

Tero Luukkonen

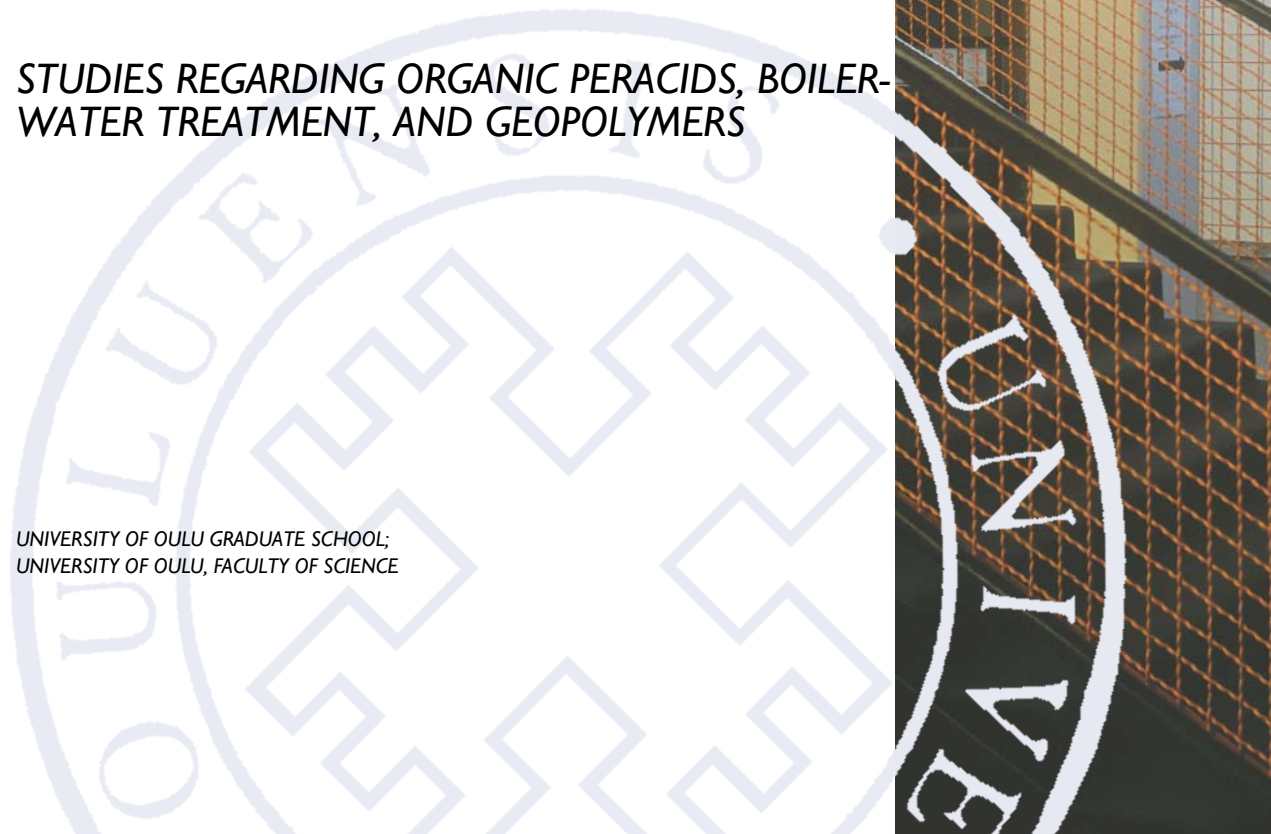
NEW ADSORPTION AND
OXIDATION-BASED
APPROACHES FOR WATER
AND WASTEWATER
TREATMENT

STUDIES REGARDING ORGANIC PERACIDS, BOILER-
WATER TREATMENT, AND GEOPOLYMERS

UNIVERSITY OF OULU GRADUATE SCHOOL;
UNIVERSITY OF OULU, FACULTY OF SCIENCE

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TERO LUUKKONEN

**NEW ADSORPTION AND
OXIDATION-BASED APPROACHES
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Studies regarding organic peracids, boiler-water
treatment, and geopolymers

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Abstract

This thesis examines three different areas of water treatment technology: the application of organic peracids in wastewater treatment; the removal of organic residues from boiler make-up water; and the use of geopolymers as sorbents.

The main advantages of peracids as alternative wastewater disinfectants are their effective antimicrobial properties and high oxidation power, as well the absence of harmful disinfection by-products after their use. Performic, peracetic and perpropionic acids were compared in laboratory-scale disinfection, oxidation and corrosion experiments. From the techno-economical point of view, performic acid proved to be the most effective disinfectant against *E. coli* and fecal enterococci. However, in the bisphenol-A oxidation experiments, no advantages compared to hydrogen peroxide use were observed. It was also determined that corrosion rates on stainless steel 316L were negligible, while carbon steel seemed unsuitable in terms of corrosion for use with peracids even in low concentrations.

Organic compounds in the boiler plant water-steam cycle thermally decompose and form potentially corrosive species. Activated carbon filtration was confirmed to be a suitable method for the removal of organic residue from deionized boiler make-up water. No significant differences in terms of treatment efficiency between commercial activated carbons were observed. However, acid washing as a pre-treatment reduced the leaching of impurities from new carbon beds. Nevertheless, a mixed-bed ion exchanger was required to remove leached impurities, such as silica and sodium.

Geopolymers, or amorphous analogues of zeolites, can be used as sorbents in the treatment of wastewater. Metakaolin and blast-furnace-slag geopolymers showed positive potential in the treatment of landfill leachate (NH_4^+) and mine effluent (Ni, As, Sb).

Keywords: activated carbon, adsorption, ammonium, antimony, arsenic, bisphenol-A, boiler water treatment, corrosion, geopolymers, nickel, peracetic acid, performic acid, perpropionic acid, wastewater disinfection

Luukkonen, Tero, Uusia adsorptioon ja hapetukseen perustuvia veden- ja jätevedenkäsittelymenetelmiä: orgaaniset perhapot, kattilaveden käsittely ja geopolymeerit.

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Tiivistelmä

Tämä väitöskirja käsittelee kolmea erillistä vedenkäsittelyteknologian osa-aluetta: orgaanisten perhappojen käyttöä jäteveden käsittelyssä, orgaanisten jäämien poistoa suolavapaasta kattilalaitoksen lisävedestä ja geopolymeerien sovelluksia vedenkäsittelysorbentteina.

Orgaanisten perhappojen pääasialliset edut verrattuna kilpaileviin tekniikoihin ovat hyvä desinfiointiteho, korkea hapetuspotentiaali ja desinfioinnin sivutuotteiden muodostumattomuus. Permuurahaishais-, peretikka- ja perpropanihapon vertailu osoitti permuurahaishapon olevan kemikaaleista tehokkain *E. coli* - ja enterokokkibakteerien inaktivoinnissa kustannus- ja teknisistä näkökulmista. Hapetuksessa, jossa käytettiin bisfenoli-A:ta malliaineena, ei kuitenkaan havaittu etua verrattuna edullisempaan vetyperoksiidiin. Ruostumattoman teräksen (316L) pinnalla ei havaittu merkittävää korroosiota, kun taas hiiliteräs ei sovellu käytettäväksi perhappojen kanssa.

Orgaaniset jäämät kattilalaitoksen vesi-höyrykierrossa hajoavat termisesti pienen moolimassan hapoiksi ja aiheuttavat korroosioriskin. Aktiivihiihluodatuksen todettiin olevan soveltuva menetelmä orgaanisten jäämien poistoon lisävedestä. Aktiivihiihlaatuojen välillä ei havaittu merkittäviä eroja, mutta happopesu aktiivihiihien esikäsitteilynä vähensi hiilestä liukenevien epäpuhtauksien määrää.

Geopolymeerit ovat zeoliittien amorfisia analogeja ja niiden ioninvaihtokykyä voidaan hyödyntää vedenkäsittelysovelluksissa. Metakaoliini- ja masuunikuonapohjaisten geopolymeerien todettiin olevan lupaavia materiaaleja malliliuosten, kaatopaikan suotoveden ja kaivoksen purkuveden käsittelyssä poistettaessa ammoniumia, nikkeliä, arsenia ja antimonia.

Asiasanat: adsorptio, aktiivihiihi, ammonium, antimoni, arseni, bisfenoli-A, geopolymeerit, jäteveden desinfiointi, kattilavedenkäsittely, korrosio, nikkeli, peretikkahappo, permuurahaishappo, perpropanihappo

Still water runs deep

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The research on the boiler water treatment was graciously funded by the Finnish Recovery Boiler Committee. Later on in the project, I continued this work at JP-Analysis (today known as Oulu Water Alliance Ltd.). Regarding the work on this particular topic, I especially would like to thank Reijo Hukkanen and Ilkka Laakso from Stora Enso Ltd., Jaakko Pellinen, and my co-authors Hanna Runtti and Emma-Tuulia Tolonen.

The work on peracetic acid in wastewater treatment was conducted during my time at PAC-Solution Ltd. I would like to thank the entire staff of the company, especially the managers Johanna Hentunen, Teuvo Kekko, and Marko Tiesmäki. The atmosphere was always ripe with innovative energy, and I could not have had a better environment in which to learn about the water industry. I continued the research of organic peroxides with funding from Maa- ja vesitekniiikan tuki ry, whose support is greatly appreciated.

Experimentation with geopolymer sorbents took place at the Kajaani University of Applied Sciences, and was funded by the Regional Council of Kainuu. Again, I had the pleasure of working with the most incredible group of colleagues: Kimmo Kemppainen, Minna Sarkkinen, Juho Torvi, Kai Tiihonen, Marjukka Hyyryläinen, and Eine Pöllänen. The work here was facilitated by the cooperation with companies such as Aquaminerals Finland Oy and Ekokymppi.

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19.11.2015, Oulu

Tero Luukkonen

List of symbols

α	Peracid degradation reaction order (0, 1, or 2)
β	Desorption constant [g/mg]
θ	Surface coverage
Λ	Chick-Watson model rate constant
v_0	Initial sorption rate [[mg/(g min)]
b	Langmuir isotherm parameter
b_1	Redlich-Peterson isotherm parameter [mg/g]
b_2	Redlich-Peterson isotherm parameter
C_0, C_t	Initial concentration and concentration at time t [mg/L]
C_e	Equilibrium concentration [mg/L]
D	Initial consumption of peracid [mg/L]
h	S-model parameter [(mg min)/L]
I_{\max}	Maximum microbial log reduction achievable at equilibrium
K	Freunlich isotherm sorption coefficient [(mg/g)/(mg/L) ^{1/n}]
k_0	Zeroth order rate constant for peracid degradation [mg/(L min)]
k_1	First-order rate constant for peracid degradation [1/min]
k_2	Second-order rate constant for peracid degradation [L/(mg min)]
k_α	Peracid degradation rate constant
k_β	Disinfection rate constant
k_H	Hom model disinfection rate constant
k_{id}	Intraparticle diffusion rate constant [mg/(g min ^{0.5})]
k_{MT}	Semi-saturation time constant [min]
k_{p1}	Pseudo-first-order sorption rate constant [1/min]
k_{p2}	Pseudo-second-order sorption rate constant [g/(mg min)]
k_S	S-model disinfection rate constant
k_{SE}	Selleck's model disinfection rate constant [(mg min)/L]
m	Empirical constant in the demand-free condition disinfection model
n	Empirical constant in the demand-free condition disinfection model
N_0, N_t	Initial number of microbes and number of microbes at time t
n_F, n_{LF}, n_T	Freundlich, Langmuir-Freundlich and Tóth isotherm exponents
n_{MF}	Multi-Freundlich isotherm exponent
q_e, q_t	Sorption amount at equilibrium and at time t [mg/g]
q_m	Maximum monolayer sorption capacity [mg/g]
$t_{1/2}$	Half-life [min]
x	Empirical constant in the demand-free condition disinfection model

Abbreviations

AC	activated carbon
AOX	adsorbable organic halogens
BOD _{7, ATU}	seven day biological oxygen demand with allylthiourea addition
CFU	colony forming units
COD _{Cr}	chemical oxygen demand using chromate as oxidizer
DOC	dissolved organic carbon
GAC	granular activated carbon
LC-OCD	liquid chromatography, organic carbon detection
NOM	natural organic matter
MPN	most probable number
PAA	peracetic acid
PAC	powdered activated carbon
PFA	performic acid
PFU	plague forming units
PPA	perpropionic acid
TOC	total organic carbon

List of original papers

This thesis is based on the following publications, which are referred to throughout the text by their Roman numerals:

- I Luukkonen, T., Teeriniemi, J., Prokkola, H., Rämö, J., Lassi, U. (2014) Chemical aspects of peracetic acid based wastewater disinfection. *Water SA*, 40: 73–80.
- II Luukkonen, T., Heyninck, T., Lassi, U., Rämö, J. (2015) Comparison of organic peracids in wastewater treatment: disinfection, oxidation and corrosion. *Water Research*, 85: 275-285.
- III Luukkonen, T., Hukkanen, R., Pellinen, J., Rämö, J., Lassi, U. (2012) Reduction of organic carbon in demineralised make-up water with active carbon filtration, *PowerPlant Chemistry*, 14: 112–119.
- IV Luukkonen, T., Tolonen, E.T., Runtti, H., Pellinen, J., Tao, H., Rämö, J., Lassi, U. (2014) Removal of total organic carbon (TOC) residue from power plant make-up water by activated carbon, *Journal of Water Process Engineering*, 3: 46–52.
- V Luukkonen, T., Sarkkinen, M., Kempainen, K., Rämö, J., Lassi, U. (2016) Metakaolin geopolymer characterization and application for ammonium removal from model solutions and landfill leachate, *Applied Clay Science*, 119: 266–276.
- VI Luukkonen, T., Runtti, H., Niskanen, M., Sarkkinen, M., Kempainen, K., Rämö, J., Lassi, U. (2016) Simultaneous removal of Ni(II), As(III), and Sb(III) from spiked mine effluent with metakaolin and blast-furnace-slag geopolymers, *Journal of Environmental Management*, 166: 579–588.

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Introduction and aims

Water is an essential resource. However, it is often taken for granted. The over-exploitation of groundwater and the unequal distribution of precipitation over the globe have led to water stress and scarcity in many areas. Additionally, industrial operations and other anthropogenic activities pollute water resources both locally and globally. These factors contribute to the increased pressure to use water more efficiently, reuse treated wastewater, and discharge only sufficiently clean effluents back into nature in order to avoid further contamination. Water can be contaminated either chemically and/or microbiologically, the latter of which causes more acute health problems. Consequently, effective and reasonably priced water and wastewater treatment methods are urgently needed.

Water quality is also a crucial factor for another current megatrend: energy efficiency. For instance, most electricity is generated using steam boilers, where water is the working fluid driving the turbines. The water quality in the boiler systems is a key determinant of the efficiency of power generation: better feedwater quality allows for the use of higher temperatures and pressures (Flynn 2009). Problems caused by impurities in feedwater include corrosion, deposit formation, foaming, and errors in on-line measurements. Again, this supports the claim that the development of effective water treatment technology is of critical importance.

This thesis discusses three different areas of water treatment technology:

1. The application of organic peracids in wastewater treatment to be used as disinfectants and oxidizers.
2. The removal of organic residues from boiler make-up water.
3. The use of geopolymers as sorbents.

The use of organic peracids and geopolymers is related to the oxidative removal of microbiological and chemical pollutants from water, respectively, whereas boiler make-up water treatment ultimately aims to improve energy efficiency. From the chemist's point of view, the core phenomena within these three kinds of treatment are oxidation (organic peracids) and (ad)sorption (boiler make-up water treatment and geopolymers). The topics, scopes, and contributions of original papers on various aspects of this thesis are shown in Fig. 1.

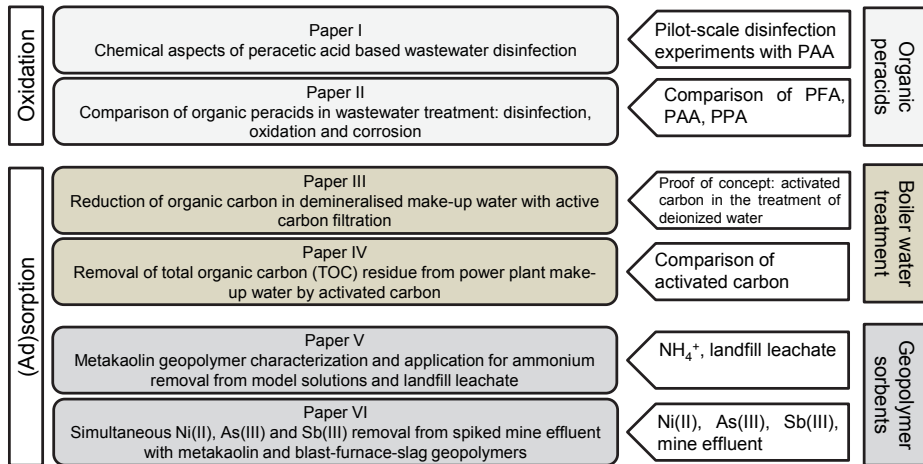


Fig. 1. Framework of the thesis: topics, scopes, and contributions of original papers.

Application of organic peracids for wastewater treatment

Peracetic and performic acids have emerged as alternative wastewater disinfectants during the last 30 and 10 years, respectively (Baldry 1983, Gehr *et al.* 2009). The most important motivating force behind their increased use has been the growing awareness of the formation of harmful disinfection by-products by such processes as chlorination or ozonation. Peracetic acid has been studied quite extensively, but research on tertiary effluent disinfection has thus far been relatively limited. Additionally, comparative studies between peracetic and performic acids are scarce in number. Furthermore, studies regarding the application of perpropionic acid in wastewater treatment do not seem to exist. Consequently, the research questions on this topic were framed as follows:

- What are the effects of peracetic acid on the physico-chemical and microbial properties of tertiary municipal wastewater on a pilot-scale (Paper I)?
- What are the differences of performic, peracetic, and perpropionic acids in terms of synthesis, decomposition kinetics, wastewater disinfection, oxidation and corrosion (Paper II)?

Removal of organic residues from boiler make-up water

Organic compounds in boiler make-up water have continued to persist as a major concern since the first published studies on the topic in 1980s (Jonas 1982). They originate mainly from natural organic matter, but they can also be from organic internal conditioning chemicals. As these compounds enter the water-steam cycle of a power plant, they gradually decompose into potentially corrosive compounds such as low molecular weight organic acids. Papers III and IV evaluate the suitability of granular activated carbon filtration in the removal of organic residues after the conventional ion exchange. The use of activated carbon at this stage of the water treatment process is a novel approach, and can potentially provide advantages such as an extended lifetime of the carbon bed. Moreover, activated carbon filtration can be more economical than other methods of removal, such as reverse osmosis or short wave-length UV treatment completed with a mixed-bed ion exchanger. The specific research questions were formulated as follows:

- Which organic fractions are present, and which ones are removed (Papers III and IV)?
- What are the differences between commercially available activated carbons (Paper IV)?
- What is the concentration and relevance of leachables from activated carbon (Papers III and IV)?

Geopolymers as sorbents

Geopolymers are amorphous, inorganic, three-dimensional polymeric materials typically consisting of an aluminosilicate network. Geopolymer technology has been in use for approx. 30 years in the development of low-CO₂ producing binders, the creation of fire-resistant materials, and the process of waste stabilization, to name a few examples (Davidovits 2011). However, the widespread use of these materials is still just beginning. Geopolymers are frequently referred as amorphous analogues to zeolites and, as such, they possess similar ion-exchange properties that allow for them to be used in wastewater treatment. Geopolymers can also be considered “green” economical materials since they can be prepared from industrial side-products such as blast furnace slag in mild reaction conditions. To date, several studies about geopolymer sorbents already

exist, although the removal of many metals and metalloids has not yet been studied, and most of the more recent studies have used only synthetic wastewater (model solutions). The following research question was formulated:

- Can geopolymer sorbents be effectively used for the removal of ammonium, nickel, arsenic, and antimony from real and synthetic wastewater (Paper V and VI)?

1 Organic peracids

Peroxides have the characteristic of containing the peroxy group (-O-O-), which is in the case of organic peroxides bound to a carbon atom either directly or via another atom. Organic peroxides can be considered derivatives of hydrogen peroxide (H₂O₂), where organic groups are substituted for hydrogen atom(s). Organic peracids, on the other hand, contain the percarboxylic group, COOOH, attached to an organic side chain which can be aliphatic, aromatic, or cyclic, to name a few examples.

Organic peracids have the highest oxidation potential of all organic peroxides, and thus have a wide range of industrial applications (Klenk *et al.* 2005). Short chain aliphatic peracids are miscible with water and have a characteristic pungent odor. They are thermodynamically unstable and have a tendency to decompose spontaneously or explode when highly concentrated, heated, under mechanical stress, or vulnerable to the catalytic effects of impurities (Giguere & Olmos 1952, Klenk *et al.* 2005, Wang *et al.* 2015). Longer carbon chain length increases stability and reduces explosiveness. Organic peracids have 3–4 units lower pK_a values (i.e., are weaker acids) than the corresponding carboxylic acids (Klenk *et al.* 2005). Peracids are used as disinfectants, sanitizers, sterilants, bleaching agents, and as reagents in the production of fine chemicals. The largest segments of users of peracetic acid were categorized as follows in 2013: the food industry (54.67 kt), healthcare (40.64 kt), water treatment (29.01 kt), production of fine chemicals (25.56 kt), and the pulp and paper industry (20.28 kt) (Marketsandmarkets 2014).

1.1 Production of organic peracids

An equilibrium solution of peracid can be prepared by mixing corresponding carboxylic acid and hydrogen peroxide according to Reaction 1, which is one of the most widely used industrial synthesis pathways (Klenk *et al.* 2005).



The reaction can be acid-catalyzed by, for example, sulfuric acid, ascorbic acid, or carboxylic acid esters (Mattila & Aksela 2000, Yousefzadeh *et al.* 2014). However, performic acid can be prepared without an additional catalyst if a large excess of formic acid relative to the amount of hydrogen peroxide is used (Klenk *et al.* 2005, Swern 1949). The composition of the equilibrium solution is affected

by both the initial molar ratios of the starting materials and the concentration of hydrogen peroxide. An example of such composition in the case of peracetic acid is shown in Fig. 2. The concentration of peracid in the equilibrium solution can be increased by vacuum distillation, among various other methods (Klenk *et al.* 2005).

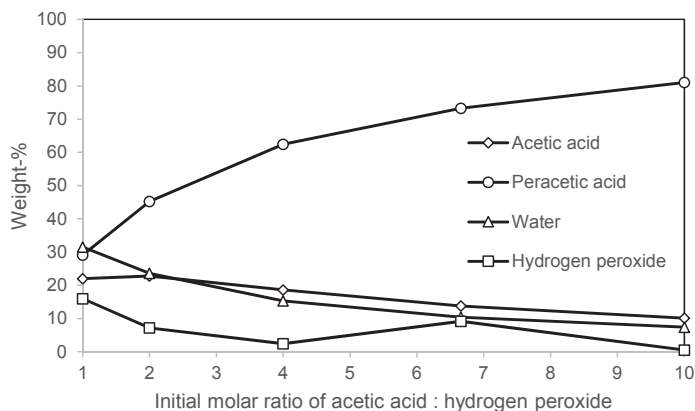


Fig. 2. The effect of the initial ratio of acetic acid to hydrogen peroxide (50% w/w) in the equilibrium composition (Klenk *et al.* 2005).

Aqueous peracids, most importantly peracetic acid, can be stabilized to increase the shelf-life of the product. Commercial solutions are stabilized with compounds such as alkali metal polyphosphates, dipicolinic acid or quinoline derivatives (Block 2001, Gunter *et al.* 1969). Furthermore, the safety hazards of peracids can be reduced by inert additives such as water, certain solvents (aliphatic and halogenated hydrocarbons, phthalate and phosphate esters, acetals), and inorganic solids (sulfates, phosphates, borates, silicates, carbonates) (Klenk *et al.* 2005).

One of the commercially available on-site performic acid production systems (Desifix, Kemira) consists of reagent (35–50% H₂O₂ and 70–90% formic acid) storages and diaphragm pumps feeding reagents to a tubular reactor submerged in a thermostatic bath (Ragazzo *et al.* 2013). Temperature, pressure, levels, and flow rates are automatically controlled. If the set threshold values are exceeded, the system automatically stops and the reactor is flushed with water. Microreactor technology (i.e., the reactor dimensions are in the range of sub-micrometer to sub-millimeter) has been studied for the production of both performic (Ebrahimi 2012, Ebrahimi *et al.* 2011, Ebrahimi *et al.* 2012) and peracetic (Jolhe *et al.* 2015) acids. The main advantages of such systems are their smaller equipment size, lower

levels of energy consumption, smaller amounts of waste production, and improved safety. The production capacities of microreactors are measured in g to kg amounts per day. They can also be readily scaled-up from laboratory to industrial use. Furthermore, the use of ultrasound technology can improve the peracid formation rate (Jolhe *et al.* 2015).

Another frequently used method of synthesis is creating a reaction between carboxylic anhydride and hydrogen peroxide (Reaction 2), which produces an anhydrous solution of peracid in the corresponding carboxylic acid. This reaction can be catalyzed by inorganic bases or metal salts (Klenk *et al.* 2005).



1.2 Disinfection and oxidation mechanisms of organic peracids

The disinfection and oxidation mechanisms of peracetic acid, which can be speculated to be the same with other organic peracids as well, are based on the formation of highly oxidative radical species such as the hydroxyl radical ($\text{HO}\cdot$), the superoxide anion ($\cdot\text{O}_2^-$), and the hydroperoxyl radical ($\text{HO}_2\cdot$). These radicals together are frequently referred to as the reactive oxygen species, or active oxygen (Fig. 3). Organic radicals can also be formed.

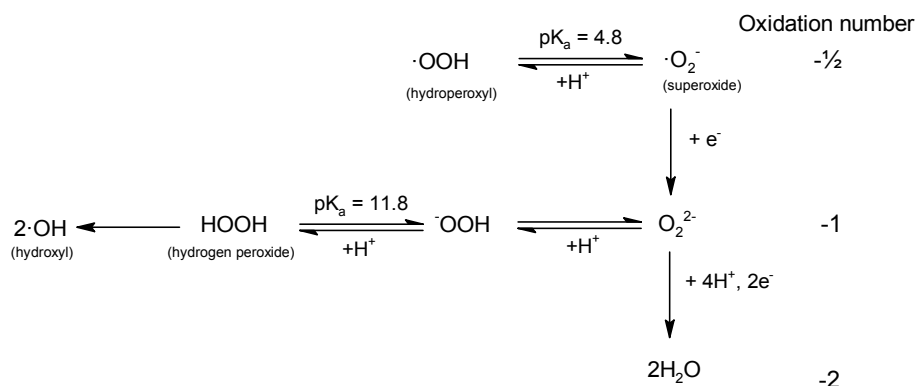
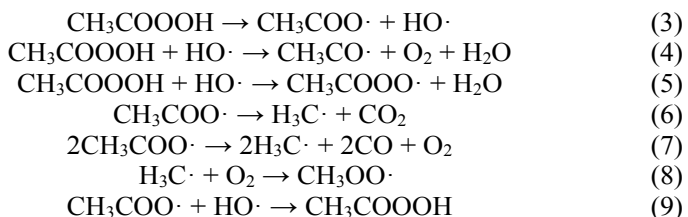


Fig. 3. Schematic presentation showing relationships between reactive oxygen species. The pK_a values are reported at 25 °C.

The formation of radicals begins with the homolysis of the oxygen-oxygen bond (Reaction 3), which is the rate-determining step in the chain reaction. The reaction requires activation in order to occur, such as a trace amount of transition

metal catalyst or UV irradiation (Bianchini *et al.* 2002a, Bianchini *et al.* 2002b). Subsequently, in the case of peracetic acid, the following aqueous chain reactions occur (Reactions 4–9) (Bach *et al.* 1996, Rokhina *et al.* 2010):



It has been suggested that all of the generated radicals contribute to the oxidation mechanism in some way, but $\text{HO}\cdot$ $\text{H}_3\text{C}\cdot$ play the most significant roles in the process (Flores *et al.* 2014). In the catalytic oxidation by peracetic acid, $\cdot\text{CH}_3$ is of limited availability due to the lower reaction rate constant (Rokhina *et al.* 2010). On the other hand, organic radicals have longer half-lives than $\text{HO}\cdot$, and thus some have argued that they are more effective in antimicrobial action as a result (Block 2001, Clapp *et al.* 1994).

Several types of specific damage to biomolecules by peracetic acid have been described by Kitis (2004) and the references therein:

- Sulfhydryl (-SH), disulfide (S-S), and double bonds in proteins, enzymes, and other biomolecules are oxidized.
- Inactivation of the catalase enzyme, which inhibits hydroxyl radical oxidation.
- Chemiosmotic function of the lipoprotein cytoplasmic membrane is disrupted.
- Protein denaturation occurs.
- Bases of the DNA molecule react adversely.
- Enzymes are oxidized and thus biochemical pathways, transport through membranes and intracellular solute levels are hindered.

In the case of viruses, inactivation might occur through the damaging of the virus surface structures, such as the protein coat, or attachment to the sites needed for infection of the host cells (Koivunen & Heinonen-Tanski 2005a). The damage caused by peracetic acid has been shown to be irreversible, i.e. microbes are unable to repair the damaged biomolecules and no regrowth takes place (Antonelli *et al.* 2006).

Hydrogen peroxide in the peracid equilibrium solution has a synergistic effect on the disinfection mechanism and serves as an additional source of hydroxyl radicals (Flores *et al.* 2014). However, hydrogen peroxide alone is a relatively ineffective disinfectant because the catalase enzyme is able to protect microorganisms from its action (Koivunen & Heinonen-Tanski 2005a, Wagner *et al.* 2002). As a result, the initial inactivation of the catalase enzyme by peracid is required to achieve the synergistic effect.

It has also been suggested that the organic part of the peracid structure might help to penetrate into microbial cells (Koivunen & Heinonen-Tanski 2005a). The increase in the chain length of the organic part might therefore increase the penetration capability as the lipophilicity increases.

1.3 Water and wastewater disinfection applications

Wastewater disinfection is conducted to prevent the spread of human pathogens and waterborne infections. Untreated wastewater is a significant contributor of bacteria and other microorganisms to aquatic ecosystems. As water resources become scarce in many areas, the need to reclaim wastewater increases. Consequently, the reuse of treated wastewater in irrigation or washing, for example, requires efficient disinfection methods.

Characteristics of an ideal disinfectant include: toxicity to microorganisms but not to higher forms of life; effectivity at ambient temperatures; stability and long shelf-life; noncorrosivity; deodorizing ability; widespread availability; and reasonable cost (Tchobanoglous *et al.* 2004).

1.3.1 Microbial quality requirements

Primary and secondary wastewater treatments can remove 90–99.9% (1–3 log units) of enteric bacteria, and tertiary treatment can eliminate a further 90–99% (1–2 log units) (Koivunen *et al.* 2003, Rajala *et al.* 2003, Verlicchi *et al.* 2011). However, these processes might still be insufficient to reach safe microbial levels.

Microbial requirements for wastewater effluents are typically expressed in terms of fecal indicator microbes (Fig. 4), which represent a substitute for actual human pathogens.

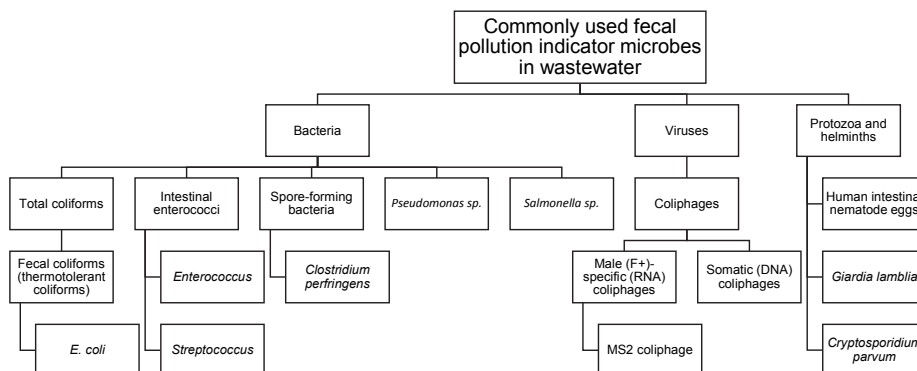


Fig. 4. Commonly used fecal contamination indicator microbes (Horan 2003).

Microbial requirements are generally implemented for the safe discharge or reuse of wastewater (Table 1). In Finland, wastewater disinfection is not a common practice, and the requirements are typically determined according to the EU bathing water requirements during the summer months (Directive 2006/7/EC 2006). Some Finnish wastewater treatment plants have additionally a 90% removal requirement for *E. coli* and enterococci in their environmental license.

Table 1. Examples of microbiological requirements for wastewater effluents.

Country / organization	Purpose	Required level	Reference
Italy	Agricultural reuse ^a	<i>E. coli</i> 10 CFU/100 mL	Decreto Ministeriale n. 185 2003
Italy	Discharge	<i>E. coli</i> 5000 CFU/100 mL	Decreto Legislativo n. 152 1999
Russia	Discharge	Total coliforms < 1000 CFU/100 mL <i>E. coli</i> < 100 CFU/100 mL Coliphages < 10 PFU/100 mL	Russian Federation Water Code 2010
WHO	Agricultural reuse ^a	<i>E. coli</i> < 1000 CFU/100 mL, helminth eggs 1 / L	WHO 2006
EU	Bathing water (excellent quality)	<i>E. coli</i> < 500 CFU/100 mL ^b <i>E. coli</i> < 250 CFU/100 mL ^c Enterococci < 200 CFU/100 mL ^b Enterococci < 100 CFU/100 mL ^c	Directive 2006/7/EC 2006

^a unrestricted use, ^b inland waters, ^c coastal and transitional waters ^{b, c} 95-percentile evaluation.

1.3.2 Disinfection by-products, mutagenicity, and toxicity

Disinfection by-products are suspected carcinogens or other toxic compounds formed by reactions between disinfectants and compounds already present in water. They include trihalomethanes (especially chloroform, bromodichloromethane, dibromochloromethane, and bromoform), bromates, aldehydes, and ketones. Concerns over disinfection by-products began in the 1970s in the USA after the discovery that trihalomethanes were extensively present in chlorinated drinking waters (USPHS Report 1970). This discovery was confirmed when it was shown that chlorine-based disinfection was capable of forming these compounds (Bellar *et al.* 1974, Rook 1974). More recently, the correlation between gastrointestinal cancer and chlorinated water consumption has been shown in epidemiological studies (Cantor 1997, IJsselmuiden *et al.* 1992, Koivusalo *et al.* 1997, Morris 1995). However, the supposed health effects of trihalomethanes have been devalued when considering the microbial safety provided by the chlorination of water (Freese & Nozaic 2004).

Peracetic acid is generally considered to produce insignificant amounts of disinfection by-products (possibly none) in typical operational conditions, which is one of the most important advantages that it has over ozone or chlorine-based disinfection (Kitis 2004). The formation of disinfection by-products caused by performic acid have not been studied extensively, however, the existing studies do point out that the amount of by-product formation is similar to, or even slightly lower than, the amount produced by peracetic acid (Chhetri *et al.* 2014). The detected amounts of aldehydes (Dell'Erba *et al.* 2007, Nurizzo *et al.* 2005, Ragazzo *et al.* 2013) and chlorinated (Dell'Erba *et al.* 2007, Monarca *et al.* 2002, Nurizzo *et al.* 2005, Booth & Lester 1995) and/or brominated (Booth & Lester 1995, Ragazzo *et al.* 2013) compounds are frequently lower than the guideline values for drinking water (Directive 98/83/EC 1998, WHO 2008). However, if the concentration of hydrogen peroxide is lower than the concentration of peracetic acid, the water matrix contains halogens, and if an excessively large dose of peracid is used, the formation of halogenated by-products is promoted (Shah *et al.* 2015).

Carboxylic acid concentrations increase as a result of peracid treatment, due to: the conjugate carboxylic acid in the equilibrium solution; the decomposition of peracid; and the oxidation of humic compounds or other organic material. Performic acid produces only a stoichiometric amount of formic acid in the wastewater in full-scale disinfection experiments, indicating that no oxidation of

organic matter took place (Ragazzo *et al.* 2013). The amounts of octanoic, nonanoic, decanoic, lauric, and myristic acids were found to increase as a result of peracetic acid treatment of surface water, but these carboxylic acids are not considered toxic or mutagenic (Monarca *et al.* 2002). The detrimental effect of introducing additional carboxylic acids to the treated wastewater is mainly related to the possible promotion of the regrowth of microbes. Formic acid is less biodegradable than acetic acid, which might indicate a lower regrowth potential of microbes after performic acid disinfection in comparison to the use of peracetic acid (Ragazzo *et al.* 2013).

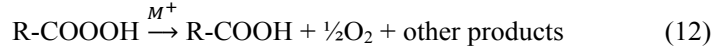
In vitro bacterial reversion assays (the Ames test) and plant genotoxicity tests showed that 2–4 mg/L of peracetic acid induced no formation of genotoxic by-products in secondary-treated municipal wastewater (Crebelli *et al.* 2005). Similar results were obtained when treating surface water with peracetic acid using a 0.2–1 mg/L dose (Monarca *et al.* 2002). However, mutagenic effects were observed occasionally depending on the season (Monarca *et al.* 2000, Collivignarelli *et al.* 2000). However, after dilution following the discharge of the water, these effects were considered negligible.

Performic acid showed only slight toxicity (or none at all) in the *V. fischeri* light suppression test in the dose range of 1–4 mg/L. Higher toxicity was observed with peracetic acid (dose 10 mg/L), and this was attributed to the slower degradation kinetics and corresponding extension in contact time. However, the toxicity diminished again as the effluent was diluted. (Chhetri *et al.* 2014, Ragazzo *et al.* 2013)

1.3.3 Peracid degradation kinetics

The degradation kinetics of organic peracids allows for the residence time of chemicals in water or wastewater to be evaluated, which is important when considering the potential regrowth of microbes, the formation of by-products, and general eco-toxicology. Hydrogen peroxide present in the peracids decomposes significantly slower than the peracid itself. The factors affecting the degradation rate include contact time, dose of the peracid, temperature, pH, amount of organic material, presence of solids or transition metals, and hardness (Falsanisi *et al.* 2006, Howarth 2003, Lazarova *et al.* 1998, Sanchez-Ruiz *et al.* 1995). In addition to those reactions in which radicals are formed (Reactions 3–9), three reaction pathways consume peracids in the aqueous environment: spontaneous decomposition, hydrolysis, and transition-metal catalysed decomposition

(Reactions 10–12, respectively) (Kitis 2004). In the pH range 5.5–8.2 the main reaction is spontaneous decomposition (Reaction 10).



The degradation rate of peracid can be presented with the following differential equation:

$$\frac{dC}{dt} = -k_\alpha C^\alpha \quad (13)$$

where k_α is the rate constant, α is the reaction order (0, 1, or 2) and C (mg/L) is the concentration of peracid. The initial consumption of peracid (D , mg/L) occurring immediately after application can be taken into account by replacing the initial concentration of peracid (C_0 , mg/L) by the term $C_0 - D$ which results in the following integrated rate laws:

$$C_t = (C_0 - D) - k_0 t \quad t_{1/2} = \frac{C_0}{2k_0} \quad (14)$$

$$C_t = (C_0 - D)e^{-k_1 t} \quad t_{1/2} = \frac{\ln 2}{k_1} \quad (15)$$

$$C_t = \frac{C_0 - D}{1 + k_2 t(C_0 - D)} \quad t_{1/2} = \frac{1}{k_2 C_0} \quad (16)$$

where k_0 (mg/(L min)), k_1 (1/min), and k_2 (L/(mg min)) are the rate constants of zeroth-order, first-order and second-order equations, respectively. Furthermore, half-lives ($t_{1/2}$, min) can be calculated as shown in Reactions 14–16. In calculating the half-lives, the initial consumption can be subtracted from C_0 .

1.3.4 Disinfection kinetics

Disinfection kinetics describe the variation of microbe amount as a function of time. The models can be divided into two categories: demand-free condition models and disinfectant demand condition models (Gyürék & Finch 1998). The demand-free condition models assume the following:

- Ideal plug-flow or batch reactor.
- No back mixing.
- Uniform dispersion of organisms and disinfectant molecules.
- Sufficient mixing to ensure that liquid diffusion is not rate limiting.
- Temperature and pH are constant.

- Disinfectant concentration remains constant during contact time.

Although demand-free condition models are clearly oversimplified in practice, they are still widely used and are able to effectively describe microbial inactivation kinetics in many cases.

The disinfectant demand condition models take into account the gradual decrease of disinfectant concentration during contact time by introducing the appropriate decomposition kinetic constants into the models. Assumptions of the disinfectant demand condition models are: negligible instantaneous disinfectant consumption (the term D in Equations 14–16) and negligible microbial inactivation during the instantaneous disinfectant consumption (Santoro *et al.* 2007).

Demand-free condition models

Most of the demand-free condition models are derived from the following differential rate law (Gyürék & Finch 1998):

$$\frac{dN_t}{dt} = -k_\beta m N_t^x C^n t^{m-1} \quad (17)$$

where dN_t/dt is the rate of inactivation, N_t is the number of surviving microbes at contact time t (min), C is the concentration (mg/L), m , n , and x are empirical constants (dimensionless), and k_β is the disinfection rate constant (unit depends on the value of m , n , and x).

The Chick-Watson model (Chick 1908, Watson 1908) (Equation 18, in integrated form) is one of the oldest disinfection kinetics models. It follows first-order kinetics, and the $C \times t$ values obtained from the model are frequently used in the designing of disinfection systems (Gyürék & Finch 1998).

$$\ln \frac{N_t}{N_0} = -\Lambda C^n t \quad (18)$$

where N_t is the amount of microbes at time t (min), N_0 is the initial amount of microbes, and Λ is the rate constant (unit depends on the value of n). The parameter n indicates the following: $n > 1$, dose is more important than contact time; $n = 1$, dose and contact time are equally important; and $n < 1$, contact time is more important than dose. Deviations from the first-order kinetics cannot be described with the Chick-Watson model. Typical deviations are shoulders or tailing-off in the survival curve, which are frequently explained by reactions with other wastewater constituents, and the protection of microbes by occurrences such

as suspended solids (Gyürék & Finch 1998, Tchobanoglous *et al.* 2004). Another reason for tailing-off could be the formation of microbe aggregates (Mattle *et al.* 2011).

The Hom model (Hom 1972) (Equation 19, in integrated form) is a more generalized first-order kinetics model which is able to account for the deviations from linearity in the survival curve.

$$\ln \frac{N_t}{N_0} = -k_H C^n t^m \quad (19)$$

where k_H is the rate constant (unit depends on the value of n and m). The parameters n and m affect the curvature of the plot: $m > 1$, the survival curve displays an initial shoulder; $m = n = 1$, the equation simplifies to the Chick-Watson model; $m < 1$, the survival curve displays a tailing-off effect. It has been suggested that the Hom model is suitable for assessing the use of peracetic acid when the dose is over 5 mg/L (Rossi *et al.* 2007).

The S-model (Profaiser 1998) (Equation 20, in integrated form) is a disinfection kinetics model frequently employed for peracetic acid disinfection (Azzellino *et al.* 2011, Rossi *et al.* 2007). It is suitable for situations where either a resistance to diffusion into the cell membrane or microbial aggregates hinder the disinfection process.

$$\ln \frac{N_t}{N_0} = -\frac{k_S C^n}{1 + (\frac{h}{Ct})^m} \quad (20)$$

where k_S is the rate constant (unit depends on the value of n) and h ((mg min)/L) is an additional model parameter. The survival curve has a characteristic S shape, consisting of three distinct phases: initial resistance, exponential inactivation, and asymptotic inactivation. The S-model has been proposed to be especially suitable for peracetic acid disinfection involving concentrations lower than 5 mg/L (Rossi *et al.* 2007). This has been explained by the negligible diffusion resistance at high peracetic acid concentrations.

Selleck's empirical model (Selleck *et al.* 1978) (Equation 21, in integrated form) is another commonly used disinfection kinetics model. However, it cannot successfully account for the kinetics of peracetic acid-based disinfection (Azzellino *et al.* 2011).

$$\log \frac{N}{N_0} = -n \log \left(1 + \frac{Ct}{k_{SE}} \right) \quad (21)$$

where k_{SE} ((mg min)/L) is the rate constant. Selleck's model was originally developed for situations where the inactivation rate decreases during the contact time, even when the concentration of the disinfectant stays constant.

A monod-type equation (Equation 22, in integrated form) of zeroth-order kinetics has been suggested for peracetic acid inactivation in some cases (Dell'Erba *et al.* 2004).

$$\log \frac{N_0}{N_t} = I_{max} \frac{t}{k_{MT} + t} \quad (22)$$

where I_{max} (dimensionless) is the maximum log reduction value achievable at equilibrium and k_{MT} (min) is the semi-saturation time constant corresponding to $I_{max}/2$.

Other demand-free condition models include the Rational model, the Hom-Power Law model, the Multiple-Target model, and the Series-Event-models, described in detail by Gyürék & Finch (1998). However, these models are not commonly applied to organic peracid-based disinfection.

Disinfectant demand condition models

The disinfectant demand condition models are based on the generalized inactivation rate law which assumes first-order kinetics for the degradation of the disinfectant (Gyürék & Finch 1998):

$$\frac{dN_t}{dt} = -k_{\beta} m N_t^x C_0^n e^{-k_1 t n} t^{m-1} \quad (23)$$

where k_1 (1/min) is the first-order rate constant for disinfectant decomposition, C_0 is the initial disinfectant concentration (mg/L), and all other terms are the same as those in Equation 17. A review of the disinfectant demand condition models is provided by Gyürék & Finch (1998). The application of the disinfectant demand condition models to peracid-based disinfection is uncommon in the literature. One of the few studies available is by Santoro *et al.* (2007), who conducted a comparison between models accounting and not accounting for peracetic acid decay. They found the best models to be the Power Law model or the Hom-Power Law model. They also noted that the residual peracid measurement method could have an effect on the selection of the best-fitting model.

1.3.5 Municipal wastewater

Combined sewer overflow

Combined sewer overflow occurs in sewer systems where wastewater and rain water are transported in the same sewer, and the increased levels of rainfall cause water levels to exceed the design capacity. The surplus effluent needs to be discharged either directly or after retention in tanks or outfall pipes, which poses potential microbial and chemical risks for the receiving water body.

The US Environmental Protection Agency lists peracetic acid as one of the potential alternative disinfectants to be used for the treatment of combined sewer overflows (US EPA 1999). In a comparison study, performic acid was found to require significantly shorter contact time than peracetic acid to reach similar disinfection result: 20 and 360 min, respectively, when using a similar (2–5 mg/L) dose (Chhetri *et al.* 2014). Additionally, performic acid was studied with full-scale experiments using 1–8 mg/L dose and a 24 min contact time, confirming the suitability of the method (Chhetri *et al.* 2015).

Primary, secondary, and tertiary municipal wastewater

Primary treatment of wastewater involves processes such as screening, (aerated) sand removal, and sedimentation. Primarily treated wastewater typically contains large amounts of organic matter and suspended solids, which complicate the disinfection processes. The required peracetic acid doses and contact times are in the ranges of 10–20 mg/L and 15–30 min, respectively, to reach a 2–6.5 log reduction in the amount of enteric bacteria detected (Koivunen & Heinonen-Tanski 2005b, Sanchez-Ruiz *et al.* 1995). In another case study, 4.5–6 mg/L of peracetic acid with a contact time of 1 h did not reach the 9000 CFU/100 mL target of fecal coliforms in the primary effluent (Gehr *et al.* 2003). As a relatively large dose of peracetic acid is needed for primary effluents, the economic viability of this treatment method is questionable (Gehr *et al.* 2003). Performic acid disinfection of primary effluents reaching 3 log removal of fecal coliforms required a dose of 3.4 mg/L and a contact time of 45 min, indicating much better efficiency than the use of peracetic acid (Gehr *et al.* 2009).

Secondary treatment of wastewater typically includes a biological treatment, such as an activated sludge process, followed by sedimentation. The organic matter and suspended solids are reduced, improving the efficiency of disinfection.

After this phase, the tertiary treatment of wastewater can be implemented via the use of processes such as sand filtration, flotation, or coagulation-flocculation. Tertiary effluents are ideal for disinfection since the amount organic matter and suspended solids are reduced even more, thus reducing the consumption of disinfectant. The combination of tertiary treatment and disinfection can be referred to as the multiple barrier concept, which has been shown to be the most effective approach for disinfection (Liberti & Notarnicola 1999). The required doses and contact times for the disinfection of secondary effluents with peracetic acid vary within the range of 0.6–10 mg/L and 10–120 min, respectively (see Table 11 in the Results section). Performic acid, on the other hand, typically requires 0.4–2 mg/L and 5–10 min (Karpova *et al.* 2013, Ragazzo *et al.* 2013). For tertiary effluents, the peracetic acid doses and contact times are typically within the range of 1.5–15 mg/L and 10–36 min, respectively (see Table 11). It has been concluded that performic acid is more effective than peracetic acid, especially in shorter contact times (Chhetri *et al.* 2014, Ragazzo *et al.* 2013). Relatively large variation within the doses and contact times can be attributed to case-dependent microbial requirements (in terms of indicator microbes and inactivation level), experimental conditions, and wastewater chemical quality.

1.3.6 Surface and ground waters

Peracids are not widely studied for the disinfection of surface or ground waters in the production of drinking or industrial water. Especially in the case of drinking water, the risk of biofilm formation increases as a result of the formation of carboxylic acids after peracid disinfection.

Peracetic acid has been recommended as a substitute for pre-chlorination, which is used at some surface water plants as a first unit process (Nurizzo *et al.* 2005). The use of peracetic acid (doses 0.2–1.0 mg/L) for surface water disinfection showed promising results in terms of disinfection efficiency and by-product formation (Monarca *et al.* 2002).

One drawback of chlorine-based disinfection is the introduction of an unpleasant flavor and odor to drinking water. Peracetic acid and sodium hypochlorite were compared in terms of the threshold flavor and odor in both surface and groundwater, respectively (Veschetti *et al.* 2010). Water treated with sodium hypochlorite was determined to have a stronger taste and odor than water treated with peracetic acid, and the threshold concentrations for odor and flavor were 0.04 and 0.23 mg/L, respectively, in the case of hypochlorite, and 6 and 11

mg/L in the case of peracetic acid. Furthermore, a 0.8–1.6 mg/L concentration of peracetic acid was proposed to be sufficient as a residual disinfectant (Veschetti *et al.* 2010).

Additionally, peracetic acid was shown to be a promising method in the remediation of groundwater contaminated with sewage (Bailey *et al.* 2011). The required dose and contact time were 4–5 mg/L and 15 min, respectively.

1.3.7 Industrial effluents

Peracetic acid has been used as a cooling water biocide (Flynn 2009, Kitis 2004), for the removal of *Legionella pneumophila* (Pradhan *et al.* 2013, Baldry & Fraser 1988, Saby *et al.* 2005), and for the disinfection of ion-exchangers (Block 2001) and membrane hollow fibers (Kitis 2004). The doses needed for *Legionella* removal have varied between 3–600 mg/L (Pradhan *et al.* 2013, Baldry & Fraser 1988, Saby *et al.* 2005), but regrowth after treatment was reported (Saby *et al.* 2005). A potentially effective approach for long-term *Legionella* control could be an initial high-shock dose, with a smaller, continuous dose administered afterwards (Baldry & Fraser 1988). As for other uses, both performic and peracetic acids have been administered to control the microbial growth in paper mill process waters (Atkinson *et al.* 2014, Jakara *et al.* 2000), and performic acid has been applied for the fouling control of reverse osmosis membranes (Vance *et al.* 2013).

1.3.8 Biosolids

Peracetic acid has been used for the reduction of pathogens in biosolids, i.e. wastewater sludges (Kitis 2004). The required dose of peracetic acid in order to remove *Salmonella* from biosolids was 300–500 mg/L (Baldry & Fraser 1988). At the dose range 150–250 mg/L, *Salmonella* was reduced significantly but not removed completely (Baldry & Fraser 1988, Fraser *et al.* 1984). The peracetic acid dose that is required to remove worm eggs is reported to be significantly higher: 500–6000 mg/L (Gregor 1990). Possible process phases for peracid dosing in sludge treatment are gravity thickening, transportation to a treatment plant, or after digestion (Fraser 1987, Fraser *et al.* 1984, Gregor 1990).

Application of peracetic acid for sludge treatment resulted in the formation of readily biodegradable and non-toxic end-products, and the process did not interfere with sludge humus improvement properties in soil constitution (Kitis

2004). Another important feature is that peracetic acid can remove odors caused by reduced compounds, such as hydrogen sulfide or mercaptans (Colgan & Gehr 2001, Fraser *et al.* 1984). However, peracetic acid does not react with ammonia, which may also cause odor problems (Fraser *et al.* 1984). The use of hydrogen peroxide (a component of peracid solutions) for odor abatement is quite common (Rafson 1998).

Peracetic acid was also applied in wastewater sludge pre-oxidation before anaerobic digestion (Appels *et al.* 2011). Solubilization of organic matter, an increase in biogas production by up to 21%, and increased formation of volatile fatty acids were observed. The optimum dose was 25 g peracetic acid / kg dry solids.

1.3.9 Advanced oxidation processes for disinfection

In advanced oxidation processes, the formation of radicals is enhanced either by combining two methods, such as UV/H₂O₂ or O₃/H₂O₂, or by using a catalyst, such as the Fenton oxidation (Fe²⁺/H₂O₂).

The combination of UV and peracid has synergistic effects; in other words, the combined disinfection efficiency is larger than the sum of individual efficiencies (Caretti & Lubello 2003, Koivunen & Heinonen-Tanski 2005a, Lubello *et al.* 2002). Synergy values (i.e. how many more log units of inactivation were achieved than was initially expected from summing up the individual log inactivation values) of 2 log units for enteric bacteria have been reported (Koivunen & Heinonen-Tanski 2005a). Slightly lower synergy for viruses was observed (Koivunen & Heinonen-Tanski 2005a, Rajala-Mustonen *et al.* 1997). As a result of the following conclusions, combined treatment has been recommended (Caretti & Lubello 2003, Koivunen & Heinonen-Tanski 2005a):

- Microbes are unable to repair the damage caused by combined treatment, which might otherwise be a problem when using only UV treatment.
- There is a lower dependency on wastewater quality as compared to sole UV treatment.
- Better disinfection results occur on a wider scale of microorganisms.
- A lower peracid dose and contact time is needed.
- A smaller UV unit is needed.
- The cost of disinfection (investment and operational) might become competitive, especially in the case of large wastewater treatment plants.

Regular wastewater disinfection UV systems (i.e., low pressure lamps with a wavelength maximum of approx. 254 nm) can be used in the combined treatment (Koivunen & Heinonen-Tanski 2005a). The tested UV and peracetic acid doses in the combined treatment have been in the range of 10–300 mWs/cm² and 0.5–15 mg/L, respectively (Caretti & Lubello 2003, Koivunen & Heinonen-Tanski 2005a, Lubello *et al.* 2002). Considered in terms of cost, the most efficient range is possibly 1–2 mg/L peracetic acid and 200–225 mWs/cm², where the operational cost would be 0.031–0.036 €/m³ (Caretti & Lubello 2003). The UV doses of regular wastewater disinfection systems, according to the guidelines, are 50, 80, and 100 mWs/cm² for membrane filtration effluent, granular medium filtration effluent, and reclaimed water systems, respectively (Tchobanoglous *et al.* 2004).

Synergistic effects were also observed when using peracetic acid, silver, and/or copper (Luna-Pabello *et al.* 2009). Most importantly, the addition of these metals decreased the required contact time (De Velásquez *et al.* 2008). The proposed mechanism was the oxidation of silver and copper to more oxidative and toxic forms, in addition to the formation of hydroxyl and other radicals.

1.4 Oxidation applications

The oxidation potential of peracetic acid is larger than that of many other oxidizers, but the oxidation potential of performic or perpropionic acids has not yet been reported (Table 2). Peroxides require activation before efficient oxidation of pollutants can occur (Jones 1999), and activators for peracetic acid have included transition metal ions (N'Guessan *et al.* 2004, Rothbart *et al.* 2012) as homogenous catalysts, metal oxides (Rokhina *et al.* 2010) and carbon fibers (Zhou *et al.* 2015) as heterogeneous catalysts, and UV radiation (Daswat & Mukhopadhyay 2012, Daswat & Mukhopadhyay 2014). The beneficial features of peracids in oxidation, especially in advanced oxidation processes, include a weaker O-O bond compared to hydrogen peroxide, technical ease of application, and activity in a wide pH range (Bianchini *et al.* 2002b, Bokare & Choi 2014, Koivunen *et al.* 2005, Kitis 2004).

Table 2. Redox potentials of commonly used oxidizers (Awad *et al.* 2004, Jones 1999, Rafson 1998).

Chemical	E° [V]
Hydroxyl radical ($\cdot\text{OH}$)	2.80
Ozone (O_3)	2.01
Peracetic acid (CH_3COOOH)	1.96
Hydrogen peroxide, low pH (H_2O_2)	1.78
Permanganate (MnO_4^-)	1.70
Hypochloric acid (HOCl)	1.49
Chlorine gas (Cl_2)	1.27
Chlorine dioxide (ClO_2)	1.27
Hydrogen peroxide, high pH (H_2O_2)	0.85

1.4.1 Oxidation of pollutants in wastewater

Landfill leachate refractory organics

Performic acid was studied for the oxidation of refractory organics in a landfill leachate sample (Hagman *et al.* 2008). No reduction in the total organic carbon content was observed, whereas the color of the samples improved. Similar results were obtained by Ragazzo *et al.* (2013) for municipal wastewater, indicating that performic acid has a low oxidative effect on organic matter in wastewater. This is possibly due to the more favorable reaction with other constituents in wastewater, such as reduced sulfur species, which also cause a dark colour, or microbes.

Pharmaceuticals

The removal of anionic active pharmaceutical ingredients with peracetic acid (diclofenac, ibuprofen, clofibric acid, naproxen, gemfibrozil, and mefenamic acid) from spiked municipal wastewater (concentration 40 $\mu\text{g/L}$) was studied by Hey *et al.* (2012). Mefenamic acid was removed most effectively, although the amount of high organic matter in wastewater inhibited oxidation. Diclofenac and naproxen were removed to some extent, whereas ibuprofen, clofibric acid, and gemfibrozil were not degraded. High doses of peracetic acid ($> 15 \text{ mg/L}$) were required to initiate degradation. Ultimately, it was determined that chlorine dioxide was more effective than peracetic acid (Hey *et al.* 2012).

Another study involved performic acid (dose 6 mg/L) as an oxidizer of salicylic acid, clofibric acid, ibuprofen, 2-hydroxy-ibuprofen, naproxen, triclosan, carbamazepine, and diclofenac (Gagnon *et al.* 2008). The studied effluent was municipal primary effluent, where the concentrations of pharmaceutical compounds were in the range of 43–2556 ng/L. The removal efficiency was poor (< 8%) for all compounds.

Dyes

Orange II was oxidized with peracetic acid catalysed by Mn(II) in a bicarbonate buffered solution (Rothbart *et al.* 2012). The oxidation mechanism (Fig. 5) involved the formation of reactive Mn(IV)=O species, which is the actual oxidant of Orange II. Interestingly, hydroxyl radical did not play an important role in the oxidation, whereas hydrogen peroxide acted as a reducing agent of oxidized manganese species, and when hydrogen peroxide was no longer present, the reaction proceeded in a stoichiometric manner and an inert MnO₂ precipitate was formed. The optimum pH was 9.4. An increased peracetic acid or Mn(II) amount showed an increased initial oxidation rate, whereas an increased hydrogen peroxide or bicarbonate amount decreased the rate. The reaction rate started to saturate after approx. 0.01 M peracetic acid (= 760 mg/L). The oxidation of Orange II caused the cleavage of azo-bond (N-N) and destroyed the aromatic structures.

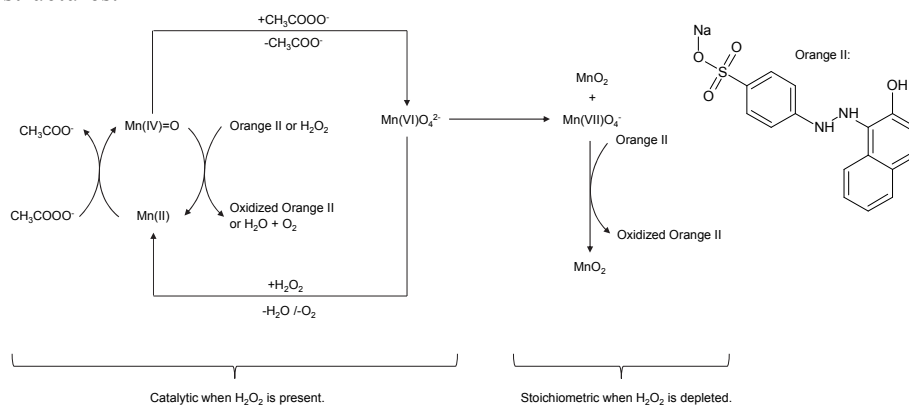


Fig. 5. Reaction pathways in catalytic and stoichiometric Orange II oxidation in the peracetic acid, hydrogen peroxide, and Mn(II) system (Rothbart *et al.* 2012).

Reactive Brilliant Red X-3B was oxidized using peracetic acid (5 mM \approx 380 mg/L) with activated carbon fibers as a catalyst (Zhou *et al.* 2015). Activated carbon fibers generate no secondary pollution due to the metal ions leaching; they also have a sustained catalytic ability, reusability, and a wide operational pH area. The mechanism of oxidation was suggested to be the homolytic cleavage of the peroxy group of peracetic acid and the subsequent formation of radicals (Reaction 3).

Phenols

Peracetic acid catalysed by manganese oxide (MnO₂) particles was used to degrade phenol from aqueous solutions (Rokhina *et al.* 2010). The oxidation was supposed to occur through the action of radicals ($\cdot\text{CH}_3$, $\cdot\text{OH}$, and $\text{CH}_3\text{COO}\cdot$). The optimum conditions were: a catalyst dose of 7 g/L, a peracetic acid concentration of 50 mg/L, and a reaction time of 120 min. The increase of peracetic acid concentration decreased the degradation significantly due to the radical scavenging by the excess oxidizing agent (Mijangos *et al.* 2006). In the absence of a catalyst, no degradation of phenol occurred by peracetic acid, which clearly identifies the need to activate peroxides in oxidation applications.

The oxidation of 4-chlorophenol (100 mg/L) was studied with an UV/PAA system involving 125–400 W UV irradiation and 1020–3040 mg/L peracetic acid (Daswat & Mukhopadhyay 2014). Over 95% mineralization was observed. Similar experiments using an industrial wastewater sample (total chlorophenol concentration 142 mg/L) revealed the optimum conditions in that case to be 250 W UV input, pH 11, and 4053 mg/L peracetic acid (Daswat & Mukhopadhyay 2012). The obtained 4-chlorophenol and COD reductions were 97 and 94%, respectively.

2 Removal of organic residues from boiler make-up water

An industrial boiler system consists of processes shown in Fig. 6. Make-up water treatment includes the physico-chemical and demineralization phases, which together produce ultrapure water with conductivity of $0.1 \mu\text{S}/\text{cm}$ or less (Flynn 2009, Hussey *et al.* 2009). Make-up water is a major contributor to organic contamination in the water-steam cycle. Organic residues are typically present in relatively small concentrations, ranging from tens to several hundred $\mu\text{g}/\text{L}$ (ppb) measured as total or dissolved organic carbon (TOC or DOC) (Huber 2006). However, these low concentrations can still cause problems in the operation of a plant or even damage the cycle materials. The problems arise from the thermal decomposition of organic residues in the water-steam cycle. The removal of organic residues is especially important for power plants with high condensate or steam losses, i.e. industrial power plants.

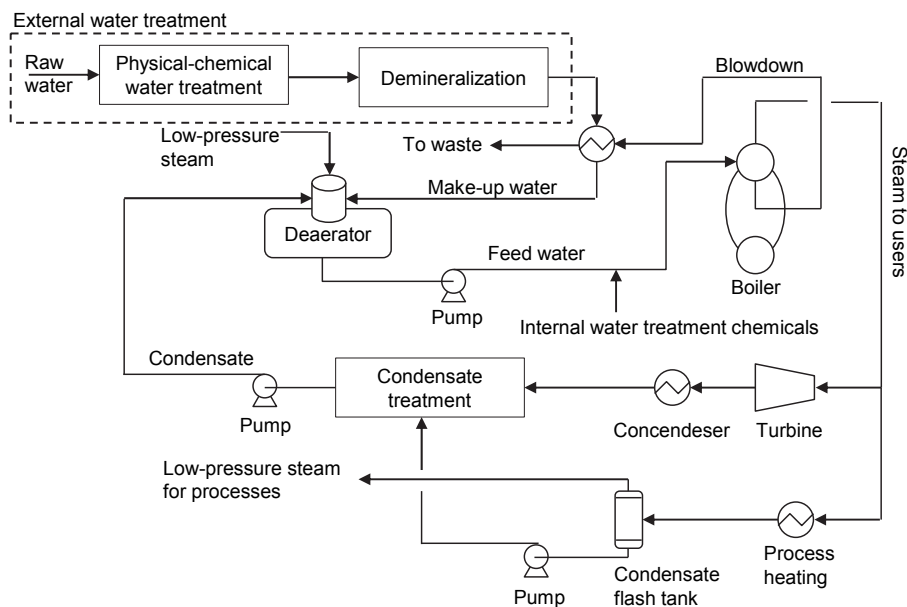


Fig. 6. Schematic presentation of an industrial boiler system (Flynn 2009).

2.1 Sources of organic residues

2.1.1 Natural organic matter

Natural organic matter (NOM) is ubiquitous in surface waters at concentrations ranging up to tens of mg/L (ppm) of TOC. NOM is a heterogenous mixture of different kinds of organic molecules with varying molecular weight, charge density, and hydrophobicity. Although the majority of organic matter is effectively removed through chemical water treatment processes and demineralization, there are still traces of organics remaining in make-up water. Generally, residues with very low molecular weight and low charge density fractions are the most difficult to remove (Moed *et al.* 2014a).

NOM can be qualitatively and quantitatively characterized with the liquid chromatography – organic carbon detection (LC-OCD) method (Huber & Frimmel 1992, Huber & Frimmel 1991), which has been frequently applied to power plant water samples (Huber 2006). This method allows for the fractionating of NOM into hydrophobic and hydrophilic fractions, of which the latter can be further classified into five parts:

- Biopolymers (polypeptides, polysaccharides, proteins, and amino sugars), >> 20 000 g/mol.
- Humic substances (fulvic and humic acids), approx. 1000 g/mol.
- Building blocks (hydrolysates of humic substances), 300–500 g/mol.
- Low molecular weight humic substances and acids, < 350 g/mol.
- Low molecular weight neutrals (alcohols, aldehydes, ketones, and amino acids), < 350 g/mol.

Of these fractions, the most problematic for boiler water treatment are the extremes in terms of molecular weight: the biopolymers and the low molecular weight neutrals (Ender *et al.* 2006).

2.1.2 Internal organic treatment chemicals

The internal water treatment chemicals are administered to the feed water (Fig. 6) in order to prevent problems caused by impurities remaining after the external water treatment. The aims of internal water treatment include pH adjustment, corrosion protection, oxygen removal, and cleaning, to name just a few examples.

There are both inorganic and organic internal treatment chemicals available. Typically, the organic chemicals are the more modern, and thus many boiler water quality recommendations do not acknowledge their use (Mathews 2008a). The dosing amounts of organic conditioning chemicals range from 10 µg/L to over 10 mg/L (Svoboda *et al.* 2006).

Neutralizing amines

Neutralizing amines, such as morpholine, cyclohexylamine, or ethanolamine (general formula R-NH₂), are employed to neutralize carbonic or other acids, and to buffer the pH to the optimal range for the preservation of the magnetite (Fe₃O₄) film on the boiler steel (Flynn 2009, Mathews 2008a). The benefit of organic amines compared to traditionally used ammonia (NH₃) is that they have a higher neutralizing capacity. The use of neutralizing amines is especially beneficial in the wet steam regions of the water-steam cycle, the air cooled condensers, and the heat recovery steam generators (Mathews 2008a). They operate by volatilizing into the steam phase and redissolving back into the condensate with carbon dioxide (Flynn 2009). Typically, amines are used in blends that consequently have a combination of several beneficial characteristics. The thermal stability of neutralizing amines varies between 400–600 °C (Flynn 2009). However, the amine provides cations for pH counterbalancing after the acidic degradation product formation (Svoboda *et al.* 2006).

Filming amines

Filming amines (also referred to as polyamines or fatty amines) are relatively volatile oligoalkylamine fatty amines with a general formula of R₁-[NH-R₂]_n-NH₂ where n = 0–7, R₁ is an unbranched alkyl chain (12–18 carbons), and R₂ is a short chain alkyl group (1–4 carbons) (Hater *et al.* 2009). Some examples include octadecylamine or oleyl propylene diamine. The film that forms on the metal surface acts as a barrier against corrosive substances such as oxygen and carbon dioxide (Flynn 2009). The hydrophobic alkyl group makes the metal surface unwettable. Additionally, the filming amines can gradually remove deposits such as calcium scale. However, despite its advantages, the application of filming amines is less common than the use of many other internal treatment chemicals.

Oxygen scavengers

Oxygen scavengers, such as carbohydrazide, diethylhydroxylamine, or hydroquinone, are used to reduce the residual dissolved oxygen (approx. 10 µg/L) from feed water to less than 1 µg/L after mechanical oxygen removal. Some oxygen scavengers also accelerate metal passivation and act as neutralizing agents after decomposition (Frayne 2002). The traditionally used hydrazine (NH₂-NH₂) is carcinogenic, and thus alternative chemicals are generally preferred. Many oxygen scavenger chemicals require the use of a catalyst such as copper or cobalt. Unlike organic amines, organic oxygen scavengers do not provide pH counterbalancing cations, and thus are potentially more corrosive after decomposition (Svoboda *et al.* 2006). The decomposition of oxygen scavengers produces mainly short-chain organic acids and carbon dioxide (Svoboda *et al.* 2006).

2.1.3 Other sources

Cleaning agents

Organic cleaning agents, such as ethylenediaminetetraacetic acid (EDTA), ammoniated citric acid, and hydroxyaceticformic acid, are used to remove deposits from once-through supercritical units, superheaters, and reheater sections (Mathews 2008b).

Ion exchanger leachable

Ion exchanger leachables, i.e. decomposition products and manufacturing impurities, are a less-recognized source of organic contamination, as they are often masked by other sources (Daucik 2008). New resins release considerably more organic compounds than older resins. The leachables include monomers (styrene, acrylate, and derivatives), organic reactants (alkyl chloride), organic solvents, by-products, and oligomers. Within a few months of use, the amount of initial leachables decreases, and the release of so-called permanent leachables begins: sulfonated monomer and oligomer derivatives in the case of cation exchangers, and aliphatic amines in the case of anion exchangers. The amount of TOC resulting from ion exchanger leachables is in the range of tens of µg/L.

However, a substantial amount of sulfate may be released as a result of the thermal decomposition of sulphur containing compounds.

2.2 Problems caused by organic residues in the water-steam cycle

Decomposition

Organic compounds in the power plant water-steam cycle decompose by thermolysis or hydrothermolysis, i.e. decomposition caused by heat, or hydrolysis caused by pure water at elevated temperatures, respectively (Moed *et al.* 2014a). For instance, a well-known decomposition of morpholine starting at approx. 590°C is presented in Fig. 7 (Flynn 2009, Moed *et al.* 2014b, Moed *et al.* 2014c, Moed *et al.* 2015). The main decomposition products of organic impurities are formic acid, acetic acid, and carbon dioxide, but if only a partial decomposition takes place, then propionic, glycolic, butyric, and oxalic acids (which are present as anions) with toluene, naphthalene, acetone, xylenes, benzene, lactate, and levuline can also be detected (Jiricek 2000, Lépine & Gilbert 1995, Moed *et al.* 2014a, Svoboda *et al.* 2006). Two pathways, reductive and oxidative, may be initialized simultaneously (disprotonation) for a given molecule (Huber 2006).

The data on the kinetics of the decomposition of NOM and other organic residues in the water-steam cycle conditions is minimal. However, despite this absence in the literature, the main factors affecting the decomposition appear to include temperature, retention time, concentration of TOC, and redox-conditions (Moed *et al.* 2014a). Reductive conditions increase the stability of all organic acid anions (Moed *et al.* 2014a).

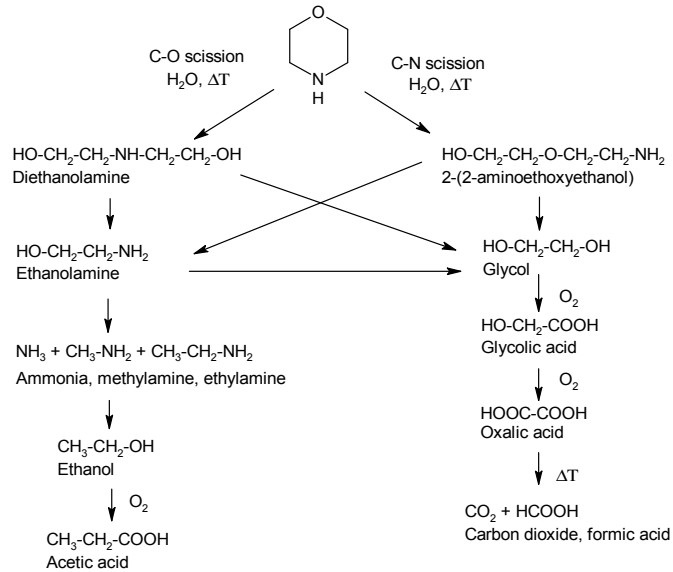


Fig. 7. The thermal decomposition (at $T > 590\text{ }^\circ\text{C}$) of morpholine (Flynn 2009).

Corrosion

The concentration of acidic decomposition products can be significantly high in the first few droplets of condensing steam (early condensate). This is due to the increased boiling (and condensation) temperature of water containing solutes. For example, the concentration of acetate in early condensate can be 600–6000 $\mu\text{g/L}$ while the stress corrosion cracking can be initiated at a concentration of 1000 $\mu\text{g/L}$ (Maeng & Macdonald 2008). Due to the lowered local pH of the condensate, the risk of corrosive damage increases in areas such as the turbine or boiler (Bodmer 1978, Svoboda *et al.* 2006). The specific types of corrosion that have been suspected to be related to organic contamination are pitting, flow accelerated corrosion, corrosion fatigue cracking, and stress corrosion cracking (Bödeker *et al.* 2002, Svoboda *et al.* 2006). However, there is no irrefutable quantitative evidence on the role of organic compounds or decomposition products on corrosion and thus this topic remains controversial (Bursik 2008, Daniels 2002, Mathews 2008a). A more serious corrosion-related concern is the release of possible heteroatoms (such as Cl and S) from organic compounds as a result of decomposition (Bursik 2008).

Increased cation conductivity

Another problem arising from the presence of anionic decomposition products is that they increase the cation conductivity (conductivity measured after cation exchange) of steam and condensate. Cation conductivity is one of the most important online measurements implemented at power plants, since it gives an indication about the presence of sulphate or chloride, among other factors. Problems such as cooling water inleakage or contaminated make-up water can be detected with the cation conductivity measurement (Svoboda *et al.* 2006). The recommended level for cation conductivity is 0.2 $\mu\text{S}/\text{cm}$ (Bursik 2008). Cation conductivity measurements can be coupled with a degassing unit which removes the problem related to carbon dioxide (Leleux *et al.* 2008). Another problem related to online measurements is the formation of interfering films on the instrument sensors (conductivity, pH, oxygen etc.) by film forming amines (Bursik 2008).

2.3 Water quality recommendations

Experimental work and practical experience indicate that organic acids can have detrimental effects in the steam-water cycle (Bursik 2008, Mathews 2008a). However, the general concensus is that a well-founded TOC guideline cannot be drawn on basis of existing data. The current guidelines generally recommend a TOC level between 100–200 $\mu\text{g}/\text{L}$ (Eskom 1999, VGB PowerTech 2002), although it has been suggested that the recommendations should be site or unit specific (Bursik 2008). In a survey of 27 power plants, the typical TOC amount in make-up water was within the range of 100–300 $\mu\text{g}/\text{L}$ and only 60% met the proposed 200 $\mu\text{g}/\text{L}$ quality recommendation (Huber 2006).

2.4 Organic residue removal methods

The general features of the TOC removal methods are summarized in Table 3.

Table 3. General features of the TOC removal methods.

Removal method	Principle	Required water pre-treatment	Achievable water quality in terms of organics	References
Enhanced coagulation	Optimized coagulation to remove TOC in terms of coagulant dosing amount, choice of chemical, and other operational parameters.	None	Significant improvement when compared to regular coagulation. Most efficiently removed fractions: BP and HS. LMW compounds are not removed effectively.	Aguiar <i>et al.</i> 1996, Budd <i>et al.</i> 2004, Chow <i>et al.</i> 1999, Gericke & Aspden 2008, Nagel <i>et al.</i> 2008
Granular activated carbon	Adsorption of organic molecules and possibly biological decomposition on the carbon surface.	Coagulation and sand filtration	Removal efficiency: LMW acids and neutrals > building blocks > HS. BP are not effectively removed.	Velten <i>et al.</i> 2011, Scholz & Martin 1997, Schönfelder & Keil 2002
Ion exchange (cation, anion, and mixed bed ion exchangers)	Reversible displacement of counter ions on the resin surface by the ions in the solution.	Chemical water treatment	DOC ≈ 100–300 µg/L. Anion exchangers remove mostly HS and building blocks while BP and LMW neutrals are not removed.	Bolto <i>et al.</i> 2002, Bödeker <i>et al.</i> 2002, Huber 2006, Nagel <i>et al.</i> 2008, Sadler & Shields 2006, Sillanpää & Levchuk 2015
Membrane filtration (Fig. 8)	The pressure difference across a semipermeable membrane is used as the separation driving force.	Reverse osmosis: chemical water treatment and for example activated carbon filter, microfiltration, or ultrafiltration	Reverse osmosis: DOC < 50 µg/L. All NOM fractions can be removed (see Fig. 8).	Cuda <i>et al.</i> 2006, Manth <i>et al.</i> 1998, Nagel <i>et al.</i> 2008, Sillanpää <i>et al.</i> 2015
Electrodeionization (Fig. 9)	Continuously regenerated ion exchange combined with a membrane filtration.	Chemical water treatment and membrane filtration or similar	DOC ≈ 100–300 µg/L, comparable to ion-exchange	Alvarado & Chen 2014, Fedorenko 2004, Matejka 1971, Wood 2008
Short wave length (185 nm) UV radiation	Oxidation by hydroxyl radicals resulting from photolysis of water.	Deionization or similar	DOC < 5 µg/L, an anion exchanger is required after UV treatment.	Baas 2003, Saitoh <i>et al.</i> 1994

BP = biopolymers, HS = humic substances, LMW = low molecular weight

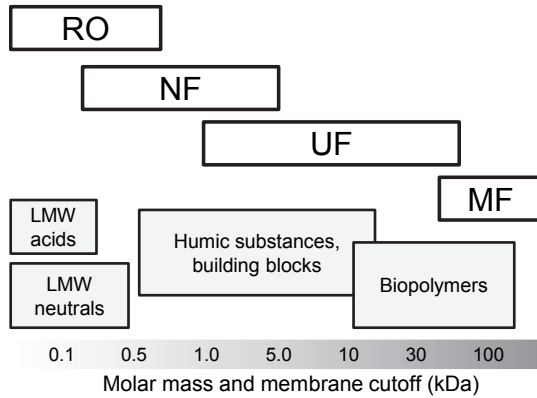


Fig. 8. The removal of NOM with reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and microfiltration (MF). LMW = low molecular weight. The cutoff value tells the maximum molar mass of a molecule or ion that can pass through the membrane. Modified from Sillanpää *et al.* 2015.

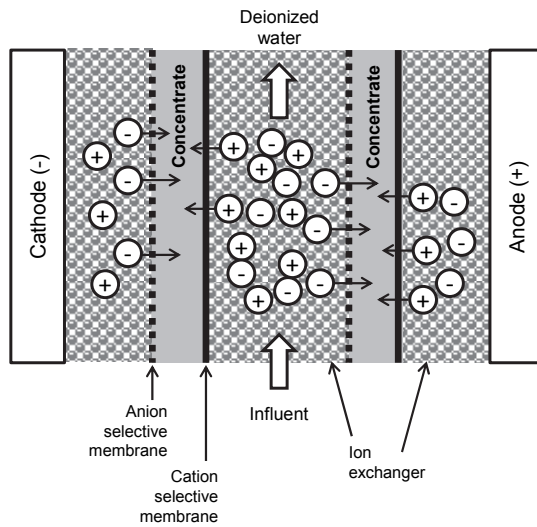


Fig. 9. Electrodeionization process: 1) mixed bed ion exchange of influent water; 2) transport of ions through anion and cation selective membranes to the concentrate channels (electrodialysis), and 3) a continuous regeneration of the ion exchanger by a DC current induced electrolysis of water. Modified from Fedorenko 2003.

3 Geopolymers as sorbents

Geopolymers are three-dimensional cross-linked inorganic polymers with an amorphous, semi-, or polycrystalline structure (Palomo & Glasser 1992, Palomo & Glasser 1992, Rowles & O'connor 2003, Van Jaarsveld *et al.* 2002). The term geopolymer was initially proposed by Davidovits in the 1970s (Davidovits 2011, Davidovits 1991). Geopolymers are prepared by establishing a reaction between aluminosilicate raw materials (such as fly ash, slags from metal industry, calcined clays or other natural minerals) and alkali metal hydroxide and/or silicate or phosphoric acid solution. The synthesis in alkaline media is more widely studied and industrially considered to be more important. Consequently, geopolymers (prepared in alkaline media) are frequently referred to as alkali activated materials. Geopolymers have been applied in low CO₂ producing binders, composite materials, waste stabilization and encapsulation processes, catalyst support material, and water treatment sorbents, to name a few examples (Davidovits 2011, Gasca-Tirado *et al.* 2012, Li *et al.* 2006, Yunsheng *et al.* 2007). Beneficial features of geopolymers are thermal and corrosive stability, a (micro)porous structure, high compressive strength, fast consolidation, and low shrinkage. Additionally, these materials can be considered environmentally friendly and economical, since they can be prepared from industrial side-products with mild reactions.

Chemical structure and synthesis

Geopolymers closely resemble zeolites in many ways and are in fact frequently referred to as amorphous analogues. Geopolymers (and zeolites) consist of an anionic framework of corner-sharing SiO₄ and AlO₄ tetrahedra (Fig. 10). The valency difference of Al(III) and Si(IV) results in a net negative charge, which is balanced by exchangeable cations (most frequently Na⁺, K⁺, or Ca²⁺). The exact structure of geopolymers is still unclear, but Barbosa *et al.* (2000) have proposed a semi-schematic presentation in the case of the Na-polysialate geopolymer as shown in Fig. 10. The possible Si and Al environments are denoted with SiQ₄(1–4Al) or AlQ₄(4Si), indicating that Si and Al are tetrahedral and are connected to 1–4 or 4 Al or Si atoms, respectively, through oxygen. Furthermore, the structure illustrates the exchangeable hydrated sodium cations within the voids of the framework.

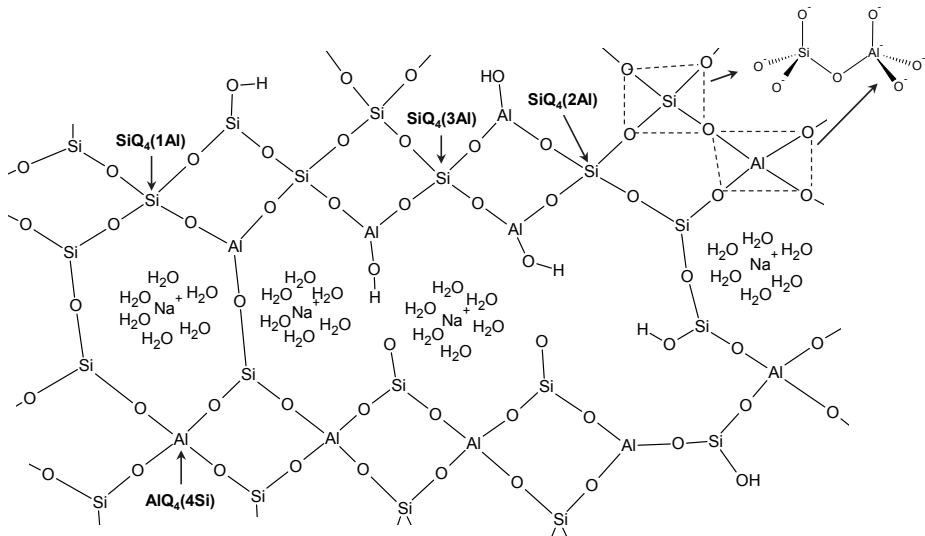


Fig. 10. Semi-schematic presentation of Na-polysialate type geopolymer structure as proposed by Barbosa *et al.* (2000). The different Si and Al environments are marked with arrows and a three dimensional presentation of the Si and Al tetrahedron are shown in the upper right corner.

For comparison, the general simplified formulas of geopolymers (polysialate type) and zeolites can be presented as follows:

- Poly(sialate) type geopolymer: $M_m[AlO_2(SiO_2)_z]_m \cdot wH_2O$, where m is the degree of polycondensation, $z = 1, 2, 3$, and M represents a cation (usually K^+ , Na^+ , or Ca^{2+}) (Davidovits 1991).
- Zeolite: $M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot qH_2O$ where n is the valence of the exchangeable cation M (Meier 1986).

The exact mechanism of formation of geopolymers is still unclear. The structure of geopolymers has been thought to contain sialate, sialate-siloxo, and sialate-disiloxo units: $-Al-O-Si-O-$, $-Si-O-Al-O-Si-$, and $Si-O-Al-O-Si-O-Si-O-$, respectively (Davidovits 1991). The formative reactions of these structures are shown in Fig. 11. However, despite the clarification they may offer, these chain structures are considered a rough simplification (Provis *et al.* 2005).

3.1 Geopolymers in water and wastewater treatment

3.1.1 Sorbents

Removal of cationic pollutants

The successful utilization of geopolymers in the removal of cations from aqueous solutions is based on their ion-exchange capacity (Bortnovsky *et al.* 2008, O'Connor *et al.* 2010, Skorina 2014). The main advantages of geopolymers compared to synthetic zeolites are the milder synthesis conditions and the simpler preparation. Interestingly, geopolymeric materials exhibit relatively low surface areas (tens m²/g) and are still effective sorbents (Bortnovsky *et al.* 2008, Wang *et al.* 2007). Sorption results obtained with geopolymers are shown in Table 4.

Table 4. Geopolymer sorption results in the treatment of synthetic wastewaters.

Raw material	Adsorbate	C ₀ [mg/L]	Optimum pH	q _{max} [mg/g]	Reference
Metakaolin ^a	Methylene blue	10–50	3	4.26 ^b	Khan <i>et al.</i> 2015
Coal fly ash	Methylene blue	32	n.d.	18.3 ^b	Li <i>et al.</i> 2006
Coal fly ash	Crystal violet	41	n.d.	17.2 ^b	Li <i>et al.</i> 2006
Metakaolin	Cs ⁺	50–500	n.d.	57.8 ^{b,c}	López <i>et al.</i> 2014b
Metakaolin	Cs ⁺	50–500	n.d.	50.8 ^b	López <i>et al.</i> 2014a
Metakaolin, fly ash	Cs ⁺	266	7	565 ^b	Chen <i>et al.</i> 2013
Coal fly ash	Cd ²⁺	10–100	5	26.5 ^b	Javadian <i>et al.</i> 2013
Metakaolin, fly ash	Sr ²⁺	175	7–11	85.1 ^b	Chen <i>et al.</i> 2013
Metakaolin, fly ash	Co ²⁺	118	5–11	153 ^b	Chen <i>et al.</i> 2013
Metakaolin	Pb ²⁺	50–500	n.d.	63.4 ^{b,c}	López <i>et al.</i> 2014b
Metakaolin	Pb ²⁺	50–300	4–5	147 ^b	Cheng <i>et al.</i> 2012
Fly ash	Pb ²⁺	100	5–6	167 ^b	Al-Zboon <i>et al.</i> 2011
Fly ash	Cu ²⁺	50–250	n.d.	92 ^d	Wang <i>et al.</i> 2007
Fly ash (A type)	Cu ²⁺	350–748	n.d.	77.3 ^d	Mužek <i>et al.</i> 2014
Metakaolin	Cu ²⁺	50–500	n.d.	59.2 ^{b,c}	López <i>et al.</i> 2014b
Metakaolin	Cu ²⁺	10–120	5	52.6 ^b	Ge <i>et al.</i> 2015a
Kaolinite, zeolitic tuff	Cu ²⁺	10–100	6	52.7 ^b	Yousef <i>et al.</i> 2009
Metakaolin, zeolitic tuff	Cu ²⁺	250	n.d.	7.80 ^d	Alshaaer <i>et al.</i> 2014
Metakaolin	Cu ²⁺	50–300	5	48.8 ^b	Cheng <i>et al.</i> 2012
Metakaolin	Cr ³⁺	50–300	4	19.9 ^b	Cheng <i>et al.</i> 2012

n.d. = not determined, ^a = prepared with phosphoric acid, ^b = calculated from the Langmuir isotherm, ^c = competitive sorption in multi-adsorbate solution, ^d = experimental capacity

Geopolymeric materials combining both sorptive properties and mechanical strength have been prepared by adding zeolitic tuff as a filler material to a kaolinite-based geopolymer (Alshaaer *et al.* 2010, Alshaaer *et al.* 2012, Yousef *et al.* 2009). It is worth noting that kaolinite was used without calcination. The compressive strength increased up to 22 MPa and the removal of methylene blue as a model compound was increased up to 90% when using 3.2 mg/L as the initial concentration (Yousef *et al.* 2009). It was proposed that these materials were to be used in water storage containers, channels and pipes, and water filters. Furthermore, a geopolymeric membrane was fabricated from metakaolin to remove Ni²⁺ in a recent study (Ge *et al.* 2015b).

Geopolymer sorbents have a certain measure of selectivity towards cations. For example, metakaolin-based geopolymers had the following selectivity (from the most to least easily removable): Cs⁺ > Pb²⁺ > Cu²⁺ > Zn²⁺ > Ni²⁺ > Cd²⁺ (López *et al.* 2014b). In addition, it was shown that NaCl at relatively high concentrations of up to 10% (w/w) had no inhibiting effect on sorption, indicating that geopolymer sorbents could work in difficult water matrixes, such as industrial wastewater (López *et al.* 2014a, López *et al.* 2014b).

Synthesis of geopolymer sorbents

The synthesis of geopolymer sorbents usually follows the method of hydrothermal processing, or the fusion method (Fig. 12). In the hydrothermal method, the raw material is mixed with an alkaline solution, and the mixture is left to cure at ambient or elevated temperatures. The fusion method, on the other hand, was developed more recently and involves the mixing of the solid raw material with the solid hydroxide at elevated temperatures, followed by the addition of water, and then filtration, washing and drying.

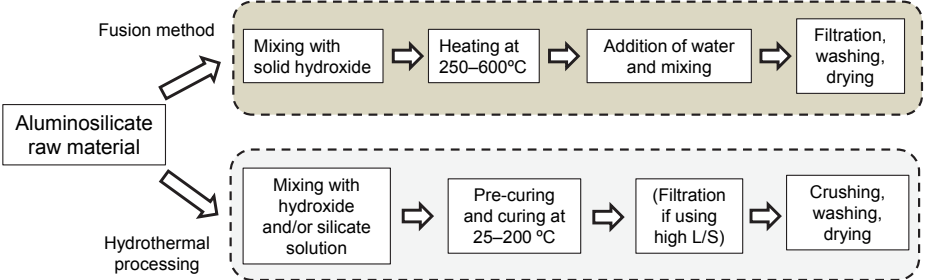


Fig. 12. The synthesis of geopolymer sorbents.

The optimum conditions for hydrothermal processing and the fusion method, as reported in the literature, are shown in Table 5.

Table 5. Optimal hydrothermal processing conditions in geopolymer sorbent synthesis reported in the literature.

Hydrothermal processing									
Raw material	T [°C]	t [h]	Si/Al ^a	Na/Si ^b	SiO ₂ / Al ₂ O ₃ ^c	NaOH [mol/L]	H ₂ O/ Na ₂ O	L/S (w/w)	Reference
Fly ash (A type)	85	24	n.r.	n.r.	n.r.	16	n.r.	0.40	Mužek <i>et al.</i> 2014
Fly ash (F type)	25 + 105	24 + 24	7.3	n.r.	n.r.	14	n.r.	0.80	Al-Zboon <i>et al.</i> 2011
Metakaolin, fly ash	100	24	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	Chen <i>et al.</i> 2013
Metakaolin	80 + 200	12 + 12	2	0.6	n.r.	8	20	n.r.	López <i>et al.</i> 2014b
Metakaolin	100 + 150	12 + 2	10	n.r.	n.r.	n.r.	n.r.	n.r.	López <i>et al.</i> 2014a
Metakaolin	25	72	7.6	0.8	n.r.	10	n.r.	0.77	Cheng <i>et al.</i> 2012
Metakaolin, zeolitic tuff	40	24	2.3– 3.7	0.2– 0.3	1	6	13	n.r.	Alshaaer <i>et al.</i> 2014
Fusion method									
Raw material	T [°C]	t [h]			NaOH/fly ash (w/w)	L/S (w/w) ^d	Reference		
Coal fly ash	250–350	1			1.2	4.0	Li <i>et al.</i> 2006		
Fly ash	600	2			1.2	4.5	Javadian <i>et al.</i> 2013		
Fly ash	550	1			0.8	4.0	Wang <i>et al.</i> 2007		

n.r. = not reported, ^a = determined from cured geopolymer, ^b = composition of alkaline solution ("alkaline activator"), ^c = SiO₂ in sodium silicate / Al₂O₃ in metakaolin, ^d = water / fused solid

If a higher temperature is used during geopolymer synthesis, this increases the crystallinity, pore volume, and surface area (Provis *et al.* 2005, Wang *et al.* 2007). With the fusion method, the increased temperature improves the sorption efficiency (Li *et al.* 2006, Wang *et al.* 2007). However, in terms of energy consumption, ambient or only slightly increased temperatures are preferable. The Si/Al ratio of the geopolymer determines the negative charge in the geopolymer framework structure (López *et al.* 2014b). However, it has to be noted that all Si and Al determined by XRF, for example, are not necessarily related to the geopolymer matrix but instead to impurity phases such as quartz. The specific surface area of the geopolymer decreased significantly when Si/Al ratio was increased from 1 to 2 or more (López *et al.* 2014b). An increase in the water

content leads to the increased formation of zeolites (Duan *et al.* 2015, Provis *et al.* 2005). Another factor affecting the crystallinity is the Na/Al ratio: a high ratio increases again the formation of zeolites, while a low ratio promotes the formation of amorphous structures (Duan *et al.* 2015). An increased curing time promotes the formation of more crystalline phases (Duan *et al.* 2015, Provis *et al.* 2005).

Spherical metakaolin geopolymers with a diameter of 2–4 mm were prepared for removing Cu(II) (Ge *et al.* 2015a). The spheres were prepared by mixing metakaolin, sodium silicate, and foaming agents (H₂O₂ and lauryl alcohol), finally adding polyethylene glycol into an 80 °C water bath. Spherical geopolymers could be used as a filter in a continuous column treatment of industrial wastewater.

The first study involving a phosphoric acid-based geopolymer prepared from metakaolin and used as an adsorbent was recently published (Khan *et al.* 2015). The geopolymer was prepared by mixing metakaolin with α -Al₂O₃ powder and adding a phosphoric acid solution. The mixture was cured at 80°C for 12 h. The adsorbent was successfully applied for methylene blue removal (Table 4).

The high CaO content of raw material, which is typical for some fly ashes, results in a microstructural porosity and increased strength due to the formation of Ca-Al-Si gel (Van Jaarsveld *et al.* 1998, Xu & Van Deventer 2000, Yunsheng *et al.* 2007).

Regeneration

Chen *et al.* (2013) have shown that a metakaolin-fly-ash geopolymer used for Co²⁺, Sr²⁺, and Cs⁺ removal could be regenerated with KCl or HCl solutions. Similar results were obtained by Cheng *et al.* (2012) in desorption studies of a spent metakaolin geopolymer using 2 M HCl. Javadian *et al.* (2013), on the other hand, were able to regenerate the spent coal fly-ash-based geopolymer using a NaOH solution, whereas HCl or HNO₃ were not suitable regenerants. Additionally, the surface area of geopolymers was found to increase when repeatedly equilibrated with KNO₃ solution or if washed with deionized water (Skorina 2014). These results indeed suggest that the removal mechanism of cationic pollutants by geopolymers is based on reversible ion exchange.

Phosphoric-acid based geopolymers used for methylene blue removal could be regenerated thermally (400 °C for 2 h) at least five times, which resulted in an increase in the sorption capacity (Khan *et al.* 2015). This could be due to the

increased porosity (Liu *et al.* 2012). As geopolymers generally have high thermal resistance, it could be speculated that other types of geopolymers used to remove organic pollutants could also be thermally regenerated.

3.1.2 Photocatalysts

Photocatalysts are semiconductor materials that produce reactive radicals when exposed to irradiation (such as UV) with the energy equal to or larger than the band energy. Radicals can be used to oxidize organic aqueous pollutants, for example. Photoactive geopolymers containing TiO₂ have been prepared via ion exchange from metakaolin geopolymers (Gasca-Tirado *et al.* 2012, Gasca-Tirado *et al.* 2012). A geopolymer-supported photocatalyst containing Cu₂O was used for the sorption and UV photodegradation of methylene blue in one study (Fallah *et al.* 2015). The presence of Cu₂O improved the sorption capacity, possibly by increasing the pore size. Fly ash frequently contains photoactive constituents, and thus the fly ash-based geopolymers can be used as photocatalysts without the addition of metal oxides (Zhang & Liu 2013). For example, fly ash-based geopolymers containing 0.94% TiO₂ (w/w) adsorbed methylene blue and degraded it under UV radiation, reaching removal levels of up to 90% (Zhang & Liu 2013).

3.2 Adsorption isotherms

The sorption equilibrium data is used to assess the sorption process and the design of adsorbers. Isotherm models describe the amount of adsorbate in the liquid phase (C_e , mg/L) and at the adsorbent surface (q_e , mg/g), respectively, when equilibrium is reached. The parameter q_e is the equilibrium sorption capacity (Equation 24).

$$q_e = \frac{(c_0 - c_e)V}{m} \quad (24)$$

where c_0 (mg/L) is the initial concentration, V (L) is the volume, and m (g) is the mass of the adsorbent.

Single-solute isotherms

Single-solute isotherms describe the situation that arises with a single adsorbate, which is an exceptional case in typical water treatment situations.

The Freundlich (1906) isotherm (Equation 25) is empirical and it is based on the assumption that the uptake of ions occurs on a heterogeneous surface.

$$q_e = KC_e^{1/n_F} \quad (25)$$

where K ((mg/g)/(mg/L)^{1/n_F}) is the sorption coefficient: a higher K indicates a higher sorption level that can be achieved. The exponent $1/n_F$ (dimensionless) describes the energetic heterogeneity of the sorbent surface. Isotherms with $1/n_F < 1$ are described as favorable (i.e. high loadings can be achieved at low concentrations) and $1/n_F > 1$ as unfavorable (i.e. loadings are low at low concentrations).

The Langmuir isotherm (Langmuir 1918) (Equation 26) is based on the assumptions that only monolayer sorption occurs, that all sorption sites are energetically homogenic, and no interactions between adsorbate molecules on the surface of the sorbent occur.

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (26)$$

where q_m (mg/g) is the maximum monolayer sorption capacity and b (dimensionless) is related to the energy of sorption. Additionally, the Langmuir isotherm allows for the monolayer surface coverage to be calculated as θ (dimensionless) (Equation 27).

$$\theta = \frac{b C_e}{1 + b C_e} \quad (27)$$

The Langmuir-Freundlich isotherm (Sips 1948) (Equation 28) contains a third parameter, n_{LF} , which is analogous to the parameter $1/n_F$ in the Freundlich isotherm. The Langmuir-Freundlich isotherm describes saturation at high concentrations thus being able to effectively account for wide concentration areas (Worch 2012).

$$q_e = \frac{q_m (b C_e)^{n_{LF}}}{1 + (b C_e)^{n_{LF}}} \quad (28)$$

The Redlich-Peterson isotherm (Redlich & Peterson 1959) (Equation 29) reduces to the linear isotherm at a low concentration area, but no leveling off at a high concentration area occurs.

$$q_e = \frac{b_1 C_e}{1 + b_2 C_e^n} \quad (29)$$

where b_1 (mg/g) and b_2 are the isotherm parameters.

The Tóth (1971) isotherm (Equation 30) is linear at low concentrations and saturates at high concentrations. Again, the parameters q_m and b are analogues of the Langmuir parameters, and n_T is the analogue of $1/n_F$ in the Freundlich isotherm.

$$q_e = \frac{q_m b C_e}{[1 + (b C_e)^{n_T}]^{1/n_T}} \quad (30)$$

Multi-solute isotherms

Multi-solute isotherms represent the competitive sorption which is typical of water treatment applications.

The extended Langmuir isotherm (Butler & Ockrent 1930) (Equation 31) is based on the assumption that all adsorbates have the same q_m value (Worch 2012). If this assumption is not fulfilled, the isotherm can still be applied but it has an empirical character.

$$q_{e,i} = \frac{q_{m,i} b_i C_i}{1 + \sum_{j=1}^N b_j C_j} \quad (31)$$

Another multi-solute isotherm model is the Freundlich isotherm for N components (DiGiano *et al.* 1978) (Equation 32), which is based on the assumption that all adsorbates have a similar value for the exponent, $1/n_{MF}$, and differ only in their sorption coefficient (K) (Worch 2012).

$$q_i = \frac{K_i^{1/n_{MF}} C_i}{(\sum_{j=1}^N K_j^{1/n_{MF}} C_j)^{1-n_{MF}}} \quad (32)$$

3.3 Sorption kinetics

The time dependence of the sorption process is referred as sorption kinetics. The sorption amount (q_t , mg/g) at time t (min) can be determined as follows:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (33)$$

The phases of sorption, where steps 2 or 3 are usually rate-limiting, involve (Worch 2012):

1. Transporting of adsorbate from the bulk liquid to the hydrodynamic boundary layer around the adsorbent.
2. Transporting of adsorbate through the boundary layer to the external surface of adsorbent, i.e. film or external diffusion.
3. Transporting of adsorbate into the interior of the adsorbent (i.e., intraparticle or internal diffusion) by diffusion in the pore liquid (pore diffusion) and/or by diffusion in the adsorbed state along the internal surface (surface diffusion).
4. Attachment to the final sorption sites.

The reaction kinetic models are appropriate to describe sorption kinetics only for weakly porous adsorbents, where chemisorption is the main sorption mechanism, and film diffusion resistance does not exist (Worch 2012). However, reaction kinetic models are frequently discussed and used in the literature.

The pseudo-first-order rate equation (Lagergren 1898) (Equation 34) can be integrated with the condition $q_t = 0$ when $t = 0$ which results in Equation 35. The parameter k_{p1} (1/min) is the pseudo-first-order rate constant.

$$\frac{dq_t}{dt} = k_{p1}(q_e - q_t) \quad (34)$$

$$\ln \frac{(q_e - q_t)}{q_e} = -k_{p1}t \quad (35)$$

The pseudo-second-order rate equation (Ho & McKay 1999) (Equation 36) can be similarly integrated to obtain Equation 37. k_{p2} (g/(mg min)) is the pseudo-second-order rate equilibrium constant.

$$\frac{dq_t}{dt} = k_{p2}(q_e - q_t)^2 \quad (36)$$

$$\frac{t}{q_t} = \frac{1}{k_{p2}q_e^2} + \frac{t}{q_e} \quad (37)$$

The Elovich equation (Zeldowitsch 1934) (Equation 38) integration ($q_t = 0$ when $t = 0$) results in Equation 39.

$$\frac{dq_t}{dt} = v_0 e^{-\beta q_t} \quad (38)$$

$$q_t = \frac{1}{\beta} \ln(v_0 \beta) + \frac{1}{\beta} \ln t \quad (39)$$

where v_0 (mg/(g min)) is the initial sorption rate, and β (g/mg) is the desorption constant.

The Weber-Morris model (Equation 40) (Weber & Morris 1963) can be used to evaluate whether the rate-limiting step in the sorption is the film or the intraparticle diffusion.

$$q_t = k_{id}t^{0.5} + C \quad (40)$$

where k_{id} ($\text{mg}/(\text{g min}^{0.5})$) is the intraparticle diffusion rate constant and C (dimensionless) is the intercept related to the thickness of the boundary layer.

4 Materials and methods

4.1 Peracids in wastewater treatment

4.1.1 Preparation of peracids

Peracids were prepared by mixing 10 mL of carboxylic acid (98–100%, w/w) with 0.94 mL of 95–97% (w/w) sulfuric acid, followed by the slow addition of 10 mL of 30% (w/w) hydrogen peroxide. The flask was kept in an ice bath, mixed with a magnetic stirrer (250 rpm) for 90 min, and then moved to a refrigerator. Performic acid was used within two hours while peracetic and perpropionic acids were usable for several days. The commercial peracetic acid (Desirox 12:20) was obtained from Solvay.

4.1.2 Determination of peracid concentration

The concentration of concentrated peracid solutions (% range) was determined according to a cerimetric-iodometric titration method (Gehr *et al.* 2009, Greenspan & Mackellar 1948). The concentrations of the dilute peracid solutions (mg/L range) were analyzed with the cerimetric-iodometric titration according to the instructions of Cavallini *et al.* (2013a). Details of these methods are presented in Paper II.

A quick test employing a pre-calibrated handheld photometer (Chemetrics, V2000) and cuvettes K-7913 and K-5543 (Chemetrics) for peracetic acid and hydrogen peroxide, respectively, was used during the pilot experiments. The peracetic acid test was based on the treatment of sample with excess of potassium iodide which reacts to iodine. Iodine oxidizes the DPD (N,N-diethyl-p-phenylenediamine) into a pink-colored species from which absorbance is determined. The method is suitable for the 0–5.00 mg/L range. The hydrogen peroxide test was based on the oxidation of ferrous ions into ferric ions in an acidic ammonium thiocyanate solution (Boltz & Howell 1978). As a result, a red thiocyanate complex formed from which absorbance was measured. The method is suitable for hydrogen peroxide concentrations of 0–6.00 mg/L. The interference caused by peracetic acid was quenched by the addition of an excess (five drops) of 11% (w/w) potassium iodide, which reacted with the peracetic acid but not with the hydrogen peroxide.

4.1.3 Laboratory-scale disinfection experiments

A wastewater sample from Taskila municipal wastewater treatment plant (Oulu, Finland) was obtained for laboratory-scale disinfection experiments. The plant process is described in detail in Paper I. The wastewater sample was characterized as described in Paper II.

Peracid concentrations 1.5, 3.0, and 5.0 mg/L were dosed to wastewater samples that were constantly mixed with magnetic stirrers. Experiments were performed at a water temperature of 15 °C to simulate typical temperatures during the process. Samples at different time intervals were taken and peracids were quenched with 9% (w/V) sodium thiosulfate (1 µL to 1 mL sample). Samples were stored at a temperature of approx. 5 °C and analyzed within 6 h. The number of *E. coli* and enterococci were estimated using membrane filtration methods (SFS-EN ISO 7899-2 2000, SFS-EN ISO 9308-1 2014). The presence of *E. coli* was confirmed using cytochrome oxidase detection quick test strips (Merck Microbiology Bactident Oxidase). Disinfection experiments were conducted in duplicates.

4.1.4 Pilot-scale disinfection experiments

Pilot-scale disinfection tests were performed at the Taskila wastewater treatment plant (Oulu, Finland). The pilot plant contained a circular contact basin where tertiary effluent from the full-scale wastewater treatment process was fed by using a submersible pump. Peracetic acid was dosed with a diaphragm pump. Peracetic acid and wastewater were mixed with an overflow weir in the basin. Contact time was adjustable by controlling the inlet valve and was tested visually using dye and a timer.

4.1.5 Oxidation of bisphenol-A

Bisphenol-A solution (60 mg/L) was prepared in deionized water. Bisphenol-A oxidation was performed as a batch treatment in an open glass reactor ($V = 500$ mL) with the solution volume 200 mL at an ambient temperature. Continuous mixing was applied. The concentrations of oxidizers were 25 or 50 mg/L in the case of hydrogen peroxide and 20 mg/L in the case of peracids. The first oxidation experiment was done without pH adjustment or the addition of catalysts. In the Fenton or Fenton-like oxidation experiments, 0.4 mM

concentration of Fe^{2+} or Cu^{2+} was added and the pH of the solution was adjusted to 3.5. Samples ($V = 2 \text{ mL}$) were taken at different time intervals (0–60 min) and the oxidation reaction was quenched by the addition of $20 \mu\text{L}$ of 20% (w/V) sodium thiosulfate solution. The concentration of bisphenol-A was estimated with a Shimadzu SPD-10A high performance liquid chromatograph using an UV detector at 226 nm.

4.1.6 Steel corrosion rate measurements

Corrosion rate, current density, and potential were determined electrochemically using a three electrode system consisting of a working electrode (steel samples), a reference electrode (saturated calomel electrode), and a counter electrode (a platinum foil), with a Versat4 potentiostat (Princeton Applied Research). During the measurement, the current between the working and counter electrodes changed and the resulting potential between the working and reference electrodes was measured (Fig. 13). The overpotential (the x-axis of the Tafel plot, see Fig. 22) was obtained by determining the difference between the potentials, measured with or without current, in the working circuit.

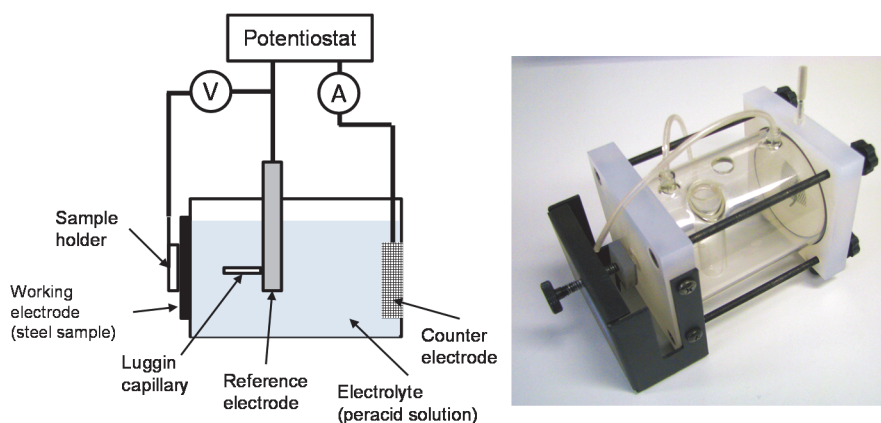


Fig. 13. Schematic presentation of the measurement arrangement (left) and the flat cell (right).

The electrolyte solution was a 500 mg/L sodium sulfate solution containing 2 or 15 mg/L of peracids to simulate regular disinfection and shock treatment concentration levels, respectively. Steel samples consisted of a stainless steel alloy (316L) with the following composition: (w/w %): 0.02% C, 17.2% Cr,

10.2% Ni and 2.10% Mo; and a carbon steel alloy composed as follows: (w/w %): 0.17% C, 1.50% Mn, 0.46% Si 0.03% Cr and 0.03% Ni. The samples were polished with SiC polishing paper grades 120, 240, 600 and 1200, and rinsed with acetone before measurements were taken. Steel samples were allowed to equilibrate with peracid solutions on an open circuit for 2 h before measurements were taken. The measurements were conducted at room temperature using a flat cell set-up.

Tafel plots were obtained by polarizing to ± 250 mV with respect to the free corrosion potential (E_c) using a scan rate of 0.5 mV/s. Pictures of the corroded surfaces were taken with a laser microscope (Keyence VK-X200 series). A uniform corrosion rate (CR, mm/year) was calculated in terms of the penetration rate using Equation 41.

$$CR = K_1 \frac{i_{cor}}{\rho} EW \quad (41)$$

where K_1 (3.27×10^{-3} (mm g)/($\mu\text{A cm year}$)) is a constant, i_{cor} ($\mu\text{A/cm}$) is the corrosion current density, ρ (g/cm) is the density of the sample and EW is the equivalent weight (dimensionless) calculated according to the standard (ASTM G102.). The corrosion measurements were done at least three times each.

4.2 Removal of organic residues from boiler make-up water

4.2.1 Pilot and full-scale activated carbon filtration experiments

The experiments were conducted in a side-stream at the demineralization plant of a power plant in Oulu, Finland (the process is described in Paper IV) and carried out in three stages: the long-term experiment, the full-scale experiment, and the comparison of activated carbons (AC). The set-ups are shown in Fig. 14 and the properties of the AC used at each stage in Table 6. The mixed bed (MB) ion exchanger resin employed was the commercially available Purolite MB 400.

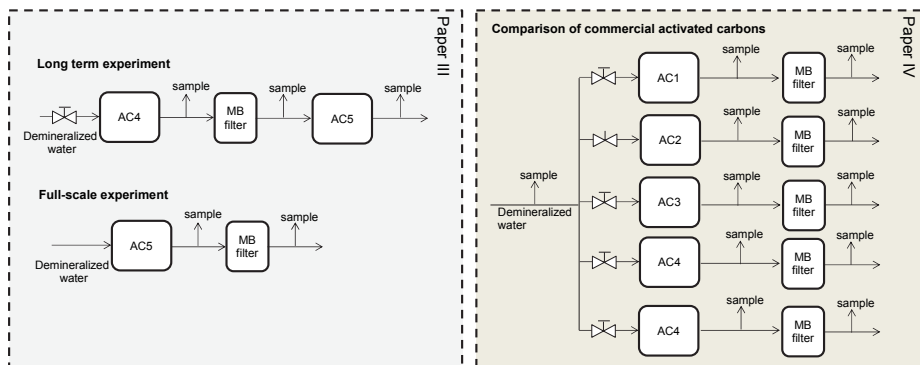


Fig. 14. The set-up of the make-up water treatment experiments.

Table 6. The properties of activated carbons used in Papers III and IV as reported by manufacturers.

	AC1	AC2	AC3	AC4	AC5
Raw material	Coal	Coconut shell	Coconut shell	Coal	Coconut shell
Pretreatment	Acid washed	Acid washed	-	Acid washed	Acid washed
Particle size [mm]	0.425–2.00	0.425–1.4	0.425–1.7	1.2–1.4	0.42–1.7
Iodine number [mg/g]	990	1100	1050	≥ 950	-
Methylene blue number	-	230	-	-	-
Surface area [m ² /g]	-	1100	1150	-	-
Density [kg/m ³]	460	450	540	450	450
pH	7.9	6–8	> 7	-	-
Moisture [w/w %]	1.0	< 10	1.5	≤ 3	-
Ash content [w/w %]	0.20	< 1.0	3	≤ 0.5	-
Manufacturer	Norit	Chemviron Carbon	Norit	Calgon Carbon	Chemviron Carbon
Tradename	GAC 1240 Plus	Aquacarb 607C 14X40	GCN 1240	CPG LF 12X40	Aquacarb 608C 12X40

Volumes of the filters in the long-term experiment were 18 L, 18 L, and 34 L for AC3, MB, and AC5, respectively, and the water flow was 1.5 L/min (approx. 9 min contact time). The volumes of the filters employed during the comparison experiments (AC1-AC4) were 5 L, and the water flow was 0.42 L/min (12 min contact time, 2.9 m/h surface load). The filters were filled 3/4 full (as dry volume of AC or resin). The full-scale experiment was done using a 3.86 m³ volume filter unit containing 2.2 m³ AC and 8 L/s water flow. The AC beds were allowed

to wet for about 24 h and then rinsed continuously until the conductivity measurements settled at a constant value. The water temperature during the experiments was approx. 20 °C.

4.2.2 Water quality measurement methods

The total organic carbon content (TOC, mg/L) of the water samples was measured with a Sievers 900 Portable TOC analyzer. Organic compounds were further characterized with a liquid chromatography - organic carbon detection (LC-OCD) system (Model 8, DOC-LABOR, Karlsruhe, Germany) (Huber & Frimmel 1991, Huber *et al.* 2011). The details of the method are presented in Paper IV. Conductivity of the deionized water before and after the use of activated carbon filters was measured online (Kemetron online conductivity probe) and the values were logged directly into a computer. Sodium, calcium and magnesium ion concentrations were measured with the atomic absorption spectrometer (Varian, SpectrAA 220). The dissolved silicic acid (reported as SiO₂) concentration was measured with a UV-VIS spectrophotometer (Shimadzu, UV-2401 PC) using a colorimetric method, the details of which are reported in Paper IV. Additionally, silica concentrations were also measured online (Braun & Blubbe 6 channels analyser) during the full-scale activated carbon filtration experiment.

4.2.3 Characterization of activated carbons

The surface morphology of AC samples was observed using a Zeiss Ultra plus FE-SEM (field emission scanning electron microscope) with Oxford Instruments INCA system EDS software. Accelerating voltages of 15 kV were used. The samples were dried at +105 °C for 24 h before analysis. The samples were not sputtered prior to analysis.

Analysis of the elemental composition (C, H, N, S and O) of the samples was performed with an automatic Thermo Scientific FLASH 2000 Series CHNS/O Analyzer. Details of the method are described in Paper IV.

Specific surface area and pore volumes of samples were determined using N₂ gas sorption-desorption isotherms at the temperature of liquid nitrogen (-196 °C) by using a Micrometrics ASAP 2020 instrument. Specific surface area was calculated based on the Brunauer–Emmett–Teller (BET) equation. Pore size distributions were calculated from desorption data using the Barrett–Joyner–Halenda (BJH) method.

4.3 Geopolymers as sorbents

4.3.1 Preparation of geopolymers

A 10 M NaOH solution was mixed with sodium silicate (1:1 w/w) and allowed to stand for 24 h. Metakaolin (Aquaminerals Finland Ltd.) and blast furnace slag (Finnsementti Ltd.) were mixed with the alkaline solution at ratios (w/w) of 1.3:1 and 1.5:1, respectively. The formed paste was mixed for 15 min, vibrated for 30 s to remove gas bubbles, and allowed to consolidate at room temperature for 3 days. Geopolymer specimens were crushed and sieved to the particle size of 63–125 μm (batch sorption experiments), 0.5–1.0 mm (regeneration), or 2–8 mm (field experiment). Before use, the materials were washed carefully with distilled water, dried at +105 °C, and stored in a desiccator.

4.3.2 Characterization of geopolymers

Powder X-ray diffraction (XRD) patterns were measured with a PanAnalytical Xpert Pro diffractometer with Co K α radiations generated at 40 kV and 40 mA. Patterns were collected from 5 to 80°2 θ using a scan time of 1.25 s per 0.02°2 θ . Samples were prepared by dispensing a finely ground specimen with ethanol onto a glass plate and allowing the ethanol to vaporize before measurement. Diffractograms were interpreted using Highscore software (version 3.0) and the Crystallography Open Database 2013 version.

The chemical composition of the samples was obtained semi-quantitatively using an X-ray fluorescence (XRF) spectrometer (PanAnalytical Minipal 4) equipped with Omnian software. Samples were ground to fine powder and compressed to tablets before analysis.

²⁷Al and ²⁹Si MAS NMR (magic angle spinning nuclear magnetic resonance) spectrums at 7 T (Bruker Avance 300 spectrometer) were analyzed under the following conditions: ²⁷Al: 1 μs ($\pi/10$) RF pulse followed by a 2 s relaxation delay, using MAS spin rate of (3 or) 7 kHz. ²⁹Si: 6 μs ($\pi/2$) RF pulse with 4 to 5 s delays, using MAS spin rate of (3 or) 7 kHz.

FTIR (Fourier transform infrared) spectrums of samples were measured using an FTIR device (Perkin Elmer Spectrum One) equipped with an Attenuated Total Reflectance (ATR) unit. Measurements were done directly from solid powders at room temperature, without any pretreatment, in the range of 4000–650 cm^{-1} .

The specific surface area and pore volumes were determined similarly to the way in which the activated carbon samples were analyzed (see Chapter 4.2.3). The surface morphology was determined in the same way, except for the fact that the samples were cast in epoxy resin (Buehler, Epoxicure). Cast samples were polished by MD Allegro 9 μ diamond (Struers) grinding paper with ethanol flushing and coated with carbon before measurements.

The zeta potential was determined with the streaming potential (Fairbrother-Mastin) method using an Anton Paar SurPASS instrument. Measurements were performed at room temperature, in 1 mM KCl solution, and the pH was adjusted with 0.05 M HCl from pH 9, which was adjusted before measurement with 0.05 M KOH. Pressure differences were between 1000 mBar and -1000 mBar.

4.3.3 Laboratory-scale batch sorption experiments

Ammonium removal

A 50 mg/L NH_4^+ model solution was prepared in deionized water. Metakaolin, a metakaolin geopolymer, and a chlinoptilolite-heulandite zeolite were used as sorbents. The parameters of the batch tests are shown in Table 7. The sorbent particle size was 63–125 μm and temperature of the solution was 22°C. After each batch experiment, the sorbent was separated from the solution by filtration through a 0.45 μm filter or by centrifugation. A NH_4^+ concentration in the samples was determined using capillary electrophoresis (Beckman Coulter MDQ) according to (Jaakkola *et al.* 2012). Some of the samples were also analyzed with an ion chromatograph (930 Compact IC Flex Deg with Metrosep C4 150/4.0 column) according to a standardized procedure (SFS-EN ISO 14911 2000).

Table 7. The experimental parameters in testing ammonium removal.

Test	Initial pH of solution	Initial NH_4^+ concentration [mg/L]	Contact time [h]	Sorbent dose [g/L]
Effect of pH	4.0, 6.0 or 8.0	50	24	5
Effect of sorbent dose	6.0	50	24	0.2–15
Effect of contact time	6.0	50	0.016–6	5
Effect of initial concentration	6.0	10–1000	24	5

Nickel, arsenic, and antimony removal

A mine effluent sample was spiked with $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, As_2O_3 , and SbCl_3 to obtain approx. 2 mg/L Ni, As, and Sb concentrations, and their simultaneous removal was studied. Metakaolin, metakaolin geopolymer, blast furnace slag, and blast furnace slag geopolymer were used as sorbents. The parameters of the batch experiments are shown in Table 8. The sorbent was separated by filtration. The concentrations of Ni, As, and Sb were determined using an optical emission spectrometer (Thermo Electron IRIS Intrepid II XDL Duo) according to the SFS-EN ISO 11885 standard.

Table 8. The experimental parameters in testing Ni(II), As(III), and Sb(III) removal.

Test	Initial pH of solution	Contact time [h]	Sorbent dose [g/L]
Effect of pH	4.0, 6.0, 8.0 or 10.0	24	5
Effect of sorbent dose	7.0–8.0	24	0–25
Effect of contact time	7.0–8.0	0.016–24	5

4.3.4 Field experiment

A small scale field experiment was performed at a landfill site (Kajaani, Finland) using a stainless steel filter unit (inner diameter: 105 mm, height 600 mm and volume 5.20 l) filled with a 3140 g (approx. 4 l) metakaolin geopolymer (particle size 2–8 mm). Sorbent was washed and allowed to wet by circulating tap water through the bed for 24 h before starting the test. The first experiment was performed with a landfill leachate effluent from a well where leachate was collected before the water treatment process. Leachate was pumped through the filter unit with a submersible pump using approx. 0.75 L/min flow rate corresponding to a surface load of 5.2 m/h. Samples were taken after the installation of the filter unit for 24 h with a time-based autosampler with an interval of 2 h. Samples before the installation of the filter unit were taken once during the 24 h test. The second experiment was performed with an effluent leaving the landfill site. This effluent was treated with a biorotor unit which removed organic matter and oils and with a zeolite containing filter which removed ammonium partially. The new sorbent mass was changed in the filter unit before starting the second experiment, and an otherwise similar experimental set-up was used. Landfill leachate samples were characterized with an optical emission spectrometer (Thermo Electron IRIS Intrepid II XDL Duo) for metal

and phosphorus concentrations according to the standard SFS-EN ISO 11885. Ammonium concentration was determined again with capillary electrophoresis, as described before. A seven day biological oxygen demand with allylthiourea addition ($BOD_{7, \text{atu}}$) was performed according to the standard SFS-EN 1899-1 and chemical oxygen demand with chromate oxidizer (COD_{Cr}), according to the standard ISO 15705:2002.

5 Results and discussion

5.1 Use of peracids in wastewater treatment

5.1.1 Synthesis and shelf-life

The concentration of peracids (% w/w) during synthesis and storage are shown in Fig. 15. PFA, PAA, and PPA reached the equilibrium in approx. 75 min (9%, 1.21 g/cm³), 2 days (16%, 1.17 g/cm³), and 5 days (17%, 1.11 g/cm³), respectively. The shelf-life results of peracids (at 5 °C) indicate that PFA stays relatively stable for approx. 3 days (decomposition < 1%). PAA and PPA stayed stable for approx. 30 days. These results are consistent with the observation that the stability of aliphatic peracids increases with increased chain length (Swern 1949), although no great difference was observed between PAA and PPA.

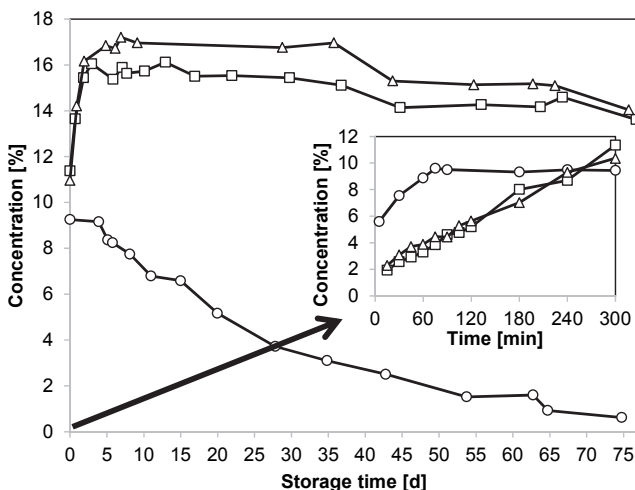


Fig. 15. Changes in the concentration of PFA (○), PAA (□), and PPA (Δ) during synthesis (small picture) and storage at 5°C.

5.1.2 Degradation of peracids

The degradation results of peracids in tap and wastewater are shown in Fig. 16. The chemical analyses of water samples are shown in Paper II.

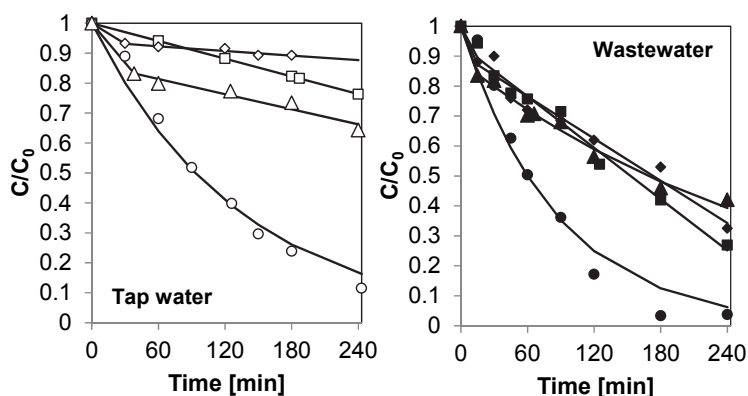


Fig. 16. The degradation of PFA (○/●), PAA (□/■), commercial PAA (◇/◆) and PPA (Δ/▲) in tap water (left) and wastewater (right). $C_0 = 15$ mg/L.

The degradation data was modelled using the kinetics equations (see chapter 1.3.3) and the obtained parameters are shown in Table 9. Based on the literature, the degradation of PAA follows first-order kinetics but in this study, a 0-order equation provided a better fit. There is a significant variation in the kinetic constants and half-lives which highlights the effect of water quality. The order of degradation (from faster to slower) was PFA > PPA > PAA > commercial PAA in tap water and PFA > PAA > commercial PAA > PPA in wastewater. The difference between PAA, commercial PAA, and PPA is relatively small, especially in wastewater. This indicates that the stabilizers in commercial PAA have only little or no effect after the chemical is dosed.

Table 9. Comparison of obtained peracid decomposition kinetics parameters to the literature.

Peracid	Dose [mg/L]	Water matrix	Order	k_d	D [mg/L]	$t_{1/2}$ [min]	Reference
PFA	15	Tap water	1st	0.007	0	99	Paper II
PFA	15	Tertiary effl.	1st	0.012	0	58	Paper II
PAA	21–28	Primary effl.	1st	0.0396	19.41	18	Falsanisi <i>et al.</i> 2006
PAA	10	Secondary effl.	1st	0.0088	-	79	Cavallini <i>et al.</i> 2013b
PAA	1.5–8.5	Secondary effl.	1st	0.0028	0.44	248	Falsanisi <i>et al.</i> 2006
PAA	1–15	Secondary effl.	1st	0.007	0.415	99	Rossi <i>et al.</i> 2007
PAA	1–15	Secondary effl.	1st	0.009	0.785	77	Rossi <i>et al.</i> 2007
PAA	4–8	Secondary effl.	0	0.016	0.8	100–225	Dell'Erba <i>et al.</i> 2004
PAA	15	Tertiary effl.	0	0.036	1.424	189	Paper II
PAA ^a	15	Tertiary effl.	0	0.042	0.925	168	Paper II
PAA	1–15	Tap water	1st	0.007	-	100	Rossi <i>et al.</i> 2007
PAA ^a	15	Tap water	0	0.010	0.810	710	Paper II
PAA	15	Tap water	0	0.016	0	469	Paper II
PPA	15	Tap water	0	0.023	1.886	285	Paper II
PPA	15	Tertiary effl.	1st	0.003	1.903	231	Paper II

^a non-stabilized PAA.

5.1.3 Disinfection of tertiary effluents

The laboratory-scale comparison of peracids was initially performed using doses 1.5, 3.0, and 5.0 mg/L to determine the required dose to reach the “excellent quality” as defined by EU bathing quality requirements (see chapter 1.3.1) (Directive 2006/7/EC 2006). These results indicated that appropriate doses would be 1.5 mg/L for PFA and 3.0 mg/L for PAA and PPA (Fig. 17). These dosing amounts were used for the cost comparison. However, the dose 1.5 mg/L was selected for the determination of kinetic parameters (Fig. 18).

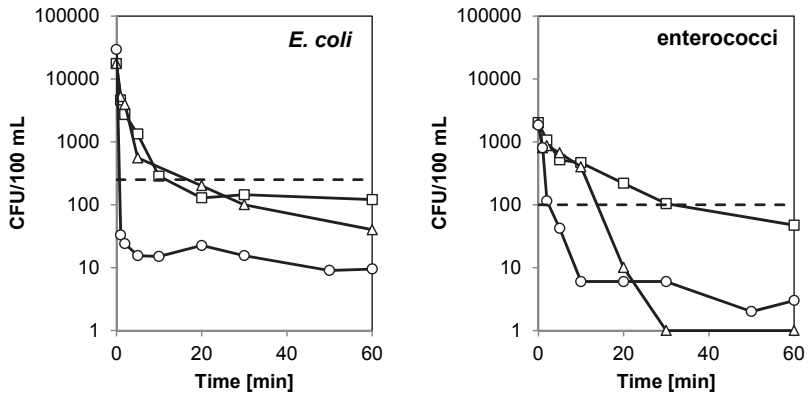


Fig. 17. The required doses and contact times of PFA (1.5 mg/L, ○), PAA (3.0 mg/L, □), and PPA (3.0 mg/L, Δ) to reach the “excellent quality” of bathing water in terms of *E. coli* (250 CFU/100 mL) and enterococci (100 CFU/100 mL) which are marked with a dotted line.

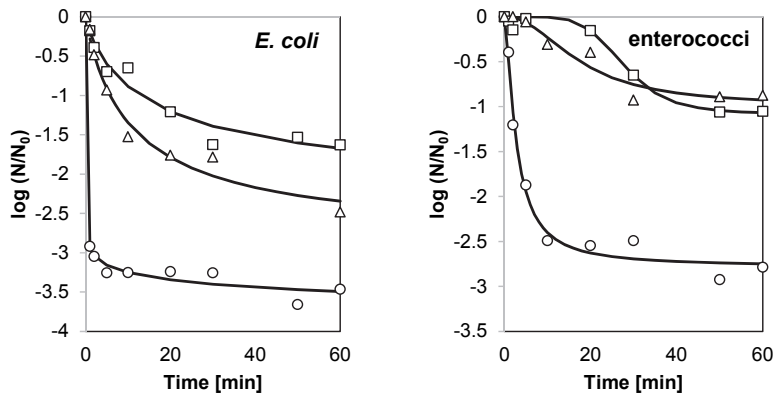


Fig. 18. The inactivation of *E. coli* (left) and enterococci (right) by PFA (○), PAA (□), and PPA (Δ) (dose 1.5 mg/L). Regressions are calculated on the basis of the S-model (Equation 20). The initial amounts of *E. coli* and enterococci were 29200 and 1840 CFU/100 mL, respectively.

The efficiency of peracids against *E. coli* is: PFA > PPA > PAA, and against enterococci: PFA > PAA ≈ PPA. The obtained results are consistent with the few existing wastewater disinfection studies comparing PFA and PAA (Chhetri *et al.* 2014, Ragazzo *et al.* 2013). Additional supporting studies outside the water treatment field showed PFA to be a more effective sporicidal agent than PPA

(Merka & Dvorák 1968), whereas PAA and PPA were determined to be equally effective virucidal agents (Vimont *et al.* 2014). However, conflicting results were obtained by Merka (Merka *et al.* 1965), who concluded that PFA, PAA, and PPA were equally effective against *E. coli*.

The kinetic data was modelled using the Chick-Watson, Hom, and S-models (see chapter 1.3.4); the S-model provided the best fit. However, the inactivation of *E. coli* with PFA fit almost equally well to the Hom model. The Chick-Watson model fits poorly ($R^2 < 0.3$) with the exception of enterococci inactivation with PAA and PPA ($R^2 = 0.925$ and 0.781 , respectively). The obtained parameters and a comparison to the literature are shown in Table 10.

The Hom parameters of PFA in *E. coli* inactivation are close to the values obtained in tap water by Yousefzadeh (2014), while the rate constant obtained in active sludge effluent is clearly smaller. It is notable that the Hom parameter n ($1.894 > m$ (0.042)) in the present study which indicates that the disinfectant dose is more important than the contact time. The S-model parameters of PAA in *E. coli* inactivation are in the same range as reported in the literature earlier. In the case of enterococci, no published disinfection kinetics data could be found for peracids. Additionally, the disinfection kinetics of PPA in wastewater treatment had not been reported on before.

The pilot-scale disinfection results from Paper I are shown in Fig. 19 for *E. coli* and total coliforms. The $C \times t$ value required to reach the bathing water quality had to be 15–30 (mg min)/L, after which the values remained within limits. These $C \times t$ values correspond to the 1.5–2 mg/L dose and the 10–15 min contact time, which are smaller than in the laboratory experiments (Paper II) due to the easier inactivation of *E. coli* and total coliforms as opposed to the more difficult inactivation of enterococci. The 99% bacterial reduction $C \times t$ value, which is frequently used for the comparison of disinfectants and conditions (Gyürék & Finch 1998), is 1.8–2.5 (mg min)/L in the case of *E. coli*. Similar values for free chlorine, chlorine dioxide, ozone, and PFA were reported to be 0.034–0.05, 0.4–0.75, 0.02, and 12.16 (mg min)/L, respectively, by Yousefzadeh *et al.* (2014) and the references therein. This indicates that the efficiency of the disinfectants would be ozone > free chlorine > chlorine dioxide > PAA > PFA which is in contradiction to the results obtained in Paper II and, for example, by Chhetri *et al.* (2014) and Ragazzo *et al.* (2013). However, the application of the $C \times t$ concept is questionable if the survival curve is not linear, i.e. contains shoulder or tailing-off, as in this study and, typically, in real conditions.

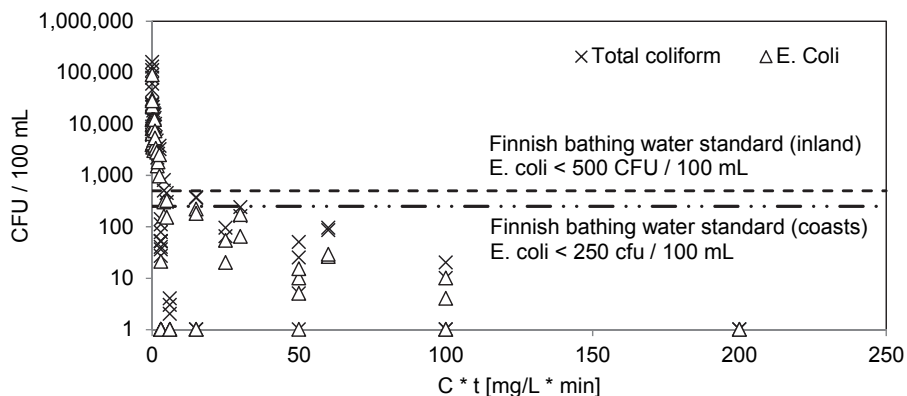


Fig. 19. The pilot-scale peracetic acid disinfection results for E. coli and enterococci using the $C \times t$ concept. The bathing water quality requirements (Directive 2006/7/EC 2006) are shown for reference.

A comparison was made between the used PAA doses, contact times, and results in secondary and tertiary municipal effluents as reported in the literature (Table 11). The required doses and contact times in the secondary and tertiary effluents have been 0.6–10 mg/L with 10–120 min and 10–400 mg/L with 20–36 min, respectively. Interestingly, the doses and contact times for the tertiary effluent are larger than for secondary effluents. The significant variation between doses and contact times can be explained by different result requirements and the variable physico-chemical characteristics of the wastewater. However, the present study indicated that 1.5–2 mg/L PAA and 10–15 min were sufficient (Paper I), which is clearly smaller than the numbers typically found in the literature.

Somatic and F-specific coliphages whose initial amounts were 1800 and 420 PFU/100 mL, respectively, were effectively removed with a 1 mg/L PAA dose and 60 min contact time in the pilot-scale experiments. The required doses for coliphage inactivation have been 3–15 mg/L PAA (Pradhan *et al.* 2013, Rajala-Mustonen *et al.* 1997). 1.5 mg/L had no effect on coliphages according to Zanetti *et al.* (2007). RNA coliphages (F-specific) are more resistant to disinfection than DNA coliphages (somatic) (Lazarova *et al.* 1998).

Table 10. Comparison of obtained peracid disinfection kinetics parameters to the literature.

Peracid	Dose [mg/L]	Contact time [min]	Wastewater matrix	Indicator organism	Hom model			S-model			Reference	
					k	n	m	k	n	m		h
PFA	2-10	30	Tap water	EC	4.25	0.35	0.35	-	-	-	-	Yousefzadeh <i>et al.</i> 2014
PFA	6-15	30	ASL	EC	0.54	0.48	0.87	-	-	-	-	Yousefzadeh <i>et al.</i> 2014
PFA	1.5	60	TE	EC	3.151	1.894	0.042	15.100	0.050	0.080	30.316	Paper II
PAA	1.5	60	TE	EC	-	-	-	5.077	0.060	0.829	25.356	Paper II
PAA	2-25	6-54	TE	EC	-	-	-	3.182	0.069	1.128	26.173	Azzellino <i>et al.</i> 2011
PAA	2-25	6-54	TE	EC	-	-	-	3.12	0.07	1.13	24.10	Mezzanotte <i>et al.</i> 2007
PAA	2	55	SE	EC	-	-	-	2.651	-0.445	1.968	15.561	Rossi <i>et al.</i> 2007
PAA	1-8	30	SE	EC	0.008	0.92	n/a	-	-	-	-	Santoro <i>et al.</i> 2007
PPA	1.5	60	TE	EC	-	-	-	6.509	0.030	0.912	17.086	Paper II
PAA	2-25	6-54	TE	TC	-	-	-	2.830	0.146	0.916	65.326	Azzellino <i>et al.</i> 2011
PAA	2-25	6-54	TE	TC	-	-	-	2.83	0.15	0.92	65.33	Mezzanotte <i>et al.</i> 2007
PAA	1-8	30	SE	TC	0.159	0.59	0.53	-	-	-	-	Santoro <i>et al.</i> 2007
PAA	2-25	6-54	TE	FC	-	-	-	2.70	0.13	0.91	50.58	Mezzanotte <i>et al.</i> 2007
PAA	1-8	30	SE	FC	0.0469	2.88	n/a ^a	-	-	-	-	Santoro <i>et al.</i> 2007
PAA	1-2	55	SE	FC	0.087	0.538	0.646	-	-	-	-	Rossi <i>et al.</i> 2007
PAA	5-15	55	SE	FC	0.260	0.430	0.4153	-	-	-	-	Rossi <i>et al.</i> 2007
PFA	1.5	60	TE	E	-	-	-	6.164	0.094	1.439	4.164	Paper II
PAA	1.5	60	TE	E	-	-	-	2.392	0.101	5.557	41.694	Paper II
PPA	1.5	60	TE	E	-	-	-	2.195	0.100	2.138	26.285	Paper II

SE = secondary effluent, TE = tertiary effluent, SBS = synthetic bacterial suspension, ASL = active sludge effluent, EC = E. coli, TC = total coliforms, FC = fecal coliforms, E = enterococci, n/a = not available

Table 11. The required doses and contact times of peracetic acid in disinfection of secondary or tertiary municipal effluents.

Secondary effluents				
Dose [mg/L]	Contact time [min]	Target organism	Result / required reduction	Reference
0.6–1.6	120	FC	2–3 log reduction	Wagner <i>et al.</i> 2002
0.6–4	60	FC	1000 CFU/100 mL	Gehr & Cochrane 2002
1	15–20	TC	20000 MPN/100 mL	Collivignarelli <i>et al.</i> 2000
1	15–20	FC	12000 MPN/100 mL	Collivignarelli <i>et al.</i> 2000
1	15–20	FS	2000 MPN/100 mL	Collivignarelli <i>et al.</i> 2000
1.5–2	20	EC	5000 CFU/100 mL	Stampi <i>et al.</i> 2001, Stampi <i>et al.</i> 2002, Zanetti <i>et al.</i> 2007
2–7	27	TC, E	3 log reduction	Koivunen & Heinonen-Tanski 2005b
4	10	EC	2 log reduction	Santoro <i>et al.</i> 2007
5	20	TC, FC	4–5 log reduction	Morris 1993
5–7	60	TC	1000 CFU/100 mL	Lefevre <i>et al.</i> 1992
5–7	60	FS	100 CFU/100 mL	Lefevre <i>et al.</i> 1992
5–10	10–50	EC	10 CFU/100 mL	Dell'Erba <i>et al.</i> 2004, Rossi <i>et al.</i> 2007
5–10	15	TC, FC	> 95% reduction	Poffe <i>et al.</i> 1978
10	10	TC, FC, FS	3 log reduction	Lazarova <i>et al.</i> 1998
Tertiary effluents				
Dose [mg/L]	Contact time [min]	Target organism	Result / required reduction	Reference
1.5–2	10–15	EC	500 CFU/100 mL	Paper I
10	30	TC	1000 CFU/100 mL	Liberti <i>et al.</i> 2000
10	30	FC	1000 CFU/100 mL	Liberti & Notarnicola 1999, Liberti <i>et al.</i> 1999
15	36	EC	4 log reduction	Mezzanotte <i>et al.</i> 2007
400	20	TC	2 CFU/100 mL	Liberti <i>et al.</i> 2000

FC = fecal coliforms, EC = E. coli, TC = total coliforms, E = enterococci, FS = fecal streptococci

The change of chemical parameters as a result of PAA dosing was studied in Paper I. Oxidation-reduction potential (ORP) rose sharply to 250–300 mV when the PAA dose was increased to 2 mg/L, and leveled off when the dose increased. ORP can be readily measured online, and therefore it offers a potential control parameter for the PAA dosing. Wastewater pH, on the other hand, was found to decrease linearly by 0.033 units per each mg/L PAA dosed ($R^2 = 0.854$). Municipal wastewater has a relatively good buffering capacity, and thus PAA dosing only slightly affects the pH value in practice. $BOD_{7,ATU}$ was found to

decrease in the PAA dose range of 0–2 mg/L and increase at larger doses. In a full-scale application of PAA in the secondary effluent, $BOD_{7,ATU}$ increased by approx. 2.8 mg/L O_2 . The BOD measurement could be interfered with by the inhibiting properties of PAA (the test is based on microbial activity) and the release of oxygen. COD_{Cr} was found to increase more than indicated by the theoretical oxygen demand, which could be due to the interfering reaction between chromate and residual hydrogen peroxide. Theoretically, the oxygen demand was 4 mg/L O_2 per 1 mg/L of PAA when using this particular PAA formulation.

5.1.4 Oxidation of bisphenol-A

The oxidative degradation of bisphenol-A (structure presented in Fig. 20) was studied: with peracids without a pH adjustment and a catalyst; at pH 3.5 and an addition of 0.4 mM Fe^{2+} ; and at pH 3.5 and an addition of 0.4 mM Cu^{2+} .

No degradation occurred with plain peracids or hydrogen peroxide without a catalyst and pH adjustment. This was an expected result, since peroxides require activation by a transition metal catalyst, and plain peracetic acid, for example, has been shown to be inert in aqueous oxidation (Jones 1999, Rokhina *et al.* 2010).

The addition of a 0.4 mM Fe^{2+} catalyst and a pH adjustment to 3.5 provided conditions for Fenton or Fenton-like reactions to occur. The bisphenol-A degradation results (effect of reaction time and oxidizer concentration) obtained at these conditions are shown in Fig. 20.

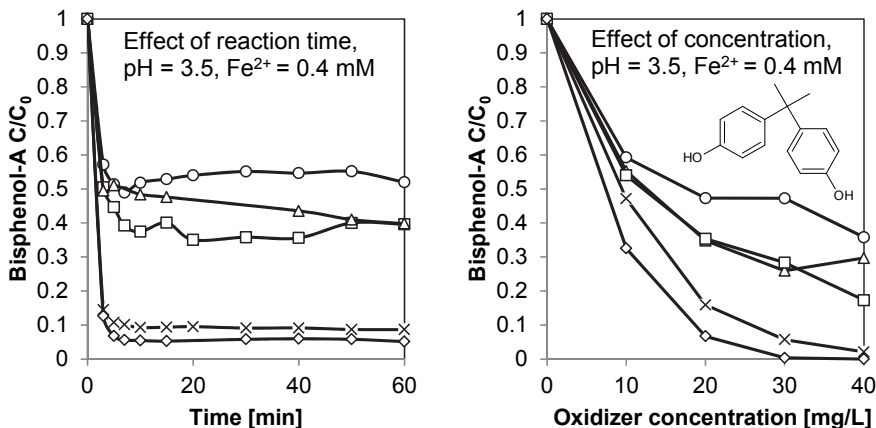


Fig. 20. The effect of reaction time using 20 mg/L peracids or 25 mg/L hydrogen peroxide (left) and the effect of oxidizer concentration (right) on the degradation of bisphenol-A with PFA (○), PAA (□), commercial PAA (◇), PPA (Δ), and hydrogen peroxide (X). The structure of bisphenol-A is presented on the right. C₀ = 60 mg/L.

The results indicate that the oxidation efficiency of chemicals is commercial PAA > hydrogen peroxide > PAA ≈ PPA > PFA. The application of ≥ 30 mg/L of commercial PAA results in a complete decomposition of bisphenol-A, and similar result is achieved using ≥ 50 mg/L of hydrogen peroxide. However, all the studied peracids contain hydrogen peroxide due to the equilibrium composition, and it was not possible to separate the Fenton oxidation resulting from hydrogen peroxide and the Fenton-like oxidation resulting from peracid. In fact, the amount of total peroxides (peracid + hydrogen peroxide) present in hydrogen peroxide, PFA, commercial PAA, PAA, and PPA was 25, 29, 53, 31, and 31 mg/L, respectively. It seems that the amount of hydrogen peroxide is more important in terms of oxidation results than the amount of peracid. This could be due to the formation of two hydroxyl radicals per each hydrogen peroxide molecule, whereas peracids form one hydroxyl radical and one corresponding organic radical. An excess oxidizer in the Fenton oxidation process is known to act as a radical scavenger (Mijangos *et al.* 2006), which could explain the poor performance of performic acid and the decrease of oxidation efficiency as the PPA concentration was increased. It can be concluded that hydrogen peroxide is the most effective oxidizer in terms of needed dose, price, and efficiency.

The use of Cu^{2+} as a catalyst was also tested based on the study by Maekawa *et al.* (2014). The results (Paper V) indicated a practically similar oxidation efficiency as with a Fe^{2+} catalyst. The dosing of soluble Fe^{2+} or Cu^{2+} to a wastewater effluent might not be feasible from an economical or environmental point of view, but these metals could still be used as heterogeneous catalysts.

5.1.5 Corrosion

The corrosion rate results (Fig. 21) with the carbon steel sample indicate that PAA was less corrosive ($< 250 \mu\text{m}/\text{year}$) than other peracids ($< 500 \mu\text{m}/\text{year}$), while the results with stainless steel (316L) indicate lower corrosion rates for other peracids ($< 2 \mu\text{m}/\text{year}$) than for PFA ($< 6 \mu\text{m}/\text{year}$). The corrosiveness of PAA has been studied in the context of pulp bleaching, and the corrosion rates have been reported to be $180\text{--}7520 \mu\text{m}/\text{year}$ using concentrations $0.005\text{--}0.485 \text{ mol}/\text{L}$, i.e. $380\text{--}36884 \text{ mg}/\text{L}$ (Qu *et al.* 2008).

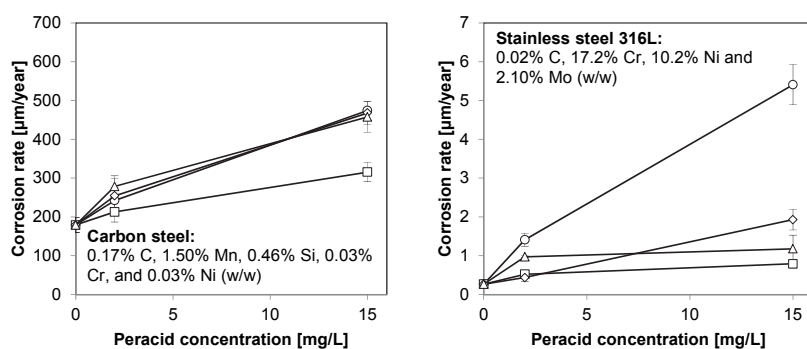


Fig. 21. Corrosion rates of carbon steel (left) and stainless steel 316L (right) exposed to PFA (○), PAA (□), commercial PAA (◇) or PPA (Δ). The error bars refer to a standard error.

It is known that pure aluminum, stainless steel, and tin-plated iron are resistant to peracetic acid, while plain steel, galvanized iron, copper, brass, and bronze are susceptible to corrosion (Fraser *et al.* 1984, Kitis 2004). Glass and most plastics are not affected by PAA while it may extract the plasticizer from vinyl-based materials and will damage natural and synthetic rubbers (Kitis 2004).

The corrosion potential and current densities were displaced in the positive direction as peracid concentrations were increased, which can be seen in Tafel plots (Fig. 22) (Paper II). Carbon steel corrosion current densities and corrosion

rates were significantly higher while corrosion potentials were clearly lower than with stainless steel 316L.

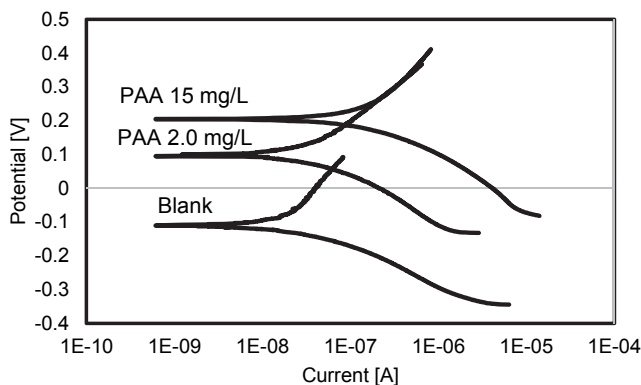


Fig. 22. An example of the obtained Tafel plots in the case of peracetic acid and stainless steel 316L.

5.1.6 Cost evaluation of disinfection

The comparison of chemical prices, operational costs, and investment costs of peracids are shown in Table 12. Operational costs include chemical consumption by the tertiary effluent to reach EU bathing water quality requirements (Directive 2006/7/EC 2006). The calculations indicate that the operational cost of peracid-based disinfection would be in the order: PAA > PPA > PFA. The investment costs of peracids are different, as PFA is prepared on-site and PAA and PPA can be supplied as a ready-to-use solution. The PFA production system would be more economical at larger capacity plants, while for small plants, PAA and PPA investment costs (storage and dosing equipment) would be lower.

Table 12. Cost comparison of disinfection with organic peracids.

Peracid	Chemical price [€/t]	Operational costs [€/m ³]	Investment costs [€]
PFA	830 ^a	0.0114 (1.5 mg/L dose)	50 000 ^d
PAA	1100–1200 ^b	0.0261 (3.0 mg/L dose)	15 000–440 000 ^e
PPA	1300 ^c	0.0207 (3.0 mg/L dose)	15 000–440 000 ^e

^a = 1:1 w/w formic acid (980 €/t) and hydrogen peroxide (670 €/t), ^b = stabilized peracetic acid, ^c = 1:1 w/w propionic acid (1900 €/t) and hydrogen peroxide (670 €/t), ^d = up to 200 000 m³/d capacity wastewater treatment plant, ^e = for 3000–200 000 m³/d capacity wastewater treatment plants, converted to 2014 price level (Collivignarelli *et al.* 2000).

5.2 Removal of organic residues from boiler make-up water

5.2.1 Characterization of activated carbons

The properties of activated carbons (AC) as reported by manufacturers were shown in the experimental section (Table 6). Additionally, the pore size distributions, specific surface areas, and chemical compositions of the ACs used in Paper IV were determined (Table 13).

Table 13. Specific surface areas and pore sizes of activated carbons studied in Paper IV.

	AC1	AC2	AC3	AC4
Specific surface area [m ² /g]	929	1150	943	976
Macropores [cm ³ /g]	0.14	0.04	0.00	0.05
Mesopores [cm ³ /g]	0.14	0.04	0.00	0.14
Micropores [cm ³ /g]	0.38	0.45	0.43	0.39

Macropores: $d_0 > 50$ nm, mesopores: $2 \text{ nm} \leq d_0 \leq 50$ nm and micropores: $d_0 < 2$ nm.

The adsorption of AC is affected by the following factors: natural organic matter (NOM) properties (including molecular weight distribution, hydrophobicity, charge distribution, and the ability to form hydrogen bonds), the solution's properties (pH and ionic strength), and the AC properties (surface area, pore volume and shape, surface charge, functional groups, and ash content) (Bjelopavlic *et al.* 1999, Summers & Roberts 1988, Velten *et al.* 2011). The most important pore sizes in NOM adsorption are large micropores (1 to 2 nm) and mesopores (Li *et al.* 2003), while macropores can also contribute to the biological activity and subsequent NOM removal of the carbon bed (Scholz & Martin 1997). Micropores smaller than 1 nm have a negligible role in the removal of NOM (Cheng *et al.* 2005). AC4 had the largest volume of combined meso and micropores (0.53 cm³/g) while AC3 had the smallest (0.43 cm³/g). Micropore volumes of ACs decreased up to 28% and total pore volumes up to 14% during the one month pilot, which could be explained by the pore blockage (Lu *et al.* 2012). Specific surface areas of AC1, AC2, and AC4 decreased up to 14% while the specific surface areas of AC3 increased 16% during the pilot. However, no correlation between pore volumes or specific surface area and the TOC removal was observed. The optimum AC for NOM adsorption, then, should have a high surface area and a large volume of 1–50 nm width pores (Velten *et al.* 2011).

Micrographs of AC surfaces (Fig. 23) show that the coconut shell-based ACs have a smooth surface with a visible pore structure, while the coal-based carbons have an irregular morphology. Similar differences were reported by Sun *et al.* (2013).

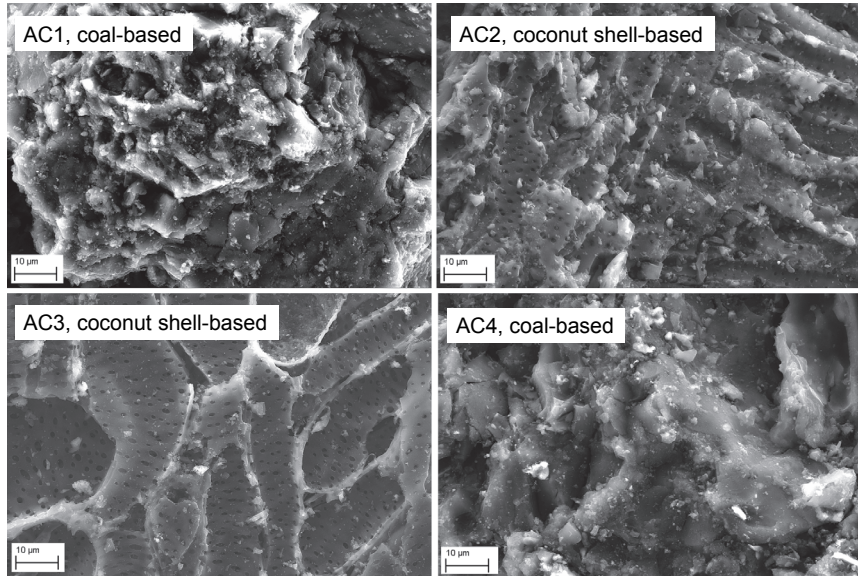


Fig. 23. Micrographs of activated carbons used in Paper IV.

5.2.2 Removal total organic carbon (TOC) fractions

The total organic carbon (TOC) removal of ACs during long-term, full-scale and comparison experiments are shown in Fig. 24.

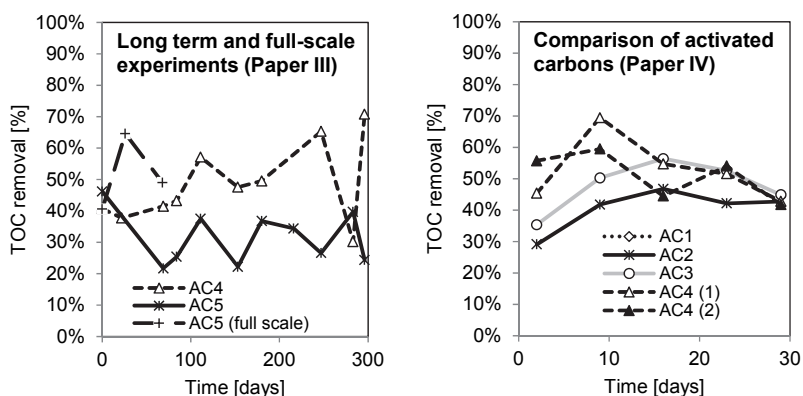


Fig. 24. TOC removal results of activated carbons during long-term, full-scale and comparison experiments.

The results of long-term experiments indicate that AC4 and AC5 remain almost constantly effective for almost one year, although the TOC of influent water varied between 250–480 $\mu\text{g/L}$. In fact, the TOC removal efficiency of AC4 seemed to improve during the operation, from 40% to 70% in 300 days. The TOC removal efficiency of AC5 (pilot-scale) is 10–40 percentage points lower than AC4. Interestingly, AC5 clearly shows higher efficiency in the full-scale than in the pilot-scale, which might be the result of more optimized flow conditions in the full-scale filter. The comparison of activated carbons revealed initial differences between AC1–AC4 which, however, decrease eventually, and, after 30 days, all ACs perform similarly. The role of the mixed bed (MB) ion exchanger after AC seemed to be minor in terms of TOC removal: only up to 12% additional TOC removal was observed. Similarly, the second AC (AC5) unit after MB removed only 13% of the remaining TOC (data not shown in Fig. 24).

Fig. 25 shows the characterization of NOM in raw water, chemically treated water, deionized water, and after each AC and MB unit. The quantity of NOM is expressed in terms of dissolved organic carbon (DOC), which was smaller than the corresponding TOC after ACs, indicating that there was particulate (over 0.45 μm) organic matter present in the water.

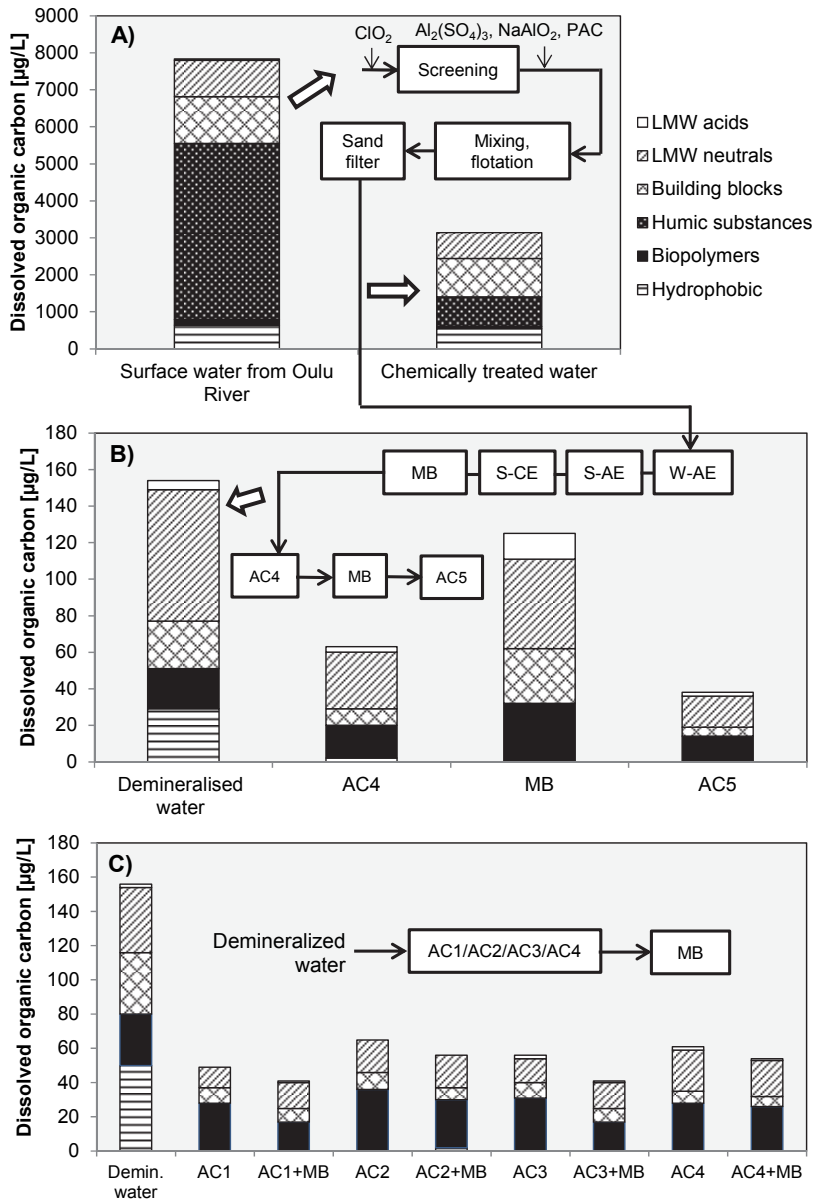


Fig. 25. Characterization of organics: A) raw water in autumn and chemically treated water, B) during long-term pilot, and C) comparison of activated carbons. The treatment process and set-ups of pilots are shown. W-AE = weak anion exchanger, S-AE = strong anion exchanger, S-CE = strong cation exchanger, MB = mixed bed.

The NOM in raw water (surface water from the Oulu River) consisted mainly of humic substances, building blocks (i.e., decomposition products of humic substances), and low molecular weight (LMW) neutrals. The DOC level was approx. 8 mg/L. The water treatment process (coagulation-flocculation-flotation and sand filtration) as shown in Fig. 25 removed mainly humic substances while other NOM fractions were not reduced efficiently. The DOC level after sand filtration was approx. 3 mg/L. Ion exchange reduced the DOC level to slightly less than 160 $\mu\text{g/L}$ and the largest fractions remaining were: LMW neutrals, hydrophobic, building blocks, and biopolymers. There are slight differences between the composition of NOM in demineralized water in Fig. 25A and Fig. 25B due to the different sampling time. AC units further reduce the DOC level to 40–60 $\mu\text{g/L}$ and the remaining fractions were (from the largest concentration to the smallest) biopolymers > LMW neutrals > building blocks. The remaining biopolymers were possibly too large to enter the pores of ACs. Generally, the removal efficiency of NOM with AC increases with decreasing molecular size (or weight) and the order is: low molecular weight acids and neutrals > building blocks > humic substances (Velten *et al.* 2011). The MB units after ACs removed mainly biopolymers (7–42%) as shown in Fig. 25C while the MB unit in Fig. 25B had started to show an increase in the DOC concentration (the sample was taken after 10 months of operation).

5.2.3 Leaching

The leaching of impurities from the AC bed was monitored with on-line conductivity measurements. The acid-washed ACs (AC1, AC2, AC4, and AC5) initially increased the conductivity up to 2.0 $\mu\text{S/cm}$, while the non-acid washed AC (AC3) increased conductivity up to 6.0 $\mu\text{S/cm}$ (Paper IV). However, conductivity of all ACs decreased as a result of continuous flushing in 7–10 days to ≤ 1 $\mu\text{S/cm}$ (Paper IV). This indicates that the effect of acid washing as a pre-treatment is primarily related to the initial release of impurities. It could be possible to use cheaper non-acid washed AC if initial and sufficient washing can be arranged. The MB unit after AC beds decreased the conductivity to the level of 0.06–0.07 $\mu\text{S/cm}$ (Paper III). As a reference, the theoretical conductivity of chemically pure water at 25 °C is 0.054 $\mu\text{S/cm}$ (Hussey *et al.* 2009) and the recommended guideline value for the conductivity of boiler make-up water is less than 0.1 $\mu\text{S/cm}$ (Flynn 2009).

The concentrations of Na, Mg, and Ca were monitored from AC filtrated water (Paper IV). The concentration of Na increased to approx. 0.04 mg/L in the case of non-acid washed AC3 while the other ACs released typically < 0.015 mg/L Na. After approx. 20 days, the release of Na was < 0.005 mg/L. The recommended Na level in make-up water is < 0.003 mg/L (Flynn 2009). In the case of Mg the initial release of impurities followed the order: AC3 (0.051 mg/L) > AC2 (0.026) > AC1 (0.021 mg/L) > AC4 (0.0030 mg/L). All ACs reached < 0.0050 mg/L Mg level after 20 days. The initial Ca release followed a similar order: AC3 (0.185 mg/L) > AC2 (0.091) > AC1 (0.014) \approx AC4 (0.010). There are no specific guideline values for Mg and Ca concentrations. However, since these cations contribute to the formation of deposits such as CaCO₃ and MgCO₃, their levels should be as low as possible. The MB unit after ACs removed 100% of the Na and Mg and 91% of the Ca on average (Paper IV).

The level of silica (SiO₂) was also monitored during the pilot (Papers III and IV): the initial release was up to 0.3 mg/L in the case of non-acid washed AC3 and < 0.22 mg/L SiO₂ with other ACs (Paper IV). The silica level after 20 days of operation was < 0.05 mg/L SiO₂. Silica forms deposits especially in the turbine area which are difficult to remove. Thus, the recommended silica guideline value is < 0.01 mg/L SiO₂ (Flynn 2009). The MB units after ACs reduced silica to the level 0.002–0.005 mg/L (Paper III).

5.3 Geopolymers as sorbents

5.3.1 Characterization of geopolymer sorbents and zeolite

The X-ray diffractograms of geopolymers, raw materials and the natural zeolite are shown in Fig. 26 (Papers V and VI).

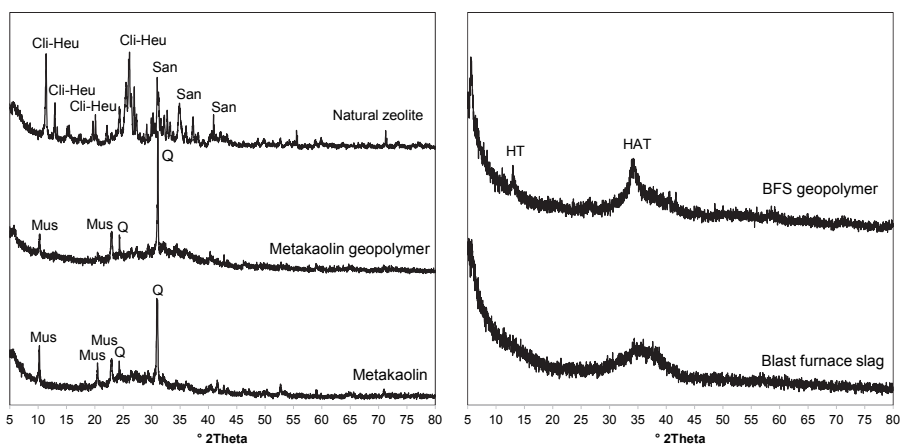


Fig. 26. The X-ray diffractograms of zeolite, metakaolin, metakaolin geopolymer, blast furnace slag (BFS), and BFS geopolymer. Cli-Heu = clinoptilolite-heulandite, San = sanidine Q = quartz, HT = hydrotalcite, HAT = hatrurite.

Metakaolin (MK) contained muscovite and quartz as impurities while the metakaolin mineral itself was X-ray amorphous. After geopolymerization, the muscovite peak intensities decreased and the maximum of the amorphous halo shifted slightly. Natural zeolites contain clinoptilolite $((\text{Na,K,Ca})_{2-3}\text{Al}_3(\text{Al,Si})_2\text{Si}_{13}\text{O}_{36} \cdot 12\text{H}_2\text{O})$, heulandite $((\text{Ca,Na})_{2-3}\text{Al}_3(\text{Al,Si})_2\text{Si}_{13}\text{O}_{36} \cdot 12\text{H}_2\text{O})$, and sanidine $(\text{K}(\text{AlSi}_3\text{O}_8))$. Blast furnace slag (BFS) contains no crystalline phases. Alkali treatment of BFS results in the formation of hydrotalcite, $(\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4(\text{H}_2\text{O}))$ and hatrurite $(\text{Ca}_3\text{SiO}_5)$.

The chemical compositions, loss on ignition, specific surface area, pore width and pore volume of raw materials, geopolymers, and natural zeolites determined semiquantitatively by XRF is shown in Table 14 (Papers V and VI).

Table 14. Chemical composition, loss on ignition, specific surface area, and pore width and volume of raw materials, geopolymers, and zeolite.

Composition [%]	BFS	BFS-GP	MK	MK-GP	Zeolite
CaO	38.5	29.9	0.06	0.09	2.00
SiO ₂	27.2	25.8	53.10	50.70	62.50
MgO	9.39	6.38	0.00	0.90	0.00
Al ₂ O ₃	8.42	5.87	40.30	31.30	10.20
SO ₃	3.76	2.66	0.00	0.00	0.00
TiO ₂	1.28	1.04	0.12	0.14	0.08
K ₂ O	0.55	0.45	2.72	2.19	4.29
Fe ₂ O ₃	0.78	0.71	1.89	1.60	1.32
Mn	0.26	0.21	0.00	0.00	0.00
Na ₂ O	0.03	8.00	0.00	8.16	0.00
Loss on ignition	0.46	12.92	3.60	8.26	8.70
Specific surface area [m ² /g]	2.79	64.5	11.5	22.4	24.0
Average pore width [nm]	12.7	5.93	18.17	30.97	13.60
Macro + mesopores [cm ³ /g]	0.008	0.070	0.047	0.165	0.071
Micropores [cm ³ /g]	0.005	0.025	0.005	0.008	0.010

The main changes during geopolymerization were the increase of Na content and loss on ignition and the decrease of Si and Al contents. The zeolite composition indicates possibly Ca or K form. The specific surface area increased as a result of geopolymerization, but still remained relatively low. The average pore width decreased in the BFS geopolymerization while the opposite happened in the case of MK geopolymerization. The geopolymerization of BFS increased all pore volumes while in the case of MK mainly the volumes of meso and macropores increased.

The MK-GP surface (Fig. 27) is frequently reported as having an irregularly porous gel structure (Alshaaer *et al.* 2014, Duxson *et al.* 2007, López *et al.* 2014b) with partially reacted metakaolin sheets being visible (marked with an arrow on Fig. 27). In contrast, the surface of BFS-GP is smoother and seems less porous, although the specific surface area is larger than that of the MK-GP. This could be explained by smaller pores: the average width is 5.93 nm (BFS-GP) vs 30.97 nm (MK-GP).

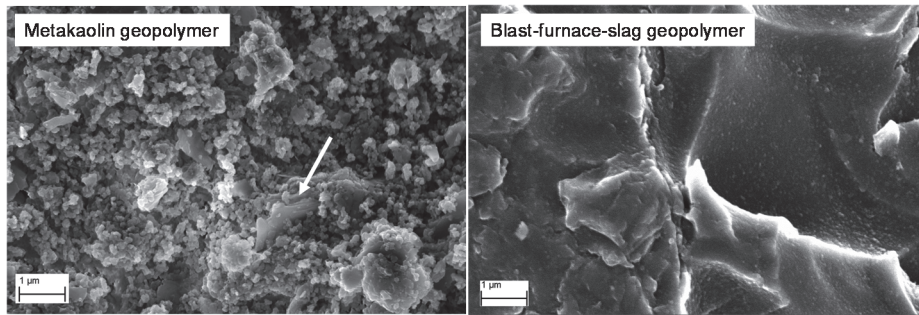


Fig. 27. Micrographs of geopolymer surfaces. Unreacted metakaolin is marked with an arrow.

The FTIR, ^{27}Al , and ^{29}Si MAS-NMR spectra (Papers V, VI, and VII) indicated change in the Al and Si environment as a result of geopolymerization, which could be seen from shifts in the signal places.

5.3.2 Sorption properties of geopolymers

Ammonium

The effects of pH, sorbent dose, ammonium concentration, and contact time on the ammonium removal are shown in Fig. 28 (Paper V).

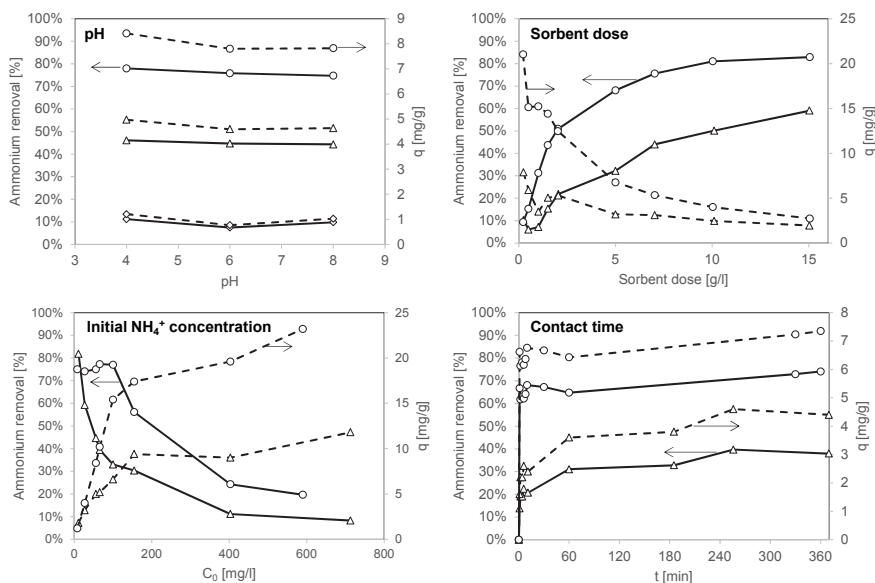


Fig. 28. The effects of pH, sorbent dose, NH_4^+ concentration and time on the NH_4^+ removal (%) and sorption capacity (q , mg/g) with metakaolin (\diamond), metakaolin geopolymer (\circ), and zeolite (Δ).

The ammonium removal efficiency of MK-GP and the zeolite stayed as constant in the pH range of 4–8, which is the typical pH of municipal wastewater, for example. The pH figure also shows data for raw material metakaolin: a significant improvement in the removal efficiency was observed as a result of geopolymerization. The increase in the sorbent dose correlated with a linear increase in ammonium removal up to 2 g/L, while a gradual saturation in the removal was observed at larger doses. The removal of ammonium was relatively constant up to an initial ammonium concentration of 100 mg/L in the case of MK-GP, while the removal efficiency of the zeolite dropped instantaneously as the ammonium concentration increased. Most of the ammonium removal occurred within 1 min contact time and was approx. 20% and 60% with zeolite and MK-GP, respectively.

The best fitting isotherm was the Langmuir-Freundlich model for both MK-GP ($R^2 = 0.965$, $\text{RMSE} = 1,720$, $X^2 = 1.212$) and the zeolite ($R^2 = 0.940$, $\text{RMSE} = 0.981$, $X^2 = 0.661$). The obtained parameters were: $q_m = 21.067$ mg/g, $b = 0.063$, $n_{LF} = 1.610$ and $q_m = 14.423$ mg/g, $b = 0.012$, $n_{LF} = 0.601$ for MK-GP and the

zeolite, respectively (Paper V). A comparison of the maximum sorption capacity (q_m) to the literature (data shown in Paper V) revealed that MK-GP is more effective than typical natural zeolites in ammonium removal, and comparable in efficacy to synthetic zeolites.

Kinetics fitted best to the pseudo-second-order model again for both MK-GP ($R^2 = 1.000$) and the zeolite ($R^2 = 0.994$). The obtained parameters were $k_{p2} = 0.074 \text{ g}/(\text{mg min})$, $q_e = 7.326 \text{ mg/g}$ and $k_{p2} = 0.032 \text{ g}/(\text{mg min})$, $q_e = 4.450 \text{ mg/g}$ for MK-GP and the zeolite, respectively. The smaller value of the rate constant (k_{p2}) in the case of the zeolite indicates slower sorption. (Paper V)

The small-scale pilot experiment at the landfill site illustrated that MK-GP is suitable for the removal of ammonium from landfill leachate in field conditions. The removal efficiency was 30–50% when treating effluent with a concentration of 55 mg/L NH_4^+ . However, when treating landfill leachate without any pre-treatment ($\text{NH}_4^+ = 624 \text{ mg/L}$), the removal efficiency dropped quickly to 0–10% due to the saturation of sorbent and blocking of sorption sites (Paper V).

The mechanism of NH_4^+ removal was ion exchange (Paper V). Furthermore, the re-usability of MK-GP was confirmed in preliminary experiments where material was successfully regenerated with 0.2 M NaCl or a combination of 0.2 M NaCl and $0.1\text{--}0.2 \text{ M NaOH}$.

Nickel, arsenic and antimony

MK, MK-GP, BFS, and BFS-GP were compared for the simultaneous removal of Ni, As, and Sb from mine effluent (Paper VI). BFS-GP proved to be the most effective, and thus only its data is discussed here. The effects of pH, sorbent dose, and contact time are shown in Fig. 29.

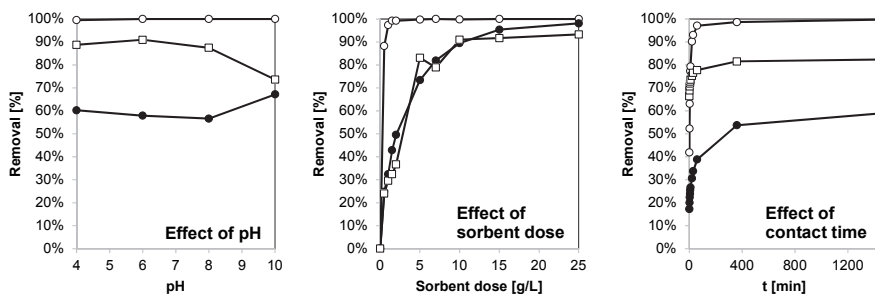


Fig. 29. The effects of pH, sorbent dose, and contact time on the removal of Ni (○), As (●), and Sb (□) with blast-furnace-slag geopolymers.

The pH of solution was increased by approx. 2 as a result of sorbent addition, although the material was carefully washed to remove any residual alkali solution. Ni removal was > 99% in the whole pH range (4–10). However, Ni(OH)₂ started to precipitate at pH > 8, and consequently only pH 4 in Fig. 29 represented a situation with sole sorption as the removal mechanism. The optimum pH for the removal of As and Sb was observed at 10 and 6, respectively. Higher pH resulted in the formation of anionic H₂AsO₃⁻ (pH > 8) and HAsO₃²⁻ (pH > 10), while Sb is present as Sb(OH)₃ in the whole pH range. The optimum sorbent dose for the removal of Ni was 1.5 g/L and for As and Sb 10 g/L. The required contact time was 60 min (Paper VI).

The best fitting isotherm for Ni removal was the Langmuir model ($R^2 = 0.968$, RMSE = 0.261, $X^2 = 0.282$) and the obtained parameters were $q_m = 4.418$ mg/g and $b = 19.41$ L/mg. A clearly positive effect of geopolymers was again observed if q_m of BFS-GP is compared to that of BFS which was 0.351 mg/g. The multi-solute Freundlich isotherm was best suited for the removal of As ($R^2 = 0.949$, RMSE = 0.054, $X^2 = 0.065$) and Sb ($R^2 = 0.772$, RMSE = 0.073, $X^2 = 0.401$). The obtained parameters were $n_{MF} = 1.120$, $K_{Ni} = 24.065$ (mg/g)/(mg/L)ⁿ, $K_{As} = 0.486$ (mg/g)/(mg/L)ⁿ, $K_{Sb} = 0.000$ (mg/g)/(mg/L)ⁿ and $n_{MF} = 1.244$, $K_{Ni} = 84.790$ (mg/g)/(mg/L)ⁿ, $K_{As} = 0.007$ (mg/g)/(mg/L)ⁿ, $K_{Sb} = 0.280$ (mg/g)/(mg/L)ⁿ, respectively. Comparison to the literature (Paper VI) revealed that several materials with significantly higher removal capacities exist, but those studies were typically conducted in more ideal conditions using a single solute system, synthetic wastewater, and higher initial concentrations.

Kinetics followed the pseudo-second-order equation ($R^2 = 0.999-1$). The obtained parameters were $k_{2p} = 1.124$, 0.233, and 1.702 g/(mg min) for Ni, As,

and Sb, respectively, and $q_e = 0.395, 0.294,$ and 0.382 mg/g for Ni, As, and Sb, respectively.

The selectivity of BFS-GP can be concluded to be $Ni > Sb > As$. The possible removal mechanism of Ni is a combination of precipitation-sorption. Sb is probably removed by sorption and the removal of anionic As species occurs through anion exchange by formed hydrotalcite.

6 Summary and concluding remarks

Organic peracids, most importantly performic (PFA) and peracetic acids (PAA), have emerged as potential alternative wastewater disinfectants and oxidizers. Their main beneficial properties over competing methods are their positive antimicrobial activity, high oxidizing power, and lack of harmful disinfection side-products. In this study, performic acid was found to be a more potent disinfectant than peracetic or perpropionic acids (PPA) when eradicating *E. coli* or intestinal enterococci from municipal tertiary effluent in order to meet the EU bathing water quality requirements. The required doses were estimated to be 1.5 mg/L of PFA and 3.0 mg/L of PAA or PPA. Furthermore, the corresponding operational costs were 0.0114, 0.0261, and 0.0207 €/m³ for PFA, PAA, and PPA, respectively. In addition to these results, a pilot-scale tertiary effluent disinfection experiment with PAA indicated high efficiency in eliminating total coliforms, *E. coli*, and coliphage viruses (somatic and F specific) already at a dose of 1.5 mg/L. No significant changes in effluent pH or biological oxygen demand were observed, whereas the increase in the redox potential could be utilized as an online control measurement. The efficiency of peracids in a Fenton-like oxidation of bisphenol-A was found to be approx. similar to or lower than the effects with the use of the much more economical hydrogen peroxide. Corrosion caused by peracids on stainless steel (316L) was negligible, whereas carbon steel seemed to be an unsuitable material for contact with even dilute peracid solutions.

Residues of natural organic matter (NOM) and organic internal treatment chemicals in a water-steam cycle of a power plant are suspected to cause corrosion due to the hydrothermal decomposition and formation of low molecular weight acids. There are several methods available to remove the residual organics: for instance, enhanced coagulation, ion exchange, membrane filtration, or short wave-length UV can all be effective. However, these methods are quite expensive in terms of operational and investment costs. Activated carbon (AC) was studied at a novel process phase: after deionization. The advantage of AC is its low operational cost due to the potentially extended operating life of carbon bed. It was confirmed that dissolved organic carbon (DOC) was decreased to less than 100 µg/L, which is comparable to the results of reverse osmosis. The most effectively removed NOM fractions were the decomposition products of humic substances (building blocks), low molecular weight neutrals, and hydrophobic compounds. However, the leaching of impurities from AC increased conductivity,

silica, sodium, calcium, and magnesium to unacceptable levels. Therefore, a mixed bed ion exchanger was required as a polishing treatment.

Geopolymers, the amorphous analogues of zeolites, are novel sorbents possessing cation exchange capacity. Geopolymer raw materials include industrial side-products or natural (clay) minerals, such as blast furnace slag, fly ash or metakaolin. Furthermore, the synthesis conditions are mild in terms of temperature. As a result, geopolymers can be considered “green” materials. In this study, geopolymers were prepared out of metakaolin and blast furnace slag. The geopolymerization induced a change in the Si and Al environment, as indicated by XRD, FTIR, and ^{27}Al , and ^{29}Si MAS-NMR measurements. The porosity and surface area increased. Metakaolin geopolymer was applied for the removal of ammonium from synthetic wastewater in batch experiments. The sorption was quick (most happened within 1 min), relatively pH independent in the range 4–8, and the removal capacity of the geopolymer was significantly higher than with the raw material. The equilibrium data fitted best with the Langmuir-Freundlich isotherm model, with the maximum capacity 21.067 mg/g. In contrast, a frequently used ammonium sorbent, clinoptilolite-heulandite zeolite, reached only 14.423 mg/g maximum capacity. Metakaolin geopolymer’s suitability for ammonium removal was further confirmed with a small-scale field experiment in a landfill leachate treatment test. Furthermore, metakaolin geopolymer could be regenerated with a NaCl/NaOH solution. Blast-furnace-slag geopolymer, on the other hand, was tested for the simultaneous removal of Ni(II), As(III), and Sb(III) from a spiked mine effluent sample. A removal rate of $\geq 90\%$ could be achieved with the selectivity being Ni > Sb > As. The required contact time was approx. 60 min. The Langmuir or multi-solute Freundlich isotherms were the best fitting. The removal mechanism was possibly a combination of precipitation (Ni(II)), (ad)sorption (Sb(III)), and anion exchange (As(III)).

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