

## Removal of trivalent chromium ions from aqueous solutions by Sodium polyacrylate beads

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**Abstract:** In the present study, the performance of sodium polyacrylate beads on the removal of trivalent chromium Cr (III) from aqueous solutions was evaluated using several techniques such as Fourier Transformed Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDAX), Inductively Coupled Plasma (ICP) and Atomic Adsorption Spectroscopy (AAS). On one hand, the characterization of dry PANa beads was carried out through FTIR and the surface morphology was analyzed by SEM and EDAX methods in order to show the loading of heavy metal on PANa beads. On the other hand, the effect of contact time, initial pH solution, initial Cr(III) concentration, adsorbent mass and temperature on the adsorption capacity of PANa was studied. All results have shown that the adsorption equilibrium was reached at about 60 minutes with an adsorption efficiency close to 90 %. Also, the study of the reliability of PANa beads was effectuated using 0.01 M nitric acid solution through six cycles of adsorption/desorption which were determined in order to study the reliability of PANa over time and to test their efficiency in industrial applications. Finally, the obtained thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) indicate that the adsorption process is spontaneous and endothermic.

**Keywords:** trivalent chromium, Adsorption, Sodium polyacrylate, thermodynamic parameters.

### Introduction

The presence of heavy metals in the environment that caused by discharges of industrial wastewater is behind considerable damage to the natural balance of the aquatic ecosystem when they are above certain concentrations<sup>1,2</sup>. Chromium exists in the environment in two forms of stable oxidation states: Cr (III) and Cr (VI)<sup>3,4</sup>. Literature has shown that it is widely used in the surface treatment industry and in the tannery, textiles, wood processing, agriculture<sup>5,6</sup>. Cr (III) is known as an essential dietary supplement in human nutrition field that helps for metabolism of lipids, carbohydrates and protein and is also considered an essential element for the regulation of insulin<sup>7-9</sup>. Cr (VI) salts with greater mobility and solubility in water<sup>10,11</sup> are more toxic than Cr (III). However, at high concentrations as a result of their accumulation, Cr (III) becomes toxic to aquatic ecosystems, living organisms, plants and humans.

To reduce the impact of water pollution, several separation techniques have been used, including chemical precipitation<sup>12,13</sup>, ion exchange resins<sup>14-16</sup>, membrane filtration<sup>17</sup>, electrocoagulation<sup>18,19</sup>, coagulation<sup>20</sup>. Nevertheless, these techniques have certain disadvantages that limit their applications, in particular, the cost and the life duration of membranes, slow kinetics and secondary contamination. The search for new supports capable to eliminate heavy metals from aqueous solutions has a crucial importance given a large number of potential applications. Last decades, a great importance was attached to the adsorption of metal ions on polymeric supports especially synthetic beads<sup>21,22</sup>, which are low cost, eco-friendly and available materials, which offer fast and easy application in wastewaters treatment<sup>23-25</sup>.

Sodium polyacrylate is a part of the compounds of polyelectrolytes ionizable groups capable to be dissociated in a polar solvent (usually water). The presence of charged groups increases solubility

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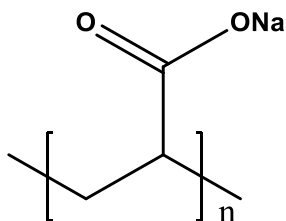
chains and has an important role in industrial applications and in biological processes, agriculture, hygiene products, medicine, pharmaceuticals, the cosmetics industry and the paper industry or also the oil industry, recovery of elements harmful to the environment, as heavy metals is an important application field.

This article is devoted to studying the removal of chromium (III) by adsorption on sodium polyacrylate beads prepared by swelling sodium polyacrylate beads in distilled water. After characterization of the polymer used as an adsorbent agent by FTIR spectroscopy, the kinetic and thermodynamic studies of the adsorption of chromium ions by PANa hydrogel were carried out. In fact, the study of the influence of various parameters (contact time, aqueous solution pH, adsorbent mass, initial heavy metal concentration, temperature) on the Cr (III) binding performance on the gel in order to optimize the adsorption process. The determination of thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ ) has described and defined the type of adsorption process.

## Material and Methods

### Preparation of adsorbent

The studied adsorbent is a sodium polyacrylate polymer whose the structure is represented in Fig. 1. These polymers are capable of retaining up to 200 times their weight in water and which are available in the transparent spherical form, non-porous surface appearance, whose diameter varies between 2 and 3.5 mm and marketed under the name: SEVEN COLOR CRYSTAL BOLL, reference SJQ-007. They are provided by Xinchang Chengtan Magic Bean & Grass Artware Doll Factory of Origin Company: Zhejiang, China. These materials have several advantages such as low cost, easy implementation and chemical stability in a wide pH range.



**Figure 1.** The structure of sodium polyacrylate (PANa)

PANa beads were introduced into a beaker containing 100 ml of distilled water for 8 hours in order to reach the limit swelling, and then they were recovered from the solution and weighed again.

PANa beads mass was calculated through the rate of swelling (swollen PANa mass / dry polymer mass).

### Preparation of aqueous solution

Aqueous solutions were prepared from high quality of hydrated chromium nitrate salt ( $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ). The stock solutions were then used to obtain the working solutions through dilution with double distilled water. Fresh dilutions were prepared and used for each experiment. The initial pH of working solutions was adjusted using 0.1 N  $\text{HNO}_3$  or 0.1 N NaOH solutions.

### Experimental techniques

The chromium concentrations of the obtained samples were measured by Atomic Absorption Spectroscopy (AAS) (air/acetylene) at 240.7 nm on a spectrometer of Jena 350 AA Spectrometer type and Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Perkin Elmer Optima, USA). The pH of solutions was controlled by a pH meter (HANNA, Model-8417).

### Adsorption experiments

Experiments were carried out to study the effect of different parameters on the adsorption of chromium by PANa beads. In fact, a swollen PANa bead mass which is equal to 7.5 g corresponds to 0.035 g of dry PANa was placed in a thermo-regulated cell at 25 °C containing 100 ml of aqueous solution containing 10 ppm of chromium ions. The experimental setup adopted for this work is illustrated in Fig. 2 and consists of a double-walled glass cell containing the metal solution, controlled by a thermometer, a glass electrode connected to a pH meter and a magnetic stirrer. At time  $t = 0$ , beads were immersed in the metal solution. Samples were then taken at regular time intervals from the aqueous phase. Each sample has been diluted in the case of its concentration does not exceed the calibration range of the spectrometer used for the determination of metal ions.

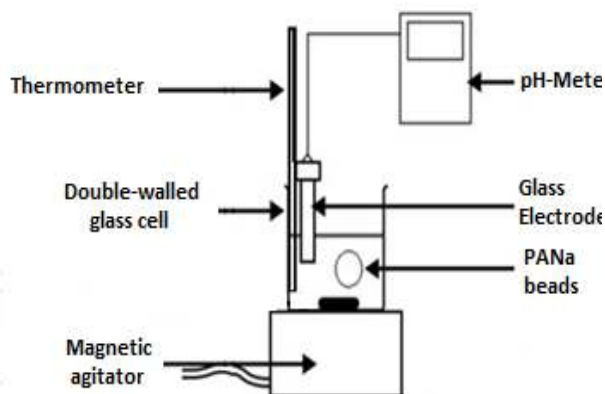
- The adsorption efficiency of chromium fixed by the gel is calculated from (Eq. 1):

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$C_0$  and  $C_e$  are the initial and the equilibrium concentrations of Cr (III) respectively.

- The number of chromium ions retained on a mass unit of coriander seeds is calculated from (Eq. 2):

$$Q = \frac{\text{Mole number of fixed } \text{Cr}^{3+}}{\text{Mole number of } \text{COO}^-} \quad (2)$$



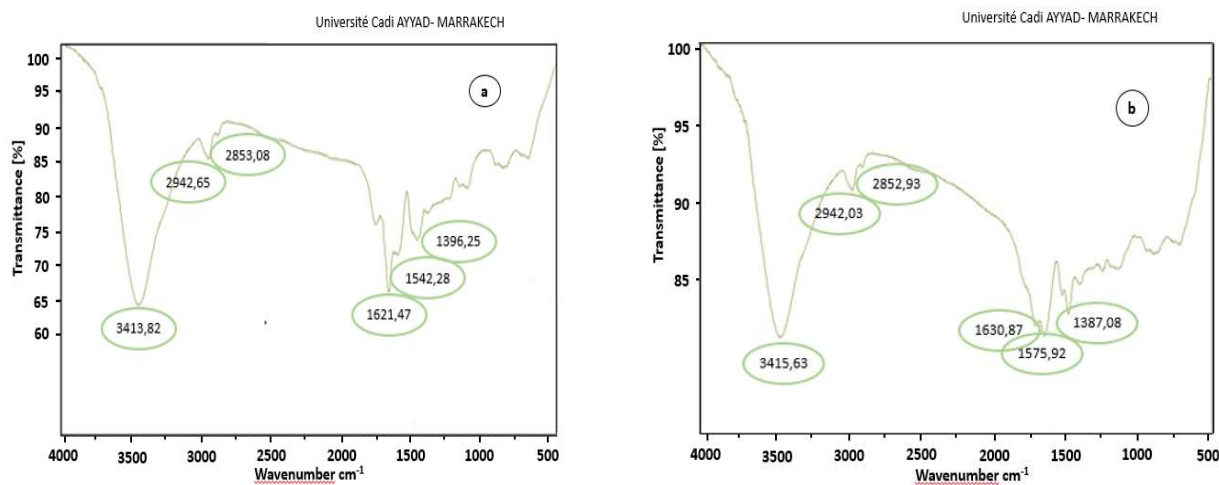
**Figure 2.** Experimental set-up adopted for adsorption experiments

## Results and Discussion

### Characterization of PANa beads by FTIR

The FTIR spectra of PANa beads were carried out using a Vertex 70 Fourier transform FTIR spectrophotometer at a rate of 400 to 4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ . The characteristic spectrum of the gel before and after adsorption of chromium ions is shown in (Fig. 3). FTIR study was effectuated in order to determine specific functional groups that

PANa beads contain. The study of this spectrum has revealed a broad peak at 3413.82  $\text{cm}^{-1}$  which is attributed to the OH stretching of the water of hydration molecules in the superabsorbent polymer (PANa) <sup>26</sup>. The vibrations at 2942.65  $\text{cm}^{-1}$  and 2853.08  $\text{cm}^{-1}$  correspond to the asymmetric and symmetric stretching of the curvatures in the  $-\text{CH}_2-$  and  $\text{CH}-$  plane, which indicates the existence of a main PANa polymer chain <sup>27</sup>. In addition, a band was observed at 1542.28  $\text{cm}^{-1}$  this peak can be attributed to the asymmetric stretching vibrations  $-\text{C}=\text{O}$  of  $-\text{COO}^-$  groups <sup>28</sup>. The peak at 1621.47  $\text{cm}^{-1}$  corresponds to the stretch  $\text{C}=\text{O}$  of the acrylate units. The infrared spectra of the polymers also contain other bands in the region of 1396.25  $\text{cm}^{-1}$  attributed to the stretching vibration of  $-\text{COO}^-$  group <sup>29</sup>. This Analysis has shown the existence of Sodium polyacrylate characteristic groups in the microstructure of PANa beads that is a very important seat for the removal of metal ions. The comparison, of both of FTIR spectra of PANa samples before (Fig.3a) and after extraction of chromium ions (Fig.3b), has shown an important difference corresponding to the band intensity values of the obtained peaks.



**Figure 3.** FTIR spectra of dry PANa beads before (a) and after (b) adsorption of chromium ions

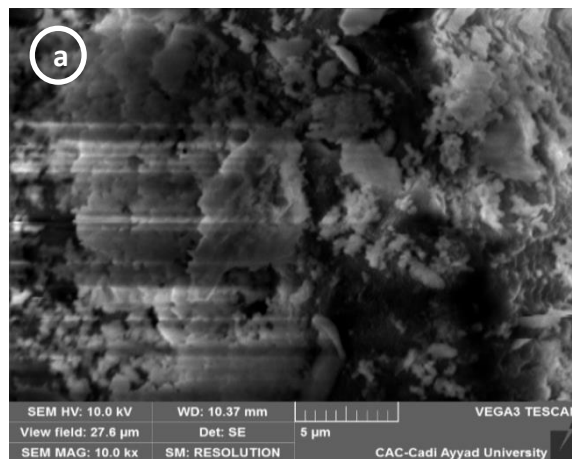
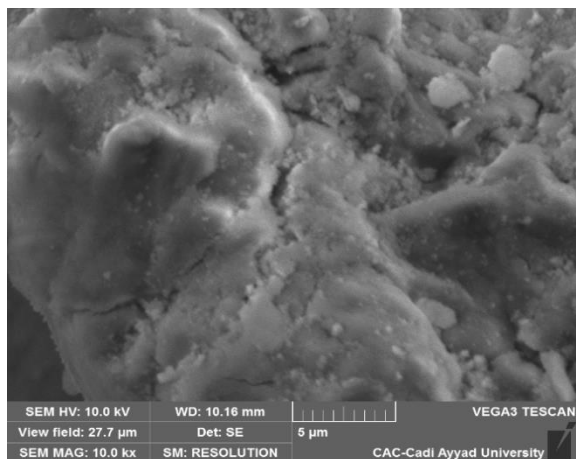
The most intense peak at about 1621.47  $\text{cm}^{-1}$ , which was attributed to the  $\text{C}=\text{O}$  stretching of the acrylate molecules, has moved to a lower wavenumber 1630.87  $\text{cm}^{-1}$ . The adsorption band saved at 1542.28  $\text{cm}^{-1}$  corresponding to asymmetric stretching vibrations  $-\text{C}=\text{O}$   $-\text{COO}^-$  groups has moved to 1575.92  $\text{cm}^{-1}$ . In addition, the adsorption bands attributed to the stretching vibration of the carboxylate group  $-\text{COO}^-$  have also increased from 1396.25  $\text{cm}^{-1}$  to 1387.08  $\text{cm}^{-1}$  that indicate the reorganisation of these groups in the polymer. In fact, these functional groups are responsible for the adsorption of trivalent chromium ions, as their chelating ability.

### SEM and EDAX analysis of PANa beads surface

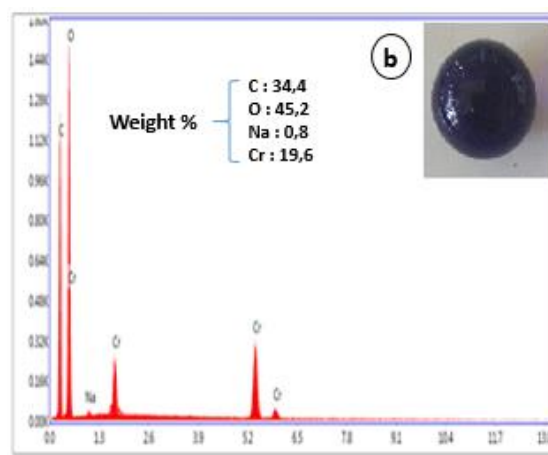
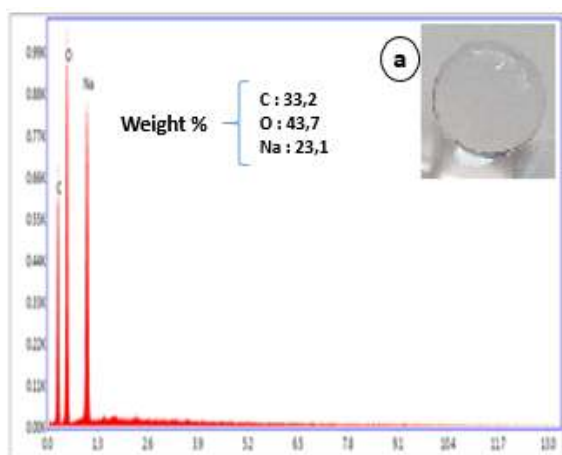
In order to characterize the surface morphology and texture of PANa beads in the absence and the presence of  $\text{Cr}(\text{III})$ , the scanning electron microscopy (SEM) and Energy Dispersive X-ray analysis were performed using VEGA3 TESCAN. The obtained images at a resolution of 5  $\mu\text{m}$  are illustrated in the Fig. 4. It can be clearly seen that the surface of the gel (PANa) is highly porous, rough and irregular (Fig. 4a). This surface was completely modified after the adsorption process (Fig. 4b), which is may be covered with chromium ions. To determine the present elements and to understand the nature of the formed film on the adsorbent surface, EDAX analysis was carried out (Fig. 5). The

obtained spectra, before adsorption of Cr(III), make it possible to deduce that the major components of the hydrogel are carbon, oxygen and sodium (Fig. 5a). After the adsorption mechanism, the Na peak intensity was decreased and several peaks corresponding to Cr (III) have appeared on PANa

beads surface (Fig. 5b). These results supposed that the adsorption of Cr (III) ions by PANa occurred through a cationic exchange mechanism, which is in a good agreement with the results obtained with the IR spectra.



**Figure 4.** SEM micrographs of dry PANa beads before (a) and after (b) adsorption of chromium ions



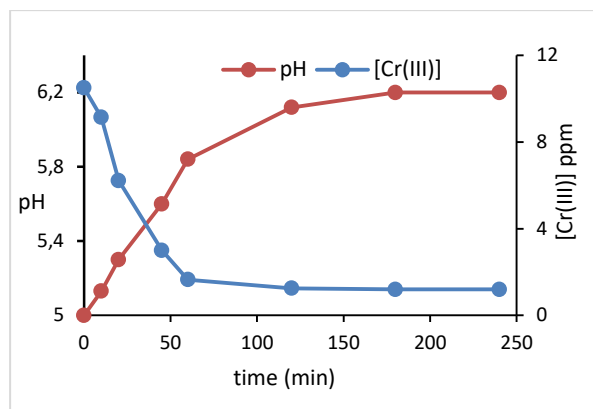
**Figure 5.** EDAX spectra of dry PANa beads before (a) and after (b) adsorption of chromium ions

#### *Effect of contact time*

The study of the evolution of chromium concentration versus time is an essential step for defining the optimal contact time necessary to reach the equilibrium of adsorption. Therefore, Fig. 6 represents the variation of Cr(III) concentration and aqueous solution pH. It appears from the obtained results a significant and rapid decrease during the

first 20 minutes of the experiment. This may be due to the availability of readily accessible active sites on the adsorbent surface<sup>30,31</sup>. At 60 minutes of contact between PANa beads and aqueous solution, the equilibrium was obtained due to the saturation of the functional groups (-COO<sup>-</sup>) by chromium ions<sup>32</sup> where about 89 % of chromium has been removed.



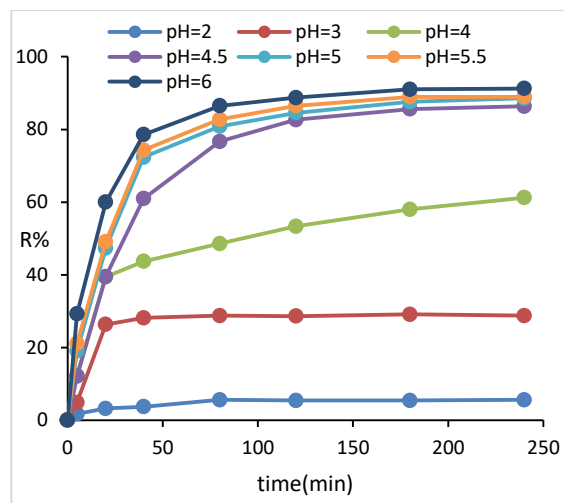


**Figure 6.** Effect of contact time on the adsorption of Cr (III) by PANa beads

Fig. 6 has shown that the decrease in the metal concentration ranging from 10.5 ppm to 1 ppm with the increase of pH values attaining 6.2 at the system equilibrium. Thus, PANa beads react with the aqueous solution by fixing the  $\text{H}_3\text{O}^+$  protons and Cr (III) ions and by releasing  $\text{Na}^+$  ions according to an ion exchange process.

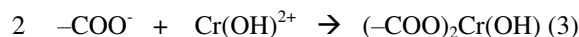
#### Effect of solution pH

The presence of hydrogen ions in the solution has a significant influence on the removal process of heavy metals in aqueous solutions, as it affects the adsorbent surface charge, the solubility of the metal ions in the solution and the degree of ionization of the adsorbate during the reaction<sup>33,34</sup>. For all these reasons, the effect of pH on the removal of Cr (III) ions by sodium polyacrylate beads was studied for different pH values: 2, 3, 4, 4.5, 5, 5.5 and 6. Fig. 7 has shown a clear variation of extraction efficiency versus time. It was found that the removal percentage of metal ion increased from 5.5 % to 90 % in increasing the pH from 2 to 4.5. Afterwards, there is a slow increase in the removal efficiency with further increase in pH. Up to pH 6, chromium exists as  $\text{Cr}(\text{OH})_3$  and forms an amorphous precipitate and therefore its sorption behaviour could not be studied<sup>35</sup>. Thus, the pH value of 5 was selected for the further studies. These results can be explained by the fact that at low values of the initial pH, the surface of the adsorbent (PANa) is surrounded by  $\text{H}_3\text{O}^+$  protons, which would reduce the interaction of chromium with the active sites of the adsorbent, under the effect of repulsive forces<sup>36,37</sup>. However, after the increase of pH values, PANa beads surface was charged negatively through



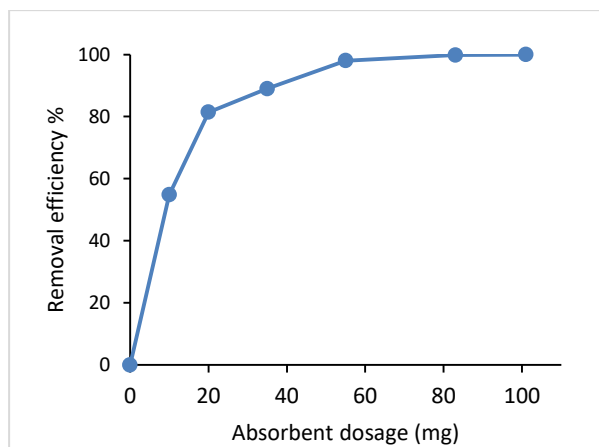
**Figure 7.** Effect of solution pH on the adsorption of Cr(III) by PANa beads

deprotonation of carboxyl groups ( $\text{COO}^-$ ) resulting in increased sorption<sup>38,39</sup>. The oxygen of each carbonyl and hydroxyl group is considered a strong Lewis base due to the presence of its vacant double electrons. Thanks to these doublets, the oxygen base forms a coordination complex with electron-poor Cr(III) ions. The dominant species of chromium in this pH range are  $\text{Cr}(\text{OH})^{2+}$ <sup>40</sup>. However, the spectroscopic study (Fig. 3) shows that the complexation of  $\text{Cr}(\text{OH})^{2+}$  ions is according to the reaction (Eq 3):



#### Effect of adsorbent dose

The study of the adsorbent influence dose on the adsorption process of chromium ions from aqueous solutions by PANa beads was effectuated. The evolution of adsorption efficiency of chromium ions by PANa beads with different adsorbent doses ranging from 0.01 to 0.1 g was followed. The measurement of the residual chromium concentration in the aqueous phase for each sample was carried out after 2 hours of contact, a time largely sufficient to reach equilibrium and at pH = 5. According to Fig. 8, the chromium removal rates increase with the increase of the adsorbent mass. At 60 mg of PANa beads, the decontamination rate of the aqueous solution has reached 98.25 % and the total purification is carried out with approximately 85 mg of adsorbent polymer. This result can be explained by the increase of the extracting sites and the contact surface following the increase of the mass of the extractant support<sup>41</sup>.

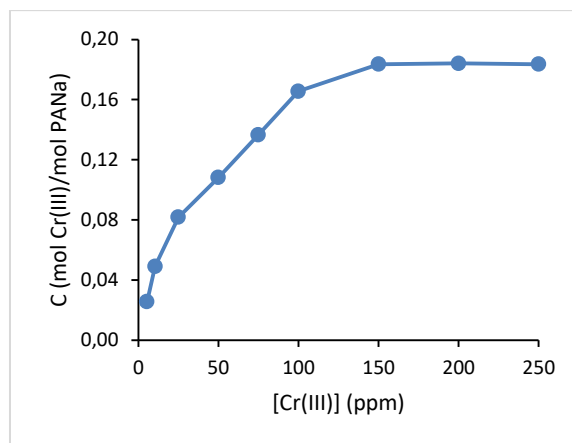


**Figure 8.** Effect of PANa beads mass on the adsorption process

#### Effect of initial Cr(III) concentration

The initial concentration of chromium ions had a considerable influence on the retention capacity of PANa beads<sup>42</sup>. Adsorption experiments were carried out under the same conditions previously defined, by varying the values of the initial concentration of the metal solution. The contact time of the adsorbent with the aqueous solution was set at 120 minutes and pH at 4.5. The evolution of the molar amount of chromium adsorption by the adsorbent versus initial heavy metal ions concentration was represented in Fig. 9.

The obtained results have shown that at low initial metal concentrations, the amount of chromium

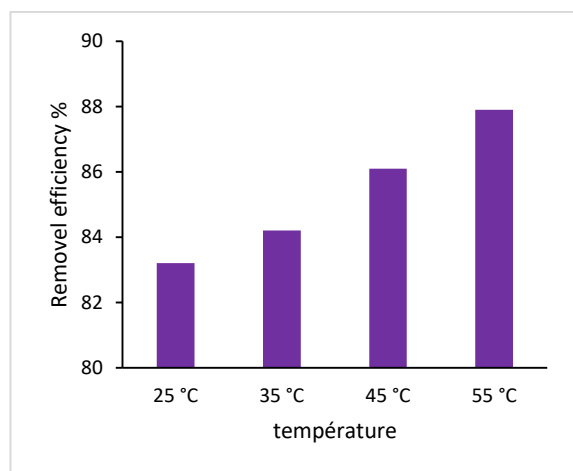


**Figure 9.** Effect of initial chromium ions on the adsorption process

retained by PANa beads increases rapidly and linearly as the concentration of chromium increases due to the increase in the driving force of the concentration gradient<sup>43</sup>. Above 150 ppm, the equilibrium was obtained corresponding to the saturation of the adsorbent with chromium ions attaining 0.18 mol of retained chromium/mole of dry polymer due to the high training force achieved by the strong tendency towards concentration<sup>44</sup>.

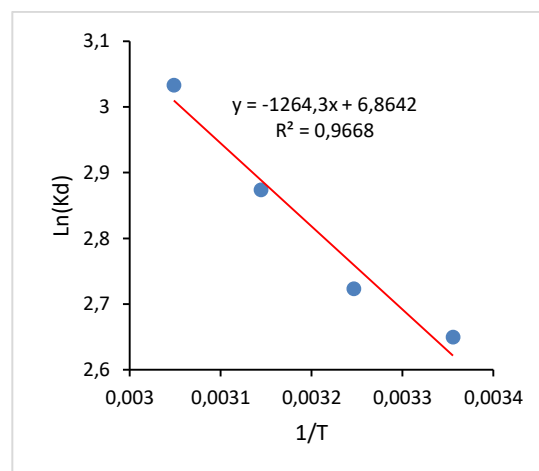
#### Effect of Temperature

The effect of temperature on the adsorption rate of Cr (III) by PANa beads was examined through temperature values ranging from 25 to 55 °C. (Fig. 10).



**Figure 10.** Effect of temperature on the adsorption of chromium ions by PANa beads

It appears from the obtained results (Fig. 10) that the temperature has an insignificant effect on the adsorption performance of Cr (III) by the hydrogel: The adsorption efficiency increases from 83.34 to 87.26 % when the temperature increases from 25 to 55 °C. This slight variation is due to an increase of active sites on the PANa surface by stretching effect of the polymeric structure.



**Figure 11.** Van'tHoff curve corresponding to the adsorption of Cr(III) by PANa beads

#### Thermodynamic study

The thermodynamic parameters of chromium adsorption process on PANa beads can be calculated from the following relation<sup>45</sup> (Eq. 4 and 5):

$$\Delta G^\circ = -RT \ln K_d \quad (4)$$

$$K_d = \frac{Q_e}{C_e} \quad (5)$$

Where  $Q_e$  ( $\text{mg g}^{-1}$ ) is the amount of metal ion adsorbed at equilibrium,  $C_e$  ( $\text{mg L}^{-1}$ ) is the concentration of heavy metal ions at the system equilibrium.  $\Delta H^\circ$  and  $\Delta S^\circ$  values were calculated from the slope and the intercept of the plot of  $\ln(K_d)$  versus  $1/T$  (Fig. 11) by the (Eq. 6):

$$\ln(K_d) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (6)$$

$\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  are related by the following equation<sup>46</sup> (Eq. 7):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (7)$$

Where  $R$  is the universal gas constant,  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $T$  is the absolute temperature (K) and  $K_d$  is the thermodynamic equilibrium constant ( $\text{L g}^{-1}$ ).

**Table 1.** Thermodynamic parameters of the adsorption process.

T(K)	$\ln K_d$ ( $\text{L g}^{-1}$ )	$\Delta H^\circ$ ( $\text{kJ mol}^{-1}$ )	$\Delta S^\circ$ ( $\text{J mol}^{-1} \text{ K}^{-1}$ )	$\Delta G^\circ$ ( $\text{kJ mol}^{-1}$ )
298	2.65	10.52	57.08	-6.56
308	2.72			-6.97
318	2.87			-7.60
328	3.03			-8.27

According to the thermodynamic parameters values obtained (Table 1), the positive value of  $\Delta H^\circ$  suggests that the adsorption of Cr (III) on PANa beads is an endothermic reaction. Negative values of  $\Delta G^\circ$  indicate that this adsorption has occurred through a spontaneous process<sup>45,47,25</sup>. While the positive value of  $\Delta S^\circ$  shows increased randomness at the PANa/metal solution interface during adsorption<sup>48-50</sup>.

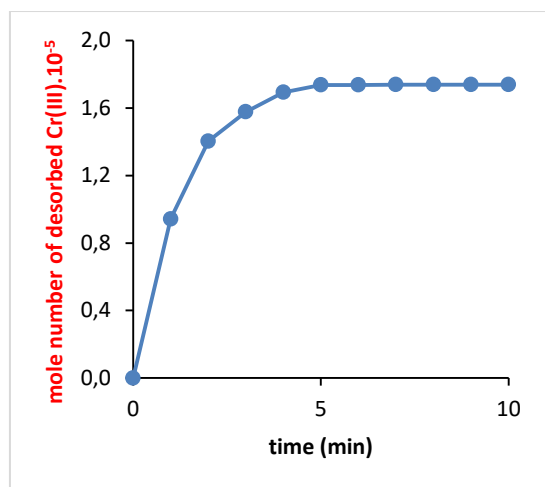
#### Regeneration of adsorbent

An effective adsorbent for the removal of heavy metals is one that has high removal efficiency as well as good desorption so that it can be recycled. Therefore, the study of the reversibility of the liquid-gel system is very interesting. Indeed, the PANa beads charged with chromium ions ( $1.72 \cdot 10^{-5}$  mol) was brought in contact with 40 ml of 0.1 M nitric acid at 25 °C and was stirred for 10 min. Samples

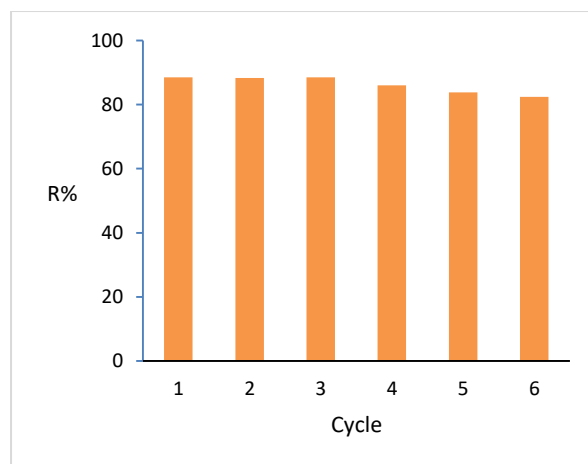
were taken from the acidic solution after each minute, diluted and then analysed.

Fig. 12 represents the variation in the mole number of chromium released in the acidic solution versus contact time, this mole number rapidly increases during the first 4 minutes, followed by the equilibrium of system where the amount of chromium recovered equal to the adsorbed one.

To test the recyclability of PANa beads, consecutive cycles of adsorption-desorption were repeated six times under the same conditions. The results of this study are illustrated in Fig. 13. It appears clear from these results that sodium polyacrylate beds retain their mechanical properties and their effectiveness despite a large number of uses. Overall results suggested that the studied adsorbent could be employed as a low-cost, sustainable, and excellent alternative material for Cr(III) ion removal from wastewater<sup>51</sup>.



**Figure 12.** Desorption of chromium ions from PANa beads in 0.1M HNO<sub>3</sub>



**Figure 13.** Adsorption / desorption cycles

## Conclusion

Sodium polyacrylate beads were investigated in the complexation of Cr (III) ions. On one hand, the characterization of the polymer by FTIR, SEM and EDAX techniques was effectuated. The adsorption performance of heavy metal ions by PANa beads depends essentially on the parameters related to the aqueous solution (pH, concentration, etc.). All results have shown that the adsorption equilibrium was reached after 60 minutes. The decrease in the concentration of chromium in the aqueous solution was accompanied by an increase in the pH values. This phenomenon is due to the acid-base rearrangement of the gel with the metal solution that results in the simultaneous consumption of protons  $H_3O^+$  and Cr (III) by the polymeric support. Moreover, the obtained thermodynamic parameters have shown that the Cr (III) adsorption process on PANa is spontaneous and endothermic. Finally, the use of PANa beads for the removal of trivalent chromium by is an efficient technique due to the several advantages of this polymer.

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