

Research Article

Optimization of the Synthetic Procedure for Functionalizing Activated Carbon Produced from *Canarium Ovatum* with Iron Oxide Nanoparticles Toward Effective Adsorption Using a Central Full Factorial Design

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Abstract

This work concerns the determination of conditions for optimizing the synthesis of a composite material consisting of activated carbon and iron (III) oxide nanoparticles in order to improve adsorptions properties such as adsorption yield and enthalpy of adsorption of malachite green. A three-point central full factorial design was used for this purpose to evaluate impact of optimal synthesis parameters namely the concentration of iron nitrate, the annealing temperature, the synthesis pH and the citric acid/iron nitrate molar ratio. The existence of interaction between the synthesis parameters increases the effects of the latter on the properties of the composite material obtained. The increase in the concentration and the decrease in the annealing temperature favors an increase in the adsorption yield from 60% to 76%. There is also an increase in the adsorption enthalpy up to values greater than or equal to 40 kJ.mol⁻¹ when there is an increase in the synthesis pH and the iron nitrate concentration simultaneously with the drop in the molar ratio citric acid/iron nitrate and the annealing temperature. Composite material obtained following the optimal conditions: annealing temperature at 400 °C, with an ionic iron concentration of 0.150 mol.L⁻¹ at pH 5 and a molar ratio close to 0.250 exhibited an adsorption yield of ~80%, higher than pristine activated carbon (~70%) and an increase in the variation of enthalpy (from -12.010 kJ.mol⁻¹ to 52.612 kJ.mol⁻¹). The results of this work provide a basis from which to effectively functionalize an adsorbent with iron oxide nanoparticles with the aim of having more improved adsorbent properties.

Keywords

Nanoparticles, Optimization, Full Factorial Design, Adsorption Yield, Enthalpy

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1. Introduction

Due to their exceptional properties resulting from their size and the impact of the surface to volume ratio, nanoparticles are increasingly used in varied fields of application [1]. Many studies show that these nanoparticles can be used in water treatment as a dopant to improve the adsorbent properties of filter materials [2-7]. Their effectiveness in this use depends on the synthesis conditions taking into account the parameters namely the synthesis pH which will influence the type of iron species obtained; the precursor concentration which has an impact on the size of particles and the quantity of nanoparticles obtained; the use of an organic compound which act as a chelating agent and consequently the chelating agent/metal precursor molar ratio (MR) which influences both the shape and size of nanoparticles obtained. The chelating agent allows the reduction of the agglomeration phenomenon of metal ions which could lead to metal oxide particles with large diameter [8-10]. Obtention of metal oxide nanoparticles also depend on annealing temperature on which the oxide phase obtained depends [11]. All this has an influence on the textural properties and the surface chemistry of the composite material obtained, which directly impacts its adsorbent properties.

Some studies show that nanoparticles of copper oxide, aluminum and iron impregnated on activated carbon are already used for the elimination of pollutants in water [12]. Researches have shown that magnetite, maghemite and hematite nanoparticles have a significant potential for adsorption of organic pollutants [13-19].

In this work, composite materials consisting of activated carbon and iron (III) oxide nanoparticles have been synthesized. Iron was obtained from inexpensive precursors and the synergism or antagonism with the high adsorbing properties of activated carbon evaluated. Central full factorial design (CFD) provides a useful tool for experimental design of interacting variables for optimization of performance of an adsorbing material [20]. However, most of the studies focus on the use of CFD for optimization of the environmental conditions of adsorption dye, such as initial dye concentration, solution pH, reaction/sonication time, adsorbent dosage, and temperature for maximum pollutant removal efficiencies [20-24]. To the best of our knowledge, experimental design is used here to study conditions of synthesis of best adsorbent before use for depollution. Hence, composite materials of activated carbon and iron (III) oxide nanoparticles in the current study are applied in adsorption studies particularly for the evaluation of the adsorption yield and adsorption heat.

2. Experimental

2.1. Materials

The precursor of the activated carbon was the kernels of

black fruits (*Canarium Ovatum*) harvested in Batcham locality of west Cameroon (10°12' longitude east and 5°30' latitude north). These nuclei were ground to powder using an industrial grinder and sieved through a 250 μm sieve. Phosphoric acid 85% (H_3PO_4), sodium hydroxide (NaOH), and hydrochloric acid 36% (HCl) were supplied by JHD Laboratories; malachite green ($\text{C}_{23}\text{H}_{25}\text{ClN}_2$) was supplied by Trust chemical eco laboratories. The hexa-hydrated iron nitrate used as a metal precursor, citric acid which acts as a chelating agent and sodium chloride are obtained from Sigma Aldrich. Ethanol of 85% purity is provided by Panreac laboratories.

2.2. Equipment

The study of the crystalline or amorphous character and the mineralogical composition of the composite material and the activated carbon was carried out using X Ray Diffraction analysis (XRD). The peaks were elucidated through Profex 5.1.1 software. Infrared (FT-IR) spectra were recorded on a Bruker Alpha IR (100 FT-IR) spectrophotometer to study the surface functional groups of materials. The determination of the specific surface area and pore width distribution was performed by using the Brunauer–Emmett–Teller and Barrett–Joyner–Halenda method (BET/BJH). An adsorption-desorption isotherm of dinitrogen (N_2) at 77 K at different relative pressures allowed the determination of the total surface area. The plot of the variation in volume based on pore width allowed to determine the porous nature of materials. Scanning Electronic Microscopy coupled to Energy-dispersive X-ray analysis (SEM/EDX) was used to complement the morphology and the detection of elemental atomic composition of materials. Thermal characteristics of the samples were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

3. Methods

3.1. Methodology

3.1.1. Experimental Design

The synthesis was carried out by a sol-gel method, to which the experimental design method was applied through the central full factorial design (CFD) at two levels with four factors (synthesis pH; metal precursor concentration; citric acid/iron nitrate molar ratio (MR) and annealing temperature) and three points in the centre using MINITAB software. This allowed the evaluation of the relationships between the synthesis factors and determined the optimal conditions for the synthesis of a composite material with maximized performance for the adsorption of malachite green. The number of experiments is given by the equation [23].

$$N=2^K + N_0 \quad (1)$$

Where:

N: is the number of experiments performed.

K: the number of factors equal to Four factors.

N_0 : the number of points in the center which is three.

Table 1 represents the different independent factors values of the high levels and low levels.

Table 1. Independent factors.

Factors	Variables	Units	values of levels		
			Hight level	Center	Low level
Iron nitrate concentration	X_1	mol.L^{-1}	0.050	0.100	0.150
Annealing temperature	X_2	$^{\circ}\text{C}$	400	450	500
Synthesis pH	X_3	-	1	3	5
Citric acid/iron nitrate molar ratio	X_4	-	0.250	1.125	2

The responses studied were the variation of enthalpy (ΔH), and the adsorption yield of malachite green.

$$k_d = \frac{Q_e}{C_e} \quad (5)$$

3.1.2. Evaluation of Adsorption Properties

The removal yield of malachite green (MG) was determined by performing adsorption in a batch mode of a mass of 0.050g of adsorbents in a volume of 30 mL of a solution of malachite green at a concentration of 55 mg.L^{-1} at different times (5min; 15min; 25min; 35min; 45min and 55min). That was done to determine the maximum adsorption time and finding the adsorption yield at that time using Equation (2).

$$\text{Yield} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

Where:

Yield: Adsorption yield at each time

C_i (mg.L^{-1}): Initial concentration of malachite green

C_f (mg.L^{-1}): Residual concentration of malachite green

The variation of enthalpy was determined by performing the thermodynamic study at temperatures varying from 30°C to 85°C . The variation of enthalpy was found with the equation (3) [25].

$$\ln(k_c) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (3)$$

$$k_c = 1000k_d \quad (4)$$

Where:

Q_e : Quantity adsorbed at each temperature (mg.g^{-1})

C_e : residual concentration of malachite green at each temperature (mg.L^{-1})

R: perfect gas constant ($8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$)

T: Temperature (K)

ΔS : Variation of entropy ($\text{kJ.mol}^{-1}.\text{K}^{-1}$).

ΔH : Variation of enthalpy (kJ.mol^{-1}).

ΔG : Variation of free energy (kJ.mol^{-1}).

$$\Delta G = -RT \ln\left(\frac{Q_e}{C_e}\right) \quad (6)$$

The most ΔS is high, the most there is disorder at the solution/ adsorbent interface.

A variation of enthalpy lower than 40 kJ.mol^{-1} traduce a physical adsorption with weak interaction [26, 27]. A negative value of ΔH means an exothermic process while a positive value translates an endothermic process.

A negative value of ΔG means a spontaneous and favorable process [28].

3.1.3. Matrix of Experiments

The CFD matrix of experiments chosen is represented in Table 2.

Table 2. Matrix of experiments.

Run order	Concentration (mol.L^{-1})	Temperature ($^{\circ}\text{C}$)	pH	MR	Yield (%)	ΔH (kJ.mol^{-1})
1	0.100	450	3	1.125	68.650	13.380

Run order	Concentration (mol.L ⁻¹)	Temperature (°C)	pH	MR	Yield (%)	ΔH (kJ.mol ⁻¹)
2	0.050	500	1	2.000	55.290	10.280
3	0.050	500	1	0.250	58.780	11.390
4	0.150	400	5	0.250	78.350	64.925
5	0.050	400	1	2.000	65.420	6.800
6	0.150	500	5	2.000	56.960	13.260
7	0.150	400	1	0.250	69.690	42.088
8	0.050	500	5	0.250	63.720	12.470
9	0.050	400	5	2.000	60.860	21.991
10	0.150	400	5	2.000	69.350	44.300
11	0.150	500	1	2.000	57.720	14.730
12	0.150	500	1	0.250	57.640	27.056
13	0.150	400	1	2.000	68.610	27.558
14	0.100	450	3	1.125	67.230	13.410
15	0.050	400	5	0.250	67.750	34.560
16	0.100	450	3	1.125	66.670	13.400
17	0.050	400	1	0.250	64.260	13.400
18	0.150	500	5	0.250	62.120	20.709
19	0.050	500	5	2.000	54.270	11.510

3.1.4. Statistical Analysis

Analysis of variances

The analysis of variances (ANOVA) makes it possible to determine whether the chosen model is statistically significant and can predict the outcomes. The relationship between the responses and the factors is statistically significant if the p-value is less than 0.050 [29].

Analysis of residues

The residuals are the difference between the calculated value of the response and its value predicted by the model [30]. Residual analysis consists of analyzing this difference. The experimental values of the adsorption yield and the variation of enthalpy should be close to the predicted values for a reliable model.

Assessment of the level of explanation of the model

The suitability and degree of explanation of the model concerning the experimental data was evaluated using the coefficient of determination (R²) values.

3.2. Preparation of Adsorbents

3.2.1. Synthesis of Activated Carbon

Activated carbon was obtained by chemical activation of black fruit powder with phosphoric acid 85%. A mass of 20g of the powder was mixed with phosphoric acid to mass ratio

powder /acid of 1/3. After complete drying at a temperature of 110 °C for 48 hours, the whole was calcined at a temperature of 450 °C with a temperature rise rate of 5 °C.min⁻¹ and a holding time of 1 hour. The product obtained was washed with distilled water until the pH of the effluent was close to 7. Finally, the activated carbon washed product was dried at a temperature of 110 °C for a duration of 48 hours and labelled AC before being preserved for subsequent steps.

3.2.2. Synthesis of Iron Oxide-Activated Carbon Composite

A mass of iron nitrate corresponding to the predefined concentrations was introduced into a 50mL volume of a mixture of ethanol/water solvent (40/60 v/v). Then, a weighted mass of citric acid was added according to the previously fixed molar ratio. The pH of the solution was adjusted using hydrochloric acid and sodium hydroxide to reach the desired pH and left under a stirring environment for 2 hours at 70 °C. Subsequently, a mass of 15g of activated carbon was introduced into the gel formed and stirred for 1 hour for homogenization. The resulting product was dried for 48 hours at a temperature of 80 °C before being calcined at the different temperatures set in the experimental design at a temperature rise rate of 5 °C.min⁻¹ for 1 hour. The composite material obtained following optimal conditions given by the design has been named ACNPS.

4. Results and Discussion

Analysis of the CFD Model Predicted Responses and Postulated Mathematical Model

Table 3. Predicted responses and residuals values.

Run order	Yield Experimental	ΔH Experimental	Yield predicted	ΔH predicted	Yield Residual	ΔH Residual
1	68.650	13.380	67.536	13.392	1.113	-0.012
2	55.290	10.280	56.613	11.450	-1.323	-1.170
3	58.780	11.390	57.445	10.984	1.335	-0.406
4	75.350	64.925	76.333	63.118	2.016	1.806
5	65.420	6.800	63.168	5.030	2.251	1.770
6	56.960	13.260	55.827	13.390	1.132	-0.130
7	69.690	42.088	70.939	44.158	-1.249	-2.070
8	63.720	12.470	62.838	11.301	0.881	1.168
9	60.860	21.991	61.772	23.990	-0.912	-1.999
10	69.350	44.300	68.712	45.330	0.637	-1.030
11	57.720	14.730	57.223	14.790	0.496	-0.060
12	57.640	27.056	58.054	24.458	-0.414	2.597
13	68.610	27.558	70.108	26.370	-1.498	1.188
14	67.230	13.410	67.536	13.392	-0.306	0.017
15	67.750	34.560	69.393	33.361	-1.643	1.198
16	66.670	13.400	67.536	13.392	-0.866	0.007
17	64.260	13.400	63.999	14.401	0.260	-1.001
18	62.120	20.709	63.448	23.058	-1.328	-2.349
19	54.270	11.510	55.217	10.050	-0.947	1.460

The predicted values of responses and residuals values are grouped in Table 3.

The experimental responses vary between 54.270% and 75.350% for the removal yield and 6.800 and 64.925 kJ.mol⁻¹ for the variation of the enthalpy while the predicted

removal yield varies between 55.218% and 76.334% and the predicted variation of enthalpy is between 10.984 kJ.mol⁻¹ and 63.119 kJ.mol⁻¹. Mathematical models generated by the Minitab software version 19 are:

$$\text{Yield} = 59.59 + 670 X_1 - 0.034 X_2 + 1.591 X_3 - 0.495 X_4 - 1737 X_1^2 - 0.633 X_1 X_2 - 0.970 X_3 X_4 \quad (7)$$

$$\begin{aligned} \Delta H = & 764 + 1029.600 X_1 - 3.548 X_2 + 25.100 X_3 - 21.51 X_4 + 0.004 X_2^2 - 1.800 X_1 X_2 - 48.100 X_1 X_4 \\ & - 0.051 X_2 X_3 + 0.046 X_2 X_4 \end{aligned} \quad (8)$$

Interactions with non-significant effects were systematically eliminated [31].

4.1. ANOVA Analysis

The values of the statistical constants of the model provided are shown in Table 4.

Table 4. Statistical constants of the model.

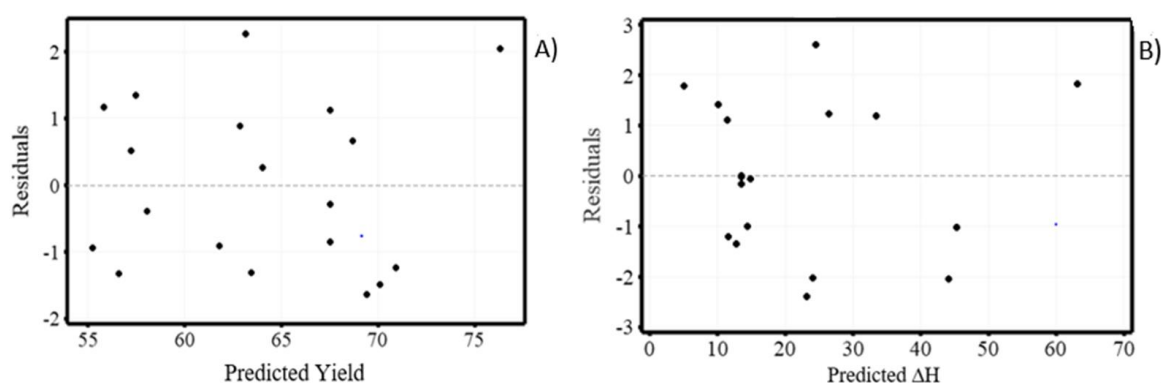
Responses	F _{tabulated}	F _{predicted}	P-values	R ²	R ² adjusted
Yield	3.220	11.310	0.000	0.960	0.961
ΔH	3.010	8.610	0.001	0.991	0.991

The F-values for the chosen model shown in Table 4 are higher than those provided in Fisher's table. This is an indication that this model is suitable for this study [32]. Moreover, the p-values obtained are less than 0.050. Thus, a statistically significant relationship between studied variables and responses [33]. The values of the coefficients of determination ranging from 0.960 to 0.991 show that the chosen variables describe only 96% of the variation of the MG adsorption yield while they make it possible to explain 99% of the variation of enthalpy [34]. However, the values of adjusted coef-

ficients of determination obtained range from 96% and 99% this proves that the mathematical models provided by Minitab make it possible to have results which agree at 96% with the values experimental results obtained for removal yield and at 99% with those obtained for enthalpy [35].

4.2. Examination of Residuals

Figure 1 below shows the spatial distribution of residuals for each response.

**Figure 1.** Distribution of residues for Yield response (A); ΔH (B).

The random distribution of the residuals on either side of the zero as well for the response of adsorption yield (figure 1A) as for the response of enthalpy variation (figure 1B) shows that residuals do not depend on predicted responses. It contributes to confirming the consistency between the variation of the responses and the predicted model [33].

4.3. Effects of Variables and Interactions

Case of yield response

Figure 2A and B show the effects of variables and their interactions on the adsorption yield.

The results of the individual effects of variables and interactions indicate that the removal yield increases with concentration and pH whereas citric acid/iron (III) nitrate molar ratio (MR) and temperature have a negative effect on the response. An increase of concentration of the metallic precursor can lead to an increase of the iron species on activated carbon since for the same solution volume, increasing iron precursor concentration involves an increase in iron precursor

mass and therefore an increase in the amount of iron species which are noticeable to be formed. Amines coordinate with iron species to form complexes with increased removal yield [36]. Chelation of metallic ions depends on the pH of the solution, it has been shown that at a pH higher than 1 all the metallic ions can be chelated and conducted to nanoparticles with a reduce size, iron oxide nanoparticles with a size between 5 and 25 nm at pH equal to 5 has been previously reported [36]. The more a nanoparticle has a small size, the more atoms there are on its surface which improves its reactivity and contributes to the adsorption capacity [37]. Some results in the literature explain that in an acid medium, a large amount of chelating agent would favor quick precipitation which would limit obtaining small-size nanoparticles [34]. The increase in annealing temperature results in the formation of an external support-iron system which could easily be subject to leaching thus reducing the adsorption capacity [36].

Case of variation of enthalpy response

Figure 3A and B show the effects of variables and their

interactions on ΔH .

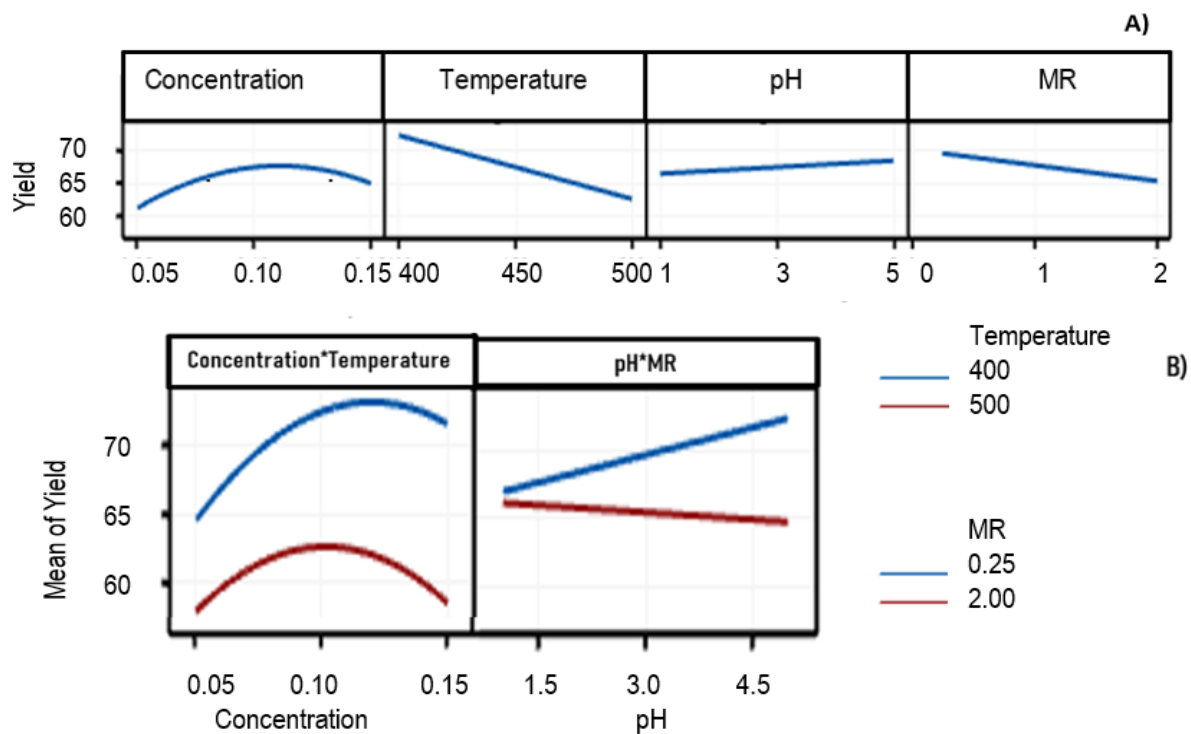


Figure 2. Effect of variables (A) and interactions (B) on yield.

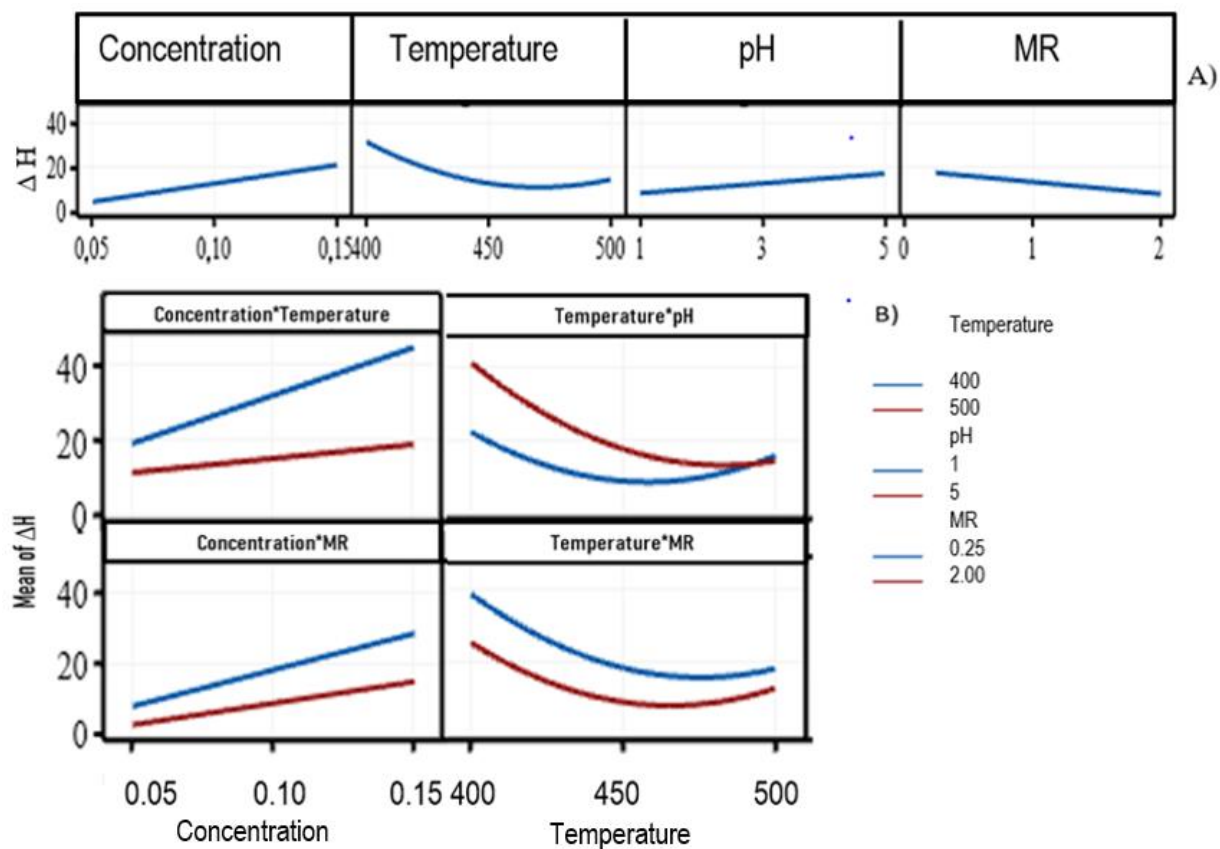


Figure 3. Effect of variables (A) and interactions (B) on ΔH .

With respect to the results observed in Figure 3, the variation of enthalpy of adsorption increases with the concentration of the metallic precursor and the synthesis pH while temperature and MR have a negative effect. In the adsorption field, the high values of enthalpy express a chemisorption involving a strong binding formation between the adsorbent and the pollutant [38, 39]. It was explained with the removal yield, that the formation of complexes between amine functional groups contained in malachite green and the iron species contained in iron oxide of the composite material is favored by the increasing of concentration and pH. That formation of complexes involves the formation of a strong

bond between malachite green and composite material and is traduced by high enthalpy while a high temperature can contribute easily to a break of the system support-iron which makes the system support-iron oxide-malachite green weak [34, 37] and impact negatively in the value of enthalpy.

The observation of contour plots shows which are the domains of variation of the variables for which we can obtain better results.

Case of yield response

Figure 4 illustrates the 3-D response surface and contour plots of the removal yield.

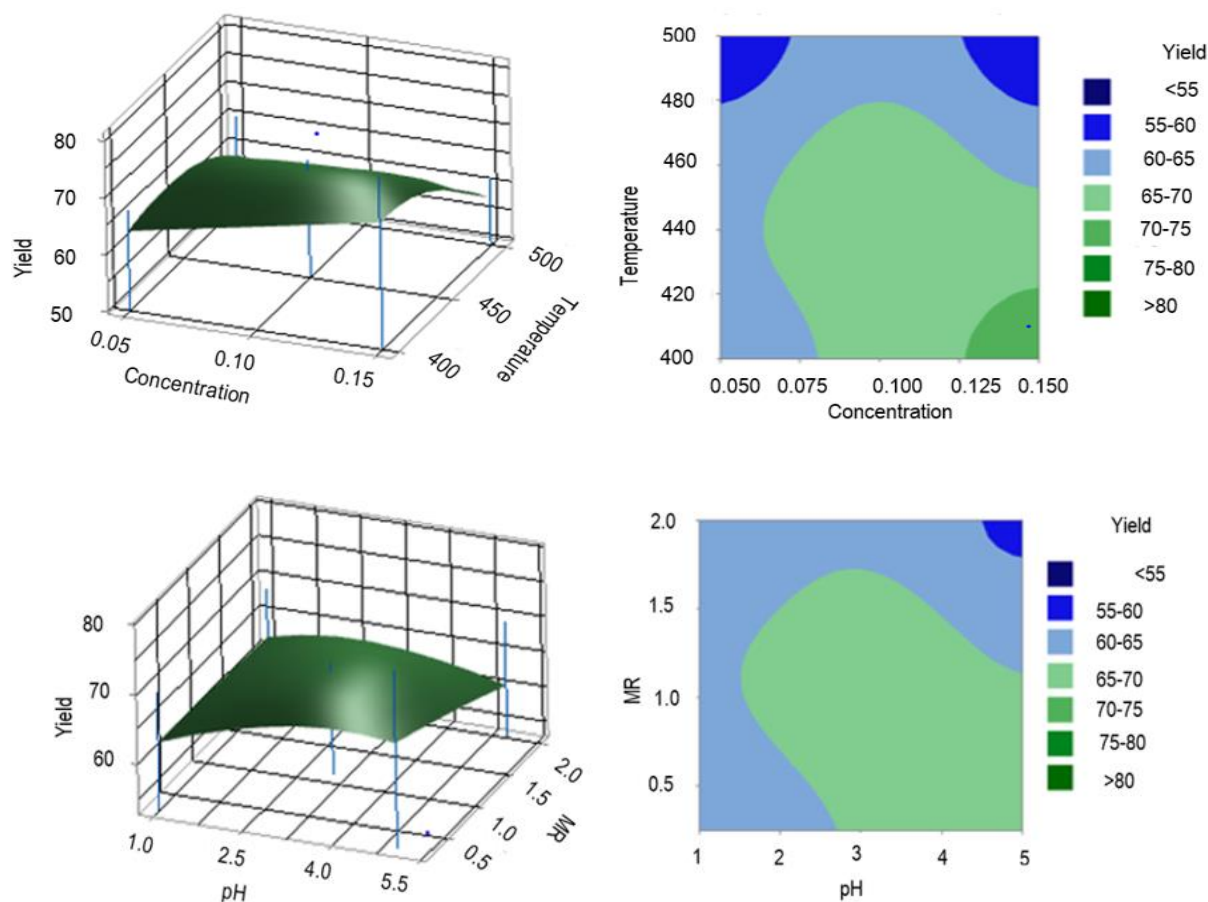


Figure 4. Responses surfaces and Contour plot of yield as a function of the variables studied.

The interaction X_1X_2 between temperature and concentration is the one on which the optimum range of the removal yield has been achieved. A removal yield higher than 70% is obtained with an iron concentration from approximately 0.125 to 0.15 mol.L⁻¹ and a temperature from 400 °C to 420 °C.

Case of variation of enthalpy response

Figure 5 illustrates the 3-D response surface and contour plots of the enthalpy variation.

The optimum range of the enthalpy variation is achieved

with the interactions X_1X_2 of concentration-temperature and X_2X_3 of temperature-pH. An enthalpy variation from 40 to 50 kJ.mol⁻¹ can be obtained with an iron (III) nitrate concentration between 0.13 mol.L⁻¹ and 0.15 mol.L⁻¹ and a temperature close to 400 °C also with a pH close to 5.

Optimal conditions

The optimal values of the different factors studied are illustrated at Figure 6.

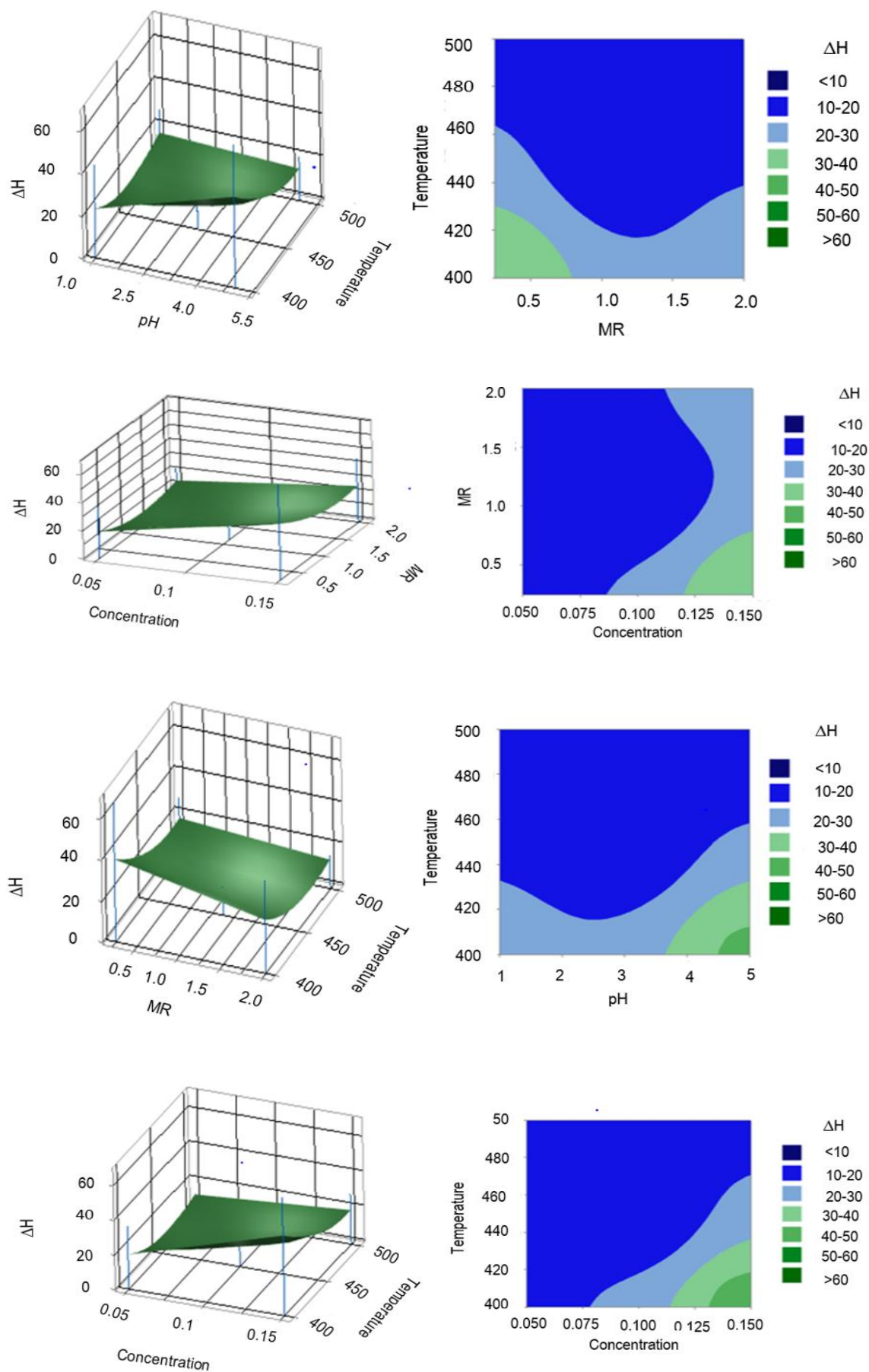


Figure 5. Responses surfaces and Contour plots of ΔH according to the studied variables.

The composite material with an adsorption capacity equal to 76.310% and an enthalpy of adsorption equal to 63.105 kJ.mol⁻¹ are obtained with a desirability upper to 0.900 at the following conditions: iron nitrate concentration of 0.150 mol.L⁻¹; annealing temperature of 400 °C; pH of 5 and molar ratio of 0.250.

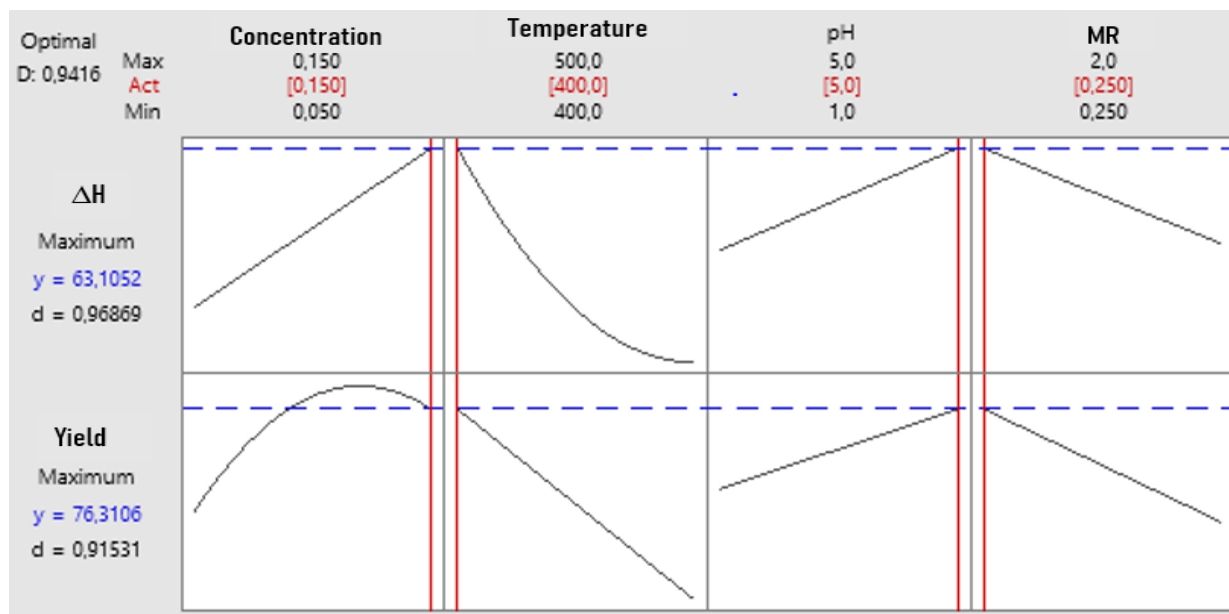


Figure 6. Optimal conditions.

5. Characterization of Activated Carbon and Composite Material

Activated carbon on which are deposited iron oxide nano-

particles and the composite material synthesized according to the optimal conditions obtained with design model have been characterized.

FT-IR

The FT-IR spectra of the two adsorbents are shown in Figure 7.

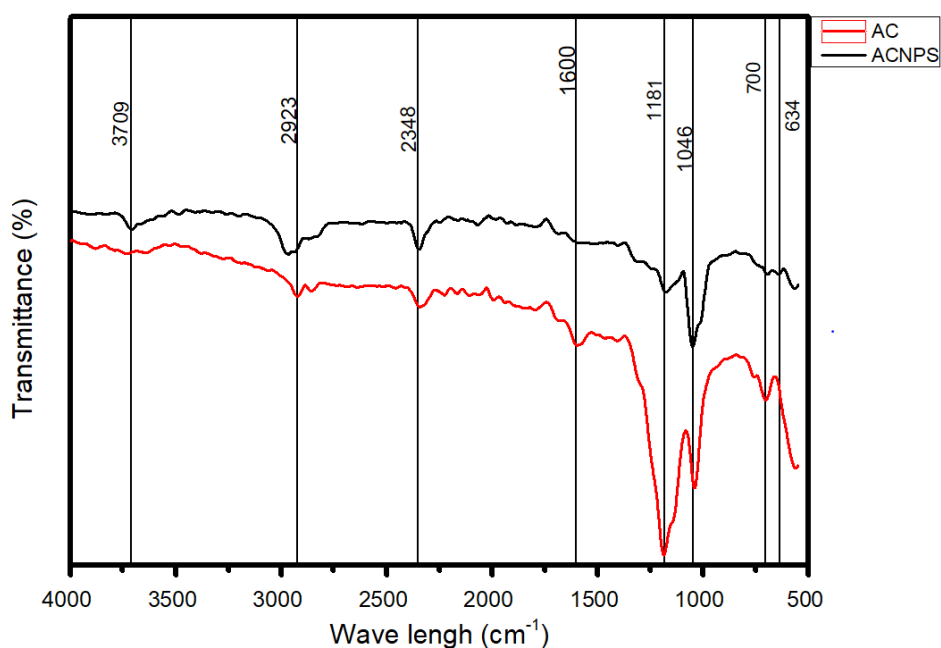


Figure 7. FT-IR spectra of AC and ACNP.

A broad peak around 3709cm^{-1} could be attributed to the stretching vibration of the OH groups of the oxygenated functions (carboxylic acids; alcohol; aldehydes, ester etc.) and adsorbed water molecules. This peak is wider for AC compared to ACNPS which could mean that the AC surface is richer in OH alcohol groups probably due to the dehydration during the annealing operation of ACNPS. The peak observed at 2923cm^{-1} corresponds to the CH vibrations of aldehydes; ketones or carboxylic acids aliphatic [40]. The peak at 1600cm^{-1} may be assigned to a combination of C=C stretching vibration of the aromatic ring structures or attributed to systems diketone, ketoester and quinone [41].

Others peaks visible between 1046cm^{-1} and 1181cm^{-1} can be attributed to the stretching C-O vibration of alcohol, carboxylate and ether structures [42]. The low intensity of these peaks for ACNPS against AC denote a decrease in C-O functions on the surface of ACNPS; these functions could be also the C-O bonds of alcohol which were broken by dehydration. The peak at 634cm^{-1} on FT-IR of ACNPS probably can be assigned to the crystalline mode vibrations of the Fe-O bond characteristic of iron oxide particles [43-45].

XRD

Figure 8, shows the different crystalline phases which have been grouped together in Table 5.

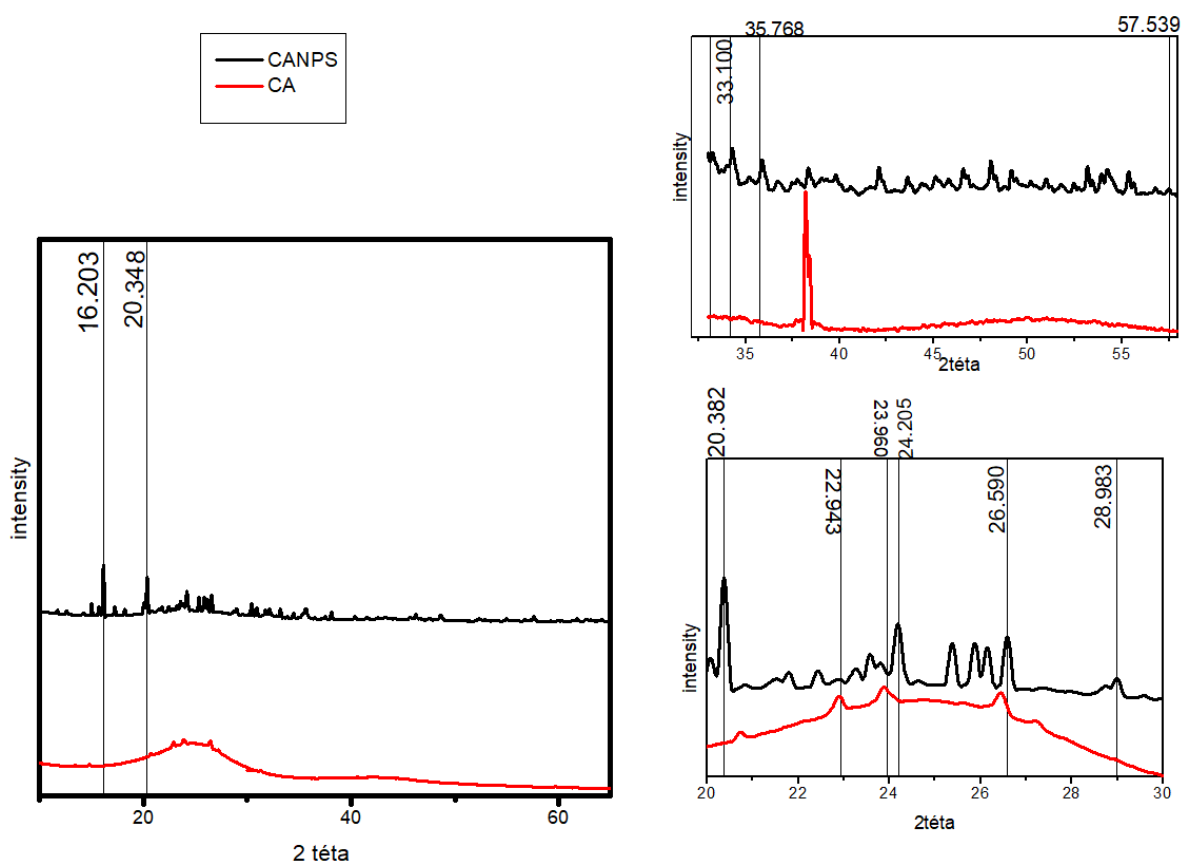


Figure 8. Diffractogram of material.

Table 5. Crystalline phases and Miller indices.

Materials	diffraction Angle (°)	crystallines Phases	Miller Indice
AC	22.943	$\text{NaAlSi}_3\text{O}_8$	(1-11)
	23.957	P_2O_6	(002)
	16.203	Acide benzoïque	(20-1)
ACNPS	20.381	$\text{Mg}_2\text{P}_2\text{O}_7$	(10-2)
	24.205; 33.100; 35.768; 57.539	Hématite	(1-12); (1-1-4); (2-10); (42-1)
	26.591	Graphite	(003)

In general, in Figure 8, two peaks which are present on the two adsorbent materials at positions 22.943° and 23.957° correspond respectively to the planes (002) and (1-11) for P_2O_6 and $NaAlSi_3O_8$ in table 5; these peaks could result from the process of activating the plant material with phosphoric acid and the calcination undergone by the silica contained in that plant material. The shape of the diffractogram of AC reveals a low crystallinity and a much more amorphous character which is an advantageous property for adsorption [46]. The diffractogram of ACNPS exhibited a visible peak at 26.591° corresponding to the plane (003) characteristic of

graphite and could result from the rearrangement of amorphous carbon during the thermal treatment. The ACNPS diffractogram also shows four visible peaks at 24.207° ; 33.099° ; 35.773° and 57.539° corresponding respectively to the planes (112); (114); (210) and (42-1) characteristics of hematite [47]. These results confirm the presence of Fe-O groups of hematite phase. The use of Profex software shows that the size of hematite crystallites varies from 25 to 37nm.

BET/BJH

Figure 9 regroupes the N_2 adsorption-desorption isotherms and the distribution pore width.

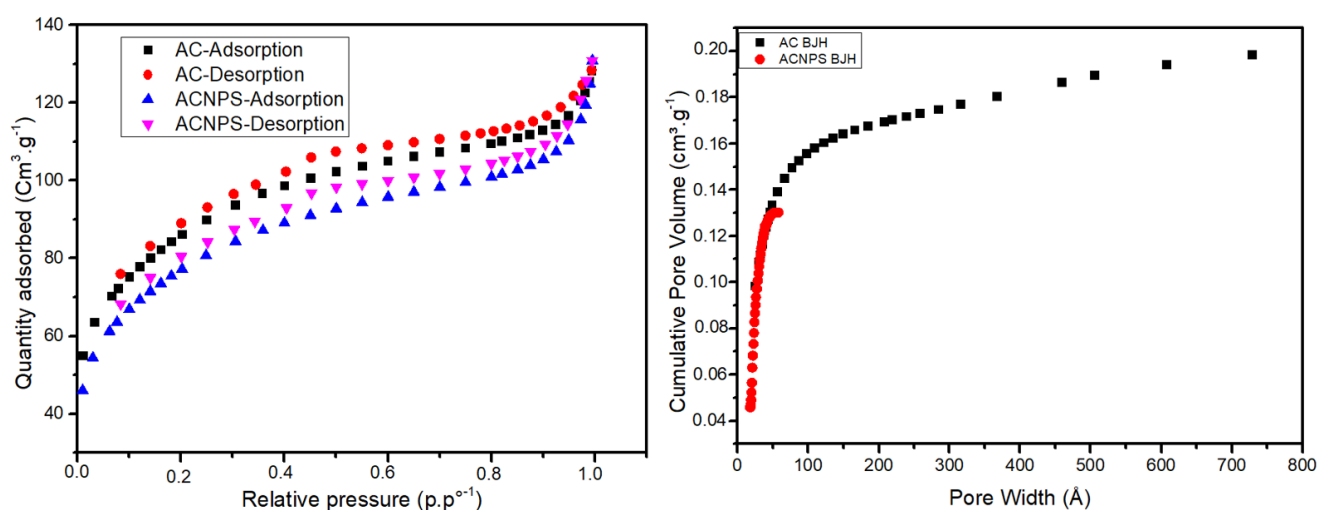


Figure 9. The N_2 adsorption-desorption isotherms and pores size distribution.

The specific area, pores width and volume are resume in table 6.

Table 6. Pore distribution of AC and ACNPS.

	Specific area ($m^2 \cdot g^{-1}$)	Median pore with (Å)	Total volume ($cm^3 \cdot g^{-1}$)
AC	312	32.797	0.202
ACNPS	282	24.603	0.199

The adsorption isotherms on adsorption-desorption graphs of AC and ACNPS are type II which involves multilayer adsorption with favorable interactions between particles and the materials surfaces. The hysteresis between adsorption isotherm and desorption isotherms on the two graphs denote the presence of mesopores [49]. The total surface area for adsorption given by BET analysis is $312 m^2 \cdot g^{-1}$ for AC and $282 m^2 \cdot g^{-1}$ for ACNPS, it reflects a reduction of the adsorption surface which is explained by the deposition of iron oxide nanoparticles on the activated carbon. The deposition of nanoparticles on the surface of the activated carbon results in the

blockage of certain pores and the reduction of the width of others. Table 6 shows a reduction of pores widths on the ACNPS surface which confirms deposition of iron oxide nanoparticles on pore openings of activated carbon. AC contains micropores (pore width $< 20 \text{ Å}$), mesopores ($20 \text{ Å} < \text{pore width} < 500 \text{ Å}$) and macropores (pore width $> 500 \text{ Å}$) while ACNPS only contains micropores and mesopores [48]. However, ACNPS is mostly mesoporous

whereas AC is meso and macroporous due to the high concentration of points at values greater than 50 Å on the BJH graphs of AC and ACNPS.

SEM/EDX Analysis of Materials

Figure 10 shows the morphology and the atomic composition of the different materials.

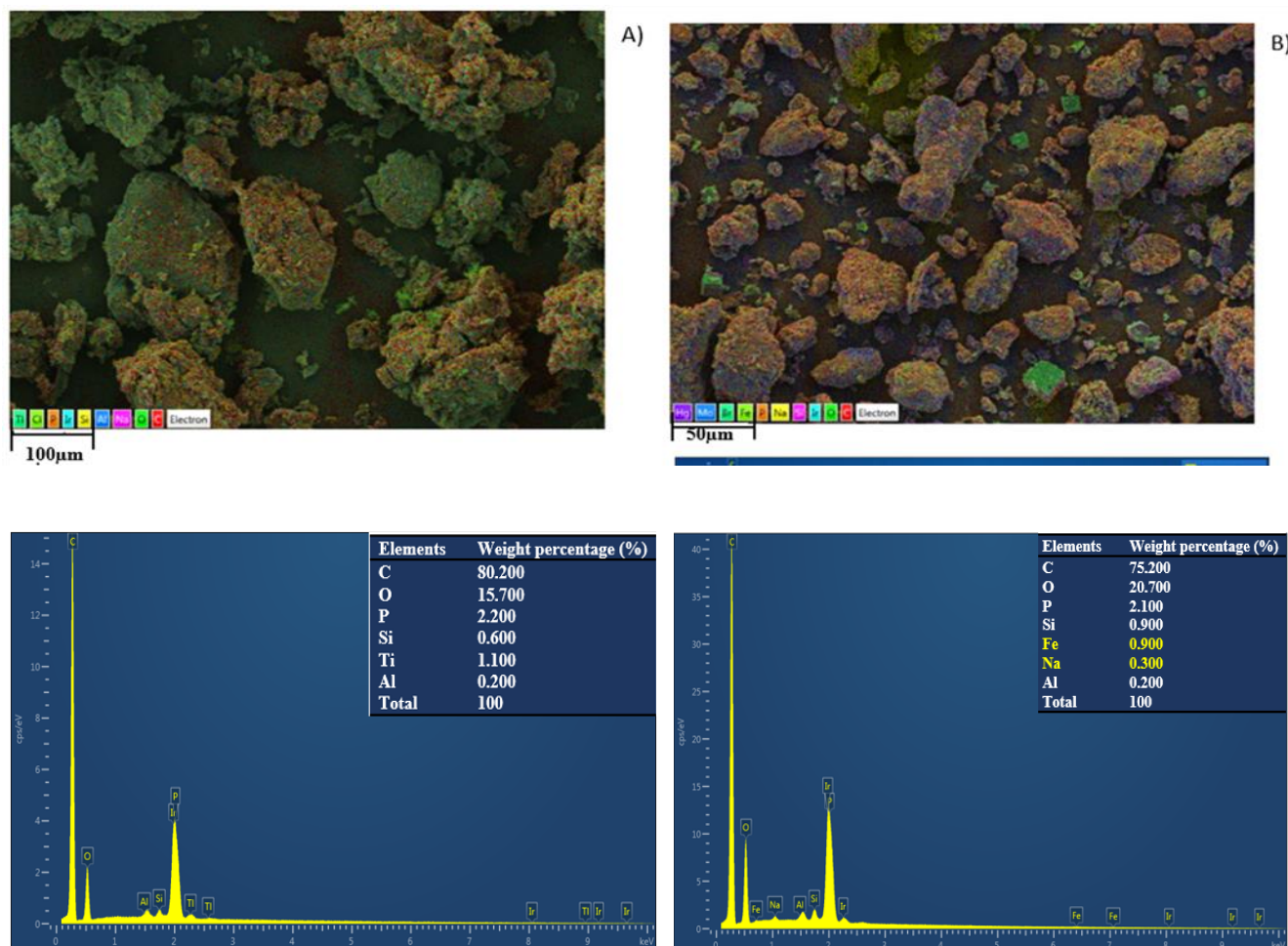


Figure 10. SEM and EDX results of AC (A) and ACNPS (B).

Micrographs show that the pores present at the AC surface are free while there are particles in the pores of ACNPS. This can be associated with the reduction of surface area for the composite material. The main common components of the two materials are carbon, oxygen and phosphorus. EDX analysis shows that ACNPS is also composed of iron (0.9%) obtained from the iron oxide nanoparticles. The percentage of oxygen has increased (from 15% to 20%) due to the addition of iron oxide whereas the carbon percentage has been reduced (from 80% to 74%) due to the double calcination. This increase in oxygen percentage and the percentage of iron on ACNPS confirm the presence of iron oxide.

DSC Analysis

Figure 11 shows the thermic behavior of adsorbents.

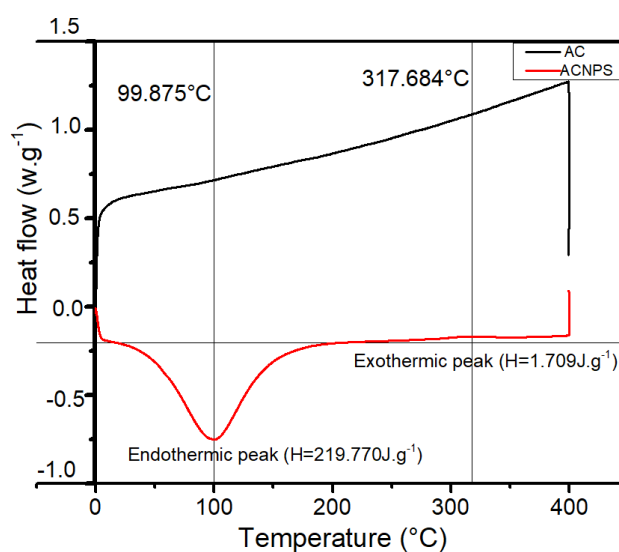


Figure 11. DSC curves of AC and ACNPS.

The DSC curve of AC does not present any endothermic or exothermic peak which expresses its amorphous character. This means that there is not any thermal transformation on the AC since the temperature of reorganization of amorphous carbon to the graphite structure which is an exothermic process has not been reached. Endothermic and exothermic peaks visible on the DSC curve of ACNPS attest to its semi-crystalline character due to the deposition of iron oxide nanoparticles [48]. The endothermic peak can be due to the

melting of crystalline hematite deposited on activated carbon. The existence of a low exothermic peak would mean that there are small amounts of noncrystalline ionic iron species on the ACNPS that would have undergone crystallization during thermal analysis.

ATG Analysis

Figure 12 below shows mass loss within the adsorbents according to temperature.

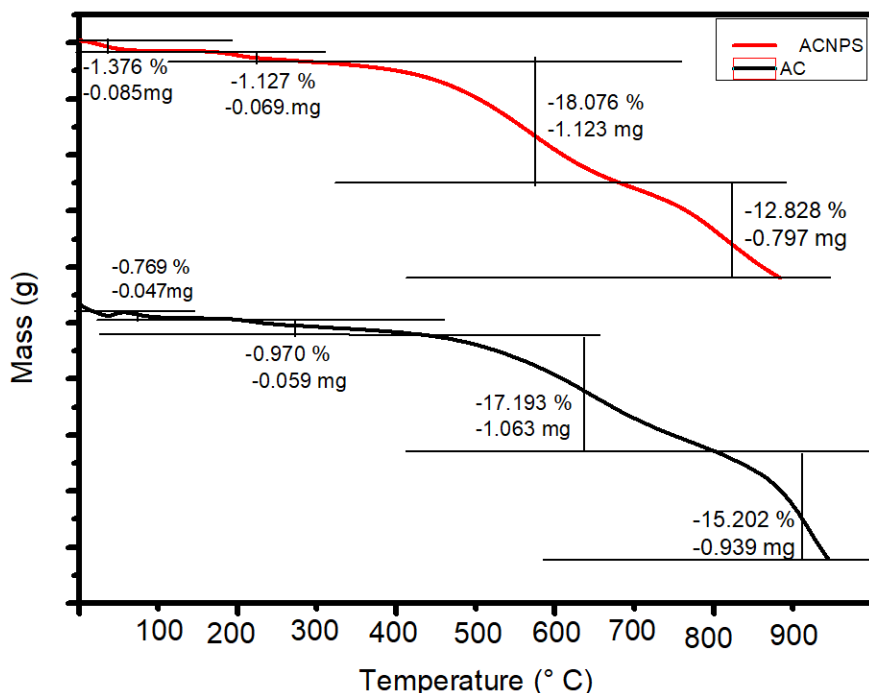


Figure 12. Thermogravimetric plot of AC and ACNPS.

Mass loss within the two materials occurs in four stages. The first mass loss happening around 100 °C is 0.769% for AC and 1.376% for ACNPS; this mass loss is attributed to dehydration of these materials. The mass loss in this area of temperature being higher for ACNPS than AC already proves a modification to the AC structure and denotes the more hydrophilic character of ACNPS due to the fact of the great affinity between the nanoparticles of iron species and water molecules. The second mass loss is observed between 200 °C and 250 °C for AC and ACNPS. This area of temperature corresponds to the decomposition temperature interval of carboxylic acid groups [41]. That mass loss observed for AC (0.970%) is less than that observed for ACNPS (1.127%); this could traduce the existence of citric acid residues used as chelating during the ACNPS synthesis process or decomposition of iron citrate residues from the chelation of iron contained in iron (III) nitrate by citric acid, literature places this decomposition between 200 and 300 °C because the decomposition of iron nitrate occurs at a temperature below 200 °C [36]. The third mass loss is in the temperature range ranging

from 500 °C to 700 °C for both adsorbents and could correspond to the decomposition of lactones, phenols and anhydride groups [41]. This mass loss is more important for ACNPS (18.076%) than AC (17.193%) which means that it could also correspond to the transformation of some forms of iron hydroxides and iron oxides on the surface of ACNPS [45]. The fourth mass loss occurs in the area of temperature between 800 °C and 900 °C. For this last range of temperature, mass loss is higher for AC (15.202%) compared to ACNPS (12.828%). This temperature area corresponds to the decomposition temperature interval of carbonyls, ethers and quinone groups. AC would be richer in these groups compared to ACNPS [41].

6. Evaluation of Adsorption Properties

Evaluation of removal yield

Figure 13 represents the evolution of the removal yield of MG with time for the two adsorbents.

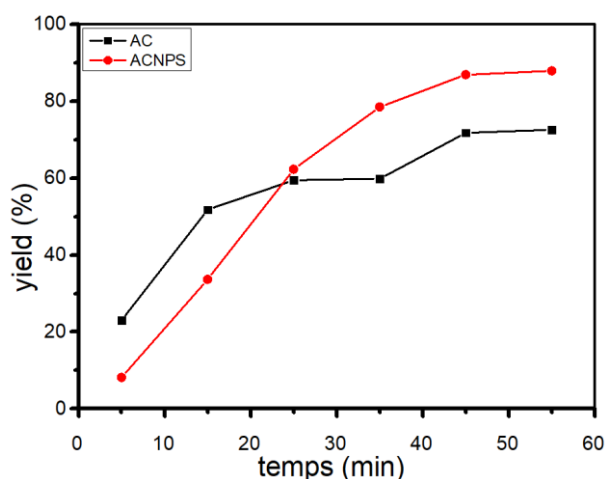


Figure 13. Evolution of the removal yield.

The adsorption on the two adsorbents surfaces takes place in three stages: the first step which is the fastest is shorter in AC (from 5 to 15 min) compared to ACNPS (from 5 to 25 min), the second stage in which we observe a reduction of the adsorption rate is however longer in AC (from 15 min to 50 min) compared to ACNPS (from 25 min to 50 min) and the third stage of 50 minutes to 60 minutes for the two adsorbents, during which we observe a bearing.

The first rapid step of adsorption on both materials is due to the presence of active sites available on the surface of the latter; however, the fact that it is even faster for AC than for ACNPS could mean that the attachment of MG molecules to the surface of ACNPS is a slow process characteristic of the establishment of strong bonds, including coordination bonds between the iron atom contained in the oxide nanoparticles and the nitrogen atom contained in the pollutant molecule. The maximum percentage of adsorption obtained in this phase is 50% for AC while it is 60% for ACNPS this could be contribute to confirming the increase in the density of active sites on the surface of ACNPS following the deposi-

tion of iron oxide nanoparticles on the surface.

The second step corresponds to the migration of MG molecules to the internal adsorbent sites through macropores and mesopores.

The last step where a bearing is observed for the two adsorbents symbolizes the stabilization of the adsorption process reflecting the saturation of all adsorption sites.

The total removal yield of the ACNPS is 80% while it is 70% for the AC. It means that the experimentation of optimal conditions determined with this design has allowed an increase of adsorption percentage by 10%.

Evaluation of thermodynamics parameters

Figure 14 shows the regression lines allowing thermodynamics parameters to be determined.

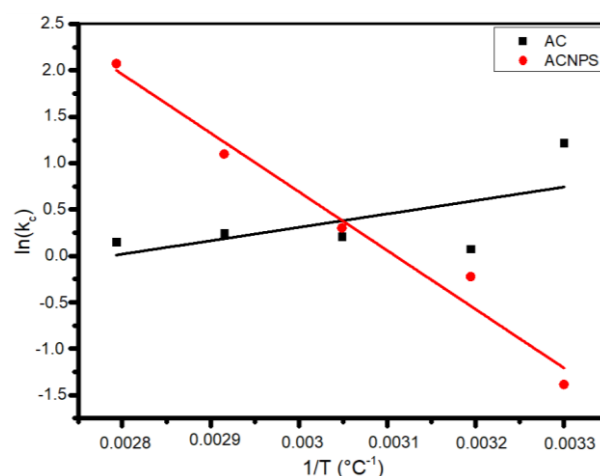


Figure 14. Thermodynamic regression linear.

The thermodynamics parameters have been grouped into Table 7.

Table 7. Thermodynamics parameters of AC and ACNPS.

	Temperature (K)	ΔG (kJ.mol ⁻¹)	ΔH (kJ.mol ⁻¹)	ΔS (kJ.mol ⁻¹ .K ⁻¹)
AC	303	-0.307	-12.010	0.033
	313	-0.198		
	328	-0.572		
	343	-0.703		
	358	-0.457		
ACNPS	303	0.349	52.602	0.026
	313	0.581		
	328	-0.818		
	343	-3.132		

Temperature (K)	ΔG (kJ.mol ⁻¹)	ΔH (kJ.mol ⁻¹)	ΔS (kJ.mol ⁻¹ .K ⁻¹)
358	-6.171		

The free energy of AC is negative for all the temperature values which correspond to a spontaneous and favourable adsorption. The negative values of the free energy for high temperatures for ACNPS imply that the spontaneity of the adsorption is ameliorated by temperature rise [49]. The variation of enthalpy increased after the deposition of the nanoparticles from -12.010 kJ.mol⁻¹ for AC to 52.602 kJ.mol⁻¹ for ACNPS. An increase in the variation of enthalpy suggests a formation of strong interaction between the material and the malachite green; in fact, a variation of enthalpy above 40 kJ.mol⁻¹ signify a chemisorption which involves strong interaction between pollutant and adsorbent such as coordination bonds or covalent bonds [27]. Adsorption is exothermic for AC due to its negative enthalpy value while it is endothermic for ACNPS due to its positive enthalpy value. The variation of entropy of the AC is greater than the one of ACNPS which denotes a more accentuated disorder at the AC interface than at the ACNPS interface [48].

7. Conclusion

It was question in this study to determine the optimal conditions that would allow us to synthesize a composite material formed of activated carbon and nanoparticles having an optimized adsorption properties. The results showed that the best adsorbent composite material would be obtained at an annealing temperature equal to 400 °C, an ionic iron concentration of 0.150 mol.L⁻¹, a synthesis pH equal to 5 and a molar ratio of 0.250. The composite material ACNPS (282 m².g⁻¹) synthesized following the conditions given by design contains a hematite phase and has a specific surface area reduced compared to that of activated carbon AC (312 m².g⁻¹) but the two adsorbents are micro and mesoporous. The synthesis conditions of composite material also allowed an increase in the adsorption yield of 10% and an increase in the variation of enthalpy thereby enabling from exothermic physical adsorption for AC (variation of enthalpy equal to -12 kJ.mol⁻¹) to endothermic chemical adsorption for ACNPS (variation of enthalpy equal to 52.6 kJ.mol⁻¹).

Abbreviations

AC	Activated Carbon
ACNPS	Activated Carbon with Nano Particles
ANOVA	Analysis of Variance
BET/BJH	Brunauer-Emmett-Teller and Barrett-Joyner-Hallenda

CFD	Central Full Design
DSC	Differential Scanning Calorimetric
FT-IR	Fourier Transform Infrared
MG	Malachite Green
MR	Molar Ratio Chelating Agent/Metal Precursor
SEM/EDX	Scanning Electronic Microscopy Coupled Energy Dispersive X Ray
TGA	Thermogravimetric Analysis
XRD	X Ray Diffraction
ΔG	Free Enthalpy Variation
ΔH	Enthalpy Variation
ΔS	Entropy Variation

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Conflicts of Interest

The authors declare no conflicts of interest.

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