A New Oil Spill Adsorbent from Sulfuric Acid Modified Wheat Straw

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Abstract: This work deals with the chemical modification of wheat straw, a common lignocellulosic agricultural residue, to obtain low cost adsorbents for diminishing an oil-products spill in seawater. The adsorbent was modified by acid hydrolysis, i.e. 0.045 N sulfuric acid as a chemical catalyst, in a PARR autoclave at 160-220°C for 0-50 min isothermal time period. The oil adsorbency tests were performed, using diesel and crude oil of predetermined quality specifications. Water adsorbency-values for reaction ending temperature at 160°C were found to increase from 4.89 g/g to a maximum of 9.08 g/g for isothermal reaction time 0 min. At 180°C the maximum was 7.05 g/g for the same isothermal reaction time. At 200 and 220°C the water adsorbency was decreasing as low as 0.93 g/g for extreme hydrolysis conditions. Diesel adsorbency-values for reaction ending temperature at 160°C were found to increase from 2.77 g/g to a maximum of 5.24 g/g for isothermal reaction time 20 min. At 180°C the maximum was 5.14 g/g for isothermal reaction time 30 min. At 200°C the maximum was 4.16 g/g for the same isothermal reaction time. At 220°C the maximum was 4.76 g/g for isothermal reaction time 50 min. Crude oil adsorbency-values for reaction ending temperature at 160°C were found to increase from 2.82 g/g to a maximum of 5.38 g/g for isothermal reaction time the same with that in the case of diesel. At 180°C the maximum was 5.17 g/g for isothermal reaction time 0 min. At 200°C the maximum was 5.16 g/g for isothermal reaction time 50 min. At 220°C the maximum was 4.78 g/g for the same isothermal reaction time.

Key-Words: adsorbent, acid hydrolysis, lignocellulosic, oil spill, pretreatment, wheat straw.

1 Introduction

The oil spills are usually results of transportation and storage activities. Dispersants, skimmers, oil-water separators, booms and adsorbents are used to remove oil from contaminated marine areas and diminish the impact on the affected ecosystems. Adsorbents can be inorganic or organic, synthetic or natural products. Waste biomass as a lignocellulosic agricultural residue or agro-industrial byproducts is a natural organic adsorbent. The chemical modification by autohydrolysis [1, 2] or acid hydrolysis of this lignocellulosic waste can provide low cost adsorbents with improved qualities for the adsorption of dyes [3-6] and oil products [7-9].

Wheat straw is a renewable source for production of energy chemicals. Wheat straw can be used during containment and cleanup of oil spills in aquatic environment. A thin wax layer covers stalks and leaves of cereals. Therefore wheat straw could favorably adsorb hydrophobic liquids. Waxes are insoluble in water, thus the coating on external surfaces of stems, leaves, flowers, fruits and seeds protects them from excessive water evaporation or outer moisture. Waxes also protect plants from microorganisms and mechanical damage. Wheat straw like the other adsorbing materials is capable of holding oil as the result of adsorption and absorption. The adsorption capacity depends primarily on the chemical structure of straw tissue that has direct contact with oil. The absorption capacity is a function of the structure of the straw stalks in the bundles, distances between them, the diameter and cross-sections of each stalk and leaf. Due to high oil adsorption by wheat straw, oil is mostly held due to capillary of straw tissue and interior part of stalk, as well as to the existence of oil bridges between stalks. Wheat straw adsorption capacity varies for many researches due to different apparent densities of wheat straw and ways of its adsorbent form. The absorption of oil depends on surface properties of wheat straw [10].

According to the technical literature, walnut shell [7], wheat and barley straw [8-10], biomass [11], raw bagasse [12], carbonized pith bagasse [13], acetylated sugarcane bagasse [14], peat [15, 16], fatty acid grafted sawdust [17] and carbonized fir fibers [18] can be used as oil-spill adsorbents.
This work deals with the modification of wheat straw to obtain low cost adsorbents for diminishing an oil-products spill in aquatic environment. The adsorbent was pretreated by acid hydrolysis at 160-220°C for 0-50 min with 0.045 N sulfuric acid as a chemical catalyst. The oil adsorbency tests were performed, using diesel and crude oil.

2 Materials and Methods

2.1 Material Development
The wheat straw obtained from Thessaly in Central Greece had a moisture content of 8.75% w/w. It was chopped with hedge shears in small pieces and the fraction with sizes 1 - 2 cm (representing more than 95% of the raw total wheat straw) was collected by sieving. This fraction was chosen because it is more suitable for scale up of the process.

2.2 Acid hydrolysis Process
The wheat straw was pretreated using acid hydrolysis; the acid hydrolysis process was performed in a 3.75-L batch reactor PARR 4843. The acid hydrolysis time was 0-50 min (not including the preheating time); the hydrolysis reaction was catalyzed by 0.045 N sulfuric acid at a liquid-to-solid ratio of 20:1; the liquid phase volume was 2000 mL and the solid material dose was 100 g. The acid hydrolysis reaction ending temperature ($T$ in °C) was 160°C, 180°C, 200°C and 220°C, reached after the 44, 47, 66 and 70 min preheating time, respectively.

2.3 Analytical Techniques
Applying the technique proposed by Saeman et al. [19], the lignocellulosic materials were quantitatively saccharified to glucose, xylose and arabinose in nearly quantitative yields. The filtrates from the quantitative saccharification, as well as those from the autoclave, were analyzed for their content of glucose, xylose, and arabinose using high-performance liquid chromatography (HPLC, Agilent 1200) with an Aminex HPX-87H Column, a refractive index detector, and 5 mM H2SO4 in water as the mobile phase. Glucose, xylose and arabinose were produced via quantitative saccharification of the solid residue in each one of the twenty-four experiments. Cellulose was estimated as glucan, and hemicelluloses were estimated as xylan and arabinan. Based on these results the cellulose and hemicelluloses content of the adsorbents were estimated. Finally, the acid-insoluble lignin (Klason lignin) was determined according to the Tappi T222 om-88 method [20].

The oil adsorbency test, defined according to the ASTM F726-06 method [21], was performed, following the procedure of this standard method, using diesel 10 PPM produced by Hellenic Petroleum S.A. and crude oil. The diesel and crude oil quality specifications are given in Table 1.

3 Results and Discussion
Cellulose is hydrolyzed to glucose, hemicelluloses are hydrolyzed to xylose and the Klason lignin is not significantly affected by acid hydrolysis. The simulation of the acid hydrolysis process can be performed using a model described in earlier work [2]. The experimental reaction temperature profiles as a function of acid hydrolysis time are presented in Fig. 1. The acid hydrolysis solid residue yield of the wheat straw (dry weight of product % w/w of the original dry material) is presented in Fig. 2 as a function of reaction time.

The experimental results of the water, diesel and crude oil adsorbency of the untreated and the acid hydrolyzed wheat straw are presented in the following Figures. The water adsorbency-values for reaction ending temperature at 160°C were found to increase from 4.89 g/g to a maximum of 9.08 g/g for isothermal reaction time 0 min (Fig. 3). The diesel adsorbency-values for reaction ending temperature at 160°C were found to increase from 2.77 g/g to a maximum of 5.24 g/g for isothermal reaction time 20 min (Fig. 4). The crude oil adsorbency-values for reaction ending temperature at 160°C were found to increase from 2.82 g/g to a maximum of 5.38 g/g for isothermal reaction time the same with that in the case of diesel (Fig. 5). At 180°C the maximum water adsorbency-value was 7.05 g/g for isothermal reaction time 0 min (Fig. 6). At the same temperature the maximum diesel adsorbency-value was 5.17 g/g for isothermal reaction time 30 min (Fig. 7). Moreover, the maximum crude oil adsorbency-value was 5.17 g/g for isothermal reaction time 0 min (Fig. 8). At 200 and 220°C the water adsorbency was decreasing as low as 0.93 g/g.

| Table 1. Diesel and crude oil quality specifications. |
|---------------------------------|----------|----------|
| Oil type                        | Diesel   | Crude oil |
| Density (kg/m³)                 | 835      | 860      |
| Viscosity (mm²/s)               | 3.7      | 40       |
| Water content (mg/kg)           | 120      | 250      |
| 3 Results and Discussion       |          |          |

for 50 min isothermal hydrolysis time (Figs. 9 and 12). At 200°C the maximum diesel adsorbency-value was 4.16 g/g for isothermal reaction time 30 min (Fig. 10). At the same temperature the maximum crude oil adsorbency-value was 5.16 g/g for isothermal reaction time 50 min (Fig. 11). At 220°C the maximum diesel adsorbency-value was 4.76 g/g for isothermal reaction time 50 min (Fig. 13). At the same temperature the maximum crude oil adsorbency-value was 4.78 g/g for isothermal reaction time 50 min (Fig. 14).

The water, diesel and crude oil adsorbency can be given as function of the autohydrolysis time as follows:

\[ A_i = a_i t^3 + b_i t^2 + c_i t + d_i \]  

(1)

where \( A \) is the adsorbency (g/g), \( t \) is the autohydrolysis time (min), and \( i = W, D, C; W \) is for Water, \( D \) is for Diesel and \( C \) is for Crude oil. The values of the coefficients of eq. (1) are given in Table 2. At the same Table the correlation coefficients are presented.

Fig. 1. Experimental reaction temperature profiles as a function of acid hydrolysis time.

Fig. 2. Wheat straw solid residue yield values as a function of acid hydrolysis time at 160-220°C with 0.045 N H\(_2\)SO\(_4\).

Fig. 3. Modified wheat straw water adsorbency vs. the acid hydrolysis time for reaction ending temperatures 160°C and 0.045 N H\(_2\)SO\(_4\).

Fig. 4. Modified wheat straw diesel adsorbency vs. the acid hydrolysis time for reaction ending temperatures 160°C and 0.045 N H\(_2\)SO\(_4\).

Fig. 5. Modified wheat straw crude oil adsorbency vs. the acid hydrolysis time for reaction ending temperatures 160°C and 0.045 N H\(_2\)SO\(_4\).
Fig. 6. Water adsorbency vs. the acid hydrolysis time for reaction ending temperatures 180°C and 0.045 N H₂SO₄.

Fig. 7. Diesel adsorbency vs. the acid hydrolysis time for reaction ending temperatures 180°C and 0.045 N H₂SO₄.

Fig. 8. Crude oil adsorbency vs. the acid hydrolysis time for reaction ending temperatures 180°C and 0.045 N H₂SO₄.

Fig. 9. Water adsorbency vs. the acid hydrolysis time for reaction ending temperatures 200°C and 0.045 N H₂SO₄.

Fig. 10. Diesel adsorbency vs. the acid hydrolysis time for reaction ending temperatures 200°C and 0.045 N H₂SO₄.

Fig. 11. Crude oil adsorbency vs. the acid hydrolysis time for reaction ending temperatures 200°C and 0.045 N H₂SO₄.
4 Conclusion
The chemical modification of wheat straw leads to low cost adsorbents for diminishing an oil-products spill in seawater. The straw was modified by acid hydrolysis catalyzed by 0.045 N sulfuric acid at 160-220°C for 0-50 min isothermal time period. The oil adsorbency tests were performed, using diesel and crude oil of predetermined quality specifications. Water adsorbency-values for reaction ending temperature at 160°C were found to increase from 4.89 g/g to a maximum of 9.08 g/g for isothermal reaction time 0 min. At 180°C the maximum was 7.05 g/g for the same isothermal reaction time. At 200 and 220°C the water adsorbency was decreasing as low as 0.93 g/g for extreme hydrolysis conditions. Diesel adsorbency-values for reaction ending temperature at 160°C were found to increase from 2.77 g/g to a maximum of 5.24 g/g for isothermal reaction time 20 min. At 180°C the maximum was 5.14 g/g for isothermal reaction time 30 min. At 200°C the maximum was 4.16 g/g for the same isothermal reaction time. At 220°C the maximum was 4.76 g/g for isothermal reaction time 50 min. Crude oil adsorbency-values for reaction ending temperature at 160°C were found to increase from 2.82 g/g to a maximum of 5.38 g/g for isothermal reaction time the same with that in the case of diesel. At 180°C the maximum was 5.17 g/g for isothermal reaction time 0 min. At 200°C the maximum was 5.16 g/g for isothermal reaction time 50 min. At 220°C the maximum was 4.78 g/g for the same isothermal reaction time.

Table 2. Coefficients of eq. (1) and correlation coefficients $R^2$.

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<th>$T$ (°C)</th>
<th>$W_i$</th>
<th>$a_i$</th>
<th>$b_i$</th>
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5 Acknowledgments
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References: