# MODIFICATION OF MATERIALS WITH EDTA AND CHITOSAN AND APPLICATION TO REMOVE PB$^{2+}$ IN AN AQUEOUS ENVIRONMENT

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**Abstract:** In this study, $SiO_2$, Zeolite materials, and activated carbon (AC) were prepared using simple methods. They were modified with ethylenediaminetetraacetic acid (EDTA) and chitosan (CS) to enhance their adsorption capacity. The adsorption capacity of as-synthesised materials was evaluated by adsorpting $Pb^{2+}$ in the aqueous environment. The characteristics of as-synthesised materials were analyzed by modern methods including X–Ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Transmission Electron Microscopy (TEM), and specific surface area analysis (BET). Surface modification of materials with EDTA and CS does not change the original structure of the materials. However, the morphology and surface of the materials have been significantly changed. Modification with EDTA and CS enhances the $Pb^{2+}$ adsorption capacity of the materials. The $Pb^{2+}$ adsorption efficiencies of EDTA/CS/Zeolite, EDTA/CS/$SiO_2$, and EDTA/CS/AC materials were 72.94, 81.67 and 84.13 %, respectively. Surface modification of materials with EDTA and CS is a promising method in the field of heavy metal treatment in an aqueous environment.

***Keywords***: *EDTA, chitosan, modification, absorption, heavy mental.*

## 1. Introduction

Water pollution is one of the alarming environmental issues in many regions around the world [1-9]. The main causes of this situation include agricultural, industrial, and domestic wastewater. Among them, industrial and domestic wastewater are the two major sources releasing large amounts of hazardous pollutants [10,11]. Heavy metals are extremely dangerous contaminants that directly affect ecosystems and human health [6,12,13].

Lead (Pb) is a highly toxic heavy metal that poses serious threats to both human health and the environment [12-14]. Once entering the body, lead can accumulate and affect the nervous system (brain development, reduced concentration, behavioral disorders, etc.), the circulatory and cardiovascular systems (hypertension, stroke, anemia, etc.), cause kidney damage, impair the reproductive system, and increase the risk of cancer.

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This situation requires solutions to address heavy metal contamination in water, especially lead pollution. Currently, adsorption is considered the most effective method for removing heavy metals from aquatic environments. Many domestic and international researchers have studied and synthesized various adsorbent materials such as activated carbon, silica, graphene oxide, and zeolite, etc. [15,16]. However, to enhance the removal efficiency of heavy metals in water, many researchers have modified the surface of adsorbent materials through methods such as thermal treatment and functionalization with chitosan and EDTA, etc. [17,18].

In this study, a series of materials including silica ($SiO_2$), zeolite, and activated carbon were synthesized using simple methods. They were functionalized with EDTA and chitosan (CS) to enhance their adsorption capacity. The characteristics of the synthesized materials were analyzed and evaluated using several modern techniques. The $Pb^{2+}$ removal performance of the synthesized materials in aqueous environments was also evaluated and compared.

## 2. Experimental

### 2.1. Materials

In March 2024, raw material samples including rice husk, bagasse, and kaolin were collected from the Hanoi area, Vietnam. The chemicals used in this study included: Complexon III (EDTA, $C_{10}H_{16}N_2O_8$, ≥ 99 %), sodium acetate ($C_2H_3O_2Na$, ≥ 99 %), chitosan (CS, $(C_8H_{13}O_5N)_n$, > 75 %), 4-(2-pyridylazo) resorcinol monosodium (PAR, ≥ 99 %), ammonia ($NH_3$, 25 – 28 %), acetic acid ($CH_3COOH$, ≥ 99 %), hydrochloric acid (HCl, 36 – 38 %), isopropyl alcohol ($C_3H_8O$, ≥ 99 %) and lead nitrate ($Pb(NO_3)_2$, ≥ 99,5 %). All chemicals were supplied from China and used directly without further purification. Distilled water was prepared in the laboratory and used for all experiments.

### 2.2. Characterization of materials

The XRD method (Bruker D8 Axe, Germany) was used to analyze the crystalline phases of the synthesized materials. XRD patterns were obtained using Cu-Kα radiation (40 kV, 40 mA) with a 2θ range from 10 to 80°. The morphology and particle size of the synthesized materials were observed using HR-TEM (JEM-JEOL 2100, Japan) operated at an accelerating voltage of 80 – 200 kV with a point resolution of about 0.19 nm, and SEM (JEOL-7600F, Japan) operated at an accelerating voltage of 0.1 – 30 kV with a maximum resolution of 1.0 nm (at 15 kV) and 1.5 nm (at 1 kV). The ASAP 2460 – Accelerated Surface Area and Porosimetry System (Micromeritics Instrument Corporation, USA) was used to analyze the structure of the modified materials.

### 2.3. Materials Synthesis

#### 2.3.1 Synthesis of silica

Rice husk was washed, dried at 100 °C, and then calcined at 600 °C for 2 h to obtain RHA. Subsequently, 5 g of RHA was stirred in 100 mL of 2 N NaOH, heated for 2 h, and filtered to obtain a $Na_2SiO_3$ solution. After that, the synthesis of $SiO_2$ was carried out following the procedure described in a previous study [7,14,19].

### *2.3.2 Synthesis of zeolite*

The synthesis of zeolite was also carried out following a previous study [16]. After collection, kaolin was treated at 600 °C for 3 h to obtain metakaolin. A mixture of metakaolin, sodium hydroxide, water glass, EDTA, and distilled water was stirred thoroughly and aged at room temperature for 48 h. The resulting gel was then crystallized at 90 °C for 24 h. After filtration and repeated washing with distilled water, the precipitates were dried, ground, and sieved to obtain zeolite Y.

### *2.3.3 Synthesis of activated carbon*

Bagasse was washed and dried at 80 °C. Next, 80 g of this bagasse was thoroughly mixed with 80 g of saturated NaOH solution, then dried and cooled, followed by calcination at 800 °C for 60 min and fine grinding. A 1 M HCl solution was added to the mixture in excess, stirred thoroughly, and aged for 24 h. Finally, the mixture was filtered, repeatedly washed with distilled water, and dried at 150 °C for 10 h to obtain activated carbon.

### *2.3.4 Material modification with EDTA and CS*

CS was stirred in 10 mL of 2 % $CH_3COOH$ solution and left overnight to obtain mixture A. The support material ($SiO_2$, zeolite, or activated carbon) was evenly dispersed in 20 mL of isopropyl alcohol and stirred at 70 °C. This mixture was then added to mixture A and stirred at 70 °C for 1 h. Subsequently, 10 mL of EDTA was gradually added to the above mixture, and stirring continued for another 1 h. Finally, the functionalized material was filtered, repeatedly washed with distilled water and ethanol, and dried at 80 °C for 12 h.

### ***2.4. Evaluation of $Pb^{2+}$ removal performance of the materials***

The adsorption capacity of the synthesized materials was evaluated by the $Pb^{2+}$ removal efficiency in aqueous solutions at room temperature. First, 0.05 g of the material was added to 100 mL of a 20 mg/L $Pb^{2+}$ solution with an initial pH of 6 and ultrasonicated for 5 min to ensure uniform dispersion. The mixture was then continuously stirred using a magnetic stirrer at 350 rpm. At predetermined time intervals, 2 mL of the reaction mixture was withdrawn and filtered through a 0.45 µm PTFE membrane to remove the material, and then used for complex formation. The complex solution consisted of: 1 mL of $Pb^{2+}$ solution, 2 mL of 0.1 M $NH_3$ solution, 3 mL of 0.1 M $CH_3COONa$ solution, and 2 mL of 100 mg/L PAR solution, made up to 25 mL. After 25 min of stabilization, the complex was measured using a UV-Vis spectrophotometer at a wavelength of 530 nm to determine the $Pb^{2+}$ concentration. The $Pb^{2+}$ adsorption efficiency was calculated using the following equation [14, 16]:

$$H\,(\%) = \frac{C_0 - C_t}{C_0} \times 100\ \% \qquad (1)$$

Where $C_0$ and $C_t$ (mg/L) are the initial $Pb^{2+}$ concentration and the $Pb^{2+}$ concentration at time t, respectively.

## **3. Results and discussion**

### ***3.1. Characterization of the materials***

In this study, the XRD method was used to observe structural changes of the materials before and after functionalization with EDTA and CS. The results are shown in Figure 1.

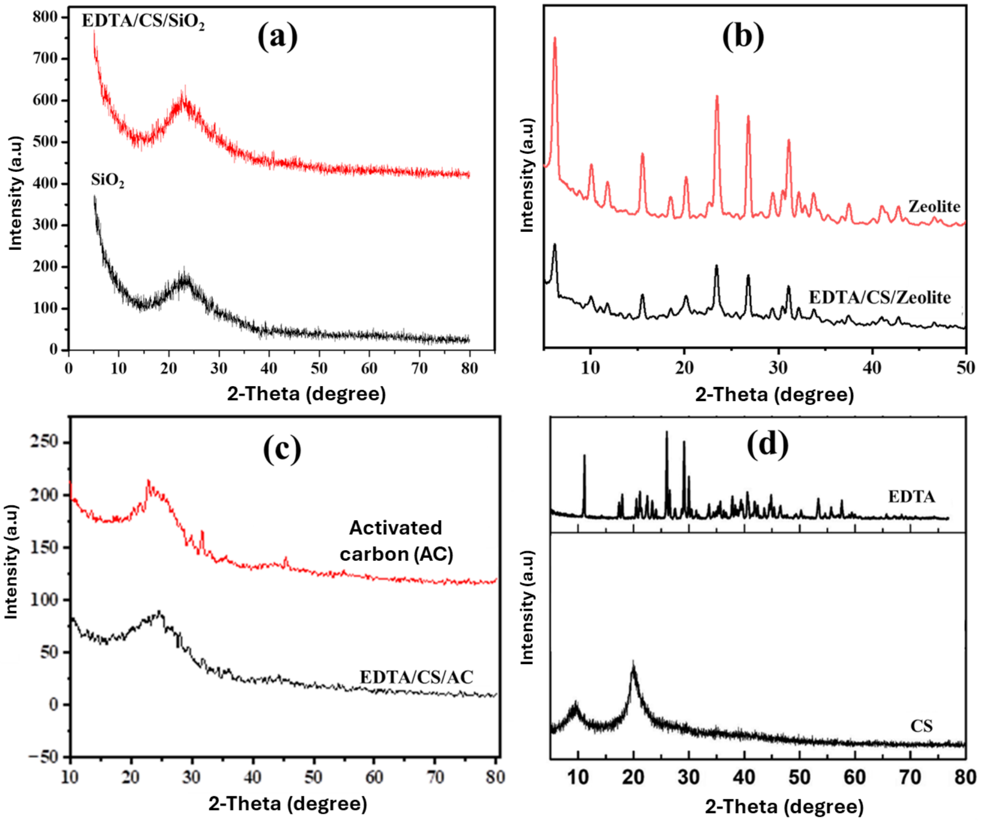

**Figure 1. XRD patterns of the materials: (a) $SiO_2$, EDTA/CS/$SiO_2$; (b) Zeolite, EDTA/CS/Zeolite, (c) activated carbon (AC), EDTA/CS/AC, and (d) pure EDTA and CS.**

As shown in Figure 1, it can be observed that surface functionalization of the adsorbent materials did not alter their original structures. The similarity between $SiO_2$ and EDTA/CS/$SiO_2$ (Figure 1(a)) indicates that the silica structure remained unchanged after surface modification with EDTA and CS. Moreover, both materials exhibit a broad diffraction peak at around 24°, suggesting that the materials are almost amorphous. As shown in Figure 1(b), the high-intensity diffraction peaks at 6.21, 15.57, 23.45, 26.79, and 31.11 ° correspond to the (111), (331), (533), (642), and (555) planes, characteristic of zeolite Y [20, 21]. In addition, several low-to medium-intensity peaks were also observed in the XRD patterns of pure zeolite and EDTA/CS/zeolite. The appearance of a broad diffraction peak between 25 and 26 ° in the XRD patterns of activated carbon and EDTA/CS/AC indicates the presence of activated carbon [22, 23]. The broad diffraction peaks indicate that the materials possess an amorphous structure. No unexpected diffraction peaks were observed in any of the XRD patterns, demonstrating that the synthesized materials are of high purity. However, in the XRD patterns of the functionalized materials, no signals corresponding to EDTA or CS were detected (Figure 1(d)). This can be explained by peak overlapping, as the peaks of the support materials mask those of EDTA and CS. Based on the analysis, the following conclusions can be drawn: (1) Zeolite Y, $SiO_2$, and activated carbon were successfully synthesized with an amorphous structure; (2) these materials were successfully functionalized with EDTA and CS; (3) surface functionalization did not alter the original crystal structure of the support materials.

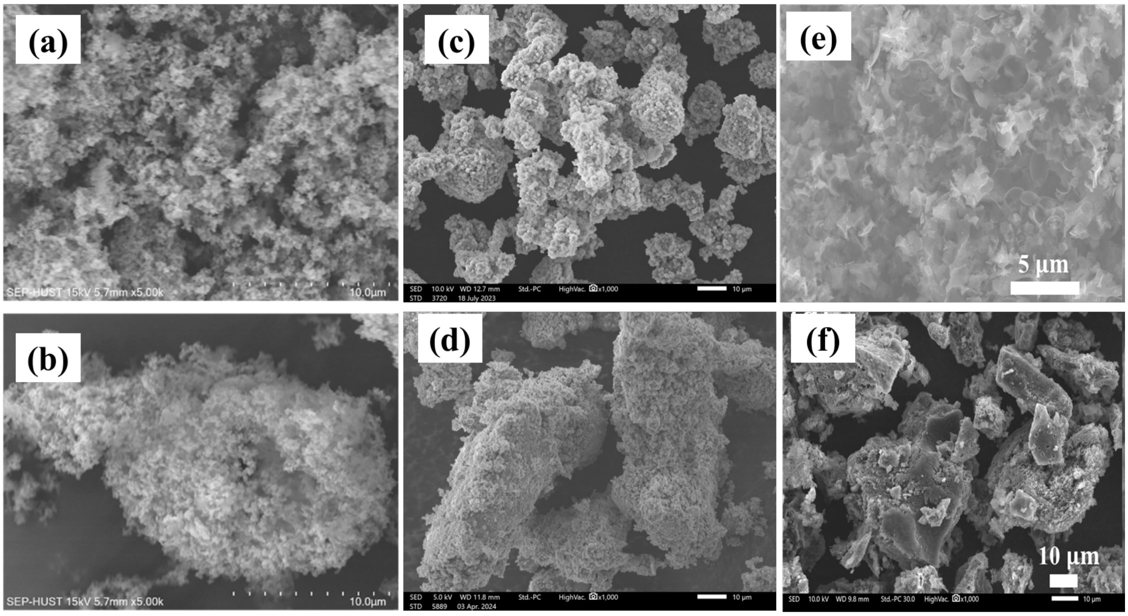

**Figure 2. SEM images of matetials (a) $SiO_2$, (b) EDTA/CS/$SiO_2$, (c) Zeolite, (d) EDTA/CS/Zeolite, (e) activated carbon, and (f) EDTA/CS/AC.**

The morphology of the synthesized materials was observed using SEM. It can be seen that $SiO_2$ exhibits a particulate and uniform morphology, aggregating into porous clusters as shown in Figure 2(a). After functionalization with EDTA and CS, EDTA/CS/$SiO_2$ formed larger cloud-like aggregates (Figure 2(b)); however, the size and shape of the particles remained similar to those of $SiO_2$. It can be observed that the nanoparticles aggregate into clusters, forming the characteristic morphology of zeolite, as shown in Figure 2(c). After functionalization with EDTA and CS, the surface of the zeolite changed significantly. The individual zeolite nanoparticles were no longer clearly observed, and the size of the clusters increased, as shown in Figure 2(d). This can be explained by the fact that CS caused the zeolite nanoparticles to aggregate into larger assemblies, forming a thick layer covering their surfaces, upon which the EDTA crystals subsequently deposited. Figure 2(e) shows that activated carbon exhibits a honeycomb structure consisting of thin layers tightly connected to form a fine porous network. AC contains numerous pores of relatively uniform size. After surface functionalization with EDTA and CS, the morphology of EDTA/CS/AC became more complex, comprising flakes and blocks of varying sizes, as shown in Figure 2(f). The surface of this material contains numerous irregularly sized pores. In addition, many grooves and voids are clearly visible on the surface (Figure 2(f)). Therefore, surface functionalization also significantly altered the original morphology of the material, which may be one of the factors contributing to the improved adsorption capacity of the support materials.

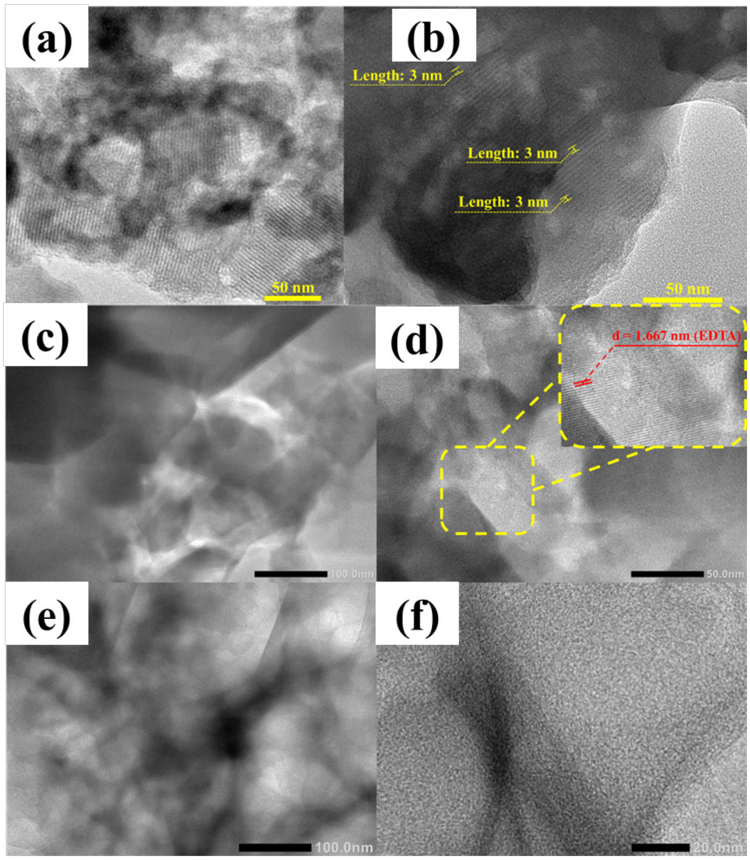

**Figure 3. HR-TEM images of materials (a-b) EDTA/CS/$SiO_2$, (c-d) EDTA/CS/Zeolite, and (e-f) EDTA/CS/AC.**

The HR-TEM images (Figure 3) of the materials functionalized with EDTA and CS all show parallel lattice fringes characteristic of crystal planes. The lattice spacings range from 1.667 to 3 nm, indicating that EDTA crystals have deposited on the surfaces of the support materials. However, in the HR-TEM images of EDTA/CS/AC (Figure 3(e–f)), the lattice fringes are not clearly observed.

### *3.2. Evaluation of $Pb^{2+}$ adsorption capacity*

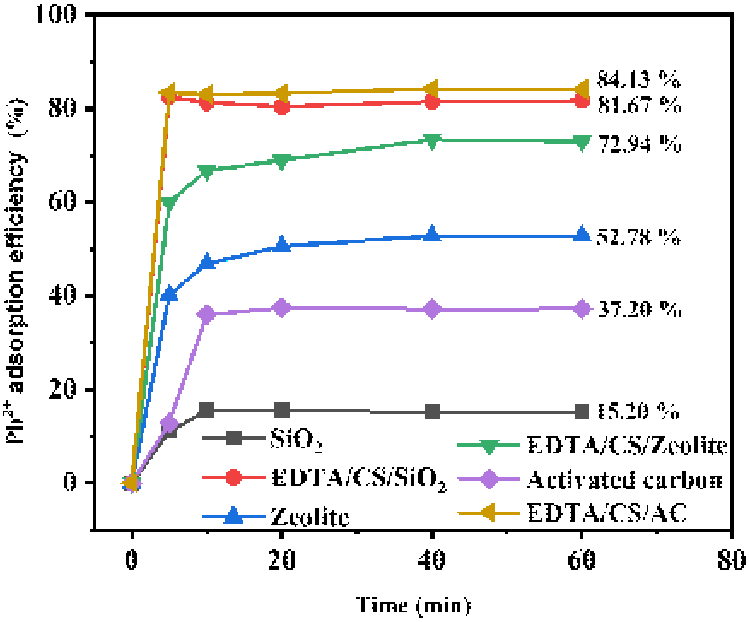

**Figure 4. $Pb^{2+}$ adsorption efficiency of the synthesized materials**

To investigate the adsorption capacity of the synthesized materials, the $Pb^{2+}$ adsorption experiments were conducted under the same reaction conditions, including 0.05 g of material, 100 mL of 20 mg/L $Pb^{2+}$ solution, and room temperature (25 °C). As shown in Figure 4, the $Pb^{2+}$ removal efficiency improved significantly after surface functionalization of the materials with EDTA and CS. The unmodified support materials exhibited relatively low $Pb^{2+}$ adsorption, ranging from 15.20 to 52.78 %. Among them, pure $SiO_2$ showed the lowest adsorption capacity with an efficiency of only 15.20 %, while pure zeolite exhibited the highest adsorption capacity, reaching 52.78 %. After functionalization with EDTA and CS, the $Pb^{2+}$ adsorption capacity of the materials increased significantly. For EDTA/CS/$SiO_2$, the $Pb^{2+}$ removal efficiency increased the most, showing a 66.47 % enhancement compared to pure $SiO_2$. EDTA/CS/zeolite exhibited a $Pb^{2+}$ removal efficiency of only 72.94 %, the lowest among the materials functionalized with EDTA and CS. For activated carbon, the $Pb^{2+}$ removal efficiency reached 37.20 %, and after functionalization, it increased to 84.13 %, the highest among all functionalized materials; however, the difference in $Pb^{2+}$ adsorption efficiency compared to unmodified activated carbon was only 46.93 %. Based on the results of the $Pb^{2+}$ adsorption evaluation of the synthesized materials, the following conclusions can be drawn: (1) The synthesized $SiO_2$, zeolite, and activated carbon all exhibited $Pb^{2+}$ adsorption capacity, with zeolite showing the highest adsorption performance among them. (2) Surface functionalization with EDTA and CS enhanced the $Pb^{2+}$ adsorption capacity of the support materials. (3) EDTA/CS/AC exhibited the highest $Pb^{2+}$ removal efficiency. This can be explained as follows: after surface functionalization with EDTA and CS, the number of functional groups

(-COOH, -OH) increased, or amide bonds were formed, leading to improved $Pb^{2+}$ adsorption efficiency [24]. Based on the structural analysis of the synthesized materials (Table 1), it can be seen that surface functionalization with EDTA and CS significantly altered the pore volume and size, particularly the specific surface area of the support materials. The decrease in these structural parameters can be attributed to the deposition of CS and EDTA molecules on the pores and surfaces of the support materials. Among the materials functionalized with EDTA and CS, EDTA/CS/AC exhibited the highest BET surface area (496.8 $m^2/g$), resulting in the most effective interaction between $Pb^{2+}$ ions and the material surface. This is also the reason why this material demonstrated the highest $Pb^{2+}$ adsorption capacity.

**Table 1. Structural properties of the synthesized materials.**

| Materials | Surface area BET ($m^2/g$) | Pore volume ($cm^3/g$) | Pore size (Å) |
|---|---|---|---|
| **$SiO_2$** | 408.3 | 0.856 | 58.2 |
| **EDTA/CS/$SiO_2$** | 352.2 | 0.114 | 55.0 |
| **AC** | 532.7 | 1.935 | 12.1 |
| **EDTA/CS/AC** | 496.8 | 1.443 | 10.0 |
| **Zeolite** | 267.0 | 0.797 | 11.9 |
| **EDTA/CS/Zeolite** | 248.7 | 0.153 | 11.4 |

## 4. Conclusion

In summary, this study successfully synthesized adsorbent materials, including $SiO_2$, zeolite, and activated carbon, using simple methods and further functionalized their surfaces with EDTA and CS. The characteristics of the synthesized materials were analyzed, evaluated, and compared. Surface functionalization with EDTA and CS did not alter the original structure of the support materials but only modified their surface morphology. The $Pb^{2+}$ adsorption capacity of the materials improved significantly after surface functionalization with EDTA and CS. Notably, surface functionalization of $SiO_2$ with EDTA and CS remarkably enhanced its $Pb^{2+}$ adsorption capacity, with an efficiency increase of 66.47 % compared to pure $SiO_2$. Therefore, surface functionalization of materials with EDTA and CS represents a highly promising and potential approach for water pollution treatment in general and heavy metal contamination in particular.

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