



Removal of polycyclic aromatic hydrocarbons (PAHs) in conventional drinking water treatment processes

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ABSTRACT

The presence of polycyclic aromatic hydrocarbons (PAHs) in water poses a serious threat to the human health due to their toxic effects. Therefore, the removal of these compounds from drinking water in Potable Water Treatment Plants (PWTs) should be evaluated and optimized to assure the quality of water intended for human consumption. In this work, changes in PAHs levels during drinking water treatment processes have been monitored to evaluate the effectiveness of conventional processes in the removal of these recalcitrant pollutants. Several chemical treatment methods based on the addition of KMnO_4 , FeCl_3 and NaClO were evaluated through jar tests. The analysis of PAH content of aqueous samples was carried out by gas chromatography coupled with mass spectrometry. The highest removal efficiency, over 90%, was obtained for benzo(a)anthracene, benzo(a)pyrene and dibenzo(a,h)anthracene. The most recalcitrant compounds to degradation were fluorene, anthracene, phenanthrene and flouranthene with reduction rates between 45 and 57%. The conventional treatment processes assessed have been proved to be effective reducing the PAH below the legal limits of drinking water quality. The definition of a parameter based on chemical properties of PAHs, i.e., sorption capacity and energy required to remove an electron, enabled the prediction of removal rate of pollutants which represents a valuable information for the plant operation.

1. Introduction

Over the last decades, the presence of persistent organic pollutant, such as polycyclic aromatic hydrocarbons (PAHs), has been detected in aquatic environment. These hazardous organic pollutants, containing two or more fused benzene rings, are generally characterized by low solubility, low vapor pressure and high melting and boiling points. Some PAHs have been classified as priority contaminants due to their toxic, mutagenic, carcinogenic and estrogenic effects on humans (Bojes and Pope, 2007). In general, PAHs are formed as product of incomplete combustion from natural (coal, oil and wood) and man-made combustion sources (automobile emissions) (Abdel-Shafy and Mansour, 2016). In addition to pyrogenic sources, PAHs can be of petrogenic and biologic origin. Petrogenic PAHs are formed during crude oil maturation and similar processes. The PAHs produced by bacteria and plants are classified as biologic (Harrison et al., 1975). Hence, the production of PAHs can be associated with either anthropogenic processes or natural

activities being the anthropogenic contribution the most relevant (Fernández et al., 2000).

PAHs has been commonly detected in air, soil and water entailing a ubiquitous environment risk. The low solubility of PAHs in water causes their attachment to the surface of particular matter which promotes they reach the hydrosphere (He et al., 2021). According to Karyab et al. (2013), PAHs enter water sources predominantly through fossils fuels combustion, petroleum spill, road runoff, industrial wastewater, leaching from creosote-impregnate wood and dry and wet deposition (Karyab et al., 2013). Hence, PAHs have been reported in drinking water, rivers and lakes, groundwater, wastewater, seawater and sediments. Mojiri et al. (2019) provided a comprehensive review on the most relevant PAHs contained in water environments. They reported benz[a]anthracene and phenanthrene in treated and untreated drinking water, respectively.

Biological and physical-chemical methods have been explored to effectively remove PAHs from aqueous solutions. Among biological

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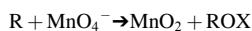
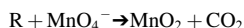
treatment methods, bioreactor, phytoremediation and bioremediation are the most common approaches proposed to reduce PAH contaminants. In Municipal Wastewater Treatment Plants (MWTPs), the biodegradation of organic pollutant, occurring both aerobically and anaerobically, is achieved through activated sludge process, sequencing batch reactors and membrane bioreactors (Fatone et al., 2011; Giordano et al., 2005; Qiao et al., 2016).

Concerning physical-chemical treatment methods, the most commonly applied to remove PAHs from water are: membrane filtration (i.e. microfiltration, ultrafiltration, nanofiltration and reverse osmosis) (Li et al., 2019), adsorption (Dai et al., 2020), advanced oxidation processes (i.e. ozonation, electrochemical oxidation, Fenton reagents and UV) (Badawy et al., 2006; Gaurav et al., 2021) and chemical precipitation (Smol and Włodarczyk-Makuła, 2017).

PAH oxidation by the addition of chemical reagents includes hydroxyl radical, ozone and permanganate ion (Boulangé et al., 2019). The production of hydroxyl radicals could be achieved by several methods, such as adding Fenton reagents and hydrogen peroxide, UV reaction and ultrasonic cavitation (Rubio-Clemente et al., 2014). The degradation of PAHs using ozone is produced not only by direct oxidation of the target compounds by O_3 but also by indirect radical oxidation at basic pH (Beltran et al., 1995).

The oxidation of PAHs contained in water using permanganate shows some important advantages: effectiveness across a wide pH range, low cost, easy and safe to use, high stability and mobility (Stewart, 1964). The oxidation of organic contaminant by permanganate ion is based on the formation of MnO_4^- ions in aqueous systems which are an efficient and strong oxidant to break alkene C=C double bonds of the PAHs structure.

In general, the oxidation of organic contaminant by permanganate ion generates manganese dioxide plus organic intermediates (ROX) or CO_2 (de Souza e Silva et al., 2009) and could be represented as:



The specific mechanisms of permanganate oxidation of PAHs are complex due to the numerous reactions in which Mn can be involved as a consequence of its multiple mineral forms and valence states (Ferrarese et al., 2008). Furthermore, some studies have concluded that the reactivity of chemical degradation of PAHs by permanganate depends on the molecular structure of the pollutant (Brown et al., 2003).

At this point, it should be highlighted that individual PAHs can differ significantly in their physical and chemical properties which difficult the development of remediation techniques for PAHs contaminated sites. Therefore, studies dealing with the simultaneous removal of PAHs from real matrices are required for a better understanding of the pollutant behaviour. These results would be really valuable not only to propose new remediation techniques but also to develop tools for the prediction of the pollutant removal under different experimental conditions.

The aim of this work was to evaluate the effectiveness of conventional treatment processes from a Potable Water Treatment Plant (PWTP) in the simultaneous removal of several PAHs. The role of three chemicals used commonly in water potabilization (i.e., potassium permanganate as oxidant, $FeCl_3$ as coagulant and $NaClO$ as disinfectant) in the degradation of PAHs from aqueous solutions has been explored through the simulation of the plant by means of jar tests. The analysis of PAH samples was carried out using gas chromatography coupled with mass spectrometry (GC/MS). Experimental results allowed to develop an approach to predict the percentage of the removal of several PAHs from water based on their chemical properties.

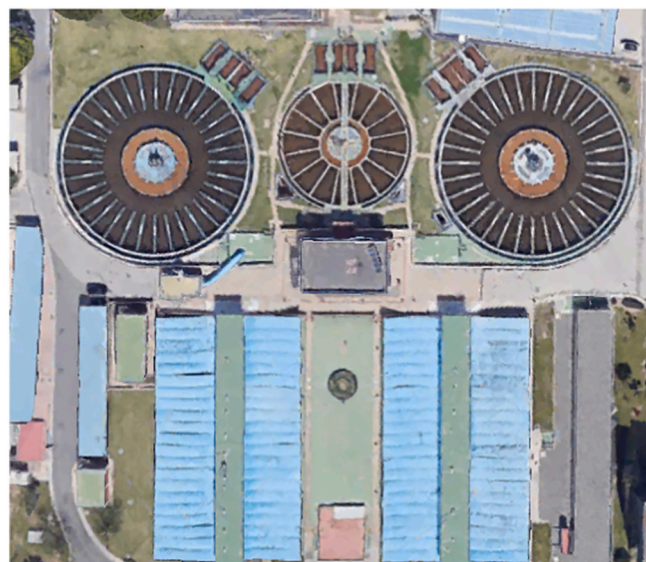


Fig. 1. Aerial photograph of PWTP (Atabal). Source: Google Earth.

2. Material and method

2.1. Water purification plant

This study was performed in the Potable Water Treatment Plant (PWTP) of Atabal (Fig. 1), operated by the Municipal Water Company of Malaga (EMASA). The plant is designed to treat a water influent of 2500 L s^{-1} collected from natural supply sources. The treatment process for potable supplies involves several steps, including coagulation-flocculation, sedimentation, and sand filtration. The conventional treatment embraces the chemical addition system. First, potassium permanganate ($KMnO_4$) is fed into the raw water in a concentration of 0.35 mg L^{-1} with a reaction time of 8 min. Then, sodium hypochlorite ($NaClO$) is added as chemical disinfectant with a final concentration of 2 mg L^{-1} of free chlorine. At the same time, ferric chloride ($FeCl_3$) is added to water as coagulant in a concentration of 18 mg L^{-1} . The contact time is also of 8 min. After chemical addition, sedimentation is performed to remove solid particles from water. The clarification system of the plant consists of an *Accelerator* clarifier with a capacity of 500 L s^{-1} and two *Accelerator IS* clarifiers equipped with a mobile diametric girded braced and a sludge scraper system with a total capacity of 2000 L s^{-1} . The clarified water is submitted to filtration to separate suspended and colloidal particles. The filtration system consists of twenty sand filters (*Acuzur type V*) with a total capacity of 2500 L s^{-1} . The treated water could be directly transported to the water supply network or pumped to the desalination plant. The generated sludge during the described process is treated in a clarifier (*Densadeg*) which combines the principle of lamellar settling with an integrated sludge thickener. After centrifugation, the dehydrated sludge is transported to the nearest Wastewater Treatment Plant (WWTP).

2.2. Water sampling and analysis

Water samples were collected from the entrance of the PWTP. The main physicochemical parameters were determined using normalized methods accredited by UNE-ISO/IEC-17025. The parameters analysed were: colour, turbidity, pH value, conductivity, chloride, calcium, magnesium and sodium content, hardness, oxidability, free residual and combined chlorine and Langelier saturation index. Experiments were performed using three different water samples to assure reproducibility of experimental conditions.

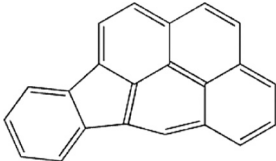
This work was focused on 13 PAHs categorized by the USEPA as

Table 1
Chemical structure and properties of the selected PAHs.

Compound	Formula	CAS number	Chemical structure	log K_{ow} ^a	Ionization potential (eV)	Solubility in water (mg L ⁻¹) at 25 °C
Fluorene (FL)	C ₁₃ H ₁₀	86-73-7		4.18	7.91	1.69
Phenanthrene (PHE)	C ₁₄ H ₁₀	85-01-8		4.57	7.89	1.15
Anthracene (ANT)	C ₁₄ H ₁₀	120-12-7		4.54	7.44	4.34 10 ⁻²
Fluoranthene (FLU)	C ₁₆ H ₁₀	206-44-0		5.22	7.90	0.26
Pyrene (PYR)	C ₁₆ H ₁₀	129-00-0		5.32	7.30	0.135
Benzo[<i>a</i>]anthracene (BaA)	C ₁₈ H ₁₂	56-55-3		5.61	7.50	9.4 10 ⁻³
Chrysene (CHY)	C ₁₈ H ₁₂	218-01-9		5.63	7.60	2 10 ⁻³
Benzo[<i>b</i>]fluoranthene (BbF)	C ₂₀ H ₁₂	205-99-2		6.06	7.32	1.2 10 ⁻³
Benzo[<i>k</i>]fluoranthene (BkF)	C ₂₀ H ₁₂	207-08-9		6.57	6.99	8 10 ⁻⁴
Benzo[<i>a</i>]pyrene (BaP)	C ₂₀ H ₁₂	50-32-8		6.84	7.11	1.62 10 ⁻³
Dibenz[<i>a,h</i>]anthracene (DahA)	C ₂₂ H ₁₄	53-70-3		6.86	7.39	2.49 10 ⁻³
benzo[<i>ghi</i>]perylene (BghiP)	C ₂₂ H ₁₂	191-24-2		7.66	7.17	2.6 10 ⁻⁴

(continued on next page)

Table 1 (continued)

Compound	Formula	CAS number	Chemical structure	log K_{ow}^a	Ionization potential (eV)	Solubility in water (mg L^{-1}) at 25 °C
Indeno[1.2.3- cd]pyrene (IcdP)	$\text{C}_{22}\text{H}_{12}$	193–39-5		7.23	6.90	$6.2 \cdot 10^{-2}$

References: (Sangster, 1989), <http://pubchem.ncbi.nlm.nih.gov>, <https://webbook.nist.gov/chemistry/>

^a Logarithm of the octanol-water partition coefficient.

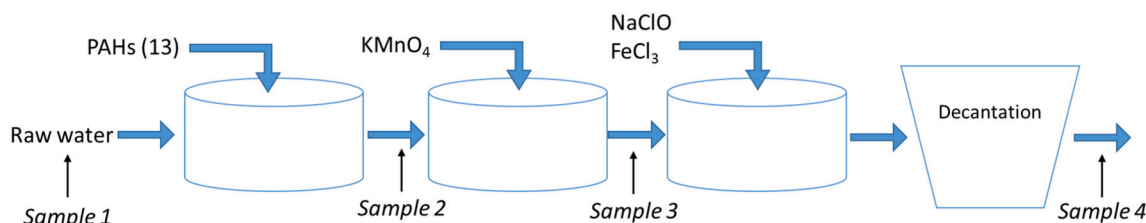


Fig. 2. Schematic diagram of experimental procedure.

priority contaminants including benzo[ghi]perylene (BghiP), chrysene (CHY), benz[a]anthracene (BaA), benzo[b]fluoranthene (BbF), anthracene (ANT), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), fluoranthene (FLU), Indeno[1,2,3-cd]pyrene (IcdP), phenanthrene (PHE), dibenz[a,h]anthracene (DahA), fluorene (FL), and pyrene (PYR). Their chemical properties can be found in Table 1.

For extraction, the commercial stir bar Twister was employed for all PAHs measurement. The stirring of the aqueous sample was carried out during 16 h at 850 rpm. When this step had been completed, the Twister was transferred to Thermal Desorption Unit to obtain the organic compounds in aqueous samples to be analysed.

Gas chromatography (GC) coupled with mass spectrometry (GC/MS) provides reliability and sensitivity for the trace analysis of organic pollutant in the environment. The advantages of using GC/MS rely on the efficiency of gas chromatography separation and the good qualitative information and high sensitivity provided by mass spectrometry (MS) (Santos and Galceran, 2003). Therefore, the PAHs content of samples was determined by a gas chromatograph-mass spectrometer (6890 N, Agilent) according to the Method 525.3 (EPA/600/R-12/010) (Munch, 2012). The column used was DB5MS-UI with helium as carrier gas. The oven temperature was programmed starting at 70 °C for 2 min, gradually increased to 285 °C where it held for 5 min. The injection was set at 40 °C, increased to 325 °C where it held for 7 min.

2.3. Jar tests

Jar tests were selected as a well-known tool to simulate full-scale PWT. The multiple stirrer jar test apparatus used (Stuart) provides a constant rotational speed of the stainless-steel paddles to assure reproducible results. The experimental procedure is schematically presented in Fig. 2.

The concentration of PAHs in raw water (sample 1) was almost negligible (FL: $2.25 \cdot 10^{-3} \mu\text{g L}^{-1}$, PHE: $3.05 \cdot 10^{-3} \mu\text{g L}^{-1}$, ANT: $3.35 \cdot 10^{-3} \mu\text{g L}^{-1}$, FLU: $2.00 \cdot 10^{-3} \mu\text{g L}^{-1}$, PYR: $7.50 \cdot 10^{-4} \mu\text{g L}^{-1}$, BaA: $3.15 \cdot 10^{-3} \mu\text{g L}^{-1}$, CHY: $1.80 \cdot 10^{-3} \mu\text{g L}^{-1}$, BbF: $5.60 \cdot 10^{-3} \mu\text{g L}^{-1}$, BkF: $1.80 \cdot 10^{-3} \mu\text{g L}^{-1}$, BaP: $1.80 \cdot 10^{-3} \mu\text{g L}^{-1}$, DahA: $5.00 \cdot 10^{-3} \mu\text{g L}^{-1}$, BghiP: $6.85 \cdot 10^{-3} \mu\text{g L}^{-1}$, IcdP: $6.20 \cdot 10^{-3} \mu\text{g L}^{-1}$). Therefore, to perform experiments, first, a standard mixture solution of the aforementioned PAHs ($100 \mu\text{g L}^{-1}$ in Methanol/Acetone) was added to the real water samples to obtain a total concentration of each PAH of $0.1 \mu\text{g L}^{-1}$. As can be seen in Table 1, the selected concentration is close to water solubility for some PAHs. Thus,

Table 2

Standard specification for potable water (European Union, 5AD; World Health Organization, 2017) and characterization of raw water.

Parameter	Standard value	Raw water
Colour (TCU)	15	5.75 ± 0.35
Turbidity (NTU)	1	29 ± 0
pH	6.5–9.5	8.2 ± 0.0
Conductivity ($\mu\text{S cm}^{-1}$)	2500	2475 ± 318
Chloride (mg L^{-1})	250	606 ± 115
Sodium (mg L^{-1})	200	395 ± 73
Calcium (mg L^{-1})	100–300	114.5 ± 3.5
Magnesium (mg L^{-1})	< 100	32 ± 3
Hardness (m L^{-1})	500	416 ± 22
Oxidizability ($\text{mg O}_2 \text{L}^{-1}$)	5 $\text{mg O}_2 \text{L}^{-1}$	2.20 ± 0.28
Free chlorine (mg L^{-1})	1 mg L^{-1}	< 0.2
Combined chlorine (mg L^{-1})	2 mg L^{-1}	< 0.2
Langelier saturation index	± 0.5	0.7

the study was not only based on the study of soluble PAH but also PAH attached to solid particles contained in the water. The experiments consisted in introducing 1 L of the spiked water sample in the jars. After that, the KMnO_4 was added and the paddle velocity was of 150 rpm during 8 min. Then, a water sample of 100 mL was collected to analyse the PAH content. Afterwards, a known mass of NaClO and FeCl_3 was added to the water samples and the agitator was set at 150 rpm during 8 min. At last, the agitation was stopped with the aim of allowing the particles to settle down during 30 min. Then, a final water sample of 100 mL was withdrawn to determine the PAH content. The reagents were added in the same proportion as in the PWT.

3. Results and discussion

3.1. Water characterization

According to the Spanish legislation (BOE-A-1988-20883, 1988), the water treatment should involve intensive physicochemical treatment, refine and disinfection in view of the characteristics of raw water (Table 2). The parametric values for potable drink water after treatment reported by the European Union (EU) and the World Health Organization (WHO) (European Union, 5AD; World Health Organization, 2017) are also presented in Table 2. The error values correspond to the standard deviation of the results for the three different raw water samples

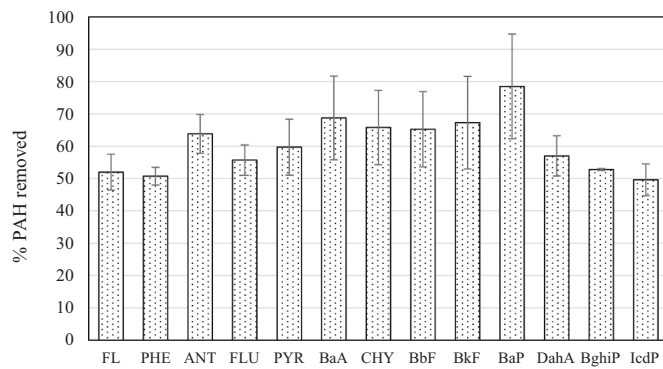


Fig. 3. Removal of PAHs by KMnO₄ oxidation.

used in this work.

The colour of raw water was within established limits whereas its level of turbidity was higher. Turbidity could be associated with suspended particles, chemical precipitates, organic particles, and organism. Although most particles that contribute to turbidity have no health significance, the aforementioned treatment entails the reduction of this parameter below the maximum recommended value. The pH value was within the recommended standard, which ranged from 6.5 to 9.5. The electrical conductivity, directly associated with the concentration of dissolved salts, was close to the maximum recommended. Contents of chloride and sodium were higher than the standard values. According to the WHO, these results could be associated with saline intrusion, mineral deposits, seawater spray, sewage effluents and salt used in road de-icing. In this particular case, high salinity is associated with saline intrusion in natural supply sources. The values of calcium and magnesium content, which are not considered of health concern by WHO, were within the taste threshold. The hardness was lower than 500 mg L⁻¹ which is the maximum value that consumers usually tolerate. The oxygen demand, free and combined chlorine content were also below the reference values. The Langelier index, which is used to predict calcium precipitation, was slightly higher than the recommended value. It should be noted that water after treatment complies with the quality values required in the current Spanish regulations.

3.2. Jar tests results

In this section, results of the jar tests simulating water treatment with KMnO₄ are firstly discussed. The chemical oxidation involving permanganate has been widely used for the destruction of organic contaminants in several matrices (Gates-Anderson et al., 2001). As shown in Fig. 3, the PAH concentration in sample 3 (Fig. 2) for all selected contaminants was reduced after permanganate treatment. The error bars for all the figures presented in this section correspond to two times the standard deviation of the triplicated experiments. The rate reduction was PAH specific varying between 50 and 80%. The higher reduction was detected for benzo(a)pyrene, while the most recalcitrant to degradation were fluorene, phenanthrene, fluoranthene, benzo[ghi]perylene and indeno[1.2.3-cd]pyrene. The divergences in PAH removal could be associated with the PAH chemical structure which directly influences on the mechanism reactions. Although several mechanisms and pathways has been reported to explain the PAH oxidation, the electrophilic aromatic substitution reaction has been proved to be the most relevant for these compounds (Forsey et al., 2010). For this pathway, the ionization potential, i.e. the ability to donate electrons, could be used as a tool to approximate the energy involved in the PAH oxidation. As the ability to donate an electron decreases, the rate of the reaction also decreases. Therefore, the higher values of ionization potential for fluorene (7.93 eV), phenanthrene (7.91 eV) and fluoranthene (7.80 eV) (Dewar et al., 1970) could explain their lower removal compared with the rest of PAHs. The recalcitrant behaviour experimentally observed for benzo

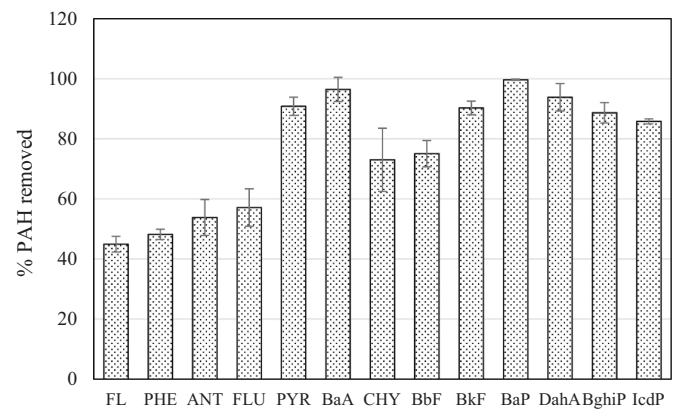


Fig. 4. Removal of PAHs after treatment with KMnO₄, NaClO and FeCl₃ and sedimentation.

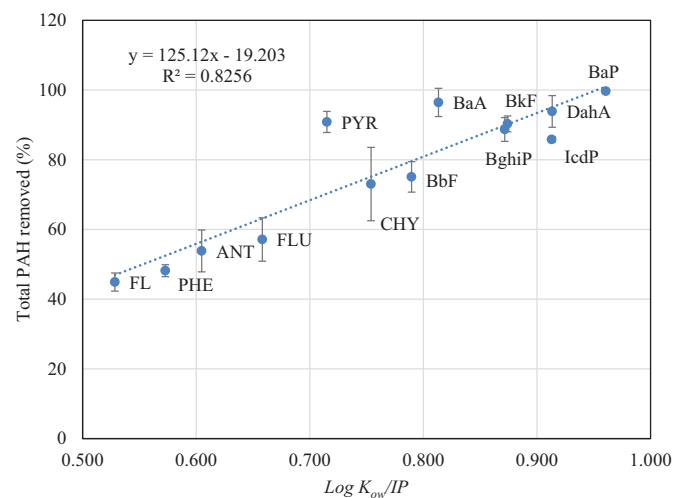


Fig. 5. Total removal of PAHs after sedimentation versus octanol-water coefficient and ionization potential ratio for each compound.

(ghi)perylene and indeno[1.2.3-cd]pyrene has been previously associated with its chemical structures: highly conjugated polyaromatic compounds with a high molecular weight and with six benzene rings (Mojiri et al., 2019). On the other hand, a higher benzo(a)pyrene reduction (80%) was achieved through permanganate treatment. Brown et al. (2003) have previously concluded that the high reactivity of benzo(a)pyrene could be explained through the Clar structural model (Brown et al., 2003). More specifically, they have associated the number of carbon-carbon double bonds, the number of stabilizing sextets and the shared carbon-carbon double bonds with the permanganate reactivity.

Results of jar tests after KMnO₄, NaClO and FeCl₃ addition and sedimentation (sample 4 according to Fig. 2) are presented in Fig. 4. Below, the effectiveness of NaClO, an economically available oxidizing agent widely used for disinfection of potable water, and of FeCl₃, a coagulation reagent, on the removal of PAHs is discussed. The results showed that the removal rate of pyrene, benzo(a)anthracene, benzo(k)fluoranthene, benzo(a)pyrene and dibenzo(a,h)anthracene was higher than 90%. The most effective removal during NaClO and FeCl₃ treatment was detected for pyrene, dibenzo(a,h)anthracene, benzo(ghi)perylene and indeno(1.2.3-Cd)pyrene which increased by more than 30% compared with water treated only with permanganate. The lowest removal efficiency, close to 55%, was reported for fluorene, anthracene, phenanthrene and fluoranthene. The most relevant positive effect of the treatment was reported for benzo(a)pyrene with an almost complete removal.

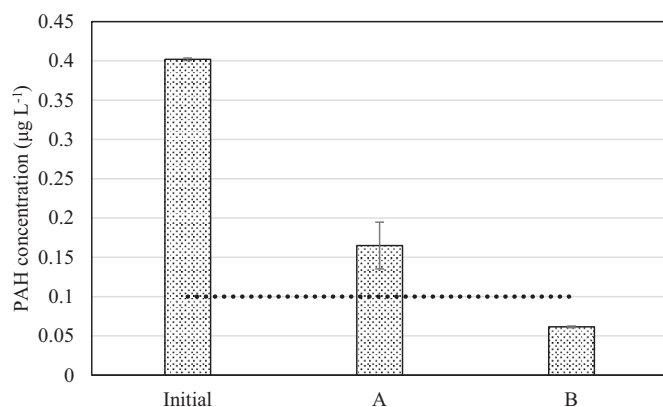


Fig. 6. Total PAH (BbF, BkF, BghiP, IcdP) concentration: Initial (sample after spiking with $0.1 \mu\text{g L}^{-1}$ of each PAH), A (sample after KMnO_4 treatment), B (sample after KMnO_4 , NaClO , FeCl_3 treatment and sedimentation).

With the purpose of comparing the behaviour of selected PAHs, $\log K_{ow}/PI$ ratio versus the total percentage of PAH removed has been presented in Fig. 5. Octanol-water partition coefficient (K_{ow}), used as indicator of sorption capacity, represents the ratio of concentration of a compound between octanol and water phases. Substances with high $\log K_{ow}$ values are more difficult to solubilize and tend to be adsorbed more readily to solid particles. For water treatment processes, the sorption entails the separation of PAHs through sedimentation of solid particles. Regarding ionization potential, as aforementioned, as values of ionization potential decreases, the ability to donate an electron increases and, subsequently, the degradation of PAHs would increase. As can be observed, the lower degradation percentages were found for compounds with the lowest values of $\log K_{ow}/PI$ (FL, PHE, ANT, FLU). A positive linear correlation between $\log K_{ow}/PI$ and the percentage of PAH ($R^2 > 0.8$) was observed (Fig. 5). From these results, it could be concluded that the evaluation of $\log K_{ow}/PI$ ratio for each PAH represents a useful tool to predict approximatively their removal percentage based on sorption capacity (K_{ow}) and energy required to remove an electron (PI).

According to the EU regulations, the limit value of the sum of four selected PAHs (BbF, BkF, BghiP, IcdP) for drinking water is $0.1 \mu\text{g L}^{-1}$ (European Union, 5AD). With the aim of evaluating the effectiveness of the treatment, the total concentration of the aforementioned PAHs has been evaluated after each treatment step (Fig. 6). Initial concentration of spiked samples was about four times higher than the standard value. After permanganate treatment, the PAH concentration was reduced by 40%. As previously discussed, organic compounds decrease can be explained by its oxidation with KMnO_4 . The sorption of PAHs onto MnO_2 and $\text{Fe}(\text{OH})_3$, precipitated as a result of the oxidation reaction of Fe (II) contained in raw water with KMnO_4 , could also contribute to the reduction of PAHs level in water (Ersoz and Barrott, 2012). Regarding final samples, the total concentration decreased by 85% of its initial value. These results showed the important role of the combined effect of NaClO and FeCl_3 , acting as oxidizing and coagulant reagents, respectively, on the degradation of PAHs. As can be observed, the total concentration of PAH in drinking water after treatment is below the limit value established by EU, which shows an effective pollutant removal through the conventional treatment evaluated. On this matter, the plant has also available two deposits of activated carbon with a surface area of $1000 \text{ m}^2 \text{ g}^{-1}$ to reduce organic contaminants by adsorption, should it be required.

4. Conclusions

The conventional treatment processes performed in a PWTP has been proved effective in the removal of PAHs from drinking water. Experimental results suggested that the water treatment with KMnO_4 allows

the oxidation of persistent organic pollutants, such as PAHs. Significant differences between rate reduction for each organic pollutant were detected, which was related to the chemical structure of the PAH. A parameter based on PAHs properties was defined to evaluate the role of the conventional treatment in the removal of the selected organic contaminants. From these results, it was established a useful methodology to predict the removal percentage of these recalcitrant organic compounds based on its chemical properties. Under the experimental conditions proposed, the plant complies with the legal limits of drinking water quality reducing the PAH concentration (BbF, BkF, BghiP, IcdP) by 85%.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Abdel-Shafy, H.I., Mansour, M.S.M., 2016. A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. *Egypt. J. Pet.* 25, 107–123. <https://doi.org/10.1016/j.ejpe.2015.03.011>.
- Badawy, M.I., Ghaly, M.Y., Gad-Allah, T.A., 2006. Advanced oxidation processes for the removal of organophosphorus pesticides from wastewater. *Desalination* 194, 166–175. <https://doi.org/10.1016/j.desal.2005.09.027>.
- Beltran, F.J., Ovejero, G., Encinar, J.M., Rivas, J., 1995. Oxidation of Polynuclear aromatic hydrocarbons in water. 1. Ozonation. *Ind. Eng. Chem. Res.* 34, 1596–1606. <https://doi.org/10.1021/ie00044a012>.
- BOE-A-1988-20883, 1988. Real Decreto 927/1988, de 29 de julio, por el que se aprueba el Reglamento de la Administración Pública del Agua y de la Planificación Hidrológica, en desarrollo de los títulos II y III de la Ley de Aguas.
- Bojes, H.K., Pope, P.G., 2007. Characterization of EPA's 16 priority pollutant polycyclic aromatic hydrocarbons (PAHs) in tank bottom solids and associated contaminated soils at oil exploration and production sites in Texas. *Regul. Toxicol. Pharmacol.* 47, 288–295. <https://doi.org/10.1016/j.yrtph.2006.11.007>.
- Boulangé, M., Lorgeoux, C., Biache, C., Saada, A., Faure, P., 2019. Fenton-like and potassium permanganate oxidations of PAH-contaminated soils: impact of oxidant doses on PAH and polar PAC (polycyclic aromatic compound) behavior. *Chemosphere* 224, 437–444. <https://doi.org/10.1016/j.chemosphere.2019.02.108>.
- Brown, G.S., Barton, L.L., Thomson, B.M., 2003. Permanganate oxidation of sorbed polycyclic aromatic hydrocarbons. *Waste Manag.* 23, 737–740. [https://doi.org/10.1016/S0956-053X\(02\)00119-8](https://doi.org/10.1016/S0956-053X(02)00119-8).
- Dai, W.-J., Wu, P., Liu, D., Hu, J., Cao, Y., Liu, T.-Z., Okoli, C.P., Wang, B., Li, L., 2020. Adsorption of polycyclic aromatic hydrocarbons from aqueous solution by organic Montmorillonite sodium alginate Nanocomposites. *Chemosphere* 251, 126074. <https://doi.org/10.1016/j.chemosphere.2020.126074>.
- de Souza e Silva, P.T., da Silva, V.L., de Neto, B.B., Simonnot, M.-O., 2009. Potassium permanganate oxidation of phenanthrene and pyrene in contaminated soils. *J. Hazard. Mater.* 168, 1269–1273. <https://doi.org/10.1016/j.jhazmat.2009.03.007>.
- Dewar, M.J.S., Haselbach, E., Worley, S., 1970. Calculated and observed ionization potentials of unsaturated polycyclic hydrocarbons; calculated heats of formation by several semiempirical scfmo methods. *Proc. R. Soc. Lond. Math. Phys. Sci.* 315, 431–442.
- Ersoz, M., Barrott, L., 2012. Best Practice Guide on Metals Removal from Drinking Water by Treatment, Best Practice Guides on Metals and Related Substances in Drinking Water. IWA Publishing.
- European Union, 05/12/1998. Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption (Council Directive). *Off. J. Eur. Communities L* 330. P. 0032 - 0054.
- Fatone, F., Di Fabio, S., Bolzonella, D., Cecchi, F., 2011. Fate of aromatic hydrocarbons in Italian municipal wastewater systems: an overview of wastewater treatment using conventional activated-sludge processes (CASP) and membrane bioreactors (MBRs). *Water Res.* 45, 93–104. <https://doi.org/10.1016/j.watres.2010.08.011>.
- Fernández, P., Vilanova, R.M., Martínez, C., Appleby, P., Grimalt, J.O., 2000. The historical record of atmospheric pyrolytic pollution over Europe registered in the sedimentary PAH from remote mountain lakes. *Environ. Sci. Technol.* 34, 1906–1913. <https://doi.org/10.1021/es9912271>.

- Ferrarese, E., Andreottola, G., Oprea, I.A., 2008. Remediation of PAH-contaminated sediments by chemical oxidation. *J. Hazard. Mater.* 152, 128–139. <https://doi.org/10.1016/j.jhazmat.2007.06.080>.
- Forsey, S.P., Thomson, N.R., Barker, J.F., 2010. Oxidation kinetics of polycyclic aromatic hydrocarbons by permanganate. *Chemosphere* 79, 628–636. <https://doi.org/10.1016/j.chemosphere.2010.02.027>.
- Gates-Anderson, Dianne D., Siegrist, Robert L., Cline, Steven R., 2001. Comparison of potassium permanganate and hydrogen peroxide as chemical oxidants for organically contaminated soils. *J. Environ. Eng.* 127, 337–347. [https://doi.org/10.1061/\(ASCE\)0733-9372\(2001\)127:4\(337\)](https://doi.org/10.1061/(ASCE)0733-9372(2001)127:4(337)).
- Gaurav, G.K., Mehmood, T., Kumar, M., Cheng, L., Sathishkumar, K., Kumar, A., Yadav, D., 2021. Review on polycyclic aromatic hydrocarbons (PAHs) migration from wastewater. *J. Contam. Hydrol.* 236, 103715. <https://doi.org/10.1016/j.jconhyd.2020.103715>.
- Giordano, A., Stante, L., Pirozzi, F., Cesaro, R., Bortone, G., 2005. Sequencing batch reactor performance treating PAH contaminated lagoon sediments. *J. Hazard. Mater.* 119, 159–166. <https://doi.org/10.1016/j.jhazmat.2004.12.002>.
- Harrison, R.M., Perry, R., Wellings, R.A., 1975. Polynuclear aromatic hydrocarbons in raw, potable and waste waters. *Water Res.* 9, 331–346. [https://doi.org/10.1016/0043-1354\(75\)90179-7](https://doi.org/10.1016/0043-1354(75)90179-7).
- He, Y., Song, K., Yang, C., Li, Y., He, W., Xu, F., 2021. Suspended particulate matter (SPM)-bound polycyclic aromatic hydrocarbons (PAHs) in lakes and reservoirs across a large geographical scale. *Sci. Total Environ.* 752, 142863. <https://doi.org/10.1016/j.scitotenv.2020.142863>.
- Karyab, H., Yunesian, M., Nasser, S., Mahvi, A.H., Ahmadkhaniha, R., Rastkari, N., Nabizadeh, R., 2013. Polycyclic aromatic hydrocarbons in drinking water of Tehran, Iran. *J. Environ. Health Sci. Eng.* 11, 25. <https://doi.org/10.1186/2052-336X-11-25>.
- Li, S., Luo, J., Hang, X., Zhao, S., Wan, Y., 2019. Removal of polycyclic aromatic hydrocarbons by nanofiltration membranes: rejection and fouling mechanisms. *J. Membr. Sci.* 582, 264–273. <https://doi.org/10.1016/j.memsci.2019.04.008>.
- Mojiri, A., Zhou, J.L., Ohashi, A., Ozaki, N., Kandaichi, T., 2019. Comprehensive review of polycyclic aromatic hydrocarbons in water sources, their effects and treatments. *Sci. Total Environ.* 696, 133971. <https://doi.org/10.1016/j.scitotenv.2019.133971>.
- Munch, D.J., 2012. EPA method 525.3. Determination of semivolatiles organic chemicals in drinking water by solid phase extraction and capillary column gas chromatography/mass spectrometry (GC/MS).
- Qiao, M., Qi, W., Liu, H., Bai, Y., Qu, J., 2016. Formation of oxygenated polycyclic aromatic hydrocarbons from polycyclic aromatic hydrocarbons during aerobic activated sludge treatment and their removal process. *Chem. Eng. J.* 302, 50–57. <https://doi.org/10.1016/j.cej.2016.04.139>.
- Rubio-Clemente, A., Torres-Palma, R.A., Peñuela, G.A., 2014. Removal of polycyclic aromatic hydrocarbons in aqueous environment by chemical treatments: a review. *Sci. Total Environ.* 478, 201–225. <https://doi.org/10.1016/j.scitotenv.2013.12.126>.
- Sangster, J., 1989. Octanol-water partition coefficients of simple organic compounds. *J. Phys. Chem. Ref. Data* 18, 1111–1229. <https://doi.org/10.1063/1.555833>.
- Santos, F.J., Galceran, M.T., 2003. Modern developments in gas chromatography-mass spectrometry-based environmental analysis. *Century Chromatogr.* 1903-2003 (1000), 125–151. [https://doi.org/10.1016/S0021-9673\(03\)00305-4](https://doi.org/10.1016/S0021-9673(03)00305-4).
- Smol, M., Włodarczyk-Makula, M., 2017. The effectiveness in the removal of PAHs from aqueous solutions in physical and chemical processes: a review. *Polycycl. Aromat. Compd.* 37, 292–313. <https://doi.org/10.1080/10406638.2015.1105828>.
- Stewart, R., 1964. *Oxidation Mechanisms: Application to Organic Chemistry*.
- World Health Organization, 2017. *Guidelines for Drinking-Water Quality: Fourth Edition Incorporating the First Addendum*. WHO Library Cataloguing-in-Publication Data, Switzerland.