

## **Role of Membrane Surface Charge and Complexation-Ultrafiltration for Heavy Metals Removal: A Mini Review**

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### **ABSTRACT**

Membrane technology is a promising water purification unit operation from household use to industrial application owing to its simplicity of operation, efficient recovery and minimum need for chemical and space allocation. Due to that reason, study on the membrane applications have becoming more popular among scientific community nowadays and one of the applications is removal of heavy metal using ultrafiltration (UF). However, a stand-alone UF will be not able to carry out the removal of heavy metals effectively. Certain modification is required in order to enhance its rejection via unique facilitated mechanism. Thus in this review, role of surface charge interaction as well as the method of complexation-ultrafiltration were discussed.

*Keywords:* Heavy metal removal, surface charge, complexation-ultrafiltration

### **1.0 INTRODUCTION**

Human activities and industrial management malpractices have mistreated the environment [1]. Untreated or incompletely-treated waste discharged into the waterbody are polluting the resources. Furthermore, unwell-managed sanitary landfill causing leachate that carries contaminants such as heavy metal could come in contact with groundwater and contaminate the soil [2]. These kind of scenarios and many other ways of heavy metal contamination will do us no good but eventually adding more stress to the current global water scarcity.

A lot of techniques have been

specialised into treatment of wastewater containing heavy metals. There goes many conventional methods have been used upon decontamination of heavy metal, such as chemical precipitation, coagulation and flocculation, ion exchange and flotation [3]. Nevertheless, inconsistency and incomplete elimination often become the major barriers of these techniques. In addition, some of the methods like flocculation-coagulation, adsorption and chemical precipitation could also generate secondary pollutants which later become uneconomically issue of disposal [4]. Therefore, it is necessary to find other methods that could serve as another alternative treatment of

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water laden with heavy metals. Among of those techniques, membrane filtration is presented as an advantageous candidate for removal of heavy metals [5].

Membrane technology in various separation applications is growing rapidly as if it is enhancing every day. Due to massive research on the membrane technology, a lot of new improvement and ground-breaking discoveries have been achieved. Technically, the membrane separation technology evolves from the traditional pressure-driven membrane separation system such as microfiltration (MF), nanofiltration (NF), ultrafiltration (UF) and reverse osmosis (RO) to the thermally driven membrane distillation (MD) and concentration driven processes for example forward osmosis (FO). Membrane operation such as RO and NF normally show good performances in term of water fluxes and rejections towards heavy metals owing to their effective steric exclusion mechanism. However, these energy-intensive-pressure-driven membrane separation systems are often known to suffer from severe fouling and lower water flux due the high pressure applied to the system [6].

Lower-pressure membrane system such as ultrafiltration which operates at pressure ranging from 1 – 4 bars will be less susceptible to fouling. Besides, their inherently larger pore (~0.01 – 0.1 microns) also help in driving high water permeation across the membrane [7]. As a consequence, larger pore size of NF membrane would make rejection of small particles by size exclusion become ineffective. Thus it is understandable to see small particles such as dissolved salt, heavy metal ions and synthetic dyes which are

rejected by UF membrane require special modification technique either upon the membrane or the system. According to Lau *et al.*, it is proven in many literatures that membranes may demonstrate better performance particularly in term of permeability and selectivity via surface modification [8]. Besides surface modification, other methods available are impregnation of adsorptive materials into the membrane sublayer which is later called mix matrix membrane [9–11]. Another interesting methods are by enhancing the surface charge of the membrane via acid or base treatment [12, 13] and finally a technique called as complexation-ultrafiltration in which water-soluble polymer is added into feed solution for enhanced rejection which is also known as polymer-enhanced ultrafiltration (PEUF) [14, 15] or polymer-supported ultrafiltration (PSU) [16] as illustrated in Figure 1. Rether and Schuster stated that the advantages of PSU over ion exchange and solvent extraction are more likely due to its highly selective separation, efficiently fast reaction kinetics and the involvement of intrinsically low-energy ultrafiltration [16]. In order to gain more insight on the techniques of heavy metal removal by ultrafiltration, it is imperative to have a review literature pertaining this topic. Thus, this mini review could serve that purpose through some overview discussed in here regarding effect of surface charge on heavy metal retention and the use of water-soluble polymer namely, carboxymethyl cellulose (CMC), polyethyleimine (PEI) and poly (sodium 4-styrenesulfonate) (PSS) in PEUF.

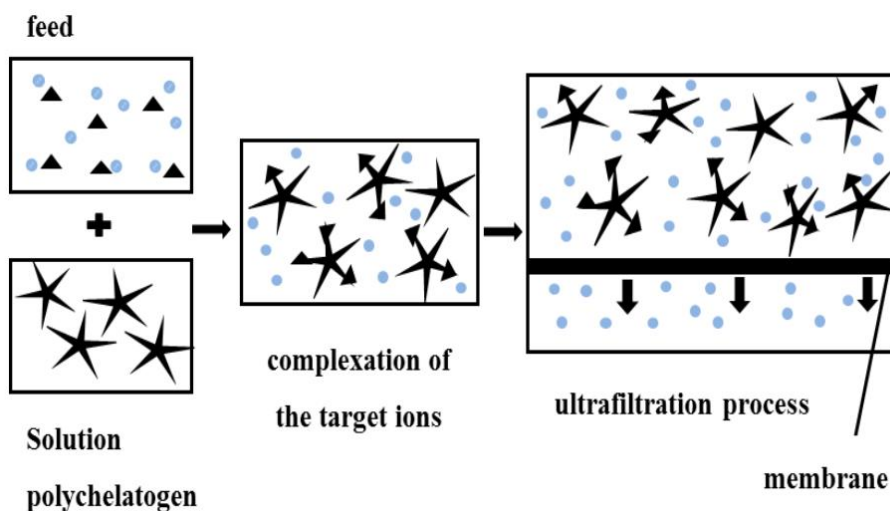


Figure 1 The schematic mechanism of PEUF [16]

### 2.1 Role of Membrane Surface Charge Toward Heavy Metal Ion Retention

Electrostatic interaction has been suggested to play an important role in the separation of charged particle [17, 18]. It is noteworthy that the performance of a membrane is significantly influenced by the effect of the surface charge of the membrane because there is electrostatic repulsion between the charged molecules and the membrane surface. Furthermore, pH also affects both the feed solution and the membrane surface charge. In feed solution, pH variation may result in protonation and deprotonation of the functional group of feed molecules while a membrane is said to be a pH-dependent because the pH of the system may affect the “openness” of the membrane due to the dissociation of membrane functional group [17].

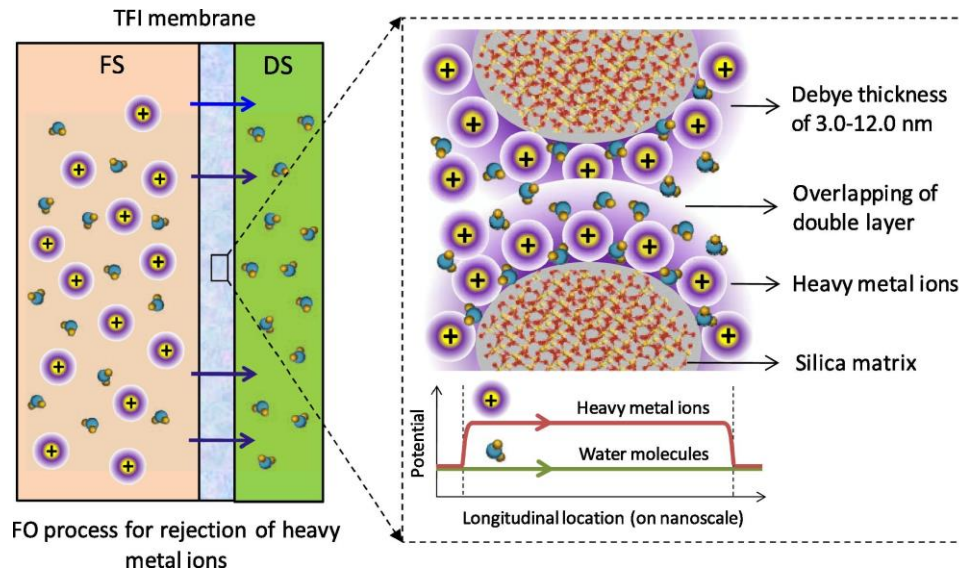
In 2008, Ortega and co-workers has studied the feasibility of using NF in the cleaning-up of acidic leachate solution generated by acid washing of contaminated soil using sulphuric acid. The experiment brought up two different NF membranes that carried different charges which were Desal5 DK (positively charged) and NF-270

(negatively charged). Essentially, charge repulsion is responsible for the effective removal of ion since ion is a charged particle. Thus, in the case of metallic ions which are positively charged, membrane with positive surface charge would be helpful in removing this type of solute [19]. Interestingly, in their experiment, both of the membranes used showed unprecedented behaviour of its metal ions rejection. NF-270 showed better metal ion retention compared to the positively charged Desal5 DK membrane due to the considerable effect of feed solution low pH. At low pH (due to acidic leachate solution) which below the isoelectric point ( $I_p$ ) caused a change on the membrane surface charge. Consequently, increased protons could possibly neutralize the negative sites on the membrane surface of Desal5 DK. In the meantime, the high retention of demonstrated by NF-270 was due to the change of charge of the membrane surface from negative to positive when  $pH < I_p$ .

Above all, the application of UF into the purification of water from heavy metal contaminants is also seen to be potentially viable. Principally, the major separation mechanism in salt separation of all of the pressurised

membrane processes can be explained in term of the steric and/or charge effect [20]. Nonetheless, the relatively bigger pore size of UF than NF hinder the effective removal of small particle such as metal ions. The size of such ions which are smaller than the pore size of UF allows the solute particle to pass through thus make the steric sieving impractical. On the other hand, researches showed that chemical modification and treatment on the membrane in order to induce a charge on the surface by incorporation of functional group could unravel this setback [21]. This claim is then confirmed by Nayak and coworkers via their research on the novel sulfanilic acid – polyvinyl chloride – polysulfone blend (PVC-SA/PSf) which was prepared via diffusion induced phase separation (DIPS). The negatively charged membrane matrix demonstrated a near complete removal (~ 95 %) of Cd (II), Pb (II), and Cr (VI) that are 1.15, 1.37 and 1.41 times respectively better compared to the commercially available NF-270 membrane [12]. Furthermore, membrane surface modification via hydrolysis of polyacrylonitrile (PAN) based UF with NaOH as shown by both Lohokare, Muthumarees-waran and their coworkers demonstrated a great deal of Donnan exclusion mechanism in enhanced rejection of arsenic and chromium ions respectively. The formation of carboxylate ( $-COO^-$ ) group on the membrane surface and within the pore wall charged the membrane negatively which in turn removed the arsenic and chromate ions effectively by excellent rejection of  $\geq 90\%$  achieved at  $pH \geq 7$ . Meanwhile, it was reported that size exclusion played insignificant role on metal ions rejection in both of the studies [13, 22]. Meanwhile You *et al.* [23] studied the effect of surface charge in pore walls of their novel thin-film inorganic forward

osmosis (TFI-FO) membrane to reduce the trade-off between water flux and selectivity. From their research, the TFI-FO membrane was synthesized via tetraethylorthosilicate (TEOS)-driven sol-gel process in which the TEOS was used as the precursor to fabricate xerogels and silica membrane. From the results, they successfully demonstrated the infamously double layer overlapping phenomenon (Figure 2) within the membrane pore induced by electrostatic interaction between the silica-made membrane pore walls and those heavy metal ions they had been experimenting. It was recorded that the TFI-FO yielded 69.0 LMH water flux using 2.0 M NaCl draw solution and averagely 94% rejection of  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  from 200 ppm feed solution. In a study by Almutairi *et al.*, selective separation, recovery and purification of heavy metals with low energy requirement have been studied using polymer enhanced ultrafiltration (PEUF). In his study, PEI was used as the "polychelator" with the cooperation of a negatively charged NADIR® asymmetric polyethersulphone (PES) membrane with MWCO of 30,000 Da. Streaming potential result of the membrane showed that the membrane portrayed negative charge over a wide range of pH with isoelectric point at pH 3.9. The results showed that the retention of heavy metal ion was the highest when the membrane had its highest negative charge. While the effect of the polymer addition was anticipated to increase the metal ion retention however reducing the water flux. As expected, the water flux was halved with the presence of PEI due to concentration polarization [24]. A deeper understanding can be achieved by briefly examining Table 1 for the comparison of the effect of surface charge according to different type of membrane filtration system.



**Figure 2** Proposed schematic mechanism double layer overlap effect within the pore of the TFI-FO membrane [23]

**Table 1** Comparison on the effect of surface charge between different type of membrane filtration systems

Author [ref]	Membrane Process	Material	Surface charge	Findings
You <i>et al.</i> [23]	FO (DS: 2M NaCl)	TFI (silica xerogel from TEOS)	Negative	Rejection avg. Efficiency of 94% with initial conc. 200 mg/L of acidic Cd, Pb, Cu, Zn.
Nayak <i>et al.</i> [12]	UF	Sulfanilic acid – PVC – PSf blend	Negative	Near complete removal ( ~95 %) of Cd (II), Pb (II), and Cr (VI)
Lohokare <i>et al.</i> [22]; Muthumareeswaran <i>et al.</i> [13]	UF	Hydrolysed PAN with NaOH	Negative	Removal of arsenic and chromate ions effectively by excellent rejection of $\geq 90\%$ achieved at pH $\geq 7$ .
Almutairi <i>et al.</i> [24]	PEUF	NADIR® asymmetric PES	Negative	Retention of heavy metal ion was the highest when the membrane had its highest negative charge.
Ortega <i>et al.</i> [19]	NF	Commercial Desal5 DK NF-270	Positive Negative	Good metal ion rejection (between 62% to 100%) with divalent ions better than monovalent ions

## 2.2 Complexation-ultrafiltration

The use of complexing agent or macroligands is basically attributed to the polymer enhanced ultrafiltration (PEUF) for heavy metal. PEUF is proposed to be a practical way to remove variety of heavy metal

contaminants from wastewater. By name, it is understandable that it uses polymer as a macroligands and in this case, a macromolecular of heavy metal ion can be formed via complexation with the help of water-soluble polymer as the complexing agent. This means, complexing a metal ion give the ion a

new molecular weight that should be larger and able to be retained when pumped through UF membrane because of size exclusion by the relatively smaller MWCO of its pores. Fu and Wang [24] however in their review paper pointed out some major concern regarding the selection of suitable polymer as the complexing agent apart from other factors affecting the degree of complexation which

include metal ion and polymer type, loading of the polymer in the metal solution, nature pH of the solution and the presence of other metallic contaminant [25]. Among vast option of polymers, Table 2 summarizes several study pertaining the use of complexing agents in PEUF for successful removal of targeted metal ions.

**Table 2** Several type of complexing agents proven to successfully remove targeted metal ions

Author [ref]	Metal	Concentration metal	Complexing agent	Findings
Chen <i>et al.</i> [28]	Cu and Pb	50 ppm	PSS (1 – 6 g/L)	Affinity of PSS towards metal ions as follows: $Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Mg^{2+} > H^+ > K^+ > Na^+ > Li^+$ . Rejection increase with increased of PSS concentration with $Pb > Cu$ .
Barakat and Schmidt [14]	Ni, Cu, Cr (III)	100 ppm	CMC (1 g/L)	With 10kDa MWCO, 1 bar, $pH \geq 7$ , rejection $Cu > Cr > Ni$ by 98.5, 97.1, and 76.4%
Aroua <i>et al.</i> [27]	Cr (III), Cr (IV)	10 ppm	Chitosan, Pectin and PEI (0.05 – 0.25 %)	Rejection of Cr (III) approaching 100% at $pH > 7$ . While Cr (IV) retention did not exceed 50% for pectin and chitosan but almost total rejection by 0.05% PEI at low pH.

Essentially, metal complexation with ligands or chelates are basically a process called chelation. There are several factors affecting the stability of the complexes formed which comprise of ligands factors, metals factors and surrounding factor. Ligands factors may include size, charge, identity of the coordinating atom(s), basicity and steric effect of the ligands [26]. For a ligand to be effective, it must have the chelate characteristic besides having highly negatively charged to form stable complex with the transition metals. Chelate characteristic refers to the number of electron donator to the metal ions (denticity) which allow the

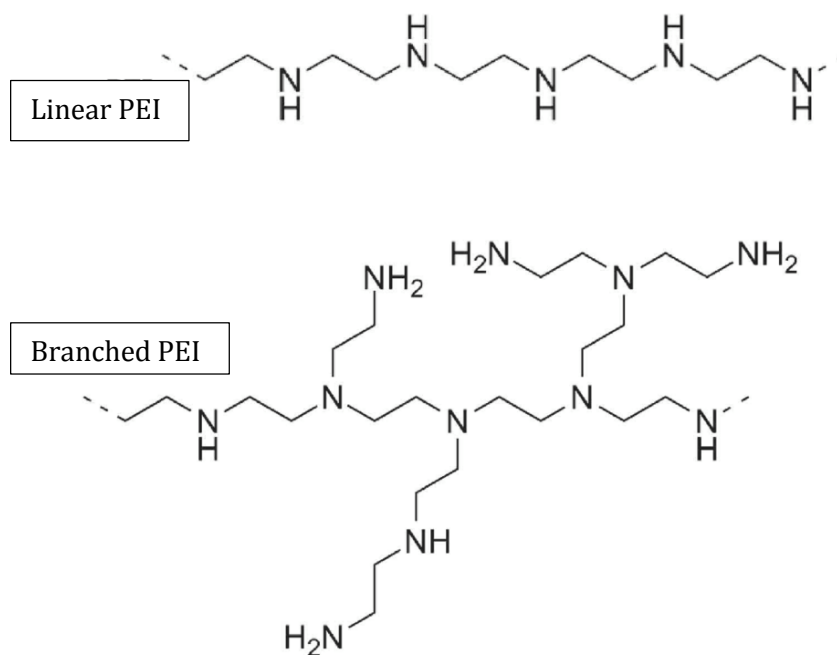
attachment of two or more donor atoms to the same metal ion simultaneously and produce one or more rings. The larger the number of chelate rings in a complex, the greater the stability of the complex.

Identity of the coordinating atom differs by each ligand. For example, the unshared electron pair on the N atom in polyethyleneimine (PEI), can form donor bonds with coordination unsaturated transition metals [27]. Meanwhile, carboxymethyl cellulose (CMC) provides different binding for different metals. For instance, oxygen of ethoxyl groups and the primary alcoholic O atom of glucopyranose

rings become the binding site for Cu (II) complexes and the etheroxygen of the hydroxyl group acts as the binding site for Cr (III) and Ni (II) [14]. On the other hands, PSS behaves like a strong-acid cation exchanger. A fraction of the initial counterion,  $\text{Na}^+$ , has a close association with the PSS functional groups, while the extent of PSS ionization can be determined by measuring free  $\text{Na}^+$  in solution. When other cations are added into the solution, they also form associations with PSS, exchanging some portions of the PSS associated  $\text{Na}^+$  into the bulk solution until equilibrium is reached [28].

Smaller size of the ligands may have advantages to easily form complexes with the metals but smaller complex does not meet the purposes of forming a complex. Therefore a larger ligand with less steric hindrance would be more preferable since high steric effect by a bulky ligand may hinder the chelation. For example in Figure 3, a linear polyethyleneimine (PEI) would have lesser steric effect and is preferred rather than the branched PEI. Basicity of the ligand may be

explained through the spectrochemical series – a list of ligands based on the strength of their interaction with metal ions. Meanwhile, from the metal factors perspectives, size and charge of the metal ions play an important role. It is plausible, a higher charged particle will form a more stable complex and on the other hands, larger size of metal ions will decrease its stability complex. In addition, a list called the Irvin-Williams stability order were often used to determine which metal gives out a stable bond with ligand since this order was found to hold for a wide variety of ligands [14]. One example of surrounding factors is pH. It is noteworthy to know that pH value carries a significant impact in the complexation process as it affect both the membrane charge as well as the chemical and physical form of the polymer ligands [15]. Normally, the metal cation retention increases as pH increases from the acidic region up to certain pH value. Moreover, at high pH region metal ions tend to form hydroxide at low solubility and may end up as precipitate [27].



**Figure 3** Linear and branched PEI

Cellulosic-based material has been deemed as a natural polysaccharide which are notably applied in various field of studies [29]. Among them, Carboxymethyl cellulose (CMC) has appeared as a viable option for an eco-friendly polymer to be used as complexing agent for PEUF. Barakat in his work, applies CMC as a complexing agent for heavy metal ion to form metal-CMC complex with increased molecular weight and size. In the study, a 10000 Da cut-off PES UF membrane is used to treat synthetic wastewater containing Cu (ii), Ni (ii) and Cr (iii) in consideration of the effect of pH value and metal/CMC ratio on percent rejection of heavy metal. As a result, maximum rejection up to 99.5% of Cr (III), 99.1% of Ni (II) and 97.6% of Cu (II) are observed as CMC/metal ratio is increased at pH 7. This is because at low pH, the presence of the positive charges hindered the affinity of CMC towards the metal ions thus reduce the stability of the complexes [30]. Meanwhile, Lam *et al.* [15], studied the performances of the PEUF which used CMC and chitosan in a certain number of conditions to remove nickel ( $\text{Ni}^{2+}$ ) from wastewater. Addition of either CMC or chitosan is proven to substantially improve the rejection of heavy metal using PEUF with the conditions of adequate amount of polymer used and the suitable pH for the complexation to occur. It is discovered that, the use of CMC is preferred to be in a natural environment ( $4 < \text{pH} < 8$ ) justifying the minor impact on the permeation flux [15]. However, treatment of complex industrial wastewater remains a challenge since the presence of numerous species impedes the chelating of the polymer with the targeted metal.

On the other hand, the adaptation of polyethyleimine (PEI) as a chelating

agent is thoroughly discussed by Aroua *et al.* In their work on PEUF to reject chromium (III) and (IV) metal ions, three water soluble polymer are used namely PEI, chitosan and pectin. Similarly, the parameters such as pH value and polymer composition in the feed solution are investigated upon their relationship towards the chromium percent retention and permeate flux at fixed pressure. As a result, it is seen that almost 100% of Cr (VI) ion removal at low pH with the help of PEI complexation while the composition of the chelating agent showed slight upshot on the rejection [27].

As for anionic polyelectrolyte such as poly (sodium 4-styrenesulfonate) (PSS), it has been studied for its selectivity towards cation affinity in binary PSS-assisted ultrafiltration system [28]. In the study, the behaviour of PSS selectivity towards several numbers of metal ion including  $\text{Mg}^{2+}$  is assessed and as a result, a selectivity sequence showing higher affinity toward divalent ion is obtained. Based on the experiment, PSS-assisted UF also has the potential to remove  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  from competitive environment even at low pH. Apart from its use as complexing agent, PSS also had been studied for its prospective as a draw solute in forward osmosis (FO) [31]. After the physical properties of PSS, they then investigate the potential of PSS as a draw agent at varying molecular weight. Interestingly, the best FO flux is exhibited by PSS (M.W: 70,000) at 0.24 g/mL concentration and in term of the PSS recovery, a simple UF system with low operating pressure (2 bar), easily manage to regenerate the draw solute. These matters may suggest new possibility for complexation of these water-soluble polymer with draw solute in forward osmosis.



### 3.0 CONCLUSION

Throughout the years have passed, environmental quality act has become more strict therefore extensive efforts have been made to address this call. The aforementioned approaches are among several methods to bring down the heavy metals content in the effluent to minimal level. The role of membrane surface charge has shown significant enhancement on the rejection of heavy metals whilst the implementation of PEUF comparatively provides better performance in term of the heavy metals retention. Despite all that, selection of proper complexing agent is important to ensure effective removal without compromising its feasibility like generating secondary pollutant for instance. In a nutshell, it is worthy to note that at the end of the day, after addressing all of the limitation, only then ultrafiltration could be found viable for the removal of heavy metals application.

### REFERENCES

- [1] M. A. Shannon, P. W. Bohn, M. Elimelech, J. G. Georgiadis, B. J. Mariñas, A. M. Mayes. 2008. Science and Technology for Water Purification in the Coming Decades. *Nature*. 452: 301-310. Doi:10.1038/nature06599.
- [2] H. B. Bradl. 2005. Chapter 1 Sources and Origins of Heavy Metals. *Interface Sci. Technol.* 6: 1-27. Doi:10.1016/S1573-4285(05)80020-1.
- [3] T. A. Kurniawan, G. Y. S. Chan, W. H. Lo, S. Babel. 2006. Physico-chemical Treatment Techniques for Wastewater Laden with Heavy Metals. *Chem. Eng. J.* 118: 83-98. Doi:10.1016/j.cej.2006.01.015.
- [4] M. A. Barakat. 2011. New Trends in Removing Heavy Metals from Industrial Wastewater. *Arab. J. Chem.* 4: 361-377. Doi:10.1016/j.arabjc.2010.07.019.
- [5] N. Abdullah, N. Yusof, W. J. Lau, J. Jaafar, A. F. Ismail. 2019. Recent Trends of Heavy Metal Removal from Water/Wastewater by Membrane Technologies. *J. Ind. Eng. Chem.* 76: 17-38. Doi:10.1016/J.JIEC.2019.03.029.
- [6] N. L. Le, S. P. Nunes. 2016. Materials and Membrane Technologies for Water and Energy Sustainability. *Sustain. Mater. Technol.* 7: 1-28. Doi:10.1016/j.susmat.2016.02.001.
- [7] Safe Drinking Water Foundation, 2008. Ultrafiltration, Nanofiltration and Reverse osmosis, Safe Drink. Water Found. 1-6. <http://www.hinesburg.org/water-project/safewaterdotorg-info-nano-and-ultrafiltration-reverse-osmosis.pdf>.
- [8] W.-J. Lau, C.-S. Ong, N. A. H. M. Nordin, N. A. A. Sani, N. M. Mokhtar, R. Jamshidi Gohari, D. Emadzadeh, A. Fauzi Ismail. 2016. Surface Modification of Polymeric Membranes for Various Separation Processes. *Surf. Treat. Biol. Chem. Phys. Appl.* 115-180. Doi:10.1002/9783527698813.ch4.
- [9] N. Abdullah, R. J. Gohari, N. Yusof, A. F. Ismail, J. Juhana, W. J. Lau, T. Matsuura. 2016. Polysulfone/hydrous Ferric Oxide Ultrafiltration Mixed Matrix Membrane: Preparation, Characterization and Its Adsorptive Removal of Lead (II)

- from Aqueous Solution. *Chem. Eng. J.* 289: 28-37. Doi:10.1016/J.CEJ.2015.12.081.
- [10] S. Shahrin, W. J. Lau, P. S. Goh, J. Jaafar, A. F. Ismail. 2018. Adsorptive Removal of As(V) Ions from Water using Graphene Oxide-manganese Ferrite and Titania Nanotube-manganese Ferrite Hybrid Nanomaterials. *Chem. Eng. Technol.* 41: 2250-2258. Doi:10.1002/ceat.201800322.
- [11] R. Jamshidi Gohari, W. J. Lau, T. Matsuura, E. Halakoo, A. F. Ismail. 2013. Adsorptive Removal of Pb(II) from Aqueous Solution by Novel PES/HMO Ultrafiltration Mixed Matrix Membrane. *Sep. Purif. Technol.* 120: 59-68. Doi:10.1016/J.SEPPUR.2013.09.024.
- [12] V. Nayak, M. S. Jyothi, R. G. Balakrishna, M. Padaki, A. M. Isloor. 2016. Synthesis and Characterization of Novel Sulfanilic Acid-polyvinyl Chloride-polysulfone Blend Membranes for Metal Ion Rejection. *RSC Adv.* 6: 25492-25502. Doi:10.1039/c6ra02590k.
- [13] M. R. Muthumareeswaran, M. Alhoshan, G. P. Agarwal. 2017. Ultrafiltration Membrane for Effective Removal of Chromium Ions from Potable Water. *Sci. Rep.* 7: 1-12. Doi:10.1038/srep41423.
- [14] M. A. Barakat, E. Schmidt. 2010. Polymer-enhanced Ultrafiltration Process for Heavy Metals Removal from Industrial Wastewater. *Desalination.* 256: 90-93. Doi:10.1016/j.desal.2010.02.008.
- [15] B. Lam, S. Déon, N. Morin-Crini, G. Crini, P. Fievet. 2018. Polymer-enhanced Ultrafiltration for Heavy Metal Removal: Influence of Chitosan and Carboxymethyl Cellulose on Filtration Performances. *J. Clean. Prod.* 171: 927-933. Doi:10.1016/j.jclepro.2017.10.090.
- [16] A. Rether, M. Schuster. 2003. Selective Separation and Recovery of Heavy Metal Ions Using Water-soluble N-benzoylthiourea Modified PAMAM Polymers. *React. Funct. Polym.* 57: 13-21. Doi:10.1016/J.REACTFUNCTPOLYM.2003.06.002.
- [17] A. E. Childress, M. Elimelech. 2000. Relating Nanofiltration Membrane Performance to Membrane Charge (Electrokinetic) Characteristics. *Environ. Sci. Technol.* 34: 3710-3716. Doi:10.1021/es0008620.
- [18] J. Zeng, H. Ye, H. Liu, H. Xie. 2006. Characterization of a Hollow-fiber Ultrafiltration Membrane and Control of Cleaning Procedures by a Streaming Potential Method. *Desalination.* 195: 226-234. Doi:10.1016/j.desal.2005.12.003.
- [19] L. M. Ortega, R. Lebrun, J. F. Blais, R. Hausler. 2008. Removal of Metal Ions from an Acidic Leachate Solution by Nanofiltration Membranes. *Desalination.* 227: 204-216. Doi:10.1016/j.desal.2007.06.026.
- [20] J. Schaep, B. Van der Bruggen, C. Vandecasteele, D. Wilms. 1998. Influence of Ion Size and Charge in Nanofiltration. *Sep. Purif. Technol.* 14: 155-162. Doi: [https://doi.org/10.1016/S1383-5866\(98\)00070-7](https://doi.org/10.1016/S1383-5866(98)00070-7).
- [21] Y. Zhang, S. Zhang, T. S. Chung. 2015. Nanometric Graphene Oxide Framework Membranes with Enhanced Heavy Metal Removal via Nanofiltration. *Environ. Sci. Technol.* 49:

- 10235-10242.  
Doi:10.1021/acs.est.5b02086.
- [22] H. R. Lohokare, M. R. Muthu, G. P. Agarwal, U. K. Kharul. 2008. Effective Arsenic Removal Using Polyacrylonitrile-based Ultrafiltration (UF) Membrane. *J. Memb. Sci.* 320: 159-166. doi:10.1016/j.memsci.2008.03.068.
- [23] S. You, J. Lu, C.Y. Tang, X. Wang, Rejection of heavy metals in acidic wastewater by a novel thin-film inorganic forward osmosis membrane, *Chem. Eng. J.* 320 (2017) 532.
- [24] F.M. Almutairi, P.M. Williams, R.W. Lovitt, Effect of membrane surface charge on filtration of heavy metal ions in the presence and absence of polyethylenimine, *Desalin. Water Treat.* 42 (2012) 131–137. doi:10.1080/19443994.2012.683097.
- [25] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, *J. Environ. Manage.* 92 (2011) 407–418. doi:10.1016/j.jenvman.2010.11.011.
- [26] G. Chauhan, K.K. Pant, K.D.P. Nigam, Chelation technology: A promising green approach for resource management and waste minimization, *Environ. Sci. Process. Impacts.* 17 (2015) 12–40. doi:10.1039/c4em00559g.
- [27] M.K. Aroua, F.M. Zuki, N.M. Sulaiman, Removal of chromium ions from aqueous solutions by polymer-enhanced ultrafiltration, *J. Hazard. Mater.* 147 (2007) 752–758. doi:10.1016/j.jhazmat.2007.01.120.
- [28] M. Chen, K. Shafer-Peltier, S. J. Randtke, E. Peltier. 2018. Competitive Association of Cations with Poly(sodium 4-styrenesulfonate) (PSS) and Heavy Metal Removal from Water by PSS-assisted Ultrafiltration. *Chem. Eng. J.* 344: 155-164. Doi:10.1016/j.cej.2018.03.054.
- [29] H. Ibrahim, N. Sazali, I. Naiman, M. Sharip. 2019. Nano-structured Cellulose as Green Adsorbents for Water Purification: A Mini Review. *J. Appl. Membr. Sci. Technol.* 23: 45-56. Doi:10.11113/amst.v23n2.154.
- [30] M. A. Barakat. 2008. Removal of Cu (II), Ni (II) and Cr (III) Ions from Wastewater Using Complexation-ultrafiltration Technique. *J. Environ. Sci. Technol.* 1: 151-156. Doi:10.3923/jest.2008.151.156.
- [31] E. Tian, C. Hu, Y. Qin, Y. Ren, X. Wang, X. Wang, P. Xiao, X. Yang. 2015. A Study of Poly (sodium 4-styrenesulfonate) as Draw Solute in Forward Osmosis. *Desalination.* 360: 130-137. doi:10.1016/J.DESAL.2015.01.001.