



Research article

Chemically treated *Posidonia oceanica* fibers as a potential sorbent for oil spill clean up

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ABSTRACT

Posidonia oceanica (PO) fibers were used as biodegradable solid waste material in the removal of oil spills from seawater. In the present study, PO fibers were chemically treated using H_3PO_4 , KOH, $ZnCl_2$ and H_2O_2 . The Fourier Transform Infrared spectroscopy and scanning electron microscopy were used to compare and to determine the structure of the raw and the chemically-treated PO fibers. The main parameters studied in the two systems, a mixture system of oil and water and a system with only oil or only water, were the chemical solutions concentrations, initial oil concentration and time contact. The results revealed that PO fibers treated with phosphoric acid (H_3PO_4) showed an enhancement of oil sorption of 12% in oil/water layer, compared to raw PO fibers. An increase of hydrophobicity was also observed with treated fibers as revealed by the 50% decrease in water sorption capacity. The isotherm and kinetic models were determined to reveal the nature and the mechanism of the sorption. Langmuir isotherm appeared to be the best fitting model showing a one-layer oil sorption onto PO fibers. In addition, the results fitted well with the pseudo-second order kinetic model compared to pseudo-first order representing the chemical sorption of oil. The results indicated that the treated biosorbent could be used as biodegradable material to clean-up oil spills in aqueous solution.

1. Introduction

The exponential growth in global transportation and production of crude oil has increased the risk of hydrocarbon (HC) spills in fresh water and marine environment. The discharge of HCs is an international concern given their economic and environmental influence, causing adverse effects on human and aquatic life. This unquestionably pollution usually results from industries, pipelines, onshore oil wells or offshore oil platforms [1]. Several techniques were used to minimize the generated damage, namely, skimmers, oil booms, in situ burning, oil dispersants, and oil sorbents [2]. Sorption is the most recent technique used nowadays owing to its better economic and environmental benefits. There are three categories of sorbent materials especially inorganic, natural and synthetic sorbents [1]. Natural organic sorbents showed environmentally friendly characteristics, excellent properties of oil removal, bountiful abundance, costlessly and biodegradability [3,4].

Many researchers have assessed the oil sorption capacity of several organic natural sorbent materials, such as raw sunflower pith [5], rice straw [6], kapok fiber [7], palm empty fruit brunch and leaves [8], garlic and onion peels [9], banana peels [10], rice husk [11], nettle fibers [12], barley straw [3], pith bagasse [13], sawdust [14] and cotton fibers [15].

Posidonia oceanica (PO) balls are an abundant biodegradable material rejected by the sea on the beaches as a solid waste [16]. It was

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tested for sorbing oil from water and showed a great sorption oil capacity from seawater media. In addition to this outstanding ability, these fibers can also able to sorb water in large quantities [17]. To enhance the poor oleophilic/hydrophobic properties of *PO* fibers, various treatments have been applied to ameliorate the interaction between sorbent and sorbate. To this end, several mechanical, thermal and chemical modification methods were used. For instance, grinding was found to enhance the oil sorption capacity of fibers but without affecting their hydrophobicity [17]. Thermal methods, such as pyrolysis, are more expensive than chemical modification and have shown a potential efficiency removal of oil than that of natural sorbents.

Among the several chemical modifications used nowadays, we can cite the alkali treatment (mercerization) [1], acetylation [18] and acid treatment [19], which may enhance the removal of the hydrophilic hydroxyl groups, the swelling of the crystalline region and the surface impurities [20]. To the best of our knowledge, there are no researchers aimed on studying the effect of chemical treatments on the potential of *PO* fibers to remove crude oil from seawater. Therefore, the main objectives of this study were to assess the oil and water sorption capacities of the ecofriendly and available *PO* fibers, in order to clean-up oil spills. The effects of various treatment types and concentrations, initial oil concentration and time contact on performance of treated fibers in sorbing oil were evaluated. In addition, the kinetic (pseudo-first-order and pseudo-second-order) and isotherm (Langmuir and Freundlich) studies were calculated to fit the experimental data.

2. Materials and methods

2.1. Materials

The beach's ball of *PO* were collected from Tunisian beaches as solid waste. For the surface treatment, different solvents were used such as phosphoric acid, potassium hydroxide, zinc chloride and hydrogen peroxide. All chemicals were of analytical grade. The water used was seawater obtained from the same area as the *PO* balls (salinity = 42.89 g/l, pH = 7.45). Crude oil was obtained from a local oilfield and used as received (mole weight 221–225 g/mol and density 0.866 g/cm³).

2.2. Preparation of treated sorbent

PO fibers were washed, dried, crushed and sieved. Fibers with a particle size [0.5 mm–1 mm] were then-chemically treated after being over nightly soaked in potassium hydroxide (KOH), phosphoric acid (H₃PO₄), zinc chloride (ZnCl₂) and oxygenated water (H₂O₂) solutions with different concentrations. Every sample was then washed with deionized water and over-night dried in the oven at 105 °C. All the samples were kept in containers ready to be used. The *PO* fibers structure was investigated using FTIR and MEB.

2.3. Fourier-transform infrared spectroscopy (FTIR)

In order to determine the functional groups of treated-*PO* fibers, FTIR spectrum was analyzed in the range of 4000–400 cm⁻¹ by a Nicolet FTIR spectrometer. About 1 mg of each sample was mixed with 100 mg of dried KBr to be used for spectroscopic measurements. The correction of background noise was carried out using the data of pure KBr.

2.4. Scanning electron microscopy (SEM)

Surface morphology was analyzed with SEM instrument equipped with an energy dispersive X-ray microanalysis to determine the surface textural characteristics of the sample. The microscope was operated at an accelerating voltage of 15 Kv and magnification ×300.

2.5. Oil and water sorption capacity measurements

The experiments were carried out in single phase (only oil or only water) and two phases (oil/water mixture) systems. The experiments of the single system (only oil/only water) were performed by weighing the samples before and after the sorption, in order to determine the oil and water sorption capacity (g/g). The experiments were conducted by adding into a beaker containing 30 ml of crude oil or water, 0.1 g of treated *PO* fibers for 5 min. A pre-weighing mesh was used to filter the sorbent, which was then drained, wiped and weighed. Whereas in oil/water system, 0.05 g of *PO* fibers were spread over the mixture, which contain different concentrations of crude oil (2.5–40 g/l) and 50 ml of seawater. The sample was left in the mixture for few minutes after being removed, drained and weighed. The oil sorption capacity was calculated by determining the weight of sorbed oil (g). It is determined by subtracting, from the initial oil weight, the remained oil weight, after sorption. The remained oil weight is determined by the method used by Ben Jmaa and Kallel [17]. The quantity of sorbed water was determined using this formula (1).

$$M_{\text{sorbed water}} = M_t - M_i - M_{\text{sorbed oil}} \quad (1)$$

$$Q_e \text{ (g/g)} = M_{\text{sorbed water}} / M_i$$

Where Q_e = water sorption capacity (g/g); $M_{\text{sorbed water}}$ = quantity of water adsorbed by the bio-sorbent (g); M_t = total mass of oil and water adsorbed by the biosorbent (g); M_i = initial mass of biosorbent (g); $M_{\text{sorbed oil}}$ = mass of oil adsorbed by the biosorbent (g).

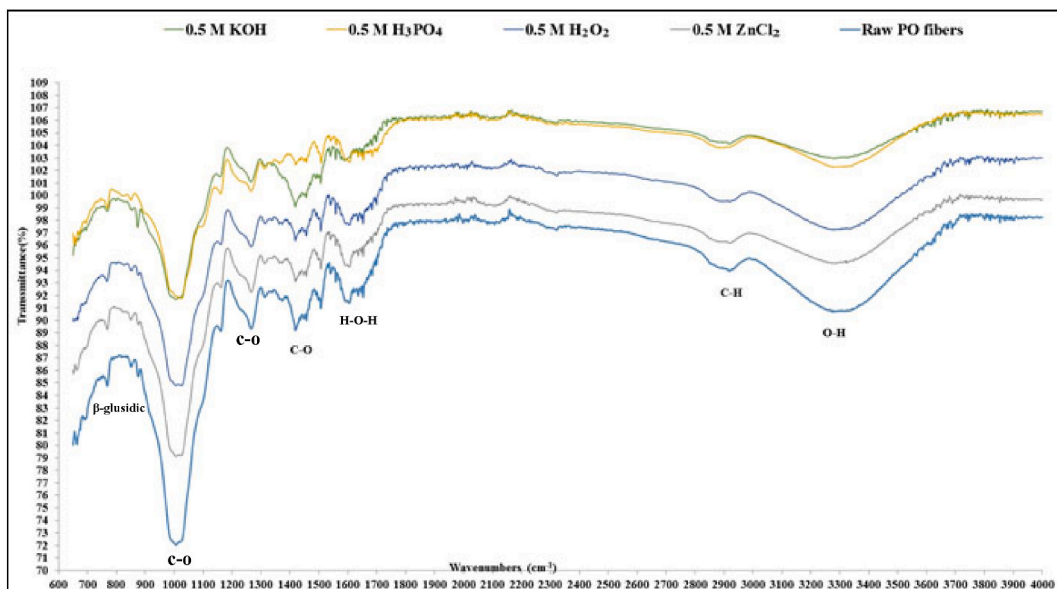


Fig. 1. FTIR spectra of raw and treated PO fibers.

2.6. Kinetics study

To know the dynamics of the sorption process, the kinetics data was processed in order to investigate the nature of sorption. Many researchers used different kinetics models to predict the sorption mechanism. The two well-known models of the kinetic study, pseudo-first order and pseudo-second order, were determined to assume the chemical or the physical sorption process [21]. The two models are expressed in the linear form in the following equations (2) and (3), respectively:

$$\text{Log}(a) = \text{log}(b) - c t \quad (2)$$

$$t / e = (1/f) + [t *(1/ h)] \quad (3)$$

Where $a = q_e - q_t$, $b = q_e$, $c = K_1/2.303$, $e = 1/qt$, $f = 1/(K_2 * qe^2)$, $h = 1/qe$.

q_t and q_e : the oil sorption capacity (g/g) at time t and at equilibrium, respectively.

K_1 (1/min) and K_2 (g/g.min-1): the first order and second order equilibrium rate constant.

2.7. Isotherm study

To determine if the sorption of oil was a monolayer or multilayer sorption on the surface of the fibers, two most widely isotherm models are performed namely Langmuir and Freundlich. Langmuir isotherm supposes that the liquid molecules are placed on only one monolayer of the fibers surface with homogeneous surface energies. The Freundlich isotherm model, however, reveals that sorption on the fibers surface occurs in the form of a multilayer sorption with heterogeneous surface energies [21]. The linear form can therefore be displayed by the succeeding equations (4) and (5).

$$V = 1/W + [(1/Z)*C_e] \quad (4)$$

$$\text{Log } G = \text{log } I + [(1/L) * (\text{log } C_e)] \quad (5)$$

$$V = C_e / q_e, W = q_0 * b, Z = q_0, G = q_e, I = K_f, L = n$$

Where q_e (mg/g) is the oil sorption capacity at equilibrium time of, C_e (mg/l) is the equilibrium oil concentration, q_0 is the theoretical maximum sorption capacity, and b is the constant related to the sorption rate, K_f (mg/g) (L/mg) is the capacity of sorption in multilayer sorption and n is the dimensionless Freundlich constant, which indicates the sorption extent and the nonlinearity degree between the solution concentration and the sorption. Whenever $\frac{1}{n}$ is between 0 and 1, the sorption process is favorable.

To determine whether the sorption is favorable or not, we could calculate the dimensionless constant separation factor R_L . The sorption forenamed favorable if R_L is between 0 and 1, unfavorable if R_L is superior to 1, linear if R_L is equal to 1, or irreversible if R_L is equal to 0. This parameter is performed using the following calculation (6):

$$R_L = 1 / S \quad (6)$$

Where $S = 1 + (b * C_0)$ and C_0 is the initial oil concentration.

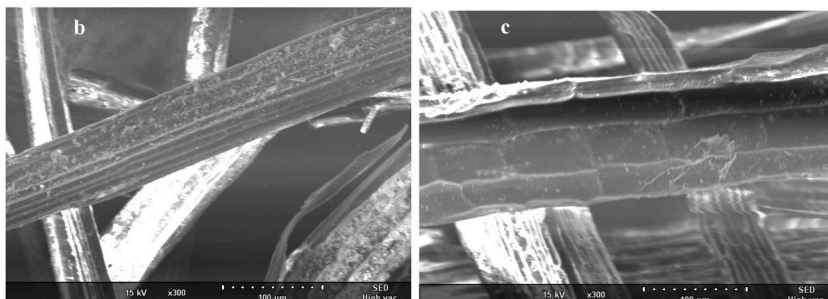
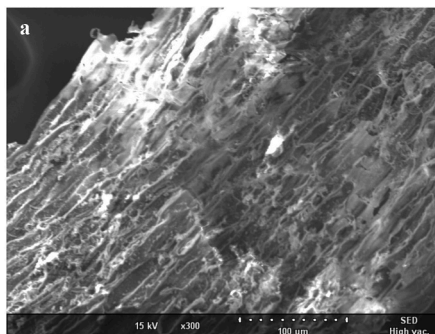


Fig. 2. SEM of (a) Raw *PO* fibers, (b) KOH treated *PO* fibers and (c) H₃PO₄ treated *PO* fibers.



Fig. 3. Real photos of (a) Raw *PO* fibers, (b) KOH treated *PO* fibers and (c) H₃PO₄ treated *PO* fibers.

2.8. Statistical analysis

The results were expressed as means \pm SD (Standard Deviation) and statistically analyzed using SPSS ver.17.0, professional edition. A one-way analysis of variance (ANOVA) was then performed to estimate the significance among means at the 5% probability level.

3. Results

3.1. Structural characterization of treated fibers

3.1.1. FTIR spectra

Fourier Transform Infrared spectroscopy spectra of raw and treated *PO* fibers are shown in Fig. 1. The FTIR spectra of raw *PO* fibers showed a number of functional groups (adsorption peaks) in the surface of the biosorbent. The peak observed at 3300-3400 cm^{-1} indicated the vibration stretching of hydroxyl groups (O-H) presented in hemicellulose, lignin and cellulose. The C-H stretching vibration was shown at 2920 cm^{-1} and 2860 cm^{-1} peaks. The peaks observed at 1636 cm^{-1} and 1267 cm^{-1} revealed the absorbed water (H-O-H) and (C-O) stretching vibration in ester. The peak observed at 1006 cm^{-1} , which is considered as the most important one correspond to C-O stretching being associated with the presence of cellulose, hemicellulose and lignin. Small peaks were seen at 888 cm^{-1} revealed the linkage between sugar units in cellulose and hemicellulose by a beta glucosidic band. The characteristic peaks of the treated fibers present higher intensities than that of raw fibers and this by changing the type of solvent. The highest intensities were observed for the acid and alkali treated-fibers, particularly in the O-H bands, compared to the raw fiber results. In addition, the width of the peak at 3300-3400 cm^{-1} corresponding to O-H stretching vibration is increasingly important when the fibers were treated.

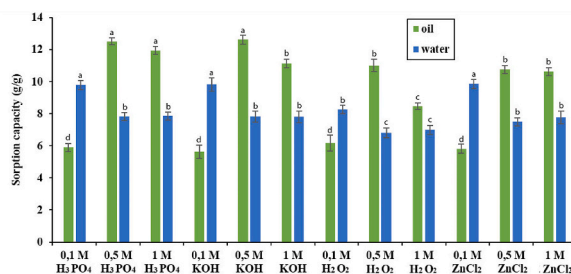


Fig. 4. Effect of the treatment type and concentration on sorption capacity in a single-phase system. ^{a,b,c,d} Different letters for the same adsorbed liquid (oil or water) for different treatments indicated significant differences ($p < 0.05$).

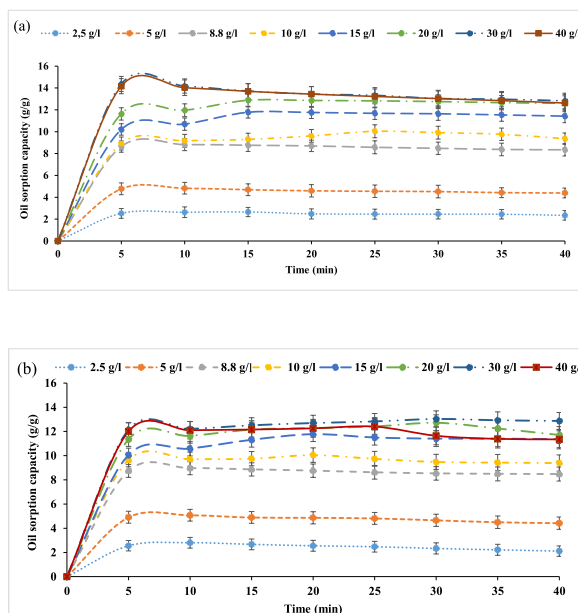


Fig. 5. Effect of reaction time and initial oil concentration on oil sorption capacity in oil/water mixture for treated *PO* fibers with 0.5 M H₃PO₄ (a) and 0.5 M KOH (b).

3.1.2. SEM morphology

The SEM technique was carried out onto the *PO* fibers to show the activation process effect on biomass structure. Fig. 2a shows that the studied fibers had a fibrous structure [22]. Fig. 2b and c illustrated the treated *PO* fibers with phosphoric acid and potassium hydroxide, respectively. A slight modification on the structure of treated the material, compared to untreated one. In fact, the fibers showed cavities that are wider and more spread out when treated with phosphoric acid and a fibrillation structure with parallel lines between them when treated with alkaline treatment. In addition, the treated fibers appeared to be more clean, clear and smooth, as shown in Fig. 3(a–c).

3.2. Oil and water sorption capacity of the treated *PO* fibers

3.2.1. Treatment concentration effect on sorption capacity in single system (only oil/only water)

Fig. 4 shows the sorption capacity of *PO* fibers treated with potassium hydroxide, phosphoric acid, oxygenated water and zinc chloride solutions for the different concentrations of 0.1 M, 0.5 M, and 1 M for 5 min. The used sorbent weight was 0.1 g. For the treated fibers, the oil sorption capacity increased with the increase of the treatment concentration of KOH, H₃PO₄, H₂O₂ and ZnCl₂ until it reached an equilibrium treatment at a concentration of 0.5 M. After equilibrium, it declined with the further rise of the chemical concentration (1 M). In addition, it was noticed that for 0.5 M and 1 M treatment concentrations, the sorption of oil was more important than that of the water compared to 0.1 M concentration. Noteworthy, when chemical was applied at 0.1 M, fibers showed the highest sorption capacity of water. The oil and water sorption capacities of modified *PO* fibers at equilibrium treatment concentration (0.5 M) were, respectively, of 12.61 g/g, 7.82 g/g for KOH, 12.51 g/g, 7.83 g/g for H₃PO₄, 11.01 g/g, 6.80 g/g for H₂O₂ and 10.75 g/g, 7.50 g/g for ZnCl₂.

It is noted that with a treatment concentration of 0.1 M, the sorption of oil slightly increased while that of water decreased by 30%

Table 1

Values of sorption constants, equilibrium sorption capacities (Qe) and correlation coefficients for different initial concentrations of treated fibers (0.5 M H₃PO₄) for both kinetic and isotherm models.

0.5 M H ₃ PO ₄ treated fibers	Initial oil concentration (g/l)							
	2,5	5	8,5	10	15	20	30	40
Qe_{exp} (mg/g)	2658	4828	8820	10039	11780	12876	14370	14166
Pseudo-First-Order								
qecal (mg/g)	50,11	54,37	69,34	1061	1396	1047	201	128,98
K ₁ (min ⁻¹)	0,044	0,057	0,046	0,034	0,046	0,046	0,057	0,068
R ²	0,519	0,920	0,558	0,350	0,67	0,58	0,75	0,82
Pseudo-Second-Order								
qecal (mg/g)	2336	4347	8333	9803	11655	12771	12594	12437
K ₂ (gmg ⁻¹ min ⁻¹)	0,0037	0,00023	0,00018	0,00033	0,000185	0,00024	7,51E-05	6,92E-05
R ²	0,9977	0,9993	0,9995	0,9962	0,9992	0,9995	0,9995	0,9991
Langmuir								
Q _{max} (mg/g)	2376	4464	8424	8928	8453	8928	5649	6944
R _L	0,996	0,991	0,998	0,982	0,402	0,155	0,018	0,013
R ²	0,9988	0,9987	0,9996	0,9993	0,9931	0,9318	0,954	0,8677
Freundlich								
K _f	2630	5495	8912	10715	10715	331131	11748975549	162181009
1/n	0,012	0,03	0,0095	0,020	0,278	0,364	1,4	0,922
R ²	0,2688	0,6324	0,655	0,746	0,858	0,505	0,865	0,596

Table 2

Values of sorption constants, equilibrium sorption capacities (Qe) and correlation coefficients for different initial concentrations of treated fibers (0.5 M KOH) for both kinetic and isotherm models.

0.5 M KOH treated fibers	Initial oil concentration (g/l)							
	2,5	5	8,5	10	15	20	30	40
Qe_{exp} (mg/g)	2803	5072	8964	10048	11776	12715	13035	12400
Pseudo-First Order								
qecal (mg/g)	125	103	116	277	1409	915	1224	167
K ₁ (min ⁻¹)	0,039	0,044	0,036	0,019	0,041	0,015	0,060	0,044
R ²	0,7	0,9	0,58	0,55	0,63	0,12	0,9	0,53
Pseudo-Second Order								
qecal (mg/g)	2061	4366	8403	9345	11614	12150	13140	11235
K ₂ (gmg ⁻¹ min ⁻¹)	0,00018	0,00015	0,00019	0,00017	0,00016	0,0042	0,00036	8,63E-05
R ²	0,9899	0,9969	0,9996	0,9987	0,9989	0,9954	0,9997	0,9966
Langmuir								
Q _{max} (mg/g)	2709	4424	8496	9407	8196	8474	6265	5434
R _L	0,973	0,984	0,999	0,997	0,358	0,143	0,023	0,0088
R ²	0,9596	0,9987	0,9999	0,9998	0,9951	0,9593	0,9577	0,6871
Freundlich								
K _f	2951	5623	9120	9772	144543	549540	229086765	1905460717
1/n	0,03	0,029	0,0098	0,0046	0,31	0,423	1004	1,17
R ²	0,086	0,709	0,42	0,15	0,92	0,68	0,84	0,39

for all the chemical treatments compared to that of the raw fibers. For the 0.5 M and 1 M treatment concentrations, the sorption capacity of oil was twice that of the raw fibers, whereas that of the water sorption was a half of the raw fibers.

3.2.2. Contact time and initial oil concentration effect in two phases system (oil/water mixture)

The optimized conditions in the single system (the two best chemical treatments giving better oil sorption capacities 0.5 M H₃PO₄ and 0.5 M KOH) allowed studying the contact time and the initial oil concentration effects on sorption capacity and the development of the kinetic and the isotherm studies. The relation between the fibers and the crude oil is noticed in the time required to eliminate the liquid from the water. Fig. 5 a,b illustrates the oil sorption capacities of PO fibers at different reaction times for both acid (0.5 M H₃PO₄) and alkali treatments (0.5 M KOH).

The oil sorption test findings in a mixture system of oil/water were performed using a dose of 1 g/l of treated sorbent (grinded fibers) while varying the time contact (0–40 min) and the initial oil concentration C₀ (2.5, 5, 8.8, 10, 15, 20, 30, and 40 g/l). Findings showed that the sorption process for acid treatment was rapid and reached saturation within the first 5 min, thereafter the sorption rate stayed perpetual with time because of the loaded PO fiber surfaces with crude oil particles as well as the occurrence of a balance between sorption and desorption process [23]. Indeed, for the acid treatment, the oil sorption capacity reached its maximum during the first 5 min with 14.37 g/g for the acid treatment. For alkali treatment, however, the sorption process was slower and took longer, about 30 min to reach maximum sorption (13.03 g/g) after that, the process became constant throughout the rest of the time.

For the effect of the initial oil concentrations, it is remarked that the oil sorption capacity increased with the initial oil concentration increase. The maximum oil sorption capacities for 0.5 M H₃PO₄ at initial oil concentrations of 2.5 g/l, 10 g/l and 30 g/l were estimated

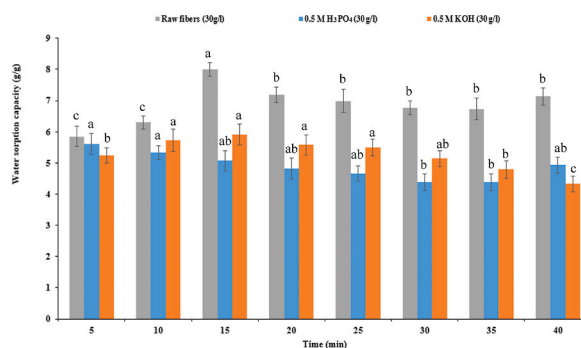


Fig. 6. Raw and treated *PO* fibers hydrophobicity at equilibrium oil concentration (30 g/l). ^{a,b,c} Different letters for the same fiber samples and different treatment times indicated significant differences ($p < 0.05$).

at about 2.65 g/g, 10.03 g/g and 14.37 g/g, respectively. For 0.5 M KOH treatment, the maximum oil sorption capacities recorded were of 2.80 g/g, 10.04 g/g and 13.03 g/g, when the oil was added at 2.5 g/l, 10 g/l and 30 g/l, respectively. It is remarked that at low concentrations, the crude oil sorption capacity was low, and considerably increased at higher oil concentrations. Maximum capacities for both treatments were reached at an oil concentration of around 30 g/l.

3.3. Adsorption mechanism of chemically modified *PO* fibers

3.3.1. Sorption kinetics

Table 1 shows the calculated constant parameters and the linear regression coefficient, R^2 of the kinetic models. Fitting calculations of the adsorption kinetics are illustrated in the Supplementary materials. It is observed that the pseudo-second order model reveals a close experimental q_e exp and theoretical q_e calc values and a higher R^2 superior to 0.996 compared to the pseudo-first order model.

3.3.2. 3.3.2. equilibrium isotherms

Tables 1 and 2 presented all the calculated values. The findings showed a higher correlation coefficient (R^2) fitted by the Langmuir isotherm model than that of the Freundlich isotherm model for both acid and alkali treated *PO* fibers. The calculated value of R_L for the treated *PO* fiber was between 0 and 1, revealing the accommodation sorption to the Langmuir model. Despite the Freundlich constant $\frac{1}{n}$ was between 0 and 1 displaying a best fitting, the calculated correlation coefficient R^2 was lower than that the one prevailing from the Langmuir model.

3.4. Assessment of the water sorption capacity of treated and raw *PO* fibers

Water sorption capacity is a key parameter to determine the tendency of fibers to swell in water. Fig. 6 shows the potential of untreated and treated biomaterial to sorb water at the optimum initial oil concentration of 30 g/l at different reaction times. It is noted that the treated biomaterial has a lower potential to sorb water compared to that of the un-treated one (8.31 g/g), against 5.91 g/g and 5.07 g/g for the treated- KOH and H₃PO₄ biomaterial.

4. Discussion

The *Posidonia oceanica* is a Mediterranean endemic alga which appears in large quantities in the form of balls (aegagropile) along many coastal beaches. It was used as a mean of water depollution as a natural biosorbent. These fibers were tested by Ben Jmaa and Kallel [17] and showed a great water sorption capacity as well as an oil biosorbent potential. So that, to reduce water sorption and to increase interfacial adhesion between the fiber surface and the oil, *PO* fibers were chemically treated with different types of solvents and were tested in the biosorption of hydrocarbons taking into account the variation of the different parameters. These fibers were subjected to FTIR and SEM characterization.

The FTIR spectra showed an increase of peaks' intensity after chemical treatment. This suggested the successful impregnation of solvent into *PO* fibers. In fact, the stretching vibration corresponding to (O–H) bond was increased which indicated that it has been turned into dissociative state or into monopolymer or even it reacted with the solvent involved. This allowed the reduction in the degree of the hydroxyl polymerization in biomass. There was a clear signal intensity increase of the –CH and C–O bands. Elenga et al. [24] observed same trends when they treated the fibers with an alkali treatment (NaOH). These results suggested that the treatment eliminated the main components of the fibers namely hemicellulose, cellulose lignin. The structure of fibers, during the alkaline hydrolysis treatment (KOH) lead to the fragmentation of the ester and glycosidic chains and the modification of lignin structure. However, during the acid treatment, it allowed further hydrolysis of hemicelluloses, especially xylan into sugar such as xylose, mannose, acetic acid, galactose and glucose [25]. These results were in good agreement with the improvement of the hydrophobicity affinity of the fibers after treatment (Fig. 6) which lead to the increase of the affinity of fibers to sorb more crude oil.

For the SEM characterization, *PO* fibers treated with phosphoric acid presented cavities, which were larger than those of raw fibers. This solution caused either the weakness of the connections between the carbohydrates or the destruction of the connections between the cell wall outer layer of lignin and carbohydrates, eliminating the primary cell wall of *PO*. This dissolution facilitated the penetration of oil and then the increase in the oil holding capacity of the biomass [19]. For the alkali treatment, it caused fibrillation of *PO* fibers by eliminating the impurities and cementing materials makes the surface fibers stonier in comparison to that of raw fibers [26]. There was also modification of *PO* fibers' color after the chemical treatment. In fact, the treatment with H_3PO_4 and KOH boosted the changes of fiber color and caused their yellowing compared to raw one (Fig. 3 a-c). This might be due to the dissolution of the cementing components of *PO* fibers (hemicellulose and lignin).

The potential of *PO* fibers as biosorbent was evaluated by determining the oil and water sorption capacities under varying conditions. These fibers treated with several solvents at different concentrations (0.1 M, 0.5 M, 1 M) showed a maximum oil sorption capacity at 0.5 M of solvent concentration, which suggested that an increase in the concentration can damage the internal structure of the fibers. Fibers treated with a 0.1 M solvent concentration adsorbed more water than oil because treatment concentration (0.1 M) failed to reduce the hydroxyl groups available in the fibers. The increase of oil sorption and the decrease of water sorption capacities were observed for both the alkali and acid treatments. In fact, the alkali treatment eliminated the impurities that cover the surface of *PO* fibers and enhanced their exposure which improved the roughness of the surface [27]. The alkali hydroxyl group (OH), within the molecules, decomposed and reacted chemically with the fibers' hydroxyl groups, eliminating the molecules of water. Therefore, it led to the reduction of the hydrophilic hydroxyl groups, which enhanced the hydrophobicity of the fibers. In addition, it improved the length/diameter aspect ratio by reducing the diameter of the fibers and therefore rising the area' specific surface for a better adhesion to crude oil [28]. Salem et al. [29], observed a similar reduction on water sorption for kenaf fiber after their treatment with stearic acid. The three OH groups of the phosphoric acid (H_3PO_4) reacted with the fibers' OH groups and reduced their sensitivity to moisture. In addition, acids allowed the hydrolysis of hemicelluloses with sparing a certain amount of cellulose. The treatment with phosphoric acid promoted better bonding at the fiber-liquid interconnection. This evade the molecules of water to enter to the treated *PO* fibers [29]. The decline in water sorption after treatment could be due to the enhancement in adhesion interface between fiber-liquid by reducing the hydroxyl moiety presenting in the cellulose surface, as proved by the Fourier Transform Infrared Spectroscopy (FTIR) results.

Further increase in solvent concentration (1 M) could cause the damage and deterioration of the fiber structure [30]. Similarly, Wang et al. [27] noted that the further increase of the treatment concentration of NaOH and HCl decreased the toluene absorbency of kapok fibers. Therefore, the chemical treatment should be performed at fixed levels to improve the oil sorption and hydrophobicity, along with preserving the fibers' structure.

The reaction time and the initial concentration of the hydrocarbons are studied in order to determine the optimal sorption conditions. Treated *PO* fibers (acid treatment) trapped the oil within 5 min (equilibrium). In fact, the vacancy of sorption sites enhanced the rapid sorption at the initial stage. When vacancy sites are saturated, the sorption slowed down and resulted in a slower increase. At equilibrium, the sorption sites were either completely filled by the crude oil [31]. This is in line with the findings reached by Banerjee et al. [32] reporting a high removing crude oil from water using oleic acid-grafted sawdust (6 g/g). These results indicated that crude oil would be quickly trapped which means that it would not be dispersed and escaped farther down the sea. This can be considered as a favor of the selected system [32]. On the other hand, the increase of oil sorption capacity with the increase of initial oil concentration was owing to the stronger driving force generated by the extreme concentration difference. The raised oil sorption at higher initial concentrations was related to the existence of more crude oil molecules to be adsorbed [32]. It was also indicated that for both alkaline and acid treatments, the sorption capacities were very close to those of low concentrations. From 20 g/l, these capacities increased for the acid treatment because of the existence of more free spaces between the molecules of the fiber (greater specific surface area). These two parameters make possible to determine kinetics and isotherms sorption. The obtained results clearly showed that the crude oil sorption onto the modified *PO* fiber did not fit the pseudo-first-order model but mainly the pseudo-second-order kinetics. Thus, we validate a chemical sorption (chemisorption) than a physical sorption (physisorption) process, which means that the interaction between crude oil and the fiber surface occurred with chemical bonds.

The chemical sorption process performed well with a largest using natural fibers such as the sorption of crude oil by modified oil palm leaves [23], the sorption of oil (diesel and soybean oil) in water by acetylated kapok fibers [21] and the removal of crude oil by acetylated oil palm empty fruit bunch fiber [8]. Concerning the nature of the sorption. The obtained results revealed that the sorbed oil onto the surface of the treated *PO* fibers realized on monolayer approach via uniform sites with homogenous energy-level dissemination [8]. Asadpour et al. [8] observed a similar trend for the treated oil palm empty fruit brunch. However, the findings achieved by Sidik et al. [23] and Wang et al. [27] showed that calculated parameters goes in line with the Freundlich model.

The hydrophobicity of treated *PO* fibers was highlighted by comparing them with the raw ones. It can be concluded that the chemical treatment improved the oil sorption capacity as well as its hydrophobicity, as it can be also by confirmed by FTIR and SEM data. In fact, the water sorption potential after acid treatment was almost half of that recorded by the untreated fibers. In fact, acids were highly vigorous and generally admitted chemicals that penetrate to glucosidic linkages in the existent carbohydrates (celluloses and hemicellulose) in biomaterials. They may also induce more hydrolysis of the xylan, the main component of the hemicelluloses, into sugars. However, during the process of alkaline hydrolysis, the structure of the biomass swelled results in the deterioration of the lignin structure and the disruption of the glycosidic chains of the ester [25]. Even if the alkaline treatment caused a small swelling of the fiber structure, water sorption was still minimal compared to that of the raw fibers.

To conclude, the acid treatment ameliorated the potential sorption of oil by only 12% in the oil/water system, which means that it was rather a poor improvement. On the other hand, it increased the fibers' hydrophobicity, reducing the water sorption capacity by almost 50% compared to that of raw fibers. The capability of the biomaterial to adsorb oil was set side by side with the findings of

Table 3

Comparison of oil sorption capacity of various sorbents.

Treated-sorbents	Oil sorption capacity (g/g)	Time (min)	Oil quantity	Type of oil	References
Lauric acid treated oil palm leaves	1.2	20	0.56 g	Crude oil	[23]
Acetylated rice husks	10.31	2	10 g	Crude oil	[33]
Oleic acid-grafted sawdust (OGSD)	6	5	0.2–1.45 g	Crude oil	[32]
Stearic acid-grafted sawdust (SGSD)	5.23				
Decanoic acid-grafted sawdust (DGDS)	4.23				
Acetylated kapok fibers	63.4	60	0.08 g	Diesel	[21]
Acetylated oil palm empty fruit bunch fiber	7	35	40 ml	Arabian	[8]
	6.8			Tapis	
Phosphoric acid treated <i>PO</i> fibers	14.37	5	1.5 g	Crude oil	This study
Potassium hydroxide treated <i>PO</i> fibers	13.03	30			

several treated agricultural biomasses as shown in Table 3. It was observed that treated *PO* fibers had the highest oil sorption compared to treated oil palm leaves [23], acetylated rice husks [33], oleic, stearic and decanoic acid-grafted sawdust [32] and acetylated palm empty fruit bunch fiber [8], but remained slightly lower than that of acetylated kapok fibers [21]. This implied that chemically treated fibers were a potential and an efficient bio sorbent for the elimination of spilled oil. Compared to other biosorbents used by several researchers, treated *PO* fibers could be considered as good natural sorbent for oil spill clean-up. In fact, they gave a fourteen times higher sorption capacity than lauric acid treated oil palm leaves [23] and three times higher than stearic and decanoic acid-grafted sawdust [27]. The obtained *PO* fiber's capacity was also twice higher than that of oleic acid-grafted sawdust [32] and even of that of acetylated palm empty fruit bunch fiber [8]. Overall results proved that the chemical treatment had a serious effect on the amelioration of the oil sorption capacity of *PO* fibers and the enhancement of their hydrophobicity compared to other treated organic natural sorbents.

5. Conclusion

In conclusion, the *Posidonia oceanica* fibers displayed a considerable capacity to be a crude oil sorbent in contaminated-oil seawater. The main benefits of using these fibers, as a natural sorbent is their low cost and abundance in all coastal zones. The magnificent impregnation of chemicals into *PO* fibers was supported by the studied analysis. In fact, the optimum oil sorption capacity 14.37 g/g was obtained for treated fibers with 0.5 M H_3PO_4 within 5 min at 30 g/l of initial oil concentration. The crude oil sorption onto treated *PO* fibers exhibited a chemisorption and monolayer sorption process, as obtained by calculated kinetics and isotherm parameters. Pretreatment of the raw *PO* fibers by chemicals effectively enhanced its surface hydrophobicity and increased its potential to sorb oil, where the best oil spill clean-up results were achieved with phosphoric acid treatment, revealing a water sorption capacity reduction by 50%, compared to the raw fibers. Further studies on the effect of the thermal treatment on *PO* fibers sorption performance need to be investigated.

Data availability statement

All analysis and experimental data used in this study are included within the present article.

CRedit authorship contribution statement

Senda Ben Jmaa: Writing – original draft, Visualization. Amjad Kallel: Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2024.e28427>.

Abbreviations

PO: *Posidonia Oceanica*

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