FUNCTIONALIZATION MESOPOROUS SILICA USING AMINOPROPYLTRIETHOXYSILANE (APTES) AS ADSORBENT FOR REMOVAL Ni (II) FROM AQUEOUS SOLUTION

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ABSTRACT

Keywords: Adsorption; APTES, Mesoporous Silica, Nickel (II)

This study successfully synthesized mesoporous silica using the template methyl ester ricinoleate (MS-TMR) and further functionalized the MS-TMR surface with 3-aminopropyltriethoxysilane (APTES). The functionalization of MS-TMR with APTES was achieved through a 48-hour grafting method. For the adsorption experiments, 20 mg of both MS-TMR and MS-TMR-APTES adsorbents were employed to remove Ni(II) from aqueous solutions at a concentration of 30 mg/L and pH 6. The objective was to assess the adsorption capacity and to characterize the synthesized adsorbents. Characterization was conducted using Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD). FTIR analysis revealed that the MS-TMR adsorbent possessed silanol (Si-OH) and siloxane (Si-O-Si) groups. Conversely, the MS-TMR-APTES adsorbent exhibited additional amine (N-H) and C-H groups after the APTES grafting. XRD results indicated that both samples were amorphous. The concentration of Ni(II) ions was determined using Atomic Absorption Spectroscopy (AAS), which facilitated the calculation of removal percentages and adsorption capacities. MS-TMR achieved a mere 3.54% removal of Ni(II) ions, corresponding to an adsorption capacity of 3.21 mg/g. In contrast, MS-TMR-APTES demonstrated significantly enhanced performance, removing 54.23% of Ni(II) ions with an adsorption capacity of 48.81 mg/g. The findings suggest that APTES-functionalized MS-TMR has considerable potential for removing Ni(II) ions and could be explored further for the adsorption of other heavy metal ions.

INTRODUCTION

The increasing pace of industrial development may contribute significantly to water pollution through industrial wastewater effluent [1]. Industrial waste, containing organic and inorganic pollutants, includes heavy metals, which are particularly hazardous due to their non-biodegradable nature. Commonly found heavy metals in industrial waste include nickel (Ni), zinc (Zn), copper (Cu), chromium (Cr), cadmium (Cd), lead (Pb), mercury (Hg), and arsenic (As). Nickel is notably carcinogenic and can cause a range of health issues, including digestive disorders, lung and kidney problems, and skin dermatitis [2]. A 2022 study highlighted the detrimental respiratory effects of nickel exposure on workers in a nickel refining factory, showing that long-term exposure to
nickel dust and fumes significantly increases the risk of developing respiratory diseases such as bronchitis, asthma, and lung cancer [3]. These health risks underscore the urgent need for effective mitigation strategies to safeguard workers in nickel-related industries and the general public from the adverse effects of nickel pollution.

Nickel is primarily sourced from mining, smelting, machinery processing, chemical production, textiles, and electroplating. The electroplating industry, in particular, utilizes substantial quantities of nickel in its coatings and discharges nickel-rich effluents with concentrations reaching up to 500 mg/L [4], far exceeding the safe limit of 1 mg/L for nickel concentration in water. Exceeding this threshold poses significant environmental and public health risks due to water pollution [5].

The conventional method for Ni(II) removal involves chemical precipitation; however, this treatment is costly and often fails to reduce the residual Ni(II) concentration in the effluent to safe levels [6]. The adsorption technique provides a superior alternative for heavy metal ion removal due to its versatility, high adsorption capacity, operational simplicity, cost-effectiveness, and the potential for adsorbent regeneration [7]. Among various adsorbents, mesoporous silica stands out due to its high surface area, uniform pore size distribution, low production cost, substantial adsorption capacity for pollutants, and the ease with which its surface can be chemically modified to enhance performance [8].

Previous research has documented the synthesis of mesoporous silica using methyl ester ricinoleate with added HCl as an adsorbent, achieving a maximum adsorption capacity of 103.10 mg/g for Cd$^{2+}$ ions and 87.03 mg/g for Cu$^{2+}$ ions [9], [10]. However, the efficiency in removing other heavy metal ions still needs to be improved [11]. Mesoporous silica's lack of diverse functional groups on its surface restricts its application to specific target molecules.

To address this limitation, mesoporous silica's surface can be modified with various ligands such as organic groups, coordination compounds, and nanoparticles to expand its application scope [12]. A common strategy for enhancing adsorbent properties includes surface modification [13]. Specifically, amine group modification is advantageous due to the simplicity of the reaction and its effectiveness in heavy metal removal [14]. Functionalizing mesoporous silica with amine groups allows it to bind several divalent cations, thus exhibiting high adsorption capacity and selectivity for heavy metal ions. The silane coupling agent 3-Aminopropyltriethoxysilane (APTES), characterized by its amine groups, plays a crucial role in this process [15].

The functionalization of mesoporous silica with APTES results in silane termination within the structure, creating a stable covalent bond between the amine group of APTES and the silanol group on the silica mesopore surface [16]. This chemical modification significantly increases the surface area and pore volume, maximizing the contact area between the adsorbent and the heavy metal ions. Consequently, Ni(II) ions in the solution form coordination complexes with the amine groups on the surface of APTES-functionalized mesoporous silica through chelation [18].
Extensive research has been conducted on APTES-functionalized mesoporous silica for various applications, such as the adsorption of Pb(II), Cu(II), and Cd(II) ions \[19\], textile dye adsorption \[20\], and CO\(_2\)/H\(_2\)O adsorption \[21\]. However, despite these advancements, studies focusing on Ni(II) adsorption are relatively scarce. This study aims to fill this gap by exploring the adsorption capabilities of APTES-functionalized mesoporous silica for Ni(II) ions, emphasizing the functionalization technique and providing crucial data that can aid in the development of effective and sustainable heavy metal ion removal technologies. Mesoporous silica synthesized using ricinoleate methyl ester from castor oil (\textit{Ricinus communis}) will be functionalized with APTES using the post-synthesis grafting method to integrate amine groups onto the silica mesopore surface. The resulting APTES-functionalized mesoporous silica will be applied as an adsorbent for Ni(II) ions in aqueous solutions.

2. Synthesis of Methyl Ester Ricinoleate from Castor Oil
The methyl ester synthesis from castor oil (\textit{Ricinus communis}) was performed following established protocols \[10\]. The process involved transesterification, where 40 grams of castor oil, 86 grams of methanol, and 0.8 grams of KOH as a catalyst were combined in a three-neck flask. This mixture was refluxed at 70°C for four hours. Subsequently, the reaction mixture was extracted with n-hexane, resulting in two phases. The upper phase was washed with distilled water, and the methyl ester was isolated using a rotary evaporator, yielding a pale yellow-colored product. The product's composition was verified by Gas Chromatography-Mass Spectrometry (GC-MS). The prepared methyl ester served as a template for synthesizing mesoporous silica.

3. Synthesis of Mesoporous Silica MS-TMR
The synthesis protocol for mesoporous silica, referred to in the literature, involved the optimization of TEOS and APMS concentrations \[22\], methanol mass \[23\], and HCl volume \[9\]. Initially, 9.04 g of methyl ester ricinoleate was mixed with 150 mL of deionized water, 15 mL of methanol, and 50 mL of 0.1 M HCl and stirred for 30 minutes (mixture A). Concurrently, 12.064 g of TEOS (0.058 mol) and 2.0764 g of APMS (0.0116 mol) were combined and stirred for 15 minutes in a sealed container (mixture B). Mixture B was then added to mixture A, and the combined mixture was stirred for an additional 2 hours. The reaction mixture was aged in an oven at 80°C for 72 hours to allow the formation of porous solids.

METHODS
1. Materials
The materials employed in this study include castor oil, distilled water, methanol (CH\(_3\)OH), potassium hydroxide (KOH), n-hexane (C\(_6\)H\(_{14}\)), tetraethylorthosilicate (TEOS), 3-aminopropyltrimethoxysilane (APMS), deionized water, hydrochloric acid (HCl), toluene, 3-aminopropyltriethoxysilane (APTES), ethanol (C\(_2\)H\(_5\)OH), and nickel nitrate hexahydrate (Ni(NO\(_3\))\(_2\).6H\(_2\)O). These materials were utilized due to their high purity levels, suitable for the chemical processes described.
Post-aging, the mixture was centrifuged, the solid washed with deionized water, and dried at 60°C. The final product was calcined at 550°C for 6 hours to obtain a white solid, designated as MS-TMR [10].

4. Functionalization of Mesoporous Silica with APTES
The mesoporous silica MS-TMR was functionalized with 3-aminopropyltriethoxysilane (APTES) following a modified post-grafting method referenced from the literature [16]. The process involved placing 1 gram of MS-TMR and 100 mL of dry toluene into a three-neck flask, stirring for 30 minutes. Afterward, 5 mL of APTES was added, and the mixture was refluxed at room temperature under a nitrogen atmosphere for 48 hours. The product was then filtered and washed sequentially with 50 mL of dry toluene and 50 mL of ethanol, followed by drying under vacuum at 80°C for 20 hours.

5. Characterization
Characterization of the synthesized materials was performed using several techniques. Gas Chromatography-Mass Spectrometry (GC-MS) analysis was carried out on a Trace 1310 GC system with a capillary fused silica column, with the temperature settings ranging from 140°C to 220°C and helium as the carrier gas flowing at 40 to 70 mL/min. Fourier-transform Infrared Spectroscopy (FT-IR) was conducted using a Shimadzu IR Prestige-21 instrument with KBr pellets to identify functional groups on the castor oil methyl esters and silica mesopore surfaces. X-ray Diffraction (XRD) was executed using an E Philip PW 3050/XPert Pro PANalytical system, utilizing Cu Kα radiation (λ = 1.542 Å) with scans at a speed of 2 deg/min over a range of 2θ = 1-15° for low angles and 2θ = 10-90° for wide angles, to assess the crystalline structure of the mesoporous silica.

6. Ni (II) Adsorption
In separate trials, the adsorption study for Ni(II) ions was conducted using 20 mg of MS-TMR and MS-TMR-APTES as adsorbents. Each adsorbent was placed in a 250 mL Erlenmeyer flask containing a Ni(NO₃)₂·6H₂O solution at 30 mg/L concentration. The flask was shaken at 150 rpm for one hour at room temperature. Subsequently, the reaction mixture was filtered, and the filtrate was analyzed using Atomic Absorption Spectroscopy (AAS, iCE 3300). The AAS was equipped with a hollow cathode lamp specific to Ni(II), and the Ni(II) absorption was measured at a wavelength of 232.2 nm. Calibration curves derived from standard solutions of known Ni(II) concentrations were utilized to ensure precise quantification of the residual Ni(II) ions not adsorbed by the silica.

7. Data analysis
The adsorption capacity using mesoporous silica adsorbent was calculated using the following equation:

\[ e = \frac{(C_0 - C_e) \times V}{m} \]  

(1)

The percentage removal of Ni (II) metal by mesoporous silica adsorbent was calculated using the following equation:

\[ R = \frac{(C_0 - C_e)}{C_0} \times 100 \% \]  

(2)

Where, C₀ (mg/L) is the initial concentration of nickel (II) metal, Cₑ (mg/L) is the final concentration, and m is the mass of the adsorbent.
concentration of Ni (II) metal. Adsorption capacity (Qe) is the amount of Ni (II) metal adsorbed per mass of mesoporous silica (mg/g). V is the volume of solution (L), and m is the mass of mesoporous silica (g) [24, 25].

RESULTS AND DISCUSSION
1. Synthesis and Characterization of Castor Oil Methyl Ester
Castor oil was chosen as the template for this study due to its wide availability and abundant raw material properties, making it a cost-effective option for biodiesel production. Unlike other vegetable oils, castor oil is unique in that it is the sole source of hydroxylated fatty acids, which are crucial for producing higher yields of methyl esters during the transesterification process [26]. In this reaction, castor oil is transesterified using popular alcohols such as methanol and ethanol, which are the most commonly utilized [27].

The conversion of castor oil into fatty acid methyl esters and other compounds was quantified using Gas Chromatography-Mass Spectrometry (GC-MS). According to the results presented in Table 1, the ricinoleate methyl ester content was determined to be 90.06%, with the remaining 9.94% comprising methyl esters of other fatty acids. This aligns with previous findings indicating that biodiesel derived from castor oil predominantly contains ricinoleic acid, constituting nearly 90% of its composition [28]. The use of high-purity materials is crucial as they are likely to yield methyl esters of superior quality, which in turn could enhance their adsorption capacity, stability, and performance across various applications [29].

The high purity of castor oil methyl ester ensures the uniformity of the template structure necessary for forming mesoporous silica with consistent pore size and morphology [30]. The direct correlation between the purity of castor oil methyl ester and the quality and performance of the synthesized mesoporous silica is pivotal, especially when modified with APTES. Ensuring the silica surface is devoid of contaminants is essential for facilitating a robust bond between the silica matrix and the APTES molecules, optimizing the functionalization process [31].

Table 1. GC–MS analysis for the methyl ester synthesized from castor oil (Ricinus communis)

<table>
<thead>
<tr>
<th>Retention time (min)</th>
<th>Name</th>
<th>Molecular Formula</th>
<th>Molecular weight</th>
<th>Area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.231</td>
<td>Hexadecanoic acid, methyl ester</td>
<td>C_{17}H_{34}O_{2}</td>
<td>270</td>
<td>1.03</td>
</tr>
<tr>
<td>17.335</td>
<td>9,12-Octadecadienoic acid (Z, Z), methyl ester</td>
<td>C_{18}H_{34}O_{2}</td>
<td>294</td>
<td>4.15</td>
</tr>
<tr>
<td>17.508</td>
<td>9-Octadecenoic acid (Z), methyl ester</td>
<td>C_{18}H_{36}O_{2}</td>
<td>296</td>
<td>3.02</td>
</tr>
<tr>
<td>17.607</td>
<td>9-Octadecenoic acid (Z), methyl ester</td>
<td>C_{18}H_{36}O_{2}</td>
<td>296</td>
<td>0.47</td>
</tr>
<tr>
<td>18.055</td>
<td>Octadecanoic acid, methyl ester</td>
<td>C_{18}H_{36}O_{2}</td>
<td>298</td>
<td>1.28</td>
</tr>
<tr>
<td>21.500</td>
<td>Methyl ricinoleate</td>
<td>C_{19}H_{36}O_{3}</td>
<td>312</td>
<td>90.06</td>
</tr>
</tbody>
</table>

The Fourier Transform Infrared Spectroscopy (FT-IR) spectrum of castor oil methyl ester, displayed in Figure 1, reveals several characteristic absorption bands indicative of its molecular structure. An absorption band at 3700 cm\(^{-1}\) signifies the presence of hydroxyl (OH) groups. The bands observed at 2922 cm\(^{-1}\) and 2855 cm\(^{-1}\)
These hydroxyl groups in the castor oil methyl esters are particularly significant as they provide potential sites for hydrogen bonding with silica precursors during the synthesis of silica mesopores. Such hydrogen bonds facilitate the condensation reactions necessary for forming silica, thereby aiding in creating organic-inorganic hybrid materials [9]. The results from both GC-MS and FT-IR analyses confirm the suitability of castor oil methyl ester as a template for synthesizing mesoporous silica. The role of the methyl ester as a surfactant is crucial; it acts as a template and significantly influences the pore size in the resultant silica structure [34].

**Figure 1.** Spectra FT-IR analysis of castor oil methyl ester

2. **Characterization of Adsorbent**

The functionalization of mesoporous silica with APTES was done through a grafting method involving a 48-hour reflux process in an inert atmosphere. This method heats the reaction mixture to its boiling point and condenses the vapors back into the reaction vessel, ensuring continuous mixing and homogeneous distribution of reactants. Such conditions are critical for effective grafting, as they maintain optimal reaction
parameters over an extended period. Toluene, chosen for its non-polar properties and ability to dissolve various organic compounds, promotes homogeneous mixing with inorganic substrates. The solvent must be dry to avoid the clustering of silanol groups on the mesoporous silica surface, as even minimal amounts of water can trigger this issue [12]. The tri alkoxy silane groups in APTES react with the silica network's silanol groups through alkoxy-silanol interactions.

Successful functionalization is evidenced by the appearance of C-H and N-H groups in the FT-IR analysis, indicating that the amine groups on the silica surface are ready to interact with target molecules. The presence or absence of water during the process influences the distribution and density of functional groups on the silica surface due to the potential hydrolysis of APTES, which can lead to additional reactions and the formation of silanol groups [35].

**Figure 2** displays the FT-IR spectra of MS-TMR (black) and MS-TMR-APTES (red). MS-TMR shows an absorption band at 3448 cm\(^{-1}\) for hydroxyl groups and a 470 cm\(^{-1}\) band for the Si-O-Si bond. Absorption bands at 1110 and 802 cm\(^{-1}\) correspond to asymmetric and symmetric vibrations of Si-O-Si, respectively. In the MS-TMR-APTES spectrum, the disappearance of the 979 cm\(^{-1}\) band post-grafting indicates that the Si-OH groups have been converted to Si-O groups with amine attachments. The presence of absorption bands at 2924 and 2854 cm\(^{-1}\) relates to the vibrations of the C-H group of the APTES propyl chain and the N-H group vibrations at 1565 cm\(^{-1}\), with the C-N bond at 1379 cm\(^{-1}\) confirming successful APTES grafting [36, 37].

Adding amine groups via APTES enhances the adsorption surface area. It improves the selectivity of the adsorbent towards Ni(II) ions, facilitating the formation of stable chelation complexes with metal ions, thus increasing adsorption efficiency [38].

**Figure 3** shows the XRD diffractograms of both MS-TMR and MS-TMR-APTES. The analysis shows a broadened peak at 2θ around 22°, and the absence of sharp peaks suggests the maintenance of an amorphous structure, which is crucial for effective adsorption due to the higher surface area and stability provided by amorphous structures [39, 40]. Introducing amine groups from APTES modifies the silica matrix's structural arrangement, as evidenced by new diffraction peaks or changes in peak intensity, demonstrating successful functionalization [41].

Preserving the amorphous structure post-APTES functionalization is key to maximizing the adsorbent's application performance, as amorphous materials typically exhibit superior adsorption kinetics and stability under various conditions. However, the synthesis techniques required to maintain this structure can be more complex and costly than those producing crystalline materials [43].
3. Adsorption Ni (II) Solution

Adsorption experiments were conducted using MS-TMR and MS-TMR-APTES adsorbents, with results detailed in Table 2 and Figure 4. The MS-TMR adsorbent achieved a removal efficiency of 3.54% for Ni (II) metal ions from an aqueous
solution, corresponding to an adsorption capacity of 3.21 mg/g. In contrast, the MS-TMR-APTES adsorbent significantly improved performance, removing 54.23% of Ni (II) metal ions with an adsorption capacity of 48.81 mg/g. The enhanced adsorption efficiency of MS-TMR-APTES is attributed to the amine groups (-NH2) introduced through APTES grafting on the silica surface, which facilitates more effective adsorption than MS-TMR. This improvement aligns with the principles of the Hard Soft Acid Base (HSAB) theory, which suggests that mesoporous silica modified with amine groups, being hard bases, effectively binds the borderline acid nature of Ni (II) metal ions [44].

The amine groups engage in complex formation with target molecules through Lewis acid-base interactions, thereby improving adsorption efficiency. The positively charged amine groups also enhance electrostatic interactions, attracting negatively charged ions. While MS-TMR primarily relies on physical adsorption mechanisms such as Van der Waals forces, MS-TMR-APTES adsorbents facilitate additional chemical interactions, including complexation and electrostatic interactions, due to the presence of amine groups [45].

However, the solution's maximum adsorption capacity is influenced by surface area, pore size, and adsorbate concentration. Although MS-TMR-APTES exhibited increased adsorption capacity for nickel, a saturation point exists beyond which further functionalization or surface modification does not significantly enhance the adsorption capacity. Practical limitations, such as the availability and cost-effectiveness of APTES reagents and the scalability of the synthesis process for large-scale applications, also need consideration [46, 47].

Table 2. Adsorption of Ni (II) by adsorbent

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Co (mg/L)</th>
<th>Ce (mg/L)</th>
<th>Q (mg/g)</th>
<th>R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS-TMR</td>
<td>30</td>
<td>28.93</td>
<td>3.21</td>
<td>3.54</td>
</tr>
<tr>
<td>MS-TMR-APTES</td>
<td>30</td>
<td>13.73</td>
<td>48.81</td>
<td>54.23</td>
</tr>
</tbody>
</table>

Figure 4. %Removal Ni (II) by Adsorbent

The strong binding affinity of the amine groups to Ni (II) ions results from the formation of stable coordination complexes. However, the affinity of amine groups to other heavy metals may vary based on factors such as charge, size, and metal coordination preferences, affecting the selectivity of MS-TMR-APTES for different heavy metal ions from industrial waste. Metals with higher charges or larger ionic radii are likely to form stronger complexes with amine groups than those with lower charges or smaller ones [45].

Additional comparative data on Ni (II) adsorption using various adsorbents are provided in Table 3, illustrating a broader context for the effectiveness of different adsorption technologies.
Table 3. Comparison of adsorption capacities Ni (II) with other adsorbent

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Q (mg/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composite material</td>
<td>199.19</td>
<td>[48]</td>
</tr>
<tr>
<td>Nano-SZO</td>
<td>32.10</td>
<td>[49]</td>
</tr>
<tr>
<td>MCA</td>
<td>167.55</td>
<td>[50]</td>
</tr>
<tr>
<td>MS-TMR</td>
<td>3.21</td>
<td>This Study</td>
</tr>
<tr>
<td>MS-TMR-APTES</td>
<td>48.81</td>
<td>This Study</td>
</tr>
</tbody>
</table>

CONCLUSION

The synthesis of mesoporous silica using a methyl ester ricinoleate template (MS-TMR) and its subsequent functionalization with 3-aminopropyltriethoxysilane (APTES), referred to as MS-TMR-APTES, was successfully conducted. Both samples were characterized using Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffraction (XRD). FTIR analysis of MS-TMR revealed the presence of Si-OH and Si-O-Si groups, indicative of the silica structure. Following the functionalization with APTES, the appearance of C-H, N-H, and C-N groups in the FTIR spectra confirmed the successful grafting of APTES onto the MS-TMR surface. XRD analysis further corroborated that both products maintained an amorphous structure. MS-TMR and MS-TMR-APTES were evaluated as adsorbents for removing Ni(II) metal ions from an aqueous solution. The experimental conditions were set at a Ni(II) concentration of 30 mg/L, a pH of 6, a contact time of 1 hour, and a stirring speed of 150 rpm. The adsorption performance was quantified using Atomic Absorption Spectroscopy (AAS) to determine the concentration of Ni(II) ions post-adsorption. The results indicated that MS-TMR achieved a removal percentage of 3.54% and an adsorption capacity of 3.21 mg/g. In contrast, the MS-TMR-APTES adsorbent significantly enhanced the removal efficiency to 54.23% and the adsorption capacity to 48.81 mg/g. These findings suggest that the functionalization of mesoporous silica with APTES improves the adsorption efficiency for Ni(II) metal ions and indicates the potential of MS-TMR-APTES to effectively adsorb other heavy metal ions. This enhancement is attributed to the increased interaction capabilities afforded by the amine groups introduced through the APTES functionalization, which facilitate stronger binding with metal ions.

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