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Kinetic Analysis and Isotherm Modeling for the Adsorption of Silver Ion from Aqueous Solution on a Superabsorbent Polymer

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Abstract

The potential of Sodium Polyacrylate (PANa) hydrogel as a low-cost sorbent was investigated for removal of silver Ag(I) ions from aqueous solution. The results of equilibrium studies showed that equilibrium was reached within 15 mn of exposure time with q_t=6.5 mg.g^{-1}. Generally the maximum percent removal of Ag(I) ion was 70%. Kinetic data were best described by the pseudo-second order model with high correlation coefficient (R^2>0.99). The equilibrium adsorption data were fitted to Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin adsorption isotherm models and the model parameters were evaluated. Adsorption isotherms predict the transition from spontaneous exothermic reaction surface type chemisorption with retention of Ag(I) ions in monolayers organized on the surface of the adsorbent.

1. Introduction

The presence of heavy metals in wastewater and surface water is becoming a severe environmental and public health problem[1,2]. Metal pollution can be due to different metals such as aluminum, arsenic, chromium, cobalt, copper, manganese, molybdenum, nickel, zinc ..., or to heavy metals such as cadmium, mercury or lead, more toxic than the previous [3]. Many human activities are responsible. This pollution is indeed essentially of factories waste, especially tanneries (cadmium, chromium) [4,5], paper mills (mercury) [6], chlorine manufacturing plants (mercury) and metallurgical plants.

Many physicochemical methods such as extraction [7-9], ion exchange, chemical precipitation, membrane filtration, adsorption [10-13] and electrodialysis [14] have been developed for the removal of heavy metals from aqueous solutions and industrial effluents, but most of these methods have significant disadvantages. They have a relatively high cost and low feasibility for use in small scale industries. In contrast, superabsorbent polymer is cheaper and more effective than conventional technologies (precipitation, ion exchange and membrane), so it has become one of the most preferred methods for the removal of heavy metals in recent years [15-17].

The main objective of this research was to evaluate the feasibility of using Sodium polyacrylate hydrogel as a sorbent for the removal of Ag(I) from the aqueous solution. The effects of different concentrations of Silver ion and contact time were studied. Additionally, the isotherm and kinetic parameters were explored to describe the experimental data.

2. Material and Methods

2.1. Adsorbent (PANa)

The sodium polyacrylate polymers used in this work, are marketed superabsorbent polymers. They are in the form of fine-grained white, sold under the name: Powdered sodium polyacrylate (Model Number SNN560-011), provided by the company Henan CXH Purity Industrial And Trading Co., Ltd. Originally: Henan, China. The fig.1 shows an image of PANa in powder form (a) and the chemical structure of PANa (b).

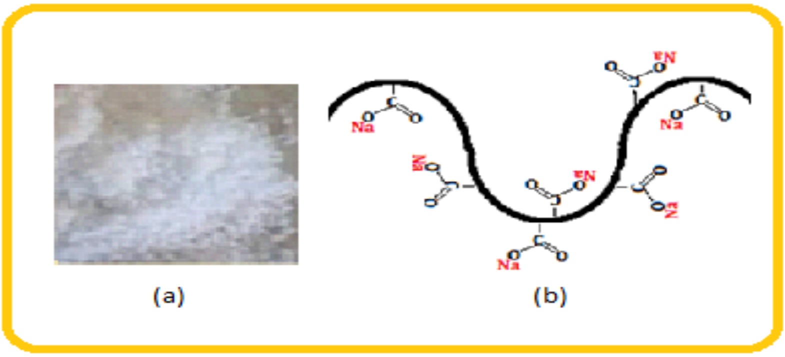

Figure1: Image of PANa in powder form (a), chemical structure of PANa (b).

The description of the characteristics of the polymeric support given by the suppliers is shown in Table (1).

Table 1: Description of the polymeric support (PANa) industrialized in powder form.

Characteristics of PANa in powder form	
Appearance	White granulated
Classification	Chemical auxiliary agent
Type	Absorbent
Chemical name	Sodium polyacrylate
Chemical formula	$(C_3H_3NaO_2)_n$
Apparent volumetric mass	0.75- 0.9 (g.ml^{-1})
Absorption capacity of deionized water	400- 600 (ml.g^{-1})
Physiological salt water absorption capacity 0.9% (ml)	50-70 (ml.g^{-1})
Moisture content	$\leq$ 6%
pH value	5.0-7.0
Gel intensity	Strong
Shelf life in dry pack	3 years
security	Non-toxic, stimulation without pollution and biodegradable

Fig. 2 shows the X-ray diffraction spectrum of the polymer in powder form. The absence of the peaks in the spectrum of this figure shows that the polymer studied is an amorphous product.

2.2. Metal ions solutions

Metal ion solution was prepared from analytical grade chemical (Merck Ltd). Stock solution of 1000 mg.l^{-1} of (Ag^+) was prepared from $Ag(NO_3)$ in double distilled water. The working solutions were prepared from the stock solutions by diluting it to appropriate volumes. The initial pH of the working solution was adjusted to 5.5 by adding 0.1 N HNO_3 or 0.1 N NaOH solutions. The flame Atomic adsorption spectrometry (AAF, nov AA350 analytik jena) was used to measure the (Ag^+) concentration.

2.3. Adsorption experiments

Adsorption experiments were conducted at different contact time (15-120 min), initial (Ag^+) ion concentration (12-200 mg.1^{-1}), and 0.035 g of PANa (equivalent to 7.5g of hydrogel). The samples were analyzed for remaining metal concentration. The amount of metal ion adsorbed by the sorbent at equilibrium q_e (mg/g) was calculated as follows:

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

Where; V is the volume of solution treated, C_o is the initial concentration of metal ion in $mg.l^{-1}$, C_e is the equilibrium metal ion concentration in $mg.l^{-1}$ and m is the amount of adsorbent used (g).

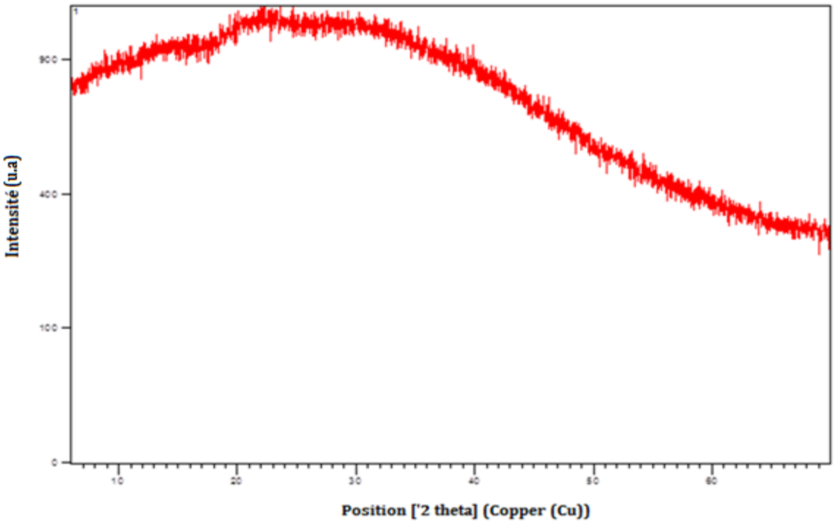

Figure 2: X-ray spectrum of the polymer in powder form.

3. Results and discussion

3.1. Effect of contact time

The sorption efficiency of (Ag^+) ions was evaluated as a function of contact time. The initial concentration of (Ag^+) ions was 12 $mg.l^{-1}$. The relationship of adsorption capacity of (Ag^+) ions by PANa hydrogel (in powder form) with contact time is shown in Fig. 3. Results showed that the q_t was relatively rapid in the initial 15 minutes, this time is rapid compared to divalent ions Cu^{2+} using PANa hydrogel (60 mn for the PANa in bead form [18] and 30 mn for the PANa in powder form [19]. This result may be due to vacant sites, and (Ag^+) could easily interact with these sites, with 70% of the (Ag^+) ions being sorbed by that time (q_t= 6.5 $mg.g^{-1}$). In addition, the sorption efficiency was almost constant such that it could be considered the equilibrium time of the (Ag^+) sorption. The same results were obtained in a previous study using the PANa in bead form by [20].

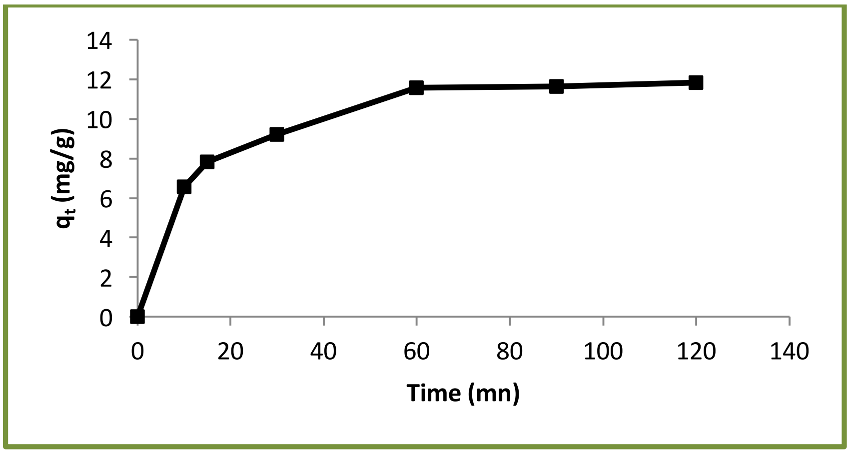

Figure 3: Evolution of the adsorption capacity of PANa in powder form as a function of contact time with the metal solution. ($[Ag^+]$=12 $mg.l^{-1}$, pH=5.5, $m_{PANa(Dry)}$=0.035 g).

3.2. Effect of initial metal concentration

The effect of initial metal concentration on the Silver (Ag^+) ions sorption was investigated in the ranges of [12-200 $mg.l^{-1}$], while the rest of the parameters were kept same as optimized in the previous experiments, i.e., pH=5.5, equilibrium time of 2 hours using 0.035 g of PANa. The results are depicted in Fig. 4. It has been found that the number of moles fixed by PANa growing rapidly at the beginning of the experiment with the increase of the concentration of the silver solution. A deceleration is observed from a feed concentration of 73 $mg.l^{-1}$ and a saturation effect appears beyond the highest concentration (200 ppm) when the number of moles of silver fixed is 4.78 .10^{-5} mol. This value is important compared with that obtained in the case of the bead adsorbing the same metal ion (4.22.10^{-5} mol) [20] and low compared to that obtained under the same experimental conditions with the divalent cation Cu^{2+} [18,19].

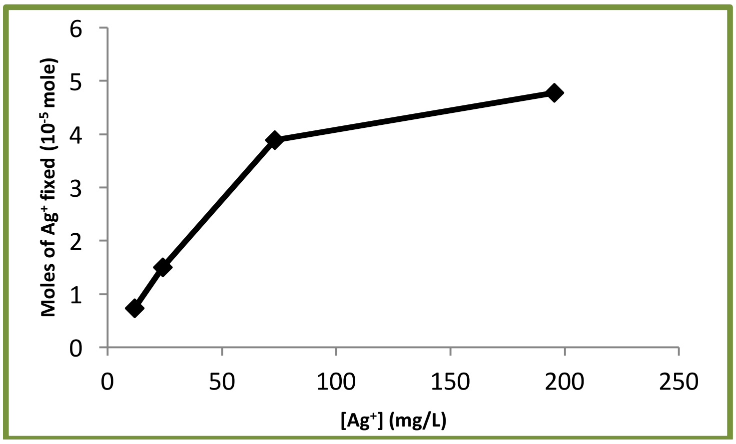

Figure 4: Evolution of the moles fixed depending on the initial concentration of the aqueous solution of Silver. (pH=5.5; $m_{PANa(Dry)}$=0.035 g).

3.3. *Kinetic studies*

For analyzing the adsorption kinetics of Silver ion five kinetic models were applied to the experimental data: Pseudo-first order model [21], Pseudo-second-order model [22], Elovich model [23], Intraparticlar diffusion [24] and Bangham model [25].

3.3.1. The pseudo-first-order

The first-order rate equation is one of the most widely used equations for the adsorption of a solute from an aqueous solution and is represented as:

$$log\ (q_e - q_t) = log\ (q_e) - \frac{k_1}{2.303} t \qquad (2)$$

Where; q_e and q_t are the amount of Ag(I) adsorbed (mg.g^{-1}) at equilibrium and time t, respectively. K_1 is the first-order reaction rate constant (mn^{-1}).

The examination of the data in Fig.5 shows that the pseudo-first order kinetic model is not applicable to silver ions adsorption onto PANa, judged by low correlation coefficient (R^2=0.66) and the significant relative difference (RD=60.75%) provided in Table 2.

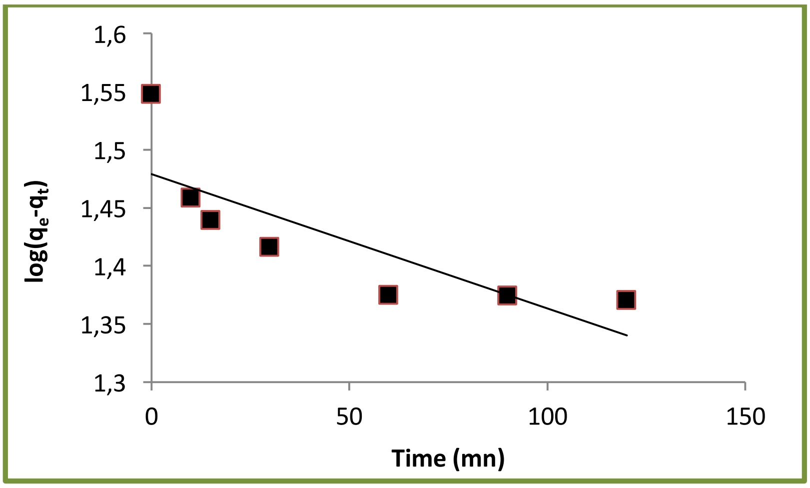

Figure 5: Pseudo-first order sorption kinetics of Ag(I) onto PANa in powder form.

Table 2: Parameters of Pseudo-first order kinetic model.

$q_{e;exp}$ (mg.g^{-1})	$q_{e;theo}$ (mg.g^{-1})	RD (%)	k_1 (min^{-1})	R^2
11.82	*30.12*	*60.75*	*2.76 10^{-3}*	*0.6647*

3.3.2. The pseudo-second-order

The pseudo-second-order equation based on adsorption equilibrium capacity may be expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \qquad (3)$$

Where; q_e is the equilibrium sorption capacity and K_2 is the pseudo-second order rate constant (g. mg^{-1}. min^{-1}). A plot of (t/q_t) versus t gives a linear relationship for the applicability of the second order kinetic model.

The straight shown in Fig. 6 shows a high correlation coefficient (R^2=0.998) and low relative difference (RD=8%) giving in Table 3, indicates that the pseudo-second order is predominant kinetic model for the (Ag^+) adsorption by PANa sorbent. Similar kinetic result was reported for the adsorption of silver by PANa in beads form [20].

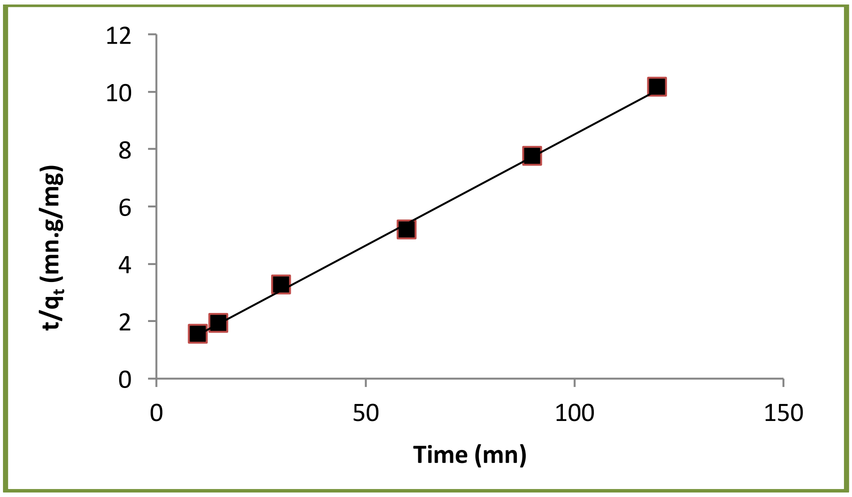

Figure 6: Pseudo-second order sorption kinetics of Ag(I) onto PANa in powder form.

Table 3: Parameters of Pseudo-second order kinetic model.

$q_{e;exp}$ (mg.g^{-1})	$q_{e;theo}$ (mg.g^{-1})	RD (%)	k_2 (min^{-1})	R^2
11.82	*12.88*	*8.23*	*7.95 10^{-3}*	*0.9985*

3.3.3. Elovich kinetic model

Elovich kinetic equation is presented as follows:

$$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln(t) \qquad (4)$$

Where; α is the initial adsorption rate (mg/g.min) and β is the desorption constant (g/mg) during any one experiment.

If the sorption of Ag^+ on PANa fits the Elovich model, a plot of q_t versus ln(t) should yield a linear relationship with a slope of (1/β) and an intercept of (1/β) ln(αβ). The experimental kinetic curve for the adsorption kinetics, modeled by the equation of Elovich is illustrated in Fig. 7

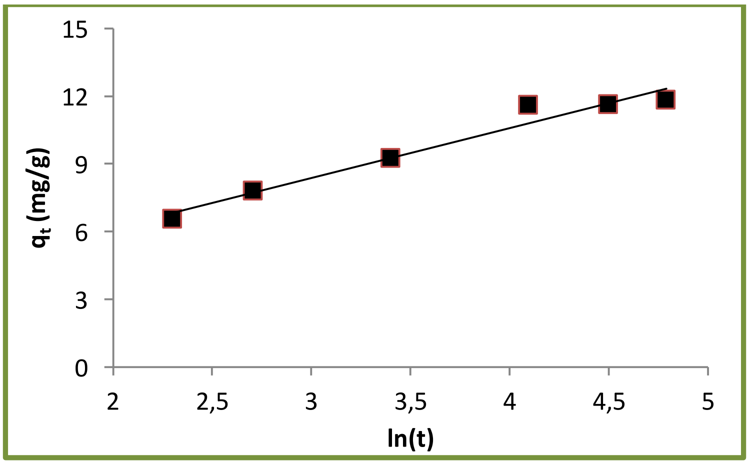

Figure 7: Elovich sorption kinetics of Ag(I) onto PANa in powder form.

. The results obtained are summarized in the table 4. The correlation coefficient (R^2) represents the success of Elovich model is greater than 0.96 with a low desorption constant. This kinetic model supports essentially the chemisorption mechanism. It is found that the results obtained from the Elovich model can explain that the adsorption of the Ag^+ ions by the hydrogel of PA-Na is dominated by a chemisorption type. In fact, the monovalent ions Ag^+ form with the $–COO^-$ groups of the hydrogel a monodentate complexes according to the reaction:

$$\mathbf{-COONa + Ag^+ \rightleftharpoons -COOAg + Na^+}$$

Table 4: Parameters of Elovich kinetic model.

α	*β*	*R^2*
4.808	*0.45*	*0.9623*

3.3.4. Intraparticlar diffusion model

To investigate the diffusivity of silver between the macromolecular chains of PANa in powder form, we applied the model of Weber and Morris, represented by the equation as follow:

$$q_t = k_i . t^{1/2} + X_i \qquad (5)$$

Where; k_i is intraparticlar diffusion constant ($mol.g^{-1}.min^{-1/2}$) and X_i is the value of the thickness of the boundary layer.

The curves obtained : $q_t = f(t^{1/2})$ with the appearance of two steps of adsorption of Silver on the PANa in powder form is shown in Fig.8. Parameters of the kinetic model of intraparticlar diffusion are summarized in the table 5. We note the occurrence of two phases: The first is linear and the second is a Plateau and also the absence of the concave part of the applied model, this may be due to the speed of adsorption to the external surface of the PANa. The same results were reported in an earlier study by studying the adsorption of copper on PANa [18,19]. These phases indicate that the adsorption process is carried out in surface first then followed by the intraparticle diffusion.

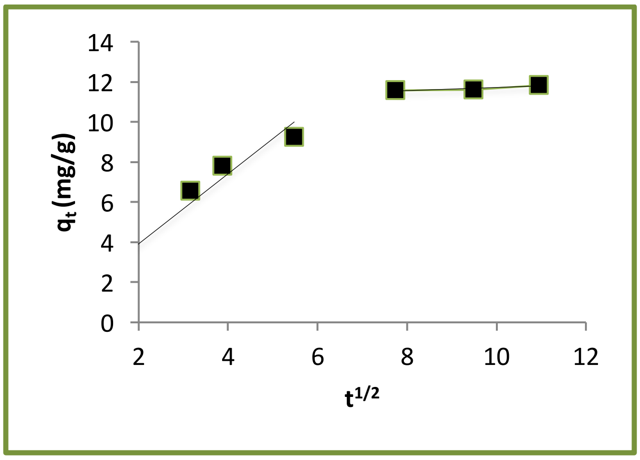

Figure 8: Intraparticular diffusion sorption kinetics of Ag(I) onto PANa in powder form.

Table 5: Parameters of Intraparticlar diffusion kinetic model.

Time (mn)	*K_i*	*X_i*	*R^2*
t<30	*1.1093*	*3.2369*	*0.9667*
t>30	*0.0749*	*10.974*	*0.8247*

3.3.4. Bangham kinetic model

Bangham's equation was used to evaluate whether the adsorption is pore-diffusion controlled. The Bangham kinetic model is expressed as:

$$\log \log\left(\frac{C_o}{C_o - q_t . m}\right) = \log\left(\frac{K_B}{2.303.V}\right) + \alpha \log t \qquad (6)$$

Where C_o is initial concentration (mg.l), V is volume of the solution (l), m is weight of the adsorbent (g), q_t is amount of adsorbate retained at time 't' (mg/g) and α, K_B are constants.

The application of this model to the experimental results of the adsorption of silver on the PANa powder form is shown in Figure 9. The parameters of this kinetic model are shown in Table 6. The experimental points are aligned on a line with a correlation coefficient close to unity: R^2=0.96, confirming that the adsorption is controlled by pore diffusion.

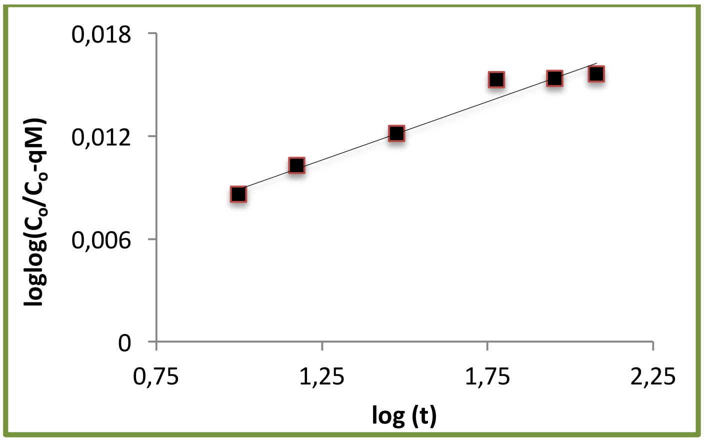

Figure 9: Bangham sorption kinetics of Ag(I) onto PANa in powder form.

Table 6: Parameters of Bangham kinetic model.

K_B	*a*	*R^2*
6.60	*0.0068*	*0.9624*

3.4. *Adsorption isotherms*

The equilibrium adsorption isotherm is fundamentally very crucial in designing adsorption systems. In this study, adsorption of silver by PANa hydrogel (powder form) was analyzed by well documented *Langmuir* [26] (Eq. 6), *Freundlich* [27] (Eq. 8), *Dubinin-Radushkevich* [28] (Eq. 9) and *Temkin* [29] (Eq. 11) isotherm models given below, respectively (Figs. 10, 12, 13 and 14). The *Langmuir* isotherm model is represented as:

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot q_{max}} + \frac{C_e}{q_{max}} \qquad (6)$$

Where; C_e is the concentration of silver solution (mg/l) at equilibrium, q_{max} gives the theoretical monolayer adsorption capacity (mg/g) and K_L is related to the energy of adsorption.

The application of this model is shown in Fig. 10. The table 7 shows that the correlation coefficient is greater than 0.99, indicating good agreement between the experimental data and Langmuir isotherm. In addition, the value of the experimental adsorption capacity ($q_{m,\ exp}$) and the capacity calculated by this model ($q_{m,\ theo}$) has an acceptable deviation (14.84%). This result indicates that the adsorption of Ag^+ on PANa occurs in monolayer.

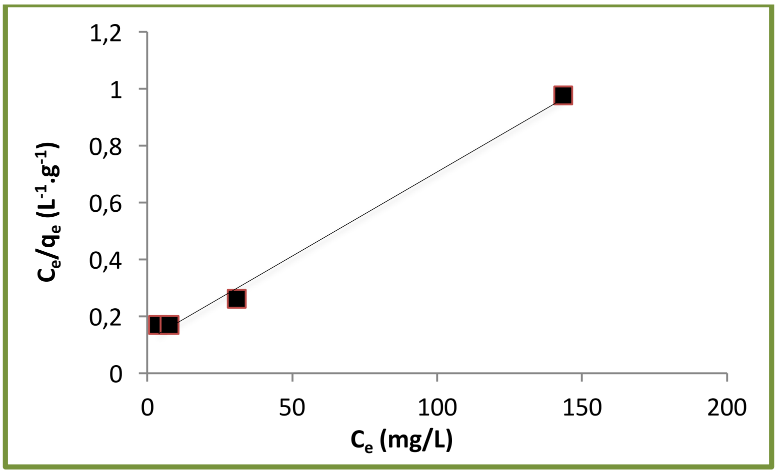

Figure 10: Langmuir isotherm model.

The essential characteristics of the *Langmuir* isotherm can be expressed in terms of dimensionless constant separation factor R_L [30] by the equation:

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

Where; C_o (mg/l) is the initial concentration of adsorbent and K_L (l/mg) is Langmuir isotherm constant. The parameter R_L indicates the nature of the shape of the isotherm accordingly.

$R_L > 1$	Unfavorable adsorption
$0 < R_L < 1$	Favorable adsorption
$R_L = 0$	Irreversible adsorption

The evolution of the value of R_L separation factor as a function of the initial concentration of silver is shown in Fig. 11. These values are less than 1 ($0<R_L<0.65$) indicates that the adsorption of Silver ion (Ag^+) on the PANa in powder form is favorable for the Langmuir model.

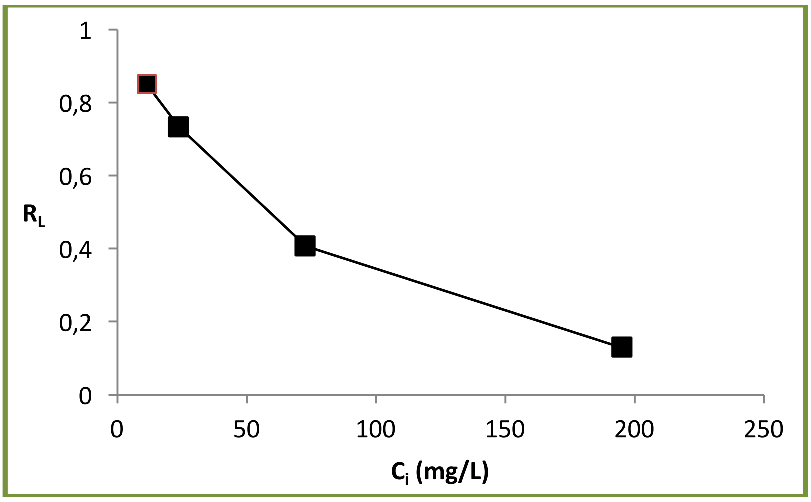

Figure 11: Evolution of separation factor with initial concentration of Ag(I).

Table 7: Parameters of Langmuir isotherm kinetic model.

q_m (mg/g)	*K_L*	*RD (%)*	*R^2*	*R_L*
169.49	*0.045*	*14.84*	*0.9944*	$0 < R_L < 0.65$

The application of the *Langmuir* isotherm to the experimental results made it possible to determine the theoretical maximum adsorption capacity of the PANa in silver ions which is 169.49 mg.g^{-1}. This value exceeds the values obtained by other studies using other natural and/or synthetic adsorbents which have been given in Table 8. This comparison led us to conclude that the sodium polyacrylate hydrogel is a better adsorbent for the noble Ag^+ ions.

Table 8: Maximum adsorption capacity of Ag^+ ions by different adsorbents.

Type of adsorbent	***C_{max}***	***Reference***
Clinoptilolite (zeolite)	*33.23 mg /g*	*[31]*
chitosan/bamboo	*52.91 mg/g*	*[32]*
Chitosan/Montmorillonite	*43.48 mg/g*	*[33]*
Na-Exchanged Mordenite	*87.72 mg/g*	*[34]*
Na- Mordenite (natural)	*57.41 mg/g*	*[34]*
Natural Bentonite	*53 mg/g*	*[35]*

The *Freundlich* isotherm model is represented as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (8)$$

Where; k_F and 1/n are the constants that can be related to adsorption capacity and the intensity of adsorption respectively. The magnitude of the exponent 1/n gives an indication of the favorability of adsorption. The value of n >1 represents favorable adsorption condition (or) the value of 1/n is lying in the range of 1 to 10 confirms the favorable condition for adsorption. This is further supported by Langmuir isotherm.

Fig.12 shows the modeled results. From the results obtained in the table 9, we find that the ratio 1/n is less than 1, the adsorption of Ag(I) on PANa is favorable. Correlation coefficient (R^2=0.89) is low compared to that of Langmuir isotherm model (R^2=0.99). We deducts that the experimental data are well represented by the Langmuir isotherm.

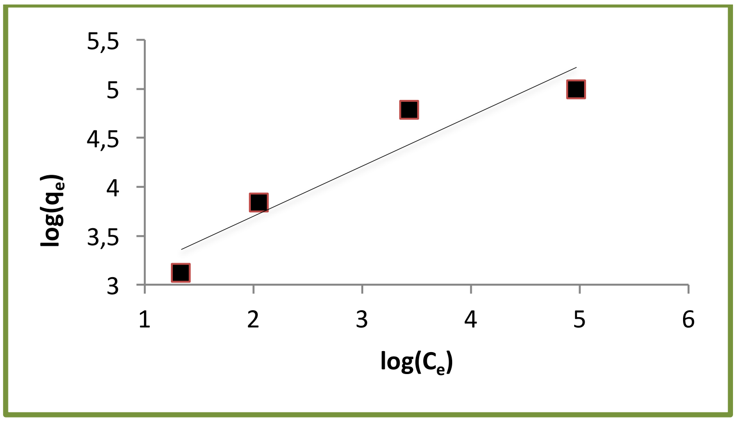

Figure 12: Freundlich isotherm model.

Table 9: Parameters of Freundlich isotherm model.

1/n	*K_F*	*R^2*
0.5118	*14.53*	*0.8932*

The *Dubinin-Radushkevich* model is expressed as follow:

$$\ln q_e = \ln(q_s) - (K_{ad}\varepsilon^2) \qquad (9)$$

Where; q_s is the theoretical saturation capacity (mg/g) and ε is the Polanyi potential. The constant B (K_{ad}) ($mg^2.KJ^2$) isotherm D-R gives the free energy average E (Kj/mol) of the adsorption per molecule of the adsorbate when it is transferred to the solid surface in of infinity in the solution and can be calculated using the following relationship [31]:

$$E = \frac{1}{\sqrt{2B}} \qquad (10)$$

The results obtained with the Dubinin-Radushkevich model are shown in Fig. 13.

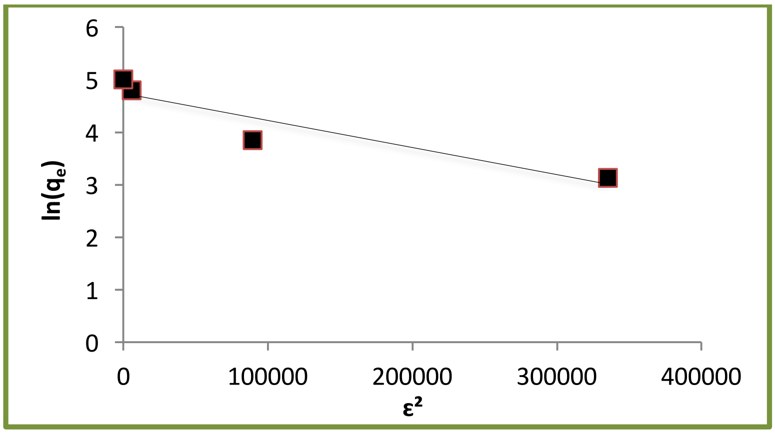

Figure 13: Dubinin-Radushkevich isotherm model.

The parameters calculated from this model are given in the table 10. The relative difference between $q_{e,;exp}$ and q_s is equal to 28%. The value of the adsorption energy calculated by this model is E=316.23 kj/mol, this value is greater than 16 kj/mol, indicating that the adsorption of Ag^+ cations on PANa is done according to a mechanism of chemisorption. This result is in agreement with that obtained from the Elovich kinetic model.

Table 10: Parameters of D-R isotherm model.

$q_{e\ ;exp}$ (mg/g)	q_s (mg/g)	RD (%)	B	E (Kj/mol)	R^2
147.576	*114.95*	*28.38*	$5.\ 10^{-6}$	*316.23*	*0.8775*

The *Temkin* isotherm model is expressed as:

$$q_e = B\ lnA + B\ ln\ C_e \qquad (11)$$

Where B (RT/ΔQ) is constant of Temkin isotherm, T is the temperature (K), R is the gas constant (8.314 $J.mol^{-1}.K^{-1}$) and ΔQ is the variation of the energy of adsorption, K_o or A is a constant of adsorption ($l.mg^{-1}$).
The Temkin isotherm may as well represent the experimental results (Fig.14), the correlation coefficient is close to unity $R^2>0.95$. The variation of the adsorption energy is positive (Table 11), indicating that the adsorption reaction is exothermic.

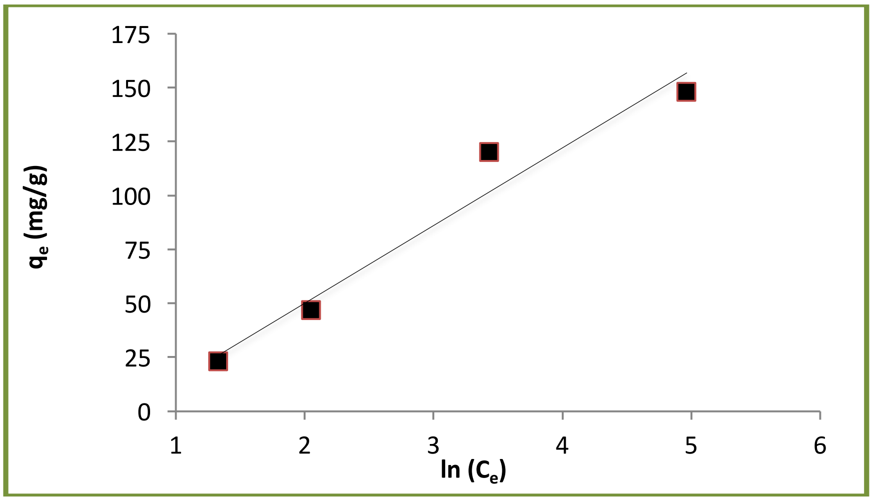

Figure 14: Temkin isotherm model.

Table 11: Parameters of Temkin isotherm model.

B_1	ΔQ ($Kj.mol^{-1}$)	K_o ($l.mg^{-1}$)	R^2
36.054	*68.753*	*0.54*	*0.9565*

Conclusion

The adsorption of silver on Sodium polyacrylate hydrogel (PANa in powder form) was found to be dependent on contact time and silver concentration. The retention of Ag(I) on PANa is fast (15 mn) and the extraction efficiency decreases with increasing concentration of the aqueous solution of silver. Mathematical modeling of experimental results by kinetic models (Pseudo-first, Pseudo-second-order, Elovich, Intraparticlar diffusion and Bnagham models) and by isotherm models (Langmuir, Freundlich, D-R and Temkin isotherms) shows that:
- The diffusion of Ag(I) is limited by the exterior layer and the presence of the pores in the structure of PANa hydrogel.
- The adsorption of Ag(I) onto PANa hydrogel is monolayer and favorable.
- The silver adsorption on PANa is dominated by chemisorption mechanism.
- The adsorption reaction is exothermic.

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