ORIGINAL RESEARCH ARTICLE

Sulfonated mesoporous polystyrene-1D multiwall carbon nanotube nanocomposite as potential adsorbent for efficient removal of xylene isomers from aqueous solution

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ABSTRACT

Xylene isomers are notorious chemical hazards, and their efficient removal from water solutions is still challenging. The current study reports a polymer nanocomposite as a potential adsorbent for successfully removing dissolved xylene isomers from contaminated water. Polystyrene-1D multiwall carbon nanotube nanocomposite (PS-MWCNT) adsorbent was prepared using the one-step bulk polymerization method. Mesoporous PS-MWCNT was prepared using the nano-crystallization phase separation method. The sulfonation of the mesoporous PS-MWCNT nanocomposites was carried out by treating the samples with concentrated sulfuric acid at elevated temperatures. The sulfonated PS-MWCNT (HO_3S-PS-MWCNT) was found to be a potential adsorbent for dissolved xylene isomers from water solution. In addition, the HO_3S-PS-MWCNT can be efficiently recycled for up to 10 consecutive cycles with negligible decline in adsorption values. The exhibited equilibrium adsorption, rate of adsorption, and rapid regeneration of the HO_3S-PS-MWCNT are clear indications for the possibility of practical utilization of these adsorbents in large-scale water treatment plants.

Keywords: polystyrene; carbon nanotube; nanocomposites; sulfonation; adsorption; xylene isomers

1. Introduction

Produced water is oil-contaminated water that is co-produced in huge quantities during oil and gas production[1,2]. The volume of water produced by the oil/gas industry does not remain constant and rapidly increases yearly[3,4]. As per the US Department of Energy, the annual production of produced water exceeds about 882 billion gallons only from the USA and about 2100 billion gallons from the rest of the world[5]. Though various efforts exist to reduce the produced water from the wells[6–12], excessive water production remains one of the biggest challenges. The high volume of the produced water demands immediate action in constructing rapid and effective treatment plants[6–9]. The water produced by gas industries contains high amounts of low-molecular-weight aromatic hydrocarbons, including saturated aliphatic hydrocarbons, polycyclic aromatics, organic acids, phenols, toluene, xylenes, and volatiles[10–13]. Notably, xylenes are one of the potentially hazardous chemicals and pose a significant threat to human health[14,15]. The excessive health risks caused by the xylene isomers are well documented in the recent literature[16–18].

Conventional contaminated water treatment technologies such as coagulation, flocculation, and gravity separations do not meet the high

purity requirement of the water treatment process[19,20]. The membrane separation processes, such as ultrafiltration (UF)[21,22] and nanofiltration (NF)[23–25], are being applied for the removal of macro/micro oil droplets present in produced water. Removing dissolved oil and organic components at their saturated concentration is still challenging[26,27]. Among the possible techniques for water treatment, adsorption by porous solids is prominent as it is one of the most efficient ways to treat organic compounds in contaminated water[19,28–31]. Adsorption has the advantage over the other simple design methodologies and low investment[32]. The search for low-cost adsorbents with high adsorption capacities has recently intensified[33–36]. There has been a constant demand for solid-phase adsorbents with improved adsorptive capacity, selectivity, stability, and analyte recoveries[37,38]. The search for a new porous solid seems to be a never-ending task, as the current efforts are at finding an optimum adsorbent for specific applications[39–42].

Since there is a growing tendency to use adsorption as an effective tool for removing dissolved aromatic hydrocarbons, discovering new porous materials exhibiting very high adsorption capacity with rapid regeneration characteristics is inevitable. Moreover, numerous absorbent polymers or porous polymer-based systems are exploited in oil and gas[9,43–57] and other industries[54,58–65]. Carbon nanostructures-based composite adsorbents are emerging as potential adsorbents for removing dissolved organic compounds from water solutions[66–68]. However, their adsorption capacity values and recyclability can further be improved. These issues can be successfully addressed by suitable processing of the composite adsorbents into mesoporous structured materials and subsequent hydrophilic surface modifications. Moreover, the application of polymers are well-known in various stages of oil and gas extraction processes[43,47,55,57,58,69–76]. Therefore, we have developed a nano-crystallization phase separation approach for fabricating mesoporous polymers from various commodity polymers[12,13,39,41,77]. These unique mesoporous polymers that contain high specific surface area and narrow pore distribution also exhibit excellent adsorption properties of different aromatic compounds dissolved in water and, at the same time, can be rapidly regenerated for repeated use in several cycles. The present study evidences the ultrafast adsorption and desorption dynamics of xylene isomers by the hydrophilically modified mesoporous PS-MWCNT composites.

2. Experimental

2.1. Materials

Polystyrene (M_w 280,000) and multiwall carbon nanotube (MWCNT, 50–90 nm diameter, >95% carbon basis) were purchased from Sigma Aldrich. Azoisobutyronitrile (AIBN, 98% purity) was also purchased from Sigma Aldrich. N, N-dimethylformamide (DMF, M_w 73.09, GC purity 99.7%), methanol (M_w 32.04, GC purity 99.8%), sulfuric acid (96% GC purity), and ethanol (99.5% GC purity) was obtained from Loba Chemie. All these chemicals were as received and without any further purification.

2.2. Methods

2.2.1. Synthesis of PS-1D MWCNT nanocomposite

The PS-1D MWCNT was synthesized using a one-step, in-situ bulk polymerization method. To prepare the sample, a mixture of 5 mL of styrene and 0.005 g of MWCNT was taken in a test tube and sonicated for 30 min. for complete mixing. Then, 0.005 mg of AIBN was added and sonicated for another 30 min. Afterwards, the mixture's temperature was raised to 70 ℃ for polymerization. The sample is kept at the same temperature for 72 h. Then, the sample is thoroughly washed with hot methanol (45 ℃) several times and dried in a vacuum oven to remove non-reacted monomers, oligomers, and homopolymers.

2.2.2. Mesoporous PS-1D MWCNT nanocomposite

To prepare mesoporous PS-1D MWCNT nanocomposite, the sample is firstly dissolved in DMF (40 wt.% of polymer nanocomposite). Then, the solution is immersed into liq. N_2 and allowed to stand for 15 min to

make the deep-frozen polymer nanocomposite solution. Excessive methanol that is pre-cooled to –80 °C was added to the above-frozen solution and subsequently transferred to a refrigerator (–80 °C) and kept for five days for the complete exchange of the DMF (solvent) with methanol (non-solvent). Then, the sample was brought to room temperature, and the excessive methanol was removed. Finally, the sample was dried in a vacuum chamber for 12 h.

2.2.3. Sulfonation of mesoporous PS-1D MWCNT nanocomposite (HO₃S-PS-MWCNT)

To prepare HO$_3$S-PS-MWCNT, the mesoporous Mesoporous PS-1D MWCNT Nanocomposite samples were treated with an excess of concentrated sulphuric acid (H$_2$SO$_4$) at 70 °C for 2 h. After the preferred reaction time, the samples were removed from the acid and subsequently washed in anhydrous methanol several times, followed by D.I. water until the pH of the washed water was around 6–7. This step ensures the complete removal of the sulfuric acid from the polymer samples. After washing, the samples were dried in a vacuum oven.

2.2.4. Determination of ion-exchange capacity (IEC) of mesoporous HO₃S-PS-MWCNT

The mesoporous HO$_3$S-PS-MWCNT was characterized by its ion exchange capacity values (IEC). The IEC of a sulfonated polymer is defined as the number of replaceable H$^+$ ions. This IEC value of the sulfonated polymer is directly related to the extent of substitution of sulfonic acid groups. When the sulfonated polymer was added to the dilute NaCl solution, the Na$^+$ ion replaced the H$^+$ ion from the introduced sulfonic acid group (-SO$_3$H) onto the polymer surface. If the replaced H$^+$ ion is back titrated with diluted NaOH solution, we can estimate the IEC of the sulfonated polymer. To determine the IEC, 100 mg of sulfonated HO$_3$S-PS-MWCNT was treated with 10 mL of 1M NaCl solution in a 50 cc glass bottle and stirred for 24 h. Then, a pH meter removed the sample from the NaCl solution and titrated it with 0.1M NaOH. The IEC can be determined by Equation (1) from the required titration volume.

$$IEC = \frac{[Vol.\,of\,NaOH\,(ml)\ \times Conc.\,of\,NaOH\,(M)]}{Weight\,of\,dried\,polymer\,(g)} \tag{1}$$

2.2.5. Adsorption of xylene isomers from aqueous solution

Equilibrium adsorption

A 0.05 wt.% of xylene isomers stock solution was prepared using D.I. water at room temperature and diluted to other subsequent experimental concentrations. In a typical equilibrium adsorption experiment, 70 g/L of mesoporous HO$_3$S-PS-MWCNT was used, whereas the xylene isomer solutions of different concentrations of 1 mg/L to 500 mg/L were used. Before use as an adsorbent, the mesoporous HO$_3$S-PS-MWCNT was added to ethanol to remove the air inside the pores. Then, the polymer is filtered and used. The adsorption reaction has been carried out at different temperatures of 30 °C and 50 °C. The mesoporous HO$_3$S-PS-MWCNT was added to the xylene isomers solution, which was continuously stirred and kept in a water bath at the abovementioned temperatures. A decrease in the concentration of xylene isomer was monitored using UV-Vis spectroscopic measurements. The adsorption experiment was stopped by filtering off the adsorbents from the solution when no more decrease in the solution concentration was observed.

Adsorption kinetics

The xylene isomer solution of 500 mg/L was used to study the adsorption kinetics. 70 g/L of sulfonated polystyrene was used in each of the experiments. The kinetics of xylene isomer adsorption onto the sulfonated mesoporous HO$_3$S-PS-MWCNT was investigated at different temperatures of 30 °C and 50 °C. The adsorbent was added to the xylene isomers solution, continuously stirred, and kept in the water bath at the above temperatures. At an equal time interval (every 10 min), a decrease in the concentration of xylene isomers was monitored using UV-Vis spectroscopic measurements. The adsorption experiment was stopped when no more

reduction in the solution concentration was observed.

Desorption kinetics

The desorption kinetics was studied by adding the xylene-adsorbed mesoporous HO_3S-PS-MWCNT in hot ethanol (60 °C). After adding the adsorbed polymer samples to the desired desorption medium, the increase in the HO_3S-PS-MWCNT concentration in the desorbing liquid was monitored by UV-Vis spectra.

2.3. Characterization

Bulk and mesoporous morphologies of the samples were analyzed using Field-Emission Scanning Electron Microscopy (FE-SEM, JEOL JSM-7401F). The surfaces of the examined sample were coated with Au nanoparticles to avoid charging. The images were recorded at an accelerating voltage of 10 kV.

3. Results and discussion

3.1. Fabrication of mesoporous PS-1D MWCNT nanocomposite

The mesoporous PS-1D MWCNT nanocomposite was prepared using the nano-crystallization-induced phase separation method (flash-freezing route). When the temperature of the polymer solution is rapidly decreased to –196 °C (liq. N_2), the solvent molecules are frozen among the polymer chains. If the temperature of the frozen polymer solution is slowly increased to a temperature (–80 °C) that is lower than the solvent's melting point, then nano-crystallization of the solvent molecules occurs. Consequently, the entangled polymer chains will be expelled due to the nano-crystallization of the solvent molecules while the forming network structure, in turn, effectively suppresses the further growth of the solvent crystals. A mesoporous structure can be obtained by extracting the size-controlled solvent crystals with a non-solvent. **Figure 1** shows the FE-SEM images of PS-MWCNT (as-prepared), mesoporous PS-MWCNT, and sulfonated PS-MWCNT (HO_3S-PS-MWCNT) samples. As evident from **Figure 1(b)**, the PS-MWCNT exhibited a disordered mesoporous structure, while the as-prepared one showed a non-porous structure (**Figure 1(a)**).
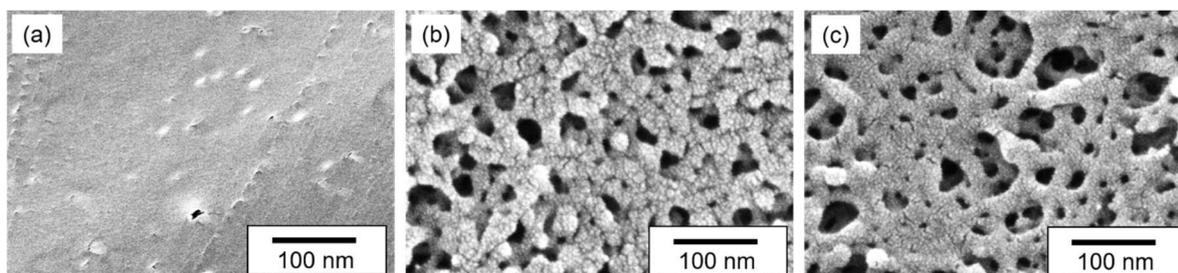
Figure 1. FE-SEM images of **(a)** as prepared PS-MWCNT; **(b)** mesoporous PS-MWCNT; and **(c)** HO_3S-PS-MWCNT.

The samples' pore sizes can be evaluated from the SEM images. The pore sizes of the mesoporous PS-MWCNT samples range from 10 nm to 25 nm. The observed mesoporous structures of PS-MWCNT support the proposed nano-crystallization-induced phase separation mechanism.

3.2. Sulfonation of mesoporous PS-1D MWCNT nanocomposite

The hydrophobicity of mesoporous PS-1D MWCNT nanocomposite highly limits its applications in aqueous mediums, but it can be hydrophilically modified to have good contact with water. The hydrophilic surface modifications of the mesoporous PS-1D MWCNT nanocomposite can be achieved by controlled sulfonation reactions without much affecting the mesoporous morphology of the polymer by treating it with a mild sulfonating agent like sulfuric acid. Electrophilic substitution introduced the hydrophilic sulfonic acid ($-SO_3H$) groups in the mesoporous PS-1D MWCNT nanocomposite surface phenyl group. The mesoporous PS-1D MWCNT nanocomposite will predominantly be homogenously sulfonated on the polymer surface in

this methodology. The extent of surface modification by sulfonation reactions was determined as ion-exchange capacity (IEC). The sulfonation conditions were optimized based on the requirement of a minimal loss in the specific surface area and the pore structure of the mesoporous polystyrene. The optimized condition was the reaction of HO_3S-PS-MWCNT with conc. H_2SO_4 for 2 h at 70 ℃, and the corresponding IEC value was found to be 0.011 meq/g. The sulfonated mesoporous PS-1D MWCNT nanocomposite shows excellent contact with water in this condition. **Figure 1(c)** shows the mesoporous morphology of the HO_3S-PS-MWCNT samples. Interestingly, the mesoporous structure of the sample was not much affected due to the sulfonation reactions.

3.3. Equilibrium adsorption

Figure 2 shows the equilibrium adsorption conditions of xylene isomers' adsorption by HO_3S-PS-MWCNT. The adsorption reaction was carried out at different times and with varying amounts of HO_3S-PS-MWCNT. As evident from **Figure 2**, the amount of xylene adsorption is increased with the increase in HO_3S-PS-MWCNT adsorbents and reaches saturated adsorption with 70 g/L of adsorbent with >99% removal. Therefore, it can be said that the optimized amount of HO_3S-PS-MWCNT was 70 g/L for the treatment of saturated concentration of dissolved xylene isomers in water. On the other hand, the amount of adsorption also increases with time. As shown in **Figure 2**, with two h of adsorption, % of removal reached a maximum of only 85%, whereas that of 4 h of adsorption time reached a maximum of >99%. Also, the adsorption time of 8 h exhibited >99% of removal. Therefore, the minimum time to reach the equilibrium adsorption of xylene isomers from water solution with optimized 70 g/L of adsorbent can be four h. The efficient and fast adsorption of xylene molecules to the HO_3S-PS-MWCNT adsorbent is correlated to the phenyl-phenyl (hydrophobic) interaction of xylene and styrene moiety of the polymeric chains.
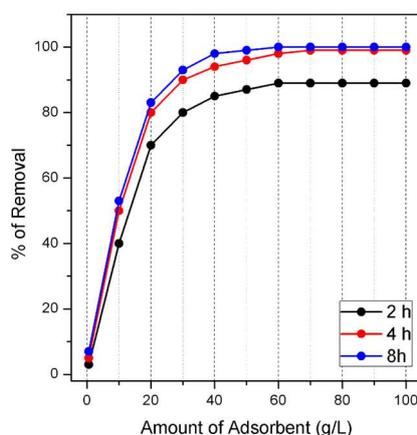
Figure 2. Adsorption of xylene isomers from water solution with different amounts of HO_3S-PS-MWCNT adsorbent and contact times.

3.4. Adsorption kinetics and effect of temperature

Figure 3 shows the adsorption kinetic curves of xylene isomers from water solutions at different temperatures of 30 ℃ and 50 ℃. The kinetic studies have been carried out with the optimized adsorbent amount of 70 g/L. Compared to 30 ℃, the adsorption rate is higher at 50 ℃ while the overall adsorption amount was decreased at higher temperatures. For instance, the maximum % of removal has reached >99% at 30 ℃ (in 4 h of contact time) while it was only 85% at 50 ℃ (in 2 h of contact time). At lower temperatures, the adsorption process is initially controlled by the concentration gradient (primary diffusion of xylene into the mesopores) of xylene molecules. Afterward, the adsorption process occurs due to the secondary diffusion of xylene molecules into the hydrophobic polymeric chains. However, the diffusion rate into mesopores is highly favored at higher temperatures due to the increased kinetic energy of the xylene molecules compared to that at lower temperatures.
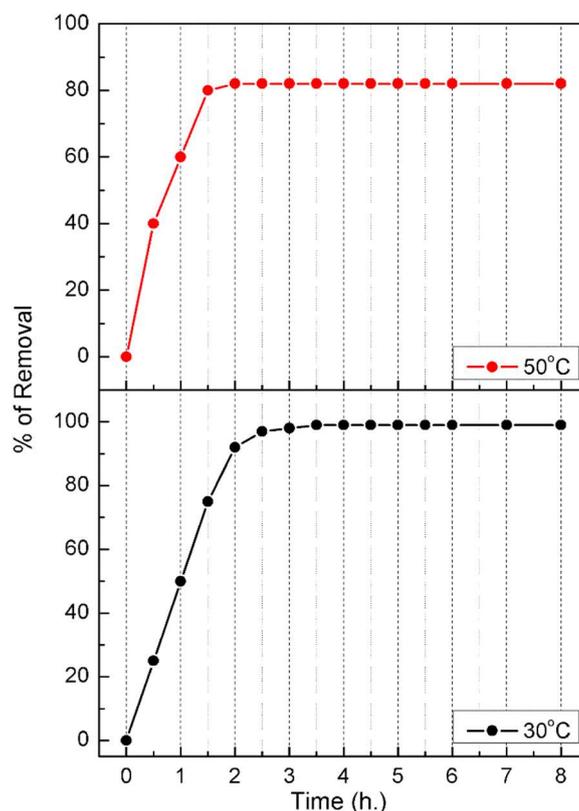
Figure 3. Adsorption kinetics of xylene isomers from water solution at different contact times and temperatures.

Table 1 shows a comparative performance of xylene removal by various solid-phase adsorbents reported in the literature against the ones reported in this study. As evident from **Table 1**, HO_3S-PS-MWCNT exhibited higher adsorption capacities (499 mg/g) and % of removal (>99%) for xylene adsorption in comparison to the other adsorbents reported in the literature.

Table 1. Xylene removal efficiency by various adsorbents.

Adsorbent	Adsorption capacity (mg/g)	% of removal	Reference
Porous biomass carbon foam	322.36	98	[78]
Polyvinyl chloride-SiO$_2$-melamine sponge	-	93	[79]
Cellulose modified Fe$_3$O$_4$ nanoparticles	595	53	[80]
Single walled-carbon nanotubes	210	-	[81]
HO$_3$S-PS-MWCNT	499	>99	This study

3.5. Recyclability

Figure 4 shows recyclability curves of HO$_3$S-PS-MWCNT adsorbent for ten consecutive adsorption-desorption cycles. After each cycle of adsorption, the desorption of adsorbed xylene molecules or regeneration of the adsorbent was carried out by treating the adsorbent in hot ethanol at 60 °C. As evident from **Figure 4**, the reduction in the amount of adsorption after each adsorption cycle is only marginal. Interestingly, the adsorbent showed >99% of removal at the first adsorption cycle, and the same adsorbent exhibited >97% of removal after the 10th cycle. The complete desorption or regeneration characteristics of adsorption sites of any porous solid in a given adsorption system are essential for their practical applications. Therefore, the demonstrated rapid regeneration of HO$_3$S-PS-MWCNT adsorbents by simple treatment with ethanol ensures they are beneficial and advantageous adsorbent materials.
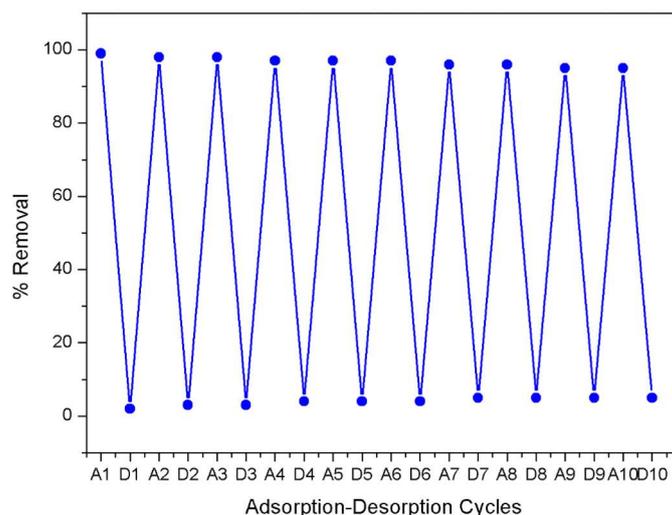
Figure 4. Recyclability of HO$_3$S-PS-MWCNT adsorbent for xylene isomers adsorption from water solutions. A1–A10: Adsorption cycles; D1–D10: Desorption cycles.

4. Conclusions

The PS-MWCNT samples were prepared using the one-step bulk polymerization method. Mesoporous structures in PS-MWCNT were created using the nano-crystallization phase separation method. Sulfonated PS-MWCNT nanocomposites were prepared by treating the samples with concentrated sulfuric acid. The sulfonated PS-MWCNT (HO$_3$S-PS-MWCNT) was found to be a potential adsorbent for dissolved xylene isomers from water solution. The sulfonated mesoporous PS-MWCNT (HO$_3$S-PS-MWCNT) has been studied as a potential adsorbent for the efficient adsorption of xylene isomers from the aqueous solution of near-saturated concentration. This unique adsorbent exhibits excellent sorption characteristics with enhanced kinetics and excellent recyclability. The equilibrium and kinetics studies indicate that the adsorption process occurs not just by simple diffusion but by strong migration between the adsorption sites or cavities.

Author contributions

Conceptualization, MRK and VR; methodology, MRK; validation, VR; formal analysis, MRK; investigation, MRK; resources, MRK; data curation, MRK and VR; writing—original draft preparation, MRK; writing—review and editing, MRK and VR. All authors have read and agreed to the published version of the manuscript.

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Conflict of interest

The authors report that there is no conflict of interest to declare.

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