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Comparison of treatment and fouling mitigation efficiency of organic and inorganic coagulants in biofilm membrane bioreactor

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Summary

Membrane bioreactors is an exemplary practice of sustainable wastewater treatment. Novel methods and approaches incorporating MBR allow not only treat wastewater with excellent efficiency, but also recover nutrients, recycle water, produce water with drinking water quality, produce and recover energy and carbon. These benefits provide limitless opportunities for MBR integration in almost any kind of field of wastewater treatment.

Still, the MBR technologies promise a lot of gains, there is a long way ahead before the MBR will overrun the world wastewater market. The most deterrent factor for MBR technology is a membrane fouling – it is evident from modern publications regarding MBR biggest fraction of which relates to the issue of membrane fouling. Numerous strategies for membrane fouling mitigation have been developed recently, starting from the upgrade of traditional mechanical cleaning, introducing adjustments in chemical cleaning and ending up in advanced biological methods for fouling control. Commonly applied chemical pre-treatment of water entering MBR has proved its reliability, enhanced treatment efficiency and ability to greatly prolong filtration time. However, it lacks sustainability, since chemical precipitation with conventional coagulants produces a large load of sludge, which is difficult for further handling due to low dewaterability and poor biodegradability. Also, residual aluminium in treated wastewater rises the risk of exposure to aluminium in food and drinking water, when recent findings assert that constant exposure to aluminium provokes Alzheimer disease and dementia. Thus, finding alternative chemical to precipitate and neutralize organic foulants (EPS and SMP) is an important task.

Chitosan is a natural polyelectrolyte produced from shells of crustaceans and is an excellent example of how wastes from food production can be converted to multi-purpose product. Ability to bind a wide range of substances makes chitosan outstanding flocculant. Chitosan proved to have the high binding ability of fats, fatty acids, polysaccharides, dyes and other organics which can contribute to biofilm growth and cause severe fouling of the membrane. Thus, it was interesting to try and investigate the anti-fouling abilities of chitosan and compare it with conventional coagulants.

Despite outstanding aggregating abilities, the results of the study show that chitosan is not so efficient in terms of fouling mitigation comparable to conventional aluminium sulfate. Moreover, low concentration of chitosan can accelerate fouling in MBR and high doses need to be applied to overcome dose range when chitosan acts as fouling enhancer. Reason for this is unclear and further study is needed, however findings from different research state the possibility of more intensive fouling due to low SMP removal by chitosan. The result of the study asserts that at optimal dosing chitosan is about 2.5 less effective than aluminium sulfate in terms of fouling mitigation.

Dedication

This thesis I dedicate for all the beauty of this world - beauty of nature, people and science; beauty of friendship and beauty of love. The world is just awesome – Boomdiada.

Acknowledgement

First of all, I would like to express my gratitude to my supervisors Dr Zakhar Maletskiy and Prof. Harsha Ratnaweera for their belief in my talent and skills. Only because of their belief and trust I was able to start performing something beautiful as this research.

Secondly, this research utterly would not be possible without colossal input of my father, Dr Bogdan Shostak. I ascribe him all the credits for making the “beautiful” part of the research, namely automated control and monitoring over the system used for testing. Restless months of work in collaboration with him, hours of brain-storming, unexpected solutions are the only reasons why this research has been brought to life. This is the 2nd thing that has made this research so exciting – opportunity to work with my family staying far away from my home.

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At last, but not the least, I am obliged to express enormous gratitude for all my family for all the moral and real support they provided me with. Their wisdom and limitless belief in me helped to overcome many problems that I faced on the way of Master research.

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List of Acronyms

AnMBR	Anaerobic membrane bioreactor
BOD	Biological oxygen demand
CAS	Conventional activated sludge
CHW	Chitosan with high molecular weight
CIP	Cleaning in place
CMW	Chitosan with medium molecular weight
CNT	Carbon nanotubes
COD	Chemical oxygen demand
DD	Deacetylation degree
DO	Dissolved oxygen
DOC	Dissolved organic carbon
EBPR	Enhanced biological phosphorus removal
EC	Electrocoagulation
EDTA	Ethylenediaminetetraacetic acid
EPS	Extracellular polymeric substances
FO	Forward osmosis
FS	Flat sheet
GO	Graphene oxide
HF	Hollow-fiber
HRT	Hydraulic retention time
IFAS	Integrated fixed-film activated sludge
MBBR	Moving bed bioreactor
MBR	Membrane bioreactor
MFC	Microbial fuel cell
MLSS	Mixed liquor suspended solids
MT	Multi-tubular
MW	Molecular weight
NOM	Natural organic matter
NP	Nanoparticles
PE	Polyethylene
PES	Polyethersulfone
PLC	Programmable logic controller
PP	Polypropylene
PVDF	Polyvinylidene difluoride
QQ	Quorum quenching
SMP	Soluble microbial products
SRT	Sludge retention time
TMP	Transmembrane pressure
TOC	Total organic carbon
TOD	Total oxygen demand
TOP	Trace organic pollutants
TRT	Total recycle test
TSS	Total suspended solids
WTP	Water treatment plant
WWTP	Wastewater treatment plant

Contents

1. Introduction

Membrane bioreactors (MBR) is an approach in wastewater treatment that combines in one unit two methods – biological water treatment and membrane separation. Since the ultra-/ microfiltration modules can be embedded in almost any kind of biological treatment system, such as CAS, IFAS, MBBR etc. for sludge separation, they were recently applied in various fields of water treatment: municipal, industrial, food and agriculture.

First MBR was introduced in the 1960s in the form of the side-stream unit which required a lot of energy to maintain high transmembrane pressure (Mohammad et. al, 2019). The research on MBR has been actively conducted for around 30 years, and for that time a lot of obstacles on the way of MBR large-scale implementation were overcome: material, capital and operation cost were substantially reduced, meanwhile performance, critical flux, stability of work and footprint were considerably improved (Xiao, Liang, Wang, Chen, & Huang, 2019). MBR based systems become more widespread – in 2019 world volume of water treated by MBR expected to reach 5 million m^3 per day, and the number of available publications is increasing exponentially (Krzeminski et. al, 2017).

Such strong growth of MBR technology is related to global changes in the water treatment sector: introduction of stricter legislation for wastewater discharge, increasing concern about nutrient recovery from wastewater, demand to reuse and recycle water in places with water scarcity, increasing importance of automation control to reduce operation cost and provide constant effluent quality, reuse of sludge after treatment and future need of removing emerging pollutants such as microplastic and TOP. MBR technology can successfully face all these challenges as recent research show (Xiao et al., 2019).

Even with such high technological advance, one problem remains unsolved up to today – membrane fouling. Membrane fouling is a gradual loss of membrane permeability over time or gradual increase of pressure required to maintain certain water flux. Rapid membrane fouling results in higher operating cost due to elevated energy consumption, higher chemical consumption for membrane cleaning, degradation of membrane integrity and loss of performance due to irrecoverable pore clogging.

Previously more attention was attracted only to membrane properties as a cornerstone of membrane performance and therefore fouling. However, recent findings show that the membrane itself is the only one side of the coin, and another mechanism contributing to fouling comes from biological processes in MBR and, moreover, there are synergetic and antagonistic effects resulting from co-performance of microorganisms and the membrane (Drews, 2010b).

One of the common strategies to reduce fouling is the addition of coagulant or flocculant. Due to the addition of aggregating chemicals plant operators aim to alter biomass properties, namely improve floc structure, increase the uniformity of particle size distribution, increase aggregation of microorganisms and dissolved matter, reduce EPS and SMP concentration in water. Most commonly applied for fouling mitigation coagulants and flocculants are similar to those used at chemical precipitation stage: inorganic soluble salts of Aluminum and Iron, metal oxides, pre-polymerized inorganic coagulants (e.g. PACl, PICl), cationic and anionic polymers: PDADMAC, ECH/DMA, CPAM, APAM, etc. The benefit of such an approach, besides prolonged filtration time, is the addition of inorganic salts also allows recovering dissolved phosphorus from wastewater, which if untreated may cause eutrophication of freshwater bodies. Therefore, it is possible to omit the chemical precipitation stage. Otherwise, the whole system will require biological phosphorus sequestration and/or tertiary treatment to remove phosphates.

Even though their performance as anti-fouling agents is well-evaluated, they possess few inherent drawbacks which can limit their applicability in the future. Most commonly applied aluminium salts possess toxicity for human (exposure to Aluminum can cause acquired dementia and Alzheimer disease in humans), also overdosing of coagulant can cause elevated residual heavy metal concentration. Sludge after treatment possesses low dewaterability and biodegradability, a nutrient in chemical sludge are presented mostly in non-available form for plans, as a result, sludge after chemical addition cannot be reused in agriculture. Also, the performance of inorganic coagulants is significantly diminished under cold temperatures and in conditions of non-optimal pH. Meanwhile, synthetic organic flocculants are not susceptible to underperformance at low temperature and at extreme pH and the produced sludge has much higher dewaterability, still, there is a big concern regarding degradability and toxicity of half-oxidized products (Oladoja, 2015). Thus, finding alternative eco-friendly, non-toxic, biodegradable coagulants and flocculants is a promising area.

The goal of this research is to prove that the addition of natural flocculant chitosan is able to significantly increase the filtration time of membrane and compare treatment efficiency and anti-fouling properties with conventional inorganic and organic chemicals.

1.1. Insights on MBR technologies

In 2016 global MBR market size was evaluated to be 1.81 billion USD. Many prognosis forecast even faster growth in upcoming years with the expected size of the market of 8.27 billion in 2025. Biggest fraction of MBR market (50.4%) is accounted for the Asia Pacific region, particularly for India and China. Around 70% of all market is represented by systems for municipal wastewater treatment (GVR, 2017).

Current MBR systems can be classified by i) system configuration ii) membrane module types iii) presence of aeration iv) membrane material.

1) According to system configuration, MBR is subdivided on:
- Submerged or immersed (iMBR)
- Side-stream (sMBR)

Globally, submerged reactors are more preferred due to lower energy consumption and simple design. Meanwhile, side-stream systems require recirculation pump, which results in higher energy consumption by up to two orders of magnitude. Moreover, submerged membranes can be cleaned more easily. As an advantage of sMBRs is they can be operated at higher fluxes than numbers (Deowan, Bouhadjar, & Hoinkis, 2015). For submerged MBR mainly dead-end filtration regime is applied and side-stream reactors are operated in cross-flow mode. Schematic drawing of two configurations is provided in figure 1.

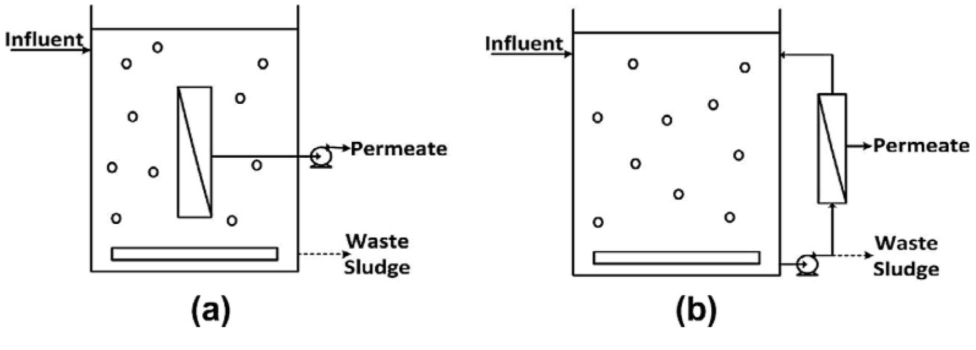


Figure 1. Configuration types of MBR. (a) – submerged MBR; (b) – sidestream MBR (Sabrina et al., 2013)

2) Membrane elements are generally presented by the next types of modules:
- Flat sheet (FS)
- Hollow-fiber (HF)
- Multi-tubular (MT)

FS and HF modules are typically used in submerged systems, meanwhile MT is more common for side-stream MBR (Sabrina et al., 2013).

3) By the presence of aeration, MBR systems can be:
- Aerobic MBR
- Anaerobic MBR (AnMBR)
- Anoxic in combination with oxic and/or anaerobic MBR (A/O and A^2O MBR)

Aerobic MBR is the most conventional type which is applied to water with low or moderate organic loading, such as municipal wastewater, discharges from textile, food and fish industries. The benefit of aeration is a simultaneous supply of oxygen to bacteria and reduction of membrane fouling due to turbulence created by coarse bubbles.

Anaerobic reactors had been mostly used for water with high organic loading since HRT in regular MBR was significantly lower than the required time for the growth of anaerobic bacteria. Later, this drawback was overcome by complete retention of slow-growing anaerobic microorganisms in the reactor. This, however, resulted in more intensive fouling (Drews, 2010; Skouteris et al., 2012). The benefit of AnMBR is the possibility of energy recovery by simultaneous biogas production. This, together with low sludge production and lower energy consumption due to the absence of aeration, significantly reduce the operational cost of the MBR system (Deowan et al., 2015).

Combination of anaerobic, anoxic and oxic processes in MBR is a relatively new approach used to achieve higher nitrogen removal rates and for enhanced biological phosphorus recovery (EBPR) (Krzeminski et al., 2017).

4) Regarding the material for membrane production, there are two main groups of the membrane:
- Ceramic membranes
- Polymeric membranes

Ceramic membranes generally can be manufactured from alumina, zirconia, silica, titania and silicon carbide. As a rule, ceramic membranes are made in form of flat-sheet modules. They are very robust and have excellent thermal and chemical resistivity, which make them applicable to the treatment of hardly contaminated industrial water. Shortcomings of ceramic membranes come from their high price and brittleness, which can require extra cost for careful handling and delivery (Mohammad et al., 2019).

Materials that are used for manufacturing of polymeric membranes include: polyvinylidene difluoride (PVDF), polyethersulfone (PES), polyethylene (PE) and polypropylene (PP). Membranes made from cellulose acetate and polysulfone are considered as obsolete and their use is very limited today. Generally, polymeric membranes are cheaper so in cases of moderate water pollution they are preferred rather than expensive ceramic membranes. Also, PDVE membranes have uniform pore size distribution, they are robust and resistant to many chemicals and oxidants, such as inorganic acids and chlorine, but moderately resistant to sodium hypochlorite. Thus, PDVE membranes represents more than a 50% share of the MBR membranes market. Second most widely applied membranes made from PES, have higher mechanical strength comparably to PDVE, have good tolerance toward NaOCl, but however susceptible to chlorine. Surface of freshly produced polymeric membranes is usually hydrophobic, but it can be modified to very hydrophilic by chemical additives and coatings. PE and PP membranes have low chemical resistance, low thermal resistance, hydrophobic and with difficulty undergo modification, however, they are the cheapest from all mentioned before (Mohammad et al., 2019).

1.2. Advances in MBR technology

Research on MBR systems is mainly going in next directions:

- reduction and prevention of membrane fouling
- improved treatment efficiency toward specific pollutants: organics, nutrients, pharmaceutical residuals, microplastic
- higher energy efficiency
- improving the sustainability of the system creating better opportunities for nutrients and energy recovery and reuse of water.

Many reviews, however, provide another subdivision of new tendencies in MBR based on the chosen approach of enhancing MBR performance. Thus, new tendencies are split into the next categories (Meng et al., 2017; Qin et al., 2018):

- Application of new strains
- New membrane materials and surface modification methods
- Introduction of additional media in reactors
- Alternatives in MBR operation: advanced aeration control and chemical cleaning
- New configurations of MBR including forward osmosis, microbial fuel cell, electrocoagulation and electrophoresis, dynamic membrane modules.

New strains of microorganisms are continuously tested in MBRs with an attempt to reduce fouling and increase removal efficiency. For example, special types of quorum quenching bacteria (QQ) can release special substances that enhance their bonding with other cells and in this way slow down biofilm formation. Addition of microalgae allows achieving high organic and nutrient removal with simultaneous production of biofuels or other target biomaterials. Microalgae require less aeration in MBR and their input to fouling formation is generally lower than of regular biological sludge. Also, the introduction of photosynthetic bacteria is one of the promising ideas, since it allows to combine water treatment with simultaneous bioenergy production in the form of biodiesel and/or hydrogen. Generally, application of such specific strains is complicated in harsh conditions and in water with rapidly changing parameters, thus these methods are not robust (Qin et al., 2018). Other studies suggest adding of bacteriophages or protozoan and metazoan species. By predation and destruction of bacteria, they prevent the formation of biofilm and/or make biofilm more loosen and thinner, which contributes to fouling reduction (Bagheri & Mirbagheri, 2018).

Several new methods for membrane modification and coating were proposed to increase permeability and robustness of conventional membranes. One of the promising highly effective approaches is modification with metal and metal oxides nanoparticles (NP). For example, Ag NP have the strong antimicrobial ability by disruption microbes' metabolism, so blended in polysulfone membrane they resulted in 94% lower biofilm formation. Metal oxides such as TiO_2 and ZnO are semiconductors with strong photocatalytic ability, so embedded on membrane surface under UV radiation they significantly improve the oxidation of organic matter and thus also grant membrane the ability for self-cleaning. The antimicrobial activity also exhibited membranes incorporated with carbon-based NP, such as single-walled carbon nanotubes (SWCNT) and membranes fabricated from graphene oxide (GO) nanosheets. Generally, membranes with embedded metal and metal oxides NP, CNT or manufactured from GO nanosheets possess significantly increased the hydrophilicity of surface which results in higher permeability. Membranes blended with Ag NP, however, are susceptible to depletion of Ag in water solution, which demands further research for more reliable Ag NP carriers (Meng et al., 2017; Qin et al., 2018).

Currently, novel methods for surface modification include surface grafting and surface coating. Meanwhile, both methods allow to substantially increase the permeability of the membrane and effectively reduce fouling, grafting method, as a rule, is very energy demanding, and hard to control a surface chemical reaction. And while coating method is simple and easy to control, the coating layer is susceptible to mechanical destruction, therefore adhesion between substrate and coating layer needs to be improved (Qin et al., 2018).

Addition of media with the high specific area is one of the approaches to decelerate biofilm growth on the membrane surface. Examples of such media can be GAC granules, PP and PE carriers, polystyrene latex and melamine beads, dispersed silica. Addition of media allows bacteria to create more stable adherence to the porous substrate rather than attach to the membrane surface. In presence of aeration, porous media also exhibits scouring effect on membrane surface reducing fouling, but on the other hand, too intensive mixing of media can cause mechanical damage to the membrane (Bagheri & Mirbagheri, 2018; Meng et al., 2017).

Many analytical studies showed that most energy demanding process in many biological treatment systems is aeration. Also, case-studies demonstrated that aeration is excessive during the time of low water loading, so at that time microbes receive more oxygen than they need for organic oxidation. Thus, the need for smart aeration control araised. In the case of MBR, there is a trade-off between anti-fouling aid of aeration and minimizing operation cost during low loading time. Experiments show that intermittent aeration and automatically controlled aeration can reduce operation cost up to 50% without a significant increase in fouling rate (Meng et al., 2017).

Promising new approaches in membrane cleaning are using surfactants and chelating chemicals (diamine tetraacetic acid, sodium dodecyl sulfate, EDTA), rhamnolipids and nitrites (in the form of free nitrous acid). Surfactants reduce surface tension between the liquid and solid phases, therefore, weakening the interaction between bacteria and membranes. Also, they enhance micellization of fats, oils and proteins which reduce the strength of biofilm. Rhamnolipids reduce fouling by increasing surface hydrophobicity. They reported to effectively remove fouling caused by proteins. Nitrous acid in its turn does not affect the surface properties, instead, it causes strong damage to microorganisms that contribute to biofilm formation.

Advanced systems incorporating MBR were proposed. Among them, systems with electrically-assisted fouling mitigation (electrocoagulation, electrophoresis), microbial fuel cells (MFC) and integrated with forward osmosis (FO). MBR with electrocoagulation pre-treatment showed significantly diminished fouling rate. Advantages of electrocoagulation pre-treatment over the conventional addition of coagulant are more compact systems, no alkalinity change, less sludge produced and together with the destabilization of particles oxidation of organic matter occurs. MBR enhanced with electrophoresis utilize electrostatic properties of organic matter and colloids in wastewater which are usually negatively charged. Thus, the cathode is installed close to the membrane surface while the anode is submerged distantly in mixed liquor, so negatively charged particles and microorganisms moves toward anode far from the membrane. MFC are known for their ability to convert energy from oxidation of organic matter by microorganisms to electricity. Due to oxidation of organics, sludge modification occur therefore reducing fouling. FO systems gained a lot of attention in the last years due to less expensive, more robust membranes and more energy efficient approaches. In MBR systems integrated with FO, water from mixed liquor is extracted through a semipermeable membrane to recirculating brine solution due to osmotic forces. Later the water from diluted brine is separated on RO membrane, meanwhile, re-saturated brine returns to FO stage by the recirculating pump. All these approaches resulted in significant fouling mitigation, however still a lot of research need to be performed regarding optimization of process and material selection, for FO systems also the problem of salt accumulation in the reactor should be overcome (Bagheri & Mirbagheri, 2018; Meng et al., 2017; Qin et al., 2018).

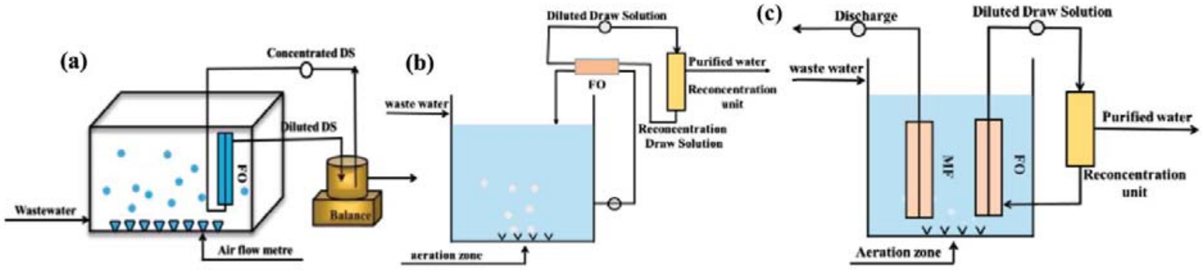


Figure 2. Forward osmosis (FO) systems incorporated in MBR (Qin et al., 2018).

1.3. Applications of MBR

MBR systems are currently applied in various systems. This is caused mainly by fact that membrane modules can be introduced to almost any kind of biological treatment systems: aerated, anaerobic, anoxic; with low and high organic loadings. Other benefits that contributed to the wide application includes: robustness, excellent chemical resistance, constant high treatment efficiency, small footprint, easy in operation, automated control systems can be easily introduced, easy to scale-up or down simply by changing the number of membrane modules. Also, the introduction of the membrane allows to uncouple HRT and SRT for CAS process. Therefore, MBR are intensively applied for the treatment of different types of wastewater: municipal, leachate, dye and textile, pulp and paper, food and beverages industries, petrochemical factories, pharmaceutical, electrochemical industries, after shipping (Krzeminski et al., 2017).

Reported treatment efficiencies are presented in table 1.

Table 1. Application of MBR

Industry and wastewater properties	Type of MBR	Treatment efficiency	Reference
Municipal wastewater	iMBR A^2O (anaerobic-anoxic-oxic) Polymeric mem.	BOD – 98% COD – 98% NH4-N – 99% TN – 74% TP – 97%	(Dohare & Trivedi, 2014)
Municipal wastewater	iMBR A^2O (anaerobic-anoxic-oxic) Polymeric mem.	COD – 94% TN – 89-93% TP – 80-92%	(Mohammad et al., 2019)
Municipal wastewater	iMBR Polymeric mem.	TSS – 99.9% COD – 93% TP – 91%	(Mohammad et al., 2019)
Oil High organic loading	iMBR Mesophilic-thermophilic conditions	COD – 78-96% BOD_5 – 87-99%	(Dohare & Trivedi, 2014)
Food Ice-cream production water	iMBR Ceramic mem.	COD – 83-97% BOD – 90-98%	(Dohare & Trivedi, 2014)
Leachate	iMBR Polymeric mem.	BOD > 95%	(Mohammad et al., 2019)
Leachate	iMBR Polymeric mem.	Caffeine – 99.95% Al – 99.93% As – 97% Ba – 98.99% B – 82.74% Cr – 98.75% Co – 97.27% Ir – 99.87% Pb – 99.9% Mn – 99.95%	(Mohammad et al., 2019)
Dye and Textile	iMBR Polymeric mem.	Color – 100% COD – 98% BOD5 – 96% SS – 100%	(Mohammad et al., 2019)
Dye and Textile	sMBR Polymeric mem.	COD – 99.1% TN – 97% TP – 65.1%	(Mohammad et al., 2019)
Textile High concentration of poorly degradable organic	iMBR	COD – 90%	(Dohare & Trivedi, 2014)
Shipboard	MBR Ceramic mem. + integrated biofilm	TSS – 42.03% TCOD – 35.41% SCOD – 31.07%	(Mohammad et al., 2019)

2. Theoretical background

2.1. Membrane fouling

Membrane fouling represents a major limitation for the wide-scale application of membrane technologies. Fouling remains the most important problem in MBR, hindering the filtration process with a followed increase in operational costs as well as a dramatic decline of the filtration velocity.

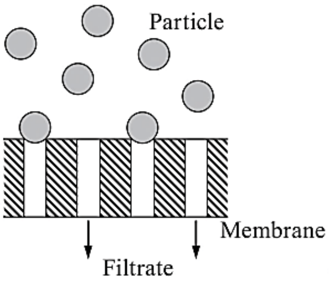
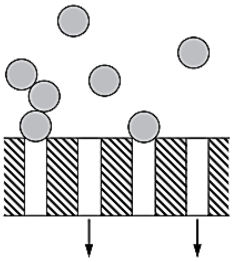
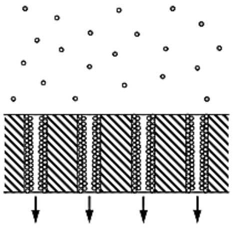
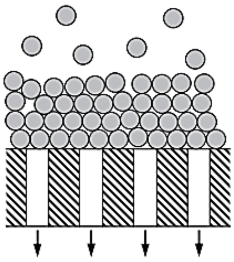
Fouling derives from the interaction between mixed liquor and membrane surface that induces accumulation and storage of solute species on the membrane surface and within the pores.

There are many factors affecting the membrane fouling including (Iritani & Katagiri, 2016):

- *pore narrowing:* particles with a smaller size than the membrane pore size, due to pressure and sticky properties, attach or adsorb as passing through the membrane and it leads to the pore constriction;
- *pore blocking/cake layer resistance:* larger particles attach onto the pore entrance with followed pore plugging they also further can retain smaller particles, creating cake layer (Geilvoet, 2010)*;*
- *adsorption of solute species:* foulants are adsorbed by the pore walls with zeroth-order kinetics;
- *concentration polarization:* comparison of *solutes* concentration near and far from the membrane surface. Retention of the solutes can cause the pressure difference resulting in need of high TMP, nevertheless, it is common to neglect this value for MF and UF membranes due to higher molecular weight cut off than in the RO membranes (Geilvoet, 2010)*;*

Four basic models could be distinguished (table 2) (Iritani & Katagiri, 2016).

Table 2. Basic models of the fouling mechanisms

• complete blocking (a):		Foulants larger than pore size, therefore unavoidably stay on the membrane surface and clog pores	*The blocking filtration law:* describes mechanisms of pore blockage
• standard blocking (b);			
• intermediate blocking (c);		Foulants smaller than pore size and can entail pore narrowing with further blocking	
• cake filtration (d).		Rather than block pores, particles form a granular bed that resulting in membrane resistance increase, but filtration still continues	*The cake filtration law*: describes cake growth and particles accumulation on the membrane surface

All models represent the influence of the particle size/pore size ratio on the flux (Drews, 2010a).

When designing the process of membrane cleaning followed factors should be taken into account (Chang et al., 2002; Guo, Ngo, & Li, 2012; Zhang et al., 2006):

- nature of feeding wastewater and its characteristics:
    1. MLSS;
    2. EPS & SMP;
    3. flocs size and structure;
    4. dissolved matter content;
    5. cations in water;
    6. viscosity (temperature);
    7. nutrient content;
    8. organic loading rate (OLR) & F/M ratio;

- membrane properties:
    1. membrane configuration;
    2. material;
    3. relative hydrophobicity;
    4. porosity;
    5. pore size;
    6. membrane charge;
- Hydrodynamics and process operation of the filtration process;
    1. configuration;
    2. aeration;
    3. HRT/SRT;
    4. TMP;
    5. cross-flow velocity (CFV);
- properties of activated sludge (Geilvoet, 2010).

Separation chamber contains a high concentration of organic matter, hence fouling stars to form in the first minutes of operation (Drews, 2010a). Fouling occurs unevenly and divides into three stages (Le-Clech, Chen, & Fane, 2006):

- *conditioning fouling*: interaction between membrane surface and EPS; passive adsorption of colloids and organic compounds; initial foulants attachment and pore blocking;
- *steady fouling*: after previous stage membrane covered with SMP, that makes the surface more suitable for further attachment of biomass particles and colloids; initiation of cake formation even with the irregular pattern;
- *rapid fouling with followed TMP jump*: since fouling distributes unevenly on the membrane surface, for regions with the less polluted surface, flux exceeding critical values and accelerates further fouling.

The more detailed fouling development is shown in figure 3 (Zhang et al., 2006).

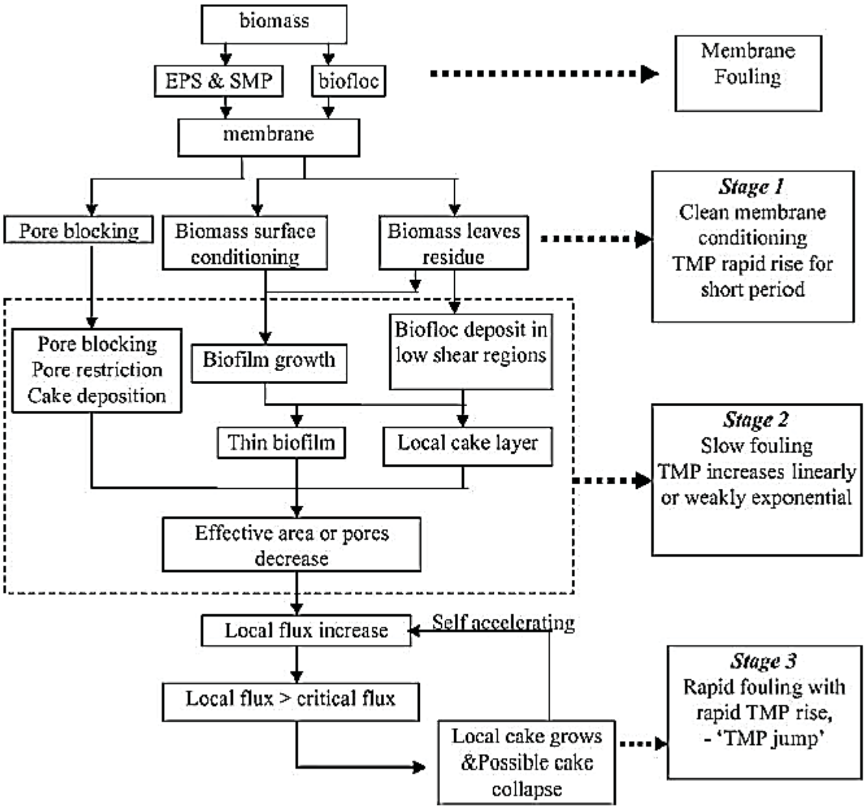


Figure 3. Fouling mechanism stages

At first, during the time, when filtration was initiated, reversible fouling occurs on the membrane. However, this type of fouling could be removed with simple physical cleaning. After a particular time even with optimized operational parameters and efficient physical cleaning, fouling becomes more severe and requires special treatment such as chemical cleaning. But even then, some of the permanent fouling structures cannot be removed.

Due to different fouling components, fouling could be divided into 3 types:

Biological fouling. This type of fouling refers to the bacteria cells or flocs on the membrane surface it is an especially big concern for the systems with low pressure, such as MF or UF (Meng et al., 2017). Entire biofilm can develop from a single cell or cell cluster on the membrane surface. Furthermore, it creates a base for the cake layer formation.

Organic fouling. Mixed liquor in the MBR is comprised of different-nature substances as particles, colloids and a dissolved fraction (Drews, 2010a). At first main focus was MLSS concentration in order to control the fouling rate. Nevertheless, what initially interested was changed to the investigations of substances with the adhesive ability for fast floc formation and further precipitation. Such substances could be divided into extracellular polymeric substances (EPS) and soluble microbial products (SMP). On the contrary to the SMP, EPS is bounded to the flocs. Recently, two other groups were added: biopolymeric clusters (BPC) and transparent exopolymer particles (TEP).

All these compounds derive not just as products of vital activity of microorganisms, but also terrestrial and manmade. Usually, attention mostly focused on EPS and SMP, which comprise of proteins and polysaccharides (main fracture), as well as lipids, nuclear acids, etc.

Almost half of the compounds that deposit on the membrane surface biofilm are related (Pikkarainen et al., 2004).

Also, mixed macromolecules formed by aggregation of different compounds behave completely differently from ordinary interaction foulant-membrane and foulant-foulant (Y. N. Wang & Tang, 2011) and in some cases can influence on the fouling rate more than separate foulants (Zator et al., 2009). To avoid the formation of the aggregation stickiness of particles could be reduced, which results in slower fouling (figure 4) (Cai & Schwartz, 2018).

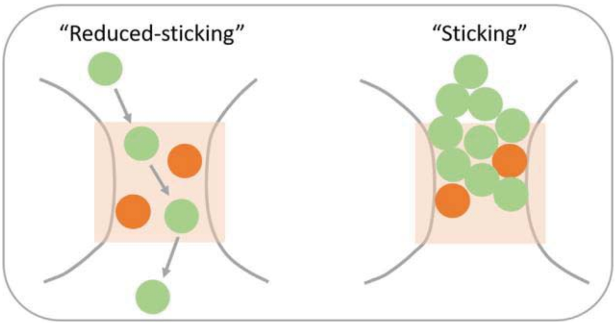


Figure 4. Fouling mechanism under "reduced sticking" in compare to "sticking" conditions.

Inorganic fouling. Even though fouling mostly formed by biological and organic compounds, all types of fouling occur simultaneously (Meng et al., 2017). Inorganic compounds take part in the cake layer formation and its enhancing. Sometimes inorganic fouling caused by inorganic scaling and hardly removed by chemical cleaning. It is possible to avoid or control inorganic fouling by special pretreatment or chemical cleaning.

2.2. Strategies to mitigate membrane fouling

Figure 5 summarizes all parameters influencing membrane fouling. Therefore, strategies for fouling mitigation are based on adjusting of one or several parameters presented on the figure. However, such information does not say anything about the practical sides of strategies, it is still useful for the understanding of fundamentals.

Generally, fouling mitigation strategies can be subdivided into three main groups (Bagheri & Mirbagheri, 2018): i) physical, ii) chemical and iii) biological.

2.2.1. Physical methods

Physical approaches for fouling reduction imply applying physical forces, such as shear and/or tension, or just increasing turbulence at the interface between mixed liquor and membrane surface. These kinds of strategies involves (Z. Wang et al., 2014):

- Hydraulic cleaning: backwashing with water, relaxation, aeration,
- Mechanical cleaning: addition of biofilm carriers and beads; rotation, vibration and oscillation of membrane modules; scraping.
- Ultrasound cleaning.

Physical methods generally do not require the addition of chemicals, which make them environmentally safer, also they are more robust since they are not dependent on water composition. However, most of the mechanical methods are proven to be very energy consuming, which make them not cost-effective. Also, for many of them, there is a high risk of mechanical abrasion of the membrane surface and damaging membrane integrity (Z. Wang et al., 2014).

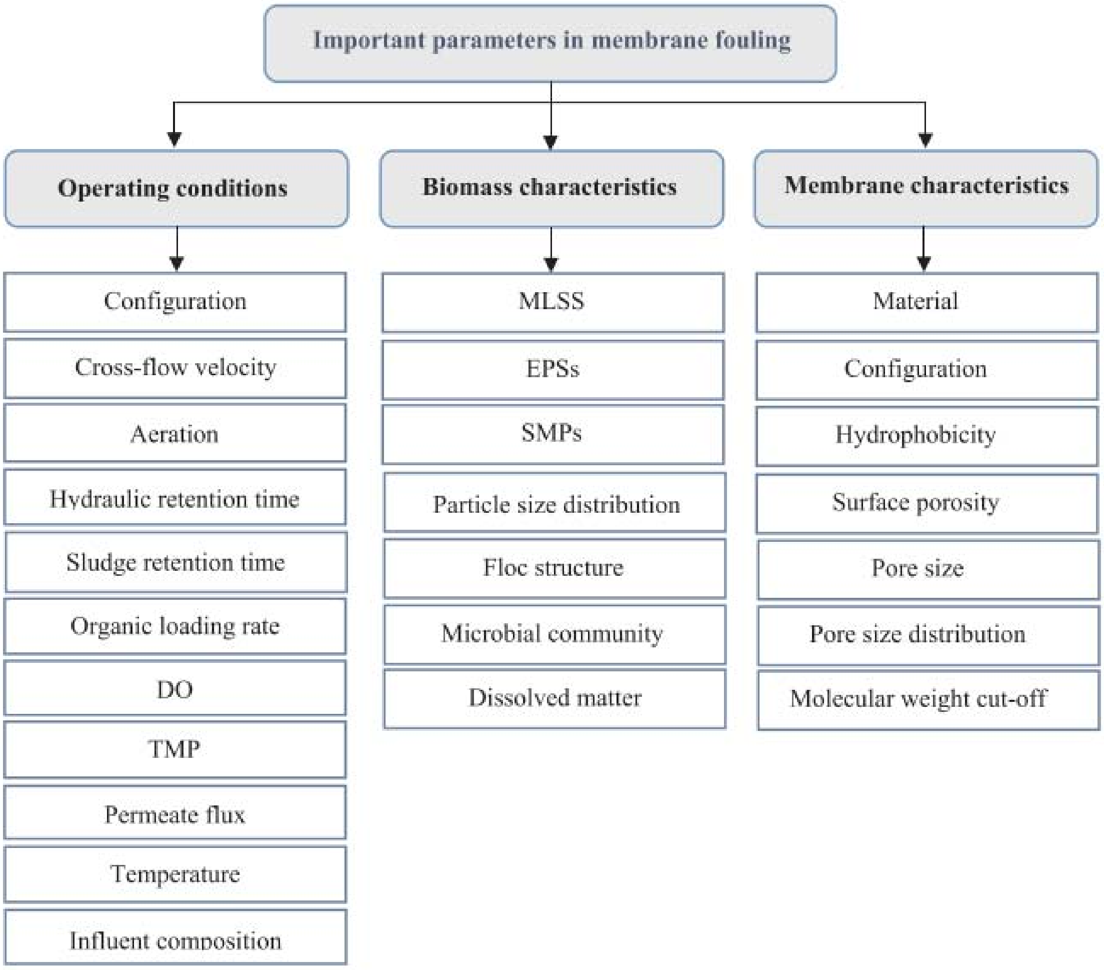


Figure 5. Factors contributing to membrane fouling (Bagheri & Mirbagheri, 2018).

2.2.2. Chemical methods

Chemical fouling mitigation strategies can be classified based on reagent that is applied for cleaning:

- Cleaning with acids
- Cleaning with bases
- Cleaning with oxidants
- Cleaning with combined reagents
- Fouling mitigation with alternative chemicals: EDTA, STP, surfactants.
- Fouling control with the addition of coagulants and flocculants

Chemical cleaning is important and at the same time also an expensive method to control fouling and permeability of membranes. Traditionally, for membrane cleaning agents are represented by the next 3 classes of substances: acids, bases and oxidants. Acids, such as oxalic, citric, nitric, hydrochloric and phosphoric are proven to be effective toward inorganic salt scaling on membranes. They effectively remove depositions of iron hydroxides, calcium and magnesium carbonates. However, acids reported being not efficient toward silicates. Bases, such as sodium hydroxide, are used generally for hydrolysis of proteins, fats and carbohydrates accumulated on the membrane surface. Application of oxidants such as sodium hypochlorite, hydrogen peroxide, polyvinylpyrrolidone is proved to be the most effective cleaning method, especially for MBRs treating municipal wastewaters, where the main fouling caused by growing biofilm. Use of combined chemicals simultaneously or sequentially can possibly reduce the dose of both with achieving higher cleaning efficiency, for example, mixtures of NaClO and NaOH (Bagheri & Mirbagheri, 2018; Z. Wang et al., 2014). Application of alternative chemicals was discussed in the section above.

Overall, chemical cleaning and fouling control methods lack in sustainability and environmental friendliness. Application of oxidants, such as hypochlorite is connected with a high risk of DBP production such as trihalogenomethane, it requires a big volume of water and neutralizing reagent to remove remaining hypochlorite from MBR, which otherwise can cause the death of microorganisms in the tank. Oxidants can disrupt membrane integrity if frequent chemical cleaning is applied. Generally, the efficiency of chemical mitigation methods is dependent on fouling nature, therefore cleaning agent should be carefully chosen, otherwise can be ineffective for fouling removal.

A promising strategy which can be considered as part of chemical methods is the addition of aggregating reagents, such as inorganic salts of aluminium, iron and calcium, synthetic and natural polymers. Changing particle size distribution, floc structures, EPS and SMP properties it allows to significantly reduce membrane fouling rate, without causing damage to the membrane surface. Several drawbacks connected to the production of big volumes of sludge and that sludge characteristics make it hard to reuse. Also, addition aggregating chemicals is cost-consuming due to their high cost and necessity of preparation before use (dilution and mixing) (Park, Yamashita, & Tanaka, 2018).

2.2.3. Biological methods

Biological fouling mitigation is based on disrupting the normal process of biofilm development or destroying substances that contribute to bacterial adherence. Currently, it is a novel set of approaches that seems to be promising due to its sustainability and gentle impact on the membrane material. Biological methods include (Bagheri & Mirbagheri, 2018):

- Bacterial quorum quenching (QQ)
- Enzymatic cleaning
- Energy uncoupling
- Nitric oxide
- Introduction of bacteriophages and protozoan
- Application of D-amino acids

QQ is a promising approach based on the idea of disruption of intracellular communication. The research proved the presence of autoinducers, molecules sensing of which trigger cell cooperation and biofilm formation, in MBR. QQ approach, therefore, aims to mitigate formation or destroy target autoinducers. This can be implemented via disrupting of production, interference with signal receptors, elimination or transformation of signal molecules. Two ways of QQ to reduce the concentration of autoinducers were adopted: enzymes-based and bacteria based. The last one was proven to be more robust since tested enzymes have a short catalytic lifetime and are difficult to recover (Bagheri & Mirbagheri, 2018).

Enzymatic cleaning is a broad set of methods since introduced enzymes are very selective in their action toward specific molecules. Enzymatic action can be aimed to reduce production or enhance degradation of various EPS and organic foulants, increase quorum quenching, slow down bacterial metabolism or promote cell's wall degradation (Z. Wang et al., 2014).

D-amino acids have been proven to provoke disassembly of biofilm, therefore providing a tool for fouling control. Both exogeneous and endogenous D-amino acids exhibited abilities to reduce fouling via diminished microbial attachment to a membrane, while also reducing the concentration of autoinducers and EPS formation.

Energy uncoupling methods based on the idea of deterioration of microbial metabolic activity, namely inhibit the synthesis of ATP, through the addition of weak acids – energy uncouplers, such as 3,3′,4′,5-tetrachlorosalicylanilid, 2,4-dichlorophenol, carbonyl cyanide chlorophenylhydrazone etc. Besides, of energy uncoupling decelerated metabolism resulted in lower production of autoinducers. Thus, it can be concluded that biological fouling mitigation methods are tightly related to each other while utilizing one approach can stipulate different mechanisms simultaneously.

Nitric oxide is one of the promising non-toxic methods. It based on the ability of nitric oxide (nitrous acid in solution) to stimulate "phosphodiesterase activity and degrades cyclic diguanylate monophosphate by changing gene expressions that favour the planktonic mode of growth" (Bagheri & Mirbagheri, 2018). Such an approach is still on the initial stage of investigation and further studies need to be done.

Introduction of bacteriophages and protozoan aims to destroy biofilm via interspecific interaction. Bacteriophages kill bacteria through the lytic or lysogenic cycles, finally causing lysis of bacteria. Protozoans reduce biofilm formation by direct predation of biofilm-forming bacteria.

Despite, the high perspectives of biological fouling control, it is at a very early stage of full-scale implementation. A lot of further research needs to be done in order to overcome current limitations, such as high cost, selectivity toward specific microorganisms or molecules, long time to achieve steady-state operation and high susceptibility to change in physical-chemical properties of water. Also, biological systems prone to develop resistance toward bacteria, bacteriophages, enzymes and chemicals.

Finalized table of currently applied methods for fouling control is presented on figure 6.

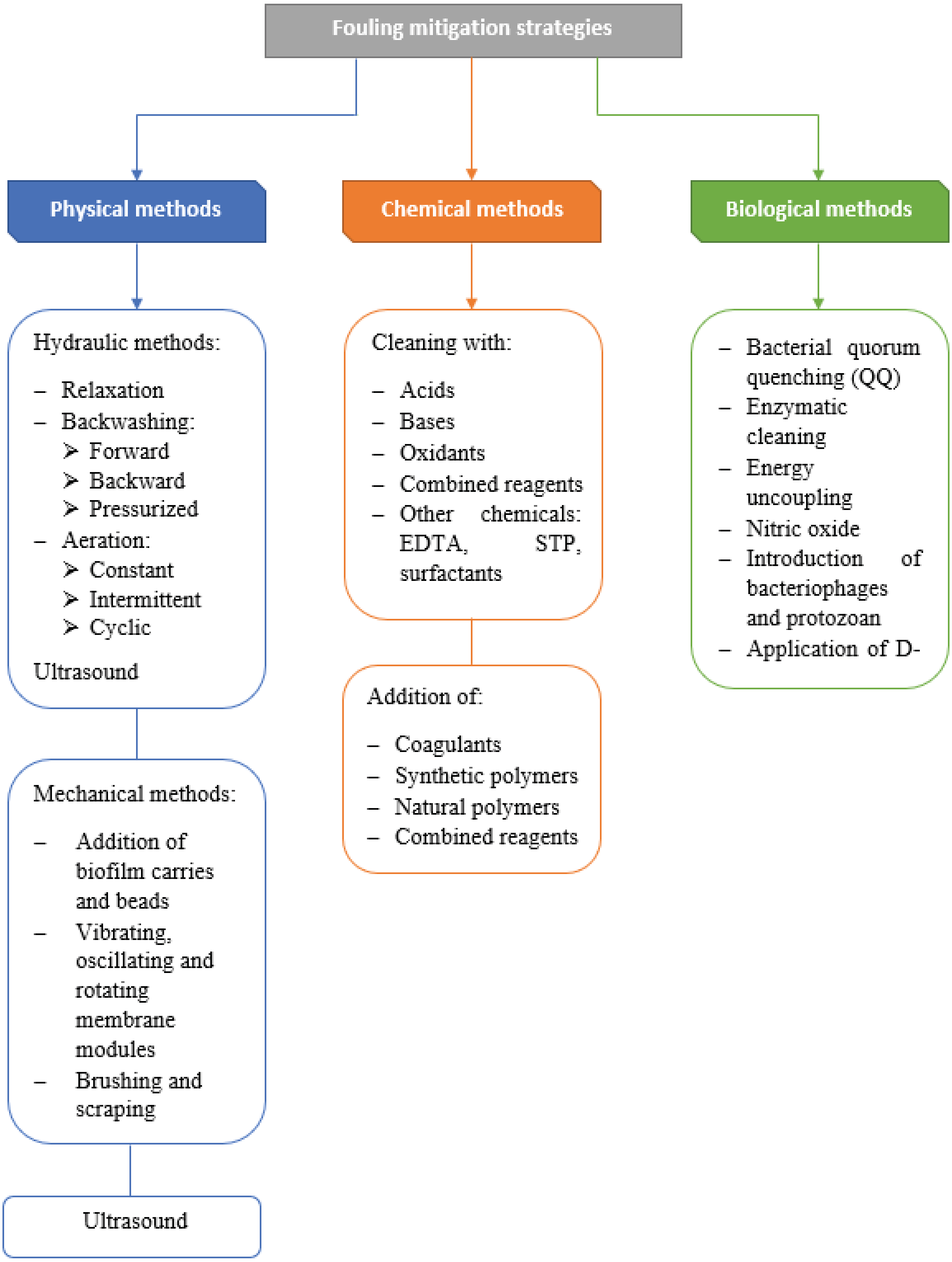


Figure 6. Strategies for fouling mitigation.

2.3. Chemical precipitation

2.3.1. Metal-based inorganic coagulants

The global market of flocculants and coagulants was evaluated to be $10,270.2 million in 2017 with a coagulant share of 45% (Prescient&Strategic Intelligence, 2018). Among them most frequently applied are so-called conventional metal-based coagulants such as alum (aluminium sulphate), aluminium chloride, ferric sulphate, ferric chloride, ferrous sulphate, ferrous chloride, polyaluminium chloride, polyaluminium sulphate polyferric chloride and polyferric sulphate (Bratby, 2016). These coagulants are produced mainly from mineral fossils, such as bauxites (Bratby, 2016), however new methods and sources for metal-based coagulants production were developed. For example, coagulant recycle from water treatment sludge (Keeley, Jarvis, & Judd, 2014; Okuda et al., 2014) and application of metal industrial wastes for production of Al- and Fe-containing coagulants (S. Wang, Ang, & Tadé, 2008).

Wide application of metal-based coagulants related to several main factors: suitable chemical properties, simplicity and low-cost of production, the possibility for transportation by major types of vehicles, long-span storage (Bratby, 2016). They can be supplied as a powder, but most frequently they are supplied in a liquid form.

When the metal-based coagulants react with water they produce a wide range of hydroxides with different degree of hydrolysis forming an amorphous precipitate. In neutral and acidic pH products of hydrolysis possess positive charge (pH up to 6 for Al coagulants, pH up to 7 for Fe). Distribution of Al (III) and Fe (III) species in water at different pH are well studied, the summarized graph if presented on the figure 7. pH and temperature strongly affect the efficiency of coagulants presented as inorganic soluble salts. (Jiang & Graham, 1998).

Currently, the field of conventional metal-based coagulants is the most extensively studied among all coagulants and flocculants (Bratby, 2016; Jiang, 2015). Influence of water composition and parameters, such as: pH, temperature, concentrations of colloidal particles, DOC (COD in case of wastewater), ionic strength, presence of specific cations and anions (Ca^{2+}, Mg^{2+}, Cu^{2+}, Mn^{2+}, PO$_4^{3-}$, SO$_4^{2-}$, F$^-$, AsO$_4^-$), as well as operation conditions: coagulant dosing, mixing conditions, retention time, effect of pre-oxidation, were investigated in depth. The results of research and most important conclusions about the chemistry of the metal-based coagulants based on laboratory and industrial scale studies are presented elsewhere (Bratby, 2016). The valuable point that should be outlined is an existence of optimal dosing range for metal-based coagulant – when in a relatively narrow range of coagulant concentration the coagulation occurs effectively. Lower dose results in poor charge screening of negatively charged contaminants, smaller flocs and diminished precipitation rate and hence poor removal efficiency, meanwhile, overdosing cause restabilization of colloidal particles and precipitated hydroxides via recharge of particles which leads to escalation of residual turbidity. Optimal range of concentration can be observed during the coagulation of drinking water and diluted wastewater, since the addition of coagulants to heavily contaminated water instantly results in co-precipitation of metal hydroxides and enmeshed in its amorphous structure colloidal particles and organic molecules. Illustration of the concept of optimal coagulant dose is presented on figure 8.

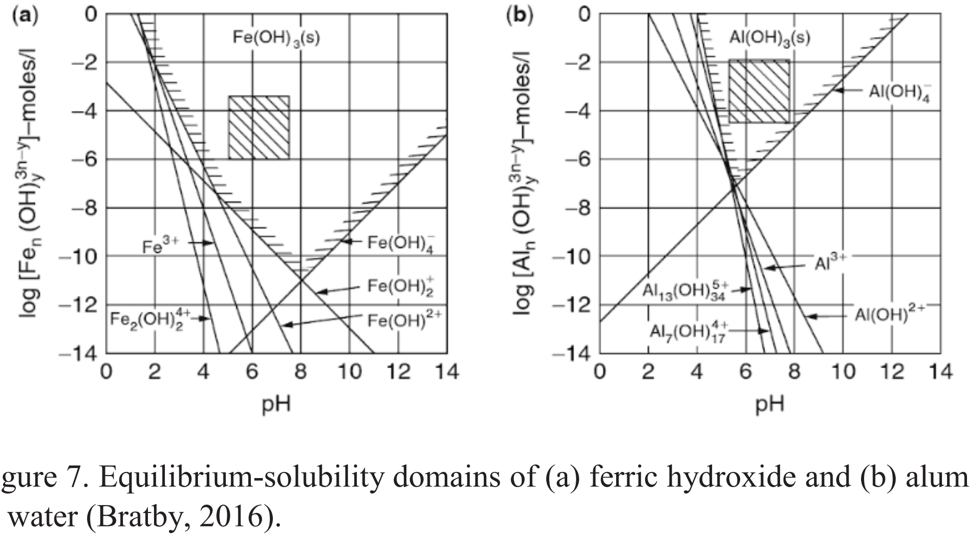


Figure 7. Equilibrium-solubility domains of (a) ferric hydroxide and (b) aluminium hydroxide in water (Bratby, 2016).

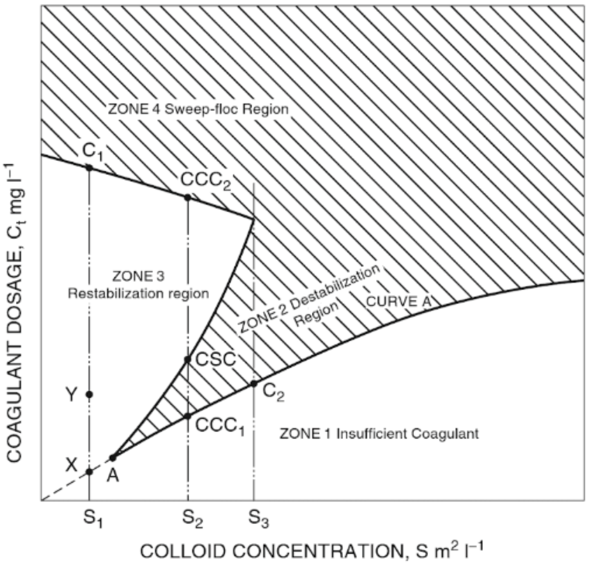


Figure 8. Zones of destabilization and restabilization at certain pH (Bratby, 2016).

Mechanisms of coagulation for metal-based coagulants are deeply investigated. Two mechanisms of prior importance are charge adsorption/neutralization and sweep-floc, to the minor role can be referred double-layer compression (Bratby, 2016). Prevalence of each mechanism strongly dependent on pH, type and concentration of contaminant, a dose of coagulant. Charge adsorption/neutralization mechanism ascribed to process when charged species (ions or molecules) are adsorbed on substances with opposite sign, therefore, reducing the total charge of the agglomerated particle. The sweep-floc or enmeshment mechanism occur when relatively high doses of coagulant are applied so, besides reaction with the negatively charged particle, an excess of the coagulant forms the wide structure of hydroxide in which contaminant become enmeshed and resulting aggregates of hydroxide and enmeshed impurities settle down. The sweep-flock mechanism tends to be dominant in cases when:

- The solution has neutral or alkali pH, so coagulants in water produce neutral hydroxides which rapidly grow forming a wide precipitate network.
- At high coagulant dosages or in case of high contaminant concentration so elevated coagulant dosages should be applied to destabilize the system. Due to high coagulant dosages, hydrolysed salts creates oversaturated solution contributing to the instant formation of large hydroxide flocs in which different sorts of impurities become enmeshed in.
- When the contaminant of interest possesses a neutral or positive charge. In this case, hydrophobic interactions between formed hydroxide network and hydrophobic tails or surfaces of contaminant become more significant. Aggregation of particles occur via co-precipitation or by adsorption on hydroxide surface

With some assumption it is fair to say that in opposite cases of i) acidic pH, ii) low coagulant dose and low water contamination and iii) negatively charged colloids and molecules the charge neutralization plays a dominant role.

Double layer compression cannot be neglected as an important process, but its effect is relatively small in comparison with charge neutralization, however, both occur due to electrostatic interaction. Double-layer compression diminishes the value of effective charge and subsequently repulsion forces. This magnifies the probability of effective particle collision.

Meanwhile, charge adsorption/neutralization screens the charge of colloids completely or locally. An important consequence is that a complete double-layer compression requires a much higher dose of coagulant. Bridging is rather insignificant in case of metal-based coagulants because metal hydroxides are not capable to build long interparticle chains and even in optimal growth conditions formed flocs are very susceptible to breakage. Pre-polymerized inorganic coagulants, on the other hand, possess significantly improved bridging properties.

Metal-based coagulants have a long story of commercial application. They are still commonly applied at municipal WTP and WWTP to remove: colloids, organic substances, microorganisms, phosphates, heavy metals, arsenic, fluorides (Bratby, 2016). To destabilize emulsions and suspensions in petrochemical, grease, pulp and paper industries. Remove organic substances from textile, dye, food and brewery industries, metals and oxides in metallurgy and galvanic industry (Sahu & Chaudhari, 2013). Summarized data is presented in table 3.

Table 3. Removal efficiencies of metal-based coagulants for treatment water and wastewater from different sources

Water source	Coagulant	Optimized removal	Reference
Domestic and municipal wastewater	Polyaluminium chloride (PAC), polyferric sulphate, alum, aluminium chloride, ferric chloride, ferric sulphate, ferrous sulphate	TSS ≥ 90% COD ≥ 70 % BOD ≥ 60% TP ≥ 90%	(Bratby, 2016)
Drinking water	Polyaluminium chloride (PAC), polyferric sulphate, alum, aluminium chloride, ferric chloride, ferric sulphate, ferrous sulphate	Color ≥ 90% NOM (TOC) ≥ 30% Turbidity ≥ 90% Bacteria ≥ 99,9% Viruses ≥ 99%	(Bratby, 2016; Matilainen, Vepsäläinen, & Sillanpää, 2010; Sillanpää, Ncibi, Matilainen, & Vepsäläinen, 2018)
Textile industry	PAC, Alum, ferric chloride, ferric sulphate, ferrous sulphate	Color ≥ 90% COD ≥ 90%	(Sahu & Chaudhari, 2013; Verma, Dash, & Bhunia, 2012)
Dye industry	Alum, ferric chloride, polyferric chloride	Color ≥ 60%	(Lee, Robinson, & Chong, 2014; Sahu & Chaudhari, 2013)
Food industry	Ferrous sulphate, ferric chloride, alum	COD ≥ 70% TSS ≥ 90% TP ≥ 90%	(Sahu & Chaudhari, 2013)
Pulp and paper	(PAC), aluminium chloride, alum	Color ≥ 90% COD ≥80 Turbidity ≥ 90	(Lee et al., 2014; Sahu & Chaudhari, 2013)
Heavy metals containing Industry effluents	Ferric chloride, polyferric sulphate, lime	Zn, Cd, Cu, Mn, Ni ≥ 99%	(Kurniawan, Chan, Lo, & Babel, 2006)

Despite the good performance in many fields and well-studied properties of inorganic coagulants, their use rather seems as unattractive in future callings. First, poor coagulation control and optimization results in high residual metal content, which lead to adverse health effects – the positive correlation between aluminium level in the human body and Alzheimer disease was found. Besides toxicity, residual metal content negatively influences subsequent water disinfection and can precipitate in the distribution network (Choy, Prasad, Wu, Raghunandan, & Ramanan, 2014). Besides, commonly applied coagulation control strategies on municipal water treatment facilities usually are not feasible and/or robust. This frequently results in insufficient treatment in case of underdosing or oppositely to excess dosing at extreme events, such as rains and floods. Meanwhile, advanced control methods whether have not been fully developed yet or require significant funding (Ratnaweera & Fettig, 2015). During treatment with metal-based coagulants, a significant change of pH may occur, which has a detrimental effect on coagulation itself and further treatment (e.g. disinfection), therefore, in many cases, additional pH adjustment procedure is required which leads to additional operational and capital cost.

Some inherent properties of metal-based coagulants cause limitations which cannot be overcome with advanced coagulation control. Conventional coagulants greatly lose their efficiency at cold temperature and much higher dosing is required to achieve equal treatment efficiency at same water composition - temperature drop of 20 degrees may cause doubling of coagulant dose for sufficient treatment (H. Ødegaard, 1992). However, the major concern of inorganic coagulant application is connected to produced chemical sludge. Poor dewaterability of chemical sludge leads to the increased cost of sludge storage and transportation. Slow biodegradation and insignificant nutrient bioavailability provide limited options for sludge reuse and recycle in agriculture (Choy et al., 2014; Oladoja, 2015; Wei, Gao, Ren, Li, & Yang, 2018).

Several efforts were made to increase dewaterability of sludge – a combination of conventional coagulants with polymeric flocculants allows reduction of coagulant dose up to 40-60% with an increase of dry matter content up to 6% in comparison with 1% when just salt applied (Keeley et al., 2014; Volk et al., 2002).

Pre-polymerized coagulants show constantly high removal rates at a wide range of pH and at colder temperatures with the same efficiency to remove dissolved contaminants such as phosphates and heavy metals. Also, they tend to form stronger and bigger flocs, therefore, increasing sedimentation rate (Bratby, 2016; Jiang & Graham, 1998; Zouboulis & Tzoupanos, 2007).

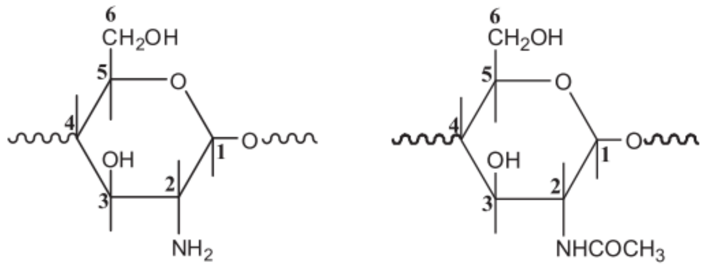
Advances in the field of conventional coagulants also include (Jiang, 2015):

- ballasted coagulation with kaolin, montmorillonite clays which increase settling speed and strength of flocs (Borchate, Kulkarni, Kore, & Kore, 2014);
- application of magnetic composite coagulants (Fe_3O_4–SiO_2) in combination with external magnetic field contributes to rapid settling;
- Application of alternative zirconium and titanium coagulants which possess higher effective positive charge, therefore require less dosing with the possibility of coagulant recovery from precipitated sludge
- electrocoagulation (EC), when metal electrodes under applied current serve as a source of coagulant. During EC, highly charged species are formed together with common hydroxides, for example $Al_8(OH)_{20}^{4+}$, $Al_{13}O_4(OH)_{24}^{7+}$ and $Fe(H_2O)_8(OH)_2^{4+}$. EC enhance destabilization of suspensions and emulsions significantly (Natarajan, Al Fazari, & Al Saadi, 2018; Song et al., 2017).

- simultaneous chemical precipitation – a combination of biological and chemical treatment in one reservoir. To increase sludge flocs aggregation addition of coagulant/flocculant is applied. This strategy increases TSS, COD and dissolved ions removal rates at lower doses of coagulant, meanwhile dewaterability, degradation and nutrient bioavailability of produced sludge remain higher in comparison with chemical sludge. Also, alternative coagulants such as hydroxyapatites and magnesium chloride can be utilized in this process (Ma, Zhang, Xue, & Li, 2018).

2.3.2. Chitosan

Chitosan is a product of alkaline deacetylation of chitin, the second most abundant polymer in the world, after cellulose. Chitin is a building material for protective cuticles of arthropods, crustaceans (shrimps, lobsters, crabs etc.) and in specific stamps of fungi and yeasts (Fabris, Chow, & Drikas, 2010). Chitosan is present in a form of aminosaccharide linear copolymer D-glucosamine and N-acetyl-D-glucosamine. Chitin as itself is insoluble in water, however, chitosan with deacetylation degree (DD) more than 50% can be dissolved in weak acidic solutions pH<6.5 (Bijan Bina, Ebrahimi, & Hesami, 2014).



(a) **(b)**

Figure 9. The chemical structures of chitosan (a) and its precursor chitin (b) (Yang, Li, Huang, Yang, & Li, 2016)

Such advantages of chitosan as high molecular mass, high cationic charge density, solubility in slightly acidic solutions, high dewaterability of sludge after coagulation, biocompatibility and non-toxicity, the ability for natural degradation and low-expense production resulted in the wide use of chitosan in water treatment. Successful application of chitosan was reported in treatment of wastewater contaminated with heavy metals (electrochemical industry), dyes, oil, treatment of effluent from textile industry, food industry, breweries, paper and pulp industry, livestock, treatment of surface water (B Bina, Mehdinejad, Nikaeen, & Attar, 2009; Oladoja, 2015; Renault, Sancey, Badot, & Crini, 2009; W. Pontius, 2016; Yang et al., 2016).

Two inherited properties of chitosan affecting the coagulation and flocculation efficiencies are deacetylation degree (DD) and molecular weight (MW). With the increase of DD cationic charge density also increase resulting in higher adsorption of negatively charged components. However, overall charge density strongly depends on the pH and salinity of the solution. 90% of all chitosan amine groups estimated to be protonated at pH 5 and most amine groups were deprotonated at pH>9 (Li, Jiao, Zhong, Pan, & Ma, 2013). High MW lead to the more extended conformation of the macromolecule and longer polymeric chains that can form chitosan between enmeshed particles (Yang et al., 2016). Generally, the effect of higher DD and MW are synergetic and results in enhanced adsorption and bridging effect, however, coagulation efficiency depends not only the properties of chitosan but on the type of contaminant and external water parameters. Influence of water parameters is discussed in the next paragraph.

Renault presented a very comprehensive review on application of chitosan in water treatment (Renault et al., 2009). Based on numerous researches, main mechanisms involved in chitosan coagulation and flocculation were reported to be charge adsorption/neutralization, bridging, precipitative coagulation and electrostatic patch. Prevalence of certain mechanism was affected by properties of contaminant (polarity and hydrophobicity) and water composition: pH, salinity, the concentration of other impurities. For example high molecular organic compound such as dyes, humic acids and oils mainly reported to be removed by charge neutralization mechanism, so highest removal rates were achieved by chitosan with a high DD in acidic pH, meanwhile change in MW does not significantly influence on removal rate. For bentonite, kaolin clay, bacteria and other charged particles, bridging was reported as a dominant mechanism, therefore main factors affecting removal rates of particulate matter are Molecular Mass of Chitosan and SS concentration. In the case of dominating bridging mechanism, chitosan proved to be efficient in a broad range of pH.

Li and colleagues in their research work (Li et al., 2013) deeply investigated factors influencing mechanism of coagulation and flocculation of chitosan in kaolin suspensions, such as DD and MW of chitosan, pH, salinity and turbidity of raw water. Charge neutralization and bridging were estimated as two major mechanisms responsible for coagulation of chitosan. The extent of each was very dependent on pH: with an increase of pH amine groups become the deprotonated reducing amount of available positively charged adsorption sites hence at pH>9 particle removal occurred mainly due to the bridging mechanism. During coagulation of water with high ionic strength, jar-tests showed the very certain point of optimal dose meanwhile rather a range of optimal doses were observed during coagulation of water with low ionic strength, which implies the importance of a bridging mechanism for water with low salinity and charge-neutralization for water with high salt content. The increase of turbidity shifts predomination of charge neutralization mechanism to bridging since at low particle concentration there is a lower probability of creation of polymeric linkages between particles. Chitosan with high MM improved interparticle bridging resulting in bigger and stronger flocs formed during coagulation. Application of chitosan with higher DD reduced the value of the optimal dose of coagulant, however, the range of optimal dosing also became narrower. These findings were very relevant in later researches and overviews as well (Yang et al., 2016).

Chitosan (and its derivatives) coagulation treatment were successfully implemented in small and industrial scale for numerous contaminants: colloidal particles, heavy metals, dyes, dissolved organic, oil emulsions, humic acids, NOM, bacteria, phosphorus etc. Removal efficiencies for specific contaminants are presented elsewhere (Lürling et al., 2017; Renault et al., 2009; Yang et al., 2016).

Table 4. Removal efficiencies of chitosan for treatment of different types of water and wastewater

Chitosan parameters	Water source	Optimized removal efficiency	Reference
Chitosan	Drinking water treatment	BOD – 35% Color – 80% Turbidity – 93% Total coliform – 80%	(W. Pontius, 2016)
Chitosan (DD=85%)	Drinking water	DOC – 18% Color – 68%	(Fabris et al., 2010)
Chitosan + dissolved air flotation	Food processing industry effluent	SS – 77-82% COD – 46-62%	(Renault et al., 2009)
Chitosan (LMW and HMW)	Vegetable wash-water	Turbidity – 90% Total coliform – 99%	(Van Haute, Uyttendaele, & Sampers, 2015)
Chitosan	Brewery wastewater	TSS – 80% COD – 50%	(Cheng, Chi, Yu, & Lee, 2005)
Chitosan (DD=90%, LMH, MMW, HMW)	Aquaculture wastewater	Turbidity – 88% TSS – 62.6% BOD – 52.3% COD – 62.8% NH3 – 91.8% PO43- – 99.1% Bacteria – 99.998%	(Chung, Li, & Chen, 2005)
Chitosan/CHPATC	Yeast factory effluent	Turbidity – 90% Color – 76.2%	(Momeni, Kahforoushan, Abbasi, & Ghanbarian, 2018)
Chitosan from shrimps industry	Synthetic solutions of heavy metals	Co2+ - 80% Ni2+ - 90% Cu2+ - 95%	(Assaad et al., 2007)
Chitosan of various DD and MW	Bentonite clay solution	Turbidity – 90%	(Li et al., 2013)
Chitosan of various DD and MW	Synthetic solutions of humic acids	Color – 90% UB-absorbance – 60% TOC – 40%	(Yang et al., 2016)
Chitosan of various DD and MW	Synthetic solutions of dyes, humic acids, bentonite clays	Dye removal – 99% Humic acids removal – 95% Turbidity – 90%	(Eric Guibal, Van Vooren, Dempsey, & Roussy, 2006)
Chitosan (LMW and HMW)	Dye solution	Dye removal – 90%	(E. Guibal & Roussy, 2007)
Chitosan + PAM	Dyeing Wastewater	Color – 99%, COD – 90%	(Chen, Sun, & Pan, 2006)

Early research reported poor removal of dissolved organic compounds, dissolved nutrients and not sufficient treatment in case of highly turbid water for application of chitosan as a single coagulant (Fabris et al., 2010; Hu et al., 2013). Therefore, mixtures of chitosan with conventional inorganic coagulants such as alum, ferric sulphate, polymerized aluminium and ferric chlorides were suggested and extensively studied (Hu et al., 2013; Ng et al., 2012; Rozainy, Hasif, Syafalny, Puganeshwary, & Afifi, 2014; W. Pontius, 2016).

Other limitations of chitosan relate to its poor solubility and shielding of protonated amine groups at neutral and alkaline pH, narrow range of optimal dosing, inactive chemical properties. Several methods of chitosan modification were proposed, the most relevant for chitosan-based flocculants are etherification/amination and graft copolymerization (Agbovi & Wilson, 2018; Yang et al., 2016). Modified chitosan allowed to overcome all mentioned limitations and increase charge density and molecular weight resulting in higher charge neutralization abilities and bridging properties (Lu, Xu, Sun, Sun, & Zheng, 2017; Momeni et al., 2018).

3. Materials and methods

To investigate and compare the anti-fouling abilities of inorganic and natural coagulants 3-stage experiment was proposed:

- 1st stage - Jar-tests
- 2nd stage – Recycle tests
- 3rd stage – experiment on continuous installation

Jar-tests are necessary to determine optimal dosages of coagulants and flocculants for effective removal of colloids and organic molecules with subsequent separation of destabilized particles by gravity settling. The optimal dosages determined on this stage of the experiment are supposed to be the starting point for the selection of appropriate dosages during recycle tests and continuous operation at lab installation.

Total recycle tests (TRT) set a goal to determine doses of coagulants and flocculants optimal for reduction of fouling. The TRT is considered as "study in static" since water parameters are not fluctuating during the experiment. Conduction of TRT aims to narrow dose range optimal for fouling mitigation.

Experiment on continuous installation was conducted to imitate industrial processes with fluctuating parameters of water entering the MBR. The experiment was done to evaluate the stability and robustness of MBR performance under the influence of added coagulant/flocculant over long time run.

3.1. Jar-tests

Jar-tests were performed using Kemira 2000 programmable flocculator. 6 mixers were connected to the programmable controller, so simultaneously 6 dosages of coagulants/flocculants could be tested. Samples of water were taken from the biological treatment stage at installation described in section 2.3. Each sample with a volume of 1 l was poured in glass beakers in which mixers were inserted. Jar-tests involved 3 step procedure: fast mixing (400 rpm) with a duration of 60 sec, slow mixing (30 rpm) for 10 min and settling (no mixing) for 20 min. After the end of the sedimentation step, samples from beakers were extracted using a plastic syringe (vol. 100 ml) and placed in glass bottles. Correction of pH was established by addition of NaOH (2M) solution. The volume of base solution for each dose was empirically estimated during pre-tests, pH was maintained at a level between 6-7. Jar-tests for each dose were performed in 2 replicas for validation. All samples were analyzed for the next parameters: pH, SS, Turbidity, Zeta potential, TOD total, TOD filtered, PO_4^{3-}, Total Phosphorus.

3.2. Total Recycle Test (TRT)

TRT test was partly performed in a rectangular plastic tank with a volume of 8 l. The tank was equipped with blowers on the bottom to simulate turbulence of water near the membrane surface as in real treatment plants. Tested membranes were set inside the reactor and connected to a peristaltic pump. Filtration was performed in dead-end mode and permeate after filtration was returned to membrane tank. Between pump and membrane outlet digital manometer with an accuracy of 0.1% was installed. The manometer was connected to data-logger which allowed to save measured TMP data on PC. Flux was maintained at a level of 50 LMH. After a test with each dose, the membrane was chemically cleaned with NaClO (0.5%) to ensure equal start conditions for each run.

Coagulants/flocculants and pH adjusting reagent were added instantly at the beginning of the test. Then, 60-sec delay was held to provide time for mixing with water before filtration starts. Filtration was performed until TMP reached -25 kPa. Then, samples were taken by plastic syringe (vol. 100 ml) and tested for the same parameters as in Jar-tests, namely: pH, SS, Turbidity, Zeta potential, TOD total, TOD filtered, PO_4^{3-}, Total Phosphorus.

Later, to avoid the transfer of membranes between facilities, TRT was performed directly in installation described in section 2.3 with the only difference that permeate after the filtration was returned to MBR instead of discharging to the sewer.

3.3. Tests in continuous mode

For the Master research IFAS-MBR installation that imitates treatment of real wastewater was assembled. The principal drawing of installation is presented in figure 2. First raw wastewater from the sewer is collected in equalization tank (RAW WATER on the figure), then by peristaltic pump water is directed to aeration tank filled with plastic beads which imitate IFAS treatment system (Aeration tank on the figure). Activated sludge for biological water treatment was taken from Bekkelaget wastewater treatment plant (Oslo, Norway). Water after biological treatment step was split into three different lines. Line 1 (blue rectangle on the figure) played the role of control line – conventional coagulant aluminium sulfate $Al_2(SO_4)_3$ was applied to serve as the reference of fouling mitigation reagent. Line 2 (green rectangle) was used to test natural flocculant (chitosan). And in the Line 3 electrocoagulation unit with tubular electrodes was integrated. Therefore, each line included chemical (electrochemical) pre-treatment of water entering to the bioreactor. Line 1 and Line 2 were equipped with inlet mixers – to provide equal distribution of reagent in the flow; and tubular flocculators - to create conditions for steady mixing and floc development. Coagulant, flocculant and pH adjusting reagent were dosed by peristaltic pumps. For the Line 1 correction of pH was provided in the form of addition of sodium hydroxide. Then, in MBRs sludge was separated and periodically discharged via solenoid valves installed at the bottom of each reactor. Filtrated water was collected in intermediate tanks before discharged to the sewer. Sludge was also stored in a collection tank (not shown at the figure) and partially returned to the aeration unit to maintain MLSS concentration in Aeration tank. Rest of sludge was discharged to the sewer.

Before start testing anti-fouling abilities of coagulant and flocculant, overall system performance was evaluated. Water parameters were measured every 2 days operating system for 1 week to check the performance stability of each unit. The lowest doses of coagulant and flocculant were applied during the evaluation test.

Tests with different coagulants doses were performed 15-24 h for each dose. When the run with certain dose was over, the membrane underwent CIP, which procedure is described in section 2.3.3. Overall system's parameters are provided in table 5. Calculation of parameters and reasoning behind variable adoption are provided in Appendix A.

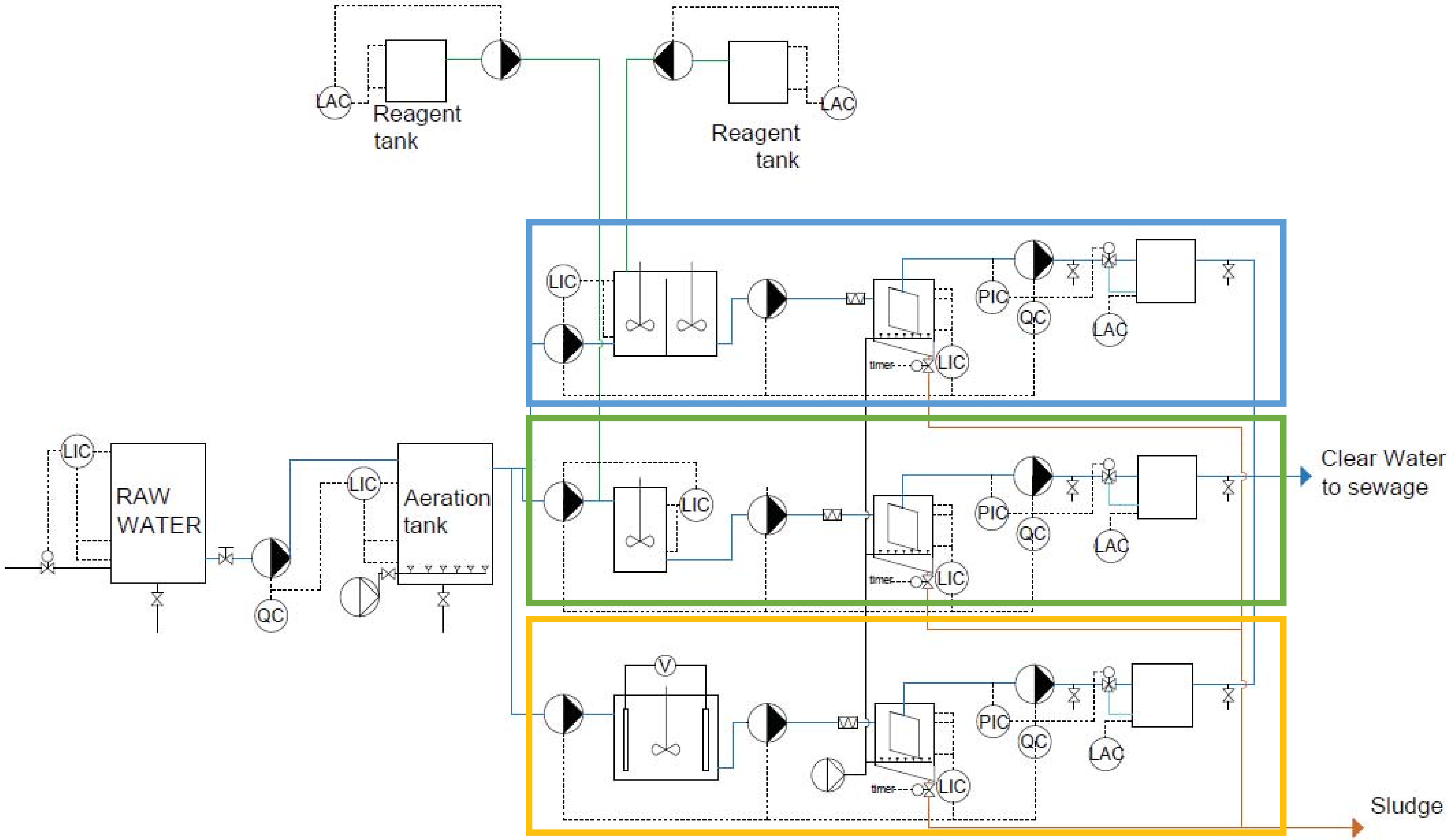


Figure 10. Principle drawing of experimental installation for tests in continuous mode.

A) B)

Figure 11. Pictures of assembled installation. A) Front view; B) Side view.

Table 5. Parameters of experimental system for continuous operation.

Parameter	Value
Operating flux (for each Line), LMH	50
Ratio of operational volume to effective membrane surface in MBR, m	0,05
Gross Flow through 1 MBR, l/h	3.15 (52.5 ml/min)
Net Flow through 1 MBR, l/h	2.076 (34.6 ml/min)
Max Total Gross Flow, l/h	9.45 (157.5 ml/min)
Max Total Net Flow, l/h	6.23 (103.8 ml/min)
Total HRT, h	19.3
Aeration tank	
Total volume, l	195
Operational volume, l	148.2
HRT, h	15.7
Filling ratio	60%
Flocculating tubes	
Volume, l	0.86
Tube inner diameter, mm	10
Tube length, m	10
HRT, min	15
Water linear velocity, cm/s	1.114
Number of turns in the tube coil	24.5
The diameter of one tube turn, cm	12
G-value, s^{-1}	5.8
Reynolds value (Re)	38.75
MBR	
Volume, l	4.41
Membrane area, m^2	0.063
HRT, h	1.4
Filtration time, sec	300
Relaxation 1 time, sec	30
Backwash time, sec	20
Relaxation 2 time, sec	60
Filtration flux, LMH	50
Backwash flux, LMH	75
Filtration flow, ml/min	52.5

To establish control over the installation and create the possibility for automatic operation, a special control unit was created on the basis of Siemens PLC (S7-1200). The created unit allowed to directly control: valves position (Open/Closed); pumps start/stop, speed and rotation direction; and monitor: pressure sensors and level switches. Interaction between user and PLC was provided through sensor panel HMI KTP700 (Siemens).

3.3.1. Raw water withdrawal

Raw water was pumped out from sewer channel leading from NMBU's Sørhellinga library. A significant issue for water withdrawal was the low level of wastewater flow in the sewer. This factor limited the possibility of water suction only to periods of high water loading. To overcome this temporary movable barrier was installed in the channel, resulting in water level increase up to 15-20 cm. Installation of such barrier was followed by another issue - clogging of suction pipe with paper and solid sediments which also posed a threat for normal pump operation. Thus, additional barrier before the suction pipe was installed which blocked paper and heavy solids coming into suction pipe. Also, an inlet of pipe was equipped with double sieving system. The withdrawal was done using jet-pump 800W 3.6 m^3/h (Biltema, Norway).

3.3.2. Reagents for filtration tests

To conduct filtration tests, coagulants and flocculants were prepared by dilution of standard products. This was done since the resolution of dosing pumps were not high enough to dose concentrated product obtained directly from suppliers. Aluminium coagulant was prepared by dissolution of ALS coagulant (Kemira, Finland) in 10 times and acidification it with concentrated sulfuric acid H_2SO_4 (Merck, Germany) to pH 1.9. Chitosan flocculant was prepared by step dissolution of powder product to a concentration of 2 g/l. Solubilization of chitosan was achieved by the addition of concentrated hydrochloric acid HCl (Merck, Germany). Total solubilization of chitosan was reached only at the point of pH 1.4, therefore, the pH of the working solution was also maintained at 1.4. Since only one pump (with multiline head) was used for dosing of aluminium coagulant and sodium hydroxide in Line 1, pH adjusting was performed proportionally to flow of coagulant solution. Preliminary tests showed that for the range of doses 1.0-2.0 mmol-Al/l concentration of 0.5 M NaOH was optimal to keep pH during coagulation in range 6-7. The preparation procedure of reagents for filtration tests is shown in table 6.

Table 6. Recipes of reagents for filtration tests.

Reagent	Raw material	Volume of working solution, l	Volume of pH adjusting reagent	Final pH
Working solution – aluminium coagulant (5.68 g-Al/l)	ALS – 100 ml	1	2 ml of H2SO4 conc.	1.9
NaOH 0.5 M	NaOH pow. -20 g	1		
Chitosan Stock solution (10 g/l)	Chitosan - 5 g	0.5	4 ml of HCl conc.	1.4
Chitosan working solution (2 g/l)	Chitosan stock sol. – 200 ml	1	2.72 ml of HCl conc.	1.4

3.3.3. Working protocol for filtration tests and CIP

Each run on the installation was performed following the next procedure.

1) The tested membrane is placed in the clean MBR tank.
2) Set up of filtration parameters: duration of stages, flows of wastewater, BW, the flow of coagulant/flocculant.
3) Filling the MBR tank with wastewater after coagulation/flocculation to level when water covers whole membrane surface – controlled by level-switch in MBR.

4) Filtration cycle run for 15-24 h.
5) After 18-24 h filtration run is stopped.
6) Samples are taken from Raw Water tank, Aeration Tank, MBRs, Permeate tanks.
7) All mixed liquor from MBRs is discharged to the sludge collection tank.
8) Recycle of sludge from collection tank to inlet of IFAS treatment step.

After every filtration run, cleaning-in-place (CIP) was performed. CIP followed the next steps:

1) Backwashing with tap water. When MBR is empty BW is started with tap water or water from permeate tank maintaining flux 1.5 times higher than flux at filtration. BW is performed until the water reaches the upper edge of the membrane – controlled by a level switch in MBR.
2) Then, the membrane is left to soak in the water for 2 hours in order to remove the cake layer on the membrane. Later water is discharged from tank to sewer. The direction of discharge – to a collection tank or to sewer, was controlled by manual valves.
3) Backwashing with the oxidant. For this, tube after the peristaltic pump is disconnected from the permeate tank and connected to a temporary portable tank filled with 0.5% NaClO. BW is started maintaining flux of 1.5xFiltration Flux. Again, BW is performed until the water level in the tank reaches the top of the membrane.
4) The membrane is left to soak in the oxidant solution for 2 hours to dissolve remains of the cake layer on the membrane. Then, the solution is discharged to the sewer. MBR and membrane are washed with tap water several times.
5) If even after CIP some cake stains are observed on the membrane surface – it was removed from the tank and scraped with a soft brush.
6) Tube after the peristaltic pump is connected back to permeate tank.
7) Continue with filtration tests.

3.3.4. Data acquisition and processing

Data from digital manometers were collected in two ways. The first approach was based on the utilization of PLC internal memory which allows saving data with a limit up to 5 MB. The special data-logging algorithm was created for Siemens PLS and TMP was registered and saved every 30 sec. Later the data was transferred to PC through PROFINET connection.

The second approach was designed by PhD student at REALTEK Abhilash Nair. The approach is based on the remote control of PLC by Raspberry Pi PC via PROFINET and recording data from PLC in PC's memory. Pi was also connected to university Wi-Fi, therefore providing the possibility of remote control and monitoring of PLC and installation trough "VNC viewer" software. To read and save data from PLS on PC special algorithm was created based on Python. Since Pi has significantly bigger memory reserve, TMP was recorded every 5 sec.

Peristaltic pumps due to their construction are known to create sinusoidal pressure trend over time. Such feature produces a considerable noise in obtained data. To filter this noise Fitting Curve Toolbox in MATLAB was utilized (MathWorks, 2019). Smoothing of data was performed according to moving average filter (Booth, Mount, & Viers, 2006). Comparison of filtered and unfiltered data is presented in figure 12.

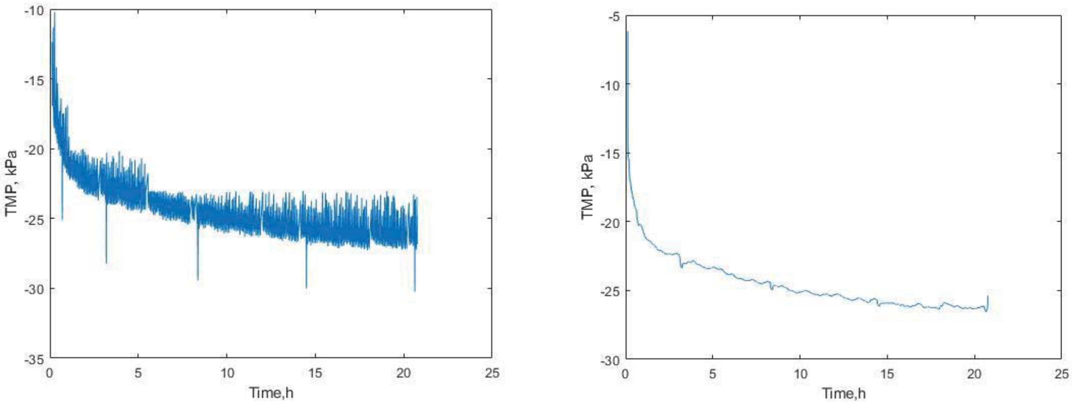


Figure 12. Example of mean average filtration for fluctuating TMP.

3.4. Analytical procedures

3.4.1. pH

pH was measured directly in sample bottles by portable pH-meter with a glass electrode (Metler Toledo, Spain). The final value was registered when the pH remained still for 1 minute.

3.4.2. Suspended solids and turbidity measurements.

Turbidity was measured by standard technic on portable turbidimeter 2100Q (Hach, USA). Analysis for Total suspended solids was performed according to standard procedure ISO 11923:1997. 50- or a 25-ml aliquot of the sample (dependently on measured turbidity) was filtered through the paper filter with 0.45 µm pores. The filter paper was preliminarily weighted on analytical balances (Metler Toledo, Spain) with ±0.0001 g resolution before filtration. Then, the filter was placed in the oven at a temperature of 105° C for 1 hour to remove all water from it, afterwards, the filter was placed in a desiccator to let it cool to room temperature. After some time, filter paper with captured solids was weighed again and the difference in measured mass of initial and filter paper after filtration provide information of suspended solids in the sample. The TSS value was calculated using the formula:

$$TSS = \frac{m_{fin.filt} - m_{in.filt}}{V_{aliq}} \left(\frac{mg}{l}\right);$$

Where $m_{fin.filt}$ – is a mass of a filter after filtration and drying, mg; $m_{in.filt}$ – is a mass of initial filter paper before filtration, mg; V_{aliq} – the volume of aliquot, l.

3.4.3. Phosphates measurement

Measurement of phosphorus is based on standard colorimetric analysis originally proposed by USEPA Method 365.1 Reference (Section 16.1) utilized by Systea EasyChem analyzer (Spain).

Table 7. Reagents and their volume for colorimetric analysis of phosphates.

Reagent	Concentration	Volume, µl
Sample	-	100
Sulfuric acid H_2SO_4	5N	71,4
Ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	40 g/l	21,4
Antimony potassium tartrate $K(SbO)C_4H_4O_6$	3 g/l	7,2
Ascorbic acid $C_6H_8O_6$	18 g/l	400

Reagents used for analysis and their characteristics are listed in table 7. Before analysis samples were prefiltered on 0.45 µm glass-fibre filter.

Ammonium molybdate and antimony potassium tartrate form with PO_4^{3-} ions antimony-1,2-phosphorous molybdenum acid. Afterwards, ascorbic acid is applied to reduce this salt of polyphosphoric acid to lower hetero-polyacid (molybdenum blue) with intensive blue color which optical density measured on 880 nm light filter.

3.4.4. Total Phosphorus measurement

For total phosphorus measurement, 2.5 ml of each sample was digested in an autoclave with potassium persulfate ($K_2S_2O_8$, 5%, 3 ml) and concentrated sulfuric acid (H_2SO_4, 95-97%, 75 µl). Digestion was performed in firmly closed glass tubes in electric oven Hach Lange at 120 °C for 30 minutes. The concentration of phosphorus in digested samples was measured applying the technique described in section 3.4.3. In the end, the concentration was recalculated to make a correction on dilution with persulfate and sulfuric acid solutions.

$$TP = PO_4^{3-} \cdot \frac{5.575}{2.5};$$

Where TP – total phosphorus concentration, mg-P/l, PO_4^{3-} - measured colorimetrically dissolved phosphorus concentration in samples after digestion, mg-P/l.

3.4.5. Ammonia measurement

Measurement of ammonia ions is based on standard procedure USEPA Method 350.1 performed on Systea EasyChem analyzer (Spain).

Table 8. Reagents and their volume for colorimetric analysis of ammonia.

Reagent	Concentration	Volume, µl
Sample	-	30
EDTA	15 g/l	180
Nitroferricyanide ($Na_2[Fe(CN)_5NO]\cdot 2H_2O$)	0.2 g/l	240
Sodium Phenoxide ($NaOC_6H_5$)	45 g/l	90
Sodium Hydrogen Carbonate $NaHCO_3$	8.25 g/l	90
Sodium Hypochlorite NaClO	2%	80

Table 8 contains concentration and volume of reagents added to each sample. Optical density was measured at 670 nm light filter. Samples were pre-filtered on 0.45 µm glass-fibre filters.

3.4.6. Zeta potential measurement

Zeta potential (ζ) was measured by special instrument Malvern Zetasizer Nano (United Kingdom). The principle of the analysis can be described as measuring the difference between incident and scattered light of a laser beam which passed through the cuvette with the sample. This special cuvette has built-in electrodes, through which electrical current is applied to the cuvette with the sample. Charged particles start to move with the speed of electrophoretic mobility that connected to zeta potential by Henry's equation.

3.4.7. Total oxygen demand (TOD) measurement

TOD analysis was performed on QuickCODlab instrument (LAR, Germany). The analysis is based on combustion of the sample at the temperature of 1200 ºC and measuring the drop of oxygen concentration in combusted air flow by the gas sensor.

Measurement of TOD was performed as an equivalent for COD, but comparable to standard COD measurement, which requires toxic and carcinogenic chemicals, TOD analysis is reagent-free and therefore eco-friendlier. Still, a strong correlation between COD with chromate method and TOD exists.

3.4.8. Polyelectrolyte titration

To estimate charge (equiv./l) of chitosan applied for aggregation, polyelectrolyte titration in the streaming current cell was utilized. Special instrument Particle Charge Analyzer (Micrometrix, USA) was applied to measure streaming potential during titration to determine the endpoint of zero charge. Titration was performed on 1 mg/l solution of chitosan 3 times with 0.0005 N solution of PVSK as a titrant. Results of titration are presented in Appendix B.

Charge of chitosan was calculated according to the formula:

$$Charge\left(\frac{equiv.}{g}\right)=\frac{AP}{V\cdot C}\cdot N$$

Where: AP – the volume of anionic PVSK (ml);

V – volume of test sample (ml);

C – concentration of test sample (g/l);

N – Normality of PVSK.

4. Results and discussions

4.1. Raw water parameters

Composition of raw wastewater and range of parameters' fluctuation is presented in table 9.

Table 9. Averaged parameters of raw water monitored over the time of experiment run.

Parameter	pH	Turbidity, NTU	TSS, mg/l	PO_4^{3-}, mg-P/l	TP, mg-P/l	NH_4^+, mg-N/l	tTOD, mg/l	fTOD, mg/l	Zeta, mV
Value	7.92 ±0.5	64.8 ±22.5	82.4 ±34.4	10.2 ±0.4	12.5 ±0.6	48.3 ±7.2	345.3 ±115.8	227.8 ±87.6	-15.7 ±2.76

Generally, water composition represents typical values of municipal wastewater, with a high fraction of soluble organic matter in the total amount of organics (Ødegaard, 1999). Low solid content can be explained by the design of a system for wastewater withdrawal and fact that wastewater first was collected in the collection tank, where solids had the possibility to settle down in stagnant zones.

4.2. Jar tests.

Jar tests were performed for 6 doses (2 replicas for each) of ALS coagulant in the range from 0.25-1.5 mmol-Al/l with the step of 0.25 mmol-Al/l. Two sets of jar-tests were performed – with and without pH correction prior to the addition of coagulant. Water parameters of supernatant such as turbidity and phosphate concentration are presented in figure 13. Removal of turbidity is not changed significantly with pre-adjusted pH. However, phosphates removal is significantly improved when pH correction is implemented. This corresponds with higher solubility of aluminium phosphate at acidic pHs (Bratby, 2016). This observation has led to setting up additional dosing point for the addition of pH correction reagent in continuous installation because in the original design of installation pH adjusting was not foreseen.

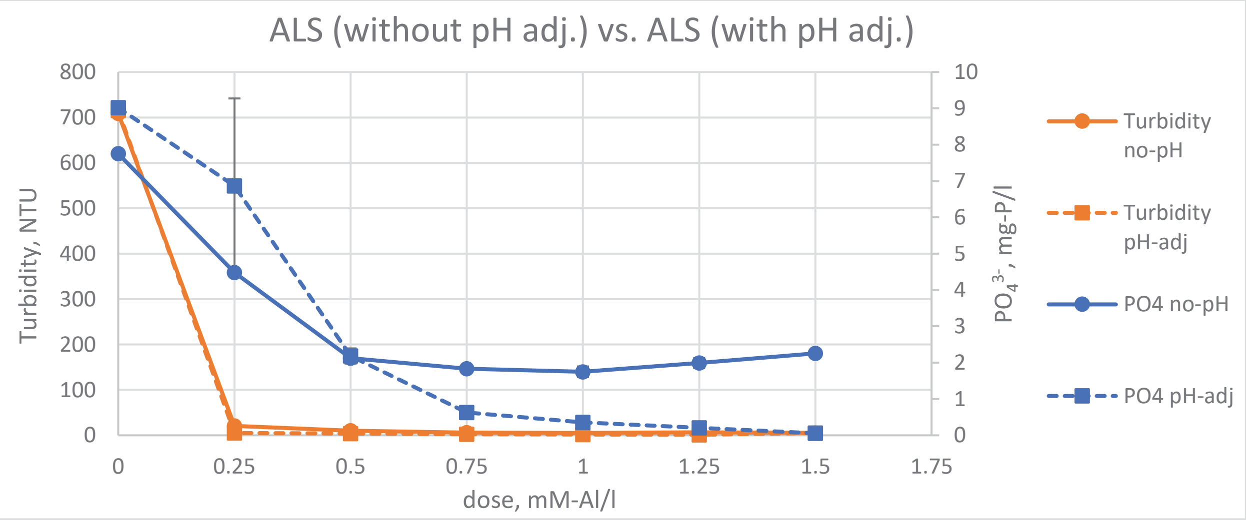


Figure 13. Comparison of turbidity and phosphates concentration in the supernatant after jar tests with and without prior pH correction.

Values of supernatant's Zeta potential and pH during coagulation is presented in figure 14. It is clear that without pre-adjusting pH Zeta potential growths with increasing of coagulant dose, which implies the importance of charge adsorption-neutralization mechanism at low pH. However, with pH correction, Zeta potential with growing dose remained far beyond an isoelectric point, which may be interpreted as the dominance of enmeshment mechanism at neutral pHs.

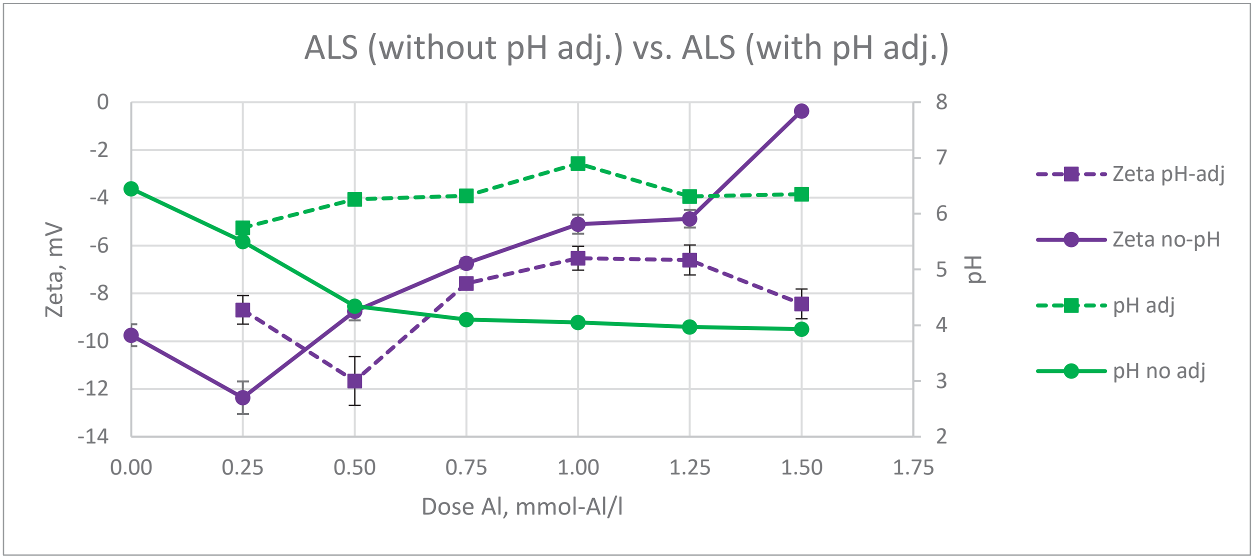


Figure 14. The dependency of supernatant's Zeta potential and pH during coagulation from coagulant dose during jar-tests with and without pH adjustment.

Since 90% phosphates removal is reached at higher doses than turbidity removal, the optimal dose for aluminium coagulant was set at the first dose where 90% phosphorus removal was achieved – 1.0 mmol-Al/l (27 mg-Al/l).

Jar-tests were performed as well for two chitosan flocculants: with high molecular weight (CHW) and moderate molecular weight (CMW). Next doses of flocculants were tested (mg/l): 0.1, 0.25, 0.5, 0.75, 1, 5, 10, 15, 20, 25, 30. Such a wide range of doses was applied to determine the lowest possible applied dose to achieve high turbidity removal, since it is not possible to determine for optimal phosphorus removal. Chitosan flocculants have no influence on phosphorus removal. Stable high turbidity removal efficiency was achieved at a dose of 1 mg/l for both flocculants, however, to be on the safe side during the tests at the continuously operated installation, the optimal dose was set at 5 mg/l for chitosan flocculants.

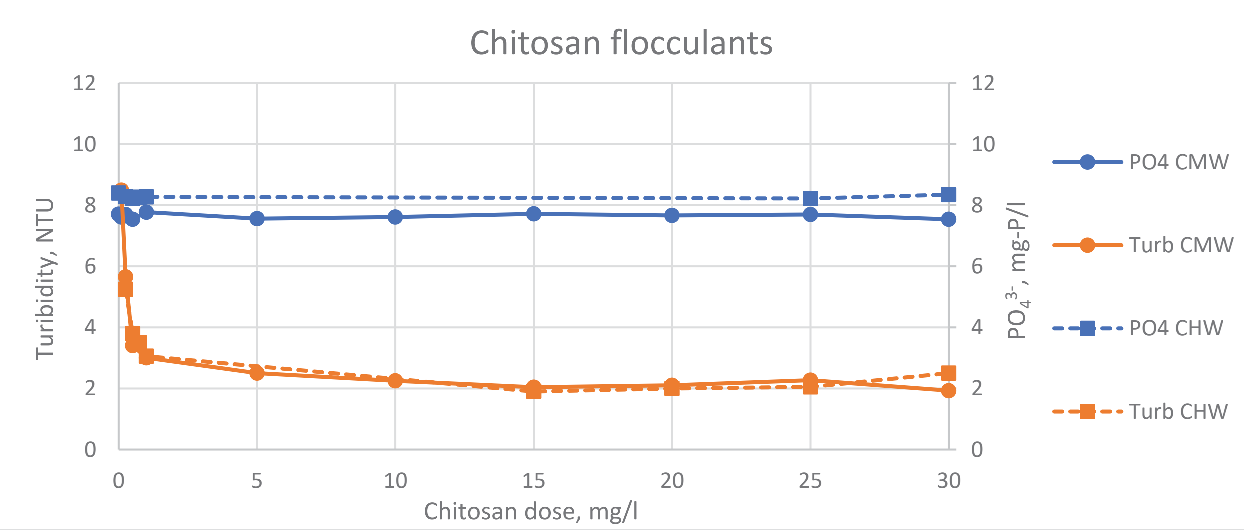


Figure 15. Turbidity and phosphates concentration in the supernatant after jar-tests with chitosan flocculants. (Turbidity of raw water – 582 NTU).

On figure 16 presented data about pH during flocculation with chitosan and Zeta potential of supernatant. As expected, chitosan does not influence pH during flocculation, since no hydrolysis occurs. However, Zeta potential increase with dosage increase and reach an isoelectric point at doses of 25-30 mg/l. Since optimal removal of particles occurs already at doses of 1 mg/l it implies to the fact that bridging mechanism is dominant for flocculation with chitosan, however, charge neutralization also takes place especially at high chitosan doses. Also, CHW reach the point of zero-potential at lower doses than CMW, which implies higher charge density of CHW.

For further tests on CMW was used since its solution is less vicious therefore simpler for handling and dilution.

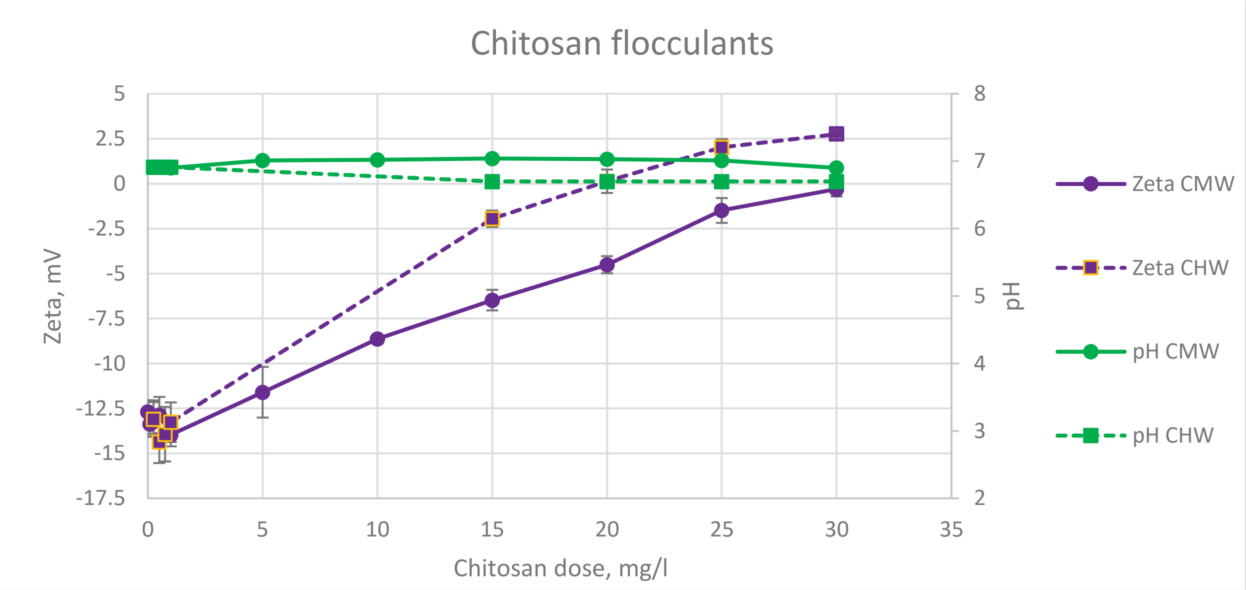


Figure 16. Zeta potential of supernatant and pH during flocculation with chitosan.

4.3. Total Recycle Test

Recycle tests were performed for 3 doses of ALS: 1 mmol-Al/l, 2 mmol-Al/l, 3 mmol-Al/l; and 3 doses of Chitosan: 5 mg/l, 10 mg/l, 15 mg/l. The doses for TRT were selected based on the principle of optimal dose from jar-tests and its doubled and tripled concentration. The results of recycling tests are presented on figure

A clear trend for aluminium coagulant is the increase of aluminium concentration positively influence on fouling mitigation. Addition of ALS reduced the drop of TMP over time and increased filtration time: filtration time at a dose of 2.0 mmol-Al/l is almost double of filtration time without the addition of coagulant. The TMP drop curves for water filtration with addition of 2.0 mmol-Al/l and 3.0 mmol-Al/l are very similar, so we assumed that at dose of 2 mmol/l the highest fouling reduction already occurs. So, for further tests at the continuous installation, ALS dose was limited to a range of 1.0-2.0 mmol-Al/l.

However, antifouling abilities are not so clear for chitosan. At a low dose of 5 mg/l chitosan possesses an antagonistic influence on membrane fouling since filtration time is significantly reduced. With the further increase of chitosan concentration, filtration time increases and at a dose of 15 mg/l slight fouling improvement can be observed. Due to such controversy, it was decided to test a wider range of chitosan doses at continuous installation to find if chitosan can be applied as fouling mitigation reagent. The dose range was widened to 5-

25 mg/l, further range increase was considered as unnecessary since there is no chance that it will be economically feasible to apply at real treatment stations such high doses.

The chemical parameters of water in MBR and permeate during TRT are presented in Appendix C.

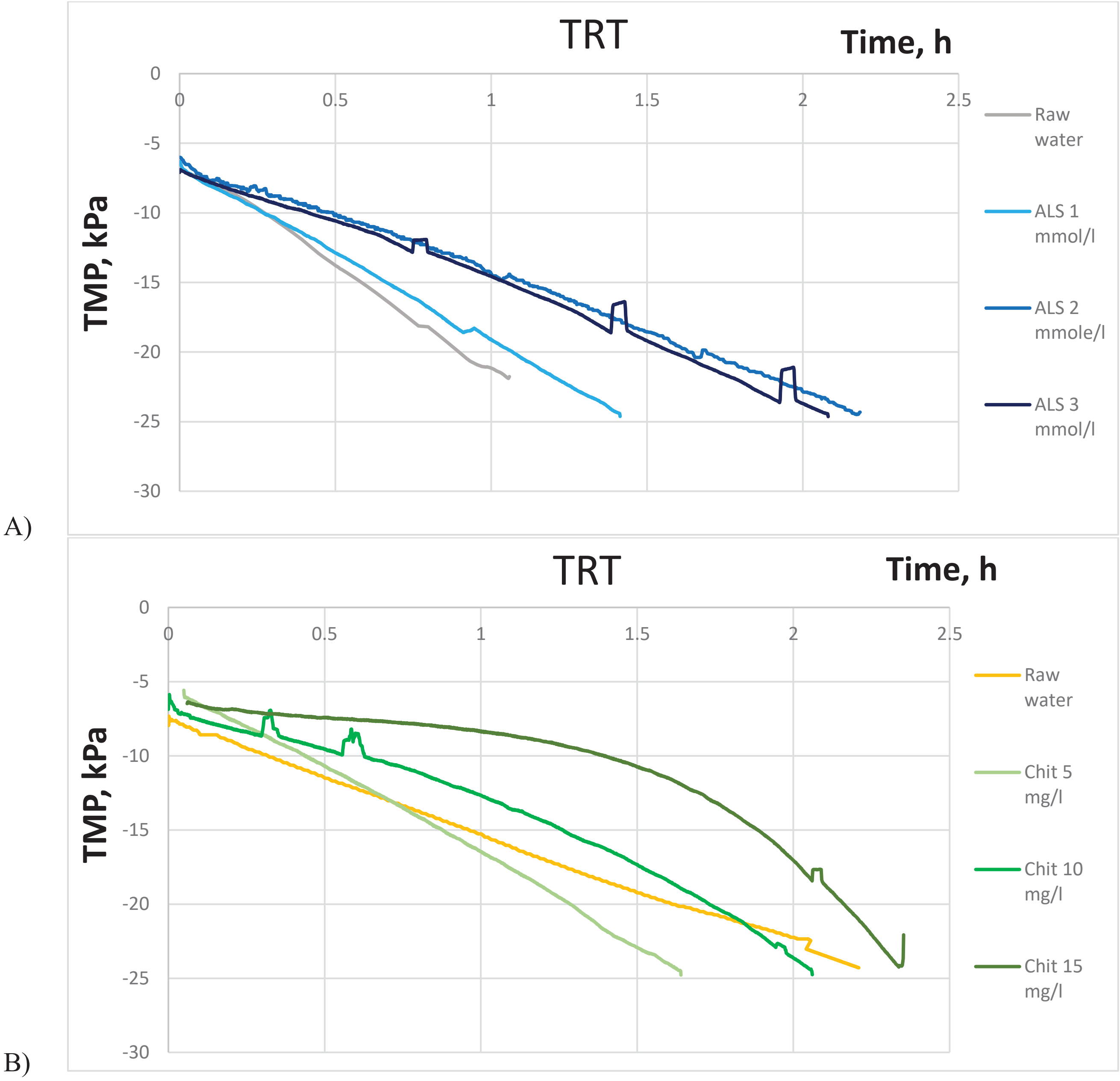
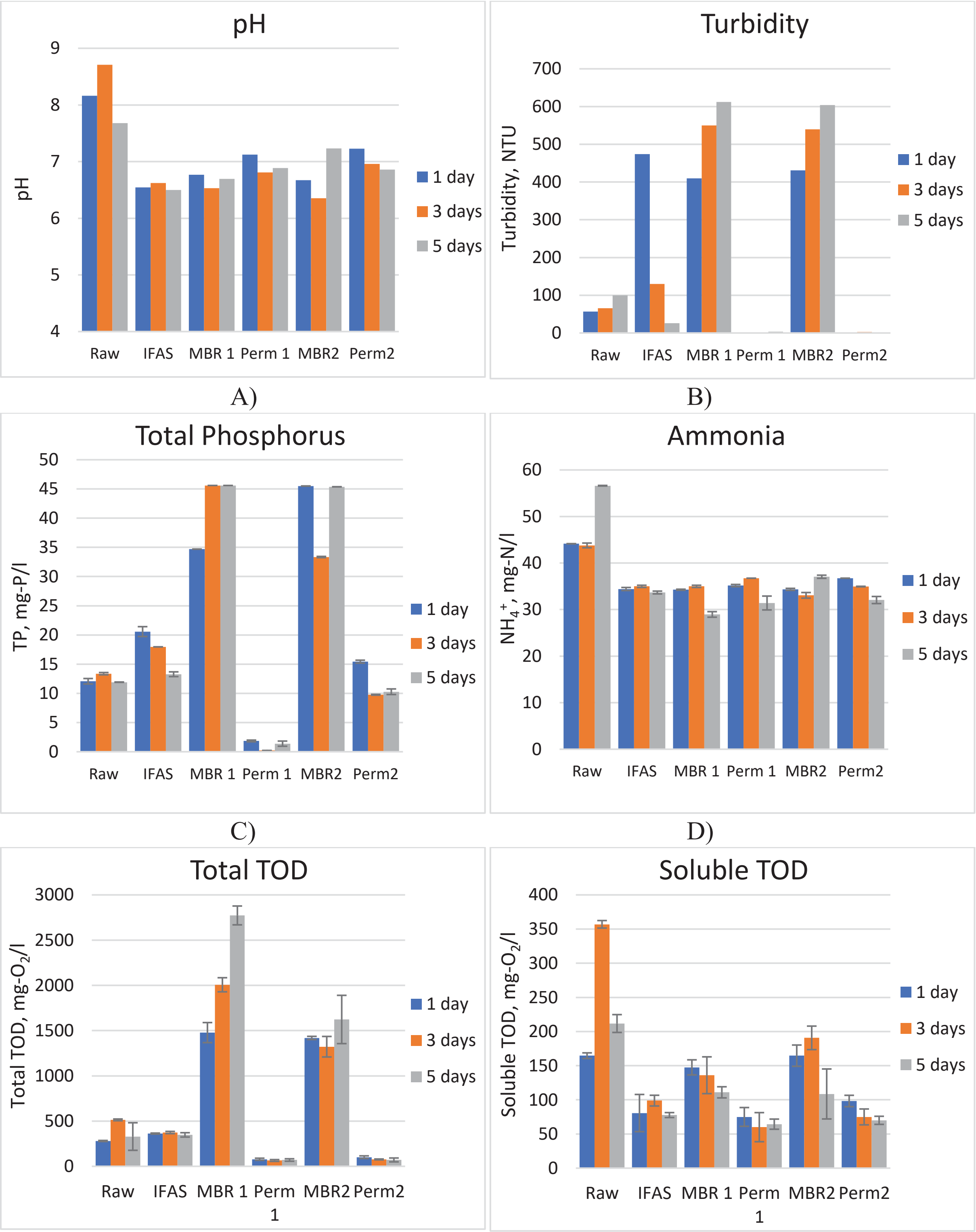


Figure 17. Increase of TMP over time during TRT with different doses of A) ALS coagulant B) Chitosan.

4.4. Tests on continuous installation.

Before starting continuous operation, activated sludge from Bekkelaget wastewater treatment plant was left for adaptation in the aerated tank for 2-3 weeks. Exhausted water was discharged and fresh raw water was supplied every 3 days to keep TOD and nutrient concentration on the same level in the aeration tank.

After 2-3 weeks of sludge adaptation, experiments were started on the installation first with TRT tests and then shifting to continuous tests. Another 2 weeks were spent to optimize operational parameters, such as the timing of filtration cycle, sludge discharge, flux and improve automated control algorithm. Overall performance of the system after all commissioning work is presented in figure 18. The trial run of the system was performed applying the lowest doses of coagulant and flocculant – 1 mmol-Al/l ALS and 5 mg/l of chitosan.



A) B)

C) D)

E) F)

Figure 18. Monitoring of system performance over 5 days after first commissioning. Change of A) pH; B) Turbidity; C) Total Phosphorus D) Ammonia; E) Total TOD; F) Soluble TOD.

After 3 days of operation, the system reached stable operating conditions, such conclusion was derived from stable pH, phosphorus and ammonia concentrations in aeration tanks and MBRs and stable removal of organic matter. Accumulation of suspended solids and organic matter in MBRs is visible on the graphs. This issue was later solved by more frequent sludge discharge. Table 10 contains data about total removal efficiency of pollutants after each stage on the 5th day of operation.

However, removal of ammonia was not so high as expected (only 40% to expected >60%), still system was working stably in terms of removal, achieving good treatment efficiency for the rest of parameters.

Table 10. Total removal efficiency after each stage of treatment.

Parameter	Turbidity, NTU	TSS, mg/l	PO_4^{3-}, mg-P/l	TP, mg-P/l	NH_4^+, mg-N/l	tTOD, mg/l	fTOD, mg/l
IFAS	-	-	10-20%	15-20%	20-40%	-	60-80%
MBR1 (ALS)	>98%	>98%	>95%	>90%	35-50%	70-90%	70-90%
MBR2 (Chitosan)	>98%	>98%	10-20%	15-30%	35-50%	70-90%	60-80%

After stability of system performance was confirmed, tests with variating of chemicals' dose started. Finalized results of membrane separation tests in continuous operation mode at different doses of chemicals are presented on figures 19 and 20.

Clearly seen that the addition of aluminium sulfate negatively affects fouling rate – increasing concentration of coagulant successfully reduce fouling and TMP increase rate reaches lowest values already at doses of 1.4-1.6 mmol/l. TMP increase curves at doses of 1.0-1.2 mmol/l show transition process when not all foulants are effectively neutralized and agglomerated, therefore they adhere to membrane surface contributing to irreversible fouling.

Influence of chitosan on membrane fouling is controversial, which is consistent with observations from TRT tests. Low doses of chitosan (5 mg/l and 10 mg/l) significantly deteriorate membrane performance leading to a significant increase in TMP already after 2 h of operation. Further increase of dose, however, has a positive impact on filtration performance. At doses higher than 15 mg/l TMP growth is decelerated, whereas at doses of 20-25 mg/l effective fouling reduction occurs.

Such controversy can be commonly found on the ground of chitosan application in MBR. Meanwhile, all reports are consistent on excellent aggregation abilities of chitosan, difference in estimated fouling mitigation abilities was found. Some studies outline 6.7 times improvement in filtration time with chitosan addition (Ji et al., 2010), other claim decrease of permeability and higher TMP during filtration (Koseoglu et al., 2012), the rest report no effect of critical flux with low fouling mitigation properties (Iversen, 2010).

Koseoglu et al. (2012) reported a 10% increase of mean TMP and 6% increased fouling at low doses of chitosan. They explained low anti-fouling efficiency through the poor ability to remove SMP and proteins, however, the reason for increased fouling at low doses was not clearly discussed. At higher doses of chitosan, enhanced fouling mitigation was observed, however with lower permeability ad higher mean TMP.

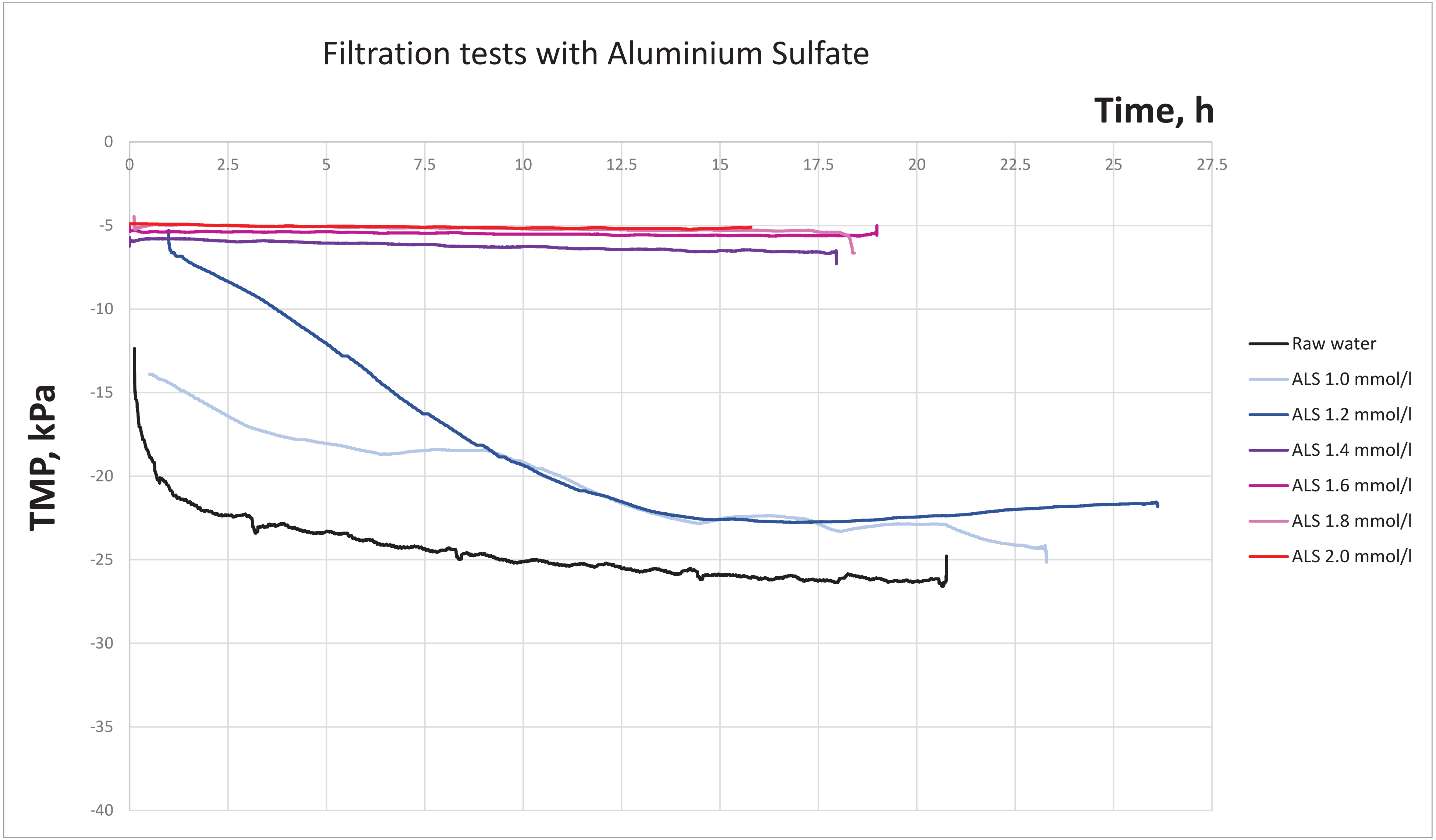


Figure 19. TMP increase over time during filtration tests at different doses of aluminium sulfate as an antifouling reagent.

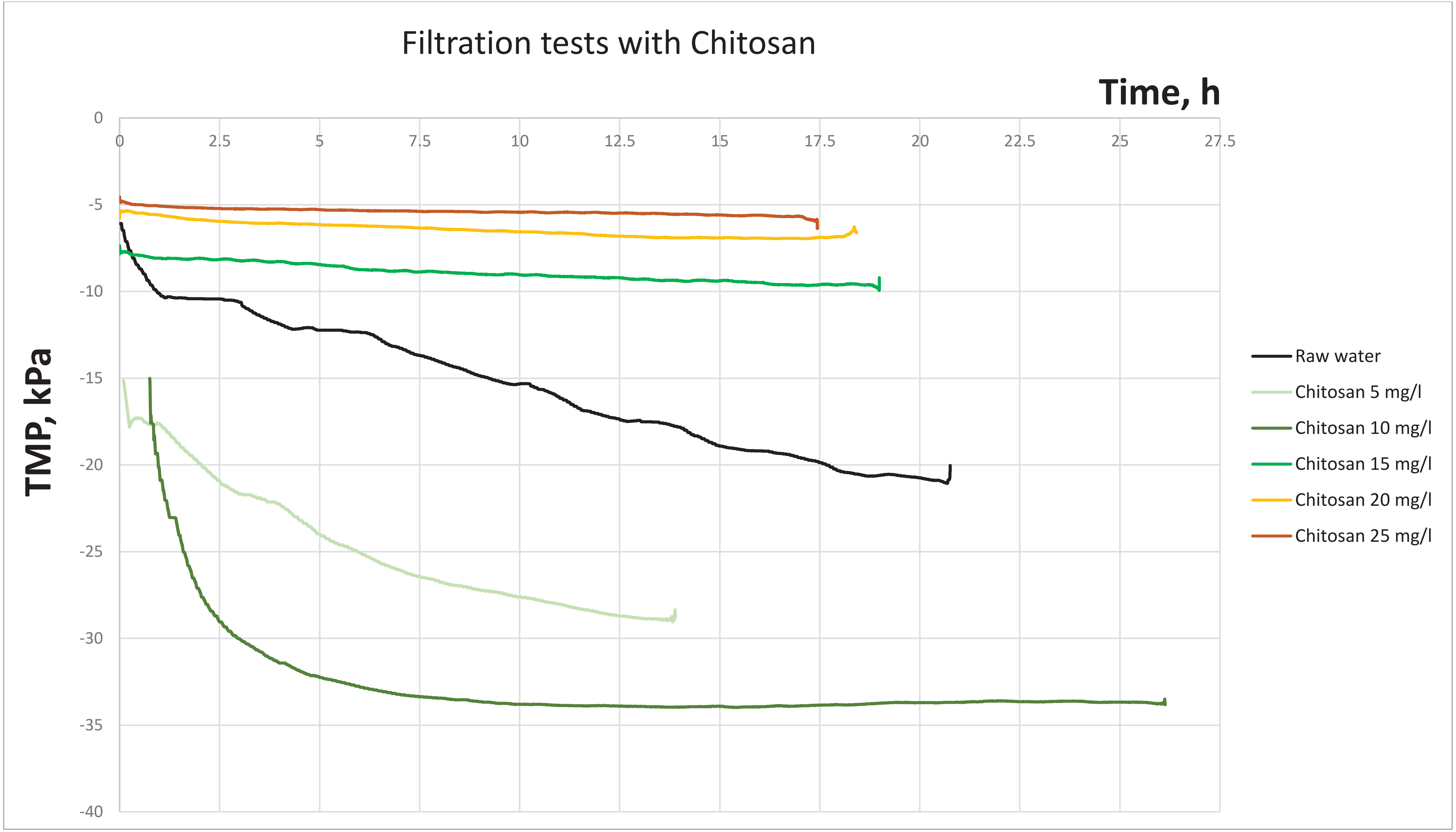
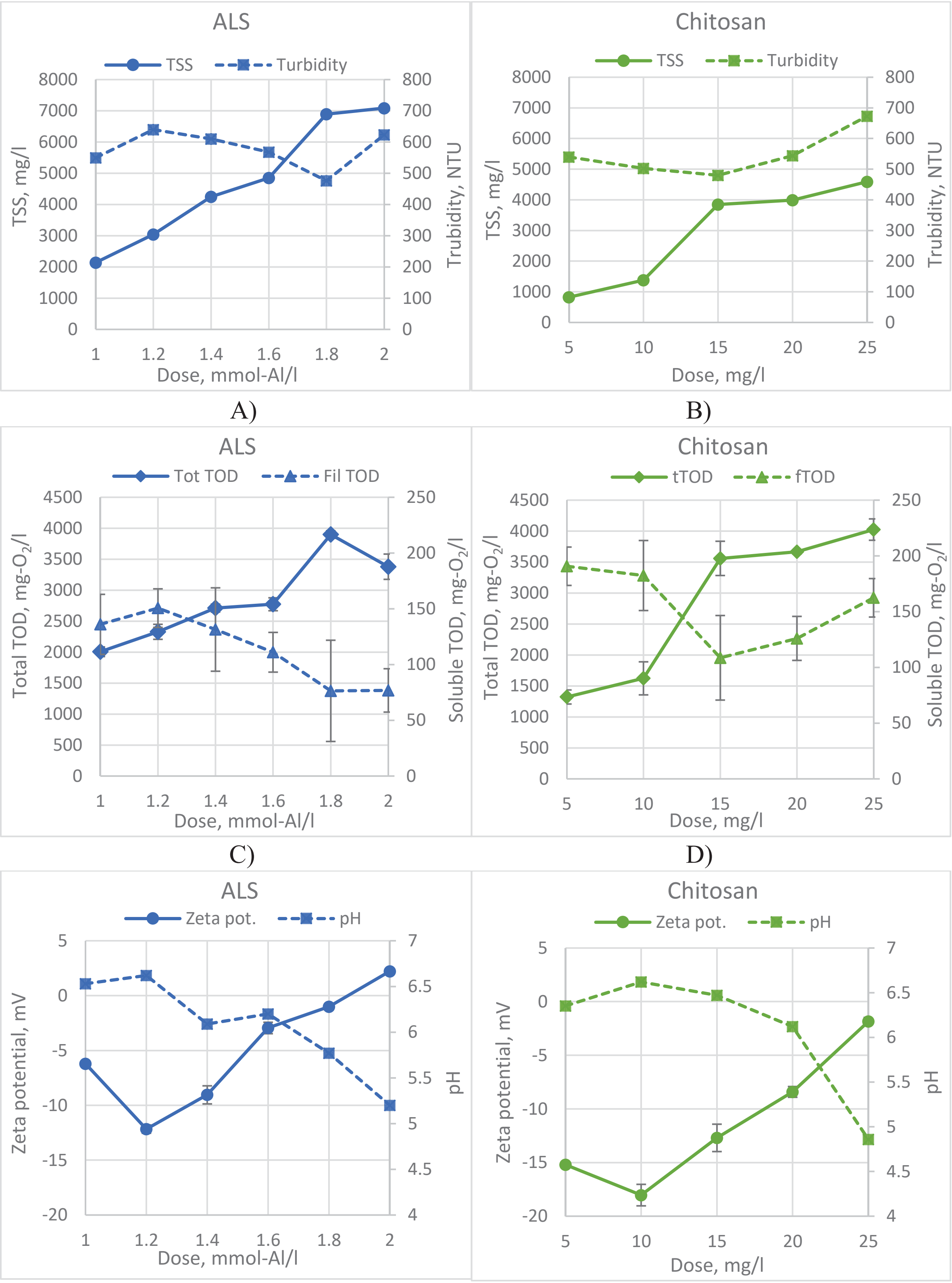


Figure 20. TMP increase over time during filtration tests at different doses of chitosan as an antifouling reagent.



A) B)

C) D)

E) F)

Figure 21. Water parameters in MBRs during filtration tests at different doses of chemicals. A) Turbidity and TSS (ALS); B) Turbidity and TSS (Chitosan); C) Total and Soluble TOD (ALS); D) Total and Soluble TOD (Chitosan); E) pH and Zeta potential (ALS); F) pH and Zeta potential (Chitosan).

At first glance, it was assumed that more severe fouling occurs due to hydrophobic interactions between non-polar chitosan branches and membrane, because visually chitosan acted as a very hydrophobic substance, making sludge attach to surfaces of silicon pipes and plastic reactors. However, after the decrease of fouling rate alongside with increasing chitosan dose and hydrophilicity of membrane surface, this hypothesis was disregarded. Most probably such phenomenon takes place due to delayed neutralization of SMP and other high molecular hydrophilic organic foulants. As it was mentioned, charge adsorption/neutralization is a dominant mechanism for removing of charged organic polymers by chitosan. Since tested chitosan has low charge density, at low concentration it is not efficient toward SMP and proteins. The remaining SMP attach to membrane surface through hydrophilic interactions providing a good substrate for biofilm growth. Due to the formation of well-structured heavy flocs bonded by chitosan and their attachment to biofilm, produced cake layer is much thicker, comparable to filtration without the addition of flocculant. At higher doses, charge neutralization started occurring more prominently, thus neutralizing a bigger fraction of SMPs, therefore biofilm growth is significantly suspended. Such hypothesis corresponds with measured Zeta potential in MBR: at higher doses, Zeta potential of biomass is close to isoelectric point (figure 21), which implies significant neutralization of charged substances and particles. However, at the current stage of research, it is not possible neither to confirm this hypothesis nor disregard and further investigation is required to determine the concentration of EPS and SMP, study biofilm formed at different doses of chitosan with microscopic technics, evaluate rheological and morphological properties of biomass. Parameters of raw water, water after biological treatment and quality of permeate is presented in Appendix D.

Some odds in the dependencies of water parameters in MBRs can be observed. For example, a sharp increase in TSS and TOD for chitosan at the dose of 15 mg/l, which expected to have a linear dependency with dose increment. Such jump is caused mainly due to the recycling of a large fraction of sludge back to IFAS treatment step and refilling of the raw water tank with fresh water from the sewer before conducting the test. Data in Appendix D shows that TSS and TOD in Raw water and water after IFAS are much higher than at previous tests. Another issue that seems strange is abnormally low pH during the tests with 25 mg/l of chitosan. Jar-tests showed that chitosan does not influence pH during coagulation, meanwhile, pH in the biological treatment tank was 6.6, so it is not caused by biological processes. The reason is the acidification by the flocculant itself. As it was mentioned in section 3.2.2, the working solution of flocculant was prepared by dilution of stock 10 g/l with hydrochloric acid because of the low resolution of a dosing pump. And meanwhile, at lower doses, wastewater could cope with of flocculant (flow of reagent was between 0.15-0.6 ml/min for 52.5 ml/l of wastewater), the last dose (flow of 0.75 ml/min) contained enough acid to neutralize alkalinity of wastewater and reduce pH. For further tests, a higher concentration of chitosan working solution should be considered.

To estimate antifouling abilities of ALS and Chitosan, filtration time, mean TMP and relative TMP increment were compared. From figures 19 and 20, it was decided to define filtration time as the time when TMP reaches value 1.5x of the starting TMP. For doses at which 1.5 TMP increase had not been achieved during filtration, linear approximation was applied. Using the obtained linear equations, the time required for 1.5 TMP increase was calculated. This approach was applied for doses: 1.4-2.0 mmol-Al/l for aluminium sulfate and for 15-25 mg/l of chitosan. Graphs comparing filtration time of water with added ALS and Chitosan are presented in figure 22.

ALS has outstanding anti-fouling abilities, meanwhile, chitosan still can significantly increase filtration time, its overall effect fades comparable to aluminium sulfate. Optimal fouling mitigation by aluminium sulfate occurs at a dose of 1.6 mmol/l. This relates to effective charge neutralization at this dose and further increment in concentration does not affect the neutralization of particles and EPS.

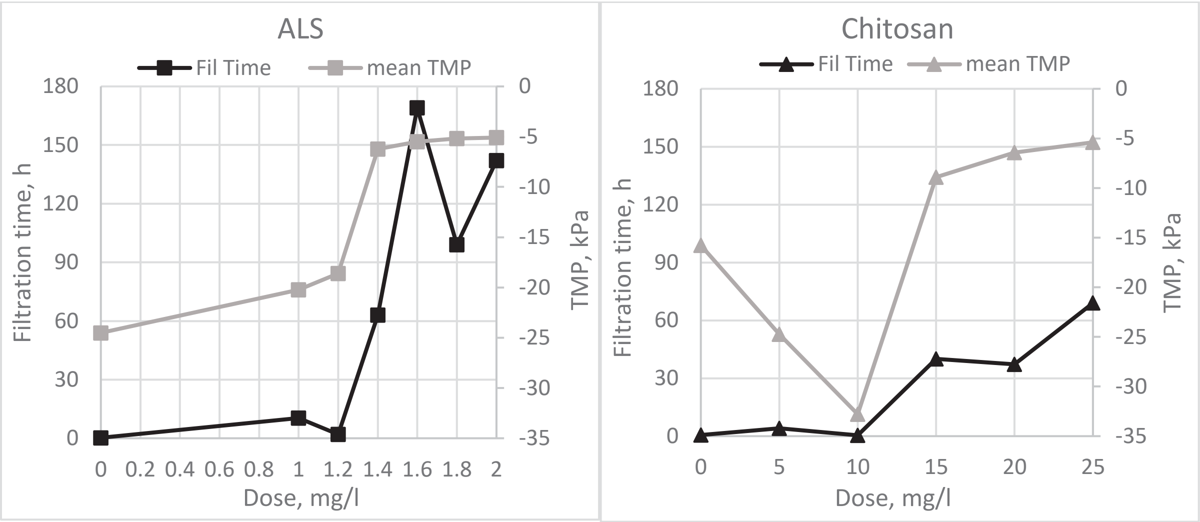


Figure 22. Comparing the performance of ALS and Chitosan as anti-fouling agents. Filtration time is time for which TMP is increased in 1.5 times comparable to starting values.

Table 11. Comparison of fouling mitigation abilities of aluminium coagulant and chitosan.

	Filtration time, h	**Mean TMP, kPa**	**Mean TMP change, %**
Raw 1	0.26	-24.5	-
ALS 1.0 mmol/l	10.4	-20.2	17.4
ALS 1.2 mmol/l	2	-18.6	24.1
ALS 1.4 mmol/l	63	-6.2	74.6
ALS 1.6 mmol/l	169	-5.4	77.6
ALS 1.8 mmol/l	99	-5.2	78.8
ALS 2.0 mmol/l	142	-5.1	79.2
Raw 2	0.7	-15.8	-
Chitosan 5 mg/l	4.0	-24.7	-57.0
Chitosan 10 mg/l	0.4	-32.8	-108.0
Chitosan 15 mg/l	40.0	-8.9	43.4
Chitosan 20 mg/l	37.3	-6.4	59.1
Chitosan 20 mg/l	69.0	-5.4	65.8

5. Conclusions and needs for further research

Chitosan flocculant despite remarkable aggregation abilities, possess low efficiency as fouling mitigation agent. Moreover, at low doses, it can induce more severe fouling significantly deteriorating membrane performance. Such dualistic behaviour of chitosan most probably can be attracted to a dual mechanism of chitosan aggregation – bridging and particle neutralization. While at low doses - bridging is dominant, the big fraction of SMP and soluble proteins remain in solution, thus not preventing them from the attachment on the membrane surface and serving as a further substrate for biofilm. Formed in this way the cake layer cannot be removed by regular backwashing due to strong interactions between the membrane and formed cake. Flocks adsorbed on the biofilm are larger and heavier due to the formation of interparticle bridges, thus cake layer is much thicker compared to filtration without the addition of chitosan. At higher doses, charge neutralization takes place more intensively inactivating bigger fraction of SMP, thus decelerating biofilm growth.

Despite the fact that at higher doses chitosan exhibited some anti-fouling abilities, overall its fouling mitigation effect was substantially lower than of aluminium coagulant. Aluminium coagulant, however, still was proven to be an excellent fouling reduction agent.

Further research is needed to investigate the true mechanism of chitosan fouling reduction. Microscopical analysis of biofilm formed on the membrane surface, measurement of EPS and SMP contented as well as measuring of fractions of soluble proteins, polysaccharides and nucleic acids should shed a light on the issue. Rheological and morphological properties of sludge and estimation of membrane surface charge can also be measurements that will help to find out the reason.

Different direction of study also should be considered. For example. simultaneous addition of chitosan together with aluminium sulfate should be a promising approach, resulting in reduction aluminium dose, therefore more biodegradable and dewaterable sludge. Degradability and dewaterability of sludge produced by chitosan, aluminium slufate and their mixture should be compared. Possibility to recover nutrients from effluent of the MBR in form of struvite or hydroxyapatites is also an interesting direction of further study. At last, LCA analysis and comparison of aluminium coagulants and natural polyelectrolytes should be done before irrevocable shift to alternative aggregation chemicals.

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7. Appendixes

Appendix A. Design of continuous installation.

MBR installation design

Flux of 50 LMH and working volume/effective membrane surface ratio was chosen based on previous publications of Master and PhD students worked on similar types of ceramic membranes (Kulesha et al., 2019; Zigta, 2017).

1) MBR

Flux=50 MLH.

Width of membrane (W) = 14 cm;

Height of membrane (H)= 22.5 cm;

1 Membrane Area (A)= W·H·2=0.225·0.114·2=0.063 m^2;

Flow (Q) through the installation = Flux·A·3=50·0.063·3=9.45 l/h (0.2268 m^3/d);

Working volume/effective membrane surface ratio (R) ≈ 0.05 m;

Reserve = 30%;

Volume of membrane tank (V_{MT}) $=R \cdot A \cdot 1.3 =$0.05·0.063 ·1.3·1000=4,095 l

Dimensions:

Width (W_{MT}) = 0.07 m; - according to size of 1 membrane

Height (H_{MT}) = 0.3 m; - according to size of 1 membrane

Length (L_{MT})= V_{MT}/(W_{MT}· H_{MT})= 4.095/1000/0.07/0.3 ≈ 0.2 m;

V_{MT}=0.07*0.2*0.3*1000= 4.2 l,

HRT $= \frac{V_{ef}}{Q} = \frac{4.2}{1.3 \cdot \frac{9.45}{3}} = 1.02\ h.$

Drawings of MBR tank are provided on figure.... Sharp angle in the bottom was made specifically for better sludge collection and discharge. The final reservoirs were made in China and delivered to Norway.

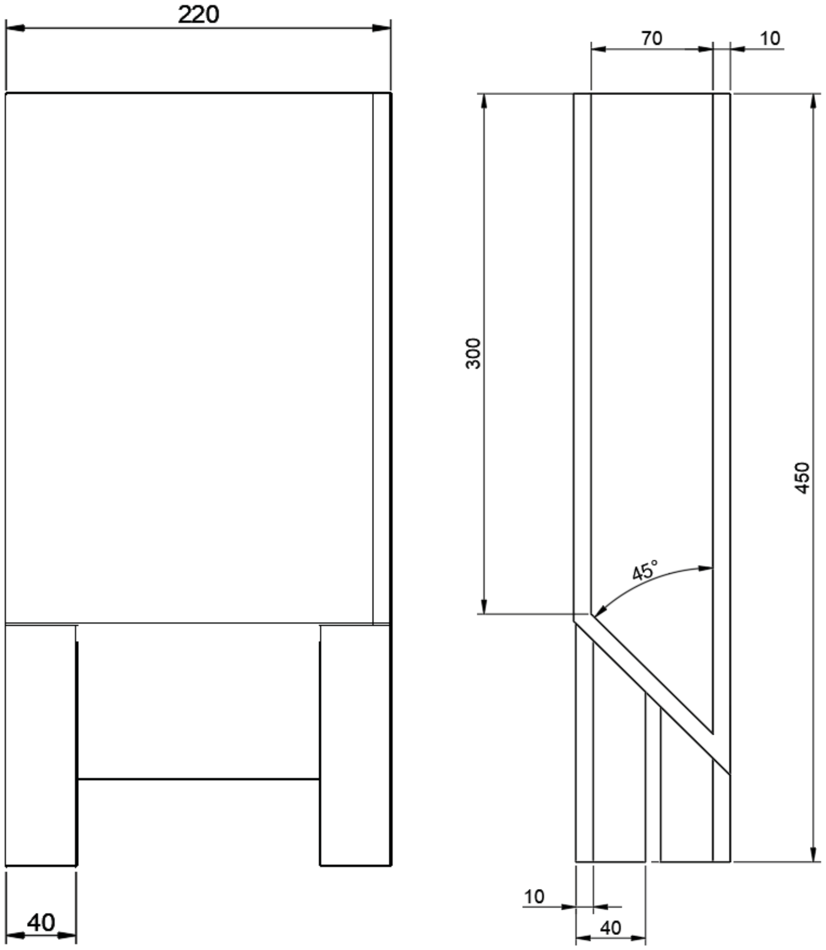

Figure A1. Schematic drawing of MBR tank

2) Flocculation tubes

Figure A2. Flocculating tubes

Since coagulant and flocculant are dosing through the inlet mixers, we assume uniform mixing of reagents with wastewater, therefore omitting module for fast mixing.

The next task is to provide gentle mixing to ensure steady conditions of floc formation. Mixing conditions can be reflected by G-value. Optimal conditions of slow mixing reflected by G-values in range between 5-100 (Crittenden et al., 2012).

Recommended values of variable for slow mixing stage were taken as (Crittenden et al., 2012):

Variable	Value
Flocculation time (T), min	15-30

Constants for calculation were taken from online directories.

Constants	Value
Water density (ρ), kg/m^3	1000
Wastewater viscosity (μ), Pa·s	0.002875
Dynamic viscosity (ν), m^2/s	$2.5075 \cdot 10^{-6}$

Knowing goal variable (G-values) and assuming that optimal flocculation time as 15 minutes it is possible to calculate diameter of flocculating pipes. For this next formulas were used (Crittenden et al., 2012):

$$G = \sqrt{\frac{g \cdot h_L}{\nu \cdot \mathrm{T}}};$$

$$h_L = \left(f \cdot \frac{L}{D} + \sum K\right)\frac{\omega^2}{2g};$$

$$\sum K = 4 \cdot K_{90} \cdot n;$$

$$n = \frac{L}{2 \cdot R_{st} \cdot \mu};$$

$$f = \frac{Re}{64} \text{ - for laminar flow;}$$

$$Re = \frac{\rho \cdot \omega \cdot d}{1000 \cdot \mu};$$

$$\omega = \frac{Q}{A};$$

$$L = \frac{Q \cdot T}{A};$$

$$A = \left(\frac{D}{2}\right)^2 \cdot \pi;$$

Where g – gravitational constant (m/s^2); h_L – head loss over mixing tank (m); f – friction factor, L – pipe length (m), D – pipe diameter (m), ω – linear velocity (m/s); ΣK – sum of all head loss coefficients; K_{90} – head loss due to 90º turn in pipe coefficient; n – number of turns in tube coil, R_{st} – radius of tube coil (m); Re – Reynolds number; Q – water flow (m^3/s); A – area of tube cross-section (m^2); D – tube diameter (m).

According to this thinking next table was obtained.

Diameter, mm	Area, m^2	Velocity, m/s	Length, m	Re	f	n	ΣK	h_L	G, s^{-1}
5	1.96E-05	0.045	53.47	77.5	0.83	131	105	0.9	54
10	7.85E-05	0.011	10	38.75	1.65	24	20	0.01	6
15	0.000178	0.00495	5.94	25.83	2.48	15	12	0.00124	2
20	0.000314	0.00278	3.34	19.4	3.3	8	6.5	0.000221	0.85
25	0.00049	0.00178	2.14	15.5	4.13	5	4.2	5.79E-05	0.4
50	0.00196	0.000445	0.535	7.8	8.26	1	1	9.05E-07	0.054

From the table the diameter of 10 mm for flocculation tubes was chosen as suitable to provide optimal mixing with relatively small length of tube.

Appendix B. Polyelectrolyte titration of chitosan with PVSK. Procedure and results.

Stock solution of 10 g/l chitosan was diluted 100 times in volumetric flask to concentration of 0.1 g/l. 1 ml of 0.1 g/l solution was placed in streaming current cell and diluted with 100 ml of water. Titrated solution of chitosan had pH equal 7. As a titrant 0.0005 N solution of PVSK was used. Data of measurement is presented below

Step	Value
1 titration	
Starting value potential, mV	175
Volume of 0.0005 PVSK used for titration	1.196
2 titration	
Starting value potential, mV	168
Volume of 0.0005 PVSK used for titration	0.8264
3 titration	
Starting value potential, mV	205
Volume of 0.0005 PVSK used for titration	1.004
Mean value of PVSK volume used for titration, ml	1.0088

Therefore, charge of chitosan can be calculated as:

$$Charge\left(\frac{mequiv.}{g}\right) = \frac{1.0088 \cdot 0.0005}{1 \cdot 0.1} \cdot 1000 = 5.044$$

Appendix C. Water parameters during TRT tests.

Doses: ALS – 1 mmol-Al/l, Chitosan – 5 mg/l.

Parameter	MBR (ALS)	Perm (ALS)	MBR (Chit)	Perm (Chit)
Turbidity, NTU	410	0.493	431	0.565
TSS, mg/l	832	8	612	8
PO_4^{3-}, mg-P/l	0.994	1.074	12.546	13.5295
TP, mg-P/l	34.69434	1.84867	45.49869	15.42937
Zeta, mV	-13.4667	-4.65	0.492	0.157633
St.Dev	0.61101	0.841487	0.398636	0.633047

Doses: ALS – 2 mmol-Al/l, Chitosan – 10 mg/l.

Parameter	MBR (ALS)	Perm (ALS)	MBR (Chit)	Perm (Chit)
Turbidity, NTU	713	0.356	718	0.494
TSS, mg/l	2872	6	2460	2
PO_4^{3-}, mg-P/l	0.698	0.757	8.842	8.579
TP, mg-P/l	46.54679	1.48964	24.74631	9.72503
Zeta, mV	-12.96666667	-8.12667	-9.87333	-9.46667
St.Dev	1.096965511	0.22053	0.382797	0.540123

Doses: ALS – 3 mmol-Al/l, Chitosan – 15 mg/l.

Parameter	MBR (ALS)	Perm (ALS)	MBR (Chit)	Perm (Chit)
Turbidity, NTU	671	2.24	384	0.585
TSS, mg/l	1818	4	712	2
PO_4^{3-}, mg-P/l	0.174	0.227	8.391	8.538
TP, mg-P/l	44.04473	0.12488	31.67938	8.7416
Zeta, mV	-13.8	-12.6333	-12.9	-10.2667
St.Dev	1.808314132	1.289703	0.87178	0.208167

Appendix D. Water parameters at different stages during filtration tests in continuous mode.

Doses: ALS – 1.2 mmol-Al/l, Chitosan – 10 mg/l.

	Raw	IFAS	MBR (ALS)	Perm (ALS)	MBR (Chit)	Perm (Chit)
pH	7.5	6.4	6.6	7.9	6.6	7.4
Turbidity, NTU	40.0	93.0	640.0	1.5	503.0	1.7
TSS, mg/l	52.0	254.0	3044.0	4.0	1376.0	8.0
PO_4^{3-}, mg-P/l	10.2	7.1	0.1	0.1	6.0	5.8
St.Dev	0.02	0.04	0.01	0.13	0.00	0.07
TP, mg-P/l	12.1	20.6	40.6	0.3	34.1	7.3
St.Dev	0.47	0.84	0.00	0.14	0.00	0.25
Zeta, mV	-14.0	-13.7	-12.2	-15.3	-18.0	-13.9
St.Dev	0.61	0.31	0.38	1.80	1.00	1.50
Tot TOD, mg-O_2/l	259.2	247.8	2328.0	54.0	1623.0	84.0
St.Dev	27.69	12.76	121.26	2.78	266.74	10.61
Removal tot, %	0.0	18.9	-661.9	82.3	-431.1	72.5
fil TOD, mg-O_2/l	185.8	84.9	150.6	50.9	182.4	80.5
St.Dev	10.44	6.07	17.29	14.94	31.40	2.57
Removal tot, %	0.0	64.6	37.1	76.2	23.9	61.8

Doses: ALS – 1.4 mmol-Al/l.

	Raw	IFAS	MBR (ALS)	Perm (ALS)
pH	7.5	6.4	6.1	6.0
Turbidity, NTU	52.0	135.0	610.0	0.5
TSS, mg/l	56.0	384.0	4244.0	6.0
PO_4^{3-}, mg-P/l	10.0	6.2	0.0	0.0
St.Dev	0.01	0.01	0.00	0.00
TP, mg-P/l	12.7	18.2	42.2	1.1
St.Dev	0.60	1.17	0.17	0.47
Zeta, mV	-14.3	-18.0	-9.0	-9.6
St.Dev	0.75	1.23	0.82	1.04
Tot TOD, mg-O_2/l	328.3	347.5	2711.0	70.2
St.Dev	96.10	23.94	64.26	5.58
Removal tot, %		-13.7	-787.2	90.9
fil TOD, mg-O_2/l	203.7	92.8	131.4	68.9
St.Dev	10.23	16.36	37.39	11.11
Removal tot, %		61.3	45.1	71.2

Doses: ALS – 1.6 mmol-Al/l, Chitosan – 15 mg/l.

	IFAS	MBR (ALS)	Perm (ALS)	MBR (Chit)	Perm (Chit)
pH	6.8	6.2	6.3	6.5	6.2
Turbidity, NTU	125.0	568.0	0.7	480.0	0.8
TSS, mg/l	358.0	4852.0	4.0	3852.0	0.0
PO_4^{3-}, mg-P/l	5.7	0.0	0.0	4.5	4.9
St.Dev	0.01	0.00	0.00	0.00	0.01
TP, mg-P/l	23.2	42.3	0.5	42.0	5.6
St.Dev	0.03	0.00	0.02	0.11	0.13
Zeta, mV	-20.0	-3.0	-9.8	-12.7	-7.3
St.Dev	0.99	0.52	1.73	1.28	1.35
Tot TOD, mg-O_2/l	362.1	2773.0	68.8	3560.0	76.0
St.Dev	5.56	104.11	3.80	295.57	12.30
Removal tot, %	-18.5	-807.5	87.3	-1065.0	75.1
fil TOD, mg-O_2/l	101.0	111.0	58.2	108.6	74.1
St.Dev	19.66	17.81	24.39	37.92	99.32
Removal tot, %	57.8	53.7	75.7	54.7	48.1

Doses: ALS – 1.8 mmol-Al/l, Chitosan – 20 mg/l.

	IFAS	MBR (ALS)	Perm (ALS)	MBR (Chit)	Perm (Chit)
pH	6.8	5.8	5.9	6.1	5.9
Turbidity, NTU	132.0	476.0	1.2	544.0	0.8
TSS, mg/l	402.0	6892.0	6.0	3988.0	4.0
PO_4^{3-}, mg-P/l	4.2	0.0	0.0	2.5	3.0
St.Dev	0.06	0.00	0.00	0.02	0.11
TP, mg-P/l	23.9	44.0	0.6	43.0	3.5
St.Dev	0.26	0.06	0.09	0.00	0.02
Zeta, mV	-19.8	-1.0	-8.8	-8.4	-9.9
St.Dev	0.76	0.29	1.91	0.50	0.85
Tot TOD, mg-O_2/l	373.8	3899.0	67.2	3665.0	100.5
St.Dev	12.29	60.71	18.75	33.47	14.08
Removal tot, %	-22.3	-1176.0	87.1	-1099.4	74.1
fil TOD, mg-O_2/l	58.1	76.4	63.5	126.0	97.8
St.Dev	11.02	45.39	31.51	19.74	28.02
Removal tot, %	75.7	68.1	73.5	47.4	59.2

Doses: ALS – 2.0 mmol-Al/l, Chitosan – 25 mg/l.

	IFAS	MBR (ALS)	Perm (ALS)	MBR (Chit)	Perm (Chit)
pH	6.6	5.2	5.2	4.9	4.8
Turbidity, NTU	44.8	623.0	1.6	673.0	0.5
TSS, mg/l	187.2	7088.0	10.0	4592.0	2.0
PO_4^{3-}, mg-P/l	1.4	0.1	0.0	0.5	0.9
St.Dev	0.10	0.01	0.00	0.00	0.19
TP, mg-P/l	11.0	43.6	0.5	42.5	1.2
St.Dev	0.20	0.00	0.06	0.06	0.08
Zeta, mV	-18.5	2.2	-6.1	-1.9	-1.2
St.Dev	0.61	0.14	1.00	0.38	0.38
Tot TOD, mg-O_2/l	164.4	3379.0	31.6	4025.0	103.2
St.Dev	6.41	204.00	4.02	172.48	21.34
Removal tot, %	46.2	-1005.8	89.7	-1217.2	66.2
fil TOD, mg-O_2/l	98.1	76.8	28.3	162.4	98.5
St.Dev	53.40	19.44	101.08	17.25	20.36
Removal tot, %	59.0	67.9	62.3	32.2	58.9

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