Mg Al-layered double hydroxide (LDH)-assisted multiwalled carbon nanotube (MWCNT) grafting on poly-2-aminothiazole (PAT)/chitosan (CS)-blend matrix for Cd$^{2+}$ removal and 4-nitrophenol reduction

Mohammad Saeid Rostami  
Razi University  
Mohammad Mehdi Khodaei (✉ mmkhoda@razi.ac.ir)  
Razi University

Research Article

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Abstract

The present study evaluated the performance of multiwalled carbon nanotube (MWCNT)@MgAl-layered double hydroxide (LDH) nanoparticles loaded on poly-2 aminothiazole (PAT)/chitosan (CS) matrix to remove Cd\textsuperscript{2+} ions from aqueous solution. We created a new PAT-based adsorbent by mixing PAT and CS nanoparticles, and surface modification by MWCNT@LDHs. For preparing the adsorbent, first, the PAT surface was modified by CS as an excellent candidate with a large number of –OH functional groups for interfacial adhesion improvement of the composite and enhancing the adsorption of the polymer. Then, to the homogeneous distribution of MWCNT in the matrix (CS/PAT), the surface of the functionalized MWCNT (MWCNT-COOH) was covalently modified by LDHs. Finally, the nanocomposite (NC) films were fabricated by ultrasonication using various loadings (30–70 wt %) of MWCNT@LDH. The prepared films were labelled CP-30%, CP-50%, and CP-70%. By adding MWCNT@LDH to the matrix network, the removal efficiency was increased significantly compared to CS/PAT. The influence of heavy metal ion concentration, pH, temperature, adsorbent dosage, and contact time on the adsorption.

The maximum absorption capacity of 1106.19 mg/g was measured for Cd\textsuperscript{2+}. The pseudo-first-order kinetics (PFO) and the Langmuir model were selected as the best models for the adsorption process. Also, the NC was successfully tested for p-nitrophenol (p-NP) reduction in the presence of NaBH\textsubscript{4}. The reaction was nearly completed in 6 min. Studies showed that the fabricated NC could be reused for three consecutive cycles.

1. Introduction

Unfortunately, harmful metal ions and other contaminants have entered water environment as a result of excessive chemical output from various chemical businesses. These harmful contaminants cause environmental contamination, which makes drinking water sources unsafe. They can also spread down the food chain, causing severe and irreparable damage to humans [1–4]. For example, Cd\textsuperscript{2+} can cause bone decay, breathing disorders, and cancer [5]. Also, nitrophenols, particularly para-nitrophenol (p-NP), have been considered by US Environmental Protection Agency (USEPA) as highly hazardous substances due to their environmental persistence and carcinogenicity [6]. Hence, it is necessary to develop new strategies to purify and remove these pollutants from aquatic environments [7].

The absorption technique is known as one of the most effective methods for removing pollutants due to its high efficiency, easy operation, cost-effectiveness and no secondary contamination [8, 9]. A perfect adsorbent for metal ion removal should have a lot of surface area, high adsorption capacity, availability, affordability, mechanical stability, compatibility, appropriate pore size and volume, environmental compatibility, ease of regeneration, and high selectivity for removing a variety of metal ions [10]. Polymers used as adsorbents should have characteristics such as good mechanical strength, recyclability, and degradability [11, 12–18].
Therefore, making polymer-based composites to obtain polymers with the aforementioned properties can be a suitable strategy to remove pollutants, and increase the surface adsorption capacity of the host polymer [17]. Therefore, in recent years, the fabrication of composites based on natural polymers, including chitosan, has increased as an alternative adsorbent with high absorption capacity [19].

For instance, Lan and coworkers [20] prepared NCs based on CS grains combined with La-Fe (LaFe@CS) and investigated it for Cd\(^{2+}\) adsorption from aqueous solution. According to the results, the maximum absorption capacity was 35.50 mg g\(^{-1}\) at pH 5.6 based on the Langmuir model. Also, the adsorption capacity remained at about 80% after four adsorption cycles. They suggested that electrostatic attraction and ligand exchange influence the adsorption behaviors. In addition, Parastar and colleagues used a CS/graphene oxide (GO)/iron (III) oxide hydroxide NC to remove Cd\(^{2+}\) ions from an aqueous solution. The results revealed that the functional groups containing oxygen on the surface of graphene oxide, iron (III) oxide nanoparticles, and abundant amino and hydroxyl functional groups of the CS chain have a very good potential to absorb Cd\(^{2+}\). It was reported that the percentage of Cd\(^{2+}\) removal was 95% [21].

Moreover, recently Fajardo and coworkers [22] reported the fabrication of Alginate/Phosphine/CS beads for removal of Cd\(^{2+}\) from water media. According to the results, the maximum adsorption capacity for Cd\(^{2+}\) (78.20 mg g\(^{-1}\)) was calculated.

CS is a biopolymer that is achieved from the deacetylation of chitin with various properties, which is considered an efficient bio-adsorbent for purifying water environments due to the presence of functional groups such as hydroxyl and amine in its structure [23–25]. On the other hand, in recent years, the use of conductive polymers as new absorbents to remove pollutants from the water environment has increased [26–32]. In the meantime, it has been reported that PAT has a high performance in absorbing heavy metal ions due to its properties of thiophene, pyrrole, and aniline as a unique polymer. For instance, Wang and coworkers reported the adsorption of Hg\(^{2+}\), Cd\(^{2+}\), Pb\(^{2+}\), and Ni\(^{2+}\) from an aquatic solution using PAT [25]. Connecting PAT to CS creates a unique matrix network with excellent properties not found in either [33].

Investigations have shown that the presence of MWCNT-COOH nanoparticles in the structure of NCs improves their potential and performance compared to conventional composites in the absorption process [34] However, MWCNTs have a high tendency to aggregate in polymer networks, which makes it difficult for homogeneous dispersion of these materials in composites [35]. The better dispersion and stability of MWCNTs in polymeric networks can be created by modifying their surface with LDHs [36]. The anion exchange properties of LDHs and their potential application in various fields have recently attracted the attention of researchers [37]. By linking LDHs to polymers having functional groups, they form strong bonds with pollutants and improve adsorption capacity [38]. Mallakpour et al. examined the fabrication of PET/MWCNT@LDH NC for the Cd\(^{2+}\) uptake from an aqueous solution, and their results showed that LDH-modified MWCNT and dispersed it on the Polymer.

In this study, the CS surface was treated with PAT for improving dispersion and compatibility with MWCNT@LDH hybrids and absorbing heavy metals. A variety of filler amounts were then used to make
films. Finally, various techniques were used to investigate NC properties. CS/PAT showed high adsorption capacity compared to pure PAT reported by previous researchers [25].

2. Experimental Section

2.1. Material and methods

Chitosan (degree of deacetylation, 75–85%; Medium molecular weight 190,000-310,000) was obtained from Sigma-Aldrich. Al(NO$_3$)$_3$·9H$_2$O, 2-aminothiazole (AT), Mg(NO$_3$)$_2$·2H$_2$O, CuCl$_2$·2H$_2$O, 4-nitrophenol (4-NP), NaOH, sodium borohydride (NaBH$_4$), and Na$_2$CO$_3$ were bought from Merck Co. (Darmstadt, Germany). MWCNT-COOH was purchased from US, INC. [Cd (OAc)$_2$·2H$_2$O (purity 98%)] was obtained from Honeywell, Fluka Co.

2.2. Characterization

The FT-IR spectrum of the samples was recorded using a Bruker Alpha 27 spectrophotometer. XRD (Equinox 3000, Inel) analysis was applied to determine crystal structures in the 2θ ranging from 10–80° using Cu K$_\alpha$ radiation and $\lambda = 0.154$ nm. The morphology of the samples was analyzed using SEM (FEI-Quanta 450 (USA)). The Cd$^{2+}$ concentration was computed using a flame atomic absorption spectroscopy (AAS) (Varian Spectra AA 220 FSVariant). Also, the measurement of p-NP was carried out using a UV/VIS spectrophotometer (Perkin-Elmer-Lambda 25). The average pore size and surface area were calculated using BET analysis. The BJH method was used to determine the pore size of PAT and CP-NC. The thermal stability of the samples was measured by thermogravimetric analysis (TGA) (Waltham, USA, STA 6000)

2.3. Synthesis of PAT

The synthesis of PAT was conducted according to the previous work [39]. Briefly, 0.1 g of AT and 30 ml of H$_2$O were transferred into a 100 ml round bottom flask. Next, 30 ml of an oxidant solution of CuCl$_2$·2H$_2$O was then added dropwise to the solution followed by heating to 70°C. The reaction continued for another 24 h. Afterwards, the obtained product was thoroughly washed with ethanol and deionized water (DI).

2.3.1. Synthesis of MWCNT@LDH nanoparticles

The fabrication of MWCNT@LDH was conducted using ultrasonic technique. First, the mixture of Al (NO$_3$)$_3$·9H$_2$O (1mmol), Mg (NO$_3$)$_2$·6H$_2$O (2 mmol) and 50 ml of DI water was prepared (1). Then, a solution containing Na$_2$CO$_3$ (0.16 g), NaOH (0.08 g) and MWCNT (0.1 g) was prepared (2). By mixing solutions (1) and (2) followed by stirring for 2 h, the resultant mixture was sonicated for 60 min. A 16 h drying process was then carried out on the obtained product at 50°C.

2.4. Fabrication of CP-NCs
CP-NCs were formed by a simple method (mixing solution). First, 25 ml of DI water was mixed with 0.1 g of PAT and heated simultaneously to 70°C for 30 min. An aqueous solution of CS was formed by transferring 0.1 g of CS into 25 ml of aqueous acetic acid solution (2% (v/v)) [38]. Then, two solutions of PAT and CS were then mixed and stirred for 1 h. Next, quantities of 30–70 wt% of filler were added to fabricate CP-NCs and stirred for 24 h. To neutralize the acetic acid, the fabricated NCs were immersed to NaOH (1 M) for 30 min. Scheme 1 shows the structure of CP-NC. In CS/PAT and MWCNT structures, hydrogen bonds form between carboxyl, hydroxyl, and amino groups, and electrostatic interactions occur between MWCNTs and LDHs nanostructures. Depending on the components of the composite structure, the presence of anionic and other functional groups will affect the ability to absorb metal ions.

2.5. Adsorption experiment

The Cd\(^{2+}\) ion adsorption process was performed by adding CP-NC (0.06 g) into a solution containing 20 ml of Cd\(^{2+}\) (100 mg L\(^{-1}\)), time (6 h), and pH = 8 to examine the efficiency of the adsorbent. The effect of pH on Cd\(^{2+}\) adsorption by CP-NC was investigated and 0.06 g of CP-NC was transferred into a Cd\(^{2+}\) solution (20 ml, 100 mg L\(^{-1}\)). The expected pH was adjusted from 4 to 8 using NaOH (1 M) and HNO\(_3\) (1 M). After equilibration, the residual concentration was assessed by AAS. To assess the impact of the adsorbent dosage, various amounts of sorbent (0.01–0.06 g) were added to a Cd\(^{2+}\) solution (20 ml, 100 mg L\(^{-1}\)), and the adsorptions were carried out at RT for 6 h. To investigate the impact of the initial metal ion concentration, adsorbent (0.06 g) was added to a Cd\(^{2+}\) solution (20 ml, 100–500 mg L\(^{-1}\)) at pH 8 at RT for 6 h to examine the effect of the initial metal ion concentration. The adsorption capacity (\(q_e\), mg g\(^{-1}\)) was determined using Eq. (1):

\[
q_e = \frac{C_0 - C_e}{m} v
\]

Where \(C_e\) and \(C_0\) are the equilibrium and initial concentration (mg L\(^{-1}\)), respectively, \(m\) (g) is the amount of the adsorbent and \(V\) (L) is the volume of the Cd\(^{2+}\) solution. Also, the removal percentage (R\(\%\)) was calculated by the Eq. (2):

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

3. Results And Discussion

3.1. Characterization of CP-NCs
The XRD patterns of prepared samples are reported in previous work [39]. In MWCNT’s graph four peaks at 2θ = 26.03° (002), 38.19 (100), 44.43 (101), and 77.8° (006) correspond to MWCNT’s hexagonal graphite structure. In the XRD pattern of MWCNT@LDH, the peak at 26.03° (002) can be related to the graphite carbon sheet in the nanotube structure (JCPDS No. 41-1487). There are also peaks at 11.29° (003), 35.14° (009), and 64.16° (110) which correspond to LDH structures (JCPDS No. 14–191), confirming the formation of LDHs on MWCNT surfaces. The XRD pattern also shows an amorphous structure for CS/PAT. A comparison of MWCNT@LDH and CP-NCs diffraction patterns revealed well-incorporated LDH nanosheets in the CS/PAT matrix.

The FT-IR spectra of MWCNT, CS/PAT, PAT, MWCNT@LDH, and CP-NC (in this manuscript CP-NC means CP-NC 30 wt %) are available [39]. The CS/PAT spectrum shows peaks around 1156, 2168, and 3418 cm$^{-1}$ correspond to the C–O–C stretching of CS, C–N asymmetric stretching, and O–H stretching (overlapped with N–H), respectively [40]. In the PAT spectrum, there is a wide peak around 3416 cm$^{-1}$ that is attributed to N-H stretching. Also, the peaks about 612, 1508, 3246, and 1610 cm$^{-1}$ are attributed to C-S in the ring poly (2-aminothiazole), C = C, C = N, and aromatic sp$^2$ C-H, respectively [25]. MWCNT-COOH spectra display a peak at 3414 cm$^{-1}$ corresponding to carboxylic acid’s O-H stretching, and a peak at 1727 cm$^{-1}$ is attributed to the COOH group. The like-hydrotalcite network bands in the MWCNT@LDH spectrum can also be attributed to metal-oxygen bonding (M–O) [41]. The band at 3414 cm$^{-1}$ in the spectra of CP-NC is attributed to overlapping –NH and –OH stretching.

Figure 1 illustrates scanning electron microscopy (SEM) analysis of CP-NCs, MWCNT@LDH, and CS/PAT. Figure 1c displays a honey-comb structure for CP-NC 30 wt %. It is clear that MWCNT@LDH is well-embedded and distributed throughout in CS/PAT matrix. The electrostatic attraction bonding between MWCNT and LDH sheets prevents the agglomeration of filler in the matrix. Modifying the surfaces of PAT and MWCNT lead to a suitable distribution of filler in the matrix. Moreover, by increasing adaptability between the MWCNTs and the matrix, the surface adhesion of the modified nanofillers was improved.

TGA graphs for MWCNT@LDH and MWCNT are available [39]. MWCNT shows a weight loss of less than 1 wt%. whereas in the MWNT@LDH graph a small demolition (13 wt %) between 30 and 250°C was observed. Weight loss related to MWCNT@LDH at temperatures between 30–600°C can be explained by the presence of H$_2$O and the breakdown of modifiers. The MWCNT@LDH graph clearly shows that LDH is bonded to MWCNT. Figure 5b illustrates how the filler effects the breakdown of the matrix network. CP-NCs show a higher char yield than pure CS/PAT. This can be attributed to nanostructures in CP-NCs reducing heat transitions during ignition, contributing to higher char yields [42, 43].

According to the N$_2$-adsorption-desorption curve for PAT and CP-NC [39] the CP-NC offers more active sites for Cd$^{2+}$ uptake due to its larger surface area (424.60 m$^2$g$^{-1}$). Based on their isotherms and pore sizes (8.52 nm for PAT and 7.78 nm for CP-NC) both display type IV hysteresis and a mesoporous structure.

### 3.2. The impact of pH on the sorption
Figure 2 shows the impact of pH on the sorption. As can be seen a sudden increase in absorption is obtained at pH = 8, indicating that at pH < 7, the CP-NCs surface is protonated and has charged positively, while at pH > 7, it is deprotonated and becomes negatively charged. Hence, the adsorption process is explained by the electrostatic adsorption mechanism of adsorbent surfaces. The adsorption efficiency decreases when the pH decreases, because of the unfavorable interaction force between the adsorbent surface and Cd\(^{2+}\) ions [44–48]. At a lower pH, there are more H\(^+\) ions present, which causes the absorption sites to become protonated. Lower Cd\(^{2+}\) ion removal results from competition between the Cd\(^{2+}\) ions and H\(^+\) ions for the same adsorption sites. At a higher pH level, on the other hand, the concentration of H\(^+\) is diminished, which causes the composite's propensity to adsorb Cd\(^{2+}\) ion to increase. Further investigation for higher pH values was not performed due to the formation of Cd(OH)\(_2\) precipitate [49].

3.3. The impact of the adsorbent dosage

Figure 3 compares the removal efficiency of Cd\(^{2+}\) ions versus adsorbent dose for CS/PAT and CP-NC. The results show that the removal efficiency for pure CS/PAT and CP-NC attained 75.8% and 98.2%, respectively when the adsorbents dose reach to 600 mg. The Cd\(^{2+}\) adsorption rate of CP-NC is higher than CS/PAT due to the presence of MWCNTs and LDHs in CP-NC samples which they have more available -OH functional groups and anionic groups on the MWCNT and LDH surfaces for metal ion adsorption.

3.4. Kinetic studies

The kinetic studies of Cd\(^{2+}\) ion adsorption using CP-NC were investigated under optimal conditions. The results indicated that by increasing reaction time, adsorption quantity increases. The following equations were used to fit the data and study the absorption characteristics.

Pseudo-first-order (PFO) 
\[ \ln(q_e - q_t) = \ln q_e - K_1 t \] (3)

Pseudo-second-order (PSO) 
\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \] (4)

Intra-particle diffusion 
\[ q_t = k_i t^{1/2} + C \] (5)

Where \( q_e \) and \( q_t \) (mg g\(^{-1}\)) represent the metal adsorption capacities at equilibrium and time t, respectively. The absorption rate constants are denoted by \( k_1 \) (min\(^{-1}\)), \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)), and \( k_i \) (mg g\(^{-1}\) min\(^{-1/2}\)), while C denotes the boundary layer's thickness. \( k_1, k_2, k_i \), equilibrium absorption (\( q_a \)), and \( C_i \) are obtained using the slope and intercept of the diagram [50, 51]. The kinetic data for Cd\(^{2+}\) removal are collected in Table 1. Figure 4 displays the line diagrams of each of the different models in the data set. PFO kinetic model (\( R^2 = 0.9906 \)) was used to fit the kinetic results. Comparing the experimental and calculated values of \( q_e \) also shows that a PSO kinetic model is more appropriate.
### Table 1
Kinetic parameters of Cd$^{2+}$ ions removal with CP-NC

<table>
<thead>
<tr>
<th>Kinetics</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_e^1$ (mg g$^{-1}$)</td>
<td>541.20</td>
</tr>
<tr>
<td><strong>Pseudo-second-order</strong></td>
<td></td>
</tr>
<tr>
<td>$q_e^2$ (mg g$^{-1}$)</td>
<td>26.52</td>
</tr>
<tr>
<td>$k_2$ (g mg$^{-1}$ min$^{-1}$)</td>
<td>0.0019</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9799</td>
</tr>
<tr>
<td><strong>Pseudo-first-order</strong></td>
<td></td>
</tr>
<tr>
<td>$k_1$ (min$^{-1}$)</td>
<td>0.00006</td>
</tr>
<tr>
<td>$q_e^2$ (mg g$^{-1}$)</td>
<td>525.31</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9906</td>
</tr>
<tr>
<td><strong>Intra particle diffusion</strong></td>
<td></td>
</tr>
<tr>
<td>$K_i$ (mg g$^{-1}$ min$^{-1/2}$)</td>
<td>0.6573</td>
</tr>
<tr>
<td>$C_i$</td>
<td>13.36</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9311</td>
</tr>
</tbody>
</table>

1 Experimental
2 Theoretical

### 3.5. Adsorption isotherm

The influence of filler loading on Cd$^{2+}$ removal efficiency was conducted using 0.06 g of each adsorbent. The results showed that increasing the MWCNT@LDH content decreases the Cd$^{2+}$ removal efficiency from 98.2–70% and 56% for CP-NCs 30, 50 and 70 wt%, respectively. CP-NC showed the highest adsorption amount for Cd$^{2+}$. It seems that with MWCNT@LDH content, more volume of active sites in the matrix is occupied by the filler. Figure 5d shows the effect of the metal ion concentration on the adsorption capacity and removal percentage (R%) using 0.01g of CP-NC. Accordingly, with increasing Cd$^{2+}$ concentration, decreasing R% and increasing adsorption capacity in aquatic medium was observed.
Decreasing R% result from a further increase in Cd\(^{2+}\) concentration can be related to the availability of more sites for adsorption at low concentrations (100 ppm).

Moreover, with increasing concentration of Cd\(^{2+}\) the adsorption sites become saturate. Consequently, Cd\(^{2+}\) trapping will be tricky. The common isotherms Freundlich and Langmuir were used to investigate experimental data. Also, the Dubinin-Radushkevich isotherm model (DR) was utilized to determine the energy and description of the adsorption mechanism.

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad \text{Langmuir (6)}
\]

\[
Ln q_e = \frac{1}{n} Ln C_e + Ln K_F \quad \text{Freundlich (7)}
\]

\[
Ln q_e = Ln q_m - K_D R \varepsilon^2 \quad \text{Dubinin-Radushkevich (8)}
\]

The equilibrium concentration is \(C_e\) (mg L\(^{-1}\)), the equilibrium adsorption capacity is \(q_e\) (mg g\(^{-1}\)), \(K_L\) (mg L\(^{-1}\)) represents the sorption energy, and \(q_m\) (mg g\(^{-1}\)) is the theoretical adsorption capacity. Also, \(n\) and \(K_F\) are absorption constants. \(K_D R\) is the Polanyi potential derived from Eq. 9 and is the isothermal constant (mol\(^2\) kJ\(^2\)):

\[
\varepsilon = RT Ln(1 + \frac{1}{C_e})
\]

9

\(R\) and \(T\) are the universal gas constant and absolute gas temperature, respectively. Based on the D-R model, \(E\) (free energy change) is related to the transfer of 1mol Cd\(^{2+}\) from aqueous solution to the adsorbent surface, which is obtained by Eq. (10):

\[
E = \frac{1}{\sqrt{2K_D R}}
\]

10

The results related to different isotherms are listed in Table 2, and Fig. 5 shows the linear regression of the Langmuir and Freundlich adsorption models of Cd\(^{2+}\) ions adsorption by CP-NC.
Table 2

The data related to different isotherms for Cd\textsuperscript{2+} adsorption on CP-NC

<table>
<thead>
<tr>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Dubinin-Radushkevich</th>
</tr>
</thead>
<tbody>
<tr>
<td>q\textsubscript{m} (mg g\textsuperscript{-1})</td>
<td>K\textsubscript{L} (L g\textsuperscript{-1})</td>
<td>R\textsuperscript{2}</td>
</tr>
<tr>
<td>1106.19</td>
<td>0.0042</td>
<td>0.9865</td>
</tr>
</tbody>
</table>

The Langmuir isotherm model provided a better fit to the results using CP-NC as the adsorbent, showing that the adsorption is monolayer and that the distribution of adsorption sites on the surface of CP-NC is homogeneous. The value of n > 1 (1.33) also reveals the suitable performance of CP-NC.

The performance of CP-NC adsorbent with other adsorbents is shown in Table 3. The performance of pure CS/PAT on Cd\textsuperscript{2+} adsorption along with CP-NC was also compared to assess the effect of MWCNT@LDH content on CS/PAT sorption. The findings disclose that the CP-NC is a potential adsorbent for removing Cd\textsuperscript{2+} from aquatic media.
Table 3
The results for the Cd\(^{2+}\) adsorption based on different adsorbents.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Adsorbent</th>
<th>Reaction conditions</th>
<th>(q_m) (mg g(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>R -PET/MWNT/LDH</td>
<td>(T = 298,^\circ)K; 0.02 g; 20–100 mg L(^{-1}); (pH = 6)</td>
<td>38.91</td>
<td>[40]</td>
</tr>
<tr>
<td>2</td>
<td>DMSA-CS beads</td>
<td>(T = 298,^\circ)K; 50–600 mg L(^{-1}); (pH = 6)</td>
<td>183.1</td>
<td>[4]</td>
</tr>
<tr>
<td>3</td>
<td>PEDGE cross-linked chitosan/activated carbon</td>
<td>(T = 298,^\circ)K; 15–200 mg L(^{-1}); (pH = 5)</td>
<td>357.14</td>
<td>[52]</td>
</tr>
<tr>
<td>4</td>
<td>BMMCs</td>
<td>(T = 298,^\circ)K; 0.0062–0.062 g L(^{-1}); 200 mg L(^{-1}); (pH = 6.5)</td>
<td>610.67</td>
<td>[53]</td>
</tr>
<tr>
<td>5</td>
<td>MgCl(_2)-modified biochar (MBC)</td>
<td>(T = 298,^\circ)K; 0.025 g; 20-1500 mg L(^{-1}); (pH = 5)</td>
<td>763.12</td>
<td>[54]</td>
</tr>
<tr>
<td>6</td>
<td>Fe(_3)O(_4)/SiO(_2)/m-SiO(_2)-NH(_2)</td>
<td>(T = 298,^\circ)K; 0.05 g; 0.870 g L(^{-1}); (pH = 6)</td>
<td>884.9</td>
<td>[55]</td>
</tr>
<tr>
<td>7</td>
<td>PAT</td>
<td>(T = 298,^\circ)K; 0.02 g; 100 mg L(^{-1}); 0.02 g; 100 mg L(^{-1}); (pH = 4.5)</td>
<td>(~20)</td>
<td>[25]</td>
</tr>
<tr>
<td>8</td>
<td>CS/PAT</td>
<td>(T = 298,^\circ)K; 0.06 g; 100–500 mg L(^{-1}); (pH = 8)</td>
<td>202.43</td>
<td>This study</td>
</tr>
<tr>
<td>9</td>
<td>CS/PAT/MWCNT@LDH</td>
<td>(T = 298,^\circ)K; 0.06 g; 100–500 mg L(^{-1}); (pH = 8)</td>
<td>1106.19</td>
<td>This study</td>
</tr>
</tbody>
</table>
The anion exchange properties of LDHs and the high surface area of MWCNTs make these nanostructures excellent candidates for the degradation of heavy metal ions and other pollutants [50]. The obtained $q_{\text{max}}$ for CP-NC is higher than those obtained from bentonite, pure CNTs, and pure PAT adsorbents (Table 3).

### 3.6. Thermodynamic Studies

To determine how temperature affects the adsorption process, the thermodynamic parameters Gibbs free energy ($\Delta G^0$), enthalpy change ($\Delta H^0$), and entropy change ($\Delta S^0$) are determined by Eqs. 12 and 13.

$$\Delta G^0 = -RT \ln K$$

$$\ln K = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \tag{13}$$

Where $K$ is the standard thermodynamic constant (L g$^{-1}$), which will be determined by dividing $q_e$ to $C_e$, and $T$ is the temperature (K), $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$). The linear Von't Hoff equation's slope and intercept were used to calculate the values for $\Delta H^0$ and $\Delta S^0$ [28]. $\ln K$ vs. 1/T (Fig. 6). Cd$^{2+}$ sorption on the CP-NC is spontaneous and endothermic when the $\Delta G^0 < 0$ and the $\Delta H^0 > 0$. The positive $\Delta H^0$ value reveals that the process facilitates with increasing the temperature. In contrast, the negative value of $\Delta G^0$ indicates that the adsorption process reduces with increasing the temperature. The results are afforded in Table 4. Thus, adsorption efficiency increased when the temperature changed from 25 to 70°C, indicating that the reaction is endothermic. It is interesting to note that the binding strength of the adsorbate-adsorbent interactions is due to isosteric heat [56]. A positive value of $\Delta S^0$ indicates a random process at the solid and liquid interface in which its irregularities increases [57]. In general, when $-20 < \Delta G^0 < 0$ kJ mol$^{-1}$, the adsorption method is physical adsorption, while the value between $-400 < \Delta G^0 < -80$ kJ mol$^{-1}$ suggests chemical adsorption [39, 58]. The values obtained for $\Delta G^0$ in this adsorption process indicate that the primary mechanism is chemical adsorption.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\Delta G^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^0$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^0$ (J mol$^{-1}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>-93.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>-98.52</td>
<td>86.83</td>
<td>314.50</td>
</tr>
<tr>
<td>323</td>
<td>-101.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>343</td>
<td>-107.96</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The adsorption of Cd\(^{2+}\) by CP-NC (Scheme 2) occurs through two pathways [59]. The hydroxyl and carboxylic groups on the CP-NC's surface form internal complexes with Cd\(^{2+}\) ions in the first route. In the second, Cd\(^{2+}\) forms exterior complexes with negative charges on the surface of the CP-NC. The isotherms and thermodynamic data reveals that both chemisorption and physisorption processes are responsible for adsorption, however chemical adsorption is the main factor in the adsorption process between CP-NC and Cd\(^{2+}\) ions.

4. Reduction Of P-np

The catalytic behavior of the obtained CP-NC was examined by the reaction of p-NP with NaBH\(_4\).

Electrostatic repulsion between p-nitrophenolate (p-C\(_6\)H\(_4\)NO\(_3\)\(^-\)) and BH\(_4\)\(^-\) ions [60], prevents the progress of the reaction even if it is thermodynamically [61]. As shown in Fig. 7, the reaction in the presence of CP-NC causes the p-NP to turn p-AP in 360 sec. A solution of 4-nitrophenol indicates its distinct absorption peak at 306 nm, which shifted to 400 nm with the addition of NaBH\(_4\), and the color of the solution changed from light to deep yellow, which could be corresponded to the formation of 4-nitrophenolate. The formation of 4-aminophenol was associated with destroying 4-nitrophenolate when the CP-NC was added into the solution of 4-nitrophenol and NaBH\(_4\). As a result, the solution turns from deep yellow to colorless and the height of the absorption peak at 400 nm decreases while the height of a new peak at 298 nm increases. Factors such as high surface area, better distribution of hybrid nanoparticles on the matrix, and a large amount of hydroxide group on the NC surface lead to improvement in the performance of the CP-NC for catalytic reduction of nitrophenols.

4.1. Kinetic study of reduction reaction

To manage the reaction's progression, UV-vis spectroscopy was also used to assess the reaction's kinetics. A PFO kinetic model for the reduction reaction with the CP-NC is shown in Fig. 8. Because the NaBH\(_4\) concentration is much larger than the p-NP concentration, the reduction rate is independent of the reducing concentration. And it can be assumed that its concentration is constant. Therefore, this reaction follows the PFO kinetic model [62–64], which is represented by Eq. (14) or (15) [65].

\[
\frac{-dc_t}{dt} = K_{app}C_t
\]

14

\[
\ln\left(\frac{C_t}{C_0}\right) = \ln\left(\frac{A_t}{A_0}\right) = -K_{app}t
\]

15

\(K_{app}\) is the apparent rate factor that will obtain using Eq. (15). Where \(A_0\) and \(A_t\) indicate adsorption at \(t\) and \(t = 0\), respectively, which directly related to its concentration in solution.
Figure 8 shows a linear relationship between \( \ln \left( \frac{A_t}{A_0} \right) \) and the reduction time. The \( k_{\text{app}} \) is calculated using the negative slope of the graph. The value obtained for the reduction reaction of p-NP is \( 5.0 \times 10^{-3} \) s\(^{-1}\). This result shows that despite the absence of metals such as (Au, Ag, Fe, Ni, etc.) in the CP-NC structure, the synthesized NC showed a relatively high potential for this reduction reaction. To examine the catalytic activity of the CP-NC, the results of this catalyst for the reduction reaction of p-NP as a model reaction were compared with the results of the reported catalysts (Table 5).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time (s)</th>
<th>( k (\text{min}^{-1}) )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co@INCl</td>
<td>120</td>
<td>2.50</td>
<td>[66]</td>
</tr>
<tr>
<td>Ni/C-800</td>
<td>240</td>
<td>1.04</td>
<td>[67]</td>
</tr>
<tr>
<td>Au/graphene</td>
<td>720</td>
<td>0.190</td>
<td>[68]</td>
</tr>
<tr>
<td>Ag@KF-HTO-PDA</td>
<td>900</td>
<td>0.138</td>
<td>[69]</td>
</tr>
<tr>
<td>Au/MWCNTs</td>
<td>7200</td>
<td>0.006</td>
<td>[70]</td>
</tr>
<tr>
<td>CS/PAT/MWCNT@LDH</td>
<td>360</td>
<td>0.311</td>
<td>This study</td>
</tr>
</tbody>
</table>

### 5. Cp-nc Recyclability Experiment

CP-NC recyclability test was investigated after each absorption. Therefore, after separation, the adsorbent was cleaned with distilled water and sodium hydroxide and used for other absorption steps. The adsorption-desorption process was performed for three cycles. The regenerated CP-NC relatively reduced its activity compared to the first case even though the reduction is not significant (Fig. 9).

### 6. Conclusions

This research introduced the construction of a new CS/PAT NC reinforced with MWCNT@LDH. According to the result obtained from various analyses, the filler was well distributed in CS/PAT, which caused good surface adhesion between the matrix and the filler and thus improved the thermal properties of CS/PAT. The results of Cd\(^{2+}\) adsorption showed that pH, contact time, adsorbent dosage, and concentration of Cd\(^{2+}\) ions had a decisive effect on adsorption. Increases in MWCNT@LDH content resulted in a reduction of the removal from 70–30%, which showed that more active sites were occupied on the matrix surface. A PFO kinetic model and the Langmuir isotherm were found to be better fitted, and as a result, they demonstrated chemical adsorption across the Cd\(^{2+}\). According to the results, the electrostatic force is the dominant factor in metal ion adsorption. The obtained \( q_{\text{max}} \) for Cd\(^{2+}\) adsorption using the Langmuir isotherm was 1106.19 mg g\(^{-1}\). Moreover, the catalytic activity of CP-NC on p-NP reduction with NaBH\(_4\) was studied. The obtained rate constants showed excellent performance for the bio-NC in the reduction
reaction. The findings also showed a reversible method for the adsorption by CP-NC due to the recyclability and reusing the adsorbent. According to the obtained results, it can be claimed that CP-NC is an active adsorbent with a high potential for removing heavy metal ions.

**Declarations**

**Acknowledgments**

The authors would like to acknowledge the financial support of Razi University.

**Ethical Approval**

This declaration is "not applicable".

**Competing interests**

The authors declare that they have no competing interests as defined by Springer, or other interests that might be perceived to influence the results and/or discussion reported in this paper.

**Authors' contributions**

Mohammad Saeid Rostami investigated and wrote original draft; Mohammad Mehdi Khodaei supervised and revised the manuscript.

**Funding**

The authors declare that they have no known competing financial interests or personal relationships.

**Availability of data and materials**

Some of the data and materials are available.

**References**


70. Mohamed, M. M., Khairy, M., & Ibrahim, A. "P-n junction based Ag\(_2\)O@ Ag@ Coated functionalized carbon nanotubes and their efficient visible-light photocatalytic reduction performances." Microporous and Mesoporous Materials. 292, 109734 (2020).
Schemes

Schemes 1 and 2 are available in the Supplemental Files section.

Figures

Figure 1
SEM images of (a) pure CS/PAT, (b) MWCNT@LDH, (c) CP-NC 30 %, (d) CP-NC 50 %, (e) CPM-NC 70 %, and (f) CP-NC structure.

Figure 2

The impact of pH on CP-NC's Cd$^{2+}$ sorption
Figure 3

Comparing the removal efficiency of Cd^{2+} ions versus adsorbent dose for CS/PAT and CP-NC.
Figure 4

Kinetic investigation of CP-NC-assisted Cd$^{2+}$ adsorption
Figure 5

(a) Freundlich, (b) Langmuir, (c) Dubinin-Radushkevich isotherms, and (d) Absorption capacity and removal efficiency vs. initial concentration (adsorbent dose: 0.01g, T = 298 °C)
**Figure 6**

Linear diagram of lnK vs. 1/T for the Cd$^{2+}$ adsorption by CP-NC.
Figure 7

UV-vis spectra for p-NP reduction using CP-NC
Figure 8

The PFO kinetic for the p-NP reduction using CP-NC.
Figure 9

Diagram of recyclability test for CP-NC.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Scheme1.jpg
- Scheme2.png