

Journal of Petroleum & Environmental Biotechnology

Open Access

β -Cyclodextrin Polyure thanes Copolymerized with Beetroot Fibers (Bio-Polymer) to Clean-Up Water Polluted by Organics and Spilled-Oil

Jamil Rima^{1*} and Karine Assaker²

¹Faculty of Sciences, Section II, Physical Chemistry and Environmental Engineering Laboratory, Lebanese University, Fanar, Lebanon ²Platform for Research and Analysis in Environmental Sciences (PRASE), Doctoral School, Lebanese University – Hadath Campus, Lebanon

Abstract

Spilled polycyclic aromatic hydrocarbons (PAH), oils and dyes on water surface involve a big environmental risk. The clean-up of such pollutants consist a challenge from economic and environmental points of view. The absorbent of oils or PAH must have buoyancy, high uptake ratio oil/water, reusable and biodegradable. In this study, β-Cyclodextrin polymerized with beetroot fibers (Bio-polymer), was prepared and applied to remove oil, polycyclic aromatic hydrocarbons (PAH) and dyes from water. The Bio-polymer was prepared by copolymerization of beetroot with β-cyclodextrin polyurethane at 70°C. The prepared new material was characterized by means of granulometry, Scanning Electronic Microscopy and FTIR. The investigation into the use of cross-linked cyclodextrin polyurethanes with beetroot fibers as adsorbents for organic pollutants showed significant results. The effectiveness to eliminate dyes such as methylene blue and Rhoda mine B with concentrations around 100 ppm and 150 ppm respectively. was more than 99%, while the pyrene, which was chosen as an example among PAHs, showed a potential of elimination exceeding the 96 % for solutions of 30 ppm. Furthermore, spilled motor oils were tested and showed an efficacy exceeding the 90g oil per one g of biopolymers. The results indicated that the biopolymer developed in this study is a promising material for the removal of mixed pollutants from industrial wastewater and good sorbent for spilled oil clean-up applications. After the biopolymer's application, yeast has been used for its biodegradation. The biodegradation, led to complete mineralization of organic contaminants and transform them into carbon dioxide, water, and inorganic compounds. The biopolymer weight polluted was reduced by biodegradation process to 15% of its initial mass

Keywords: β -cyclodextrin-polyurethane-beetroot fibers; Spilled oil clean-up; Removal of PAH and dyes; Biodegradation of non-recyclable bio-polymers

Introduction

When oil is explored, transported and stored, there is a risk of spillage which causes significant environmental impact [1]. Due to its destructive properties, oil can damage the entire contaminated area. When oil encounters something to stick to (e.g., beach, rocks, feathers of a duck or a bathers hair), it is difficult to be removed [2]. Oil settles on beaches and kills organisms that lie there, such as crabs. Oil endangers fish hatcheries in coastal areas as well as contaminates the flesh of commercially valuable [1,3]. Therefore, pollution by petroleum oils affects sea life, economy, tourism and leisure activities due to the coating properties of these materials.

Effective decontamination and oil clean-up are necessary after a spill for the protection of the environment and human health. Sorption techniques are one of the most effective approaches for the removal of oil spills. Many types of sorbents are used; one of them is natural sorbents which include a wide variety of organic vegetable products, such as rice straw, peat moss, wood, and cotton [4,5]. Natural organic sorbents or fibers are known for their good affinity for oil. Usually, natural fibers are cheap, abundant, eco-friendly and have low density so that they can float on water. Kapok, cotton fibers, silk floss, rice husk and straw, feathers, bagasse and many others were tested as natural sorbents [1,2,6–10]. Most of these materials have high sorption capacity but no more than 30 g/g. They are also limited by their affinity to water. Once plant-derived sorbents are applied to saturated environments, preferential water sorption is favored over the sorption of oil because the sorbents are typically hydrophilic in nature. The main drawbacks of these plant-derived sorbents are their relatively low oil sorption capacity, low hydrophobicity and poor buoyancy compared to synthetic sorbents, such as polypropylene [10,11].

Synthetic sorbents have oleophilic and hydrophobic characteristics in addition to their low density. Moreover, they are readily available in large scale fabrication. Among the various synthetic sorbents that have been employed for oil spill remediation, synthetic polymers, such as polypropylene and polyurethanes were experimented [12]. Synthetic Cyclodextrin polymers have demonstrated the capacity to remove organic species in water at concentration levels as low as ng [13]. Cyclodextrins are capable of polymerization via chemical bonding formation between their surficial hydroxyl groups. These polymers have shown in several studies their capacity to trap organic pollutants in water, especially polycyclic molecules. A study conducted by Allabashi et al. [14] showed that modified cyclodextrin polymers with silvlated functions present a retention capacity of PAH up to 90%. In another study, Ding et al. optimized the synthesis of a crosslinked cyclodextrin polymer for its use as oil sorbent. They showed the potential efficiency of cyclodextrin polymer on adsorbing different kind of oils by comparing its performance to other synthetic polymers [15]. Furthermore, it has been found that cyclodextrin polymers can be recycled several times while still maintaining high adsorption efficiency [13,16]. The modification of commercial organic sorbents, such as cyclodextrin polyurethanes showed good oil/water selectivity and a high sorption capacity up to 150 g/g [17,18].

Corresponding author: Jamil Rima, Faculty of Sciences, Section II, Lebanese University, Fanar, Lebanon, Tel: +961 3 321833; E-mail: jamil.rima1@gmail.com

Received May 20, 2018; Accepted June 02, 2018; Published June 08, 2018

Citation: Rima J, Assaker K (2018) β -Cyclodextrin Polyurethanes Copolymerized with Beetroot Fibers (Bio-Polymer) to Clean-Up Water Polluted by Organics and Spilled-Oil. J Pet Environ Biotechnol 9: 368. doi: 10.4172/2157-7463.1000368

Copyright: © 2018 Rima J, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

Also, some natural fibers, having highly oleophilic surfaces such as kapok, have been modified to render them more hydrophobic and oleophilic [19]. A super hydrophobic kapok fibre was made by sol-gel method [20]. Kapok was prepared in presence of silica precursor and surfactant. This modification improved the oil sorption capacity and the buoyancy after oil absorption. Lee et al. [21] used the combination of kapok with polypropylene nonwoven fabrics (pp/kapok) to clean-up oil spill on water. This combination allowed kapok fibers to be used as pads with higher hydrophobicity. Authors showed the ability of pp/kapok to absorb maximum quantity of highly viscous oil in short time (5 minutes). In addition, the new fabricated pads of pp/kapok are biodegradable.

Synthetic sorbents have the disadvantage of the nonbiodegradability, which is their major disadvantage. Usually landfill and incineration are used to dispose of non-recyclable synthetic sorbents. Whereas, both disposals are environmentally undesirable [4,5]. On the other hand, natural sorbents suffer from their hydrophilicity. From this point, the combination of natural and synthetic materials for oil sorption is likely to both eliminate organic pollutants from water and be able to biodegrade the used materials after several cycles of use.

A huge number of bacterial and fungal generations possess the capability to degrade organic pollutants. Biodegradation is defined as the biologically catalyzed reduction in complexity of chemical compounds. Generally, petroleum compounds or organic compounds are biodegraded into various small molecules by microorganisms [22]. At present, many researches have showed that the degradation way of all sorts of petroleum components (e.g., alkane, polycyclic aromatic hydrocarbons, etc.) is an oxidizing process [23–25].

In this work, we developed a new synthetic/natural material for organic pollutants removal from water, with combined characteristics of both synthetic and natural sorbents. The synthesized biopolymer is insoluble in water and thus it can be used to decontaminate polluted water. It is capable of removing non-polar organic compounds like PAH by their insertion into the cavities of the cyclodextrin and still able to retain the polar compounds such as dyes by the chemical functions existing on the surface of the fibers. This double function gives an advantage to this bio-polymer over other sorbents.

Another interest property is due to the biodegradability of the materials when they become expired. The biodegradability of natural fibers and the high oil/water uptake of synthetic sorbents provide high efficient oil sorbent. We used beetroot fibers combined with β -cyclodextrin synthetic polyurethane in order to profit of this efficiency. The biodegradability of the natural/synthetic sorbent has been carried out by using the beer yeast as the microscopic unicellular fungus *Saccharomyces cerevisiae*.

Materials and Methods

Materials

Sugar beets were collected from industries in Lebanon Bekaa, air dried and crushed to powder in a mill. The meal obtained was sieved through a sieve of 250 μ m. The powder of fiber was soaked in distilled water for 24 hours at room temperature, and air-dried and stored for use. All reagents used for the preparation of solutions were of analytical grade. Methylene blue (MB), Rhodamine B (RB), Pyrene, HCl (aq), were purchased from Prolabo and used without further purification. Toluene diisocyanate (TDI), pyridine and β -cyclodextrin were purchased from Sigma. Petroleum oil is a commercial product.

Page 2 of 7

Preparation of the β -Cyclodextrin (β -CD) polyurethanes and β -CD polymerized with beetroot fibers (Bio-polyurethane)

To prepare β -CD polyurethane, 100 g of β -CD were dissolved by stirring in 300 ml of pyridine at a temperature of 70°C. Then 100 ml of TDI (toluene diisocyanate) were added gradually in the solution. To copolymerize β -CD with beetroot fibers, the initial weight of β -CD of 60 g were dissolved to 300 ml of pyridine at 70°C until dissolution, and then 28 g of beetroot fiber (250 μ m) were added and stirred until homogenization of the mixture. The following steps are the same for both preparations. The reaction time was 30 min. An off white solid starts to appear called β-cyclodextrin polymer-fibers or polyurethane reinforced by beetroot fiber (Bio-polymer). The off white solid obtained was washed with water to remove pyridine remaining in the material and an additional washing with ethanol was done to improve removal of pyridine. For more security we have washed the bio-polymer with water and ethanol five times to remove completely the traces of pyridine. Schematic reaction of the polymerization of β-cyclodextrin, toluene diisocyanate (TDI), and beetroot fibers in pyridine as solvent at 70°C is shown in Figure 1.

The reaction between β -Cyclodextrin, Polyurethanes and Beetroot fibers is interpreted by the polymerization reaction between them. The general reaction of polymerization can be completed by the following reaction [26].

$$HO - R - OH + OCN - R' - NCO \rightarrow \begin{bmatrix} 0 \\ -C - O - R - O - \parallel -N - R' - N \\ -N - \parallel -N - \parallel$$

The β -CD, was polymerized using toluene diisocyanate (TDI) as co-polymer, and pyridine as solvent. The polyurethane is insoluble due to the formation of urethane or carbamate function (-NHCOO-). CD is a molecule based on sugar (D (+) - glucopyranose), this means that this molecule has free primary hydroxyl groups localized on the outer surface of the molecule that can react with various reagents such as diisocyanates that we have used to prepare the polyurethane of cyclodextrin. Pyridine was chosen as solvent for the selective esterification of the primary hydroxyl groups of CD with the TDI [27]. Beetroot fibres, as well, contain free hydroxyl groups and react with TDI in through the same reaction. The schematic reaction for biopolymer is presented in Figure 1.

Analysis

The infrared spectra were recorded in the mid-infrared range on a Fourier transform infrared spectrometer JASCO 6300 apparatus. To perform the analysis, we first diluted thesamples as powder in a KBr matrix (1 wt %). The spectra are shown in transmittance mode.

The spectrum resolution was 4 cm⁻¹, and the acquisition time was





Citation: Rima J, Assaker K (2018) β-Cyclodextrin Polyurethanes Copolymerized with Beetroot Fibers (Bio-Polymer) to Clean-Up Water Polluted by Organics and Spilled-Oil. J Pet Environ Biotechnol 9: 368. doi: 10.4172/2157-7463.1000368

1 min. Laser granulometric tests of fractioned fillers were made with Horiba LA-950V2 instrument that works in wet method. Ultrapure Water was used while carrying out experiments. A small amount of samples was spread into the water and ultrasonic treatment at medium power 5 was also used for 20 seconds. Samples for Scanning electron microscopy (SEM) were prepared by spreading some materials into ethanol, then a drop of it was taken and spread on a carbon coated copper grid. Observations were made using a TESCAN VEGA3 SB microscope with SEI mode operated at voltage of 20 kV. The Shimadzu UV-1601 UV-VIS spectrometer was used in the range from 190 nm to 1100 nm to monitor the organics removal by the biopolymer filter. The pH values were measured with a WTW pH/mV Hand-Held Meter 330/ SET. The pH meter was calibrated by using pH-Buffer solutions.

Column procedures to remove dyes and some hydrocarbons

The column consisted of a Plexiglas tubing (30 cm height, φ 4.0 cm) perforated at the bottom and connected to a pumping system. In order to assure homogeneity and reproducibility of the results, the column was filled for all experiments by 30 g of biopolymer. Also, we proceeded with the passage of 50 ml of solution. Methylene blue and Rhodamine B were used to test the remediation of water polluted by dyes. These dyes are chosen because they present significant sources of industrial pollution. In order to test the effectiveness of the biopolymer in the treatment of water polluted by PAHs, Pyrene standard solution was prepared in ethanol/water 50/50 (v/v) with a concentration of 30 mg /L. The pH values were adjusted by the addition of aqueous HCl solution. Free filtration is applied; the residence time of each solution in the column was 20 minutes of free, non-forced filtration. The concentrations before and after the injection were measured by UV spectroscopy.

Spill oil clean up test

The spilled oil tests were followed as per Bayat et al. [10]. A common dynamic sorption method was employed to determine the oil sorption capacity of the sorbents. A specified amount of oil pollutants (10 g, 20 g and 30 g) was added to a 600 ml beaker containing 400 ml of simulated seawater and placed on a shaker apparatus. A sorbent was weighed (1,000 g) and added to the system, which was shaken for 5 min at 90 cycles/ min. The wetted sorbent was removed from the polluted water, drained for 2 min and then carefully weighed. The water content (quantitative) of the sorbent was determined by the ASTM D 95 distillation technique [28]. The material to be tested is heated under reflux with a water-immiscible solvent, which co-distilled with the water in the sample. Condensed solvent and water are continuously separated in a trap, the water settling in the graduated section of the trap and the solvent returning to the still. We calculate the water in the sample, as weight or volume percent, in accordance with the basis on which the sample was taken, as follows:

Water, % (V/V) = {[(Volume in water trap, ml - Water in solvent blank, ml)]/ (Volume in test sample, mL)} \times 100

Water, % (V/m) = {[(Volume in water trap, ml - Water in solvent blank, ml)]/(Mass of test sample, g)} \times 100

The total net amount of sorption is the difference between the weights of the initial sorbent and the drained sorbent. Finally, the net oil sorption was determined by subtracting the water content from the total net amount of sorption. Oil recovery efficiency is considered as a measure of the hydrophobicity and the oleophilicity of sorbent through of the following relation:

$R=100 (M_0/Mt)$

Where, R is the oil recovery efficiency. M_0 is the net oil sorption, and Mt is the total net amount of sorption. Experiments were repeated 3 to 5 times. Experiments were repeatable and results were reproducible by mean of 5% deviation.

Biodegradation process

90 g of expired bio-polymer which is charged with petroleum oil during the sorption and desorption process were transferred into 250 ml beaker. 1g of yeast mixed, 1g of sugar (sucrose) and 10 ml of distilled water were added to the biopolymer polluted. The set was kept under the hood and the Erlenmeyer was weighed every 24 hours. The beaker is weighed once a day for 30 days.

Results and Discussion

Materials characterization

After the preparation of materials the granulometric analyses were conducted to examine the particles size distribution. As shown in Figure 2, the beetroot fibers particle size distribution is large and centered around 230 µm. This beetroot fiber' particles size was expected since fibers were sieved through a 250 µm pores. The prepared β-cyclodextrin polyurethane showed a larger distribution of particles size than that of beetroot fibers. As presented in Figure 2, the distribution of particles diameter of β -CD polyurethane is between 10 μ m and 500 µm showing two maximum particles size at 60 µm and 230 µm. When the β -CD polyurethane is prepared in the presence of beetroot fibers to obtain the bio-polyurethane, the particles size distribution of the prepared materials becomes larger than that of the beetroot fibers and stated between 20 µm and 1000 µm. The distribution of the bio-polyurethane particles size is centered at 380 µm. To understand better the particles size distribution of all prepared materials, scanning electronic microscopy (SEM) analyses were recorded. Figure 3 shows the SEM analyses of beetroot fibers, β -cyclodextrin polyurethane and the bio-polyurethane. Beetroot fibers pictures present long fibrotic sticks of more than 500 µm long and a diameter of less than 100 µm. The longitudinal shape of the fibers can explain the large particles size distribution obtained by granulometric analysis, since the measurement takes in consideration the dynamic circular diameter of the analyzed particles. Concerning $\beta\text{-}\mathrm{CD}$ polyurethane, the analyses depicted small round shaped and agglomerated particles of almost 50 µm. This result corroborates with the one obtained by granulometric analysis, since the distribution of particles size showed two maximum sizes one of them is around 60 µm. The other particles size around 230 µm can be obtained of



Figure 2: Granulometric particle size distribution of beetroot fibres, β -CD polyurethane and the copolymerized bio-polymer.

J Pet Environ Biotechnol, an open access journal ISSN: 2157-7463

several agglomerated particles of the polymer. The SEM pictures of the bio-polyurethane show a mixture of the two already described textures. We can see small round shaped particles aggregated around long sticks. These results, on one hand, suggest that the bio-polyurethane is a physical mixture between beetroot fibers and β-CD polyurethane. On the other hand explain the enlargement of the particles size distribution of the bio-polyurethane by granulometric analysis.

FTIR spectra of beetroot fibers, cyclodextrin polyurethane and the bio-polyurethane are shown in Figure 4. The FTIR spectrum of beetroot fibers shows OH stretching at 3423 cm⁻¹ as large and sharp peak, as small peaks at 2923 cm⁻¹ and OH bending between 1500 and 1000 cm⁻¹.



Figure 3: SEM images of beetroot fibers, β-CD polyurethane and the copolymerized biopolymer.



Figure 4: FTIR spectra of beetroot fibres, β-CD polyurethane and the copolymerized biopolymer.

C=O stretches are shown in the spectrum at 1763 cm⁻¹ and 1636 cm⁻¹ ¹. In order to be able to compare, and because we couldn't record the FTIR of the bare β -cyclodextrin before polymerization, we compared our results with the recorded FTIR spectrum of β - cyclodextrin from Stanculescu et al. study [29]. As shown in the FTIR spectrum of β-cyclodextrin, the presence of surficial OH functions is shown very obviously by OH stretching at 3392 and 2927 cm⁻¹, and OH bending as sharp and small peaks between 1411 and 100 cm⁻¹. At 1630 cm⁻¹ we note a small peak representing C=C vibration [29]. These results corroborate with the molecular structure of β-cyclodextrin composed of linked C and a lot of OH functions at its surface. Cyclodextrin polymer FTIR spectrum shows the large peak of OH stretching at 3423 cm⁻¹ but none at 2923 cm⁻¹. At the same time, we remark less noticeable peaks between 1500 and 1000 cm⁻¹. Similar results are represented in the mixture biopolyurethane spectrum. These results may depict the chemical reaction occurring while polymerization either of cyclodextrin or beetroot with cyclodextrin engaging the OH functions at the surface of the starting materials. This is shown by the polymerization reaction in Figure 1.

Removal of motor oil and organic compounds using the copolymerized bio-polymer

β-CD polyurethane and the biopolymer keep the hydrophobic cavities of the molecules origins of β -CD; this suggests that the efficiency of inclusion of organic compounds by their cavities are very similar. The test performed on the retention efficiency by β -CD polyurethane was a valid model for polymer and bioploymere. The solutions models we tested are: Rhodamine B, methylene blue and Pyrene. Thus, three different solutions of methylene blue (100 ppm), Rhodamine B (150 ppm) and Pyrene (30 ppm) in different pH values ranging from 1.5 to 7.5 were prepared. For each solution we determined the maximum of absorbance obtained after their filtration through β-CD polyurethane column. The plot (Absorbance in function of pH) is presented in Figure 5. According to these results when the pH is between 6 and 6.5 the maximum of absorbance of all organic compounds tested is obtained. For this reason, experiments to remove these chemicals using the bio-polymer were performed in aqueous solutions adjusted to pH 7. Solutions of Methylene Blue 100 ppm, Rhodamine B 150 ppm and Pyrene 30 ppm were used to test the performance of the prepared biopolymer. The experimental results showed that the biopolymer is able to eliminate the dyes with an efficiency of 99% (Figures 6 and 7). Figure 8 shows the UV spectra of Pyrene solution before and after injection inside the biopolymer column. It is also obviously that the removal of Pyrene is efficient and the removal percentage is higher than 96%.



The oil sorption capacities of different sorbents are presented in

Figure 5: Effect of pH on the encapsulation of Methylene Blue [100 ppm], Rhodamine B [150 ppm] (aqueous solutions) and pyrene [30 ppm] in 50/50 ethanol water using the bio-polymer as sorbent.

Page 4 of 7



Figure 6: UV spectrum of Rhodamine B 150 ppm before and after filtration through the bio filter (pH=7, free filtration).



Table 1. The results represent the average oil sorption capacities (as mass of sorbed oil per unit of sorbent mass) for different pollutantto-sorbent ratios (10 g/g, 20 g/g and 100 g/g). Also, in this table, the standard deviations of all experiments are given. The results reveal that the biopolymer has a significant oil sorption capacity for different oils and can sorb 85 to 90 g of different oils per each gram of sorbent.

 β -cyclodextrin polymers are known to be efficient for oil and organic molecules adsorption from water due to their hydrophobic cavities. In this work, the prepared bio-polymer showed its ability to eliminate organic polar and non-polar pollutants. The copolymerization of β -CD with beetroot fibers showed a great oil and organic molecules adsorption rate due to the combined characteristics of CD and fibers. The use of CD in previous work [30] showed a great absorption efficiency of pyrene, whereas, Rima et al. found that pyrene forms a complex with β -CD due to the β -CD cavity hydrophobic characteristics. Beetroot fibers were used to eliminate heavy metals and charged compounds as well [30]. The absorbent activity of fibers is usually high; Rima et al. showed a high efficiency adsorption of beetroot toward charged metals [31].

In a similar study, Ding et al. [15] showed many experiments using CD polymer copolymerized with co-polymers. They changed the concentration of the copolymer and presented different results illustrating the effect of an excess cross-linking agent to the surface of CD. The formation of too dense network on the surface decreases the polymeric chains and lowers the oil absorbency of the material. The copolymerization of β -CD with beetroot fibers in the presence of TDI results in long chains, where TDI is incorporated between the

cyclodextrin and fibers. With this structure, the cyclodextrin cavities are non-perturbed, while the hydrophobic properties of the cavities are preserved and the active sites of the fibers still capable of retaining the polar compounds. Comparing to our results, and as shown in SEM figures the CD polymers are attached onto the surface of beetroot fibers which increases contact area of the material with oil and aqueous solutions. Ding et al. [15] compared the capacity of absorbance of oils by oil-absorbents with and without CD as well.

Results found show that polymers containing CD are more efficient for oil removal. This corroborate with our results as well, showing that the main absorbent of pollutants and oil is the β -CD polyurethane having an enhanced action when copolymerized with the natural beetroot fibers.

Biodegradation of the expired biopolymer charged with crude oil

The biodegradation process was followed during 30 days. The total mass of the bio filter charged with the pollutants constitutes crude oil is reduced by 85%. The residues have not been analyzed, which morphologically appears like a hard solid mass. The residues are likely to be mineral compounds. Figure 9 shows the evolution of degradation as a function of time. The fundamental reactions of the aerobic hydrocarbon decomposition have been well known for several decades [22,32,33].

The key step of hydrocarbon degradation is the addition of one oxygen atom, in some cases, two oxygen atoms, to the hydrocarbon molecule to be converted to an alkanol (in the case of aliphatic hydrocarbons) or to a phenol (in the case of aromatic molecules). This oxidation introduces a reactive site for the next reactions. Complete mineralization is taken mainly by bacteria. The monoaromatic molecule or one ring of the polyaromatic system is oxidized stepwise via formation of a diol and subsequent ring cleavage. The main products are biomass and carbon dioxide. An accumulation of deadend products is rare and occurs mostly when cells are deficient in their degradation pathway. The disadvantage of this pathway is that only ring systems of up to four rings are mineralized. Systems with a higher number of rings seem to be recalcitrant [34]. In order to understand the biodegradation obtained in our case, we make a comparison approach with the microbial biodegradation of petroleum oil by microbial communities. Some microorganisms, such as A. borkumensis, are able to use hydrocarbons as a carbon source in the metabolism (Figure 10). They are able to oxidize environmentally harmful hydrocarbons while producing harmless products, following the general equation:





J Pet Environ Biotechnol, an open access journal ISSN: 2157-7463



Figure 9: Evolution of biofilter biodegradation as a function of time at 25°C.



Figure 10: Schematic presentation of biodegradation of organic pollutants.

Oil Sorption (g/g sorbent)	Recovery Efficiency (%)	Maximum of sorption (g/g)	Standard Deviation
3.7	100	95	4
4.5	100	92	5
12	95	90	5.5
50	85	89	5.5
100	80	85	5.7

 Table 1: Experimental results of oil sorption capacities, recovery efficiencies and standard deviations.

 $C_nH_n + O_2 \rightarrow H_2O + CO_2$.

This type of special metabolism allows these microbes to grow well in areas affected by oil spills and play an important role in the removal of environmental pollutants [35,36].

Conclusion

 β -Cyclodextrin polymerized with beetroot fibers (Bio-polymer), was prepared and applied to the remove oil, PAH and dyes from wastewater. The bio-polymer was experimented as a filter using free non-forced filtration. The results show that the elimination of the pollutants was very effective, up to 99% for dyes removal and up to 96% for PAH removal. The bio-polymer was tested also for adsorption of crude oil. The maximum sorption is 90 g crude oil per gram of sorbent. After several times of use, the bio-polymer has been subjected to degradation by the yeast. After thirty days of monitoring, the mass of the biopolymer polluted was reduced to 15% while leaving mineral residues. According to the results this bio-polymer can be used to remedy the polluted water with organic compounds and spilled oil.

Acknowledgments

This work was supported by the Lebanese University and the Doctoral School at Lebanese University PRASE. Analysis and discussions were made in PRASE-Hadath Campus.

References

1. Hussein M, Amer A, Sawsan I (2008) Oil spill sorption using carbonized pith

bagasse. Application of carbonized pith bagasse as loose fiber. Int J Environ Sci Tech 5: 233–242.

Page 6 of 7

- Thompson NE, Emmanuel GC, Adagadzu KJ (2010) Sorption studies of crude oil on acetylated rice husks. Arch Appl Sci Res 2: 142–151.
- Badejo OT, Nwilo PC (2003) Waterways, management of oil spill dispersal along the Nigerian coastal areas, Delta. 2002.
- Choi HM, Cloud RM (1992) Natural sorbents in oil spill cleanup, Environ Sci Technol 26 772–776.
- Deschamps G, Caruel H, Borredon ME, Bonnin C, Vignoles C (2003) Oil removal from water by selective sorption on hydrophobic cotton fibers. 1. Study of sorption properties and comparison with other cotton fiber-based sorbents. Environ Sci Technol 37: 1013–1015.
- Lim T, Huang X (2007) Evaluation of kapok (*Ceiba pentandra* (L.) Gaertn.) as a natural hollow hydrophobic-oleophilic fibrous sorbent for oil spill cleanup, Chemosphere 66: 955–963.
- Dong T, Xu G, Wang F (2015) Adsorption and adhesiveness of kapok fiber to different oils, J Hazard Mater. 296: 101–111.
- Praba Karana C, Rengasamy RS, Das D (2011) Oil spill clean-up by structured fibre assembly. Indian J Fibre Text Res 36: 190–200.
- Bazargan A, Tan J, Hui CW, McKay G (2014) Utilization of rice husks for the production of oil sorbent materials. Cellulose. 21: 1679–1688.
- Bayat A, Aghamiri SF, Moheb A, Vakili-Nezhaad GR (2005) Oil spill cleanup from sea water by sorbent materials. Chem Eng Technol. 28: 1525–1528.
- Nwadiogbu JO, Okoye PAC, Ajiwe VI, Nnaji NJN (2014) Hydrophobic treatment of corn cob by acetylation: Kinetics and thermodynamics studies. J Environ Chem Eng 2: 1699–1704.
- Saleem J, Adil Riaz M, Gordon M (2018) Oil sorbents from plastic wastes and polymers: A review. J Hazard Mater 341: 424–437.
- Mamba BB, Krause RW, Malefetse TJ, Mhlanga SD, Sithole SP, et al. (2007) Removal of geosmin and 2-methylisorboneol (2-MIB) in water from Zuikerbosch treatment plant (Rand Water) using β-cyclodextrin polyurethanes. Water SA 33: 223–227.
- Allabashi R, Arkas M, Hörmann G, Tsiourvas D (2007) Removal of some organic pollutants in water employing ceramic membranes impregnated with cross-linked silylated dendritic and cyclodextrin polymers. Water Res 41: 476–486.
- Ding L, Li Y, Jia D, Deng J, Yang W (2011) β-Cyclodextrin-based oil-absorbents: Preparation, high oil absorbency and reusability, Carbohydr Polym 83: 1990–1996.
- Appell M, Jackson MA (2012) Sorption of ochratoxin A from aqueous solutions using β- cyclodextrin-polyurethane polymer. Toxins 4: 98–109.
- Zhu H, Qiu S, Jiang W, Wu D, Zhang D (2011) Evaluation of electro spun polyvinyl chloride/polystyrene fibres as sorbent materials for oil spill clean-up. Environ Sci Technol 45: 4527–4531.
- Li H, Liu L, Yang F (2013) Oleophilic polyurethane foams for oil spill cleanup. Environ Sci Procedia 18: 528–533.
- Asadpour R, Bin Sapari N, Tuan Z, Jusoh H, Riahi A, et al. (2013) Application of Sorbent materials in Oil Spill management: A review. Casp J Appl Sci Res 2: 46–58.
- Wang J, Zheng W, Wang A (2001) Kinetic and thermodynamic studies on the removal of oil from water using superhydrophobic Kapok fiber. Water Environ Res 86(4): 360-365.
- Lee Y, Lee E, Chang G, Lee D, Jung Y, et al. (2014) Comparison of oil sorption capacity and biodegradability of PP, PP/kapok (10/90 wt%) blend and commercial (T2COM) oil sorbent pads. Text Color Finish 26: 151–158.
- Atlas RM (1995) Petroleum biodegradation and oil spill bioremediation Mar Pollut Bull 31: 178–182.
- Chaîneau CH, Rougeux G, Yéprémian C, Oudot J (2005) Effects of nutrient concentration on the biodegradation of crude oil and associated microbial populations in the soil. Soil Biol Biochem 37: 1490–1497.
- Blumer M, Ehrhardt M, Jones JH (1973) The environmental fate of stranded crude oil. Deep Res Oceanogr Abstr 20: 239–259.
- Robador A, Brüchert V, Jørgensen BB (2009) The impact of temperature change on the activity and community composition of sulfate-reducing bacteria in arctic versus temperate marine sediments. Environ Microbiol 11: 1692–1703.
- 26. Flores C, Lopez M, Tabary N, Neut C, Chai F, et al. (2017) Preparation and

Citation: Rima J, Assaker K (2018) β-Cyclodextrin Polyurethanes Copolymerized with Beetroot Fibers (Bio-Polymer) to Clean-Up Water Polluted by Organics and Spilled-Oil. J Pet Environ Biotechnol 9: 368. doi: 10.4172/2157-7463.1000368

characterization of novel chitosan and β -cyclodextrin polymer sponges for wound dressing applications, Carbohydr Polym 173: 535–546.

- 27. Kawano S, Kida T, Miyawaki K, Noguchi Y, Kato P, et al. (2014) Cyclodextrin polymers as highly effective adsorbents for removal and recovery of polychlorobiphenyls (PCBs) contaminants in insulating oil. Environ Sci Technol 48: 8094-8100.
- American Association State (2002) Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation, American National Standard: pp: 1–5.
- Stanculescu P, Dobrica I, Mandravel C, Mindrila G (2010) FTIR and Molecular Modeling Study of the Interaction Between B -Cyclodextrin and Polychlorobiphenyls. Ann Uni Bucharest 19: 47–52.
- 30. Rima J, Kyriacos S, Rida MA (2009) Effect of the acyl group and the dodecylsulfonate chain on the inclusion of pyrene inside the cavity of β-cyclodextrin, Spectrochim. Act Part A Mol Biomol Spectros 74: 10–15.

- Rima J, Ghauch A, Ghaouch M, Martin- Bouyer M (2000) Cleaning of water contaminated by heavy metals using beetroot fibres as bio filter. Toxicol Environ Chem 75: 89–97.
- Brooijmans RJW, Pastink MI, Siezen RJ (2009) Hydrocarbon-degrading bacteria: The oil-spill clean-up crew. Microb Biotechnol 2: 587–594.
- Atlas RM (1984) Petroleum Microbiology. Technology & Engineering, Macmillan, Basingstoke, UK. pp: 1-692.
- Dinand E, Chanzy E, Vignon MR (1996) Parenchymal cell cellulose from sugar beet pulp: preparation and properties. Cellulose 3: 183–188.
- Hassanshahian M, Cappello S (2013) Crude Oil Biodegradation in the Marine Environments. Biodegradation, IntechOpen Limited, London: pp: 101-135.
- Button DK, Schut F, Quang P, Martin R, Robertson BR (1993) Viability and isolation of marine bacteria by dilution culture: Theory, procedures, and initial results. Appl Environ Microbiol 59: 881–891.

Page 7 of 7