

**UNIVERSIDADE DE SÃO PAULO ESCOLA POLITÉCNICA  
DEPARTAMENTO DE ENGENHARIA HIDRÁULICA E AMBIENTAL**

**POTASSIUM PERMANGANATE APPLICATION  
TOGETHER WITH POWDERED ACTIVATED  
CARBON FOR THE REMOVAL OF TASTE AND ODOR  
CAUSING COMPOUNDS**

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"There is no question that our health has improved spectacularly in the past century. One thing seems certain: It did not happen because of improvements in medicine, or medical science, or even the presence of doctors, much of the credit should go to the plumber sand sanitary engineers of the western world."

Lewis Thomas (speech, 1984)

## Abstract

The removal of odor and taste causing compounds is one of the most important issues in drinking water treatment. They can be removed with different treatments, but the most used is probably the adsorption on Powdered Activated Carbon (PAC). PAC has a lot of good features that allow an efficient removal of taste and odor, but its removal capacity is often influenced by the action of some oxidants used in the pre-oxidation stage. The aim of this study was to evaluate the interference of a specific oxidant, potassium permanganate ( $KMnO_4$ ), in PAC removal efficiency of two odor and taste causing compounds: 2-Methylisoborneol (MIB) and geosmin. Different tests were conducted and it was observed that there is an interaction between  $KMnO_4$  and PAC that can be well described by a second order kinetic model. It was noted a rapid consumption of  $KMnO_4$  which oxidizes the carbon surface and reduces its adsorption efficiency.

In this study appears that potassium permanganate, also being less aggressive than other oxidants, can influence PAC adsorption capacity, therefore the conclusions suggest that it should be used only the quantity of oxidant needed for the pre-oxidation, avoiding the contact between PAC and  $KMnO_4$  in following phases of the treatment which causes PAC surface oxidation and the decrease of its adsorption capacity.

## Resumo

A remoção de compostos causadores de gosto e odor é um dos principais problemas no tratamento de águas de abastecimento podendo ser removidos com diversos tipos de tratamentos. Entretanto o mais utilizado é provavelmente a adsorção em carvão activado em pó. Este possui várias boas características que permite uma eficiente remoção de gosto e odor, contudo sua capacidade de remoção é influenciada pela ação de alguns agentes oxidantes utilizados na fase de pré-oxidação. O objetivo deste estudo foi avaliar a interferência de um oxidante específico, permanganato de potássio ( $KMnO_4$ ), na capacidade do PAC de remover dois compostos causadores de gosto e odor: 2-Methylisoborneol (MIB) e a geosmina. Foram realizados diversos experimentos e foi observado que existe uma interação entre  $KMnO_4$  e o carvão que pode ser descrita com um modelo cinético de segunda ordem. Foi notada um rápido consumo de  $KMnO_4$  que oxida a superfície do carvão e reduz a capacidade de adsorção dele.

Neste estudo parece que o  $KMnO_4$ , mesmo sendo um oxidante menos agressivo que outros, pode influenciar a capacidade de remoção do carvão. Isso levou a conclusão que ele deve ser utilizado só nas doses requeridas na pré-oxidação, evitando o contato entre o  $KMnO_4$  e o carvão nas fases sucessivas do tratamento que causaria a oxidação da superfície do carvão e resultaria na diminuição da capacidade de remoção do mesmo.

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## **GLOSSARY**

AOPs	Advanced Oxidation Processes
EDS	Energy-Dispersive X-ray Spectroscopy
ET	Electric Tongue
FPA	2170 Flavor Profile Analysis
GAC	Granular Activated Carbon
HAAs	Haloacetic acids
IBMP	2-isobutyl-3-methoxy pyrazine
IPMP	2-isopropyl-3-methoxy pyrazine
MBM	Membrane Based Method
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
MIB	2-Methylisoborneol
NOM	Natural Organic Matter
OTC	Odor Threshold Concentration
P&T	Purge and Trap Method
PAC	Powdered Activated Carbon
SEM	Scanning Electron Microscopy
SPE	Solid Phase Extraction
SPME	Solid Phase Microextraction
TCA	2,3,6-trichloroanisole
TCP	Trichloropropane
THMs	Trihalomethanes
TON	Threshold Odor Number
VOCs	Volatile Organic Compounds

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## 1 INTRODUCTION

One of the biggest challenges in drinking water treatment, even in developed countries, are taste and odor problems.

Consumers complaints about drinking water taste and odor are very common all around the world, and often they correlate taste and odor with drinking water actual potability.

In the late 19th century, water professionals and consumers throughout the world used tastes and odors to assess water quality (Dietrich, 2006) and currently taste and odor are still perceived as the primary indicators of drinking water safety and acceptability (Srinivasan and Sorial, 2011). An American nation wide survey of 1,754 bottled water consumers found that 39% of the consumers chose bottled water because it tasted better, while only 18% said it was because of safety (Srinivasan and Sorial, 2011). In a survey concerning home plumbing and drinking water, 34% of the interviewed said aesthetic factors (taste, odor and color) were important (Dietrich, 2006). Another survey on 377 water utilities in Canada and in US by the American Water Works Association (AWWA) stated that “fiscal resources spent by water utilities to control taste and odor problems averages \$67,800, representing an average of 4.5 percent of their total budget” (Suffet et al., 1996).

There are a lot of factors influencing water taste and odor and they can be summarized in three main groups (Dietrich, 2006):

1. water chemical and microbial content, which depends on geology and ecology conditions;
2. chemicals used or removed from water during treatments;
3. reactions occurring during storage and distribution.

Consumer perception depends also on the temperature (high temperature is often a damaging factor) and on the concentration of responsible compounds (perception can occur with concentrations of pg/l to mg/l).

During the last decades odor and taste problem has increased because of water reservoirs eutrophication due to industrial and urban wastewater discharge and the resulting excessive growth of algae and microorganism (cyanobacteria) which generate, through their metabolic processes, some organic substances responsible for water bad taste and odor (Zhang et al., 2010; Watson et al. 2008; Suurnakki et al., 2015). The major taste and odor-causing substances in drinking water are geosmin and 2-Methylisoborneol (MIB) which derive from cyanobacteria's metabolism (Pirbazari et al., 1993). There are currently no regulations for these two compounds as they have not been associated with any health effects, but they must be removed because of the earthy and musty odors they generate even at low concentrations. The Odor Threshold Concentration (OTC) for MIB and geosmin can range from 4 to 20 ng/l (Srinivasan and Sorial, 2011).

The conventional treatment methods to remove MIB and geosmin are adsorption by activated carbon or oxidation with strong oxidants. The best alternative is the use of Powdered Activated Carbon (PAC) because oxidation with strong oxidants is very expensive, causes the formation of by products and it is not flexible enough to follow the seasonality of the pollutants (Srinivasan and Sorial, 2011).

In drinking water treatment it is common to apply, together with PAC, potassium permanganate ( $\text{KMnO}_4$ ) which is a strong oxidant of iron and manganese in raw water. Moreover, potassium permanganate has other good features:

- differently from other oxidants like chlorine, it causes a low oxidation of the PAC surface, avoiding reduction of the PAC removal efficiency (Gillogly et al., 1998);
- it avoids the production of chlorine typical by products like trihalomethanes (THMs) and haloacetic acids (HAAs) (Ficek and Boll, 1980; USEPA, 1999).

There are a lot of papers demonstrating the efficacy of  $\text{KMnO}_4$ , but a specific study about the effect of  $\text{KMnO}_4$  on PAC removal performance of odor and taste compounds is not available.

To deeply analyze the above mentioned issue, it would be necessary a more detailed research in this field to know more about the relation between KMnO<sub>4</sub> oxidation and PAC removal capacity.

## 2 PURPOSE

The purpose of this work is the assessment of the application of potassium permanganate in drinking water treatment with reference to PAC performances for odor and taste causing compound removal. More specifically, 3 purposes can be identified:

1. analysis of the influence of the application of  $\text{KMnO}_4$  on PAC performance in the removal of MIB e geosmin;
2. description by a kinetic model of the interaction between PAC and potassium permanganate;
3. study of  $\text{KMnO}_4$  interferences in PAC adsorption process.

### 3 LITERATURE REVIEW

#### 3.1 Taste and odor issues

One of the greatest challenges of the last years in the drinking water treatment is the elimination of water odor and taste causing compounds because of the socio-economic effects they generate, since consumers normally use their presence as the primary measure of drinking water safety.

In fact taste and odor are the biggest cause of consumer complaints even if they are rarely produced by pathogens or toxic compounds and so are not dangerous for health. Therefore, it is fundamental to detect taste and odor compounds, also because their presence can help to identify short and long-term issues of the water supply network: in the short term, they can signal treatment or distribution network malfunction or chemical/biological hazards in source water, while in the long term they can provide an early warning of fundamental changes in a freshwater resource (Watson, 2004).

Odor and taste issue often occurs because water supplies are localized near to big urban centers and so the eutrophication events are very common. Algae and bacteria are one of the most frequent source of drinking water taste and odor through the production of Volatile Organic Compounds (VOCs). Some VOCs are unique to algae or bacteria, while others are produced by both groups of organisms. There are a lot of algae in the water supplies and they can produce similar or different VOCs that contribute to the overall taste and odor. The situation can appear complicated, but three factors support in the identification of taste and odor origin (Watson, 2004):

- a small quantity of VOCs are responsible of most algae derived tastes and odors;
- only 0.5% of all the algae species present are responsible for odor and taste issues;
- VOCs can be produced throughout algae growth or released mainly through cell senescence, death, or mechanical damage.

Facing a taste and odor event is often quite complicated, since (Watson, 2004):

- the event is not predictable in occurrence and characteristics;
- the causing compounds can have different threshold concentrations ranging from 4 to 20 ng/l (Srinivasan and Sorial, 2011);
- odor and taste causing compounds require sophisticated analytical techniques for their identification, they must be monitored and show different responses to treatments;
- a mix of compounds can produce similar or different odors or tastes in source and finished water;
- specific treatments, like chlorination or ozonation, can exacerbate odors and tastes because of the generated by products.

Therefore, it is important to clearly identify the sources and the characteristics of odor and taste causing compounds to treat them in the best way and to limit their negative effects (Watson, 2004).

### 3.2 Odor and taste causes

There are a lot of taste and odor causing compounds and their sources are numerous. They are summarized in a review by Suffet et al. (1999).

Of particular interest are compounds which produce earthy-musty odors and tastes, because, even at low concentration, they could result in consumers complaints. Among these compounds the most important are: 2-isopropyl-3-methoxy pyrazine (IPMP), 2-isobutyl-3-methoxy pyrazine (IBMP), 2,3,6-trichloroanisole (TCA), geosmin and 2-methylisoborneol (MIB). Specifically, MIB and geosmin are considered the major and more identified compounds in the earthy-musty category (Lalezary et al., 1986).

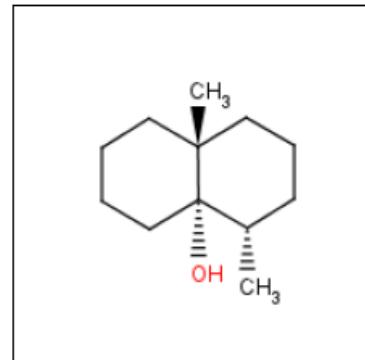
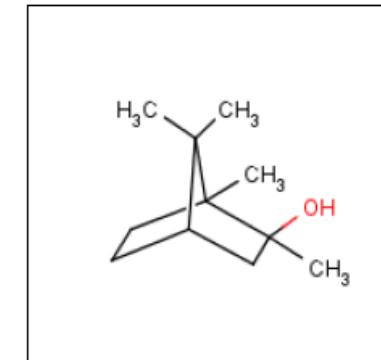
MIB and geosmin physical and chemical characteristics are summarized in Table 1. They have a low molecular weight and a low Octanol/Water Partition coefficient ( $K_{ow}$ ) meaning their low solubility and high volatility. MIB has a

hydrocarbon skeleton containing one hydroxyl group, making it relatively hydrophobic and it is roughly spherical in shape with a diameter of 0.6 nm (Pendleton et al., 1997). Geosmin and MIB are tertiary alcohols, each of which exists as (+) and (−) enantiomers. Odor phenomena are caused by biological production of the naturally occurring (−) enantiomers, which are almost 10 times more potent than the (+) molecules (Jüttner and Watson, 2007).

Geosmin and MIB are produced by members of certain groups of benthic and pelagic aquatic microorganisms that normally bloom in presence of nutrients at warmer temperatures (Srinivasan and Sorial, 2011). Most of the producers are prokaryotes, heterotrophs and photoautotrophs, but have also been identified as sources some eukaryotes which has not been systematically investigated yet. There are several groups of heterotrophic microorganism producers (Table 2) and it is important to highlight that their activity in distribution pipes or filtration beds can originate odor also downstream of water treatment.

For a long time aerobic filamentous actinomycete bacteria (*Streptomyces*) (heterotrophs) were considered the most important source of MIB and geosmin. Actinomycetes can be found in soil and during high terrestrial runoff they and their odorous metabolites are introduced into surface waters, causing episodic odor outbreaks in rivers, particularly in areas of intensive livestock operations. Tabachek and Yurkowski (1976) recognized cyanobacteria (photoautotrophs) as a more frequent source of geosmin and MIB in water than actinomycetes (Jüttner & Watson, 2007). Cyanobacteria synthesize MIB/geosmin during growth and release or store these compounds depending on the growth phase and based on environmental factors. Most of the MIB/geosmin is released during the death and biodegradation of these cells. Fewer than 50 species of Cyanobacteria out of more than 2000 have been confirmed as producers of MIB and geosmin, while the others have still to be investigated. No marine Cyanobacteria has been identified as MIB/geosmin producer, but it is not demonstrated that salinity preclude the production of these compounds.

Table 1: Chemical and physical characteristics of geosmin and MIB (Pirbazari et al., 1992; Smith, 2011).

Name	Geosmin	2-Methylisoborneol (MIB)
Molecular structure*	 The chemical structure of Geosmin is a bicyclic compound consisting of a decalin system with a methyl group (CH <sub>3</sub> ) and a hydroxyl group (OH) at the 10-position, and two methyl groups (CH <sub>3</sub> ) at the 7 and 9 positions.	 The chemical structure of 2-Methylisoborneol (MIB) is a bicyclic compound with a methyl group (CH <sub>3</sub> ) at the 2-position of the isoborneol ring system.
Molecular formula	C <sub>12</sub> H <sub>22</sub> O	C <sub>11</sub> H <sub>20</sub> O
Molecular weight	182 g/mol	168 g/mol
K <sub>ow</sub>	3.70	3.13

\*Image source for structures: National Library of Medicine, ChemIDplus Advanced, <http://chem.sis.nlm.nih.gov/chemidplus/>

Table 2: Actinomycetes and other noncyanobacterial that produce geosmin (GE) and 2-MIB (Jüttner and Watson, 2007).

VOCs	Taxon	Reference
MIB, GE	<i>Penicillium</i> and <i>Aspergillus</i> species	Saadoun et al., 1997
GE	<i>P. expansum</i>	Dionigi et al., 1992
GE	<i>Streptomyces albidoflavus</i>	Sunesson et al., 1997
GE	<i>S. avermitilis</i>	Rezanka et al., 1994
GE	<i>S. citreus</i>	Pollak and Berger, 1996
GE	<i>S. griseus</i>	Whitmore and Denny, 1992
GE, MIB	<i>S. griseofuscus</i>	Aoyama et al., 1993
GE	<i>S. halstedii</i>	Schrader and Blevins, 2001
GE	<i>S. psammoticus</i>	Jensen et al., 1994
GE	<i>S. tendae</i>	Dionigi et al., 1992
GE, MIB	<i>S. violaceusniger</i>	Saadoun et al., 1997
GE, MIB	<i>Streptomyces</i> spp.	Various
GE	<i>Symphyogyna brongniartii</i> (liverwort)	Spörle et al., 1991
GE	<i>Vannella</i> sp. (heterotrophic amoeba)	Hayes et al., 1991

### 3.3 Health effects of MIB and geosmin

Numerous studies stated that the presence of MIB and geosmin can't be associated with any health effect. Dionigi et al. (1993) carried out a study about the mutagenic properties of MIB and geosmin and demonstrated the complete absence of this characteristic at concentrations of many orders of magnitude higher than those

normally observed in water resources. Some studies have detected the presence of MIB/geosmin in some fish species, but they demonstrated that the two compounds are not dangerous to either the fish or to the humans (Srinivasan and Sorial, 2011). Therefore, it is impossible to define a Maximum Contaminant Level (MCL) or Maximum Contaminant Level Goal (MCLG) for either MIB/geosmin.

The biggest problems of MIB/geosmin is their low OTC ranging from 4 to 20 ng/l and their persistence to elimination with conventional treatments (coagulation, sedimentation, filtration, chlorination). That is why consumers can easily perceive them. The consequence is a decrease of the trust in drinking water quality and the use of other water supply, such as bottles (Srinivasan and Sorial, 2011).

### **3.4 Detection methods for MIB and geosmin**

Detection and quantification of taste and odor causing compounds have always been quite difficult due to the characteristics of the compounds and their extremely low OTC. The methods can be divided in two groups: quantitative and qualitative.

The quantitative methods are Purge and Trap method (P&T) and liquid-liquid extraction. P&T method is a valuable concentration method applied to VOCs. The compounds are concentrated by bubbling an inert gas through the sample followed by collection in and desorption from a sorbent trap and then this extract is analyzed (APHA, 2005).

The liquid-liquid extraction method separates compounds based on their relative solubilities in two different immiscible liquids. It consists of transferring one (or more) solute(s) contained in a feed solution to another immiscible liquid (solvent). The solvent that is enriched in solute(s) is called extract. The two methods were effective but expensive, leading to the development of alternative methods like the Membrane Based Method (MBM) or the Solid Phase Extraction (SPE). With these methods it was possible to measure concentrations of the order of part per trillion in water, but the apparatus setup was complex and involved a lot of equipment (Srinivasan and Sorial, 2011), so that, in 1996, a new method called Solid-Phase Micro Extraction (SPME) was introduced. It is an adsorption/desorption process using coated fibers into a syringe like device (Figure 1). The automation of

the solid phase micro-extraction can ease the method, bringing the following advantages (Yean-Woong You, 2012):

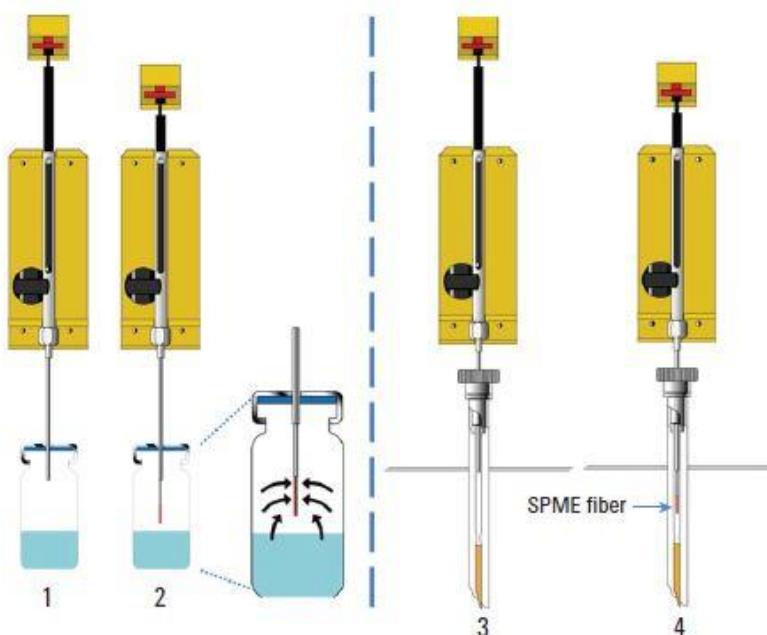
- lower costs and less environmental impacts since liquid extraction solvents are not required;
- increase in analytical sensitivity and precision.

Some studies have compared P&T method with SPME and it was seen that the precision and limits achieved with SPME are comparable to P&T, detecting concentrations of the order of ng/l, with SPME offering faster analysis with smaller sample size. Therefore, currently SPME is the standard quantitative method (Srinivasan and Sorial, 2011).

Since SPME is quite costly, time consuming and it can't be applied for real time monitoring because it is difficult to implement at remote locations, Braga et al. (2012) developed an Electronic Tongue (ET) system based on non-specific polymeric sensors and impedance measurements to monitor MIB and geosmin in water samples. They showed that this equipment can perform with remarkable reproducibility the discrimination of these two contaminants in both distilled or tap water, in concentrations as low as 25 ng/l. They concluded that in some cases this equipment can be useful because of its lower costs and good efficiency.

Among the qualitative methods the most used are Threshold Odor Number (TON) and 2170 Flavor Profile Analysis (FPA) (APHA, 2005). The qualitative methods can be an important solution to detect odor and taste because they are very cheap and often efficient. Specifically, they can be very useful when the purpose is not to detect pollutants concentration but only to evaluate taste and odor intensity. Ferreira Filho and Alves (2006) conducted a series of tests, using water treated in a Brazilian plant, about the consumer complaints to compare the results of FPA and P&T method. They showed that FPA is very efficient and produces similar results as P&T in the detection of musty/earth odors, therefore in many cases, FPA can substitute P&T method being the first one easier and cheaper than the second. They highlighted that the greatest problem using FPA method is the presence of free chlorine that can influence the odor perception. Specifically, the influence of free

chlorine is more intense on MIB than on geosmin, so that using FPA method it is important to analyze the original samples and then the dechlorinated ones to compare the results and note how the chlorine can influence the perception.



*Figure 1:Solid phase microextraction (SPME). In (1) and (2) the syringe plunger is depressed to expose directly the fibers to the the sample or to the headspace above the sample and the organic compounds are adsorbed on the fiber. In (3) and (4), once equilibrium is attained, the fiber is withdrawn from the sample and the compounds are thermally desorbed to carry out the analysis(Yean-Woong You, 2012).*

### 3.5 Taste and odor treatment technologies

Several studies, conducted in water treatment plants, have shown that MIB/geosmin are extremely resistant to removal by conventional water treatment processes such as coagulation, sedimentation and filtration (Srinivasan and Sorial, 2011; Ferreira Filho and Alves, 2006).

It has been seen that also common oxidants such as  $\text{Cl}_2$ ,  $\text{ClO}_2$  and  $\text{KMnO}_4$  are not very effective to remove these compounds (Lalezary et al., 1986). Lalezary et al. (1986) conducted some laboratory tests using a synthetic water and simulating water treatment conditions to study the removal efficiency with  $\text{Cl}_2$ ,  $\text{KMnO}_4$  and  $\text{ClO}_2$ . They obtained unsatisfactory results. For example,  $\text{Cl}_2$  at a dose of 20 mg/L reduced geosmin from 120 to 80 ng/l (33 percent removal) after a 16 h contact time. With a

dose of 4 mg ClO<sub>2</sub>/l for the same period, removal was somewhat better (60 percent), but for some reason higher dosages were no more effective. Potassium permanganate did not oxidize geosmin under the conditions used (2 h contact time, up to 50 mg KMnO<sub>4</sub>/l) (Lalezary et al., 1986; Glaze et al., 1990). Therefore, potassium permanganate has low removal capacity even at higher dosages than chlorine. Srinivasan and Sorial (2011) stated that chlorine residual, in some cases, masks the musty/earthy odors rather than removing them. Moreover, chlorination often creates problems because of the by products such as THMs and HAAs.

That's why other technologies have been developed and used for the treatment of taste and odor causing compounds, like:

- Advanced Oxidation Processes (AOPs) such as ozone (O<sub>3</sub>), O<sub>3</sub> and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>);
- UV radiation;
- Granular Activated Carbon (GAC) or PAC and biological treatment.

Collivignarelli and Sorlini (2004) investigated MIB/geosmin removal using ozone and UV. Different batch tests were performed with ozone concentration up to 10 mg/l, UV dose up to 14,000 J/m<sup>2</sup> and a maximum contact time of 10 minutes, noting that both MIB and geosmin were persistent to reaction with ozone and showed low (about 50%) removal rates. However, ozone followed by exposure to UV increased the removal close to 90%. Molecular ozone had limited reaction with these two compounds and UV radiation was required to decompose the ozone molecule for generation of hydroxyl radicals (·OH) which subsequently reacted with MIB/geosmin. Moreover, they showed that this process did not result in complete removal of MIB/geosmin and the resulting effluent concentrations were higher than the OTCs.

Looking at UV oxidation of MIB/geosmin, Rosenfeldt et al. (2005) found that dosages higher than the normally used for disinfection are required for complete removal. In fact, they ran tests, using raw water, with Low Pressure (LP) and Medium Pressure (MP) direct UV photolysis noting that it was reached a removal of 10% for MIB and 25–50% for geosmin by 1000 mJ/cm<sup>2</sup> UV fluence. It was also found that water quality parameters, such as turbidity from NOM, influence the

removal rates, as the destruction in clear well water was much higher than in raw river water.

Koch et al. (1992), Carollo (2000) and Westerhoff et al. (2006) studied the  $O_3/H_2O_2$  application to understand the influence of parameters such as pH, ozone,  $H_2O_2$  dosage and water quality parameters, such as temperature, on the removal of MIB/geosmin. The results showed that removal efficiencies for both MIB/geosmin increased with increase in temperature, ozone dosage, pH and  $H_2O_2$  concentration. Specifically, Koch et al. (1992) through a study of Colorado River water concluded that ozone dosages of 1, 2, and 4 mg/l removed 58%, 65%, and 75% of the MIB, respectively, and that an ozone dose addition of hydrogen peroxide (0.2 mg $H_2O_2$ /mg $O_3$ ) improved MIB removal by approximately 20%. Carollo (2000) showed that ozonation (1.5 to 2 mg/l) of Arizona surface waters during different seasons achieved only 10% MIB removal in 19 °C water but 85% in 27 °C water. Westerhoff et al. (2006) also developed an empirical model to predict contact time requirement, odorant oxidation and bromate formation, that is the biggest limiting factor using these oxidants.

Removal of MIB/geosmin by AOPs depends on various water quality parameters, such as pH and NOM concentrations. The capital and energy costs associated with these technologies can be significantly high, especially for large scale applications. It must be considered also the risk of formation of harmful disinfection by products through these processes; for instance, ozonation could generate byproducts such as aldehydes, ketones and brominated compounds in water containing bromide. However, these technologies are being used more commonly and could be optimized for effective removal of these odorants (Srinivasan and Sorial, 2011).

Another alternative that can be considered is the biological treatment, often used in combination with ozonation. Ho et al. (2007) showed the removal of odor/taste causing compounds by biological sand filtration and identified four different bacteria responsible for biodegradation. Guo et Al. (2016) evaluated MIB and geosmin removal in Shanghai water treatment plant, which was equipped with coagulation, sedimentation, ozonation, Biological Activated Carbon (BAC) filtration, sand filtration, and chlorination. They demonstrated, through a 13 months monitoring

using FPA method, that the combination ozonation-biological treatment can be effective in the removal of taste and odor causing compounds. The ozone dose was 1.0 mg/l with reaction time of 15 min. The empty bed contact time and filtration velocity of the activated carbon filter were 16 min and 8.3 m/h, respectively. They noted that the musty odor typical of MIB and geosmin was completely removed. Another solution to treat taste/odor causing compounds could be the adsorption on activated carbon. Some studies showed that Granular Activated Carbon (GAC) filters, can be very efficient for MIB/geosmin treatment, by removing the compounds below the OTC. Generally, the vegetal GACs have better affinity to MIB/geosmin than mineral GACs, and the performances of the regenerated GACs are comparable to the virgin ones. The biggest issue is the long-term performance, because it is demonstrated that after 1-2 years the performance drops significantly, resulting in higher concentrations in the effluents (Srinivasan and Sorial, 2011). PAC is another way of using activated carbon for facing taste and odor episodes and it is normally used prior to filtration. PAC biggest issue is the competition with NOM. Ho and Newcombe (2005) found that NOM, especially lower MW fractions, comparable in size with MIB, reduced MIB adsorption by PAC due to competitive adsorption. Moreover, an increase in turbidity resulted in larger coagulation floc size which in turn reduced MIB adsorption further due to incorporation of the PAC particles into these flocs. They ran tests using a raw water of a reservoir, treated with alum as coagulant,  $PAC = 15 \text{ mg/l}$  and contact time of 15 min. They showed that increasing alum concentration from 20 ng/l to 120 ng/l the turbidity decreases of 97%, but MIB concentration increases from 25 ng/l to 30 ng/l. However, PAC has a lot of important features, such as high removal efficiency and great flexibility in the application, allowing to turn on/off dosages and also to adjust dosages depending upon the severity of the event. These are fundamental features in MIB/geosmin treatment because of the seasonality that characterizes odor and taste episodes (Srinivasan and Sorial, 2011).

Every study about MIB and geosmin removal shows that, regardless of the type of treatment used, geosmin is more easily and efficiently removed than MIB.

Because of the features of each alternative described above, PAC is probably the most efficient and currently the most commonly practiced technology for MIB/geosmin removal.

### 3.6 Adsorption with Powdered Activated Carbon (PAC)

Activated carbon can be produced from almost any carbonaceous material. Common materials include bituminous coal, lignite coal, coconut shells and wood. The preparation of the activated carbon includes two steps:

1. the carbonization of the raw materials that are fired in the absence of oxygen;
2. the carbon activation, through a heating process at extremely high temperatures (315 – 925 °C) in the presence of carbon dioxide or steam.

If compared with the granular form the powdered one has some advantages, such as the smaller dimension of the particles and the possibility to vary the dose applied according to the treatment demand (Najm et al., 1991).

Matsui et al. (2015) showed that depending on the raw material of the carbon it is necessary to vary the dimension of the powder to maximize the efficiency. For example, they showed that with hydrophobic compounds, like geosmin, if it is used a carbon coming from coconut it is recommended a particle with a diameter of a few micrometers.

Najm et al. (1991) showed that PAC removal efficiency depends on its concentration and on the type of compounds to be removed, being more efficient in the removal of geosmin than of MIB. They carried out some tests, using raw water, about trichloropropane (TCP) removal with PAC and noted that with an isotherm conducted with an initial TCP concentration of 500 mg/l a carbon dosage of 1 mg/l is required to reduce the concentration of TCP in ground water from 10 to 0.5 mg/l. However, an isotherm conducted with an initial concentration of 10 µg/l leads to the prediction that a carbon dosage of 6.5 mg/l is required for the same removal. It is fundamental to define the right PAC dose, the contact time needed and the application point of the PAC in the water treatment plant to obtain a high removal efficiency (Najm et al., 1991; Ferreira Filho and Fernandes, 2005). About PAC

application point in a drinking water treatment plant there are several alternatives, each one with the pros and the cons that should be evaluated (Edzwald, 2011). The addition of PAC at the raw water intake (point A, Figure 2) is a good solution because it allows the highest possible contact time between PAC and pollutants, enhancing the adsorption, but at this point there are still a lot of organic compounds that could be adsorbed by the PAC, decreasing its adsorption capacity towards MIB and gesomin. Another alternative is the addition of PAC immediately before the addition of the coagulants (point B, Figure 2), but the metal hydroxide, formed during coagulation, precipitates and may occupy PAC active sites decreasing the adsorption capacity. To solve the obstacles of the above-mentioned alternatives, a solution may be adding the PAC only before the filtration (point C, Figure 2), as suggested by Sontheimer et al. (1988), even if the structure of most of the drinking water treatment plants doesn't allow the PAC addition at this point. The most common choice among the above mentioned is PAC addition at the raw water intake, usually together with an oxidant for the pre-oxidation stage. The action of some oxidants can interfere in the PAC adsorption capacity, oxidizing its active sites. A typical example of this phenomena is the free chlorine that, as demonstrated in several studies, reduce PAC adsorption capacity significantly (Gillogly et al., 1998; Srinivasan and Sorial, 2011). It is important to find an alternative oxidant that can substitute chlorine, in order to avoid a PAC over-dosage to compensate the decrease in its adsorption capacity.

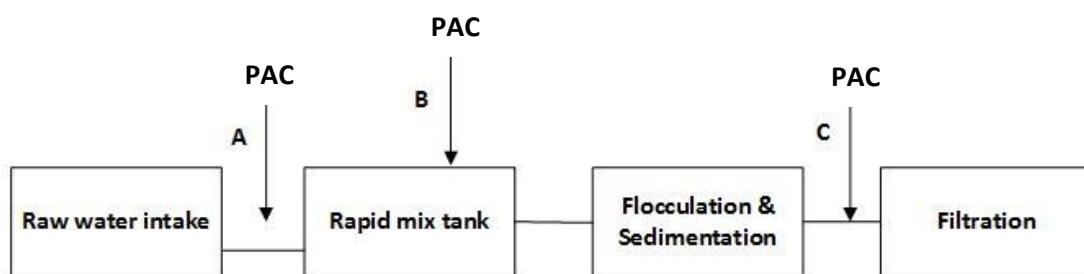


Figure 2: Alternative application points of PAC in drinking water treatment plant.

### 3.7 PreOxidation- Potassium permanganate: an alternative to chlorination

Drinking water production from natural sources needs the removal of many compounds, mainly humic substances, inorganic and organic species and toxic micropollutants. Part of these compounds can be removed through the pre-oxidation treatment. Usually pre-oxidation goal is the removal of mineral compounds, color, turbidity and suspended solids, bad tastes and odors; in addition, this step partly degrades natural organic matter (NOM) and inactivates microorganisms (Camel and Bermond, 1998).

Among the available oxidizing compounds the most used are: chlorine, chlorine dioxide, ozone and potassium permanganate.

During the last years potassium permanganate (Figure 3) use has become very common, due to its special features such as (USEPA, 1999):

- it is a strong oxidant;
- it can be used to control taste, odors, and biological growth in treatment plants;
- it removes colors, iron and manganese;
- it can inactivate various bacteria and viruses even it is not used as disinfectant.

Potassium permanganate is not used directly as a disinfectant, however its capacity of bacteria and virus inactivation allows to use less disinfectants during the treatment, limiting the production of disinfection typical byproducts like THMs. Besides, potassium permanganate can limit by products production oxidizing their precursors (USEPA, 1999). A potassium permanganate concentrate solution (typically 1% to 4%) (USEPA, 1999) is generally used and dosed in the rapid mix tank in conjunction with coagulants. Potassium Permanganate doesn't require a special mixing equipment at the point of injection to be effective and it gives water a pink color. In some cases it can be added in

crystal form (Edzwald, 2011). During the last years the addition of potassium permanganate before coagulation has become quite common, because in this way longer contact time are allowed (Edzwald, 2011; Naceradska et al., 2017).

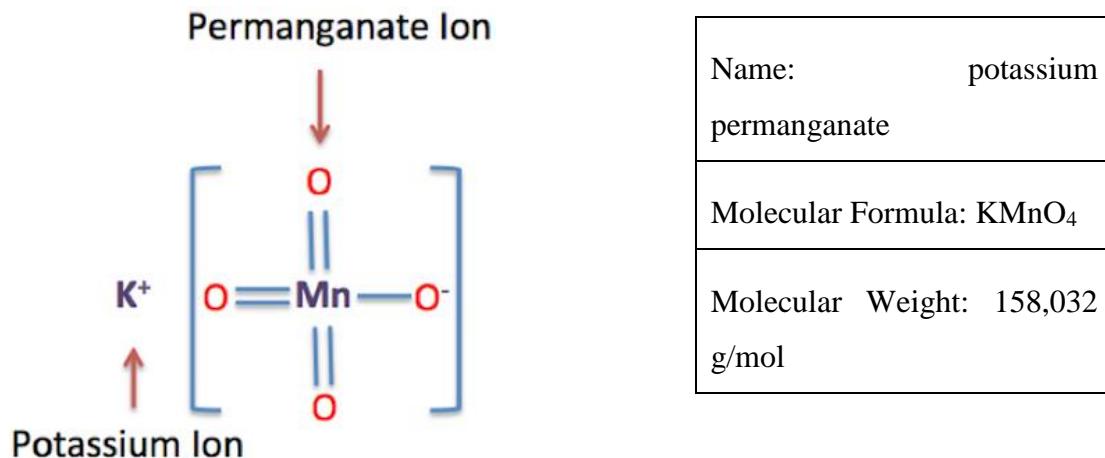
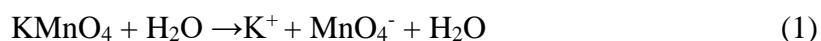
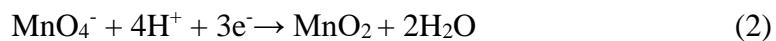


Figure 3: Physical and chemical characteristics of potassium permanganate.

The permanganate behavior in water is described by equation 1:



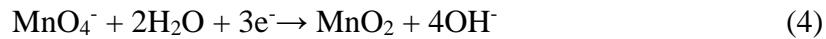
The oxidation depends on the pH (USEPA, 1999). Under neutral conditions (pH = 7-8) the oxidation half-reaction is:



With pH more acid, approximately 3, the reaction is:



Under alkaline conditions (pH>8), the half-reaction is:



All the reactions are exothermic.

It means that at basic or neutral pH the formation, and subsequent precipitation, of manganese dioxide occurs and the precipitate must be removed during the following treatments (Edzwald, 2011).

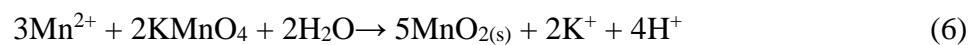
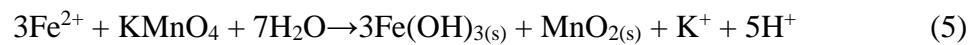
A potassium permanganate primary use is the oxidation of iron and manganese. Iron and manganese are not health hazardous but they can cause aesthetic problems and bad taste. Manganese can be objectionable in water even when present in smaller concentrations than iron (Dvorak et al., 2014).

EPA classify the drinking water standards in two categories (Dvorak et al., 2014):

- Primary Standards - based on health consideration and enforceable.
- Secondary Standards - based on aesthetic factors that may affect the suitability of water supplies. They are recommended but not enforceable.

Either iron and manganese belong to Secondary Standards (Dvorak et al., 2014).

Permanganate oxidizes iron and manganese to convert ferrous (2+) iron into the ferric (3+) state and manganese (2+) to the (4+) state. The oxidized forms will precipitate as ferric hydroxide and manganese dioxide. The equations 5 and 6 describe these reactions (USEPA, 1999):



It can be observed that iron and manganese oxidation needs alkalinity (1.49 mg/L as  $\text{CaCO}_3$  per mg/L of  $\text{Fe}^{+2}$  and 1.21 mg/L as  $\text{CaCO}_3$  per mg/L of  $\text{Mn}^{+2}$  oxidized). The potassium permanganate dosage required for oxidation is 0.94 mg/mg iron and 1.92 mg/mg manganese.

Another important characteristic of potassium permanganate, as already mentioned, is the limitation of disinfection by products formation. Ficek and Boll (1980) show using potassium permanganate as oxidant, it can be achieved a great reduction of THMs and HAAs. C. Blanck (1979) reported that a 76% reduction in finished water THMs was achieved when the point of chlorination was moved from the raw water, and potassium permanganate was used as a preoxidant agent. A report from the Frankfurt Water Plant in West Germany indicated an overall reduction of 50% in HAAs generation moving chlorination from raw water and adding permanganate (Ficek and Boll, 1980). However, the reduction of THMs is mainly due to the elimination of raw water chlorination.

In addition, some studies show an increase in THM concentration when  $\text{KMnO}_4$  and free Cl were present simultaneously. A test in California shows that chlorination of the raw water produced a concentration of 83 ppb THM. By eliminating prechlorination, adding  $\text{KMnO}_4$ , coagulating, filtering, and then post-chlorinating, the final THM concentration was reduced to between 30 and 40 ppb. By adding  $\text{KMnO}_4$ , and chlorine together (no coagulation or filtration) the final THM concentration was increased to 99 ppb, higher than the one produced by chlorination of the raw water alone. This test indicated that permanganate should be added, the water coagulated, and only then should the water be chlorinated to produce the best results (Ficek and Boll, 1980).

To remove taste and odor from drinking water Glaze et al. (1990) demonstrated that potassium permanganate could be very efficient, but for MIB and geosmin its removal performance is not satisfactory (13% for MIB and 15% for geosmin). It

means that the sole application of potassium permanganate would not be sufficient, but it must be applied in conjunction with other technologies like activated carbon.

It should be mentioned the influence of  $\text{KMnO}_4$ , as other oxidants, on the adsorption of PAC. Specifically  $\text{KMnO}_4$  can create functional groups on the PAC surface, such as carboxyl, ketyl and ether groups, which have weak reaction with non-polar organic matter and can reduce PAC removal performances. Potassium permanganate can also change the PAC physical characteristics, limiting its adsorption capacity. Zhang et al. (2013) compared the characteristics and the NOM removal performances of a normal and an oxidized PAC. They showed that the isotherms of the oxidized and normal PAC had a similar shape, while the specific surface area, pore total volume and average pore radius of the oxidized PAC all decreased because  $\text{KMnO}_4$  oxidized some of the PAC adsorption capacity. It was also demonstrated that the main surface functional groups of the PAC don't not vary. Ferreira Filho and Fernandes (2005) demonstrated that the application of chlorine and PAC decreases the removal performance of MIB and geosmin, proportionally to chlorine dosage. They carried out adsorption kinetic tests using raw water, different doses of chlorine, PAC and showed that with a dose of 4.0 mg  $\text{Cl}_2/\text{l}$  MIB residual value was 54 ng/l, while without chlorine this value was only 14 ng/l. Potassium permanganate also influences the removal performances, especially when it is applied in dosages greater than the needed ones, but its negative effect is lower than the chlorine one and can be almost cancelled by using the right dosage (Ferreira Filho and Fernandes, 2005). Ferreira Filho and Fernandes demonstrated it through tests with raw water where  $\text{KMnO}_4$  demand was 1 mg/l. They showed that when  $\text{KMnO}_4$  was used according to the demand MIB and geosmin residual values were lower than when it was over dosed. Therefore, it is fundamental to define the right permanganate dose that, usually, depends on the concentrations of iron, manganese and organics compounds in raw water.

## 4 MATERIALS AND METHODS

### 4.1 Reagents

The water used during the experiments was a synthetic water, produced in the laboratory mixing ultrapure water (milli-Q), sodium chloride (NaCl), calcium chloride (CaCl) and sodium bicarbonate (NaHCO<sub>3</sub>). The reagents were purchased from the Polytechnic School of the University of São Paulo's laboratory. The salts were added to reach a pH between 7.0 e 8.0, alkalinity of 100 mg/L as CaCO<sub>3</sub> and hardness between 30 and 40 mg/L as CaCO<sub>3</sub>, which are typical characteristics of the raw water commonly treated in São Paulo.

The samples of MIB and geosmin and the micro syringe used to add them to the synthetic water came from the Basic Sanitation Company of São Paulo State (SABESP) with a concentration of 100 µg/mL.

The activated carbon used has bituminous origin (WPH-M) supplied by Calgon (Table 3). It is recommended for the removal of MIB and geosmin in drinking water treatment.

*Table 3: Calgon WPH-M PAC's specifications ([www.calgoncarbon.com](http://www.calgoncarbon.com)).*

Iodine number	500 mg/g (min)
Moisture by Weight	8% (max)
Screen size by Weight:	
Through 100 mesh	99% (max)
Through 200 mesh	95% (max)
Through 325 mesh	90% (max)

## 4.2 Jar Test equipment

The tests were performed using a jar test equipment, with six jars each of 2.5 liters volume capacity (Figure 4). The equipment had the possibility to regulate the speed gradient. All the tests were carried out at room temperature (25 °C).



Figure 4: Jar-test equipment used for the tests.

## 4.3 Tests

The tests were divided in 4 different stages. In stage 1 and 3 the first step was the preparation of synthetic water, with the characteristics explained in paragraph 4.1, MIB and geosmin were added, using the samples and the micro syringe, to the synthetic water to reach a concentration of 200 ng/l, which is typical of Southeast Brazil raw water supplies. Then the solution was mixed for approximately 10 minutes to reach a homogeneous concentration in the volume.

Afterwards, the water was put in the jar test equipment to begin the tests and the rotation was set on 125 rpm, to simulate the hydraulic behavior and the speed gradient in the rapid mix tank during the raw water intake.

In stage 4 the procedure was the same as in stage 1 and 3 but also adding iron (2+) ( $Fe^{2+}$ ) in the synthetic water.

In stage 2 was not used the jar test equipment but it was run using a 1.5 l beaker mixed with a magnetic stirrer. The contact time between PAC and permanganate was 2 hours. In this stage the pollutants were not present in the water.

All the samples resulting from the tests and the ones containing the synthetic water were collected, for the purpose of having a double test, in two test-tubes and sent to the SABESP laboratory for the residual MIB/geosmin analysis.

#### **4.3.1 Analytical methods**

Residual potassium permanganate was detected using the 4500Cl F - DPD Ferrous Titrimetric Method (DPD) (APHA, 2005). It is usually used to detect residual chlorine, but with a correction factor (0,893) (Carus Chemical, 2004) it can also be applied with other oxidants like KMnO<sub>4</sub>.

To detect the residual concentration of MIB and geosmin it was used the 6040 D-Solid-Phase Microextraction (SPME) (APHA, 2005) in the SABESP laboratory.

Some membranes used in stage 3 were analyzed through the Scanning Electron Microscopy with Energy-Dispersive X-ray Pectroscopy method (SEM with EDS), to observe PAC particles and the elements retained on them.

#### **4.3.2 Stage 1: application of KMnO<sub>4</sub> and PAC with different concentrations to assess the removal efficiency of MIB and geosmin**

In stage 1 two types of tests were conducted: one without KMnO<sub>4</sub> and six different PAC concentration (0, 5, 10, 20, 30, 40 mg/l) (Figure 5), the second one with the same PAC concentrations as the first test and the addition of KMnO<sub>4</sub> in three different concentrations (1, 2, 4 mg/l) (Figure 6).

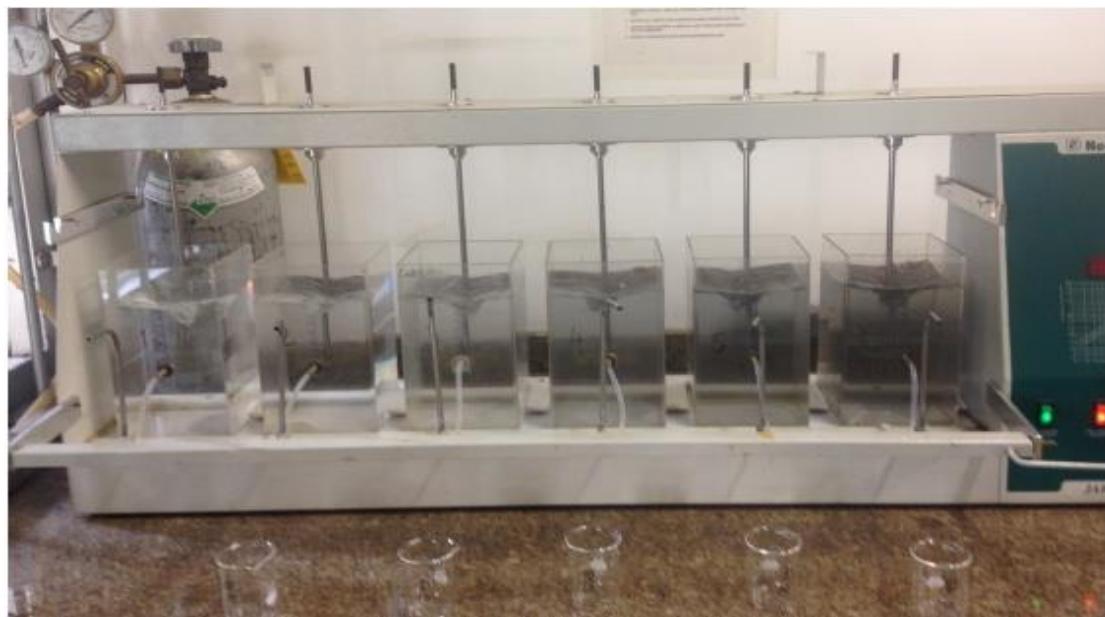


Figure 5: Water in the jar test equipment with different PAC concentrations (0, 5, 10, 20, 30, 40 mg/l). It can be noted the water colour change increasing PAC concentration.



Figure 6: Water in the jar test equipment with six different PAC concentrations and addition of  $KMnO_4 = 2$  mg/l.

After 30 minutes a sample of 200 ml of water was collected from each jar: 100 ml were used for the residual  $KMnO_4$  analysis; to the other 100 ml a solution of sodium thiosulphate was immediately added to precipitate  $KMnO_4$  and then a filtration with a 0.45  $\mu m$  pore-size membrane was applied to retain the PAC (Figure 7).

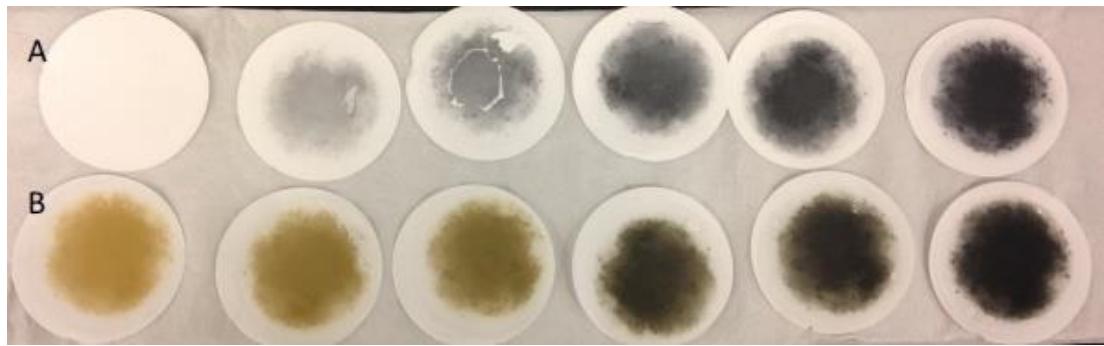


Figure 7: Membrane used to filter the samples treated with PAC only (A) and with the combination of PAC- $KMnO_4 = 2\text{ mg/l}$  (B). It can be noted the typical yellow colour due to the presence of permanganate.

#### 4.3.3 Stage 2: kinetic test with $KMnO_4$ and PAC and without pollutants

In stage 2 tests with different PAC and  $KMnO_4$  concentrations were performed. Specifically, three PAC concentrations (10, 20, 40 mg/l) were used and for each of them three concentrations of  $KMnO_4$  (1, 2, 4 mg/l); nine tests were carried out.

100 ml were collected for the residual permanganate analysis at 9 different times: 10, 20, 30, 45, 60, 75, 90, 105 and 120 minutes. In Figure 8 it can be observed the change of the water's color due to the adsorption of the oxidant on PAC.



Figure 8: Sample with the application of 40 mg/l of PAC and 1 mg/l of  $KMnO_4$  at times 0, 30, 60 e 120 minutes.

#### 4.3.4 Stage 3: kinetic test with $KMnO_4$ , PAC and pollutants

In stage 3 initially the PAC concentration used was 20 mg/l, combined with three different  $KMnO_4$  concentrations (0, 1, 2 mg/l). Afterwards it was decided to

apply a greater PAC concentration (40 mg/l). The water samples were collected at six different times: 5, 10, 15, 30, 45, 60 minutes.

Approximately 200 ml of water were collected from each jar; half of the collected quantity was used for the residual KMnO<sub>4</sub> analysis while the remaining 100 ml were used as follows:

- in a part was added a solution of sodium thiosulphate to precipitate KMnO<sub>4</sub> and then was applied a filtration with a 0.45 µm pore-size membrane to retain the PAC;
- another part was filtered without the precipitation of KMnO<sub>4</sub> to obtain a membrane where was possible to observe the KMnO<sub>4</sub> retained on the PAC through SEM with EDS analysis. Specifically, were analized the membranes collected at times 45 minutes and 60 minutes of each experiment.

#### 4.3.5 Stage 4: kinetic test with KMnO<sub>4</sub>, PAC, Fe<sup>2+</sup> and pollutants

In the last stage the same experiments as in stage 3 were performed, but also adding iron (+2) (Fe<sup>2+</sup>) in the synthetic water.

An iron concentration of 2 mg/l was used and 15 ml of HCl 0.5N for 15 l of synthetic water were also added to avoid iron precipitation. Adding this acid the water assumed new characteristics, specifically pH around 6 and alcalinity of 50 mg/l as CaCO<sub>3</sub>.

PAC concentration of 40 mg/l and three different concentrations of KMnO<sub>4</sub> X, X/2 and 2X were used, where X = 1.89 mg/l is the potassium permanganate concentration deriving from the stoichiometric reaction with iron (equation 5, paragraph 3.7). The water samples were collected at six different times: 5, 10, 15, 30, 45, 60 minutes. From each jar approximately 200 ml of water were collected and they were used as already explained in stage 1. For each test, at the times 5 and 60 minutes were filtered 250 ml more of water which were collected in other samples to analyze the iron residual. To allow the conservation of the residual iron and permit the analysis execution in the SABESP laboratory, in every sample were added 0.5 ml of nitric acid (HNO<sub>3</sub>).

## 5 RESULTS AND DISCUSSION

### 5.1 Stage 1

The purpose of the first stage was to verify the influence of potassium permanganate on PAC adsorption of MIB and geosmin.

Analyzing the results in Figure 9 a and b it can be noted that the influence of  $\text{KMnO}_4$  is not so important both for MIB and geosmin.

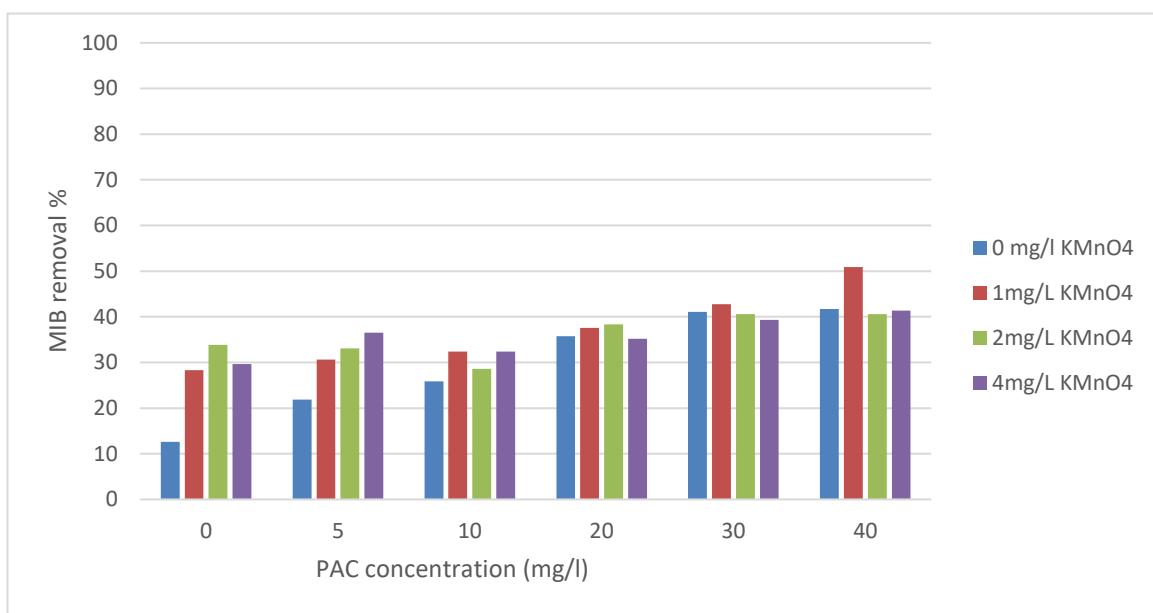
Observing specifically MIB removal (Figure 9a), it can be noted that for high PAC concentrations ( $> 20 \text{ mg/l}$ ) there is not a high difference in the removal, it is always around 40%, despite different  $\text{KMnO}_4$  concentrations. With lower PAC concentrations (PAC = 0, 5, 10 mg/l) the removal is less efficient, around 30%, independently from  $\text{KMnO}_4$  and PAC concentrations.

Observing geosmin behaviour (Figure 9b), it can be noted a greater variation in the removal at different PAC concentrations, ranging from 22% to 61% for 5 mg/l and 40 mg/l PAC respectively. The influence of permanganate once again doesn't appear so strong. The trend that can be noted from these data is that geosmin removal increases, for every PAC concentration, when  $\text{KMnO}_4$  increases (1 and 2 mg/l), however when  $\text{KMnO}_4$  reaches 4 mg/l geosmin removal decreases. Consequently, it seems that  $\text{KMnO}_4$  high concentrations can influence geosmin removal more than the MIB one. This trend is typical of conflicting processes where a trade-off for the best efficiency must be found.

Analyzing the trend of potassium permanganate residual concentration it can be noted a consumption of this oxidant (Figure 10). The oxidation power of  $\text{KMnO}_4$  on MIB and geosmin is not so strong (Srinivasan and Sorial, 2011; Glaze et al., 1990), therefore there is an interaction between  $\text{KMnO}_4$  and PAC that causes the consumption of the oxidant. That's why  $\text{KMnO}_4$  decreases when PAC concentration increases.

Results here obtained seem to contradict other studies (Ferreira Filho and Fernandes, 2005; Zhang et. Al, 2013) showing a little influence of potassium permanganate in PAC adsorption efficiency, even if the  $\text{KMnO}_4$  is dosed with higher concentrations than the needed ones. Moreover, geosmin seems to be more influenced by  $\text{KMnO}_4$  high concentrations than MIB and this contradicts the literature (Srinivasan and Sorial, 2011). Therefore, other tests must be carried out to better evaluate  $\text{KMnO}_4$  influence on PAC adsorption of MIB and geosmin.

a)



b)

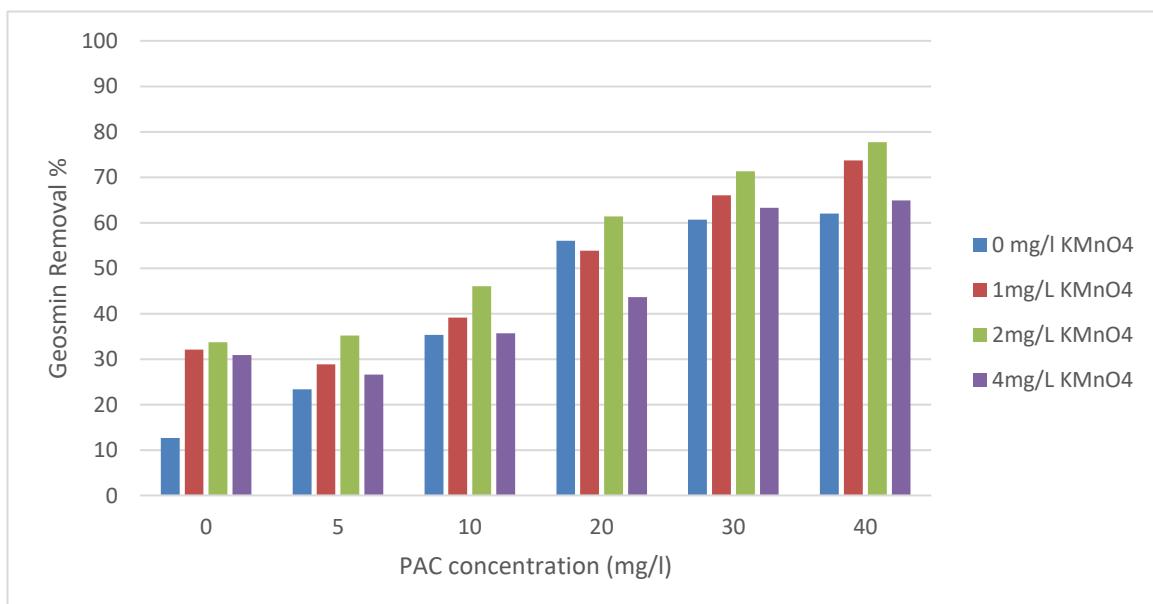


Figure 9: MIB (a) and geosmin (b) removal with different PAC and potassium permanganate concentrations (contact time = 30 min).

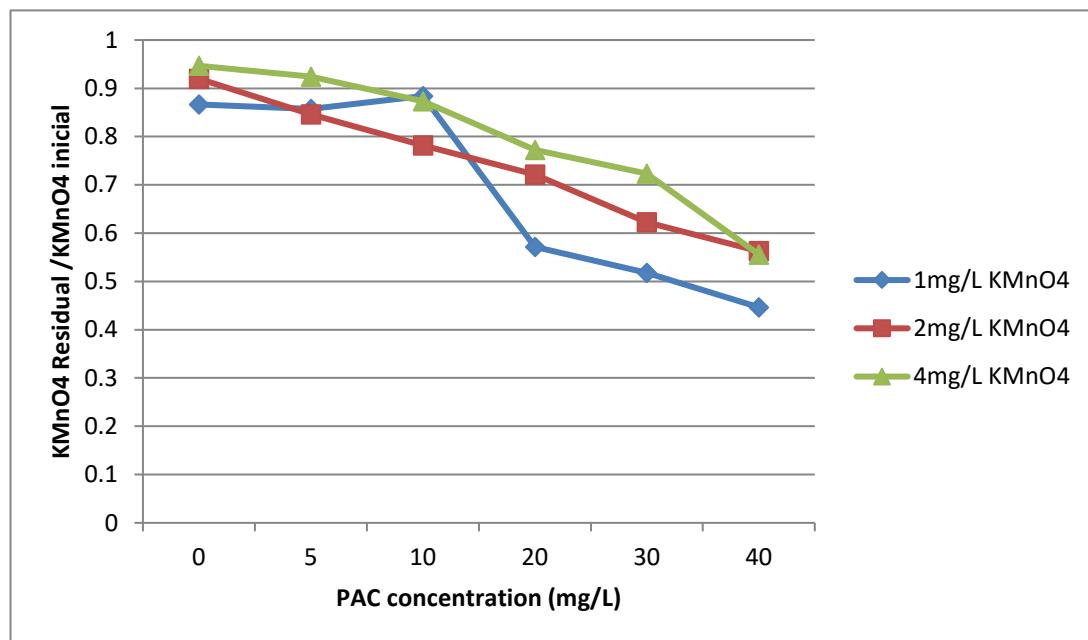


Figure 10: Residual potassium permanganate trend with different PAC concentrations.

## 5.2 Stage 2

The purpose of stage two was to evaluate the interaction between  $\text{KMnO}_4$  and PAC and to find the best kinetic model to describe it.

The kinetic model chosen to describe the interaction was a second order one, represented in equation 11. It was formulated by Bocelli et al (2003), who obtained it starting from the global equation of the chemical irreversible reaction with a second order kinetic, studied by Levenspiel (1972). Bocelli et al. used this equation to describe chlorine decay in disinfection. They noted that this model was the best to describe the rapid initial chlorine decay and the slower long-term chlorine consumption that happened. Analyzing the residual  $\text{KMnO}_4$  data it was observed a behavior similar to the chlorine one, characterized by a rapid initial consumption and a slower long-term decay, so it was decided to try to describe the adsorption with the same model.

$$C_A(t) = \frac{C_{A,0} - a}{1 - (a/C_{A,0})e^{-(C_{A,0}/a-1)\beta t}} \quad (11)$$

$$\alpha = \frac{aC_{B,0}}{b} \quad (12)$$

$$\beta = C_{B,0}k_A \quad (13)$$

Where,  $C_{A,0}$  and  $C_{B,0}$  are, respectively, the dosage of  $\text{KMnO}_4$  and PAC used;  $a$  and  $b$  are stoichiometric coefficient of the chemical reaction between PAC and  $\text{KMnO}_4$ ;  $k_A$  is the decay tax of  $\text{KMnO}_4$ . Because  $a$ ,  $b$  and  $k_A$  are not known, new parameter with a physical meaning were created to solve the equation. That's why were introduced the following parameters:

- $\alpha (\text{M/L}^3)$  that represent the stoichiometric concentration of permanganate necessary for the reaction;
- $\beta$  that is the oxidant's tax decay related to PAC concentration, like a first order reaction (equation 15).

$$\frac{dC_A}{dt} = -k_A C_B C_A \quad (14)$$

$$\frac{dC_A}{dt} = -\beta C_A \quad (15)$$

Equation 11 was solved to minimize the sum of the square of the errors between the observations and the results of the model. Then to evaluate the quality of

the model representation was used the Root-Mean-Square of the errors (SMQE) (WILKS, 2006).

The results of the application of the second order model are reported in Figure 11 a, b and c. The values of the parameters  $\alpha$ ,  $\beta$ , which characterize the curve, and of the RMSE, to evaluate the adaptation of the model to the observations, are reported in Table 4.

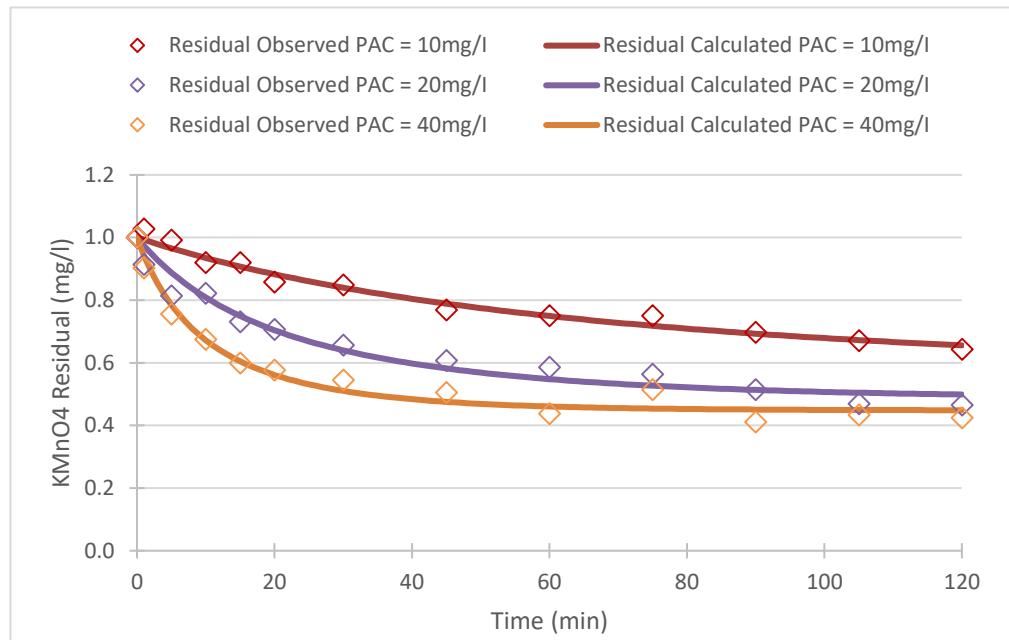
It is important to highlight that in the test with 1 mg/l of permanganate and 40 mg/l of PAC,  $\text{KMnO}_4$  concentration measure was quite difficult because of the high PAC concentration that gives to the water a black color which interferes in the titration of pink color. Probably that's why this curve has a trend a little bit different if compared with the curves with the same permanganate concentration (1 mg/l), but lower PAC concentrations (10 mg/l and 20 mg/l).

It can be noted a consumption of potassium permanganate in the first 30-45 minutes: 60% removal was obtained in 45 min, while almost 100% removal was reached in 75 min, after that  $\text{KMnO}_4$  concentration stabilizes on a constant value.

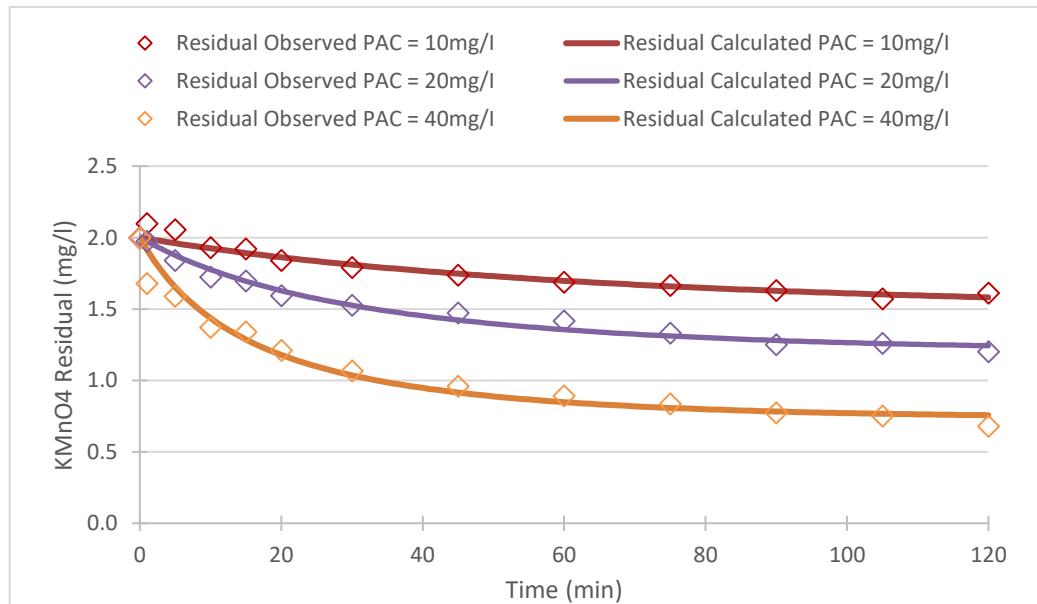
This behaviour can be explained by the interaction between PAC and potassium permanganate, already observed during stage 1 and reported in other studies (Gillogly et al., 1998; Ferreira Filho and Fernandes, 2005), where chlorine was used as oxidant. The behaviour of chlorine and potassium permanganate in contact with PAC can be compared: potassium permanganate, being an oxidant, oxidizes rapidly the adsorption sites on PAC surface and PAC adsorption capacity progressively decreases. Afterwards, the oxidizable fraction of PAC surface decreases, so less permanganate is consumed, until a point when no more PAC surface can be oxidized and the residual oxidant stabilizes on a constant value. The limiting factor for  $\text{KMnO}_4$  removal is therefore PAC surface. It can also be observed that  $\text{KMnO}_4$  consumption increases with PAC concentration (Figure 12a). The reason is that with higher PAC concentrations there is more oxidizable surface, so more oxidant is consumed. This is also highlighted by the values of the parameters  $\alpha$  and  $\beta$  of Table 4: at the same concentration of oxidant, the values of  $\alpha$ , which represent the quantity of permanganate that participates in the reaction, and  $\beta$ , that is the oxidant

decay, increase with the PAC concentration. This means that the kinetic reaction of potassium permanganate oxidation is mainly influenced by PAC concentration.

a)



b)



c)

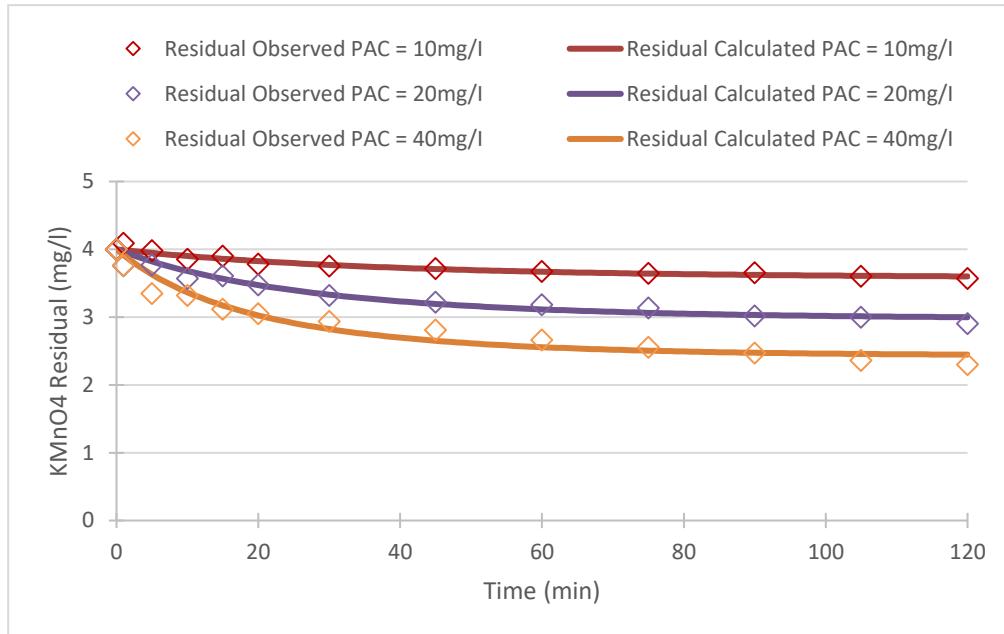


Figure 11: Application of the second order kinetic model to represent potassium permanganate residual with different PAC concentrations and: a)  $KMnO_4 = 1\text{ mg/l}$ ; b)  $KMnO_4 = 2\text{ mg/l}$ ; c)  $KMnO_4 = 4\text{ mg/l}$ .

Table 4: Parameters  $\alpha$ ,  $\beta$  and RMSE of the second order kinetic model for stage 2 (a) and 3 (b).

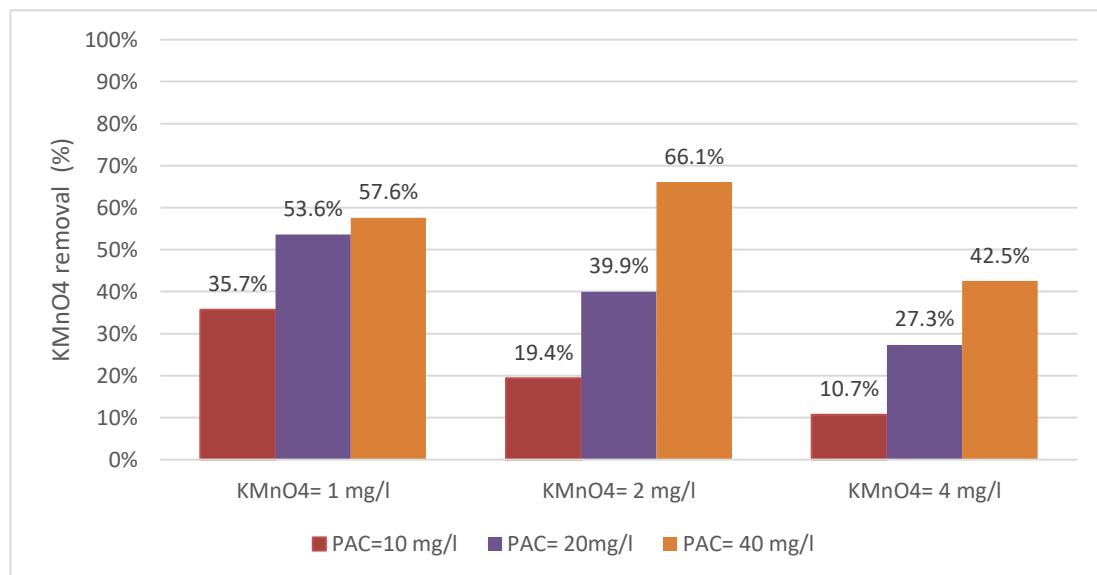
a)

$KMnO_4$ (mg/L)	PAC (mg/L)	$\alpha$ (M/L <sup>3</sup> )	$\beta$ (T <sup>-1</sup> )	RMSE (mg/L)
1	10	0.438	0.007	0.019
	20	0.597	0.018	0.035
	40	0.552	0.062	0.030
2	10	0.514	0.004	0.043
	20	0.796	0.014	0.033
	40	1.265	0.045	0.079
4	10	0.419	0.003	0.039
	20	1.024	0.010	0.077
	40	1.569	0.022	0.121

b)

KMnO <sub>4</sub> (mg/L)	PAC (mg/L)	$\alpha$ (M/L <sup>3</sup> )	$\beta$ (T <sup>-1</sup> )	RMSE (mg/L)
1	20	1.529	0.018	0.041
	40	0.648	0.030	0.031
2	20	0.588	0.023	0.100
	40	0.822	0.028	0.036

a)



b)

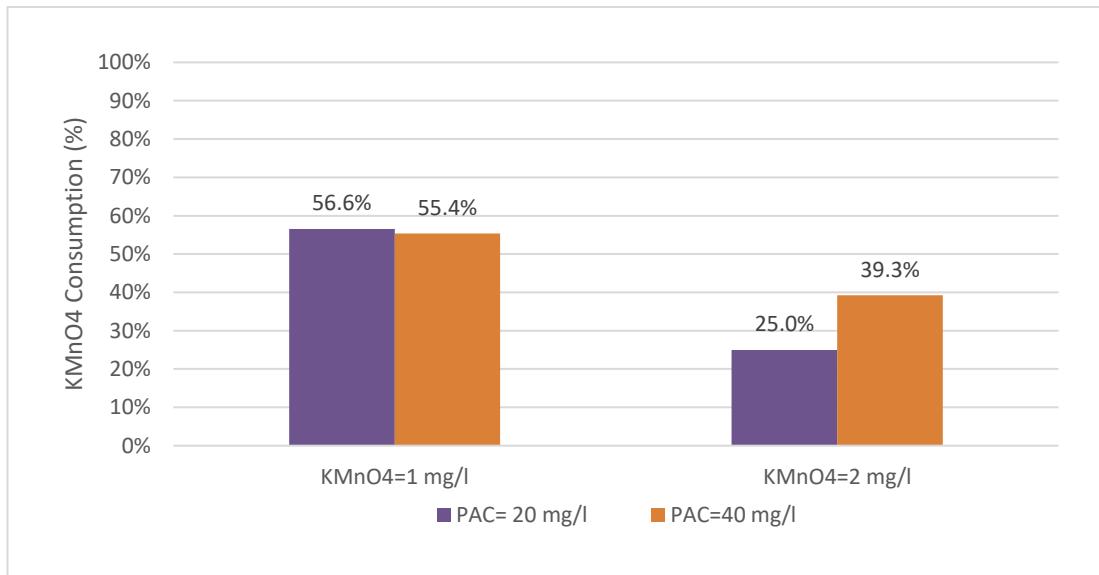


Figure 12:  $KMnO_4$  consumption with different initial permanganate and PAC concentrations in stage 2 (a) and in stage 3 (b).

### 5.3 Stage 3

The main purpose of this stage was to analize PAC removal efficiency of MIB and geosmin in presence of potassium permanganate with different concentrations. In this way it would be possible to evaluate potassium permanganate influence on PAC adsorption of the pollutants.

MIB and geosmin removal are reported in Figure 13, it can be noted a decrease of the pollutants removal efficiency when  $KMnO_4$  is added.

Analyzing MIB removal with  $PAC = 20 \text{ mg/l}$  (Figure 13a, Table 5), a high difference in the removal efficiency with or without the oxidant can be observed. Without  $KMnO_4$  the removal reaches, after 60 minutes, 75.3%, while with  $KMnO_4 = 1 \text{ mg/l}$  and  $KMnO_4 = 2 \text{ mg/l}$  it reaches, respectively, 52.3% and 36.1%. Anyway the differences among the removal values with or without the oxidant, except at time = 5 min, are always between 20% and 45%. It can also be noted that the removal difference between  $KMnO_4 = 1 \text{ mg/l}$  and  $KMnO_4 = 2 \text{ mg/l}$  is not so important, always less than 10%, except at time = 60 min where is 16%.

These results show that the influence of  $\text{KMnO}_4$ , regardless of its concentration, on PAC removal of MIB is quite important and MIB removal appears strongly affected by the presence of the oxidant.

Analyzing Table 5 and Figure 13b it can be noted that geosmin removal is more efficient and it also seems less influenced than MIB removal by the presence  $\text{KMnO}_4$ . Specifically the highest removal value, at time = 60 minutes, without  $\text{KMnO}_4$  is almost 95%, while with  $\text{KMnO}_4 = 1 \text{ mg/l}$  and  $\text{KMnO}_4 = 2 \text{ mg/l}$  it is respectively 81.2% and 56.5%. Therefore as demonstrated in stage 1 and as the literature (Srinivasan and Sorial, 2011) shows, PAC is more efficient in the removal of geosmin than MIB. Geosmin removal appears less influenced by  $\text{KMnO}_4 = 1 \text{ mg/l}$ . Comparing the removal values with and without that concentration of oxidant the values are often lower than 20%, while if  $\text{KMnO}_4 = 2 \text{ mg/l}$  the differences in the removal values are similar to the MIB ones, always between 20% and 45%.

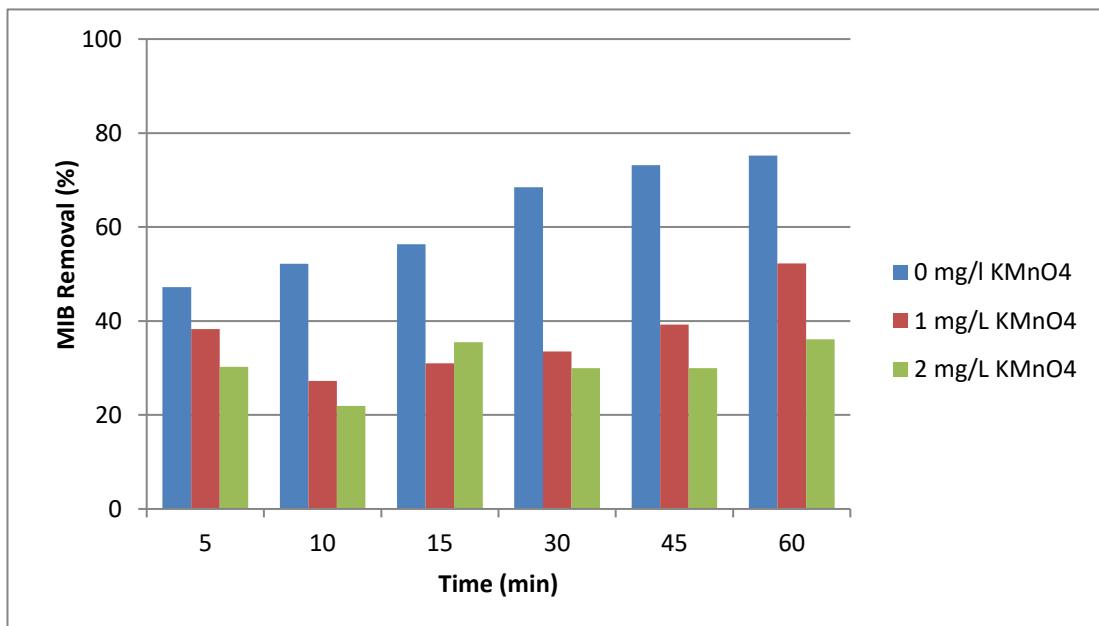
Therefore the influence of the oxidant is lower for geosmin adsorption, but with  $\text{KMnO}_4 = 2 \text{ mg/l}$  PAC performance seems still strongly affected.

The same tests were repeated with a double PAC concentration ( $\text{PAC} = 40 \text{ mg/l}$ ) to observe the differences in the trends. The result of this second test was similar to the first one, with a very strong influence of the oxidant in the adsorption of MIB and geosmin. Analyzing MIB (Figure 13c, Table 6), it can be noted that the maximum removal value after 60 minutes is 92.9% without  $\text{KMnO}_4$ , while it decreases to 54.7% and 52.3% when, respectively,  $\text{KMnO}_4 = 1 \text{ mg/l}$  and  $\text{KMnO}_4 = 2 \text{ mg/l}$ . The differences among the removal values with or without the oxidant, except at time = 5 min, are still between 20% and 40%. The removal difference between  $\text{KMnO}_4 = 1 \text{ mg/l}$  and  $\text{KMnO}_4 = 2 \text{ mg/l}$  is confirmed little, the maximum value is 7% at time = 15 minutes.

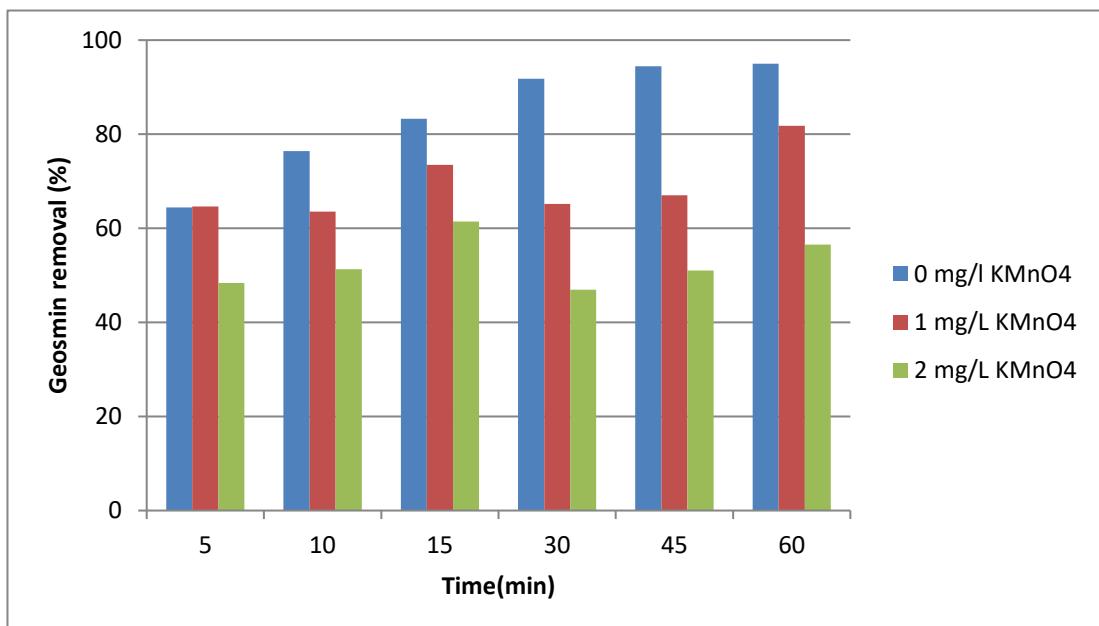
Geosmin removal (Figure 13d) is clearly confirmed as more efficient and still appears less influenced by the action of the oxidant. More specifically the maximum removal is 97.5% without oxidant and it decrease only up to 81.5% and 80.5% if, respectively,  $\text{KMnO}_4 = 1 \text{ mg/l}$  and  $\text{KMnO}_4 = 2 \text{ mg/l}$ ; the difference in the removal with and without  $\text{KMnO}_4$  ranges between 10% and 20%. A very little difference

between  $\text{KMnO}_4 = 1 \text{ mg/l}$  and  $\text{KMnO}_4 = 2 \text{ mg/l}$  is confirmed too, with values always under 4%.

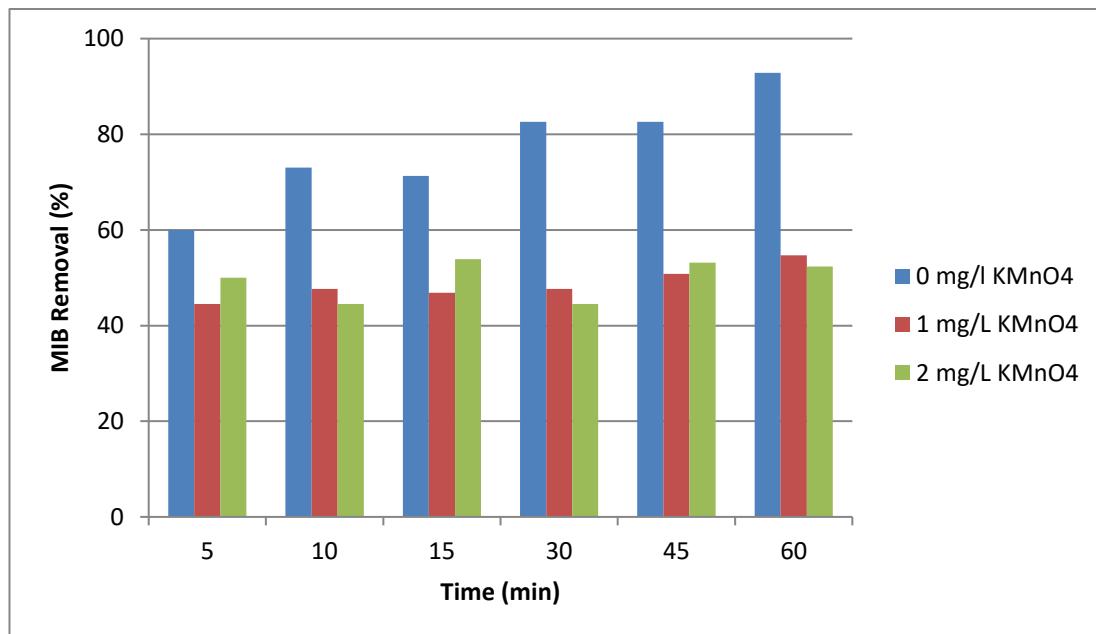
a)



b)



c)



d)

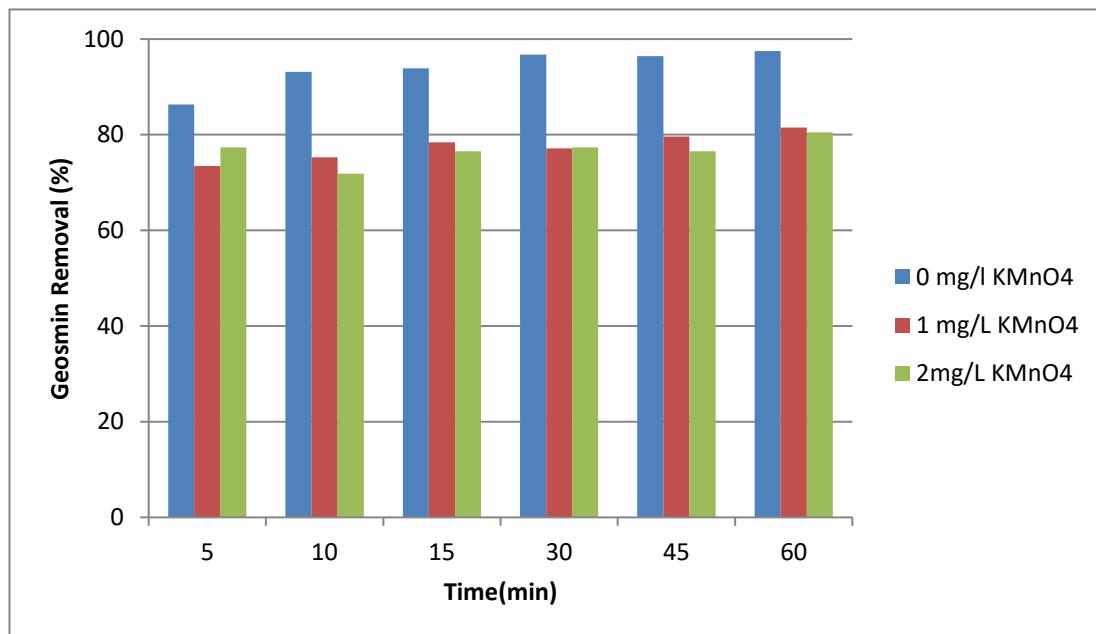


Figure 13: MIB and geosmin removal with PAC = 20 mg/ (a & b) and with PAC = 40 mg/ l (c & d).

Table 5: MIB and geosmin removal with different  $KMnO_4$  concentrations and  $PAC = 20\text{ mg/l}$ .

$KMnO_4$ (mg/l)	Time (min)	MIB removal (%)	Geosmin removal (%)
0	5	47.2	64.5
	10	52.2	76.4
	15	56.3	83.3
	30	68.4	91.8
	45	73.2	94.4
	60	75.2	95.0
1	5	38.3	64.6
	10	27.2	63.5
	15	31.0	73.5
	30	33.5	65.1
	45	39.2	67.0
	60	52.2	81.8
2	5	30.2	48.4
	10	21.9	51.3
	15	35.5	61.4
	30	29.9	47.0
	45	29.9	51.0
	60	36.1	56.5

Table 6: MIB and geosmin removal with different  $KMnO_4$  concentrations and  $PAC = 40\text{ mg/l}$ .

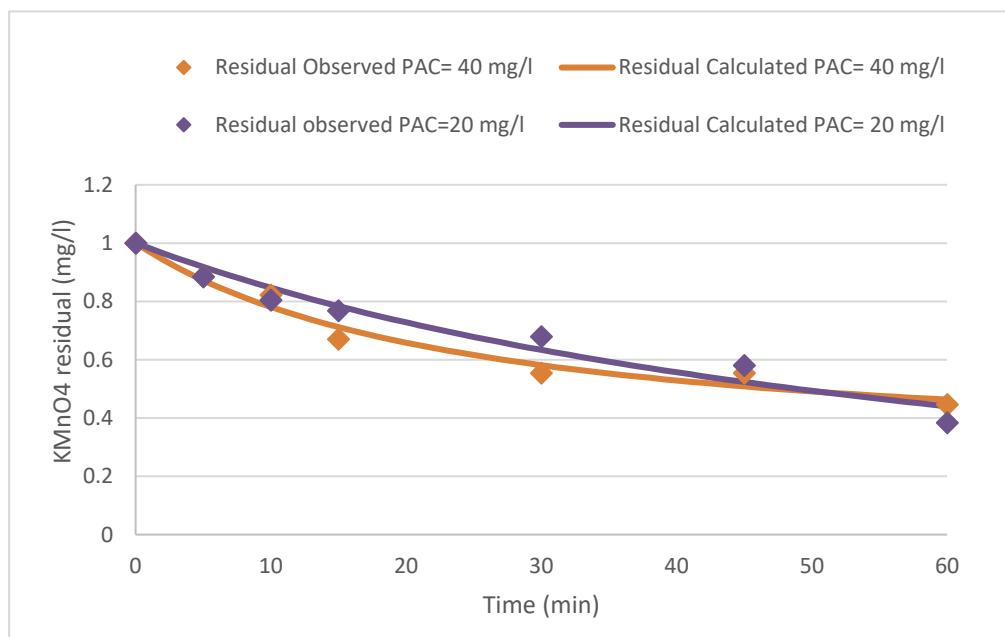
$KMnO_4$ (mg/l)	Time (min)	MIB removal (%)	Geosmin removal (%)
0	5	60.0	86.3
	10	73.0	93.2
	15	71.3	93.9
	30	82.6	96.8
	45	82.6	96.5
	60	92.9	97.5
1	5	44.5	73.5
	10	47.7	75.3
	15	46.9	78.4
	30	47.7	77.2
	45	50.8	79.6
	60	54.7	81.5
2	5	50.0	77.3
	10	44.5	71.9
	15	53.9	76.6
	30	44.5	77.3
	45	53.1	76.6
	60	52.3	80.5

Residual permanganate interpolation curves with the second order kinetic are shown in Figure 14. As in stage 2, it can be noted a rapid consumption of potassium permanganate, specifically for  $KMnO_4 = 2\text{ mg/l}$ , when most of the oxidant is consumed in the first 30 minutes and then its concentration stabilizes on a constant value. When  $KMnO_4 = 1\text{ mg/l}$ , instead, this behaviour is not so clear and the concentration decrease constantly in 60 minutes. The reason is, probably, still related to the oxidation of PAC surface caused by potassium permanganate.  $KMnO_4 = 1\text{ mg/l}$  is a low concentration, it doesn't oxidize all PAC surface in the first minutes, as happens when  $KMnO_4 = 2\text{ mg/l}$ , and the permanganate decreases constantly during 60 minutes.

The relation between PAC concentration and permanganate removal efficiency is reported Figure 12b. With  $KMnO_4 = 1\text{ mg/l}$  there is no difference in the

consumption despite PAC concentration, probably because the oxidant concentration is so low that it is removed regardless of PAC concentration, but with  $\text{KMnO}_4 = 2 \text{ mg/l}$  the consumption is confirmed, as in stage 2, more efficient when PAC concentration is higher. The parameter  $\alpha$  and  $\beta$  of Table 4b highlight this behavior, increasing as PAC concentration increases. These considerations confirm that the kinetic reaction of potassium permanganate oxidation is principally influenced by PAC concentration. Comparing Figure 12 a and b it can be noted that in case b the removal efficiency with  $\text{KMnO}_4 = 2 \text{ mg/l}$  are lower. This difference is probably due to the presence of the pollutants in stage 3 that, being adsorbed by the PAC, reduce its oxidizable surface and consequently  $\text{KMnO}_4$  consumption.

a)



b)

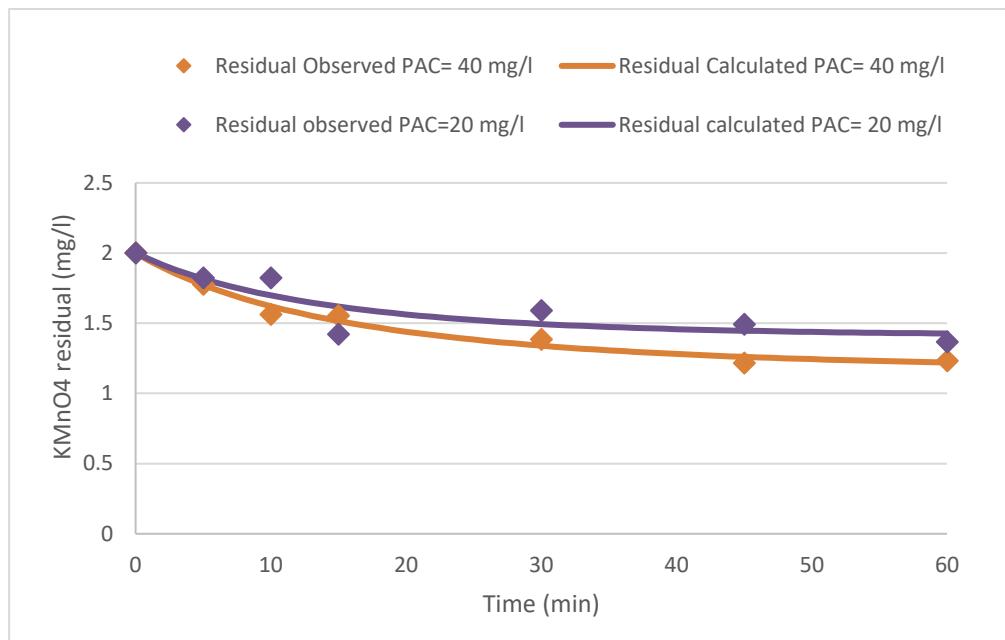


Figure 14: Application of Second order kinetic model to represent potassium permanganate residual with  $KMnO_4 = 1 \text{ mg/l}$  (a),  $KMnO_4 = 2 \text{ mg/l}$  (b) and different PAC concentrations.

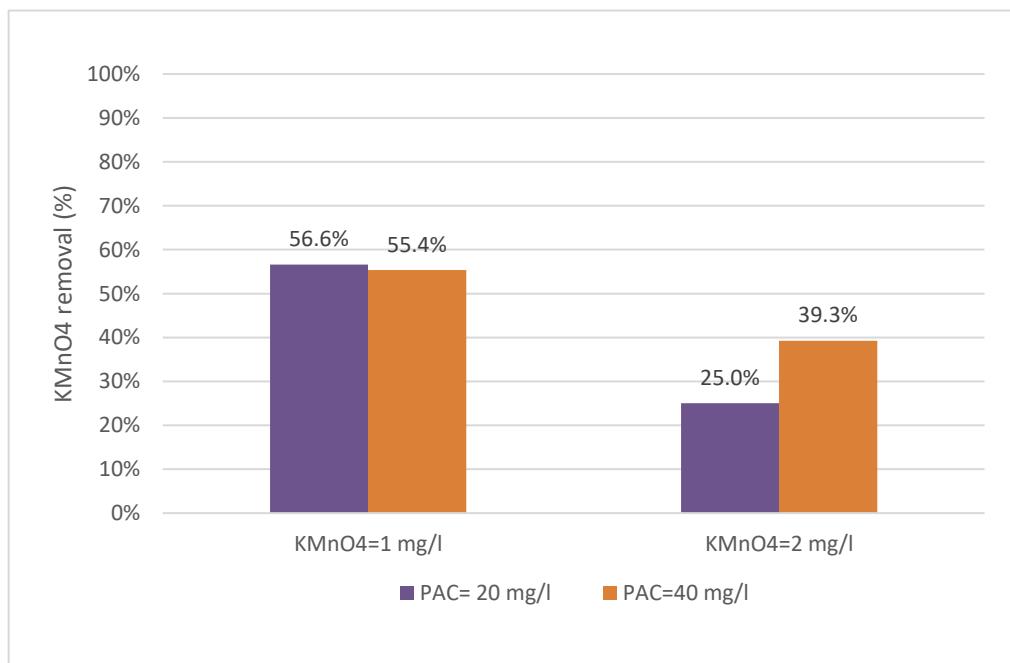


Figure 15:  $KMnO_4$  consumption with different initial permanganate and PAC concentrations.

For each jar-test carried out the membrane at 45 minutes and 60 minutes were collected, to observe through SEM with EDS the compounds retained on the carbon surface. Specifically the purpose was to observe how potassium permanganate oxidizes PAC surface. As an example, in Figure 16 is represented the SEM image of the membrane collected after 45 minutes in the test with  $KMnO_4 = 2\text{ mg/l}$  and  $PAC = 40\text{ mg/l}$ . It can be observed that the carbon surface is not homogenous and there are some specific points, highlighted in green and tagged with numbers, with different colors that seem to have particular characteristics. These points were analyzed through EDS to observe their characteristics and the compounds that are retained there. In Figure 17a the characteristics of point 1, that was highlighted because of its particular color, can be observed: it can be noted that there is a great concentration of carbon and an important quantity of manganese, therefore there are particles of activated carbon that, as a result of the oxidation by  $KMnO_4$ , have manganese retained on the surface. It can be noted that there are a lot of other compounds retained on the membrane, also in considerable quantities, as calcium, sulfur, silica and aluminium. The origin of these compounds is not clear, but probably the reasons are the compounds that were present in the jars and that couldn't be cleaned or a contamination happened during the transport of the membrane to the laboratory. These compounds can be noted also observing Figure 17b, representing EDS of point 2 which was highlighted because of its particular white color. The most present compounds in this part of the membrane are aluminium and silica, there is also a considerable quantity of potassium as a result of the oxidation of the surface by  $KMnO_4$ . In point 3, represented in Figure 17, the most present element is carbon and there are little quantities of other compounds, so in this part of the membrane, characterized by a grey color, there was only activated carbon without big quantities of other elements retained.

In Figure 18 and Figure 19 are represented through a color contrast the part of the membrane where are retained the greatest quantities of manganese and potassium as a result of potassium permanganate oxidation effect on the PAC surface. It can be noted that there are parts of the membranes, highlighted with more intense color, where the two elements are concentrated, specifically manganese is widespread in the membrane. These figures, together with the EDS of the highlighted points, allow

to observe that there is an interaction between PAC and  $KMnO_4$  that results in an oxidation of PAC surface.

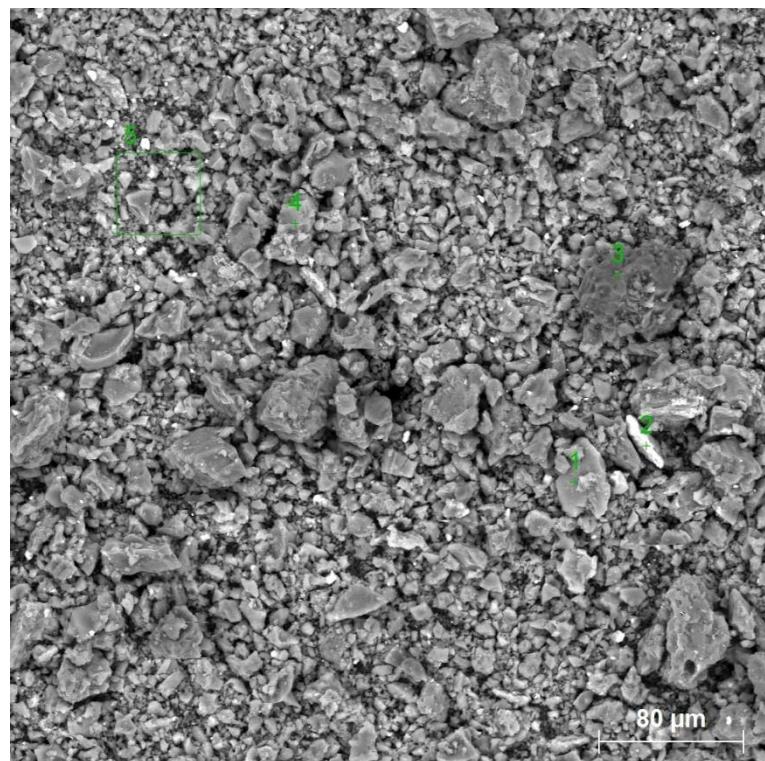
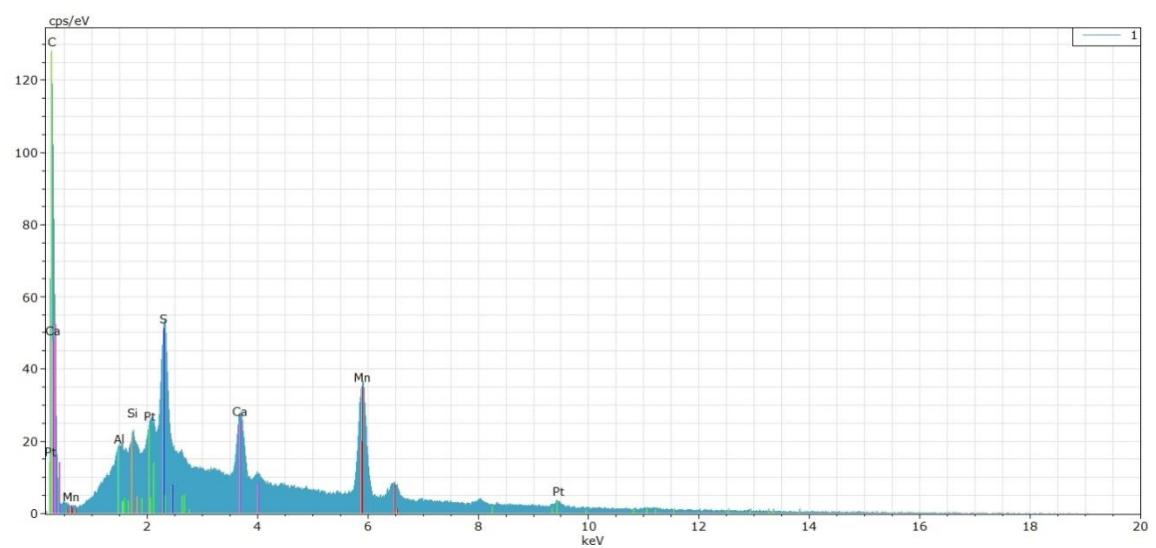


Figure 16: SEM image of the membrane collected at time = 45 minutes in the test with  $KMnO_4 = 2 \text{ mg/l}$  and  $PAC = 40 \text{ mg/l}$ . Some important points are highlighted with the numbers 1, 2, 3, 4, 5.

a)



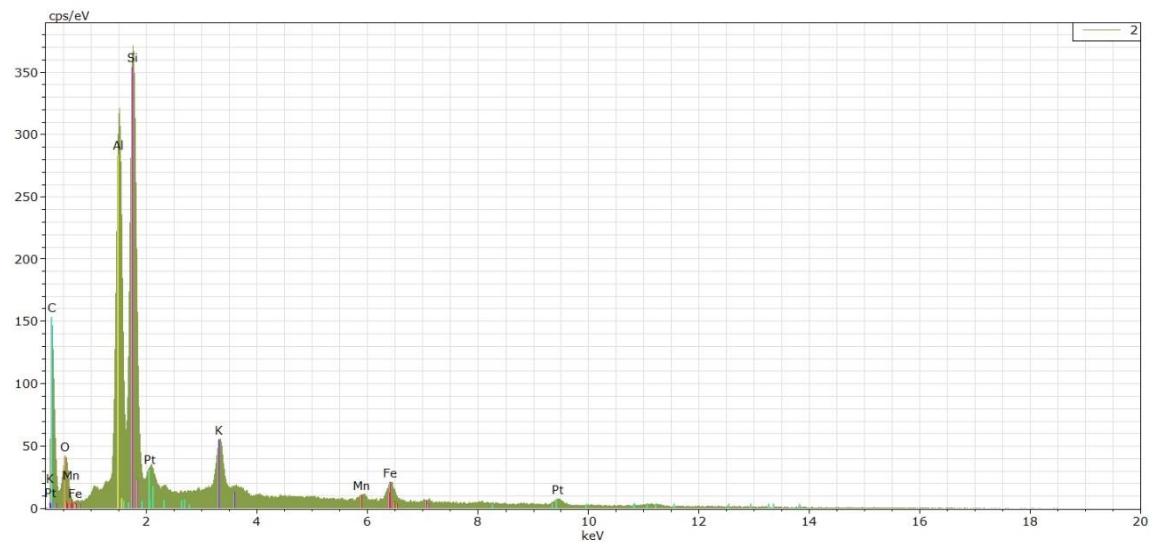
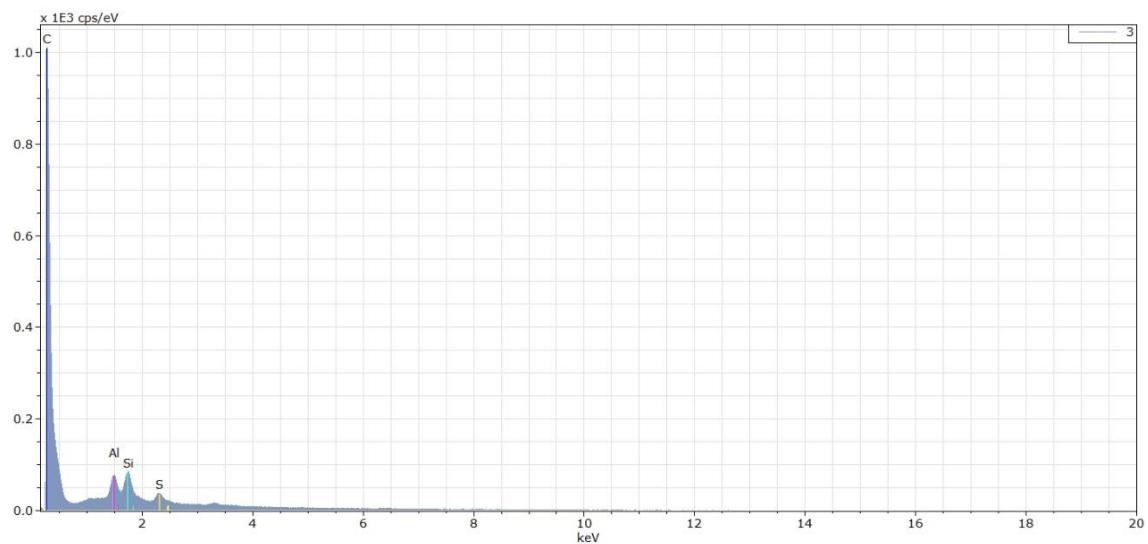
**b)****c)**

Figure 17: EDS of point 1 (a), 2 (b) and 3 (c).

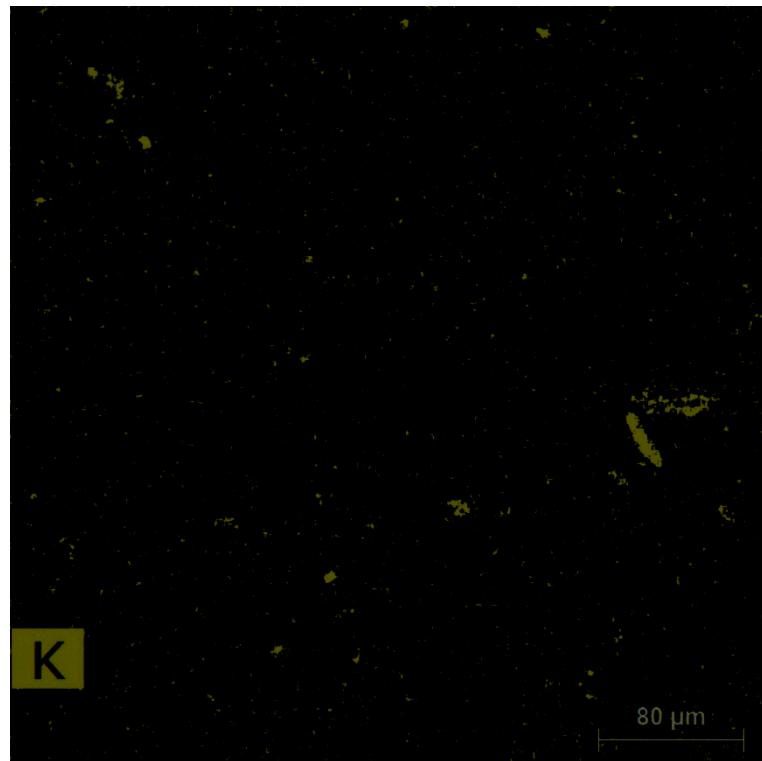


Figure 18: Traces of potassium (yellow parts) retained on the PAC in the membrane.

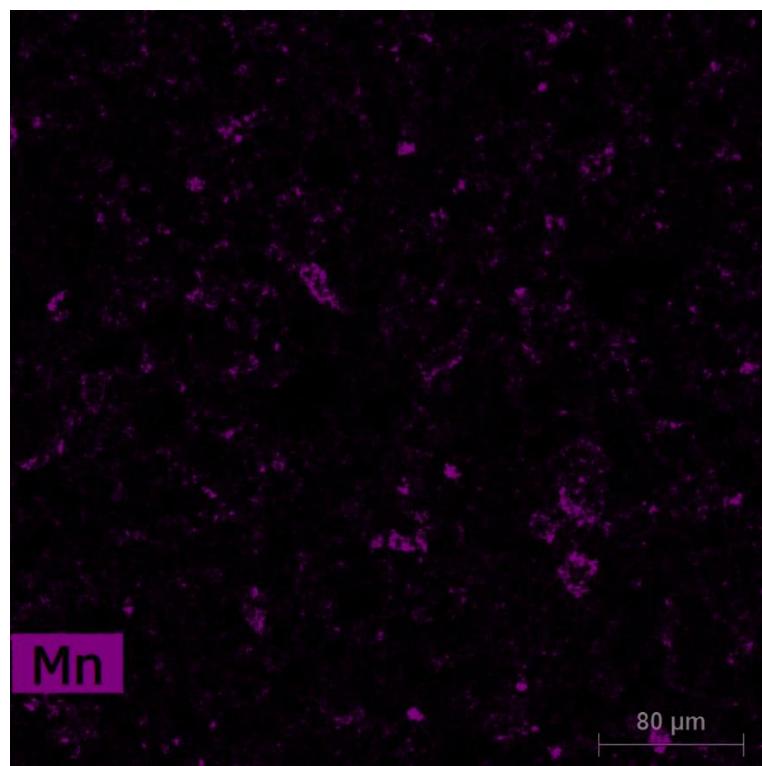


Figure 19: Traces of manganese (purple parts) retained on the PAC in the membrane.

## 5.4 Stage 4

The main purpose of stage 4 was to evaluate the potassium permanganate influence on the PAC adsorption of MIB and geosmin when also iron is present in the water.

Results as MIB and geosmin removal as summarized in Figure 20. A high decrease of the removal efficiency of both MIB and geosmin can be noted when permanganate is applied, especially at concentrations higher than the ones needed to oxidize iron.

Analyzing MIB removal (Figure 20, Table 7) a great difference in the removal values due to the application of different concentrations of potassium permanganate can be noted, specifically at 60 minutes the removal reaches 85.5% when  $KMnO_4 = X \text{ mg/l}$ , it goes up until 92.5% with  $KMnO_4 = X/2 \text{ mg/l}$  but it decreases until 39.3% if  $KMnO_4 = 2X \text{ mg/l}$ . Therefore, it doesn't appear a big difference if the oxidant is used with concentration  $X$  or  $X/2$ , in both cases high removal efficiencies are reached, but when  $KMnO_4$  is used with a concentration twice than the stoichiometric one the removal seems to suffer a big decrease.

Therefore, permanganate should be used at the stoichiometric concentration requested to oxidize  $Fe^{2+}$  because in case of higher dosage the residual permanganate can reduce PAC performance.

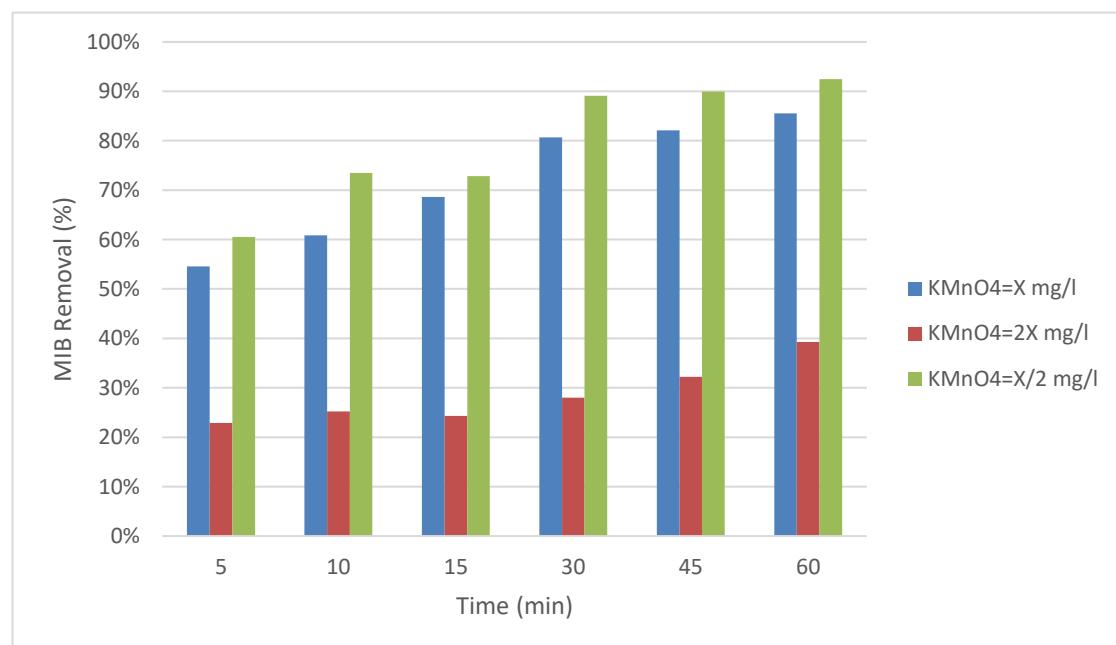
Analyzing Table 7 and Figure 20b geosmin removal is confirmed as more efficient and it still appears less influenced by potassium permanganate action. Specifically, the maximum removal values reached at time = 60 minutes are 97.1% if  $KMnO_4 = X \text{ mg/l}$ , 97.4% with  $KMnO_4 = X/2 \text{ mg/l}$  and 72.4% if  $KMnO_4 = 2X \text{ mg/l}$ . Therefore, the removal decreases because of the high permanganate dosages but the decrease is lower if compared with the MIB one.

Geosmin can be removed with high efficiency, higher than 95% with contact time > 30 minutes, when permanganate is dosed with the stoichiometric concentration. When permanganate is dosed with a concentration twice than the stoichiometric the

removal is quite influenced, anyway geosmin appears less influenced than MIB by the presence of the PAC.

The analysis of the data on the residual iron in the water (Figure 21) showed a great removal of  $\text{Fe}^{2+}$ , always higher than 95% regardless of  $\text{KMnO}_4$  concentration. This high removal efficiency is due to the action of two oxidants  $\text{KMnO}_4$  and the oxygen present in the water, since iron was removed even at under-stoichiometric concentrations of  $\text{KMnO}_4$  due to dissolved oxygen.

a)



b)

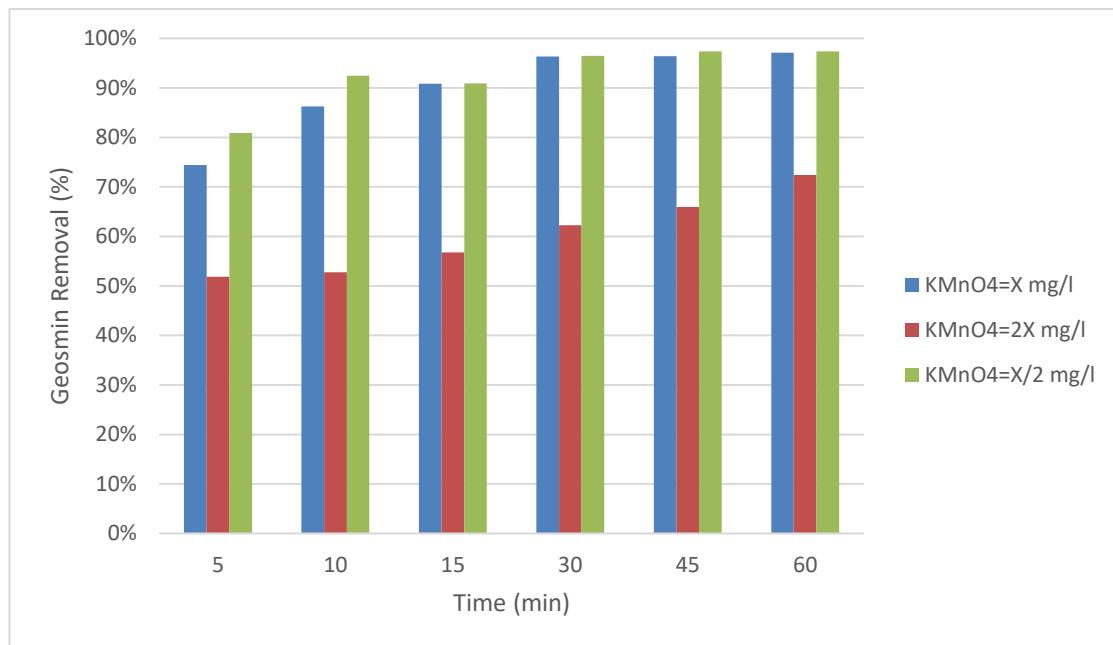


Figure 20: MIB (a) and geosmin(b) removal with  $PAC = 40 \text{ mg/l}$ ,  $Fe^{2+} = 2 \text{ mg/l}$ , different  $KMnO_4$  concentrations and different contact times ( $X = 1,89 \text{ mg/l}$ ).

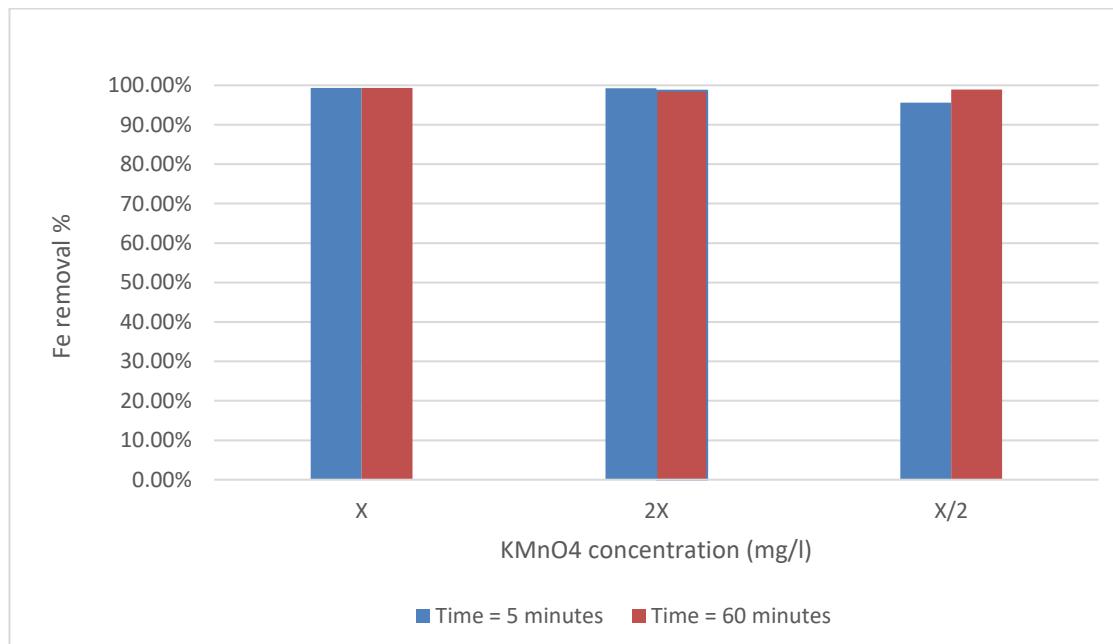


Figure 21: Iron removal with different KMnO<sub>4</sub> concentrations at time = 5 minutes and time = 60 minutes.

Table 7: MIB and geosmin removal with different  $KMnO_4$  concentrations,  $Fe^{2+} = 2 \text{ mg/l}$  and  $PAC = 40 \text{ mg/l}$ .

	Time (min)	MIB removal (%)	Geosmin removal (%)
$KMnO_4 = X \text{ mg/l}$	5	54.6%	74.4%
	10	60.9%	86.2%
	15	68.6%	90.8%
	30	80.7%	96.3%
	45	82.1%	96.4%
	60	85.5%	97.1%
$KMnO_4 = 2X \text{ mg/l}$	5	22.9%	51.8%
	10	25.2%	52.8%
	15	24.3%	56.7%
	30	28.0%	62.3%
	45	32.2%	66.0%
	60	39.3%	72.4%
$KMnO_4 = X/2 \text{ mg/l}$	5	60.5%	80.9%
	10	73.5%	92.4%
	15	72.8%	90.9%
	30	89.1%	96.5%
	45	89.9%	97.4%
	60	92.5%	97.4%

## 6 CONCLUSIONS

MIB/geosmin have been identified as the main taste and odor causing compounds in drinking water. Even if these two compounds have not been associated with any serious health effects, the resulting taste and odor from their presence is perceived as unsafe by consumers. Studies have demonstrated that it is extremely difficult to remove these two compounds by conventional water treatment methods such as coagulation, sedimentation and chlorination. Currently, adsorption by PAC is the most effective and widely used technology to treat these compounds. PAC shows a lot of good features that make it suitable for treatment of MIB and geosmin, such as its high removal efficiency and its flexibility in the application. The greatest challenge related to PAC use is the competitive adsorption of NOM, that decreases the adsorption capacity of carbon and consequently its removal capacity of MIB and geosmin. That's why usually treatment with PAC is preceded by a pre-oxidation stage that removes the competitive compounds. The most important drawback of pre-oxidation treatment is the oxidation of PAC surface, with reduction of its adsorption capacity, caused by the oxidant used (for example chlorine). That's why in this study it was evaluated the effect of an alternative oxidant, like potassium permanganate, on PAC adsorption of MIB and geosmin. Through the four stages described it was possible to reach important conclusions about the interaction between PAC and  $\text{KMnO}_4$ .

It is important to highlight that all the conclusions reached through this study are not definitive and can not be a reference describing  $\text{KMnO}_4$ -PAC interaction, because the sample were not collected from independent tests and so they haven't statistical relevance. However, through this study it was possible to note an important interaction between PAC and  $\text{KMnO}_4$  that could be studied more in depth in future studies.

A strong interaction between PAC and  $\text{KMnO}_4$  was observed causing an increase of oxidant consumption as the carbon concentration increased.

A kinetic model describing the interaction between  $\text{KMnO}_4$  and PAC was interpolated based on experimental data. It describes the rapid  $\text{KMnO}_4$  consumption in the first minutes and the stabilization of the residual permanganate on a constant value.

KMnO<sub>4</sub> had a great influence in the adsorption of the pollutants, specifically, as the literature suggested, MIB adsorption resulted more affected by permanganate action than geosmin one and it was removed with lower efficiency. It was also noted that the removal capacity was compromised regardless of potassium permanganate concentration as both the removal values with KMnO<sub>4</sub> = 1 mg/l and KMnO<sub>4</sub> = 2 mg/l were lower than the ones without the oxidant. Experimental data suggested that even low permanganate concentrations can strongly influence PAC adsorption performance. Therefore, even if the influence of potassium permanganate is lower if compared with other oxidants like chlorine, it would be necessary to dose KMnO<sub>4</sub> in the right way, adding only the quantity needed in the pre-oxidation and avoiding the contact between residual permanganate and PAC, so that it can be taken advantage of the PAC adsorption capacity to remove MIB and geosmin allowing a drinking water supply without taste and odor problems.

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