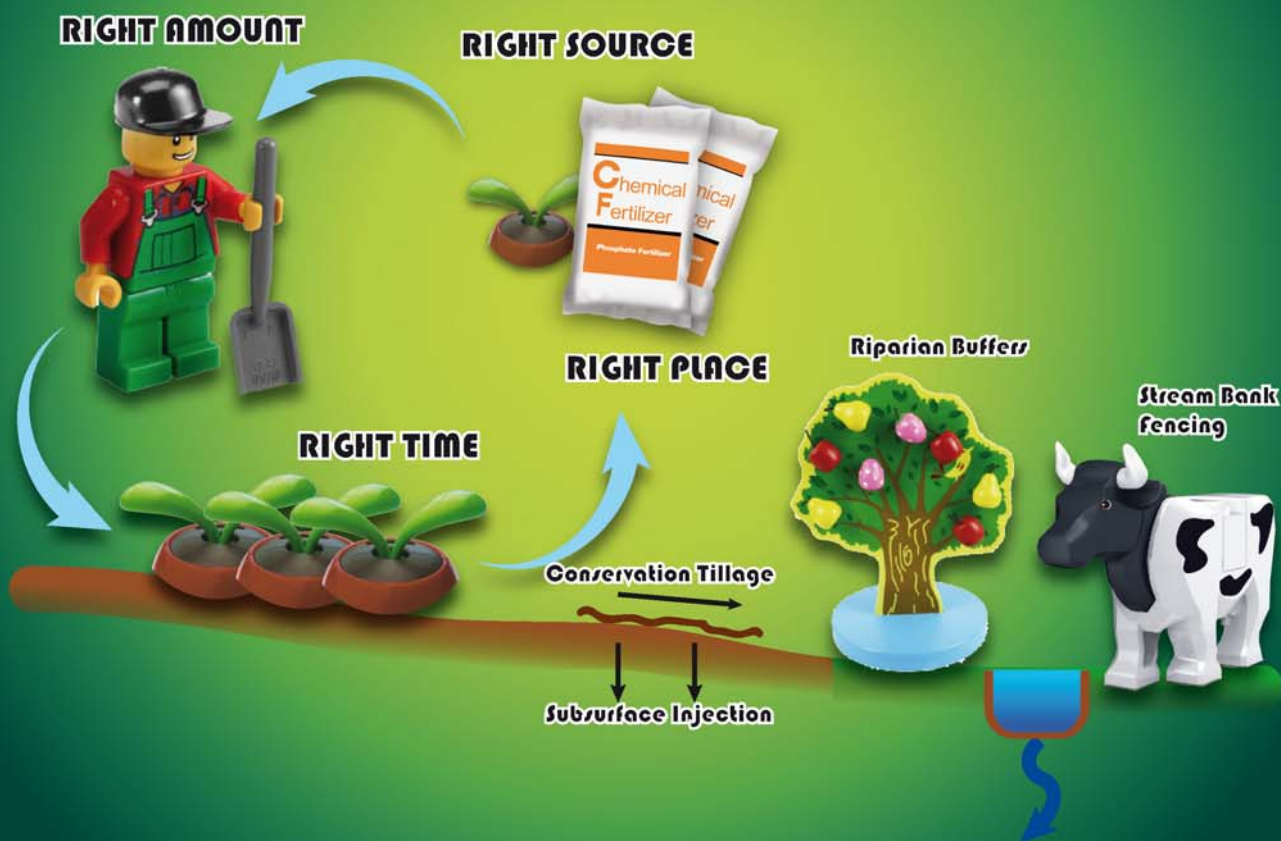


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Removal of cobalt(II) ion from aqueous solution by chitosan–montmorillonite

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ABSTRACT

Montmorillonite (MMT) modified with chitosan (CTS, molecular weight = 5×10^4) was applied to remove heavy metal cations by using Co²⁺ as a model ion. An increase in MMT interlayer distance observed from X-ray diffraction indicates the intercalation of CTS into MMT. Together with the results of scanning electron microscopy and Fourier transform infrared spectroscopy, it was concluded that the composite material of CTS and MMT (CTS–MMT) was prepared successfully. The mass ratio of CTS to MMT had a strong influence on the adsorption performance of CTS–MMT. The highest adsorption value of 150 mg/g was obtained over the composite material with CTS to MMT mass ratio of 0.25, which is much higher than those reported in other studies. The adsorption isotherms and kinetic results indicated that Co²⁺ was adsorbed over CTS–MMT in a multilayer model, and the chemical sorption of Co²⁺ was determined to be the rate-limiting step.

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Introduction

Treatment of industrial wastewater with heavy metal ions is a major issue and the development of effective adsorbents for removal of those metal ions is of great importance. Activated carbon has been widely studied and used for the removal of mercury, cadmium, lead, cobalt, copper and so on in terms of cost, simplicity of design and operation (Netzer and Hughes, 1984; Corapcioglu and Huang, 1987; Gomez-Serrano et al., 1998). However, high capital and regeneration cost limit its large scale application. Recent studies have focused on relatively low cost adsorbents such as zeolite, montmorillonite, kaolinitic clay, mineral silicates, sepiolite and others (Ali and El-Bishtawi, 1997; Orumwense, 1996; Sanchez et al., 1999; Brigatti et al., 2000; Green-Pederson et al., 1997). Chitosan

(poly-β-(1,4)-2-amino-2-deoxy-glucopyranose, CTS) is a product of the deacetylation of chitin (Septhum et al., 2007), which is the second most abundant natural biopolymer on earth after cellulose. CTS is an excellent natural adsorbent in that its amine (–NH₂) and hydroxyl (–OH) groups may serve as coordination sites to form complexes with various heavy metal ions. It can remove metal ions effectively by adsorptive enrichment. Compared with activated carbon, CTS is self degradative, non-toxic, low cost, and environmentally benign. Thus, it is widely used in many fields such as textiles, leather, food, bioengineering, agriculture, sewage treatment and so on. However, the poor selective adsorption, small surface area and low porosity of chitosan limit its application in pollutant adsorption (Ahmaruzzaman, 2008). Montmorillonite (MMT) is a 2:1 layered aluminosilicate of smectite-type clay, which is

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composed of two tetrahedral sheets with Si in the cationic sites sandwiching an octahedral Al sheet. The partial substitution of Al^{3+} for the tetrahedral Si^{4+} and Mg^{2+} makes the layers negatively charged, which is neutralized by exchangeable cations in the interlayer space. Commonly, alkali or alkaline earth metal cations like Na^+ , Ca^{2+} , etc., are in the interlayer of natural MMT. The porous structure, high surface area, capability of exchanging interlayer cations, and environmental compatibility make MMT one of the most promising candidates for decontamination and disposal of wastewater with high-level heavy metal cation content (Bhattacharyya and Gupta, 2008).

It is hypothesized that the combination of CTS with MMT may create a more efficient adsorbent. Thus, in this work, we developed a simple method to prepare a composite of MMT and CTS, and Co^{2+} was selected as a typical heavy ion to test the adsorption with the aim of testing the removal efficiency of this new material.

1. Materials and methods

1.1. Preparation of CTS–MMT

CTS of 0.5 g with molecular weight 5×10^4 (>90% degree of deacetylation, Golden-Shell Biochemical Co., Ltd., China) was dissolved in 50 mL, 5% (V/V) acetic acid (China Pharmaceutical Group Co., Ltd., China) to form a sol, and the sol was stirred at 60°C for 3 hr. After cooling to 30°C, a certain content of MMT (Zhejiang Sanding Technology Co., Ltd., China) was added into the sol according to the designed mass ratio (CTS:MMT = 1, 0.5, 0.25, 0.1, 0.05) and stirred for 24 hr. After drying the solid in a vacuum oven at 70°C, it was ground and sieved to 100 mesh particles that were then collected for adsorption studies.

1.2. SEM, XRD and FT-IR characterization

Scanning electron microscope (SEM) observations were carried out (Quanta 200 Philips, USA). X-Ray diffraction patterns (XRD) were recorded in the range of 2–40° (2 θ) with a diffractometer (D/max 2550 VB+/PC Rigaku, Japan) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154$ nm). The applied voltage and current were 30 kV and 40 mA, respectively. Fourier transform infrared spectroscopy (FT-IR) was also performed using a spectrometer (Avatar 360 Nicolet, USA). FT-IR spectra in the transmittance mode were recorded in the range of 500–4000 cm^{-1} at a resolution of 4 cm^{-1} .

1.3. Co^{2+} adsorption tests

Co^{2+} adsorption experiments were carried out by adding 0.1 g CTS–MMT into 25 mL, 8.25×10^{-4} g/mL $\text{Co}(\text{NO}_3)_2$ (China Pharmaceutical Group Co., Ltd., China) solution at 30°C for 1, 2, 4, 8, 12 and 24 hr, respectively. The slurry after adsorption was filtered and centrifuged. The concentration of Co^{2+} in the solution was measured with an atomic adsorption spectrophotometer (AAS, Beijing Purkinje, China), and the interaction of Co^{2+} with the adsorbent was studied using a UV–Vis diffuse reflectance spectrophotometer (UV-3000, Hitachi, Japan), and thermodynamic and kinetic studies of Co^{2+} adsorption were also carried out.

2. Results and discussion

2.1. Properties of CTS, MMT and CTS–MMT

SEM micrographs of CTS, MMT and CTS–MMT are shown in Fig. 1. CTS displays an irregular particulate morphology having smooth surfaces. The MMT is composed of flakes or agglomerated flakes with varied sizes. In the case of CTS–MMT, larger seemingly gelled particles with small flakes and rough surfaces were observed.

The XRD patterns of CTS, MMT and CTS–MMT are given in Fig. 2. From the characteristic (001) diffraction, structural changes of the MMT are clearly observed. The (001) diffraction peak of MMT occurred at 2θ of 7.545°, corresponding to a d001 spacing of 1.1707 nm. However, the d001 spacing of CTS–MMT was slightly increased to 1.3497 nm ($2\theta = 6.543^\circ$), indicating that the MMT interlayer expanded, which can be reasonably ascribed to the intercalation of CTS into the MMT interlayer region, leading to the formation of CTS–MMT.

The FT-IR spectra of CTS, MMT and CTS–MMT are shown in Fig. 3. The IR spectra of CTS exhibit an –OH stretching vibration at around 3400 cm^{-1} , –CH stretching vibration at 2932 cm^{-1} , and –NH bending vibration at 1650 cm^{-1} , respectively. The –CH₂ bending vibration observed at 1451 cm^{-1} and the peaks at 1018 and 1110 cm^{-1} belong to the –CO stretching vibration in the –COH group. The shoulder IR adsorption at 3625 cm^{-1} originates from the stretching of hydroxyl groups coordinated to octahedral cations. The 3442 and 1639 cm^{-1} bands for MMT are assigned to stretching and bending vibrations of hydroxyl groups in molecular water present in MMT. The most intense peak at 1040 cm^{-1} derives from the stretching vibration of Si–O in the tetrahedral sheet. In comparison with the spectra of CTS and MMT, two characteristics of CTS–MMT are observed, one is that an intense new peak and a small new peak appear at 2355 cm^{-1} and 1554 cm^{-1} , the other is that –OH, –NH, and –CH group positions clearly shifted. These changes indicate that strong interactions are present in CTS–MMT.

2.2. Adsorption behavior

Fig. 4 shows the adsorption results of Co^{2+} on CTS–MMT for different times (1, 2, 4, 8, 12 and 24 hr). It was found that the adsorption amounts for these CTS–MMT materials increased quickly in 4 hr and then became slow and reached the maximum value at 12 hr. CTS–MMT with a mass ratio of 0.25 showed the highest adsorption amount (150 mg/g) at 12 hr. The adsorption potential of CTS–MMT for cobalt in this study was compared with that of other reported adsorbents as summarized in Table 1 (Manohar et al., 2006; Yavuz et al., 2003; Parab et al., 2006; Anoop Krishnan and Anirudhan, 2008; Ahmadpour et al., 2009; Suhasini et al., 1999; Erdem et al., 2004; Smiciklas et al., 2006; Repo et al., 2009; Bhatnagar et al., 2010). It can be seen that the prepared adsorbent in this study shows good performance for cobalt removal, which might be related to the combination of the advantages of both CTS and MMT.

As mentioned above, CTS is known as a good adsorbent due to its abundant amine (–NH₂) and hydroxyl (–OH)

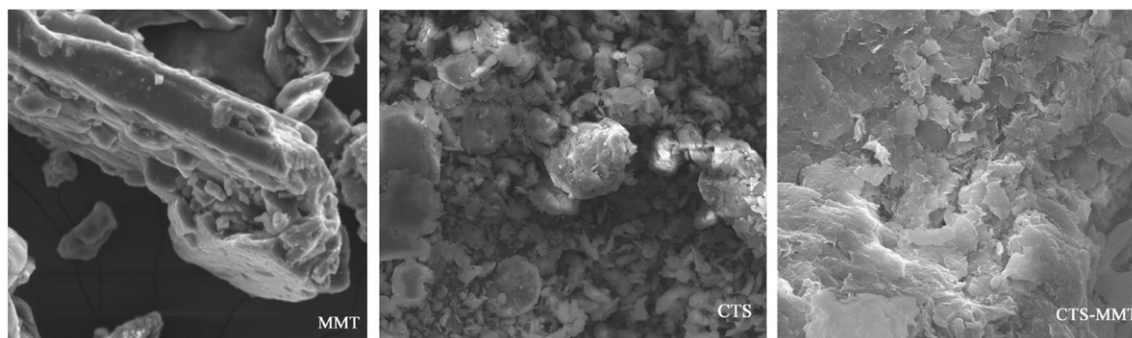


Fig. 1 – SEM images of MMT, CTS, and CTS-MMT.

groups, which can form complexes with various heavy metal ions. Here, the prepared CTS-MMT maintains the adsorption characteristics of CTS, and $-OH$ and $-NH$ groups are also observed via FT-IR, which might serve as coordination sites to form complexes with Co^{2+} . The UV-Vis diffuse reflectance spectra of Co^{2+} -absorbed CTS-MMT are shown in Fig. 5. It can be observed clearly that the spectrum is dominated by two peaks occurring at 250 nm and 300–600 nm, respectively. The narrow peak at 250 nm can be attributed to the absorption of CTS-MMT. Meanwhile, the broad peak occurring at 300–600 nm is characteristic of Co^{2+} (Zhang et al., 2011). Furthermore, no peak attributable to Co^{3+} is detected. Thus, the removal of Co^{2+} is carried out by the formation of Co^{2+} complexes, and the adsorption is a chemical adsorption process.

Langmuir, Freundlich and Temkin isotherms are widely used to describe the adsorption characteristics of adsorbents. Important information about adsorbent surface properties can be known from the adsorption isotherms (Liu et al., 2011; Juang and Shao, 2002), and the linear form of Langmuir, Freundlich and Temkin isotherms can be written as Eqs. (1)–(3), respectively.

$$\frac{C_e}{Q_e} = \frac{1}{BQ_m} + \frac{C_e}{Q_m} \quad (1)$$

$$\log Q_e = \log K + \frac{1}{n} \log C_e \quad (2)$$

$$Q_e = A + B \log C_e \quad (3)$$

where, C_e (g/L) is the equilibrium concentration of Co^{2+} in solution, Q_e (mmol/g) is the amount adsorbed per unit mass of adsorbent, Q_m (mmol/g) is the maximum sorption capacity, and B , K , n , and A are adsorption constants. The correlation coefficients based on the three isotherms are summarized in Table 2. Independent of the adsorbents, the Temkin equation gave the best fit for all the results, indicating multilayer adsorption of Co^{2+} on adsorption sites having different energies.

The efficiency of an adsorbent for the removal of metal cations is essentially determined by adsorption kinetics. In order to determine the controlling steps such as mass transfer and chemical reaction, different kinetic models are used to fit the experimental data (Annadurai et al., 2008; Zhou et al., 2009). The linear form of the pseudo first-order kinetic model, pseudo second-order kinetic model, and intraparticle diffusion kinetic model can be written as follows, respectively.

$$\frac{1}{q_t} = \frac{k_1}{q_e t} + \frac{1}{q_e} \quad (4)$$

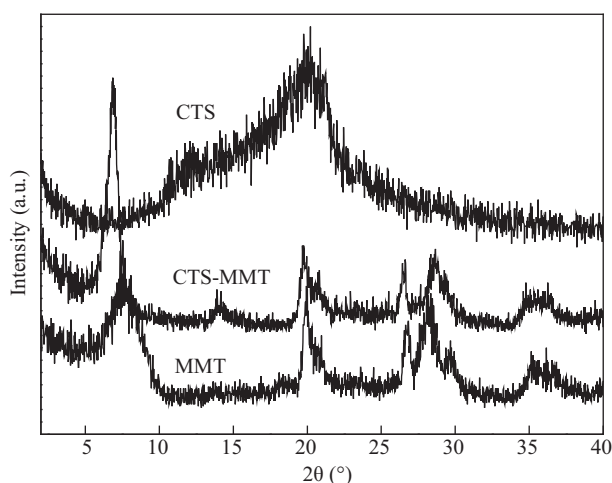


Fig. 2 – XRD patterns of MMT, CTS, and CTS-MMT.

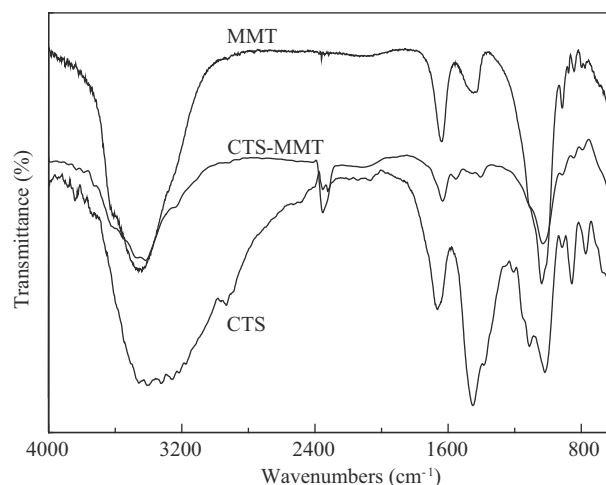


Fig. 3 – FT-IR spectra of CTS, MMT, and CTS-MMT.

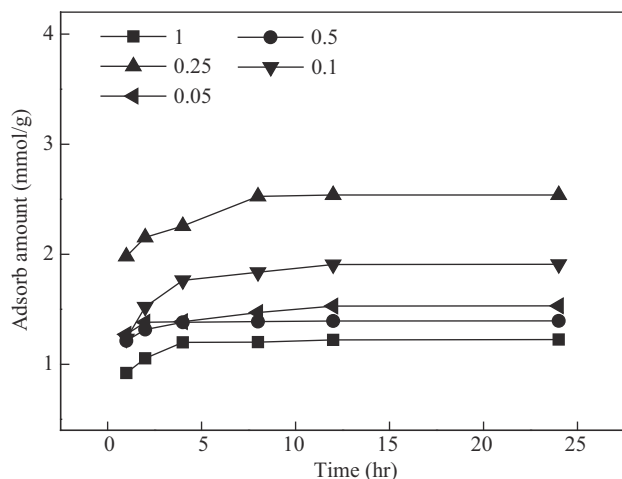


Fig. 4 – Adsorption of Co^{2+} on the CTS-MMT with different mass ratios.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \quad (5)$$

$$q_t = k_i t^{\frac{1}{2}} + c \quad (6)$$

where, q_t (mg/g) is the amount of Co^{2+} at time t (min), q_e (mg/g) is the equilibrium adsorption capacity, and k_1 (min^{-1}), k_2 ($\text{g}/(\text{mg}\cdot\text{min})$) and k_i ($\text{mg}/(\text{g}\cdot\text{min}^{0.5})$) are the rate constants of the pseudo first-order kinetic model, pseudo second-order kinetic model and intraparticle diffusion kinetic model, respectively. According to the three kinetic models, the correlation coefficients are listed in Table 3. The adsorption of Co^{2+} on CTS-MMT best fits the pseudo second-order equation, indicating that chemical sorption is the rate-limiting step.

The calculated values of free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) are given in Table 4. They were calculated using the following equations.

$$K_c = \frac{C_A}{C_s} \quad (7)$$

$$\Delta G^\theta = -RT \ln K_c \quad (8)$$

$$\ln K_c = \frac{\Delta S^\theta}{R} - \frac{\Delta H^\theta}{RT} \quad (9)$$

where, K_c is the equilibrium constant, C_A (g) is the amount of Co^{2+} adsorbed in per unit mass of absorbent at equilibrium, C_s (g/L) is the equilibrium concentration of the Co^{2+} in solution, ΔG^θ (kJ/mol) is the adsorption free energy change, ΔH^θ (kJ/mol) is the enthalpy change, ΔS^θ (J/(K·mol)) is the entropy change, R (kJ/(K·mol)) is the gas constant, and T (K) is the absolute temperature. The values of enthalpy (ΔH^θ) and entropy (ΔS^θ) were obtained from the slope and intercept of $\ln K_c$ vs $1/T$ plots.

The calculated values of free ΔG , ΔH and ΔS were obtained according to the methods in other studies (Septum et al., 2007; Choudhari and Kariduraganavar, 2009). The value of ΔH^θ is positive (14.00 kJ/mol), suggesting that the adsorption of Co^{2+} is endothermic. The value of ΔG^θ (−1.66 kJ/mol) is negative, indicating that the reaction is spontaneous at 30°C. The positive value of ΔS^θ (51.67 J/(mol·K)) shows that particles in equilibrium solution decrease randomness compared to the initial solution. Before adsorption, there were only metal ions and water molecules, but metal ions were combined with water molecules, forming aquo-metal ions. When adsorption equilibrium was reached, some metal ions in the solution were absorbed by CTS, and water molecules were released from the aquo-metal ions, thus the total particles in equilibrium solution increased.

3. Conclusions

A simple method was developed to prepare CTS-MMT composites, whose formation was confirmed by XRD and FT-IR results. Greatly enhanced adsorption of Co^{2+} was achieved on CTS-MMT in comparison with CTS or MMT alone, and was dependent on the specific experimental conditions and the molecular weight of CTS. Irrespective of the initial concentration of Co^{2+} , CTS-MMT with mass ratio 0.25 (CTS:MMT) showed better performance for Co^{2+}

Table 1 – Comparison of Co^{2+} adsorption over different adsorbents.

Adsorbent	Co^{2+} (mg/L)	Adsorbent dose	Reaction time (hr)	Adsorption capacity (mg/g)	Reference
Clay	25	2.0 g/L	24	38.6	Manohar et al. (2006)
Kaolinite	2400	1.0 g/L	2	0.9	Yavuz et al. (2003)
Coir pith	50	2.0 g/L	2	12.8	Parab et al. (2006)
Activated carbon	1000	2.0 g/L	4	153.6	Anoop Krishnan and Anirudhan (2008)
Almond green hull	50	5.0 g/L	0.1	45.5	Ahmadpour et al. (2009)
Biosorbent	500	2.0 g/L	24	190.0	Suhasini et al. (1999)
Zeolites	400	20 g/L	5.5	14.4	Erdem et al. (2004)
Hydroxyapatite	5–1000	–	24	20.9	Smiciklas et al. (2006)
Silica gel	400	2.0 g/L	4	20	Repo et al. (2009)
Lemon peel	1000	10 g/L	10	22	Bhatnagar et al. (2010)
CTS-MMT	825	4 g/L	12	150	This study
–: not mentioned.					

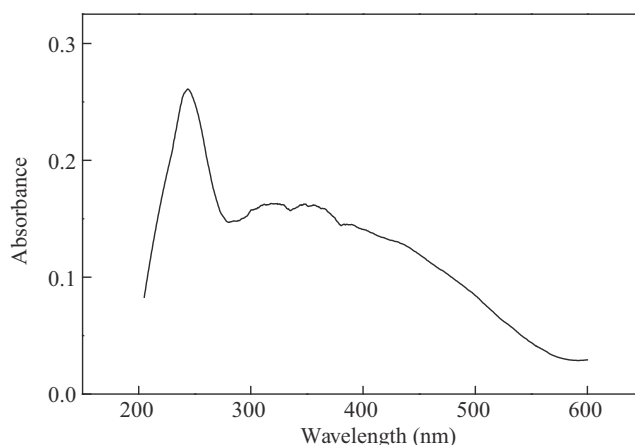


Fig. 5 – UV-Vis pattern of Co^{2+} absorbed CTS-MMT.

Table 2 – Parameters of three kinds of adsorption models.

Mass ratio	Langmuir				Frenudlich			Temkin	
	Q_m	B	R^2	$1/n$	k	R^2	A	B	R^2
1	1.91×10^{-3}	-2.53	0.9945	-2.26	1.77×10^{-3}	0.9972	-1.7×10^{-3}	-0.033	0.9998
0.5	2.84×10^{-3}	-3.08	0.9986	-2.91	1.90×10^{-3}	0.7942	-8.5×10^{-4}	-0.029	0.9999
0.25	8.64×10^{-3}	-10.24	0.9946	-0.53	6.88×10^{-3}	0.9905	4.5×10^{-3}	-0.016	0.9962
0.1	4.00×10^{-3}	-4.05	0.9842	-1.22	3.44×10^{-3}	0.9870	3.14×10^{-4}	-0.026	0.9974
0.05	3.30×10^{-3}	-3.39	0.9958	-1.49	2.88×10^{-3}	0.9972	-4.28×10^{-4}	-0.028	0.9996

Table 3 – Correlation coefficients (R^2) of Co^{2+} adsorption by CTS-MMT.

Mass ratio	Pseudo first-order	Pseudo second-order	Intraparticle diffusion
1	0.8172	0.9966	0.8156
0.5	0.6476	0.9997	0.7768
0.25	0.2867	0.9935	0.8246
0.1	0.6228	0.9918	0.864
0.05	0.3912	0.9918	0.9226

adsorption than other samples, and the maximum value was 150 mg/g. The adsorption isotherms of Co^{2+} on the composites were best fitted by the Temkin equation, indicating multilayer adsorption of Co^{2+} . Kinetics study revealed that the adsorption of Co^{2+} on CTS-MMT followed the pseudo second-order equation, indicating that chemical sorption is the rate-limiting step. Thermodynamic parameters such as ΔG^θ , ΔH^θ , and ΔS^θ were also evaluated to understand the nature of sorption.

Table 4 – Thermodynamic parameters.

Metal ions	T (°C)	$\ln K_c$	ΔG^θ (kJ/mol)	ΔS^θ (J/(mol·K))	ΔH^θ (kJ/mol)
Co^{2+}	30	0.68	-1.66	51.67	14.00
	60	1.12	-3.10	/	/
	90	1.61	-4.86	/	/

As discussed above, the adsorption of Co^{2+} over CTS-MMT is a chemical process due to the formation of Co^{2+} complexes with amine ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$) groups and the parameters ΔG^θ and ΔS^θ also suggest that the process is spontaneous and irreversible. Thus, the regeneration of this synthesized material is difficult using common methods such as washing, calcination and others. Considering the low cost of CTS-MMT and the highly enriched Co^{2+} content of spent adsorbent, centralized disposal with other treatments to recycle Co-related materials might be a more economical option than regeneration.

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