*water*

MDPI

*Editorial*

# Recent Advances in Water and Wastewater Treatment with Emphasis in Membrane Treatment Operations

**Anastasios I. Zouboulis * and Ioannis A. Katsoyiannis**

Department of Chemistry, Laboratory of Chemical and Environmental Technology, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece; katsogia@chem.auth.gr

* Correspondence: zoubouli@chem.auth.gr

Received: 6 December 2018; Accepted: 22 December 2018; Published: 27 December 2018

check for updates

**Abstract:** The present Special Issue brought together recent research findings from renowned scientists in this field and assembled contributions on advanced technologies that have been applied to the treatment of wastewater and drinking water, with an emphasis on novel membrane treatment technologies. The 12 research contributions highlight various processes and technologies that can achieve the effective treatment and purification of wastewater and drinking water, aiming (occasionally) for water reuse. The published papers can be classified into three major categories. (a) First, there are those that investigate the application of membrane treatment processes, either directly or in hybrid processes. The role of organic matter presence and fouling control is the main aim of the research in some of these studies. (b) Second, there are studies that investigate the application of adsorptive processes for the removal of contaminants from waters, such as arsenic, antimony, or chromate, with the aim of the efficient removal of the toxic contaminants from water or wastewater. (c) Lastly, there are studies that include novel aspects of oxidative treatment such as bubbleless ozonation.

**Keywords:** membranes; adsorption; natural organic matter; arsenic; chromate; antimony; ozonation

---

Worldwide, an estimated 800 million people remain without access to an appropriate source of drinking water, and in parallel, the global water demand for manufacturing is expected to increase by 400% between 2000–2050 [1]). Although between 2001–2010 more than one billion Euros were invested by the European Commission to tackle this problem, it is evident that the targets of the Millennium Development Goals have not been fully met by 2015 [2]. In September 2015, the United Nations adopted the Sustainable Development Goals for 2030, one of which was to ensure the availability and sustainable management of water and sanitation for all. Given the time frame of less than 15 remaining years to accomplish this, the achievement of these important goals requires immediate action and the translation of knowledge into practice. This special issue was intended to bring together recent research findings from renowned scientists in this field, presenting certain recent advanced technologies as applied to the treatment of wastewater and of drinking water, with a specific emphasis given to novel membrane treatment operations. Twelve research contributions have highlighted various processes and technologies that can achieve the effective treatment and purification of wastewater and of drinking water, aiming (occasionally) for water reuse.

In particular, the work of Keucken et al. [3], entitled "Combined Coagulation and Ultrafiltration Process to Counteract Increasing NOM in Brown Surface Water", describes and evaluates a 30-month UF pilot (coagulation-coupled ultrafiltration) trial, treating the surface water of Lake Neden (Sweden) and providing drinking water to 60,000 residents. With an optimal aluminum coagulation dosing (0.5–0.7 mg $L^{-1}$), efficient NOM removal was achieved. UV absorbance, the freshness index, and the liquid chromatography-organic carbon detection (LC-OCD) measurements were used to optimize the respective treatment process.

The next study reviewed one of the most pressing problems regarding membrane operation, i.e., the fouling caused by organic matter. The study entitled "Membrane Fouling for Produced Water Treatment: A Review Study from a Process Control Perspective", by Jepsen et al. [4] reviewed and analyzed the fouling detection, removal, prevention, and the dynamical and static modeling approaches, with an emphasis on how the membrane process can be manipulated from a process control perspective to overcome this problem. They showed that the majority of the respective models rely on static descriptions that are limited to a narrow range of operating conditions, which subsequently limits their usability. This work concluded that although the membrane filtration has been successfully applied and matured in several industrial areas, important challenges regarding the cost-effective mitigation of fouling, especially for the offshore de-oiling applications, still exist.

In a relevant study [5] it was examined the "Membrane Fouling Patterns in Biofilm Ceramic Membrane Bioreactor". This study dealt with the determination of the fouling propensity of filtered biomass in a pilot-scale biofilm membrane bioreactor to enable the prediction of fouling intensity. The system was designed to treat domestic wastewater with the application of ceramic microfiltration membranes. Partial least squares regression analysis of the data, which was obtained during the long-term operation of the used biofilm membrane bioreactor (MBR) (BF-MBR) system, demonstrated that the Mixed Liquor Suspended Solids (MLSS), the Diluted Sludge Volume Index (DSVI), the Chemical Oxygen Demand (COD), and their slopes were detected as the most significant parameters for the estimation and prediction of fouling intensity, whereas the normalized permeability and its slope were found to be the most reliable fouling indicators. Three models were derived, depending on the applied operating conditions, which enabled an accurate prediction of the fouling intensities in the system. These results can help prevent severe membrane fouling through the appropriate modification of operating conditions, aiming to prolong the effective operative lifetime of membrane modules, and saving energy and resources for the efficient maintenance of this treatment system.

Further studies regarding membrane fouling were carried out by Sun et al. [6], performing "Quantitative Analysis of Membrane Fouling Mechanisms", which are involved in the "Microfiltration of Humic Acid–Protein Mixtures at Different Solution Conditions". This paper argues that a systematical quantitative understanding of different mechanisms, although of fundamental importance for the better control of fouling, is still unavailable for the microfiltration (MF) of humic acid (HA) and protein mixtures. Based on extended Derjaguin–Landau–Verwey–Overbeek (xDLVO) theory, the major fouling mechanisms, i.e., Lifshitz–van der Waals (LW), electrostatic (EL), and acid–base (AB) interactions were for the first time quantitatively analyzed, considering model HA–bovine serum albumin (BSA) mixtures at different experimental conditions. The obtained results indicated that the pH, ionic strength, and calcium ion concentration of the solution can significantly affect the physicochemical properties and the interaction energy between the poly(ether sulfone) (PES) membrane and the HA–BSA mixtures. The free energy of cohesion of the HA–BSA mixtures was minimized at pH 3.0, ionic strength 100 mM, and [$Ca^{2+}$] 1.0 mM. The AB interaction energy was a key contributor to the total interaction energy when the separation distance between the membrane surface and the HA–BSA mixtures was less than three nm, while the influence of EL interaction energy was found to be of lower importance, considering the total interaction energy. The attractive interaction energies of membrane–foulant and foulant–foulant were increased at lower pH values and at higher ionic strength and calcium ion concentrations, thus aggravating the membrane fouling problem, which was also supported by the respective experimental results. The obtained findings would provide valuable insights for the quantitative understanding of membrane-fouling mechanisms, which were caused by the treatment of mixed organics during the MF process.

The next study by Arahman et al. [7] investigated the functionalization of membranes to increase efficiency by studying the "Effect of Ca and Mg Ions on the Filtration Profile of Sodium Alginate Solution in a Poly(ether sulfone)-2-(methacryloyloxy) Ethyl Phosphorylchloline Membrane". This work explained the filtration performance of a hollow fiber membrane that was fabricated from poly(ether sulfone)-2-(methacryloyloxy) ethyl phosphorylchloline, while using a sodium alginate (SA) feed solution. The filtration process was applied in a pressure-driven cross-flow module, using a single-piece hollow fiber membrane in a flow of outside–inside operating mode. The effect of the presence of Ca and Mg ions in the SA solution on the relative permeability, membrane resistance, cake resistance, and cake formation on the membrane surface was examined. Furthermore, the performance of membrane filtration was predicted by using mathematical models, which were developed based on Darcy's law. The results show that the presence of Ca ions in the SA solution has the most prominent effect on the formation of a cake layer, which showed a significant effect for lowering the relative permeability.

Further to these studies, Lintzos et al. [8] examined the influence of "Backwash Cleaning Water Temperature on the Membrane Performance in a Pilot SMBR Unit". In this work, different backwash (BW) schemes were applied on identical hollow fiber (HF) membranes in a membrane bioreactor (MBR), treating municipal wastewater. The effect of BW duration (one minute, three minutes, and eight minutes) and of water temperatures (8 °C, 18 °C, 28 °C, and 38 °C) on membrane fouling was investigated. Specifically, the transmembrane pressure (TMP) drop and the membrane permeability increase, due to the BW, were investigated. Furthermore, the time required for the membrane to return to the initial stage, just before each BW experiment, was also examined. It was found that the membranes presented better operating performance as the BW temperature and the backwash duration were increased, which also improved the membrane permeability. By using higher BW water temperatures, more hours were required to return the membranes to the initial condition (just before cleaning), noting also that the examined BW water temperatures did not adversely affect the permeate quality.

The following work by Karanasiou et al. [9] examined the efficiency of a modified membrane process by using "Vacuum Membrane Distillation and Employing Hollow-Fiber Modules". Vacuum membrane distillation (VMD) is an attractive variant of the novel membrane distillation process, which is promising for various separations, including water desalination and bioethanol recovery (through the fermentation of agro-industrial by-products). This publication is part of an effort to develop a capillary membrane module for various applications, as well as a model that would facilitate the process design of VMD. Experiments were conducted in a pilot-scale VMD unit, comprising polypropylene capillary membrane modules. Performance data that was collected at modest temperatures (37–65 °C) with deionized and brackish waters confirmed the improved system productivity with the increase of feed water temperature; simultaneously, excellent salt rejection was obtained. The recovery of ethanol from ethanol–water mixtures—as well as from fermented winery by-products—was also studied, in continuous, semi-continuous, and batch operating modes. At a low feed solution temperature (27–47 °C), ethanol solution was concentrated 4–6.5 times in continuous operation and two to three times in the semi-continuous mode. Taking advantage of the small variation of properties in the module axial-flow direction, a simple VMD process model was developed, satisfactorily describing the obtained experimental data. This VMD model appears to be promising for several practical applications and warrants further research and development (R&D) work.

Apart from the studies dealing with membrane treatment applications for water and wastewaters, in this special issue, some interesting research, examining other processes, such as ozonation, coagulation, and adsorption, were also included. In particular, in the work of Zoumpouli et al. [10], entitled "A Single Tube Contactor for Testing Membrane Ozonation", a membrane ozonation contactor was built to investigate ozonation by using appropriate tubular membranes. Non-porous tubular poly(dimethylsiloxane) (PDMS) modified membranes of 1.0–3.2 mm inner diameter was tested at ozone gas concentrations of 110–200 g/m$^3$ and liquid side velocities of 0.002–0.226 m/s. In this case, the application of modeling could sufficiently predict the final ozone concentrations. Model contaminant degradation experiments (evaluated by UV light absorption measurements) of ozonated water samples were also used to generate information on the reactivity of ozone with different water matrices. The combination of simple membrane contactors with modeling approaches has allowed the prediction of ozonation performance under a variety of experimental conditions, leading to an improvement in the efficiency of bubbleless ozone systems, especially applied for water treatment.

The study titled the "Removal of Antimony Species, Sb(III)/Sb(V), from Water by Using Iron Coagulants", by Mitrakas et al. [11] systematically investigated the removal of the most commonly found antimony species in water, namely, Sb(III) and Sb(V), by the addition of iron-based coagulants. The applied coagulants were Fe(II), Fe(III), and the equimolar mixed Fe(II)/Fe(III) salts, and the experiments were performed using realistic (low) antimony concentrations in the range 10–100 µg/L, by examining artificially polluted tap water solutions. Sb(III) removal by Fe(III) provided better adsorption capacity at a residual concentration that was equal to the drinking water regulation limit (five µg/L), that is, $Q_5$ = 4.7 µg Sb(III)/mg Fe(III) at pH 7, which was much higher than the respective value achieved by the addition of Fe(II) salts, i.e., $Q_5$ = 0.45 µg Sb(III)/mg Fe(II), at the same pH value. Similarly, Sb(V) was removed more efficiently by Fe(III) addition, than by the other examined coagulant agents. However, the Fe(III) uptake capacity for Sb(V) was found to be significantly lower, i.e., $Q_5$ = 1.82 µg Sb(V)/mg Fe(III), than the corresponding value for Sb(III). The obtained results can give a realistic overview of the efficiency of conventionally used iron-based coagulants and their mixture for achieving Sb concentrations below the respective drinking water regulation limit; therefore, they can be subsequently applied for the design of real-scale water treatment units.

The next study, which was by Smoczynski et al. [12], analyzed certain important aspects of coagulation efficiency. The authors studied the sludge particles that were formed during the coagulation of synthetic and municipal wastewaters for increasing the sludge dewatering efficiency. In this work, municipal wastewater sludge was produced by the chemical coagulation of synthetic wastewaters (SWW), which was based on Synthene Scarlet P3GL disperse dye, as well as on real municipal wastewater (MWW), which was coagulated by the addition of commercial coagulants PAX (i.e., preliminarily hydrolyzed aluminum coagulant) and PIX (i.e., a ferric pre-polymerized coagulant based on $Fe_2(SO_4)_3$). It was found that the presence of phosphate ions in the system facilitates the removal efficiency of the examined dye due to the interaction between the dye molecules and $H_2PO_4^-$ ions. These results suggested that flocs composed of spherical $\{Al(OH)_3\}$ units possessed more internal space for water than the respective aggregates, consisting of rod-shaped $\{Fe(OH)_3\}$ units. The obtained results showed that smaller-sized particles are dominating in SWW sludge, whereas larger-sized particles are prevalent in MWW sludge. The parameters studied were the size distribution and the specific surface area of the particles.

The following work by Usman et al. [13] examined the "Efficiency of Small-Sized Powdered Ferric Hydroxide as Arsenic Adsorbent". In this study, batch adsorption experiments were carried out to remove arsenic species from water. The dust ferric hydroxide (DFH) was characterized in terms of zero point charge, zeta potential, surface charge density, particle size, and moisture content. Batch adsorption isotherm experiments indicated that the Freundlich model described the isothermal adsorption behavior of arsenic species notably well. The results indicated that the adsorption capacity of DFH in deionized ultrapure water, when targeting a residual equilibrium concentration of 10 µg/L at the equilibrium pH value of 7.9 ± 0.1 and with contact time of 24 h (i.e., $Q_{10}$), was 6.9 µg/mg and 3.5 µg/mg for As(V) and As(III), respectively, whereas the measured adsorption capacity of the conventionally used granular ferric hydroxide (GFH), under similar conditions, was found to be lower, i.e., 2.1 µg/mg and 1.4 µg/mg for As(V) and As(III), respectively. Furthermore, the adsorption of arsenic species onto DFH in the Hamburg tap water matrix, as well as in the National Science Foundation (NSF) challenge water matrix, was found to be significantly lower. The lowest recorded adsorption capacity at the same equilibrium concentration was 3.2 µg As(V)/mg and 1.1 µg As(III)/mg for the NSF water. Batch adsorption kinetics experiments were also conducted to study the impact of different water matrixes on the behavior of removal kinetics for the As(V) and As(III) species by the addition of DFH, and the respective data were best fitted to the second-order kinetic model. The outcomes of this study confirmed that the small-sized iron oxide-based material, being a by-product of the production process of GFH adsorbent, has significant potential to be used for the adsorptive removal of arsenic species from water, especially when this material can be combined with the subsequent application of low-pressure membrane filtration/separation in a hybrid water treatment process, as has been previously demonstrated by the use of Fe(II) and microfiltration, and provided excellent overall results [14].

The last work, which was by Tatoulis et al. [15], investigated the possibilities for the "Simultaneous Treatment of Agro-Industrial and Industrial Wastewaters: Case Studies of Cr(VI)/Second Cheese Whey and Cr(VI)/Winery Effluents". Hexavalent chromium (Cr(VI)) was co-treated either with second cheese whey (SCW) or with winery effluents (WE) by using pilot-scale biological trickling filters in series under different operating conditions. Two pilot-scale filters in series, using plastic support media, were used for each case. The first filter (i.e., Cr-SCW-filter or Cr-WE-filter) aimed at Cr(VI) reduction and the partial removal of dissolved Chemical Oxygen Demand (d-COD) from SCW or WE, and it was inoculated with indigenous microorganisms, originating from industrial sludge. The second filter in the series (i.e., SCW-filter or WE-filter) aimed for the further removal of d-COD, and it was inoculated with indigenous microorganisms that were isolated from the raw SCW or WE wastewaters. Various Cr(VI) concentrations (5–100 mg $L^{-1}$) and SCW or WE wastewaters (having d-COD, 1000–25,000 mg $L^{-1}$) were tested as feed concentrations. Based on the experimental results, the sequencing batch reactor operating mode with a recirculation of 0.5 L $min^{-1}$ proved very efficient, since it led to the complete Cr(VI) reduction in the first filter in series, and achieved overall high Cr(VI) reduction rates (up to 36 mg $L^{-1}d^{-1}$ and 43 mg $L^{-1}d^{-1}$ for the SCW and WW cases, respectively). The percentage of d-COD removal for the SCW and WE wastewaters in the first filter was rather low, ranging 14–42.5% and 4–29% for the cases of the Cr-SCW-filter or Cr-WE-filter, respectively. However, the addition of the second filter in the series enhanced the total d-COD removal to above 97% and 90.5% for the SCW and WE cases, respectively. These results indicated that agro-industrial wastewater could be used as a carbon source for the efficient Cr(VI) reduction, while the use of two trickling filters in the series could effectively treat both industrial and agro-industrial wastewaters with relatively low installation and operational costs. This technology uses indigenous microorganisms, and therefore can be classified as a biological treatment method.

In conclusion, this special issue contains 12 studies with important results, covering several aspects of water and wastewater treatment, by the application mainly of membranes, but also examining the application of other important technologies, such as ozonation, adsorption, and coagulation. Some of these studies refer specifically to the pollution problems of the Mediterranean region, covering important issues, because of the severe problems of water scarcity that this area is particularly facing and is expected to face more severely in the near future.

**Author Contributions:** A.I.Z. and I.A.K. have both conceived the idea and wrote the manuscript.

**Acknowledgments:** We thank all the authors of the papers for the great support to the realization of the present special issue.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Mekonnen, M.M.; Hoekstra, A.Y. Sustainability: Four billion people facing severe water scarcity. *Sci. Adv.* **2016**, *2*, e1500323. [CrossRef] [PubMed]
2. Hering, J.G.; Maag, S.; Schnoor, J.L. A call for synthesis of water research to achieve the sustainable development goals by 2030. *Environ. Sci. Technol.* **2016**, *50*, 6122–6123. [CrossRef] [PubMed]
3. Keucken, A.; Heinicke, G.; Persson, K.M.; Köhler, S.J. Combined coagulation and ultrafilltration process to counteract increasing NOM in brown surface water. *Water* **2017**, *9*, 697. [CrossRef]
4. Jespen, K.L.; Bram, M.V.; Pedersen, S.; Yang, Z. Membrane fouling for produced water treatment: A review study from a process control perspective. *Water* **2018**, *10*, 847.
5. Kulesha, O.; Maletskyi, Z.; Ratnaweera, H. Multivariate chemometric analysis of membrane fouling patters in biofilm ceramic membrane bioreactor. *Water* **2018**, *10*, 982. [CrossRef]

6. Sun, C.; Zhang, N.; Li, F.; Ke, G.; Song, L.; Liu, X.; Liang, S. Quantitative anallysis of membrane fouling mechanisms involved in microfiltration of humic acid-protein mixtures at different solution conditions. *Water* **2018**, *10*, 1306. [CrossRef]
7. Arahman, N.; Satria, S.; Razi, F.; Bilad, R.M. The effect of Ca and Mg ions on the filtration profile of sodium alginate solution in a polyethersulfone 2-(methacryl-oxy)-ethyl-phosphorychloline membrane. *Water* **2018**, *10*, 1207. [CrossRef]
8. Lintzos, L.; Chatzikonstantinou, K.; Tzamtzis, N.; Malamis, S. Influence of the backwash cleaning water temperature on the membrane performance in a pilot SMBR unit. *Water* **2018**, *10*, 238. [CrossRef]
9. Karanasiou, A.; Kostoglou, M.; Karabelas, A. An experimental and theoretical study on separation by vacuum membrane distillation employing hollow fiber modules. *Water* **2018**, *10*, 947. [CrossRef]
10. Zoumpouli, G.A.; Baker, R.; Taylor, C.M.; Chippendale, M.J.; Smithers, C.; Ho, S.S.X.; Mattia, D.; Chew, Y.M.J.; Wenk, J. A single tube contactor for testing membrane ozonation. *Water* **2018**, *10*, 1416. [CrossRef]
11. Mitrakas, M.; Mantha, Z.; Tzollas, N.; Stylianou, S.; Katsoyiannis, I.; Zouboulis, A. Removal of antimony species, Sb(III)/Sb(V) from water by using iron coagulants. *Water* **2018**, *10*, 1328.
12. Smoczynski, L.; Kalinowski, S.; Cretescu, I.; Smoczynski, M.; Ratnaweera, H.; Trifescu, M.; Kosobucka, M. Study of sludge particles formed during coagulation of synthetic and municipal wastewater for increasing the sludge dewatering efficiency. *Water* **2018**, in press.
13. Usman, M.; Katsoyiannis, I.; Mitrakas, M.; Zouboulis, A.; Ernst, M. Performance evaluation of small sized powdered ferric hydroxide as arsenic adsorbent. *Water* **2018**, *10*, 957. [CrossRef]
14. Katsoyiannis, I.A.; Zouboulis, A.I.; Mitrakas, M.; Althoff, H.-W.; Bartel, H. A hybrid system incorporating a pipe reactor and microfiltration for biological iron, manganese and arsenic removal from anaerobic groundwater. *Fresenius Environ. Bull.* **2013**, *22*, 3848–3853.
15. Tatoulis, T.I.; Michailides, M.K.; Tekerlekopoulou, A.G.; Akratos, Ch.S.; Pavlou, S.; Vayenas, D.V. Simultaneous Treatment of Agro-Industrial and Industrial Wastewaters: Case Studies of Cr(VI)/Second Cheese Whey and Cr(VI)/Winery Effluents. *Water* **2018**, *10*, 382. [CrossRef]