Anion Exchanger on the base Polyvinylchloride for Efficient Removal Hexavalent Chromium Ions in Aqueous Media

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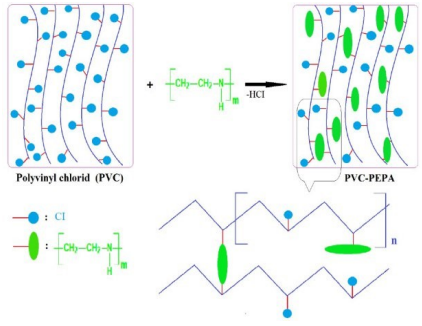
Abstract

Chemical modification of plasticized polyvinylchloride with polyethylenepolyamine (PEPA) leads to anion exchange resin (PPE-1). Different characterization techniques, such as XRD, FTIR, and SEM of PPE-1 anion exchanger revealed weak base amino groups as well as macroporous structure morphology. PPE-1 turned out effective to remove hexavalent chromium ions from aqueous media. Corresponding adsorption kinetics best fit the pseudo-second order model that followed a Freundlich isotherm. In the case of hexavalent chromium ions, the maximum adsorption capacity of PPE-1 was 218,4 mg/g. Thermodynamic data revealed spontaneous endothermic processes and was a chemisorption reaction. In addition, results show that the anion exchanger (PPE-1) has 98% for removing hexavalent chromium ions containing from wastewater.

Present work, we studied the process of obtaining anion exchanger by chemical modification of plasticized polyvinylchloride with polyetilenpolyamine (PEPA). To study the structure morphology of the PPE-1 anion exchanger different characterization techniques such as XRD, FTIR, and SEM were applied. Moreover, the synthesized anion exchanger PPE-1 was used as effective removal for hexavalent chromium ions in aqueous media. Among the toxic metal ions, chromium is one of the widely used elements in industrial processes, such as metal finishing, textile dyeing, coating, pigments, batteries, leather tanning, etc. [1, 2]. Therefore, the wastewater of such an enterprise contains huge amounts of chromium ions. That why The World Health Organization (WHO) has recommended that the maximum permissible concentration of total chromium in drinking water be less than 0.05 mg/L [2].



Scheme 1 Scheme of the reaction of PVC with PEPA

Scheme 1 sketches the synthesis procedure of anion exchange resins: for the synthesis of anion exchanger, we mixed 4.0 g granular PVC and 5.0 ml PEPA polyethylenepolyamine. The reaction shows that the anion exchange resin contains groups of basic nature >NH. The amount of elements contained in the samples was determined by using the EuroEA Elemental Analyzer. The static exchange capacity (SEC) of the obtained PPE-1 anion exchanger with respect to HCl is 6.58 mg-eq g^{-1}. Potentiometric titration of the obtained anion exchanger showed that the anion exchanger has two functional groups, weakly and strongly basic, respectively, with pK_b 10.4 and 7.6.

Fig.1 (b) shows the FT-IR spectra of PVC and the ampholyte, i.e. before and after synthesis. PPE-1 reveals spectral bands in the region around 1680 cm^{-1}, which are characteristic of bond valence vibrations >C=C<. These lines are associated to dehydrochlorination of vinyl groups. Absorption lines in the region of 1480 cm^{-1} are from skeletal C-C, deformation C-N, and deformation CH_2 vibrations [42]. Lines in the range of 690 cm^{-1} characterize C-Cl valence oscillations [42,43]. The broad band at around 3288 cm^{-1} marks the biggest difference between the two spectra. It characterizes deformation vibrations of N-H-bonds [43] and thus clearly demonstrates that the material.

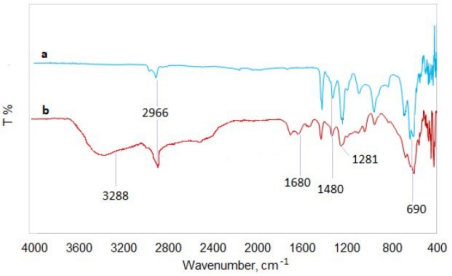


Figure 1 IR spectrum of polymer materials, (a) - PVC, (b) - PPE-1

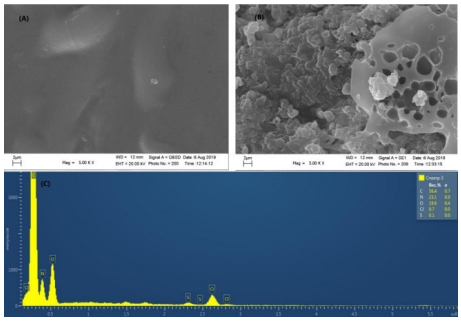


Figure 2 SEM microphotographs of PVC and polymers based on it (a) - PVC, (b) - PPE-1 anion exchanger and (d)-X-ray (EDS) element analysis of anion exchanger PPE-1

The SEM image in Fig.2 (a) shows that the plasticized polyvinylchloride has a smooth surface. Extracting the plasticizer and introducting amine groups, leads to granules with porous structure as shown in Fig.2 (b). This may indicate that the PVC-based anion exchanger has a large surface area. Such a morphological structure gives us high sorption properties. Fig.2 (c) shows quantitative microanalysis of energy-disperse X-ray (EDS) which reveals that the mass fractions of nitrogen in the anion exchange resin is 23,1%. This is in line with nitrogen contents resulting from elemental analysis.

According to the values of the Freundlich parameters, Cr (VI) ions n= 2.3. Which indicates a high degree of sorption of hexavalent chromium ions into the anion exchange resin. The correlation coefficients R^2 is 0.9982; the change in concentration indicates that the adsorption process is best describe by Freundlich-type adsorption theory. Parameter estimation of expressions representing each model yields a range of physico-chemical information such as adsorption capacity, surface properties, adsorbent affinity, and interactions between hexavalent chromium ions and adsorbent explain the process more clearly. Hexavalent chromium ions penetrate in anion exchanger PPE-1 pores and due to the high density of Cr (VI) ions in the anion exchanger.

Table 1 Langmuir and Freundlich isotherm models for sorption of Cr (VI) onto anion exchanger PPE-1.

Isotherm models	Parameters					
	q_{max} (mg/g)	K_F	K_L	n	R_L	R^2
Langmuir	*218,4*	-	*0,0077*	-	*0,998*	*0,9666*
Freundlich	-	*11,66*	-	*2,3*	-	*0,9982*

Table 2 Thermodynamic characteristics for sorption of hexavalent chromium ions

Metal ions	T, K	q_{max}, mg/g	R^2	ΔG, kJ/mol	ΔH, kJ/mol	ΔS, J/mol·K
Cr(VI)	293	194	0,9215	-3,283		
	303	203		-3,962	16,632	67,97
	313	218,4		-4,642		

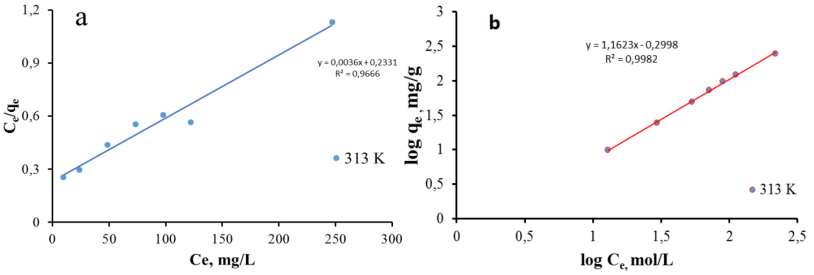
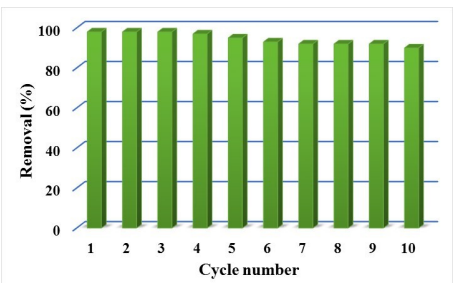


Figure 3 Langmuir isotherm (a) and Freundlich isotherm (b) for Cr (VI) ions



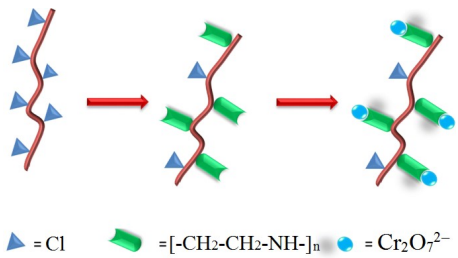


Figure 4. Sorption cycles of Cr (VI) ions by anion exchanger and scheme reaktions.

After ten cycles of the sorption–desorption process, about 90% of the Cr (VI) removal ability remained, which indicated that PPE-1 anion exchanger was suitable to be used as a recyclable sorbent for hexavalent chromium ions. Furthermore, after ten sorption–desorption cycles, PPE-1 could still be easily separated from the solution due to its chemically and mechanically stable monolithic structure.

It can be seen that a new anion exchanger has been obtained as a result of the assurance obtained on the basis of PVC in this study. It was proved by the methods of physic-chemical analysis that the obtained anion exchange resin, as well as their binding to the PVC chain, forming amine-groups. Sorption of the obtained anion exchanger, in artificial solutions containing chromium (VI) ions at different initial concentrations and temperatures, showed that the subordination to the theory of Freundlich adsorption show the absorption of Cr (VI) ions into PPE-1 anion exchange resin.The above data will show that, obtaining anion exchange resin PPE-1 can be used multiple times as an effective ion exchange for the purification of wastewater from hexavalent chromium ions.

References

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