RESEARCH ARTICLE

OPTIMIZATION BY FULL FACTORIAL DESIGN OF LEAD ADSORPTION CONDITIONS ON ACTIVATED CARBONS FROM COCONUT SHELLS.

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Manuscript Info

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Abstract

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Adsorption of heavy metals on activated carbons is influenced by various factors that must be controlled. This study investigates the optimal conditions for removal lead on activated carbon using experimental designs. Thus, influence of three parameters (pH, lead concentration and activated carbon) on adsorption rate was studied. Activated carbons was prepared from coconuts shells of Côte d'Ivoire by using chemical activation method. pH, lead concentration and coal nature are the factors considered in the two-level complete factorial plan used for optimization. values of lead elimination rate are between 87 % and 96 % thus indicating pertinence of choice of the experimental domain. Moreover, two of the three factors; pH and lead concentration have a significant influence on the lead removal rate. Also, interactions between carbon type and lead concentration and those between pH and concentration have a significant influence on adsorption. Thus, the optimal adsorption conditions of 50 mL of lead at 150 mg / L of concentration are obtained with 0.3 g of activated carbon, at pH 6 and at a temperature of 25 ° C. Experimental designs therefore make it possible to optimize lead removal conditions from wastewater.

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Introduction:-

Water pollution by heavy metals is a source of environmental degradation and is of interest internationally (Demim et al. 2013). Lead is one of the most toxic heavy metals, it is found most often in environmental compartments in the form of traces. Its presence in wastewater is due to its use in many industrial processes such as production of paint, dyes, glass, fuel and batteries. This pollutant can concentrate along the food chain and accumulate in certain organs of the human body including central nervous system, kidneys and hematopoietic system (Song et al., 2010). Removal of (Pb_2^+) ions from wastewater can be achieved by processes such as chemical precipitation, ion exchange, reverse osmosis and activated carbon adsorption (Yobouet et al., 2018). Among these methods, activated carbon adsorption is the most efficient and economical technique for the removal of lead (Gbamele et al., 2016; Murat et al., 2018). Moreover, adsorption phenomena are controlled by adsorption parameters such as nature of the activated

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carbon, effect of the mass ratio of the carbon/volume of the solution, pH, temperature and contact time. Thus, in order to optimize the operating conditions, mathematical models are increasingly used (Tchakala et al., 2012). Optimization tools generally used are experimental designs that reduce the number of experiments to be carried out without losing on quality of the results sought. There are several types of experiment designs. But the most commonly used because simple, is the complete two-level factorial design and is noted 2^k (Aboua et al., 2010). In this work, it is therefore a question of optimizing the lead elimination conditions considering nature of active carbon, pH of the reaction medium and initial concentration of lead. Process of removing lead is based on activated carbon adsorption synthesized from coconut shells, an abundant and cheap material in Côte d'Ivoire.

Material and methods:-
Reagents and solutions
Orthophosphoric acid (85%), sodium hydroxide (98%), hydrochloric acid (37%), lead nitrate and nitric acid (98%) are mainly the chemicals used. They are of analytical quality and are provided by Prolabo, Suvchem, Panreac Quimica S.A.U.

Coconut shells, precursors of activated carbon, come from agricultural waste in Côte d'Ivoire.

The synthetic lead solutions used in the various tests were obtained by dissolving the lead nitrate in distilled water. The main physico-chemical characteristics of lead are given in Table I.

Table 1:-Physico-chemical characteristics of lead (Me Convey et al., 1985; Mazet et al., 1990).

Atomic number	82
Atomic mass	$207,2 \pm 0,1$ u
Density	$11,44$ g.cm^{-3} à 20 °C
Melting temperature	260 °C
Boiling temperature	1755 °C
Electronegativity of Pauling	1,8
Atomic radius (Van der Waals)	0,154 nm
Ionic radius	0,132 nm (+II) ; 0,084 nm (+IV)

2.2. Preparation of activated carbons
Activated carbons were prepared by chemical activation with orthophosphoric acid 30% according to the method described below.

Coconut shells (300g) having undergone pretreatment removing the impurities are impregnated in 300 mL of a solution of orthophosphoric acid 30% for 24 h. After 24 hours, the impregnated samples are dried in an oven at 110°C until complete evaporation of the impregnating liquid. Dried samples are placed in crucibles and carried in an oven to be carbonized respectively at different temperatures 400°C and 600°C for three (3) hours. The charred samples are washed with distilled water while stirring until the pH of the rinsing water is between 6.5 and 7. These samples are finally dried in an oven at 110 °C for 24 hours and packaged in ready-to-use glass jars.

2.3. Characterization of coals
Different parameters were determined on the carbons obtained to understand their behavior during lead adsorption tests.

2.3.1. Ash rate
A mass of 5 g of activated carbon dried in an oven at 110°C until stabilization of the mass of dry matter and placed in crucibles. Samples are then baked at 500°C for 8 hours. These crucibles are finally weighed after being cooled. calculation of the ash rate (TC) is as follows:

$$TC(\%) = \frac{m_2 - m_0}{m_1 - m_0} \times 100 \qquad (1)$$

m_0: mass of the empty crucible
m_1: crucible mass + oven-dried sample at 110°C
m_2: mass of the crucible + calcined residue

2.3.2. Humidity rate
Moisture content (TH) is a ratio expressed as a percentage; it is determined by the drying of the adsorbent in an oven. 5 g of activated carbon are placed in a crucible. It is then dried in an oven at 110°C. for 24 hours. After 24 hours, the crucible is removed from the oven and weighed to determine the moisture content. The following equation is used to determine the moisture content.

$$TH(\%) = \frac{m_1 - m_2}{m_1} \times 100 \tag{2}$$

m_1: mass of activated carbon before drying at 110 °C
m_2: mass of carbon dried at 110°C for 24 hours

2.3.3. Iodine number
Iodine number, expressed in mg/g, is the quantity of iodine adsorbed per gram of activated carbon in an aqueous solution of iodine I_2 of normality 0.02 N. It characterizes the accessible zones any particle smaller than or equal to that of the iodine molecule (Gueye, 2015). To determine the iodine value, we used a method that is an adaptation of the 1989 CEFIC method and AWWA B600-78 (Mazet et al., 2017).

In a 100 ml beaker, about m = 0.2 g of previously dried carbonic weighed in an oven at 110° C. for 24 hours. 20 ml of the 0.02 N iodine solution are pipetted and stirred for 4-5 minutes. The mixture is filtered on ash less filter paper and 10 ml of the filtrate is taken and placed in an erlenmeyer flask. From the burette, sodium thiosulphate is poured into the erlenmeyer flask containing the filtrate in the presence of starch until the solution is completely bleached. V_{thio} is the volume in mL of thiosulfate equivalence. The iodine number expressed in mg/g is given by the following relation:

$$Q_{I2} = \frac{C_0 \times C_{th} \times V_{th}}{2 V_{I2}} \times \frac{M_{I2} \times V_{ads}}{m_{CA}} \tag{3}$$

C_0: concentration of the initial solution of iodine (L)
C_{th}: concentration of sodium thiosulfate (mol / L)
Vth: volume of sodium thiosulfate poured (L)
V_{I2}: volume of the measured solution (L)
M_{I2}: molar mass of iodine (g/mol)
V_{ads}: adsorption volume (L)
m_{CA}: mass of activated carbon (g)

2.3.4. Specific surface
Specific surface of the prepared carbons is determined according to the adsorption method of the acetic acid molecule developed by (Avon et al., 2001). In Erlenmeyer flasks, a mass of 1 g of carbon and a volume of about 50 ml of acetic acid of known concentration ranging from 0.015 to 0.15 mol are placed. L^{-1} is added. These erlenmeyer flasks are then closed and placed in a thermostat bath set at the appropriate temperature and stirred regularly for thirty minutes (30 minutes). The mixture is left to stand during an hour before being filtered. After filtration, a volume of 5 or 10 ml of solute is titrated with a 0.1 mol^{-1} solution of sodium hydroxide.
The amount of solute adsorbed per liter of solution is determined by the difference between the initial concentration (Ci) and the equilibrium concentration (Ce), then the amount of acetic acid adsorbed at equilibrium is deduced according to the following relationship:

$$Qe = \frac{Ce - Ci}{m} \tag{4}$$

Qe: amount of acetic acid adsorbed at equilibrium (mol/g)
Ce: equilibrium concentration of acetic acid (mol /L)
Ci: initial concentration of acetic acid (mol / L)
m: mass of activated carbon (g)

For the determination of the specific surface area SL (m^2/g), the Langmuir equation is written in the form:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m}$$

(5)

C_e: Concentration of acetic acid solution at equilibrium (in mol /L)

qe: Amount of acetic acid equilibrated with carbon (in mol/g)

qm: Maximum saturation capacity of the carbon (in mol /g)

b: Thermodynamic constant of the adsorption equilibrium (in L/mol)

qm: Deduced from the slope of the $\frac{C_e}{q_e}$ curve as a function of Ce.

Knowledge of qm leads to the determination of the surface SL by the relation:

$$S_L = q_m \times S \times N_0$$

(6)

S = 21 Å^2 is the area occupied by a molecule of acetic acid

$N_0 = 6,02.10^{23}$ mol^{-1} is the number of Avogadro.

2.4. Experimental design
2.4.1. Methodology of the experimental designs

There are different types of experimental models. The most commonly used, because of its simplicity, is the complete factorial plane, denoted 2^k, which is the combination of all levels (2) of all factors (k) (Feinberg, 1996; Massart et al., 1988). This method consists in using all the data simultaneously to calculate each factor. The results are processed using multiple linear regression and variance analysis. It states that the answer is a linear function of all factors. Thus, to determine this function is to find the coefficients of the following polynomial equation:

$$Y = a_0 + a_1 X_1 + a_2 X_2 + \ldots + a_k X_k + \ldots + a_{12} X_1 X_2 + \ldots + a_{k-1k} X_{k-1} X_k + a_{1\ldots k} X_1 X_2 \ldots X_k \quad (7)$$

a_i: Effect of the factor X_i

a_{ij}: Effect of the interactions between factors X_i and X_j.

The determination of experimental domain, experimental designs, estimates and statistics of the polynomial coefficients is carried out using NEMRODW software (Mathieu et al., version 9901).

2.4.2. Choice of factors

An appropriate choice of parameter variation domains is an essential condition for establishing a precise model that perfectly describes the studied process (Choumane et al., 2016; Depci et al., 2012). Type of activated carbon, pH and initial concentration of lead were selected as parameters of the study. Lead removal rate, Y, is the measured response. Each factor (X_i) at a low level and a high level denoted respectively (-1) and (+1) in coded variable (Table 2).

Table 2:-Experimental field

Facteurs	Variable	Niveau bas (-1)	Niveau haut (+1)
Type of activated carbon	X_1	CAT1	CAT2
pH	X_2	4	6
Initial concentration of lead (mg/L)	X_3	30	150

2.5. Analytical technique

Lead adsorption was performed in batches at room temperature (30 ± 2°C). For each test, a volume of 50 mL of synthetic solutions containing lead was used. The operating conditions for the optimization are fixed by the experimental plan. The activated carbon/metal solution mixture is stirred for a period and filtered before analysis by the Shimadzu Type AA6500 flame atomic absorption spectrometer (SAA). The quantity of lead adsorbed at equilibrium is calculated according to the expression:

$$q_e = \frac{(C_o - C_e) \times V}{m}$$

(8)

m: Mass of the sample (g),

V: Volume of the solution (L)
Co: Initial concentration of lead (mg / L)
C_e: Concentration of metals at equilibrium (mg/L)
qe: Amount of metals adsorbed at equilibrium (mg/g of adsorbent).

For determination of the lead adsorption rate (T), the following expression is used.

$$T(\%) = \frac{(C_o - C_r) \times 100}{C_o} \tag{9}$$

Co: Initial concentration of lead (mg / L)
Cr: Residual concentration of lead (mg / L).

Results:-
3.1. Characterization of activated carbons
Two types of carbons CAT1 for T = 400 ° C and CAT2 for T = 600 ° C are obtained. Results of characterization tests for both types of carbon are shown in Table 3.

Table3:-Characterization of activated carbons

Types of carbons	Specific surface (m^2/g)	Iodine number (mg/g)	Ash rate (%)	Humidity level (%)	returns (%)
CAT1 à 400 C	97,96	456,86	1,50	8,00	37,17
CAT2 à 600 C	75,72	426,40	2,50	2,00	34,83

Determination of equilibrium times
The influence of stirring time is used to determine time required to reach the adsorption equilibrium for each activated carbon. Results obtained are presented in figure1.
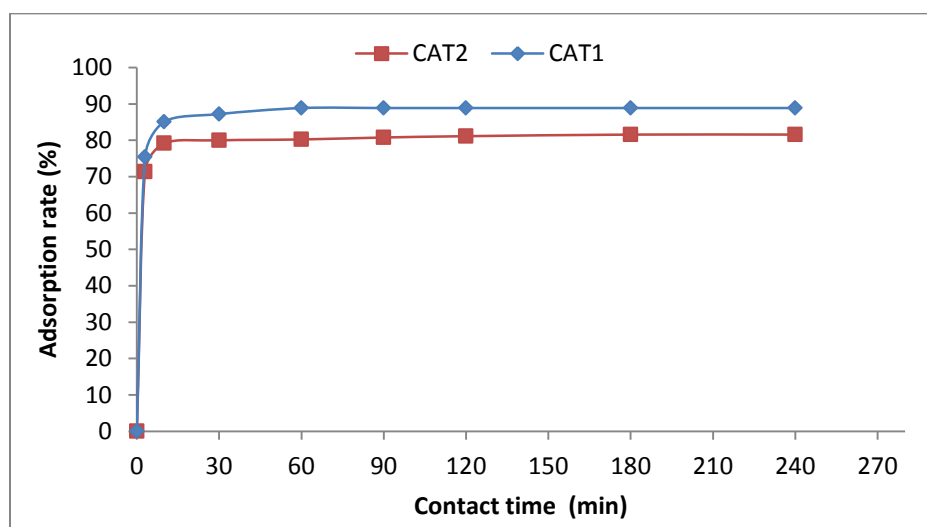

Figure 1:-Effet of contact time on lead adsorption.
(T = 25°C, m = 0,3 g, V = 50 mL et [Pb] = 30 mg/L)

Optimization of lead adsorption conditions
Experimental design and coefficient of factors
The table 4 presents the experimental design and the experimental results for the three factors studied.

Table 4:-Experimental design for the three factors

N° Expérience	Type of CA	pH	Concentration	Adsorption rate (%)
1	CAT1	3	30	89,78
2	CAT2	3	30	91,84
3	CAT1	6	30	89,06
4	CAT2	6	30	88,01
5	CAT1	3	150	88,91
6	CAT2	3	150	86,91
7	CAT1	6	150	96,15
8	CAT2	6	150	93,72

This table includes the eight experimental conditions in a random order and the lead adsorption rate associated with each test

Estimation and statistics of coefficients
The table 5 presents estimate and statistics of coefficients of the polynomial (equation 7).

Table 5:-Estimation and statistics of coefficients

Name	Coefficient	Ecart-Type	Signif. %
b0	90,548	0,335	0,236 **
b1	-0,428	0,335	42,3
b2	1,188	0,335	17,5*
b3	0,875	0,335	23,3*
b12	-0,443	0,335	41,3
b13	-0,680	0,335	29,1*
b23	2,325	0,335	9,1*

The significance test of each coefficient of the model was performed by taking the absolute value of the coefficients which must be greater than twice the standard deviation.

3.3.3. Effects of different factors
The importance of factor effects as well as their interactions is illustrated in **Figure 2**.
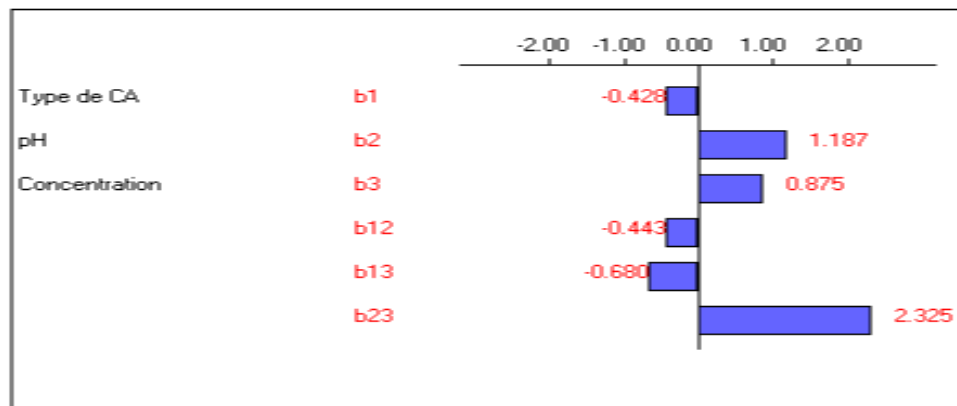
Figure 2:-Graphical study of the effects of factors on the response (adsorption rate).

Figures 3 and **4** show respectively interactions between the type of carbon and the concentration and that between the pH and the concentration. The values in each small square represent the combinations of the levels of the two factors.
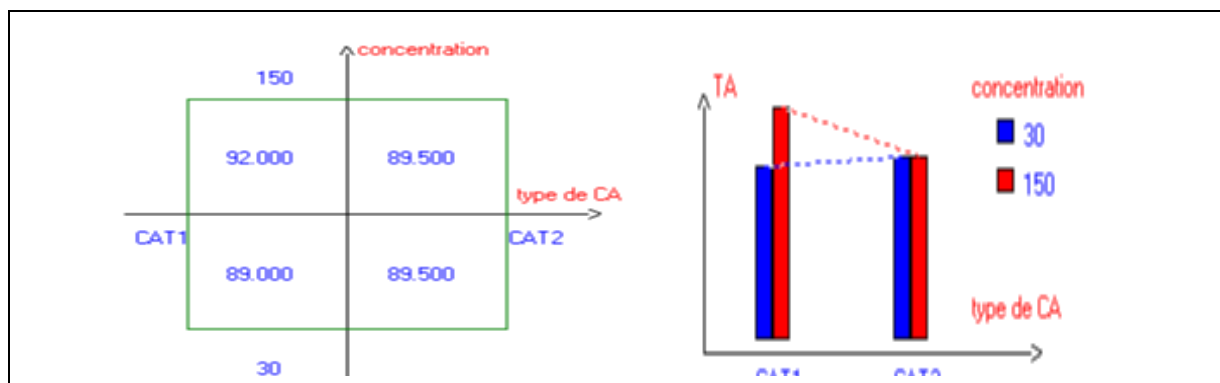
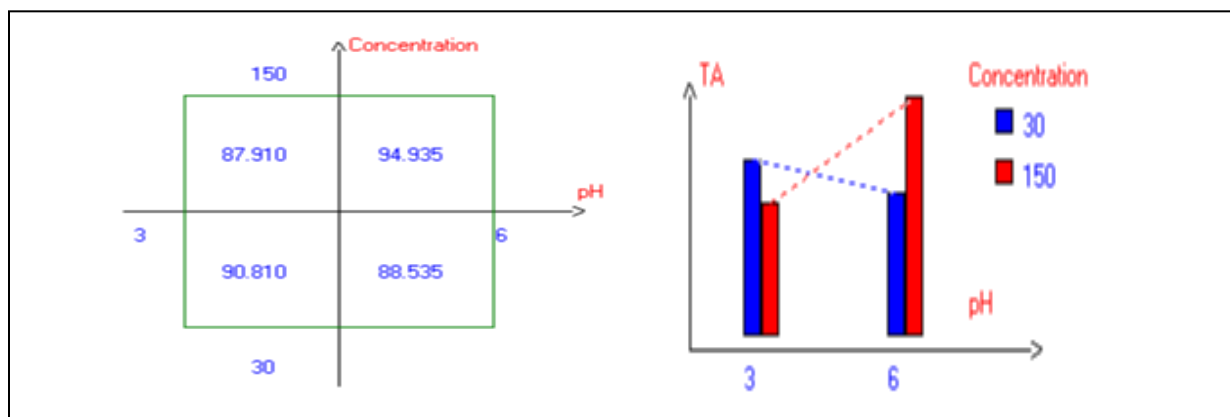**Figure 3:-**Graphical Study of Typical AC Interaction / Lead Concentration

Figure 4:-Graphical study of the pH / lead concentration interaction

Discussion:-

Both types of carbon have been characterized to appreciate their adsorption capacity. Indeed, a carbon is better than it has a low rate of ash and moisture and a large surface area (Gueu et al., 2006). In this study, the ash content is less than 3% and the moisture content does not exceed 8%. As for the values of the adsorption capacity, they are above 400 mg/g. These values, comparable to those obtained by Zeroual et al., (2011) and Mamane et al., (2016), indicate that the carbons obtained are of good quality.

The study of the adsorption kinetics gives an equilibrium time of 30 minutes and 10 minutes respectively for CAT1 and CAT2 with more than 80% removal of lead. The rapid adsorption observed during the first few moments may be due to the availability of active sites for the removal of lead (Khattria et al., 2009; Bouhamed et al., 2013). The difference in adsorption rate (after 10 min, for example, 85.81% of lead adsorbed on CAT1 and 79.17% on CAT2) at this phase, could be related to the nature of the pores at the surface of the activated carbon. It could therefore be deduced that the carbonization temperature has an influence on the development of the porosity on the surface of the carbon. According to Mohanty et al., (2005), when temperature reaches the value of 600°C, a restructuring takes place causing a decrease in the adsorption capacity of the activated carbon. These authors emphasize that at these temperatures the micropores are destroyed in the profile of macropores.

The optimization of the operating conditions for removing lead from water led to the choice of an experimental domain with the three study factors. In this field, the tests carried out give adsorption rates of between 87% and 96% thus showing the relevance of this choice. Table 4 and figure 2 also show that two of the three factors have a significant influence on the rate of removal of lead by prepared coals. This is the pH (Variable X_2) and the lead concentration (variable X_3). In addition, interactions between carbons type (Variable X_1) and concentration (Variable X_3) and that between pH (Variable X_2) and concentration (Variable X_3) significantly influence adsorption. Indeed, the absolute value of the pH and lead concentration coefficients and those of the interactions is greater than twice the standard deviation (Assidjo et al., 2005). In the predefined experimental field, the equation of the adsorption rate (Y) of lead as a function of the different parameters is thus given by the following mathematical model.

Y= 90,548 + 1,188X$_2$ + 0,875X$_3$ + 2,325X$_2$X$_3$ - 0,680X$_1$X$_3$ **(10)**

Detailed study of the different coefficients of factors having a significant influence on lead adsorption makes it possible to understand the effect of these and their interactions. Thus, for pH, when the value goes from 3 to 6, the adsorption capacity of lead increases 2.38% (value of b2 = 1.188). From this it can be deduced that a rise in pH in an acidic medium causes a rise in the rate of adsorption of lead. These results are consistent with those obtained by (Hamane et Bendjama., 2005; Arris, 2008; Boudrahem et al., 2011). The latter studied the adsorption of Pb2+ ions on materials derived from biomass. For these authors, this increase could be explained by the fact that in acidic medium there is production of H$^+$ ions which would make the adsorption of Pb$_2^+$ ions less favorable. The increase of the pH which indicates the decrease of the protons, thus releases the sites of adsorption of the coal thus rendering them more available for the adsorption of Pb$_2^+$ ions. The maximum fixation of these is obtained at a pH equal to 6. This observation was also noted for the adsorption of lead from river sediments on spruce sawdust (Marin et Ayele, 2002).

Regarding the influence of the initial concentration of lead, there is an average increase of 1.75% of the adsorption capacity when the concentration of lead increases from 30 to 150 mg/L. An increase in the concentration therefore has a positive effect on the adsorption capacity. These results are supported by those of (Mouni et al., 2014) who worked on the removal of Pb$_2^+$ ions by adsorption on activated carbons prepared and encapsulated in a closed stirred reactor. For these authors, the increase in the quantity adsorbed with the concentration can be explained by a great variability of the adsorption sites and the presence surface. Thus, the transfer of the solute would be all the better that the concentration of the solutions is high. Knappe et al., (1998) have achieved the same result and claim that the higher the concentration, the higher the adsorption.

The results of the typical interaction-concentration interaction indicate that when the concentration goes from 30 mg / L to 150 mg / L, the average lead absorption rate increases from 89% to 92% for CAT 1 carbon. On the other hand, for the same variation in the concentration of lead, the adsorption rate remains unchanged in the case of CAT2 carbon. In this area, the effect of lead concentration depends on the type of carbon. The best lead adsorption rate is reached at the maximum value of the concentration (150mg/L) with the CAT1 carbon. These results show that increasing the concentration of lead improves the lead adsorption rate with CAT1.

Concerning pH and concentration interaction, we notice an increase of 7.03% when the pH goes from 3 to 6 and that the concentration is at its high level (150 mg/L). However, when the concentration of lead is low (30 mg/L), the adsorption rate is reduced by 2.28% for the same pH change. In this field, the effect of the lead concentration on the adsorption rate depends on the level of the pH factor. Finally, the optimal conditions for lead adsorption, in the experimental field, are obtained with 0.3 g of carbon, at pH 6 and at a temperature of 25 °C. Under these conditions, for 150 mg/L of lead, after 30 minutes, an adsorption rate of 96% is obtained.

Conclusion:-
This work is based on the use of experimental designs to optimize the operating conditions for the elimination of lead by activated carbons. The carbon used was obtained by the chemical preparation process, from coconut shells abundantly available in Côte d'Ivoire. The complete two-variable factorial design technique determined the effect of three factors and their interactions on lead adsorption. It should be noted that lead adsorption depends on the pH and concentration of the pollutant and their interactions. A removal rate of nearly 95% is obtained for a concentration of 150 mg/L at pH = 6. It is therefore possible to optimize, using mathematical tools, the operating conditions for the purification of wastewater using the activated carbon adsorption process from agricultural waste.

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