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RESEARCH ARTICLE

DEVELOPMENT OF A NEW ADSORBENT MATERIAL BASED ON MARINE SPONGES OF THE GENUS *IRCINA*: APPLICATION OF THE EXPERIMENTAL DESIGN METHODOLOGY "SCREENING AND OPTIMIZATION".

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Abstract

In this work, activated carbon was prepared from the by- product of marine sponges. The objective of this study is summarized in the development of an adsorbent material with a very interesting adsorption capacity, hence the interest to control the parameters influencing the functioning of the development process by exploiting it The screening plan "Factoriel Complet". This technique minimizes the experiments and allows detecting the factors influencing the quality and the quantity which are: temperature, time and mass. Then the next step in this study was devoted to the optimization of the process of elaboration, using the response surface methodology "Composite centered plan". The optimal conditions with 55% of methylene blue adsorption capacity are obtained with 180.9minas activation time, 118.9°C as activation temperature and 7.33g for the mass of the raw material.

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Introduction:-

Liquid industrial effluents present a great danger to the aquatic environment which is the main site of industrial and urban waste. Industrial wastewater is causing enormous damage to the environment and health **(Oumam et al.,2003)** . These releases have different degrees of harmfulness and this pollution is all the more dangerous because it is not known. In order to combat this dissolved pollution, several studies have been oriented towards economically acceptable processes using several techniques **(Souabi et al., 1993 and Altinbas et al., 1995)**. These techniques could be divided into three types of treatment, namely biological, dielectric and physico-chemical treatments **(Wanassi et al., 2017**). These include adsorption and ion exchange (**Tzvetkova et al., 2016)**.The aim of this work is to develop adsorbent materials having an adsorption capacity from the extraction residues of the *Ircinia* marine sponge, adopting the experimental design methodology in first the screening plan in order to master the influence of factors on the process of elaboration, followed by an optimization of the process by adopting a composite plan centered. This study has guided us in translating the evolution of the performance of the materials developed according to the different operating factors influencing the process.

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Materials and methods:-

Sample:

The marine sponges were collected in winter 2015 at the littoral Atlantic of El-Jadida (Morocco). All the sponges were identified by Dr. Maria-Jesús Uriz, Research Professor at the Centro de Estudios Avanzados de Blanes (CEAB) and Consejo superior de investigaciones científicas (CSIC) Spain. The collected materials were immediately frozen for one night prior to extraction **(Rhandour et al., 2016).**

Preparation of samples:-

The extraction residues obtained from these sponges were chemically activated using (phosphoric/ sulfuric) acid 2M. The samples were baked overnight at 120 ° C. and heat-treated in air, in a muffle furnace, at different temperatures, the treatment time varied. The samples are then washed with distilled water in a Soxhlet for 72 hours, in order to extract the excess acid and the soluble material and then dried in the oven at 120 ° C. The products are ground (granulometry less than 100 µm) **(Tarbaoui et al., 2014).**

Experimental design methodology:-

Screening plan :-

The first problems which experimental design can give the solution are these of screening parameters “Complete factorial plans “. This study permitted to determine easily, among a large number of factors (k), those are significantly influenced to improve extraction process. This study will allow determining the "effect" of each level and for every factor, in objective to classify them in ascending order **(Fadil et al., 2014).** The table (tab.1) presents the factors studied with real and coded level.

Table 1: Factors and their coded levels

Factors	Levels	Coded Levels
Temperature (°C)	180	-1
	350	+1
Time (mn)	90	-1
	180	+1
Mass (g)	5	-1
	10	+1
Type of acid	sulfuric	-1
	phosphoric	+1
Pretreatment	yes	-1
	no	+1

Optimization plan:-

Response surface methodology (RSM) is a statistical method that uses quantitative data from appropriate experiments to determine regression model equations and operating conditions (**Alam et al., 2007)**. RSM is a collection of mathematical and statistical techniques for modeling and analysis of problems in which a response of interest is influenced by several variables (**Chaudhary et al., 2014**). A standard RSM design called central composite design (CCD) **(Tarbaoui et al., 2015).**Which allow solving the optimization problems by determining the optimal levels of the factors giving rise to a desired response. They constitute a second stage of the study after screening plans designed to identify the most influential factors **(Oumam et al., 2003).** In order to optimize the production conditions of our adsorbent material, the composite centered plane was used in order to reduce the number of experimental tests necessary for the evaluation of the parameters determined by the screening plan (activation temperature, time, and the treated mass of the material) and their effects on the adsorption capacity of methylene blue (**Marouane et al., 2012)**.

Statistical analysis:-

The treatment of the results for the experimental models was carried out using experimental design software JMP. The adsorption capacity was compared with the ANOVA test, the Fisher Snedecor test and the student test. All statistical analyzes were carried out in P values ($P < 0.05$).

Results and discussion:-

Screening plan:-

The "Complete factorial plan" is a pre-established plan in the JMP software. The experiment matrix is a table L8 (Tab. 2) which allows establishing the experimental plan**.**

Table 2:- Experiment matrix of the material produced from the sponge

N° Test	code	Temperature (°C) X_1	Time (mn)X_2	Mass (g)X_3	Acid X_4	Pretreatment X_5	Adsorption capacity %
1	+−−++	350	90	5	phosphoric	no	75.8
2	+++++	350	180	10	phosphoric	no	55.3
3	−−−−+	180	90	5	sulfuric	no	55.196
4	−++−+	180	180	10	sulfuric	no	21.41
5	−+−+−	180	180	5	phosphoric	yes	13.4
6	−−++−	180	90	10	phosphoric	yes	9.13
7	++−−−	350	180	5	sulfuric	yes	13.17
8	+−+−−	350	90	10	sulfuric	yes	7.3

Validation of the model :-

The quality of the adjusted model was expressed by the coefficient of determination R^2, and its statistical significance was verified by an F test (analysis of variance) at the significance level of 5%.

The linear regression of the model:-

R^2 measures the proportion of the total change in the mean response explained by the regression, it is the correlation between the observed and predicted response **(Franco ., 2008)**. The goodness of the model is judged if the linear of regression coefficient is equal to or higher than 0.80 **(Rhanzi. N et al., 2015)**. The linear analysis of regression as established by the experimental design JMP software are shown in the Figure 1. The calculated values of the coefficients of determination of the multilinear regression R2 equal to 0.99 is close to 1 and adjusted R^2_A which is 0.97 (Tab.3) make it possible to confirm the validity of the model.

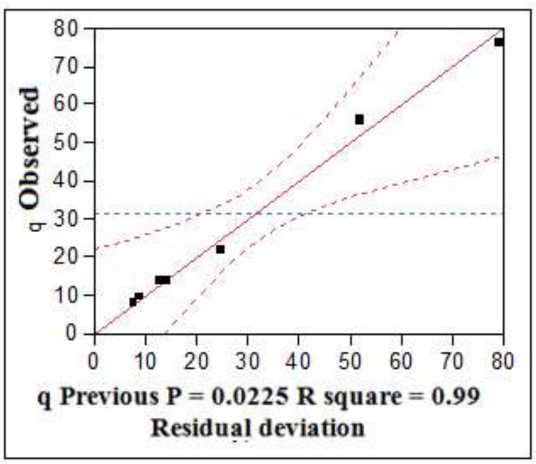


Figure 1:- Linear regression of Adsorption capacity

Table 3:- Adjusted regression analysis of adsorption capacity.

R square	0.99
Adjested R square	0.97
Root of square error of average	4.73
Average of the reponse	31.33
Observations (or weighted sums)	8

Variance analysis:-

The variance analysis is based on the comparison of the variance of the established model with the variance of the residue, using the Fisher Snedecor test. For the model to be very significant at 95%, it is necessary that: Fexp >> $F\alpha$, ν_{mod}, ν_{res} where $\alpha = 0.05$. The results of the ANOVA given by the JMP software are shown in Table 4. The results of analysis of the variance between the established model and the residue give an experimental factor Fexp (variance of the model / variance of the residue) = 43.75.

From the results, we have Fexp = 43,75 >> Fthéo, the condition of the Fisher Snedecor test is verified, so the regression is significant with a confidence threshold of 5%.

The probability Prob> F is the P-value associated with F value given by the statistical software JMP. It was compared to the risk $\alpha = 0.05$, then the P-value is strictly less than $\alpha = 0.05$, this model is significant.

Table 4:- ANOVA test

Source	Degrees of freedom	Sum of squares	Average square	F value
Modele	5	1224.22	244.84	43.75
Residue	2	11.19	5.59	Prob. > F
Total	7	1235.42		0.0225

Study of selected factors:-

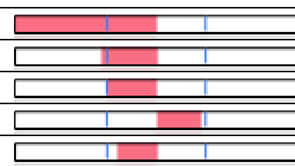
Factors Statistically not negligible:-

Table 5 shows an increase in the adsorption capacity of methylene blue from low temperatures to high temperatures, while with the increase in processing time and mass a decrease in adsorption capacity is observed. The t-test for the temperature, processing time, and mass coefficients showed that these factors influence process operation because their risks are significant (<0.05).

Factors Statistically negligible:-

The pretreatment and the type of acid are the factors which do not affect the process of production of adsorbent, and therefore will be removed from the study. The screening plan helps to demonstrate the parameters which have little influence on the adsorption capacity and therefore choose those which appear to be more influential. These will be studied more precisely in the next section to allow better control of the process.

Table 5:- Significant effects

Terme	Estimation	Standard deviation	T value	T value	Prob.>|t|
Temprature	-10.29	0,83	-12.31		0.0065
Time	-4.026	0.83	-4.81		0.04
Mass	-3.53	0.83	-4.23		0.05
Acid (sulfu)	3.27	0,83	3.92		0.0594
Pretraitement (yes)	-2.75	0.83	-3.30		0.0809

Optimization of the conditions for the preparation of adsorbent materials by the experimental design method "Composite centered plan":-

The results obtained in the previous part of this study allowed to choose the most influential variables on the adsorption capacity of the prepared material namely temperature, treatment time and mass. The next step of this study will be devoted to the optimization of the process of elaboration. The easiest way is to choose a plan of experiments with faces centered whose matrix and the experimental values of adsorption capacity are represented in Table 6.The exploitation of the results obtained for the response was carried out with the same approach. The evaluation of the overall quality of the postulated model makes it possible to know whether it adequately summarizes the results of the tests of the experimental design. The evaluation of the overall quality of the postulated model allows knowing if it adequately summarizes the results of the tests of the experimental design.

Table 6:- Factors studied and field of study

	Limit of Domain	
Factor	Minimum value	Maximum value
Temperature X_1	180	400
Treatment time X_2	90	180
Mass X_3	5	10

The equation of quadratic model is expressed by a mathematical equation of 2nd degree written in the following polynomial form:

$Y_i = b_0 + \Sigma\, b_i X_i + \Sigma\, b_{ii} X_i^2 + \Sigma\, b_{ij} X_i X_j + £_i$

b_0 is the constant of the model. bi is the effect of factor Xi. bij is the effect of the interactions between factors i and j. bii is the quadratic effect and £i is the residue.

Matrix of experiments and realization of tests:-

The realization of tests consists of measuring the responses for all combinations of the factors indicated in the test matrix and requires certain precautions both statistical order as practical. This is firstly the randomization of the order of the tests which consists in randomly sorting the order of the tests in order to eliminate the influence of the unknown process disturbing factors which may possibly be correlated with the order of the tests. If the order of the trials is not randomized the interfering factors correlated with certain factors of the plan can only be demonstrated by confirmatory tests carried out at the end of the analysis of the results. The optimum configuration obtained by modeling may not be reproduced due to external disturbances. The influence attributed to the factors of the plan can be distorted and the difficulty will then be to detect which factor is affected and by what disturbance. Similarly, during the tests, test sheets were prepared to report the process and to mark the observations and incidents that occurred during the experiments. This will help the experimenter to make a better analysis and an explanation of the obtained results. The response studied is the adsorption capacity. The test matrix is given in Table 8.

Table 7:- Experimental design in coded and reels variables for centered composite design, and test results

Test number	Configuration	Temperature	Time	Mass	Adsorption capacity %
1	00a	290	135	5	11.5
2	−−−	224	108	6	25.6
3	+−−	355	108	6	12.5
4	−+−	224	162	6.	47.6
5	++−	355	162	6.012	6.4
6	0a0	290	90	7.5	9.7
7	a00	180	135	7.5	54.3
8	000	290	135	7.5	7.3
9	000	290	135	7.5	12.9
10	000	290	135	7.5	12.6
11	000	290	135	7.5	11.9
12	A00	400	135	7.5	11.8
13	0A0	290	180	7.5	13.3
14	−−+	224	108	9	26.7
15	+−+	355	108	9	10
16	−++	224	162	9	40
17	+++	355	162	9	2.8
18	00A	290	135	10	12.9

Analysis of test results:-

The linear regression of the model:-

The essential characteristics of the fit of the quadratic model are given in Table 9. The regression is illustrated by the graph of the responses measured as a function of the estimated responses which show the distribution of points around the regression line Fig. 2. The coefficient of determination R^2=0.98 is close to 1. This coefficient reflects the contribution of the model in the restitution of the variation of the observed response. It expresses the ratio between the variation due to the regression and the total variation. In the presence of several explanatory variables, we use the adjusted coefficient of determination (adjusted R^2) (adjusted R^2 is equal to 96%). which reflects a good fit of the model and that the descriptive quality of the postulated model is satisfactory.

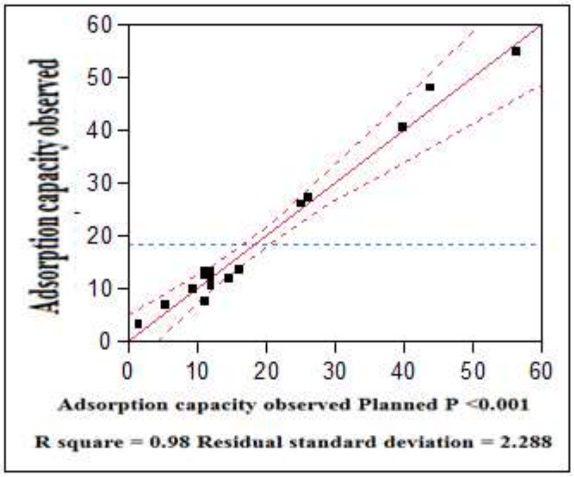


Table 8:- Adjusted regression analysis of adsorption

R square	0.98
R square adjusted	0.96
Residual standard deviation	2.88
Average response	18.32
Observations (or weighted sums)	18

Analysis of variance and lack of adjustment:-

According to Table 9. The Fisher Snedecor Fobs value is very high. Moreover. the probability that the variance of the model is significantly equal to the residual variance is less than the risk $\alpha = 0.05$. This proves that the postulated model is consistent since the variance of the model is distinctly different from that of the residue. The lack of adjustment measures the difference between the a priori model (postulated model) chosen by the experimenter and the real model that governs the phenomenon studied. The sum of the squares of the lack of adjustment is equal to the difference between the sum of the squares of the residuals and the sum of the squares of the pure error.

Table 9:- Analysis of variance.

Source	Degree (s) of freedom	Sum of squares	Average square	Report F
Model	9	3607.36	400.818	48.24
Residues	8	66.46	8.308	Prob. > F
Total	17	3673.83		<.0001

The results presented in Table 10 show that the probability that the variance of the postulated model is significantly equal to the variance of the real model is lower than the 5% risk. This allows us to deduce that the lack of fit is not due to the quadratic model.

Table 10:- Lack of adjustment

Source	Degree (s) of freedom	Sum of squares	Average square	Report F
Lack of adjustment	5	45.919676	9.18394	1.3409
Pure error	3	20.547500	6.84917	**Prob. > F**
Total error	8	66.467176		0.4306
				R carré max.
				0.9944

Estimation of model coefficients:-

The analysis of the variance makes it possible to determine the factors and the most influential interactions on the performance of the coal elaborated in order to have an attractive adsorption capacity. The statistical analysis of the coefficients constituting the equation of the quadratic model is based on the null hypothesis H0 which states that the coefficient is zero. The diagrams shown in Table 11 make it possible to visually identify the factors most influential on the response. To achieve the objective of this study, which is summarized in the determination of the input factors that maximize the adsorption capacity, we validated the quadratic model.

Table 11:- Significant effects coefficients of established equation model.

Terme	**Estimation**	Standard Deviation	Report t	Report t	**Prob.>|t|**
Constant	11.075145	1.439098	7.70		<.0001
Temperature	-13.15648	0.77998	-16.87		<.0001
Temperature*Temperature	8.1808174	0.810453	10.09		<.0001
Temperature* Time	-6.075	1.019093	-5.96		0.0003
Time	2.0542398	0.77998	2.63		0.0300
Time*Mass	-1.225	1.019093	-1.20		0.2637
Mass*Mass	0.8092292	0.810453	1.00		0.3473
Mass	-0.750209	0.77998	-0.96		0.3643
Time*Time	0.5617419	0.810453	0.69		0.5079
Temperature*Mass	0.05	1.019093	0.05		0.9621

According to this graphic representation, the effects of temperature and time factors are significant, as is the effect of the interaction between temperature and time, and even the quadratic effect of temperature.

Therefore the estimated model relating to the adsorption capacity is written as indicated by the following formula:

$$Y=11,075-13,156*X_1+2,054*X_2-6,075*X_1*X_2+8,180*X_1X_1$$

The equation of the established model shows that the temperature has a negative effect, which means that the increase of this factor gives a decrease in the adsorption capacity. While the effect of treatment time is positive, indicating that our response increases with increasing contact time.

Optimization and Desirability:-

The overall desirability reflects a particular adjustment of the input factors which allow to obtain, from the empirical models, the values of responses within the tolerance intervals. This search is done iteratively in dedicated software. The modeled responses were transformed into desirability functions ranging from 0 to 100%. This desirability reflects the degree of satisfaction of the experimenter as a function of the obtained value of the modeled response, after assigning it a target value to be achieved. A satisfaction index equal to 100% is assigned when the objective is reached, this index is equal to zero if the value of the modeled response is outside the tolerance interval associated with it. As soon as the level of a response does not belong to the tolerance interval associated with it, the value of the desirability function is zero.

The figure 3 shows the desirability functions of the adsorption capacity. It illustrates a case study where we set the target at 48.6%, with a temperature equal to 180.9 ° C. We then varied the other parameters in the field of study using the predictive profiler which allowed the values of the other input factors to be obtained with a processing time equal to 118.9 min and a mass Equal to 7.33g.

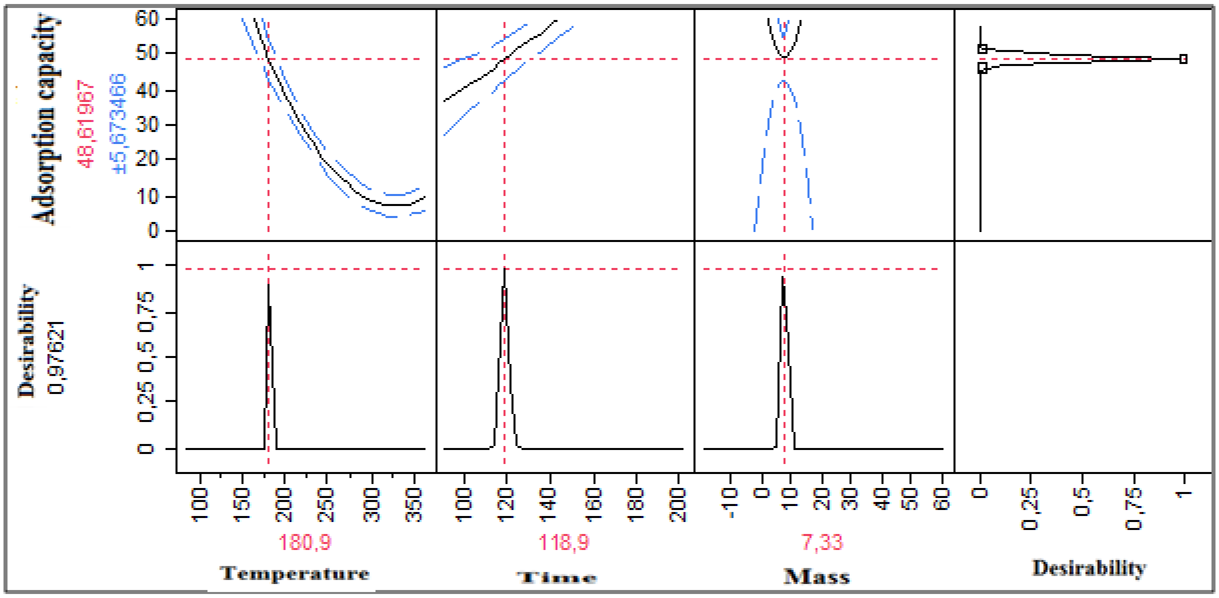


Figure 2:- Prediction profiler

Conclusion:-

In this work, the effect of each factor involved in the process of preparation of the adsorbent materials was determined with the methodology of the experimental plans using a "Factoriel Complete" screening plan to have an adsorption capacity interesting. This method allowed us to select the factors influencing the performance of adsorbent elaborated which are the temperature, the time, and the mass of the raw material. Then, the central composite plan, established for the study of the quality of the adsorbent produced, was used to determine the optimum conditions for the development of adsorbent.

The results of the optimization of the operating conditions allowed us to obtain a material which has an adsorption capacity equal to 55%. The three parameters were set at T = 180.9 ° C, m = 7.33 g, for 118.9 min.

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