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Ozonation/adsorption hybrid treatment system for improved removal of natural organic matter and organic micropollutants from water – a mini review and future perspectives

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Abstract

Elevated concentrations of natural organic matter (NOM) and organic micropollutants (OMPs) can contaminate the quality of drinking water, and current water treatment technologies are not always successful in removing all their constituents. Ozonation and adsorption are two advanced processes with different removal mechanisms used to treat NOM and OMPs. Their treatment efficiency depends on the strength and kinetics of adsorption and ozonation (ozone molecule and OH radical (OH•) reaction) of the individual NOM constituents and OMPs. They are individually able to remove many of the NOM fractions and OMPs but not satisfactory in removing the vast array of their components which differ in their physico-chemical characteristics, for example molecular weight, charge, functional groups, aromaticity, and hydrophobicity/hydrophilicity. Significant progress has been made by integrating these processes (ozonation followed by activated carbon (AC) adsorption) but they need further improvement to efficiently target all NOM fractions and the various OMPs.

Ozonation transforms the larger NOM molecules into smaller molecular sizes with lower aromaticity and hydrophobicity, subsequently resulting in reduced adsorption. The reduced adsorption of these molecules diminishes their competition against OMP adsorption resulting in increased OMP removal. Adsorption can remove unoxidized pollutants as well as the by-products of ozonation, and some of them are suspected to be human carcinogens. Of the commonly used adsorbents, anion exchange resin and AC, the former has higher affinity towards negatively charged humic fraction and OMPs. Conversely, the latter has higher affinity towards the hydrophobic constituents and smaller sized constituents which diffuse into AC pores and get adsorbed. Biofilm formed by long-term use of AC also contributes to enhanced removal of NOM and OMPs. This paper briefly reviews the currently available literature on removing NOM and OMPs by the ozonation/adsorption integrated process. It also suggests a new method for further increasing the efficiency of this process.

Keywords: natural organic matter, organic micropollutants, adsorption, ozonation, activated carbon, ion exchange resin

Highlights

- Ozonation/adsorption hybrid process is very efficient in removing NOM and OMPs.
- Adsorption after ozonation is more efficient than when they are used individually.
- Ozonation reduces adsorption competition of NOM with OMPs; so, more OMPs are removed.
- Using two adsorbents with different properties after ozonation is more efficient.
- Anion exchange resin after commonly used activated carbon is a preferred option.

1. Introduction

Natural organic matter (NOM) and organic micropollutants (OMPs) are two major groups of pollutants in natural water that at elevated concentrations can cause adverse outcomes in drinking water. NOM is a complex mixture of zooplankton, phytoplankton, clay-humic acid complexes, humic acids, proteins, polysaccharides, fluvic acids, and very small molecules such as fatty acids, carbohydrates, amino acids, and hydrocarbons (Bolto, 1995). The constituents vary in size including molecular weight, charge on the functional groups, hydrophobicity/hydrophilicity, aromaticity, etc. (Loganathan et al., 2020). NOM is operationally divided into different fractions by measuring them using a liquid chromatography-organic carbon detection unit (LC-OCD) (DOC-Labor Dr. Huber, Germany) (Huber et al., 2011). LC-OCD separates the NOM into five fractions of organic carbon with different molecular weight ranges and chemical polarity (hydrophobic and hydrophilic (biopolymers, humics, building blocks, and low molecular weight substances)) (Huber et al., 2011; Velten et al., 2011; Jamil et al. 2021). OMPs in water consist mainly of pharmaceutical and personal care products, endocrine disruptors, pesticides, and industrial by-products (Lee and von Gunten, 2016; Ullberg et al., 2021).

NOM is known to produce colour, taste, and odour problems, and acts as a substrate that can increase microbiological growth. It is also a major contributor to disinfectant by-product formation and potentially toxic to humans. In some cases, it has reduced the treatment capacity of direct filtration in treatment plants. OMPs at high concentrations are toxic to aquatic organisms (Fick et al., 2010; Pal et al., 2010). Human and animal exposures to certain OMPs have been linked to an array of carcinogenic, mutagenic, and reproductive toxicity risks (Cizmas et al., 2015; Zhang et al., 2020). Some OMPs are known to be toxic to humans, especially to embryonic cells, even at very low concentrations. The increased concern of the potential adverse impacts on human health has enforced surveillance of several OMPs. Surveillance of OMPs has become mandatory with the latest revision of the EU Drinking

Water Directive and noted also in the 3rd Watch List under the Water Framework Directive (Cortes et al., 2020).

The traditional treatments to remove these pollutants such as chlorination and flocculation are not always successful. Therefore, advanced treatments using adsorption, and ozonation technologies having different physical and chemical mechanisms of removal are employed to improve the removal efficiencies. On their own, however, they have not been found to be successful in removing all NOM fractions and the various OMPs to required levels. This is because both NOM (Loganathan et al., 2020) and OMPs (Zhang et al., 2020) consist of components with different functional groups, molecular weights, charges, aromaticity, and hydrophobicity, which make them behave differently towards ozonation and the various adsorbents used. However, some studies have reported combining these two processes. For example, installing adsorption treatment (e.g. activated carbon (AC) filters) downstream of an ozonation stage has led to some improvements (Zietzschmann et al., 2015; Guillosoou et al., 2020a; Sauter et al., 2021; Ulberg et al., 2021).

Some studies have combined ozonation with UV, hydrogen peroxide, catalysts and electrocoagulation and improved the removal of organic contaminants from industrial wastewaters containing recalcitrant compounds that can resist biodegradation (Malik et al., 2020; Rekhate and Srivasta, 2020). In one such process AC was combined with ozone to accelerate the generation of hydroxyl radicals from ozone. Here AC, due to its surface properties, acts as a catalyst helping the ozonation process.

This paper presents a brief review of the processes discussed above and recommends a scheme of combining ozonation and adsorption using two adsorbents having contrasting properties to improve further the degree of removal of all components of NOM and the different OMPs. Recent studies have shown that adsorbents having contrasting properties were able to remove different OMPs and NOM fractions which have properties that match

with the different affinity-preferences of the respective adsorbents (Hu et al., 2014; Shanmuganathan et al., 2014; Jamil et al., 2021). Previously there were excellent reviews on the removal of NOM or OMP by adsorption (Delgado et al., 2012; Jeirani et al., 2017; Korotta-Gamage and Sathasivam, 2017; Sophia and Lima, 2018; Neha et al., 2021) or ozonation (Van Geluwe et al., 2011; Rekhate and Srivastava, 2020; Derco et al., 2021). However, this was not evident when these processes are integrated, and when NOM and MOPs coexist. Thus, the review presented here is new and the recommendation of using two adsorbents having contrasting properties downstream of an ozonation stage represents an advance on previous ones using only one adsorbent.

2. NOM and OMP removal using ozonation

Ozone is one of the strongest and fastest commercially available disinfectants and oxidants used for water treatment. It is a more powerful oxidant than the traditionally used chlorine (Beltrán et al., 2021). Ozone can directly oxidise NOM or indirectly by decomposing in water forming the free radicals, hydrogen peroxy ($\text{HO}_2\bullet$) and hydroxyl ($\text{OH}\bullet$) which causes the oxidation and disinfection (EPA, 1999; Snyder et al., 2006; Lee and van Gunten, 2016; Malik et al., 2020; Rekhate and Srivasta, 2020; Beltrán et al., 2021).

The mechanism and reaction products of ozone oxidation have been well documented in many review articles on this subject (Stahelln and Hoigné, 1985; von Gunten, 2003; Van Geluwe et al., 2011; Malik et al., 2020; Rekhate and Srivastava, 2020). The powerful oxidizing ability of ozone, and its high reactivity is due to the unique electronic configuration of this molecule. It comprises of one-weak single bond and one strong double bond (Van Geluwe et al., 2011; Malik et al., 2020). There exist two possible resonance structures of ozone causing it to act as a dipole agent either as electrophile (accept electrons) or nucleophile (donate electrons) (Fig. 1). The positive charges on the central oxygen atom in both resonance

structures explains the electrophilic character of ozone, and the negative charge presents in one of the terminal atoms gives a nucleophilic character to it (Van Geluwe et al., 2011). The electrophilic character of ozone accounts for its very fast and preferential reaction with unsaturated bonds to oxygenated saturated functional groups, such as aldehydic, ketonic and especially carboxylic groups.

Ozone with a high oxidation potential of 2.07 V reacts with organic compounds either directly (Equation 1, 2) or indirectly through hydroxyl free radical generation (Equation 3, Malik et al., 2020). In direct oxidation reaction ozone reacts with the unsaturated bonds in NOM to produce various oxidation products of NOM (NOM_{ox} , Equation 1) or the production of an ozonide ion radical (O_3^-) by an electron transfer reaction (Equation 2). This reaction is due to the dipolar structure of ozone which helps in splitting the double bond.



These reactions are generally attributed to double bonds, electron-rich aromatic systems, amine, and sulphides (Van Geluwe et al., 2011). They control the decomposition of ozone during the initial phase of ozonation, in which very high amounts of $\text{OH}\cdot$ radicals are generated. Many intermediate chain reactions (involving oxygen and oxygen/hydrogen radicals) are responsible for the oxidation which are summarised by an overall reaction in Equation 3 (Malik et al., 2020). This reaction indicates that three ozone molecules are required to produce two hydroxyl radicals



The hydroxyl free radical, which is a highly reactive and unstable compound has a higher oxidation potential (2.8 V) than ozone (2.07 V). Due to the unstable nature of $\text{OH}\cdot$ radical it immediately undergoes a chemical reaction to become stable (Van Geluwe et al.,

2011). It oxidises the organic molecules (RH) by extracting a hydrogen atom from the molecules with the production of organic radicals (R•) as shown in Equation 4 (Malik et al., 2020; Rekhate and Srivastava, 2020). Although the OH• radical is thought to be an unselective oxidant, organic molecules with unsaturated bonds react faster with OH• radicals than saturated C-C bonds or C-H bonds. As in the case of ozone oxidation (Equation 1), OH radical oxidation also gives oxidation products (NOM_{ox}) (Equation 5).

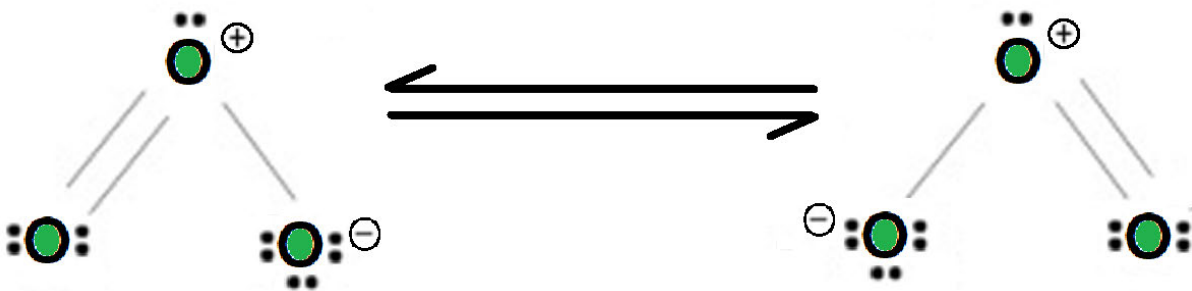


Fig. 1. Resonance structure of Ozone (redrawn from Van Geluwe et al. (2011) and Malik et al. (2020))

Ozone is more effective than chlorine in destroying viruses, protozoa, and bacteria (EPA, 1999). Beltrán et al. (2021) compared the CT values (product of the disinfectant concentration and the detention time) calculated by Doré and des Oxydants (1989) for four drinking water chemical oxidants (chlorine, chlorine dioxide, chloramine, and ozone) to remove five types of common microorganisms. In all cases ozone presented the lowest CT value. Utilising ozone avoids the formation of halogenated organics inherent in the practice of

chlorine treatment. However, it can lead to the formation of other undesirable by-products resulting from incomplete oxidation.

Ozonation of natural waters has been shown to have little effect on the removal of NOM at low ozone doses (Marhaba et al., 2000; Ullberg et al., 2021) and moderate effect at high doses (Sketchell et al., 1999). This is because ozone oxidation converts large organic molecules into smaller molecules such as aldehydes, ketones, carboxylic acids, etc., without completely oxidising them to carbon dioxide gas (Zietzschmann et al., 2015; Sauter et al., 2021). The incomplete oxidation is due to ozone's rapid decomposition in water (Sketchell et al., 1999). Sketchell et al. (1999) reported that ozonation with 2 mgL⁻¹ ozone dose had only a minimal effect on DOC concentration (10% removal), whereas a very high dose of 3.5 mgL⁻¹ resulted in approximately 60% DOC removal. Zietzschmann et al. (2015) also reported that ozone dose up to 1.64 mg.mg⁻¹ DOC did not reduce DOC concentration but reduced the aromaticity, hydrophobicity, and molecular size of the organic compounds. They showed that the LC OCD analysis peaks for biopolymers and humics decreased but those of building blocks and low molecular weight acids increased after ozonation. This demonstrated that the larger molecules were broken down into smaller ones without changing the total DOC concentration in the water. Filloux et al. (2012) stated that ozonation of biologically treated water modified the molecular weight distribution by breakdown of larger organic molecules. Using LC OCD measurement, they showed that the concentration of biopolymers dropped by 44% whereas those of low molecular weight acids and building blocks increased.

Removal percentage of individual OMP by ozonation depends on the kinetic rate constant for the reactions of ozone molecule and OH radicals (OH•) with the OMP (k_{O_3} and k_{OH} values, respectively) (Lee et al., 2013; Sauter et al., 2021). These constants are higher for OMPs containing electron-rich moieties (ERMs), such as phenols, anilines, olefins, reduced sulphur, and amine moieties (Lee and von Gunten, 2010; von Sonntag and von Gunten, 2012; Lee et al., 2013). Lee et al. (2013) spiked 16 OMPs into 10 different secondary wastewater

effluents collected from facilities in Australia (AU), Switzerland (CH), and the U.S. and determined these two rate constants for reaction of ozone at different doses. They grouped the OMPs into 5 classes according to the k_{O_3} and k_{OH} values and found that the percentage of OMPs removed generally increased when the values of these rate constants rose. It was proposed that using these values and ozone dose one can predict the percentage of the OMPs removed. Many of the OMPs were not satisfactorily removed at the normal doses of ozone. Also, of the OMPs removed at high percentages, their oxidation products might have remained in the treated water.

Ullberg et al. (2021) reported that ozonation (0.75 mgL^{-1}) was efficient in reducing the concentrations of a wide range of OMPs, with reduction $>70\%$ for most of them (21 of 29 compounds), but the DOC concentration was reduced only by 4%. They cautioned that although ozonation was efficient in removing the target compounds it creates stable transformation products, and therefore the concept “removal of OMPs” by ozonation may be misleading. When ‘removal’ is commonly referred to in literature, only target compounds are considered, and the potential co-existing transformation products are not accounted for.

In a recent pilot-plant study (Sauter et al., 2021) on the removal of OMPs from municipal wastewater secondary effluent by ozonation prior to biological AC post-treatment, it was reported that the percentage removal was related to the k_{O_3} and k_{OH} values of the respective OMPs. This scenario supports the findings of Lee et al. (2013). The OMPs were classified into fast ($>90\%$ removal), moderate (40-80% removal), and slow (0-70% removal) reactivity with ozone (Fig. 2). Furthermore, the quantity and type of NOM in water often influences the ozonation effectiveness of OMPs. van Gijn et al. (2021) reported that OMP removal from a municipal wastewater effluent spiked with 18 OMPs was affected by the type of organic matter (organic matter fractions) and its size. Within the various fractions, hydrophobic neutrals and hydrophilics had higher interference with OMPs than other

fractions. The smallest size fraction (<1 kDa) was found to have the lowest interference, and this interference depended on the ozonation kinetic rate constants of individual OMPs.

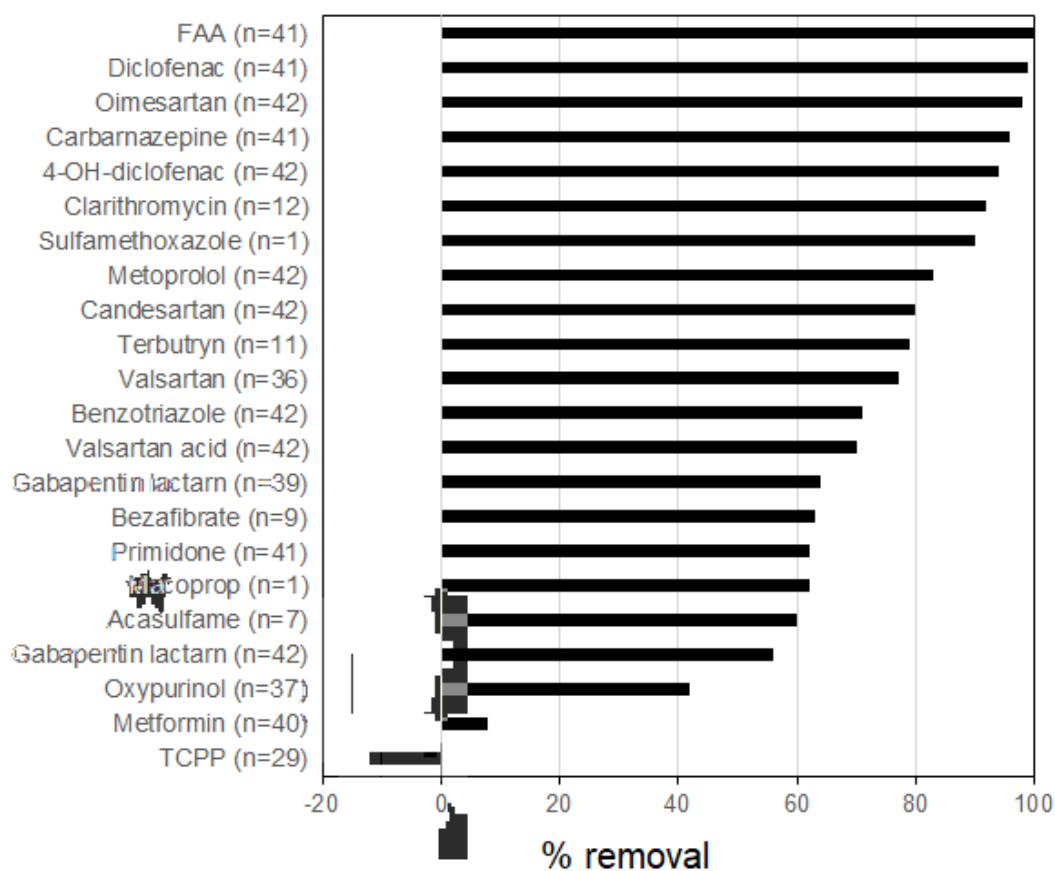


Fig. 2. Average percentage removal of 22 monitored OMPs during ozone treatment (n is the number of data points) (redrawn from Sauter et al. (2021)).

3. NOM and OMPs removal using adsorption

Adsorption is one of the most cost-effective, simple, and efficient processes for removing NOM and OMPs because it can even remove tiny amounts of these pollutants from water, and for this reason it has been widely employed. Moreover, it produces minimum chemical or biological sludge waste, no undesirable by-products and the adsorbent can be restored and reused, thus curtailing operation costs. The efficiency of removal of NOM and OMP using

adsorption depends on the properties of both the adsorbent and adsorbate. The main properties of adsorbent and adsorbate that influence the removal efficiency are surface charge, hydrophobicity, and surface functional groups that promote hydrogen bonding, π - π electron donor-acceptor interaction, and van der Waals' forces (Delgado et al., 2012; Hu et al., 2014; Liu et al., 2014; Shanmuganathan et al., 2014; Jamil et al., 2019; Zhang et al., 2020; Jamil et al., 2021). In addition, the molecular size of the adsorbate, surface area and porosity of the adsorbent influence the degree of adsorption (Liu et al., 2014; Loganathan et al., 2014; Zhang et al., 2020). A scheme for possible mechanisms of ozonation and AC adsorption of NOM constituents and various OMPs is presented in Fig. 3.

NOM is generally negatively charged because of the predominant presence of humic acids having carboxylic groups (Loganathan et al., 2020). Therefore, positively charged adsorbents such as anion exchange resins are well suited to remove them by electrostatic attractive forces. NOM also has a significant percentage of hydrophobic fraction and to remove this fraction adsorbent it is necessary to have a hydrophobic characteristic adsorbent. The OMPs can have positive, negative, or neutral charge and possess hydrophobic or hydrophilic character (Shanmuganathan et al., 2017; Haddad et al., 2019; Guillosoy et al., 2020b). The adsorbent must be compatible with these characteristics of OMPs if they are to be removed efficiently.

Carbon-based materials such as AC, carbon nanotubes, graphene and its derivatives, biochar, engineered hierarchical porous carbon materials, and ion exchange resins are the most successful group of adsorbents used to remove OMPs (Wang and Wang, 2016; Zhang et al., 2020; Zhang et al., 2021). Of these, AC as a traditional adsorbent has been widely used in full scale water treatment plants (Wang and Wang, 2016). However, it has not been always successful in removing all OMPs, especially the hydrophilic and negatively charged ones because it has mostly negative surface charges and hydrophobic character. Other adsorbents (e.g. ion exchange resins, other carbon-based adsorbents) are also not fully successful

because, individually, they do not favourably interact with all the properties of OMPs (e.g. charge, hydrophobicity/hydrophilicity) for effective removal.

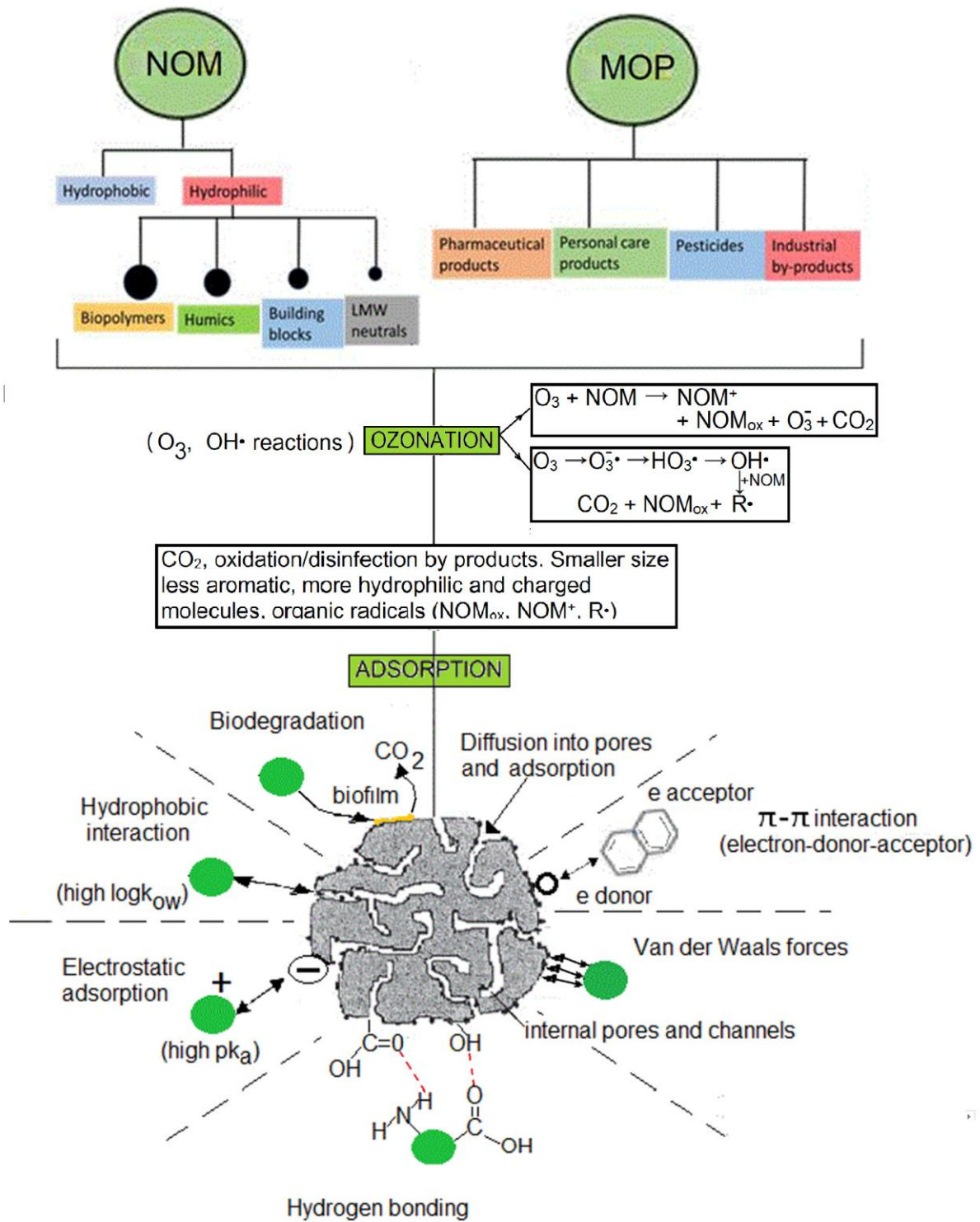


Fig. 3. Possible mechanisms for NOM constituents and various OMPs removal from water by ozonation and adsorption processes.

In an experiment on the comparison of GAC and an anion exchange resin as pre-treatment for nano-filtration of microfiltered water from a water reclamation plant, Jamil et al. (2021) found that humic fraction of the DOC was completely removed by Purolite by electrostatic attractive forces between the negatively charged humics and positively charged anion exchange resin (Fig. 4a). On the other hand, complete removal of the hydrophobic fraction was obtained by GAC adsorption. The latter was explained as due to hydrophobic interactive forces. The hydrophobic interaction is explained as being caused by π - π bonding between aromatic rings in the hydrophobic molecules in DOC and GAC surface (Moreno-Castilla, 2004; Valderrama et al., 2009). In this type of bonding, oxygen groups on the GAC surface act as electron donors, while the aromatic rings of the hydrophobic molecules act as electron acceptors (Dąbrowski, 2005; Tran et al., 2017). Jamil et al. (2020, 2021) reported that in addition to the hydrophobic fraction, GAC also removed larger amounts of building blocks and low molecular weight neutrals. What made this possible was diffusion of these low molecular size molecules into the GAC pore. On the other hand, GAC removed fewer biopolymers than Purolite, probably because the larger biopolymer molecules were unable to penetrate the pores of GAC, and because biopolymers are highly hydrophilic in nature (Filloux et al., 2012).

Continuous use of GAC can result in microbial biofilm formation on the GAC surface which can assist in the decomposition of DOC (Sketchell et al., 1999; Moona et al., 2018). Several studies on wastewater applications have demonstrated that the presence of such a biofilm may enhance the overall DOC removal and the removal of individual micropollutants (Alonso et al. 2021). Sketchell et al. (1999) developed a biological activated carbon by continuously pumping reservoir water through GAC for a long time and used it in their water filtration experiments. The authors observed very high removal of DOC mainly because of the decomposition of the biodegradable DOC by the biofilm in GAC.

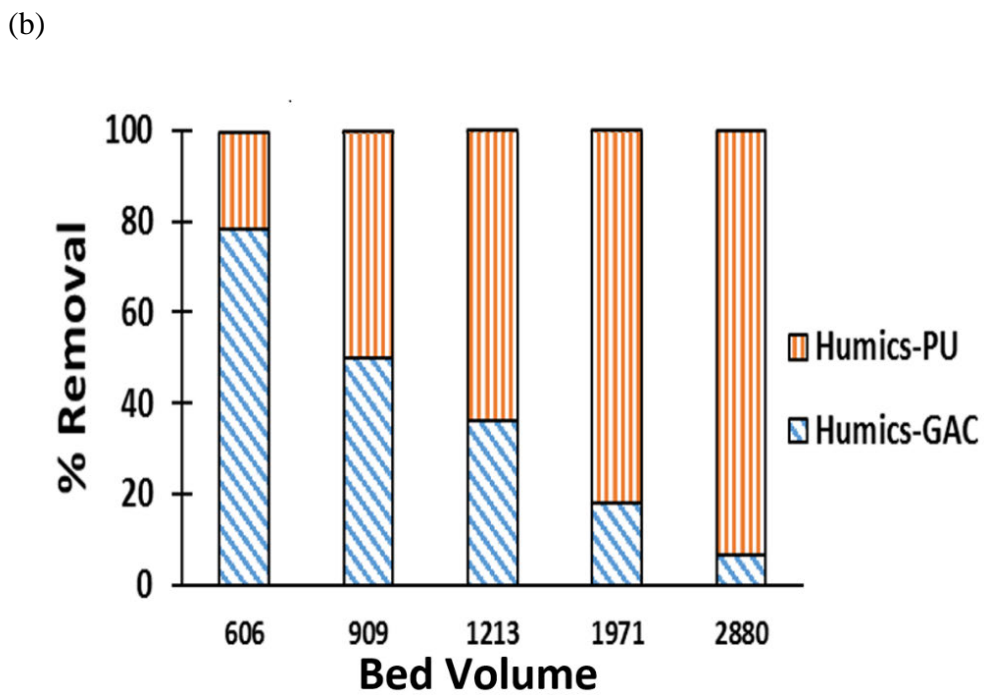
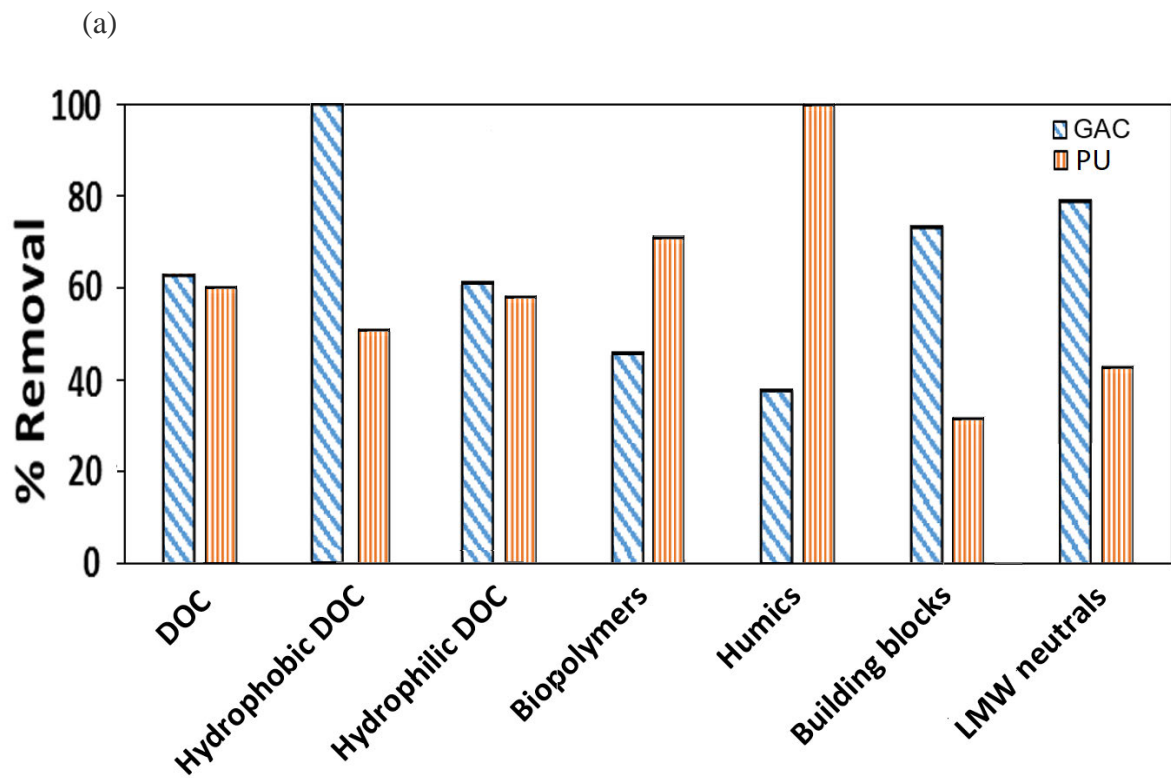


Fig. 4 (a) Comparison of DOC fractions removal from microfiltered water from a water reclamation plant by GAC and Purolite anion exchange resin (PU) columns (redrawn from Jamil et al. (2021)). (b) Humics fraction removal, firstly by the GAC column and then by the Purolite (PU) column (redrawn from Jamil et al. (2020))

Regarding OMPs removal, in the study of Jamil et al. (2021), the GAC removed a higher percentage of diclofenac (91%) than the anion exchange resin (76%) because of the much higher hydrophobicity of this OMP ($\log K_{ow}$ 4.0-4.5) which caused greater affinity to the hydrophobic GAC. On the other hand, the hydrophilic OMPs with very low $\log K_{ow}$, benzotriazole (1.44), carbamazepine (2.45), and trimethoprim (0.91) were removed at higher percentages by the hydrophilic anion exchanger (98, >98, >97, respectively) than by the GAC (75, 48, 85, respectively). Instead of the hydrophilic anion exchange resin had a neutrally charged hydrophobic resin was used the hydrophobic OMPs can be effectively removed. Haddad et al. (2019) used three neutral polymeric resins with high porosities and satisfactorily removed nine OMPs having positive, negative, or neutral charge at pH 7 and varied $\log K_{ow}$ values. They reported that this type of resin was a promising alternative to activated carbon for micropollutants sorption in drinking water treatment.

Others have also shown that hydrophobic interaction is an important property in the removal of OMPs by activated carbon (Westerhoff et al., 2005; Snyder et al., 2007; Nam et al., 2014; Wang and Wang, 2016). For example, Snyder et al. (2007) reported that two different types of GACs removed several OMPs (endocrine disruptors, pharmaceuticals, and personal care products) spiked to municipal wastewater effluent in accordance with their degree of hydrophobicity ($\log K_{ow}$). OMPs exhibiting less hydrophobicity resulted in rapid breakthrough from the column because of their weaker adsorption to GAC. Jamil et al. (2019) reported that the removal efficiency of 18 OMPs in GAC columns depended on both hydrophobicity and charge. They classified the OMPs removal into four groups based on charge and $\log K_{ow}$. The four positively charged OMPs having high $\log K_{ow}$ (< 3.5) showed the highest percentage removal (95-100%).

OMP adsorption can be reduced by NOM due to competition for adsorption sites on the activated carbon surface and inside pores, and blockage of activated carbon pores with larger molecules of the NOM (Li et al., 2003; Snyder et al., 2007). Generally, micropores

(pore diameter < 2 nm) play a major role in providing sorption sites, whereas mesopores (2 nm < pore diameter < 50 nm) and macropores (pore diameter > 50 nm) act as diffusion channels (Liu et al., 2014; Zhang et al., 2020). Kinetics of adsorption will also influence the degree of competition between OMP and NOM for adsorption. Liu et al. (2014) reported that in the presence of humic acid, three OMPs and smaller size humic acid molecules would occupy the adsorption sites first, followed by the adsorption of the higher molecular weight components of humic acid. Therefore, pores blockage resulting from the non-preferential adsorption of large size humic acid molecules did not affect the OMPs adsorption much. However, excessive deposition of biofilm growth inside the pores of previously used GAC can prevent larger sized OMPs from entering the pores and prevent OMPs adsorption in pores.

4. NOM and OMPs removal using ozonation/adsorption hybrid process

Though ozone is a powerful oxidising agent in removing microorganisms and most of the NOM and OMPs, by-products of oxidation are generated. Also, as discussed previously, it does not remove all DOC constituents. Generally, the larger organic molecules are broken down into smaller ones during ozone oxidation. In the case of OMPs, some of them are not removed by ozonation because their oxidation rates are slow (Lee et al., 2013; Sauter et al., 2021). Another concern is that, when ozone is applied at practical doses, because NOM and OMPs compete for oxidation, some of them remain unoxidized in the water (van Gijn et al., 2021).

Considering the above problems of ozonation, many have added an adsorption post-treatment step to ozonation to remove the unoxidized NOM and OMPs and their by-products. Activated carbon has been a popular adsorbent used in many studies (Müller et al., 1996; Matsui et al., 1999; Sketchell et al., 1999; Zietzschmann et al., 2015; Bourgin et al., 2018;

Guillossou et al., 2020a; Sauter et al., 2021; Ullberg et al., 2021). However, the improvements achieved by the adsorption process have not been reported in quantitative terms in all the studies.

One of the earliest analyses conducted on coupling ozonation and adsorption was using biological activated carbon (BAC) filter after ozonation in removing DOC, colour and trihalomethane from reservoir water in a laboratory trial (Sketchell et al., 1999). The BAC used was from a long-term field trial where biofilm was allowed to grow on the GAC. The results showed that the biodegradable proportion of DOC increased with ozone dose. Both ozonation and adsorption individually decreased DOC concentration (Fig. 5), colour and trihalomethane concentration. However, when the treatments were combined the reduction of these concentrations was much greater which others had observed (Guillossou et al., 2020a). The biofilm in AC would have decomposed the biodegradable DOC and therefore this biological process further assisted the removal of OMPs and NOM in addition to the adsorption process.

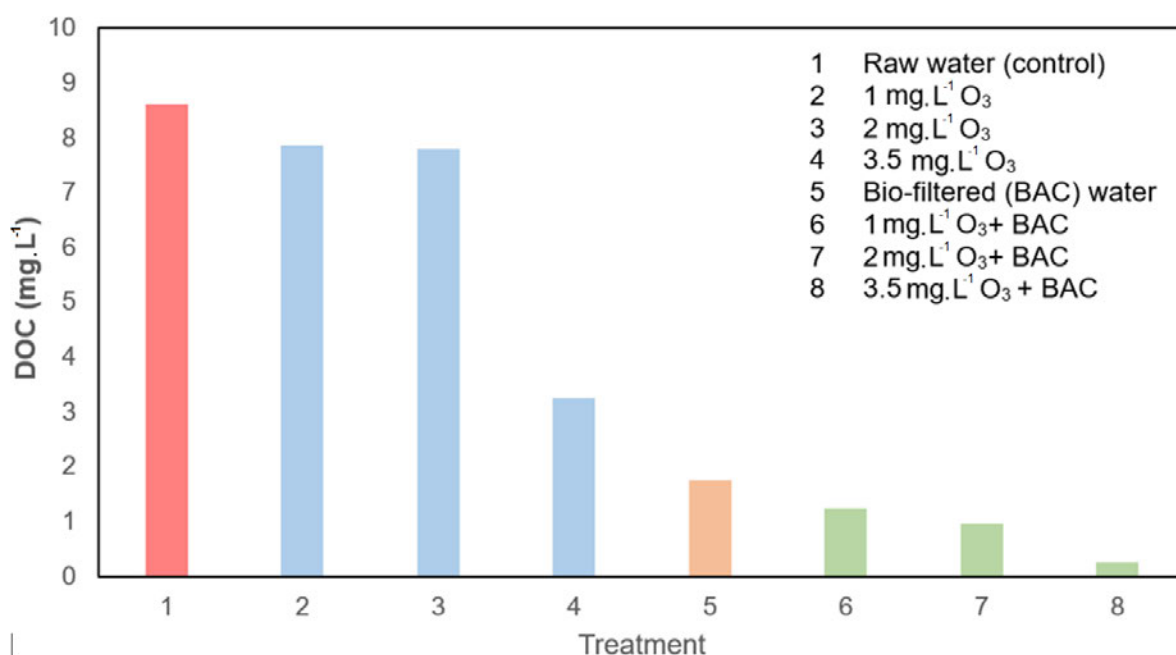


Fig. 5. Decrease in DOC after ozonation, biofilm-developed AC (BAC) column adsorption, and ozonation + adsorption treatments (the figure is prepared using the data of Sketchell et al., (1999)).

Zietzschmann et al. (2015) studied the removal of NOM and some OMPs from a wastewater effluent by ozonation using different doses of ozone followed by adsorption of the oxidised products and unoxidized NOM and OMPs onto powdered AC. They concluded that: firstly, combining ozonation and AC adsorption benefited the removal of OMPs more than using the treatments individually; and secondly, ozonation can alleviate adsorption competition caused by the NOM constituents. Reducing the adsorption competition was explained as being due to ozonation diminishing the adsorption capacity of various NOM constituents owing to their transformation into compounds having lower aromaticity, molecular size, and hydrophobicity. Ozone preferentially reacts with aromatics than non-aromatics by selective destruction of the electron-rich aromatic ring systems (Westerhoff et al., 1999; Wenk et al., 2013; Zietzschmann et al., 2015). For OMPs having stronger adsorbing affinities to AC, a smaller ozone dose was found to be sufficient, whereas for weakly adsorbing OMPs higher ozone doses were necessary to avoid the competition.

In a one-year pilot plant study on the removal of NOM and OMPs from a lake water, Ullberg et al. (2021) reported that breakthrough of OMPs was delayed when GAC columns were used after ozonation compared to without prior ozonation treatment. A possible explanation for this was lower adsorption competition with low-molecular-weight natural organic matter (NOM) fraction decreasing the aromaticity produced by ozonation. They concluded that ozonation enabled the GAC filters to run for longer time.

Ozonation with post-AC filtration in a full-scale waste treatment plant was tested by Bourgin et al. (2018). They reported that treatment with fresh AC filter after ozonation improved OMPs removal compared to solely ozonation treatment or an identical AC filter without prior ozonation treatment running parallel to the ozonation + AC treatment. The concentrations of oxidation by-products and NOM transformation products were reduced by the post-treatment with AC. The breakthrough of OMPs and DOC was delayed and occurred after an increased number of effluent bed volumes. The later breakthrough of OMPs and DOC in the ozonation + AC treatment compared to ozonation alone or AC alone treatment and the explanation was ozonation broke down NOM into less competitive species for OMP adsorption.

Less competition was reported because of NOM was being transformed into smaller compounds with less aromaticity and more hydrophilicity possessing more charges which caused reduced adsorption of NOM constituents. This has also been commented on by others (Zietzschmann et al., 2015). Guillosoy et al. (2020a) reported a similar study in removing 10 OMPs from a wastewater effluent by ozonation followed by adsorption onto powdered AC (PAC) at different doses of ozone and PAC in a batch experiment. They too found that adsorption after ozonation was more efficient in removing OMPs than when these processes were used individually. Low ozone doses did not improve OMPs removal in comparison to higher doses, yet low doses coupled with AC adsorption was reported to be complementary and an adequate process for the removal of OMPs. The increased OMPs removal was

attributed to the decreased NOM adsorption which led to a reduced adsorption competition with OMPs as reported by others (Zietzschmann et al., 2015; Bourgin et al., 2018).

The degree of adsorption competition of NOM depends on the composition of the NOM which varies with the type of water and ozone rate used. Wang et al. (2020) compared three ozonated natural waters and one synthetic water (standard humics solution) with highly heterogeneous NOM compositions to study NOM competition against adsorption of 2-methylisoborneol (MIB) on AC. They reported that the competition waned with increasing ozonation rates in the natural waters. In contrast, in synthetic water, ozonation at low/moderate ozone rates increased NOM adsorption and competition; only at high ozone rates did this competition decline because of the decreased NOM adsorption. The increased NOM adsorption and competition against MIB adsorption at low/moderate ozone rates, was explained as likely due to more pore accessibility or blockage by humic substances with lower molecular weight. For higher ozone rates, this effect was outweighed by the competition-alleviating aromaticity reduction of NOM by ozonation and its adsorption. Aromaticity reduction lowers the intensity of π - π electron donor-acceptor interaction and hydrophobic attraction of NOM on AC leading to reduced adsorption (Castan et al., 2020). Castan et al. (2020) conducted adsorption batch experiments with three types of NOM (humic acid, river water, and a compost extract) and three types of carbonaceous adsorbents (graphite, carbon nanotubes, and biochar) of different geometries and surface complexities. It was reported that aromatic NOM fraction generally had preferential sorption regardless of NOM type. They used $SUVA_{254}$ value (UV absorbance at 254 nm/ DOC concentration x100) as a measure of aromaticity. Exceptions to aromaticity controlling adsorption are other factors such as NOM molecular weight, adsorbent functionality, and adsorbent geometry which were less favourable for adsorption.

Biological process besides adsorption is important in the removal of NOM and OMPs when AC is continuously used for a long period and biofilm grows on the AC (Alonso et al.,

2021; Sauter et al., 2021,). This is an attractive feature of AC compared to other adsorbents and a possible reason for its popular use in removing these pollutants. Sauter et al. (2021) compared three deep-bed-filter (1.2-1.8 meters) post-treatments to ozonation, namely biological AC (BAC), BAC/sand and anthracite/sand in the removal of NOM and OMPs in a long-term (1.5 years) study. They reported that ozonation without the filters reduced DOC only marginally at the low ozone dose used, but UV_{254} reduced substantially due to oxidation of aromatic compounds to aldehydes, ketones, and carboxylic acids. These oxidation products are largely biodegradable and consequently, BAC filtration following the ozonation treatment increased the removal of DOC. However, this did not apply to the anthracite-based filter because of the biological activity of BAC degrading the bioavailable carbon source. Similarly, with respect to OMPs abatement, BAC containing filters showed additional removal of OMPs after ozonation even after a long duration of filtration (>50,000 bed volumes), whereas no additional removal was noticed when the anthracite-based filter was employed. Because OMPs removal in BAC filters remained constant even after 50,000 bed volumes, it was assumed that a biological process besides adsorption was operating as part of the treatment. If the removals were due to only adsorption, the adsorption sites would have become saturated within a short period of time and subsequently no more OMPs removal would have occurred. In another study investigating the removal of NOM and OMPs from municipal wastewater using 6 types of GAC over 32 months the biological processes accounted for about 25 – 42% of the totally removed DOC at the end of the operation (Fundneider et al., 2021). MOPs removal by these processes were also highly significant. Alonso et al. (2021) cited several studies where the presence of biofilm on AC enhanced the overall NOM and OMPs removal in wastewater treatment plants.

5. Two contrasting adsorbents in sequence after ozonation treatment

To date, all adsorption/ozonation hybrid processes for the removal of NOM and OMPs used one type of adsorbent, namely different forms of AC as the post-treatment to ozonation. Although this treatment system was found to be satisfactory for most NOM fractions and large number of OMPs, several were not removed to the required levels. This is because the properties of AC were insufficiently favourable to adsorb them. For example, metformin was not removed at all with ozonation and the subsequent 1.5 yr of pilot plant column adsorption on biological AC was also poor (Sauter et al., 2021). The poor adsorption was explained as stemming from the extremely polar nature of this OMP ($\log D_{7.4} = -5.6$). Such a polar type of OMP would be favourably adsorbed if a hydrophilic type of adsorbent was used, instead of the hydrophobic AC. Another important property of adsorbent influencing adsorption is the surface charge on the adsorbent. AC, being negatively charged around neutral pH, has high affinity to positively charged OMPs but expected to have poor adsorptive capacity towards negatively charged NOM fractions such as humics and negatively charged OMPs (Shanmuganathan et al., 2014; Jamil et al., 2019; Guillossou et al., 2020b). The data of Guillossou et al. (2020b) clearly demonstrate the influence of charge and hydrophobicity of NOM fractions and OMPs on their adsorption on a powdered AC. They reported that, of the various NOM fractions, the negatively charged humic acids fraction exhibited the lowest adsorption capacity. Of the various OMPs tested the smallest percentages of OMPs removed were the negatively charged and the most hydrophilic ones (Diclofenac ($\log_8 = 0.26$, 27% removal), sulfadiazine ($\log_8 = 0.66$, 31% removal) and ibuprofen ($\log_8 = 0.69$, 24% removal). Similar findings were reported by Jamil et al. (2019).

The findings of the studies discussed in the preceding paragraph indicate that a combination of different adsorbents having contrasting surface charge, hydrophobicity, and other properties is required to remove all the different NOM fractions and OMPs **having positive, negative or neutral charge with hydrophobicity or hydrophilicity characteristic**. An example of such adsorbents and how they were able to differentially remove the various

NOM fractions was discussed previously with supporting data (Fig. 4a). Differences in the adsorption of two OMPs, namely benzotriazole and diclofenac by the adsorbents used (GAC and Purolite (anion exchange resin)) were also recently reported (Jamil et al., 2021). GAC adsorption removed a higher percentage of diclofenac (high log K_{ow} of 4-4.5) than Purolite (91% by GAC and 76% by Purolite), but the opposite occurs with benzotriazole (low log K_{ow} 1.44) (75% by GAC and 99% by Purolite). This is because GAC being hydrophobic had higher affinity to hydrophobic OMPs (high log K_{ow}) and Purolite being hydrophilic had higher affinity to hydrophilic OMPs (low log K_{ow}). This study demonstrated that combining adsorbents having different affinities towards the variety of DOC fractions and OMPs should be a more effective method of removing all these pollutants with varied characteristics. Therefore, GAC and Purolite adsorbents were combined and used in sequential order of GAC followed by Purolite in a long-term column study to investigate the removal of NOM fractions from a wastewater reverse osmosis concentrate (Jamil et al., 2020). This investigation demonstrated that the adsorbents did complement each other, and together they removed 100% of humics, whereas the initial GAC column alone removed only 5-75% during the 9.5 days (2880 bed volumes) of the experiment (Fig. 4b).

These results suggest that using such a sequential combination of adsorbents having contrasting properties can be a better treatment system than using one adsorbent as in previous studies of the ozonation/adsorption process. The additional cost involved in using two adsorbents is expected to be overcome by the superior quality of the treated water that is produced. This can be even blended with less pure water to produce increased volume of water and still meet the permissible limits of pollutant concentrations. Furthermore, the quantity of each adsorbent used can be halved when two adsorbents are used compared to when one adsorbent is used.

Other adsorbents having similar properties as GAC and Purolite anion exchange resins can be explored for use in the sequential hybrid treatment process. Hydrophobic polymeric

resins have been shown to effectively remove many hydrophobic OMPs due to their high porosity and accessible internal adsorption sites (Haddad et al., 2019). Therefore, they can be used as an alternative to GAC. However, as in the case of GAC, they were not able to remove the hydrophilic OMPs and therefore another adsorbent needs to be used in sequence to deal with this problem. Moreover, removals by biodegradation process caused by biofilm growth on GAC is not possible with other adsorbents. Exchange resins other than Purolite can be tested for removing negatively charged hydrophilic OMPs. For example, a magnetic ion exchange resin (MIEX) which is a polyacrylate macroporous polymer with strong base quaternary ammonium functional group (positively charged) and a magnetic iron oxide core to assist with resin agglomeration and recovery have been successfully used as an anion exchanger to remove the negatively charged OMP, estrone (Neale et al., 2010). Bäuerlein et al. (2012) reported that ion-exchange polymers may be effective as alternative adsorbents, because adsorption of all charged OMPs to oppositely charged polymers was stronger than to AC, especially for the double-charged cation metformin. Their research also showed that sorption of cationic OMPs was reduced in Ca^{2+} solutions compared to similar concentrations of Na^+ , while that of anionic OMPs was much weaker in SO_4^{2-} solutions compared to equal concentrations of Cl^- . Amine-grafted agricultural wastes (Kalaruban et al., 2016a), iron modified exchange resins (Kalaruban et al., 2016b) and iron modified AC (Kalaruban et al., 2019) which were successfully used to remove inorganic anionic pollutants are other possibilities that can be tested as a replacement for Purolite to remove OMPs. Because these modifications produced positive surface charges on the adsorbents, they are expected to remove negatively charged OMPs as Purolite did. They also have surface functional groups which can adsorb the OMPs by H-bonding mechanism.

6. Conclusions

Ozonation and adsorption on their own are effective processes for removing most of the OMPs and many of the NOM constituents from water to acceptable levels. However, when combined in the order of ozonation followed by adsorption, their performance is greatly enhanced. Ozonation not only completely oxidises most of these pollutants but also converts large organic molecules into smaller ones such as aldehydes, ketones, carboxylic acids, etc., without completely oxidising them to carbon dioxide gas. Therefore, the DOC concentration does not reduce much at low ozone doses. The transformed molecules generally have less aromaticity, molecular size, and hydrophobicity resulting in reduced adsorption on the commonly used adsorbent, AC. The reduced adsorption of these molecules curtails their competition against OMP adsorption resulting in increased MOP removal. The effectiveness of ozonation to remove OMPs increases when there is an increase in the kinetic rate constant for the reactions of ozone molecule and OH radicals (\bullet OH) with the MOP.

The main properties of adsorbent and adsorbate that influence the removal efficiency of NOM and OMPs are surface charge, hydrophobicity, and surface functional groups that promote hydrogen bonding, π - π electron donor-acceptor interaction, and van der Waals' forces. Additionally, the molecular size of the adsorbate, and surface area and porosity of the adsorbent influence the degree of adsorption. The NOM and OMPs removals by AC are achieved not only by adsorption mechanism but also by biological transformation produced by the microbial biofilm development on the AC surface. The intensity of biofilm formation gets stronger with longer period of AC usage. Because the NOM constituents and the different OMPs have a variety of properties, a combination of different adsorbents having contrasting surface charge, hydrophobicity, and other properties is required to remove all of them. In the past only different types of AC were used as adsorbents after ozonation treatment and this has not always been completely successful in removing all NOM constituents and OMPs. Based on some recent studies, recommendations are made here to use two adsorbents, namely, AC and an anion exchange resin in sequential order after ozonation treatment to

improve the process. AC is hydrophobic, porous and has net negative surface charges whereas the anion exchange resin is hydrophilic and has surface positive charges. With these contrasting properties, the two adsorbents when combined were able to adsorb all the different NOM constituents and the various types of OMPs and ensure their complete removal. Further research is recommended on the sequential use of alternative adsorbents with contrasting surface charge and hydrophobic/hydrophilic properties and testing their application as a post treatment process to ozonation. The trials with these alternative adsorbents need to be of long-term duration and comparison needs to be made with using AC as the first adsorbent in the sequence. This is because unlike other adsorbents where the removal decreases with time due to adsorption sites getting saturated, in the case of AC it may increase because of biodegradation caused by the continued growth of microbial biofilm on AC.

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