Selective Absorption of Aromatic Compounds by Syndiotactic Polystyrene Aerogels

Antonietta Mancuso, Olga Sacco,* Vincenzo Venditto, Wanda Navarra, Pasqualmorica Antico, Christophe Daniel, and Vincenzo Vaiano

Experimental measurements are combined with mathematical modeling in order to investigate the selective absorption of aromatic molecules (benzene, phenol, and toluene) from aqueous solutions by syndiotactic polystyrene (sPS) monolithic aerogels. The experimental results with aqueous solutions of a single aromatic compound show high absorption efficiency for the non-polar compounds (toluene: ≈94%; benzene: ≈77%), whereas phenol (polar compound) is poorly absorbed with an efficiency of about 12%. Furthermore, phenol is no way removed from aqueous phase in presence of NaCl while the water salinity do not affect the absorption efficiency toward toluene and benzene in ternary aqueous solution, evidencing also that toluene is preferentially uptaken by aerogels with a superior kinetic and higher diffusivity constant with respect to benzene. The results obtained in this work underline that sPS aerogels can be interesting materials to selectively recover non-polar compounds from seawater by means of an absorption process.

1. Introduction

Ecological disasters due to accidents involving tankers and cargo cause the release of large volumes of organic compounds in water bodies. For this reason, in the last decades, a great requirement for researchers has been to find more efficient materials for the recovery of crude oil and petroleum products that are spilled at sea.[1–4] In addition, the research attention was also focused on the utilization of the large brine wastewater stream that is produced during oil and gas exploration and production activities. It is a mixture of dissolved and particulate inorganic and organic substances that has intermediate characteristics of fresh water and concentrated saline brine.[5] The produced water composition during recovery of oil and gas is very complex and, it includes hydrocarbons, metals, additives, and solubilized gases (especially

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hydrogen sulfide and carbon dioxide). In particular, these oil-additives contain different recalcitrant organic compounds such as benzene, toluene, ethylbenzene, xylene (BTEX), polycyclic aromatic hydrocarbons (PAHs), phenols, organic acids, waxes, surfactants, and biocides that must be removed in order to not increase the pollution load in water.[1,G,7]

Sorption-based processes are among the most frequently used conventional technologies to recover organic compounds from water.[8] Different classes of materials such as activated carbon, zeolites, clays, and natural organic substances were used as adsorbents.[9–11] However, despite their excellent adsorption performances, they bear some drawbacks including limited working capacity and/or selective removal of target molecules.[12]
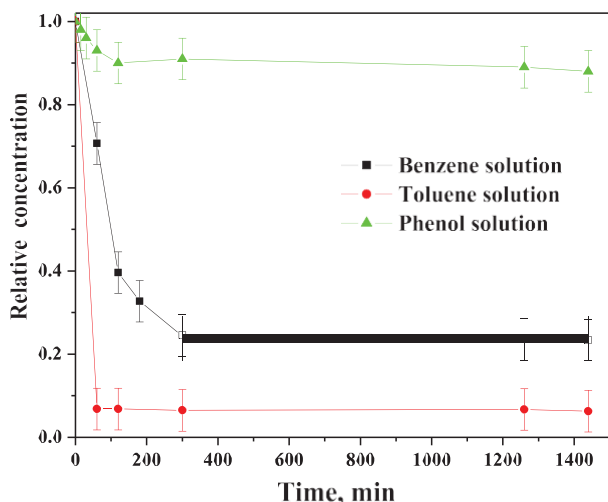
In recent years, polymeric aerogels have been developed as an alternative to common sorption substrates.[13–20] Thermoplastic polymers are considered economic, recyclable, and easy-to-handle materials which can act very effectively in the absorption of organic molecules from aqueous solutions. In this perspective, monolithic aerogels based on thermoplastic polymers such as syndiotactic polystyrene (sPS),[21] being hydrophobic in nature, are able to concentrate the non-polar organic molecules, making easy their recovery.[22] sPS aerogels have the peculiarity that, both the amorphous phase, which has disordered cavities typical of aerogels, and the crystalline phase, when it is one of the sPS porous forms, contribute to aerogel porosity. sPS aerogels, based on a porous crystalline form of this polymer (nanoporous sPS aerogels), allow to trap non-polar compounds both in the perfectly identical and ordered nanocavities of crystal lattice, and in those of random shape and randomly distributed of the amorphous phase.[23] Therefore, sPS aerogels seem to be promising materials to selectively recover some useful aromatic molecules from aqueous solutions. Therefore, in the present study, nanoporous sPS (n-sPS) monolithic aerogels were employed to test the capacity of the polymer to absorb benzene, phenol, and toluene allowing their recovering and potential subsequent utilization. In particular, the sorption kinetics and diffusion apparent constants on benzene, toluene and phenol solution and on binary/ternary systems of these aromatic compounds in liquid phase were evaluated. Furthermore, the influence of water salinity on the absorption process of aromatic compounds by n-sPS aerogels was investigated

Figure 1. Benzene, toluene and phenol relative concentration (C/C_0) in aqueous solution as a function of run time using n-sPS aerogel ($C_{0\,benzene}$ = 50 mg L^{-1}, $C_{0\,toluene}$ = 50 mg L^{-1}, $C_{0\,phenol}$ = 50 mg L^{-1}).

in order to evidence the possible separation and selective recovery of these functional organic compounds from sea water. On the other hand, they are also important chemicals that can have many distinctly different applications in the industrial fields. Indeed, benzene and toluene are major components of gasoline,[24] and they are commonly used as solvents and feedstocks by the chemical industry to produce paints, adhesives, medicines, dyes, detergents, rubbers, and polyurethane resins.[25,2G] For instance, phenols are widely used (in low concentrations) as a disinfectant in household cleaners and as intermediates for industrial synthesis. In industry, phenol is used as a starting material to make plastics, explosives, and drugs.[27]

2. Results and Discussion

2.1. Benzene, Toluene, and Phenol Absorption in n-sPS Aerogels

Absorption tests by n-sPS aerogels were first performed on aqueous solution of a single aromatic compound: benzene (initial concentration: 50 mg L^{-1}), toluene (initial concentration: 50 mg L^{-1}) or phenol (initial concentration: 50 mg L^{-1}), and subsequently, on binary and ternary mixtures of these organic compounds. With the exception of iodine, the sorption capacity of sPS δ-form nanoporous crystalline phase is characterized by a maximum guest molecule/monomer unit molar ratio 1/4. Since, in the used aerogels, sPS crystalline fraction was 40%, all the absorption tests were carried out with a solute molecule/monomer unit ratio larger than 1/11, therefore with an excess of polymer with respect to the solute molecules. Under these experimental conditions, the solute molecules are absorbed only in the nanoporous crystalline lattice of sPS δ-form.[28]

The relative concentration in liquid phase of these organic compounds as a function of run time is displayed in **Figure 1**.

A very high absorption efficiency of toluene ($\approx$94%) and benzene ($\approx$77%) by n-sPS aerogels after 1440 min of run time were found, whereas phenol was poorly absorbed in the same conditions with an efficiency of about 12%.

In agreement to the literature, this result can be explained by the ability of the n-sPS, due to its hydrophobic nature, to absorb non-polar aromatic compounds (benzene and toluene), compared to polar compounds (phenol), in the cavities of its nanoporous lattice.[21,23,29] Benzene and phenol relative concentration, in the binary mixture of such compounds, as a function of absorption time is shown in **Figure 2**a.

The affinity of n-sPS aerogel towards non-polar compounds was more emphasized in presence of a binary aqueous solutions containing benzene and phenol. Indeed, benzene was selectively retained into the cavities of sPS nanoporous lattice with an efficiency equal to 80% while the phenol was absorbed by the aerogel for only 2%. This behavior was further demonstrated with a toluene-phenol binary aqueous solution (Figure 2b) where the decrease of toluene relative concentration was very fast and, therefore, the toluene was largely absorbed by polymer with an efficiency equal to 88% after G0 min of run time, whereas the phenol absorption efficiency was very low and equal to 2.5%.

Furthermore, the absorption capacity of non-polar compounds by n-sPS polymer was investigated in **Figure 3** considering benzene-toluene binary aqueous solution.

Both non-polar aromatic compounds were remarkably entrapped into crystalline nanoporous cavities of sPS. However, toluene was absorbed by n-sPS aerogel more rapidly than benzene obtaining a high absorption efficiency of toluene equal to 84% after G0 min of run time compared to that of benzene (47%). In detail, toluene reached the absorption equilibrium with an efficiency of $\approx$92%, whereas the benzene was uptaken by n-sPS aerogel for about 75% after 1440 min. This result further confirms the very high affinity of n-sPS aerogel toward the absorption of non-polar aromatic compounds.

Moreover, it was examined as the n-sPS polymer selectively absorbs benzene and toluene with respect to phenol considering benzene-toluene-phenol ternary mixture (Figure S1, Supporting Information).

Figure S1 (Supporting Information) underlines as toluene and benzene were absorbed strongly into n-sPS aerogel with sorption efficiency of about 87% and 7G% after 1440 min of treatment time, respectively, while phenol was hardly absorbed in the same conditions, achieving a sorption efficiency of $\approx$2%. In particular, it was possible to notice as the relative concentration of toluene decreases more rapidly than that of benzene already after G0 min, showing a preferential absorption of toluene by n-sPS aerogel also in the case of benzene–toluene–phenol ternary mixture.

Furthermore, it was investigated the influence of salinity on n-sPS aerogel absorption properties using both binary and ternary aqueous solutions. To this purpose, 35 g L^{-1} of sodium chloride (NaCl) aqueous solution was used in order to achieve the typical salinity of sea water.[30] **Figure 4**a shows the behavior of relative concentration with a binary benzene-phenol mixture as a function of run time.

It is possible to observe that, in this case, n-sPS aerogel was not able to absorb phenol from the solution. This result could be explained considering that the addition of NaCl increased the liquid medium ionic strength. Phenol in water is partially dissociated into phenoxide ion and, its solubility increases as the ionic strength increases (salting-out effect).[31]

However, it is worthwhile to note that benzene was absorbed by n-sPS aerogel with an absorption efficiency of approximately
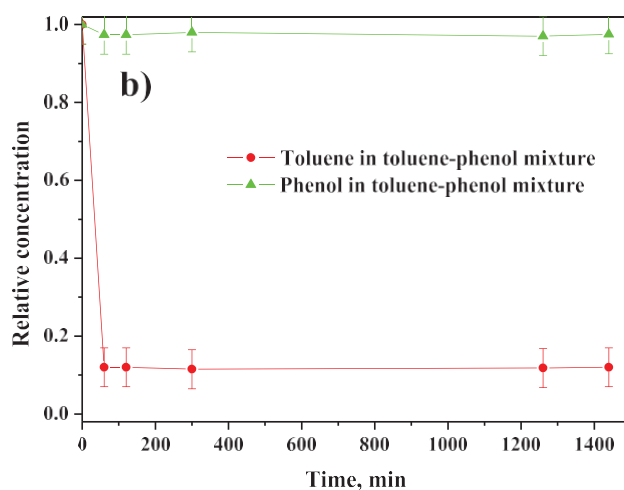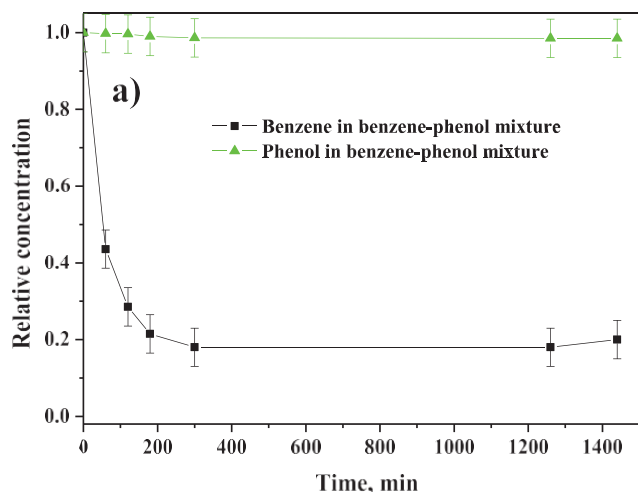
Figure 2. a) Benzene and phenol relative concentration (C/C_0) in benzene-phenol binary mixture as a function of run time using n-sPS aerogel ($C_{0\,benzene}$ = 50 mg L^{-1}, phenol $C_{0\,phenol}$ = 50 mg L^{-1}) and b) Toluene and phenol relative concentration (C/C_0) in toluene-phenol binary mixture as a function of run time using n-sPS aerogel ($C_{0\,toluene}$ = 50 mg L^{-1}, $C_{0\,phenol}$ = 50 mg L^{-1}).
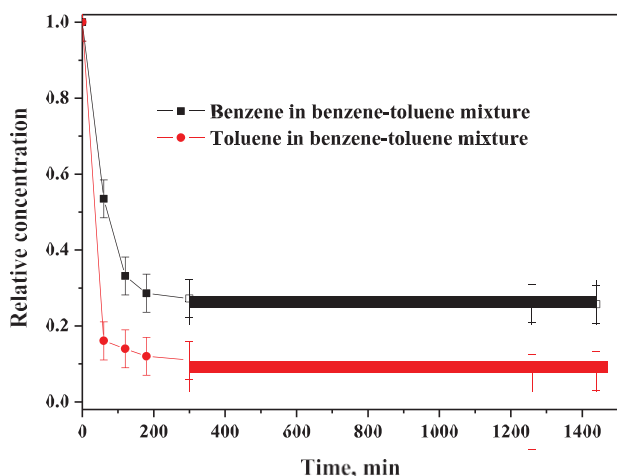
Figure 3. Benzene and toluene relative concentration (C/C_0) in benzene-toluene binary mixture as a function of run time using n-sPS aerogel ($C_{0benzene}$ = 50 mg L^{-1}, $C_{0toluene}$ = 50 mg L^{-1}).

70%. Similar result was obtained considering a binary toluene-phenol aqueous solution in presence of NaCl (Figure 4b).

Figure 4b highlights that n-sPS aerogel absorbed toluene with a high efficiency (99%) after 1440 min of run time. Also in this case, no phenol absorption by n-sPS aerogel was observed.

Figure S2, Supporting Information, displays the behavior of relative concentration with a benzene–toluene binary mixture as a function of run time.

Benzene and toluene were absorbed by n-sPS aerogel with an absorption efficiency equal to about 71% and 85%, respectively. Finally, the behavior of relative concentration as a function of run time was evaluated considering the benzene-toluene-phenol ternary aqueous solution in presence of NaCl (Figure S3, Supporting Information).

No decrease in the relative concentration of phenol was evidenced during all the treatment time. On the other hand, the n-

sPS aerogel retained benzene into the nanocavities of its crystal lattice with the absorption efficiency (7G%), while the toluene was more absorbed after 1440 min of run time, achieving a sorption efficiency of ≈92% in presence of NaCl. All the achieved experimental results are summarized and reported in **Table 1**.

2.2. Evaluation of Diffusivity Constant in n-sPS Aerogel

To calculate the diffusivity coefficient of guest aromatic molecules inside the n-sPS aerogel structure for the tested operating conditions, it was first simulated the concentration profile of each compound as a function of run time, using a pseudo-first-order kinetics model for the absorption process, in agreement with the literature concerning the removal of aromatic compounds from the liquid phase by means of PS nanofibers.[32] In detail, the mathematical model was developed considering that, in the closed pyrex flask, n-sPS aerogel absorbs aromatic compounds from aqueous solution, causing a decrease of their concentration during the run time until to reach the equilibrium conditions.

Therefore, the concentratration of benzene, toluene, and phenol in liquid phase was calculated by the following mass balance (Equation 1):

$$V \frac{dC}{dt} = -k \left(C(t) - C_\infty \right) \cdot m \tag{1}$$

where, C_∞ is equilibrium concentration of benzene, toluene, and phenol (ppm); k is absorption kinetics constant (L g^{-1} min^{-1}); m is n-sPS aerogel mass (g); V is aqueous solution volume (L).

The initial condition is: t = 0 C = C_0.

Equation (1), together with the initial condition, was solved by the Eulero iterative method.

The simulation goal by mathematical model was to identify the absorption constant k by fitting the achieved experimental data. The fitting procedure was done by using the least squares approach. **Figure 5**a compares the model calculations and the
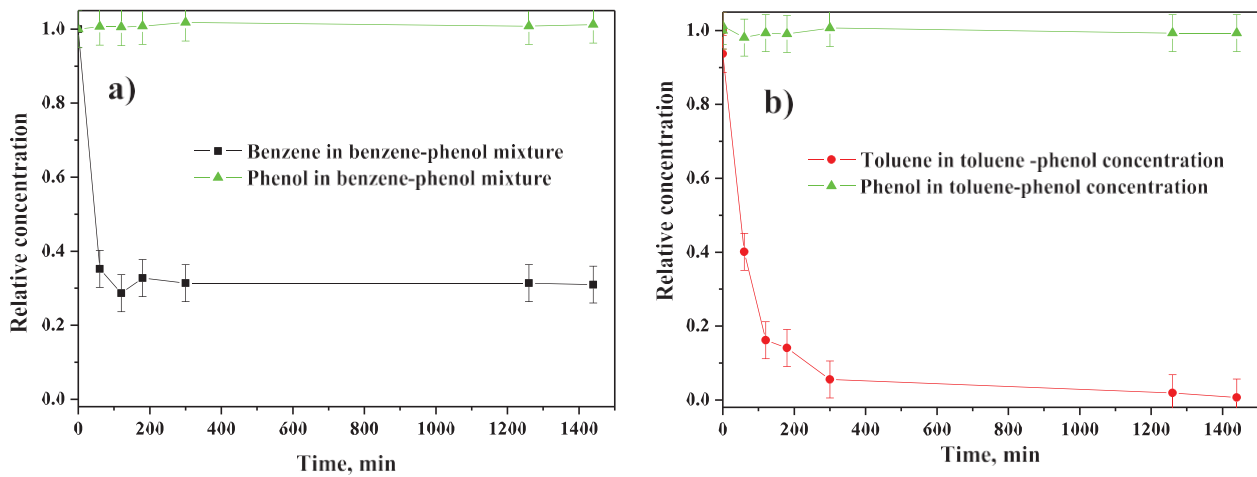
Figure 4. a) Benzene and phenol relative concentration (C/C$_0$) in binary benzene-phenol mixture as a function of run time with the addition of sodium chloride (35 g L^{-1}) using n-sPS aerogel (C$_{0\ benzene}$ = 50 mg L^{-1}, C$_{0\ phenol}$ = 50 mg L^{-1}) and b) Toluene and phenol relative concentration (C/C$_0$) in binary toluene-phenol mixture as a function of run time with the addition of sodium chloride (35 g L^{-1}) using n-sPS aerogel (C$_{0\ toluene}$ = 50 mg L^{-1}, C$_{0\ phenol}$ = 50 mg L^{-1}).

Table 1. Equilibrium absorption efficiency of aromatic compound by sPS aerogel in absence and in presence of NaCl.

Aromatic compound aqueous solution	Equilibrium absorption efficiency	
Benzene	77%	
Toluene	94%	
Phenol	12%	
Binary aqueous mixture		Equilibrium absorption efficiency (NaCl)
Benzene in benzene–phenol	80%	70%
Phenol in benzene–phenol	2%	–
Toluene in toluene–phenol	88%	99%
Phenol in toluene–phenol	2.5%	1%
Benzene in benzene–toluene	75%	71%
Toluene in benzene–toluene	92%	85%
Ternary aqueous mixture		
Benzene in benzene–toluene–phenol	76%	76%
Toluene in benzene–toluene–phenol	87%	92%
Phenol in benzene–toluene–phenol	2%	–

experimental data for the aqueous solutions containing a single aromatic compound. It was important to underline that the concentration values predicted by the model are in agreement with the experimental data in all cases, validating the use of the pseudo-first order type kinetic model for the absorption process. The obtained k values are reported in **Table 2**.

The obtained concentration profiles allow to calculate the amount of aromatic compounds absorbed by the aerogel at any given time t (Equation 2) and when the equilibrium condition is achieved (Equation 3).

$$M\ (t) = \frac{\left(C_0 - C\ (t)\right)}{m} \cdot V \tag{2}$$

$$M_\infty = \frac{\left(C_0 - C_\infty\right)}{m} \cdot V \tag{3}$$

The apparent diffusivity constants (D) take into account the diffusion both in the amorphous phase and in the crystalline phase. D values (Table 2) were calculated from the slopes of linear region of the curves reporting the behavior of $M(t)/M_\infty$ as a function of time square root divided by the macroscopic thickness ($t^{1/2}/L$) of n-sPS aerogel (Figure 5b) to evidence the Fick diffusion phenomena into n-sPS, as described in literature.[21,33]

It is worth noting that n-sPS aerogel showed the highest absorption kinetics for toluene ($k = 4 \times 10^{-2}$ L (g min^{-1})$^{-1}$). However, the aerogel exhibits a phenol absorption kinetic ($k = 4.2 \times 10^{-3}$ L (g min^{-1})$^{-1}$) slightly higher than that obtained for benzene ($k = 3.4 \times 10^{-3}$ L (g min^{-1})$^{-1}$). Similarly, the diffusivity constant found for phenol ($D = $ G.2 $\times 10^{-3}$ cm^2 s^{-1}) is a little higher than the diffusivity value obtained for benzene ($D = 5.5 \times 10^{-3}$ cm^2 s^{-1}). This result evidences that, despite it is absorbed in lower extent
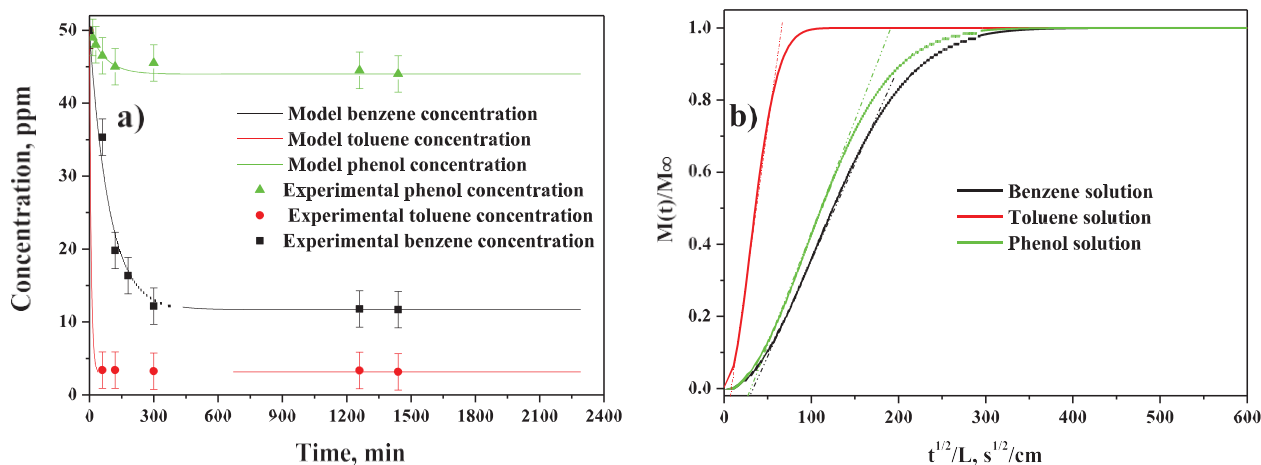
Figure 5. a) Comparison between model calculation and experimental data to find the model absorption constant k for the aqueous solutions containing a single aromatic compound ($C_{0\ benzene}$ = 50 mg L^{-1}, $C_{0\ toluene}$ = 50 mg L^{-1}, $C_{0\ phenol}$ = 50 mg L^{-1}) and b) Estimation of diffusivity constants for aqueous solution of aromatic compound.

Table 2. Absorption kinetics and apparent diffusivity constants for aromatic compounds aqueous solution in n-sPS aerogel.

Aromatic compound aqueous solution	Absorption kinetics constant (k) [L (g min^{-1})$^{-1}$]	Diffusion constant (D) [cm^2 s^{-1}]
Benzene	3.4×10^{-3}	5.5×10^{-3}
Toluene	4×10^{-2}	1.9×10^{-2}
Phenol	4.2×10^{-3}	6.2×10^{-3}

$C_{0\ benzene}$ = 50 mg L^{-1}, $C_{0\ toluene}$ = 50 mg L^{-1}, $C_{0phenol}$ = 50 mg L^{-1}.

with respect to benzene and toluene, phenol is able to diffuse into the crystalline phase of n-sPS aerogel when it is the only aromatic compound present in the aqueous medium.

The mathematical kinetic modeling was also performed on binary aqueous mixtures (Figure S4, Supporting Information).

The trend of curves in Figure S4, Supporting Information, evidenced as the concentration of non-polar aromatic compounds decreased progressively over the time indicating that benzene and toluene were widely absorbed by n-sPS aerogel, whereas phenol, being a polar aromatic compound and, therefore, being not affine with the n-sPS hydrophobic nature,[21,22,34] poorly entered into the polymer crystal structure. This result was also confirmed by the curves related to the behavior of $M(t)/M_\infty$ (Figure S5, Supporting Information) since for benzene and toluene, $M(t)/M_\infty$ achieved the equilibrium value at shorter times than that of phenol.

The values of k and D constants for binary aqueous solutions are reported in **Table 3**.

The data collected in Table 3 evidence as n-sPS aerogel more rapidly absorbed benzene or toluene considering their binary mixture with phenol while, in presence of toluene and benzene aqueous mixture, toluene was preferentially uptaken by the aerogel with a superior kinetic ($k = 1.0 \times 10^{-2}$ L (g min^{-1})$^{-1}$) and higher diffusivity constant ($D = 8.7 \times 10^{-3}$ cm^2 s^{-1}) with respect to benzene.

The mathematical kinetic modelling and the behaviour of $M(t)/M_\infty$ were also performed and analyzed for binary aqueous mixtures in presence of NaCl to calculate absorption kinetic con-

stants and the apparent diffusivity constants, respectively. The obtained results are displayed in **Table 4**.

As previously observed from Figure 2 and according to literature[31] no absorption of phenol by sPS is observed with the addition of NaCl in binary aqueous solution. Therefore, absorption kinetics and diffusivity constants for phenol are undetectable. On the other hand, an improvement of absorption kinetic and diffusion phenomenon for both non-polar aromatic compounds was revealed by adding NaCl in binary aqueous solutions (Table 4). Finally, the simulation through mathematical model was also performed for a benzene-toluene-phenol ternary mixture both in the absence and in presence of NaCl with the aim to estimate k and D values (**Table 5**).

Figure 6a shows the decrease of benzene and toluene concentration during the time indicating that n-sPS aerogel tends to preferentially absorb non-polar aromatic compounds and, in particular toluene with higher absorption rate ($k = 1 \times 10^{-2}$ L (g min^{-1})$^{-1}$) (Table 5). The absorption of phenol by sPS is negligible proving again the low affinity of polymer toward polar compounds.

This behavior was also confirmed by trend of $M(t)/M_\infty$ for toluene (Figure Gb) that achieves the equilibrium at slightly lower times than benzene with a diffusivity constant for toluene equal to about 9.0×10^{-3} cm^2 s^{-1} and for benzene of $\approx 7.8 \times 10^{-3}$ cm^2 s^{-1} (Table 5).

The data reported in Table 5 evidence that phenol was not absolutely removed from aqueous phase both in presence and in absence of NaCl. Additionally, it is worthwhile to note that

Table 3. Absorption kinetics and apparent diffusivity constants for binary aqueous mixture in n-sPS aerogel.

Binary aqueous mixture	Absorption kinetic constant (k) [L (g min^{-1})$^{-1}$]	Diffusion constant (D) [cm^2 s^{-1}]
Benzene in benzene-phenol	6.4×10^{-3}	7.0×10^{-3}
Phenol in benzene-phenol	4.3×10^{-4}	2.3×10^{-3}
Toluene in toluene-phenol	4.5×10^{-2}	1.9×10^{-2}
Phenol in toluene-phenol	4.8×10^{-4}	2.4×10^{-3}
Benzene in benzene-toluene	5.4×10^{-3}	6.5×10^{-3}
Toluene in benzene-toluene	1.0×10^{-2}	8.7×10^{-3}

$C_{0\,benzene} = 50$ mg L^{-1}, $C_{0\,toluene} = 50$ mg L^{-1}, $C_{0phenol} = 50$ mg L^{-1}.

Table 4. Absorption kinetics and apparent diffusivity constants for binary aqueous mixture in presence of NaCl with n-sPS aerogel.

Binary aqueous mixture	Absorption kinetics constant (k) [L (g min^{-1})$^{-1}$]	Diffusivity constant (D) [cm^2 s^{-1}]
Benzene in benzene–phenol	1.5×10^{-2}	1.1×10^{-2}
Phenol in benzene–phenol	–	–
Toluene in toluene–phenol	6.1×10^{-3}	7.4×10^{-3}
Phenol in toluene–phenol	–	–
Benzene in benzene–toluene	7.8×10^{-3}	8.0×10^{-3}
Toluene in benzene–toluene	1.0×10^{-2}	9.1×10^{-3}

$m_{NaCl} = 35$ g L^{-1}, $C_{0\,benzene} = 50$ mg L^{-1}, $C_{0\,toluene} = 50$ mg L^{-1} $C_{0phenol} = 50$ mg L^{-1}.

Table 5. Absorption kinetics and apparent diffusivity constants for benzene–toluene–phenol ternary aqueous solution in n-sPS aerogel with and without NaCl presence.

Ternary aqueous mixture	Absorption kinetics constant (k) [L (g min^{-1})$^{-1}$]	Diffusivity constant (D) [cm^2 s^{-1}]
Benzene in benzene–toluene–phenol	7.6×10^{-3}	7.9×10^{-3}
Toluene in benzene–toluene–phenol	1×10^{-2}	9.0×10^{-3}
Phenol in benzene–toluene–phenol	–	–
Benzene in benzene-toluene-phenol with NaCl	7.2×10^{-3}	7.8×10^{-3}
Toluene in benzene–toluene–phenol with NaCl	1×10^{-2}	9.2×10^{-2}
Phenol in benzene–toluene–phenol with NaCl	–	–

$C_{0\,benzene} = 50$ mg L^{-1}, $C_{0\,toluene} = 50$ mg L^{-1}, $C_{0phenol} = 50$ mg L^{-1}.
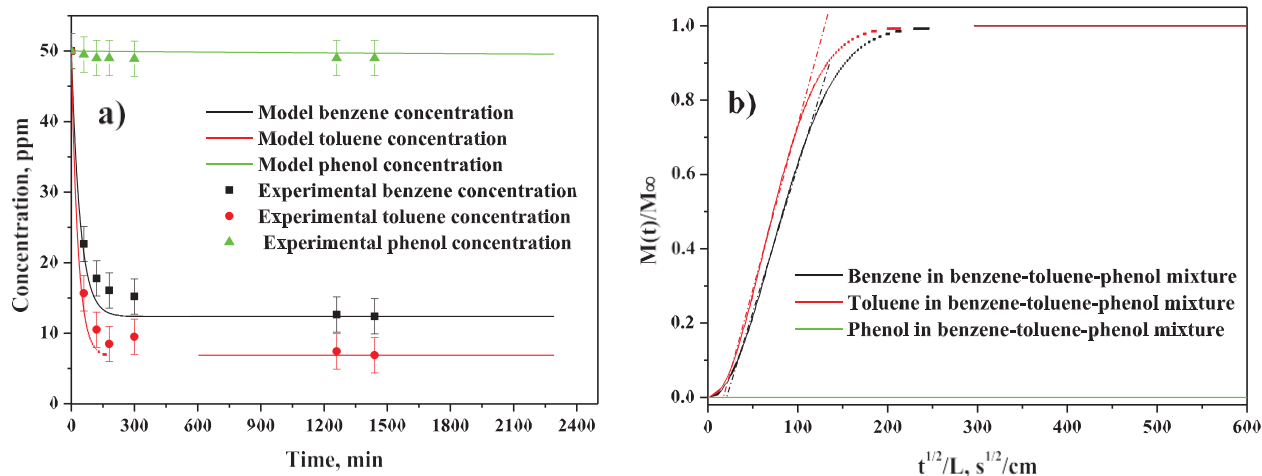
Figure 6. a) Comparison between model calculation and experimental data to find the model absorption constant k for benzene–toluene–phenol ternary aqueous solution ($C_{0benzene} = 50$ mg L^{-1}, $C_{0\,toluene} = 50$ mg L^{-1} $C_{0phenol} = 50$ mg L^{-1}) and b) Estimation of diffusivity constants for benzene–toluene–phenol ternary aqueous solution.

the addition of NaCl did not affect the sPS absorption properties towards toluene and benzene in ternary aqueous solution (being their *D* and *k* values in presence of NaCl very similar to those achieved when such salt is absent in the liquid medium), thus evidencing that n-sPS aerogel may be a suitable material for the possible recovery of these high value-added compounds from seawater through a selective absorption process.

3. Conclusions

In the present study, nanoporous sPS (n-sPS) monolithic aerogels were employed to test, for the first time, their capacity of selectively absorbing aromatic molecules (benzene, phenol and toluene) and their mixtures from aqueous solutions both in the absence and in presence of NaCl. The n-sPS aerogels were prepared starting from syndiotactic polystyrene gels, obtained by dissolving the polymer in chloroform. After this step, the aerogels are obtained by supercritical carbon dioxide treatment, which extracts the solvent avoiding the gel collapsing. Experimental results in the absence of NaCl showed that n-sPS aerogel absorbed phenol in very low extent, whereas higher toluene and benzene absorption efficiency was observed in the same conditions. These results can be explained considering the high affinity of sPS aerogels toward non-polar compounds (toluene and benzene) and its very low affinity with polar compounds (phenol). In presence of NaCl in the liquid medium, n-sPS aerogel does not absorb phenol, possibly because the addition of NaCl increased the solution ionic strength, leading to the increase in the solubility of the phenoxide ions (formed by the dissociation of phenol in water) in the aqueous phase (salting-out effect).

Kinetic studies showed that the absorption of n-sPS aerogels followed pseudo first-order model for all the tested guest molecules and for all the investigated operating conditions. The obtained values of kinetic constants evidenced as n-sPS aerogels more rapidly absorbed benzene or toluene considering their binary mixture with phenol while, in presence of toluene and benzene aqueous mixture, toluene was preferentially uptaken by the aerogel with a superior kinetic because of the lower solubility of toluene in water with respect to benzene. Moreover, diffusivity constants of the tested aromatic compounds into n-sPS crystalline structure were evaluated, showing that, despite it is absorbed in a lower extent with respect to benzene and toluene, phenol is able to diffuse into the nanoporous crystalline phase of n-sPS aerogels when it is the only aromatic compound present in the aqueous medium. However, for a benzene-toluene-phenol ternary mixture, phenol was not absolutely removed from aqueous phase both in presence and in absence of NaCl. Furthermore, the addition of NaCl did not affect the n-sPS absorption properties towards non-polar compounds (toluene and benzene) in ternary aqueous solution (being their diffusivity and kinetic constant values in presence of NaCl very similar to those achieved when such salt is absent in the liquid medium). Therefore, the obtained results underline that n-sPS aerogels may be interesting materials to selectively separate some useful non-polar aromatic compounds from seawater through an absorption process.

4. Experimental Section

Chemicals and Reagents: Aerogels synthesis was made using sPS which was manufactured by Idemitsu Kosan Co., Ltd. under the trademark XAREC© 90ZC. The polymer was highly stereoregular with a content of syndiotactic triads over 98% (13C nuclear magnetic resonance data). Benzene (CAS number 71-43-2) with purity greater than or equal to 99.7%, phenol (CAS number 108-95-2) with purity greater than to 99% and toluene (CAS number 108-88-3) with purity greater than to 99.8% were purchased from Sigma Aldrich. Water (CAS number 7732-18-5) was acquired from Carlo Erba with purity greater than or equal to 99.9%. Chloroform used as solvent without further purification to prepare the gels were purchased from Aldrich. Sodium chloride (CAS number 7647-14-5) with purity greater than to 99% was acquired from Sigma Aldrich.

n-sPS Aerogel Preparation: sPS polymer was dispersed in chloroform inside a hermetically sealed test tube at 100°C until complete polymer dissolution. The obtained mixture was sonicated at room temperature until complete gelation of the polymer and then cooled to produce a gel. The monolithic aerogels (D = 0.5 cm and h = 5 cm) were obtained by treating the gels with supercritical carbon dioxide (by using an ISCO SFX 220 extractor), for 4 h at T = 40°C and P = 20 MPa, to extract the solvent. The obtained aerogel was deeply characterized from physical-chemical point of view in our previous papers.[35,36] In summary, X-ray diffraction pattern shows typical signals of sPS delta crystal form (n-sPS) in the 2θ range 8–25° with a degree of crystallinity of c.a. 40% and BET analysis evidences a high specific surface area equal to 260 m^2 g^{-1}.

Experimental Setup for Absorption Tests: The absorption tests were performed in 35 mL aqueous solution containing benzene (initial concentration: 50 mg L^{-1}), toluene (initial concentration: 50 mg L^{-1}) and phenol (initial concentration: 50 mg L^{-1}) using 3 g L^{-1} of n-sPS aerogel under continuous stirring for 1440 min to obtain absorption equilibrium of aromatic compounds. All the absorption tests were performed using a closed pyrex flask filled with the aqueous solutions maintained under continuous stirring. During each test, liquid samples were withdrawn from the pyrex flask at different times and analyzed quantitatively by an Agilent gas chromatograph (model 7820 A) equipped with a flame ionization detector (FID) to evaluate the benzene, toluene, and phenol concentration.

GC separation was achieved with a DB Heavy Wax fused-silica capillary column (30 m × 0.35 mm i.d. × 0.25 μm) under the following conditions: column temperature 40–300°C (40°C held 2 min, rate 5°C min^{-1} to 90°C, rate 20°C min^{-1} to 250°C, held 10 min); helium at a constant flow rate of 1 mL min^{-1}; injection port operated at 10:1 split mode; temperature of injector and detector at 180°C and 300°C, respectively. The chromatographic conditions were: oven temperature 35°C; flow rate 0.8 mL min^{-1}; injection volume 50 μL and UV detector at 270 nm.

Supporting Information

Supporting Information is available

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the cor- responding author upon reasonable request.

Keywords

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