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Mathematical Modeling Of The Adsorption Of Trivalent Chromium By The Sodium Polyacrylate Beads

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Abstract

The objective of this work is thus to study the kinetics and adsorption isotherms of Chromium (III) on a superabsorbent polymer PANa (Sodium Polyacrylate). In first, the study of some parameters like contact time and metal concentration, show that the extraction efficiency reaches 80% at a concentration of chromium equal to 4 mg/L. The extraction equilibrium time decreases from 60 mn for 4 mg/L to 30 mn for raised concentrations of Cr(III). In a second step, the study of the kinetics show that the adsorption of Cr(III) onto PANa from aqueous solution is well described by the pseudo-second order kinetic model (the correlation coefficient R^2>0.98). The adsorption isotherms of the adsorbent/adsorbate systems studied are described satisfactorily by the mathematical model of Langmuir. Furthermore, the isotherm study revealed that the adsorption is spontaneous and is carried out in monolayer.

1. Introduction

The release 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 [1-4]. Moreover, these toxic metals can accumulate in the tissues of the living beings, causing various undesirable effects and disorders in human beings [5, 6] and especially chromium. The latter is one of the most known metals for the toxicity of its salts [7, 8]. The data in the literature show that it is widely used in the surface treatment industry and in the tannery [9-11].

To remedy this problem, several chromium removal techniques have been applied [12] of example: chemical precipitation [13, 14], ion exchange [15], membrane filtration [16], electrocoagulation [13, 17] … Attention was focused thereafter on the use of new adsorbents based on abundant natural materials [18, 19], inter alia, natural and synthetic zeolites [20-22], clays [23, 24] and especially hydrogel [25-27].

The aim of this work is the liquid-gel extraction of Cr(III) from dilute aqueous solutions by a hydrogel based on sodium polyacrylate in the form of beads. To determine the adsorption performance of Cr(III) on PANa, several mathematical models were applied to the experimental results

2. Experimental details

2.1. *Adsorbate*

Fresh Superabsorbent polymers used in this work are presents in spherical beads transparent, named: SEVEN COLOR CRYSTAL BOLL; they are supplied by the company Xinchang Chengtan Magic Bean & Grass Doll Artware Factory of Origin: Zhejiang, China (Reference SJQ-007).

2.2. *Preparation of adsorbate*

Superabsorbent polymer has the drawback of being hygroscopic; to remedy this problem we worked with gels (PANa swolled with distilled water). We introduce a mass of gel equivalent to 0.035 g of dry polymer in a filter bag to avoid breaking the bead swelled by stirring the metal solution. Thus the gel is protected and levies can be made directly in the solution without problem drive from the gel grains in the samples assayed.

2.3. *Preparation of the metal solution*

Different solutions of known concentrations of chromium metal are prepared from salt of chromium nitrate ($Cr(NO_3)_3$).

2.4. *Analysis method*

The chromium solution was assayed by flame atomic absorption (air/acetylene) on a type of nov AA350 analytik jena spectrometer (CUAE2TI of the University Ibn Tofail of Kenitra). Calibration of the spectrometer was carried out using metal standard solutions.

Calculating the retention capacity q_e (mg/g) and chromium removal rate R (%) was carried out by the equations (1) and (2), respectively.

$$q_e = (C_o - C_e).\frac{V}{m} \qquad (1)$$

$$R(\%) = (C_o - C_e).100/C_o \qquad (2)$$

With C_o and C_e are respectively the initial concentrations and at equilibrium; m is the mass of the support and V is the volume of solute.

2.5. *Effect of initial concentration*

The effect of initial concentration was studied by agitating 0.035 g of sodium polyacrylate (7.5 g of hydrogel) and 100 mL of metal solution of Cr(III) at 20 ± 2 °C. The experiment was conducted at different initial concentration ranging from 4 to 60 mg/L. Agitation was provided for 2 hours contact time at a constant agitation speed of 130 rpm. The pH was adjusted at 5 by adding a few drops of diluted 1.0N NaOH or 1.0N HCl and measured by using a pH meter.

3. Results and Discussion

3.2. Effect of contact time and initial concentration on chromium adsorption

The adsorption of Cr(III) by PANa was studied at different initial Cr(III) concentrations (4, 8.43, 20 and 60 mg/L). Figure 1 and Table.1 shows the result for effect of time and initial concentration on adsorption of chromium onto PANa beads, respectively. As can be seen from Figure 1, the amount of the adsorbed Cr(III) at low initial concentration (4 mg/L) achieve adsorption equilibrium in approximately 60 mn, while at high initial Cr(III) concentration (20 mg/L), the time necessary to reaches equilibrium was 30 mn. However, the experimental data were measured at 120 min to be sure that full equilibrium was attained.

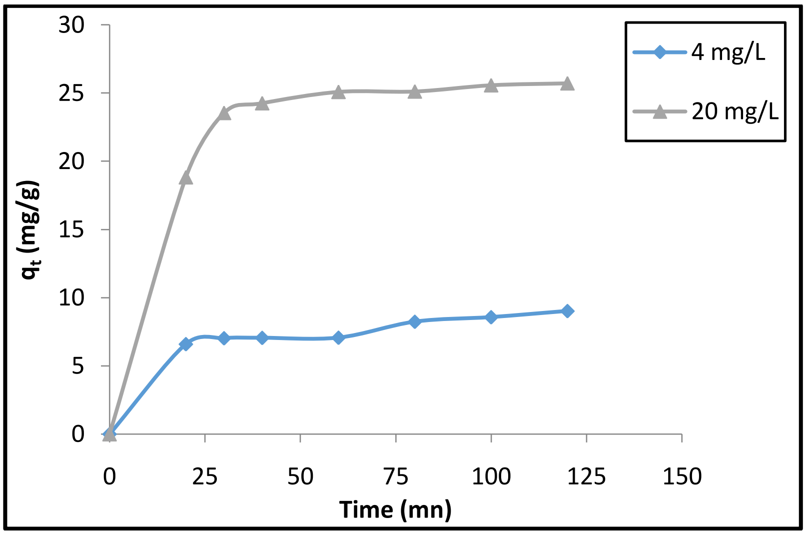

Figure 1: Effect of initial concentration and contact time on Cr(III) adsorption by PANa; ($m_{PANa\ dry}$= 0.035 g; V = 100 mL; pH=5; T=20°C) measurements.

Table 1 shows that an increase in initial Cr(III) concentration leads to increase in the adsorption of Cr(III) on PANa. Indeed, the adsorption capacity increases from 9.02 to 34.57 mg/g, with increase in the initial Cr(III) concentration from 4 to 60 mg/L and the % removals of Cr(III) at equilibrium were 80 and 20.39 % for initial concentration of 4 and 60 mg/L, respectively. This indicates that initial concentrations played an important role in the adsorption of Cr(III) on PANa beads.

Table 1: Evolution of the retention capacity of Cr(III) on PANa beads with the variation in the initial concentrationof Cr(III); ($m_{PANa\ dry}$= 0.035 g; V = 100 mL; pH=5; T=20°C).

	4 mg/L	**8.34 mg/L**	**20 mg/L**	**60 mg/L**
q_m (mg/g)	9.023	20.14	25.71	34.57
%Removel of Cr(III)	80	83.63	47.37	20.39

3.2. *Adsorption kinetics*

The modeling of the kinetics of adsorption of Cr(III) on PANa beads was investigated by three common models, namely, the Lagergren pseudo-first order model [28], pseudo-second order model [29] and Elovich model [30].
Lagergren proposed a method for adsorption analysis which is the pseudo-first order kinetic equation (3) in the linear form:

$$log(q_e - q_t) = log(q_e) - \frac{k_1}{2.303}t \qquad (3)$$

Where q_e and q_t are the amounts of chromium ion adsorbed at equilibrium in mg/g, and at time *t* in mn, respectively, and k_1 is the pseudo-first order rate constant (mn^{-1}).
A linear plot of ln(q_e−q_t) against time allows one to obtain the rate constant (Figure 2). The Lagergren's first-order rate constant (k_1) and q_e determined from the model are presented in Table 2 with the corresponding correlation coefficients.

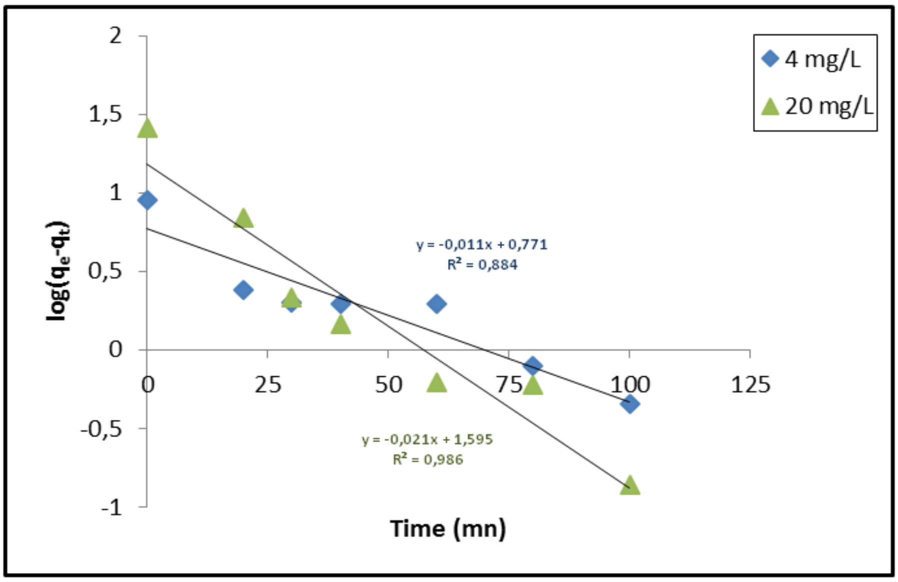

Figure2: Pseudo-first order kinetic model of the adsorption of Cr(III) on PANa beads.

The pseudo-second order kinetic model is expressed in the linear form as the following equation (4):

$$\frac{t}{q_t} = \frac{1}{k_2.q_e^2} + \frac{1}{q_e}t \qquad (4)$$

Where k_2 (g/mg.mn) is the rate constant of adsorption, qe (mg/g) is the amount of chromium adsorbed at equilibrium and q_t (mg/g) is the amount of Cr(III) adsorbed at time t. The equilibrium adsorption capacity (q_e), and the second-order constants k_2 (g/mg.mn) can be determined experimentally from the slope and intercept of plot t/q_t versus t (Figure3).

The k_2 and q_e determined from the model are presented in Table 2 along with the corresponding correlation coefficients.

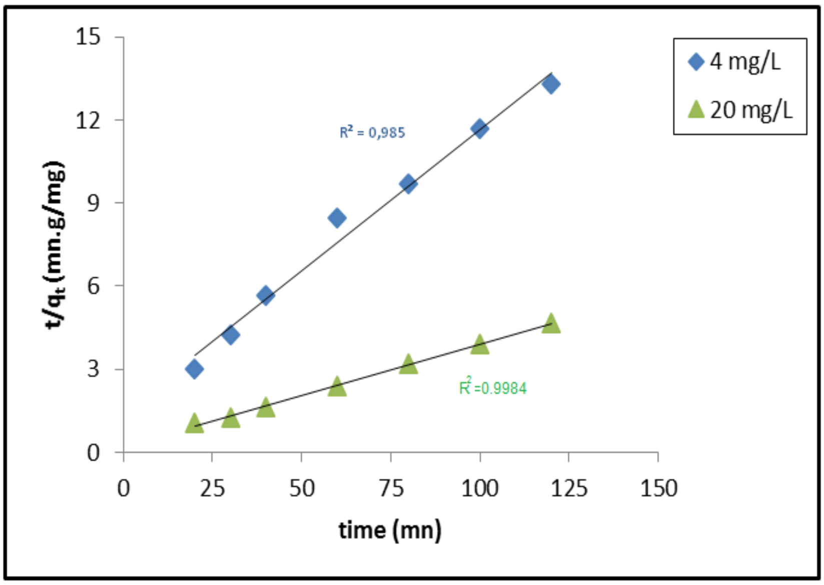

Figure3: Pseudo-second order kinetic model of the adsorption of Cr(III) on PANa beads.

It can be seen from Table 2 that the values of correlation coefficients in the pseudo-second order model are close to unity $R^2>0.98$ for both initial concentration of chromium(III), this values are high compared to those obtained in the case of pseudo-first order kinetic model. Indicating that pseudo-second order equation is appropriate to the adsorption of Cr(III) on PANa beads.

It is clear from the table 2 that the relative difference values of the pseudo-second order model for Chromium are very low (DR<8%) than those obtained for the pseudo-first order model (DR>52%). So, the adsorption process is a pseudo-second order process. A similar result was reported for the adsorption of Chromium (III) from aqueous solution by *Chen et al., 2012* [31], using bentonite.

The same result was found in the case of using the same adsorbent PANa hydrogel (in beads and in powder form) to remove other heavy metals from aqueous solution by *Ismi et al., 2014* [32, 33].

Table 2: Parameters of pseudo-first order and pseudo-second order kinetic model.

Kinetic model	**Parameters**					
	$[Cr^{3+}]$(mg/L)	$q_{e\,;\,exp}$ (mg.g^{-1})	$q_{e\,;calcul}$ (mg.g^{-1})	DR%	k_1 (min^{-1})	R^2
Pseudo-first order	4	9.022	5.91	52.66	0.025	0.8847
	20	25.71	15.17	69.48	0.047	0.932
Pseudo-second order	$[Cr^{3+}]$(mg/L)	$q_{e\,;\,exp}$ (mg.g^{-1})	$q_{e\,;calcul}$(mg.g^{-1})	DR%	k_2 (min^{-1})	R^2
	4	9.022	9.78	7.75	0.0072	0.9854
	20	25.71	27.1	5.13	0.0062	0.9984

3.3. Adsorption mechanism

In order to gain insight into the mechanisms of adsorption, the kinetic experimental results were fitted to the Elovich model.

The Elovich model is expressed in the linear form by the following equation (5):

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \qquad (5)$$

Where, α ($mg.g^{-1}.min^{-1}$) is the initial adsorption rate and β ($g.mg^{-1}$) is the constant of the desorption related to the activation energy for chemisorptions. This equation was used to correct our experimental data by tracing q_t = f (ln (t)) curves. The results are shown in (Figure 6). The constants α, β and R2 are summarized in Table 3. The R2 values are close to unity for both initial concentration of Cr(III) $R^2>0.95$, confirming that the adsorption is likely to be dominated by chemisorptions process. The initial rate α of adsorption of Cr(III) on the PANa beads are equal to 2.18 and 7.37 mg.g-1.min^{-1}; while the constant of desorption of chromium β for the PANa are low 0.55 and 0.18 $g.mg^{-1}$, for initial concentration of Cr(III) equal to 4 and 60 mg/L, respectively.

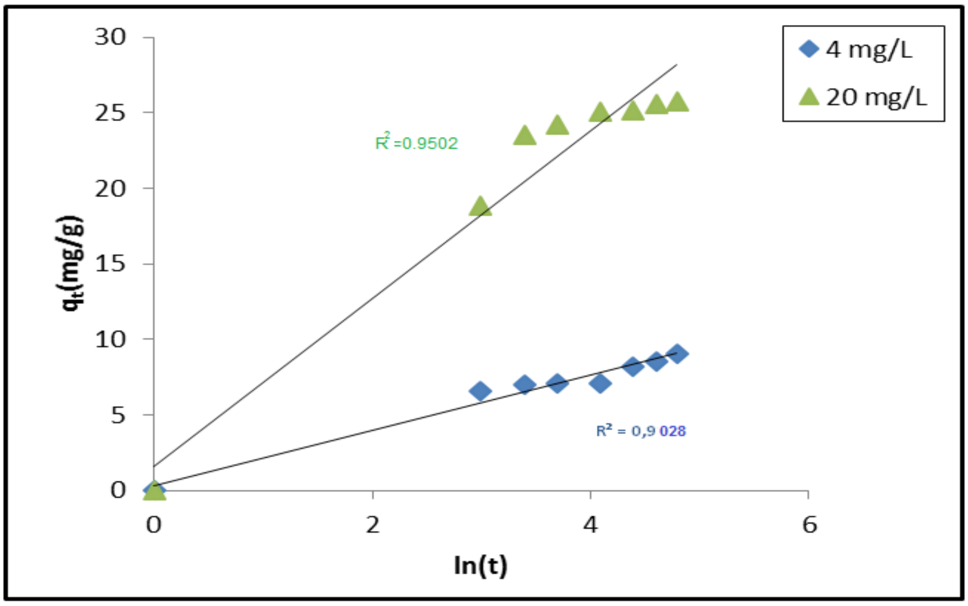

Figure 4: Elovich kinetic model for the adsorption of Cr(III) on PANa beads.

Table 3: Parameters of Elovich kinetic model for the adsorption of Cr(III) on PANa beads.

	Parameters		
[Cr^{3+}](mg/L)	**α**	**β**	**R^2**
4	2.18	0.55	0.9028
20	7.37	0.18	0.9502

3.4. Equilibrium modeling

Three isotherms were tested for their ability to describe the experimental results, namely the Langmuir isotherm, the Freundlich isotherm and the Temkin isotherm.

The Langmuir adsorption model [34, 35] is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the sorbed molecules. The linear expression of the Langmuir model is given by Eq. (6):

$$\frac{c_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L.q_m} \qquad (6)$$

Where q_e (mg/g) and C_e (mg/L) are the amount of adsorbed Cr(III) per unit mass of adsorbent and chromium ion concentration at equilibrium, respectively. qm is the maximum amount adsorbed of the Cr(III) and KL is a constant related to the affinity of the binding sites (L/mg). The plot of specific adsorption (C_e/q_e) against the equilibrium concentration (C_e) represented in (Figure 5). The Langmuir constants q_m and KL were determined from the slope and intercept of the plot and are presented in Table 4.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor RL that is given by Eq. (7):

$$R_L = \frac{1}{(1+K_L.C_o)} \qquad (7)$$

Where C_o is the highest initial concentration of adsorbate (mg/L), and K_L (L/mg) is Langmuir constant. The value of RL indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The R_L values between 0 and 1 indicate favorable adsorption. The variation of R_L values is represented in (figure 6).

At a given temperature, free enthalpy of adsorption $\Delta G°_{ads}$ (kj/mol) can be calculated by the following equation:

$$\Delta G^o_{ads} = -RT(lnK_L + 4.02) \qquad (8)$$

R, T and K_L represent the constant of ideal gases, the absolute temperature and the Langmuir constant, respectively. The free enthalpy of adsorption calculated is given in Table 4.

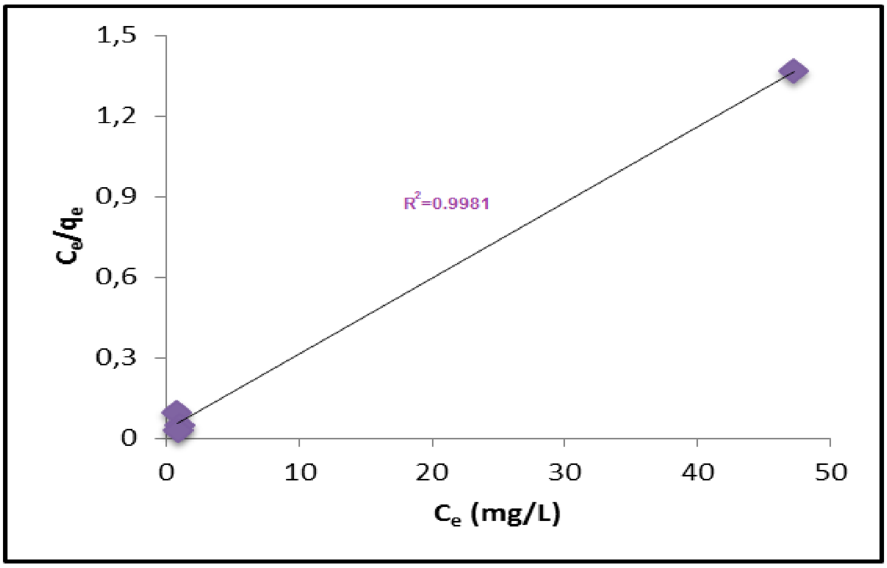

Figure 5: Langmuir isotherm model for the adsorption of Cr(III) on PANa beads.

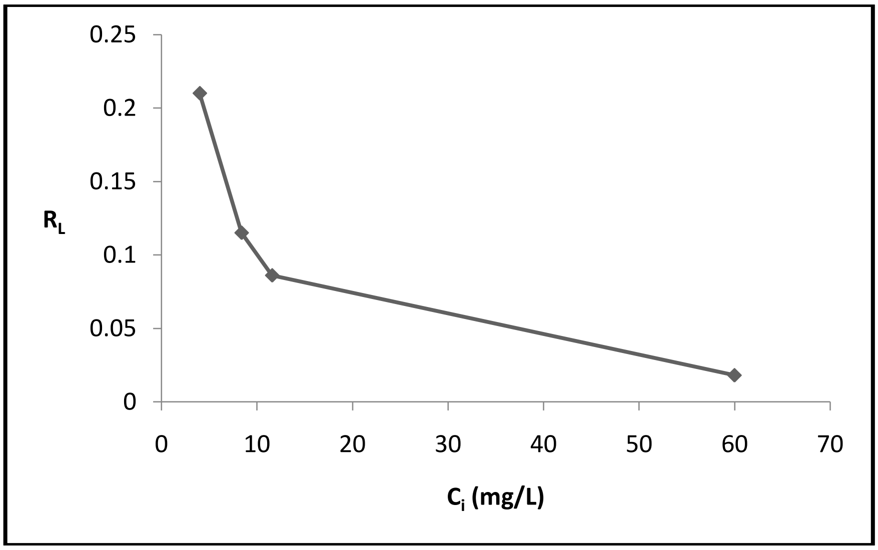

Figure 6: Evolution of separation factor values with initial concentration of Cr(III).

The Freundlich isotherm [36] is an empirical equation employed to describe heterogeneous systems. The linear form of Freundlich equation is given as:

$$logq_e = logK_F + \frac{1}{n} logC_e \qquad (9)$$

Where K_F and n are Freundlich constants with K_F (L/g^{-1}) is the adsorption capacity of the sorbent and n giving an indication of how favorable the adsorption process. The magnitude of the exponent, 1/n, gives an indication of the favorability of adsorption, n>1 represent favorable adsorption condition. Values of K_F and n are calculated from the intercept and slope of the plot represented in (Figure 7) and listed in Table 4.

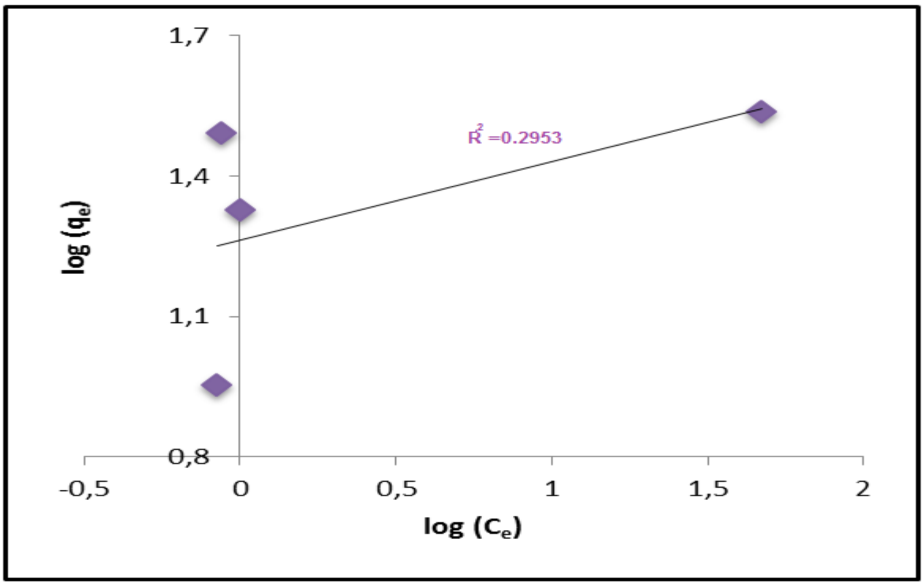

Figure7: Freundlich isotherm model for the adsorption of Cr(III) on PANa beads.

The Temkin isotherm [37] has generally been applied in the linear form:

$$q_e = B_1 lnA + B_1 lnC_e \qquad (10)$$

Where $B_1 = RT/\Delta Q$, ΔQ is the variation of the energy of adsorption (J/mol); A is the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol.K) and T the absolute temperature (K). Therefore, by plotting q_e versus lnC_e (Figure 8) the constants A and B can be determined. The constants A and B are listed in Table 4.

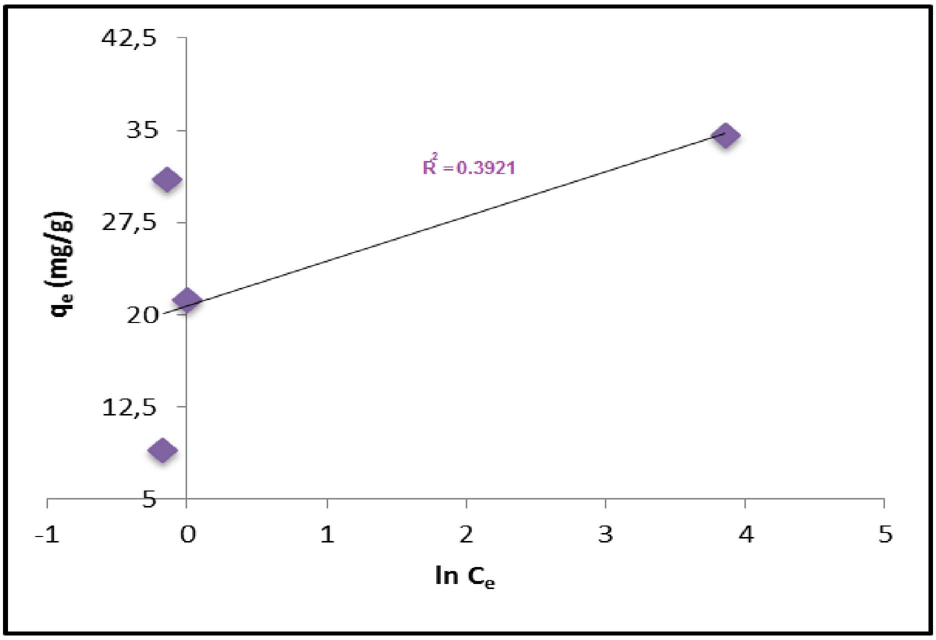

Figure 8: Temkin isotherm model for the adsorption of Cr(III) on PANa beads.

As seen in Table 4, the Langmuir isotherm fits quite well with the experimental data (R^2>0.99). The monolayer adsorption capacity according to this model was 35.34 mg/g. The calculated $q_{m;\ calc}$ values agreed with the experimental $q_{m;\ exp}$ values with low relative difference 2.18% (Table 4). It was found in figure 6 and table 4 that The value of R_L in the present investigation less than 0.21 indicating that the adsorption of Cr(III) on PANa hydrogel is favorable.

The fact that the Langmuir isotherm fits the experimental data very well may be due to homogeneous distribution of active sites onto PANa surface, since the Langmuir equation assumes that the surface is homogenous. A similar result was reported in literature for the adsorption of Copper (II) and Sliver (I) from aqueous solution using PANa in bead form by *Ismi et al., 2014* [38]. The adsorption is exothermic because the free enthalpy of the reaction calculated from Langmuir isotherm is negative $\Delta G°_{ads}= -9.60$ *Kj/mol* . The value of the free enthalpy of adsorption demonstrates the spontaneous nature of the process involved. The same results was found by studyng the adsorption of chromium(III) on lignin by Wu and al., 2008 [39] and on resins by Gode and Pehlivan, 2003 [40].

Table 4: Parameters of isotherm models (Langmuir Freundlich and Temkin).

Isotherm model	**Parameters**						
Langmuir	$q_{m;exp}$ **(mg/g)**	$q_{m;calc}$ **(mg/g)**	**Relatif difference (%)**	K_L	ΔG^o_{ads} **(Kj/mol)**	R^2	R_L
	34.57	35.34	2.18	0.92	-9.60	0.9981	0
Freundlich	**1/n**		**n**		K_F	R^2	
	0.1674		5.97		10.63	0.2953	
Temkin	B_1	ΔQ **(Kj.mol^{-1})**		K_o **(L.mg^{-1})**		R^2	
	3.62	0.673		307.97		0.3921	

Conclusions

The present study shows that hydrogel prepared by swelling sodium polyacrylate in beads form can be used as an adsorbent for the removal of Chromium (III) from aqueous solutions. The effect of contact time and the initial concentration of Cr(III) shows that the adsorption of Cr(III) on PANa is fast and depends upon the initial concentration of Cr(III).

The suitability of the kinetic models for the adsorption of Cr(III) on the PANa was discussed. It was found that the adsorption kinetics of Cr(III) obeyed pseudo-second order adsorption kinetics and the adsorption mechanism was determined by applying the kinetic model Elovich. It was found that the adsorption of Cr(III) onto PANa is chemisorptions type.

The equilibrium data were also fitted to the Langmuir, Freundlich and Temkin isotherm models, and the equilibrium data were best described by the Langmuir isotherm model, which shows that the adsorption of Cr(III) on PANa hydrogel is favorable, spontaneous and monolayer.

It may be concluded that PANa beads may be used as low-cost adsorbent for the removal of Cr(III) and it may also be effective in removing as well other harmful or undesirable species present in the wastewater.

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References

1. Varol M., *J. Hazard. Mater.*, 195 (2011) 355-364.
2. AL-Jaboobi, M., Zouahri, A., Tijane, M., El Housni, A., Mennane , Z., Yachou, H., Bouksaim, M., *J. Mater. Environ. Sci.*, 5 (2014) 961-966.
3. Boularbah A., Schwartz C., Bitton G., Aboudrar W., Ouhammou A., Morel J. L., *Chemosp.*, 63 (2006) 811-817.
4. Mouradi Az., Bennasser B., Gloaguen V., Mouradi Ah., Zidane H., Givernaud T., *Wor. J. Biol. Res.*, 6 (2014) 1-9.
5. Lee SM., Lalhmunsiama, Tiwari, D., *Environ. Sci. Pollut. Res.*, 21(2014) 3686.
6. Järup L., *Br Med Bull.*, 68 (2003) 167-82.
7. Khan S., Cao Q., Zheng Y. M., Huang Y. Z., Zhu Y. G., *Environ. Poll.*, 152 (2008) 686-692.
8. Costa M., *Critic. Rev. Toxicol.*, 27 (1977).
9. Tiglyene S., Jaouad A., Mandi, L., *Environ. Technol.*, 29 (2008) 613-624.
10. Elabbas S., Mandi L., Berrekhis F., Noelle Pons M., Leclerc J. P, Ouazzani N., *J. Environ. Manag.*, 166 (2016) 589-595.
11. Gupta V. K., Mohan, D., Sharma S., Park K. T, *Environ.* 19 (1998) 129-136.
12. Gupta V. K., Ali I., Saleh T. A., Siddiqui M. N., Agarwal S., *Environ. Scie. Poll. Res.*, 20 (2013) 1261-1268.
13. Meunier N., Drogui P., Montané C., Hausler R., Mercier G. Blais JF., *J. Hazard. Mater.*, 137 (2006) 581-590.
14. Rendón-Ángeles J. C., Valadez-Farias L. M., Rodríguez-Galicia J. L., Méndez-Nonell J., López-Cuevas J., *Bol. Soc. Esp. Ceram.*, 43(2004) 869-876.
15. Sahu SK., Meshram P., Pandey BD, Kumara V., Mankhand TR., *Hydrométal.*, 99 (2009) 170-174.
16. Religa P., Kowalik A., Gierycz P., *Separ. Purif. Technol.*, 82 (2011) 114-120.
17. Golder AK., Samanta UN., Ray S., *Separ. Purif. Technol.*, 53 (2007) 33-41.
18. Santhana Krishna Kumar A., Kalidhasan S., Rajesh V., Rajesh N., *Ind. Eng. Chem. Res.*, 51 (2012) 58-69.
19. Namasivayam C., Sureshkumar M. V., *Biores. Technol.,* 99 (2008) 2218-25.
20. Covarrubias C., Arriagada R., Yáñez J., García R., Angélica M., Barros SD., Arroyo P., Falabella Sousa-Aguiar E., *J. Chem. Technol. Biotechnol.*, 80 (2005) 899-908.
21. Wu D., Sui Y., He S., Wang X., Li C., Kong H., *J. Hazard. Mater.*, 155 (2008) 415-423.
22. Yusof AM., Malek NN., *J. Hazard. Mater.*, 162 (2009) 1019-1024.
23. Akar ST., Yetimoglu Y., Gedikbey T., *Desalin.*, 244 (2009) 97-108.
24. Fonseca MG., Oliveira MM., *J. hazard.*, 137 (2006) 288-292.
25. Abdel-Halim E. S., Al-Deyab S. S., *Carbohy. Polym.*, 68 (2011) 1306-1312.
26. Patel AM., Patel RG., Patel MP., *J. Macrom. Scie., Part A: Pur. App. Chem.*, 48 (2011) 339-347.
27. Yu Z., Zhang X., Huang Y., *Ind. Eng. Chem.*, 52 (2013) 11956-11966.
28. Lagergren S., *Kung. Sven. Vetenskaps. Handl.*, 24 (1898) 1-39.
29. Ho Y., Ofomaja A. E., *J. Hazard. Mater. B*, 129 (2006) 137-142.
30. Ho Y. S., McKay G., *Adsor. Scie. Technol.*, 20 (2002).
31. Chen Y-G., He Y., Ye W-M., Lin C-H., Zhang X-F., Ye B., *Environ. Earth Scie.*, 67 (2012) 1261-1268.
32. Ismi I., Rifi E. H., Lebkiri A., 2014, *Mor. J. Chem.*, 2 (2014) 403-414.
33. Ismi I., Elaidi H., Lebkiri A., Skalli A., Rifi E. H, *Intern. J. Advan. Res. Technol.*, 3 (10) (1014).
34. Langmuir I., *J. Amer. Chem. Soc.*, 38 (1916) 2221-2295.
35. Chafai H., Lotfi H., Bazzaoui M., Albourine A., *J. Mater. Environ. Sci.*, 4 (2013) 285-292.
36. Freundlich H., *Zeitsch. Physik. Chem.*, 57 (1907) 385-471.
37. Tempkin M.I., Pyzhev V., *Acta Phys. Chim. USSR*, 12 (1940) 327-356.
38. Ismi I., Elaidi H., Rifi E. H, Lebkiri A., Skalli A., *Inter. J.l Scie. Eng. Res.*, 5 (8) (2014).
39. Wu Y., Zhang S., Guo X., *Huang H., Bior. Technol.*, 99 (2008) 7709-7715.
40. Gode F., Pehlivan E., *J. Hazard. Mater.*, 100 (2003) 231-243.

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