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Evaluation of Butyl Rubber as Sorbent Material for the Removal of Oil and Polycyclic Aromatic Hydrocarbons from Seawater

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Ecological disasters resulting from oil spills have created a great need to find more efficient materials for oil spill cleanup. This research highlights the use of a novel macroporous polymeric material based on butyl rubber (BR) as a sorbent in an oil spill cleanup. The sorption capacity of BR for crude oil and petroleum products is 15–23 g g⁻¹ as compared to the value of 10–16 g g⁻¹ obtained using a nonwoven polypropylene (PP), a widely used commercial oil sorbent. BR sorbent is reusable after simple squeezing and its continuous sorption capacity for crude oil is 7.6 g g⁻¹ in each cycle, about 3 times the capacity of the PP sorbent. BR sorbents also remove efficiently polycyclic aromatic hydrocarbons (PAHs) such as acenaphthene and pyrene from seawaters. The results suggest that the rubber sorbents are a better alternative to the widely used PP sorbents by improving the efficiency of oil sorption and the reusability of the sorbent.

Introduction

Accidents involving tankers and cargo ships can result in the release of large volumes of crude oil, and this risk significantly increases along narrow seaways with heavy maritime traffic. Therefore, removal of crude oil and petroleum products that are spilled at sea is a serious problem of the last decades (1). Another important threat to the environment comes from polycyclic aromatic hydrocarbons (PAHs), a large group of organic compounds with two or more fused aromatic rings. PAHs have been known to affect a variety of biological processes and can be potent cell mutagens and carcinogens (2). A typical crude oil may contain from 0.2% to more than 7% total PAH (1); in addition to oil spills, sources of PAHs in aquatic environments include wastewaters, surface runoff, industrial processes, atmospheric deposition, biosynthesis, and natural events such as forest fires (1, 3). As a consequence, large amounts of PAHs have been discharged to the aquatic environment (1, 4).

Among existing techniques for the removal of oil and PAHs from waters, the use of sorbents is generally considered to be one of the most efficient techniques (5, 6). Properties of an ideal sorbent material for oil spill cleanup include (a)

hydrophobicity, (b) high uptake capacity and high rate of uptake, (c) buoyancy, (d) retention over time, (e) durability in aqueous media, (f) reusability or biodegradability, and (f) recoverability of oil. Although several materials have been proposed as sorbents for oil removal (7–11), polymeric materials based on nonwoven polypropylene (PP) are the most commonly used commercial sorbents in oil spill cleanup. This is due to the fact that the properties of PP sorbents closely match those of an ideal oil sorbent (12–14). Furthermore, sorbents such as natural materials, activated carbon and macroporous polymers have been evaluated for the removal of PAHs from waters (15–17).

Butyl rubber (BR) is a low-cost but an important commercial elastomer with many desirable and interesting properties such as low air permeability, a good resistance to aging and weatherability (18). The principal applications of BR are in tire industry for the preparation of inner tubes and inner lines. Although cross-linked BR exhibits a high sorption capacity for organic solvents, its sorption rate is so slow that it has not been used as an oil sorbent (19). Recently, we have reported the preparation of macroporous BR able to absorb large volume of organic solvents in a short period of time (20, 21). It was shown that the frozen solutions of BR in organic solvents at subzero temperatures can easily be vulcanized using sulfur monochloride (S₂Cl₂) to produce responsive and durable materials with a macroporous structure. The BR materials thus obtained were very tough; they can be compressed up to about 100% strain without any crack development, during which the total organic liquid (toluene) inside the sorbent is removed (20). Further, the compressed BR immediately absorbs in contact with toluene to recover its original shape. Due to the hydrophobicity, fast-responsivity, and reusability, macroporous BR seems to be a suitable sorbent material in various applications.

This paper is the first report on the application of macroporous BR sorbents in the oil spill cleanup from surface waters as well as for the removal of PAHs from waters. Here, a series of BR sorbents were prepared and their sorption capacities for crude oil, petroleum products, vegetable oil as well as for PAHs were determined. The results were compared with the performance of a commercial sorbent based on nonwoven polypropylene fiber.

Materials and Methods

Sorbent Preparation. Butyl rubber (Butyl 365, Exxon Chemical Co.) with 2.3 mol % isoprene units and a Mooney viscosity of 33 was used for the sorbent preparation. The cross-linking agent sulfur monochloride, S₂Cl₂, was purchased from Aldrich Co. Benzene, toluene, and methanol (all Merck grades) were used as the solvent for the solution cross-linking reactions, swelling and deswelling experiments.

The sorbents in the form of cylindrical tissues of about 14 cm in diameter were prepared by solution cross-linking technique at a butyl rubber (BR) concentration of 5 w/v % and a cross-linker concentration of 6 v/v % (with respect to butyl rubber) according to the following scheme: BR (50 g) was first dissolved in 1 L of benzene at room temperature (20 ± 1 °C) overnight. After addition of sulfur monochloride (3.0 mL) under rigorous stirring, the solution was transferred into several glass Petri dishes of 140 mm in diameter and 20 mm in height. The dishes were sealed with glass plates and the reaction was conducted for 24 h at a given temperature T_{prep} . After the reaction, the reaction system was thawed at room temperature for 1 h and the sorbent formed was squeezed to remove benzene. It was then washed several times first with toluene then with methanol and finally dried under

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TABLE 1. Properties of the Model Chemicals and Mixtures Used in the Experiments^a

chemical/mixture	origin and properties
toluene	technical grade, purity = 98%, $d = 0.865 \text{ g mL}^{-1}$, viscosity = 0.59 cP (20 °C)
gasoline	BP super, 95 octane, lead-free, $d = 0.720 - 0.775 \text{ g mL}^{-1}$, viscosity = 0.75 cP (38 °C)
diesel fuel	BP ultimate diesel, setan number = 55, $d = 0.85 \text{ g mL}^{-1}$, viscosity = 5.0 cP (25 °C)
no. 6 fuel oil	$d = 1.03 \text{ g mL}^{-1}$ (15 °C), viscosity = 130 cP (25 °C)
crude oil	from Ozan Ungurlu wells, Turkey. $d = 0.89 \text{ g mL}^{-1}$, viscosity = 350 cP (25 °C)
olive oil	from Kent Boring, $d = 0.918 - 0.923 \text{ g mL}^{-1}$, viscosity = 69 cP (25 °C). It is a mixture of saturated (11.4%) and unsaturated fatty acids.
acenaphthene	from Sigma-Aldrich. Solubility in distilled water at 25 °C = 4.5 mg L ⁻¹ .
pyrene	from Sigma-Aldrich Solubility in distilled water at 25 °C = 0.13 mg L ⁻¹ .

^a Viscosities of liquid chemicals and mixtures were measured between the parallel plates of the rheometer (Gemini 150 Rheometer system, Bohlin Instruments) equipped with a Peltier device for temperature control. The upper plate (diameter 40 mm) was set at a distance of 500 μm before the measurements.

vacuum at room temperature. Extraction tests showed that the sorbents are insoluble in toluene, i.e., the gel fraction equals to unity (20).

To visualize the morphology of the sorbents, they were investigated by scanning electron microscopy (SEM) at various magnifications between 20 and 300 times (Jeol JSM 6335F Field Emission SEM). Prior to the measurements, the samples were sputter-coated with gold for 3 min using Sputter-coater S150 B Edwards instrument. The pore volume V_p of the sorbents was estimated through uptake of methanol of dry samples. Since methanol is a nonsolvent for the polymer, it only enters into the pores of the polymer network (20). Thus, V_p (mL pores in 1 g of dry sorbent) was calculated as $V_p = (m_M - m_{dry}) / (d_M - d_{dry})$, where m_M and m_{dry} are the mass of the sorbent immersed in methanol after 2 h and its dry mass, respectively, d_M is the density of methanol (0.792 g mL⁻¹).

For comparison, commercial nonwoven propylene sorbent, Mavisorb, obtained from Mavideniz Cevre Hizmetleri A.S. (Istanbul, Turkey) was used as a reference in the sorption experiments.

Model Chemicals and Complex Mixtures. Three model chemicals and five mixtures were used to investigate removal of contaminants from water. These include toluene, gasoline, diesel fuel, crude oil, no. 6 fuel oil (Bunker C), olive oil, and two PAH compounds with different properties, namely acenaphthene, and pyrene. Characteristics of the model chemicals and mixtures are provided in Table 1. Among the chemicals, toluene was chosen as a model compound for the aromatic hydrocarbons.

Procedure for Oil Removal Tests. All tests were performed at 20 $\pm$ 1 °C. The kinetics of the oil sorption process was determined by immersing 2 g of dry sorbent into 500 mL of test solution and then monitoring the mass of the sorbent as a function of time. For this purpose, the sorbent was removed from the test solution at selected time intervals (30

s to 5 min) and weighed. The uptake capacity at time t , i.e., g of pollutants absorbed by 1 g of sorbent was calculated as $(m_t - m_{dry}) / m_{dry}$ where m_t is the sorbent mass at time t .

The uptake capacity of the sorbents at time $t = 2$ min for pollutants that spread on the water level was determined by the method described previously (22). In a crystallizer containing 1 L of water at 20 °C, the test solution (280 mL) was poured to obtain a layer of approximately 1 cm thickness on the water surface. Then, dry sorbent (2 g) was put onto the solution and, after a sorption time of 2 min, the sorbent was left to drip for 30 s and weighed. The uptake capacity was calculated as the amount of pollutant absorbed by 1 g of sorbent within 2 min.

Sorbent reusability as well as the continuous extraction capacity of the sorbents was determined by subjecting the sorbents to successive sorption-squeezing cycles under identical conditions. Dry sorbent cylinder of about 50 mm in diameter and 4 mm in width having a mass of about 0.7 g was first immersed into 500 mL of test solution for 1 min and then, it was left to drip for 30 s. The saturated sorbent was weighed and put into a Büchner funnel and squeezed for 30 s under 7.2 g cm⁻², with a 50 mm vacuum. The sorbent cylinder was then weighed again to calculate the amount of sorbed pollutant by 1 g of dry sorbent. This sorption-squeezing cycle was repeated 30 times to obtain the recycling efficiency and continuous extraction capacity of the sorbents.

Procedure for PAH Removal Tests. Stock solutions of acenaphthene (Ace) and pyrene (Pyr) were prepared by dissolving each PAH in acetone. Solutions used for the PAH removal tests were prepared by diluting stock solutions with filtered (Active carbon + 0.45 μm) natural seawater (22 ppt) to final concentrations of 1500 μg Ace and 50 μg Pyr each in 1 L of seawater. PAH removal tests were performed by placing 2 g of cylindrical sorbent materials onto 1 L seawater solution and stirring on a magnetic stirrer for 24 h at 20 $\pm$ 1 °C. Since PAHs are known to degrade through the process of photo-oxidation, the test solutions were covered with dark sheets. Control solutions containing either Ace or Pyr were also prepared and checked for their PAH contents throughout the experiments. Samples were taken at various time intervals between 1 min and 10 h, and the measurements were performed using fluorescence spectrometer (Perkin-Elmer LS 55) at excitation and emission wavelengths of 218 and 328 nm for Ace, 265 and 390 nm for Pyr, respectively. FLWinlab software was used for calculations.

Results and Discussion

Characteristics of the Sorbents. Butyl rubber (BR) sorbents were prepared at three different temperatures T_{prep} , namely at 17, -2, and -18 °C. In the following paragraphs, these sorbents will be called +17BR, -2BR, and -18BR, respectively, where the first two numbers refer the preparation temperature T_{prep} . Pictures of some BR sorbents in the dry state are shown in Figure 1A. SEM analysis of the sorbents prepared at room temperature (+17BR) revealed that they are nonporous and exhibit glasslike fracture surfaces but without pronounced microstructure. However, as seen in Figures 1B and C, where SEM images of -2BR and -18BR are given, respectively, the low temperature sorbents consist of irregular pores of 10¹–10² μm in diameter. The total volume of pores V_p of the BR sorbents was found to be 0.5, 2.2, and 8.9 mL g⁻¹ for +17BR, -2BR, and -18BR, respectively, i.e., V_p increases with decreasing preparation temperature. This trend can also be seen from the SEM images in Figures 1B and 1C; -18BR sorbent consists of larger number of millimeter-sized macropores as compared to -2BR sorbent.

For comparison, a commercial polypropylene (PP) sorbent, Mavisorb, was also used in the sorption tests. SEM image of the PP sorbent given in Figure 1D illustrates the porous web structure of the nonwoven fiber of about 10 μm

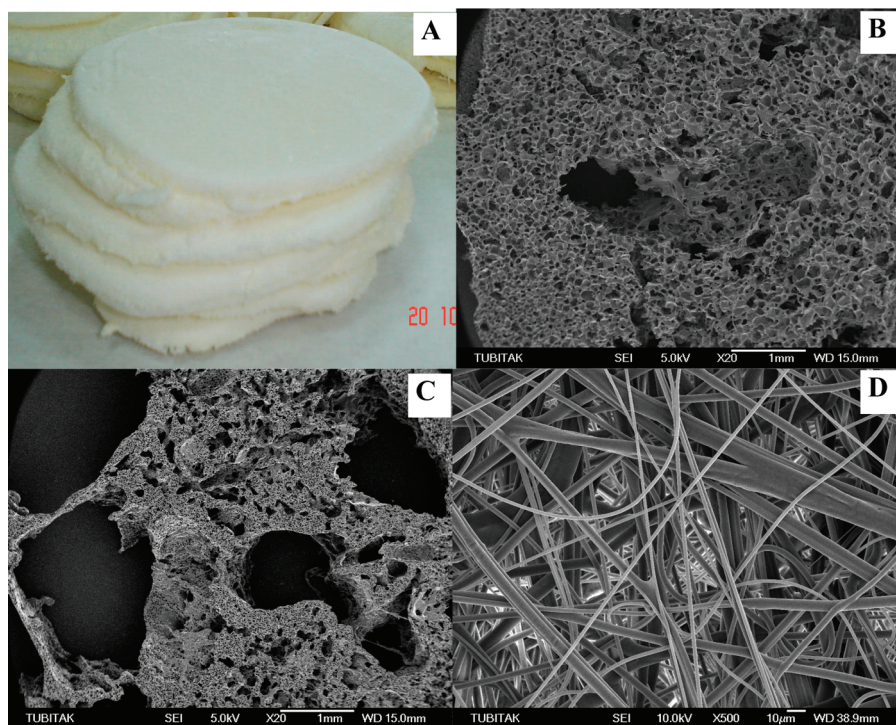


FIGURE 1. A: Pictures of -18BR sorbents. B and C: SEM of -2BR and -18BR, respectively, at a magnification of $\times 20$. Scaling bars = 1 mm. D: SEM of the PP sorbent Mavisorb. Scaling bar = 10 μm . Magnification = $\times 500$.

in diameter with interstices of 10^1 – 10^2 μm in width. The total volume of pores in the PP sorbent measured by the methanol uptake test was 10.1 mL g^{-1} , the largest among the sorbents studied.

Sorption of Crude Oil, Petroleum Products, and Olive Oil. To investigate the maximum sorption capacity of the sorbent materials, their sorption properties were first analyzed in oil medium without any water. The results of the sorption kinetics of the sorbents in contact with various pollutants are shown in Figure 2, where the sorbed amount of pollutants is plotted against the contact time. The sorption rate of the nonporous +17BR is very slow (see also Supporting Information Figure S1), while macroporous rubber sorbents -2BR and -18BR as well as the commercial PP sorbent absorb the pollutants in less than 5 min to attain the thermodynamic equilibrium. The fast sorption rate is due to the interconnected pore structure of these materials (Figure 1); the pollutants are sorbed through the micrometer-sized pores by convection, which is much faster than the diffusion process that dominates the nonporous +17BR sorbent.

Figure 2 also shows that, the lower the preparation temperature of the rubber sorbent, the larger the sorption capacity and the faster the uptake rate for the pollutants. This is a consequence of the increasing volume of pores with decreasing preparation temperature. In Figure 3, the maximum sorption capacity of the best rubber sorbent, namely -18BR is compared with that of PP. For crude oil and petroleum products, -18BR exhibits sorption capacities that are higher than those of the PP sorbent. One g of -18BR sorbs about 23 g crude oil or 20 g diesel as compared to the values 15 g g^{-1} and 11 g g^{-1} , respectively, obtained using the PP sorbent. In contrast, however, the sorption capacity of -18BR for olive oil is much lower than PP (8 g g^{-1} versus 15 g g^{-1}), indicating that the rubber sorbent is not suitable for the removal of vegetable oils from water. Sorption capacity of -18BR sorbent increased in the following order: Olive oil < fuel oil < gasoline < toluene < diesel < crude oil. Thus, the sorption capacity of -18BR is the highest for crude oil, i.e., for the pollutant with highest viscosity. This implies that, although increased viscosity of the pollutant decreases the

rate of sorption, favorable hydrophobic interactions between the crude oil and hydrophobic polymer increases the adherence of oil onto the surface of the polymer so that more oil is retained within the rubber sorbent.

Visual observations showed that, while PP sorbent does not change its volume during the sorption process, BR sorbents shrink or expand in contact with the pollutants. This indicates that the process of sorption by the BR sorbents involves both the filling of the pores with liquid and the absorption of liquid by the polymer regions. As a consequence, the sorption capacity of BR sorbents greatly varies depending on the type of the pollutant. For example, olive oil sorption capacity of -18BR is 7.9 g g^{-1} , i.e., 8.6 mL g^{-1} , which is close to its pore volume (8.9 mL g^{-1}), indicating that olive oil is a poor swelling agent for the rubber and thus, it only fills the voids. However, the crude oil sorption capacity of -18BR is about 3 times larger than its pore volume indicating that crude oil is a good swelling agent for the rubber. In contrast, the sorption capacity of PP does not change much depending on the type of the pollutants. As mentioned in the literature (23), this is due to the fact that the oil sorption of polypropylene mainly occurs by filling the voids between the fibers with the liquid components.

In this connection, one should also compare the capacities of the BR sorbents with the other sorbents. Agricultural products such as cotton, kapok, and milkweed with a natural hydrophobic character have sorption capacities of about 30–40 g g^{-1} (24–26). Thus, these natural materials sorb larger amounts of crude oil than both BR and PP sorbents. However, these materials are characterized by a lack of stability in aqueous media over time after oil sorption so that they can be used to treat pollution, not to prevent it. In comparison, PP sorbents as well as BR sorbents were stable over time; those subjected to oil sorption tests showed that they are stable at least for 6 months.

The sorption capacities of the sorbents were also measured in the water medium. For this set of experiments, the contact time of the sorbent with pollutant that spread on water level was set to 2 min. The results of the measurements are collected in Supporting Information Table S1. For both -18BR

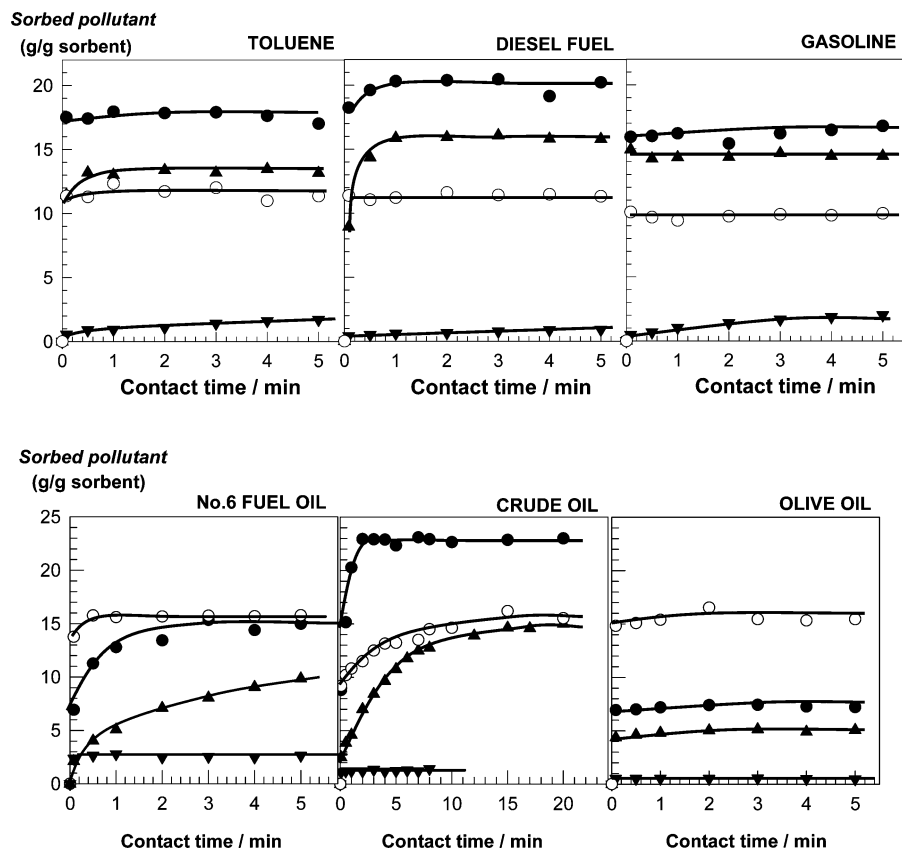


FIGURE 2. Sorption capacities of sorbents vs contact time with various pollutants. Type of sorbents: -18BR (●), -2BR (▲), +17BR (▼), and PP (○). The lines are to guide the eye.

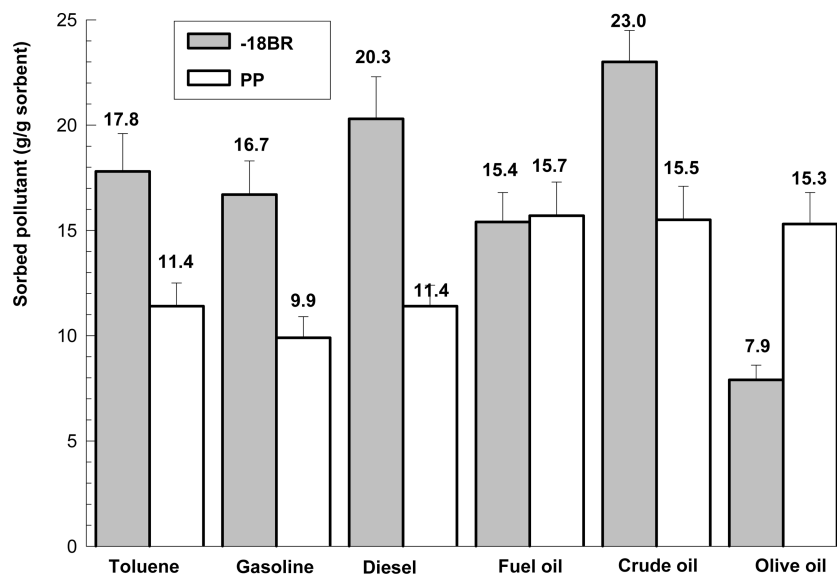


FIGURE 3. Maximum sorption capacities of -18BR and PP for various pollutants. Amounts of sorbed pollutants are shown on the bars.

and PP, the amount of pollutant sorbed within 2 min on the water level is close to their maximum capacities and the difference between the two values is within the limits of the experimental error (10%). Thus, decreasing both the contact time and the contact area do not affect the sorption behavior of these sorbents.

The reusability of the sorbents and the recoverability of the pollutants are important aspects in the oil spill cleanup procedures. This behavior of the sorbents was checked by repeated sorption-squeezing cycles. Results of 30 successive tests conducted using -18BR and PP are shown in Figure 4A by the filled and open symbols, respectively. After an initial

decrease in the uptake capacity of the sorbents, the amount of the sorbed pollutant approaches a limiting value. The average of these limiting values for the number of cycles larger than 9, i.e., the continuous extraction capacities are collected in Figure 4B. The results clearly demonstrate high reusability of -18BR and recoverability of crude oil and petroleum products, indicating that this sorbent could be applied as an efficient oil sorbent for several uses. The continuous extraction capacity of -18BR is 2–3 times larger than the capacity of PP for gasoline and crude oil, respectively. Further, although the maximum capacity of PP for fuel oil is slightly larger than -18BR (Figure 3), the continuous

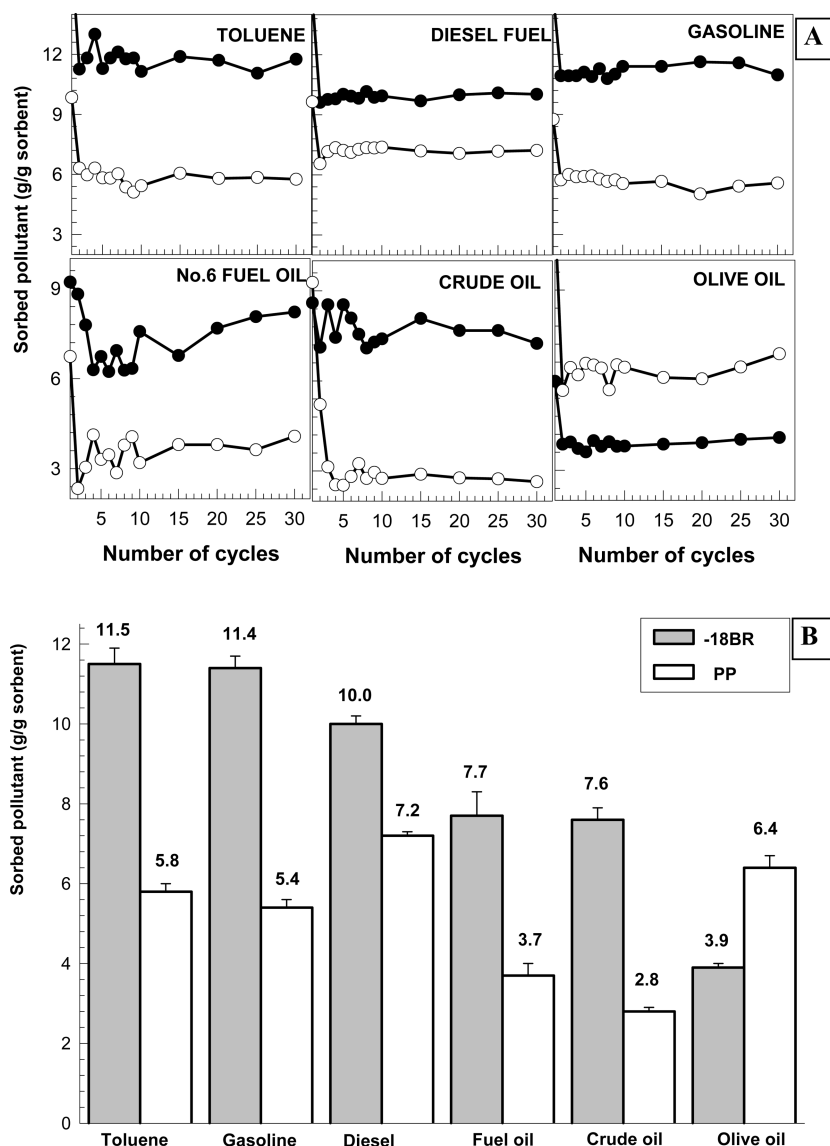


FIGURE 4. A: Continuous extraction capacities of the sorbents –18BR (●) and PP (○) for various pollutants as a function of the number of cycles. The lines are to guide the eye. B: Average of the extraction capacities of –18BR and PP sorbents for various pollutants.

capacity of the latter is twice the capacity of PP. Higher continuous extraction capacity of the rubber sorbent originates from the elasticity of polymer regions separating the pores so that the material can totally be compressed without any damage (20).

Sorption of Acenaphthene and Pyrene. During the screening procedure of the individual PAHs used in this study, two criteria were considered: (a) the priority pollutants indicated by the U.S. Environmental Protection Agency Clean Water Act and (b) the number of aromatic rings in their structures. The latter was due to the fact that the sources, fates, bioaccumulation tendencies, and effects of PAHs may show variations depending on the number of aromatic rings (27). The two PAH compounds selected for the sorption experiments, namely acenaphthene (Ace) and pyrene (Pyr) with two and four aromatic rings, respectively, are widespread pollutants and found in different matrices of the aquatic environments (28, 29).

Sorption tests on seawater samples containing Ace and Pyr were conducted using –18BR and PP sorbents. For this purpose, seawater solutions containing $1500 \mu\text{g L}^{-1}$ Ace or $50 \mu\text{g L}^{-1}$ Pyr were stirred in the presence of the sorbents for 24 h during which the concentrations of the individual PAHs were monitored as a function of the contact time. After 24 h,

the sorbents were transferred to freshly prepared solutions and the tests were repeated for 8 times. Results of the first four measurements are shown in Figure 5A, where the concentrations of Ace (C_{Ace}) and Pyr (C_{Pyr}) in seawater are plotted against the contact time t . PAH concentration (C_{PAH}) rapidly decreases with increasing contact time up to about 6 h and then levels off. The decrease of C_{PAH} in the aqueous phase is greater for –18BR sorbent than for PP due to better sorption properties of the butyl rubber sorbent. The initial sorption rate is faster and the final C_{PAH} remaining in the seawater is lower when –18BR is used in the PAH removal tests. For example, in solutions treated with –18BR, the concentrations of Ace after the first and fourth sorption cycles were 57 and $235 \mu\text{g L}^{-1}$, respectively, as compared to the values of 269 and $820 \mu\text{g L}^{-1}$ obtained using the PP sorbent. However, in solutions containing Pyr, the difference between the efficiencies of the sorbents was not significant. Assuming a first order kinetics, the sorption process of PAH by the sorbent can be described by the following equation (30, 31):

$$\frac{dq_t}{dt} = k(q_e - q_t) \quad (1)$$

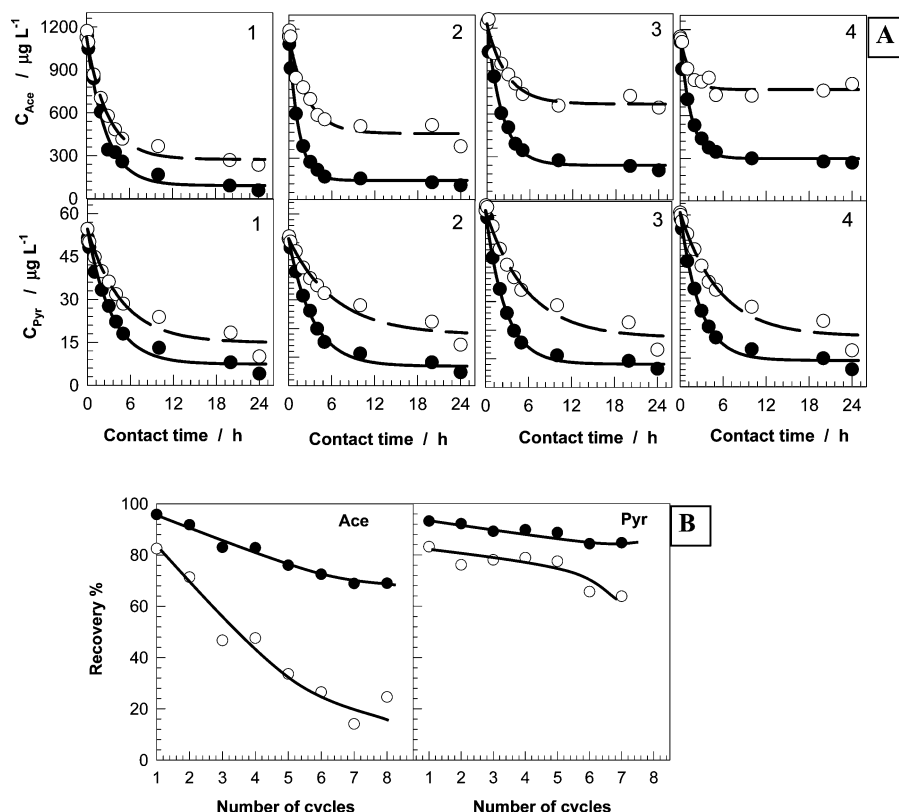


FIGURE 5. A: The concentrations of Ace (C_{Ace} , upper panel) and Pyr (C_{Pyr} , lower panel) vs contact time with -18BR (filled symbols) and PP (open symbols). The curves were calculated using eq 1a. Number of cycles is indicated. **B:** Recovery percentages of Ace (left) and Pyr (right) from seawater as a function of the number of successive removal tests using -18BR (filled symbols) and PP (open symbols). The lines are to guide the eye.

where q_t and q_e are the amounts of PAH absorbed at time t and at equilibrium, respectively, k is the rate constant. Solution of eq 1 gives

$$C_{PAH} = C_0 - q_e(1 - e^{-kt}) \quad (1a)$$

where C_0 is the initial concentration of Ace or Pyr in the solution.

Curves in Figure 5A were calculated by fitting the experimental data to eq 1a. Excellent agreement between the prediction of eq 1a and the experimental data is seen from the figure. Note that assuming a second order sorption kinetics in the form of the equation, $dq_t/dt = K(q_e - q_t)^2$, the results provided a poorer fit to data at shorter contact times ($t < 6$ h). The values of the rate constant k extracted from the fits to the Ace removal data were $0.57 \pm 0.17 \text{ h}^{-1}$ and $0.46 \pm 0.20 \text{ h}^{-1}$, for -18BR and PP sorbents, respectively. From the Pyr removal data, k value found for -18BR sorbent was also larger than that found using PP sorbent ($0.33 \pm 0.04 \text{ h}^{-1}$ versus $0.18 \pm 0.02 \text{ h}^{-1}$) also indicating higher affinity of butyl rubber compared to polypropylene. Moreover, within the limits of the standard deviations, k is slightly increasing function of the number of cycles, probably due to the fact that the absorption of PAH on the surface of the pores increases attractive interactions between PAH molecules and the polymer chains. In Figure 5B, the percentages of the recovery of the PAHs by the sorbents -18BR and PP are shown for eight successive tests. More than 70% Ace recovery could be achieved using -18BR after eight cycles, while it decreased to 10% in case of PP verifying higher efficiency of the rubber sorbent. For the Pyr removal tests, both sorbents were found to be effective, probably due to the low concentration of Pyr in the solution. The results thus suggest that, after taking necessary cautions to not remove natural

hydrophobic chemicals that are important for the biological life (32, 33), the rubber sorbents can be installed to several locations in natural waters to ensure a continuous sorption of those pollutants.

The results in this study demonstrate that the rubber sorbent -18BR is an efficient material for oil spill cleanup as well as for the removal of PAHs from seawaters. The most important feature of the rubber sorbent is its reusability after simple squeezing; its continuous sorption capacity for crude oil is about 3 times the capacity of the PP sorbent, suggesting that -18BR is a better alternative to the widely used PP sorbents by improving the efficiency of oil sorption and the reusability of the sorbent.

Acknowledgments

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Supporting Information Available

Figure S1 shows the sorption kinetics of +17BR sorbent and Table S1 shows uptake capacities of the sorbents within 2 min for pollutants on the water level. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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