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PHENOL ADSORPTION ONTO OLIVE POMACE ACTIVATED CARBON: MODELLING AND OPTIMIZATION

Purpose. To depollute water contaminated by phenol using the adsorption process in a batch reactor with valorization of olive pomace for the preparation of activated carbon to be used as an adsorbent.

Methodology. In this present work, study on the influence of four principal parameters on the adsorption yield during the treatment of polluted water by the process of adsorption were studied, namely: the activated carbon mass, the contact time, the phenol initial concentration and the stirring speed. In addition, the process was optimized with full factorial designs using the response surface methodology by the MINITAB software.

Findings. The phenol removal by adsorption on the activated carbon made from olive pomace makes it possible to achieve an adsorption efficiency of 91 % with the use of following optimal conditions: adsorbent mass of 0.48 g, a contact time of 110.80 min, a phenol concentration of 100.98 mg/L, and a stirring speed of 462.89 rpm. Contact time and adsorbent mass showed a positive effect on phenol removal efficiency. The principal effect results illustrate that all four examined factors significantly affected the phenol removal by olive pomace activated carbon with a confidence level of 95 %.

Originality. The experimental data of the phenol adsorption on the olive pomace activated carbon were examined by adjustment of a second-degree polynomial model. This model is validated by a statistical method using an analysis of variance (ANOVA). Numerical optimization was performed by the desirability function to identify the optimal parameters for maximum phenol recovery.

Practical value. In order to highlight a process for treating waters contaminated with phenol, we have chosen the processes that are considered to be best suited, which is adsorption with the recovery of a waste such as an adsorbent, which is prepared by physical and chemical activation of olive pomace. The full factorial design applied makes it possible to show the influence of each parameter independently and their dependencies, as well as to find the optimal experimental conditions quickly which lead to the realization of this process.

Keywords: *adsorption, phenol, olive pomace, activated carbon*

Introduction. Water is a major element of the world, in addition to being the symbol of life and all human activities [1]. Currently, the risk of water lack is rapidly growing and negatively influences all water consumers worldwide, namely: commercial, industrial, and agricultural activities [2, 3]. Potable water is the central point of concern for public opinion and leaders [1], but in the long term it is clear that any polluting discharge, in particular not very biodegradable or toxic, is a threat and/or a difficulty in the production of drinking water [4]. Surface water is found to be more vulnerable to pollution due to the presence of organic matter in water discharged from industries [4]. All human activities (agricultural, industrial, and others) dare to threaten all water resources as well as climate change, which has become a major danger to the planet, at all stages of development, being of great importance today [5]. This pollution causes a change in the smell, color and flavor of the water and among the dreaded organic compounds we find phenol and its derivatives [6].

Aromatic compounds in general and phenols in particular are now considered carcinogenic micropollutants even in trace amounts [7]. Phenol and its derivatives are very dangerous pollutants, once dissolved in water, they will often be difficult to treat [8]. These compounds, which are found in many industrial effluents, are often discharged into the natural environment without any prior treatment [8]. Their presence in nature is a permanent threat to any biological organism. The elimination of these contaminants is therefore a major necessity for the protection of the environment.

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All the researchers in the fields (medicine, chemistry, agronomy, geology, plant physiology, etc.), are very interested in identifying and eliminating different pollutants. There are various chemical, physical and biological techniques for treating and removing polluted compound, among these techniques we distinguish coagulation-flocculation, ionizing radiation, deep degradation, precipitation, membrane filtration, chemical oxidation, ion exchange, reverse osmosis, bioremediation by algae, electrochemical methods and adsorption [9]. Today, adsorption separation is one of the most important techniques for removal of pollutants, considered to be a better water treatment technique in terms of cost and performance; it is a technique that presents simplicity of design, ease of use and insensitivity to toxic substances, and it has become an analytical method of choice. Adsorption is commonly used in the industry to treat water containing phenolic compounds [10].

Many studies have highlighted the interest of using activated carbons, whatever their origin, as adsorbents to eliminate the pollutants contained in industrial liquid waste. These carbonaceous materials are the most used and the most studied because of their interesting physico-chemical properties. Indeed, a large specific surface, a microporous structure, high pore volume, and a high adsorption capacity and relatively fast retention kinetics make these adsorbents the materials of choice when it comes to eliminating organic contaminants such as phenolic compounds in wastewater.

Several types of adsorbents are developed and used in the adsorption process of both organic and mineral pollutants; clays, zeolites, activated alumina and activated carbon. However, activated carbon is still the most used adsorbent despite

its high price [11]. Lots of adsorbents based on biomass have recently been used to eliminate organic pollutants from wastewater [12], including olive pomace.

The purpose of the present article is to study the influence of the main experimental parameters, namely: the initial concentration of phenol, the activated carbon mass, the contact time and the stirring speed, on the yield of the adsorption technique as well as to determine the optimal experimental conditions by the response surface method.

Materials and methods. ***Preparations of sorbate and adsorbent.*** The phenol chemical formula is C_6H_6O, the pollutant is used as an adsorbent and prepared by dissolved in the aqueous solution (distilled water). The phenol structure is illustrated in Fig. 1.

The solution concentration was prepared at 1000 ppm (1000 mg/L). The concentrations prepared for each test were obtained by the dilution method of the stock solution.

The olive pomace was collected from the modern oil refinery in the wilaya of Bejaia-Algeria. Olive pomace was treated according by the procedures of the previous study with some modification in the laboratory to improve the adsorbent produced.

The experimental protocol used in the sample activation process is as following: the olive pomace is washed with hot distilled water to eliminate all the solid impurities, dust and water-soluble substances, and in the second one with cold distilled water, then introduced into the oven dried with a time of 24 h at a constant temperature of 105 °C. The sample having been dried in the oven and having constant weight, the olive pomace undergoes a chemical activation step with the following reagents ($ZnCl_2 + H_3PO_4$). The desired sample activated is obtained as follows: we placed a mass of 50 g of the olive pomace in a beaker with the adequate volume of an equal-molecular solution (1 mol/L) of the reagents ($ZnCl_2 + H_3PO_4$) for a time period of 24 h in a batch reactor. The previous activated sample is afterwards oven dried with a temperature of 100 °C for 2 h; the chemically activated sample undergoes thermal activation, calcination in a muffle furnace with a temperature of 600 °C for 45 min. After sample cooling, the raw activated carbon is washed with dilute acid HCl (10 %) in order to remove the excess of dehydrating agents and the fine fraction of soluble ash in water, then washing with distilled water to eliminate all the residual mineral and organic matter. The goal washing with distilled water is total elimination most of the residues from used activating agents. The finalization of washing in the distilled water ends once the conductivity measurements are minimal and become stable. Activated carbon is dried at the temperature of 105 °C for 48 h. The product is crushed with a grinder and sieved to a uniform and particle size lower of 30 μm and stored in tightly sealed bottles.

Physical and chemical characterization method of the adsorbent. Chemical and physical characterization of activated carbon made from olive pomace (ACOP) was realized by several methods, namely:

1. X-ray diffraction (XRD) was analyzed employing the Cu-Kα radiation source (X'Pert MPD PANalytical diffractometer) with λ = 0.15418 nm in the 2θ range 5–80° with a step size 0.025° and accounting time of 10 s [13].

2. For the determination of the sample chemical composition, analysis of fluorescence X (Philips Magix Pro PW-2440) was done.

3. ACOP morphology and microstructure were examined by scanning electron microscopy (high-resolution scanning electron microscopy using JEOL SM 840 operating at 20 kV) [14].

4. To get details on the chemical bond's structure of ACOP, an identification of the functional groups was performed by FTIR (Shimadzu 8400 spectrophotometer in the range of 400–4000 cm^{-1}).

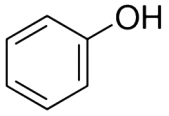


Fig. 1. Chemical structure of phenol

Adsorption experiments. Preliminary experiments carried out as part of the parametric study have identified the main factors influencing the elimination of phenol using CAOP. Among the parameters investigated in the process optimization are the following: adsorbent mass, contact time, the initial phenol concentration, and stirring speed. The other parameters were held with the following values: room temperature of 25 °C, the pH of the solution bet between (7–9). The amount of phenol adsorbed (q_e, mg · g^{-1}), and the phenol elimination yield (removal efficiency) was calculated using equation, in which the phenol removed is the phenol percentage that is absorbed by activated carbon in the aqueous solution.

$$R = \frac{C_0 - C_e}{C_0} \cdot 100;$$

$$q_e = \frac{(C_0 - C_e) \cdot V}{W},$$

where C_0 is the phenol initial concentration; C_e is the equilibrium concentration of the phenol (mg/L). V is the volume of the solution with L, and W is the activated carbon mass used (g).

Experimental design. The effect of adsorbent mass, contact time, phenol initial concentration and stirring speed as an input variable on the phenol removal efficiency as a response were studied. The experimental position of the variables of input was obtained from the design constituted by the methodology of the central composite design (CCD). Experimental design, data guidance, and statistical analysis were performed using the MINITAB software. The predefined value of the input variables was achieved from the actual value in applying the equation

$$x_i = \left(\frac{X_i - \bar{X}}{\frac{\Delta X}{2}} \right), \quad (3)$$

where x_i is the coded value (dimensionless) of x_i variable. $\bar{x}$ and Δx are the mean and the fork of X_i, respectively. The independent variable values coded and actual and their fork are illustrated in Table 1.

The full factorial design method was used to investigate the influence of experimental parameters in the yield of phenol adsorption on ACOP. The full factorial design was implemented to achieve the effect of four factors using an independent variable. To estimate the magnitude of the model, 95 % of the confidence interval (p_value ≤ 0.05) was used. The levels for each parameter are provided in Table 1.

Response surface methodology (RSM) Analysis. RSM is established by the calculation method by which the experiment analysis, modeling, and optimization are taken. The RSM was used to investigate the optimal adsorption condition and the effect of different adsorption factors on the adsorption capacity, was used to examine the interactive effect of study adsorption factors. In the RSM statistical model, a response (y) is given by a number of influential variables ($x_1, x_2, ..., x_n$). Response (capacity of adsorption process) was used to build a model using a quadratic model

Table 1

The values of actual and coded for the experimental design factors

Factors	Unit	Symbol	Levels				
			–2	–1	0	+1	+2
Adsorbent mass	g	x_1	0.2	0.4	0.6	0.8	1.0
Contact time	min	x_2	30	60	90	120	150
Phenol concentration	mg/L	x_3	40	80	120	160	200
Stirring speed	rpm	x_4	200	350	500	650	800

or second-order polynomial equation (considering the relation existed between the response and the input variables with first degree, and interactive impacts between variables), which offers the correlation between the response adsorption process input variables. The response model is described using the equation

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{1 \le i \le j}^{k} \beta_{ij} x_i x_j + \varepsilon,$$

where k is the number of all model variables, the coefficient β_0 is the number of constant. The coefficients β_i, β_{ii}, β_{ij} are respectively the linear, quadratic, and interaction, ε is an error related to the experiments. With the object of study is of concordance of RSM model and ANOVA test.

***Analysis of variance* (*ANOVA*).** The variance analysis (ANOVA) was carried out to determine the optimum model by analyzing the effects of the main factors: adsorbent mass, contact time, initial phenol concentration, and stirring speed. To determine the best possible combinations of the four factors, which leads to find the best phenol removal efficiency, numerical optimization was used. The suggested solution of the numerical optimization method with high desirability was validated and confirmed the results in the laboratory using actual runs.

The significant factors were determined in the results analysis using a significance level of 0.05. The factor effect on phenol removal was realized and illustrated using contour and 3D plots affected by Minitab software.

Results and discussion. ***Physical and chemical characterization of ACOP*.** The chemical composition results of ACOP are shown in Table 2, we see that our adsorbent contains a major element which is carbon (26.9 %), followed by secondary elements like (Na, Mg, Al, Si, P, S, Cl, K, Ca and Fe), and other trace elements (Cu, Zn, Rb and Sr). Plant waste is essentially made up of cellulose, hemicellulose and lignin, their main elements are: carbon, oxygen, nitrogen and hydrogen [15].

Fig. 2, a illustrates the X-ray diffractograms of ACOP. The results show the presence of a typical amorphous carbon observed at positions 2θ 20,86 and 43,41, these peaks correspond to planes (002) and (100), respectively, and these are graphite-like reflections that indicate the arrangement of graphite on the molecular planes [16]. The results of the analysis show no presence of the activating agents used in chemical activation were identified in X-ray diffraction analysis, which means that the acid cleaning step followed by washing with distilled water is very effective in eliminating any residual material that is found on the outer grain surface of the carbonized material.

FTIR spectrum for the ACOP is present in Fig. 2, *b*. One could deduce from this that the FTIR spectrum had similar bands. We see that there is a strong peak observed at 3353.77 cm^{-1} attributed to O—H stretching which represents the hydroxyl groups. A pronounced bond observed in 2922.51 cm^{-1} attributed to =C—H stretching of aldehyde group and another peak observed at 2852.40 cm^{-1} assigned to C—C stretching of aliphatic (C—C of CH_2 and CH_3). The peaks observed in the absorption bands 1710.17, 1662.72 and 1447.45 cm^{-1} were attributed to groups: aldehyde (C=O), Alkene (C=C), and aromatic (C=C), respectively. In addition, the elongation located between 1000 and 1250 cm^{-1} is attributed to the bond C—O of oxidized carbons for the following compounds: ester, alcohols, acids, phenols, and ethers. Furthermore, the peaks observed at 755.59 cm^{-1} are related to the aromatic groups' deformation δ_{C-H}. Infrared spectroscopy made it possible to obtain information on the ACOP chemical structure. The analysis revealed the presence of the compounds namely: hydroxyl, carboxyl, ethers, acids, and aromatic compounds suggest the lignocellulosic structure chemical properties of olive pomace.

The micrographics illustrated in Fig. 3 for ACOP present a high magnification that indicates modification and improvement in the grain form and surface as well as the repartition and dispersal of pores caused to use chemical and thermal activation of the olive pomace. The ACOP presented various surfaces on the grain and the appearance of multi-dimensional cavities. In addition, formation of an important number of pores which have various sizes and texture was noticed and well created, we also observed the presence of macropores and micropores. Pore size indicates randomness, and we can compare it to a sponge form. As a result, the solid pores were unobstructed, suggesting that it performed well as an adsorbent material.

***Experimental*.** The full factorial design was based with two levels and four factors, 2^4 experimental designs with 4 center points and experiments were conducted with three replicates, the matrix of experience is formed of 16 combinations of the four factors retained in our study. In total, sixteen experiments are included in this study to estimate the impact of the four main factors on the adsorption process efficiency.

The responses y_i, which are the adsorption capacities of the phenol adsorbed by the ACOP, were measured for the sixteen experimental points. For each test, a parameter is fixed at one of the extremes, and the other three are adjusted to their maximum or minimum levels, for all possible combinations. For each test point, three repetitions were carried out in order to guarantee the applicability of the results. The matrix of the experimental design is gathered in Table 3.

***Determination of the model equation*.** The aim of our modeling is to calculate the impact of all the factors on the efficiency of the adsorption process, in order to find a relationship between these four parameters and the adsorption capacity of phenol. The mathematical model associated with the full factorial design 2^4 is written in the following form

$$\hat{y} = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \\ + \beta_{14} x_1 x_4 + \beta_{23} x_2 x_3 + \beta_{24} x_2 x_4 + \beta_{34} x_3 x_4 + \beta_{123} x_1 x_2 x_3 + \\ + \beta_{124} x_1 x_2 x_4 + \beta_{134} x_1 x_3 x_4 + \beta_{234} x_2 x_3 x_4 + \beta_{1234} x_1 x_2 x_3 x_4.$$

With $\hat{y}$ being the estimated response, the following variables x_1, x_2, x_3 and x_4 are the reduced centered ones corresponding respectively to the real variables Z_1, Z_2, Z_3 and Z_4. β_0 is the mean value of the response; β_{12}, β_{13}, β_{14}, β_{23}, β_{24}, β_{34} are the dual interaction effects; β_{123}, β_{124}, β_{234} are the triple interaction effects; β_{1234} is the quadratic interaction effect.

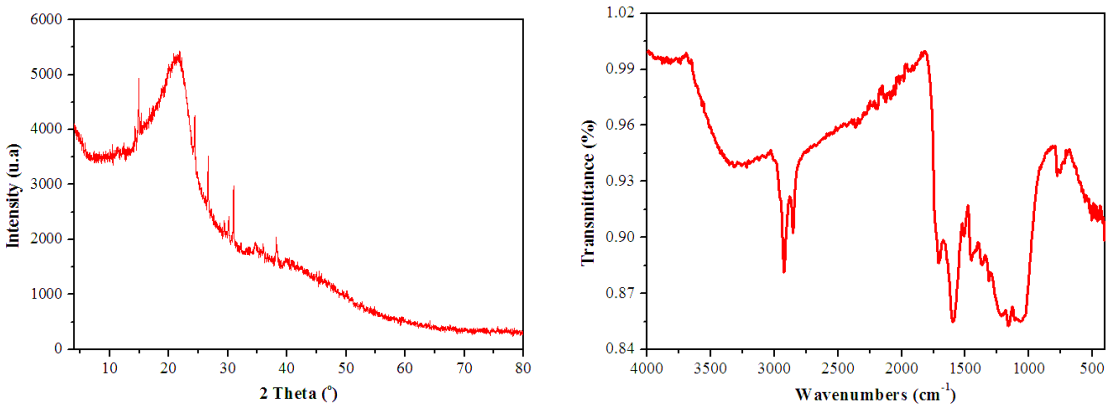
The goal of our modeling was to calculate the impact of all factors on efficiency, a way to capture the empirical relationship between the four main parameters and the yield of the phenol elimination by adsorption process. The values of the coefficients of the regression equation are determined by the matrix product: $(x^T x)^{-1} x^T y$. Equation is the realized model equation which is represented as follows

$$\hat{y} = 86.74 - 31.45 x_1 + 1.75 x_2 + 59.46 x_3 - 1.68 x_4 + 0.35 x_1 x_2 - \\ - 22.47 x_1 x_3 + 0.47 x_1 x_4 + 1.76 x_2 x_3 - 1.75 x_2 x_4 - 0.15 x_3 x_4 - \\ - 0.74 x_1 x_2 x_3 + 0.86 x_1 x_2 x_4 + 0.46 x_1 x_3 x_4 - 0.76 x_2 x_3 x_4 + \\ + 0.62 x_1 x_2 x_3 x_4.$$

Table 2

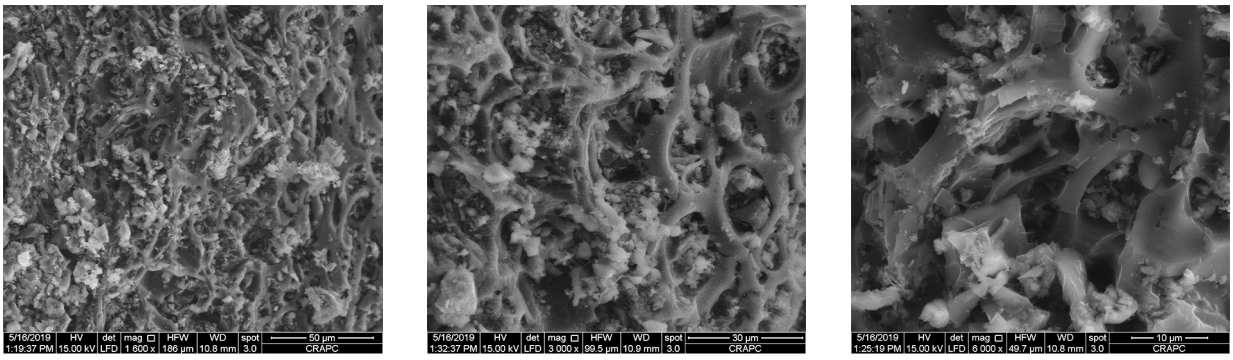
Chemical composition of olive pomace activated carbon

Element	C	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	Cu	Zn	Rb	Sr
Mass composition (%)	26.900	0.0205	0.0351	0.0168	0.0378	0.0409	0.0697	0.0610	0.4560	0.2350	0.0107	0.0005	0.0005	0.0002	0.0014



a *b*

Fig. 2. Characterization of ACOP:
a – X-ray diffractogram; b – FTIR vibrational spectrum



a *b* *c*

Fig. 3. SEM micrograph of olive pomace activated carbon:
a – enlargement of 1600; b – enlargement 3000; c – enlargement of 6000

The previous equation indicates that the following four parameters: absorbent mass, contact time, initial phenol concentration and stirring speed have both positive and negative effects on the response. This refers to the fact that the regression coefficients, which are associated with them, some are positive, while others are negative. A positive value is indicative of an effect favoring optimization, while a negative value is indicative of the reversal of the relationship between the factor and response.

Table 3

Experimental design matrix with corresponding responses

Test	x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_m
1	–1	–1	–1	–1	58.87	57.12	58.37	58.12
2	+1	–1	–1	–1	15.12	15.08	15.49	15.23
3	–1	+1	–1	–1	51.76	51.81	52.54	52.04
4	+1	+1	–1	–1	79.13	79.58	80.05	79.59
5	–1	–1	+1	–1	81.89	81.45	81.68	81.67
6	+1	–1	+1	–1	38.38	38.42	39.56	38.79
7	–1	+1	+1	–1	46.49	46.81	47.46	46.92
8	+1	+1	+1	–1	80.71	80.28	89.53	80.17
9	–1	–1	–1	+1	81.13	81.02	82.24	81.46
10	+1	–1	–1	+1	11.78	11.10	12.24	11.71
11	–1	+1	–1	+1	22.47	22.41	21.60	22.16
12	+1	+1	–1	+1	33.19	33.74	33.26	33.40
13	–1	–1	+1	+1	86.69	86.47	87.18	86.78
14	+1	–1	+1	+1	84.54	84.76	84.04	84.45
15	–1	+1	+1	+1	73.48	73.14	73.80	73.47
16	+1	+1	+1	+1	12.43	12.69	13.72	12.95

Residual analysis. The distribution of the model residuals compared to the experimental values is represented by the graphs grouped in the following Figures:

Fig. 4, *a* (Normal probability plot) shows that the values of the residues found by subtracting the calculated values with that of the experiment are divided around a straight line, which proves that the obtained values are symmetric and that there are no outliers.

Fig. 4, *b* shows the plot of residues as a function of the quantity adsorbed, does not reveal any relationship between the predicted values and the residues; the dots appear randomly arranged. It indicates that the variances are constant being no outliers.

Fig. 4, *c* represented residuals as a function of the order of observations, the residuals seem to be scattered randomly around zero, and there is no correlation between the errors.

Fig. 4, *d* illustrated the histogram of the distribution of errors which represents another form of analysis compared to the previous figures; these errors are distributed in a random manner and are distributed according to the Gaussian form.

The method of validation of the developed model was analyzed by calculation of residuals (calculated subtraction of the difference of the predicted and experimental values). Determined residues by software are considered incomprehensible parameters of the elaborated model, and the residuals are expected to follow a distribution that favors the distribution of the normal law [17]. The phenol removal plot is calculated in comparison to residual values (Fig. 4, *d*), all plotted values are correct with no outlier values among them, all the plotted points are placed in the interval of +1 to –1, this result suggests that the model developed shows a small difference between the values calculated by the model and those given by the experiment.

The factors effect and their interactions on the response. The factors effects on the response. Based on experimental results of the full factorial design (results in Table 3), establishment of a mathematical model that gives the relationship between the response and the various factors in the form of a quadratic polynomial. The equation is formulated by the model response made in (1). The interaction effect of the studied parameters on the adsorption efficiency.

According to this equation, we can deduce that the four factors studied have positive and negative effects with respect to the response, since among the regression coefficients associated with them there are some positive and some negative. The positive value of the coefficient signifies an effect which improves the response crosswise, contrary to the negative value which affirms the fact that the coefficient gives an effect which decreases the response.

Study on the interaction effects of factors. To study the combined interaction of two factors on the response, the responses of the two levels (low and high) of each factor are determined; if these responses vary inversely, then the interaction is effective of the same levels of the second factor, that is to say when the two lines are not parallel [17]. Fig. 5 illustrates the plots of the interactions of each of the two factors on the response. It is noteworthy that there is an important interaction effect between the adsorbent mass and the three other factors as well as between the phenol initial concentration with both contact time and stirring speed factors. However, the interaction among contact time and stirring speed was not effective. The effect of interactions relates to the combined influence of the four factors in the response. Some interactions have a positive effect, while others negatively affect the course of the adsorption process.

The coefficients β_1, β_2, β_3 and β_4 (the effects of the factors) with positive signs, have their factors varying in an increasing direction with the response, thus marking a positive slope. Conversely, the coefficients with negative signs have the factor oriented in the decreasing direction with the response, hence they feature negative slope.

The coefficients with positive signs β_{12}, β_{13}, β_{14}, β_{23}, β_{24} and β_{34} (the double interaction effects on the response), form a case where each pair of factors is oriented in the same direction, thus excluding the possibility of crossing of the two straight lines. Conversely, coefficients with negative signs display factors varying opposite directions, letting their respective lines intersection. We can effectively say that the data in Fig. 5 confirm the results.

Statistical analysis. Confirmation of experimental design. Statistical calculations that indicate the significance of the effects, calculate the confidence intervals or confirm the linearity of the implicated model on the one hand the residuals ei, In other words, the difference between the investigational value and the model's intended value. The results of the comparison of the average responses given by the experiment with those given by the model are shown in Table 4.

The trace of the predicted responses as a function of the experimental responses, we notice a strong linearity between the values, the latter are characterized by correlation coefficients R^2, which is equal to 1. This indicates that the model perfectly simulates the considered phenomenon.

Contour curves. The model equation allowed us to plot contour curves to better see the impact of various parameters on the percent adsorbed phenol. The contour curves are grouped together in Fig. 6.

1. The contour curve (speed-mass) shows that the best phenol adsorption efficiency is obtained when working with speeds between 200–300 rpm and with a mass of activated carbon close to 1 g.

2. The contour curve (speed-time) shows that the phenol adsorption efficiency is obtained when working with stirring speeds between 200–450 rpm and residence times between 90–120 min.

3. The contour curve (concentration-mass): it is noted that the best phenol adsorption efficiency is obtained at a phenol concentration close to 80 mg/l and a mass of activated carbon close to 0.8 g.

4. The contour curve (concentration-speed): we note that the best phenol adsorption efficiency is obtained at phenol concentrations between 85–108 mg/l and a stirring speed close to 400 rpm.

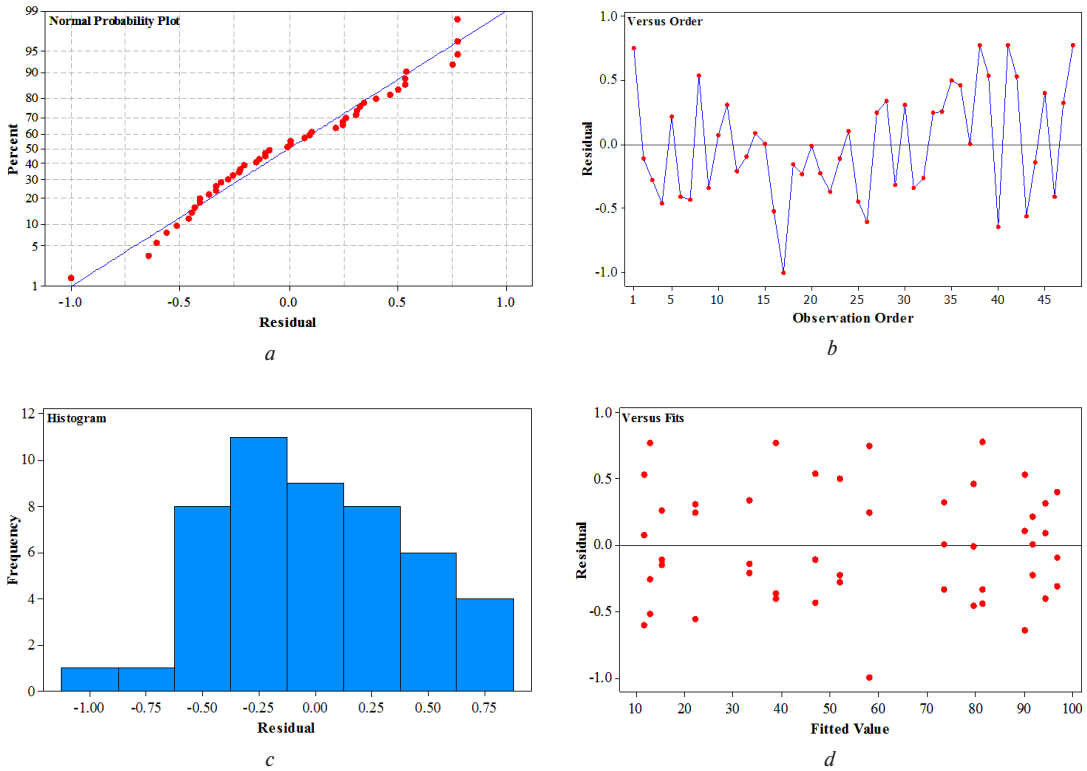


Fig. 4. Residual analysis:

a – Normal probability plot; b – Versus order; c – Histogram; d –Versus fits

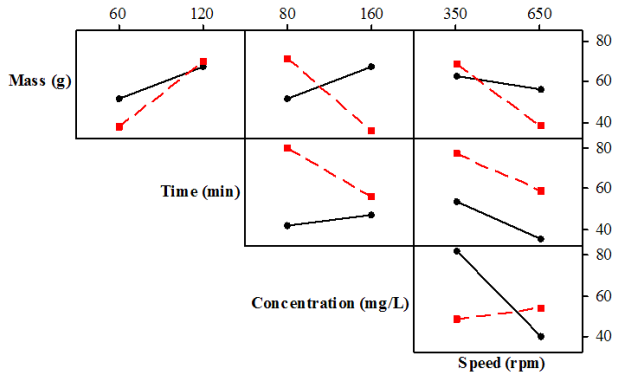


Fig. 5. Interaction effects as the percentage of phenol removal

5. The contour curve (time-mass), we note that the best adsorbed quantities of phenol are obtained at a residence time close to 120 min and a mass of activated carbon close to 0.8 g.

6. The contour curve (time-concentration): we note that the best phenol adsorption efficiency is obtained at a contact time close to 115 min and a phenol concentration close to 90 mg/l.

Response surface. Table 5 represents the responses of the 31 tests for phenol adsorption by ACOP, with the aim of tracing the curves of the response surface and the iso-response curves.

It can be said that the response surfaces are three-dimensional graphs, the horizontality of the figure materializes the domain of change in two parameters; on the other hand, the secondary axis implement the model's response. Over and above of two factors, the factors whose variations are not depicted in the horizontal plane must be maintained at a constant level.

The experimental range designed has been determined from combined tests of the factors studied, the model graphical analysis consists in restoring the equation of the latter in the form of response surfaces in a three-axis reference, and to follow the effect of the variation of two parameters simultaneously on the response, while keeping the third and fourth factor in its minimum, average and maximum values.

It is possible to project the surface in the horizontal plane in order to obtain iso-response curves; this gives us another vision of analysis from another angle, which makes it possible to complete the response surfaces. They are interpreted as

Table 4

Comparison between the means given by the experiment with those given by the model

Test	Experimental Response	Predicted responses	Residues e_i
1	58.12	57.34	00.78
2	15.23	16.12	–00.89
3	52.04	50.44	01.60
4	79.59	80.48	–00.89
5	81.67	81.95	–00.28
6	38.79	37.80	00.99
7	46.92	48.12	–01.20
8	80.17	79.14	01.03
9	81.46	82.12	–00.66
10	11.71	10.18	01.53
11	22.16	22.61	–00.45
12	33.40	34.21	–00.81
13	86.78	85.96	00.82
14	84.45	83.66	00.79
15	73.47	74.87	–01.40
16	12.95	12.59	00.36

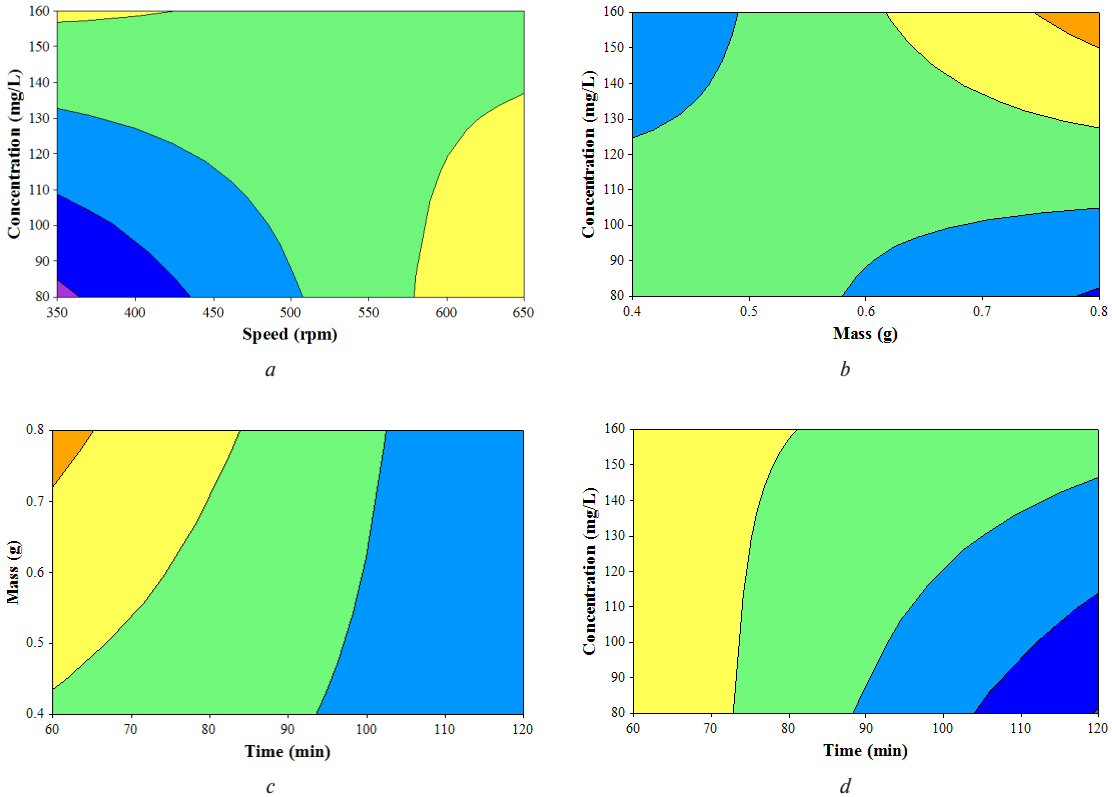


Fig. 6. Contour plots of the phenol adsorption efficiency according to the variables:

a – contour curve (*speed-concentration*); *b – contour curve* (*mass-concentration*); *c – contour curve* (*time-concentration*); *d – contour curve* (*time-mass*)

contour lines, drawn on a topographic map. Just like for the response surfaces, there are only two factors involved in the representation, the rest should be set at a constant level.

Iso-response curve analysis. The model equation allowed us to plot the iso-response curves (Fig. 8) to better see the impact of different factors on adsorption yield. The graphical representation of the pre-established model, in the space of variables, makes it possible to obtain iso-response curves. These allow us to visualize the response according to the various synthesis parameters. Their analysis underscoring the factors impact on the response and likewise makes it possible to determine an optimal region where the adsorption efficiency is optimal. The iso-response curves make it possible to identify the range of optimal variation of the studied factors.

Desirability. The study on the main effects and on interaction allows us to distinguish the influence separated or not of the four investigation factors on the response amplitude, that is to say, to evaluate each effect in absolute terms, or in the abstraction of other influences. Once the responses are modeled, we can find the optimal composition that corresponds to the highest adsorption efficiency. The result was found using the Minitab software.

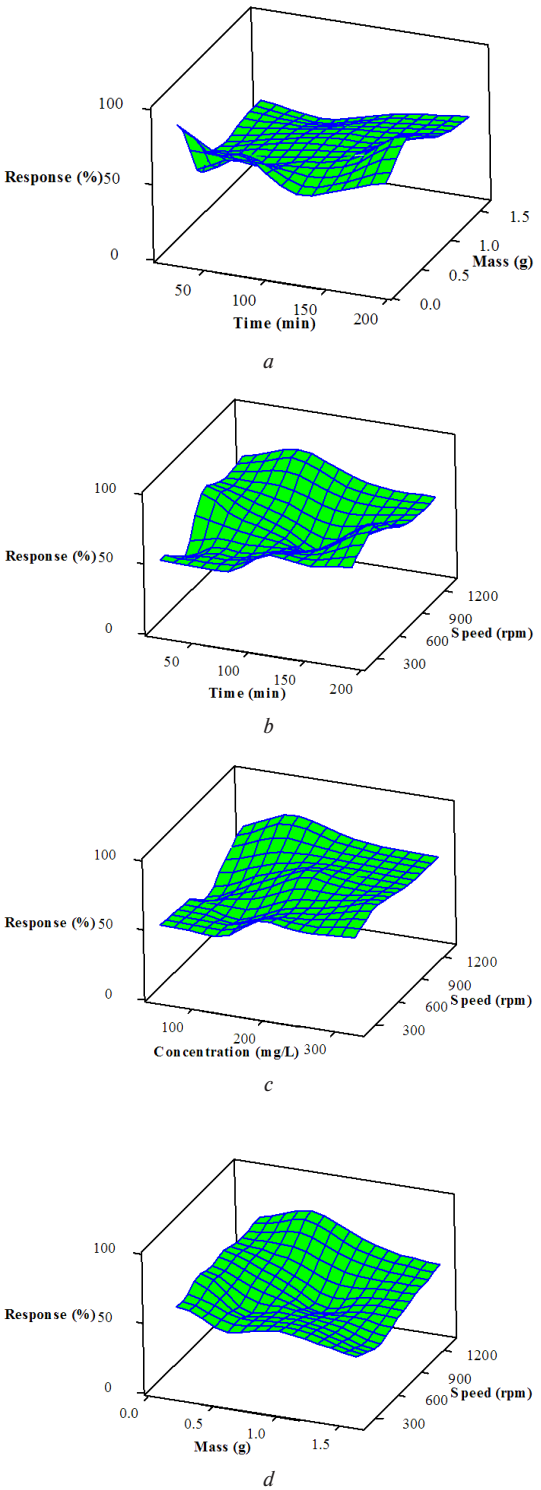
Table 5

Results of the response surface matrix

Test	x_1	x_2	x_3	x_4	y
1	0	0	+2	0	71.58
2	–1	–1	+1	–1	81.67
3	+2	0	0	0	38.49
4	+1	–1	–1	–1	15.23
5	0	0	0	+2	77.03
6	0	0	0	0	32.66
7	–1	+1	+1	+1	73.47
8	–1	–1	–1	–1	58.12
9	0	+2	0	0	81.18
10	0	0	0	0	75.94
11	–2	0	0	0	69.38
12	+1	+1	+1	–1	80.17
13	0	0	0	0	31.99
14	0	0	0	–2	49.56
15	+1	+1	–1	+1	33.40
16	0	0	0	0	32.42
17	–1	–1	+1	+1	86.78
18	0	–2	0	0	35.36
19	0	0	–2	0	49.65
20	+1	+1	–1	–1	79.59
21	0	0	0	0	31.86
22	–1	+1	+1	–1	46.92
23	0	0	0	0	32.07
24	+1	–1	–1	+1	11.71
25	+1	+1	+1	+1	12.95
26	–1	+1	–1	+1	22.16
27	+1	–1	+1	+1	84.45
28	–1	+1	–1	–1	52.04
29	0	0	0	0	32.11
30	+1	–1	+1	–1	38.79
31	–1	–1	–1	+1	81.46

For an overall desirability of 99.998 %; the following optimal composition is obtained: adsorbent mass (g), contact time (min), phenol initial concentration (g/L) and stirring speed (rpm).

Similar of phenol removal from activated carbon. The phenol removal efficiency by adsorption onto ACOP in the best conditions of the parameters was 91 %. In the works already carried out, which are found in the bibliography, the phenol removal was obtained from 87.6 % on tobacco residue activated carbon [18]; an adsorption efficiency of 95.31 % – when



a

b

c

d

Fig. 7. Response surface plots of the phenol adsorption efficiency according to the factors:

a – response surface curve (mass-time); b – response surface curve (speed-time); c – response surface curve (speed-concentration); d – response surface curve (speed-mass)

treated with activated carbon prepared using seaweed [19], a yield is between 79 and 98 % – if adsorbed on African beech sawdust activated carbons [20], and the percentage of 85 % – using activated carbon made from Rhazya stricta [17].

Conclusions. This study deals, on the one hand, with the valorization of an agricultural waste which is olive pomace in the manufacture of activated carbon at a lower cost. The latter was characterized textually, morphologically, structurally and thermally. On the other hand, it focuses on utilization of activated carbon development in the treatment of wastewater contaminated with phenolic compounds by the adsorption process.

The results of the characterization of various physical-chemical analysis methods (FTIR, DRX, FRX, SEM), show that the Fourier transform infrared spectroscopy indicates the presence of the functional groups which characterize an organic matter; the diffraction analysis X-rays show that the activated carbon has an amorphous structure; X-ray fluorescence analysis shows that carbon is the major element; scanning microscopic analysis shows the presence of a porous structure.

With this aim, we carried out a systematic study on the impact of the main factors affecting the efficiency of the phenol adsorption, in a batch reactor, on elaborated activated carbon. The optimized parameters are: the adsorbent mass, the contact time, the initial concentration of phenol, and the stirring speed.

The study on the variation of the adsorption parameters and their interaction effects allows us to distinguish the separate influence or not of the four factors studied on the amplitude of the response, that is to say, to evaluate each effect in absolute terms, or in abstraction of other influences. After modeling the response using the design of experiment method, the optimum composition corresponding to the highest adsorption efficiency was determined.

The modeling of the phenol adsorption process of olive pomace activated carbon by the full factorial design method of experiments with two levels and four parameters makes it possible to achieve a quadratic model with interactions. The response surface method made it possible to optimize the quantity of phenol adsorbed by acting on the operating conditions.

The investigation of the impact of the various parameters studied demonstrates that the phenol adsorption is more favorable for the following optimal composition: $m = 0.48$ g, $t = 110.80$ min, $C = 100.98$ mg/L and $V = 462.89$ rpm. The result of the validation of the experiment carried out with the optimal composition obtained from the response surface, confirms to us that elaboration of the model in the adsorption of phenol on activated carbon is valid.

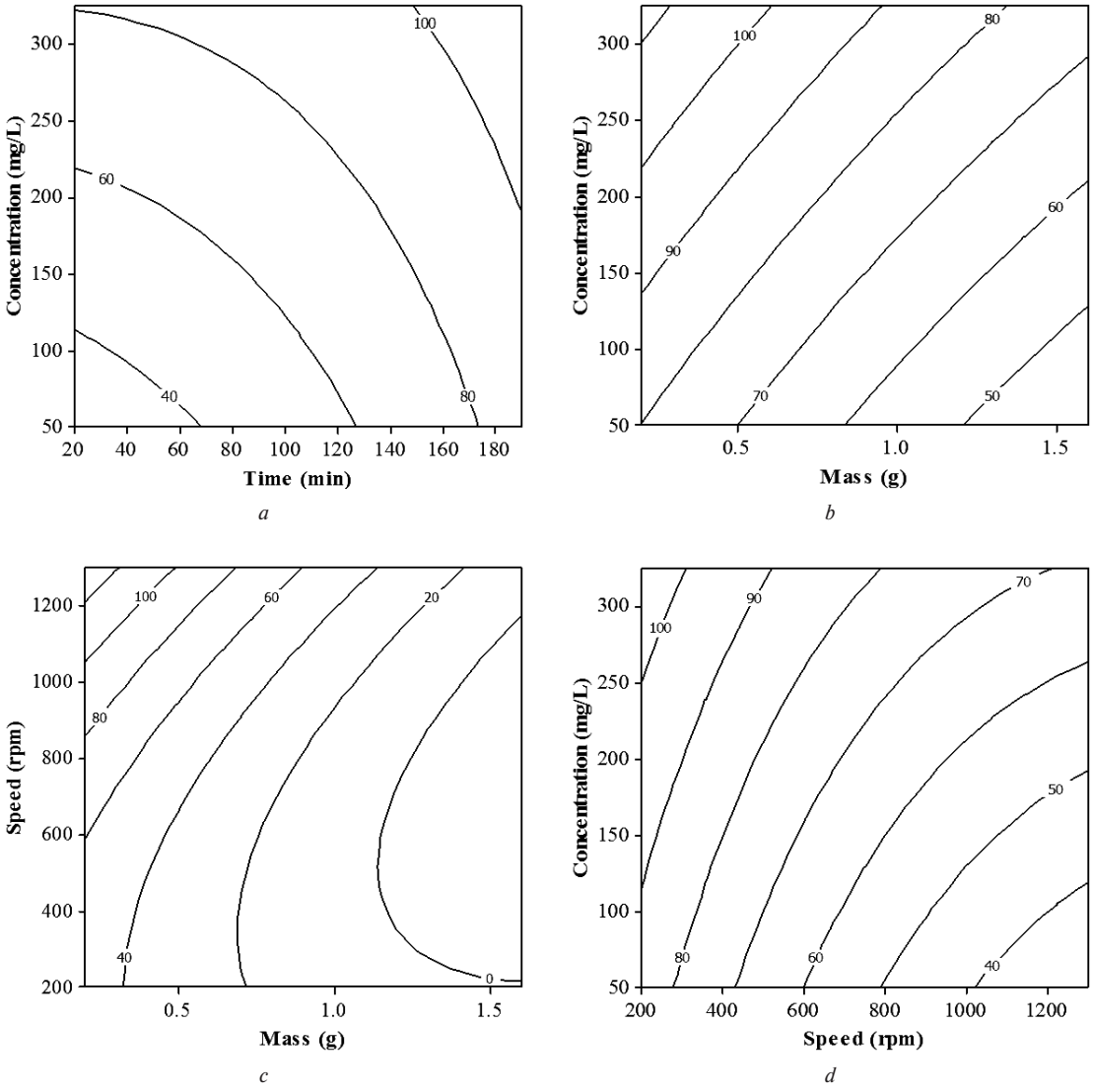


Fig. 8. Iso-response plots of the phenol adsorption efficiency according to the factors studied:

a – iso-response curve (*time-concentration*); *b – iso-response curve* (*mass-concentration*); *c – iso-response curve* (*mass-speed*); *d – iso-response curve* (*speed-concentration*)

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Адсорбція фенолу активованим вугіллям з оливкових вичавків: моделювання та оптимізація

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Мета. Очищення води, забрудненої фенолом, за допомогою процесу адсорбції в реакторі періодичної дії з валоризацією оливкових вичавків для приготування активованого вугілля задля подальшого використання як адсорбент.

Методика. У цій роботі вивчався вплив чотирьох основних параметрів на результат адсорбції при очищенні забрудненої води за допомогою цього процесу, а саме: маси активованого вугілля, часу контакту, початкової концентрації фенолу та швидкості перемішування. Крім того, процес був оптимізований за допомогою факторного аналізу із застосуванням методики поверхні відгуку програмного забезпечення MINITAB.

Результати. Адсорбція фенолу на активованому вугіллі з оливкових вичавків дозволяє досягти ефективності адсорбції 91 % за таких оптимальних умов: маса адсорбенту – 0,48 г, час контакту – 110,80 хв, концентрація фенолу – 100,98 мг/л та швидкість перемішування – 462,89 об/хв. Час контакту й маса адсорбенту позитивно впливають на ефективність видалення фенолу. Основні результати впливу показують, що всі чотири досліджені фактори значно вплинули на видалення фенолу активованим вугіллям з оливкових вичавків зі ступенем достовірності 95 %.

Наукова новизна. Експериментальні дані з адсорбції фенолу активованим вугіллям з оливкових вичавків досліджували шляхом побудови поліноміальної моделі другого ступеня. Ця модель перевіряється статистичним методом із використанням дисперсійного аналізу (ANOVA). З метою визначення оптимальних параметрів для максимального вилучення фенолу була виконана чисельна оптимізація за допомогою функції бажаності.

Практична значимість. Щоб висвітлити процес очищення води, забрудненої фенолом, ми вибрали процеси, які вважаємо найбільш підходящими, а саме адсорбцію з відновленням відходів, таких як адсорбент, що отримують шляхом фізичної та хімічної активації оливкових вичавків. Повний факторний аналіз, що застосовується, дозволяє показати індивідуально вплив кожного параметра та їх залежності, а також швидко знайти оптимальні експериментальні умови, які призводять до реалізації цього процесу.

Ключові слова: *адсорбція, фенол, оливкові вичавки, активоване вугілля*

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