ADSORPTION OF USED MOTOR OIL ONTO LIGNOCELLULOSE MODIFIED WITH SILOXANES

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ABSTRACT

In this study, lignocellulose was modified with N-terminated siloxanes and then used as adsorbent for the removal of used motor oil from water.After modification, Fourier-transform infrared spectroscopy (FTIR) showed that N-terminated siloxanes were grafted onto lignocellulose. The adsorbents prepared showed very good adsorption properties for the removal of used motor oil in aqueous medium: up to 90 mg of COD were removed per g of lignocellulose modified with N-terminated siloxanes. Some Langmuir isotherms were not very high, but a reasonable fit for adsorption of used motor oil onto lignocellulose modified with siloxanes was obtained, suggesting that the oil uptake occurred onto a monolayer adsorbent surface. Whereas Freundlichisotherms could not be applied because linear plots appeared not to fit. The correlation coefficient ($R2 \geq 0.9997$) from pseudo-second order equations suggested that adsorption couldhave involved chemisorption.

Key Words: Lignocellulose, Chemical modification, N-terminated siloxanes, Adsorption, Used motor oil.

1. Introduction

Oil plays a central role in lubricating parts of the engine so that they move easily and smoothly. However, routine maintenance (servicing) of vehicles results in soil pollution which ends up in water bodies with water runoff. Such disposal of used motor oil (especially in developing countries) is an environmental concern. Another source of environmental concern (worldwide) comes from oil spills due to different accidents. The biodegradation of this fossil oil can last for

years depending on biological and physicochemical factors, such as: low numbers of microbes, insufficient oxygen or nutrient availability, temperature and water availability (Troquet*et al*., 2003; Antizar-Ladislao*et al*., 2005; Antizar-Ladislao*et al*., 2006).

Researchers (Vazquez-Duhalt, 1989 and Clonfero, 1996) have pointed out the adverse effects of used motor oil on the environment. These adverse effects varied from the disruption of food chains to oil toxicity. Lefcort*et al*. (1997) found that such negative effects of oil may interfere with respiration across gill surfaces of fishes and other animals. Also, oil is regarded as capable of generating carcinogens and endocrine disrupters (Granella*et al*., 1995; Nash *et al*., 1996; Onwurah*et al*., 2007). Therefore, disposal of used motor oil should be done with due environmental concerns; hence it is important to consider effluents containing oil as a very dangerous polluting product.

Different techniques have been used for cleaning up water. Adsorption, with sorbent materials,is the most use for the removal of oil from water (Johnson &Manjrekar, 1973; Teas *et al*., 2001; Wei *et al*., 2003; Sayed &Zayed, 2006; Gammoun*et al*., 2007; Rajakovic-Ognjanovic*et al*., 2008; Moriwaki*et al*., 2009). Lignocellulosic materials have been recognized as sorbent materials after modification of the hydroxyl groups by esterification with a combination of monocarboxylic and dicarboxylic acid ester groups. The modified sorptive material is effective for the removal of oils and other contaminants, including heavy metals from fluids such as contaminated water by combined sorption of hydrophobic contaminants and ion exchange (Eriksen*et al.* 2008). Researchers (Dizhbite*et al.,* 1999) have reported an interaction between hydroxyl and carbonyl groups (of lignocellulose) with polyphenols or heavy metal ions through hydrogen bonding or complexation in the removal of these pollutants. Telysheva*et al*. (2006) described a high potential of the water-insoluble lignins as raw materials for design of sorbents intended for decontamination of soil and water from organic/biological pollutants.

Different natural materials, such as: cotton, milkweed, kenaf vegetable, and wool fibres have been assessed as adsorbents. Researchers have reported that some of these materials have higher oil-sorption capacity over synthetic adsorbents (Rajakovic*et al,* 2007; Moriwaki*et al.,* 2009). The increased interest in natural materials for reinforcement has paved the way for increased research activities in the field of natural fibres (Pothan& Thomas, 2003). To improve the cellulosic fibres' properties for diverse applications, different authors have suggested various chemical modifications (Botaro&Gandini, 1998). It has been reported that chemical modification has a profound influence on the polarity of lignocellulose fibres (Pothan and Thomas, 2003). In the process, methods such as mercerization, silane treatment, acetylation, benzoylation, plasma treatment etc. have been reported for lignocellulose modification (Gadhe*et al.,* 2006; Baltazar-Y-Jimenez and Bismarck, 2007; Kekalo*et al.,* 2008), leading to different applications. The hydroxyl groups are the most interesting functional groups targeted for lignocellulose chemical modifications. Appearance, wetting and coating characteristics, sorption, adhesion and friction, as well as biocompatibility are primary properties dependent on the surface of lignocellulose to be modified (Torstensson& Hult, 1992). Therefore, adsorbents from lignocellulosic material(Kikuyu grass) was chemically modified to assess its sorption properties toward used fossil oil.

Chemical Oxygen Demand (COD) was selected as the most valuable measurement technique to monitor the effectiveness of oil removal by the prepared adsorbents because oil is a mixture of a wide range of chemicals. COD is a test through which organic matter is oxidized by a boiling mixture of dichromate ion and sulfuric acids. $K_2Cr_2O_7$, H_2SO_4 and heating (reflux or digestion) are used to oxidize organic carbon to CO_2 and H_2O in the presence of silver sulphate catalyst (Baumann, 1974). During digestion, the sample material is oxidized and $K_2Cr_2O_7$ readily "gives up" oxygen to bond with carbon atoms to form carbon dioxide (CO_2). The oxygen transaction reduces the hexavalent $Cr_2O_7{}^{2-}$ ion to the trivalent Cr^{3+} ion as shown in the Scheme.

$$Cr_2O_7{}^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$
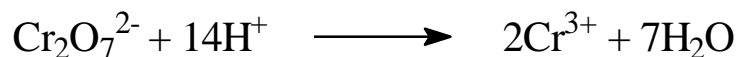
Scheme: Reduction of $Cr_2O_7{}^{2-}$ *during COD test*

Mercuric sulphate is used to suppress interference mainly due to chloride. The COD test measures the amount of dichromate consumed in the breakdown of organic matter, which is proportional to COD. In essence, COD is a measure of the amount of oxygen used in the chemical oxidation of organic matter (organic pollutants) contained in a sample (such as wastewater). It is also considered an indicator of the degree of pollution in the effluent and of the potential environmental impact of the discharge of the liquid effluent.

2. Material and Method

2.1. Chemicals

Grass (Pennisetumclandestinum,Kikuyu grass)was collected from gardens within Alice Town (Eastern Cape, South Africa) and used as source of lignocellulose.

Chemicals: Dibutyltindilaurate (DBTDL) was supplied by Sigma-Aldrich. Three siloxanes: 3-aminopropyl-terminated polydimethylsiloxanes(NH15D, NH40D and NH130D,Mw = 1,000, 2,600, and 11,000 g/mol, respectively) weresupplied by Wacker Chemie AG/Germany. Dibutyltindilaurate(DBTDL) and dimethylformamide (DMF) by SigmaAldrich. Used motor oil (collected from a garage in Alice, Eastern Cape,South Africa) was filtered (Whatman filter paper, 150 mm ø)and oven-dried in an open vessel for 48 h at 60 °C with frequentshaking(in order to remove suspended matter and reduce moisture).

2.2. Preparation of materials

2.2.1. Lignocellulosic material:grass material was pre-treated according to the procedure obtained from Ruiz and Ehrman (1996) and Palmowski& Muller (1999). Soluble substances and hemicellulose were extracted by decoction for 30 min. The residue obtained after filtration was extensively washed with water until the filtrate became "colourless". The solid residue (lignocellulose) was oven-dried overnight to constant weight at 65°C;it was then fractionated (hydrolysed) in H_2SO_4 according to the procedure obtained from Shibazaki*et al*. (1995), Curreli*et al*. (2002), Xiang et al. (2003) and Hong &Qiu (2008), prior to chemical modification. The chemical modification of lignocellulosic material by siloxanes was adapted from the work of Matías*et al*. (2000) and Le Digabel*et al*. (2004) and carried out as follows: In a 3-neck round

bottomed flask, 10 mL of 3-aminopropyl-terminated polydimethylsiloxane was added to 1.5 g of lignocellulose (from acid hydrolysis) in 30 mL of DMF and refluxed for 5 h at 130°C. The reaction was carried out under a nitrogen atmosphere, in the presence of 200 μL of dibutyltindilaurate. The products were Soxhlet-extracted with 100 mL THF for 5 h. The obtained products (modified lignocellulose) were oven dried overnight at 65°C. The resulting materials were designated as followed: LNH15D (lignocellulose modified with siloxane NH15D), LNH40D (lignocellulose modified with siloxane NH40D and LNH130D (lignocellulose modified with siloxane NH130D while grass with H_2SO_4 was considered as the product obtained after treatment with sulfuric acid.

2.2.2. Experimental procedure for the adsorption of motor oil

Sorption experiments were conducted with used motor oil emulsified in deionised water and then used as a simulation of oily wastewater. The sorption of oil was adapted from the procedure of Radetic*et al.* (2008); Ji*et al.* (2009); Moriwaki*et al.* (2009); Srinivasan &Viraraghavan (2010) as follows: A known amount (200, 400, 600, 800, 1000 mg) of used motor oil was ultrasonicated for 20 min with 100 mL of deionized water in order to form a water emulsion in a conical flask (500 mL) and 0.1 g of adsorbent added to the mixture. Each mixture (oil-in-water emulsion + adsorbent) was shaken on an orbital laboratory shaker (mrc Orbital shaker) at 160 rpm. Aliquots of the mixture were collected after 5, 15, 30, 60, 180, 300 min. The oil-in-water emulsion was filtered through a 0.45 µm syringe filter after sorption experiments and was taken for COD measurements. Initial COD (before adding the adsorbent) and a blank were recorded for each run. All experiments were conducted in duplicate and mean values were used in the analysis of data.

Equilibrium was considered to be reached when at least 3 consecutive measurements of the COD of oil were similar in the batch experiments. Aliquots of oil-in-water were taken and the initial and the equilibrium CODs were measured using a COD SpectroquantPharo 100 spectrophotometer (Merck).The COD was calculated using the formula:

$$Q_t = \frac{V(COD_o - COD_t)}{m}$$

Q_t is the COD amount of oil adsorbed (mg/g) at time t, COD_o and COD_t are the initial and COD at time t (in mg/L), m is the mass of adsorbent (g) and V is the volume of solution (L).

It is important to notice that although ultrasonication was used for the oil-in-water emulsion preparation, aliquots for COD analysis before adsorption (adding of adsorbent) could only be collected at specific sites (of high oil-in-wateremulsion), since it was not possible to obtain a perfect emulsion without using a surfactant.

3. Results and discussion

3.1. Physicochemical properties of oil

Wet chemistry was used to obtain the water and inorganic contain and the density of the used motor oil. Some physicochemical properties of oil are summarised in Table 1.

Table 1: Properties of waste motor (engine) oil

Parameter	Value
Water contain (w/w %)	6.9
Density (kg/m^3)	882
Viscosity (mPa·s) (by DV-E Viscometer at 50rpm)	420
Inorganic content (w/w %)	0.5

3.2. FT-IR of Lignocellulosic materials

FT-IR spectra (Figure 1) were examined in order to confirm (or otherwise), the chemical modification of lignocellulosic material following grafting with siloxane. The evidence of chemical modification of grass lignocellulose is observed from the spectral bands between 808 and 1460 cm^{-1} and similar bands have been observed in literature when a silane coupling agent was used (Colom *et al*., 2003). These bands can only be attributed to the presence of siloxaneon the matrix; because that region is the main IR absorption region of siloxane. The presence of Si–O–Si bridges is not easily detected by FT-IR, since the typical vibration frequencies of this group, around 950 and 1100 cm^{-1}, are easily masked by the large and intense cellulose C–O stretching bond (Coates, 2000). The appearance of a peak at 1266 cm^{-1} can be assigned to C-NH$_2$ bond, ending the siloxane moiety or its Si-CH$_3$ bond.
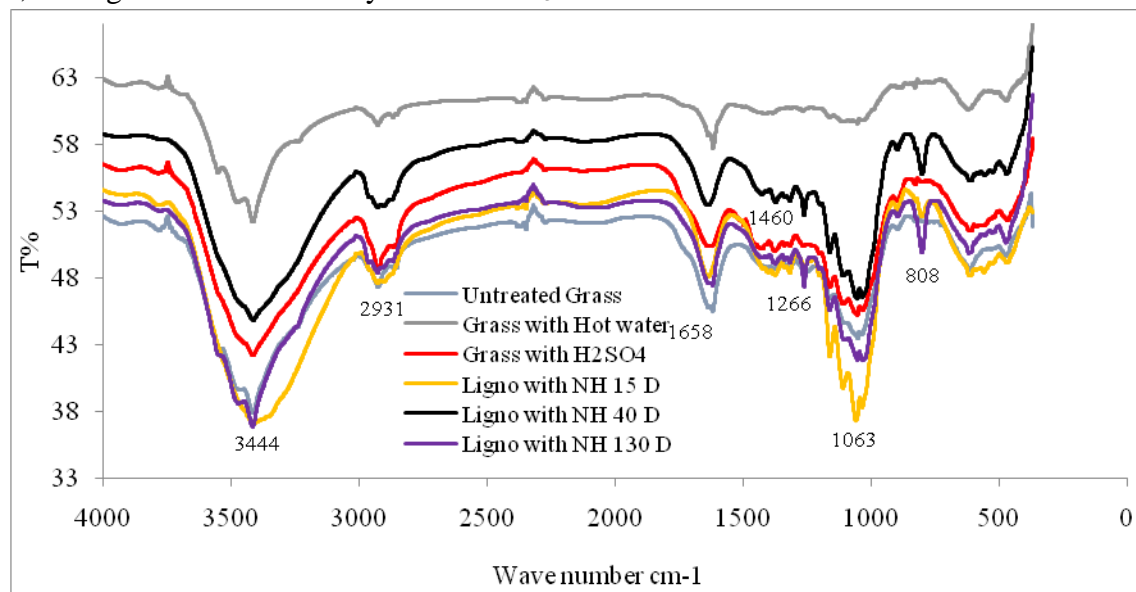

Figure 1: FT-IR of untreated and modified lignocellulosic materials

The assignment of other main peaks is reported in Table 2 below; this was done as reported in literature (Brown *et al*, 1988; Adams, 1963; Kemp, 1991; Homma *et al*., 1999; Coates, 2000; Hamciuc*et al*., 2007).

Table 2: Assignment of FT-IR peaks

Band position (cm⁻¹)	Functional group
3444	O–H
2964	C–H
1658	C=O
1266	C-NH$_2$/Si-CH$_3$
1063	Si-O-Si/C-O
808	Si-C

The lignocellulosic materials prepared were soaked in water for 24 h in order to ensure the stability of the prepared materials in water, since they were intended to be used for the removal of pollutants in water treatment. The obtained FT-IR spectra (after soaking the materials) did not reveal any changes amongst the different peaks, as shown in Figure 2.
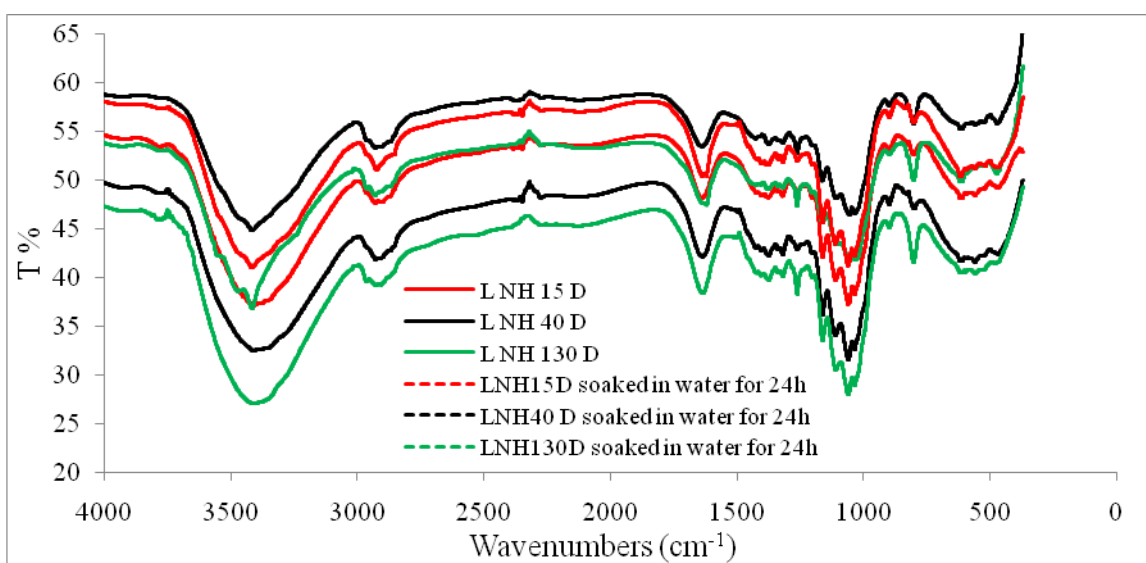

Figure 2: FT-IR of soaked and non-soaked materials (stability of bonds in water)

The soaking of the prepared materials was conducted to appreciate the stability of the chemical bond formed between the matrix (lignocellulose) and the siloxanes. It is most likely that an ether linkage was formed between the OH group of the lignocellulosic matrix and one of the NH$_2$ groups of the coupling agent (N-terminated siloxane), with elimination of ammonia.

3.3. SEM of lignocellulose

Scanning electron microscope (SEM) micrographs were obtained with the intention to explore the impact of siloxane on the morphology of the modified lignocellulose. The SEM images of the modified lignocellulose and grass (source of lignocellulose) treated with hot water are presented in Figure 3 below.

The SEM micrographs showed that the siloxanes coupling agents had an impact on the surface of the lignocellulosic fibres. The modified lignocelluloses appear drier, firmer, smooth and brush-like. Their surfaces show the absence of surface impurities whilst the surface of grass treated with hot water appears rougher.
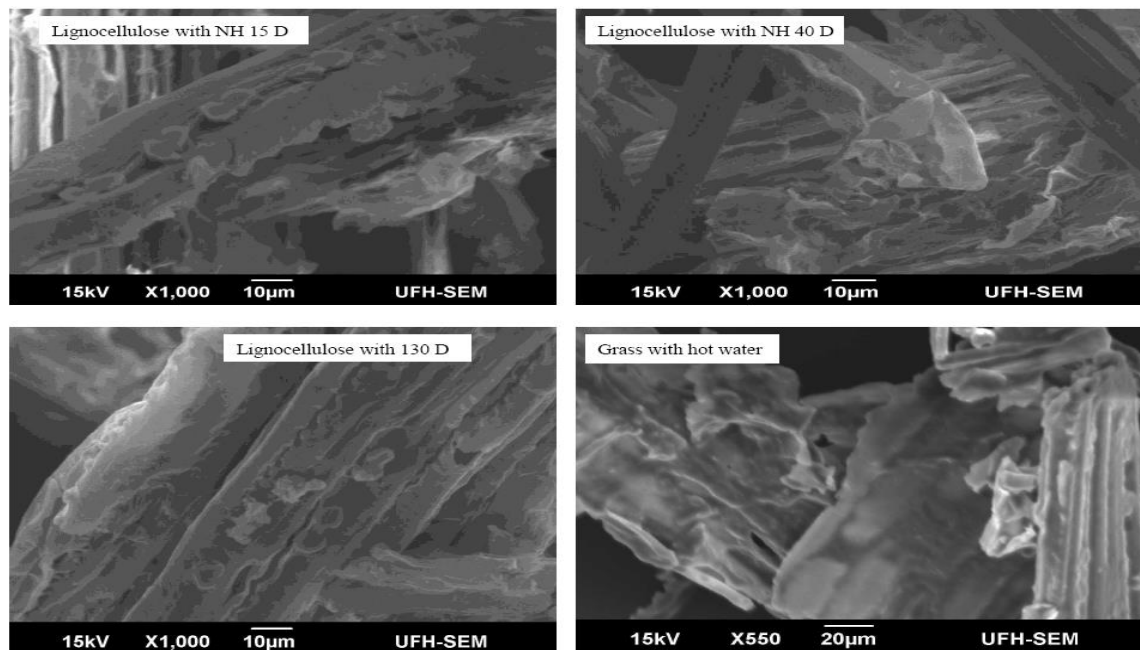
Figure 3: SEM micrographs of grass and modified lignocellulose with siloxane

3.4. TGA of lignocellulose

The thermal stability of lignocellulose modified with siloxanes was evaluated by thermogravimetric analysis (TGA). Figures 4 (A, B) present the TGA and DTG curves of unmodified and modified lignocellulose from grass. Both lignocelluloses showed weight loss around 100°C due probably to the elimination of moisture. However, lignocellulose modified with siloxanes had slightly higher resistance to heat than unmodified lignocellulose. The unmodified grass decomposed in the range of 233-377 °C and 421-590 °C.
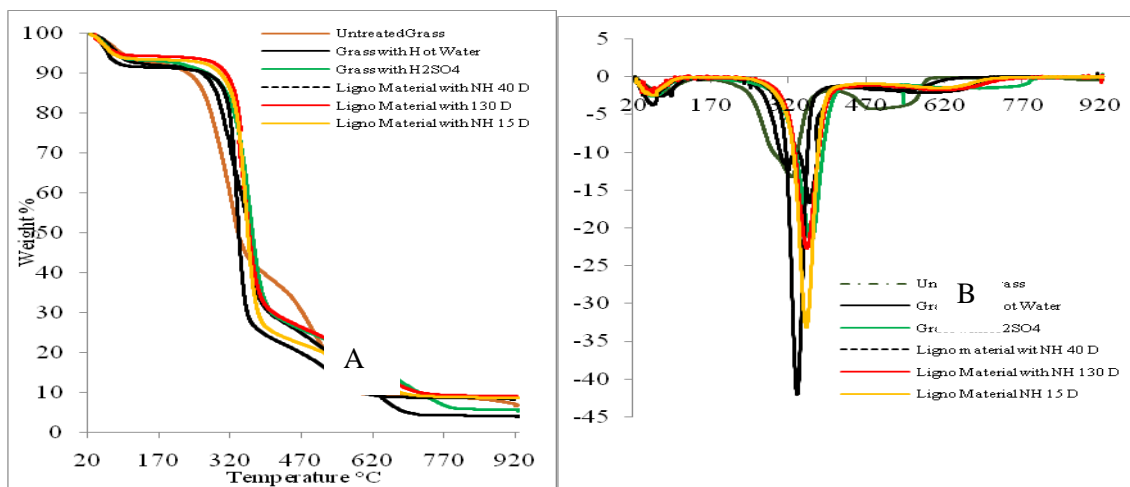
Figure 4: TGA and DTG of untreated and treatedgrass and modified lignocellulose A) TGA, B) DTG (derivative)

The modified lignocellulose with siloxane NH40D showed significant decomposition in the range of 256-383°C; and also in the range 383-616°C. In both cases, between 233 and 616°C, weight loss was probably due to the release of volatile matter from the materials. From around 372°C, the sample mass decreased slightly, although it seemed to be influenced by siloxane moiety of the product. As deduced, the modification of the biopolymer with siloxane segments had an impact on the thermal stability of the product obtained.

3.2. Adsorption of used motor oil onto lignocellulose modified with siloxanes
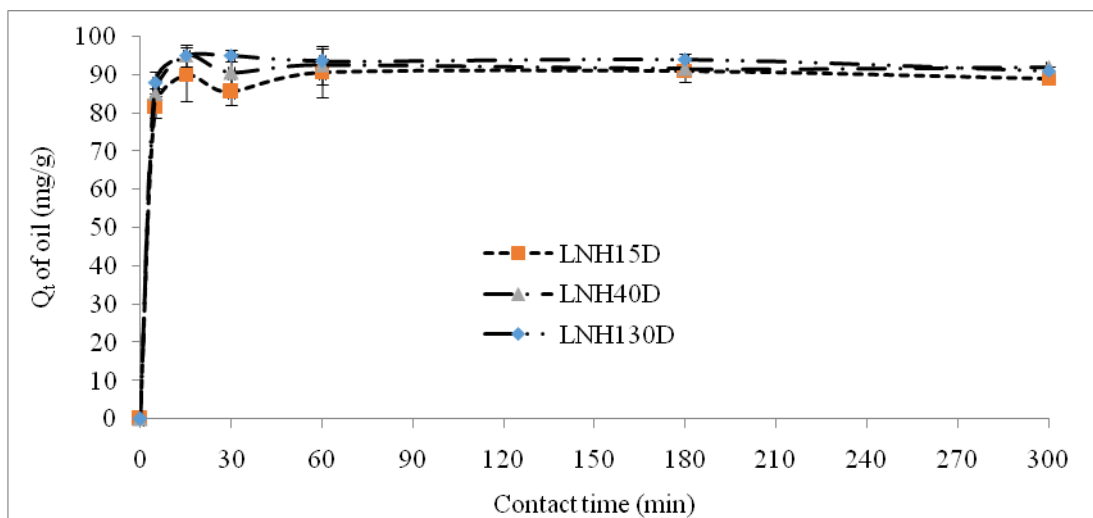
3.2.1.   Kinetics of adsorption of motor oil adsorption on lignocellulose modified with siloxanes

3.2.1.1.   Effect of contact time and molecular weight

Contact time between used motor oil and lignocellulose modified with siloxanes was examined and the results are showed in Figure 5. It can be seen that the initial adsorption process (onto the adsorbents) takes few minutes (~10 min). After a small fluctuation (desorption-adsorption) onto LNH15D and LNH40D, equilibrium was reached. Adsorption onto LNH130D appeared to be slightly higher than onto others adsorbents. High molecular weight of LNH130D may be responsible of this results.

Although the composition of motor oil has not been defined, it is known that mineral-based oils contain a substantial fraction of nitrogen- and sulfur-containing compounds (ABB Environmental, 1990). The nitrogen- and sulphur-containing compounds could have played an important role in the sorption of oil onto the modified lignocellulose by probably establishing hydrogen bond between OH (of lignocellulose) and nitrogen (N) and sulphur (S) of oil.
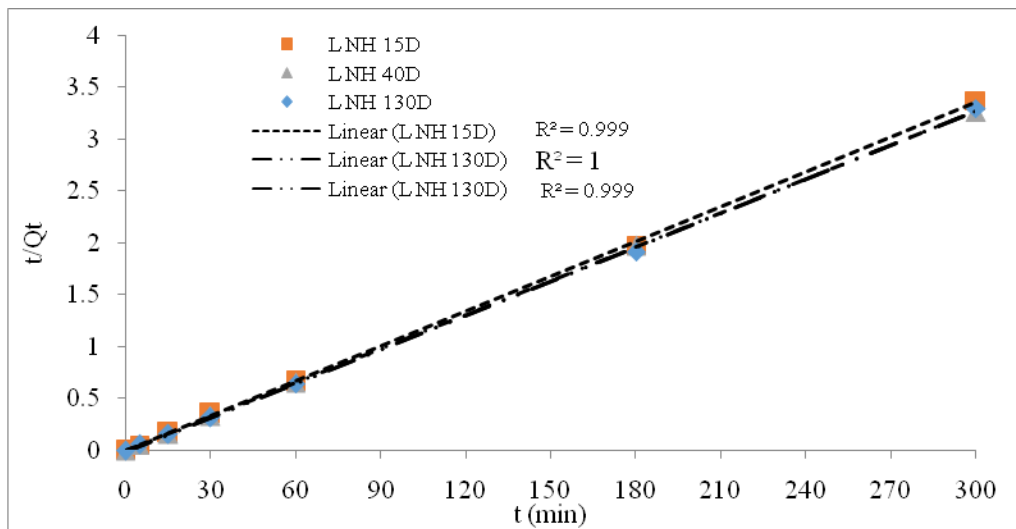
Figure 5: Effect of contact time and molecular weight on adsorption of oil onto lignocellulose modified with siloxanes

3.2.1.2.   Pseudo second order of adsorption of oil adsorbed onto lignocellulose modified with siloxanes

In the attempt of studying the kinetics, it was found that the pseudo first order could not be applied to the adsorption of used motor oil onto lignocellulose modified with siloxanes. When plotted, the correlation coefficient (R^2) was found to be very low (less than 0.1).

Instead, the pseudo second-order, in Figure 2, showed R^2 values of almost unity. This then, depicts the possibility of a chemical bond amongst interacting species during the sorption process of used motor oil onto lignocellulose modified with siloxanes. Ho& McKay (1999) stated that high values of correlation coefficient($R^2> 0.99$, in this study), suggests formation of a chemical bond between adsorbent and adsorbate. As suggested above, adsorption could have been due to the hydrogen bond.

Figure 2: Pseudo second-order

3.2.2. Isotherms of COD of used motor oil adsorbed onto lignocellulose modified with siloxane

Langmuir isotherms of used motor oil adsorbed onto lignocellulose modified with siloxanes were plotted and the results are displayed in Figure 3. Correlation coefficients (R^2) of Langmuir model were not very high, but a reasonable fit for adsorption of used motor oil onto lignocellulose modified with siloxanes was obtained. Freundlichmodel could not be applied for adsorption of used motor oil onto lignocellulose modified with siloxanes because linear plots appeared not to fit.
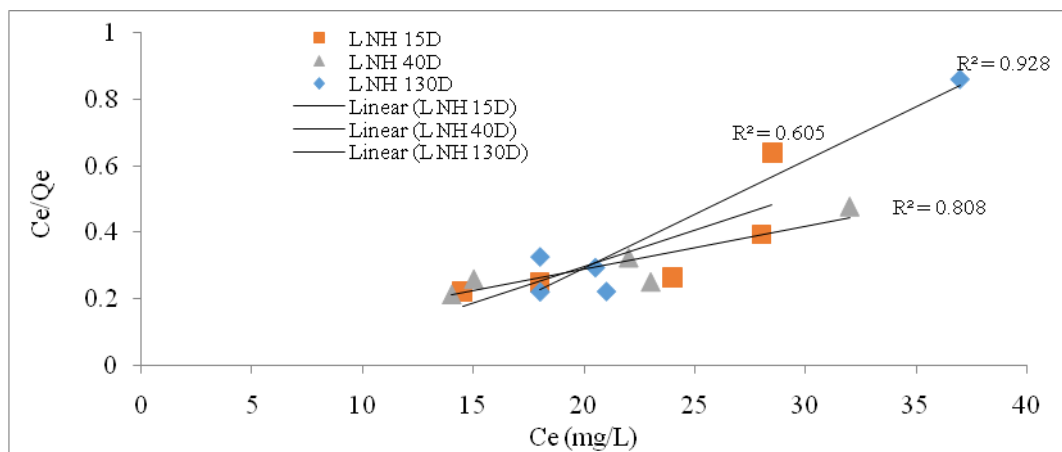
Figure 3: Langmuir isotherms of oil onto lignocellulose modified with siloxanes

This means that Langmuir isotherms were the best fit for adsorption of used motor oil onto lignocellulose modified with siloxanes suggesting that the oil uptake occurred onto a monolayer surface, possibly because the material do not form layers (according to SEM results).

Conclusion

Lignocellulose was chemically modified with N-terminated siloxanes after extraction of soluble substances by decoction. FTIR, TGA, andSEM were used to assess the chemical modification. The stability of the grafting was checked by socking the materials in water for 24 h. Used as adsorbent, up to 90 mg of COD were removed per g of lignocellulose modified with N-terminated siloxanes. This means that the materials can be good candidates for the removalof used motor oil from water.

Acknowledgement

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