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Petroleum Absorbers Based on CNSL, Furfural and Lignin – The Effect of the Chemical Similarity on the Interactions among Petroleum and Bioresins

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Summary: The petroleum has become our most important source of energy since the mid-1950s. It is due to its high energy density, easy transportability and relative abundance. However, along extraction, storage or transportation of oil, spill accidents may happen. This kind of accident causes severe impacts on the environment, being directly responsible for the destruction of the marine life, which affects the fishing and even tourism industries. Main goal of this work is related to the use of renewable sources aiming to obtain "absorbent green materials". These materials were synthesized by a typical phenolic resin polycondensation route using cashew nut shell liquid (CNSL) as main phenolic compound. Focused on keep the green characteristic of the materials, furfuraldehyde from hemicellulose was used as aldehyde and the reaction was catalyzed using a small amount of sulfuric acid. Resins were characterized using Optical Microscopy, Scanning Electron Microscopy, Infrared Spectroscopy with Fourier Transformed (FTIR) and density tests. In addition, contraction of the oil spilled was studied in presence of resins. Obtained results demonstrated that synthesized resins present a good chemical similarity with oil, which produces a good interaction among resins and oil, making easy the contraction of the oil spot on the water and, consequently, the removal process of oil spilled on water.

Keywords: cashew nut shell liquid; experimental design; furufuraldehyde; lignin; petroleum

Introduction

Humanity is still very dependent on crude oil. In spite of the large efforts related to the reduction of the petroleum consumption, our society remains depending on this resource as an energetic source besides raw material for the production of several commodities. In addition, petroleum is, principally, carried through far distances by marine routes, increasing the chances of accidents. These accidents involving oil spill produces devastating impacts on the environment, since the lipophilic hydrocarbons of the petroleum present a strong interaction with the similar tissue of the higher organisms. This assimilation produces intoxication and even death. Unfortunately, the traditional cleanup process, which involves the use of dispersants and surfactants,[1–2] often presents a larger impact to the environment than the spill, as seen in Torrey Canyon (1967)[3] and Alaska (1989)[1–2] spills. In these spills, the cleanup processes were not effective and also contributed for increasing the amount of toxic elements in the environment, making harder the biorecovery of the

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ecosystem. This larger environmental impact is related to the absorption of the dispersed oil by organisms, which leads to a greater time for the biorecovery of the degraded environment.[4] The devastation extension caused by accidents, as in Dalian/China (2010), Gulf of Mexico (2010), as well as in Campos/Brazil (2011), shows that new strategies of remediation must be continuously studied. The goal of spill response in any habitat it to minimize the damage caused by the accident.[5] Several variables are present, such as type and amount of oil spilled, geology of the shoreline, rate of water flow, weather, and availability of equipment for salvage will determine which options can be considered during a response. Among possible clean-up methods, some are frequently cited such as (i) *booms and skimmers*, useful to limit and concentrate the spread oil; (ii) *sorbents and vacuum pumping* which could be used in lagoons; (iii) *low-pressure flushing* which is a way to accelerate the natural removal; (iv) natural cleansing which can be more efficient in the presence nutrients able to increase the bacterial biodegradation; (v) in situ burning, useful in situations where there is a safe distance from the populated areas and (vi) *dispersants*, which should be restricted to deep water, away from the shore and away from environmentally fragile habitats.[5–7]

In this specific context, our group is focused on the use of renewable resources able to be transformed in polymer materials useful to the absorption of petroleum from the water.[8–11] Among these renewable resources, good absorption results are provided by resins prepared using the cashew nutshell liquid and lignin from Kraft process. Cashew nut shell liquid (CNSL) is an important byproduct of the cashew nut industry.[12–14] The potential annual availability of this material, which accounts for about 32 wt% of the cashew shell, is enormous. Industrial application of CNSL-based products are numerous, including brake linings, paints and primers, foundry chemicals, lacquers, cements, coatings and transformed cardanol for gasoline stabilization.[15] The main component of CNSL is cardanol, a phenol derivative that presents a C15 unsaturated hydrocarbon chain with 1–3 double bonds in the meta position.[16–20] Pure cardanol can be obtained from CNSL by distillation technique. Because of its structure, cardanol can also be used as a stabilizer of liquid–liquid dispersions and/or a plasticizer.

Lignin is a complex hydrocarbon polymer with both aliphatic and aromatic constituents.[15,21–24] Besides largely available, - world's production is around 30 million tons per year[25] - the complex structure of lignin is very interesting since it can be useful to tuning aromatic/aliphatic balance in resins, making them better petroleum absorbers. From the environmental point of view, this strategy is interesting because it avoid the use of non-renewable materials inside impacted areas.

In this context, this work aims employing CNSL, lignin and furfuraldehyde, all obtained from renewable sources, to produce ‘‘absorbent green materials’’. These materials were synthesized by a typical polycondensation route used to produce phenolic resin, using CNSL as main phenolic compound and furfuraldehyde as green aldehyde, catalyzed by sulfuric acid. Lignin was included in the materials to change the hydrophilic/lipophilic ratio. Synthesized resins present a good chemical similarity with petroleum, which produces a good interaction among them, making easy the contraction of the oil spot on the water and, consequently, the removal process of oil spilled on water.

Experimental Part

Materials

Sulfuric acid (H_2SO_4) and furfural ($C_5H_4O_2$) were purchased from Vetec (Rio de Janeiro, Brazil). The lignin was kindly provided by KABLIN (Rio de Janeiro, Brazil). This lignin presented Mw and Mn equal to 2351 g/mol and 1396 g/mol, respectively. The cashew nut shell liquid (CNSL) was kindly provided by RESI-

BRAS (Ceará, Brazil). The petroleum, API degree around 21 and density equal to 0.92 g/cm^3 (@ 25 °C), was kindly provided by REDUC-PETROBRAS (Rio de Janeiro, Brazil).

Equipments used in this research: magnetic stirrer (Fisatom/753A); vacuum pump (Prismatec/131); analytical scale (Bioprecisa/Fa 2104n); picnometer 50 mL (Vibrolabor); Vibrating Sample Mill (Heiko Co., TI-100); metallic sieve (Bert - 230#); optical microscope (Bel Photonics BE221); scanning electron microscope (JEOL – JSM6460-LV) and Infrared Spectroscopy with Fourier Transformed (Thermo Nicolet - iN10). In addition several glasses, such as beakers, Petri plates, Büchner flasks, Dewar flasks and glass flasks were also used.

Bioresins Synthesis

The bioresins were synthesized by polycondensation route following an experimental design (or Design of Experiments - DoE). The CNSL amount was always equal to 20 mL. Therefore, main factors studied in experimental design were the amount of furfuraldehyde, lignin and H_2SO_4. DoE was performed at two levels plus a central point, comprising eleven experiments. Lowest (−1) and highest (+1) levels to furfuraldehyde, lignin and sulphuric acid are presented in Table 1. In addition, three DoE central point experiments were also performed.

In all of the cases, CNLS, furfuraldehyde and lignin were poured inside a beaker on a hot plate stirrer. Stirring was started in fastest possible level and the temperature was set to 80 °C. Sulfuric acid was added in the reaction medium and experimental conditions were kept up to the increase of the viscosity. Soon afterwards the magnetic stirring be stopped by the increase of the viscosity, the bioresin was poured in a Petri plate and carried to the furnace at 100 °C to finish the polymerization. After the polymerization the bioresins were milled using Vibrating Sample Mill Ti-100 and passed through a 230 mesh sieve.

Characterization

The bioresins synthesized were characterized chemically by Infrared Spectroscopy with Fourier Transformed (FTIR). Moreover, density tests were carried out to estimate their potential use in aquatic environment. The contraction of the oil spot on the water tests were performed to evaluated the oil absorption by the bioresin.

Optical microscopy: Resins were studied using an optical microscope (Bel Photonics BE221) using zoom equal to 45x.

Scanning Electron Microscopy (SEM): Resins were also studied using a Scanning electron microscope (JEOL – JSM6460-LV). The specimens were examined under an accelerating voltage of 15 kV, using magnifications equal to 1000X, 3000X and 5000X.

Table 1.
Experimental design used to prepare the resins.

Bioresins Synthesized	Amounts used in the synthesized bioresins					
	Furfural (mL)	Lignin (g)	H_2SO_4 (mL)	$X^{(a)}_1$	$X^{(a)}_2$	$X^{(a)}_3$
1	6.6	0.4	0.16	−1	−1	−1
2	6.6	0.4	0.48	−1	−1	+1
3	6.6	2.0	0.16	−1	+1	−1
4	6.6	2.0	0.48	−1	+1	+1
5	12.4	0.4	0.16	+1	−1	−1
6	12.4	0.4	0.48	+1	−1	+1
7	12.4	2.0	0.16	+1	+1	−1
8	12.4	2.0	0.48	+1	+1	+1
9	9.6	1.2	0.32	0	0	0
10	9.6	1.2	0.32	0	0	0
11	9.6	1.2	0.32	0	0	0

[a] Lowest (−1); highest (+1) and central point (0) levels of furfuraldehyde (X_1), lignin (X_2) and H_2SO_4 (X_3) amounts.

Infrared Spectroscopy with Fourier Transformed: The FTIR analyses were performed in the Thermo Nicolet iN10 equipment, using an attenuated total reflection accessory (FTIR-ATR) equipped with a zinc selenide crystal. The analyses were made with accumulation of 128 scans, resolution of 4 cm^{-1}, in the wavenumber range from 4000 to 675 cm^{-1}.

Bulk density: The density tests were performed using glass recipients of (1.4586 ± 0.0238) mL where a known mass of the resin was compacted. Tests were performed in triplicate.

Oil contraction tests: The contraction of the oil spot on the water tests were carried out using 2 g of spilled petroleum on the water in the beaker of 300 mL. In each one of the cases, one gram of the resin was poured on the petroleum. Contraction of the oil was evaluated in times equal to 1, 3, 5 and 10 minutes.

Results

The main goal of this work is related to obtain an absorber with good properties such as: low density, good chemical affinity and good oil absorption capability. Therefore, pointing to reach these goals, resins were prepared in accordance with the experimental design presented in Table 1. Obtained samples were characterized using optical microscopy, FTIR-ATR, density and oil absorption tests and the results are summarized in Table 2. Results are presented in terms of size distribution, relative density, contraction of the oil spill in presence of resin and the root mean squared error (RMSE) among the FTIR absorbance of the oil and resins. RMSE was chosen because it is very useful to study the misfit between experimental data and model.[27]

Optical micrographs of the resins were used to determine the morphology and size distribution of the particles. All samples presented very similar morphology, predominantly in the granular shape. One example is shown in Figure 1. The obtained particle size distribution of the resin particles is also shown in the same figure. According to Figure 1, resin particles present a granular morphology with a certain degree of aggregation. Particle diameters were calculated with the *ImageJ* software,[28] while particle size distributions were computed as described in other works of our group.[29,30]

Figure 1 shows that particle size distributions present a single mode, which is asymmetric, concentrating 95% of the particles in the range 39^{+79}_{-17} um. In addition, particle size distributions showed in Table 2 allow inferring that samples present statistically equal diameters. In turn, Scanning electron micrographs of the resins were

Table 2.
Characterization of the resins.

Experiment	Furfural	Lignin	H_2SO_4	S.D. (um)[a]	Density (g/cm^3)	ContrMax (%)[b]	RMSE[c]
1	−1	−1	−1	43^{+86}_{-23}	0.5901	0.0000	0.2010
2	−1	−1	1	40^{+84}_{-19}	0.6364	15.7895	0.1884
3	−1	1	−1	41^{+86}_{-22}	0.4768	18.1818	0.1789
4	−1	1	1	39^{+86}_{-19}	0.6113	27.7778	0.1525
5	1	−1	−1	41^{+81}_{-19}	0.4954	20.0000	0.1945
6	1	−1	1	39^{+83}_{-21}	0.6587	32.6923	0.1630
7	1	1	−1	40^{+84}_{-19}	0.4663	24.0000	0.1563
8	1	1	1	40^{+86}_{-22}	0.6330	45.4545	0.1591
9	0	0	0	41^{+77}_{-19}	0.4756	33.8983	0.1847
10	0	0	0	39^{+79}_{-17}	0.4831	28.0702	0.1787
11	0	0	0	41^{+81}_{-17}	0.5271	34.9206	0.1702

[a]Size distribution of resins' particles. [b]Maximum contraction of the spilled oil in presence of the resin. [c]Root mean squared error between resin and oil.

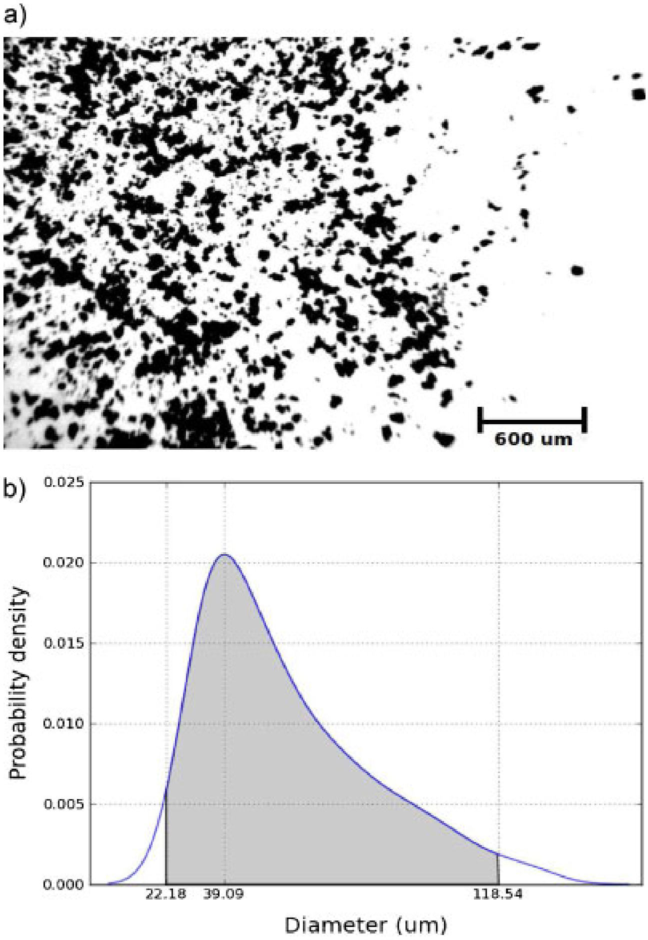

Figure 1.
Optical micrograph of sample 8 (a) and respective diameter distribution of the particles (b).

used to study the surface morphology of the samples (see Figure 2). In complete agreement with the optical microscopy studies, the samples presented very similar morphology, predominantly in the granular shape, presenting a certain degree of aggregation and a rough surface.

Figure 2 shows surface details of the sample 8. As one can see, the granules present smaller particles attached on their surfaces, probably due to the presence of static charges among them. On the other hand, the particles do not present pores, which would be able to enlarge their surface area, constituting an efficient absorption mechanism.[31] Therefore, shape, diameter and surface morphology of the particles are not sources of divergences among the properties of the synthesized materials and the morphology of the samples will be not considered in further discussions.

In order to investigate the possible existence of correlations among the used preparation conditions and observed results, a standard correlation analysis was performed.[32–36] The calculation of the correlation matrix is a common first step of many data analyses that involve more than two variables, aiming to examine the data looking for expected and unexpected significant relations. This calculation is performed taking the quotient between

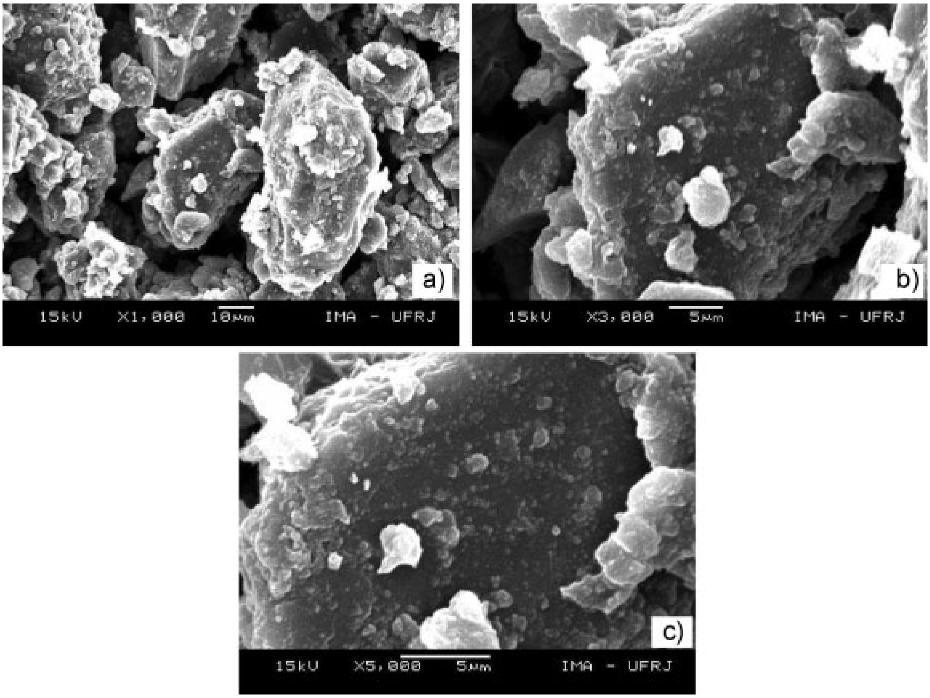

Figure 2.
Scanning electron micrographs of the sample 8 with magnifications equal to 1000X (a), 3000X (b) and 5000X (c), respectively.

the covariance of the two variables and the product of their standard deviations.[37,38] Obtained results are presented in Table 3.

Correlation matrices were calculated with Statistica®. Statistically significant results are obtained whenever the P-level (p) is lower than the selected critical significance level (SL), which was selected to be 5%. The P-level is an estimated measure of the degree to which it is representative of the population and represents the probability of error when the observed result is assumed to be correct.[32,33] In many areas of research, the p-level of 0.05 is customarily treated as a "border-line acceptable" error level.[38,39]

Results presented in Table 3 indicate the existence of some reliable correlations (in bold) among some of the analyzed properties. However, correlation values are usually small (smaller than 0.70), indicating that the distinct evaluated properties respond differently to modifications of the reaction media. The exception is the

Table 3.
Correlation matrix for observed values.

	Furfural	Lignin	H_2SO_4	Density	Contraction	RMSE
Furfural	1.00	0.00	0.00	−0.09	0.56	−0.33
Lignin	0.00	1.00	0.00	−0.29	0.44	−0.69
H_2SO_4	0.00	0.00	1.00	0.75	0.55	−0.47
Density	−0.09	−0.29	0.75	1.00	0.07	−0.20
Contraction	0.56	0.44	0.55	0.07	1.00	−0.67
RMSE	−0.33	−0.69	−0.47	−0.20	−0.67	1.00

Marked correlations are significant at $p < .05000$.

correlation between density and H_2SO_4, which is equal to 0.75. This result is due to the intrinsic density of the acid, which is trapped by the resin, producing higher values of this property.

The results showed in Table 3 encourage the development of independent statistical analysis for the distinct analyzed properties. In order to analyze the effects of system compositions on the characterized properties, a standard empirical modeling approach is used. Empirical models are based on data and they are not derived from assumptions concerning the relationship between variables and they are not based on physical principles.[40,41] After several tests, it is assumed that the process response can be modeled as

$$y_n = \sum_{i=1}^{N} \alpha_i^{\mu} x_i + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \sum_{k=j+1}^{N} \beta_{ijk}^{\mu} x_i x_j x_k \quad (1)$$

where y_n is an experimental response, x_i ($i = 1, \ldots, N$) is an experimental design variable; α_i^{μ} and β_{ijk}^{μ} ($i = 1, \ldots, N; j = 1, \ldots, N, k = 1, \ldots, N$) are model parameters; α_i^{μ} represents the linear effects, while β_{ijk}^{μ} represents the nonlinear synergistic effect, which refers specifically to the structural or functional effects that are produced by various combinations of things.[42] Therefore, experimental data could be appropriately fitted using the previous empirical model which takes in to account the sum of the linear effects among the concentrations of the reactants and the synergistic effects produced by the combination effect of the used reactants.

Table 4–6 present the parameter estimates for Equation (1) and respective confidence levels (p) for the different analyzed process responses. Based on Tables 4–6 it is possible to discriminate the most influential composition effects on the analyzed responses and to observe whether important nonlinear (synergistic) effects are present.

Density is a very important characteristic of materials which will be used as oil absorbers on the water. So, density values higher than the one of the water are unsuitable and values lower than this last must be pursuit. Thus, density was studied and obtained values are presented in Table 2. Among obtained values, the lowest and the highest were equal to (0.47 ± 0.03) g/cm^3 and (0.66 ± 0.04) g/cm^3, respectively. Therefore, from the flotation point of view, the density of the resins, in comparison with the one of the water, can be considered as very good. Main effect analysis of density was performed according Equation (1) and led to correlation of 0.89116 between model and observed data. This value is larger than the ones presented in Table 3, indicating that model is able to fit suitably the experimental data. The results are summarized in Table 4. The strongest positive and significant effect on the density is provided by H_2SO_4. On the other hand, in spite possessing $p > 0.05$, the increase of the furfural and lignin amount produced a decrease of the density. The first case is related to the sulfate ions trapped inside resin producing the observed increase of the density while the decrease produced by organic species is due to the formation of a more random polymer structure. However, as H_2SO_4 is the unique statistically significant value, no further analyses were performed.

The chemical nature of the resins and petroleum was studied by FTIR. Spectra are shown in the Figure 3.

Spectra of the resins are very similar, it means that all resins present the same functional groups. On the other hand, the intensity of the characteristics bands are distinct, meaning that the functional groups are present in different amounts. Thus, the higher intensity the larger the functional

Table 4.
Main effect analysis for density (**y_1**).

	Effect	Std.Err.	p
Mean/Interc.	0.570994	0.012499	0.000000
Furfural (α_1^1)	−0.015327	0.024997	0.566593
Lignin (α_2^1)	−0.048296	0.024997	0.111194
H_2SO_4 (α_3^1)	0.127713	0.024997	0.003741
$\beta_{123}^{1\,*}$	−0.021167	0.024997	0.435754

* Synergism; $R^2 = 0.89116$.

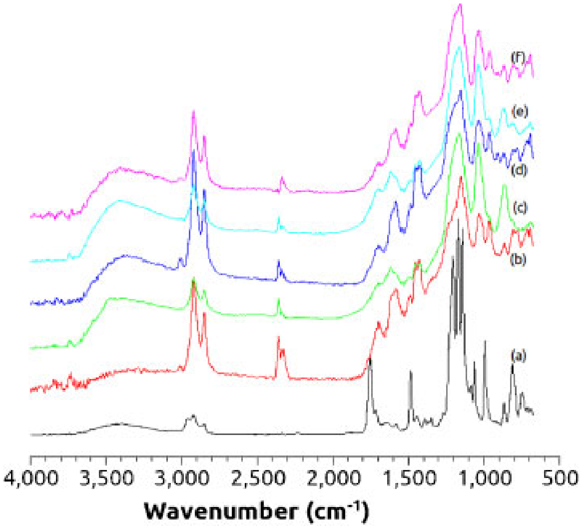

Figure 3.
FTIR-ATR spectra of petroleum (a) and CNSL bioresins prepared through the conditions 1 (b), 4 (c), 5 (d), 8 (e) and 10 (f) presented in Table 1.

group amount. Therefore, results demonstrated the presence of resins possessing larger amount of the aliphatic groups or aromatic groups, such as the resins prepared according conditions 1 and 8, respectively. The wide band around 3320 cm^{-1} is related to the stretching of OH, which is able to produce hydrogen bounding. The band at 3000 cm^{-1} corresponds to stretching of CH and the doublet at 2950 and 2790 cm^{-1} is related to stretching of CH_2 and CH_3. The stretching of the aromatic double bonds ($C=C$) takes place at 1460 and 1454 cm^{-1}. The C-O stretching of the phenol group can be observed at 1180 and 1040 cm^{-1}. The characteristic band at 970 cm^{-1} corresponds to the $C=C$ asymmetric stretching of the aromatic ring, while the bands at 887 and 721 cm^{-1} are the characteristic scissoring deformation of ring out-of-plane hydrogen. The O-H scissoring deformation appears at 580 cm^{-1}.[23,24] These results indicate that the obtained resins are typical phenolic resins with the polymerization occurred through the aromatic rings. In spite very similar, obtained spectra presented differences. These differences can be expressed using appropriate statistical tools. Among them, the root mean squared error (RMSE) is very useful to study the misfit between experimental data and model.[26] Therefore, RMSE was calculated through linear regressions between absorbances of the resin and oil, using the *least squares* approach. The obtained results are shown in Table 2. In addition, the main effect analysis of RMSE was performed according Equation (1) and led to correlation of 0.92255 among calculated and observed data. The results are summarized in Table 5.

All of the tested effects and synergism were significant. Among them, only synergism presented a positive value. Therefore, the increase of the used amount of reactants produced a decrease of the RMSE. In other words, the increase of the reactants amount led to materials more and more similar to

Table 5.
Main effect analysis for RMSE (**y_2**).

	Effect	Std.Err.	p
Mean/Interc.	0.174235	0.002259	6.95E-09
Furfural (α_1^2)	−0.011986	0.004519	4.53E-02
Lignin (α_2^2)	−0.025046	0.004519	2.62E-03
H_2SO_4 (α_3^2)	−0.016918	0.004519	1.34E-02
β_{123}^2 *	0.012033	0.004519	4.47E-02

* Synergism; $R^2 = 0.92255$.

the petroleum. The observed decrease of the RMSE among resins and petroleum is due to the increase of the aromatic and polar characteristic of the prepared materials. This hypothesis is in agreement with FTIR results which showed the discreet increase of aromatic bands, at 887 and 721 cm^{-1}, and the more pronounced increase in the polar bands, at 3320, 1180 and 1040 cm^{-1}.

Due to the lack of chemical attraction between oil and water, the spilled oil tends to spread up and the distribution of the spilled oil on the water occurs due to the gravitation forces. According literature,[36,43] one ton of petroleum spilled on the water can be dispersed over a radius of fifty meters in less than ten minutes, forming an oil slick of 10 mm thick which can becomes thinner and thinner as oil continues to spread, covering even an area of up to twelve square kilometers.[36] Therefore, keep the oil molecules together is an important goal and the effect of the synthesized resins on oil slick was tested in small scale (see Figure 4). In average, the oil spots present diameter equal to (5.7 ± 0.4) cm and the maximum contraction of the sample occurs after (3.2 ± 1.1) min. The maximum contraction of the spilled oil due to the presence of each one of the resins is showed in Table 2.

Table 6.
Main effect analysis for contraction of the oil (**y_3**).

	Effect	Std.Err.	p
Mean/Interc.	22.98699	1.226837	0.000008
Furfural (α_1^3)	15.09945	2.453675	0.001648
Lignin (α_2^3)	11.73309	2.453675	0.004963
H_2SO_4 (α_3^3)	14.88307	2.453675	0.001758
β_{123}^3 *	3.73894	2.453675	0.188061

* Synergism; $R^2 = 0.95852$.

The main effect analysis of contraction of the oil slick was also performed according Equation (1) and led to correlation of 0.95852 among calculated and observed data. The results are summarized in Table 6.

All of the tested effects were significant and presented positive values. Therefore, the increase of the used amount of reactants produced an increase of the oil slick contraction. In other words, the increase

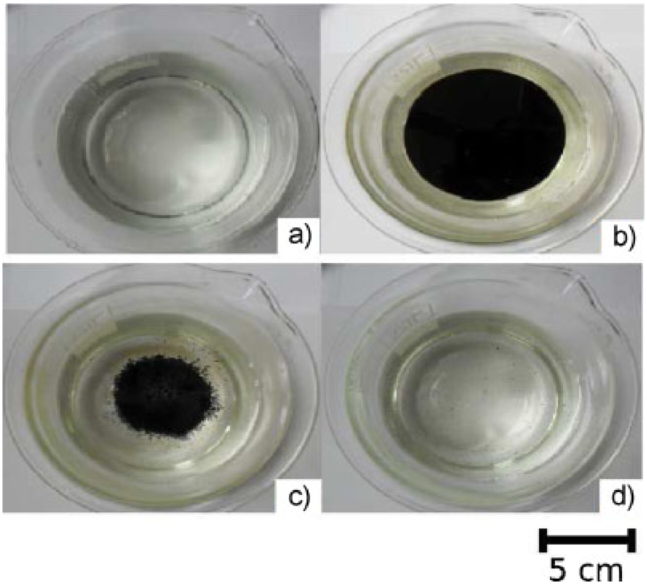

Figure 4.

of the reactants amount led to materials more and more able to absorb the petroleum. This result is in complete agreement with the RMSE analysis indicating that the increase of reactants amount produce resins more and more similar to the tested petroleum. Thereby, seeking to provide an overall view of the obtained responses, response surfaces are presented in Figure 5.

The response surfaces of RMSE are shown in Figure 5 (a), indicating graphically that the increase of the used levels of the reactants produced a decrease of the RMSE. So, as discussed earlier, resins prepared according these conditions (see Table 1) present the larger similarity with tested oil. In its turn, Figure 5 (b) presents the surface responses of oil slick contraction in presence of resin. Unlike previous case, the increase of the used levels of the reactants produced an increase of the observed contraction. In addition, RMSE and contraction responses are almost diametrically opposed. Therefore, presented modeled surfaces are able to show that the oil slick contraction (or oil absorption) is inversely related with the RMSE or in other words, the absorber material is more efficient to capture the petroleum as the oil and the resin become more and more similar.

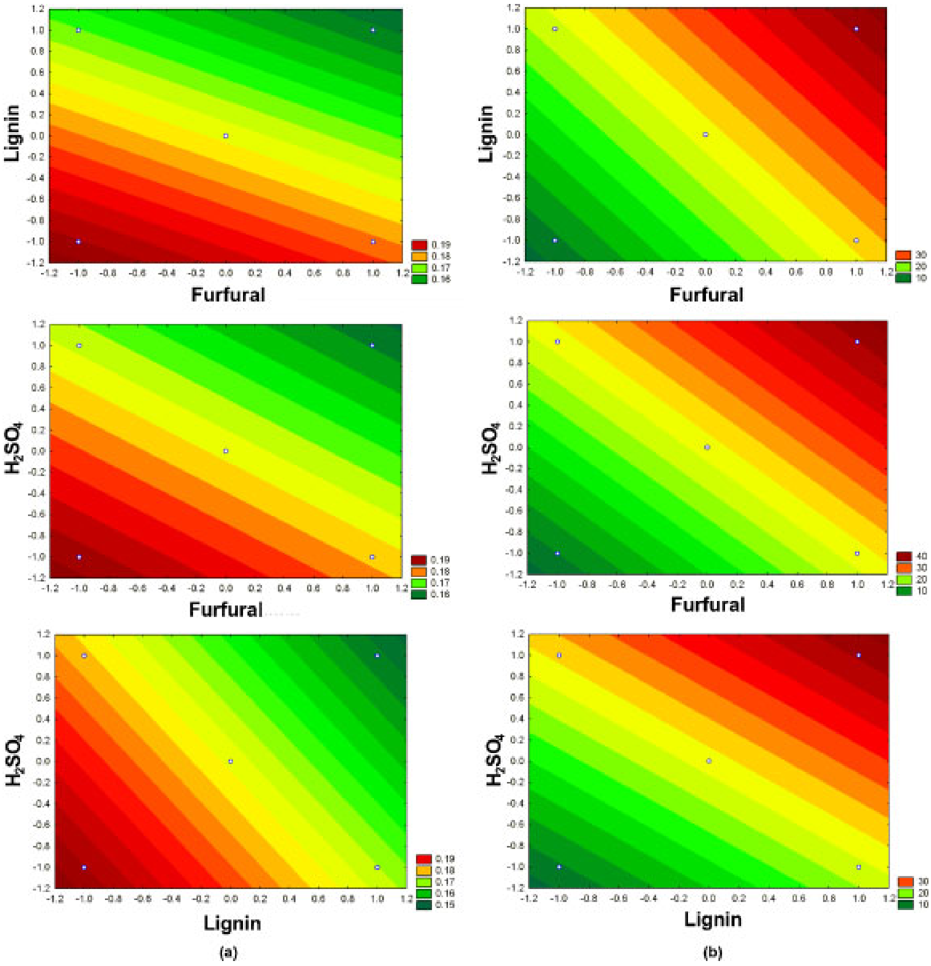

Figure 5.
Surface responses for RMSE (a) and oil slick contraction (b) of tested materials.

Conclusion

Bioresins able to absorb petroleum spilled on the water can be obtained from CNSL, furfuraldehyde and lignin. Interactions among resins and petroleum were studied through an oil slick contraction test. In a general way, these contraction processes were very fast, taking less than three minutes and the mass constituted by oil and resin was easily removed from the water using a skimmer. In addition, the use of statistical tools allowed for infer about the influence of chemical composition of the resins on their oil contraction capability. Obtained results showed that the increase of the oil slick contraction is inversely related to the root mean squared error among FTIR absorbance of the oil and resins. So, the increase of the chemical similarity between synthesized materials and petroleum leads to the increase of the oil slick contraction capability by the resin. Therefore, beyond the environmental concerns related to the synthesis of nature friendly absorbers, this work was also able to show that the RMSE of the FTIR data constitutes an important tool to adjust the chemical composition of resins, allowing the engineering of more efficient petroleum absorbers.

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