ORIGINAL ARTICLE

Removal of Heavy Metals from Oil Refinery Effluent by Micellar-Enhanced Ultrafiltration (MEUF)

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Received: 11 April 2018
Revised: 10 May 2018
Accepted: 12 June 2018

Abstract

Background: One of the major pollutants in the environment is heavy metals. The stability of heavy metals in the environment has created a lot of problems. Refinery effluents are one of the most important sources of heavy metals and should be treated before being discharged into the environment.

Methods: This interventional experimental study aimed to remove heavy metals from petroleum effluent by using the micellar-enhanced ultrafiltration (MEUF) at Kermanshah Oil Refinery. Since ultrafiltration membranes alone cannot remove the heavy metals, surface active agents, such as surfactants, are injected into the effluent. Surfactant monomers in reaction to metal ions creating a complex that cannot cross the ultrafiltration membrane. Heavy metals are removed from the effluent stream. In the present study, Sodium Dodecyl Sulfate (SDS) as surfactant was used to add the effluent to improve the process of heavy metal removal.

Results: The results showed that heavy metals such as nickel, lead, cadmium and chromium decreased by 96%, 95%, 92% and 86%, respectively. In the inlet effluent with increasing pH, the efficiency of the processes for metal removal increased, so that at pH=10, the highest removal efficiency was observed.

Conclusion: According to the results of this study, the use of membrane processes as a practical and efficient method in industrial wastewater treatment can be applied in various industries, especially refinery ones.

Please cite this article as: Hashemi F, Hashemi H, Dehghani M, Hoseini M. Removal of Heavy Metals from Oil Refinery Effluent by Micellar-Enhanced Ultrafiltration (MEUF). J Health Sci Surveillance Sys. 2018;6(3):123-129.

Keywords: Heavy metals removal, Oil refinery, Micellar-enhanced ultrafiltration (MEUF), Sodium Dodecyl Sulfate, Effluent

Introduction

The development of urbanization and the industrialization process are two important factors in causing environmental pollution by heavy metals, which has been increasing since the 1940s to the present day.[1-3] Hence, heavy metals pollution is a major challenge in the current societies. In developing countries, the release of heavy metals to the environment, either directly or indirectly, is increasing. Various industries, such as refineries and petrochemicals, paint manufacturing, pesticides, melting and plating of metals, tannery, military products, etc., are considered as sources of production and release of heavy metals to the environment.[4, 5] Heavy metals have the characteristics of persistence and non-biodegradability, which can accumulate in the human tissues by entering the food chain.[6] Although some heavy metals are essential for biological systems, they can cause toxicity, cancer, and ultimately death depending on the dose and duration of exposure to them. Unnecessary heavy metals include mercury, cadmium, lead, and arsenic, which can also be toxic in very low concentrations.[1] Table 1 summarizes the Maximum Contaminated Level (MCL) standards, for Nickel, Lead, Cadmium and Chromium identified

Table 1: The Maximum Contaminated Level (MCL) standards for heavy metals

Heavy Metal	Toxicities	MCL(mg/L)
Nickel	asthma, coughing, human carcinogen	0.20
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system and nervous system	0.006
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogen	0.05

by USEPA.[7] Since heavy metals are very toxic in low amounts, considering strict rules to minimize exposure, removal of heavy metals from industrial effluent before discharging into the environment and receiving the water is essential. The effluent of oil-refineries and petrochemical industries has various chemical pollutants such as Polycyclic Aromatic Hydrocarbons (PAHs), Phenols, Heavy Metals, Surfactants, Sulfides and other chemicals.[8] In terms of physical characteristics, heavy metals generally have an atomic weight of 63.5 to 200.6 and gravity of more than 5.[9, 10] Depending on the industry, industrial effluent is different in terms of the nature and concentration of pollutants, and the treatment and disposal methods. Therefore, the selection of the treatment method depends on the parameters such as the volume of the treated effluent, type and concentration of the pollutant, and level of toxicity.[9] According to research conducted by Fenglian et al. (2011) and Rao et al. (2011), methods such as ion exchange, chemical precipitation, membrane processes, coagulation and flocculation, and electrodialysis can be used as an efficient method for the removal of metals at medium and high concentrations.[11, 12] On the other hand, using these methods at low concentrations of heavy metals is ineffective and non-economic.[6] Methods used for removing and separating heavy metals from wastewater streams are of three types of physical, chemical and biological. These methods have certain limitations. In physical removal methods, parameters that can affect the effectiveness of this method include size and shape of the particulate, magnetic properties, humic content, hydrophobic properties of the particle surface, and clay content.[13, 14] Some of the methods of physical separation of heavy metals from wastewater include Membrane filtration, hydrodynamic classification, flotation, magnetic separation, gravity concentration, and mechanical screening.[15] Ion exchange, chemical precipitation, adsorption, electrochemical deposition of chemical treatment, and flotation are used as conventional chemical methods for the separation of heavy metals. One of the limiting factors in using these methods is the calcite, high buffering capacity, anions, and high content of clay/silt.[11] Some disadvantages of physical and chemical methods include the costs related to the purchase of chemicals, the cost of sludge disposal and high energy consumption. The use of physico-chemical methods is the most appropriate approach if chemical costs are reduced in any way possible.[14] Ultrafiltration is a membrane separation process with a pore size of 0.1 to 0.001 microns and is capable of removing and separating high molecular weight materials, organic and inorganic polymers, turbidity, suspended solids, and microorganisms. The separation mechanism in this method is based on the particle size.[16] Today, the use of membrane methods, especially the ultrafiltration process due to non-use of chemicals, ability to be set up in limited space and high efficiency at low pressures, is of interest to various industries for water and wastewater treatment. This method has high efficiency in the removal of microorganisms, turbidity, suspended solids, organic compounds and inorganic contaminants such as heavy metals.[14] The purpose of this study was to use the ultrafiltration process to remove heavy metals including nickel, lead, cadmium and chromium from oil refinery effluent.

Materials and Methods

This is an intervention-experimental study conducted at Kermanshah Oil Refinery. In this study, we used the ultrafiltration process for the removal of heavy metals. At first, sampling was performed from the refinery effluent, and based on the available parameters (pH, Temperature and Turbidity), the membrane was provided for the ultrafiltration process. The sampling was done for 4 months (weekly) from the inlet and outlet effluent from the pilot. For increasing the accuracy, 20% of the samples were duplicate. Therefore, 40 samples were taken and analyzed. All experiments were carried out according to Standard method guidelines.[17] Heavy metals (nickel, lead, cadmium and chromium) were measured by Atomic Absorption Spectrometry(AAS) according to the Standard method guidelines (Standard Test Number, 3111B). The pH of the inlet and outlet effluent was measured using a pH meter (Product by Insmark Co, Model: is136). Turbidity measurement was performed in accordance with the Standard method guidelines (Standard Test Number, 2130), using a Turbidity meter, Model: 2100Q, Product by HACH Co (Measurement Accuracy: 0-1000 NTU). Since membrane technology, such as ultrafiltration for the separation of heavy metals, is prone to degradation in certain amounts of pH, the use of appropriate membranes applicable to a wide range of pH is essential. The membrane properties used in the ultrafiltration process are shown in Table 2.

Membrane Preparation

The schematic of the purification process is shown in Figure 1. The soluble metal ions are low in hydrate formations or molecular-weight complexes, which are smaller than the size of membrane cavities

Table 2: Specifications for polysulfone membrane (PS)

Membrane type	MWCO	Functional range in operational conditions		
Polysulfone	30 kDa	T (ºC)	P (bar)	pH
		0-75	1-10	1-13

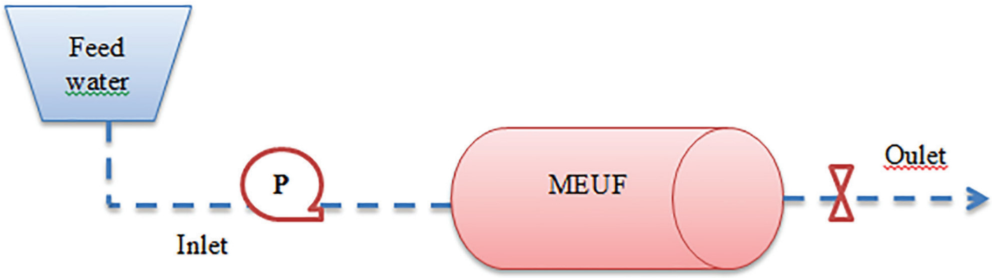

Figure 1: The schematic of the treatment process

and easily pass through the membrane. Therefore, in order to overcome this problem and increase the removal efficiency, we should use the membrane of ultrafiltration with micelles or polymer improvers. This process is based on the addition of surface active agents (Cationic or anionic surfactants) to the effluent. Surface active agents accumulate on the surface of the micelles and bond with metal ions, and by forming larger structures, they easily trap inside membrane cavities. Therefore, in this study, Micellar enhanced ultrafiltration (MEUF) was used. Since one of the most effective factors for the removal of metals using the MEUF method is pH, in this study, sodium hydroxide (NaOH) and HCl were used for pH adjustment. The type of anionic surfactant used in this work was sodium dodecyl sulfate (SDS).

Statistical Analysis

After subsequent experiments, the data were analyzed using Excel and SPSS software. Kolmogorov-Smirnov test was used to investigate the normal distribution of data. The removal efficiency of heavy metals was investigated before and after the treatment method, using paired t-test.

Results

Table 3 shows the average concentration of heavy metals and other parameters in the feed water to the ultrafiltration process. The efficiency of MEUF in the removal of heavy metals and the trend of changes in the concentration of heavy metals in the inlet and outlet effluent from the pilot are shown in Figures 2-6.

In Figure 2, Nickel concentration changes before and after the process MEUF are shown in 20 operating runs. According to Table 3, the Nickel concentration in the feed water was 0.176 mg/l; after passing through the MEUF membrane, it was 0.007 mg/l. The results of this study showed that the percentage of nickel removal increased by increasing the pH. At pH=10, the removal percentage increased to 98%.

Figure 3 shows the trend of changes in the concentration of Lead in the effluent. According to the results of this study (Table 3), the average lead concentration in the effluent was 0.03 mg/l, which decreased after passing the ultrafiltration process to 0.001 mg/l. Therefore, this reduction in concentration indicates the effective efficiency of this process in reducing this heavy metal. The results of this study showed that the removal efficiency of lead in the MEUF process was 95%.

According to Table 3, the mean concentration of Cadmium in the effluent was 0.045 mg/l which decreased to 0.003 mg/l after passing the ultrafiltration membrane. The cadmium removal efficiency was 92%, using the method investigated in this study.

In Figure 5, Chromium concentration changes before and after the process MEUF are shown in 20 operating runs. According to Table 3, the chromium concentration in the feed water was 0.022 mg/l, which reaced 0.003 after passing through the MEUF membrane mg/l. The removal efficiency of chromium was 86%, using the method investigated in this study.

Table 3: Quality of Feed water

Parameter	Mean±SD	Range
pH	7.56±0.75	6.1–8.9
Turbidity	8.68±1.73	4.3–12
Nickel	0.176±0.013	0.149–0.197
Lead	0.03±0.005	0.021–0.040
Cadmium	0.045±0.006	0.032–0.055
Chromium	0.022±0.003	0.017–0.029

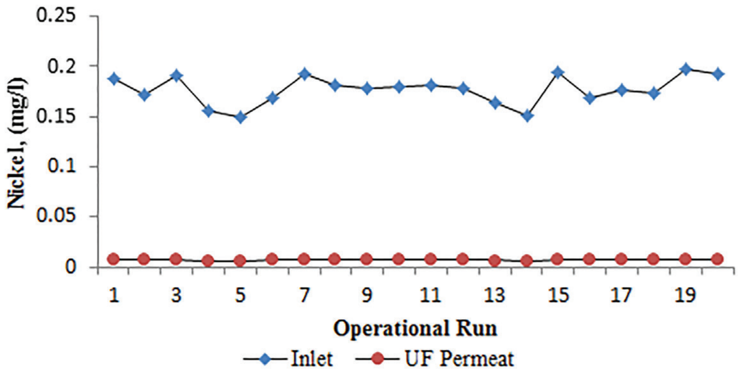

Figure 2: The trend of changes in the concentration of Nickel before and after the pilot

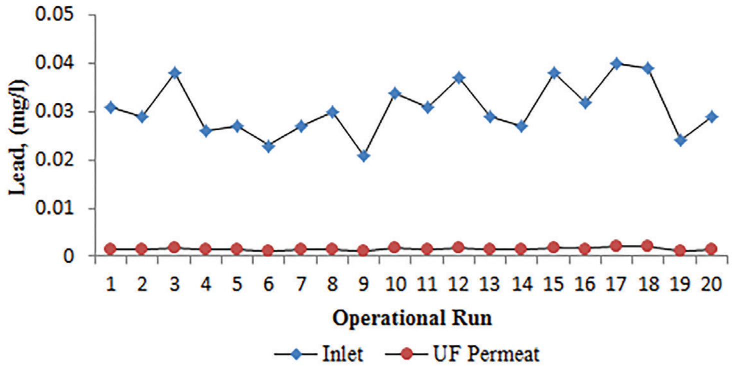

Figure 3: The trend of changes in the concentration of Lead before and after the pilot

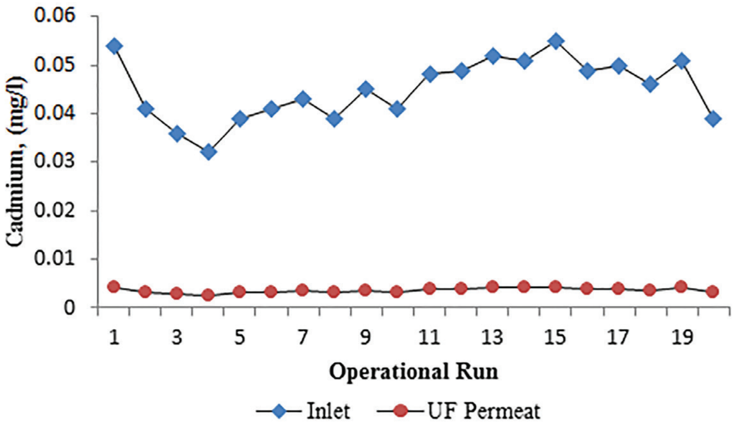

Figure 4: The trend of changes in the concentration of Cadmium before and after the pilot

Discussion

The efficiency of the micellar-enhanced ultrafiltration (MEUF) method in reducing the amount of Nickel in the effluent was reported 96%. In a study by Encarnacion Samper et al., (2010), using the MEUF, the nickel removal rate was reported 70%.[18] In another study by Fang et al. (2011), it was shown that the effluent treatment process using micellar-enhanced ultrafiltration (MEUF) could reduce the nickel content by more than 98%.[19] Statistical analysis indicated that the MEUF method was significant in reducing nickel (P<0.001).

Lead is one of the most important pollutants that can cause serious risks in the air and water. The efficiency of the micellar-enhanced ultrafiltration (MEUF) method in reducing the amount of Lead in the effluent was reported 95%. This removal percentage was due to an increase in the amount of injectable surfactant up to 4 g/L. In a study by Xue Li et al. (2017) entitled "Adsorption of metals by micellar-enhanced ultrafiltration (MEUF)", the removal efficiency of lead by increasing the surfactants up to 4.5 g/l was reported 93%.[20] In another study conducted by Rahmanian et al. (2012) entitled "Investigating the efficiency of the MEUF process in removing lead from aqueous solution", the results showed that if optimal conditions were provided, such as pH and

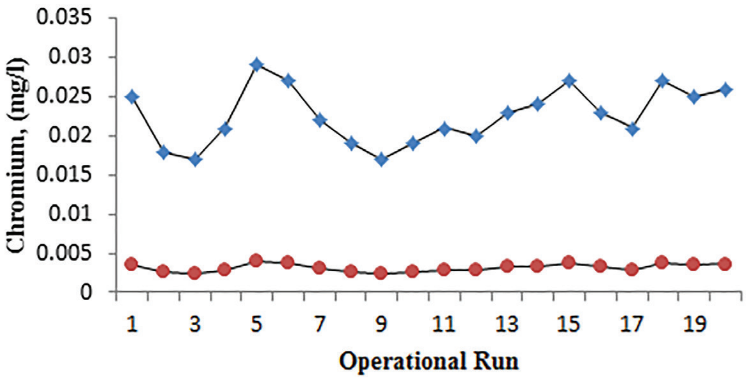

Figure 5: The trend of changes in the concentration of Chromium before and after the pilot

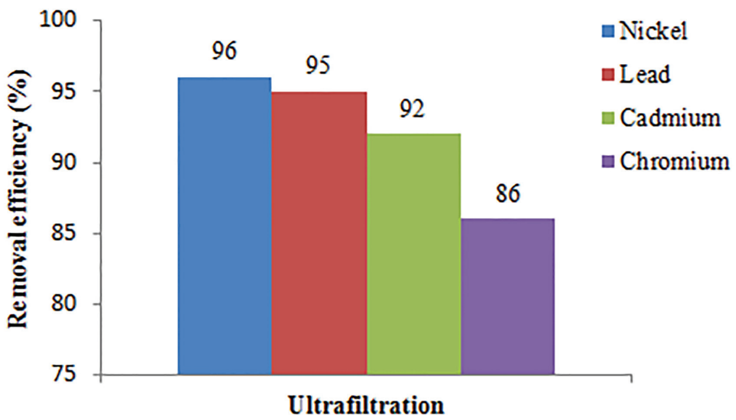

Figure 6: Removal efficiency of heavy metals

concentration of surfactants, up to 99% of the lead could be removed.[21] Statistical analysis indicated that the MEUF method was significant in reducing the amount of lead (P<0.001).

Cadmium is one of the most dangerous heavy metals that has adverse effects on human health. The efficiency of the micellar-enhanced ultrafiltration (MEUF) method in reducing the amount of Cadmium in the effluent was reported 92%. El Zeftawy et al. (2011) in a study entitled "Removal of Heavy Metals Using MEUF in the Presence of a Bio-Surfactant," 99% cadmium removal efficiency was reported using a membrane with a characteristic of 30000 MWCO.[22] In the study of Xue Li et al. (2017), the rate of cadmium removal by (MEUF) method was reported 97%.[20] Aguirre et al. (2012) removed some heavy metals in phosphorus-rich drainage water using ultrafiltration. The removal efficiency of cadmium was reported to be 84% in the study.[23] The MEUF method in this study was significant in reducing the cadmium content (P<0.001).

The efficiency of the micellar-enhanced ultrafiltration (MEUF) method in reducing the amount of Chromium in the effluent was reported to be 86%. The MEUF method in this study was significantly effective in reducing the cadmium content (P<0.001). In similar studies conducted by Baek et al. (2004) and Ghosh et al., (2006) aiming to remove the chromium using MEUF, the effective removal of this method was 98% and 99%, respectively.[24, 25] The results of Lassâad Gzara et al. showed that the ultrafiltration method was able to remove chromium by 88%.[26] One of the differences between Lassâad Gzara et al.'s study and the present study was the type of the surfactant used. The type of the surfactant used in the present study and that of Lassâad Gzara was anionic and cationic, respectively. It should be noted that the type of surfactant used did not make a significant difference in chromium removal efficiency.

Generally, in the present study, the removal efficiency of heavy metals (Nickel, Lead, Cadmium and Chromium) by MEUF process was 96%, 95%, 92% and 86%, respectively. The results of statistical analysis using SPSS software indicated that the MEUF process was significant in the removal of heavy metals.

Conclusion

All industrial wastewater, depending on the type of reuse or disposal in the environment, should be treated as much as possible to avoid environmental problems. Nowadays, membrane methods are one of the effluent treatment methods used for treatment of industrial effluent containing heavy metals. The most important factors affecting the process of removing heavy metals from aqueous solutions through ultrafiltration are pH, operating pressure, surfactant concentration, membrane type and its pore size and temperature. The results of this study showed that the presence of surfactants, especially SDS, has been successful in the removal of multivalent metal ions when using the micellar-enhanced ultrafiltration (MEUF). In this study, pH was determined as an effective factor in the removal of heavy metals, and with the increase of pH, the removal efficiency was also increased. Although the MEUF process in the presence of surfactants is used as an effective method for the removal of heavy metals, it has not yet been completely applied in the industrial scale. According to the statistical analysis of the data and results obtained in this study as well similar studies showed that the filtration process was effective in the removal of heavy metals.

Acknowledgment

This article was extracted from an MSc thesis of Environmental Health Sciences (approved No 16091), which was financially supported by Shiraz University of Medical Sciences. Also we would like to thank Kermanshah oil Refinery Company.

Conflict of Interest: None declared.

References

1 Ali H, Khan E, Ilahi I. Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity, and Bioaccumulation. Journal of Chemistry. 2019;2019.

2 Khan F, Rahman A, Jan A, Riaz M. Toxic and trace metals (Pb, Cd, Zn, Cu, Mn, Ni, Co and Cr) in dust, dustfall/soil. JOURNAL-CHEMICAL SOCIETY OF PAKISTAN. 2004;26:453-6.

3 Merian E. Introduction on environmental chemistry and global cycles of chromium, nickel, cobalt beryllium, arsenic, cadmium and selenium, and their derivatives. 1984.

4 Kadirvelu K, Thamaraiselvi K, Namasivayam C. Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. Bioresource technology. 2001;76(1):63-5.

5 Huang Y, Miao YE, Liu T. Electrospun fibrous membranes for efficient heavy metal removal. Journal of Applied Polymer Science. 2014;131(19).

6 Lakherwal D. Adsorption of heavy metals: a review. International journal of environmental research and development. 2014;4(1):41-8.

7 Babel S, Kurniawan TA. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. Journal of Hazardous Materials. 2003;97(1):219-43.

8 Marcus A, Ekpete O. Impact of Discharged Process Wastewater from an Oil Refinery on the Physicochemical Quality of a Receiving Waterbody in Rivers State, Nigeria2014.

9 Bazrafshan E, Mohammadi L, Ansari-Moghaddam A, Mahvi A. Heavy metals removal from aqueous environments by electrocoagulation process- a systematic review2015. 74 p.

10 Srivastava N, B Majumder C. Novel biofiltration methods for the treatment of heavy metals from industrial wastewater2008. 1-8 p.

11 Fu F, Wang Q. Removal of heavy metal ions from wastewaters: a review. Journal of environmental management. 2011;92(3):407-18.

12 Rao L, Hayat K, Lv Y, Karangwa E, Xia S, Jia C, et al. Effect of ultrafiltration and fining adsorbents on the clarification of green tea. Journal of Food Engineering. 2011;102(4):321-6.

13 Smith L. Contaminants and remedial options at selected metal-contaminated sites. Technical resource report. Battelle, Columbus, OH (United States); 1995.

14 Gunatilake S. Methods of removing heavy metals from industrial wastewater. Methods. 2015;1(1).

15 Dermont G, Bergeron M, Mercier G, Richer-Laflèche M. Metal-contaminated soils: remediation practices and treatment technologies. Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management. 2008;12(3):188-209.

16 Cheryan M. Ultrafiltration handbook: Technomic Publishing Co. Inc.; 1986.

17 Association APH, Association AWW. Standard methods for the examination of water and wastewater: American public health association; 1989.

18 Samper E, Rodríguez M, Sentana I, Prats D. Removal of nickel by means of micellar-enhanced ultrafiltration (MEUF) using two anionic surfactants. Water, air, and soil pollution. 2010;208(1-4):5-15.

19 Li F, Li X, Jingdong Z, Peng L, Liu C. Removal of organic matter and heavy metals of low concentration from wastewater via micellar-enhanced ultrafiltration: an overview. IOP Conference Series: Earth and Environmental Science. 2017;52:012077.

20 Li X, He S, Feng C, Zhu Y, Pang Y, Hou J, et al. Non-Competitive and Competitive Adsorption of Pb2+, Cd2+ and Zn2+ Ions onto SDS in Process of Micellar-Enhanced Ultrafiltration. Sustainability. 2018;10:92.

21 Rahmanian B, Pakizeh M, Maskooki A. Optimization of lead removal from aqueous solution by micellar-enhanced ultrafiltration process using Box-Behnken design. Korean Journal of Chemical Engineering. 2012;29(6):804-11.

22 El Zeftawy MM, Mulligan CN. Use of rhamnolipid to remove heavy metals from wastewater by micellar-enhanced ultrafiltration (MEUF). Separation and Purification Technology. 2011;77(1):120-7.

23 Landaburu-Aguirre J, Pongrácz E, Sarpola A, Keiski R. Simultaneous removal of heavy metals

from phosphorous rich real wastewaters by micellar-enhanced ultrafiltration. Separation and Purification Technology. 2012;88:130–7.

24 Baek K, Yang J-W. Effect of valences on removal of anionic pollutants using micellar-enhanced ultrafiltration. Desalination. 2004;167:119-25.

25 Ghosh G, Bhattacharya PK. Hexavalent chromium ion removal through micellar enhanced ultrafiltration. Chemical Engineering Journal. 2006;119(1):45-53.

26 Gzara L, Dhahbi M. Removal of chromate anions by micellar-enhanced ultrafiltration using cationic surfactants. Desalination. 2001;137(1):241-50.