Surface Functionalization of Mesoporous Carbon for the Enhanced Removal of Strontium and Cesium Radionuclides

Munzir Hamedelniel Suliman, Mohammad Nahid Siddiqui * and Chanbasha Basheer

Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia; g201304270@kfupm.edu.sa (M.H.S.); cbasheer@kfupm.edu.sa (C.B.)

* Correspondence: mnahid@kfupm.edu.sa; Tel.: +966-138-602-529

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Abstract: Mesoporous carbons (MPC) and modified mesoporous carbons (MMPC) were prepared from asphalt for the adsorption of several metal ions from the aqueous solution. In this study, we investigated the adsorption efficiency of Cesium (Cs⁺) and Strontium (Sr²⁺) ions using mesoporous and modified mesoporous carbons. The optimum conditions for the removal of Cs⁺ and Sr²⁺ were at 10.0 pH, 1.00 ppm (1000.0 µg/L) concentration, 20.0 min contact time, 0.20 g/L adsorbent dose, 25.0 °C temperature with more than 95.0% removal of Cs⁺ and Sr²⁺ ions using MMPC. The limit of detection (LOD) was found to be 0.030 ppb and 10.00 ppb for Sr²⁺ and Cs⁺ metals ions, respectively, while the Limit of quantification (LOQ) was calculated to be 0.10 ppb for Sr²⁺ and 35.00 ppb for Cs⁺ metals ions. The functionalization of the MPC was performed using potassium permanganate to get MMPC, which were characterized by FT-IR spectroscopy. The nature of the X-ray diffraction peaks suggests that the MPC and MMPC carbons are amorphous and semi-crystalline materials. The scanning electron microscope (SEM) and transition electron microscope (TEM) studies showed the changes in the morphology due to the adsorption on the surface of the carbons. The TEM analysis clearly showed that the metal ions blocked most of the pores on the surface. The surface area, by N₂ adsorption isotherm (BET), of MPC and MMPC were 937 and 667 m²·g⁻¹, respectively. Among the adsorption isotherms, Langmuir isotherm showed the best linearity. The Langmuir isotherm indicates that the adsorption is monolayer and homogeneous with a finite number of ions. Adsorption kinetics showed better linearity with pseudo-second-order plots and obeys this order. This process indicates that the chemical interaction, such as covalent or ionic bonding, took place between the metal ions and the carbon adsorbents.

Keywords: surface functionalization; surface modification; mesoporous carbon; adsorption; metal ions

1. Introduction

Clean water resources are vital to humans, animals, and plants. However, the extensive use of these resources, especially in the industrial process, leads to lower water quality and the availability of clean water [1–3]. The wastewater treatment for the removal of organic substances and heavy metals (such as As, Zn, Ni, Cu, Hg, Sr, Cs, and more) is considered as a significant and challenging task [4]. The contamination of water with strontium (Sr²⁺) and cesium (Cs⁺) ions especially the radioactive isotopes ⁹⁰Sr and ¹³⁷Cs represent a significant concern due to their long half-life (t¹/₂ = 29.0 and 30 years respectively) and high solubility [5]. These species are produced from the nuclear fusion and remains with nuclear wastes and emit beta and gamma radiations [6]. Thus, the development of efficient, simple, and cost-effective methods to remove these dangerous ions from wastewater and produce clean water. Different removal methods were investigated, such as liquid extraction [7],
photo-degradation [8], electrochemical techniques [9], coprecipitation [10] and adsorption using several adsorbents. Adsorptive removal of Sr and Cs ions is the preferred approach in terms of adsorption capacity, selectivity, simplicity, and cost-effectiveness. The development of low-cost adsorbent draws excellent attention, such as red mud [11], zeolite [12], bentonite [13], and eggshell [14]. Carbon nanomaterials have been wildly investigated in water treatment due to the unique properties of these materials. These materials have shown an excellent adsorption ability to organic and inorganic pollutants through a different mechanism, physiosorption and chemisorption with different adsorption capacity depend chiefly on adsorbents’ active sites and available surface area [15]. Several carbonaceous adsorbent materials, including carbon nanotubes (CNT), carbon fibers, activated carbons and more have been extensively examined for the treatment of polluted and wastewater [16–18]. The adsorption capacity of these carbonaceous adsorbents was significantly enhanced by the treatment of acids/bases, which leads to the functionalization of the carbonaceous material. This treatment introduced several relevant functional groups including some of the prominent negative functionalities such as carboxylic (–COOH), carbonyl (–C=O), and hydroxyl (–OH) which are capable of facilitating the interaction of the adsorbent with the cationic species in the aqueous medium, due to the replacement of the weak interaction (van der Waals) with stronger electrostatic interactions [19]. The most used standard functionalization system is the mixture of potassium permanganate with nitric and sulfuric acids on the surface of several carbon adsorbents [20–22]. In another study, functionalized CNT showed a substantial enhancement in their adsorption capacity compared to other non-functionalized CNT for the removal of Cu\(^{2+}\), which showed an excellent removal by 94.5% at pH of 5.0 for 101 min [23]. A similar comparison was reported for oxidized CNT for the removal of several ions (Cd\(^{2+}\), Zn\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), and Pb\(^{2+}\)), which showed higher removal efficiency than the pristine. This enhancement could be explained by the interaction of the metal ion with the functionalities mentioned above [24]. The removal of both Cs\(^{+}\) and Sr\(^{2+}\) was investigated by using sodium cobalt hexacyanoferrate encapsulated in alginate vesicle with CNT [25]. Generally, the adsorption capacity of carbon absorbent increased by the enlargement of the surface area. The introduction of porosity on the carbon also increases the surface area.

In this study, a simple approach to prepare high surface area functionalized mesoporous carbon from an inexpensive petroleum matrix source, asphalt, was adopted and was tested for the adsorption of Sr\(^{2+}\) and Cs\(^{+}\) metal ions from aqueous solution. Asphalt is very inexpensive and widely accessible heavy crude oil fraction obtained after all boiling fractions have been removed and there is no scope to upgrade further. Asphalt contains the highest portion of carbon (85%–90%) with approximately 10%–12% of hydrogen, therefore, economically not many useful fractions except is being used in roads and roofs. Asphalt has unique physicochemical properties, which afforded a very high surface area porous carbon (MPC) that can be easily tailored to suit many applications. The performance of MPC and oxidatively modified MMPC nanoporous carbon materials were tested as nanoporous filters to remove radioactive metal ions and polynuclear aromatic hydrocarbons (PAHs) from water. Compared with other porous activated carbon materials, the MMPC performance was much better and the production cost was much cheaper than other reported carbon materials. Thines et al. [18] reported that the mesoporous functionalized carbons may induce exceptional metal-carbon interaction, causing a significant effect on several critical processes, including the interfacial equilibrium, desorption, and adsorption of highly reactive classes and their interaction with the surface. The mesoporous functionalized carbons were characterized using several spectroscopic techniques. The adsorption parameters, kinetic (pseudo-first and second orders), and the adsorption isotherms (Langmuir, Freundlich, and Temkin) were investigated and optimized. The thermodynamic parameters such as entropy (\(\Delta S\)), enthalpy (\(\Delta H\)), and the Gibbs free energy of the processes were calculated and confirmed that the metal ions removal process is exothermic and spontaneous.
2. Materials and Methods

Asphalt was procured from the Ras Tanura refinery through the Research and Development Center of Saudi Aramco at Dhahran, Kingdom of Saudi Arabian. The following reagents were purchased and used in this work; which includes potassium hydroxide (85%, Sigma Aldrich, Louis, MO, USA), hydrochloric acid (37%, Merck, Kenilworth, NJ, USA), sulfuric acid (95%–97%, Merck), potassium permanganate (99.5%, Sigma Aldrich). 1.0 and 0.1 M solution were prepared by using nitric acid, ACS reagent 70% from Sigma-Aldrich Company. 1.0 and 0.1 M solution were prepared by using sodium hydroxide pellets from Fluka. Strontium standard 1000 ug/mL from ULTRA SCIENTIFIC Analytical Solution. Cesium chloride salt from Puratronic brand with Johnson Matthey Chemicals Limited (London, UK) as manufacturer.

2.1. Preparation of Activated and Mesoporous Carbons

Mesoporous carbon (MPC) was prepared sequentially by heating the asphaltic material in a tubular furnace (MTI Corporation, Richmond, CA, USA) at 525 °C for 7 h under a continuous stream of nitrogen gas. The resulted mixture was further carbonized by treating with potassium hydroxide (KOH) powder in a fixed mass ratio of 1:4 (carbon:KOH) at a higher temperature around 750 °C under a continuous stream of nitrogen gas. The afforded mesoporous carbon was washed several times with distilled water for extended times, followed by diluted hydrochloric acid (HCl) and, again washed by distilled water to remove all possible traces of NaCl or HCl. The MPC product was further drenched in distilled water, filtered, dried in the oven, and stored.

2.2. Functionalization of Mesoporous Carbon

The mesoporous carbon (MPC) was treated with potassium permanganate (KMnO₄), an oxidative agent, to prepare functionalized mesoporous carbon (MMPC) which possesses various oxygen functional groups. Around 10.0 g of MPC was transferred into a 1000 mL Pyrex beaker containing 150 g of 88.6% of H₂SO₄ (82 mL Conc. H₂SO₄ + 12 mL H₂O) and 6.0 g of KMnO₄ and let to rest for about one hour. Another 6.0 g dose of KMnO₄ was added to reaction mixture and left for 7 h to complete the reaction. Finally, 500 mL of distilled water was added to the resultant solution and waited 1 h to completely quench the reaction. The product obtained was functionalized mesoporous carbon (MMPC) which was washed thoroughly several times with distilled water until the pH value of 5 of the washings was obtained. The MMPC product was filtered, dried in the oven and stored [1].

2.3. Characterization of MPC and MMPC

The characteristic structure and surface morphology of the mesoporous carbon and functionalized mesoporous carbon were studied by several analytical techniques including Scanningelectron microscopy (SEM) for the morphology were obtained using FESEM/FIB/GIS (Tescan Lyra-3, Brno-Kohoutovice, Czech Republic) operated at 20.0 kV. X-ray diffraction (XRD) analysis was performed on the Rigaku Ultima IV X-ray diffractometer (RIGAKU, Tokyo, Japan). The FT-IR spectral measurements were carried out on Nicolet 6700 FT-IR spectrometer (Thermo Scientific, Waltham, MA, USA) in the range 400–4000 cm⁻¹. The Brunauer–Emmett–Teller (BET) analysis was performed using a micrometeritics (Tristar II PLUS, Norcross, GA, USA) instrument under the continuous adsorption conditions to determine the surface area. Transmission electron microscopy (TEM) of both mesoporous carbon samples were carried out using JEM2100F multipurpose (Jeol, Tokyo, Japan), 200 kV FE (Field Emission) analytical electron microscope.

2.4. Adsorption Experiments

Initially, adsorption experiments were carried out in a 50-mL Erlenmeyer flask using both MPC and MMPC under varying parameters such as solution pH, concentration (ppm), adsorption time (min), catalyst dosage (mg), solution volume (mL), and temperature (°C), the concentration of metal ions was
one ppm with 200 rpm stirring speed. The experiments were performed in triplicate. After adsorption, with a syringe and PTFE filter disc, samples were analyzed using ICP-OES with a Model PlasmaQuant® PQ 9000 (Analytik Jena, Jena, Thuringia Land, Germany) with ppt detection limits. The optimum removal parameters were at 10.0 pH, 1.00 ppm (1000.0 µg/L) concentration, 20.0 min contact time, 0.20 g/L adsorbent dose, 25.0 °C temperature. This reaction method was a very precise and accurate which also afforded limits of detection (LOD) and limits of quantification (LOQ). The LOD was found to be 0.030 ppb for Sr\(^{2+}\) and 10.00 ppb for Cs\(^{+}\) metals ions. The LOQ was calculated to be 0.10 ppb for Sr\(^{2+}\) and 35.00 ppb for Cs\(^{+}\) metals ions. After each extraction, the sorbent was washed with acid (1 M HCl) for 20 min and then heated at 150 °C to regenerate the sorbent.

3. Results and Discussion

To understand this study properly, the results and discussion is being divided into two parts: (i) characterization of MPC and MMPC, and (ii) removal of Sr\(^{2+}\) and Cs\(^{+}\) metal ions by adsorption.

3.1. Characterization of MPC and MMPC

The prepared MPC and MMPC were characterized using several spectroscopic techniques including XRD, FT-IR, SEM, TEM, and BET to study the phase, surface, the microstructural, and various physico-chemical properties of the adsorbents. Various properties of MPC, and MMPC were compared, however, the characteristic properties of MPC and MMPC were found to be of a great significance and discussed in detail. Activated carbon (AC) was the main precursor of the MPC and MMPC without any adsorptive capabilities.

FT-IR spectra in Figure 1 shows the surface modification of the MPC carbon surface on permanganate oxidation in MMPC carbon. Several vibration peaks were observed corresponding to the C=O, COOH, and OH groups. The most significant peaks observed in MMPC carbon were at 3431.8, 1738.8, 1629, 1457.4, 1392.2, and 1054 cm\(^{-1}\), while in MPC two most prominent peaks observed were at 3413 and 1629 cm\(^{-1}\) only. In the FTIR spectra, the 2356 cm\(^{-1}\) is belonging to trapped CO\(_2\). The bands at 2924 cm\(^{-1}\) are related to the C–H aldehyde group. The 1738 and 1629 cm\(^{-1}\) belongs to the carbonyl, C=C double bonds, respectively. The secondary absorptions at 1457 and 1392 cm\(^{-1}\) are peaks related to –COOH and –CH=O moieties [1]. Which makes MMPC very effective and efficient adsorbent for removing metal ions and other pollutants.

![FT-IR spectra of MPC and MMPC.](image)

Figure 1. FT-IR spectra of MPC and MMPC.

X-ray diffraction analysis of MPC and MMPC were carried out to investigate the phases which are shown in Figure 2. In MPC and MMPC, two diffraction peaks at 2θ angles of 23.5° and 43.0° ascribed
to the reflection of planes 002 and 101 respectively. The nature of the diffraction peaks confirms that the synthesized MPC and MMPC were semi-crystalline and amorphous materials.

Figure 2. X-ray diffraction of MPC and MMPC.

Figure 3 shows the microstructure and the morphology of the MPC (a) and MMPC (b) investigated by FESEM. The figures revealed the rough surface of agglomerated semi sphere particles with pores. These particles assemble in layers like morphology. SEM image was recorded after the adsorption of the cation. The porosity is relatively reduced due to adsorption of Sr$^{2+}$ metal ions as shown in Figure 3c.

Figure 3. SEM of (a) MPC, (b) MMPC, and (c) MMPC after adsorption of Sr$^{2+}$ ions metal ions.

TEM was also carried out to augment the findings of FESEM. Figure 4a shows porous layers of in the case of MPC. MMPC sample Figure 4b also revealed more homogenous pores and thinner layers of carbon. This layer could be attributed to the oxidation process which occurs on the surface and can reduce the stacking of the layers. Similarly, a TEM was investigated after the adsorption. Small clusters of metal ions were deposited on the surfaces indicating great influence of the modified surface. The pores were blocked after the adsorption of the Sr$^{2+}$ metal ions, as shown in Figure 4c.

The surface area and the type of porosity of the synthesized MPC and MMPC adsorbents were determined by the N$_2$ adsorption isotherm (BET). The surface area of the MPC has been calculated to be 937 m$^2$·g$^{-1}$. The calculated value revealed a significant drop as a result of carbon functionalization. The MMPC surface area was 667 m$^2$·g$^{-1}$. Figure 5 shows the BET isotherms of MPC and MMPC where Figure 5a compares the N$_2$ adsorption-desorption isotherms of MPC and MMPC; whereas Figure 5b comapres the pore size distribution of MPC and MMPC. The sorbent consists of both micro and mesoporous structure. However, the majority of the pores are classified as mesoporous. The adsorption isotherm in Figure 5 confirms there were two types of pores meso (36.6 Å for MPC and
33.6 Å for MMPC) and microporosity (<2 nm) and the mesopores volume were 0.62 cm³·g⁻¹ for MPC and 0.16 cm³·g⁻¹ for MMPC. MPC and MMPC were grained manually to obtain fine powder form. We may expect to have a particle size of about 100 µm size.

![Figure 4. TEM of (a) MPC, (b) MMPC, and (c) MMPC after adsorption of Sr²⁺ ions metal ions.](image)

Figure 4. TEM of (a) MPC, (b) MMPC, and (c) MMPC after adsorption of Sr²⁺ ions metal ions.

![Figure 5. BET isotherm of MPC and MMPC: (a) N₂ adsorption-desorption isotherm; (b) Pore size distribution.](image)

Figure 5. BET isotherm of MPC and MMPC: (a) N₂ adsorption-desorption isotherm; (b) Pore size distribution.

3.2. Optimization of Adsorption Parameters

MPC and MMPC were used as adsorbents for the removal of Sr²⁺ and Cs⁺ ions in aqueous solution. Several adsorption parameters were investigated and optimized to achieve the maximum adsorption capacity, such as adsorbent dosage, the time of the adsorptions, and the pH of the solution.

3.3. Dosage of the Adsorbent

The dosage of adsorbent is considered a critical parameter in the wastewater treatment process. Different amounts of MPC and MMPC (5, 10, 20, 30, and 40 mg) were studied in the removal of Sr²⁺ and Cs⁺ ions as shown in Figure 6. The adsorption took place in 30 mL aqueous solution with a pH of 10.0, MPC showed maximum adsorption efficiency for Sr with 42.8% at a dosage of 5 mg, while showed 26.7% for Cs when 10 mg used as a dosage amount. Remarkable enhancement was observed in the case of 10 mg of MMPC, which showed 93.3% and 85.6% adsorption for Sr²⁺ and Cs⁺ ions respectively. One interesting aspect of the dosage of adsorbent study is that the more adsorbent is used, the fewer cations it retains. This could be due to a hydrophobic effect that leads to the adsorbent particles’ agglutination, leading thus to a diminished total available surface.
3.4. Optimization of Time

The optimum removal time for the ions using MPC adsorbent was 45 min to remove only 11.0% and 1.5% of the Sr$^{2+}$ and Cs$^+$, respectively. The adsorption took place in 30 mL aqueous solution with a pH of 10.0, the concentration of metal ions was one ppm and 5 mg adsorbent dosage. The removal time and the adsorption capacity were enhanced significantly upon the use of MMPC in only 5 min to 85.5% and 81.0% of Sr$^{2+}$, and Cs$^+$ respectively were removed, and the optimum removal time was found to be 15 min (after 20 min, the maximum adsorption is already attained. Prolonged times would lead to increase desorption), which showed removal efficiency of 97.5% and 83.0% for Sr$^{2+}$ and Cs$^+$ respectively. The effect of time on the adsorption of Sr$^{2+}$, and Cs$^+$ metal ions on MPC and MMPC is given Figure 7.

3.5. Optimization of the pH

Figure 8 shows the effect of pH on the adsorption phenomenon of MPC and MMPC. The pH was adjusted using both 0.1 M and 1.0 M nitric acid and 0.1 M and 1 M sodium hydroxide solutions. The pH of the solution has a significant influence on the adsorption process. This effect can be attributed to the effect of the pH on the functionalities on the adsorbents, which will affect the adsorption process. At high pH, basic functionalities such as (−COO$^-\$) could enhance the binding with the cations. Several experiments took place in pH range between 3 and 12. The removal efficiency increased with increasing the pH up to 10.0, which was considered the optimum pH. Although pH 10.0 showed the highest adsorption capacity, pH 7.0 and 9.0 (normal water pH) revealed a comparable removal efficiency with pH 10.0, which means this process is suitable for industrial samples. In Figure 8b, it can be observed that there is a sharp drop in the adsorption efficiency of Cs$^+$ ions. It has been reported that at higher pH values the Cs$^+$ ions may form hydroxides leading to lower adsorption [26,27].
3.6. Adsorption Kinetics

Adsorption kinetics (pseudo-first-order and pseudo second-order) were investigated for MPC and MMPC for the removal of Sr$^{2+}$ and Cs$^+$ using Equations (1) and (2). Where ($q_e$) is the adsorption capacity at the equilibrium, ($q_t$) is the adsorption capacity at certain time, $k$ the rate of adsorption and $t$ is the time of adsorption.

\[
\log(q_e - q_t) = \log q_e - \frac{kt}{2.0303}
\]  
(1)

\[
\frac{t}{q_e} = \frac{1}{k' + \frac{t}{q_e}}
\]  
(2)

As per Figure 9, better linearity was observed in case of pseudo-second-order plots (Figure 9c,d), which is suggest that the adsorption obey that order, which indicates the interaction between the ions and the adsorbent takes place through chemical interaction such as covalent or ionic bond [28].

Figure 9. Pseudo-first-order plot for MPC and MMPC for the removal of (a) Sr$^{2+}$ and (b) Cs$^+$ and pseudo-second-order plot for MPC and MMPC for the removal of (c) Sr$^{2+}$ and (d) Cs$^+$ ions.
Langmuir, Freundlich and Temkin adsorption isotherms were plotted using Equations (3)–(5) and represented in Figure 10. From the figure, Langmuir isotherm showed the best linearity. This isotherm indicates that the adsorption is monolayer and homogeneous with a finite number of ions [29].

\[
\frac{C_e}{q_e} = \frac{1}{kq_m} + \frac{C_e}{q_m} \tag{3}
\]

\[
\ln q_e = \ln k + \frac{1}{n} \ln C_e \tag{4}
\]

\[
q_e = \frac{RT}{B} \ln K_T C_e \tag{5}
\]

3.7. Adsorption Thermodynamics

Thermodynamic parameters such as enthalpy change (\(\Delta H\)), entropy change (\(\Delta S\)), and change in the free energy (\(\Delta G\)) were calculated using the effect of three different temperatures on the adsorption process at 25, 35 and 45 °C and given in Figure 11. Equation (6) (Van’t-Hoff equation) was used to calculate \(\Delta H\) and \(\Delta S\) from the figure, and \(\Delta G\) was calculated using Equation (7), all the values are summarized in Table 1.

\[
\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{6}
\]

\[
\Delta G = \Delta H - T\Delta S \tag{7}
\]

The positive \(\Delta H\) confirmed that the reaction is endothermic, while the positive \(\Delta S\) suggests the increase of the disorder during adsorption as a result of the release of water molecules from the substantial hydration. The process was confirmed to be spontaneous from the negative values of Gibbs free energy.
were characterized using several spectroscopic techniques such as FT-IR, XRD, BET, SEM and TEM.

In this study, we investigated the adsorption efficiency of Sr\(^{2+}\) and Cs\(^{+}\) ions using mesoporous and modified mesoporous carbons (MMPC) from the asphalt. The MPC and MMPC carbon adsorbents from asphalt, which shows that our MMPC adsorbent has better properties. The MPC and MMPC carbon adsorbents from asphalt, which shows that our MMPC adsorbent has better properties. In this study, we investigated the adsorption efficiency of Sr\(^{2+}\) and Cs\(^{+}\) ions using mesoporous and modified mesoporous carbons (MMPC) from the asphalt. The MPC and MMPC carbon adsorbents from asphalt, which shows that our MMPC adsorbent has better properties.

Table 2 shows the comparison of the surface areas and pore sizes of recently developed mesoporous carbons (MPC) and modified mesoporous carbons (MMPC) from the asphalt. The MPC and MMPC carbon adsorbents from asphalt, which shows that our MMPC adsorbent has better properties.

Our study reports a straightforward, cost-effective, and efficient method to prepare mesoporous carbons (MPC) and modified mesoporous carbons (MMPC) from the asphalt. The MPC and MMPC were characterized using several spectroscopic techniques such as FT-IR, XRD, BET, SEM and TEM.

Table 2 shows the comparison of the surface areas and pore sizes of recently developed mesoporous carbons (MPC) and modified mesoporous carbons (MMPC) from the asphalt. The MPC and MMPC were characterized using several spectroscopic techniques such as FT-IR, XRD, BET, SEM and TEM.

3.8. Regeneration of Adsorbents

The reusability of the adsorbent is considered as a critical factor for the real-life application. The regeneration of MPC and MMPC adsorbents was investigated for the three-cycle for the removal of Sr\(^{2+}\) and Cs\(^{+}\) in the aqueous medium as reported in Figure 12. The MPC and MMPC showed excellent durability and reusability, with higher removal efficiency for MMPC with no significant drop in the removal percentage.

Table 1. Thermodynamic parameters calculated from Van’t-Hoff equation.

| Parameters | \(\Delta H\) (kJ·mol\(^{-1}\)) | \(\Delta S\) (kJ K\(^{-1}\)·mol\(^{-1}\)) | \(\Delta G\) (kJ·mol\(^{-1}\)) |
|------------|----------------|----------------|----------------|
| Cs\(^{+}\)  | 5.87           | 0.031          | -3.37          |
| Sr\(^{2+}\) | 4.45           | 0.029          | -4.19          |

**Figure 11.** Van’t Hoff relationship with temperature for Sr\(^{2+}\) and Cs\(^{+}\) ions.

**Figure 12.** The regeneration of MPC and MMPC for the removal of (a) Sr\(^{2+}\) and (b) Cs\(^{+}\).

4. Conclusions

Our study reports a straightforward, cost-effective, and efficient method to prepare mesoporous carbons (MPC) and modified mesoporous carbons (MMPC) from the asphalt. The MPC and MMPC were characterized using several spectroscopic techniques such as FT-IR, XRD, BET, SEM and TEM. Table 2 shows the comparison of the surface areas and pore sizes of recently developed mesoporous carbon adsorbents from asphalt, which shows that our MMPC adsorbent has better properties. In this study, we investigated the adsorption efficiency of Sr\(^{2+}\) and Cs\(^{+}\) ions using mesoporous and modified mesoporous carbons. Introduction of negative functionalities such as carboxylic (–COOH), carbonyl (–C=O), and hydroxyl (–OH) which are capable of facilitating the interaction of the adsorbent

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**Figure 11.** Van’t Hoff relationship with temperature for Sr\(^{2+}\) and Cs\(^{+}\) ions.

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|------------|----------------|----------------|----------------|
| Cs\(^{+}\)  | 5.87           | 0.031          | -3.37          |
| Sr\(^{2+}\) | 4.45           | 0.029          | -4.19          |

**Figure 12.** The regeneration of MPC and MMPC for the removal of (a) Sr\(^{2+}\) and (b) Cs\(^{+}\).
with the cationic species in the aqueous medium, due to the replacement of the weak interaction (van der Waals) with stronger electrostatic interactions. The optimum conditions for the removal of Cs and Sr were at 10.0 pH, 1.00 ppm (1000.0 µg/L) concentration, 20.0 min contact time, 0.20 g/L adsorbent dose, 25.0 °C temperature with more than 95.0% removal of Cs⁺ and Sr²⁺ ions using MMPC. Furthermore, MMPC revealed excellent durability for three regeneration cycles without a significant drop in the removal efficiency. Additionally, normal water pH, comparable removal of Cs⁺ and Sr²⁺ (around 80.0%) was achieved. The applied removal conditions and the cost-effective catalyst are considered as promising for treating the real polluted samples and other industrial applications. The Langmuir adsorption isotherm showed the best linearity indicating the adsorption process is monolayer and homogeneous with a finite number of ions. Adsorption kinetics showed better linearity with pseudo-second-order plots and obeys pseudo-second-order. This process confirms that the chemical interaction, such as covalent or ionic bonding, took place between the metal ions and the carbon adsorbents.

### Table 2. Comparison of the surface area and pore size of the mesoporous carbon obtained from different asphalt samples.

| Carbon                              | Surface Area (m²·g⁻¹) | Pore Size (nm) | Ref.       |
|------------------------------------|-----------------------|----------------|-----------|
| Activated carbon (Jordan Asphalt)  | -                     | -              | [30]      |
| Graphitic mesoporous carbon        | 479                   | 7.53           | [31]      |
| Oxidized mesoporous carbon         | 333.6                 | 3.93           | [32]      |
| Hierarchical porous carbon         | 3581                  | 2.20           | [33]      |
| MMPC                               | 667                   | 3.60           | This work |

### Author Contributions:
Conceptualization, M.N.S. and C.B.; funding acquisition, M.N.S. and C.B.; writing—original draft preparation, M.H.S.; writing—review and editing, M.H.S., M.N.S., and C.B.; supervision, M.N.S. and C.B. All authors have read and agreed to the published version of the manuscript.

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### Conflicts of Interest:
The authors declare no conflict of interest.

### References
1. Siddiqui, M.N.; Ali, I.; Asim, M.; Chanbasha, B. Quick removal of nickel metal ions in water using asphalt-based porous carbon. *J. Mol. Liq.* 2020, 308, 113078. [CrossRef]
2. Alissa, F.M.; Mohammed, D.; Osman, A.M.; Chanbasha, B.; Siddiqui, M.N.; Al-Arfaj, A.A.; Suliman, M.H. Synthesis of highly efficient asphalt-based carbon for adsorption of polycyclic aromatic hydrocarbons and diesel from emulsified aqueous phase. *Carbon Lett.* 2020, 30, 555–567. [CrossRef]
3. Basheer, A.A. New generation nano-adsorbents for the removal of emerging contaminants in water. *J. Mol. Liq.* 2018, 261, 583–593. [CrossRef]
4. Allen, H.E.; Perdue, E.M.; Brown, D.S. *Metals in Groundwater*; CRC Press: Boca Raton, FL, USA, 1993.
5. Todd, T.A.; Todd, T.A.; Law, J.D.; Herbst, R.S. *Cesium and Strontium Separation Technologies Literature Review*; INEEL/EXT-04-01895; Idaho National Engineering and Environmental Laboratory: Idaho Falls, ID, USA, 2004.
6. Aguila, B.; Banerjee, D.; Nie, Z.; Shin, Y.; Ma, S.; Thallapally, P.K. Selective removal of cesium and strontium using porous frameworks from high level nuclear waste. *Chem. Commun.* 2016, 52, 5940–5942. [CrossRef]
7. Wilmarth, W.R.; Lumetta, G.J.; Johnson, M.E.; Poirier, M.R.; Thompson, M.C.; Suggs, P.C.; Machara, N.P. Waste-pretreatment technologies for remediation of legacy defense nuclear wastes. *Solvent Extr. Ion Exch.* 2011, 29, 1–48. [CrossRef]
8. Kabra, K.; Chaudhary, R.; Sawhney, R.L. Solar photocatalytic removal of metal ions from industrial wastewater. *Environ. Prog.* 2008, 27, 487–495.
32. Zhang, X.; Lin, Q.; Luo, Q.; Ruan, K.; Peng, K. Preparation of novel oxidized mesoporous carbon with excellent adsorption performance for removal of malachite green and lead ion. *Appl. Surf. Sci.* **2018**, *442*, 322–331. [CrossRef]

33. Pan, L.; Wang, Y.; Hu, H.; Li, X.; Liu, J.; Guan, L.; Tian, W.; Wang, X.; Li, W.; Wu, M. 3D self-assembly synthesis of hierarchical porous carbon from petroleum asphalt for supercapacitors. *Carbon* **2018**, *134*, 345–353. [CrossRef]

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