Fibrous adsorbent derived from sulfonation of cotton waste: application for removal of cadmium sulfide nanoparticles from aquatic media

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Abstract

In the present research, the performance of the cellulose sulfate microfibers (CSMFs) was investigated for the removal of cadmium sulfide nanoparticles (CdS NPs). At first, cotton waste was sulfonated by chlorosulfonic acid. The high sulfur content of the CSMFs (6.54%) and the absorbance bands appeared at 610 cm^{-1} (symmetric stretching vibrations) and 1205 and 1180 cm^{-1} (asymmetric stretching vibrations) in the FT-IR spectrum of CSMFs confirmed the successful modification of cotton microfibers. Optimizing the adsorption process was achieved using the response surface methodology. The impacts of the initial concentration of CdS NPs, contact time, total dissolved solids (TDS), and adsorbent concentration on the removal efficiency were assessed. The highest removal efficiency (about 100%) was obtained under optimum conditions. By increasing the TDS, the removal efficiency decreased slightly. University of Tehran, Radke–Prausnitz, and Redlich–Peterson models exhibited low error values. The high maximum adsorption capacity of 5533 mg g^{-1} was due to the high content of anionic surface groups. The kinetics data were consistent with the Elovich, intraparticle diffusion, and pseudo-second-order models. The rate constant of the pseudo-second-order model decreased by decreasing the concentration of CdS NPs. The adsorbent recovery decreased about 10% after four cycles of regeneration.

Keywords Cadmium sulfide · Nanoparticle · Cellulose sulfate · Adsorption · Cotton

1 Introduction

Over the last decades, nanoparticles (NPs) have been considerably studied by researchers. NPs have been used in water and wastewater treatment and diverse industries such as, paint, cement, sunscreen, and electronics [1–6]. Increasing the use of nanoparticles has been led to growing the release of nanoparticles into natural aquatic systems. The toxicity of NPs is more than that of larger particles of the same substance due to their higher surface to volume ratio, higher chemical reactivity, and more particles per unit mass [7–10]. Therefore, NPs, especially metal-containing NPs that are used greatly in industries related to healthcare products, must be controlled properly

during their production, use, and disposal to prevent the living organism from the exposure to the wide range of NPs [11].

Among metal-containing NPs, CdS NPs have unique photochemical and photophysical properties [12]. They are classified as semiconductors with a direct band gap of 2.42 eV at room temperature. Their applications have been expanded into fluorescence imaging, biomedical imaging, detectors for laser and infrared, luminescence devices, optoelectronic devices, and solar cells. Therefore, the release of CdS NPs into the environment is inevitable [13–15].

Cytotoxicity and toxic effects of CdS NPs have been studied in many researches [16]. As mentioned above, the cytotoxicity of CdS NPs is dependent on the particle size.

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Lowering the size of CdS particles increases the release of Cd^{2+} ions and exposing animals and human to this toxic heavy metal ion [17, 18]. Many studies have been reported the harmful effects of CdS NPs and other chemical forms of cadmium on the environment and human health [19]. Some researchers reported that CdS NPs are dangerous not only for human health but also for all species [18].

Several methods such as phytoremediation, coagulation and flocculation, membrane filtration, and adsorption have been assessed to find suitable methods for removing metal-containing NPs from water and wastewater [20–26]. Because of the drawbacks of other methods including fouling in membrane filtration and high volume of sludge in coagulation and flocculation process, the adsorption process has been reported as the most efficient and economical method [27].

Several materials such as clays, modified plant wastes, chitin, and activated carbon have been used as adsorbents in adsorptive processes. Cellulose is a cheap, renewable, biodegradable, and the most widely available natural resource; however, it does not have suitable functional groups for the removal of pollutants. Because of its porosity, high surface area, and the presence of hydroxyl groups, cellulose is a suitable material to be converted to an adsorbent through the surface modification [28–32]. The adsorbents derived from the cellulose have been used for removing dyes [33] and heavy metals [34]. Furthermore, using cellulose wastes, especially hospital cotton wastes, for preparing the adsorbent is feasible if a strong acid is used for the preparation of the adsorbent because it can completely remove all microbial pollutants. There are various methods for recycling and reusing cellulosic wastes that makes them suitable for this purpose.

In this study, cellulose sulfate (CS) synthesized from the cotton waste was applied to remove CdS NPs from contaminated streams. The modified cellulose microfibers were characterized by FTIR, SEM, and EDX. Many factors involved in the process of CdS NPs adsorption, including contact time, pH, TDS, and the initial concentration of CS NPs were investigated. The kinetics and equilibrium experiments were also executed.

2 Experimental

2.1 Chemicals

Natural cotton waste was obtained from the Health Center of the University of Tehran and used as a source of cellulose microfibers. Before modification of its surface, the cotton was dried at 50 °C for 12 h. Other chemicals used in this research were purchased from Sigma-Aldrich (St. Louis, MO, USA) and Merck (Darmstadt, Germany). N,

N-Dimethylformamide (DMF, $\text{C}_3\text{H}_7\text{NO}$, CAS No. 68-12-2, $\geq 99.5\%$, Merck) and Chlorosulfonic acid (CSA, HClO_3S , CAS No. 7790-94-5, $\geq 97.0\%$, Merck) were used for functionalization of cotton microfibers. CdS NPs (1100 mg L^{-1}) was prepared using cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, CAS No. 10022-68-1, $\geq 97.5\%$, Sigma-Aldrich), cetyltrimethylammonium bromide (CTAB, $\text{C}_{19}\text{H}_{42}\text{BrN}$, CAS No. 57-09-0, $\geq 98\%$, Merck), and sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, CAS No. 1313-84-4, $\geq 98.0\%$, Sigma-Aldrich). The pH of the CdS NPs suspension was adjusted using a pH-meter (model B2000, Behine) with NaOH and HCl solutions (0.1 mol L^{-1}). MgSO_4 , CaCl_2 , NaHCO_3 , and KNO_3 salts were obtained from Merck Co. to attain the stock solution of TDS with the concentration of 2000 mg L^{-1} [35].

2.2 Preparation of CdS NPs

To determine the adsorption removal efficiency of CdS NPs by CSMFs, a suspension of 1100 mg L^{-1} of cadmium sulfide nanoparticles was synthesized. For the preparation of this solution, about 0.3 g of cadmium nitrate tetrahydrate was added in 25 mL of deionized water and stirred for 15 min. Then 0.1 g of CTAB dissolved in 25 mL of deionized water was added to the cadmium nitrate solution. After that, 0.078 g of sodium sulfide nonahydrate previously prepared in 50 mL deionized water was mixed with the above solution. As a consequence, a bright yellow solution was obtained, indicating the formation of CS NPs.

2.3 Preparation of the adsorbent

Anionic cellulose sulfate was prepared using dried natural cotton soaked in DMF and CSA diluted with DMF as a sulfonation reagent. Briefly, 6 g of dried natural cotton was soaked in 75 mL of DMF for 20 min at room temperature. Then 18 g of CSA was added dropwise to 75 mL of DMF in an ice bath. Subsequently, the mixture was gently added to the cotton immersed in DMF. The ultimate mixture was shaken at the rate of 120 rpm at room temperature in a sealed glass container. After 2 h of shaking, vacuum filtration through a $1 \mu\text{m}$ membrane was utilized to separate DMF from the product. After that, the residual solid was treated with deionized water and neutralized with sodium bicarbonate solution (2% w/v). Finally, cellulose sulfate sodium salt was filtered following several steps of washing with deionized water.

2.4 Characterization of the adsorbent

FTIR analyses of the natural cotton and CSMFs were performed using a Burkert spectrometer. Morphology of CSMFs was investigated with a scanning electron microscope (SEM, model: HITACHI S-4160). Energy dispersive

Table 1 Different levels of the selected independent variables

Variables	Factor	Unit	Levels		
			−1	0	+1
Time	A	min	1.0	15.5	30.0
CS dosage	B	g L ^{−1}	0.025	0.137	0.250
CdS NPs concentration	C	mg L ^{−1}	20	110	200

X-ray analysis (EDX) was used for determination of elemental composition of the adsorbent. The size of CdS NPs was determined with dynamic light scattering (DLS, Zetasizer ZEN3600, Malvern Co, England).

2.5 Design of experiments

Box-Behnken design (BBD) was applied to determine the importance of various independent factors and their interactions and to optimize experimental conditions. Some experiments were performed to select the effective factors and their ranges for the CdS NPs removal. In the present study, contact time (A), adsorbent dosage (B), and CdS NPs concentration (C) were selected as variables. Each input factor was set at '+1', '0', and '−1'. Table 1 illustrates the three different levels and the experimental ranges of each variable.

The number of total experimental runs can be calculated from Eq. 1.

$$N = 2k(k - 1) + N_0 \quad (1)$$

where N_0 and k are the number of central points and factors, respectively. Five central points and three factors were employed herein; as a result, the total number of runs was 17. The center point experiments were conducted to estimate experimental errors. The design matrix and the obtained data are given in Table 2.

The validity of the model was evaluated by the analysis of variance (ANOVA). The initial and residual concentration of CdS NPs after the adsorption process was measured using inductively coupled plasma-optical emission spectroscopy (ICP-OES, Spectro, Arcos EOP, Germany). For this purpose, 2 mL of concentrated nitric acid was added to 10 mL of the solution of CdS NPs and then heated for 10 min. Finally, the digested solution was diluted to 25 mL with deionized water. Design-Expert 10 (Stat-Ease Inc., USA) was used to set up experiments.

The kinetics experiments were executed at different CdS NPs concentrations between 20 and 200 mg L^{−1} in the range of 1–30 min on 40-mL portions of CdS NPs solutions, containing 25 mg L^{−1} of CSMFs. Adsorption isotherms were examined at the constant CSMFs dose of 25 mg L^{−1}, the initial CdS NPs concentration ranging between

Table 2 RSM design containing the predicted and actual values

Run	Factors			Removal efficiency (%)	
	Time	CS (g L ^{−1})	CdS NPs (mg L ^{−1})	Actual	Predicted
	A	B	C		
1	15.5	0.137	110	97.5	97.0
2	15.5	0.250	20	92.0	92.1
3	30.0	0.137	20	90.5	95.0
4	1.0	0.137	200	60.0	60.0
5	1.0	0.137	20	70.0	69.7
6	15.5	0.137	110	96.7	97.0
7	15.5	0.137	110	97.0	97.0
8	15.5	0.137	110	95.8	97.0
9	15.5	0.025	20	63.0	63.1
10	30.0	0.250	110	92.0	91.9
11	15.5	0.137	110	98.1	97.0
12	30.0	0.025	110	67.0	66.9
13	1.0	0.025	110	30.2	30.1
14	15.5	0.025	200	46.0	45.9
15	15.5	0.250	200	90.0	89.9
16	1.0	0.250	110	78.0	78.1
17	30.0	0.137	200	85.1	85.2

20 and 200 mg L^{−1}, and the equilibrium contact time of 15 min. For the justification of equilibrium features of the adsorption process, several were employed. The consistency between the experimental and predicted data using the investigated models was assessed using the residual root-mean-square error (RMSE) and the Chi square test (χ^2) [36].

3 Results and discussion

3.1 Characterization of CSMFs and CdS NPs

The SEM images were recorded to investigate the morphology of the cotton microfibers, CSMFs, and CSMFs containing CdS NPs. The comparison between SEM images of the cotton and CS (Fig. 1a, b) revealed considerable morphological changes due to the sulfonation process. The fibers of the natural cotton were longer and more rigid than those of the CSMFs; which is due to aging in the acidic medium. The same morphology was reported by Rajalaxmi et al. [37] for the sulfonated cellulose derived from hardwood kraft pulp. The CSMFs containing CdS NPs had a rough surface, showing NPs adsorbed on its surface. (Fig. 1c, d).

EDX analysis was used for the qualitative and quantitative analysis of elements on the surface of the cotton

Fig. 1 SEM images of **a** cotton, **b** CSMFs, **c**, **d** adsorbent containing CdS NPs with the magnification of 300× and 1500×, respectively

microfibers, adsorbent, and the adsorbent containing CdS NPs. The elemental composition of the cotton, CSMFs, and CSMFs containing CdS NPs are shown in Fig. 2a–c, respectively. The high sulfur content of the CSMFs confirmed the effective modification of the cotton microfibers. The elemental composition of the CSMFs after the adsorption process indicated a great amount of the CdS NPs adsorbed onto its surface. Figure 2d shows the FT-IR spectra of cotton and CSMFs. CSMFs spectrum exhibited bands at 1205 and 1180 cm^{-1} , corresponding to asymmetric stretching vibrations, and 610 cm^{-1} , which is related to the symmetric one of the sulfate group. The mean particle size of CdS NPs determined using DLS method was 52.8 nm (Fig. 2e).

3.2 Statistical analysis

The following model attained by the BBD is a quadratic equation, correlating the removal efficiency (%) with variables, adsorption time (A), CSMFs dosage (B) and CdS NPs concentration (C). A2, B2, and C2 are the quadratic effects, and AB, AC, and BC shows double interactions

$$Y = 97 + 12.625 \times A + 18.25 \times B - 4.875 \times C - 5.750 \times AB - 0.25 \times AC + 3.750 \times BC - 12.63 \times A^2 - 17.62 \times B^2 - 6.63 \times C^2 \quad (2)$$

The data obtained by the ANOVA for CdS NPs removal are illustrated in Table 3. The larger F-value and smaller *p* value (< 0.05) represent a great significance of the corresponding coefficient [38]. As a consequence, all three factors were found to be significant. Moreover, the interaction of CSMFs dosage with contact time and CdS NPs concentration was significant; however, there was no interaction between contact time and CdS NPs concentration (*p* value = 1). The model F-value of 1864.32 confirmed that the model is valid. On the other hand, the model *p* value was less than 0.0001, showing the validity of the model in the investigated range of variables. The lack of fit *p* value was 0.9437; as a result, the lack of fit was insignificant, showing that the data obtained by experiments were in agreement with the model output. In addition, the model accuracy was confirmed using the high values of the adjusted R^2 (99.9%) and the predicted R^2 (99.95%).

3.3 Impacts of investigated variables on the removal efficiency

The perturbation plots given in Fig. 3 indicate the effects of three main parameters on the CdS NPs removal. As can be seen, the effects of time (A) and adsorbent dosage (B) on the response were almost the same, which is consistent

Fig. 2 EDX analysis of **a** cotton fibers; **b** CSMFs; **c** CSMFs containing CdS NPs (CSMFs: 0.1 g L⁻¹; CdS NPs: 100 mg L⁻¹); **d** FT-IR spectra for cotton and CSMFs; **e** DLS analysis of CdS NPs

with the results of the F-test. However, the CdS NP concentration (C) had a less significant impact on the response.

Figure 4a displays the effect of CdS NPs concentration and contact time at a constant adsorbent content on the adsorption process. By increasing the contact time, the removal efficiency raised. In addition, the interaction between contact time and CdS NPs concentration was insignificant (p value > 0.05). Increasing the CSMFs dosage enhanced the removal efficiency (Fig. 4b), which was in accordance with the highest F-value (6155.61) and the low p value (< 0.0001). The initial concentration of CdS NPs had lower F-value in comparison with other variables, indicating its lowest impact in the adsorption process. The significant interaction of CSMFs concentration and time are presented in Fig. 4c. Low p value and the high F-value (< 0.05 and 305.53, respectively) were the meaningful indications of the strong interaction between these two factors.

3.4 Effect of pH and TDS

The effect of pH on the CdS NPs removal is shown in Fig. 5a. The removal efficiency reduced by declining the pH value because of high H⁺ concentration, competing with CdS NPs for adsorption on the adsorbent surface. Maximum removal efficiency was achieved at the neutral medium. As the pH raised, the removal efficiency improved by about 20%.

The impact of TDS (0 to 1600 mg L⁻¹) on the adsorption of CdS NPs using CSMFs was also investigated. The remaining CdS NPs in each solution was measured, and the obtained data were presented in Fig. 5b. The slight decrease observed in the removal efficiency by increasing the TDS content may be due to the existence of cations competing with CdS NPs for the anionic active sites.

3.5 Kinetic studies

The pseudo-second-order (PSO) and pseudo-first-order (PFO) models are the well-known empirical models for adsorption kinetics studies. In the PSO model, the

Table 3 The ANOVA results for the constructed model

Factor	SS ^a	dF ^b	MS ^c	F-value	p value
Model	6445.50	8	805.69	1861.32	< 0.0001
A-time	1020.10	1	1020.10	2356.67	< 0.0001
B-CSMFs	2664.50	1	2664.50	6155.61	< 0.0001
C-CdS NPs	152.10	1	152.10	351.39	< 0.0001
AB	132.25	1	132.25	305.53	< 0.0001
AC	0.000	1	0.000	0.000	1.0000
BC	56.25	1	56.25	129.95	< 0.0001
A ²	604.88	1	604.88	1397.42	< 0.0001
B ²	1139.53	1	1139.53	2632.59	< 0.0001
C ²	169.53	1	169.53	391.66	< 0.0001
Residual	3.03	7	0.43		
Lack of fit	0.25	3	0.083	0.12	0.9437
Pure error	2.78	4	0.70		
Cor total	6448.53	15			
Model	6445.50	8	805.69	1861.32	< 0.0001

$R^2 = 0.9995$, Adj $R^2 = 0.9990$, Pred $R^2 = 0.9988$

A, contact time; B, CSMFs dosage; C, CdS NPS concentration

^aSum of square

^bDegree of freedom

^cMean square

Fig. 3 Perturbation plots for CdS NPs removal by CSMFs

adsorption rate is proportional to the square of free active surface sites. When the initial concentration is high, PFO fits better, while PSO fits better when it is not too high. PSO and PFO models are supposed to fit chemical reaction

controlled kinetics, but theoretical interpretations have shown that effective fitting of these models alone is not an indication of chemisorption adsorption. Diffusion or combined diffusion–reaction control can be involved in the adsorption process. Unlike the PSO and PFO models, the Elovich model describe the chemisorption well. It is suitable for the kinetics far from the equilibrium state, at which desorption does not take place [39].

The controlling mechanisms of the adsorption process was studied by kinetic models. They were validated using the residual root-mean-square error (RMSE) and the Chi square test (χ^2).

The residuals of the studied models and the related error functions are shown in Fig. 6a–e and Table 4, respectively. Elovich, pseudo-second-order, intraparticle diffusion, liquid film diffusion, and pseudo-first-order models fitted the experimental data in the order of high to low fitness degree, respectively.

Table 5 shows kinetic parameters and the corresponding equations. In the Elovich isotherm, the constant “ α ” represents the rate of chemisorption, and the constant “ β ” represents the surface coverage. Regarding the results presented in Table 5, by increasing the initial concentration of CdS NPs, the constant “ β ” decreased, whereas the constant “ α ” increased, indicating an increase in the rate of chemisorption, and a decrease in the available sorption surface [40].

The Variation of k_2 and k_{dif} by changing the initial concentration of CdS NPs are illustrated in Fig. 6f, g. According to Fig. 6f, by rising initial CdS NP concentration, the second-order rate constant, k_2 , decreased, confirming the higher adsorption rate at the higher initial concentration of CdS NPs. In intraparticle diffusion plots (Fig. 6g), the first region represents the external surface adsorption. A slow adsorption rate was recognized in the second region where intraparticle diffusion was the rate-limiting step. The third region is related to the equilibrium stage, where the intraparticle diffusion rate begins to slow down because of the lower active sites available [41]. According to Fig. 6g, h, by increasing the initial concentration of CdS NPs, the diffusion rate constant increased as a result of increasing the adsorption driving force [42].

3.6 Equilibrium study

To describe the interactive behavior between CdS NPs and CSMFs, equilibrium adsorption experiments were executed. For the selection of the best fit line, the error analysis was applied. The model with the minimum residual root-mean-square error was considered as the best model. The residuals of experimental and calculated q_e for these three isotherm models were lower than those for other models as shown in Fig. 7. According to the errors

Fig. 4 The simultaneous interaction of **a** contact time and CdS NPs concentration; CSMFs dosage at the level of 0, **b** CdS NPs concentration and CSMFs dosage; contact time at the level of 0, **c** CSMFs dosage and contact time; CdS NPs concentration at the level of 0

Fig. 5 The effect of **a** pH and **d** TDS on the CdS NPs removal (CSMFs: 125 mg L⁻¹, CdS NPs: 50 mg L⁻¹, contact time: 15 min, and temperature: 298 K)

shown in Table 6, the fitness extent followed the following order:

UT isotherm > Redlich–Peterson > Radke–Prausnitz > Dubinin–Radushkevich > Langmuir > Temkin > Freundlich.

The equation of the investigated models and the related parameters are presented in Table 7. In the Langmuir isotherm, active sites covering with a monolayer of adsorbates are identical, and the maximum adsorption capacity (q_m) is related to monolayer adsorption [36]. The Langmuir model can also determine the maximum adsorption capacity of the adsorbent corresponding to the monolayer adsorption on the surface of the adsorbent. The value of R_L can be calculated as below:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (8)$$

where K_L (L mg⁻¹) is the Langmuir constant and C_0 is the initial concentration (mg L⁻¹). According to the following criteria, the adsorption is classified irreversible ($R_L = 0$), linear ($R_L = 1$), unfavorable ($R_L > 1$), and favorable ($0 < R_L < 1$). The R_L in this work was 0.25; therefore, the sorption was favorable. Freundlich isotherm describes a multilayer adsorption process [43]. In this study, n -value was 2.2,

indicating that the sorption was favorable [44]. Temkin isotherm considers that the binding energies are distributed uniformly [41]. In Dubinin–Radushkevich isotherm a heterogeneous surface is considered for adsorption. According to Eq. S11, the mean free energy of 0.08 kJ mol⁻¹ represents a physisorption process. Radke–Prausnitz, University of Tehran (UT), Redlich–Peterson models can be applied for heterogeneous and homogeneous surfaces. The UT isotherm is a novel adsorption isotherm having the capability to predict the q_m of the heterogeneous systems [45]. According to the UT isotherm, the free capacity fraction (FCF) can be calculated using Eq. 4.

$$FCF = \frac{k_d}{D \cdot q_m} \quad (9)$$

where K_d is the UT desorption constant, and D is the adsorbent dosage (g L⁻¹). The high FCF-value (0.07) was an indication of the homogeneous surface [45].

3.7 Desorption studies

To study the regeneration of the CSMFs for future uses, desorption experiments were done. For this purpose, a solution of CdS NPs (110 mg L⁻¹) containing 0.25 g L⁻¹ of CSMFs was stirred for 15 min. After that, the CSMFs was separated and washed with HCl 0.1 mol L⁻¹ and then with deionized water. The recovered adsorbent was used for the removal of CdS NPs under the mentioned-above conditions. The adsorption and desorption cycle was repeated four times, and the results are presented in Fig. 8. The recovered CSMFs indicated a good performance even after four cycles of the regeneration.

3.8 Performance comparison of techniques for NPs removal

The performance of the CSMFs and other methods are reported in Table 8. The high removal efficiency of CSMFs is an indication of its effectiveness for CdS NPs removal from polluted streams. In addition, the equilibrium was achieved less than 10 min.

4 Conclusion

In this research, the cellulose sulfate microfibers prepared by sulfonation of the cotton waste was introduced as an efficient adsorbent for the removal of CdS NPs from contaminated streams. The high sulfur content of the CSMFs (6.54%) and the absorbance bands appeared at 1205 and 1180 cm⁻¹ (asymmetric stretching vibrations) and 610 cm⁻¹ (symmetric stretching vibrations)

Fig. 6 Residual plots of investigated kinetic models in different CdS NPs concentrations: **a** 20 mg L⁻¹, **b** 65 mg L⁻¹, **c** 110 mg L⁻¹, **d** 155 mg L⁻¹, and **e** 200 mg L⁻¹ (adsorbent: 25 mg L⁻¹ and contact

time: 15 min); Effect of the CdS NPs concentration on the **f** k_2 and **g** k_{dif} ; **h** Intraparticle diffusion kinetics

Table 4 The performance of kinetic models for adsorption of CdS NPs onto CSMFs at different CdS NPs concentrations

Model	Error function	CdS NPs concentration		
		20	110	200
Pseudo-first-order	R ²	0.966	0.954	0.954
	RMSE	74.79	320.82	459.86
	χ^2	496.7	1614.23	1579.57
Pseudo-second-order	R ²	0.999	0.999	0.998
	RMSE	3.71	20.63	36.8
	χ^2	0.65	3.58	7.22
Intraparticle diffusion	R ²	0.945	0.944	0.944
	RMSE	3.741	20.76	37.86
	χ^2	0.69	3.80	6.91
Liquid film diffusion	R ²	0.812	0.777	0.78
	RMSE	11.08	41.21	127.72
	χ^2	8.11	21.93	76.10
Elovich	R ²	0.969	0.969	0.968
	RMSE	2.81	16.33	30.11
	χ^2	0.38	2.33	4.46

in the FT-IR spectrum of CSMFs confirmed the successful modification of cotton microfibers. The maximum adsorption capacity of 5500 mg g⁻¹ and the maximum removal efficiency of 100% were obtained. The TDS and pH did not affect the performance of the CSMFs. The adsorption process followed the UT and Redlich–Peterson isotherms. Moreover, the adsorption kinetic data followed the Elovich and pseudo-second-order models. The adsorbent recovery was performed with HCl 0.1 mol L⁻¹, and the removal efficiency dropped by approximately 10% after four cycles of the regeneration. In conclusion,

Fig. 7 Residual plots of investigated models (CSMFs: 25 mg L⁻¹, contact time: 15.5 min)**Table 6** Error values and R² for adsorption of CdS NPs onto CSMFs at 298 °C

Models	Error function		
	R ²	RMSE	χ^2
UT isotherm	0.9996	9.09	0.13
Redlich–Peterson	0.9996	9.39	0.13
Radke–Prausnitz	0.9998	19.81	0.50
Dubinin–Radushkevich	0.9818	102.43	16.41
Langmuir	0.9857	123.18	24.14
Temkin	0.9678	141.23	29.25
Freundlich	0.9377	216.75	65.84

the cellulose sulfate derived from the cotton waste is an efficient adsorbent for the removal of nanoparticles with the positive surface charge. Due to the large particle

Table 5 Adsorption kinetic parameters for CdS NPs adsorption onto the CSMFs at different CdS NPs concentrations

Model	Parameters	CdS concentration(mg L ⁻¹)		
		20	110	200
Pseudo-first-order	k_1 : min ⁻¹	0.1951	0.2258	0.2234
$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303}$ (3)	q_e (calc): mg g ⁻¹	68.779	446.416	803.357
Pseudo-second-order	k_2 : g mg ⁻¹ min ⁻¹	0.00650	0.00120	0.00063
$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t$ (4)	q_e (calc): mg g ⁻¹	148.014	828.16	1336.898
Intraparticle diffusion	k_{dif} : mg g ⁻¹ min ^{-1/2}	9.88	54.123	98.559
$q_t = k_{dif} t^{1/2} + C$ (5)	C:	94.52	535.51	804.19
Liquid film diffusion	k_{fd} : min ⁻¹	0.1951	0.2258	0.2234
$\ln(1 - F) = -k_{fd} t$ (6)				
Elovich	β : mg g ⁻¹ min ⁻¹	0.074	0.0136	0.0075
$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$ (7)	α : g mg ⁻¹	2.207×10^4	5.124×10^4	7.78×10^4

α , (mg g⁻¹ min⁻¹) and β , (g mg⁻¹) are the initial adsorption rate of the Elovich equation and the desorption constant; k_{fd} , liquid film diffusion rate coefficients (min⁻¹); C, intercept of intraparticle diffusion; k_{dif} , rate constant of intraparticle diffusion (mg g⁻¹ min^{-1/2}); k_2 , second-order rate constant of adsorption (g mg⁻¹ min⁻¹); k_1 , Rate constant of pseudo-first order adsorption (min⁻¹)

Table 7 Isotherm parameters for the adsorption of CdS NPs onto CSMFs at 298 K

Isotherm	Equation	Parameters	Values
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (10)$	q_m : mg L ⁻¹ K_L : L mg ⁻¹	5850 0.0272
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e \quad (11)$	$1/n_F$ K_F : (mg g ⁻¹)(L mg ⁻¹) ^{1/n}	0.458 547.61
Temkin	$q_e = B_1 \ln A + B_1 \ln C_e \quad (12)$	B_1 : mg g ⁻¹ A : L mg ⁻¹	1446.04 0.204
Dubinin–Radushkevich	$\ln q_e = \ln q_s - \beta \varepsilon^2 \quad (13)$ $\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (14)$	q_s : mg g ⁻¹ β : mol ² J ⁻²	4223.12 7.12 × 10 ⁻⁵
	$E = \frac{1}{\sqrt{2\beta}} \quad (15)$	E : kJ mol ⁻¹	0.08
Radke–Prausnitz	$\frac{C_e}{q_e} = \frac{1}{K_{RP} q_m} + \frac{C_e^m}{q_m} \quad (16)$	m : K_{RP} : L mg ⁻¹ q_m : mg g ⁻¹	1.69 0.00061 168,774
Redlich–Peterson	$\ln \left(K_R \frac{C_e}{q_e} - 1 \right) = g \ln C_e + \ln \alpha_R \quad (17)$	g K_R : L g ⁻¹ α_R : (L mg ⁻¹) ^g	1.69 101.63 0.00061
UT isotherm	$\ln \left(\frac{C_e}{q_e} - \frac{K_d}{q_m} \right) = \ln \frac{D^{1-b}}{q_m^b} + b \ln C_e \quad (S14)$	b FCF K_d : mg L ⁻¹ q_m : mg g ⁻¹	1.69 0.07 54.44 5533

T , absolute temperature (K); R , 8.314 gas constant (J mol⁻¹ K⁻¹); b , UT isotherm exponent; K_d , desorption constant; K_{RP} , Radke–Prausnitz constant (L mg⁻¹); β , constant of Dubinin–Radushkevich (mol² J⁻²); E , related to free energy (kJ mol⁻¹); q_s , adsorption capacity (mg g⁻¹), $1/n$ and K_F , Freundlich isotherm constant; K_L , Langmuir constant (L mg⁻¹); K_R (L g⁻¹); α_R (L mg⁻¹) and g , Redlich–Peterson constants

Fig. 8 The regeneration of the CSMFs with HCl 0.1 mol L⁻¹

size, CSMFs can be easily separated from the contaminated streams after the treatment process. On the other hand, the prepared adsorbent exhibited a considerable

Table 8 The efficiency comparison of the reported techniques for NPs removal

Method	Nanoparticle	Removal efficiency (%)	References
Coagulation	CdTe QDs	80	[44]
Coagulation	CNT	97	[45]
Coagulation	TiO ₂	80	[46]
Adsorption (adsorbent: modified paper)	Ag	80	[47]
Coagulation	CuO	80	[48]
Adsorption (adsorbent: CS)	CdS	100	Present study

adsorption capacity due to the high content of anionic surface groups.

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Compliance with ethical standards

Conflict of interest The authors confirm that this article content has no conflict of interest.

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