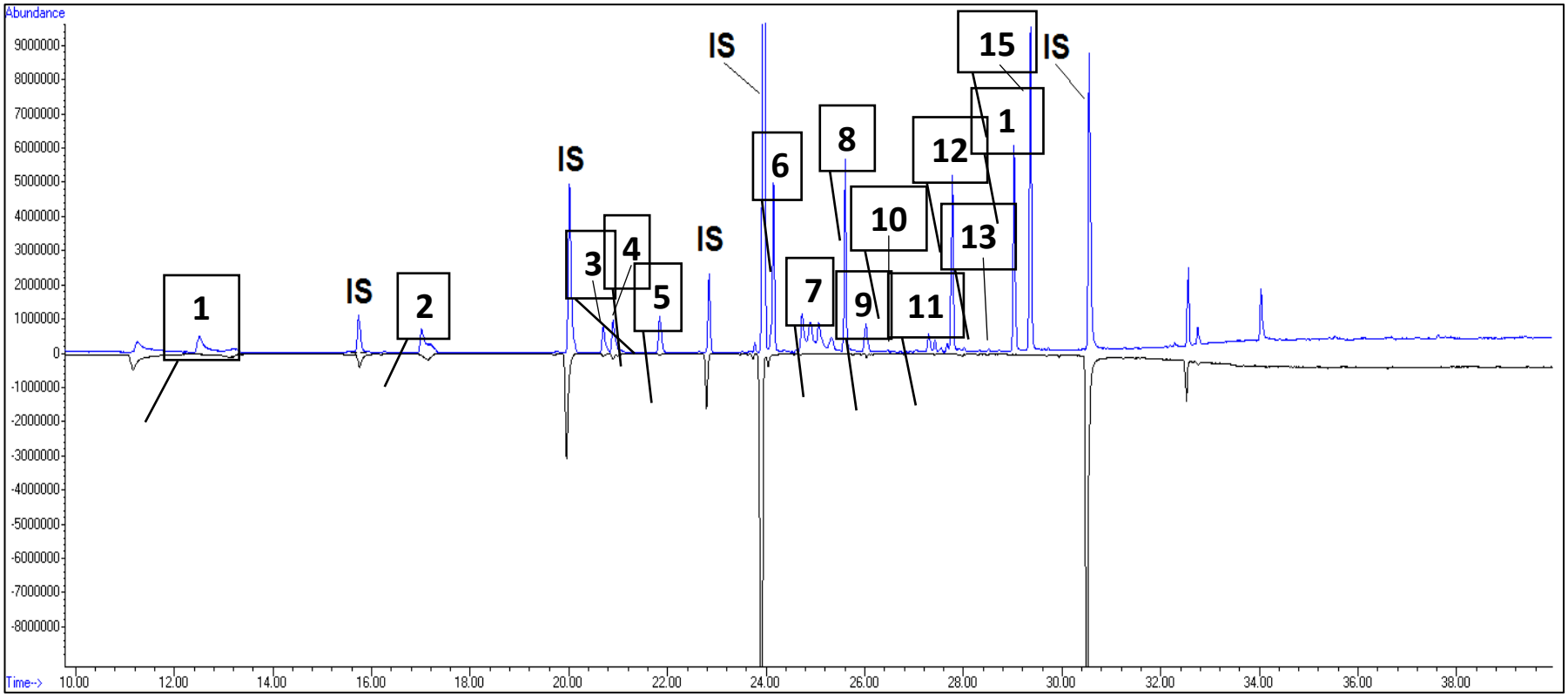

Figure 20S – Chromatogram of Na_2SO_4 process at 60 ºC with an oxidant dose of 435.39 g. Blue line represent the initial sample and the black represents the final sample, after treatment. IS – internal standards; IS – internal standards; 1 – benzene; 2 – toluene; 3 – ethylbenzene; 4 – 2-ethylthiophene; 5 – o-xylene; 6 – 2-methylcyclohexanone; 7 – 2,4,6 colidine; 8 – 2-ethyl-1-hexanol; 9 – phenol; 10 – dibutyl sulfide; 11 – 4-methylbenzaldehyde; 12 – nitrobenzene + 2,6-dimethylphenol; 13 – 2-nitrphenol; 14 – 2-nitrotoluene; 15 – 4-ethylphenol + naphthalene.

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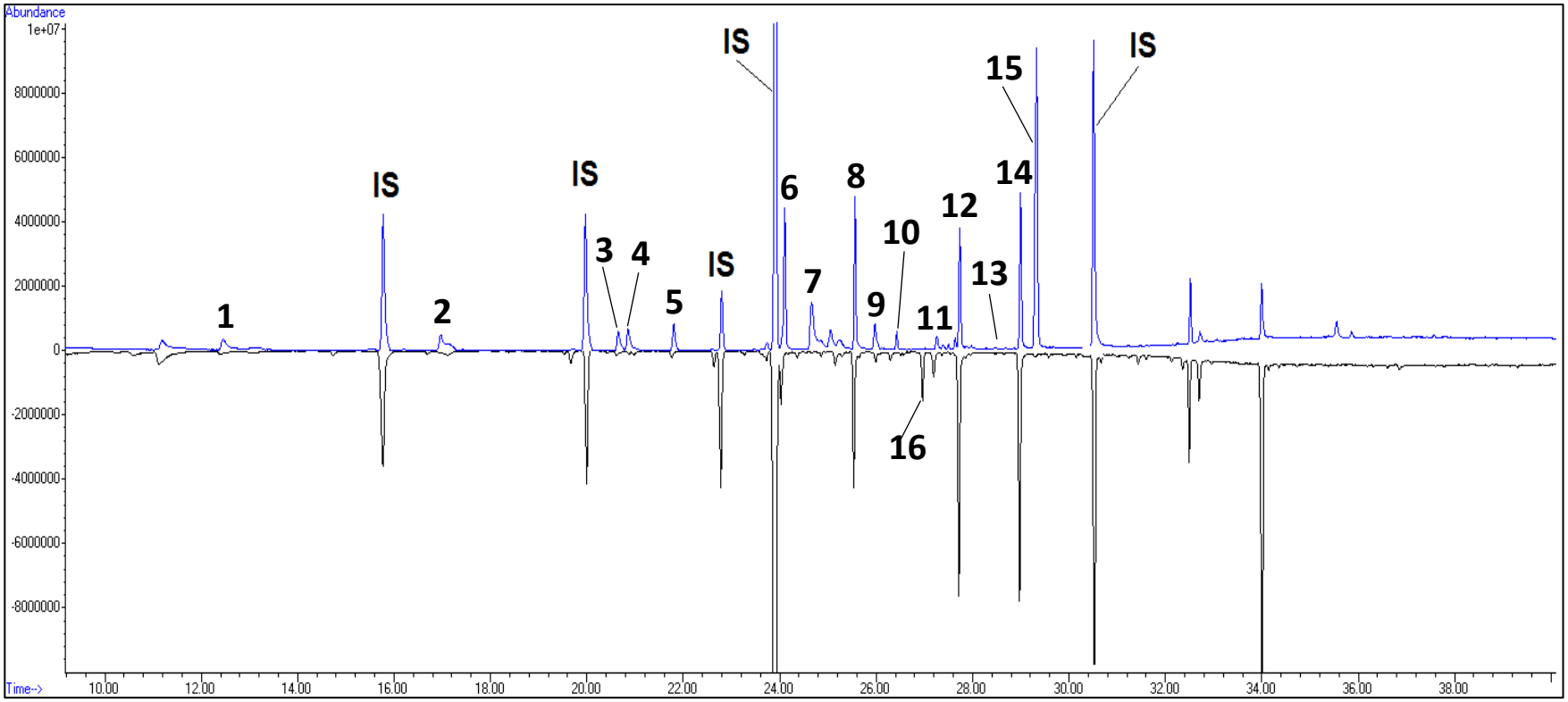

Figure 21S – Chromatogram of $KHSO_5$ process at 40 ºC with an oxidant dose of 114.3 g. Blue line represent the initial sample and the black represents the final sample, after treatment. IS – internal standards; 1 – benzene; 2 – toluene; 3 – ethylbenzene; 4 – 2-ethylthiophene; 5 – o-xylene; 6 – 2-methylcyclohexanone; 7 – 2,4,6 colidine; 8 – 2-ethyl-1-hexanol; 9 – phenol; 10 – dibutyl sulfide; 11 – 4-methylbenzaldehyde; 12 – nitrobenzene + 2,6-dimethylphenol; 13 – 2-nitrphenol; 14 – 2-nitrotoluene; 15 – 4-ethylphenol + naphthalene; 16 – acetophenone.

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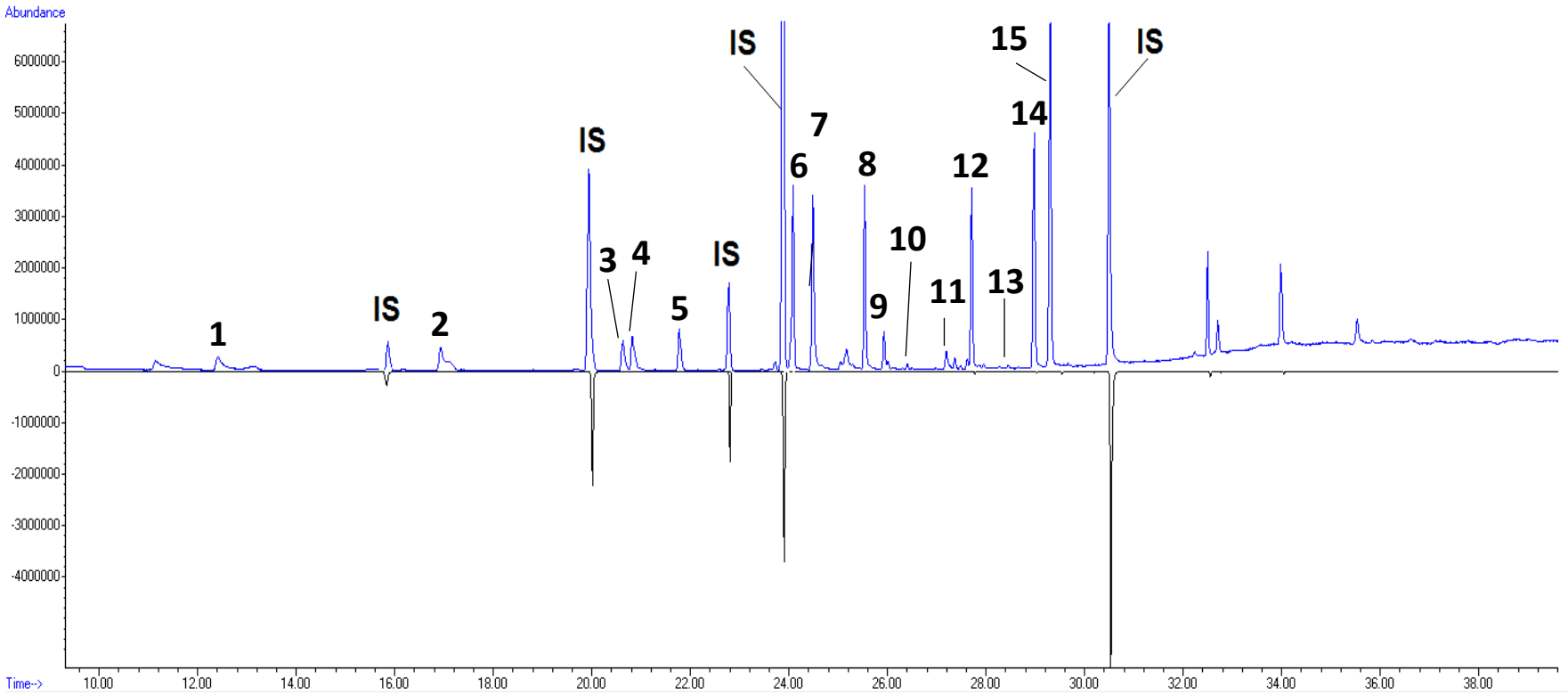

Figure 22S – Chromatogram of $KHSO_5$ process at 60 ºC with an oxidant dose of 114.3 g. Blue line represent the initial sample and the black represents the final sample, after treatment. IS – internal standards; 1 – benzene; 2 – toluene; 3 – ethylbenzene; 4 – 2-ethylthiophene; 5 – o-xylene; 6 – 2-methylcyclohexanone; 7 – 2,4,6 colidine; 8 – 2-ethyl-1-hexanol; 9 – phenol; 10 – dibutyl sulfide; 11 – 4-methylbenzaldehyde; 12 – nitrobenzene + 2,6-dimethylphenol; 13 – 2-nitrphenol; 14 – 2-nitrotoluene; 15 – 4-ethylphenol + naphthalene.

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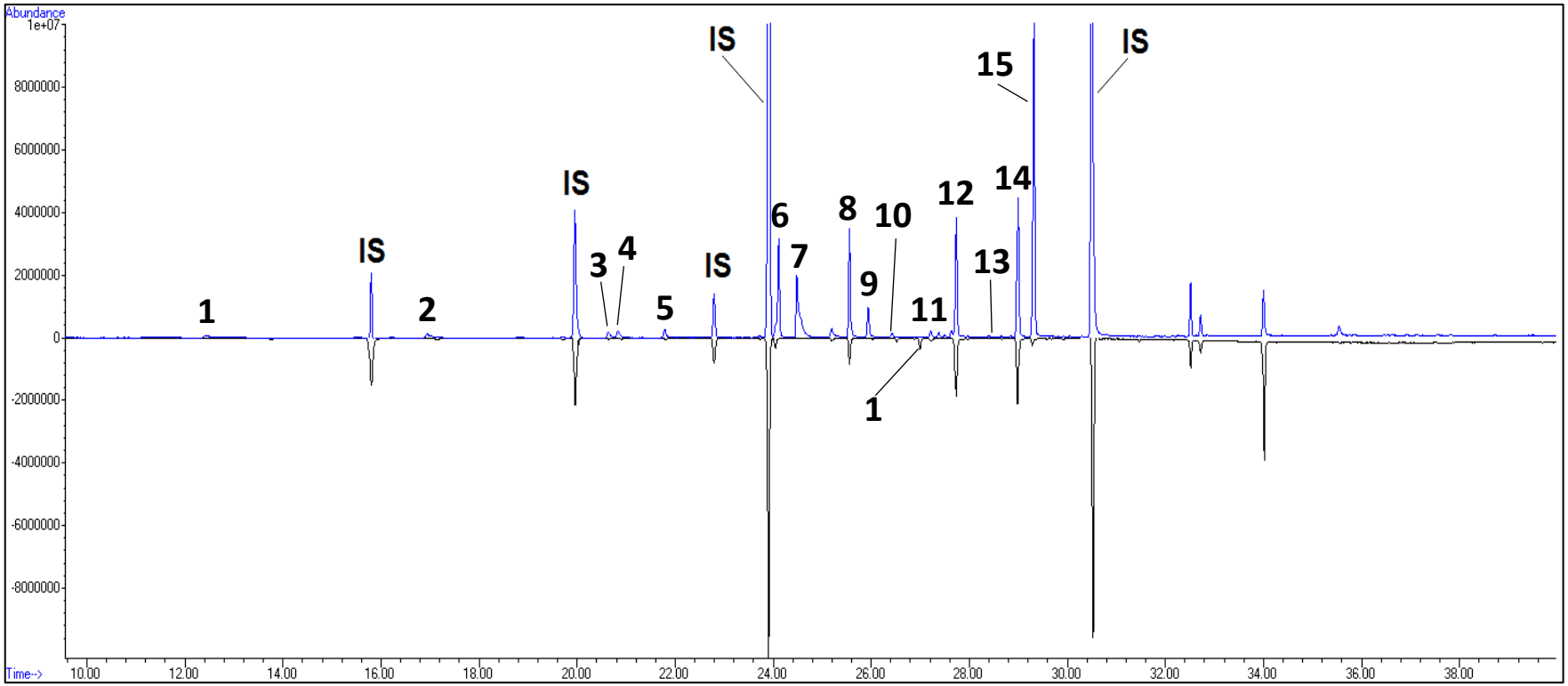

Figure 23S – Chromatogram of $KHSO_5$ process at 40 ºC with an oxidant dose of 69.67 g. Blue line represent the initial sample and the black represents the final sample, after treatment. IS – internal standards; 1 – benzene; 2 – toluene; 3 – ethylbenzene; 4 – 2-ethylthiophene; 5 – o-xylene; 6 – 2-methylcyclohexanone; 7 – 2,4,6 colidine; 8 – 2-ethyl-1-hexanol; 9 – phenol; 10 – dibutyl sulfide; 11 – 4-methylbenzaldehyde; 12 – nitrobenzene + 2,6-dimethylphenol; 13 – 2-nitrphenol; 14 – 2-nitrotoluene; 15 – 4-ethylphenol + naphthalene; 16 – acetophenone.

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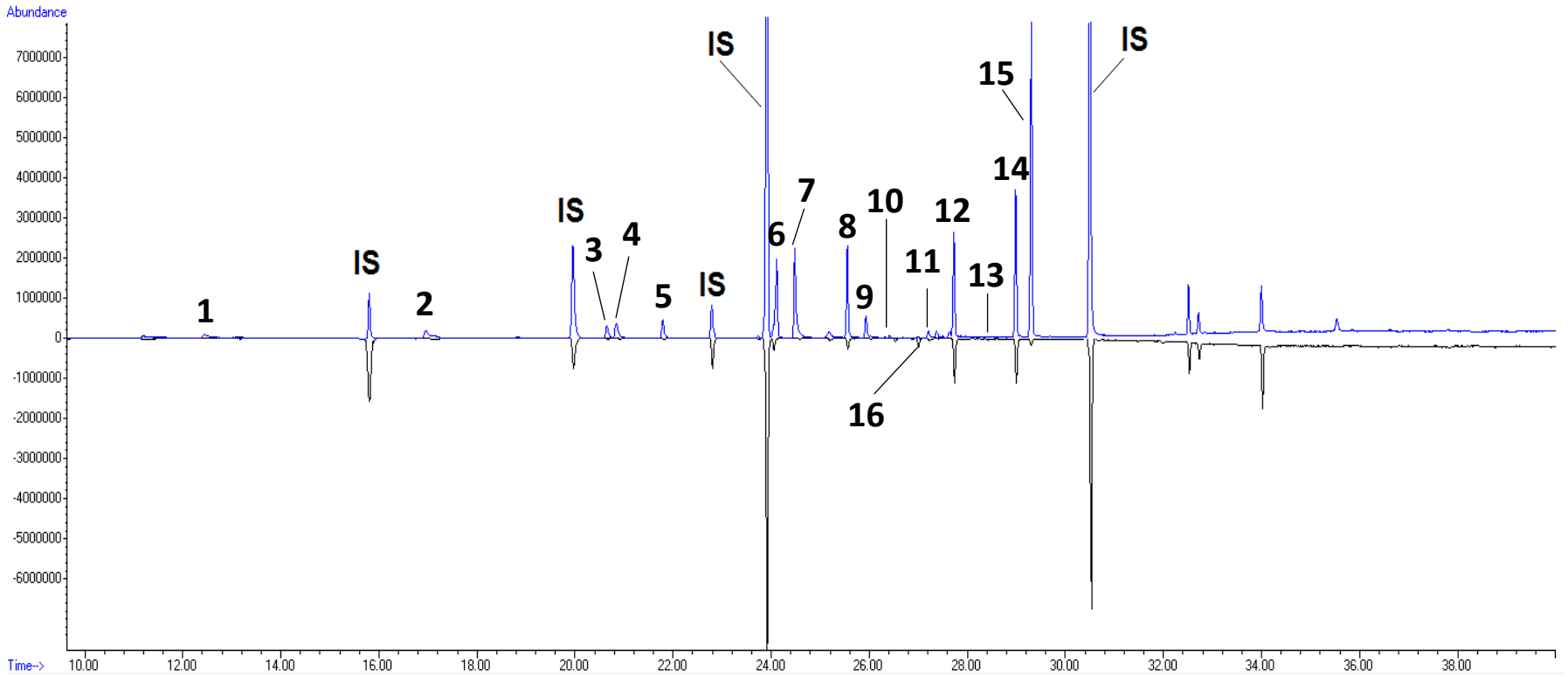

Figure 24S – Chromatogram of $KHSO_5$ process at 60 ºC with an oxidant dose of 69.67 g. Blue line represent the initial sample and the black represents the final sample, after treatment. IS – internal standards; 1 – benzene; 2 – toluene; 3 – ethylbenzene; 4 – 2-ethylthiophene; 5 – o-xylene; 6 – 2-methylcyclohexanone; 7 – 2,4,6 colidine; 8 – 2-ethyl-1-hexanol; 9 – phenol; 10 – dibutyl sulfide; 11 – 4-methylbenzaldehyde; 12 – nitrobenzene + 2,6-dimethylphenol; 13 – 2-nitrphenol; 14 – 2-nitrotoluene; 15 – 4-ethylphenol + naphthalene; 16 – acetophenone.

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