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Characterization and coagulation of impurities in water treatment

DISSERTATION

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Charakterizace a koagulace znečišťujících příměsí při úpravě vody

DISERTAČNÍ PRÁCE

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ABSTRACT

Undesirable natural or anthropogenic compounds are commonly present in drinking water supplies. An ongoing challenge for water treatment is algal organic matter (AOM) produced by phytoplankton. A part of this thesis is devoted to the coagulation of AOM, specifically cellular organic matter (COM) and its peptide/protein and non-proteinaceous fraction. Besides investigating the coagulation in relation to the COM character, attention was paid to its interactions with other compounds and to the subsequent impacts on coagulation. Additionally, the involvement of an ozonation step was assessed. Another part of the thesis is focused on emerging anthropogenic water pollutants microplastics (MPs), particularly on their quantification and characterization at drinking water treatment plants (DWTPs).

It has shown that the optimum coagulation conditions differ for the COM peptides/proteins and the non-proteinaceous fraction. While the former were effectively removed at slightly acidic coagulation pH, the latter required coagulation pH around neutral and much higher doses of coagulant. The maximum removal efficiency for the non-proteinaceous fraction was much lower compared to that of the peptides/proteins (25% versus 75%), owing mainly to the high content of low-molecular weight (< 10 kDa) compounds. Further, it was found that when COM, namely the peptide/protein fraction, occurs in water together with other organic or inorganic compounds such as humic substances or clay colloids, deterioration in coagulation can be avoided by optimization of coagulation conditions, especially of the coagulation pH. In case of the organic compounds mixture, even better coagulation efficiency and lower coagulant demand (compared to coagulation of the compounds alone) was achieved. Mutual coagulation optimum was determined also for a mixture of cyanobacterial cells and COM, while the removal of 99% and 57% was attained, respectively. When pre-ozonation was applied prior to coagulation of the non-proteinaceous COM, either increased or decreased removal was observed depending on the pre-ozonation conditions, i.e., O_3 dose and ozonation pH, while aldehydes were found to be formed as ozonation by-products.

With regard to MPs, their occurrence was revealed in both raw and treated water of different DWTPs supplied by surface water. The average numbers ranged from 1473 ± 34 MPs L^{-1} to 3605 ± 497 MPs L^{-1} in raw water and from 338 ± 76 MPs L^{-1} to 628 ± 28 MPs L^{-1} in treated water, depending on the DWTP; the removal was 70-83%. The prevailing shapes were fibres and fragments, major materials were polyethylene terephthalate, polypropylene, and polyethylene, and the vast majority of MPs was < 10 μm in size.

ABSTRAKT

Zdroje pitné vody běžně obsahují nežádoucí látky přírodního i antropogenního původu. Problémy při úpravě vody působí látky produkované fytoplanktonem (algal organic matter – AOM). Část této práce je věnována odstraňování AOM pomocí koagulace; konkrétně byly studovány celulární AOM (cellular organic matter – COM) a jejich peptidová/proteinová a neproteinová složka. Kromě výzkumu koagulace COM ve vztahu k jejich charakteru byla pozornost věnována interakcím COM s dalšími látkami a jejich následným dopadům na koagulaci. Testováno bylo také využití ozonizace. Další část práce je pak věnována poměrně nově sledovaným antropogenním polutantům vodního prostředí – mikroplastům (MPs), a to zejména jejich kvantifikaci a charakterizaci na úpravnách pitné vody.

Optimální podmínky koagulace jsou rozdílné pro COM peptidy/proteiny a neproteinovou složku. Zatímco peptidy/proteiny byly nejúčinněji odstraňovány při mírně kyselém pH, neproteinová složka koagulovala v oblasti kolem neutrálního pH, přičemž bylo zapotřebí vyšších dávek koagulačního činidla. Lišila se i maximální účinnost koagulace, která byla 75 % pro peptidy/proteiny a jen 25 % pro neproteinovou složku, zejména z důvodu vysokého obsahu nízkomolekulárních látek (< 10 kDa). Dále bylo zjištěno, že výskyt COM peptidů/proteinů ve vodě obsahující další organické či anorganické znečištění, jako např. huminové látky nebo koloidní jílové minerály, nemusí vést ke zhoršení účinnosti koagulace, pokud jsou přizpůsobeny podmínky koagulace, zejména reakční pH. V případě organických látek bylo dokonce pozorováno zlepšení účinnosti koagulace a současně snížení potřebné dávky koagulačního činidla (v porovnání s koagulací daných látek samostatně). Koagulační optimum bylo určeno také pro současné odstraňování sinicových buněk a COM, přičemž bylo dosaženo účinnosti až 99 % pro buňky a 57 % pro COM. Využití pre-ozonizace ve spojení s koagulací bylo testováno pro neproteinovou složku COM a v závislosti na podmínkách pre-ozonizace (dávka O_3 a pH ozonizace) bylo pozorováno zvýšení či snížení celkové účinnosti odstranění, přičemž při zapojení ozonizace docházelo ke tvorbě aldehydů.

Přítomnost mikroplastů byla zjištěna jak v surové, tak upravené vodě na úpravnách zásobovaných z povrchových vodních zdrojů. Průměrné množství MPs v surové vodě bylo 1473 ± 34 MPs L^{-1} až 3605 ± 497 MPs L^{-1}, v upravené pak 338 ± 76 MPs L^{-1} až 628 ± 28 MPs L^{-1}; účinnost odstranění dosahovala 70-83 %. Z tvarů převažovaly fragmenty a vlákna, z materiálů polyetylentereftalát, polypropylen a polyetylen, přičemž naprostá většina MPs byla < 10 μm.

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1 INTRODUCTION

Removing a variety of compounds, both those of natural and anthropogenic origin, is required during drinking water treatment, particularly in case of surface water resources. This PhD thesis is devoted to the characterisation and removal of two important groups of impurities, i.e., algal organic matter (a part of natural matter) and microplastics (emerging anthropogenic contaminants). The literature background is provided in the following sub-sections.

1.1 Algal organic matter

The occurrence of phytoplankton, including cyanobacteria, green algae, or diatoms, etc., is ubiquitous in surface water bodies (Hallegraeff, 1993; Paerl et al., 2001; Dixon et al., 2011; Zhou et al., 2017). Nowadays, environmental conditions that favour proliferation of phytoplankton, such as elevated temperature and enhanced nutrient supply (especially nitrogen and phosphorus), are quite common (Paerl et al., 2001; Heisler et al., 2008; Zhou et al., 2017). Resulting massive occurrences of phytoplankton are recognized as algal blooms, or also harmful algal blooms (HABs) owing to their detrimental effects on water quality (Hallegraeff, 1993; Paerl et al., 2001; Anderson et al., 2002; Zhou et al., 2017). The content of phytoplankton cells in surface waters currently affected by the blooms was reported to reach up to millions of cells per mL (Hallegraeff, 1993; Dixon et al., 2011).

The presence of phytoplankton then leads to a release of algal organic matter (AOM) into water. AOM is a varied mixture of organic compounds (Henderson et al., 2008; Fang et al., 2010; Villacorte et al., 2015), and can be divided into extracellular organic matter (EOM) and (intra)cellular organic matter (IOM/COM), according to its origin. EOM is produced extracellularly as a result of metabolic processes of living phytoplankton cells; COM is formed when they die and decompose (Pivokonsky et al., 2006, 2014, 2016; Henderson et al., 2008). Additionally, surface-retained organic matter (SOM) is sometimes distinguished (Takaara et al., 2007, 2010).

AOM commonly forms a substantial part of natural organic matter (NOM) present in surface waters, and it can account for nearly all NOM content in some eutrophic water bodies (Zhang et al., 2010; Pivokonsky et al., 2016; Adams et al., 2018). To illustrate, different phytoplankton species at cell concentrations of $12 \cdot 10^6$, $12 \cdot 10^4$, and $18 \cdot 10^6$ cells mL^{-1}, respectively, were observed to correspond to stationary phase EOM concentrations of approximately 20, 40, and 60 mg L^{-1} as DOC (dissolved organic carbon) under laboratory

conditions (Pivokonsky et al., 2014). Henderson et al. (2008) quantified EOM DOC per cell, and it ranged from approximately 0.001 to 0.65 ng DOC cell^{-1} depending on the species and its growth phase, while generally higher numbers were observed during stationary compared to exponential growth phase. Additionally, in natural water bodies, particularly high content of COM DOC is released after the bloom decay (Zhang et al., 2010). Increase in DOC as a result of cell decomposition was observed also in laboratory cultures at the decline phase, during which the DOC content approximately doubled compared to the stationary growth phase (Leloup et al., 2013). Additionally, COM may also be discharged as a result of cell damage during some water treatment processes, e.g., pre-oxidation (Ma et al., 2012; Coral et al., 2013; Wen et al., 2017).

Removal of AOM during drinking water treatment is required because of several reasons. AOM produced by some (especially cyanobacterial) species may contain toxins harmful to human health, mostly hepatotoxins or neurotoxins (Carmichael, 1992; Pearson et al., 2016), and AOM can be a source of undesirable taste and odour of water (Zhang et al., 2010; Srinivasan and Sorial, 2011; Li et al., 2012). Further, AOM serves as a precursor for the formation of disinfection by-products (DBPs) (Fang et al., 2010; Li et al., 2012; Goslan et al., 2017; Liu et al., 2018), many of which pose a health hazard owing to carcinogenic, mutagenic, or other adverse health effects (Richardson et al., 2007; Hamidin et al., 2008). The most pronounced DBPs include trihalomethanes (THMs) and haloacetic acids (HAAs), which both belong to carbonaceous DBPs (C-DBPs) (Zhou et al., 2015; Liu et al., 2018; Hua et al., 2019). Another group are nitrogenous DBPs (N-DBPs) such as haloacetonitriles (HANs) (Zhou et al., 2015; Goslan et al., 2017; Liu et al., 2018). These all are formed after chlorination or, to a lesser extent, after chloramination of AOM or other organic precursors (Fang et al., 2010; Li et al., 2012). For example, specific THM, HAA, and HAN yields for AOM of different species were reported to be approximately 20-60, 15-80, and 0-1 µg mg^{-1} C, respectively (Goslan et al., 2017; Hua et al., 2019). Moreover, AOM may be a source of assimilable carbon in water distribution system, which can threaten microbiological quality of water (Hammes et al., 2007; Wen et al., 2017). The influence of AOM on the removability of other water impurities is also worthy attention. For example, AOM may interfere with coagulation of other compounds (Bernhardt et al., 1985; Takaara et al., 2007; Ma et al., 2012), cause membrane fouling (Her et al., 2004; Zhang et al., 2016), or compete with target pollutants for adsorption onto activated carbon (Hnatukova et al., 2011; Pivokonsky et al., 2016).

1.1.1 Composition and properties of AOM

AOM (both EOM and COM) contains a range of compounds, e.g., peptides and proteins, carbohydrates, lipids, various organic acids (amino acids, nucleic acids, uronic acids, etc.), amino sugars, or lipopolysaccharides (Myklestad, 1974, 1995; Weckesser et al., 1974; Bertocchi et al., 1990; Pivokonsky et al., 2006, 2014; Henderson et al., 2008; Fang et al., 2010; Takaara et al., 2010; Markou et al., 2012; Laurens et al., 2014; Villacorte et al., 2015). Composition of AOM is species-dependent and also varies with the growth phase of the organisms (Pivokonsky et al., 2006, 2014; Henderson et al., 2008; Laurens et al., 2014). Moreover, external factors such as temperature, light intensity (van der Westhuizen and Eloff, 1985), and nutrient availability (Myklestad, 1995; Markou et al., 2012) are also influential.

A significant proportion of AOM is usually formed by peptides/proteins (Her et al., 2004; Henderson et al., 2008; Pivokonsky et al., 2006, 2014; Li et al., 2012; Villacorte et al., 2015). They were reported to comprise up to 60-70% of AOM DOC. In laboratory cultivations of various phytoplankton species (cyanobacteria *Anabaena flos-aquae*, *Microcystis aeruginosa*; green algae *Chlamydomonas geitleri*, *Scenedesmus quadricauda*; diatom *Fragilaria crotonensis*), the relative proportion of peptides/proteins in EOM increased with the age of the culture, and reached the maximum in COM. In general, the content of peptides/proteins was the highest for cyanobacteria and the lowest for green algae (Pivokonsky et al., 2006, 2014). An overview of the peptide/protein and non-proteinaceous fraction share on EOM/COM DOC in dependence of the species and growth phase is provided by Fig. 1. Additionally, substantial protein content, up to approximately 50%, was reported also when determined as phytoplankton dry weight (DW) (Myklestad, 1974; Laurens et al., 2014).

Other significant AOM constituents are carbohydrates (Myklestad, 1974, 1995; Bertocchi et al., 1990; Laurens et al., 2014; Villacorte et al., 2015). For example, the proportion of carbohydrates on DW was up to 90% for marine diatoms (Myklestad, 1974) and up to approximately 50% for green algae (*Chlorella* sp., *Scenedesmus* sp.) (Laurens et al., 2014). Similar to peptides/proteins, the proportion of carbohydrates also changes during the growth of a culture (Myklestad, 1974; Laurens et al., 2014).

Especially undesirable substances produced by some phytoplankton species are toxins and taste and odour (T&O) compounds. The most common toxins include hepatotoxic peptides microcystins and nodularin, hepatotoxic alkaloid cylindrospermopsin, and neurotoxic alkaloids anatoxin-a, saxitoxin, and neosaxitoxin (Carmichael, 1992; Pearson et al., 2016).

The most pronounced T&O compounds with very low odour threshold levels are terpenes geosmin, 2-methylisoborneol, or β-cyclocitral (Huang et al., 2007; Srinivasan and Sorial, 2011; Li et al., 2012).
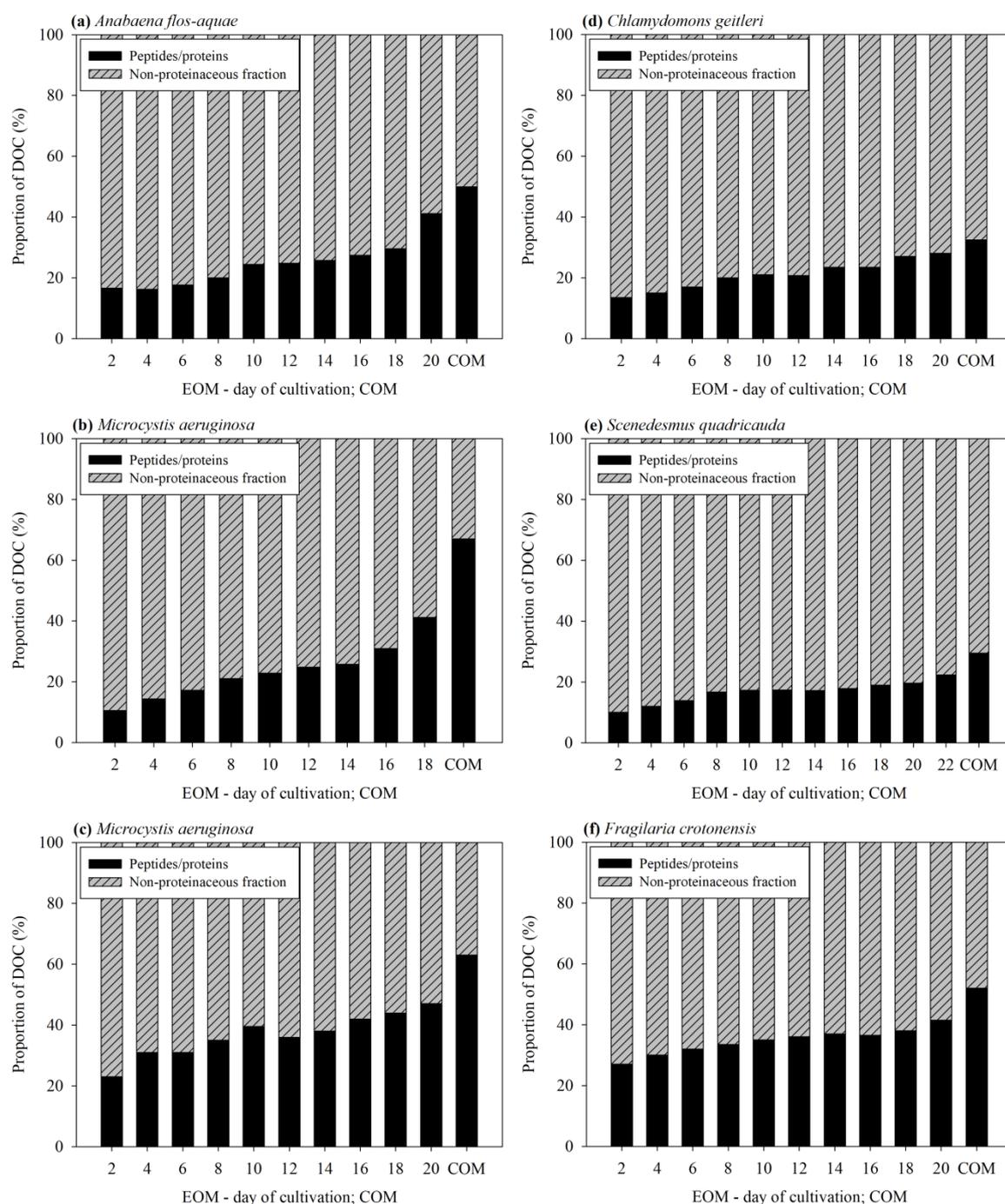
Figure 1. The proportions of peptides/proteins and non-proteinaceous fraction expressed as the corresponding percentage of dissolved organic carbon (DOC) for cyanobacteria (a-c), green algae (d-e), and a diatom (f). Extracellular organic matter (EOM) was analysed at different stages of growth; cellular organic matter (COM) was derived during the stationary growth phase. The data were adopted from studies Pivokonsky et al. (2006) (a, b, e) and Pivokonsky et al. (2014) (c, d, f).

The AOM components greatly differ in their molecular weight (MW) that ranges from several hundred daltons to hundreds kilodaltons (Pivokonsky et al., 2006, 2014; Henderson et al., 2008; Fang et al., 2010; Li et al., 2012). Typical high-MW compounds are biopolymers such as proteins and polysaccharides (Myklestad, 1995; Henderson et al., 2008; Pivokonsky et al., 2014). The lower-MW AOM fractions comprise a range of compounds, e.g., peptides, amino acids and other organic acids, or hydrocarbons (Huang et al., 2007; Li et al., 2012; Pivokonsky et al., 2014; Villacorte et al., 2015). Also the cyanobacterial toxins and T&O compounds belong to the low-MW components (Carmichael, 1992; Li et al., 2012; Pivokonsky et al., 2014). In general, the MW distribution of AOM is very variable, and differs not only between the species, but also between EOM and COM and changes with the age of a phytoplankton culture (Pivokonsky et al., 2006, 2014). For example, Henderson et al. (2008) conducted MW fractionation of stationary phase EOM of different species, and the proportion of DOC in the largest (> 500 kDa) and in the lowest (< 1 kDa) MW fraction ranged from negligible to almost 50% and from approximately 30% to 80%, respectively. Pivokonsky et al. (2014) determined MWs of peptide/protein and non-proteinaceous fractions of exponential and stationary phase EOM and COM of different species, and in most cases observed increasing proportion of larger-MW fractions from exponential to stationary phase, and from EOM to COM.

As opposed to some other NOM components, i.e., humic substances, AOM is predominantly hydrophilic. In addition to the hydrophilic (HPI) fraction, contents of hydrophobic (HPO) and transphilic (TPI) fractions are usually reported (Her et al., 2004; Henderson et al., 2008; Leloup et al., 2013; Pivokonsky et al., 2014; Goslan et al., 2017). In some studies, HPI compounds are further distinguished into neutral hydrophilic (NHPI) and charged hydrophilic (CHPI) (Li et al., 2012; Huang et al., 2014). The HPI content was reported to comprise majority (54-90%) for either EOM and COM of many different species (cyanobacteria *Anabaena flos-aquae*, *Aphanizomenon flos-aquae*, *M. aeruginosa*; green alga *Chlorella vulgaris*, *Scenedesmus subspicatus*, *Scenedesmus obliquus*, *C. geitleri*; diatom *Asterionella formosa*, *F. crotonensis*, *Cyclotella*, *Melosira* sp.) (Her et al., 2004; Henderson et al., 2008; Li et al., 2012; Huang et al., 2014; Pivokonsky et al., 2014; Goslan et al., 2017). Besides the species-dependence, differences occurred between EOM and COM, while COM was generally more hydrophilic (Pivokonsky et al., 2014), but only slight variations in the HPI/HPO/TPI partitioning were observed in EOM during the growth of the culture (Henderson et al., 2008; Pivokonsky et al., 2014). The high content of HPI compounds is

supported by low specific ultraviolet absorbance (SUVA) values of AOM, ranging from 0.5-1.7 L m^{-1} mg^{-1} for different species (Her et al., 2004; Henderson et al., 2008; Fang et al., 2010; Li et al., 2012; Goslan et al., 2017).

With regard to drinking water treatment, also charge properties of AOM are important (Bernhardt et al., 1985; Pivokonsky et al., 2009a, b, 2012, 2016; Guo et al., 2017). In general, AOM is negatively charged in a wide range of pH values (Bernhardt et al., 1985; Henderson et al., 2008). For example, Henderson et al. (2008) reported negative zeta potential values in the pH range of 2-10 for AOM of different species (cyanobacteria *M. aeruginosa*, green alga *C. vulgaris*, diatoms *A. formosa* and *Melosira* sp.). However, the charge density varied between the species and also changed during the growth of a phytoplankton culture, ranging from 0.1 to 3.2 meq g^{-1} C. The charge of AOM is associated to the presence of ionisable functional groups. The peptide/protein fraction of AOM is in principle amphoteric due to the content of diverse functional groups, both acidic and basic, i.e., OH, COOH, SH, NH^{3+}, or NH^{2+} (Creighton, 1993). Peptides/proteins with isoelectric points (pI) ranging from 4.8 to 8.1 were identified in COM of *M. aeruginosa* (Pivokonsky et al., 2012; Safarikova et al., 2013). Nevertheless, negative charge of AOM peptides/proteins prevails within pH values of approximately > 4 (Pivokonsky et al., 2012). The charge of non-proteinaceous AOM fraction can be related e.g. to the presence of uronic acids that contain COOH group (Bertocchi et al., 1990; Ozturk et al., 2014).

1.1.2 Removal of AOM by coagulation

A fundamental step in drinking water treatment, which is commonly utilized also for phytoplankton-laden waters, is coagulation followed by separation of the formed aggregates (via sedimentation, flotation, and/or filtration) (Duan and Gregory, 2003; Matilainen et al., 2010). Very high removal efficiencies (94.8-99.7%) were achieved for cells of cyanobacteria (*M. aeruginosa*), green alga (*C. vulgaris*), as well as diatoms (*A. formosa*, *Melosira* sp.) when using conventional Al- or Fe-based coagulants (aluminium sulphate, ferric chloride) under optimized coagulation conditions (Henderson et al., 2010; Gonzalez-Torres et al., 2014).

However, the removal of AOM by coagulation is generally less effective than the removal of cells, while more research was devoted to EOM compared to COM in this regard. For example, Henderson et al. (2010) obtained maximum removal of 71, 55, and 46% for AOM (primarily EOM possibly accompanied by a little proportion of COM) of *C. vulgaris*, *M. aeruginosa*, and *A. formosa*, respectively, by using aluminium sulphate as a coagulant

(doses corresponding to 0.8, 1.2, and 1.5 mg Al mg^{-1} DOC, respectively). Zhang et al. (2014) attained removals of approximately 60-70% for *M. aeruginosa* EOM by using different Al/Fe coagulants (aluminium sulphate, aluminium chlorohydrate, ferric sulphate, ferric chloride; 1.2 mg Al mg^{-1} DOC or 2.3 mg Fe mg^{-1} DOC). Lower removals were reported by Widrig et al. (1996), i.e., 49, 29, and 20% removal for EOM of *Dictyosphaerium pulchellum*, *S. quadricauda*, and *M. aeruginosa*, respectively, despite using very high doses of coagulant (ferric chloride; up to 34.4 mg Fe mg^{-1} DOC). Maximum EOM removals within the mentioned range of approximately 20-70% were determined also in other studies (Yan et al., 2017; Ly et al., 2019). The removal of COM also did not exceed 70%, similar to that of EOM. Maximum of 46-66% and 39-41% removal efficiency was reported for the coagulation of *M. aeruginosa* COM by ferric and aluminium sulphate, respectively (Pivokonsky et al., 2009a, b; Guo et al., 2017). The differences in removal efficiency, even for one phytoplankton species, may stem from several reasons. One of them is supposed to be a lack of thorough optimization of coagulation pH in some studies, since pH value determines forms and charge of both coagulants and impurities to be removed, and subsequently the course of coagulation (Duan and Gregory, 2003; Pivokonsky et al., 2012, 2016). Those studies that performed pH optimization for AOM coagulation usually reported an optimum within the pH range of 4.5-6.5 (Pivokonsky et al., 2009b; Guo et al., 2017), while the optimum may slightly differ for Al- and Fe-based coagulants owing to the different proceeding of Al and Fe hydrolysis (Duan and Gregory, 2003) and also to the variable character and associated charge properties of AOM. Under the slightly acidic pH values, the main coagulation mechanism involved in AOM removal is anticipated to be electrostatic interaction (charge neutralization) between negatively charged AOM and positively charged Al/Fe hydroxopolymers (Pivokonsky et al., 2009b).

Another influential factor is the intra-species variability in AOM character (Pivokonsky et al., 2006, 2014; Henderson et al., 2008) and different removability of distinct AOM fractions (Pivokonsky et al., 2009a, b, 2012; Guo et al., 2017; Naceradska et al., 2017). Pivokonsky et al. (2009a) coagulated COM of *M. aeruginosa* with maximum efficiency of 46 and 41% when using ferric sulphate and aluminium sulphate, respectively, and analysed residual COM after coagulation. It was found that COM peptides/proteins were primarily removed, while the majority of residual COM was formed by non-proteinaceous matter. Pivokonsky et al. (2012) isolated the peptides/proteins from *M. aeruginosa* COM and coagulated them by ferric sulphate. Very good removal with the maximum of approximately 80% was obtained within

the coagulation pH of 4.0-6.0. Similar results for COM peptides/proteins were reported also by Naceradska et al. (2017). However, peptide/protein fraction can also pose deterioration of coagulation. Pivokonsky et al. (2012) observed that under certain pH conditions (around pH of 6.2), COM peptides/proteins produced by *M. aeruginosa* form soluble complexes with Fe supplied as a coagulant. It prevents peptides/proteins as well as Fe from coagulation, which results in increased DOC and Fe residuals. Formation of metal-protein complexes was proposed as a reason for COM driven disruption of coagulation also when using pre-polymerized coagulant polyaluminium chloride (PACl) (Takaara et al., 2007).

Further, AOM components of distinct MWs are removed to a different extent. To illustrate, Guo et al. (2017) coagulated a range of MW-fractions of *M. aeruginosa* COM separately and while the fraction > 100 kDa was removed by up to almost 45%, the removal of 30-100 kDa compounds was approximately half-effective, and the fractions < 30 kDa were removed by less than 10%. Better removal of high-MW components was observed also in other studies that analysed AOM MWs before and after coagulation (Pivokonsky et al., 2009b; Zhang et al., 2014; Yan et al., 2017) and when coagulating COM peptide/protein fraction separately (Pivokonsky et al., 2012; Naceradska et al., 2017). Additionally, also the proportion of HPI/TPI/HPO fractions in AOM may affect coagulation efficiency, since HPO compounds are more amenable to coagulation (Croué et al., 1993; Matilainen et al., 2010; Guo et al., 2017).

In addition to the problematic removal of AOM itself, it affects coagulation of other impurities. Either negative or positive effects of EOM on the coagulation of inorganic particles (quartz) were reported in dependence of the mutual ratio of the components and coagulant. Deterioration of coagulation resulting in increased demand of coagulant was observed; however, under certain conditions, EOM improved the coagulation performance since it acted as anionic polyelectrolyte that formed bridges between the particles (Bernhardt et al., 1985). Takaara et al. (2007) coagulated inorganic particles (kaolin) alone and in the presence of EOM or COM derived from *M. aeruginosa*. Under otherwise fixed coagulation conditions, both EOM and COM inhibited kaolin removal, more with increasing EOM/COM concentration. Stronger adverse effect was observed for COM, presumably owing to the presence of inhibitory proteins. The effects of *M. aeruginosa* peptides/proteins on kaolin coagulation were investigated by Safarikova et al. (2013), and while the peptides/proteins slightly worsened kaolin removal within the pH range previously determined as optimal for kaolin alone (i.e., pH of 7.0-8.5 and 6.4-8.0 for Al- and Fe-based

coagulant, respectively), the peptides/proteins enhanced kaolin removal in slightly acidic pH region. Contradictory effects of AOM were observed also in the case of cell + AOM coagulation. While low-MW AOM and complex-forming proteins impaired coagulation performance, high-MW AOM served as coagulation aid (Ma et al., 2012).

Coagulation is commonly connected to other treatment steps. Pre-oxidation by using various oxidants is often applied as coagulation pre-treatment, aiming to improve the coagulation performance (Widrig et al., 1996; Bose and Reckhow, 2007; Chen et al., 2009; Coral et al., 2013; Xie et al., 2013, 2016; Naceradska et al., 2017). There are several studies devoted to the effects of pre-oxidation on phytoplankton cells, and advantages (cell inactivation and destabilization) as well as disadvantages (cell breakage and low-MW AOM release) were observed, while the choice of an oxidant and optimization of oxidation conditions are of a great importance (Chen et al., 2009; Miao and Tao, 2009; Coral et al., 2013; Xie et al., 2013). However, pre-oxidation of AOM is less explored. Pre-oxidation by ozone was reported to improve *S. quadricauda*, *D. pulchellum*, and *M. aeruginosa* EOM removal (by up to 5, 12, and 15%, respectively) owing to alterations in EOM character when sufficiently high doses of ferric chloride (approximately 34 mg Fe mg^{-1} DOC) were used for subsequent coagulation (Widrig et al., 1996). Permanganate pre-oxidation enhanced removal of *M. aeruginosa* COM peptides/proteins (by up to 12%) with a benefit of microcystin degradation (Naceradska et al., 2017). However, application of some oxidants to organic material may result in the formation of hazardous by-products, e.g., THMs, HAAs, or HANs in case of chlorine (Xie et al., 2013; Zhou et al., 2015; Goslan et al., 2017; Liu et al., 2018; Hua et al., 2019); bromo-organic compounds or odorous and toxic aldehydes in case of ozone (Huang et al., 2005), etc. Additionally, oxidation of AOM can lead to undesirable degradation of organic material into low-MW compounds (Xie et al., 2013); thus, possible drawbacks of AOM pre-oxidation should be better understood.

Coagulation is also important for the efficiency of downstream treatment processes, such as membrane filtration. Different AOM components were identified as membrane foulants, e.g., protein-like and polysaccharide-like compounds (Her et al., 2004; Huang et al., 2014; Zhang et al., 2014), and AOM was reported to cause more severe flux decline compared to other NOM fractions, such as humic substances (Her et al., 2004). The fouling potential appeared to depend on AOM characteristics as well as on the membrane properties (Huang et al., 2014; Zhang et al., 2016). Nevertheless, performing coagulation prior to membrane filtration was highly beneficial in different cases (Zhang et al., 2014, 2016; Yan et al., 2017). For example,

Zhang et al. (2014) reported much better performance of microfiltration membrane when the influent EOM-containing water was pre-treated by coagulation, i.e., 90 and 65% reduction in reversible and irreversible fouling resistance was attained, owing mainly to the removal of EOM high-MW biopolymers.

1.2 Microplastics

In addition to natural water impurities, such as AOM and other NOM, water resources commonly contain also various compounds of anthropogenic origin (Wilkinson et al., 2017; López-Pacheco et al., 2019). Currently, microplastics (MPs) are being detected in various aquatic environments worldwide (Andrary, 2011; Cole et al., 2011; Eerkes-Medrano et al., 2015; Auta et al., 2017). MPs are most often defined as plastic particles not exceeding 5 mm in size (Eerkes-Medrano et al., 2015; Koelmans et al., 2015; Auta et al., 2017; Hahladakis et al., 2018), while the lower size boundary of MPs is not clearly defined; plastic particles smaller than 100 nm (Koelmans et al., 2015; Hahladakis et al., 2018) or 1000 nm (da Costa et al., 2016) are sometimes recognized as nanoplastics (NPs). Nevertheless, owing to the limits of methods utilized for the identification of plastic particles in water samples, the knowledge of NP occurrence in natural aquatic environments is lacking (Koelmans et al., 2015; da Costa et al., 2016). Additionally, the lower size boundary of MPs determined in different studies greatly varies – from 1 μm (Oßmann et al., 2018; Tong et al., 2020; Wang et al., 2020) to several hundred of μm (Zhao et al., 2014; Eerkes-Medrano et al., 2015), which results in difficult comparability of the studies.

MPs can be divided into primary and secondary, according to their origin (Cole et al., 2011; Auta et al., 2017). Primary MPs are plastic particles directly produced in the corresponding size range (Cole et al., 2011); these are utilized e.g. in cosmetics and other personal care products (Gregory, 1996; Napper et al., 2015; Lei et al., 2017) or in air-blasting technology (Gregory, 1996; Cole et al., 2011). Secondary MPs arise from a breakdown of larger plastic items. Besides simple mechanical disruption, weathering driven by UV radiation or temperature alterations can be also influential (Andrary, 2011; Cole et al., 2011). Disintegration of plastic items into MPs may take place also before entering the environment. For example, large quantities of MPs (particularly MP fibres) are released during washing of synthetic clothes (Napper and Thompson, 2016; De Falco et al., 2018).

An important route of MPs to aquatic environments is discharge from waste water treatment plants (WWTPs) (Leslie et al., 2017; Simon et al., 2018). Different MP abundancies were reported for the effluent water, ranging from < 1 MP L^{-1} to approximately 400 MPs L^{-1} (Murphy et al., 2016; Leslie et al., 2017; Mintenig et al., 2017; Simon et al., 2018). Additionally, some studies attempted to quantify the total amounts of MPs released from WWTPs, and for example, the estimation for annual WWTP discharge in Denmark based on the median effluent MP content of 54 items L^{-1} is 3 tons of MPs (10-500 µm) per year (Simon et al., 2018). An important source of MPs to the environment is also wear and tear from car tyres, and via rainwater runoff, a part of MPs from tyres may be transported to surface waters. For example, based on the calculations for the Netherlands, 6% of the tyre-derived MPs end up in surface waters directly, corresponding to 520 tonnes annually (Kole et al., 2017). Further, fishing may result in MP release to (especially marine) waters, particularly owing to the degradation of fishing gears (Andrary, 2011; Cole et al., 2011). Plastic pollution can be also associated to shipping and coastal tourism, and related inappropriate handling of plastic waste (Cole et al., 2011).

It is of note that to date, overall toxicological effects of MPs are not fully understood, and potential impacts of MPs on human health are not known (Wright and Kelly, 2017; Barboza et al., 2018; Revel et al., 2018; World Health Organization, 2019). However, MPs raise concerns for multiple reasons. Besides possible physical effects associated to particle ingestion, attention is paid also to the content of residual monomers or additives such as plasticizers, heat stabilizers, slip agents, or antioxidants in the materials forming MPs, and to their potential leaching (Hahladakis et al., 2018). Additionally, MPs are capable of adsorbing chemicals such as polychlorinated biphenyls, polycyclic aromatic hydrocarbons, pesticides, or antibiotics (Wang et al., 2018; Guo and Wang, 2019), thus are speculated as their potential carriers through the environment and possibly to humans (Wang et al., 2018; Caruso, 2019; Naik et al., 2019). Nevertheless, available data do not indicate a current need for MP limitation in drinking water, and more research is required for better understanding of this field (World Health Organization, 2019).

1.2.1 Occurrence and characterization of microplastics

MPs occur in different aquatic environments, including seawaters (Andrary, 2011; Cole et al., 2011; Auta et al., 2017) and freshwaters (Eerkes-Medrano et al., 2015), and were found also in sediments and aquatic organisms (Cole et al., 2011; Nel and Froneman, 2015; Su et al.,

2016; Auta et al., 2017; Leslie et al., 2017). In general, MPs are globally distributed and they were detected even in water bodies located within remote areas characterized by low population density and a lack of industrial or agricultural activities in surroundings (Free et al., 2014; Jiang et al., 2019). Recently, MPs were determined also in water intended for human consumption, i.e., in DWTP treated water (Wang et al., 2020), tap water (Tong et al., 2020), water from public drinking fountains (Shruti et al., 2020), or in bottled water (Mason et al., 2018; Oßmann et al., 2018; Schymanski et al., 2018).

In seawaters, MP contents ranging from negligible (Morgana et al., 2018; Pelamatti et al., 2019) to approximately 1200 MPs m^{-3} (Nel and Froneman, 2015) or, when measured in samples collected by trawling, up to 1.5-1.7 million MPs km^{-2} (Isobe et al., 2015; Abayomi et al., 2017) were reported. Similarly, greatly different MP abundancies were determined for freshwater bodies, ranging from 3.5 MPs m^{-3} (Bordós et al., 2019) to approximately 900 MPs L^{-1} (Triebskorn et al., 2019) or 6.8 million MPs km^{-2} (Su et al., 2016). Thus, MPs in different samples ranged greatly in number. In addition to the variability of samples (more MPs were detected in urban than in rural areas in comparative studies (Song et al., 2018; Yin et al., 2020)), the significant differences in MP abundancies may be related also to the dissimilarities of applied sampling and analytical methods. An important factor likely is the lower size boundary of analysed MPs, which greatly varies between the studies, from 1 μm (Oßmann et al., 2018; Tong et al., 2020; Wang et al., 2020) to 500 μm (Zhao et al., 2014).

So far, MPs down to the size of 1 μm were determined only in few studies, which were mostly devoted to drinking water (Oßmann et al., 2018; Tong et al., 2020; Wang et al., 2020). Interestingly, the reported MP numbers were higher than elsewhere. For example, Oßmann et al. (2018) determined average values of 2649, 4889, and 6292 MPs L^{-1} in water packed in single use plastic bottles, returnable plastic bottles, and glass bottles, respectively; Tong et al. (2020) reported a maximum of 1247 MPs L^{-1} in tap water; Wang et al. (2020) determined up to almost 9000 and 1000 MPs L^{-1} in DWTP raw and treated water, respectively. The size categorization of MPs revealed that vast majority (80-100%) was < 10 μm (Oßmann et al., 2018; Wang et al., 2020). Similar trend was observed in studies that determined MPs with the lower size boundary of 4-5 μm – 67-96% of MPs was < 20 μm (Schymanski et al., 2018; Triebskorn et al., 2019). The size distribution of MPs reported in studies that analysed MPs down to the size of 1-5 μm and conducted size categorization of MPs is shown in detail in Fig. 2. These observations imply that that underestimation of results presumably increase with increasing lower size boundary of analysed MPs.
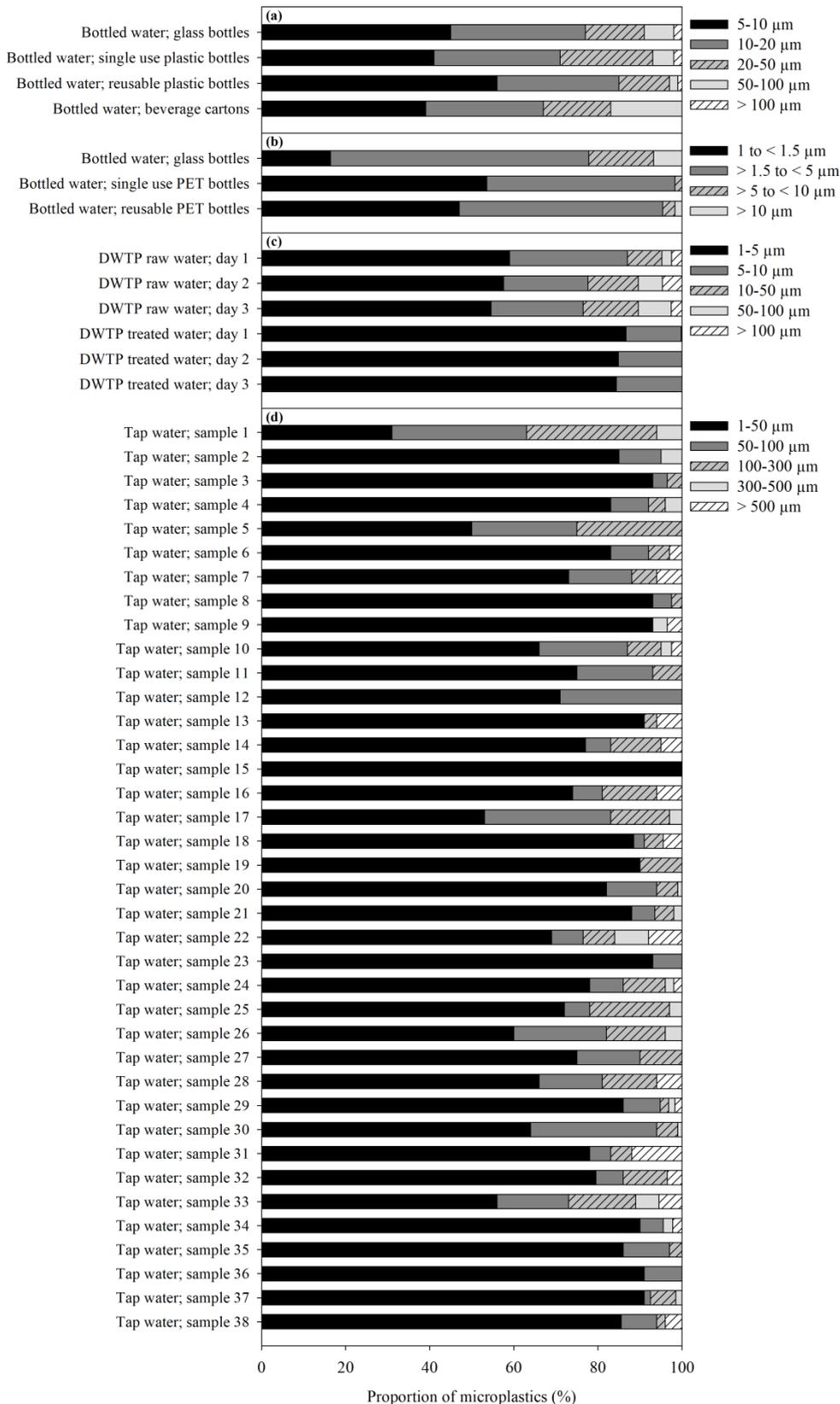
Figure 2. Size distribution of microplastics detected in bottled drinking water (a, b), raw and treated water from drinking water treatment plants (DWTPs) (c), and tap water (d). The data were adopted from studies Schymanski et al. (2018) (a), Oßmann et al. (2018) (b), Wang et al. (2020) (c), and Tong et al. (2020) (d).

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Besides the abundance and size of MPs, their shape and material composition are commonly reported. The shape categories are not uniform between the studies, while e.g. fibres, fragments, films, foils, pellets, granules, or spheres are being distinguished (Zhao et al., 2014; Su et al., 2016; Abayomi et al., 2017; Leslie et al., 2017; Lares et al., 2018; Song et al., 2018; Shruti et al., 2020; Tong et al., 2020; Wang et al., 2020). Various materials were identified to form MPs, including ethylene-vinyl acetate (EVA), polyamide (PA), polyethylene (PE), polyethylene terephthalate (PET), poly(methyl methacrylate) (PMMA), polypropylene (PP), polystyrene (PS), polytetrafluorethylene (PTFE), polyurethane (PU), polyvinyl chloride (PVC), etc. (Su et al., 2016; Lares et al., 2018; Mason et al., 2018; Oßmann et al., 2018; Schymanski et al., 2018; Simon et al., 2018; Song et al., 2018; Bordós et al., 2019; Shruti et al., 2020; Tong et al., 2020; Wang et al., 2020; Yin et al., 2020). Additionally, the colour is sometimes recorded in case of larger MPs (Zhao et al., 2014; Abayomi et al., 2017; Yin et al., 2020).

1.2.2 Removal of microplastics

The knowledge of MP removal at DWTPs is very scarce. Mintenig et al. (2019) conducted a study on MP occurrence along drinking water supply chain that involved 5 DWTPs supplied by groundwater wells of the Oldenburg-East-Frisian water board (Germany). However, only MPs > 20 μm were determined and negligible amounts of MPs were detected already in raw water; thus, the results do not enable assessing the MP removal. Very recently, MPs down to the size of 1 μm were determined at different stages of treatment at one DWTP supplied by the Yangtze River (China). Raw and treated water contained 6614 ± 1132 and 930 ± 71 MPs L^{-1}, respectively; thus, a removal of 86% was attained (Wang et al., 2020). Nevertheless, a broader overview of MP content in raw water and subsequently of their common removal at DWTPs is lacking.

To date, more attention has been paid to the MPs at WWTPs compared to DWTPs. Some studies reported very high removal of MPs at WWTPs (based on the MP number determined in influent and effluent water), up to 98-99% (Carr et al., 2016; Murphy et al., 2016; Lares et al., 2018; Simon et al., 2018), while lower removal (approximately 70%) was determined elsewhere (Leslie et al., 2017). Nevertheless, it is of note that the investigated WWTPs differed in the MP content in influent water and in the treatment chain, and also the methodology for MP determination was not uniform. Additionally, none of the studies covered MPs < 10 μm; thus, their fate at WWTPs remains unknown.

Some sporadic studies dealt also with the removal of MPs by distinct drinking water treatment technologies under laboratory conditions. Ma et al. (2019a, b) performed coagulation and ultrafiltration experiments with PE particles of different sizes (< 0.5 mm, 0.5-1 mm, 1-2 mm, and 2-5 mm). However, despite these particles fulfil the definition of MPs (Eerkes-Medrano et al., 2015; Koelmans et al., 2015; Auta et al., 2017; Hahladakis et al., 2018), the reasonability of treating particles in mm size range is doubtful. When focused on the size class < 0.5 mm, maximum removal by coagulation was 17% and 37% when using ferric and aluminium chloride, respectively, while very high doses of coagulant (corresponding to approximately 112 mg L^{-1} Fe or 405 mg L^{-1} Al) were required. The reported optimum pH was 8.0 and 6.0 for Fe- and Al-based coagulant, respectively, but only few pH values were tested and detailed optimization of coagulation pH was not performed (Ma et al., 2019a, b). Removal of smaller MPs and NPs (PS particles of 180 nm and of 1.2 μm; PE particles of 10-20, 45-53, and 106-125 μm) spiked to DWTP raw water was recently investigated by Zhang et al. (2020). Very poor removal efficiency (< 2% for all size categories) was reported for alum coagulation with subsequent sedimentation, while deep-bed filtration of MPs through anthracite was very effective (86.9-99.9% depending on the particle size). However, coagulation was performed only under fixed conditions utilized at the DWTP, and optimization was not performed. The low efficiency of coagulation is contradictory to observations of Wang et al. (2020) from a DWTP, at which approximately 50% of MPs > 1 μm was removed by coagulation-sedimentation. Noteworthy is that despite both studies (Wang et al., 2020; Zhang et al., 2020) reported the MP content as the number of items per litre, the methods applied for MP quantification were completely different.

In the study by Wang et al. (2020), the efficiency increased with increasing particle size, i.e., ranged from 30% for MPs of 1-5 μm to > 90% for MPs > 100 μm. Differences were observed also for fibres, fragments, and spheres; the removal efficiency attained by coagulation-sedimentation decreased in the mentioned order. Relationships between MP size and shape and their removability were suggested also with regard to the fate of MPs at WWTPs (Lares et al., 2018).

2 MOTIVATION AND OBJECTIVES

A range of undesirable natural or anthropogenic compounds may be present in water supplies, while their removal is subsequently required during drinking water treatment. An ongoing challenge for the treatment is AOM, which appears naturally, but its occurrence is amplified by environmental factors such as increasing temperature or enhanced nutrient loading. The character of AOM is greatly variable, which is an obstacle for optimizing the treatment processes, and AOM affects also the removal of other compounds. Better understanding of the relationships between AOM properties and removability as well as elucidating the interactions of AOM with other compounds is needed to achieve more effective removal of AOM during drinking water treatment. Additionally, limited attention has been paid to distinct AOM fractions, such as COM and particularly its non-proteinaceous fraction.

With regard to anthropogenic water pollution, MPs are an emerging issue. Currently, the removal of MPs is not a target for drinking water treatment; nevertheless, owing to the increasing production of plastic materials, their high persistence, and so far unclear toxicological effects of MPs, their occurrence and fate at DWTPs deserves attention. Moreover, quantification and characterization of MPs at different stages of treatment is a necessary step prior to further investigation of MP removability.

This work is focused on both these diverse groups of water pollutants, i.e., AOM and MPs, while the specific objectives (dealt with in the corresponding publications) are as follows:

- to describe simultaneous coagulation of COM peptide/protein fraction and other common surface water impurities, i.e., NOM (represented by humic substances; publication 1) and clay colloids (represented by kaolinite; publication 2);
- to elucidate coagulation of a little-explored cyanobacterial species *Merismopedia tenuissima*, including its cells, COM, and their mixture (publication 3);
- to assess removability of COM non-proteinaceous fraction by coagulation (publication 4) and suitability of involving ozonation step to the removal process (publication 5);
- and to determine the abundance and distinct characteristics of MPs in raw and treated water at selected DWTPs (publication 6) and to assess the current knowledge and research targets with regard to MPs and water treatment (publication 7).

3 PUBLICATIONS

3.1 Publication 1

The impact of interactions between algal organic matter and humic substances on coagulation

Martin Pivokonský, Jana Načeradská, Tomáš Brabenec, **Kateřina Novotná**, Magdalena Barešová, Václav Janda

2015

3.2 Publication 2

Effect of cyanobacterial peptides and proteins on coagulation of kaolinite

Kateřina Novotná, Magdalena Barešová, Lenka Čermáková, Jana Načeradská, Martin Pivokonský

2016

3.3   Publication 3

An application of cellular organic matter to coagulation of cyanobacterial cells (*Merismopedia tenuissima*)

Magdalena Barešová, Martin Pivokonský, **Kateřina Novotná**, Jana Načeradská, Tomáš Brányik

2017

3.4 Publication 4

Investigating the coagulation of non-proteinaceous algal organic matter: Optimizing coagulation performance and identification of removal mechanisms

Jana Načeradská, **Kateřina Novotná**, Lenka Čermáková, Tomáš Cajthaml, Martin Pivokonský

3.5 Publication 5

Consequences of ozonation for the limited coagulation of non-proteinaceous AOM and formation of aldehydes as ozonation by-products

Kateřina Novotná, Martin Pivokonský, Michaela Prokopová, Magdalena Barešová, Lenka Pivokonská

2020

3.6 Publication 6

Occurrence of microplastics in raw and treated drinking water

Martin Pivokonský, Lenka Čermáková, **Kateřina Novotná**, Petra Peer, Tomáš Cajthaml, Václav Janda

2018

3.7 Publication 7

Microplastics in drinking water treatment – current knowledge and research needs

Kateřina Novotná, Lenka Čermáková, Lenka Pivokonská, Tomáš Cajthaml, Martin Pivokonský

2019

4   SUMMARY AND CONCLUSIONS

This PhD thesis is focused on two different groups of water impurities, i.e., AOM and MPs, particularly on their characterisation and removal during drinking water treatment. The objectives of the thesis are dealt with within the listed publications, while the results are summarized as follows:

Peptide/protein fraction of *M. aeruginosa* AOM (specifically COM) appeared to interact both with organic and inorganic compounds that are commonly present in surface water (NOM – represented by peat humic substances (HS); clay colloids – represented by kaolinite), which affected the course and efficiency of coagulation. Optimum coagulation pH for the removal of the COM peptides/proteins and HS alone was in the slightly acidic pH region (pH of 5.2-6.7 and 5.5-6.0, respectively), owing to the electrostatic interactions between negatively charged functional groups of the compounds and positively charged hydroxopolymers formed by a coagulant (aluminium sulphate). It was similar also for the mixture of the compounds (optimum pH of 5.5-6.2); however, the required dose of coagulant significantly changed. Optimum doses were 2.0 mg L^{-1} Al for the COM peptides/proteins and 5.5 mg L^{-1} Al for HS (both at the initial concentration of 5 mg L^{-1} DOC), while only 2.8 mg L^{-1} Al was sufficient for the COM peptides/proteins and HS mixture (at the initial concentration of 5 mg L^{-1} DOC each, thus 10 mg L^{-1} DOC in total). The removal efficiency for the COM peptides/proteins and HS, respectively, was 75% and 65% when coagulated separately, and 80% and 70% when coagulated in mixture. Peptides/proteins of higher MWs (approximately > 10 kDa) were better removed and the residuals after coagulation composed of mainly the low-MW fraction. The importance of coagulation pH was observed also for the mixture of *M. aeruginosa* COM peptides/proteins and kaolinite, while ferric sulphate was used as a coagulant in this case. Optimum coagulation pH for the COM peptides/proteins alone was again within the slightly acidic pH region (pH of 4.2-5.9); however, it did not overlap with that for kaolinite alone (optimum pH of 6.5-8.0). Interestingly, when the mixture of the compounds was coagulated, a mutual optimum pH occurred. Within the pH range 4.0-5.5, both the peptides/proteins and kaolinite were removed with an efficiency comparable to that obtained by coagulation of each compound alone (approximately 75% for peptides/proteins, > 90% for kaolinite) without a requirement of increasing coagulant dose. Noteworthy is that in every case the peptide/protein fraction was involved, the optimum coagulation pH range was close to the region of the maximum formation of dissolved complexes between the peptides/proteins and metals (either Al or Fe), which resulted in a serious deterioration of coagulation and

should be therefore avoided. Nevertheless, it can be concluded that when AOM (COM) with a high proportion of the peptide/protein fraction appears in water that already contains humic substances or clay colloids, deterioration in coagulation may be avoided by careful optimization of coagulation conditions, particularly the pH of coagulation; and even better removal efficiency accompanied by a lower coagulant demand can be achieved for the organic compounds mixture (publication 1, publication 2).

Coagulation was successfully applied also to the emerging cyanobacterial species *M. tenuissima*. Its cells alone were efficiently coagulated within the pH range of 6.0-7.7 (with ferric sulphate as a coagulant) and the maximum removal was as high as 99%. Different patters were observed for its COM (that composed of 43% peptides/proteins and 57% non-proteinaceous matter). Optimum coagulation pH was in the range of 5.4-6.2, and the maximum removal did not exceed 53%. The optimum dose of coagulant coincidently corresponded to 1 mg Fe mg^{-1} DOC, and increasing the dose did not lead to better efficiency. The limited removal was ascribed to a significant content of HPI and low-MW fraction in COM. When the mixture of the cells and COM was coagulated, a similar phenomenon as that observed for COM peptides/proteins and kaolinite occurred – COM contributed to the cell removal at pH < 6.0, which was unsuitable for the coagulation of cells alone. Thus, the highest removals of both cells and COM were achieved at almost the same pH as of COM alone and the removal rates were comparable to that for the compounds alone, while no increase in coagulant dose was required (publication 3).

Coagulation of the non-proteinaceous fraction (that was derived from COM of *C. vulgaris*) appeared to greatly differ from the peptides/proteins. Optimum coagulation pH was not in the slightly acidic pH region; it was close to neutral/slightly alkaline (pH of 7.1-7.5 and 7.6-8.0 when using aluminium sulphate and polyaluminium chloride, respectively). Thus, the main coagulation mechanism was anticipated to be adsorption involving mainly the colloidal or solid precipitates of the coagulants. The maximum coagulation efficiency of the non-proteinaceous fraction was only 25%, thus much lower than that of COM peptides/proteins, and high dose of coagulant was required, i.e., 10 mg L^{-1} Al at the initial concentration of 5 mg L^{-1} DOC (five times higher optimal dose than for the peptides/proteins). The difficulties in the coagulation of the non-proteinaceous fraction were ascribed particularly to a very high proportion of the low-MW fraction (the components > 10 kDa were almost completely removed by coagulation, and > 95% of the residuals after coagulation were < 10 kDa) and lower content of ionisable functional groups. Further, ozonation (at various O$_3$ doses and pre-

ozonation pH values) was applied in combination with coagulation (with aluminium sulphate as a coagulant) to the non-proteinaceous COM fraction; pre-ozonation-coagulation and coagulation-post-ozonation were investigated in this regard. Pre-ozonation either increased or decreased the removal efficiency, depending on the ozonation conditions. In general, the lowest O_3 dose tested (0.01 mg O_3 mg^{-1} DOC) applied at the pre-ozonation pH of 5.5 and 7.8 and the highest O_3 dose tested (0.8 mg O_3 mg^{-1} DOC) applied under any pH improved the removal; by contrast, the intermediate O_3 dose (0.1 mg O_3 mg^{-1} DOC) applied at the pre-ozonation pH of 5.5 and 7.8 decreased the removal. The maximum removal of the non-proteinaceous fraction accompanied by the lowest residuals of coagulant was achieved within the coagulation pH range of 6.6-7.5 regardless the pre-ozonation mode, similar to that without pre-ozonation. Additionally, pre-ozonation conducted under certain conditions improved the removal of the non-proteinaceous fraction in the slightly acidic pH region optimal for the coagulation of COM peptides/proteins. The positive effects of ozonation were ascribed to the increased content of ionisable functional groups and to a partial mineralization of the non-proteinaceous fraction, the adverse effects to increased proportion of the low-MW fraction. When post-ozonation using the highest O_3 dose was applied after coagulation, additional removal occurred owing to the partial mineralization. In addition to evaluating the removal efficiency, formation of aldehydes as ozonation by-products was monitored. Aldehydes were detected in every case the ozonation step was involved, while the aldehyde yield was low for the lowest O_3 dose and significantly increased with increasing O_3 dose, and it was independent of the ozonation pH. To conclude, the results revealed the optimum coagulation conditions for the removal of the COM non-proteinaceous fraction, and also pointed out to the limits of coagulation for the removal of low-MW and/or uncharged compounds. Additionally, the importance of careful considering and alternatively optimization of the ozonation step was emphasized in order to achieve and improvement (and not worsening) of the removal efficiency and the quality of treated water (publication 4, publication 5).

Compared to the topic of AOM, the research on MPs with regard to drinking water treatment is in its beginnings. It is therefore important to focus on the MP content, characteristics, and also on the MP fate during conventional water treatment practice first. The results from three different DWTPs revealed the presence of MPs (those ≥ 1 μm were determined) in both raw and treated water in all cases. The average content of MPs in raw water was 1473 ± 34, 1812 ± 35, and 3605 ± 497 MPs L^{-1} at the three DWTPs, respectively; the average content of MPs in treated water was much lower, i.e., 443 ± 10, 338 ± 76, and 628 ± 28 MPs L^{-1}.

The corresponding average removal was 70-83%. Three different shapes of MPs were distinguished – fibres, fragments, and spheres. Fibres and fragments prevailed, while spheres comprised no more than 20%. Also the material composition of MPs was determined, and the majority was composed of polyethylene terephthalate, polypropylene, and polyethylene. Additionally, MPs were categorized according to their size and majority was always < 10 µm (approximately 30-60% were in the size range of 1-5 µm and 30-50% in the size range of 5-10 µm). By contrast, only < 2% of MPs detected in raw water were > 100 µm, and no MPs > 100 µm occurred in treated water. The results imply that with regard to drinking water and its sources, it is important to focus on MPs within the smallest size ranges. The knowledge of the occurrence of such small MPs needs to be widened, and the observed characteristics of MPs should be then taken into account when preparing MP samples for laboratory experiments aimed at the detailed investigation of MP removal. Since the removal efficiency for MPs was quite high at the DWTPs operated under their ordinary conditions, the involved steps (coagulation with sedimentation and/or sand filtration; granular activated carbon filtration) may be a promising solution if MP removal is desired (publication 6, publication 7).

To conclude, coagulation is very useful for the treatment of algae-laden waters. It is highly effective in the removal of phytoplankton cells and AOM (both peptides/proteins and non-proteinaceous fraction) with higher-MWs (> 10 kDa). Additionally, it has shown that the occurrence of AOM in water comprising HS or clay colloids does not necessarily lead to a deterioration of coagulation; by contrast, particularly the high-MW proteins may rather improve the coagulation performance. Noteworthy is that both the dose of a coagulant and coagulation pH must be always optimized for particular AOM and overall raw water composition to achieve the maximum removal efficiency. It has shown that the optimum conditions vary for AOM of different composition, and coagulation is affected also by the interactions between AOM and other common raw water components. Nevertheless, certain AOM (specifically the low-MW fraction < 10 kDa) is not amenable to coagulation and requires further treatment. Further, ozonation is commonly applied as a pre-treatment step before coagulation to improve its performance. However, in case of water comprising AOM, its suitability is highly dependent on the ozonation conditions such as O_3 dose and pH value at which the ozonation is performed. Finally, based on the observations from DWTPs, coagulation is a promising treatment also for the removal of MPs; nevertheless, more research is required in this regard, while focus should be laid particularly on MPs in the µm size range.

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LIST OF ABBREVIATIONS

AOM	algal organic matter
C-DBPs	carbonaceous disinfection by-products
COM	cellular organic matter
DBPs	disinfection by-products
DOC	dissolved organic carbon
DW	dry weight
DWTP	drinking water treatment plant
EOM	extracellular organic matter
EVA	ethylene-vinyl acetate
HAA	haloacetic acid
HAB	harmful algal bloom
HAN	haloacetonitrile
HPI	hydrophilic
HPO	hydrophobic
HS	humic substances
CHPI	charged hydrophilic
IOM	intracellular organic matter
MPs	microplastics
MW	molecular weight
N-DBPs	nitrogenous disinfection by-products
NHPI	neutral hydrophilic
NOM	natural organic matter
NPs	nanoplastics
PA	polyamide
PACl	polyaluminium chloride
PE	polyethylene

PET	polyethylene terephthalate
pI	isoelectric point
PMMA	poly(methyl methacrylate)
PP	polypropylene
PS	polystyrene
PTFE	polytetrafluorethylene
PU	polyurethane
PVC	polyvinyl chloride
SOM	surface-retained organic matter
SUVA	specific ultraviolet irradiation
T&O	taste & odour
THMs	trihalomethanes
TPI	transphilic
WWTP	waste water treatment plant