

Adsorption of Silver (Ag^+) from aqueous solution by the Sodium Polyacrylate in bead form

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ABSTRACT

The adsorption of the silver (Ag^+) is performed in aqueous medium, of a superabsorbent polymer, sodium polyacrylate (PANa) in the form of bead. The kinetic study shows that the pseudo-second-order and Bangham models are best suited. The equilibrium isotherms, for the sorption of silver, was analyzed using four widely used isotherm models (Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models). Error analysis, using the linear correlation coefficient (R^2), showed that the Langmuir isotherm best fits the silver adsorption data on PANa bead form. The monolayer coverage capacity of the PANa in bead form, obtained from Langmuir isotherm studies, was 147.06 mg/g. The thermodynamics showed that the adsorption of silver on PANa was most favorable and spontaneous; the value of R_L is lower than 1 and the free energy value is -2.64 KJ/mol.

Keywords : Adsorption, kinetics, isotherms, heavy metal, silver, sodium polyacrylate.

1 INTRODUCTION

The heavy metal pollution is a sneaky because, unlike plastic waste or of the hydrocarbons, it does not notice it and its effects on organisms or the environment rather belated.

Although heavy metals exist naturally in sea water [1,2], minerals and volcanic compounds, the human with his activities which is responsible for the release of a large amount of these elements in environment. Lead, mercury, arsenic and cadmium entering the food chain [3,4]. The industry is responsible for almost all releases of heavy metals in water [5,6], such as burning coal [7], oil [8], waste and certain industrial processes rediffuse however in large amounts in the environment [9]. The heavy metals are biopersistent; disrupt ecosystems [10,11], deteriorating soil [12,13], surface water, forests and cultures and bioaccumulate in the food chain [3,4]. Some are carcinogenic to humans [14]. They cause nuisance even when discharged in very small quantities (toxicity develops through bioaccumulation). It is therefore necessary to treat and reduce wastewater.

In this context, the use of gels in the treatment of wastewater constitutes an original application [15-18]. This time, they are used not for their exceptional ability to swell [19,21], but for their character and chelating polyelectrolyte allowing them to complex metal salts while at collapsing on themselves.

The aim is the use of sodium polyacrylate gels in bead form, for the recovery of the silver present in the synthetic aqueous solutions. It is necessary to better understand the phenomena at the interface between PANa and ions of silver in terms of diffusion and adsorption mechanism to optimize their use.

The adsorption performance of the PANa bead form was estimated on the basis of kinetic models (First order [22], Second order [23], Elovich [24] and Bangham [25]) and adsorption isotherms (Langmuir [26], Freundlich [27], Dubinin-Raduchkevich [28] and Temkin [29]).

2 MATERIALS AND METHODS

2.1 Silver solutions

Silver solutions that we used are prepared by dissolving the salt of Silver nitrate $\text{Ag}(\text{NO}_3)$ in distilled water. The pH of the solution is adjusted with concentrated hydrochloric acid.

2.2 Preparation of sodium polyacrylate

The sample used in this work is superabsorbent polymer which is present in spherical beads transparent, the diameters ranging between 2 and 3.5 mm. They introduce oneself in many colors from which the name: SEVEN COLOR CRYSTAL BOLL, reference SJQ-007, supplied by the company Xinchang Chengtan Magic Bean & Grass Doll Artware Factory of Origin: Zhejiang, China (Mainland).

Sodium polyacrylate has the drawback of being hygroscopic. This poses a problem for stability weighing especially when using very small quantities. To remedy this, we worked with gels (PANa swolled with distilled water).

3 RESULTS AND DISCUSSION

3.1 Effect of contact time

In order to optimize the contact time and determining the kinetics of adsorption of Ag^+ unto sodium polyacrylate in bead form, an amount of gel equal to 7.5 g (equivalent to 0.035 g of dry PANa) was contacted with 100 ml of the metal solution at a concentration of 11.79 mg/L and agitated [at 200 rpm] for 120 minutes. The adsorption is carried out at 25°C and atmospheric pressure. The figure 1 shows the capacity retention of Ag^+ cations of the polymeric support as a function of contact time.

The time $t=0$ corresponds to the contact of the gel with the metal solution. The equilibrium adsorption capacity, q_e (mg/g) of Ag^+ on PANa bead form surface was calculated by using

following equation 1:

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

Where C_o is the initial adsorbate concentration, C_e is the adsorbate concentration at equilibrium (mg/L), V is the volume of the solution (L) and m is the mass of adsorbent (g).

However, the adsorption capacity at pre-determined time intervals was calculated by using following equation 2:

$$q_t = (C_o - C_t) \cdot \frac{V}{m} \quad (2)$$

Where C_t is the adsorbate concentration (mg/L) at time t (min).

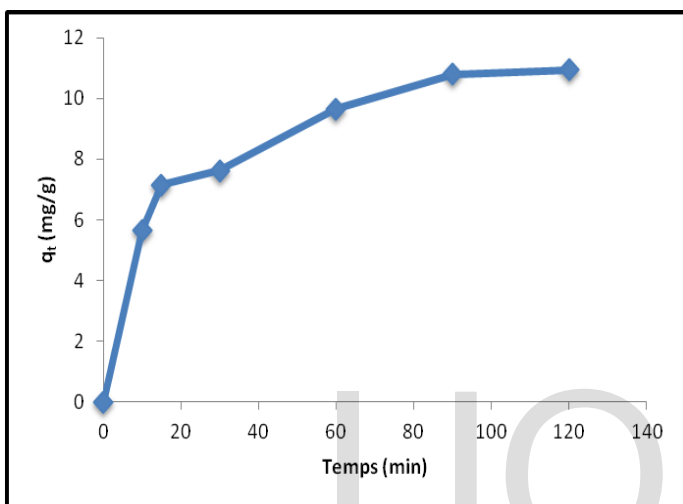


Fig. 1. Adsorption kinetics Ag+ unto PANa in bead form

The amount of Ag^+ cations adsorbed (mg/g) increased with increase in agitation time and reached equilibrium. The equilibrium time was found to be 90 min, then a plateau, This indicates that the gel is in equilibrium with the metal solution.

3.2 Effect of the concentration of silver

The effect of the concentration of Ag^+ cations on the adsorption capacity of PANa was also studied. The Fig.2 shows the evolution of the adsorption capacity of the PANa bead form as a function of the initial concentration of Ag^+ cations.

The amount of Ag^+ removed at equilibrium increased from 22 to 130mg/g with increase in Ag^+ concentration from 11.74 to 195.4 mg/L. It shows that the adsorption at different concentrations was rapid in the initial stages and gradually decreased with the progress of adsorption until the equilibrium was reached.

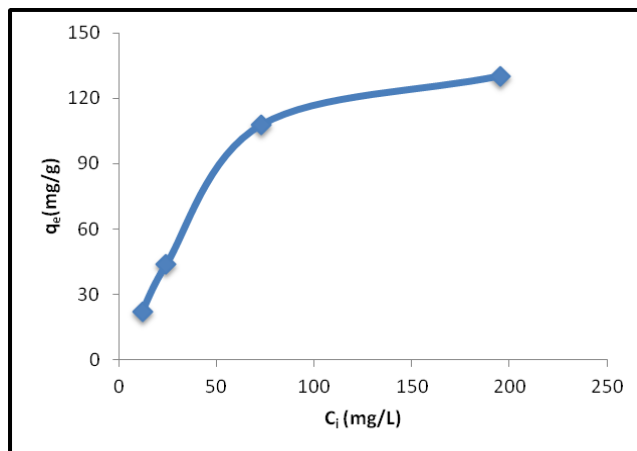


Fig. 2. Effect of Ag^+ cation concentration on the adsorption capacity of PANa

3.3 Adsorption kinetics

Adsorption kinetic models correlate the adsorbate uptake rate with bulk concentration of the adsorbate. Kinetic data were fit into Lagergren, second order, Elovich and Bangham models. The first order kinetic model is represented as:

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

Where; q_e and q_t are the amounts of Ag^+ adsorbed (mg/g) at equilibrium and at time t , respectively, and k_1 is the Lagergren rate constant of first order adsorption (min^{-1}).

The second order kinetic model is expressed as:

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

Elovich kinetic equation is presented as follows:

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

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 $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha\beta)$.

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

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

Where C_o is initial concentration (mg/L), V is volume of the solution (L), M is weight of the adsorbent (g), q_m is amount of adsorbate retained at time 't' (mg/g) and α , K_0 are constants.

The application of these models to the experimental results of the adsorption of silver on the PANa bead form is shown in Figures 3, 4, 5 and 6, respectively to the models described pre-

viously. The parameters of the Pseudo-first order, Pseudo-second order, Elovich and Bangham kinetic models are shown in Tables 1 and 2.

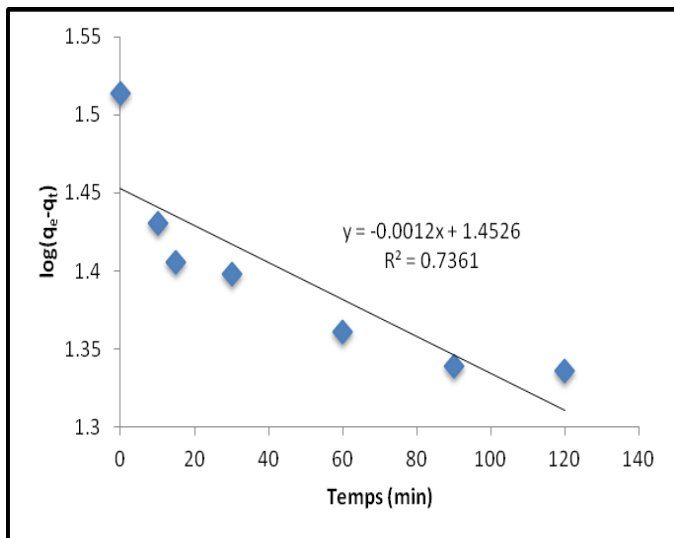


Fig. 3. Pseudo-First order kinetic model

The variation of $\log(q_e - q_t)$ versus time has not been very linear, and the regression coefficient R^2 is unsatisfactory because its value does not exceed 0.75, and the relative difference between q_e experimental and q_e calculated by this model is very large, it is around 62%. Finally we can conclude that the kinetics does not respond to the pseudo first-order kinetic model.

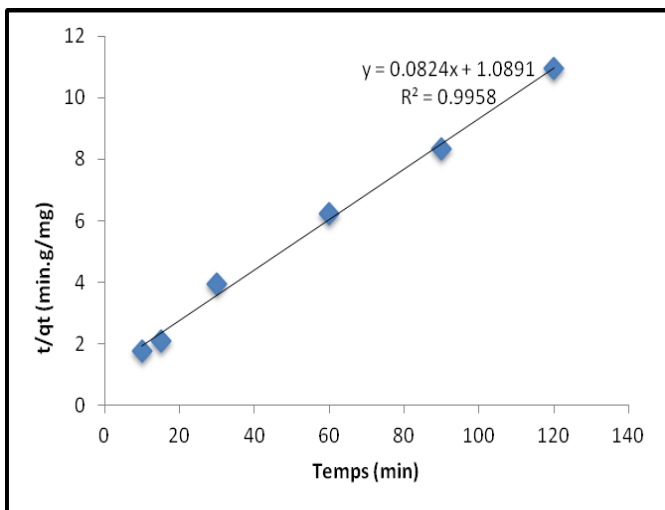


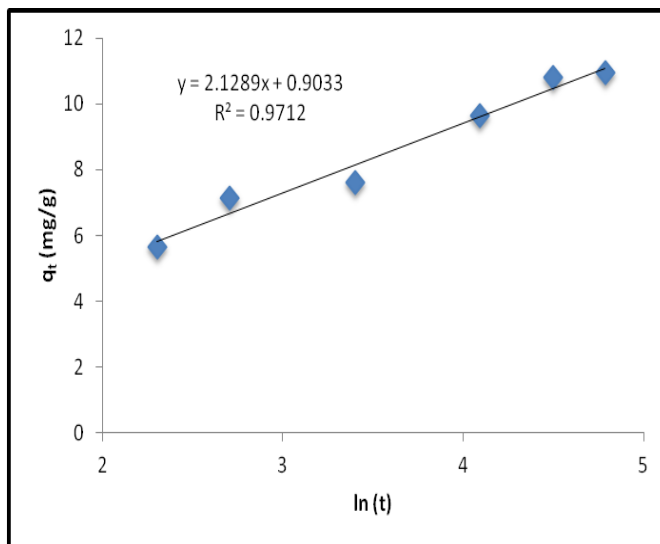
Fig. 4. Pseudo-Second order kinetic model.

Based on the parameters of the pseudo-second order kinetic model, it is clear that the adsorption capacity (q_e exp) of PANa, coincides with that obtained by the pseudo-second order model. Indeed, the relative difference is very small ($RD < 10\%$). The rate constant k_2 shows a fairly rapid retention ($k_2 = 6.23 \cdot 10^{-3} \text{ min}^{-1}$). So we conclude that the adsorption capacity of the silver on the PANa is a fast and speed adsorption process appears to follow a kinetic law second order rather than

first order.

Fig. 5. Elovich kinetic model

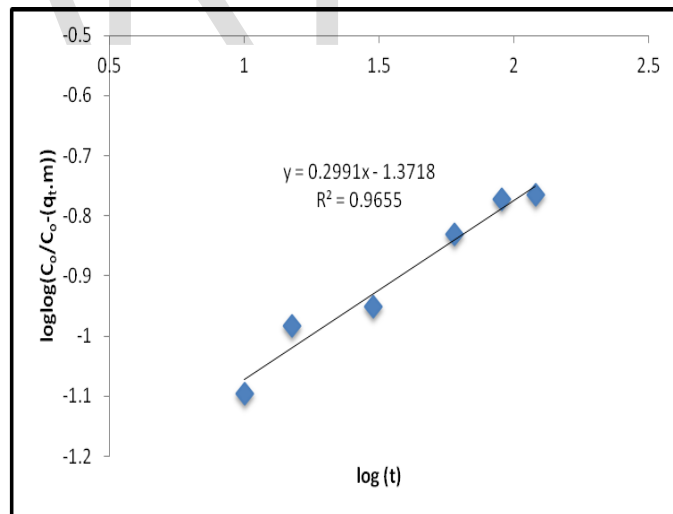
The correlation coefficient of the Elovich model is close to



unity, which probably means that the adsorption is chemisorption kind confirming the kinetic model valabilité Pseudo second-order.

The initial rate α adsorption of copper on the PANa powder form is 3.25. Whilst the constant β is weak, it is equal to 0.47.

Fig. 6. Bangham kinetic model.



Plots of $\log \{ \log [C_o / (C_o - qM)] \}$ vs $\log t$ ($R^2 = 0.97$) was found to be linear at 25°C (Fig. 6) which confirms that the adsorption is pore-diffusion controlled.

The plot was found to be linear with good correlation coefficient (> 0.9) indicating that kinetics confirmed to Bangham's equation and therefore the adsorption of silver onto PANa bead form was pore diffusion controlled.

TABLE 1
PSEUDO-FIRST ORDER AND PSEUDO-SECOND ORDER PARAMETERS

Pseudo first-order model	q _{exp} (mg.g ⁻¹)	q _{calculated} (mg.g ⁻¹)	Difference Relative (%)	k ₁ (min ⁻¹)	R ²
	10.94	28.35	61.41	2.76 10 ⁻³	0.7361
Pseudo second-order model	q _{exp} (mg.g ⁻¹)	q _{calculated} (mg.g ⁻¹)	Difference Relative (%)	k ₂ (min ⁻¹)	R ²
	10.94	12.14	9.88	6.23 10 ⁻³	0.9958

TABLE 2
ELOVICH AND BANGHAM PARAMETERS

Elovich model	a	β	R ²
	3.25	0.47	0.9712
Bangham model	K _B	a	R ²
	9.79	0.2991	0.9655

3.4 Determination of adsorption Isotherms

The equilibrium adsorption isotherm is fundamentally very crucial in designing adsorption systems. In this study, adsorption of silver by PANa bead form was analyzed by well documented Langmuir (Eq. 7), Freundlich (Eq. 10), Dubinin-Radushkevich (Eq. 11) and Temkin (Eq. 13) isotherm models given below, respectively (Figs. 7, 9, 10 and 11).

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad (7)$$

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 essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L [14,15] by the equation:

$$R_L = \frac{1}{1 + K_L \cdot C_o} \quad (8)$$

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 calculated R_L, q_{max} and K_L values are given in Table 3.

The free energy ΔG°_{ads} (kJ/mol) of adsorption process considering the adsorption equilibrium constant K_L is given by the equation:

$$\Delta G_{ads}^{\circ} = -RT(\ln K_L + 4.02) \quad (9)$$

Where T is the temperature in Kelvin and R is the universal gas constant (8.314 J/mol.K).

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The Freundlich isotherm model is represented as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (10)$$

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. The constant K_F and n values are given in table 3.

The Dubinin-Radushkevich model is expressed as follow:

$$\ln q_e = \ln(q_s) - (K_{ad} \epsilon^2) \quad (11)$$

With q_s is the theoretical saturation capacity (mg/g) and ε is the Polanyi potential. The constant B (K_{ad}) (mg².KJ²) 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:

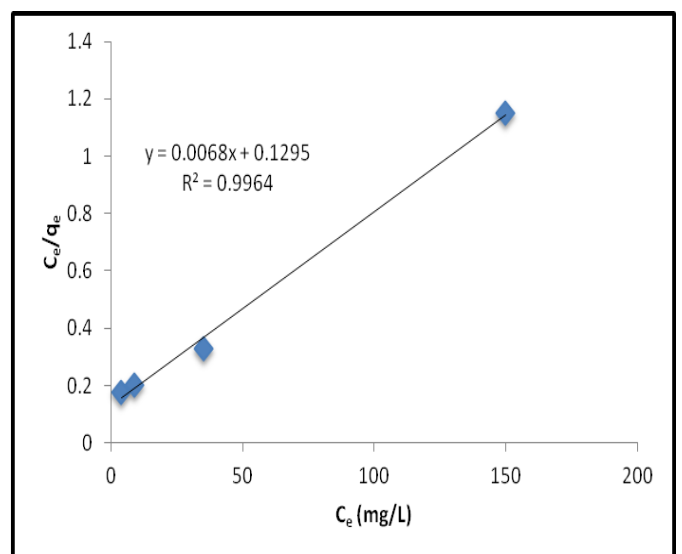
$$E = \frac{1}{\sqrt{2B}} \quad (12)$$

Temkin isotherm model is expressed as:

$$q_e = B \ln A + B \ln C_e \quad (13)$$

Where; B (RT/ΔQ) is constant of Temkin isotherm, T is the temperature (K), R is the gas constant (8.314 J/mol.K) and ΔQ is the variation of the energy of adsorption, K_o or A is a constant of adsorption (L/mg).

Fig. 7. Adsorption isotherms of silver on the PANa according to the Lang-



muir model.

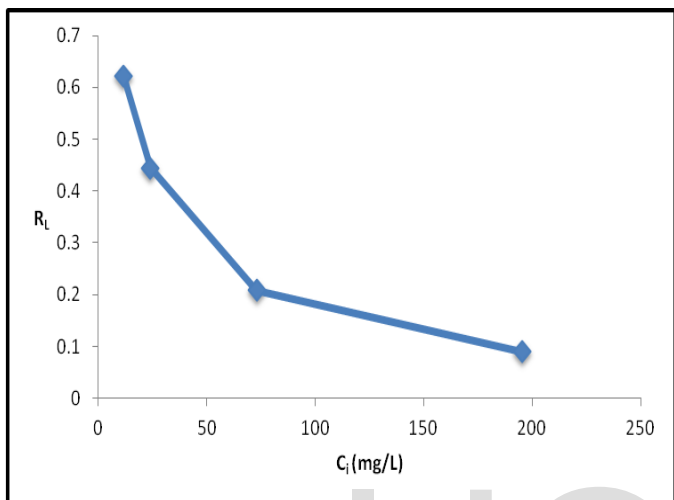
The data showed correlation coefficient, R² for silver adsorption unto PANa bead form was 0.9964 (Table 3).

The Gibbs free energy for silver metal value is -2.64 kJ/mol, shows that the adsorption process is spontaneous. The maximum adsorption capacity (monolayer) q_m on PANa bead form was 147.06 mg/g, it is the same obtained experimentally. Indeed, q_{exp} is equal to 149.9 mg/g.

The evolution of the separation factor (R_L) as a function of the initial concentration of Ag^+ in the supernatant solution, is shown in Figure 8.

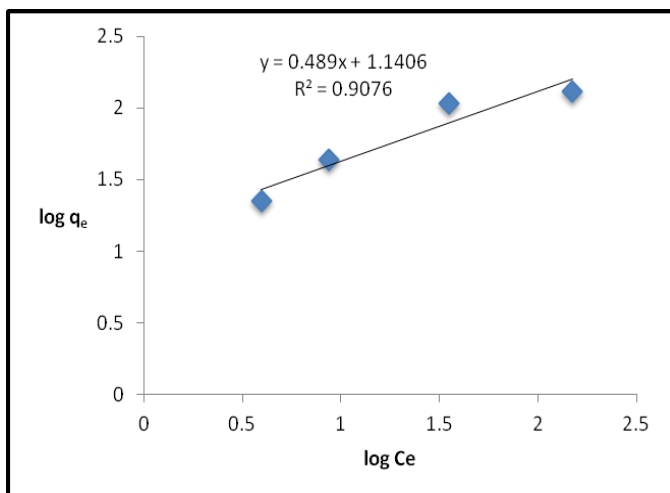
Fig. 8. Evolution of separation factor

For an initial silver concentration equal to 11.74mg/L, the



value of separation factor (R_L) is 0.62. This estimated value of R_L that is less than unity, clearly show a favorable silver adsorption on the PANa bead form. Adsorption becomes more favorable as the initial concentration of Ag^+ ions increases. The increased presence of Ag^+ ions in the supernatant solution favors adsorption on PANa bead form; effectively for an initial concentration of Ag^+ equal to 194.5 mg/L, the R_L value is 0.09.

Fig. 9. Adsorption isotherms of silver on the PANa according to the Freun-

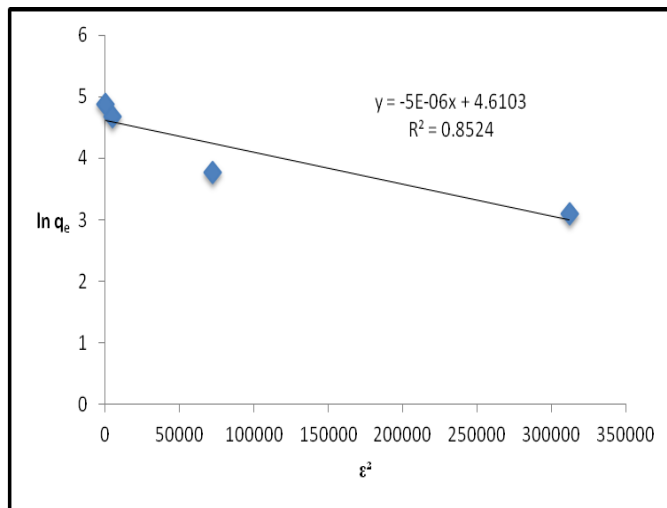


dlich model.

The Freundlich constants, k_F and n were evaluated from the linear plots of $\log q_e$ vs $\log C_e$ and found to be 13.82 and 2.045,

respectively. The value of n is in the range of favorable adsorption ($1 < n < 10$) showing that adsorption process was favorable.

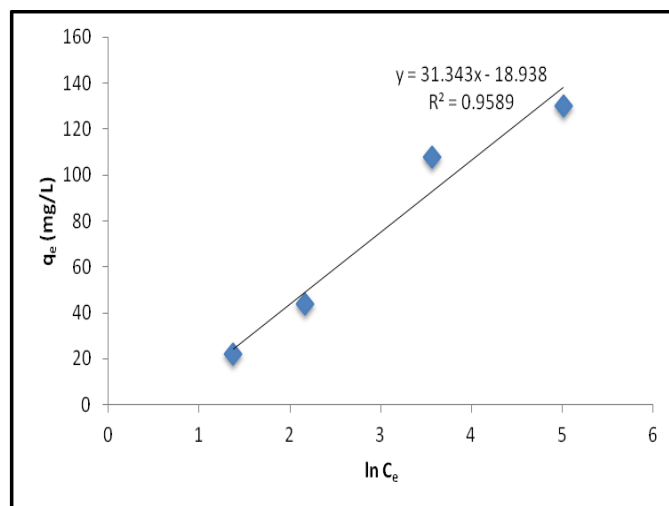
Fig. 10. Adsorption isotherms of silver on the PANa according to the D-R



model.

The Langmuir isotherm constants do not explain the chemical or physical properties of the adsorption process. However, the mean adsorption energy (E) calculated from the D-R isotherm provides important information about these properties. For $E < 8$ kJ/mol, physisorption dominates the sorption mechanism. If E is between 8 and 16 kJ/mol, ion-exchange is the dominant factor. If $E > 16$ kJ/mol, sorption is dominated by particle diffusion. The adsorption energy was 316.23 kJ/mol at a temperature of 293°K (Table 3), suggesting that the sorption process was dominated by particle diffusion and that these forces were more important than ion-exchange and physical forces. This confirms the results of Bangham kinetic model.

Fig. 11. Adsorption isotherms of silver on the PANa according to the Tem-



kin model.

The Temkin isotherm constants A and B were found to be 0.55 L/mg and 31.343 mg/g, respectively (Table 3).

Langmuir model showed higher values of R^2 compared with Freundlich, D-R and Temkin models indicating better applicability of Langmuir model. Langmuir model was an indication of surface homogeneity of adsorbent. Therefore, it can be concluded that the adsorption on PANa bead form surface was homogeneous. Similar results have been reported using the same polymer for the adsorption of copper (II) [30].

TABLE 3
PARAMETERS OF THE FOUR ISOTHERMS ADSORPTION

Freundlich isotherm				
$1/n$	n	K_F	R^2	
0.489	2.045	13.82	0.9076	
Temkin isotherm				
B	ΔQ (Kj/mol)	A (L.mg ⁻¹)	R^2	
31.343	79.087	0.55	0.9589	
Langmuir isotherm				
q_m	K_L	ΔG_{ads} (KJ/mol)	R_L	R^2
147.06	0.052	-2.64	0 < R_L < 0.7	0.9964
D-R isotherm				
q_s	$E(\%)$	K_{ad}	$E(KJ/mol)$	R^2
100.51	29.47	$5 \cdot 10^{-6}$	316.23	0.8524

4 CONCLUSION

The adsorption of silver unto sodium polyacrylate in bead form, have been tested by four kinetic models (First order, second order, Elovich and Bangham) and performed by Lngmuir, Freundlich, Dubinin-Radushkevich and Temkin adsorption isotherms. Adsorption kinetics followed second order, Elovich and Banghams model. Equilibrium adsorption data fit better into Langmuir isotherms. It can be concluded that:

- The adsorption was dominated by particle diffusion
- The adsorption was chemisorptions kind.
- The adsorption process is spontaneous and the surface was homogeneous

This study shows that PANa bead form is an effective adsorbent for the removal of Ag⁺ cation from aqueous solution. Therefore, it could be used as a substitute cheap adsorbents commercially available for the removal of heavy metals present in the wastewater.

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