

## CHROMIUM IONS REMOVAL FROM GROUNDWATERS BY FUNCTIONALIZED ULTRA-FILTRATION MEMBRANES

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**Abstract.** This paper aims to summarize techniques that are used in functionalized ultrafiltration membranes for chromium ions removal. Since pore size of ultrafiltration membranes are not suitable to separate heavy metal ions, water-soluble polymers are used to bind the metals to form macromolecular complexes that will be retained, while the non-complexed ions pass through the membrane. With this method, using different water-soluble polymers or introducing new functional groups to the polymer, it is possible to achieve selective separation and recovery of heavy metals with low energy requirements.

**Keywords:** chromium removal, functionalized ultrafiltration membranes.

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### 1. Introduction

Heavy metals, such as Cd, Cr, Cu, Ni, As, Pb, and Zn, because of their high solubility in the aquatic environments, can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders. Therefore, it is necessary to treat metal contaminated water. (Barakat, 2011).

Membrane separation has been increasingly used recently due to its convenient operation. There are different types of membrane filtration such as Microfiltration (MF) ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Ultrafiltration (UF) utilizes permeable membrane to separate macromolecules and suspended solids from aquatic solutions on the basis of the pore size (5–20 nm) and molecular weight of the separating compounds (1000–100,000 Da). (Barakat, 2011).

Low energy driven membranes, such as Microfiltration or Ultrafiltration cannot therefore separate dissolved ions from water. Their removal is normally accomplished by adsorption on suitable solid media, which is able to bind the toxic components from the water. Basically, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/ or chemical interactions. (Barakat, 2011).

Recently, researchers have used adsorption or coagulation for removal of arsenic or chromate and then they used membrane filtration to separate the solids created and thus achieve high rates of water purification (Katsoyiannis *et al.*, 2013; Stylianou *et al.*, 2018). These are called hybrid treatment methods, because they use two different techniques to combine their advantages and achieve more efficient treatment.

Another hybrid separation technique is polymer-enhanced ultrafiltration (PEUF). PEUF is the combination of two phenomena; binding of metal ions to a water-soluble polymer, and ultrafiltration. Since pore size of ultrafiltration membranes are not suitable to separate heavy metal ions, water-soluble polymers are used to bind the metals to form macromolecular complexes. These large molecules, having a larger molecular weight than the molecular weight cut off of the membrane, will be retained, while the non-complexed ions pass through the membrane. With this method, using different water-soluble polymers or introducing new functional groups to the polymer, it is possible to achieve selective separation and recovery of heavy metals with low energy requirements (Aroua *et al.*, 2007). Several experiments have been done using biopolymer macroligands able to complex heavy metal ions such as chitosan. The other group of macroligands is the synthetic macroligands such as carboxyl methyl cellulose. (Barakat *et al.*, 2010).

In view of the demand for more versatile and highly tailored membranes, membrane scientists are currently engaged in the development of new polymeric materials. Cellulose Acetate (CA) has been considered as an important membrane material because of its advantages such as moderate flux and high salt rejection properties. However, the application of CA in ultrafiltration (UF) membrane preparation is limited because of the drawbacks such as fairly narrow temperature and pH range of usage (maximum 30°C, pH 2–8), and high biodegradability, which reduces the membrane lifetime. Moreover, CA is not suitable for aggressive cleaning, has low thermal, oxidation and chemical resistance; thus, the modification of CA membranes is the endless necessity of time. Another important membrane material, poly(ether-sulfone) (PES) is a versatile high-performance polymer with high thermal, mechanical and chemical stability. However, application of PES as a membrane material is limited because of its drawbacks such as strict membrane casting conditions, relatively low rejection and high hydrophobic nature which leads to severe fouling during macro molecular separations. Thus, in order to develop membranes with enhanced fouling resistance and separation efficiency, it is desirable to make PES membrane more hydrophilic and it can be achieved by functionalization. Thus, in order to develop cellulose acetate UF membranes with better separation efficiency it had been blended with epoxidated PES. To improve the hydrophilicity and selectivity of PES membranes, researchers introduced epoxy groups into PES backbone. (Jayalakshmi *et al.*, 2012)

Polysulfone (PSf) is a widely used material in the preparation of membranes for the variety of membrane separation processes. The need for an efficient membrane especially for heavy metal ion separation necessitates the matrix or surface modification of the membranes. The necessity arises from the incapability of the manufactured membranes in rejection or adsorption of small molecules or stems from the hydrophobic nature of the membrane. Nano-materials such as SiO<sub>2</sub>, have been popularly incorporated into polymer matrix of membranes. Among different surface modifiers, polydopamine (PDA) has drawn considerable attention as a universal membrane surface modifier for improving hydrodynamic permeability and antifouling properties. The PDA coating on the surface of substrates is typically thin and offers highly robust structure at a wide range of pH and on pressure driven flow conditions. (Habibi *et al.*, 2015)

Artificial mesoporous silica materials were extensively used to remove heavy metals from aqueous medium. Among the series of the mesoporous silica sieves, MCM-41 possesses a unique large surface area, well-defined pore size and shape, MCM-41 and organic/inorganic modified MCM-41 were widely used as catalysts or adsorbents

and showed many excellent performances. As a common and multi-purpose modification method, numerous studies manifested the excellent application prospect of amine-functionalized MCM-41 (NH<sub>2</sub>-MCM-41) in adsorption. For dealing with heavy metals, NH<sub>2</sub>-MCM-41 was also reported as high-effective adsorbent for heavy metals from aqueous solutions. NH<sub>2</sub>-MCM-41 with PVDF UF membrane which may provide a facile route to endow membrane with ability to extract heavy metals from aqueous solution, and to enhance its anti-fouling performance. (Bao *et al.*, 2015).

Chemical structure of graphene oxide (GO) is reported as oxidized graphene, decorated with various oxygenated functionalities such as hydroxy, epoxy on the basal plane and carbonyl, carboxylic acid at the edges. Through the sharing of the lone electron pair on oxygen, it can efficiently bind the metal ion to form metal complex, thereby, rendering it an effective adsorbent for removal of heavy metal ions. In spite of having high adsorption efficiency, GO has some disadvantages: (i) possibility of leaching of GO nanoparticles, due to high affinity towards water and (ii) high cost of synthesis. Considering the above challenges, a mixed matrix membrane (MMM) of ultrafiltration (UF) grade can offer an attracting alternative. The GO impregnated MMM has the following advantages: (i) no leaching of GO nanoparticles; (ii) the membrane can be easily regenerated and (iii) as the required amount of GO is less, the process will be cost effective. MMM is defined as a class of composite membrane where one or more inorganic additives are dispersed in polymeric matrix. (Mukherjee *et al.*, 2016)

The continued attention of membranes scientists for polysulfone (PSf) is due to its excellent characteristics such as solubility in a large range of aprotic polar solvents (dimethylformamide, dimethylacetamide, dimethylsulfoxide), high thermal resistance (150–170<sup>0</sup>C), chemical resistance on the entire pH range, resistance in oxidative medium (hypochlorite, hydrogenperoxide) and also due to the high mechanical resistance of the films (fracture, flexure, torsion). Applications of the PSf membrane are often limited because of its hydrophobic nature. Because of its hydrophobic properties, performance of PSf membranes results in low water flux and serious membrane fouling. Carboxylated or sulfonated polysulfone showed increased hydrophilicity. The large surface and the nano size diameters of the CNTs could be effectively used in modifying the polysulfone membrane, a step forward in transforming an ultrafiltration membrane to a nanofiltration membrane. (Shah *et al.*, 2017)

The pH value is a very important factor in most cases of polymeric binding since either protons or hydroxyl anions can compete with metal to be bound to the polymer. Generally, for example, the presence of protons influences the equilibrium of ion-exchange processes and also, of complex equilibria. If several metal ions form macromolecular complexes with different stability constants, it is possible to separate them by varying the pH. (Aroua *et al.*, 2007)

Chromium is a unique toxic element, regulated with respect to its oxidation stages between Cr(III) and Cr(VI). Chromium (VI) is recognized to be much more toxic than chromium(III). Hexavalent chromium compounds are carcinogenic and corrosive on tissue, and are found to be toxic to bacteria, plant, animals and people. Human toxicity includes lung cancer, as well as kidney, liver, and gastric damage. (Aroua *et al.*, 2007). In natural waters, the species which is mainly present is the Cr(VI) species, because the Cr(III) species are much less soluble. Conventional removal of chromate by water employs the use of Fe(II) salts, which react with Cr(V). This reaction results in the reduction of Cr(VI) to Cr(III) and in the oxidation of Fe(II) to Fe(III), which in the pH values of natural waters (i.e., 6-8) forms insoluble iron oxides, which are able to

precipitate and adsorb the Cr(III), which is the result of Cr(VI) reduction (Stylianou *et al.*, 2018). However, this technology is only chromate specific and has some limitation, such as the high ratio of Fe(II)/Cr(VI) which is required for efficient removal of chromate, thus the formation of high amounts of toxic sludge which has to be handled and the possibility to have residual iron concentrations in the treated water, if high dosages of Fe(II) are used.

Therefore, the present review article aims to explore the use of modified UF membranes as an alternative solution for chromium removal from water. Studies on the application of PEUF for the removal of chromium species are scarce in the open literature. Pectin, polyethyleneimine (PEI) and chitosan, are water-soluble polymers that are frequently used. (Aroua *et al.*, 2007). The objective of the present study is to summarize the main studied investigating the removal of chromium species by modified polymer membranes or by polymer enhanced ultrafiltration as a viable alternative to the traditional removal of chromate by reaction by Fe(II).

## 2. Pectin, polyethyleneimine (PEI) and chitosan PEUF

The effect of pH on rejection of chromium ions using pectin has been studied by Aroua *et al.* Cr(III) rejection is much higher than that of Cr(VI) over the entire tested pH range. At pH 3, the Cr(III) rejection is low due to the protonation of chelating groups which in this case are carboxylic functions. As expected the retention of Cr(III) increases with increasing pH due to the deprotonation of the carboxylic groups of pectin that results in an increase in Cr(III) complexation. At pH greater than 6, the Cr(III) retention reaches a plateau at a value of 99%. The rejection of Cr(VI) is found to be independent of pH. Over the entire investigated pH range, the retention of Cr(VI) remained almost constant around a value of 30%. This result indicates lower ability of Cr(VI) ion to be bound with pectin. This is in line with the Cr(VI) speciation profiles which indicate that Cr(VI) is mainly present as anionic species. (Aroua *et al.*, 2007).

Chitosan is the most prominent modified natural polymer as cationic polyelectrolyte. Commercial chitosan is the medium molecular weight and has a charge density, which is pH dependent and can be as high as 80 mol%. The rejection for both Cr(III) and Cr(VI) increases with increasing pH especially at higher pH started from neutral pH in the order  $R_{Cr(III)} > R_{Cr(VI)}$ . Cr(III) rejection increases with increasing pH and then reaches plateau at near 10. For Cr(VI), the rejection first decreases with the pH and then gradually increases to reach a plateau starting from pH 9. (Aroua *et al.*, 2007).

Cr(III) rejection with PEI first decreases at low pH values. Then the Cr(III) retention increases very sharply at a pH more than 5 to reach a plateau at pH 7 and above. This behaviour is similar to that of chitosan. Different behavior is found for Cr(VI) where the rejection values are constant very high near 1 at low pH up to pH 9 and then suddenly it decreases at pH 9 and above. This behaviour is in concordance with the Cr(VI) speciation profiles which show that only anionic species exist in solution. These anionic species can be complexed by the protonated PEI. It is also well known that PEI is very effective for neutralization of excess anionic colloidal charge, especially under acidic and neutral pH conditions. (Aroua *et al.*, 2007)

### 3. Carboxyl methyl cellulose (CMC) PEUF

The membrane material is polyethersulfone polymer, which is hydrophilic. CMC form polymer complexes with transition metal ions. The binding sites in Cr (III) complexes were the etheroxygen of the hydroxyl group. These complexes would most likely exhibit an octahedral geometry with Cr (III). (Barakat *et al.*, 2010).

The effect of pH on the rejection of the metal ions from aqueous solutions using polyethersulfone ultrafiltration membrane has been studied by Barakat *et al.* The studied pH range was from 3 to 9, the CMC/metal ratio was 100 and the applied pressure was 1 bar. The metal ion rejection efficiency was increased with pH increase, reaching maxima values at  $\text{pH} \geq 7$ . The metal rejection efficiency value was 99.5% for Cr (III) ions, at pH 7. This can be attributed to the stability of the formed M–CMC complexes which is pH dependent. The rejection of metals depends strongly on the pH due to the higher binding with the polymeric ligands at higher pH values. At low pH, the affinity of CMC towards the metal ions is weak due to the presence of positive charges and so the stability of the complex is low. As pH increases, the affinity and stability of CMC–metal complexes increases. On another hand, there is a higher possibility for precipitation of metal hydroxide at neutral or alkaline pH values. (Barakat *et al.*, 2010)

Also, the effect of CMC/M ratio on the complexation and filtration processes has been studied. Increasing the CMC ratio enhanced the metal bonding process. This is due to that, the molecules of the metal hydroxyl complexes with CMC particles start to agglomerate forming bigger particles that are rejected by the membrane. The maximum metal rejection was achieved at CMC/M ratio of 50. (Barakat *et al.*, 2010)

### 4. CA/EPES blend membranes

The effect of pH on the rejection behavior of CA/EPES membranes, rejection experiments was carried out in two different pH, 4 and 7. For the sake of reproducibility the chromium ion rejections studies and simultaneous permeate flux measurements were repeated three times and average was reported. The rejection performance of pure CA and CA/EPES blend membranes for the metal complexes of Cr(III) and Cr(VI) has been studied by Jayalakshmi *et al.* From the rejection studies, it was clear that as the concentration of EPES in the blend system increased, rejection of chromium ions enhanced due to the smaller pore size of the membranes as shown in morphological study. The increase in rejection of chromium ions was increased up to 80/20 blend composition and further increase in EPES content decreased the rejection. These values at 70/30 blend composition are lower than that of the blend membranes at 80/20 composition due to the heterogeneity arising as a result of the higher EPES content creating gaps between the polymer chains. Thus the rejection of chromium ions by the membranes was in the order CA/EPES (80/20 wt%) > CA/EPES (90/ 10 wt%) > CA/EPES (70/30 wt%) > CA (100 wt%). Incorporation of PEG 600 into the casting solution decreased the rejection of chromium ions and it may be ascribed to the rapid leaching out of PEG 600 during gelation because of the tendency to lower the free energy of the system. It was found that the rejection behavior of the CA/EPES membranes was similar to that of membrane without additive and was higher at pH 7. (Jayalakshmi *et al.*, 2012).



## 5. SiO<sub>2</sub> nano-particles and/or polydopamine layer modified PSF membrane

At higher pH values, the retention of Cr(VI) by all of the membranes is less than 40%. In contrast, at lower pH values (pH < 5), the retention of Cr(VI) enhanced, although this remained low for PSF and PSF/SiO<sub>2</sub> membranes, indicating that the separation capability of the membranes was mainly due to size exclusion mechanism. Presumably, steric repulsion between the hydroxyl groups of the silica nano-particles and chromium ions in the membrane matrix reduces the separation capability of PSF/SiO<sub>2</sub> membrane. Moreover, according to the speciation profile of chromium, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> is the major species in solution at low pH, HCrO<sub>4</sub><sup>2-</sup> exists in solution up to pH = 8 and CrO<sub>4</sub><sup>2-</sup> species start to appear at high pH and it is the only species at pH = 10 and higher. Since at low pH the amino groups of the polydopamine are protonated, the Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ions adsorption to the polydopamine selective layer was most ascribed to the electrostatic attraction between the anion and the positively charged PDA layer. Additionally, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> molecular size was estimated to be 1.34 nm, which is in agreement with the literature. Therefore, it was inferred that the separation capability of PSF and PSF/SiO<sub>2</sub> membranes was based on the difference between the molecular size of the chromium ion and the pore size of the membranes. While, PSF/PDA and PSF/SiO<sub>2</sub>/PDA membranes separation capability was not solely because of the size exclusion mechanism or the hindered transport theory, but also due to the chromium adsorption on the polydopamine layer at pH = 3. The maximum separation of 94% occurs at pH = 3, therefore this value was opted as an optimum value of pH for the further study of the membranes. (Habibi *et al.*, 2015).

In order to investigate the effect of initial concentration of chromium on the adsorption property of the membranes, four different initial concentrations (5, 15, 25 and 50 mg L<sup>-1</sup>) were chosen and examined at pH = 3 (i.e. at the obtained optimum pH value). The running time was 555 min. Separation of chromium by PSF and PSF/SiO<sub>2</sub> membranes are not higher than 30%. It could be attributed to the lack of main functional groups on the membranes surface. However, maximum separation percentage (about 94%) occurred at 5 mg L<sup>-1</sup> by PSF/SiO<sub>2</sub>/PDA. The high separation capability of PSF/SiO<sub>2</sub>/PDA in comparison with the three other membranes can be due to the homogeneous and thicker deposition of PDA on the membrane surface, as discussed before using AFM results. However, separation percentage decreased with increasing the initial concentration of chromium, associated with gradual saturation of the active sites. (Habibi *et al.*, 2015).

## 6. NH<sub>2</sub>-MCM-41 with PVDF UF membrane

The static adsorption results of Cr (VI) and Cu (II) on both c-PVDF and g-PVDF were conducted to examine the effects of grafted NH<sub>2</sub>-MCM-41. The c-PVDF had no adsorption capacity of metal ions at set solution conditions. On contrast, the g-PVDF showed the well affinity to Cr (VI), the maximum adsorption capacity of g-PVDF was 2.8 mg Cr/g membrane. Meanwhile, the adsorption processes reached equilibrium around 5 min, which would promote the effectiveness to extract heavy metals from the water. The most favorable pH for extraction of Cr (VI) was around 3.5. The electrostatic interaction between Cr (VI) which exists as anion in solution and protonized amino group in acidic solution was the main force that conducted the adsorption process. (Bao *et al.*, 2015).

The continuous adsorption process was conducted at driven pressure of 1 bar in the dead-end device. The heavy metal concentration (Cr (VI)) in filtrates increased with adsorption time. However, it was maintained stably below initial concentration during 7 h filtration even though its initial concentration was rather low already (Cr (VI) = 0.5 mg/L). The metal adsorbed g-PVDF was regenerated by being submerged in 50 mL solution (0.5 mol/L HNO<sub>3</sub>), and C/C<sub>0</sub> vs. time curve of regenerated membrane showed same tendency of first cycle. (Bao *et al.*, 2015).

## 7. Graphene oxide (GO) impregnated mixed matrix membrane (MMM)

A GO impregnated MMM was designed and prepared using polysulfone (PSF) in N, N-dimethylformamide (DMF) for the adsorption of heavy metal ions such as Cr(VI). As PSF has high thermal and chemical stability in aqueous environment, it is selected as the polymeric matrix. (Mukherjee *et al.*, 2016).

Maximum adsorption capacity of different Cr by different GO membranes has been studied by Mukherjee *et al.* Adsorption capacity in acidic solution is considerably lower than that at neutral or basic solution. GO 0.2 MMM can reject 90% of Cr in its natural pH (3.5). This membrane has high adsorption capacity even at natural pH (154 mg/g), leading to high rejection. However, rejection decreases for MMM with higher GO concentration. Solute rejection depends on electrostatic interaction with the membrane surface and its pore size. Since the effect of pore size is dominant for MMM with higher GO concentration, the solute rejection decreases. The permeate flux increases steadily with GO concentration due to higher membrane permeability. Interplay of these two phenomena, higher adsorption and higher permeability of membranes with more GO concentration lead to maximum rejection of Cr by GO 0.2. As this membrane results considerably high permeate flux, GO 0.2 was selected as optimum membrane for subsequent experiments. (Mukherjee *et al.*, 2016).

The GO with adsorbed heavy metal molecules were regenerated in acidic solution. The membrane was first thoroughly washed with distilled water for 10 min. Then an acidic solution of pH 5.5 (prepared by addition of HCl solution) was passed over the membrane for 30 min for regeneration. (Mukherjee *et al.*, 2016).

## 8. Multi-walled carbon nanotube/polysulfone (MWNT/PSf) composite membranes

Tests were carried out at different pressures 0.49, 0.686 and 0.882 MPa and at various pH 2.6, 6.8, 9.5 for chromium. The permeation tests were conducted at 25°C, effective membrane area was 16 cm<sup>2</sup>, and feed flow rate was 12 mL/min. (Shah *et al.*, 2013).

Percentage rejection of Cr(VI) at 0.49 Mpa and 2.6 pH for composite membranes containing 0.1% and 1% amide functionalized CNT was 80.4 and 94.2, respectively, which is reduced to 62.3 and 75.3, respectively, when pressure used is increased to 0.882 Mpa and 2.6 pH. Similar rejection experiments confirmed that maximum rejection for Cr(VI) was found at pH 2.6 (acidic), which could be explained as high complex at ion tendency of surface active sites of the blend membranes. There is decrease in rejection at pH 6.8, which again increases at basic pH (9.5) due to hydroxide formation of Cr(VI) (Shah *et al.*, 2013).

The metal removal was found to be more pronounced in case of membranes containing amide and azide functionalized CNTs. The presence of amide and azide groups are expected to have better metal binding capacity as compared to carboxylic group, and thus only 33.6% of Cr(VI) is rejected using an oxidized CNT/PSf blend while 80.4% of Cr(VI) is rejected using amide functionalized CNT/PSf. Similar observations were made for oxidized CNT/PSf composite membranes. In case of amide functionalized CNT/PSf membranes, 0.1% amide gave 80.4% rejection of Cr(VI) while 1% amide gave 94.2% rejection. On increasing carbon nanotubes, there is decrease in pore size, which gives reduced flow rate and reduced flux, and thus better removal of heavy metal ions on the surface. On the contrary plain polysulfone membranes (without carbon nanotubes) show very less or negligible rejection. Plain polysulfone membranes gave only 10.2% rejection of Cr(VI), which is very less as compared to blended membranes. (Shah *et al.*, 2013).

## 9. Conclusions

A comparison between all the techniques mentioned is shown in the following table. The conclusion is that each technique can be chosen in relation to the pH of the procedure and the desirable separation percentage.

**Table1.** Comparison of the mentioned above techniques for optimum pH and rejection percentage values

Technique	Rejection Percentage %		pH	
	Cr (III)	Cr (VI)	Cr (III)	Cr (VI)
Pectin	99	-	7	-
Chitosan	99	70	10	4, 11
PEI	99	100	7.5	3-9
CMC	99.5	-	8	-
80/20 CA/EPES	94	98	7	7
PSF/SiO <sub>2</sub> /PDA	-	94	-	3
PVDF	-	95	-	3.5
GO 0.2 MMM	-	90	-	3.5
Amide CNTs	-	94.2	-	2.6

The most appropriate technique for separation of both Cr(III) and Cr(VI) is the 80/20 CA/EPES blended membrane and polymer-enhanced ultrafiltration with polyethyleneimine (PEI), at neutral pH. For Cr(III) separation, the optimum membrane is the CMC at basic pH and for Cr(VI) is polymer-enhanced ultrafiltration with polyethyleneimine (PEI) at a wide range of pH (3-9).

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