

Empirical models for the correlation of input-output analysis on wheat straw samples

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Abstract

The use of wheat straw, a lignocellulosic material, as an adsorbent of hydrocarbons in water has been investigated after acid hydrolysis pretreatment. Experiments designed in a 3-level Box-Behnken fashion were made to determine the effect of various parameters affecting the behavior of the treated wheat straw as an adsorbent. The kinetics of the acid hydrolysis of cellulose, the reaction kinetics, adsorption isotherm and thermodynamic parameters are presented, as well as the empirical models for the acid hydrolysis and adsorption steps. The responses of several analytical methods such as Mercury Porosimetry, Thermogravimetric Analysis (TGA), Total Organic Carbon (TOC) and Scanning Electron Microscope (SEM) were utilized to characterize the material and its adsorbancy potential with the use of empirical models of non-linear regression and artificial neural networks (ANN).

Keywords: wheat straw, kinetics, acid hydrolysis, non-linear regression and artificial neural networks (ANN).

Introduction

Spilled oil causes severe environmental damage. A major problem with oil spilled in waterways is that it renders their water unusable for the municipal water supply either in industry or in agriculture (Blumer, M. 1969). The public concern for a healthy environment has led to new improved techniques and methods in order to deal with hazardous materials. In an effort to devise new methods for containment/mitigation of oil spills, we experimented with agricultural waste such as wheat straw, which is inexpensive, readily available, and has oil sorption capacity as well as low hydrophobicity (Lee, B.G et al. 1999). This lignocellulosic material consists of three main components, cellulose, hemicellulose and lignin, with an average composition in the range of 40–50, 20–35 and 15–35%, respectively. Cellulose microfibrils give wood cells their superior mechanical properties while hemicellulose and lignin act as a binder for cellulose crystallites. For the preparation of an adsorbent, the raw material is subjected to heat treatment or pyrolysis, which removes organic matter from the raw material resulting in an increase of material pore volume and surface area available for adsorption. The adsorbent capability depends on its structural and physicochemical features. The surface energy of a lignin film is similar to that of cellulose, but the contact angle of water for lignin is higher than that for cellulose, i.e., lignin is more hydrophobic or less hydrophilic than cellulose. The lignin surface contains charged functional groups that may attract charged oil droplets.

Straw-like adsorbing materials are capable of holding oil as a result of two processes: adsorption and absorption. The adsorption capacity depends primarily on the chemical structure of straw tissue that is in direct contact with oil, while the absorption capacity is a function of the structure of straw stalks in bundles, the distance between stalks, and the cross-sections of each stalk and leaf. Due to high oil adsorption by straw, oil is mostly held by capillary forces on straw tissue and interior parts of stalk and by oil bridges between stalks. Absorption of oil depends on the surface properties of straw. The hydrolysis reactions using dilute acid are complex for several reasons, including the fact that the substrate is a solid and the catalyst a liquid. The reaction rate of hydrolysis depends on temperature, acid concentration, time, and substrate concentration and composition. Previous studies showed that the cellulose fractions are hydrolyzed to water soluble glucose (Lenihan, P. et al 2011).

In previous works, thermo-hydrolyzed wheat straw treated under several conditions with maleic acid has been examined as adsorbent of hydrocarbons in water (Chatzizacharia et al. 2015, Tsiodra et al. 2015). Here, the kinetics of the acid hydrolysis of cellulose, the reaction kinetics, adsorption isotherm and thermodynamic parameters are going to be presented, as well as the empirical models for the acid hydrolysis and adsorption steps.

Material and Methods

The wheat straw used in this work was obtained from the Kapareli village, close to the city of Thiva in the Kopaida area of central Greece (harvesting year 2012), as a suitable source for full-scale industrial applications. The moisture content of the material when received was 8.8% w/w. After screening, the fraction of particle sizes between 10 and 20 mm was isolated.

The straw autohydrolysis process was performed in a 3.75-L batch reactor PARR 4843. The autohydrolysis isothermal time was 0-50 min (not including the preheating time). The reaction was catalyzed by organic acids produced by the wheat straw itself during autohydrolysis at a liquid-to-solid ratio of 20:1. The liquid phase volume (water) was 2000 mL and the solid material dose (wheat straw) was 100g. The temperature at reaction completion was 200°C, and it was reached after 66 min of preheating. The autohydrolysis took place at 200°C for 10min isothermally. In the modified wheat straw oil absorbance method, the ratio of water or oil absorbed to dry adsorbent weight was based on the ASTM F726-06 method. Following the standard method, 10PPM diesel produced by Hellenic Petroleum SA as well as crude oil was used (Chatzizacharia, K. et al. 2013). In the analysis that follows, the kinetics of the acid hydrolysis of cellulose, the reaction kinetics, adsorption isotherm and thermodynamic parameters are presented, as well as the empirical models for the acid hydrolysis and adsorption steps. The responses of several analytical methods such as Mercury Porosimetry, Thermogravimetric Analysis (TGA), Total Organic Carbon (TOC) and Scanning Electron Microscope (SEM) were utilized to characterize the material and its adsorbancy potential by use of mechanistic models of non-linear regression and artificial neural networks (ANN).

Results and Discussion

Kinetics of acid hydrolysis of cellulose

The hydrolysis reactions using dilute acid are complex for various reasons, including the fact that the substrate is a solid and the catalyst in a liquid. The reaction rate of hydrolysis depends on temperature, acid concentration, substrate concentration and composition. Previous studies showed that the cellulose fractions are hydrolyzed to water-soluble glucose. A fraction amounting to 80% of hemicellulose is hydrolysed to water-soluble xylose and the remaining fraction together with lignin remains insoluble. The model which has

been developed in order to describe the acid hydrolysis kinetics is presented below in Fig. 1, where RRH is the Reaction Resisting Hemicelluloses, ERH the Easily Reacting Hemicelluloses, WSOH the Water Soluble Oligosaccharides from Hemicelluloses, CC the Crystalline Cellulose, AC the Amorphous Cellulose, WSOC the Water Soluble Oligosaccharides from Cellulose, 5-HMF the 5-hydroxymethyl furfural (Katsamas and Sidiras 2014).

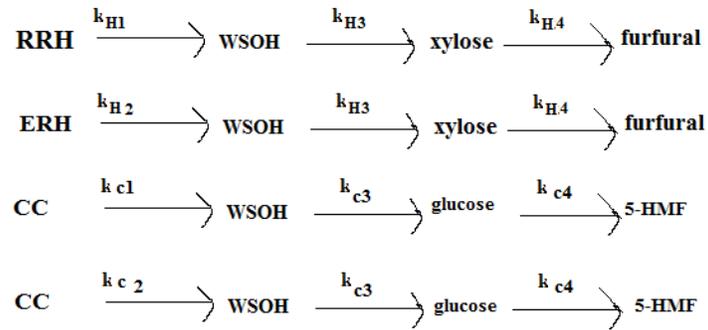


Fig. 1. Acid hydrolysis kinetics model

The reactions in acid hydrolysis treatment of xylan 1 and xylan 2 are described by a system of first-order kinetic equations. The hydrolysis of amorphous and crystalline cellulose, the hydrolysis of oligosaccharides and the degradation of xylose/glucose can be modeled by first-order kinetic expressions. Thus, the acid hydrolysis reactions of lignocellulosic materials are described as follows:

$$-(dC_{i1})/dt = k_{i1}C_{i1} \quad (1)$$

$$-(dC_{i2})/dt = k_{i2}C_{i2} \quad (2)$$

$$-(dC_{i3})/dt = k_{i1}C_{i1} + k_{i2}C_{i2} - k_{i3}C_{i3} \quad (3)$$

$$-(dC_{i4})/dt = k_{i3}C_{i3} - k_{i4}C_{i4} \quad (4)$$

$$k_{ij} = p_{ij} a e^{-E_{ij}/RT} \quad (5)$$

where $i=1$ is for cellulose hydrolysis and $i=2$ for hemicellulose hydrolysis, and $j=1,2,3$ or 4 for reaction-resisting and reacting hemicellulose, and crystalline and amorphous cellulose, respectively; p_{ij} and E_{ij} are the pre-exponential factor (min^{-1}) and activation energy ($\text{kJ}\cdot\text{mol}^{-1}$), respectively, a is the activity of the sulfuric acid and can be estimated by the equation $a = 10^{-\text{pH}}$ or $\text{pH} = -\log a$, and C_a is the sulfuric acid concentration. The concentration of the acid hydrolysis products obtained from the polysaccharides (cellulose and hemicellulose) is given by the following equation:

$$C_j = \frac{\sum_{i=C,H} C_{i,0,0} C_{ij}}{\sum_{i=C,H} C_{i,0,0}} \quad (j=0, 3, 4, T) \quad (6)$$

where $C_{i,0}$ is the initial experimental concentration of barely straw cellulose and hemicellulose.

$$R_0 = \int_0^1 e^{-T_\theta} \frac{T_r \theta}{\omega} dt \quad (7)$$

where T_θ is temperature in $^\circ\text{C}$, t is the time in min, T_r ($^\circ\text{C}$) is the reference temperature in $^\circ\text{C}$ and ω an empirical parameter related with the activation energy, which can be expressed as

$$\omega = RT_r^2 / E_{H_2} \quad (8)$$

where $R = 0.0083 \text{ kJ} / (\text{mol}\cdot\text{K})$ and E is the activation energy (kJ/mol).

The R_0 -model can be expressed as follows, taking into account eq.1-5 and 9-11.

$$C_{i0} = D_i e^{-k_{i1} R_0} + (1 - D_i) e^{-k_{i2} R_0} \quad (9)$$

$$C_{i3} = D_i L_{i13} e^{-k_{i1} R_0} + (1 - D_i) L_{i23} e^{-k_{i2} R_0} - [D_i L_{i13} + (1 - D_i) L_{i23}] e^{-k_{i3} R_0} \quad (10)$$

$$C_{i4} = D_i L_{i13} L_{i14} \frac{k_{i3}}{k_{i1}} e^{-k_{i1} R_0} + (1 - D_i) L_{i23} L_{i24} \frac{k_{i3}}{k_{i2}} e^{-k_{i2} R_0} - [D_i L_{i13} + (1 - D_i) L_{i23}] L_{i34} e^{-k_{i3} R_0} - [D_i L_{i13} \left(L_{i14} \frac{k_{i3}}{k_{i1}} - L_{i34} \right) + (1 - D_i) L_{i23} \left(L_{i24} \frac{k_{i3}}{k_{i2}} - L_{i34} \right)] e^{-k_{i4} R_0} \quad (11)$$

Reaction kinetics

The formation rate of the product glucose with respect to time is represented by equation below

$$dC/dt = kC \quad (12)$$

Adsorption Isotherms

The comparison of the adsorption capacity of the untreated and pretreated straw samples was based on the Freundlich and Langmuir and many other isotherm models. The first two models are both widely used for the adsorption of a plethora of oil on various lignocellulosic materials. The Freundlich isotherm is given by the following expression:

$$q = K_F C_e^{1/n} \quad (13)$$

where q is the amount adsorbed per unit mass of the adsorbent ($\text{mg} \cdot \text{g}^{-1}$), C_e is the equilibrium concentration of the adsorbate ($\text{mg} \cdot \text{L}^{-1}$) and K_F , n are the Freundlich constants related to adsorption capacity and intensity, respectively. The Langmuir adsorption isotherm has been successfully used to explain the adsorption of basic dyes from aqueous solutions. The Langmuir isotherm is given by the following expression:

$$q_e = Q_m b C_e / (1 + b C_e) \quad (14)$$

where q_e is the equilibrium concentration of oil in the adsorbed phase ($\text{mg} \cdot \text{g}^{-1}$), Q_m is the maximum adsorption capacity ($\text{mg} \cdot \text{g}^{-1}$), b is a constant related to energy of adsorption and C_e is the equilibrium concentration of oil in liquid phase ($\text{mg} \cdot \text{L}^{-1}$).

Thermodynamic parameters

The change in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) are related through the equations below (Vaishya and Gupta 2002):

$$\Delta G^0 = -RT \ln K \text{ with } \ln K = \frac{\Delta S}{R} - \frac{\Delta H}{R} T \quad (15)$$

where K is the adsorption equilibrium constant, R is the gas constant, T is the absolute temperature. The change in enthalpy and entropy, ΔH^0 and ΔS^0 , respectively, can be obtained from the slope and intercept of the Van't Hoff plot of $\ln K$ versus T^{-1} (Dermidas, et.al. 2008).

Empirical models for the correlation of input-output analysis on wheat straw samples

Acid hydrolysis evaluation- Response Surface Analysis

In the following analysis, the effect of the acid hydrolysis conditions of wheat straw on porosity, specific surface area, bulk density, TOC and TGA mass loss is evaluated. In Figure 1, the plots of the effects of the acid hydrolysis factors (maleic acid concentration- MC , reaction temperature- T and time- t) on response are presented. Porosity and surface area are two important physical properties that impact the quality and utilization of solid phase materials as adsorbents. Differences in the surface area and porosity of particles of the material, which may have the same physical dimensions, can greatly influence sorption performance characteristics and play a major role in adsorbency, efficacy and stability. From the plots, it is obvious that porosity variation means are highly affected by T , with an almost constant negative slope, and less by MC and t . The specific surface area variation mean is affected by all the three parameters, where MC has a clear negative effect, with T in the range from 180 to 200 °C and t in the range from 0 to 25 min having the greater effects. The efficiency of an adsorbent is also related to its bulk density, as the lower the bulk density is, the higher is its adsorbency. Low bulk density means less solid material in a specific volume indicating high porosity, which is an essential factor for efficient adsorbency. The bulk density variation mean is much affected by T , with a positive effect, and by MC values from 0.010 to 0.055 M. The TGA mass loss needs to be increased in the case of acid treated wheat straw material because of the removal of cellulose and hemicellulose, a fact that consequently increases the material adsorbency. TGA variation means appear to be

affected by MC , t and T from 180 to 220 °C. Finally, regarding TOC, it is expected to be lower in the case of acid hydrolyzed wheat straw adsorbents than that of raw material, because of the removal of cellulose and hemicellulose, a fact that also increases the final adsorbency. The mean values of TOC variation are negatively affected by MC , T , and t values from 25 to 30 min.

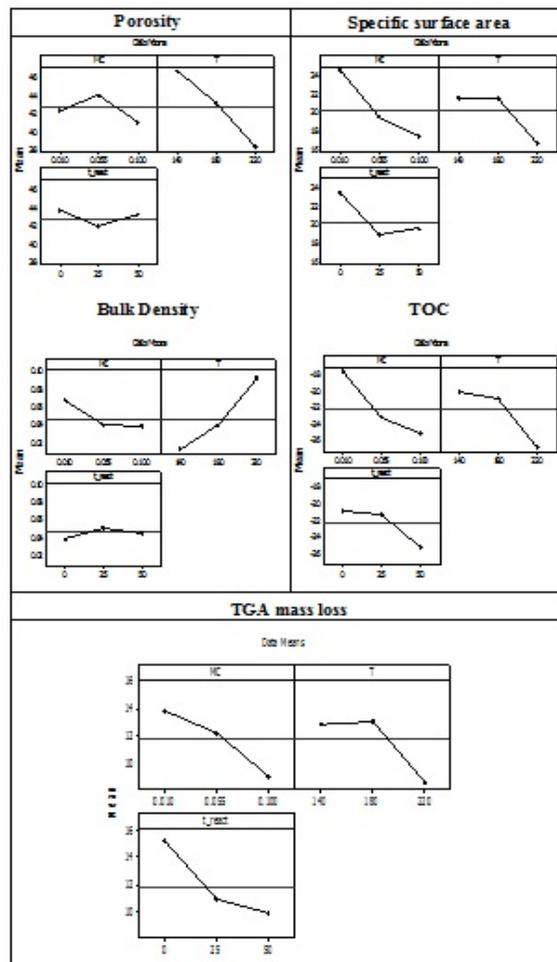


Fig. 2. Main effects plots of the acid hydrolysis factors on the responses variation from the raw wheat straw samples means

A response surface analysis of the designed and performed experiment is shown in Table 1. Coded units were used in order to compare the impact of various factors on responses. Regression analysis and Analysis of Variance show a good stability and inherent variability of the center point responses. Porosity is found to be a strong function of the treatment temperature (T), with statistical significance $p=0.002$, total specific surface area ($Surf. Area$) is a strong function of T , maleic acid concentration (MC), reaction time (t), and quadratic terms and interactions, with statistical significance $p<0.05$, and bulk density ($Bulk Density$) is a strong function of T , with statistical significance $p=0.001$. Finally, TOC is a strong function of MC and T , and TGA Mass loss ($Mass loss$) of MC and t , with statistical significance $p<0.05$. The resulting regression models are presented in Eqs. 16a-e.

$$Porosity = -0.032 * T + 49.790 \quad (16a)$$

$$Surf. Area = -564.922 * MC + 0.317 * T - 0.396 * t - 0.001 * T^2 + 0.004 * t^2 + 2.370 * MC * T + 2.385 * MC * t + 20.902 \quad (16b)$$

$$BulkDensity = -0.002 * T + 0.136 \quad (16c)$$

$$TOC = -354.917 * MC + 0.463 * T - 39.792 \quad (16d)$$

$$TGAMassloss = -114.806 * MC - 0.468 * t - 12.424 \quad (16e)$$

Table 1. Acid hydrolysis designed experiment and responses variation from the raw wheat straw samples

Run Order	Pt Type	Blocks	Maleic C (M)	T (oC)	t (min)	Porosity variation	Spec. surface area variation	Bulk Density variation	TOC variation	TGA mass loss variation
1	2	1	0.100	140	25	46.53	12.00	0.009	-22.51	10.65
2	2	1	0.010	180	50	43.90	20.70	0.050	-23.25	5.93
3	2	1	0.100	220	25	36.45	16.46	0.085	-27.58	3.50
4	2	1	0.100	180	0	39.33	20.55	0.032	-23.97	10.73

5	2	1	0.010	180	0	45.44	31.15	0.060	-10.27	25.35
6	2	1	0.100	180	50	42.23	20.84	0.025	-26.46	11.02
7	2	1	0.055	220	0	40.26	17.77	0.060	-25.72	11.27
8	2	1	0.010	220	25	37.20	16.88	0.120	-25.14	9.39
9	2	1	0.055	140	50	47.47	20.91	0.000	-22.27	12.70
10	0	1	0.055	180	25	43.29	20.40	0.054	-23.47	14.47
11	2	1	0.055	220	50	39.64	16.03	0.104	-28.64	9.95
12	2	1	0.010	140	25	43.13	29.47	0.042	-11.57	14.60
13	0	1	0.055	180	25	42.52	18.90	0.017	-15.36	9.06
14	0	1	0.055	180	25	45.22	19.01	0.036	-22.71	14.47
15	2	1	0.055	140	0	49.85	24.27	0.003	-23.48	13.43

The surface and contour plots of the response variables are presented below in Fig.3. The surface plots help the visualization of the response surface and show how a response variable relates to factors based on model equations. On the other hand, contour plots show combinations of factors on a plane that produce same value responses. Moreover, the interaction plots of the response variables are presented, where an interaction occurs when the effect of one factor is dependent upon a second factor. Thus, these plots are used to compare the relative strength of the effects across factors.

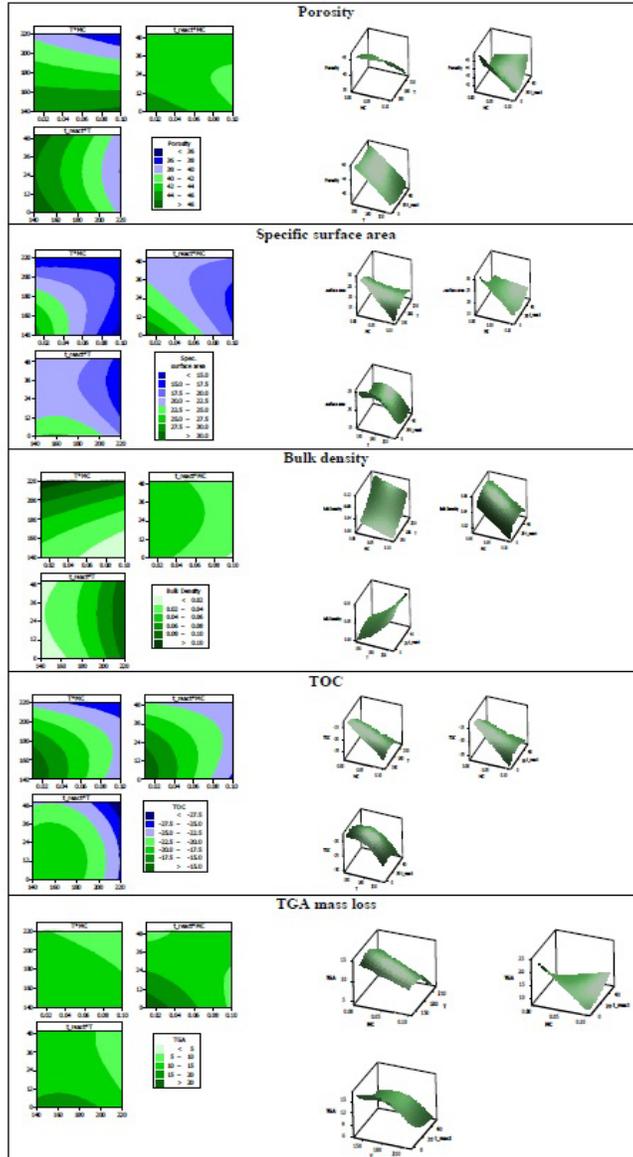


Fig. 3. Surface and contour plots of the acid hydrolysis factors on the responses variation from the raw wheat straw samples means

In order to optimize the adsorption capability of the wheat straw samples examined, the porosity, surface area and TGA mass loss variations must be maximized, while the bulk density and TOC variations must be minimized.

Porosity, and capillary structure develop differently under different wheat straw acid hydrolysis conditions. Associated with porosity is material permeability, i.e. the extent to which the pores and capillary structures are interconnected throughout the material. These networks, their size, structure and orientation affect the degree and depth to which moisture, vapors and liquids can be absorbed into the interior of the material or migrate from the substrate by capillary action through the material. Permeability may be greater in some directions than others based upon the pore size, shape and the distribution of the interconnectedness of the system. Adsorbency is the result of these two properties and is an important determining factor in material sensitivity to stains. The size of the pores, their orientation, how well they are connected into networks and the type of finish the material has are important contributing factors to a material's overall adsorbency.

The specific surface area, which is important for transport and chemical reaction, increases when particle size decreases and its particle porosity increases. Even for materials with the same weight and volume, the surface activity and adsorption volume vary with specific surface area. So the specific surface area plays an important role in the evaluation of activity and adsorption capacity of materials (e.g. catalysis and adsorbent). The usefulness of acid hydrolyzed wheat straw adsorbent derives mainly from its large micropore (and sometimes mesopore) volume and the resulting high surface area. At the same time, low values of bulk density show less solid material in a specific volume indicating high porosity. Therefore, it is expected that the bulk density of the acid hydrolyzed wheat straw adsorbents will be lower than the raw material.

Regarding the TGA mass loss, needs to increase in the case of acid treated wheat straw material because of the removal of cellulose and hemicelluloses. Lignin pyrolysis is accelerated as some hemicelluloses are extracted from wheat straw at the same temperature, when temperatures exceed 350 °C. Most decomposition products are volatile, according to the results of the total decomposition of cellulose and hemicelluloses during wheat straw pyrolysis. The main residue of lignin pyrolysis char. Finally, because of the removal of cellulose and hemicellulose, TOC is expected to be lower in the acid hydrolyzed wheat straw.

A graphical representation of the acid hydrolysis conditions that lead to such results and consequently to optimal adsorption is presented in Fig. 4. The contours of the responses are placed on top of each other, and each set of them defines the boundaries of acceptable response values. The white area represents the feasible region of acceptable limits from all the responses, simultaneously. In this figure, any combination of acid hydrolysis conditions, within the experimental limits, can be easily evaluated whether it results in acceptable responses, i.e. in wheat straw with high adsorptive performance or not. For example, the conditions of $MC = 0.05$ M, $t = 50$ min and T ranging from 140 to 180°C result in optimal adsorption performance, while T values above 180°C result in non-acceptable samples.

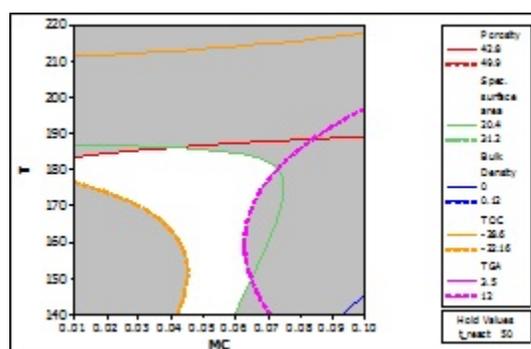


Fig. 4. Overlaid contour plot of acid hydrolysis conditions resulting in high adsorptive performance of wheat straw samples

Acid hydrolysis evaluation- Artificial Neural Networks Analysis (ANN)

In recent years, it has been shown that Artificial Neural Networks (ANN) can provide an alternative approach to traditional mathematical approaches, by applying mathematical constructs that are capable of “learning” relationships within data, with no prior knowledge required from the user. A neural network composed of an input and output layer with one hidden layer, i.e., a three-layer back propagation network was chosen for the purposes of this study. A sigmoidal function was used as the transfer function for the hidden layer and back propagation of errors, while a linear transfer function was used for the output layer. The Mean Squared Error (MSE) was used as the performance function of different number of nodes in the hidden layer and the optimal ANN structure was used for each data set. The network with 10 nodes in the hidden layer is selected as optimal with the maximum regression value of 99%. The efficiency of the network depends on the number of nodes, due to possible under- or over-training of the network. The optimal hydrolysis conditions calculated by ANN with 10 nodes is $MC = 0.055 \text{ M}$, $t = 50 \text{ min}$ and $T = 150^\circ\text{C}$. This result is in agreement with the acceptable (white) area of Fig. 4. It has been demonstrated that ANN is as effective and sometimes superior to polynomial equations in predicting quantitative non-linear relationships between variables and responses, with benefits like effective use of incomplete data sets, rapid analysis of data, ability to accommodate more data and retrain, and ability to generate understandable rules. However, some drawbacks are the trial-and-error procedure of best node number choice for training, the fact that the problem must be numeric in nature and that reasonable quantities of data should be available to train an adequate model. The greatest benefits are

achieved for multidimensional problems where it is difficult to express any analytic model and to abstract the rules by any other mechanism than neural computing.

Acid hydrolysis hydrocarbons adsorbance evaluation on different hydrocarbon and water media-

Response Surface Analysis

The performance of the hydrolyzed samples' absorptive capability on different hydrocarbon and water media (i.e. crude oil, diesel, their respective oil spills and water) is evaluated by the variation in porosity, specific surface area, bulk density, TOC and TGA mass loss. In Fig.5, the plots of the effects of acid hydrolysis factors on response means of hydrocarbon media are presented. It is obvious that for wheat straw samples in crude oil, porosity and bulk density variation means are highly affected by *T*, surface area variation is affected by *MC*, especially in the range from 0.01 to 0.055 M, while TOC and TGA mass loss variations are affected by *MC* and *T*. The same behavior is detected for the oil spill crude oil as well. For wheat straw samples in diesel, porosity and surface area variations are affected by *MC*, and bulk density, TOC and TGA variations by *T*. The oil spill, is strongly affected by *MC* (especially in the range from 0.01 to 0.055 M) and *T*. Finally, for wheat straw samples in water media, *MC* and *T* have a strong effect, especially on middle to high values of response variation.

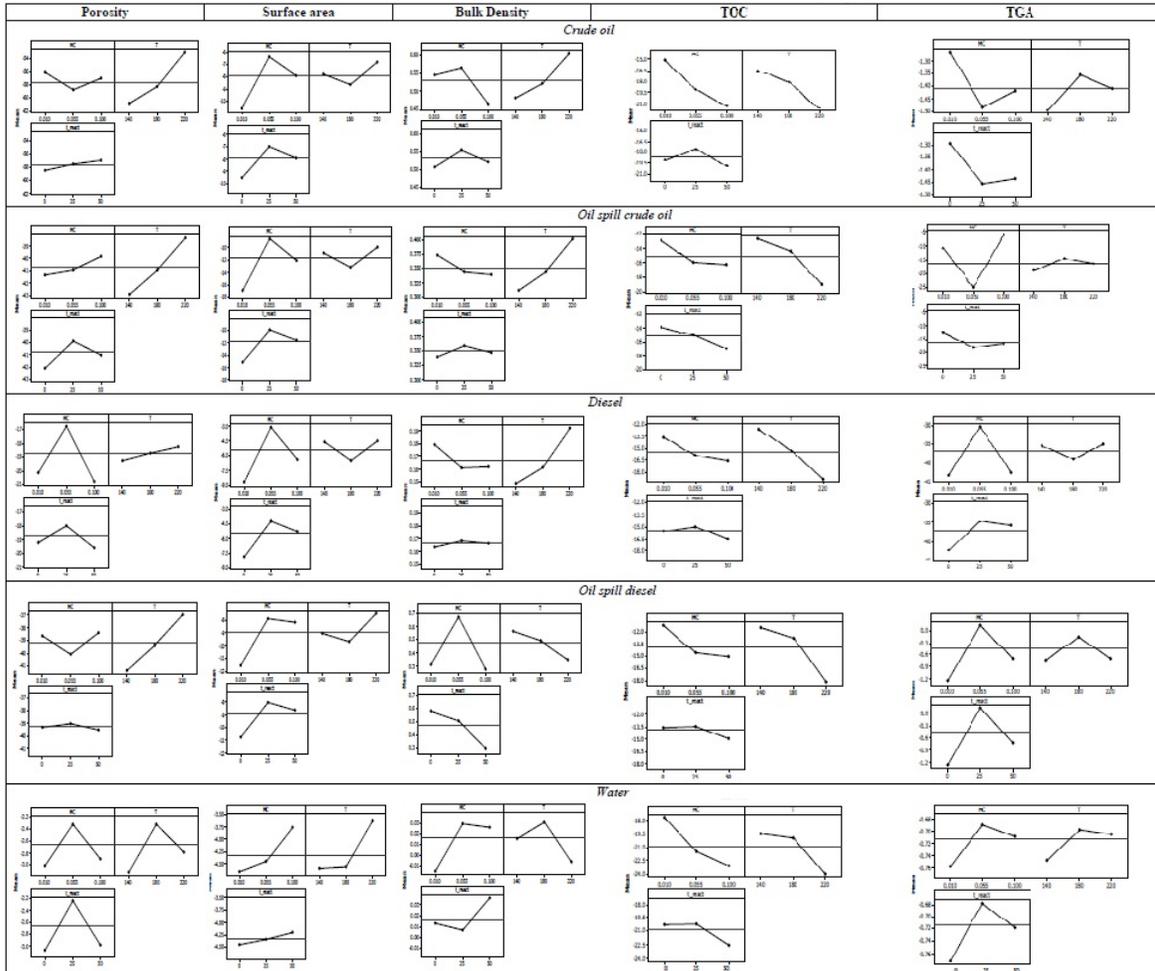


Fig. 5. Main effects plots of the acid hydrolysis factors on the responses variation from the wheat straw samples and hydrocarbon media mean values

A response surface analysis is presented. The resulting effects seem to agree with the results of the means from Fig.5. The regression models are well presented by Eqs. 17-22. Bulk density variation for wheat straw in diesel oil spill and water, as well as porosity and TGA variation for water show no significant terms with acceptance level 95%. The resulting surface and contour plots are shown in Fig.6.

$$\text{porosity_crude oil} = 0.07 * T - 67.59 \quad (17a)$$

$$\text{Surf.area_crude oil} = -1415.66 * MC^2 - 23.25 \quad (17b)$$

$$\text{Bulk density_crude oil} = 0.002 * T + 0.211 \quad (17c)$$

$$\text{TOC_crude oil} = -68.58 * MC - 2.70 \quad (17d)$$

$$\text{TGA_crude oil} = -1.69 * MC - 1.44 \quad (17e)$$

$$\text{porosity_crude oil spill} = 0.04 * T - 48.55 \quad (18a)$$

$$\text{Surf.area_crude oil spill} = -2934.13 * MC^2 - 35.51 \quad (18b)$$

$$\text{Bulk density_crude oil spill} = -0.978 * MC + 0.001 * T - 0.176 \quad (18c)$$

$$\text{TOC_crude oil spill} = -0.08 * T + 2.53 \quad (18d)$$

$$\text{TGA_crude oil spill} = 54.3 * MC - 22.77 \quad (18e)$$

$$\text{porosity_diesel oil} = -1836.51 * MC^2 - 22.04 \quad (19a)$$

$$\text{Surf.area_diesel oil} = -2211.74 * MC^2 - 17.40 \quad (19b)$$

$$\text{Bulk density_diesel oil} = 0.001 * T + 0.087 \quad (19c)$$

$$\text{TOC_diesel oil} = -0.08 * T + 0.95 \quad (19d)$$

$$\text{TGA_diesel oil} = 8.25 * MC - 41.59 \quad (19e)$$

$$\text{porosity_diesel oil spill} = 0.04 * T + 772.99 * MC - 44.83 \quad (20a)$$

$$\text{Surf.area_diesel oil spill} = 321.40 * MC - 981.91 * MC^2 - 0.98 * MC * T - 26.12 \quad (20b)$$

$$\text{TOC_diesel oil spill} = -0.08 * T + 4.18 \quad (20c)$$

$$\text{TGA_diesel oil spill} = 5.95 * MC - 1.16 \quad (20d)$$

$$\text{Surf.area_water} = -0.47 * MC * T - 11.54 \quad (21a)$$

$$\text{TOC_water} = -60.31 * MC - 6.38 \quad (22b)$$

It is obvious that the same factors tend to affect the crude oil adsorbance and its respective spill response variables. The wheat straw in water adsorbance capability is affected by the interaction of MC and T , a fact that is noted in the response of the diesel oil spill as well. This is expected as diesel is lighter than crude oil and obviously can play a more important role in the oil spill.

For wheat straw in crude oil, the highest porosity and bulk density differences are calculated for the raw crude oil, because of its heavy fractions. For diesel, the highest differences are noted for the spill case, because water acts as a vehicle that transfers diesel molecules in the inner layers of the adsorbent increasing the overall diesel uptake. For both cases, TOC shows the highest differences for the raw crude and diesel oil, as the hydrocarbons are at highest concentration. Finally, TGA for raw hydrocarbons and their spills is only affected by the MC factor and shows higher results for the crude oil spill and the raw diesel. In the TGA results of the samples with crude oil and diesel (Tsiodra et al. 2015), it is observed that crude oil removal starts at lower temperature compared to that for diesel removal, because of the presence of volatile fractions. Moreover, the rate of weight loss for crude oil is smoother compared to that for diesel, because of heavy fractions.

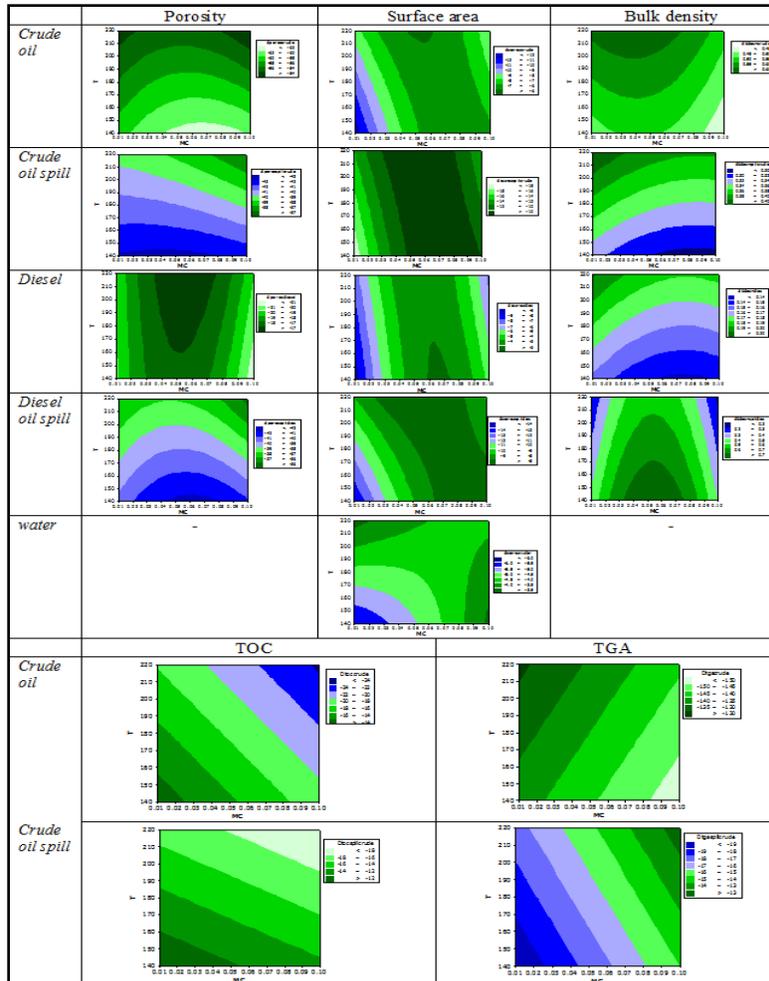


Fig. 6. Surface and contour plots of the acid hydrolysis factors on the responses variation from the wheat straw samples and hydrocarbon media

**Acid hydrolysis hydrocarbons adsorbance evaluation on different hydrocarbon and water media-
Artificial Neural Networks Analysis**

As before, a neural network composed of an input and output layer with one hidden layer, i.e., a three-layer back propagation network was chosen for the purposes of this study. A sigmoidal function was used as the transfer function for the hidden layer and back propagation of errors, while a linear transfer function was used for the output layer. The MSE was used as the performance function of different number of nodes in the hidden layer and the optimal ANN structure was used for each data set. The network with 5 nodes in the hidden layer is selected as optimal with the maximum regression value of 99.1%. In this case, due to the large number of response variables per hydrocarbon media and per absorbance parameter, the use of ANN method offers great benefits, as it is difficult to efficiently express an analytic model and abstract the rules by any other mechanism than neural computing. Moreover, the optimal solution from the raw to acid hydrolyzed wheat straw, i.e. $MC = 0.05$ M, $t = 50$ min and T ranging from 140 to 180°C, with the ANN method results in an optimal point for the absorbance performance parameters as well. Every other combination of hydrolysis parameters can be easily evaluated through the resulting responses calculations and vice versa.

Conclusion

The maleic acid hydrolysis of wheat straw in batch mode was studied. The hydrolysis kinetics of cellulose and hemicellulose were fitted with a first and second order model. Sorption equilibrium isotherms were modeled by Langmuir, Freundlich and Temkin expressions. The effect of acid hydrolysis conditions on porosity, specific surface area, bulk density, TOC and TGA mass loss of wheat straw was evaluated with regression and ANN models. The adsorption capability of wheat is maximized, when the porosity, surface area and TGA mass loss are maximized, while the bulk density and TOC variations are minimized. A graphical representation of acid hydrolysis conditions provide a way of defining an overlapping region in which various combinations of acid hydrolysis conditions, within experimental capabilities, lead to high adsorption

performance. The optimal hydrolysis conditions calculated by an ANN model with 10 nodes are $MC = 0.055$ M, $t = 50$ min and $T = 150^\circ\text{C}$, a result in agreement with that of the regression analysis.

Finally, the absorptive capability of hydrolyzed samples' indifferent hydrocarbon and water media (i.e. crude and diesel oils as well as their respective oil spills in various types of water) was evaluated. For wheat straw in crude oil, the highest porosity and bulk density are observed for raw crude oil, because of its heavy fractions. Surface area is higher for samples in crude oil spills. For diesel oil, the highest values are observed for the spill case, because here the water acts as a vehicle that transfers diesel molecules into the inner layers of the adsorbent, thus, increasing the overall diesel uptake. TOC shows the highest differences for raw crude and diesel oil, as the hydrocarbons are at higher concentrations. Finally, for both types of raw oil and their spills, TGA is affected by the MC factor and shows higher values for the crude oil spill and the raw diesel oil cases. It is observed that crude oil removal starts at lower temperature than that in the case of diesel oil, because of the presence of volatile fractions. The rate of weight loss for crude oil is smoother than that for diesel oil, because of heavy fractions. As before, a neural network model was utilized to find the optimal conditions of adsorbance.

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