Adsorption of Cr (III) from aqueous solution by two forms of a superabsorbant polymer : parametric study and effect of activation mode

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Abstract. The adsorption of chromium ions Cr3+ using two forms of a superabsorbant polymer PANa from aqueous solution was investigated. On one hand the equilibrium pH with the distilled water and the pH of point of zero charge have been studied in order to characterize the acid-base behavior of both of PANa forms. On the other hand, the effect of contact time between PANa and the metallic solution and stirring speed of aqueous solution on the adsorption rate were established to highlight the importance of PANa as an efficient adsorbent of chromium ions Cr3+.
Keywords: adsorption, Chromium, ICP, superabsorbant polymer.

1. Introduction

 The presence of heavy metals in the environment caused by discharges of industrial wastewater is behind considerable damage to the aquatic ecosystem, when they are above certain concentrations. Literature shows that it is widely used in the surface treatment industry and in the tannery[1, 2]. To remedy this issue, various removal techniques have been applied[3], for example: chemical precipitation, ion exchange, membrane filtration, electrocoagulation [4]… Last decades, attention was focused on adsorption method[4–7] and the use of new adsorbents based on abundant natural materials, natural [8, 9]and synthetic zeolites, clays [11, 12] and especially hydrogel [10, 11].

Sodium polyacrylate PANa superabsorbent polymer is a part of the compounds of polyelectrolytes ionizable groups capable of dissociating in a polar solvent (usually water). The presence of charged groups increases solubility 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 fields [15].

The objective of the present work is to investigate the possible use of PANa in two forms (beads and powder) as a removal of chromium (III) ions from contaminated solutions. Some adsorption parameters such as contact time and stirring speed werestudied using Inductively Coupled Plasma (ICP) in order to evaluate the adsorbent-metal ion interactions.

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2. Material and methods
2.1. Adsorbent material

The adsorbent used in this study is a superabsorbent polymer based on sodium polyacrylate. PANa is able to retain up to 200 times their weight in water, which are in the form of transparent spherical beads, non-porous surface appearance and in the form of a fine white powder, sold under the reference SJQ-007, is provided by Xinchang Chengtan Magic Bean & Grass Artware Factory of Origin Doll: Zhejiang, China [16].

2.2. Aqueous solution

Aqueous solutions were prepared from hydrated chromium nitrate salt (Cr (NO3)3, 9H2O) purchased from Sigma Aldrich. The stock solutions were prepared and then used to obtain the working solutions through dilution with distilled water. Fresh dilutions were prepared and used for each experiment. 10-1 mol /L HNO3 or NaOH solutions were used to adjust the initial pH of working solutions[7].

2.3. Adsorption experiments

The adsorption process was followed by adding 7.5 g the gel (PANa) corresponding to 0.035 g of the dry polymer placed in a thermo-regulated cell at room temperature (25°C) containing 100 ml of the 10 ppm chromium metal solution with magnetic stirring. All the adsorption tests were carried out at an initial pH of 5 and the evolution of the pH during the reaction was followed by a pH meter. The reaction time was set at 3 hours except in the case of kinetic studies. At the end of the reaction, the suspension is filtered and the filtrate is assayed by inductively coupled plasma (ICP) emission spectroscopy.

2.4. Data evaluation

The adsorption process of chromium ions by PANa was evaluated using the following parameters, which were calculated from experimental results:
Rate of copper ions removed (R, %):

$$R = \frac{C0 - Ce}{C0} * 100$$

C0 is the initial concentration of Cr3+ in the solution (ppm).
Ce is the equilibrium concentration of heavy metal ions in the solution (ppm).
All the data are the mean values of three replicate measurements, and the standard deviation calculated in each case was lower than ± 1.0%.

3. Results and discussion
3.1. Behavior of PANa in contact with distilled water (equilibrium pH)

The equilibrium pH was determined after putting 1 g of each form of the material (0.315 mm) in contact with 100 ml of distilled water (pH = 5.2 ± 0.2). The sample was stirred at 300 rpm for 6 hours. The pH measurements were made at regular time intervals minutes using a pH meter pHM210 (Standard pH meter, MeterLab).
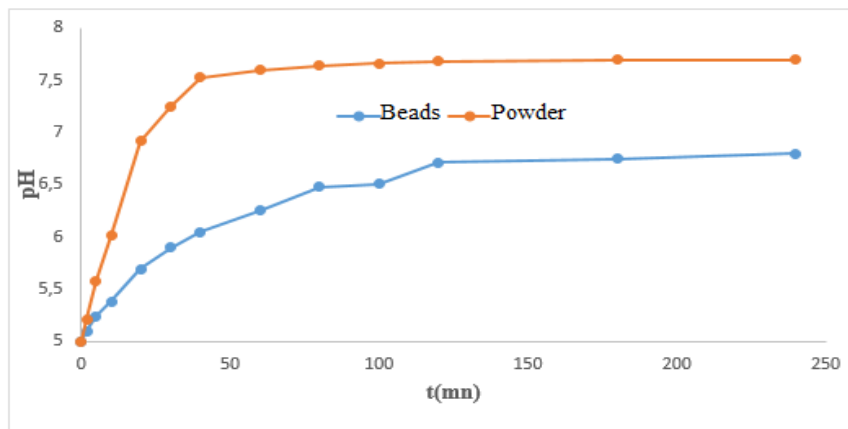
Fig.1. Equilibrium pH of PANa (beads and powder)

The evolution of the pH of PANa in contact with distilled water is shown in fig.1. The curve obtained shows an increase in pH values during the experiment. At (t = 0), we recorded a value of pH = 5, after this value the pH increases gradually until the equilibrium pH = 6.5 for beads and 7.7 for powder, which prove the acid-base rebalancing of the gel with the aqueous solution. It therefore appears obvious that the PANa gel equilibrates with the aqueous phase by consuming protons according to an exchange process of Na+ ions of PANa against protons of the aqueous solution according to:

$$-COONa + H^+ \rightleftharpoons -COOH + Na^+$$

3.2. Determination of pHpzc

The point of zero charge (pHpzc) of adsorbent was determined by the method described elsewhere [17]. In brief, 100 ml of 0.01M NaCl solutions were placed in various Erlenmeyer flasks. Their pH was adjusted to different values between 2 to 12 by the addition of 0.1 M HCl or NaOH solutions. Now the mass adsorbent beads and powder was added into each solution and the final pH of these solutions was recorded after 48 hours of agitation [18].
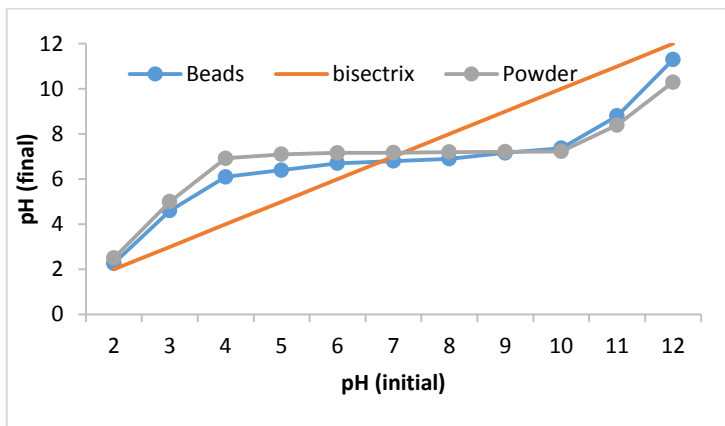
Fig.2. Point of zero charge

The pHpzc is the point where the curve pHfinal verses pHinitial intersects the straight line corresponding to: pH initial = pHfinal. The point of zero-charge, as shown in Fig.2, was evaluated to be equal to 7.12 for PANa beads and 6.8 powder form [19].

3.3. Adsorption of Chromium (III) by PANa
3.3.1. Effect of contact time

The study of adsorption kinetics has a great importance. In fact, it makes it possible to determine the adsorption process and subsequently to calculate the time required to eliminate the heavy metal ions. In figure (3(a) and 3(b)), the kinetics of adsorption of Cr3+ ions in the nitrate medium from an aqueous solution by a PANa in two forms (beads and powder) have been represented. The curves show the evolution of the concentration and the adsorption rate of chromium versus time of contact of the gel with the aqueous solution. It appears from the results a significant and rapid removal of the heavy metal ions after 20 minutes for the powder form and 40 minutes in the case of beads of PANa which can be attributed to the presence of a large contact surface of PANa powder in comparison with beads form. After equilibrium where the concentration of Cr3+ ions becomes independent of time, the contact time required to reach equilibrium is about 30 minutes and 85 minutes for PANa powder and beads respectively. This translates the extraction performance of chromium ions, related to the form of the gel. The evolution of the adsorption rate versus contact time with the heavy metal solution shows that more than 70% of Cr3+ is adsorbed after 30 minutes; R (%) reaches its limit value 95% at 45 minutes for the powder and about 89% for beads at 85 minutes.
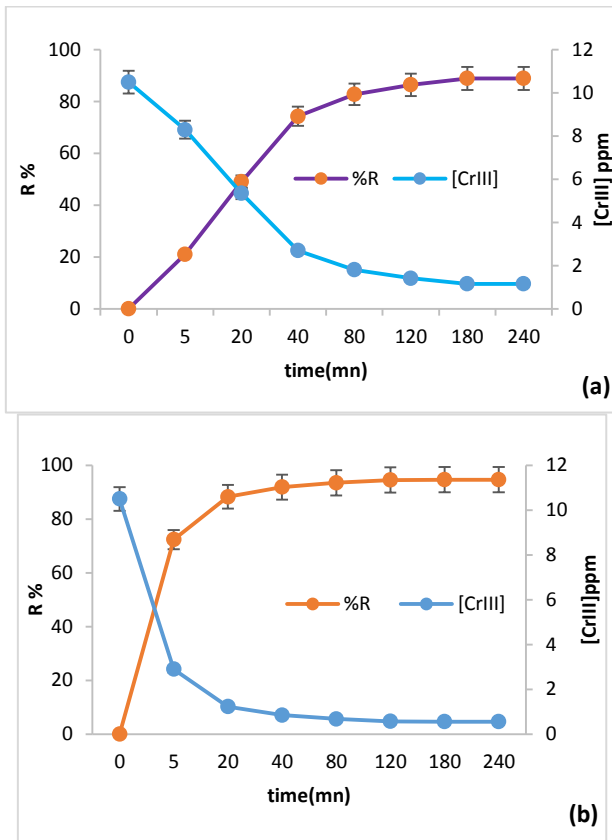
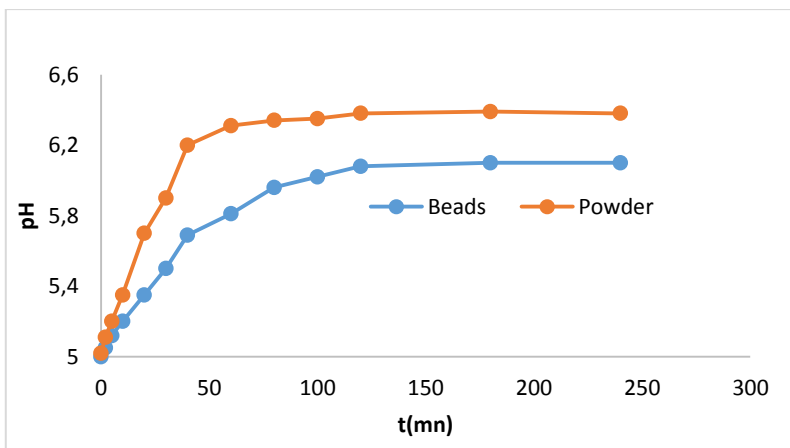**Fig.3.** Evolution of adsorption rate (a) PANa beads and (b) PANa powder

Fig.4. Evolution of pH of PANa in contact with Cr^{3+}

The decrease in metal concentration of aqueous solution in contact with PANa Beads form (from 10.5 to 1.16 ppm) and powder form (from 10.5 to 0.56 ppm) is accompanied by an increase in pH values, which shows that the hydrogel equilibrates with the metal solution by fixing H + protons and Cr3+ ions by releasing Na+ ions in the aqueous solution, according to an exchange process.

3.3.2. Effect of stirring speed

By the same experimental protocol previously described, we introduce volumes of 100 ml of 10 mg / l solution in chromium with 0.035 g of dry polymer at room temperature. The stirring speed is varied between 100 and 1000 rpm until equilibrium. The samples have been taken after 120 minutes of PANa contact with the metal solution and analyzed by ICP. The curve (fig.5) represents the evolution of removal rate versus the stirring speed.
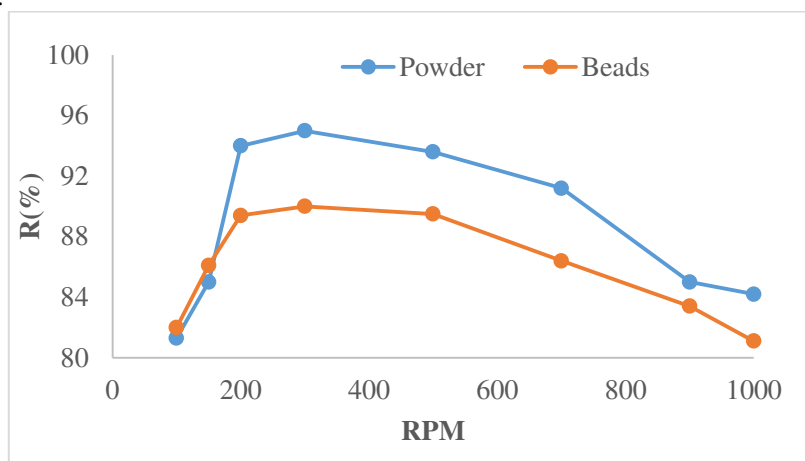

Fig.4. Evolution of adsorption rate versus stirring speed

Stirring of the system generally decreases the thickness of layer around the adsorbent particles that results from the increase in the speed of mixing. When the system is agitated, the suspensions move rapidly with the solution, thereby increasing the concentration of the metal near the surface of the extractant, probably to a value close to the concentration within the solution. The results reveal that the Cr (III) removal efficiency is influenced by the stirring speed. However, the speed corresponding to 300 rpm with both types of PANa gives better results, and it is found that at low stirring speed the retention is less favored. Beyond a stirring speed of 500 rpm there is an important rate in the removal efficiency of Cr (III) this may be due to additional energy sufficient to destroy the bonds possibly formed between the ions chromium and the surface of the PANa hydrogel[15].

4. Conclusion

The results obtained by equilibrium pH after contact of PANa with distilled water have shown an acid-base rebalancing of material with the double distilled water. The study of point of pH zero charge of each form of PANa indicated that the PANA beads acquires a positive charge below pH 7.12 while the powder form have a positive charge below pH

6.8. The study of the chromium ions Cr3+ extraction by PANa through following the evolution of the concentration and the rate of adsorption versus time has shown that the fixation of Cr3+ on the area of our material has been detected on a short time. The pH measurements have increased with time; this is the rebalancing of the acid - base of PANa (beads and powder) with the solution of the metal Cr3+. In brief, PANa can be an effective adsorbent potential of heavy metals contaminating wastewaters.

Acknowledgment

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