

## Application of Kinetic and isotherm models to the Sorption of Copper (II) on to superabsorbent polymer in powder form

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### Abstract

Equilibrium sorption of the sodium polyacrylate (PANa) in powder form was studied. The Elovich model and the Pseudo-second order model both provided a high degree of correlation with the experimental data for most of the sorption process. The equilibrium sorption data were also fitted into Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D-R) isotherms. Of the four adsorption isotherms, the  $R^2$  value of Langmuir and Temkin isotherm model were the highest. The maximum monolayer coverage ( $q_m$ ) from Langmuir isotherm model was determined to be 116.8 mg/g, the separation factor indicating a favorable sorption experiment is  $0 < R_L < 0.35$ . Also from Freundlich isotherm model, the sorption intensity ( $n$ ) which indicates favorable sorption and the correlation value are 2.44 and 0.91 respectively. The heat of sorption process was estimated from Temkin Isotherm model to be 139.52 KJ/mol and the mean free energy was estimated from D-R isotherm model to be 2236 KJ<sup>1</sup>/mg which vividly proved that the adsorption experiment followed a chemical process.

**Keywords:** *Isotherm models; Kinetic models; Sodium polyacrylate; Sorption of copper.*

### 1. Introduction

Heavy metals are Naturally present in the environment [1,2] and used industrially [3,4], they are released into the air as very fine particles and end up back on the soil [5-7] contaminating the animals [8,9] and plants [10-13]. Some metals such as iron, chromium and copper are needed in small quantities to ensure the health of humans and animals. But when taken in too large quantities, these metals cause various problems. Furthermore, the uptake of heavy metals such as lead and mercury is never desirable, whatever the quantity. Once ingested, the different metals can accumulate in various organs such as the kidney, liver and spleen [14,15]. For all these conditions, and to prevent them, a good detox is needed, and fortunately, it can be done by the use of low-cost sorbents [16-22] has been investigated as a replacement for current costly methods of removing

heavy metals from solution. The metal cations by complexation polyelectrolytes gels have been subject of several studies [23-29]. Indeed, recovery of elements harmful to the environment, as copper complexing polymethacrylic acid gels [30], the extraction of silver of polyacrylic acid, sodium polyacrylate [31], the extraction of cobalt nitrate medium and recovering cesium, strontium and europium by polyacrylic acid gels [32], is an important application fields. As the recovery of organic matter [33]. The adsorption performance of the sodium polyacrylate in powder form can be estimated through the kinetic models (pseudo first-order, pseudo second-order [34] and Elovich [35]) and adsorption isotherms namely Freundlich, Langmuir [36], Temkin and Dubinin-Radushkevich [37]. For this study the copper was chosen as the target pollutant. The results will be modeled and discussed in terms of chemical properties of PANa powder form.

## 2. Materials and methods

### 2.1. Used materials

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, under reference: Model Number SNN560-011, provided by the company Henan CXH Purity Industrial And Trading Co., Ltd. Originally: Henan, China (Mainland).

### 2.2. Preparation of sorbent

The first problem encountered in the use of sodium polyacrylate polymers resides in the weighing sample. Indeed, these polymers have the drawback of the spontaneously absorb humidity, which is an obvious problem of weighing stability, especially at very low amounts of dry polymer. To overcome this difficulty and to use small amounts of dry polymer, we have worked directly on gels swollen with distilled water. The gel thus obtained is separated from the supernatant liquid by filtration and was previously introduced into a small bag made of filter paper prepared in the laboratory, this technique allows to avoid breaking the gel grains during agitation of the aqueous solution and also allows for easy swabs supernatant solution without problems drive grains gel in the samples to be assayed. The time  $t=0$  corresponds to the contact of the gel with the metal solution. The extraction yield is calculated by the following equation, where  $C_i$  and  $C_f$  are the initial and final copper (II) concentration, respectively:

$$R\% = \frac{(C_i - C_f)}{C_i} \times 100 \quad (1)$$

### 2.3. Preparation of aqueous solution

Copper solutions that we used are prepared by dissolving the salt of copper nitrate ( $\text{Cu}(\text{NO}_3)_2$ ) in distilled water. The pH of the solution is adjusted with concentrated hydrochloric acid.

### 2.4. Adsorption kinetics

Three kinetic models are studied to describe the phenomenon of adsorption of copper (II) on the PANa powder form used: the model of pseudo-first-order, model of pseudo-second order and the Elovich model.

The adsorption capacity was calculated using the following relation (1):

$$q_e = (C_0 - C_e) \cdot \frac{V}{m} \quad (2)$$

With:  $q_e$ : adsorbed amount of copper on the sodium polyacrylate at equilibrium (mg.g<sup>-1</sup>),

$C_0$ : initial concentration of copper in solution (mg.L<sup>-1</sup>),

$C_e$ : concentration of copper in solution at equilibrium (mg.L<sup>-1</sup>),

$V$ : volume of solution (L).

Table 1 shows the various expressions of the main kinetic models.

**Table 1.** Models of adsorption kinetics

Model	Model expression	Linear expression	Plot	Reference
Pseudo first-ordre	$\frac{dq_t}{dt} = k_1(q_e - q_t)$ (3)	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t$ (4)	$\log(q_e - q_t)$ vs. $t$	[38]
Pseudo second-ordre	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$ (5)	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$ (6)	$\frac{t}{q_t}$ vs. $t$	[39]
Elovich	$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)$ (7)	$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln(t)$ (8)	$q_t$ vs. $\ln(t)$	[40]

Where  $k_1$  is the rate constant of Pseudo first-order model,  $k_2$  is the equilibrium rate constant (g/mg.min) of Pseudo-second-order chemical sorption,  $q_t$  (mg/g) is the amount of adsorbed copper at any time  $t$  (min) and  $\alpha$  is the initial copper(II) sorption rate (mg/g.min) and  $\beta$  is the desorption constant (g/mg).

## 2.4. Adsorption isotherms

The model is expected to optimize dimensioning and functioning of adsorbent through the prediction of the adsorption capacity and contact time.

Table 2 describes the different expressions of the main models used isotherms.

**Table 2.** Models adsorption isotherms

Model	Model expression	Linear expression	Plot	Reference
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$ (9)	$\log q_e = \log K_F + \frac{1}{n} \log C_e$ (10)	$\log q_e$ vs. $\log C_e$	[41]
Langmuir	$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$ (11)	$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$ (12)	$\frac{C_e}{q_e}$ vs. $C_e$	[42]
Temkin	$q_e = \frac{RT}{b} \ln(A C_e)$ (13)	$q_e = B \ln A + B \ln C_e$ (14)	$q_e$ vs. $\ln C_e$	[43]
Dubinin-Radushkevich	$q_e = (q_s) \exp(-K_{ad} \varepsilon^2)$ (15)	$\ln q_e = \ln(q_s) - (K_{ad} \varepsilon^2)$ (16)	$\ln q_e$ vs. $\varepsilon^2$	[44]

Where  $K_F$  is multilayer adsorption capacity and  $n$  is adsorption intensity for Freundlich isotherm,  $q_m$  is the monolayer adsorption capacity, and  $K_L$  is the constant of the Langmuir isotherm and  $q_s$  (mg.g<sup>-1</sup>) is the theoretical monolayer saturation capacity of the adsorbent and  $\varepsilon$  is Polanyi potential is given as follows:

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_s} \right) \quad (17)$$

The Langmuir separation factor ( $R_L$ ) was applied to estimate either the sorption system favorable ( $0 < R_L < 1$ ), unfavorable ( $R_L > 1$ ), irreversible ( $R_L = 0$ ) or linear ( $R_L = 1$ ). Is calculated from the Langmuir isotherm based equation as follow [45]:

$$R_L = \frac{1}{1 + K_L C_i} \quad (18)$$

A temperature studied, the free energy of adsorption  $\Delta G^\circ_{ads}$  can be calculated by the following equation:

$$\Delta G^\circ_{ads} = -RT(\ln K_L + 4.02) \quad (19)$$

$\Delta G^\circ_{ads}$ ,  $R$ ,  $T$  and  $K_L$  represents the free energy of adsorption, the ideal gas constant, the absolute temperature and the Langmuir constant, respectively.

The constant  $B$  ( $K_{ad}$ ) ( $\text{mg}^2 \cdot \text{KJ}^2$ ) isotherm D-R gives the free energy average  $E$  ( $\text{KJ}^{-1} \cdot \text{mg}$ ) 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:

$$E = \frac{1}{\sqrt{2B}} \quad (20)$$

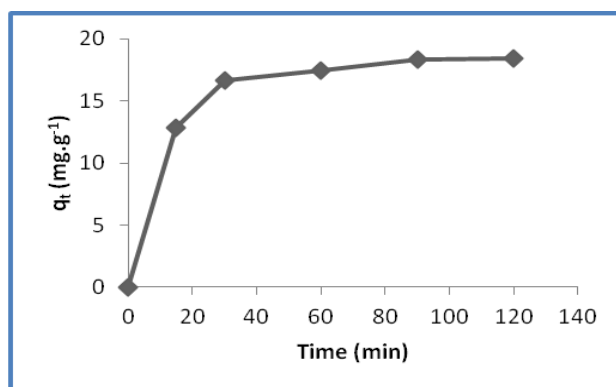
### 3. Results and Discussions

#### 3.1. Effect of contact time

The discussion of this effect is the contacting of the metal solution and the gel study PANa in powder form considered, following the variations of the metal concentration of the liquid phase by performing dosages of samples by ICP.

A quantity equivalent to 7.5 g of gel (0.035g of dry PANa in powder form) was in contact with a solution of copper nitrate at a concentration of 6.8 mg/L ( $10^{-4}\text{M}$ ), the mixture was placed under agitation.

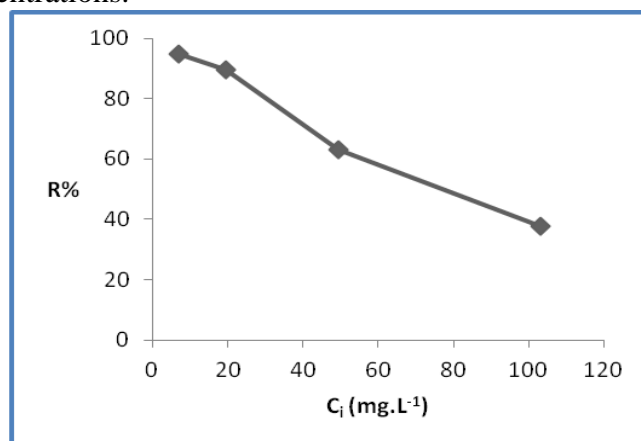
The curve of figure (1) shows that the adsorption equilibrium is fast. Indeed, it is reached after 30 minutes of immersion of the gel in the metal solution and the extraction yield was 95%. Using the PANa in bead form as is shown by a previous study [46] that time is 60 min and the extraction yield decreased from 95 to 69.11%.



**Figure 1.** Evolution of the adsorption capacity as a function of contact time with the metal solution. ( $C_o = 6.8 \text{ mg} \cdot \text{L}^{-1}$ ,  $\text{pH} = 5.5$ ,  $m_{\text{PANa(Dry)}} = 0.035 \text{ g}$ )

### 3.2. Effect of the concentration of $\text{Cu}^{2+}$ ions

The initial concentration of the metal can also have a fairly large influence on the retention capacity of the polymeric materials. The extraction tests are carried out on the same conditions: pH equal to 5.5, mass equal to 7.5 g of gel, only the metal concentration varies (6.8, 19.6, 49.2 and 103 mg/L). It can be seen from figure (2) that, the process of removing the copper by PANa gel is influenced by the value of the initial concentration of the metal species. Indeed, the figure shows an increase of the retention rate of the gel with the decrease in metal concentration. It goes from 38 to 95 %, from 103 to 6.8 mg/L. This can be explained by the fact that low concentrations of copper in the gel swell more than for high concentrations.



**Figure 2.** Evolution of the yield of extraction depending on the initial concentration of the aqueous solution of copper. (pH=5.5,  $m_{\text{PANa(dry)}}$ =0.035 g)

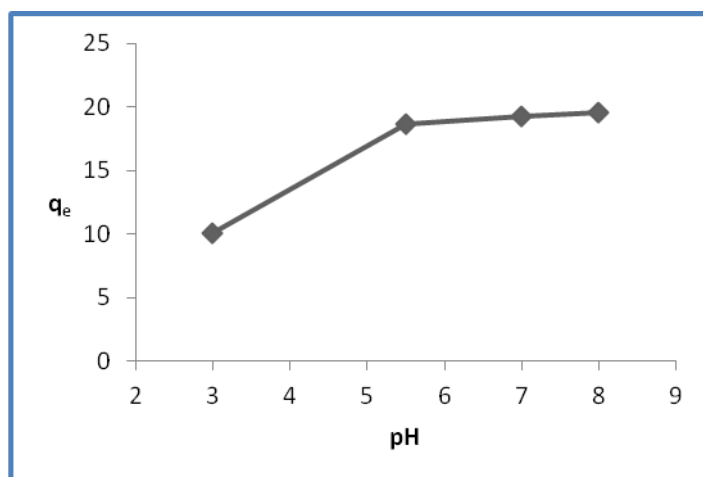
### 3.3. Effect of pH of the metal solution

Inevitably, the removal of metals by adsorption greatly depends on the pH of the metal solution by the influence of this parameter on the burden of the extracting matrix.

7.5 g gel PANa, brought into contact with 100 ml of a metal solution to 6.8 ppm, the pH range from 3 to 8, while keeping the temperature constant. Levies versus time were performed in the supernatant solutions. Then, the samples are analyzed by ICP.

The result shown in Figure (3) shows that whatever the value of this parameter affects the adsorption capacity of metal shown.

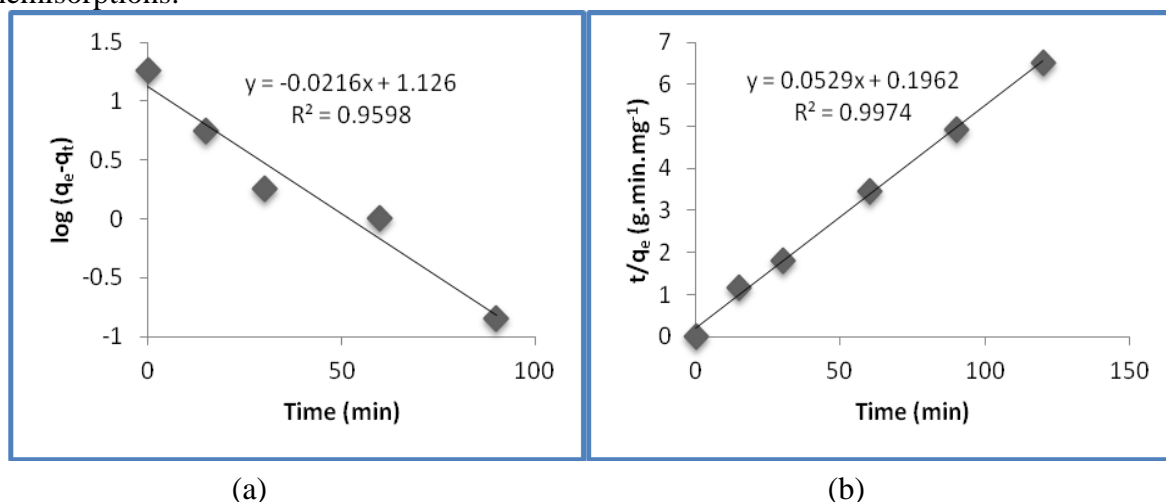
A strongly acidic pH (pH=3): the copper ions are not retained. This can be explained in that the concentration of cations  $\text{H}^+$  is high in solution which induces a competition for the cations  $\text{H}^+$ , with  $\text{Cu}^{2+}$  cations for sites negatively charged carboxylate, so there's an electrostatic repulsion between cations  $\text{Cu}^{2+}$  and frost that has acquired a positive charge. At a pH range of amongst 5.5 to 8, the substrate is very effective for the removal of  $\text{Cu}^{2+}$  ions. Indeed, at high pH values of the gel swells advantage that for low values of pH is that promotes the diffusion of metal cations.



**Figure 3.** Evolution of the adsorption capacity as a function of initial pH of the metal solution. ( $C_0=6.8 \text{ mg.L}^{-1}$ ,  $m_{\text{PANa}}=0.035 \text{ g}$ )

### 3.4. Adsorption kinetics

The model of pseudo-first-order model [47] established for the liquid phase adsorption and is applicable only in the first minutes of the adsorption phenomenon. It requires prior knowledge of the quantity adsorbed at equilibrium. This model has been applied in several liquid-solid systems. The model of pseudo-second-order is frequently used in adsorption. Unlike the first-order model, it is valid for the entire duration of the adsorption phenomenon and requires a mechanism of chemisorptions.



**Figure 4.** The Pseudo first-order (a) and Pseudo-second order kinetic models (b)

The hypotheses of this model are:

- The adsorption takes place over localized sites and there is no interaction between the adsorbed molecules,
- The desorption rate is negligible compared with that of adsorption,
- The maximum adsorption is the formation of a monolayer of adsorbates on the surface of the adsorbent (PANa).

Figure 4 (a,b) shows the application of kinetic models, pseudo first order and pseudo-second order on the experimental results obtained previously. The parameters of these models are shown in Table (3)

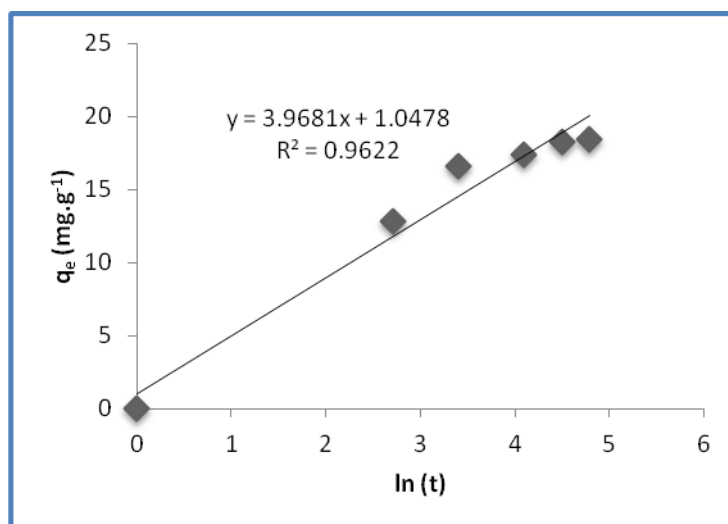
**Table 3.** The parameters of kinetic models

<b>Pseudo first-order model</b>	$q_{e\ exp}(mg.g^{-1})$	$q_{e\ calcul}(mg.g^{-1})$	<i>Difference Relative (%)</i>	$k_1 (min^{-1})$	$R^2$
	18.43	13.36	37.95	0.05	0.9598
<b>Pseudo second-order model</b>	$q_{e\ exp}(mg.g^{-1})$	$q_{e\ calcul}(mg.g^{-1})$	<i>Difference Relative (%)</i>	$k_2 (g.mg^{-1}.min^{-1})$	$R^2$
	18.43	18.90	2.486	0.014	0.9974

The relative difference between the experimental value of the adsorption capacity at equilibrium and that calculated by the model of the pseudo-second order is very low (<3%), while for the pseudo-first-order model this difference can reach 38%. We further the correlation coefficient obtained for the model of pseudo-second order is close to unity, they show that the model correctly describes the adsorption kinetics of PANa in powder form,  $R^2 > 0.9974$ . The use of the bead form gives the same results as the powder form is that the Pseudo second-order model is the dominant model [46].

The Elovich kinetic model was also applied to the experimental results. This model is one of the most used models to verify and describe the chemisorption at an adsorption. The results are shown in Figure (4) and the constants  $\alpha$ ,  $\beta$  and  $R^2$  are summarized in Table (4).

The  $R^2$  value is close to unity,  $R^2 > 0.96$ , which probably means that the adsorption is chemisorption kind confirming the kinetic model valabilité Pseudo second-order. The initial rate  $\alpha$  adsorption of copper on the PANa powder form is important. Whilst the constant  $\beta$  is negligible desorption.



**Figure 5.** Elovich model application

**Table 4.** Parameters of Elovich model

Parameter	$\alpha$	$\beta$	$R^2$
Copper (II)	5.198	0.25	0.9622

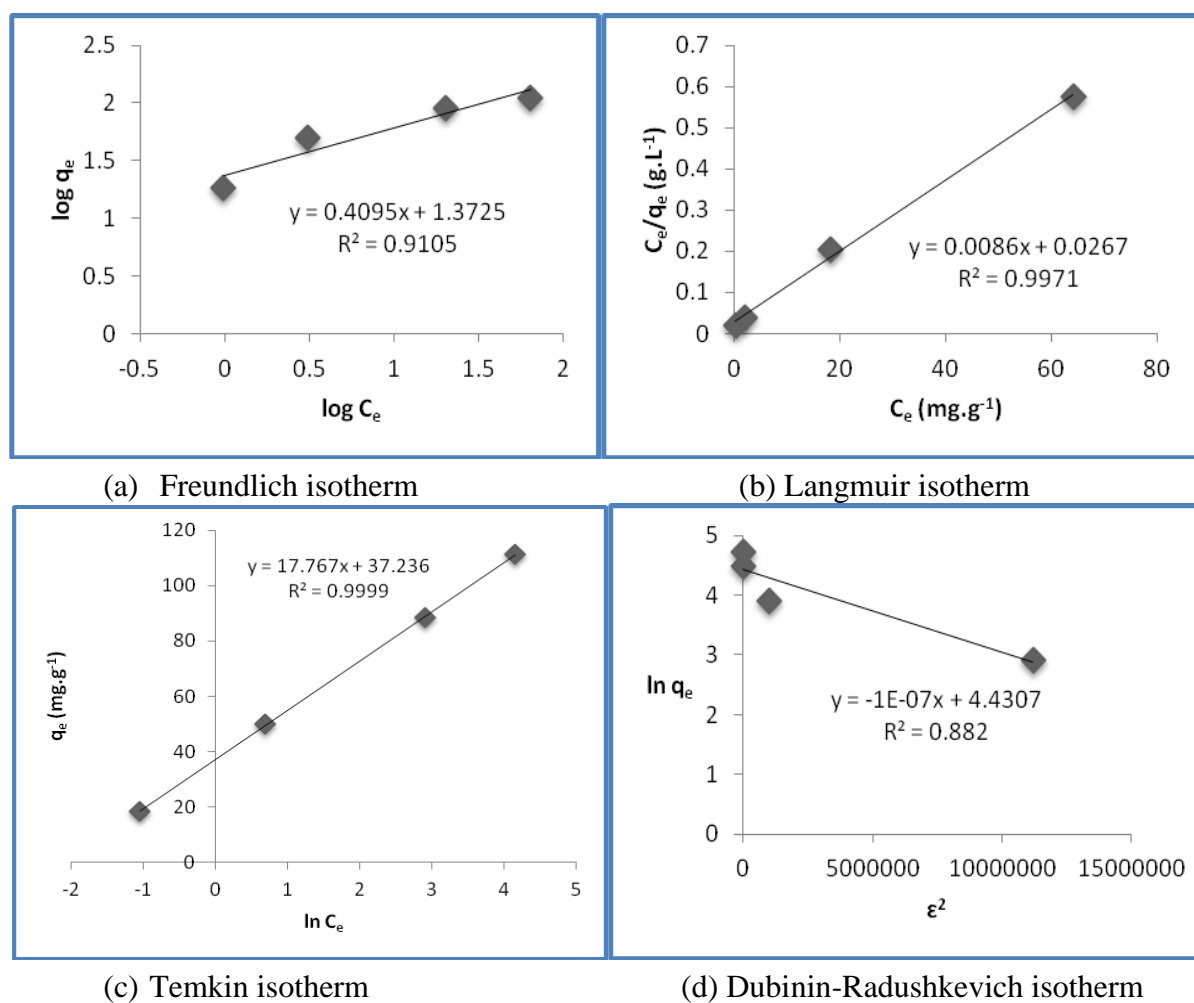
### 3.5. Adsorption isotherm

In order to identify the isotherm that best represents the adsorption of copper (II) on the PANa powder form, we tested four theoretical models namely our experimental results, the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. The four adsorption isotherms are shown in figure (5) and the constants are gathered in the table (6).

Modeling of the experimental results showed good agreement with the Langmuir model. Indeed, all the Langmuir, Freundlich and Temkin adsorption isotherms showed linear relationship on the present results shown in Fig. 5, but  $R^2$  for the Langmuir and Temkin adsorption isotherms are larger than that in Freundlich and D-R isotherms adsorption isotherms, it is close to 1. As that The monolayer adsorption capacity according to this model was  $116.8 \text{ mg.g}^{-1}$ , this value is very close to the experimental value  $111.43 \text{ mg.g}^{-1}$ . Indeed, the relative difference is very low it is in the order of 4.6%. The dominance of the Langmuir model is also found by using PANa in bead form [46]. This describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. The Langmuir isotherms model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface.

Found the value of  $\Delta G_{ads}^{\circ}$  shows that the adsorption is exothermic type, because the energy value of the reaction is negative  $-7.061 \text{ KJ/mol}$ . In this case, the solution scales its temperature by yielding heat in the environment.

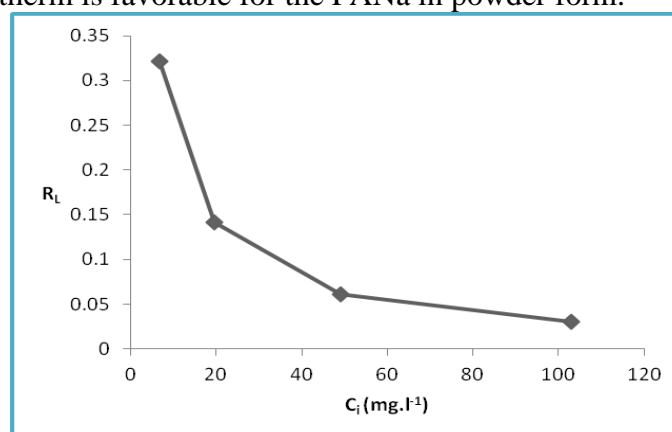




**Figure 5.** Adsorption isotherms of copper (II) on the PANa powder form

In order to predict the effectiveness of the adsorption process, separation of a dimensionless parameter noted  $R_L$  can be determined by the equation (18).

Figure (6) represents the evolution of the estimated Value of  $R_L$  depending on the initial concentration of copper (II) in the aqueous solution .  $R_L$  was found lower than 1, so we can say that the Langmuir isotherm is favorable for the PANa in powder form.



**Figure 6.** Evolution of the estimated Value of  $R_L$

**Table 6.** Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherm constants for the adsorption of Cu(II) ion unto PANa powder form

Metal ion	Freundlich isotherm				Langmuir isotherm				
	$1/n$	$n$	$K_F$ (mg/g)	$R^2$	$q_m$	$K_L$	$\Delta G_{ads}^0$	$R_L$	$R^2$
Cu(II)	0.41	2.44	23.58	0.91	116.8	0.31	-7.061	$0 < R_L < 0.35$	0.997
	Temkin isotherm				D-R isotherm				
	$B$	$\Delta Q$ (Kj.mol <sup>-1</sup> )	$A$ (L.mg <sup>-1</sup> )	$R^2$	$q_s$ (mg/g)	$E$ (%)	$K_{ad}$ (mol <sup>2</sup> /kJ <sup>2</sup> )	$E$ (KJ/mol)	$R^2$
	17.767	139.52	8.13	0.9999	83.99	32.67	$10^{-7}$	2236	0.882

## 4. Conclusion

In this study, investigation of the equilibrium sorption was carried out at 25°C and pH 5.5. The results showed that:

The retention of copper (II) on the sodium polyacrylate in powder form is fast.

The copper extraction capacity on the PANa in powder form is sensitive to the influence of pH.

The extraction efficiency decreases with increasing concentration of the aqueous solution of copper.

The kinetic model showed that the pseudo-second order is the dominant model.

The sorption data fitted into Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms out of which Langmuir and Temkin adsorption models was found to be have the highest regression value and hence the best fit.

It could be concluded that PANa in powder form is a potential and active sorbent for removal of Copper ions from its aqueous solution and industrial waste water remediation.

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