Polyurethane foam impregnated with lignin as a filler for the removal of crude oil from contaminated water

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HIGHLIGHTS

- The presence of lignin in polyurethane foams increased oil sorption capacity.
- The presence of lignin resulted in a decrease in the hydrophobicity of the foams.
- Langmuir isotherm predicted a maximum oil adsorption of $28.9\,g\,g^{-1}$ by the PUF-10.
- ΔG° ($-4.4\,kJ\,mol^{-1}$) indicated that adsorption process by PUF-10 was spontaneous.
- The recyclability of the foam showed efficiency greater than 95% after five cycles.

GRAPHICAL ABSTRACT
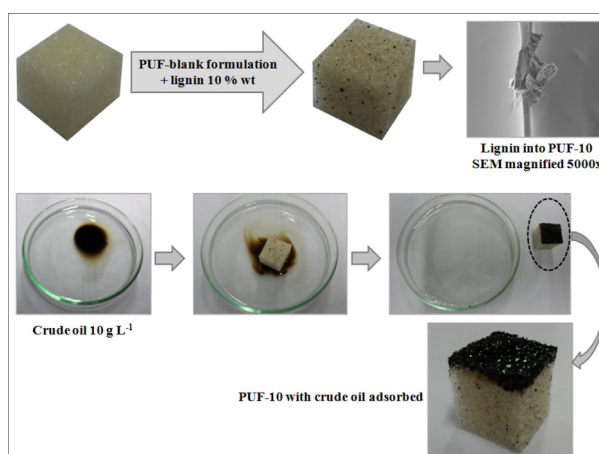
ARTICLE INFO

ABSTRACT

The present study describes the influence of the concentration of lignin when used as a filler in polyurethane foam for crude oil sorption. The foams (lignin 0–20 wt%) were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis, contact angle and density. The FTIR analysis confirmed urethane linkage formation, showing that the chemical structure of the polymer was preserved, despite the addition of different lignin concentrations. Thermogravimetric analysis showed that the presence of lignin has altered the onset temperature (T_{onset}) of the foams, decreasing as the concentration of lignin is increased. The contact angle analysis showed a decrease in the hydrophobicity of the foams with increasing lignin concentration. All modified foams showed an improvement in the oil sorption capacity in a PUF/oil/water system, and the PUF-10 showed an improvement of about 35.5% compared to the PUF-blank. The Langmuir isotherm showed a better fit to the data and predicted a maximum oil adsorption of $28.9\,g\,g^{-1}$ by the PUF-10.

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The $\Delta G\degree$ value of $-4.4\,\mathrm{kJ\,mol^{-1}}$ indicated that crude oil adsorption process by PUF-10 was spontaneous. The results of reuse of the PUF-10 showed that oil removal efficiency remained greater than 95% after five consecutive cycles.

1. Introduction

Nowadays, one of the most serious environmental problems is water contamination by oil and chemical spills. Often it occurs through contamination in the process of extraction, transportation and storage of oil. Oil spill at sea is more dangerous than on land since oil floats over the sea surface and can be distributed over wide areas by the action of wind and waves. In general, main impacts are damages to wildlife and their habitats, chemical toxicity and large ecological changes. The negative impacts of oil spills on ecosystems, and their long-term effects for environment pollution call much attention to the importance of developing materials to promote the removal of oil from impacted areas [1,2].

Many studies have approached the development of new materials for application in the remediation of impacted areas by oil spills, in particular, those materials that have large sorption capacity [3]. Some examples of materials used for the sorption of crude oil and derivatives include sugarcane bagasses [4], vegetable fibers [5], clays [6], and polyurethane foams [7], among others. Particularly for oil sorption, polyurethane foams are attractive materials, mainly due to the combination of porous structure with hydrophobic polymer matrix. Furthermore, these materials are also interesting as solid extractors of pollutants due to the possibilities of adjusting their geometric structure and pore size as well as the possibility of further chemical modifications. Due to the combination of all those properties, Bowen published, for the first time, a study of the extraction and recovery of a few inorganic and organic compounds from aqueous solutions using flexible polyurethane foams as extracting materials. In the same study was shown that the extraction was not just a surface phenomenon, but the adsorption of these substances could also occur inside in the foam as well [8]. After this first publication, the use of polyurethane foams in sorption processes has been studied in several works [9–16].

Studies reporting the development of polyurethane composites increased significantly in recent years, particularly for environmental applications. Several studies of the incorporation of fillers into polyurethane foams can be found in the literature [14,17,18]. Despite the versatility of polyurethanes, various physicochemical important properties for sorption studies such as permeability, elasticity, chemical resistance, hydrophobicity can be improved with the use of fillers. These improvements can be achieved by incorporating small amounts of fillers, generally in the range of 1–10% in mass [19]. In this context, recent studies have shown the applications of modified polyurethane foams for oil sorption as: PUF-nanoclay [14], PUF-silica-DTMS [16], PUF-activated carbon [20], PUF-ZnO-PA [21] and PUF-carbon nanotubes [22].

In this work, the influence of lignin as filler on polyurethane foam is investigated for oil removal from water. Lignin is a waste produced in large scale from the paper and cellulose industry and from ethanol generation from lignocellulosic biomass. Lignin has a complex tridimensional polyphenolic structure containing multiple responsive free groups (C=O, OH, and COOH) and may be used as a reactive filler for polyurethane materials without prior chemical treatment [23,24]. The wasted alkali lignin produced from the Kraft pulping process is inert and is usually burnt for power. However, its rich chemical functionality can be used in a better way to produce composites with chemical added value [25]. In this context, differ-

Table 1
Reagents used in the synthesis of the PUF-blank, in parts per hundred parts of polyol (php).

Reagents	PUF-blank
Water	11.1
Polyol	100
Glycerol	12.5
PEG-400	12.5
Silicon	3.3
DMCHA	1.1
Pentane	33.3
p-MDI	110

ent concentrations of lignin (0–20 wt%) on polyurethane foam was tested to optimize the oil sorption process. The oil sorption capacity was evaluated by Langmuir and Freundlich isotherms.

2. Materials and methods

2.1. Materials

The polyurethane foams were synthesized with isocyanate (Biopol p-MDI, 4,4-diphenylmethane diisocyanate, average functionality equal to 2.6 and average molar mass equal to $349.9\,\mathrm{g\,mol^{-1}}$) and a polyol (Biopol®411, 311 mg KOH g^{-1}) derivative from castor oil. These reagents were obtained from the Poly-Uretane Indústria e Comércio LTDA – Minas Gerais/Brazil and were used as received from the company, without any prior treatment. Glycerol, polyethylene glycol 400 (PEG 400), and pentane were purchased from Synth. *N,N*-dimethylcyclohexylamine (DMCHA) was purchased from Sigma Aldrich. All reagents were of analytical grade. Tegostab silicon was obtained from Evonik Industries – Minas Gerais/Brazil. The lignin was obtained from Suzano, Papel e Celulose – São Paulo/Brazil.

2.2. Polyurethane foam and composite synthesis

The PUF-blank (without lignin) was produced by a single step method from a two component (A and B) system with the ratio of NCO/OH groups equal to 1.1. The component A (polyol mixture) consisting of the mixture of polyol, water, glycerol, PEG-400, silicon, DMCHA and pentane were mixed and stirred with the component B (isocyanate, p-MDI) to prepare the foams. Table 1 summarizes the synthesis of the PUF-blank.

For synthesis of the polyurethane/lignin composites, lignin was added while mixing both components A and B from the PUF-blank formulation. Composites were synthesized with different total mass percentages (wt%) 5, 10, 15, and 20% of lignin, which were labeled PUF-5, PUF-10, PUF-15, and PUF-20 respectively. After polymerization reaction and expansion, the solution was let to cure for 48-h at room temperature.

2.3. Characterization of polyurethane foam and composites

ASTM D 1622-08 densitometer was used to determine the apparent density, performed in triplicate. The synthesized materials and lignin were also characterized by Fourier transform infrared spectroscopy (FTIR) in the range of 4000–400 cm^{-1}. FTIR spectra

were acquired in a Perkin Elmer FTIR RX System using the KBr disks, with resolution of $4\,cm^{-1}$ and 32 scans per sample. The materials morphologies were probed by scanning electron microscopy (SEM). The samples were cut into small pieces. Surfaces were metalized with a thin gold layer approximately 0.7 nm in thickness. The images were obtained in a FEG – Quanta 200 FEI scanning electron microscope. The Feret diameter of the cells (perpendicular to the foam growth direction) was studied with ImageJ software. The materials were subjected to thermogravimetric analysis to evaluate the thermal degradation process. The thermo gravimetric curves were obtained in a Shimadzu thermo balance, DTG 60. The analysis conditions included an alumina crucible and a heating rate of $10\,°C\,min^{-1}$ in air atmosphere with a flow-rate of $100\,mL\,min^{-1}$. The wettability of the surface was analyzed by measuring the contact angle between deionized water ($10\,\mu L$) and the surface of a pressed tablet of the powdered material using a DIGIDROP-DI (GBX Instruments) goniometer, equipped with a photo camcorder.

2.4. Determination of oil sorption capacity: kinetics study

The blank foam and PUF-lignin composites were cut to dimensions of $10 \times 10 \times 10$ mm and were weighted to determine their oil sorption capacity in the PUF/oil and PUF/oil/water systems. The materials were immersed into the oil at room temperatures. After maximum contact time of 48 h, the materials were weighted again. The oil sorption capacity was determined by Eq. (1) [16]:

$$S = \frac{m_f - m_i}{m_i} \qquad (1)$$

Where S is the oil sorption capacity ($g\,g^{-1}$); m_f is the mass of foam saturated with oil (g); and m_i is the mass of the foam (g).

2.5. Concentration effect: efficiency and oil removal percentage

The assays of oil removal efficiency and the oil removal percentage from water by PUF-10 were performed at different oil concentrations ($10–200\,g\,L^{-1}$). The determination of the oil sorption capacity of the PUF-10 in the PUF/oil/water system was based on the Standard Test Method for Sorbent Standards of Performance Adsorbents (ASTM F726-99) and the Method for Water in Crude Oil by Distillation (ASTM D4006). The oil sorption capacity was calculated by Eq. (2) [14,20]:

$$S_o = \frac{m_f - m_w - m_i}{m_i} \qquad (2)$$

Where S_o is the oil sorption capacity ($g\,g^{-1}$); m_f is the mass of the saturated composite (foam + oil + water) after contact time of 48 h (g); m_w is the mass of the absorbed water (g); and m_i is the mass of the composite (g).

The efficiency of oil removal was studied at different oil concentrations and was calculated by Eq. (3) [14,20]:

$$E = \frac{m_o}{m_f} 100 \qquad (3)$$

Where E is the efficiency of oil removal; m_o is the mass of oil retained in the composite (g); and m_f is the mass of the saturated composite (foam + oil + water) after contact for 48 h (g).

The oil sorption percentage was calculated at different oil concentrations by Eq. (4) [14,20]:

$$R = \frac{m_o}{m_a} 100 \qquad (4)$$

Where R is the oil removal percentage; m_o is the mass of oil retained in the composite (g); and m_a is the initial oil mass (g).

2.6. Adsorption isotherms

The study of sorption through adsorption isotherms may indicate the way in which the oil is adsorbed and estimate the maximum amount of oil that can be adsorbed by the foam. The assay was performed in different oil concentrations (10 up to $200\,g\,L^{-1}$), at a room temperature and with the PUF-10. The Langmuir and Freundlich isotherm models were analyzed to determine which model showed the greatest agreement with the experimental data on oil sorption by the PUF-10.

2.6.1. Langmuir isotherm

This model proposes adsorption onto a uniform surface, where a monolayer of the solute covers the entire surface and there is no interaction between the adsorbed molecules. This model is commonly represented by Eq. (5) [26]:

$$Q_e = \frac{Q_m\,K_L\,C_e}{1 + K_L C_e} \qquad (5)$$

The Langmuir expression can be obtained in a linear form by Eq. (6) [26]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \qquad (6)$$

Where Q_m is the maximum sorption capacity ($g\,g^{-1}$), Q_e is the amount of adsorbate on the adsorbent at equilibrium ($g\,g^{-1}$), C_e is the oil concentration at equilibrium ($g\,L^{-1}$), and K_L is the Langmuir constant ($L\,g^{-1}$). The slope and intercept of the linear regression of C_e vs. C_e/Q_e allow the determination of Q_e and K_L, respectively.

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L, and can be determined by Eq. (7) [26]:

$$R_L = \frac{1}{1 + K_L C_0} \qquad (7)$$

Where K_L (L/g) is the Langmuir constant and C_0 is the initial oil concentration ($g\,L^{-1}$). The R_L value indicates if the adsorption is favorable ($0 < R_L < 1$), linear ($R_L = 1$), unfavorable ($R_L > 1$), or irreversible ($R_L = 0$) [14,26,27].

2.6.2. Freundlich isotherm

This model describes multilayer adsorption on heterogeneous surfaces. The Freundlich isotherm is given by Eq. (8) [26]:

$$Q_e = K_F\,C_e^{1/n} \qquad (8)$$

The Freundlich expression can be expressed in a linear form by Eq. (9) [26]:

$$lnQ_e = \ln K_F + \frac{1}{n} ln\,C_e \qquad (9)$$

Where Q_e is the amount of adsorbate on the adsorbent at equilibrium ($g\,g^{-1}$); K_F is the Freundlich constant, which is related to the adsorption capacity of the adsorbent ($g\,g^{-1}$); C_e is the oil concentration at equilibrium ($g\,L^{-1}$); and n is the heterogeneity factor, which is related to the affinity of the adsorbate to the adsorbent surface, where $n > 1$ indicates that the adsorption is favorable. The slope and intercept of the linear regression of $\ln C_e$ vs. $\ln Q_e$ allows the determination of n and K_F [26,28].

2.6.3. Non-linear regression analysis

In order to evaluate the fit of the equation to the experimental data the residual root mean square error (RMSE), and the chi-square tests (X^2) were used to measure the goodness-of-fit. RMSE can be defined by Eq. (10) [29]:

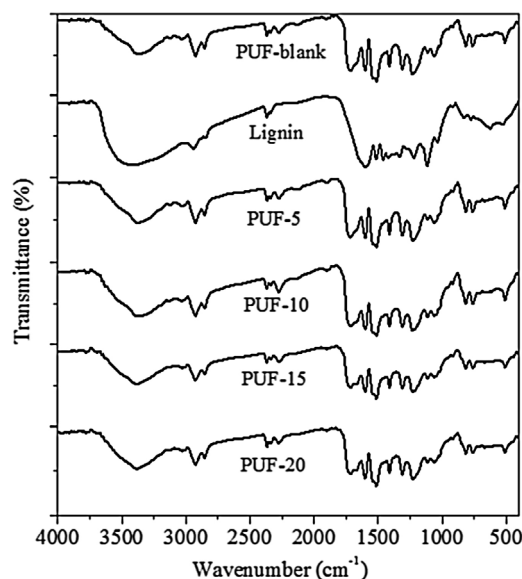$$RMSE = \sqrt{\left(\frac{1}{n-2}\right) \Sigma_1^n (Q_e - Q_i)^2} \qquad (10)$$

Fig. 1. FTIR spectra of PUF-blank and PUF/lignin composites.

Table 2
Absorption bands characteristic of the FTIR spectra for polyurethane foams in the range of 4000 down to 400 cm^{-1}.

Wavenumber [cm^{-1}]	Absorption bands
3400	N—H stretching
2925–2850	C—H stretching (CH$_2$ e CH$_3$) aliphatics
2270	N=C=O stretching
1715	C=O stretching (esters, rigid domains)
1600	N—C stretching (urethane group)
1510	N—H deformation
1215–1050	C—O and C—O—C deformation
810–600	C—H deformation (aromatic groups)

Where Q_e is the observation from the experimental data, Q_i is the estimate from the isotherm for corresponding Q_e and n is the number of observations in the experimental isotherm.

The chi-square test can be defined by Eq. (11) [29]:

$$X^2 = \Sigma_1^n \frac{(Q_e - Q_i)^2}{Q_i} \qquad (11)$$

The smaller RMSE value indicates the better fitting curve. For small value numbers of X^2, the data from model are similar to the experimental data.

2.6.4. Gibbs free energy ($\Delta G°$)

The thermodynamic parameter $\Delta G°$ (Gibbs free energy) indicates the degree of spontaneity of an adsorption process. The higher negative value of $\Delta G°$ reflects that the adsorption process is energetically favorable [30].

The most part of adsorbates studied in the literature can be divided in a simplified form into two large groups according to their charge characteristics: charged species (for example heavy metal ions) and neutral species or species with weak charges (for example organic compounds like oils). The $\Delta G°$ value of adsorption can be calculated for organic compounds by Eq. (12) [30–32]:

$$\Delta G° = -RTlnK_L \qquad (12)$$

Where K_L is the Langmuir constant, T is the temperature in Kelvin, and R is the gas constant with a value of 8.314 J mol^{-1} K^{-1}.

2.7. Reuse of the sorbent

For the reutilization tests, after the sorption experiments, the PUF-10 was washed with xylene and followed by distilled water. The foam was dried out at 50 °C for 4 h in a stove. The essay was performed in PUF/oil/water system, and the efficiency of oil removal was calculated by Eq. (3). The oil concentration used was 150 g L^{-1}.

3. Results and discussions

3.1. Fourier transformed infrared spectroscopy (FTIR)

FTIR spectra of the synthesized materials are shown in Fig. 1. The infrared absorption spectrum of the lignin shows an intense band

between 3500 and 3100 cm^{-1}, which is assigned to the OH stretching vibration. This band is caused by the presence of alcoholic and phenolic hydroxyl groups. The bands at 2934 and 2846 cm^{-1} are assigned to CH stretching in aliphatic groups. The band at 1600 cm^{-1} is due to C=O stretching (conjugated ketone) and the band in the region of 1520–1410 cm^{-1} is due to vibrations of the aromatic ring. The bands between 1328 and 1210 cm^{-1} can be attributed to the stretching of the C—O group attached to the aromatic ring while those between 1108 and 1034 cm^{-1} are ascribed to the in-plane CH bending of aromatic groups. The signals between 828 and 614 cm^{-1} are due to out-of-plane deformations of aromatic CH bonds [33].

Significant changes were not observed in the foams modified with lignin compared to the blank one. The spectra show that the characteristics of the chemical structure of polyurethane foams were preserved after the addition of lignin as filler. Table 2 shows the main characteristic bands observed for polyurethane foams [34].

3.2. SEM, density, and thermogravimetry

The addition of fillers to polyurethane foam formulations has a direct influence on the size and shape of their cells as well as on the density of the resulting composites and the appearance of pores in their three-dimensional structure [35,36]. All those properties, in turn, can also alter the sorption capacity of the composite foam in relation to the blank foam (without filler).

SEM is a common technique to evaluate changes in the size and shape of the cells of polyurethane foams due to the presence of fillers. Fig. 2 shows the SEM images of foams at 20× magnification and lignin at 100× magnification. The SEM images of the foams show a tendency toward the formation of less homogeneous and more deformed cellular structure with the addition of lignin, especially in PUF-10, PUF-15, and PUF-20. It did not significantly influence Feret diameter of the cells. This phenomenon may be related to the increase of the system's viscosity, which hinders the mixing of the reagents [37]. The SEM image of the lignin used to synthesize the PUF-lignin composites showed a Feret diameter ranging from 0.004 to 0.243 mm.

In general, the foam density depends on the mass of the expanded polymer, which in turn, is related to the amount of blowing agents. The addition of fillers may also affect these properties since a higher amount of denser solid material in the synthetic process may increase the viscosity of the system and interfere with the cells nucleation [19,35]. No significant differences were observed in the densities of the foams modified by lignin addition compared to the PUF-blank (Table 3), except for PUF-10, which showed a lower density than the other foams. This result can be related to the further expansion of the polymer mass due to the addition of the filler, which changed the mass/volume relationship of the system.

Fig. 3 shows the thermogravimetric curves and the onset temperature (T_{onset}) values for foams. It is observed that for both, blank and modified foams, thermal decomposition occurs in a similar way
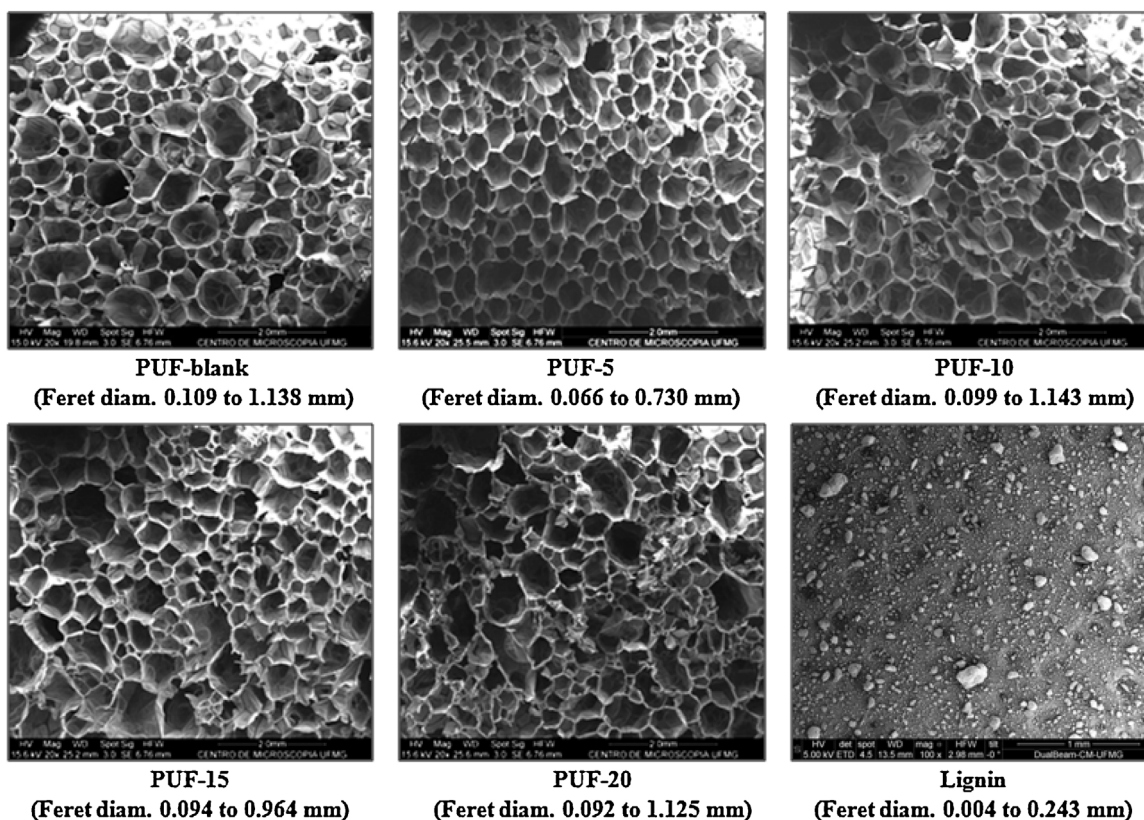
Fig. 2. SEM images of the PUF-blank, PUF-lignin composites (PUF-5, PUF-10, PUF-15, PUF-20) magnified 20 times and lignin magnified 100 times.

Table 3
Density values with standard deviations of the foams.

Foam	Density $(Kg\,m^{-3})$
PUF-blank	16.5 ± 1.82
PUF-5	16.7 ± 0.54
PUF-10	14.6 ± 0.78
PUF-15	16.1 ± 0.35
PUF-20	16.5 ± 1.30
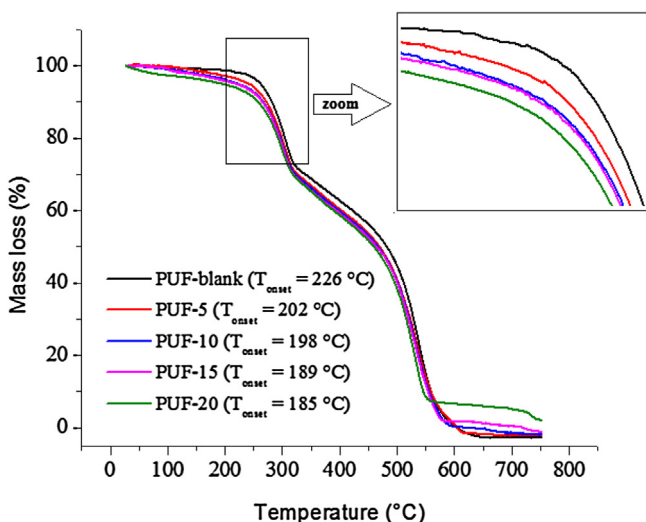
Fig. 3. Thermogravimetric curves and T_{onset} of the PUF-blank and PUF-lignin composites (PUF-5, PUF-10, PUF-15, and PUF-20).

into two stages, with an initial loss of mass between 200 and 350 °C related to the decomposition of the urethane group. A second mass loss occurs between 400 and 600 °C been related to the breakage of C—C bonds and the decomposition of the remaining materials from the first stage of thermal degradation [34,38]. With increasing lignin concentration, a decrease in the T_{onset} is observed, which can be related to the increased mobility of the polymer chains (smaller cross linking density) observed in the modified foams. In the opposite way, an improvement in the thermal stability of foams has been described in the literature. The authors showed that the incorporation of activated carbon decreased the density of soft segments in the polymer [20].

3.3. Contact angle

The contact angle (CA) between a drop of a polar liquid and the surface of a material is a function of the systems surface at free energy. When the surface energy is lowered, the hydrophobicity of the material is enhanced [39]. CA measurements were performed to analyze the behavior of different lignin concentrations as filler on foam PUF-blank (Fig. 4). During CA measurements between the PUF-blank and water there was a reduction in the CA value of 123° to 119°, characteristic values of hydrophobic material. The addition of only 5 wt% of lignin in the polymer matrix reduced the CA for values around 100°. The result may reflect the contribution of the several free polar groups from lignin. With increasing lignin content in the foam to values above 10 wt% generate CA for PUF-10, PUF-15 and PUF-20 to be reduced to less than 90°. There is no consensus in the literature about the contact angle formed between the materials surface and a given polar liquid. The material can be defined as hydrophilic or hydrophobic, however, according to the definitions of Gangnon et al. and Gupta et al. these foams have shown hydrophilic behavior [1,40,41]. In this case, the increased wettabil-
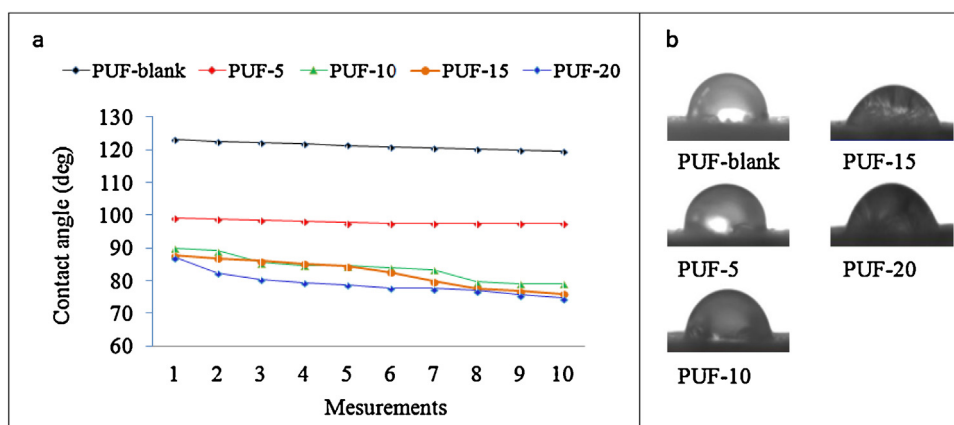
Fig. 4. a) Effect of lignin concentration on the contact angle between water and the surface of the materials and b) image of water droplet in contact with the surface of the foams.
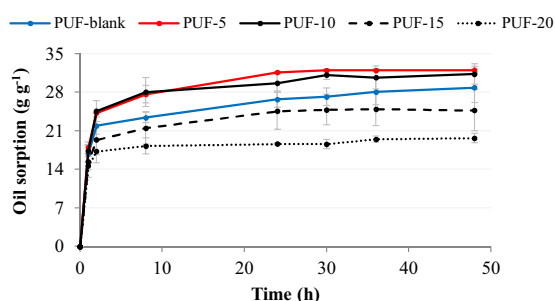

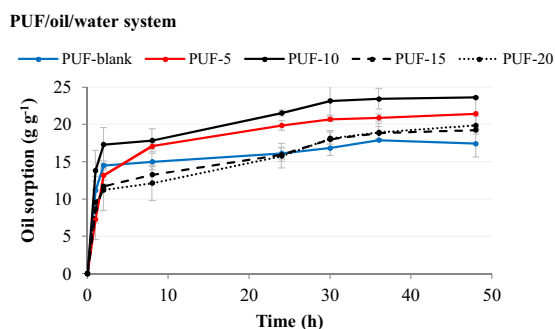**Fig. 5.** Oil sorption capacity of the foams as a function of time in PUF/oil system.

Fig. 6. Oil sorption capacity of the foams as a function of time in PUF/oil/water system.

ity of the surface is produced by the increase in surface-free energy of the material and wicking of water into cavities. Some studies show that the increase in surface foam hydrophobicity increases the oil sorption capacity [14,16,20–22]. In the present study, this behavior was not observed. Addition of lignin into foam decreased the hydrophobicity of the composite for all lignin concentrations studied and the best performance of PUF-5 and PUF-10 on oil sorption relative the PUF-blank may be associated with the molecular restructuring in the interface foam-oil for the reinstatement of equilibrium, leading to increased oil adsorption [42].

3.4. Kinetic study of oil sorption capacity in PUF/oil and PUF/oil/water systems

The Figs. 5 and 6 show the oil sorption capacities of the blank and modified foams with lignin, in PUF/oil and PUF/oil/water system as function of time, respectively. All foams showed a higher oil sorption capacity in the PUF/oil system when compared to the
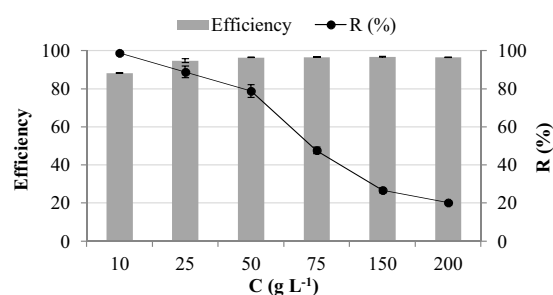

Fig. 7. Oil removal efficiency and oil removal percentage from water by PUF-10.

EPU/oil/water system after contact time of 48 h, except the PUF-20, which had approximately the same sorption capacity for both systems. This result corroborates the contact angle results, indicating that PUF-20 has a higher hydrophilicity compared to the other foams, which may favor the simultaneous sorption of water and oil. Even with a higher hydrophilicity, PUF-20 showed an improvement of about 14.1% in sorption capacity compared to the blank one in the PUF/oil/water system. Every lignin modified foams exhibited better oil sorption in the PUF/oil/water system after contact time of 48 h compared to the blank one, showing the positive influence of lignin on oil sorption in this system. Lignin reduces the hydrophobic character of modified foams due to the polar groups in the structure, but it also has aromatic groups derived from benzene, which can favor the sorption of organic compounds [43]. The PUF-10 showed an improvement of about 35.5% in sorption capacity compared with the blank one in the PUF/oil/water system. It is possible that the lower density of PUF-10 contributed to the improvement in the oil sorption capacity; since greater polymer expansion can result in finer cells that can be easily ruptured, permitting a larger amount of oil to permeate into the polymer. This behavior has been previously described in the literature [7].

3.5. Concentration effect: efficiency and oil removal percentage

Considering that the PUF-10 showed better performance for the removal of crude oil from water, its oil removal efficiency and oil removal percentage were evaluated in different oil concentrations (10 up to 200 g L^{-1}). Fig. 7 shows the oil removal efficiency and the oil removal percentage from water by PUF-10 in different oil concentrations (10 up to 200 g L^{-1}). The removal efficiency increases with increasing concentration of oil in the water. The high oil concentrations in water, disfavor water sorption by the foam, favoring greater oil sorption by the polymer. In contrast, the oil removal per-

Table 4
Estimated parameters of oil adsorption by the modified foam PUF-10 using the Langmuir and Freundlich models.

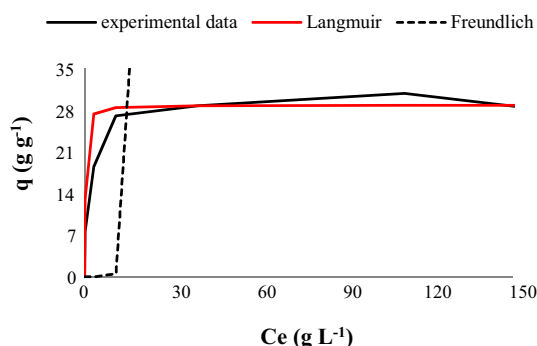| Parameters		
Langmuir		
K_L (L g^{-1})	5.86	Favorable
Q_m (g g^{-1})	28.9	
R_L	0.0147	
R^2	0.9965	
RMSE	4.79	
X^2	5.39	
Freundlich		
n	0.2175	Unfavorable
K_F	9.4E−06	
R^2	0.8802	
RMSE	6.3E+04	
X^2	5.1E+10	

Fig. 8. Comparison of Langmuir adsorption isotherm with oil adsorption by the modified foam PUF-10.

centage was diminished with the increase of the oil concentration in water. This result was expected, due to the saturation of the foam when the oil adsorption process reaches equilibrium.

3.6. Adsorption isotherms

The adsorption isotherms express an equilibrium relation between the sorbate concentration in the sorbent and in solution. According to the parameters shown in Table 4, the Langmuir model has a better fit to the experimental data. A good correlation ($R^2 = 0.9965$) and the value of $0 < R_L < 1$ obtained by the Langmuir model as well as the lowest values of RMSE and X^2 show that adsorption is favorable and occurs on a uniform surface, resulting in the formation of a monolayer of adsorbed oil that covers the entire cell surface of the foam. The Langmuir model also shows that the maximum oil adsorption by the modified foam PUF-10 would be 28.9 g g^{-1}, comparable to the experimental data, which showed a greatest oil adsorption of 30.9 g g^{-1}. The parameters presented in Table 4 show that Freundlich model is unfit to the experimental data [26,28,29].

Fig. 8 shows the fits of the experimental results and the calculated data using the Langmuir and Freundlich models. The curvature of the experimental data shows good agreement with the Langmuir model, and according to the classification in literature [44], the curves are of the L type, indicating a decrease of active sites on the adsorbent as soon as oil molecules are adsorbed. This result is consistent with the reduction of the oil removal from water by the modified foam PUF-10, due to the increased oil concentration in the system, as illustrated in Fig. 6. The curvature of the Freundlich model shows a disagreement with the experimental data, and the adsorption process does not reach the equilibrium. This model is unsuitable for theoretical explanation of the experimental data.
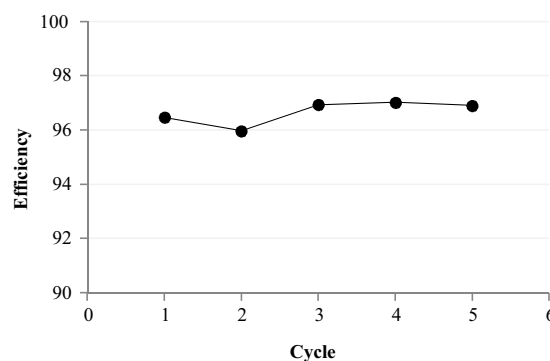

Fig. 9. Oil removal efficiency by PUF-10 for five cycles.

Table 5
Crude oil sorption capacities of some polyurethane foams reported in literature.

Sorbent	Maximum oil sorption (g g^{-1})	Reference
PUF-nanoclay (3 wt%)	21.5	[14]
PUF-silica-DTMS	25.6	[16]
PUF-activated carbon (1 wt%)	27.2	[20]
PUF-carbon nanotubes (1 wt%)	24.8	[22]
PUF-lignin (10 wt%)	28.9	This study

The negative value obtained of $\Delta G \circ$ (-4.4 kJ mol^{-1}, at 298 K) indicates that the oil adsorption process by PUF-10 is energetically favorable and happens of spontaneous way.

3.7. Reuse of the sorbent

Fig. 9 shows the PUF-10 efficiency during five continuous cycles. It is clear on the good performance of the PUF-10 since significant losses of oil removal efficiency have not been observed during the five cycles. The result also attests the chemical stability of the PUF-10 after successive washes with xylene and water. The oil removal efficiency remained greater than 95% after all cycles showing the good recyclability of the PUF-10.

The Table 5 shows a comparative study of the oil sorption for some polyurethane foams. Modification of the foams is important to improving the oil sorption capacity and all works shown in the table showed an improvement in crude oil sorption for the modified foam compared to white foam (without modification). However, large scale production of materials used for environmental remediation cannot be compromised by a high final cost of production and a great waste generation. In this context, the reuse of waste as filler in polyurethane foams may be an interesting solution under an economic and environmental aspect.

In present work, the lignin was used without any prior treatment as filler in polyurethane foam. In this context, this work has significant environmental relevance such as (i) reuse of a waste produced by industry and (ii) positive results in absorption of crude oil from water due to the presence of lignin in the foam.

The Table 5 shows a comparative study of the oil sorption for some polyurethane foams. Modification of the foams is important to improving the oil sorption capacity. All works have shown that large-scale production of materials properly used for environmental remediation cannot be compromised by a high final cost of production and a huge waste generation. In this context, the reuse of waste as filler in polyurethane foams may be an interesting solution under an economic and environmental aspect.

4. Conclusions

It is concluded that the presence of lignin in polyurethane foams increased oil sorption capacity. The kinetics study shows that equi-

librium was achieved before a time contact of 48 h, the oil sorption is higher for PUF/oil system than PUF/oil/water by all foams except for the PUF-20, which showed the same sorption capacity for both systems. In particular, the PUF-10 showed an improvement of about 35.5% compared to the blank foam in PUF/oil/water. The concentration effect showed that the oil removal efficiency increases while the oil removal percentage decreases with the increase of oil concentration (10 up to $200\,g\,L^{-1}$) for the removal of crude oil from water by PUF-10. The Langmuir isotherm showed a better fit to the experimental data and predicted a maximum oil adsorption of $28.9\,g\,g^{-1}$ by the PUF-10. The curvature of the Freundlich model shows a disagreement with the experimental data. The ΔG° value of $-4.4\,kJ\,mol^{-1}$ indicated that the crude oil adsorption process by PUF-10 was energetically favorable. The results of reuse of the foam showed that oil removal efficiency remained greater than 95% after five consecutive cycles demonstrating the good recyclability and chemical stability of the PUF-10.

Acknowledgments

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