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Removal of lead ions from aqueous solution by the sugarcane bagasse

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Abstract

The objective of this work is the use of sugarcane bagasse (SCB) for the removal of lead ions (Pb^{2+}) from aqueous solution. After realization of a reliable experimental protocol and giving reproducible results, the metal aqueous solutions are analyzed by the technique of the Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).The kinetic study at pH = 5.5, shows that the extraction equilibrium is reached after 35 min, and the process of extraction is expressed by the kinetic law of second order. The equilibrium time, the yield and the extraction capacity increase with the initial pH of the aqueous solution, the maximum extraction capacity of Pb^{2+} per the SCB is about 3.32 mg/g. In the operating conditions used, a mass of 0.8 g of the SCB is enough sufficient to purify a lead solution with 20 ppm.The treatment of a mixture of metals shows that the SCB presents the sequence of following selectivity: $Pb^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+}$.

Keywords: Extraction, lead, sugarcane bagasse, extraction kinetics.

1-Introduction

The industrial effluents liquid, containing heavy metals pose a serious environmental problem, because of the insufficiency of our water resources, and the degradation of living conditions in this natural environment, which is translated by deep changes of the watery flora and fauna and by various nuisances [1-2]. The elimination and the recovery of heavy metals from waters are carried by out means of the physicochemical conventional methods of recovery [3-6] such as: liquid-liquid extraction, membrane system, opposite osmosis, and precipitation. The latter prove very expensive especially not very powerful for little concentrated solutions. During these last years, many works were focused on the use of resins of natural origins to depollute the solutions loaded with industrial effluents of efficiently manner and economically [7-12].

In this work, we have chosen sugarcane bagasse as extractant matrix for the following reasons:

- Its high content of cellulose, hemicellulose and lignin, which are contained in their structures of the groupings hydroxyls and phenol hydroxides, which play an important role at the level of extraction mechanisms of heavy metals.
- Another essential reason, it is that the sugarcane bagasse is available and less expensive.
- Also, grace to the mechanical properties of bagasse, we can regenerate this material in several cycles of extraction - deextraction of heavy metals, and in wastewater treatment in general [13].

We chose the lead as metal to extract from aqueous solutions, because of its massive use in several industrial fields [14-15]. It is also, the lead is known to be one of the heavy metals most toxic to living organisms and it is one of the more widespread heavy metal contaminants of the environment [16].

2-Materials and Methods

2-1-Material used

The sugarcane bagasse is the fibrous residue which remains after the extraction of sugar contained in sugarcane.

2-1-1 - Chemical composition of sugarcane bagasse

The sugarcane bagasse is made up mainly by natural polymers (biopolymers) such as, the cellulose whose monomer is the glucose, the hemicellulose which is a copolymer whose principal reason is composed of xylose connected with glucose and arabinose [17], and the lignin which is a three-dimensional polymer, its pattern is constituted mainly by three different monomers such as, coniferyl alcohol, paracoumaryl alcohol and sinapyl alcohol [18]. The table (1) summarizes the percentage of cellulose, hemicellulose and lignin in the sugarcane bagasse.

Table 1: Percentage of composition of the sugarcane bagasse [17]

Compound	**Percentage (%)**
Cellulose	43.6
Hémicellulose	33.5
Lignin	18.1
Ash	2.3
Wax	0.8
Other	0.7

The chemical structures of the cellulose, hemicellulose and lignin of the sugarcane bagasse are shown on the figures 1, 2 and 3.

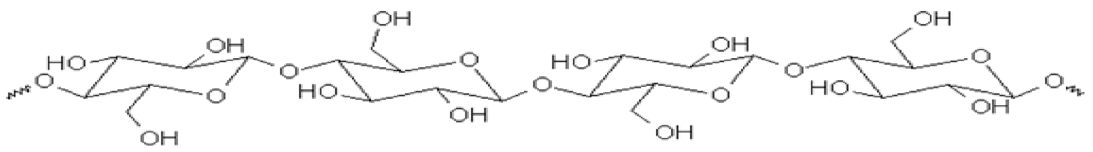

Figure 1: Chemical formula of cellulose

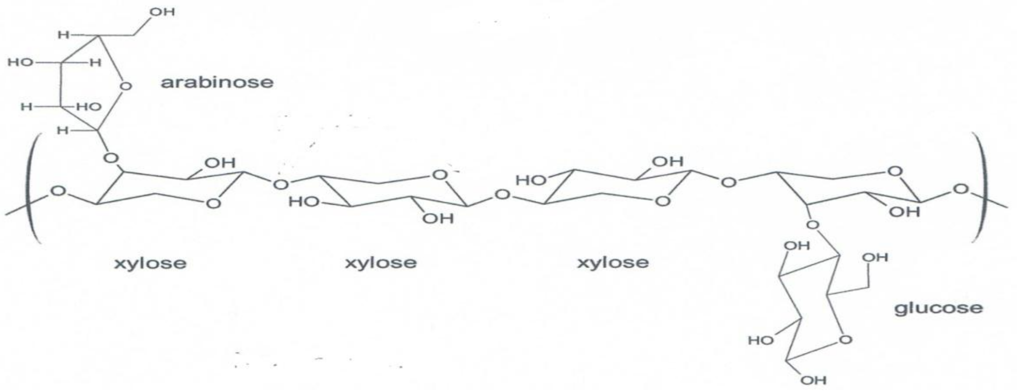

Figure 2: Chemical formula of the hemicellulose of the sugarcane bagasse [17]

2-1-2-Preparation of the sugarcane bagasse (SCB)

The sugarcane bagasse (SCB) was dried with the air, under the action of the solar rays, then crushed and tamised so as to obtain homogeneous materials for the experimental achievements, and the fraction of granularity of very low diameter.

2-2 Preparation of metallic solutions

The metallic solutions of lead are prepared by dissolving of the lead acetate salt hydrated (Pb (OAc)$_2$, 3H2O) in distilled water. The pH of each solution was adjusted by hydrochloric acid (HCl) and the sodium hydroxide (NaOH).

2-3-The yield and the extraction capacity

The evaluation of the effectiveness of extraction is carried out either by determining the extraction yield, denoted R%, or by calculating the extraction capacity, denoted q, expressed in mg of metal per g of extractant support.

The extraction yield R% is calculated using the following formula:

$$\mathbf{R\% = (C_o - C_e)\, 100/C_o}$$

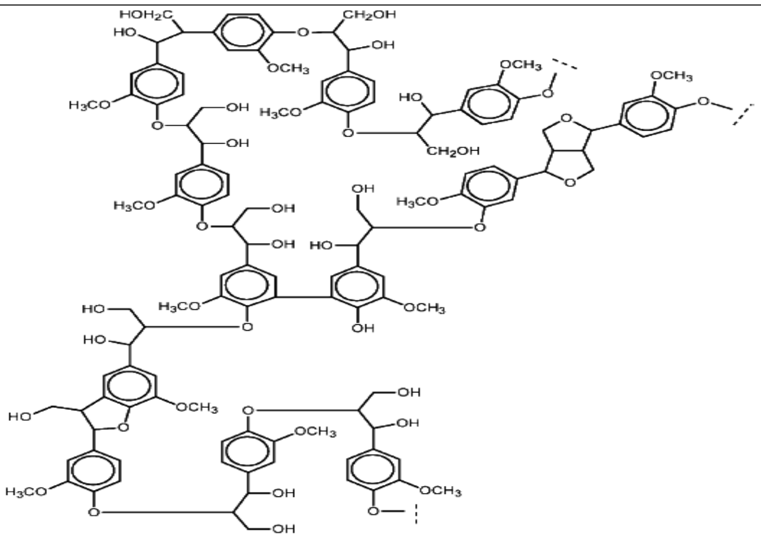

Figure 3: Chemical Formula of the lignin of the sugarcane bagasse [19]

The extraction capacity at time t is defined by the following formula:

$\mathbf{q_t}$ (mg/g) = $\mathbf{(C_o - C_t)\ V/m}$

The extraction capacity at time t is defined by the following formula:

$\mathbf{q_e}$ (mg/g) = $\mathbf{(C_o - C_e)\ V/m}$

C_o: initial concentration of metal (ppm).
C_t: residual concentration of metal at time t (ppm).
C_e: residual concentration of metal at the equilibrium extraction (ppm).
V: volume of the metallic solution (l).
m: mass of the support extractant introduced in solution (g)

2-4- Technique of extraction

The process of extraction liquid-solid of metallic cations Pb^{2+} by sugarcane bagasse was carried out by contacting a volume of 100 ml of the aqueous phase, of concentration equal to 20 ppm, with a mass of 0.5 g of SCB stirred in beakers at 25 °C until extraction equilibrium. The pH of each solution is adjusted to 5.5. The extractant matrix was previously introduced into a small sachet of filter paper closed by a wire. The homogenisation of the aqueous solutions is ensured by an agitator magnetic with a constant agitation.

The extraction kinetics of Pb^{2+} ion represents the evolution of the residual concentration of lead with time in the aqueous solution. The study was performed by performing sampling with time in the supernatant solution, and each sample is noted at the pH of the supernatant solution. Each sample was diluted with distilled water, and assayed to determine the final concentration of metal remaining to the extraction equilibrium.

2-5-Analysis Method

In this work, the dosage of metallic solutions of lead is realized at Laboratory of the National Office of Hydrocarbons and Mines (ONHYM), by the technique of the Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).The spectrometer used is of type JY-38.

3- Results and discussions

In this part, we have studied the influence of various experimental parameters on the effectiveness of extraction of Pb^{2+} by the sugarcane bagasse such as: the time of contact, the initial lead concentration, the mass of the SCB, and the initial pH of the solution.

3-1- Extraction kinetics

The extraction kinetics describes the speed of the reaction for determining the contact time taken to reach the extraction equilibrium. In this work, we followed the simultaneous evolution of the residual concentration of Pb^{2+} ions and the extraction capacity with time of contact between the aqueous phase and the solid phase (figure 4). One notices a clear decrease in the metal concentration which passes from 20 ppm to 4.75 ppm followed by a state of equilibrium. This decrease is notified by an increase in the quantity of metal fixed to the SCB. The value of the extraction yield equilibrium reached after 35min, is estimated at 76%, and the maximum extraction capacity (q_m) is equal to 3.05mg/g.

We measured the pH of different samples taken during the kinetic study, the results are presented in figure 5. We noticed a decrease in the initial pH of the solution from the first minutes of contact solution-SCB, the value of the pH passed from 5.5 to 5.18 followed by a stationary state. The decrease in pH indicates that the SCB balances each other out with the metallic solution of lead in releasing of protons H^+ in the aqueous solution.

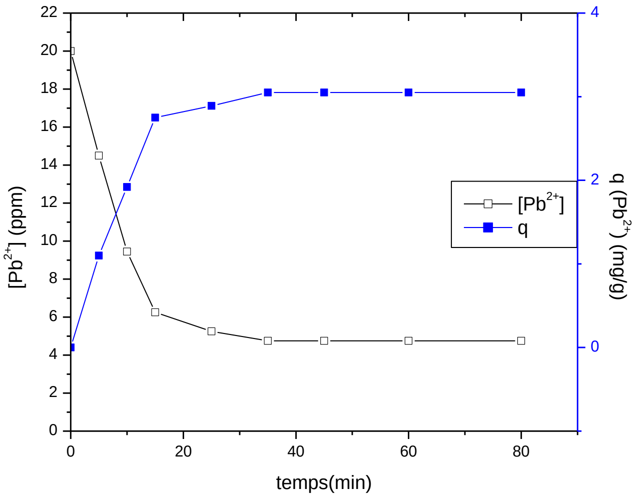

Figure 4: Extraction kinetics of lead by the SCB (V_{aq} = 100ml, $[Pb^{2+}]$ = 20ppm, pH_i = 5.5, m (SCB) =0.5g).

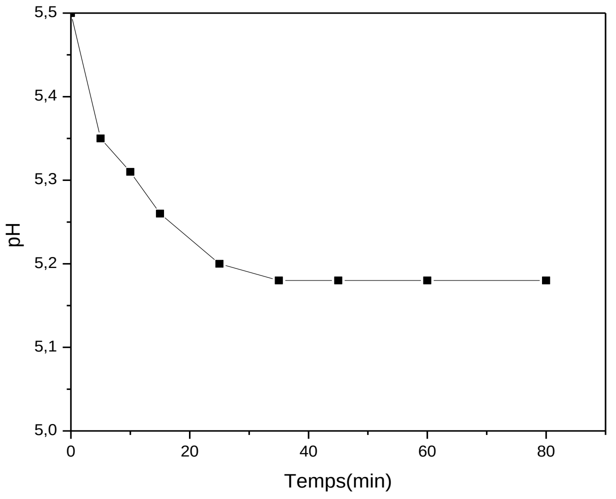

Figure 5: Variation of the pH of the solution of lead versus time (V_{aq} = 100ml, $[Pb^{2+}]$ = 20ppm, pH_i = 5.5, m (SCB) = 0.5g)

The experimental results enable us to value the kinetic models of first and second order, to determine the correlation coefficients (R), the determination coefficients (R^2), the speed constants, and to deduce the kinetic order of extraction.

3-1-1-The first order kinetics

The kinetic model of first order expressed by the equation of Lagergren [20].

$$\frac{dq}{dt} = k_1 \, (q_e - q_t)$$

After integration of this equation between t = 0 and t, q_t = 0 and q_t, the equation becomes:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

The course of the curve ln (q_e-q_t) = f (t) (figure 6) gives a straight line with the slope equal $-k_1$ and the ordinate at the origin equal to ln (q_e).

q_t = 0: the extraction capacity before beginning the extraction process.

q_t and q_e : The extraction capacities at time t and the extraction equilibrium.

k_1 (min^{-1}): speed constant of the process of extraction of the first order.

3-1-2 -The second order kinetics

The kinetic model of second order expressed by the equation of HO and MCKAY [21].

$$\frac{dq}{dt} = k_2 \, (q_e - q_t)^2$$

After integration between t = 0 and t, q_t = 0 and q_t we obtain the linear form:

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{t}{q_e}$$

The course of the curve t/q_t = f (t) (figure 7) gives a straight line with the slope equal $1/q_e$ and intercept equal to $\frac{1}{K_2 {q_e}^2}$

k_2 (g min-^{1}mg^{-1}): speed constant of the extraction process of the second order.

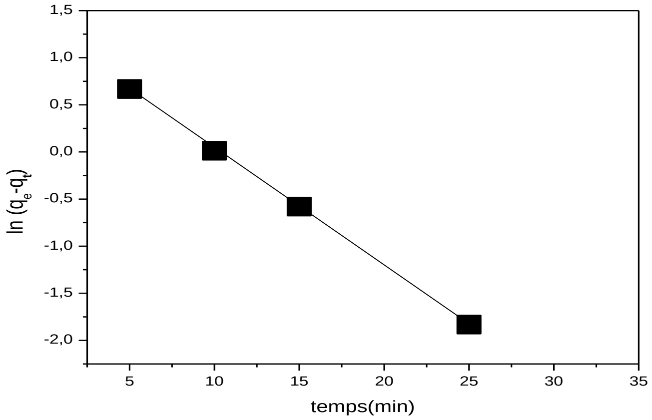

Figure 6: curve of the linear form of the first order kinetic model

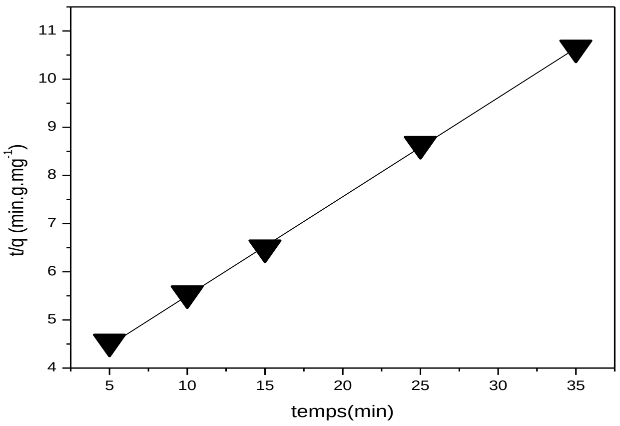

Figure 7: curve of the linear form of the second order kinetic model

The table 2 gathers the correlation coefficients (R), the determination coefficients (R^2) and the constant kinetics of extraction for the two models.

Table 2: kinetic parameters of extraction for the two models

First order kinetics			Second order kinetics		
K_1 (min^{-1})	R	R^2	K_2 (g mg^{-1} min^{-1})	R	R^2
0.92	-0.848	0.719	0.0255	0.99624	0.9925

According to these results, it is noticed that, the determination coefficient (R^2) given by the kinetic model of second order is higher than the first order. It can be inferred that the kinetic of extraction of Pb^{2+} ions by the SCB can be expressed by the kinetic law of the second order. This result is in agreement with the work carried out during the extraction of heavy metals by various extractants supports [22-24].

3-2-Effect of the initial pH on the extraction of Pb^{2+} by the SCB

In the figure 8, we followed the evolution of the fixing capacity of lead versus time for different values of initial pH.

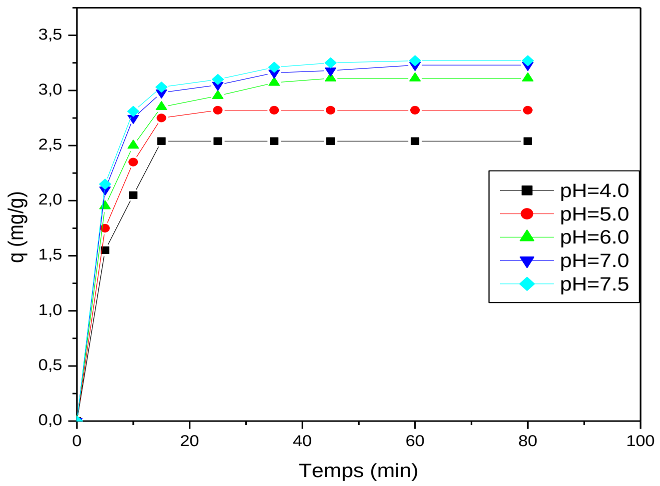

Figure 8: Effect of initial pH on the extraction of Pb^{2+} by the SCB (V_{aq} =100ml, [Pb^{2+}] = 20ppm, m (SCB) =0.5g)

We notice that the kinetic curves of lead obtained have the same allure, and the more the initial pH of the solution increases, the more the maximum quantity of metal fixed to the SCB increases. Also, the time required to reach the extraction equilibrium increases with pH. For pH = 4, the extraction equilibrium is reached at 15 min of agitation of the system, and the maximum capacity of fixing is about 2.54mg/g. In the opposite for a pH = 7, we have about 60 min for that the SCB equilibrium with the metallic solution of Pb^{2+}, and the maximum capacity is equal to 3.23 mg/g. Indeed, the increase in pH causes the dissociation of the ionizable functional groups of surface, which increases the negative charge of surface and attracts the metal cations in solution. Also, the competition of the H^+ protons in solution with the Pb^{2+} cations for the same sites of fixing is weakened considerably as pH increases. The table 3 summarizes the variation of equilibrium time, the capacity and the extraction yield as a function of initial pH of aqueous solution.

Table 3: Variation of equilibrium time, capacity and extraction yield as a function of pH_i

pH_i	**4.0**	**5.0**	**6.0**	**7.0**	**7.5**
Equilibrium time (min)	15	25	45	60	65
q_m (mg/g)	2.54	2.82	3.11	3.23	3.27
R %	63.5	70.5	77.75	80.75	81.75

3-3-Effect of the initial concentration of Pb^{2+} ions on the extraction capacity

The application of the process of extraction of lead by the sugarcane bagasse on synthetic solutions at different concentrations (20, 40, 50, 100, 150, 200, 250, 300, 400 ppm) enabled to determine the maximum quantity extracted at the equilibrium. The presented curve in figure 6, shows an increase in the fixing capacity with the concentration of lead and ends with a saturation starting from 250 mg/g, where the quantity of lead removed by sugarcane bagasse becomes constant (q_m = 3.32 mg/g).

This result enables to conclude that this value represents the maximum quantity of lead that can be fixed on one gram of the sugarcane bagasse in our operating conditions.

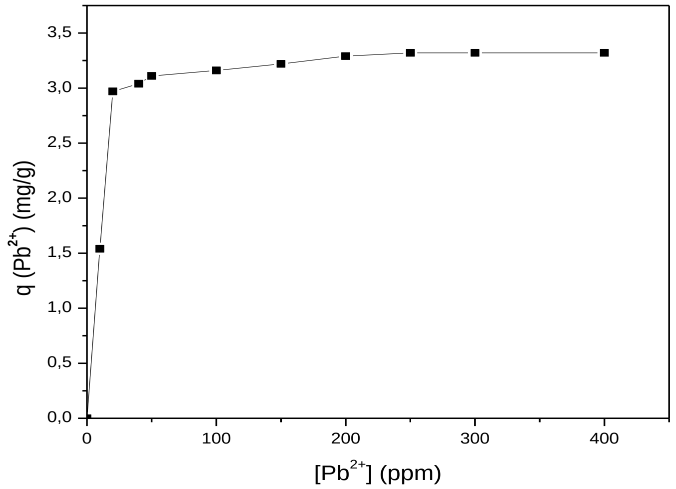

Figure 9: Effect of $[Pb^{2+}]_i$ on the extraction capacity by SCB ($[Pb^{2+}]_i$ =20ppm, 40, 50, 100, 150, 200, 250, 300 and 400 ppm, Vaq = 100ml, m (SCB) = 0.5g, pH= 5.5)

3-4-Extraction of a mixture of metals

To carry out this study, we prepared a mixture of equimolar solution containing the Pb, Cd, Co, Zn and Cu with a concentration of $9.6.10^{-5}$ mol/l for each metal. The pH of the solution obtained was fixed at 5.5. Into a volume of 100 ml of this mixture, we introduced a quantity of SCB of mass equal to 2.5g. The results illustrated on table 3, show that, the SCB presents the sequence of following selectivity: $Pb^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+}$.

The bibliographic consultation concerning the treatment of a mixture of metals in solution shows that the order of selectivity of metal ions varies from one material to another [25-29]. Indeed, during the study of the extraction of a mixture of heavy metals on two marine algas, Leusch and al obtained the affinity sequence $Pb^{2+} > Cd^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+}$ for Sargassum fluitans, and $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+}$ for Ascophyllum nodosum. Ahmady-Asbchin and al, reported the order of selectivity $Pb^{2+} \sim Cu^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+}$ for the alga Fucus serratus. Also Reddad has highlighted the fixing sequence $Pb^{2+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+}$ for the beet pulp saponified. The sequence affinity Cu^{2+}> Pb^{2+}> Ni^{2+} was demonstrated by Brady and al for fungi treated with an alkaline solution. Vaughan and al obtained the order of affinity $Cu^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+} > Pb^{2+}$ for envelopes soybean and corn cobs changed.

Table 4: Extraction selectivity of the mixture by SCB (Pb, Co, Cd, Cu, Zn)

metallics ion	Pb^{2+}	Cd^{2+}	Zn^{2+}	Cu^{2+}	Co^{2+}
$[M^{2+}]_i$ (ppm)	19.85	10.85	6.32	6.13	5.68
$[M^{2+}]_f$ (ppm)	4.367	3.038	1.96	2.03	1.93
R %	78	72	69	67.75	66

3-5-Effect of the mass of the extractant support

In this study, we plunged of quantities of the SCB, of increasing mass (0.3g, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1 g) in 100 ml of each aqueous solution of lead, of concentration equal to 20 ppm. The pH of each solution was fixed at 5.5. According to the results shown in figure 7, we notice that the yield of extraction of Pb^{2+} ions increases gradually as the mass of the SCB put in contact with the metallic solution increases, which can be explained by the fact why, the more the mass increases, the more the surface of contact offered to the extraction of lead becomes important. Also, the availability of the active sites responsible to the complexation for the metal ions increases.

A bearing is obtained from a mass of 0.8g of SCB, which corresponds to an optimal yield of 100%.

Therefore, we can conclude that in the operating conditions used, a mass of 0.8g of SCB is enough sufficient to purify a metallic solution of Pb^{2+} of concentration equal to 20ppm.

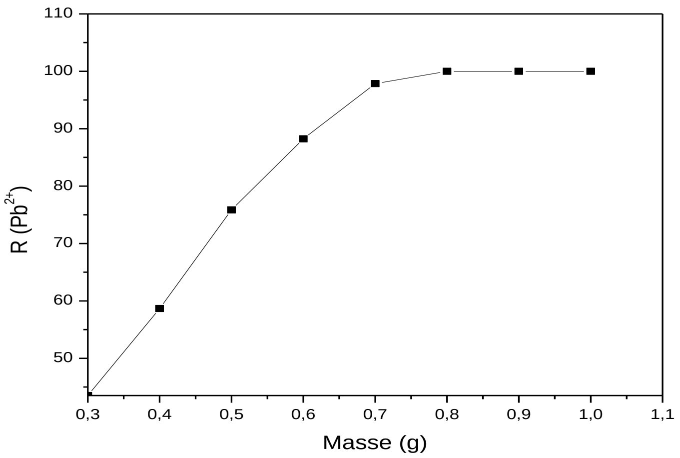

Figure 10: Effect of the mass of SCB on the extraction yield
($[Pb^{2+}]$ =20ppm, pH= 5.5)

Conclusion

The removal of lead ions from aqueous solutions by the sugarcane bagasse (SCB) was studied. The volume treated for each solution is equal to100 ml. The principal results are the following:

-The kinetic study of Pb^{2+} by the SCB at pH= 5.5 showed that the extraction process is expressed by the kinetic law of second order, and the extraction equilibrium is reached after 35min. The pH of the aqueous solution of Pb^{2+} decreases in the course of extraction by the SCB, which is due to the release of the H^+ protons by the sugarcane bagasse in the aqueous solution.

- In the operating conditions used, the maximum capacity of fixing of lead by SCB is about 3.32mg/g.

-The treatment of a mixture of divalent metals containing the Pb, Co, Cd, Cu and Zn by the SCB, shows that the SCB presents the sequence of following selectivity:Pb^{2+}> Cd^{2+} >Zn^{2+} > Cu^{2+} > Co^{2+}.

-In the experimental conditions used, a mass of 0.8g of sugarcane bagasse is enough sufficient to purify a metallic solution of lead of concentration equal to 20 ppm.

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