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MODELING EXTERNAL MASS TRANSFER DURING THE BATCH ADSORPTION OF PHENOL ON ACTIVATED CARBON USING A FRACTIONAL DESIGN

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Abstract: In this work, we have studied the variation of the external mass transfer during the adsorption of phenol on activated carbon in a batch reactor, using a 2^{5-1} fractional design. The pH of the solution being fixed at 3, we varied the phenol concentration (ph) from 20 to 30 mg/L, the temperature (T) from 25 to 35°C, the particle size of the activated carbon (dp) from 0.405 to 0.805 mm, the stirring speed (w) from 500 to 1000 rpm and the amount of activated carbon in the solution (ch) from 1 to 2g/L. A linear model with interactions is obtained and validated with an adjusted correlation coefficient of around 99.60%.The greatest effect is obtained for the interaction (ch.w), followed by the main effect (w). The external mass transfer coefficient increases with the increase of the stirring speed, the temperature of the solution, the particle size and decrease with the increase of the amount of activated carbon and initial concentration of phenol in the solution. The maximum value for the external mass transfer coefficient (k_f = 0.300 cm.min $^{-1}$) is obtained for dp= 0.805mm, T=35°C, ch= 1g/L, w=1000rpm and ph= 20mg/L.

Keywords: Adsorption; phenol, activated carbon, mass transfer, fractional design.

INTRODUCTION

Phenol is among the major organic pollutants encountered in wastewater effluents. It is introduced into the aquatic environment from the wastewater released from various industries such as pesticide, resin, petrochemicals, fertilizers, pharmaceutical industries and petroleum refineries (Zhang *et al.*, 2018). This compound is considered dangerous and harmful to living systems because of their toxicity and carcinogenicity even at low concentrations. Its permissible concentration should be less than 0.1mg/L before it is released into the aquatic environment (Zeboudj *et al.*, 2014). Therefore, there is a need to treat phenol from wastewater before it is released into the environment. Several conventional chemicals, physical and biological methods have been used for the treatment of phenolic wastewater (Girish *et al.* 2012; Girish *et al.*, 2016) .The adsorption technology with the use of activated carbon as adsorbent has been observed to be one of the most effective and widely used method for the removal of phenols and its derivatives as well as other organic compounds from liquid-phase system (Mohanty et al., 2005; Anisuzzaman *et al.*, 2015). In this paper, we propose to study the external mass transfer during the adsorption of phenol on an industrial activated carbon in a batch reactor. The influence of certain parameters such as the initial phenol concentration, the amount of adsorbent, the particle size, the temperature and the agitation speed is studied using the experimental design method. This technique remains an indispensable economic tool of any study aimed at predicting or optimizing the performance of industrial processes because it reduces the number of experiments needed to carry out a study given (Douglas, 2001; Jiju, 2003; Goupy, 2006). In this sense, in order to work out the regression equation of the model, a 2^{5-1} fractional design is chosen to allow to study the 5 influencing factors on the basis of a minimum of tests (in total 22).

MATERIALS AND METHODS

Characterization of activated carbon

The activated carbon used in our experiments is a UP07 industrial activated carbon supplied by the LA BELLE company. After grinding, the dimensional analysis of the coal obtained is carried out by sieving in a series of sieves of different diameters in order to obtain the desired particle sizes.

Table 1.

Physical characteristics of the activated carbon used

Granulometry (mm)	Density (g .cm^{-3})	Specific area (m^2.g^{-1})	Total pore volume (cm^3.g^{-1})	Porosity (%)
0.405	1.425	807.341	1.767	71.57
0.605	1.355	772.669	1.587	68.26
0.805	1.317	718.002	1.545	67.04

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Preparation of solutions

All solutions are prepared in distilled water acidulated to pH =3 with sulfuric acid H_2SO_4 according to a previous study (Hamaidi et al., 2009). All the experiments were carried out in a batch reactor on a heating plate equipped with a magnetic stirrer and a thermometer (Fig.1).

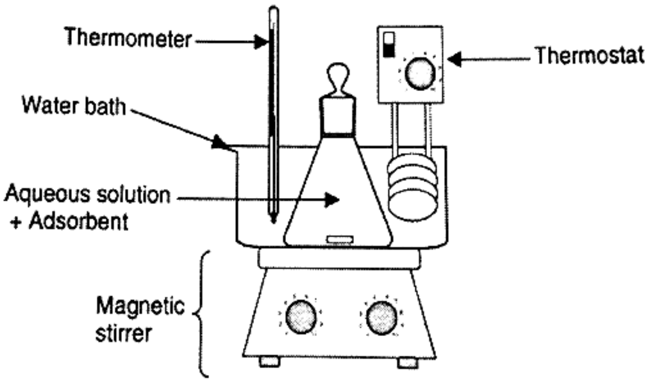


Fig. 1 Experimental apparatus.

Experiments

For each test, an experiment is carried out in a time interval, ranging from zero to fifteen minutes. Samples of 10 mL were taken at regular intervals, then filtered and the final concentrations are monitored by measuring the absorbance corresponding to a maximum wavelength (λ = 270 nm) using a visible Optizen UV spectrophotometer. 3220.

Fractional plan calculation

The factors selected in this study and their intervals of variation are grouped together in Table 2. The value -1 is assigned to the lowest level of a factor, zero for values in the center of the chosen domain, and the value +1 to the highest level (Douglas et al., 2001; Goupy, 2006). In this study, we have chosen a 2^{5-1} fractional design with six points in the center (N_0= 6), so the total number of experiments is twenty-two (Nt =22). The calculation and the processing of the results are carried out using MINITAB 1.7 and Excel 2007 software.

Table 2.

Selection of factors and field of study

Operating parameters	Abbreviation	Level -1	Level 0	Level +1
Température (°C)	T	25	30	35
Stirring speed (rpm)	w	500	750	1000
Particle size (mm)	dp	0.405	0.605	0.805
Activated carbon concentration (g. L^{-1})	ch	1	1.5	2
Initial concentration of phenol (mg. L^{-1})	ph	20	25	30

The chosen response

In any adsorption process, it is very essential to know the extent of solute or adsorbate transfer from the bulk liquid phase to the solid adsorbent surface and the solid adsorbent interface or to the liquid and solid interface (Girish *et al.* 2016; Smith *et al.*, 1973). In our case we are interested in the mass transfer on the external surface. In this context, we have applied the Mathews-Weber external diffusion model which assumes that the concentration at the surface of the adsorbent tends to zero or that the intraparticle resistance is negligible and hence the intraparticle diffusion can be neglected at an early period of contact (Prasad *et al.*, 2009). The model is derived on the basis of Fickien's law's application, where the solute concentration in the liquid-phase is expressed as a function of the solute concentration difference in the liquid-phase and at the adsorbent surface (Girish *et al.*, 2016). The external mass transfer coefficient can be expressed as given in Equation (1) (Kumar *et al.*, 2007):

$$\mathrm{kf} = -\frac{\ln\left(\frac{C_t}{C_0}\right)}{S_A t} \qquad (1)$$

where C_t is the concentration of solute in bulk liquid phase at any time t; C_o is the phenol initial concentration, kf is the external mass transfer coefficient, and S_A is the surface area of adsorbent per unit volume of particle free slurry (cm^{-1}) and is given by Equation (2) (Kumar *et al.*, 2007):

$$S_A = \frac{6M}{V d_p \rho (1-\varepsilon_p)} \qquad (2)$$

Where V is the volume of solution (L), M is the adsorbent mass (g), ε_p is the particle porosity, and ρ is bulk density ($g.cm^{-3}$). The external mass transfer coefficient k_f can be estimated from the slope of the curve ln (C_0/C_t) versus time t.

RESULTS AND DISCUSSIONS

Matrix of experiments

In Table 3. The values of the external mass transfer coefficient kf (response) are obtained by plotting the curve of ln (C_0 / Ct) as a function of time for each experiment and predicted values of kf are calculated using the model obtained. The matrix of experiences obtained is given with the real variables.

Table 3.

Matrix of experiments

Run order	T	w	dp	ch	ph	Response kf (cm. min $^{-1}$)	Predicted kf (cm. min $^{-1}$)	Relative error (%)
1	35	500	0.405	2.0	30	0.088	0.086	2.32
2	25	500	0.805	2.0	30	0.156	0.155	0.64
3	35	1000	0.805	2.0	30	0.170	0.169	0.59
4	25	1000	0.405	2.0	30	0.102	0.100	2.00
5	30	750	0.605	1.5	25	0.159	0.158	0.63
6	30	750	0.605	1.5	25	0.157	0.158	0.63
7	35	1000	0.405	1.0	30	0.193	0.193	0.00
8	30	750	0.605	1.5	25	0.156	0.158	0.63
9	35	500	0.805	2.0	20	0.207	0.207	0.00
10	25	500	0.805	1.0	20	0.150	0.148	1.35
11	25	500	0.405	1.0	30	0.138	0.138	0.00
12	25	1000	0.405	1.0	20	0.235	0.234	0.43
13	35	500	0.805	1.0	30	0.142	0.143	0.70
14	35	1000	0.405	2.0	20	0.155	0.156	0.64
15	30	750	0.605	1.5	25	0.161	0.158	1.90
16	35	500	0.405	1.0	20	0.106	0.105	0.95
17	30	750	0.605	1.5	25	0.162	0.158	2.53
18	25	500	0.405	2.0	20	0.130	0.131	0.76
19	25	1000	0.805	1.0	30	0.198	0.199	0.50
20	30	750	0.605	1.5	25	0.157	0.158	0.63
21	35	1000	0.805	1.0	20	0.300	0.298	0.67
22	25	1000	0.805	2.0	20	0.125	0.125	0.00

Modeling and analysis of variance

The Pareto chart of the effects is used to determine the magnitude and the importance of an effect. The chart displays the absolute value of the effects and draws a reference line on the chart. Any effect that extends past this reference line is statistically significant. In Fig. 2 we notice that all terms have a value greater than 2.36 so they are all representative, as we also observe in this figure that the most important interaction is (ch.w), followed by the main effects (w) and (ch). In Table 4. We have represented the results of statistical tests. The Student’s test (T-value) allows us to verify the meaning of the model terms (Goupy, 2006). The analysis of variance makes it possible to verify the adequacy of the regression equation. For this, it is necessary to carry out the Fisher-Snedecor’s test (F-value). The associated P-value expresses the probability of accidentally obtaining the result observed if the factor has no effect. If $P < 0.05$ we observe that the result is not the result of chance: the result is significant (Latifa *et al*., 2015). Otherwise, the result has, in the absence of effect of the factor, such a probability. It will not be attributed to the effect of the factor: the result is not significant. In Table 4. It can be seen that all P-values are less than 0.05 for both tests so all terms will be represented in the model equation.

Lack of fit, tests assess the fit of the model, if the P-value is less than 0.05 evidences exists that the model does not accurately fit the data (Maria *et al*., 2016). In our case the regression, then performed is very significant (P- value = 0.171 > 0.05), which means that the variations in responses observed are mainly explained by the final regression equation.

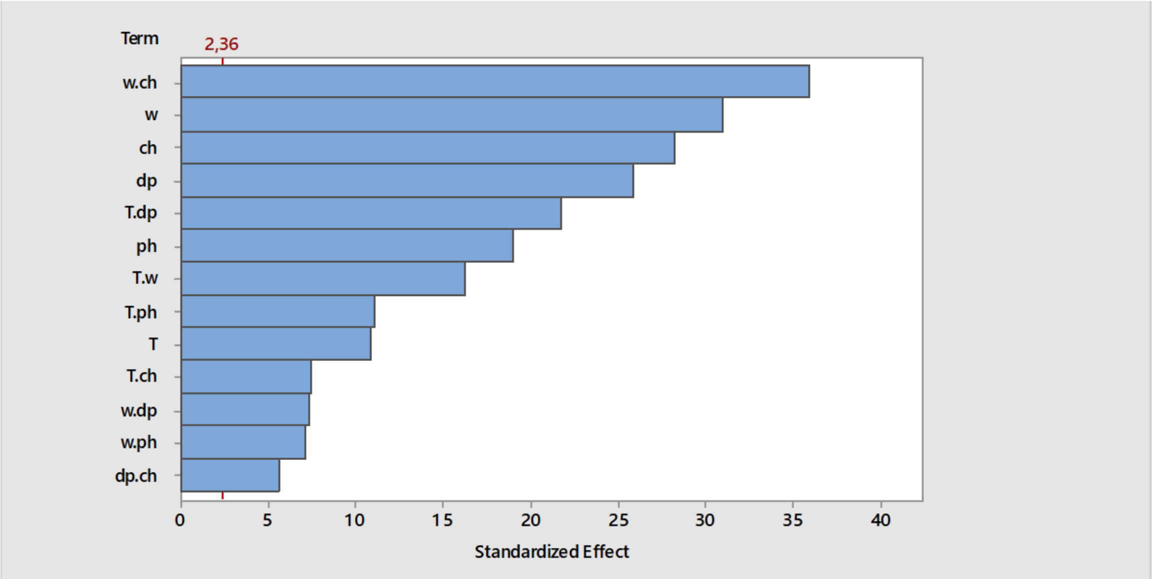


Fig. 2 Pareto Chart of the standardized effects for the level of significance α = 0.05.

Table 4.

Results of statistical tests

Terms	Coefficient	T-value	P-value	Terms	F-value	P-value
Term constant	0.1515	222.60	0.000	T	118.68	0.000
T	-0.01027	10.89	0.000	w	958.91	0.000
w	0.000289	30.97	0.000	dp	666.65	0.000
dp	-0.3616	25.82	0.000	ch	796.45	0.000
ch	0.0262	-28.22	0.000	ph	359.38	0.000
ph	0.010025	-18.96	0.000	T.w	262.84	0.000
T.w	0.000009	16.21	0.000	T.dp	470.98	0.000
T.dp	0.015813	21.70	0.000	T.ch	55.69	0.000
T.ch	0.002175	7.46	0.000	T.ph	122.45	0.000
T.ph	-0.000322	-11.07	0.000	w.dp	53.16	0.000
w.dp	-0.000106	-7.29	0.000	w.ch	1291.79	0.000
w.ch	-0.000210	-35.94	0.000	w.ph	50.69	0.000
w.ph	-0.000004	-7.12	0.000	dp.ch	31.09	0.001
dp.ch	0.04062	5.58	0.001	**Lack-of-fit**	**2.57**	**0.171**

The quality of the predicted model is evaluated by the coefficient of determination, for our model the calculated R^2 , which is equal to 99.87% indicates that the regression model is significant at 99.87% of the degree of confidence, i.e. that the model makes it possible to recover 99.87% of the measured responses. The adjusted R^2 value is also important; it's equal to 99.60%.

Regression equation

The relative error which does not reach 3% (Table 3.), the results of the analysis of variance, the Student and Fischer test and the coefficient of determination obtained, greater than 99% of the level of significance α = 0.05, allow us to validate the model and write the final regression equation in uncoded units as follows:

$$\begin{aligned} \mathrm{kf} &= 0.1515 - 0.01027\mathrm{T} + 0.000289\mathrm{w} - 0.3616\mathrm{dp} \\ &+ 0.0262\mathrm{ch} + 0.010025\mathrm{ph} + 0.000009\mathrm{T.w} \\ &+ 0.015813\mathrm{T.dp} + 0.002175\mathrm{T.ch} - 0.000322\mathrm{T.ph} \\ &- 0.000106\mathrm{w.dp} - 0.000210\mathrm{w.ch} \\ &- 0.000004\mathrm{w.ph} \\ &+ 0.04062\mathrm{dp.ch} \qquad (3) \end{aligned}$$

Study of interactions

In this case, we are only interested in the interaction (w.ch) which has the greatest T-value in absolute value (35.94) (Table 4.). This value is negative, this means that one parameter must be increased and the other decreased in parallel in order to obtain a better kf. Fig. 3 confirms this deduction moreover, we observe that it is necessary to increase w and decrease ch for a better kf.

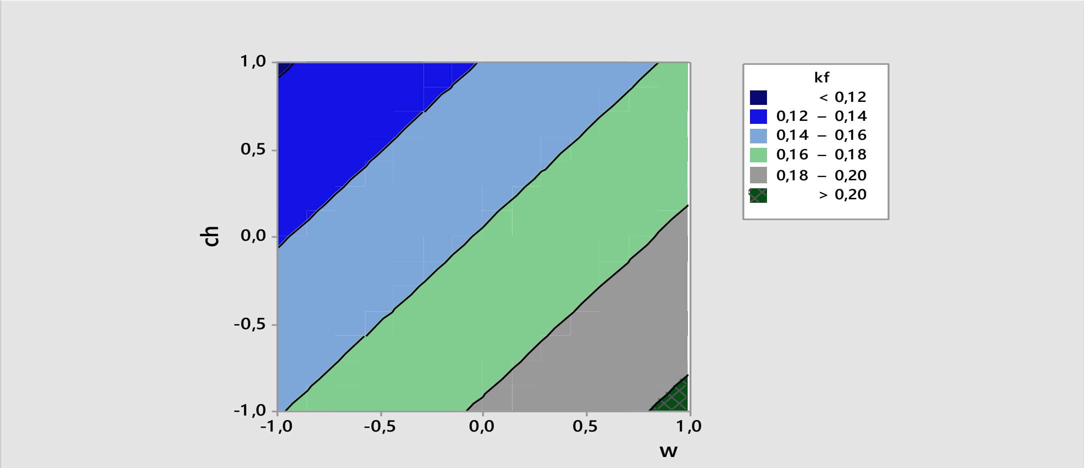


Fig. 3 Contour Plot of kf vs. ch; w.

Effect of initial concentration of phenol and the amount of activated carbon

Fig. 4 shows that the external mass transfer coefficient decreases with the increase in the initial phenol concentration, indeed a higher concentration of phenol saturates the active sites available on the surface of the activated carbon, which leads to a diffusion of the phenol molecules in the internal porosity of the activated carbon particles, consequently to a decrease in the speed at the external transfer (Nassar *et al.*, 2008). Increasing the amount of activated carbon decreases the external surface area of the particle per unit volume since the external mass transfer coefficient is inversely proportional to the latter, which results in an increase in the transfer rate (Guiza *et al.*, 2012; Mathews *et al.*, 1977).

Fig. 5 showing the contour plot of kf versus ph and ch indicates that the highest external transfer rate (kf > 0.19 cm. min^{-1}) is obtained for small phenol concentrations and smalls activated carbon's amount.

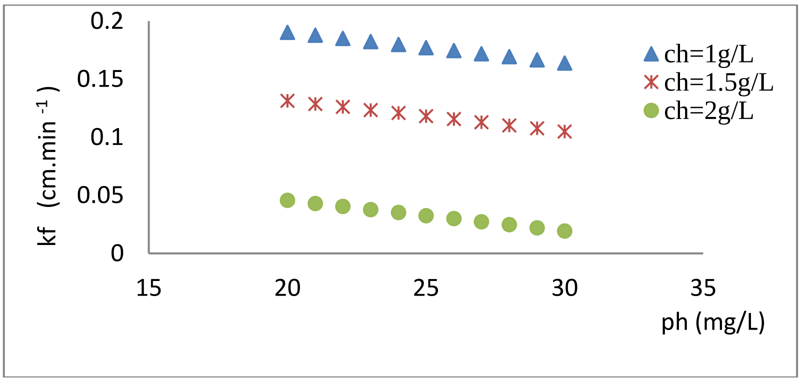


Fig. 4 Effect of initial concentration of phenol and amount of activated carbon (dp = 0,605 mm, T = 30°C, w = 750rpm.

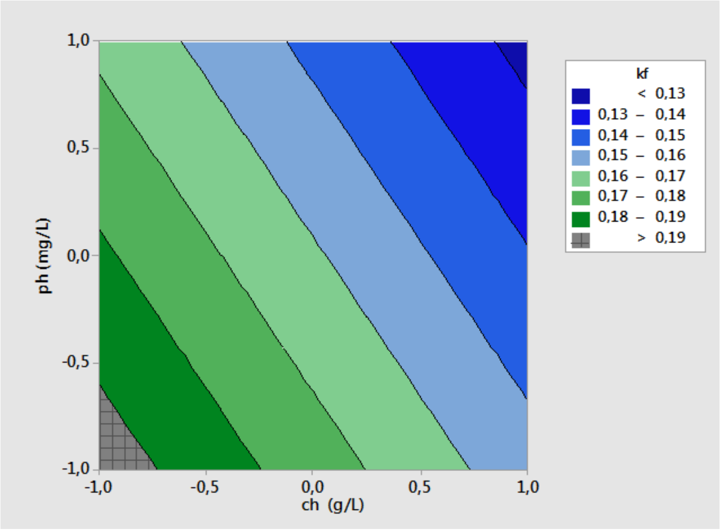


Fig. 5 Contour plot of kf vs. ph; ch.

Effect of temperature and particle size

In Fig. 6, we notice that the coefficient of external mass transfer increases with the increase of the temperature. Indeed, the effect of temperature is mainly decreasing viscosity of solution consequently decrease thickness of boundary layer resistance surrounding the adsorbate and leads to increase mass transfer (Yongli *et al*., 2014). Also on the same figure, it is noted that the increase in the diameter of activated carbon particles leads to an increase in the rate of external mass transfer. The increase in the diameter of the adsorbent particle decreases the outer surface of the particle per unit volume, which leads to an increase in the external mass transfer coefficient since it is inversely proportional to that surface (Guiza *et al.*, 2012; Mathews *et al*., 1977). Fig. 7, shows us that the best values of kf (kf > 0.18 cm.min^{-1}) are obtained for high temperatures and large particles.

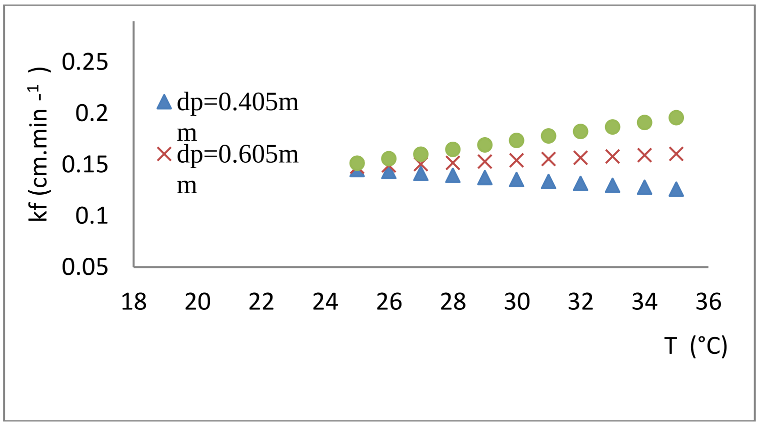


Fig. 6 Effect of temperature and particle size (ch = 1.5 g/L, w = 750 rpm, ph = 25 mg/L).

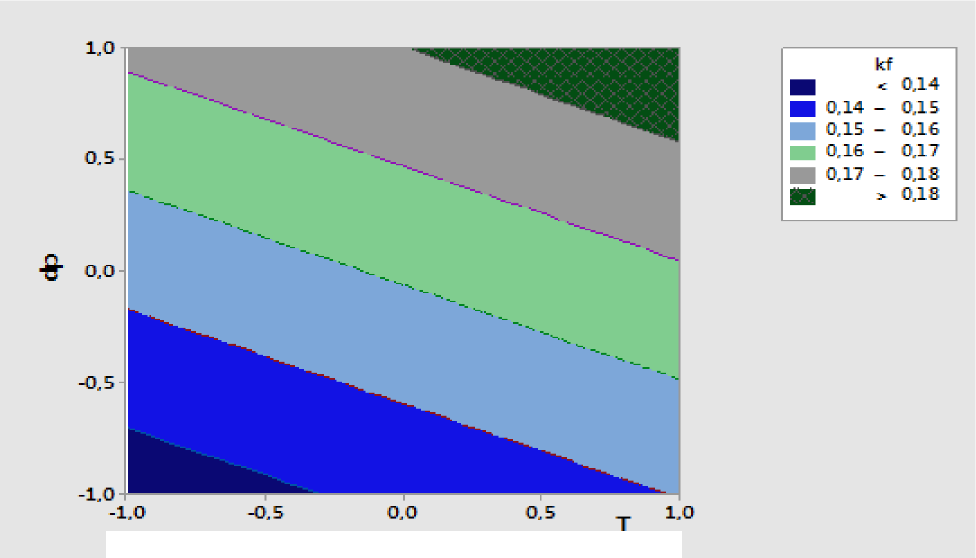


Fig. 7 Contour Plot of kf vs. dp; T.

Effect of agitation

The major controlling factor in external mass transfer is the boundary layer. The mass transfer coefficient increases with agitation see Fig. 8; consequently, the effect of agitation is to lower the boundary layer thickness or resistance surrounding the activated carbon particle (Mckay *et al*., 1982; Yeşim *et al*., 2000). The large values of kf (kf > 0.19 cm.min^{-1}) are obtained for high temperatures and great agitation (Fig. 9).

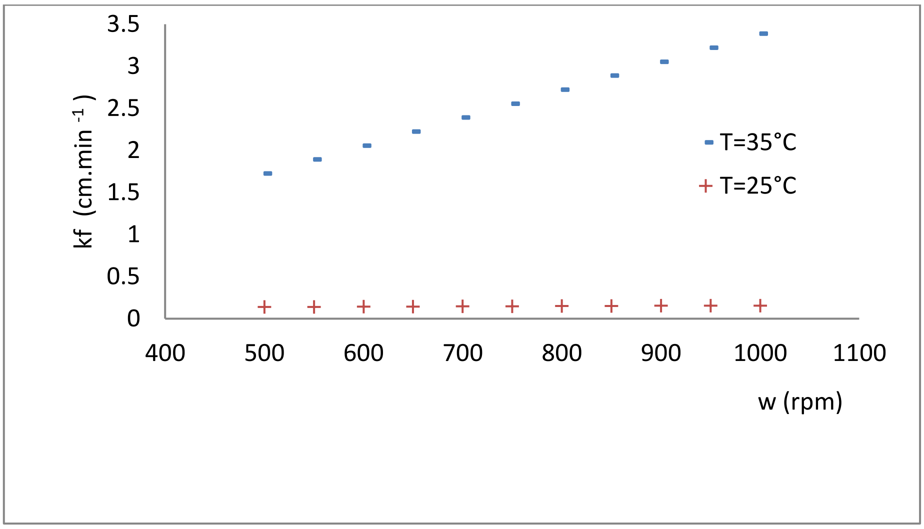


Fig. 8 Effect of agitation at different temperatures (dp = 0.605 mm, ch = 1,5 g/L, ph = 25 mg/L).

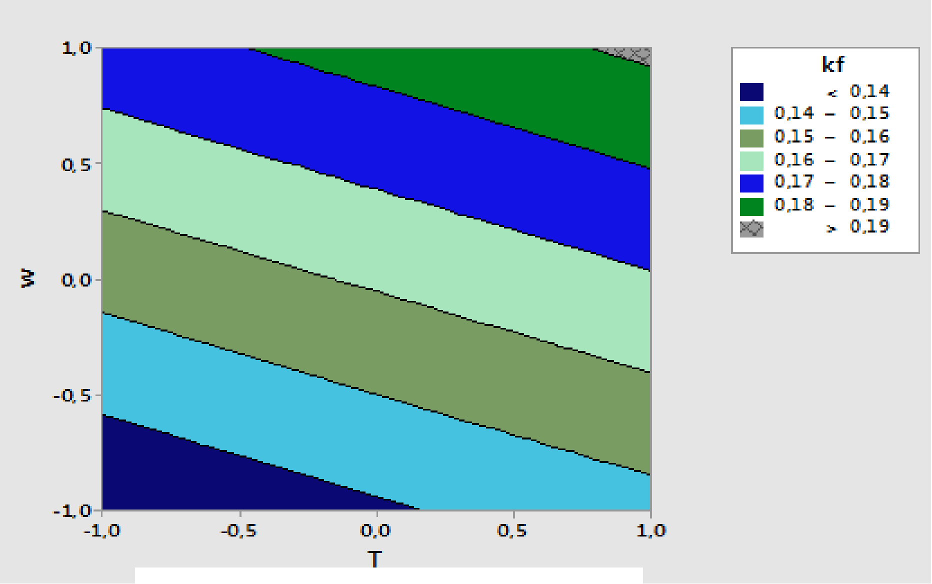
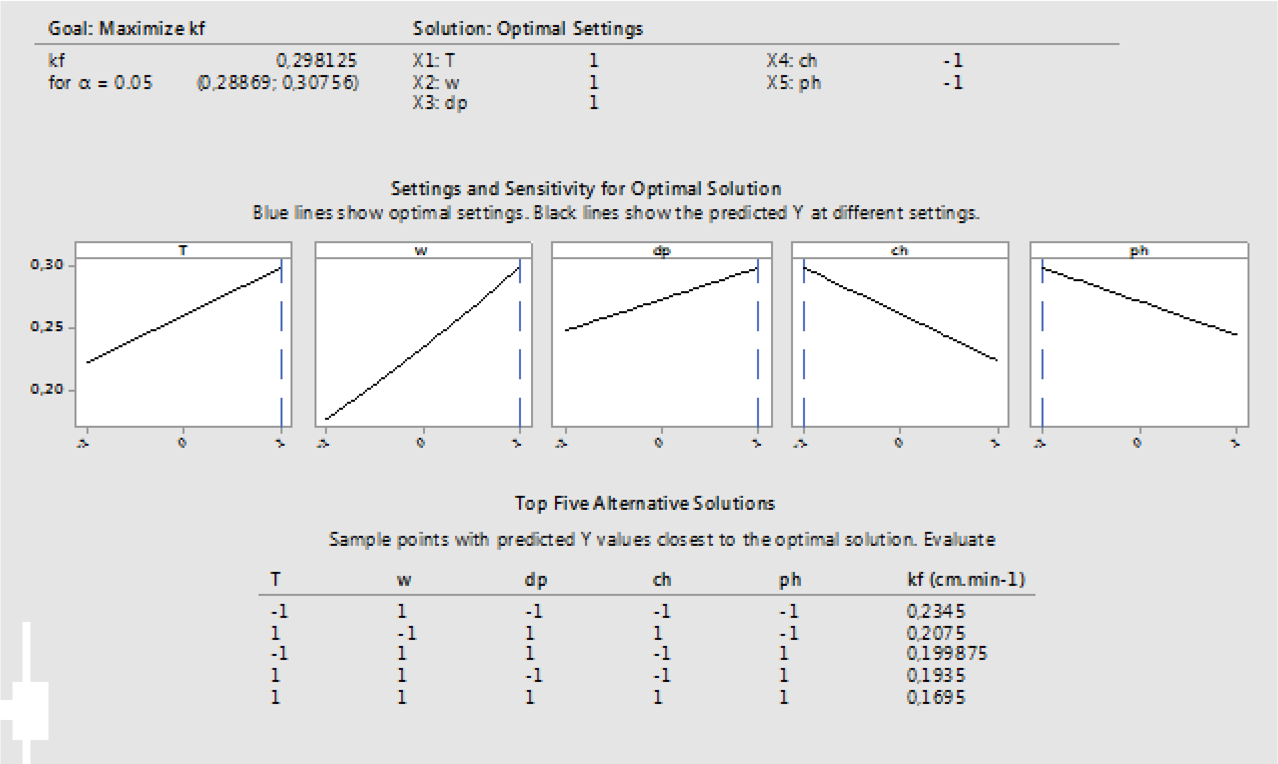


Fig. 9 Contour Plot of kf vs. w; T.

Prediction and optimization of external mass transfer coefficient

In Fig. 10, showing the optimization report, it can be seen that the best values of kf are obtained with a large stirring, a high temperature, a large particle size, a low concentration of phenol and a small amount of activated carbon in solution. The values of the parameters giving the maximum of kf (between 0.288 and 0.30756cm.min^{-1}) are therefore: T=35°C, w=1000rpm, dp =0.805mm, ch=1g/L and ph =20mg/L. In this report, we also got the top five alternative solutions to the optimal solution.



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Goal: Maximize kf                    Solution: Optimal Settings
kf                  0,298125         X1: T     1          X4: ch    -1
for α = 0.05   (0,28869; 0,30756)    X2: w     1          X5: ph    -1
                                     X3: dp    1
```

Settings and Sensitivity for Optimal Solution
Blue lines show optimal settings. Black lines show the predicted Y at different settings.

Top Five Alternative Solutions

Sample points with predicted Y values closest to the optimal solution. Evaluate

```
T     w     dp    ch    ph    kf (cm.min-1)
-1    1     -1    -1    -1    0,2345
1     -1    1     1     -1    0,2075
-1    1     1     -1    1     0,199875
1     1     -1    -1    1     0,1935
1     1     1     1     1     0,1695
```

Fig. 10 Multiple regression for kf. Prediction and optimization report.

Comparison with various studies

The comparison of the external mass transfer coefficient of this work with various adsorbents is given in Table 5. Even the studied couple's diversity, the external mass transfer kf remains in the range 0.06 – 0.30 cm.min $^{-1}$.

Table 5.

Comparison of the external mass transfer coefficient kf.

Adsorbent	Adsorbate	kf (cm.min^{-1})	Reference
Activated carbon	phenol	0.060	(Vinod *et al*., 2002)
Activated carbon	phenol	0.096 -0.149	(Lallan *et al*., 2019)
Carbon silica	phenol	0.12	(Mckay, 2001)
Activated carbon	Polyethylene glycol	0.315	(Chang *et al*., 2004)
Sodic Bentonite	Methyl violet	0.246	(Guiza *et al*., 2012)
This work		**0.088 - 0.300**	

CONCLUSION

From the results of the experiments and modeling; it appears that the R^2 indicated that the model explained approximately more than 99 % of the variability of the response. The significant value of this regression ($P< 0.05$) revealed that this model is well adjusted and statistically significant, and the non-significant value of lack of fit ($P>0.05$) shows that there is not bias in this regression. The most influential interaction is (ch.w) followed by the main effects (w) and (ch).The external mass transfer coefficient increases with the increase in the stirring speed, the temperature of the solution, the particle size and decrease with the increase of the amount of activated carbon and initial concentration of phenol in the solution. We can have five alternative combinations to get optimums, but the one that gives us the maximum (kf = 0.30 cm min $^{-1}$) is obtained with a high temperature, a great agitation, a large particles of activated carbon , small concentrations of phenol and a small amount of activated carbon. The values of the external mass transfer coefficient found in this study are of the same order of magnitude compared to those obtained in other studies already carried out, whatever the adsorbent / adsorbate couple used.

AUTHORS CONTRIBUTIONS

Conceptualization, NHM, SBB, NK and HT; methodology, NHM, SBB; data collection NHM, SBB, NK; data validation, NHM, SBB, data processing NHM, SBB; writing—original draft preparation, NHM, SBB; writing—review and editing, NHM.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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