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

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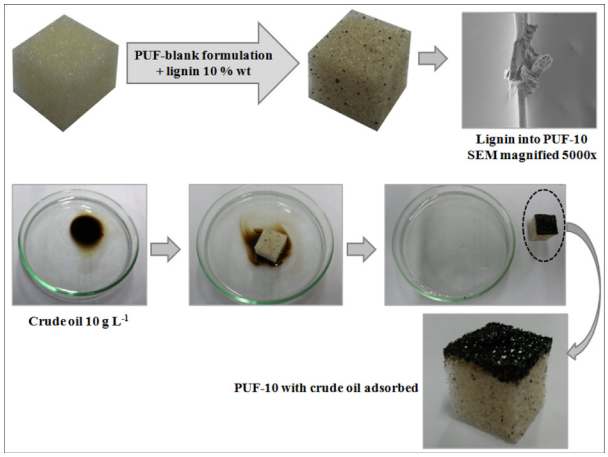
HIGHLIGHTS

- 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



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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 ΔG° value of $-4.4\,kJ\,mol^{-1}$ 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, different 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.

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

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 $349.9\,g\,mol^{-1}$) 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

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