Environmental Engineering and Management Journal
June 2021, Vol. 20, No. 6, 985-994
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

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TREATMENT OF ORGANIC POLLUTED WATER BY SPENT COFFEE GROUNDS IN THE CONTEXT OF INTEGRATED WASTE MANAGEMENT IN ALGERIA

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Abstract

This paper presents the feasibility of phenol removal from aqueous solutions by using microwaves activated spent coffee grounds. The activation of the coffee grounds made it possible to increase with 75% the quantity eliminated compared to the not activated coffee grounds. The results showed that the adsorption process was favourably fitted with the pseudo-second order kinetic model and the isotherm obeys to Langmuir model. The maximum amount of phenol adsorbed (7.35 mg/g) for optimal conditions was determined using an experimental factorial design 2^3.

Keywords: adsorption, factorial design, microwaves activation, phenol, spent coffee grounds

Received: June, 2020; Revised final: September, 2020; Accepted: October, 2020; Published in final edited form: June, 2021

1. Introduction

Water pollution has become a major problem and a major concern since it is a source of environmental degradation and phenol is recognized as a hazardous pollutant even at low concentration due to its toxicity and carcinogenicity properties (Ahmadi and Igwegbe, 2018). The ingestion of contaminated water can be the cause of the protein degeneration, the paralysis of central system nervous, and also damages the kidney, liver, and pancreas (Gardziella et al., 2000). It is worth mentioning that the permissible limit of phenol in water discharges is 0.1 mg/L (Galicia-Aguilar et al., 2017; USEPA, 1985).

This context has leaded the authorities to the imposition of severe restrictions against this pollution, which has required the development of an effective treatment technology in this field. Currently, a large number of wastewater treatment techniques, domestic or industrial, are used. They differ from each other and include, for example, adsorption, electrolysis, solubilization, flotation, precipitation, ions exchanges, liquid-liquid extraction, etc.

Among these techniques, the adsorption on which this study is based has shown great wastewater treatment capacities. It is also very simple and efficient for the removal of organic pollution. However, its effectiveness highly depends on of the nature of the carrier used as an adsorbent, particularly with respect to its cost, its availability and regeneration (Húmpola et al., 2013; Namane et al., 2005). For emerging countries, activated carbons are expensive materials. The solutions to work around this problem are to use a local adsorbent, at low cost and requiring only an investment within the reach of all. An increasing demand exists in this direction moving towards the available carbonaceous waste, being able to present real capacities of adsorption and not requiring complex treatments (Kehili et al., 2019; Kumar and Jena, 2016).

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The challenge of society is the management of residual materials generated by the consumption of raw materials. In a framework of sustainable development, Algeria has opted for a policy of organic waste management. In order to meet this objective, the transition to a circular economy is essential. Therefore, the materials must no longer be considered as waste, but as reusable materials. Overview World coffee production for 2019/20 is forecast to 10 million Tons (FAS, 2019). With more than 135.000 tons, of consumed coffee, Algeria is the leading consumer in Africa (ICO, 2020).

The coffee ground by its carbonaceous characteristics can be used eventually as an adsorbent. The management, recovering and upgrading of this solid waste quantity, which pollutes the soil, water and air, is not easy. But if done, this will have significant environmental and socio-economic benefits. Other carbonaceous wastes that are usually applied (after their conversion in activated carbons) are: the coffee grounds (Namane et al., 2005), the sawdust (Abdel-Ghani et al., 2016), the olive stones (Bohli et al., 2013), the tea waste (Girish et al., 2017).

In this context, the general objective of this work is to evaluate the relevance of specifically recovering coffee grounds and reusing them in the treatment of polluted water. Actually, we considered the elimination of phenol by coffee grounds recovered for different operating conditions of activation. The results obtained were exploited and modelled. A full 2^3 factorial design was carried out to investigate the individual and interactive effects of three operating parameters which may affect the adsorption of phenol onto coffee grounds. Several researchers use this method of exploiting experimental results to find mathematical correlations between different operating parameters (Ouriache et al., 2019; Tebbouche et al., 2015).

2. Material and methods

2.1. Adsorbents preparation and characterization

The spent Robusta coffee grounds studied are collected in the cafeterias. These residues were washed, boiled and purified in distilled water to remove dust, impurities and the water-soluble substance. Then, the resulting residues noted **NAA** (Non-activated adsorbent)) are dried at 105°C for 24 h in an oven. The previous residue was treated by activation in a microwave oven at different powers (180, 300 and 450 Watt) and different activation time (1, 2 and 3 minutes). The adsorbent obtained noted **AA** (activated adsorbent) was experimented in the removal of phenol from aqueous solutions.

2.2. Adsorbate-analysis of phenol

Phenol purchased from USA with purity greater than 99.5% was chosen in this study as a model organic molecule. The concentration of phenol was determined by spectrophotometric method using amino-4-antipyrine (Namane et al., 2014). The absorbance was read at a 510 nm wavelength using Shimadzu UVmini-1240 spectrophotometer.

Prior to analysis, the residual concentration of phenol, the calibration curve between absorbance and the concentration of the phenol solution was established.

2.3. Phenol adsorption experiments

The adsorption of phenol on coffee grounds was performed using batch method. A mass of adsorbent was introduced into 250 ml flasks Erlenmeyer, each of them containing 50 ml of phenol solution. The flasks were placed in a shaker (Fisher Bieblock Scientific) at 150 rpm and 25◦C. The carried-out samples at quite time intervals were filtered through filter paper and analyzed.

Phenol uptake at equilibrium, Q_e (mg/g), was calculated by Eq. (1) (Rushdi et al., 2011):

$$Q_e = (C_0 - C_e).V/m \tag{1}$$

when: C_0 and C_e (mg/L) are the concentrations of phenol at initial and at equilibrium, respectively; V is the volume of the solution (L) and m is the mass of dry adsorbent used (g).

Adsorption experiments were carried out for different operating conditions. Kinetics and equilibrium data were treated and exploited in accordance to different models cited.

2.4. Kinetics and adsorption modeling

The knowledge of adsorption kinetics provides important information for designing batch adsorption systems (Prasanna et al., 2007).

The kinetic rate equations of the controlling mechanism of the adsorption process can be written as (Eq. 2) (Franca et al., 2009):

$$dQ/dt = k_n (Q_e - Q_t)^n \tag{2}$$

Validation of the experimental adsorption results was evaluated by a kinetic study (Al-Zaben and Mekhamer, 2013; Azouaou et al., 2010; Franca et al., 2009; Vimala and Grace, 2013).

In order to investigate the mechanism of sorption and potential rate controlling steps such as mass transport and chemical reaction processes, kinetic models have been used to test experimental data. These kinetic models included the pseudo-first order equation (PFO), the pseudo-second order equation (PSO), intraparticle diffusion and the Elovich equation.

- *Pseudo-first order* (PFO): it was assumed that the sorption speed at time t is proportional to the difference between the quantities adsorbed at equilibrium (Q_e), the quantity (Q_t) adsorbed at the time (t), and that the adsorption is reversible.

In other words, the adsorption kinetics is faster if the system is far from equilibrium. The temporal variation of the adsorbed quantity can be written by (Eq. 3) (Grigoraș et al., 2020):

$$dQ/dt = k_1(Q_e - Q_t) \quad \Rightarrow \quad Ln(Q_e - Q_t) = LnQ_e - k_1.t \qquad (3)$$

Q_e and Q_t (mg/g), t (min), respectively and k_1 is rate constant (L/min).

- *Pseudo-second order (PSO)*: This model suggests the existence of chemisorption, an electronic exchange between the adsorbate and the adsorbent for example. It is represented by the Eq. (4) (Azouaou et al., 2010; Vimala and Grace, 2013):

$$dQ/dt = k_2(Q_e - Q_t)^2 \quad \Rightarrow \quad t/Q_1 = 1/k_2Q_e^2 + t/Q_e \qquad (4)$$

where: K_2 (g/mg. min), is the constant of the pseudo-second-order rate; Q_t and Q_e were the same as depicted above for the pseudo-first-order kinetics model.

- *Intraparticle diffusion model*: the effect of diffusion as the rate-controlling step in the adsorption was evaluated according to intra-particle diffusion (Ali et al., 2016). The model was proposed by Weber and Morris (1963). It is represented by Eq. (5):

$$Q_t = k_{int}.t^{0,5} + L_i \qquad (5)$$

where: k_{int} is the rate constant (mg/g.min$^{1/2}$). The constant k_{int} is deduced from the slope of the linear part of the equation representing this model; L_i (mg/g) is a constant that gives an idea about the thickness of the boundary layer. A value of 1 close to zero indicates that diffusion is the only controlling step of the adsorption process.

- *Elovich's model* (Elovich and Larinov, 1962) is based on a kinetic development assuming that the adsorption sites increase exponentially with adsorption, which implies multi-layer adsorption; it is expressed by Eq. (6):

$$Q_t = 1/\beta \, Ln(\alpha\beta) + 1/\beta \, Lnt \qquad (6)$$

where*:* α is the initial rate (mg /g.min). Because (dQ_t/dt) approaches β when Q_t approaches zero, the parameter β is related to the extent of activation energy and surface coverage for chemisorptions (g/mg).

2.5. Adsorption isotherms

An adsorption isotherm is the variation of the amount of compound adsorbed on a solid as a function of its concentration in the fluid in contact, at a given temperature T (Foo and Hameed, 2010).

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose. The isotherms data were modeled by Langmuir (Kumar and Jena, 2016), Freundlich (Nimibofa et al., 2017) and Temkin (Dada et al., 2012) using different phenol concentrations ranging from 50 mg/L to 500 mg/L at room temperature and at a stirring speed of 150 rpm.

2.5.1. Langmuir

Langmuir isotherm, based on a theoretical model, assumes monolayer adsorption over an energetically and structurally homogeneous adsorbent surface. It does not take into account interactions between adsorbed molecules. The Langmuir equation may be written as (Eq. 7) (Nacu et al., 2019):

$$1/Q_e = 1/Q_{max}.K_L.C_e + 1/Q_{max} \qquad (7)$$

where: Q_e (mg/g) is the adsorption capacity at equilibrium, C_e (mg/L) is the sorbate equilibrium concentration, K_L (L/mg) is the Langmuir constant associated to energy of adsorption and Q_{max} (mg/g) denotes the theoretical monolayer adsorption capacity.

2.5.2. Freundlich

The Freundlich adsorption model is used in case of possible formation of more than one adsorption monolayer on the surface and the sites are heterogeneous with different fixation energies. Generally, the Freundlich isotherm is given by Eq. (8) (Dada et al., 2012):

$$Q_{eq} = K_F.C_e^{n_F} \qquad (8)$$

where: K_F and n_F are two coefficients whose meaning is not immediately accessible; K_F (mg/g) depends on the total number of adsorption sites and n_F is a function of the distribution of adsorption energies. The application of this formulation is done by taking the logarithm (Eq. 9):

$$LnQ_e = LnK_F + 1/n_F \, LnC_e \qquad (9)$$

2.5.3. Temkin

This isotherm contains an explicit factor (B_T) which gives information on the nature of adsorption. The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent adsorbate interactions (Luo et al., 2017).

Temkin model is given by Eq. (10):

$$Q_e = B_T.LnK_T + B_T.LnC_e \qquad (10)$$

where: B_T is the Temkin constant related to heat of adsorption (J/mol); K_T is the equilibrium binding constant (L/g) corresponding to the maximum binding energy.

2.6. The factorial design

The evolutions of the characteristic variables of the process, their interactions, and their influences on the studied quantities were formalized by the factorial design, a method which highlights the links between the result and the variables.

The factorial design of experiments was used to determine the main effect of phenol concentration, activation time and activation power, as well as the interaction effects between them to optimize and predict phenol adsorption process. The experiments were arranged according to a factorial design with three factors on two distinct levels 2^3.

3. Results and discussions

3.1. Effect of contact time on adsorption

In order to determine the equilibrium time, a kinetics adsorption of phenol was made by monitoring the residual concentration.

Kinetic experiments were performed by mixing 1 g of adsorbent with 50 mL of phenol solution (C_0= 300 mg/L). The suspensions were shaken for 2 h at 25◦C at 150 rpm. Samples were collected at fixed intervals every 10 minutes and analyzed. This experiment was carried out on the two adsorbents, namely non-activated and activated adsorbents. The results have been graphically represented in Fig. 1.

Fig. 1 shows relatively low phenol adsorption kinetics, and that the equilibrium time is practically the same for the two adsorbents. On the other hand, the quantity adsorbed has been improved by the activated adsorbent as compared to the non-activated one. As well, this experiment shows that activation by microwave has no effect on the equilibrium time. Following the results, the equilibrium time will be taken equal to 90 minutes. At this point, the adsorption capacity was in state of dynamic equilibrium with the amount of phenol adsorbed from the coffee grounds. Following the inconclusive results of the adsorption of phenol by coffee grounds, microwave activation was tested in order to improve the adsorbed quantity of phenol. Kinetics tests for different operating parameters were studied for this.

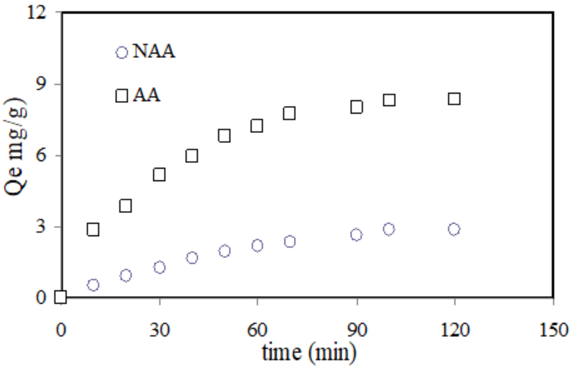


Fig. 1. Effect of contact time on the adsorption of phenol for the activated and non-activated adsorbents

3.2. Kinetics of adsorption

The adsorption process was investigated by fitting both first and second-order; intra-particle diffusion and Elovitch kinetics models to the experimental data. This study will provide valuable information on adsorption mechanism. The parameters of four kinetic models have been calculated and are presented in Table 1.

From the values found and independently of the graphs, the experimental data agree with both models (pseudo first and second order), the correlation coefficient is of the order of R^2 = 0.99. Both PSO and PFO do not explain the diffusion of solute into the adsorbent; therefore, before any conclusions are made about adsorption mechanism, other diffusion models should be investigated.

Intraparticle diffusion gives indications of the predominant steps in the adsorption mechanism unlike pseudo-diffusion. Generally, the pseudo-first-order model suggests a single-step adsorption mechanism, while the pseudo-second-order model suggests a multi-step adsorption. Intraparticle diffusion explains the different stages of the adsorption mechanism. The drawing of the Eq. (5) gives us indications on the predominant stage and if the value of intercept, obtained from the plot of data, depicts the resistance of the mass transfer in the boundary layer. The larger value, the greater is the boundary layer effect (Soto et al., 2017).

Table 1. Kinetic constants for phenol adsorption onto coffee grounds

Models		*Pseudo-first order*			*Pseudo-second order*				*Intraparticle diffusion*			*Elovich*		
Parameters		*Q_{cal} (mg/g)*	*K_1 (1/mn)*	*R^2*	*Q_{exp} (mg/g)*	*Q_{cal} (mg/g)*	*K_2 (g/mg.mn)*	*R^2*	*K_i (mg/g.mn$^{1/2}$)*	*L_i (mg/g)*	R^2	*α (g/mg.mn)*	*β (mg/g)*	*R^2*
P	*t(min)*													
0	0	3.50	0.027	0.988	2.87	5.86	0.002	0.985	0.35	-0.59	0.994	0.14	0.96	0.976
180	1	4.55	0.029	0.993	4.96	6.27	0.005	0.991	0.46	0.50	0.984	0.45	0.72	0.984
	2	5.99	0.037	0.990	8.30	11.01	0.003	0.992	0.82	0.53	0.966	0.69	0.40	0.983
	3	4.21	0.029	0.995	4.67	5.85	0.006	0.991	0.43	0.51	0.979	0.46	0.76	0.988
300	1	1.56	0.032	0.995	2.08	2.35	0.062	0.999	0.15	0.58	0.974	0.37	2.10	0.998
	2	3.82	0.025	0.991	3.64	5.5	0.016	0.997	0.41	-0.46	0.994	0.20	0.82	0.980
	3	1.75	0.036	0.991	1.59	2.6	0.031	0.996	0.16	0.04	0.977	0.12	2.01	0.992
450	1	4.97	0.028	0.993	4.53	6.84	0.017	0.994	0.51	-0.53	0.991	0.26	0.6	0.991
	2	3.27	0.027	0.993	2.94	4.79	0.014	0.991	0.34	0.47	0.991	0.15	0.97	0.984
	3	4.24	0.026	0.990	3.68	6.18	0.013	0.991	0.43	-0.65	0.996	0.19	0.77	0.984

Table 2. Isotherm constants for phenol adsorption onto coffee grounds

Langmuir										
P (W)		180			300			450		
Time (min.)	0	1	2	3	1	2	3	1	2	3
Q_{max} (mg/g)	3.54	8.53	11.12	5.99	3.90	4.21	2.40	5.32	3.14	5.69
K_L (L/mg)	0.002	0.005	0.02	0.011	0.004	0.015	0.007	0.008	0.016	0.003
R^2	0.987	0.982	0.993	0.983	0.990	0.985	0.992	0.990	0.983	0.981
Freundlich										
K_F (mg/g(l/mg)$^{1/n}$)	0.025	0.068	0.760	0.365	0.039	0.310	0.083	0.142	0.370	0.037
n_F	1.20	1.25	2.10	2.21	1.42	2.3	1.90	1.71	2.88	1.30
R^2	0.975	0.981	0.980	0.980	0.989	0.984	0.980	0.988	0.969	0.987
Temkin										
K_T (1/mol)	0.003	0.027	0.221	0.094	0.788	1.246	0.131	0.035	0.112	0.057
B_T (J/mol)	1.234	2.632	2.284	1.416	0.891	1.030	0.588	1.351	0.699	1.302
R^2	0.928	0.879	0.978	0.946	0.961	0.993	0.978	0.969	0.974	0.934

When the plot is linear and passes through the origin only, the intraparticle diffusion is the rate controlling mechanism, otherwise other mechanisms along with intraparticle diffusion are involved. In this case, the deviation of the line from the origin shows that intraparticle transport is not the only limiting step. Probably the transport of the adsorbate through the interphase liquid-solid, as well as adsorption on the surface of the adsorbent, is responsible of the adsorption. This is in agreement with the works of Belaid and Kacha (2011). This already eliminates the pseudo first order model.

The second question is whether the adsorption is physical or chemical? According to the table, we see that the coefficient (β) of Elovich model is relatively high, that is to say that the desorption is significant, this suggests physio-sorption.

3.3. Adsorption isotherms

The effect of initial phenol concentration on equilibrium was observed by mixing 1 g of adsorbent with 50 mL of phenol solutions of varying initial concentrations (0–500 mg/L). The suspensions were shaken for 2 h at P = 180Watt and 25°C (rpm = 150 rpm). The experimental data were exploited and modeled. The results obtained have been grouped in Table 2.

The Langmuir model describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Freundlich model is commonly used to describe the adsorption for the heterogeneous surface. The Temkin Isotherm takes into the account of adsorbent–adsorbate interactions. This state of the adsorption in previous models is neglected. In this case, both models seem to describe the data adequately.

What is the choice between a model demonstrating saturation (Langmuir) and one (Freundlich) associated with exponential distribution of the sites? A conclusion is that sorption isotherm is non-linear, and there is a gradual saturation of the sites. This advocates the Freundlich model (Al-Ghouti and Da'ana, 2020). The maximum monolayer adsorption capacity, Q_{max} from the Langmuir model was found to be 3.54 and 11.12 mg/g for UCG and TCG, respectively.

It should be noted that for a time of 2 minutes and a power of 180W, an improvement in the adsorption capacity of almost three times was recorded. The results suggest that the phenol is favorably adsorbed by activated coffee grounds TCG.

The lower value of K_L (0.002) for the UCG implies low surface energy, thus indicating a probable stronger bonding between phenol and UCG.

K_F and n are the Freundlich constants characteristic of the system, as indicators of adsorption capacity and adsorption intensity, respectively. In general, as the K_F value increases the adsorption capacity of the adsorbent increases. The magnitude of the exponent $1/n$ gives an indication of the favorability of adsorption. In this case, the value $n > 1$ represents favourable adsorption condition (Dada et al., 2012).

As can be seen from Table 2, the value of n is 1.07 and 2.88 for the UCG and TCG, respectively. This result indicates the favorable adsorption of phenol on the both adsorbents. Moreover, the higher value of K_F was determined to be 0.780 for the TGC.

3.4. Factorial design analysis

The objective of this study is to introduce a tool, which is the design of experiments, in the organization and optimization of trials in scientific research. It is a question of what are the links existing between a quantity (y) and its variables (x_i); of determining the identification of the factors influencing the process; and the evaluation of the interactions between these factors.

Table 3 presents the limits of variation of the variables and their coding.

Table 3. Factors and coded levels for the experiment design

Independent Variables	***Factors***	***Coded level***		
		-1	0	+1
Phenol C_0 (mol/L)	X_1	100	300	500
Activ time ta (min)	X_2	1	2	3
Activ power Pa (W)	X_3	180	300	450

The experimental tests were organized and carried out according to an experiment matrix, written in coded variables as shown in Table 4 to model the adsorption capacity (response *Y*).

Table 4. Full factorial design matrix of three variables in coded and natural units with the experimental responses

Run	***Real value***			***Response Qe (mg/g)***
	C_0	***time***	***Power***	
	(mg/L)	***(min)***	***(W)***	
1	100	1	180	1.63
2	100	1	450	1.64
3	100	3	180	2.36
4	100	3	450	1.02
5	500	1	180	7.35
6	500	1	450	4.53
7	500	3	180	5.23
8	500	3	450	3.68
9	300	2	300	3.64
10	300	2	300	3.64

For a statistical significance evaluation of the effects and interactions, 2 center points were carried out. The phenol adsorption capacity on the activated coffee grounds, were adjusted with a polynomial model of the 1st order connecting the response *Y* to variables $X_{i=1,2,3}$ given by Eq. (11).

The model coefficients were determined using JMP 8.0 statistical analysis software. The coded mathematical model for 2^3 factorial designs can be given as:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{12}X_1X_2 + a_{13}X_1X_3 + \\ + a_{23}X_2X_3 + a_{123}X_1X_2X_3 \tag{11}$$

where: *Y* is the theoretical response function, a_0 is the global mean; a_i; a_{ij} and a_{ijk} represent the regression coefficient corresponding to the main factor effects and interactions, respectively.

By substituting the regression coefficients in Eq. (11) by their numerical values as given in Table 5 we get (Eq. 12):

$$Y = 3.472 + 1.766X_1 - 0.357X_2 - 0.714X_3 - 0.386X_1X_2 - \\ - 0.379X_1X_3 - 0.010X_2X_3 + 0.325X_1X_2X_3 \tag{12}$$

3.4.1. Regression models and statistical testing

The experiment is in perfect agreement with the predicted responses (Fig. 2). The Square correlation coefficients R^2 and adjusted R^2 respectively, equal to 0.999 and 0.996 (i.e. the unity). The high values of the two coefficients ensure a good descriptive quality of the model.

3.4.2. Student's t-test

The regression coefficients significance in Eq. (12) was verified by the Student t- test application (Goupy and Creighton, 2006). An effect will be considered if the associated absolute t-value is greater than t-critic equal to 4.303 (Student table) for 95% confidence level.

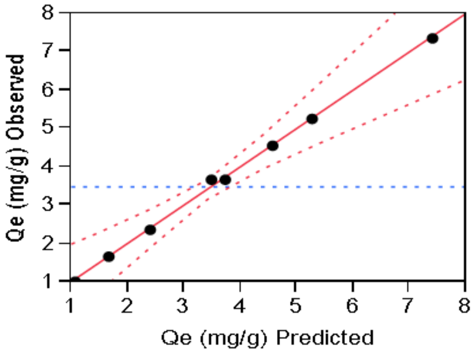


Fig. 2. Q_e observed vs. Q_e predicted response plot

Another method is to consider the probability value (p-value) of each model term closer to zero and which must be less than or equal to the threshold p of 0.05. These tests, from the review of t values and p-values (Table 5) highlighted 1 non-significant coefficient (a_{23}) for *Y* response.

Table 5. Estimated regression coefficients for the adsorption capacity of phenol

Parameter error	***Estimate***	***Standard error***	***T-value***	***P-value***
Constant	+3.472	0.059	58.80	0.0003*
X_1	+1.766	0.066	26.75	0.0015*
X_2	-0.357	0.066	-5.41	0.0325*
X_3	-0.714	0.066	-10.81	0.0084*
X_1X_2	-0.386	0.066	-5.85	0.0280*
X_1X_3	-0.379	0.066	-5.75	0.0290*
X_2X_3	+0.010	0.066	- 0.16	0.8909
$X_1X_2X_3$	+0.325	0.066	4.93	0.0387*

Note: * *Values which respond to significant tests*

The results were also confirmed by the Pareto Chart test (Fig. 3), which shows each effects and interactions estimated by decreasing order of importance, where the vertical line defines 95% of the confidence interval.

It arises from the different significance tests, that the variable X_1, X_2, X_3 and the interactions X_1X_2, X_1X_3, and $X_1X_2X_3$ affect significantly the adsorption capacity (response *Y*). As a result, the model was adjusted by considering only the influential linear and interaction effects (Eq. 13):

$$Y = 3.472 + 1.766X_1 - 0.357X_2 - 0.714X_3 - 0.386X_1X_2 - \\ - 0.379X_1X_3 + 0.325X_1X_2X_3 \tag{13}$$

These results are represented graphically by the Pareto test (Fig. 3). They show the estimated effects and interactions in decreasing order of importance. The vertical lines define the confidence interval (0.95%).

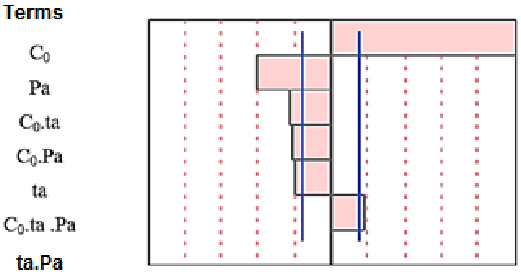


Fig. 3. Pareto Chart for standardized effects

3.4.3. Analysis of variance (ANOVA)

To check the significance of the model variables retained, a Fisher test was established. Analysis of variance (ANOVA) showed a fairly high mean square of regression compared to the main square of residues (Table 6) and consequently a Fisher value (F = 136. 226) much higher than the critical one ($F_{0,05;7;2}$= 19.532) and the P-value inferior to 0.5 (0.073). This means a good adequacy of model regression to experimental data at a 95% confidence level.

Table 6. Analysis of variance (ANOVA)

Source of variation	*Degrees of freedom*	*Sum of squares*	*Mean square*	*F-value*	*P>F*
Model Residues	7	33.254896	4.75070	136.2266	0.0073
2	0.069747	0.03487			
Total	9	33.3332463			

3.4.4. Main interaction effects

The main effects represent deviations of the average between the high and the low levels for each factor. When the effect of a factor is positive, *Y* increases and the factor changes from low to high levels (Goupy and Creighton, 2006).

Analysis of the adjusted model given in Eq. (13) indicated that the phenol concentration (X_1) is the key factor affecting the adsorption capacity (response Y) since its coefficient is the higher modulus. In addition, its positive sign means that adsorption capacity increases significantly with phenol concentration. These results corroborate the experimental results obtained in the first stage while varying phenol concentration only (Zeboudj et al., 2014). However, the effects of ta and Pa factors are negative, which indicates the decreases of the response with the two factors increase.

The plots of interaction effects evidenced interaction existence between two factors, when the two lines of levels -1 and 1 are not parallel. The parallel lines indicate the absence of interaction between factors. The interaction plot for the adsorption capacity of phenol is shown in Fig. 4. It could be seen that there is an important interaction effects between the concentration and the time (X_1X_2), concentration and the power (X_2X_3) and concentration, the power and the time ($X_1X_2X_3$). The negative sign of the interaction effect coefficient (-0.386) between the concentration of phenol and the activation time means that adsorption capacity decreases with the increasing initial concentration for high level of time. The interaction effect coefficient between the concentration and the power activation is also negative. Thus, adsorption capacity increases with the power activation when the concentration is weak. The positive sign of interaction effect coefficient between the three parameters reveals that the response *Y* decreases with weak values of these.

In the same way, the surface plots are useful approach in terms of optimization of the adsorption of phenol as a function of significant variables and interactions.

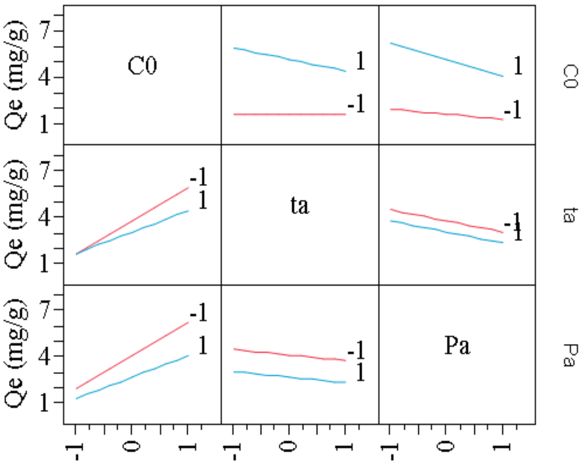


Fig. 4. Interaction plot for Q_e

Fig. 5a represents the surface plot of the response *Y* (Qe) as a function of the levels of (C_0) and (ta) for a value (Pa) fixed at the zero level. This figure illustrates and highlights the significant interaction effect of C_0-ta (X_1 X_2) and shows that with an increase in the amount of (C_0), the adsorption capacity increases with a reduction in that of (ta). The variations of (C_0) and (Pa) for a value (ta) fixed at level zero (Fig. 5b) promoted the phenol removal.

3.4.5. Estimation of optimal design conditions by the method of desirability function

The desirability function is generally used to optimize multi performance indicators of a given process. The individual desirability function (*d*) values are between 0 and 1 and reflect the satisfaction degree taken by a performance indicator (response *Y*) (Ouriache et al., 2019; Tebbouche et al., 2015).

The d value of 0 is assigned when the factors lead to an unacceptable response ($Y < Ymin$) and that of 1 when the response presents the desired maximum performance ($Y > Ymax$) for the considered factors, the individual desirability value (*d*) is determined as given in Eq. (14) (Jayaraman and Kumar, 2015).

$$d = \begin{bmatrix} 1 \\ \dfrac{Y - Y_{max}}{Y_{min} - Y_{max}} \\ 0 \end{bmatrix}^{s} \qquad \begin{matrix} Y < Y_{min} \\ Y_{min} \le Y_{min} \le Y_{max} \\ Y > Y_{max} \end{matrix} \tag{14}$$

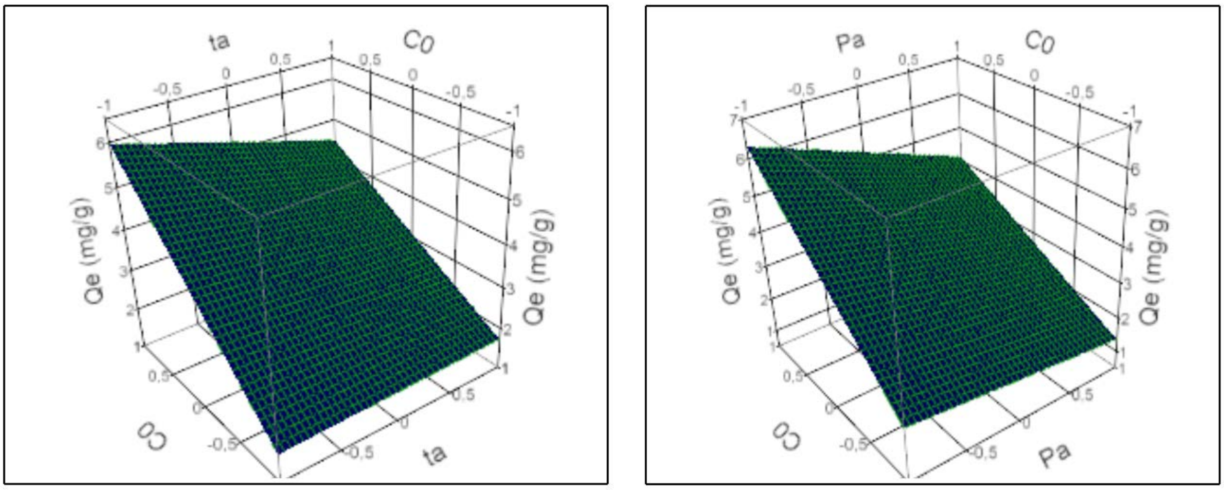
where Y_{min} and Y_{max} are respectively the minimum and maximum values of the response and *s* is the factor modifying the importance of an increase in the response *Y* for the considered individual desirability. The search for the optimal operating conditions leading to the optimization of phenol adsorption, from previously established model, was achieved using the response profiler of Fig. 6, whose desirability value close to 1 corresponds to maximum values of adsorption capacity of phenol.

More the desirability function tends towards 1 more the response represents a maximum performance for the considered factors. The optimum condition, i.e. the best combination of factor settings for achieving the optimum response was found to be: initial phenol concentration 500 mg/L, time activation 1min and power activation 180 W for a predicted response of 7.39 mg/g with a desirability value of 0.897.

4. Conclusions

This study highlighted the possibility of using a recovery waste (the spent coffee grounds) in the treatment of organic water pollution.

A simply activation by microwaves improved its adsorption capacity at about 7.4 mg/g, corresponding to the following conditions: initial phenol concentration 500 mg/L, activation time of 1min and power activation of 180 W.



(a) (b)

Fig. 5. (a) Surface plot of effects of C_0 phenol and ta on phenol adsorption, (b) Surface plot of effects of C_0 phenol and Pa on phenol adsorption

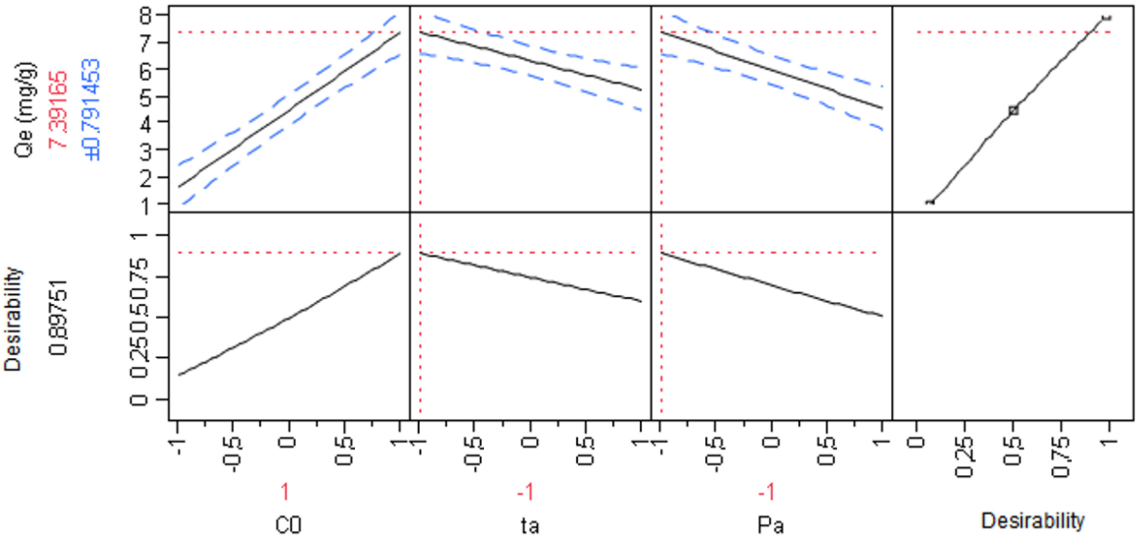


Fig. 6. Desirability functions for the optimization of the response

Experimental results have shown that adsorption is physical that it follows a pseudo-second order kinetics and that the isotherm is governed by the Langmuir and Freundlich models.

The application of a factorial design methodology showed that activation depends on the different ways of the three study parameters. The statistical analysis showed a good fit with the R^2-value of 0.997 and the F-value of 136.226.

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