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# MODELING OF POLLUTANT ADSORPTION ON NOVEL MODIFIED BIOMASS AS A MEANS OF SEAWATER DECONTAMINATION

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## ABSTRACT

This work focuses on the adsorption of diesel/crude oil on modified biomass. The experiments were performed using real and substitute seawater. The effect of fluids/colloids (hydrocarbons, salts, dispersants, pigments and heavy metals) was studied. Agitation was induced to simulate the sea wave's movement in the case of shoreline flows.

## INTRODUCTION

Hydrocarbon spills (diesel, crude oil etc.) cause great damage to the shorelines which usually include sensitive marine ecosystems. Moreover, there are significant negative economic impacts on tourism and fisheries. Chemical dispersion, in situ burning, mechanical containment and adsorption are some of the cleanup methods to combat the oil spills pollution. Adsorbents collect liquid hydrocarbons on the solid phase, thus they can remove oil spills from the sea surface water. Waste lignocellulosic biomass is such a natural organic product. The thermochemical treatment of lignocellulosic waste biomass can provide a fraction that can be used as a low-cost adsorbent with increased sorption capacity and biodegradability for cleaning by adsorption the oil spills. The modification of lignocellulosic wastes can provide adsorbents with relatively high sorption capacity, biodegradability, and cost-effectiveness for the adsorption of dyes, heavy metals and oil products (1-6).

A survey of literature shows that cotton (7), kapok (8), wool (9), raw bagasse (10), acetylated sugarcane bagasse (11), peat (12), fatty acid grafted straw (13), barley straw (14-16), wheat straw (17), rice straw (18), rice husk (19-20), garlic and onions peels (21), banana trunk fiber (22), and groundnut husks (23), can be used as adsorbents for oil-spills.

Acid hydrolysis can fractionate (24) the three basic components of lignocellulosic: hemicelluloses, cellulose and lignin. Dilute sulfuric acid has been used to commercially manufacture furfural from cellulosic materials (25). The hydrolysis of cellulose is a significant entry point into the biorefinery scheme based on carbohydrates for the production of biofuels and biochemicals. The long-term

success of the biorefinery concept depends on the development of energetically efficient processes to convert cellulose into biofuels and chemicals (26).

In this work we focus primarily on modeling the process of adsorption of diesel and crude oil on modified biomass fraction. The experimental measurements were performed using mainly seawater, and simulated/substitute seawater. This work includes the modeling of adsorption of mixtures of fluids and colloids, containing water, hydrocarbons, salts, dispersants and predetermined contaminants. Agitation was induced to simulate the sea wave's movement in the case of shoreline flows.

## **MATERIALS AND METHODS**

**Material origin:** The wheat straw used in this work was obtained from the Kapareli village, close to the Thiva city at the Kopaida area in central Greece (harvesting year 2012), as a suitable source for full-scale industrial applications. The moisture content of the material when received was 9% w/w and the particle size  $19\pm 5$   $\mu$ m; after cutting and screening, the fraction with particle sizes between 1 and 2 mm was isolated for small scale experiments. Diesel and crude oil was provided by Hellenic Petroleum SA, decane was from Sigma-Aldrich and n-dodecane was from Alfa Aesar. They were used as adsorbates.

**The sulfuric acid hydrolysis modification process:** The wheat straw sulfuric acid hydrolysis pretreatment was performed in a 20 L CHEMGLASS glass reactor. The acid hydrolysis isothermal time was 4 h (not including the preheating time); the reaction was catalyzed by sulfuric acid 0.45 M at a liquid-to-solid ratio of 20:1; the liquid phase volume (water) was 10 L and the solid material dose (wheat straw) was 500 g. The reaction ending temperature was 100 °C reached after the 1 h and 50 min preheating period. The solid residue yield was 55.34% w/w on dry basis.

**Kinetic studies:** The adsorbent sample to be tested was 4 g. In the case of oil spills, a 2 L jar was filled with 1 L freshwater, seawater or substitute seawater, stream water and lake water with 50 mL of test liquid (diesel, crude oil, decane, n-dodecane). The container was then placed on a shaker table, at a frequency of 150 rpm for 2, 5, 15, 30, 60, 120, 240 and 1440 min and allowed to settle for a period of 2 min for keeping the lignocellulosic material in suspension. The various adsorption tests were conducted at pH 7.7 as regards freshwater and 7.9 as regards seawater.

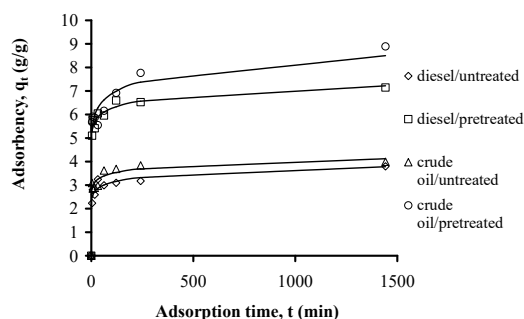
**Analytical Techniques:** The water and oil adsorbency test, defined as the ratio of water or oil adsorbed to dry adsorbent weight, according to the ASTM F726-06 method (27), was performed, following the procedure of this standard method.

## **RESULTS AND DISCUSSION**

The modeling of the adsorption process of diesel, crude oil, decane and n-dodecane on untreated and modified biomass fraction was studied. In the following Table 1, the four kinetic models examined herein are presented. Kinetic results of the adsorption rate batch experiments, in the cases: (a) of diesel and (b) crude oil adsorption on UWS (Untreated Wheat Straw) and MWS (Modified Wheat Straw) when the oil spill is formed on seawater (i.e., Piraeus Port) are given in Fig. 1.

**Table 1.** Kinetic models.

Model	Equation	Parameters	Ref.
Lagergren	$q - q_t = q \cdot e^{-k \cdot t}$	$q$ , $q_t$ are the amounts of oil adsorbed quantity (in g) per g of straw after equilibrium time and adsorption time $t$ , respectively; $k$ is the pseudo-first order rate constant (in $\text{min}^{-1}$ )	(28)
Second order	$q_t = q - [q^{-1} + k_2 t]^{-1}$	$k_2$ is the pseudo-first order rate constant	(29)
Intra-particle diffusion model	$q_t = c + k_p \cdot \sqrt{t}$	$q_t$ is the amount of MB adsorbed at time $t$ , $c$ is a constant ( $\text{mg g}^{-1}$ ), $k_p$ is the intra-particle diffusion rate constant in ( $\text{mg g}^{-1} \text{min}^{-0.5}$ )	(30)
Elovich	$\frac{dq_t}{dt} = a \exp(-\beta q_t)$	$q_t$ is the amount of oil adsorbed quantity after adsorption time $t$ , $a$ is the initial oil sorption rate ( $\text{g g}^{-1} \text{min}^{-1}$ ) and $\beta$ is the desorption constant ( $\text{g/g}$ )	(31)
Fractional	$q_t = a t^b$	$q_t$ is the amount of the adsorbate sorbed by the adsorbent at a time $t$ , while $a$ and $b$ are constants with $b < 1$	(32)

**Fig. 1:** Oil adsorbency for untreated and pretreated wheat straw vs. adsorption time; oil spill on seawater; the fractional kinetic model was applied.**Table 2.** Fractional kinetic model parameter values for oil spill adsorption on seawater by untreated and pretreated wheat straw.

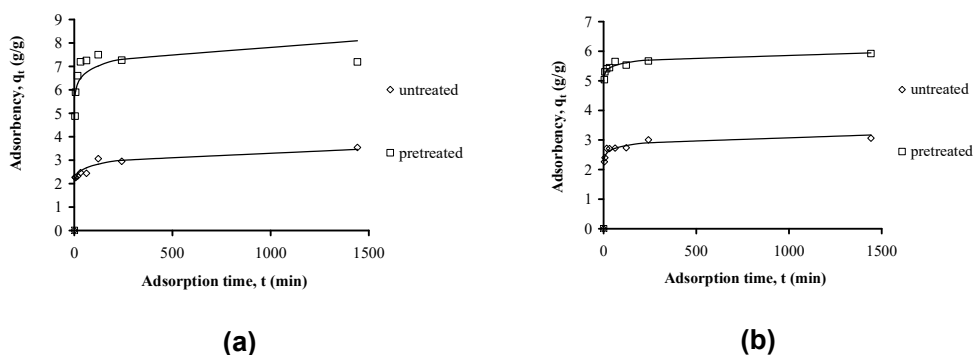
Case	Diesel/UWS	Diesel/MWS	Crude oil/UWS	Crude oil/MWS
b	0.0730	0.0535	0.0626	0.0795
a	2.223	4.894	2.615	4.765
SEE	0.0799	0.0409	0.0713	0.0747

In Fig.1, oil adsorption on wheat straw vs. adsorption time in the case of the fractional power function kinetic model is shown, while in Table 2 sum,  $n'$ ,  $p'$ , SEE and  $\ln a$ ,  $b$ ,  $a$  values are performed. With regard to the second order kinetic model the diesel and crude oil amount adsorbed after equilibrium was also found to be higher for the MWS comparing to the UWS (Table 3).

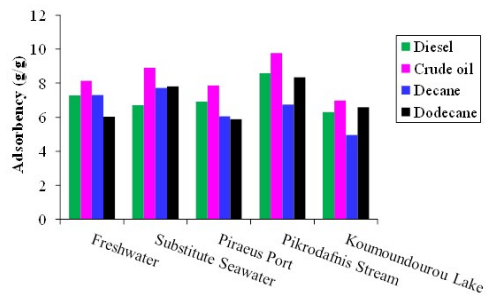
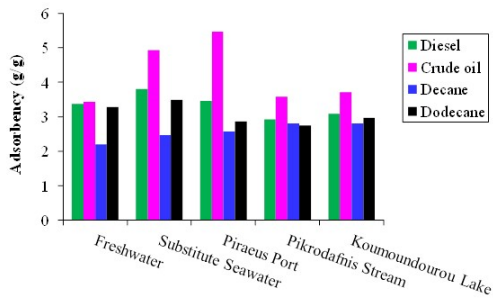
**Table 3.** Diesel and crude oil amount adsorbed on MWS and UWS for five types of water estimated according to the second-order kinetic model.

$q$ (g g <sup>-1</sup> )	Diesel/UWS	Diesel/MWS	Crude oil/ UWS	Crude oil/ MWS
Fresh Water	2.970	7.257	3.532	8.027
Sea Water	3.301	6.488	3.624	7.177
Substitute Water	3.225	6.554	4.151	7.533
Stream Water	3.402	6.908	3.923	8.918
Lake Water	3.314	5.407	3.905	5.720

In general the Elovich rate constant  $\beta$  was significantly higher for MWS comparing to the UWS. The Elovich model gave SEE values relatively lower than the other kinetic models while the fractional power or power function kinetic model gave SEE values significantly lower than the Elovich model. Kinetic results of decane and n-dodecane adsorption: With regard to the Lagergren kinetic model, the decane and dodecane oil amount adsorbed after equilibrium time were significantly higher for the MWS (7.18 and 5.51 g g<sup>-1</sup>, respectively) comparing to the UWS (2.78 and 2.81 g g<sup>-1</sup>, respectively). In the case of the second kinetic model, the decane and n-dodecane oil amount adsorbed after equilibrium time were also higher for the MWS (7.44 and 5.67 g g<sup>-1</sup>, respectively) comparing to the UWS (2.94 and 2.90 g g<sup>-1</sup>, respectively). In Fig.2, decane and n-dodecane adsorption on UWS/ MWS vs. time are presented with regard to the fractional kinetic model. The fractional power or power function kinetic model gave the lowest SEE values kinetic model in both cases.



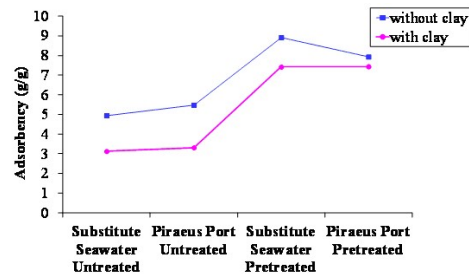
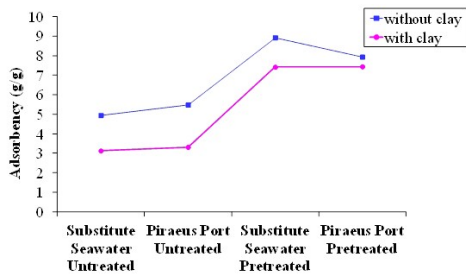
**Fig. 2:** Oil adsorbency for untreated and pretreated wheat straw vs. adsorption time: for (a) decane and (b) n-dodecane; hydrocarbon spill on freshwater; the fractional kinetic model was applied.



(a)

(b)

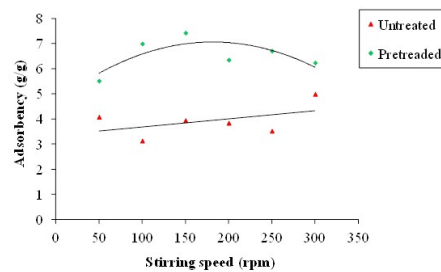
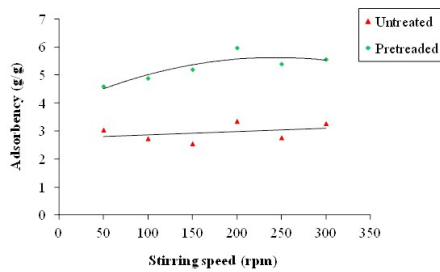
**Fig. 3:** Adsorbencies of diesel, crude oil, decane and dodecane (a) on untreated and (b) on modified wheat straw; hydrocarbon spill on freshwater, substitute seawater, seawater, stream water and lake water.



(a)

(b)

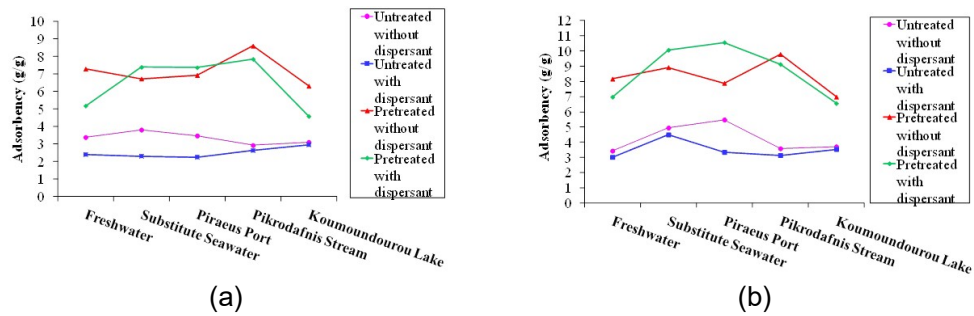
**Fig. 4:** Adsorbencies on untreated and modified wheat straw of (a) diesel and (b) crude oil spills with or without clay on substitute seawater and seawater.



(a)

(b)

**Fig.5:** Adsorbencies on untreated and pretreated wheat straw (a) diesel and (b) crude oil spills on seawater under the effect of stirring.



**Fig. 6:** Adsorbencies on untreated and modified wheat straw of (a) diesel and (b) crude oil spills with or without dispersant on freshwater, substitute seawater, seawater, stream water and lake water.

The adsorbency of diesel, crude oil, decane and n-dodecane spills formed on various types of water can be observed in the Fig.3. The adsorbent was UWS and MWS. The crude oil adsorption on original and modified wheat straw was significantly the highest of all other adsorbates on all types of water (see Fig.3).

In Fig.4, the effect of clay (simulating suspended solids in shoreline waters) in the case of diesel (see Fig.4a) and crude oil (see Fig.4b) adsorption on UWS and MWS, when the oil spill is formed on seawater (Piraeus port) and substitute seawater is shown.

The effect of continuous stirring (simulating sea waves) is presented in Fig.5, in the case of diesel (Fig. 5a) and crude oil (Fig. 5b) adsorption on UWS and MWS, when the oil spill is formed on seawater (i.e., Piraeus port) and substitute seawater.

In Fig.6, the effect of chemical dispersant is shown in the cases of diesel oil and crude oil adsorption on UWS and MWS. The oil spills were formed on freshwater, sea water (Piraeus port), lake water (Koumoundourou Lake), stream water (Pikrodafnis stream) and substitute seawater.

## CONCLUSIONS

The fractional power kinetic model presented the best fitting on the experimental data of the adsorption process for diesel, crude oil, decane and n-dodecane spills on untreated and modified lignocellulosic biomass. Crude oil adsorption on original and modified wheat straw showed significantly the highest adsorbency on all types of water. The oils' adsorbencies were higher on modified wheat straw comparing to the untreated one in all oil kinds and water types. The presence of clay (simulating suspended solids in shoreline water) had negative impact in all cases of oil adsorbency on wheat straw and especially in the case of crude oil spill on seawater and substitute seawater. The effect of stirring (simulating sea waves) was positive as regards oil spill adsorbency, especially in the case of diesel and crude oil on modified wheat straw. The effect of chemical dispersant had negative impact on diesel and crude oil spills adsorbency regarding all types of water.



## ACKNOWLEDGMENT

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