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Removal of Cadmium from aqueous solution by polysaccharide produced from *Paenibacillus polymyxa*

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ABSTRACT

This paper deals with the removal of Cadmium from aqueous solutions by polysaccharide produced from *Paenibacillus polymyxa*. The effects of contact time, initial metal ions concentration, mass of the polysaccharide and pH were studied. The Freundlich and Dubinin–Radushkevich (D–R) models have been applied and the equilibrium adsorption was found to best fit the Dubinin–Radushkevich adsorption isotherm based on the coefficient of correlation, R^2. The maximum Cd^{2+} uptake was 520.09 mg g^{-1}. An empirical modeling was performed by using a 2^3 full factorial design and a regression equation for adsorption of Cd^{2+} was determined from the data. The pH and the initial concentration of Cadmium are the most significant parameters affecting Cd^{2+} adsorption followed by the mass of the polysaccharide.

1. Introduction

Contamination of the environment with hazardous and toxic compounds such as heavy metals is one of the major problems facing the industrialized nations today. Many industries including metal plating, battery, pigment and chemical industries release heavy metals like Cadmium. Wastewaters from these industries have permanent toxic effects to living organisms and constitute a threat for the environment [1,2].

A variety of traditional methods such as precipitation, coagulation, ion-exchange [3–5] can be used to remove toxic metals from industrial effluents but they are expensive, relatively inefficient and in most cases they generate a great amount of waste which is difficult to eliminate.

Recently, increasing interest in the application of a safe method for removing heavy metals from discharging effluents have resulted in the search for other unconventional materials like those of biological origin.

Many microbial species are known to have high metal adsorbing capacities [6–8], extracellular polymeric substances have been shown to bind metal ions selectively [9,10] they contain ionic functional groups such as carboxyl, phosphoric, amine and hydroxyl groups which enable the exopolysaccharide to sequester heavy metals [11,12]. Furthermore, work on a variety of microorganisms has clearly shown that bacteria excreting extracellular polysaccharides have high metal adsorption potential [9,13–15]. *Paenibacillus polymyxa* is known to produce substantial amounts of polysaccharides when it is cultured in adequate medium [16].

The aim of the present study is to investigate Cadmium sorption capacity by exopolysaccharide produced by *P. polymyxa*. The influence of various parameters like contact time, initial metal concentration, adsorbent mass and pH of the solution on metal sorption has been investigated. Various isotherm models including Freundlich and Dubinin–Radushkevich (D–R) were used for fitting the data. The experiments have been carried out using a 2^3 full factorial design to study the effect of the main and interaction parameters and to optimize the adsorption process.

2. Materials and methods

2.1. Microorganism

The bacterial strain used in this study (Strain CHL 0102), was provided from the collection of the laboratory of soil biology from the faculty of biological science (USTHB). It was isolated from the wheat rhizosphere (*Triticum durum* L.) in the area of Chlef town

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(Algeria). This strain was identified by comparision of its DNA 16S sequence with the Genebank data base. Strain CHL0102 attired to belong to the species *P. polymyxa* (access number FJ468003). It produces in solid medium (Petri dishes) 7 g of EPS/ml of medium and is known for its production of Levan:homopolysaccharide (polyfructane) [16].

2.2. Production of the polysaccharide

The production of the polysaccharide is carried out on a solid medium composed of: sucrose ($20\,g\,l^{-1}$), yeast extract ($0.2\,g\,l^{-1}$), K_2HPO_4 ($0.25\,g\,l^{-1}$), $MgSO_4(7H_2O)$ ($0.1\,g\,l^{-1}$), NaCl ($0.05\,g\,l^{-1}$), Agar agar ($15\,g\,l^{-1}$). The culture medium is distributed in Petri dishes of 90 mm of diameter; 0.1 ml of a culture of 24 h is inoculated in every Petri dish then spread out. After 5 days of incubation at 30 °C, the "bacterial must" is recovered in aseptic conditions, and then preserved at 4 °C. This "bacterial must" is approximately composed of 90% of polysaccharide (dry weight) [16] (studies conducted in the laboratory of soil biology, USTHB), it is transparent, very viscous and its water content is determined by the use of a "thermo balance". The result obtained gives a percentage of 89.67% of water; this enables us to calculate the wet weight of polysaccharide necessary for a given dry weight.

2.3. Chemicals

The Cadmium salt ($Cd(NO_3)_2,4H_2O$) of analytical grade was provided by ACROS ORGANICS and used without purification to prepare $1000\,mg\,l^{-1}$ of cadmium solution. The demineralized water was used for all dilutions and reagents preparations.

2.4. Metal adsorption experiments

Batch equilibrium sorption experiments were carried out in 250 ml conical Erlenmeyer flasks with 100 ml of demineralized water. Known amounts of the polysaccharide were added and the mixture was agitated until total dispersion of the polysaccharide. The pH of the solution was adjusted to the required value by using HCl or NaOH. After this, the metal solution is added and the mixture was stirred with an orbital shaker at 120 rpm and 30 °C. After the sorption equilibrium was reached, the solution was separated from the polysaccharide by ultra filtration membrane (30 kDa) and the filtrate is analyzed for the remaining metal ions using a spectrophotometer with atomic absorption (SAEB ERAKAT, UNICAM 929) with 228.8 nm wavelength. All kinetic experiments were carried out in triplicate and the mean values were used in calculations.

2.5. Cadmium uptake capacities and sorption isotherm

The amount of Cd^{2+} sorbed at equilibrium, q_e ($mg\,g^{-1}$), which represent the metal uptake, was calculated according to the following equation:

$$q_e = (C_0 - C_e)\frac{V}{m} \tag{1}$$

where V is the volume of the solution (l), m the mass of the polysaccharide (g), C_0 the initial concentration of Cd^{2+} in the solution in ($mg\,l^{-1}$) and C_e the equilibrium concentration of metal in the solution in ($mg\,l^{-1}$).

To examine the relationship between the amount of Cd^{2+} sorbed and aqueous concentration at equilibrium, sorption isotherm models, Freundlich and Dubinin–Radushkevich (D–R) were used for fitting the data.

2.5.1. Freundlich adsorption model

The Freundlich model [17] is purely empirical based on sorption on a heterogeneous surface, which is commonly presented as

$$q_e = K_F C_e^{1/n} \tag{2}$$

where K_F and n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. Many researchers have used this model to interpret their sorption data for various systems [18–21]. The model constant will be calculated from the linear form of the Eq. (2)

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \tag{3}$$

2.5.2. Dubinin–Radushkevich (D–R) model

The D–R isotherm also does not assume a homogeneous surface; it is given by the following equation [22]:

$$q_e = q_{\max} \exp(-Be^2) \tag{4}$$

where e is given like:

$$e = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{5}$$

where R ($8.314\,J\,mol^{-1}\,K^{-1}$) is the gas constant, T (K) is the absolute temperature and B ($mol^2\,kJ^{-2}$) is a constant related to adsorption energy; it can be computed using the relationship [23]:

$$E = \frac{1}{(2B)^{1/2}} \tag{6}$$

This parameter gives information about chemical or physical adsorption. The magnitude of E between 8 and $16\,kJ\,mol^{-1}$, the biosorption process follows chemical ion-exchange, while for the values of $E < 8\,kJ\,mol^{-1}$, the biosorption process is of physical nature [24]. The linear form of D–R equation is:

$$\ln q_e = \ln q_{\max} - Be^2 \tag{7}$$

3. Results and discussion

3.1. Effect of contact time

In this part of study, the experiments of adsorption were undertaken in the aim of determining the contact time at equilibrium. The analysis of Cd^{2+} concentration during the first 30 min showed many fluctuations, this can be attributed with the fact that the Cadmium was not uniformly distributed in the solution. The great viscosity of the medium seems to be at the origin of the heterogeneity of the solution. From 60 min, the Cd^{2+} contents are very close and equilibrium is reached. For example in Table 1(a) we can notice that for $m = 0.5$ g, pH = 6.68 and initial Cadmium concentration (C_0) of $30\,mg\,l^{-1}$ the equilibrium concentrations of the metal in the solution (C_e) at 60 and at 120 min are equal to 22.64 and $22.10\,mg\,l^{-1}$, respectively. These results enabled us to fix the contact time at 60 min for the whole of the experiments.

Table 1
Kinetics of Cd^{2+} sorption by polysaccharide produced from *Paenibacillus polymyxa*.

Time (min)	$[Cd^{2+}]_e$ ($mg\,l^{-1}$)	
	60	120
(a) $[Cd^{2+}]_0 = 30$ ($mg\,l^{-1}$)	22.64	22.10
$[Cd^{2+}]_0 = 60$ ($mg\,l^{-1}$)	31.40	32.01
(b) pH = 3	74.72	75.01
pH = 4	73.98	74.20
(c) $m = 0.5$ (g)	42.50	41.88
$m = 1.0$ (g)	36.02	35.68

(a) $m = 0.5$ g, pH = 6.68; (b) $[Cd^{2+}]_0 = 100\,mg\,l^{-1}$, $m = 0.5$ g; (c) $[Cd^{2+}]_0 = 100\,mg\,l^{-1}$, pH = 6.68.

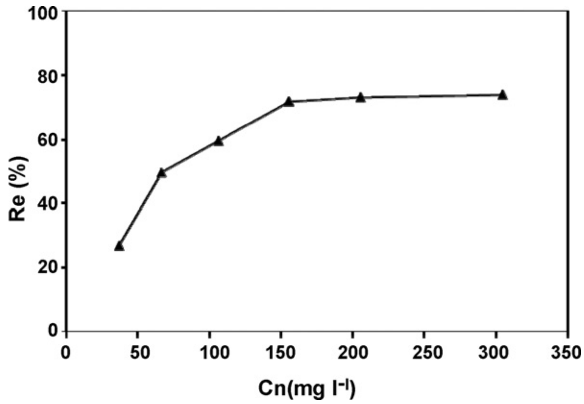

Fig. 1. Effect of initial Cadmium concentration on the rate of adsorption for polysaccharide produced from *Paenibacillus polymyxa* (pH = 6.68, m = 0.5 g, contact time = 60 min, T = 30 °C).

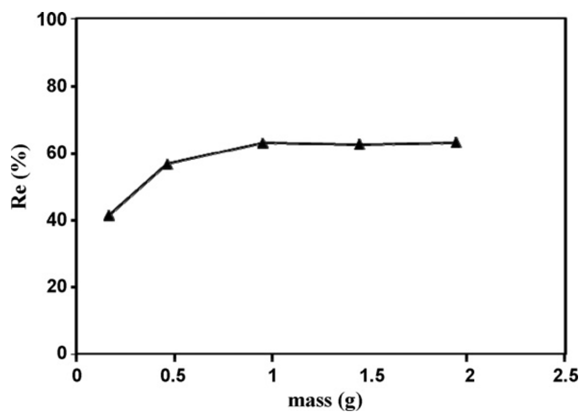

Fig. 2. Effect of the mass of polysaccharide produced from *Paenibacillus polymyxa* on the rate of adsorption (pH = 6.68, $[Cd^{2+}]_0$ = 100 mg l^{-1}, contact time = 60 min, T = 30 °C).

3.2. Effect of initial metal concentration

The adsorption of Cd^{2+} was carried out at different initial Cd^{2+} ion concentrations ranging from 30 to 300 mg l^{-1}. The output sorption increases from 24.53% to 70.08% with increasing initial Cadmium concentration from 30 to 150 mg l^{-1} (Fig. 1), due to the increase in the number of ions competing for the available binding sites in the polysaccharide. The uptake of Cd^{2+} gave a plateau at 150–300 mg l^{-1} showing the saturation of binding sites at higher concentration levels.

3.3. Effect of the mass of the polysaccharide

The initial polysaccharide mass in solution will affect the metal adsorption capacity. The results are shown in Fig. 2. We can see that the adsorption rate increases from 42% to 63.98% as the adsorbent mass increases from 0.2 to 1.0 g, further increase of the mass do not have any effect on the adsorption rate of Cadmium. This will be attributed to metal concentration shortage in solution [25].

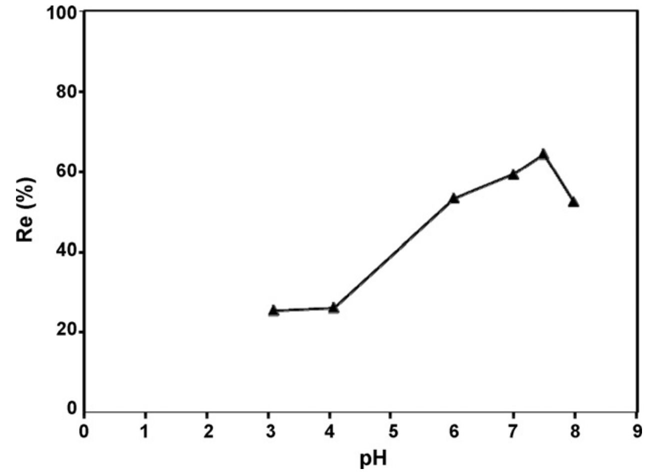

Fig. 3. Effect of initial pH on sorption of Cd^{2+} by polysaccharide produced from *Paenibacillus polymyxa* ($[Cd^{2+}]$ = 100 mg l^{-1}, m = 0.5 g, contact time = 60 min, T = 30 °C).

3.4. Effect of initial pH

Earlier studies on heavy metal adsorption have showed that the initial pH of the solution is a critical parameter for adsorption experiments [26–28]. The adsorption of Cadmium increased with pH and then declined with further increase in pH as shown in Fig. 3. The decrease of adsorption rate at pH = 8 might be attributed to the beginning of the insoluble hydroxide precipitating from solution, making true metal adsorption studies impossible [29,30].

At low pH the adsorption capacity of the metal is very low because large quantity of hydrogen ions competes with metal ions at sorption sites. In addition, in acid medium the viscosity of polysaccharide decreases, which allows a greater availability of interstitial water and consequently more free Cd^{2+}. The increase in Cadmium uptake when the pH increases, could be due to the interaction between the cations and the negative charges of the functional groups of polysaccharide [31,32]. In the other hand, the increase in the pH value induces a greater viscosity of polysaccharide, which enables it to trap more water and thus more Cd^{2+} [33]. Maximum adsorption capacity was obtained at pH 7.5.

4. Equilibrium models to fit experimental data

Adsorption isotherm plays a crucial role in the predictive modelling procedures for the analysis and design of an adsorption system. Therefore, in this study, the adsorption data of Cadmium were tested with Freundlich and Dubinin–Radushkevich (D–R) isotherm models within metal ion concentration range from 30 to 300 mg l^{-1} at 30 °C. The various constants relating to the two models were calculated and are gathered on Table 2.

The equation of Freundlich is based on an adsorption on heterogeneous surfaces [34] or surfaces supporting sites of varied affinities and has been used widely to fit experimental data. The Fig. 4 indicates that the Freundlich model does not fit well the

Table 2
Freundlich and D–R models parameters for Cd^{2+} sorption on the polysaccharide of *Paenibacillus polymyxa*.

Model parameters						
Freundlich			Dubini–Radushkevich			
K_F (l g^{-1})	n	R^2	q_{max} (mg g^{-1})	B (mol^2 kJ^{-2})	E (kJ mol^{-1})	R^2
0.00592	0.381	0.923	520.09	310.4	0.04	0.987

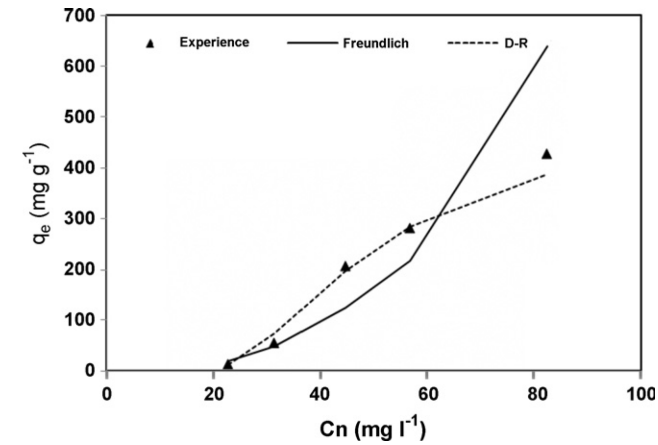

Fig. 4. Adsorption isotherms for Cadmium on polysaccharide produced from *Paenibacillus polymyxa* (pH = 6.68, m = 0.5 g, contact time = 60 min, T = 30 °C).

experimental data (R^2 = 0.923). For the low concentration range, the calculated Freundlich uptakes are lower, whereas in the high concentration range they are higher than the experimental uptake values. Hence, the Freundlich model is not the suitable model for describing the sorption process with sorbent used in the present study, as R^2 value is lower than the D–R model, as shown in Table 2.

The experimental data are fitted well by the Dubinin–Radushkevich (D–R) isotherm showing high value of the correlation coefficient (R^2 = 0.987). The magnitude of E value obtained is useful for estimating the type of sorption reaction. The E value obtained was around 0.04 kJ mol^{-1}, which is in the energy range of a physical adsorption, i.e., <8 kJ mol^{-1} [24].

Table 3 lists some reported sorption capacity values for Cd^{2+} uptake by different microorganisms. The polysaccharide of *P. polymyxa* tested in this study exhibited sorption capacity value greater than to those reported elsewhere for various adsorbents.

5. Empirical modelisation

In order to obtain the optimum conditions for the adsorption process, a full factor design of the type n^k has been used, where n is the number of levels and k is the number of factors under verification. In this study, n = 2 and k = 3. Thus, the total number of trial experiments needed for an investigation is 2^3 (8 experiments). If R which is the rate of adsorption is the response variable, then the regression equation [39] is given by Eq. (8). The 2^3 factorial design and the parameters studied in their reduced and normal form are resumed in Tables 4 and 5.

$$R = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3 + a_{123}X_1X_2X_3 \quad (8)$$

where a_0, a_1, a_2 and a_3 are the main factors coefficients, a_{12}, a_{13}, a_{23} are the second-order interaction terms and a_{123} is the third-order interaction term. X_1, X_2, X_3 are the dimensionless coded factors of the following parameters studied: initial Cadmium concentration, pH and mass of the polysaccharide, respectively.

The different coefficients were evaluated and the insignificant terms were neglected. The regression equation was tested to see how it fitted with the experimental values. It was found that the confidence level is at about 99% (Fig. 5). The significant coefficients for Cadmium adsorption are shown in Fig. 6. On deleting the coef-

Table 3
Sorption capacities for Cd^{2+} using different adsorbents.

Adsorbents	Sorption capacity (mg g^{-1})	Refs.
Penicillium simplicissimum	52.50	[34]
Chlorella vulgaris	67.00	[35]
Pantoea sp.	52.00	[36]
Staphylococcus xylosus	250.00	[37]
Pseudomonas sp.	278.00	[37]
Pseudomonas veronii 2E	54.00	[38]
Polysaccharide produced from *Paenibacillus polymyxa*	520.09	This study

Table 4
The 2^3 factorial design for Cadmium adsorption onto polysaccharide produced from *Paenibacillus polymyxa*.

Natural variables	Coded variables	Low level	High level
Initial Cadmium (II) concentration C_0, (mg l^{-1})	(X_1)	100	200
pH	(X_2)	7.0	7.5
Mass of the polysaccharide (m, g)	(X_3)	0.5	1.0

Table 5
Parameters studied in their reduced and normal form.

Experiment	C_0 (mg/l)	X_1	Ph	X_2	m (g)	X_3	R_{exp} (%)	R_{th} (%)
1	100	−1	7.0	–	0.5	–	60.01	60.57
2	200	+1	7.0	–	0.5	–	70.44	69.88
3	100	−1	7.5	+	0.5	–	65.32	64.78
4	200	+1	7.5	+	0.5	–	73.52	73.25
5	100	−1	7.0	–	1.0	+	55.80	55.49
6	200	+1	7.0	–	1.0	+	58.25	58.56
7	100	−1	7.5	+	1.0	+	71.73	71.22
8	200	+1	7.5	+	1.0	+	75.43	75.16

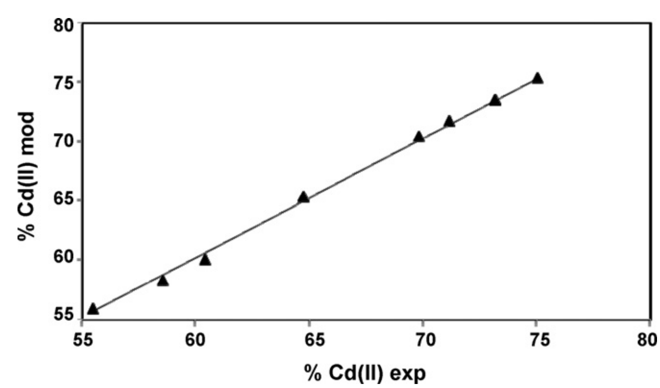

Fig. 5. Scatter diagram of the investigated adsorption model of Cadmium.

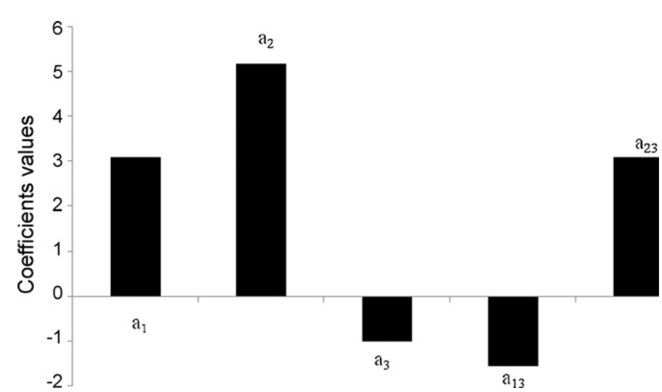

Fig. 6. Significant main and interaction empirical coefficients.

ficients not significant, the regression equation Eq. (8) becomes:

$$R = 66.3125 + 3.0973X_1 + 5.1875X_2 - 1.01X_3 - 1.56X_1X_3 + 3.09X_2X_3 \quad (9)$$

Substituting the coded factors in Eq. (2) by their original values, we obtain the following equation:

$$R = 164.41 + 0.1555C_0 - 16.33\,\text{pH} - 343.76m + m(49.44\,\text{pH} - 0.1248C_0) \quad (10)$$

It can be seen from Fig. 6, that the initial Cadmium concentration and the pH have the most positive pronounced effect in increasing the Cadmium adsorption, followed by the interaction pH–mass of the polysaccharide, whereas the mass of the polysaccharide and the interaction initial Cadmium concentration–mass of the polysaccharide have a negative effect on the process.

The coefficient of determination r^2 which measure the quality of the model is defined by the following expression [40]:

$$r^2 = \frac{\left(\sum_{i=0}^{8}(R_{i\text{exp}} - \overline{R_{\text{exp}}})(R_{ith} - \overline{R_{th}})\right)^2}{\sum_{i=0}^{8}(R_{i\text{exp}} - \overline{R_{\text{exp}}})^2 \sum_{i=0}^{8}(R_{ith} - \overline{R_{th}})^2}. \quad (11)$$

According to Eq. (11), r^2 is equal to 0.995 it is close to 1, therefore, the model enable us to find measured values.

6. Optimisation of parameters

The aim of the process development is to determine the optimum conditions (initial Cadmium concentration, pH, mass of the polysaccharide) from the model obtained,

$R = 66.3125 + 3.0973X_1 + 5.1875X_2 - 1.01X_3 - 1.56X_1X_3 + 3.09X_2X_3$. For this we used the “isoréponse curves”, the finding values were, $X_1 = +1$, $X_2 = +1$, $X_3 = +1$ which corresponds to:

$$C_0 = 200\,\text{mg}\,\text{l}^{-1};\ \text{pH} = 7.5 \ \text{and} \ m = 1\,\text{g}.$$

The experience in these optimal conditions was performed and the result is shown in Table 5 (experiment no. 8), a maximum rate of adsorption of 75.43% was found for these conditions.

7. Conclusion

Adsorption is one of the promising technologies involved in the removal of heavy metals from wastewaters. Adsorption performances of exopolysaccharide produced by *P. polymyxa* are studied for the removal of Cadmium from aqueous solution. The kinetic experiments show that the maximum sorption rate achieved in 60 min, the sorption rate of Cd^{2+} increased with initial metal ion concentration and the mass of the polysaccharide, the initial pH significantly influenced Cd^{2+} uptake. Experimental data were analyzed using Freundlich and Dubinin–Radushkevich isotherm models. It was found that Dubinin–Radushkevich model presented a better fit. The adsorption activation energy, *E*, was equal to 0.04 kJ mol^{-1}, which implied that Cadmium was mainly adsorbed physically onto the polysaccharide. The maximum capacity of metal adsorption, as calculated using *D–R* adsorption isotherm is 520.09 mg g^{-1}. Statistical design of experiments for the adsorption of Cadmium was an efficient technique to quantify the effect of variable parameters. The initial Cadmium concentration and the pH are the most significant parameters affecting Cadmium adsorption. The study revealed that exopolysaccharide produced by *P. polymyxa* may be used as an inexpensive, effective and easily cultivable adsorbent for the removal of Cd^{2+} from aqueous solutions.

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