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Study of Lead Adsorption from Aqueous Solutions on Agar Beads with EPS Produced from Paenibacillus Polymyxa

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Heavy metals ions in water have been a major preoccupation for many years because of their toxicity toward aquatic life, plants, animals, human beings and the environment. Water contaminated by heavy metal ions had become much more serious with a rapid development of industries and competitive use of fresh water in many parts of world. Therefore, heavy metals ions removal from water has become an important subject today. This present work reports a study about lead adsorption from aqueous solution onto agar beads with an extracellular polysaccharide (EPS) produced by the bacterium *Paenibacillus polymyxa*. The ability of produced beads to adsorb lead has been studied at different optimized conditions such as contact time, solution pH, biomass dosage and initial lead concentration. According to the experiments results, it was shown, that equilibrium was achieved in less than 120 min. The effect of pH investigated for values ranging from 1 to 5, showed maximum adsorption for pH 5. In order to determine the adsorption characteristics, Langmuir, Freundlich and Dubinin –Radushkevich adsorption isotherms were applied to the experimental data. The Freundlich isotherm provided the best fit for lead adsorption onto agar beads and the maximum adsorption capacity was found to be 111.11 mg.g^{-1} according to the Langmuir model. The results suggested that (Agar + EPS) beads could be suitable as a sorbent material for removal of lead ions from aqueous solutions.

1. Introduction

Heavy metals have many applications due to their technological importance. Both soil and aqueous effluents have been contaminated with these heavy metals as the result of numerous industrial activities including mining, smelting, automobile battery production, vehicle emission and pigment. This kind of contamination cause serious threat to environment, animals and human (Bayhan et al., 2001). A variety of traditional methods including precipitation, coagulation, ion exchange, etc (Basha and Murthy, 2007) 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 (Lavecchia et al., 2010) like those based on biological origin. Many microbial species are known to have high metal adsorbing capacities (Wang and Chen, 2006; Chatterjee et al., 2010), extracellular polymeric substances have been shown to bind metal ions selectively (Pal and Paul, 2008), they contain ionic functional groups such as carboxyl, phosphoric, amine and hydroxyl groups which enable the exopolysaccharide to sequester heavy metals (Morillo Pérez et al., 2008; Mokaddem et al., 2009; Farooq et al., 2010). The present study investigates lead sorption capacity by agar beads with exopolysaccharide produced by *Paenibacillus polymyxa* . The adsorption process was studied through batch experiments with regard to the effects of contact time, pH, biomass dose and initial metal concentration.

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2. Materials and methods

2.1 Microorganisms

The bacterial strain used in this study was isolated from the wheat rhizosphere (*Triticum durum* L.) in the area of Chlef town (Algeria). This strain was identified by comparison of its DNA 16S sequence with the Genebank data base. Strain CHL 0102 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).

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 hours is inoculated in every Petri dish then spread out. After five 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), 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 Production of the beads

Agar and (agar + EPS) beads were prepared by using a syringe to drop 2 % aqueous solutions of agar into cold oil of sunflower. The beads were collected by filtration, washed with distilled water in order to eliminate oil and dried with the free air. The procedure for production of (agar + EPS) beads was the same as that described above except that 2 % agar was replaced by an aqueous solution of 1.5 % agar and 0.5 % crude EPS.

2.4 Chemicals

The lead salt PbN_2O_6 of analytical grade was provided by BIOCHEM Chemopharma and used without purification to prepare 1000 mg.L^{-1} of lead solution. The distilled water was used for all dilutions and reagents preparations.

2.5 Metal adsorption experiments

Batch equilibrium sorption experiments were carried out in 250 mL erlenmeyer flasks. Known amounts of agar or (agar + EPS) beads were added to 100 mL of lead solution of known initial concentration and the solution was stirred continuously at 120 rpm. The pH of the solution was adjusted to the required value by using HCl or NaOH. After the sorption equilibrium was reached, the residual liquid was separated from the biomass with filter paper (type Double Rings 102) and the filtrate was adjusted to pH 2.0 with nitric acid before analysis by atomic adsorption spectrophotometry (SAEB ERAKAT, UNICAM 929) at 228.8 nm wave length.

2.6 Lead uptake capacities and sorption isotherms

The amount of Pb (II) sorbed at equilibrium, q_e (mg.g^{-1}) and the metal uptake were calculated according to the following equations:

$$q_e = (C_0 - C_e)\ V/m \qquad (1)$$

$$Re\ (\%) = [(C_o - C_e)/\ C_o\ ]*100 \qquad (2)$$

Where V is the volume of the solution (L), m the mass of the polysaccharide (g), C_0 the initial concentration of Pb (II) in the solution (mg.L^{-1}) and C_e the equilibrium concentration of metal in the solution (mg.L^{-1}).

To examine the relationship between the amount of Pb (II) sorbed and aqueous concentration at equilibrium, sorption isotherm models of Langmuir, Freundlich and Dubinin –Radushkevich (D-R) were used for fitting the experimental data.

2.6.1 Langmuir adsorption model

The Langmuir adsorption isotherm is given by the following equation:

$$q_e = q_{max} b C_e/(1+bC_e) \qquad (3)$$

Where, q_{max} (mg.g^{-1}) is the amount of adsorption corresponding to complete monolayer coverage, i.e., the maximum adsorption capacity and b (L. mg^{-1}) is the Langmuir constant. The model constants will be calculated from the linear form of equations (3)

.

$$1/q_e = (1/q_{max}b).1/C_e + 1/q_{max} \quad (4)$$

2.6.2 Freundlich adsorption model

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

$$q_e = K_F C_e^{1/n} \quad (5)$$

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. The model constant will be calculated from the linear form of the equation (5)

$$\ln q_e = \ln K_F + (1/n) \ln C_e \quad (6)$$

2.6.3 Dubinin-Radushkevich model

The D-R isotherm also does not assume an homogeneous surface, it is represented by the following equation :

$$q_e=q_{max}\exp(-Be^2) \quad (7)$$

$$e = RT \ln (1+1/C_e) \quad (8)$$

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:

$$E=1/(2B)^{1/2} \quad (9)$$

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

$$\ln q_e = \ln q_{max} – Be^2 \quad (10)$$

3. Results and discussions

3.1 Effect of contact time

High biosorption rates were observed at the beginning, and adsorption equilibrium was gradually reached within 120 min. after this period, the concentration of adsorbed metal ions did not change with time. From Figure 1, it is evident that agar beads adsorb Pb (II) ions far less than (EPS + agar) beads. Ozdemir et al. (2005) carried out two kinetics, one for alginate beads alone and the other for alginate beads-EPS produced by the bacterium Chryseomonas luteola TEM 05; they reported identical results, this enables us to conclude that the improvement of the output is made by the introduction of polysaccharide into the beads. For the further experiments we will be interested in the (agar + EPS) beads because of their better performance.

3.2 Effect of solution pH

Earlier studies on heavy metal adsorption have showed that the initial pH of the solution is a critical parameter for adsorption experiments (Park et al., 2004; Azouaou et al., 2013). The adsorption of lead increased with pH as shown in Figure 2. At low pH values the adsorption capacity of the metal is very low because large quantity of hydrogen ions compete with metal ions at sorption sites and compete significantly with metal binding. Maximum adsorption capacity was obtained at pH 5 with a rate of 90 %. Indeed, capacity of fixing metal depends also on the density of surface charge of the adsorbent i.e. in relation with the isoelectric point of adsorbent material. In our case, the pH of the lead solution is lower than the pH_{ZC} (7.29) thus the surface of the (EPS + agar) beads is positively charged, so the fixing of the Pb (II) ions on the surface of the adsorbent could be due to the complexation with the functional groups of (EPS + agar) beads (Holan and Volesky, 1994) or by ions exchange. Additional increase in the pH was not considered because the beginning of the insoluble hydroxide precipitating from solution makes true metal adsorption studies impossible (Comte et al., 2008)

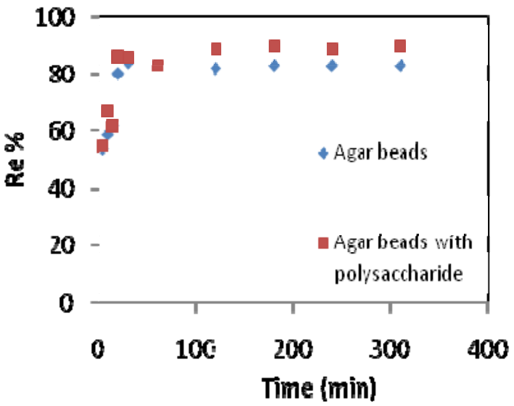

Figure 1: Kinetic of Pb(II) sorption on agar and (EPS+agar) beads, (initial Pb(II) concentration: 100 mg.L^{-1}, pH: 5.0, (EPS+agar) beads concentration: 5 g.L^{-1}, pH: 5.0)

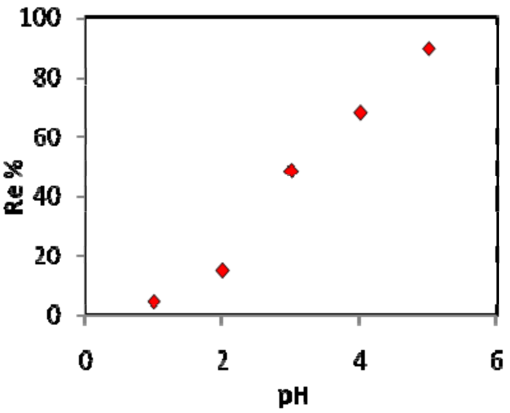

Figure 2: Effect of initial pH on sorption of Pb^{2+} by (*EPS+agar) beads (initial Pb(II) concentration: 100 mg.L^{-1}, (EPS+agar) beads concentration: 5 g.L^{-1}, contact time :120 min).*

3.3 Effect of the concentration of (agar + EPS) beads

Adsorbent dose is a significant factor to be considered for an effective metal removal. The effect of the biomass dose on the lead sorption was studied. Various biomass concentrations were considered: 1, 2, 4, 5, 7 and 10 g.L^{-1} the results are shown in Figure 3. At lower concentrations (1 to 4 g.L^{-1}), we note an increase of the adsorption rate of lead; the maximum value was obtained at 5 g.L^{-1}. This effect can be explained by the increase in the surface of adsorption and consequently in the number of active sites with the rise in the concentration of beads. This is in agreement with the results obtained by Cheng et al (2009). According to these authors, the adsorption of copper is improved from 45 to 80 % when the concentration of the immobilized micro-organism varies from 1 to 5 g.L^{-1}. Though, further increase in biomass dose, don't affect the adsorption capacity. This will be attributed to metal concentration shortage in solution (Fourest and Roux, 1992).

3.4 Effect of initial lead concentration

The effect of initial metal concentration on the yield of adsorption on (EPS + agar) beads is illustrated in Figure 4.The results obtained show that the elimination of lead is more effective with the weak concentrations with a higher yield of adsorption; indeed, it reaches a value of 92.7 % for an initial concentration of 30 mg.L^{-1} then starts to decrease as the initial concentration increases to reach 27.03 % for an initial concentration of 2000 mg.L^{-1} which is explained perfectly by the abundance of the metal ions likely to be fixed on the active sites on the (EPS + agar- beads.

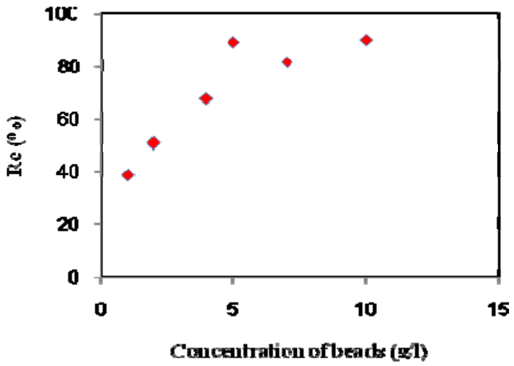

Figure 3 : Effect of (EPS+agar) beads on yield adsorption of lead. (Initial lead concentration :100.mg L^{-1}, pH:5, contact time :120 min).

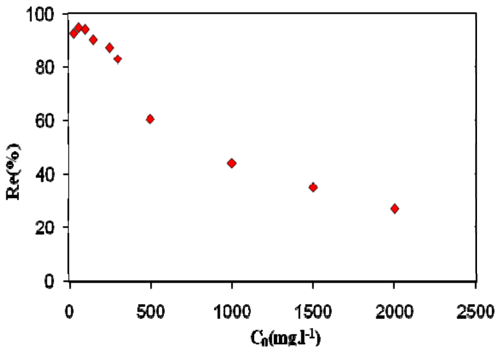

Figure 4 : Effect of initial lead concentration on yield adsorption on (EPS+agar) beads. ((EPS+agar) beads concentration :5 g L^{-1}, pH:5, contact time :120 min).

3.5 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 lead were tested with Langmuir, Freundlich and D-R isotherm models within initial metal ion concentration range from 30 to 2000 mg.L^{-1}. The various constants relating to the models were calculated and are gathered on Table 1. The experimental results are well represented by the Freundlich model, with higher value of correlation coefficient. The value of n ranging between 1 and 10, indicating that the lead adsorption was favourable (Gokand and Aytas, 2009). We also note that the value of q_{max} (111.11 mg.g^{-1}) obtained from the Langmuir model is in adequacy with the experimental value (figure 5).

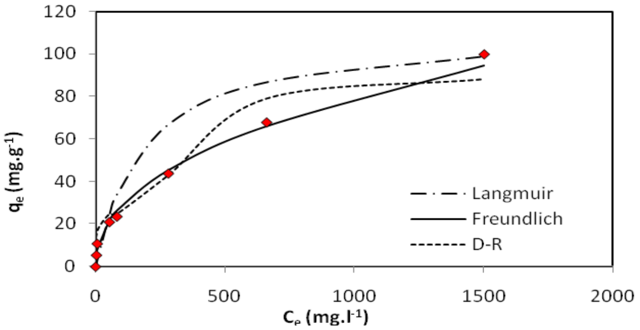

Figure 5: Adsorption isotherms of lead on (EPS + agar) beads. (pH=5, concentration of (EPS+agar) beads= 5 g.L^{-1}, contact time.=120 min).

Table 1: Langmuir, Freundlich and D-R models parameters for Pb (II) sorption on the (EPS + agar) beads.

Concentrations range	**Langmuir**			**Freundlich**			**Dubinin-Redushkevich (D-R)**		
	q_{mL} (mg/g)	**b** (L/mg)	**R^2**	**K_F** (mg$^{(11/n)}$.L$^{1/n}$)/g	**n**	**R^2**	**q_{mDR}** (mg/L)	**B** (mol^2/kJ^2)	**R^2**
Feeble	**111.11**	0.0054	0.924	3.834	2.28	0.983	24.78	2.673	0.94
High							90.38	9301	0.884

Table 2 lists some reported sorption capacity values for Pb (II) uptake by different immobilized microorganisms. The comparison of the maximum capacity of adsorption of the various adsorbents is difficult considering the experimental conditions vary from one study to another. However, we can conclude that our result is in conformity with the results of former works and that the (EPS+agar) beads tested in this study exhibited a reasonable capacity of adsorption compared to the other adsorbents.

Table 2: Sorption capacities for Pb (II) using different adsorbents

Adsorbents	q_{max} (mg.g^{-1})	References
Alginate of calcium beads	58.02	(Zhang et al., 2013)
F.Vesiculosus - Alginate of calcium beads	468.27	(Mata, 2008)
Magnetic alginate beads	50.00	(Ani et al., 2012)]
Magnetic alginate beads (called magsorbent)	100.00	(Bée et al., 2011)
Alginate-SBA-15 (ALG-SBA-15)	222.22	(Cheraghali et al., 2013)
(EPS+agar) beads	**111.11**	**This study**

4. Conclusions

The results demonstrate that (EPS+agar) beads were able to remove lead from aqueous solution. The study of the influence of various operating parameters on the biosorption showed that the maximum sorption capacity was achieved in 120 min of contact time and the yield of lead adsorption depends on the adsorbent dosage, the initial metal concentration and particularly on the pH of the solution. The application of several isotherms models show that the adsorption of lead is represented better by the model of Freundlich. The maximum adsorption capacity of 111.11 mg.g^{-1}, estimated using Langmuir model was very near to the experimental value.

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