

Increasing the clay membranes' Cr³⁺ Ions removal ability by coating a bentonite-CMC composite

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Abstract. In this research, bentonite was intercalated with CMC and then two different percentages of glutaraldehyde (5 & 10%) were added as a crosslink agent to achieve non water-soluble composites. Then the composites were coated on clay-based microfiltration membranes which were synthesized in the previous work of the authors. The XRD technique was used to track the intercalation mechanism and FTIR was used to study the crosslink procedure. SEM was used to study the microstructure and morphology of the coated samples and then the ability of non-coated and coated samples for removal of Cr³⁺ ions was studied and compared. It was seen that the samples coated with the synthesized composite including 10% of glutaraldehyde showed the best results and removed 99.7% of Cr³⁺ ions from water polluted with 5 ppm of Cr³⁺ ions.

Keywords: adsorptive membrane; clay-polymer composite; heavy metals; low cost; water treatment

1. Introduction

Heavy metal ions such as chromium are one of the most hazardous pollutions of water and wastewater (Kashaninia *et al.* 2019, Ghanbarpourabdoli *et al.* 2016). Chromium interferes into the natural water sources from the wastewater of leather tanning, electroplating, mining, chemical manufacturing and metal finishing industries and is non-biodegradable (Parlagici *et al.* 2015). Cr⁶⁺ is the most hazardous cation of chromium and is carcinogen. Cr³⁺ is less poisonous but when released into the nature, in the presence of high amounts of oxygen or in contact with MnO₂ would convert to Cr⁶⁺ (Hammami *et al.* 2017, Stoquarta *et al.* 2012, Xu *et al.* 2019). A variety of methods can be used for removing heavy metals from polluted water such as precipitation, solvent extraction, vacuum evaporation, membrane technology, adsorption, ionic exchange and hybrid mechanisms (combination of membrane filtration with other mechanisms) (Bedelean *et al.* 2009, El-gendi *et al.* 2016, Zhang *et al.* 2016).

Clays are effective low cost adsorbents and among different types of clay minerals, montmorillonite (MMT) has thrown a lot of attention to itself (Mitra *et al.* 2014, Xu *et al.* 2006). Montmorillonite consists of thin platelets with thickness of less than 1 nm. Each platelet is comprised of aluminum octahedral layer which is linked to oxygen and is covered with two silicon tetrahedral layers. These layers are linked together by Van der Waals forces and are formed as stacks of plates (Validi *et al.* 2012). As a result of cation substitution in tetrahedral and octahedral sites, a negative charge occurs on the layers. Changeable interlayer cations

like Ca²⁺ and Mg²⁺ and water molecules counterbalance the layer charge (Kozak *et al.* 2010 and Krupskay *et al.* 2017). These cations can be changed with some of the solved cation in the solutions such as heavy metal cations, which make clays suitable for heavy metals removal from water (Shaheen *et al.* 2012). Bentonite is formed from decomposition of fly ash and contains high values of clay minerals especially montmorillonite (Jana *et al.* 2010). Other clay minerals like stilbite, a mineral from zeolite groups which can eliminate heavy metals from water by two mechanisms of ion-exchange and absorption (Zorpas *et al.* 2011) can exist in bentonite and increase its efficiency in heavy metal removal. Natural polymers are other types of adsorbents which are harmless to the environment and human beings. Cellulose is the most abundant natural polymer, but inter and intra molecule hydrogen bonds between hydroxyl (-OH) groups have limited its activity. In modified derivative of cellulose, carboxymethyl cellulose (CMC), carboxymethyl groups (-COOH) are adsorption sites for heavy metal cations and cationic dyes, but its high water solubility is the complicity of using CMC in water treatment, which is subjected by crosslinking. Crosslinking severely decreases the solubility of CMC and is usually accomplished with glutaraldehyde (Braihi *et al.* 2014 and Saber-Samandari *et al.* 2016). Crosslink forms a three dimensional network which is unsolvable in water. The crosslinker is a monomer with one or more double bonds and by connecting the polymer chains with ionic or covalent bonds limits water solvability (Migneault *et al.* 2004). Glutaraldehyde, a dialdehyde containing 5 carbon atoms, being non-poisonous, reactive, commercially available and low cost attracts a lot of attention (Sathiyarayanan *et al.* 2015). Furthermore, addition of glutaraldehyde leads to the formation of a porous film (Braihi *et al.* 2014). As a result of crosslinking with glutaraldehyde, the crystallinity of the structure decreases and leads to increase the free space between polymer chains

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and hence increases the adsorption capacity (Meneghetti *et al.* 2010).

Intercalating of CMC in montmorillonite structure leads to achieve a super adsorbent (Mitra *et al.* 2014). In order to synthesize an intercalated composite, the clay surface should be compatible with that of polymer. The suitable solvent should solve the polymer molecules and also be compatible with the clay surface. When the polymer is hydrophobic, an organo clay is needed; but for water solvable polymers such as CMC, both polymer and clay surfaces are hydrophilic and no extra procedure is needed (Henderson *et al.* 1971, Jana *et al.* 2011).

Sathiyarayanan *et al.* (2015) intercalated montmorillonite with CMC and poly ethylene glycol and crosslinked it with glutaraldehyde to remove Cu^{2+} from water. In another paper, Wang *et al.* (2013) intercalated organo-montmorillonite with CMC to remove Congo Red from water. Saber-Samandari *et al.* (2016) also studied synthesize of a nano-composite layer including montmorillonite, CMC and glutaraldehyde to remove Cd^{2+} ions and Crystal Violet from water.

In this research, two different bentonite-CMC composites were synthesized and coated on clay micro-filtration membranes and then their abilities for Cr^{3+} ions removal from a feed solution (containing 5 ppm of Cr^{3+} ions in deionized water, which is much more than the concentration of Cr^{3+} ions in real drinking water resources) were verified and compared with that of a non-coated clay membrane.

2. Materials and methods

In this research, bentonite-CMC composites were synthesized with three different percentages of glutaraldehyde (i.e., 0, 5 & 10); XRD technique was used to track the intercalation mechanism and FTIR was used to study the crosslink procedure. The composites then were coated on clay microfiltration membranes which were synthesized by the authors in the previous work and then their microstructures and abilities for the removal of Cr^{3+} ions from water (including 5 ppm of Cr^{3+} ions in deionized water) were evaluated and compared.

2.1 Materials

Chemical analysis of the bentonite used in this work (an Iranian bentonite) is shown in Table 1 and the physical and mechanical properties and also the semi-quantative analysis of the substrates are shown in tables 2 and 3, respectively. Carboxymethyl cellulose (CMC) was purchased from Aldrich (C5678) and the crosslink agent, glutaraldehyde (25% w/v) was purchased from Merck (K41618603 241). Chromium nitrate (Merck, code: 102481) was used to create Cr^{3+} ions.

2.2 Synthesize of the composites

Three clay suspensions were prepared with less than 1% wt of bentonite in deionized water. They were then stirred with medium speed overnight at 50°C to make sure that the

Table 1 Chemical analysis of the Iranian bentonite

SiO_2 (wt%)	Al_2O_3 (wt%)	Fe_2O_3 (wt%)	MgO (wt%)	CaO (wt%)	K_2O (wt%)	L.O.I. (wt%)
67.8	11.7	0.9	2.3	4	1.1	11.9

Table 2 Physical and mechanical properties of the substrates

Apparent porosity (%)	Bulk Density (g/cm^3)	Mean pore size (μm)	Modulus of rupture (MOR)
28	1.69	2.5	29

Table 3 Semi-quantative phase analysis of the substrates

Cristobalite (wt%)	Anorthite (wt%)
67	23

Table 4 Samples coding

Sample code	Coating	Glutaraldehyde (vol%)
B	No	0
B-5%	Yes	5
B-10%	Yes	10

clay particles' layers are separated. Then the CMC solution (1 g CMC in 40 ml deionized water) were added to the clay suspensions slightly and the mixtures were stirred vigorously for 20 min to achieve intercalated composites. The desirable concentrations of clay suspensions and CMC solutions and also the sufficient time and speed for stirring were achieved through multiple tests and comparing the XRD patterns. After that, three different amounts of glutaraldehyde (25 % w/v) (i.e., 0, 5 & 10 vol%) were added to the suspensions as a crosslink agent drop wisely and then the mixtures were stirred for extra 30 min. The mixtures were first poured into Petri dishes and then were dried at 60°C for 24 h and then were evaluated with XRD and FTIR techniques to study the intercalation and also the crosslink mechanisms. Then the similar mixtures were prepared and coated on microfiltration clay membranes by dip coating method for 2 min. The samples are identified in Table 4.

2.3 Characterization techniques

Phase analysis of raw bentonite was studied through X-ray diffraction (PANalytical, Cu $K\alpha$, 40kV). A comparison between the results of quantitative phase analyses derived from chemical analyses and the results of Rietveld method show a satisfactory agreement (Ufer *et al.* 2008) though the approximate amounts of the phases were calculated with regarding to the chemical analyses of the starting materials (Table 1). The XRD technique was also used to track the intercalation mechanism.

The crosslink mechanism was verified by FTIR (8400-S Shimadzu) and the microstructure and morphology of the coated surfaces were studied by scanning electron microscope (Vega-TScan II) and the approximate pore size distributions were derived from the SEM micrographs using the ImageJ software (Monash and Pugazhenthii 2011 and Vasanth *et al.* 2011).

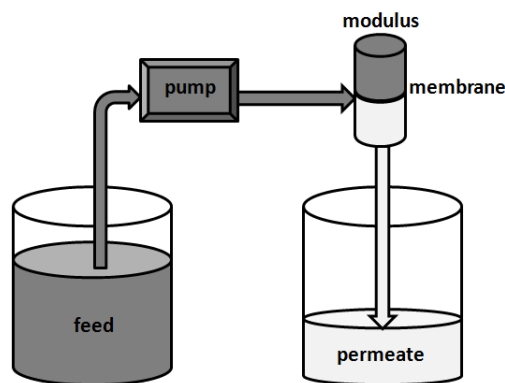


Fig. 1 The filtration set up

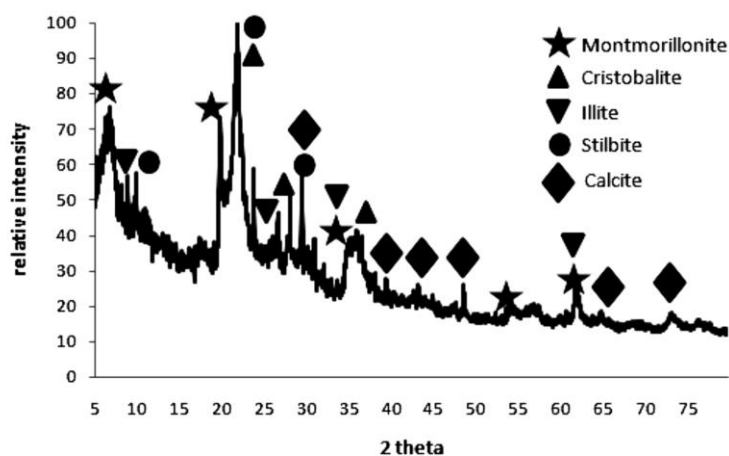


Fig. 2 The XRD pattern of raw bentonite

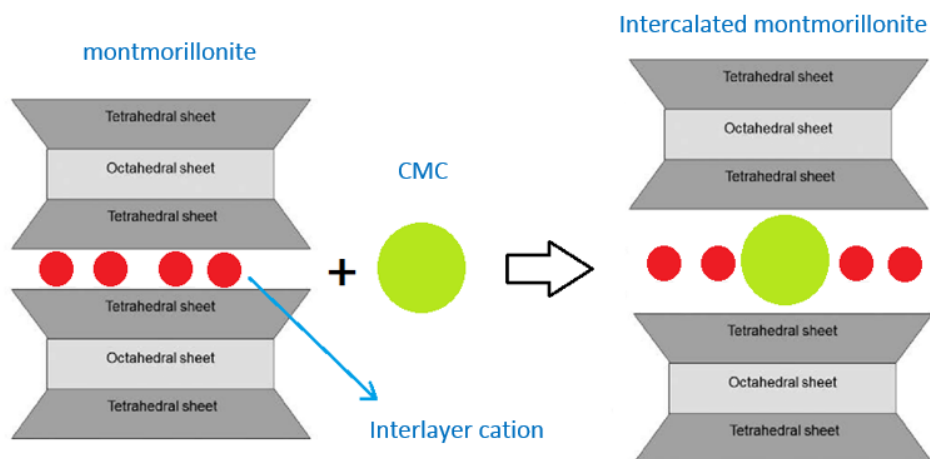


Fig. 3 Schematic of intercalation mechanism

The filtration test was performed with a home-made dead-end set up (Fig. 1) in which the feed solution is passed through the membrane module with the aid of an HPLC pump (Flow rate= 3 ml/min) and then the filtrate of each sample was examined by Atomic Absorption (Shimadzu-AA 6300). The feed solution includes 5 ppm of Cr^{3+} ions in deionized water (which is more than the concentration of Cr^{3+} ions in real drinking water resources even near the sea shores).

3. Results and discussion

3.1 Verifying the intercalation mechanism

Phase analysis of raw bentonite in 2θ ranges of 5-80 is shown in Fig. 2. It can be seen that montmorillonite, cristobalite, illite, stilbite and calcite are detected in bentonite which is corroborated with clay analysis (Karlund *et al.* 2006) and the approximate amounts of the

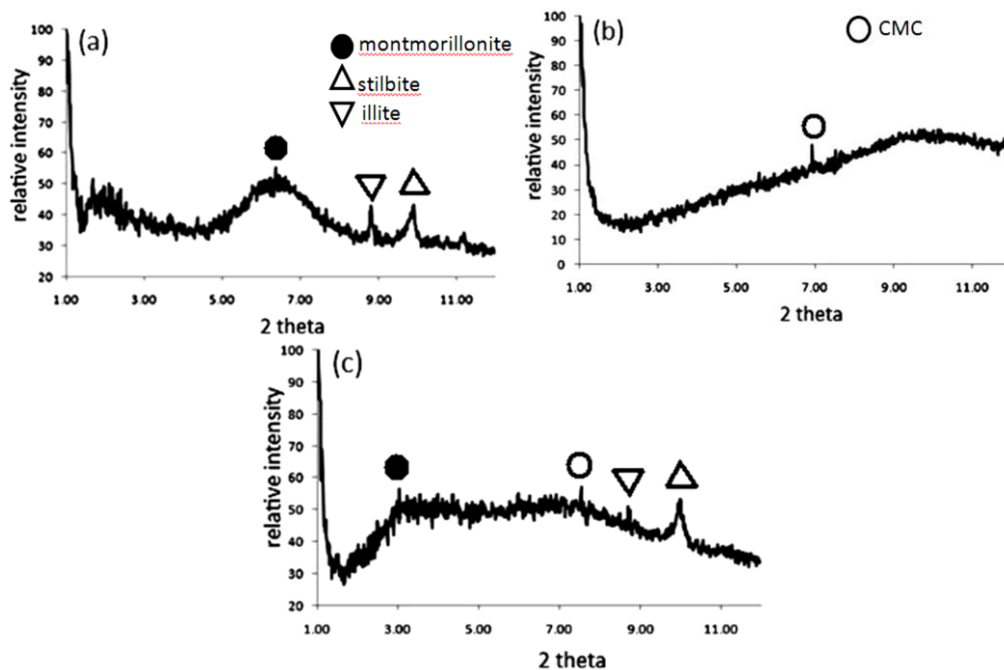


Fig. 4 The XRD pattern of: (a) raw bentonite, (b) CMC and (c) the mixture of raw bentonite and CMC (Intercalated composite)

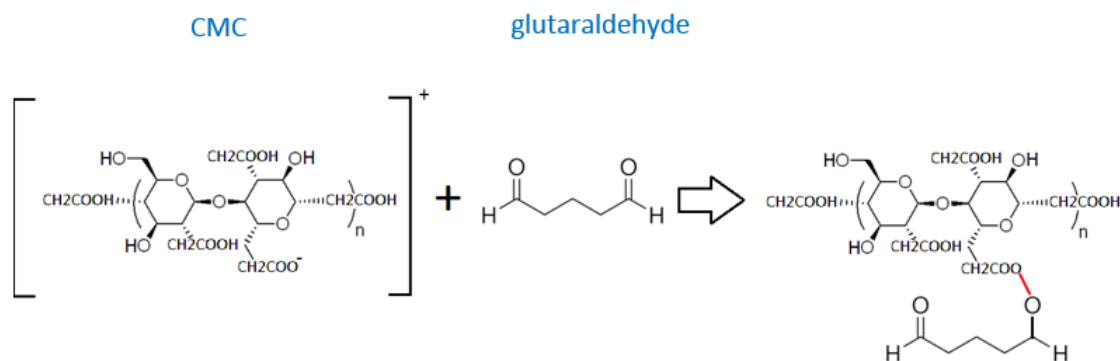


Fig. 5 Schematic of crosslink mechanism

phases, with regarding to Table 1 (chemical analyses of raw bentonite), are around 46%, 25%, 9%, 8% and 6%, respectively. Schematic of intercalation mechanism is shown in Fig. 3.

The XRD patterns of bentonite, CMC and their mixture (the intercalated composite) in 2θ ranges of 1-12 are shown in Fig. 4.

XRD is used to determine the intercalation mechanism. If the polymer intercalates the clay, the basal distance between the clay planes increases and the fwhm of the peaks (i.e., the system order) decreases (Pavlidou and Papaspyrides 2008).

Fig. 4 shows that the characteristic peak of montmorillonite in bentonite (at $2\theta = 6.47^\circ$, relevant to $d = 13.75\text{\AA}$, according to the Bragg's Law) (Fig. 4(a)) is decreased to $2\theta = 3.09^\circ$ (i.e., the d -spacing is increased to $28.57\text{\AA}$) as a result of mixing with CMC (Fig. 4(c)) which means that CMC is intercalated in the structure of bentonite. It can be also seen that the addition of CMC lead all of the characteristic peaks to decrease and means that the system's

regularity is diminished which is another sign of intercalation. Basal distances in illite and stilbite are not changed as expected which means that their structures are not expandable hence they don't participate in the intercalation mechanism. Fig. 3(b) shows the XRD pattern of CMC that indicates a characteristic peak at $2\theta = 6.93^\circ$ which is also seen in the pattern of intercalated bentonite (Fig. 4(c)).

3.2 Verifying the crosslink mechanism

Schematic of crosslink mechanism is shown in Fig. 5.

FTIR spectra of the intercalated bentonite without glutaraldehyde and with 5 and 10% of glutaraldehyde are shown in Figs. 6(a)-6(c) and interpreted in Table 5. In FTIR spectra, the range of $4000\text{--}1500\text{ cm}^{-1}$ refers to the functional groups and the range of $1500\text{--}400\text{ cm}^{-1}$, which is known as the fingerprint region, includes complicated peaks and refers to the molecular structures which are unique for each composition (Gonenc and Us 2018).

Table 5 The interpret of the FTIR spectra of CMC intercalated bentonite: (a) without and (b) with 5% and (c) with 10% of glutaraldehyde (c)

	(c) (Wave Number (cm ⁻¹))	(b) (Wave Number (cm ⁻¹))	(a) (Wave Number (cm ⁻¹))
O-H bonds in montmorillonite and CMC (Sathiyarayan and Karunakaran 2015, Ouali <i>et al.</i> 2013, Owoeye <i>et al.</i> 2012)	3406	3431	3444
C-H bonds (Methyl group) in CMC and glutaraldehyde (Sathiyarayan and Karunakaran 2015)	2923	2929	2941
C=O bonds (Carbonyl group) in CMC and glutaraldehyde (Owoeye <i>et al.</i> 2012)	–	1722	1720
Asymmetric stretching vibrations of COO bonds (Carboxyl groups) in CMC (Wang and Wang 2013)	1622	1623	1681
Symmetric stretching vibrations of COO bonds (Carboxyl groups) in CMC (Wang and Wang 2013)	1423	1382	–
Stretching vibrations of Si-O-Si bonds (Klosek-wawrzyn <i>et al.</i> 2013, Wang and Wang 2013)	1045	1043	1041
Vibrations of SiO ₄ tetrahedrals/ Stretching vibrations of structural O-H (Klosek-wawrzyn <i>et al.</i> 2013, Ouali <i>et al.</i> 2013)	792	792	792
Bending vibrations of Si-O-Si (Klosek-wawrzyn <i>et al.</i> 2013, Ouali <i>et al.</i> 2013)	476	462	452

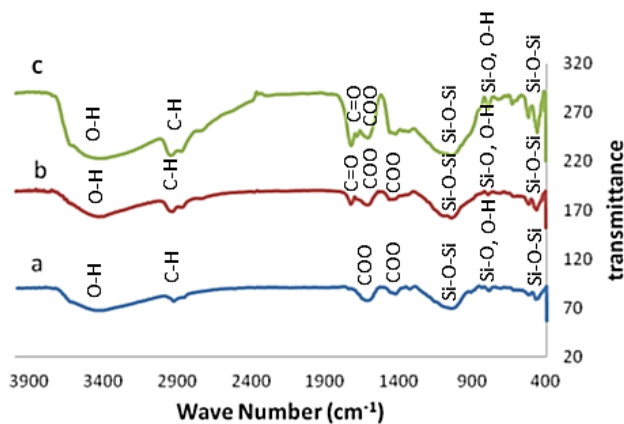


Fig. 6 The FTIR spectra of CMC intercalated bentonite: (a) without and (b) with 5% and (c) with 10% of glutaraldehyde.

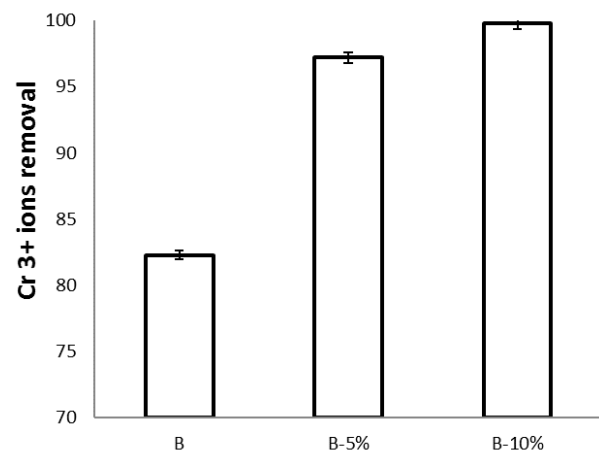
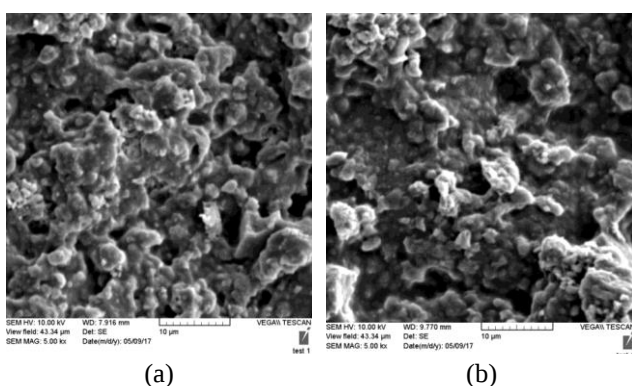
Fig. 8 Effect of coating on Cr^{3+} removal of the samples

Fig. 7 The coated surfaces of samples, crosslinked with (a) 5% and (b) 10% of glutaraldehyde (in magnitude of 5000)

According to Fig. 6 and also Table 5, it can be seen that by addition of glutaraldehyde, characteristic bands of bentonite (related to Si-O-Si and O-H bonds) aren't changed which means that glutaraldehyde approximately hasn't reacted with phases in bentonite; But it can be seen

that addition of 5% of glutaraldehyde lead the characteristic bands of CMC (related to COO bonds or carboxyl groups) to decrease which means that glutaraldehyde has reacted with CMC and the crosslink mechanism has happened. By increasing the amount of glutaraldehyde to 10%, more structural bonds of CMC are deteriorated and so the crosslink has improved. It can be also seen that by addition of glutaraldehyde, the band related to C=O bonds (related to glutaraldehyde's structure) is appeared and the band related to C-H bonds (methyl group) is increased due to the addition of C-H bonds of glutaraldehyde structure.

3.3 SEM analyses

Microstructure of the coated surfaces of the samples, crosslinked with 5 and 10% of glutaraldehyde are shown in Fig. 7.

Depending on the proportion of CMC to montmorillonite, a dense or macro porous layer can be formed (Zhou *et al.* 2012). When the amount of dry mass in the coating composition is around 1%, only the large pores of the support are partially covered and by increasing the

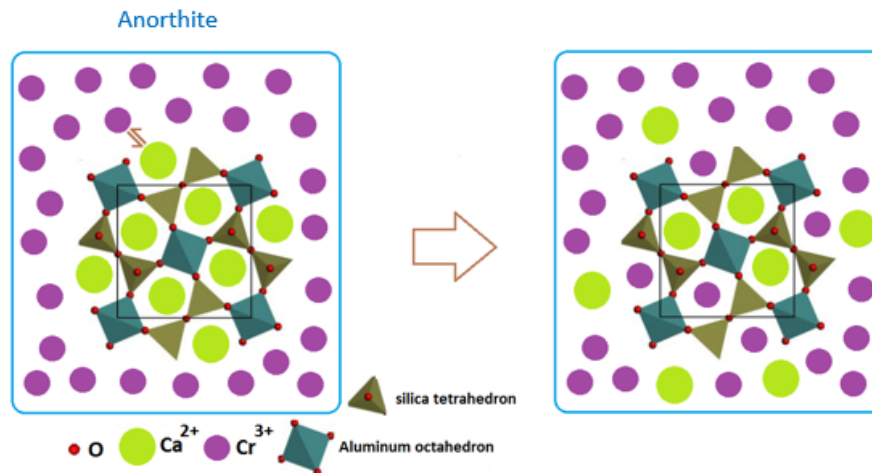


Fig. 9 Schematic of cation exchange mechanism in anorthite phase (in the substrate)

amount to 1.5%, a thin layer appears over the top surface (Jana *et al.* 2010), so in this research, due to the total amount of bentonite and CMC (around 1%), no distinct layer was formed and so it couldn't be detected in the cross-section images.

According to Fig. 7, the surface of the coated samples are porous and using the ImageJ software (Abramoff *et al.* 2003), the mean pore sizes in the surfaces of the samples coated with the composites crosslinked with 5% and 10% of glutaraldehyde are 1.63 μm and 1.47 μm , respectively, which are in the range of micro filter membranes (0.1-10 μm). It can be also seen that the surfaces of the coated samples are very rough which leads the surface area and hence the adsorption sites to increase.

3.4 Filtration test

The amount of Cr^{3+} ions in the treated water passed from the non-coated sample and the samples coated with the composite crosslinked with 5% and 10% of glutaraldehyde are shown in Fig. 8 (The mean error is considered as the error bar).

Fig 8 shows that coating of the membrane increased the Cr^{3+} removal ability from 82.28% to 99.7%. It can be also seen that increasing the amount of glutaraldehyde lead the Cr^{3+} removal to increase.

Comparing the mean pore sizes of the samples (1.47-2.5 μm) with the size of Cr^{3+} ions (0.615 $\text{\AA}$), it can be deduced that Cr^{3+} ions couldn't be removed through microfiltration mechanism. The substrate contains anorthite phase, which tends to adsorb heavy metal cations due to the presence of exchangeable Ca^{2+} ions. The coating composition includes raw bentonite, CMC and glutaraldehyde. The raw bentonite includes montmorillonite, cristoballite, illite, stilbite and calcite. Among these, montmorillonite and stilbite have high tendency to remove heavy metal cations. Heavy metals are removed by montmorillonite through two mechanisms:

1. Ion exchange between layers, which happens as a result of interactions between ions and the negative charge on the layers.

2. Formation of complexes with Al-O- and Si-O- on the edges of the clay layers (Akpomie *et al.* 2015).

As a result of intercalating montmorillonite with CMC, the inter-layer distances increase and hence the ion exchange mechanism happens much easier and so the ability for heavy metal cations adsorption increases.

Stilbite is a zeolite; Zeolites also remove heavy metal ions through ion exchange and adsorption. Ion exchange, contrary to adsorption, is an stoichiometric mechanism, i.e., each ion extracted from the solution replaces with equivalent amount of another ion with the same charge, which remains the electric conductivity of the solution constant; but in adsorption, the solute comes out from the solution without any replacement (Zorpas 2011).

Carboxy methyl cellulose (CMC) includes carboxy methyl groups ($-\text{CH}_2\text{COOH}$) on some of the hydroxyl groups ($-\text{OH}$) of cellulose. Polar carboxyl groups ($-\text{COOH}$) in CMC are the adsorption sites (Jana *et al.* 2010). As a result of intercalating CMC in montmorillonite layers, a super adsorbent of heavy metal cations and cationic dyes is achieved (Mitra *et al.* 2014). Crosslink mechanism decreases the cristallinity degree which is of critical role in availability of the ions to adsorption sites (Meneghetti *et al.* 2010). Regarding the FTIR results, increasing the amount of glutaraldehyde and so the degree of crosslinking leads the energy of COOH bonds to decrease, but regarding that the Cr^{3+} removal is increased, it can be said that the decrease in structural order and cristallinity degree affects much more on increasing the adsorption capacity, due to increasing the availability of adsorption sites and adsorptive groups for cations. Schematic of happened cation exchange and adsorption mechanisms are shown in Figs. 9 and 10.

Fig. 11 shows the concentration of Ca^{2+} ions in the filtered water, passed from samples B and B-10% (The mean error is considered as the error bar). In ion exchange mechanism, Cr^{3+} ions should be replaced with 3/2 of Ca^{2+} ions (due to the charge neutral). It can be seen that in sample B, which has removed 82.28% of Cr^{3+} ions (i.e., 4.136 ppm), 2.8005 ppm of Ca^{2+} ions have been pushed into the water, which means that 1.867 ppm of Cr^{3+} ions have been exchanged with Ca^{2+} ions and else (i.e., 2.269 ppm)



In another research of the authors (Kashaninia *et al.* 2019), a little change in the composition of the membranes (addition of calcium carbonate) and also a decrease in the flow rate of the pump from 3 ml/min to 0.3 ml/min lead the

ability of the clay membranes for Cr^{3+} ions removal to increase to 99.97% from a polluted water, including 1000 ppm of Cr^{3+} ions (i.e., in the range of wastewater of tanning industry)(in this research, the concentration of Cr^{3+} ions in the polluted water was 5 ppm, which is in the range of drinking water resources) and hence by coating of those membranes with the optimal composition of coating gained in this research and in lower flow rates of the pump, high efficient membranes would be achieved which can treat wastewaters highly polluted with heavy metals in a very low cost.

4. Conclusions

- Clay membranes coated with bentonite-CMC composites successfully removed Cr^{3+} ions from water (including 5 ppm of Cr^{3+} ions, which is more than the concentration of Cr^{3+} ions in drinking water resources, even near the sea shores) up to 99.7%.

- Adsorption and ion exchange were the main mechanisms of Cr^{3+} ions removal.

- By increasing the amount of glutaraldehyde to 10 vol%, due to the decrease in the structural order and crystallinity and so the ease of accessibility to adsorption sites, better results and higher amounts of Cr^{3+} removal were achieved.

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