Removal of Cd2+ from Water Containing Ca2+, Mg2+ using Titanate Nanotubes Modified by Carbon

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2.1 Materials and reagents

  TiO₂(anatase, 2-5 nm, 98%) and Cadmium standard solution (1000 ug/mL in 1 mol/L HCl) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Furfuryl alcohol (>99%), Ethanol, Calcium chloride anhydrous (CaCl₂, >99%) and Cadmium nitrate tetrahydrate (>99%) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Magnesium chloride hexahydrate (MgCl₂·6H₂O) and Sodium hydroxide (NaOH, >99%) were both acquired from XiLong Scientific Co., Ltd (Guangdong, China).

2.2 Preparation of TNT, TNT/C and TNT/HC

2.2.1 Preparation of TNT

Mix 1.2 g of TiO2 with 60 mL of 10 M NaOH solution. After stirring overnight, the mixture was poured into a container lined with polytetrafluoroethylene, and then heated at 130°C for 3 days. Until the temperature of the mixed solution was consistent with room temperature, rinsed the sample with pure water until the supernatant reached neutrality. Then the target product was sonicated in alcohol and lastly dried at 80°C (Li et al. 2015).

2.2.2 Preparation of TiO₂/C and

TNT/C

3 g TiO₂ and 1 g Furfuryl alcohol were mixed with 10 mL Ethanol. After stirring for 12 hours, the furfuryl alcohol in the mixed suspension was polymerized at 80°C, and then calcined at 600°C for 3 hours under a nitrogen atmosphere. This was how TiO2/C was made. he making process of TNT/C was the same as that of TNTs, except that the TiO2 was replaced with TiO2/C.

2.2.3 Preparation of TiO₂/HC and TNT/HC

Treat TiO2/C in boiling HNO₃ for 6 hours. After standing, the supernatant was poured out, washed with deionized water to neutrality, and dried at 105°C to obtain a TiO2/HC sample (Maroto-Valer et al. 2004). The making process of TNT/HC was the same as that of TNT, except that the TiO₂ was replaced with TiO₂/HC.

The synthesis process of the adsorbent is shown in figure 1.

2.3 Characterization of adsorbent

The morphology of these adsorbents was observed by SEM (Tescan, A VEGA) and TEM (JEM-2100Plus). The structures of these three samples were studied by XRD (Panalytical X'Pert PRO MPD). The carbon

content of the composite material was determined from TGA (NETZSCH STA 409 PC/PG). FT-IR (TENSOR 27, resolution 4 cm^{−1}, Bruker, Billerica, MA, USA) was used to analyze the functional groups and bonding conditions on the surface of the adsorption material. XPS (K-ALPHA, Thermo Fisher, Waltham, MA, USA) was used to analyze the surface element composition and valence state of the surface. The concentration of Cd²⁺ was detected by A flame atomic absorption spectrophotometer (FLAAS) (AA900T, PerkinElmer, Waltham, MA, USA).

2.4 Adsorption experiments

All batch experiments were repeated 3 times and oscillated at a speed of 200 rpm at the set temperature. The general experimental procedure is described as follows: All batch experiments were carried out by adding 0.02g adsorbent to polyethylene pipe (50 ml) with 40 ml solutions. When Initial solution concentration is 200 mg/L with the pH from 2 to 6, the most suitable pH for the adsorption of Cd²⁺ by TNT, TNT/C, and TNT/HC is first determined. At 25°C and the optimum pH, the adsorption isotherm is obtained by experimenting with initial solutions of different concentrations. At the same time, the adsorption kinetic

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66 After the set adsorption time is reached, the supernatant obtained
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72 2018)
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74 src="https://myfiles.space/user_files/69515_16346c490bab499e/695
75 15_custom_files/img1635490867.png">
76 Where co (mg/L) is the concentration of initial Cd2+
77 concentration and Ce (mg/L) is the equilibrium Cd2+ concentration,
78 respectively, V (L) is the volume of the solution and m (g) is the
79 weight of sorbent. Removal of Cd^{2+} from water containing Ca^{2+},
80 Mg^{2+} using Titanate nanotubes modified by carbon

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Abstract

Ca^{2+} and Mg^{2+} usually exist in natural water. When Cd^{2+} is removed from water by adsorption, it will be inhibited by these two ions. Titanate nanotubes (TNTs) have an effective adsorption capacity for Cd^{2+} due to extraordinary ion-exchange property. However, TNTs also adsorb Ca^{2+} and Mg^{2+} in water. In this study, carbon-modified TNT (TNT/C or TNT/HC) was synthesized by hydrothermal synthesis. The transmission electron microscope (TEM) images show that TNT/C or TNT/HC still keep nanotube morphology. The experimental results show the order of adsorption amount to Cd^{2+} is TNT > TNT/C > TNT/HC when there is no Ca^{2+} or Mg^{2+}. But when there is Ca^{2+} or Mg^{2+} in the water, the order of Cd^{2+} adsorption capacity becomes TNT/HC > TNT/C > TNT. It indicates that the surface carbon-modification can alleviate the hindrance of Ca^{2+} or Mg^{2+} to Cd^{2+} removal. This is because the carbon on the surface of TNT captured part of Ca^{2+} or Mg^{2+}, it made more Cd^{2+} be successfully absorbed by TNT through ion exchange. This mechanism was confirmed by XPS spectra analysis. The results of this paper can provide ideas for the adsorption and removal of Cd^{2+} in water in the presence of Ca^{2+} or Mg^{2+}.

Keywords

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1. Introduction

With the increase of cadmium production year by year, a considerable amount of cadmium is discharged into the environment, and many natural water systems are polluted by cadmium (Zhao et al. 2011). Unreasonable disposal of heavy metal-containing wastewater poses a huge threat to human health (Zhou et al. 2018). Cadmium ion (Cd^{2+}) is on is one of the toxic ions, and the In the World Health Organization's regulations on qualified drinking water, the maximum concentration of Cd2+ is limited to 5 ug/L (Sriram et al. 2020). The effects of intaking the drinking water whose Cd^{2+} concentration exceeds the limit ingestion are inducing kidney disease and

bone disease (Zhang et al. 2019). The Japanese “itai-itai” disease is the worst event in the Cd^{2+} pollution incident, and it is included in the eight major pollution incidents(Huang et al. 2020a).

There are many methods to treat water with heavy metal ions, including physical methods, chemical methods, membrane treatment methods, and electrolysis methods (Bolisetty et al. 2019). Among them, the adsorption method has become one of the most promising methods for the treatment of metal ions due to its low cost, simple operation process, and less post-treatment (Mudhoo et al. 2020). However, traditional adsorbents, such as carbon-based adsorbents and organic polymer adsorbents, do not have a good adsorption capability on Cd^{2+} (Lu &Astruc 2018). In contrast, nano-metal oxide materials have shown potential applications in anchoring Cd^{2+}. Among them, magnesium oxide, iron oxide, manganese oxide, and aluminum oxide have all been used as adsorbents for heavy metal ions (Boparai et al. 2011, Mahdavi et al. 2013, Yusuf et al. 2020, Zhang et al. 2020). However, due to the instability of these substances in water, these oxides are not enough to be perfect Cd^{2+} adsorbent materials. Titanate nanotubes have attracted the attention of researchers since it successfully prepared by Tomoko Kasuga in 1998 (Kasuga et al. 1998), it has received extensive attention from researchers due to their excellent specific surface area, excellent hydrophilicity and stability in complex water environments. This material is generally obtained by one-step hydrothermal treatment of titanium dioxide in a high-concentration NaOH aqueous solution at medium temperature (90-180°C), and could be obtained from various crystal forms of titanium oxide raw materials (Bi et al. 2020). Allen J. Du et al. found that when there are both inner sphere complexation and ion exchange, the multi-site ion complexation (CDMUSIC) model based on charge distribution is the most consistent with the process of TNT adsorption of Cd^{2+} (Du et al. 2011). Xiong et al. found that with the pH of the initial solution changed from 2 to 6, the ability of Cd^{2+} adsorbed by TNT was increased (Xiong et al. 2011). In addition, it was confirmed that 0.1 M hydrochloric acid can desorb 85% of Cd^{2+} from the adsorbent (Xiong et al. 2011). Liu

et al. found that Na^+, K^+, Ca^{2+} and Mg^{2+} will compete with Cd^{2+}, which greatly inhibited the adsorption of Cd^{2+} (Liu et al. 2013). Moreover, it is proposed that EDTA and HNO_3 can also be used as desorption agents to desorb Cd^{2+} from TNT, and the desorption rate can reach more than 90% (Liu et al. 2013). Moreover, it was proved that the [TiO_6] octahedral structure of TNTs hardly changed during the entire adsorption process(Duan et al. 2021). This shows that TNT has high structural stability when facing the complex environment of the waste water (Wang et al. 2013a). Wang et al. used 0.1 M HNO_3 to desorb the Cd^{2+} in TNT, and then only 0.2 M NaOH at room temperature could easily achieve the regeneration of TNT. Even after six cycles, the regenerated TNT can adsorb Cd^{2+} (Wang et al. 2013b). The research results show low NaOH concentration is required to prepare TNT with the largest adsorption capacity for Cd^{2+} (Liu et al. 2014). Yang et al. successfully prepared a magnetite-graphene oxide-titanate composite material, which made the titanate material easier to recycle. (Yang et al. 2020).

Although titanate materials (TNT or TNs) have great potential as cadmium ion adsorbents, when it is surrounded by Na^+, K^+, Ca^{2+}, Mg^{2+} and natural organic matter (NOM), the adsorption capacity of Cd^{2+} would be greatly reduced. The powdered activated carbon supported TNTs (TNTs@PAC) synthesized by Ma et al. showed high adsorption capacity for Pb(II) and strong resistance to natural organic matter (Ma et al. 2017). This shows that the researchers found that the environment affects the adsorption of titanate. However, few researchers are interested in the effect of inorganic ions on the adsorption of titanate. $Ca^{2+}$and Mg^{2+} often appear in polluted water bodies, they would reduce the adsorption capacity of titanate materials for Cd^{2+}: from 2.02 mmol/g to 1.17 mmol/g (Liu et al. 2013). According to the soft and hard acid-base theory, $Ca^{2+}$and Mg^{2+} belong to the ranks of hard acid, while Cd^{2+} is classified as soft acid(Esrafili et al. 2021, Wang et al. 2019). In addition, some carbon-containing functional groups, such as -COOH, -C=O and C-OH, are in the category of hard bases (Di Natale et al. 2020, Zhao et al. 2011). If the surface of the Titanate material is functionalized with -COOH, -C=O and -OH, they would be used to capture Ca^{2+}, Mg^{2+},

and the probability of ion exchange between these interfering ions and the sodium ions in the titanate layer would be reduced. It is beneficial to the adsorption of Cd^{2+}.

Based on the above statement, after carbonizing the furfuryl alcohol on the surface of the titanium oxide, it was further processed by alkaline hydrothermal method to obtain in-situ carbon-supported TNT.

This article aims to:

1）Synthesis of Titanate nanotubes modified by carbon (TNT/C);

2）Evaluate the selective adsorption performance of TNT/C;

3）Explore the mechanism of resisting interference from non-target ions by oxidizing surface carbon with nitric acid.

2. Experimental

2.1 Materials and reagents

TiO_2(anatase, 2-5 nm, 98%) and Cadmium standard solution (1000 ug/mL in 1 mol/L HCl) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Furfuryl alcohol (>99%), Ethanol, Calcium chloride anhydrous ($CaCl_2$, >99%) and Cadmium nitrate tetrahydrate (>99%) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) and Sodium hydroxide (NaOH, >99%) were both acquired from XiLong Scientific Co., Ltd (Guangdong, China).

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2.2.3 Preparation of TiO_2/HC and TNT/HC

Treat TiO2/C in boiling HNO_3 for 6 hours. After standing, the supernatant was poured out, washed with deionized water to neutrality, and dried at 105°C to obtain a TiO2/HC sample (Maroto-Valer et al. 2004). The making process of TNT/HC was the same as that of TNT, except that the TiO_2 was replaced with TiO_2/HC.

The synthesis process of the adsorbent is shown in figure 1.

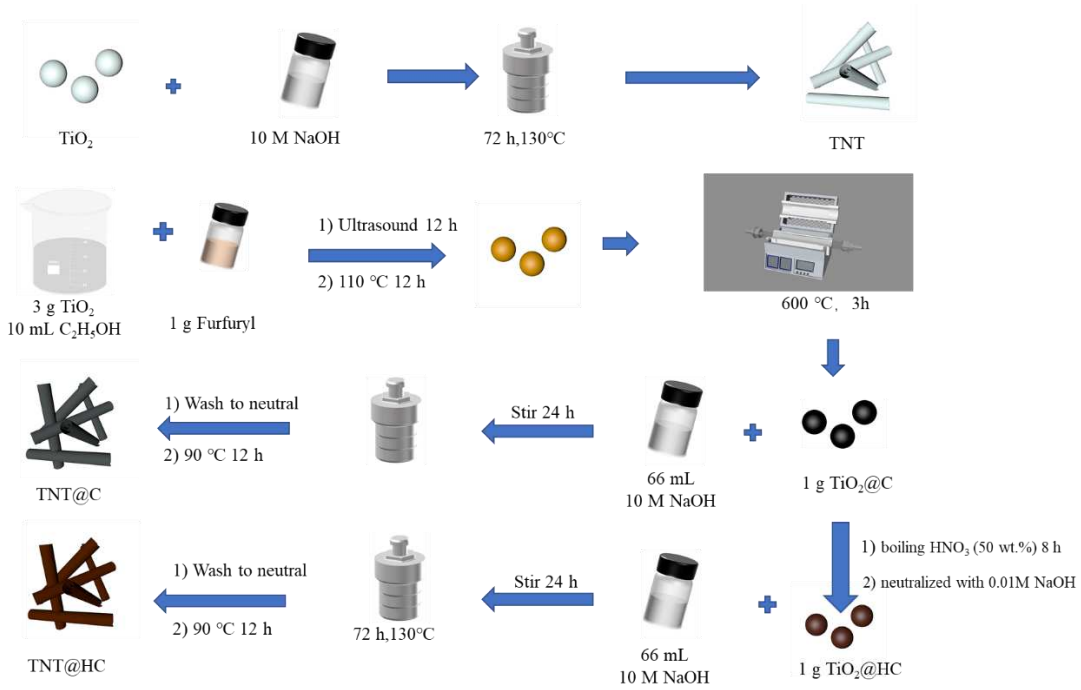

Fig. 1. The scheme of the synthesis of TNT, TNT/C and TNT/HC.

2.3 Characterization of adsorbent

The morphology of these adsorbents was observed by SEM (Tescan, A VEGA) and TEM (JEM-2100Plus). The structures of these three samples were studied by XRD (Panalytical X'Pert PRO MPD). The carbon content of the composite material was determined from TGA (NETZSCH STA 409 PC/PG). FT-IR (TENSOR 27, resolution 4 cm^{-1}, Bruker, Billerica, MA, USA) was used to analyze the functional groups and bonding conditions on the surface of the adsorption material. XPS (K-ALPHA, Thermo Fisher, Waltham, MA, USA) was used to analyze the surface element composition and valence state of the surface. The concentration of Cd^{2+} was detected by A flame atomic absorption spectrophotometer (FLAAS) (AA900T, PerkinElmer, Waltham, MA, USA).

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After the set adsorption time is reached, the supernatant obtained after filtering the aqueous suspension through a 0.45um filter membrane can be used for the measurement of Cd^{2+} concentration.

The data is the average of three experiments. The adsorption capacity q_e (mg/g) was calculated by the Eq. (1) (Zhu et al. 2018)

$$q_e = (c_0 - c_e) * V/m \quad (1)$$

Where c_0 (mg/L) is the concentration of initial Cd^{2+} concentration and c_e (mg/L) is the equilibrium Cd^{2+} concentration, respectively, V (L) is the volume of the solution and m (g) is the weight of sorbent.

3 Results and discussions

3.1 Characterization

Figure 2 shows the SEM images of three adsorbents (TNT, TNT/C, TNT/HC). The samples all showed some aggregation. In order to prove that these bundles or clusters of material structures are nanotubes rather than nanowires, TEM was used for further characterization.

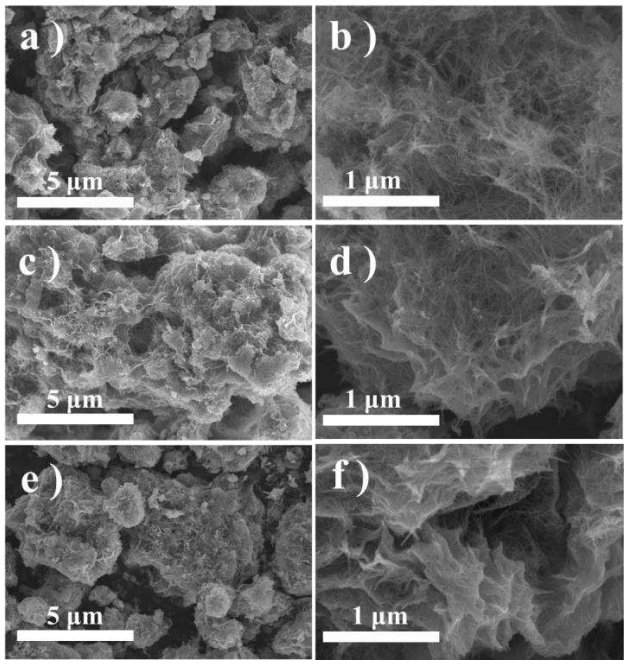


Fig. 2. SEM images of TNT (a, b), TNT@C (c, d) and TNT@HC (e, f)

Figure 3 demonstrates a typical TEM image of titanate nanotubes, which are approximately 5-10 nm in diameter. Figure 4.a. shows the XRD patterns of the TNT, TNT/C and TNT/HC. It is assumed that the peaks at the center of 10°, 24.3°, 28.5° and 48.2° are their characteristic diffraction peaks, which indicates that the synthesized titanate nanotubes have the chemical formula of $Na_xH_{2-x}Ti_3O_7$ (Duan et al. 2021). The peak at 10° is an indication of the interlayer distance of titanate (Zhao et al. 2016). The SEM/TEM images and XRD patterns of TNT, TNT/C and TNT/HC are similar, which

means that carbon loading on the TiO_2 surface does not affect the growth of TNT.

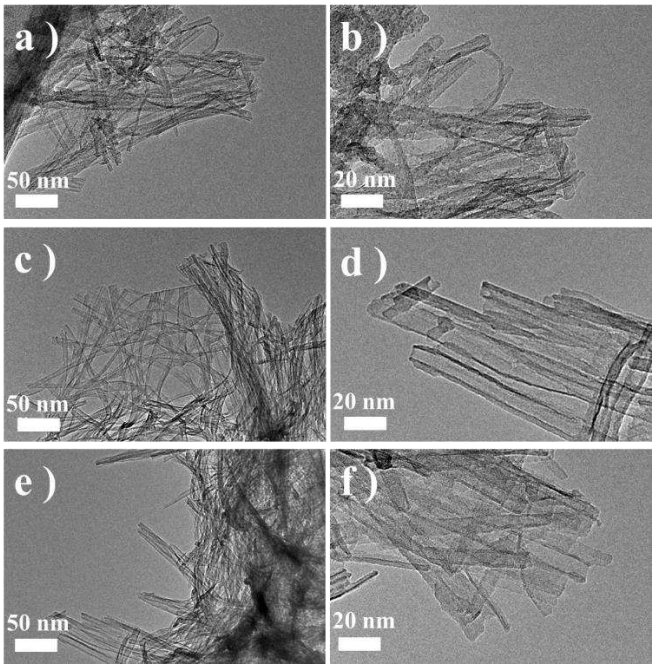


Fig.3. TEM images of TNT (a, b), TNT/C (c, d) and TNT/HC (e, f)

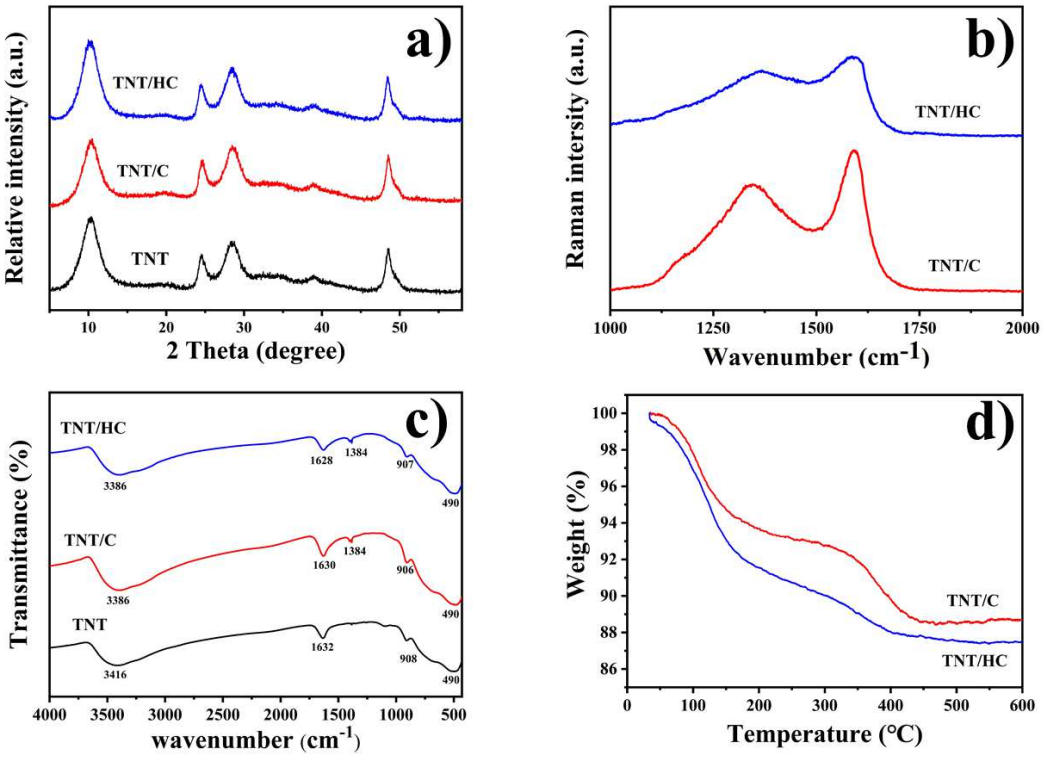


Fig. 4. Characterizations of the TNT, TNT/C and TNT/HC. (a) XRD pattern, (b) Raman spectra, (c) FT-IR spectra, (d) Thermogravimetric profiles.

The Raman spectra of TNT/C and TNT/HC are shown in Figure 4.b. The two

peaks at 1358 cm^{-1} and 1600 cm^{-1} correspond to the G peak and D peak of carbon, which indicates the successful introduction of carbon (Pyrzyńska &Bystrzejewski 2010). The $I_D/I_{G\ TNT/HC}$ (0.884) exceeding $I_D/I_{G\ TNT/C}$ (0.806) indicates that the degree of non-graphitization of TNT/HC is greater than that of TNT/C, which is caused by nitric acid treatment. The FT-IR spectra of TNT, TNT/C and TNT/HC are given in Figure 4.c. For the neat TNT, the strong absorption bands in the region of 3416 cm^{-1} and the band at 1632 cm^{-1} could be attributed to the hydroxyl groups stretching vibration and water molecules binding vibration, respectively, indicating the presence of hydroxyl groups and water molecules in the TNT (Wang et al. 2018, Zhu et al. 2018). The band at 908 cm^{-1} might be related to a four-coordinate Ti−O stretching vibration (Wang et al. 2013b). The band at 490 cm^{-1} was assigned to the vibration of [TiO_6] octahedron (Xiong et al. 2011). For TNT/C and TNT/HC, the new peak at 1384 cm^{-1} is the carbonyl vibrations of ketone groups peak (Wang et al. 2013a). The thermogravimetric profiles of TNT/C and TNT/HC could be seen in Figure 4.d. The weight loss at temperatures below 100°C is due to the evaporation of free water on the surface of the adsorbent (Yuan et al. 2017, Zhou et al. 2020). The weight loss at 100-350°C is attributed to the loss of chemically bonded water of the crystal layer. The weight loss after 350°C is due to the oxidation of carbon. TNT/HC has no obvious plateau at 200-350°C, which is caused by the superposition of the loss of chemically bonded water in the crystal layer and the loss of carbon oxidation (Yuan et al. 2017).

3.2 Effects of pH

The pH value of the experimental solution has a great influence on the adsorption results. According to previous studies, in order to avoid precipitation of Cd^{2+} hydroxide, it was decided to choose an initial solution with a pH of 2-6 for exploration (Kim et al. 2020). The experimental results are shown in Figure 5. The adsorption capacity of TNT and TNT/C for Cd^{2+} changes with the change of pH, and the relationship between them is positively correlated. The maximum adsorption capacity occurs when the pH is 6.

Whether the adsorption mechanism is ion exchange or surface action, the adsorption of positively charged Cd^{2+} and positively charged H^{+} on the surface of the adsorbent is in a competitive relationship. Therefore, when the pH is lower, the concentration of hydrogen ions is also higher, and the competition between hydrogen ions and Cd^{2+} is quite fierce. As we all know, pH is the negative logarithm of hydrogen ion. Because an increase in the pH value by one value could cause the hydrogen ion concentration to drop by an order of magnitude, so at the same time the ratio of Cd^{2+} to H^{+} concentration would increase. So, the adsorption capacity gradually increases with the increase of pH.

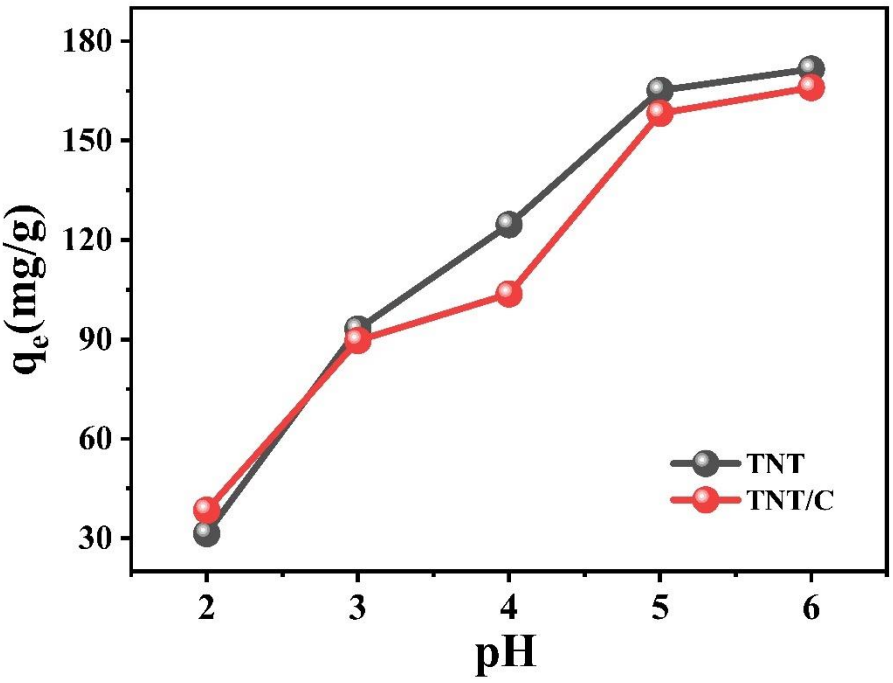


Fig. 5. Effect of initial pH on adsorption capacity of TNT and TNT/C.

3.3 Effects of contact time and adsorption kinetic

Figure 6.a shows the kinetics of Cd^{2+} adsorption on the TNT, TNT/C at 25 °C and pH=6. Obviously, the adsorption capacity increases with the prolongation of the contact time, and the adsorption equilibrium is reached within 150 minutes. The Cd^{2+} absorption amounts of TNT, TNT/C are 171.56 $mg \cdot g^{-1}$and 166 $mg \cdot g^{-1}$. Kinetic studies have profound guiding significance for the explanation of the experimental mechanism

and the selection of the best adsorption time for the adsorbent. There are two commonly used semi-empirical models, namely pseudo-first-order (PFO) dynamics and pseudo-second-order (PSO) dynamics (Dalvand et al. 2018, Dolatyari et al. 2016). The pseudo first order dynamics is as follows

$$ln(q_e - q_t) = lnq_e - k_1 * t \quad (2)$$

Where k_1 is the rate constant of pseudo-first-order adsorption, q_e(mg/g) and q_t(mg/g) is the amount of Cd^{2+} adsorbed at equilibrium and at time (t) (Goyal et al. 2020). The pseudo first order dynamics is as follows

$$t/q_t \ = 1/(k_2 * q_e\text{^}2\ ) + t/q_e \quad (3)$$

Where k_2 is the rate constant of pseudo-second-order adsorption (Rahman et al. 2020). The corresponding kinetic parameters are shown in Table 1. The pseudo -first-order kinetics and pseudo-second kinetics determination coefficient (R^2) of TNT/C are 0.7623 and 0.9999. Similarly, the value of TNT/HC are 0.7396 and 0.9999. This indicates that pseudo-second-order kinetics is more suitable for the process of Cd^{2+} adsorption by TNT and TNT/C. Since the PSO model assumes that the chemical surface reaction is the rate-limiting step (Zhao et al. 2020), we concluded that the rate-determining step of Cd^{2+} adsorption on TNT and TNT/C was chemisorption (Zheng et al. 2021).

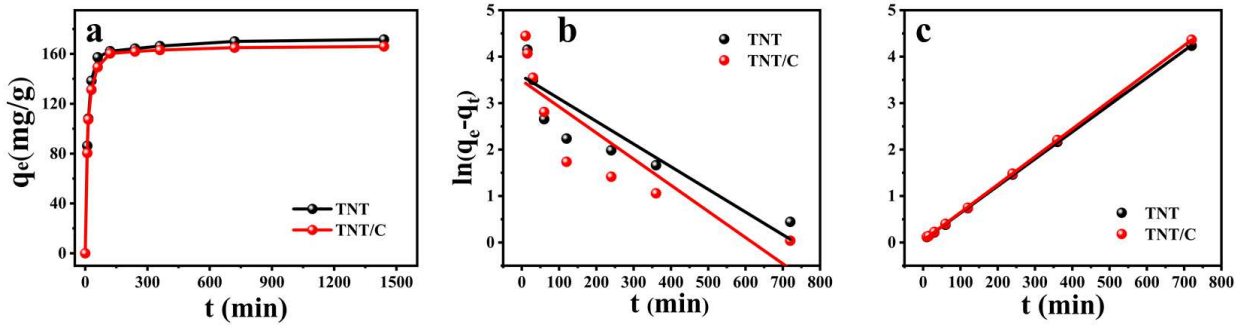


Fig. 6. Adsorption kinetics (a), the Pseudo-first-order model(b) and the Pseudo-second-order model fitting curve of Cd^{2+} on TNT and TNT/C (c).

Table 1

Pseudo-first-order and pseudo-second-order parameters for adsorption of Cd^{2+} by TNT

336 and TNT/C

Sample		pseudo-first-order kinetic			pseudo-second-order kinetic		
	$q_{e,exp}$ (mg/g)	$q_{e,cal}$ (mg/g)	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg/g)	k_2 (g/(mg*min))	R^2
TNT	171.56	36.0313	0.0049	0.7623	171.5266	0.4066	0.9999
TNT/C	166	32.6329	0.0056	0.7396	16.9449	0.3738	0.9999

337

338 ## 3.4 Adsorption isotherms.

339 For the design and operation of adsorption systems, the correlation of equilibrium
340 adsorption data is important. Langmuir and Freundlich isotherms models were applied
341 to fit the obtained adsorption data (Wang et al. 2020). The Langmuir equation has been
342 used extensively for dilute solutions in the following form:

343 $$q_e = (q_m * K_L * c_e)/(1 + K_L * c_e) \quad (4)$$

344 Where c_e ($mg \cdot L^{-1}$) is the equilibrium concentration of Cd^{2+} remained in solution,
345 q_e ($mg \cdot g^{-1}$) is the amount of solution adsorbed per unit mass of the adsorbent, q_m
346 ($mg \cdot g^{-1}$) is the maximum adsorption capacity, K_L is the Langmuir adsorption
347 equilibrium constant (Tang et al. 2020). The Freundlich equation has been used
348 extensively for dilute solutions in the following form:

349 $$\ln q_e = \ln K_F + 1/n * \ln c_e \quad (5)$$

350 Where K_F and n are the Freundlich constants related to the adsorption capacity
351 and adsorption intensity, respectively (Mao et al. 2018). The curve of the adsorption
352 isotherm model and the fitting data are shown in Figure 7 and Table 2. The results show
353 the Langmuir isotherm model better fits the experimental results with high correlation
354 coefficients (>0.97). The Langmuir model indicates that it is monolayer adsorption on
355 the structurally homogeneous TNT and TNT/C.

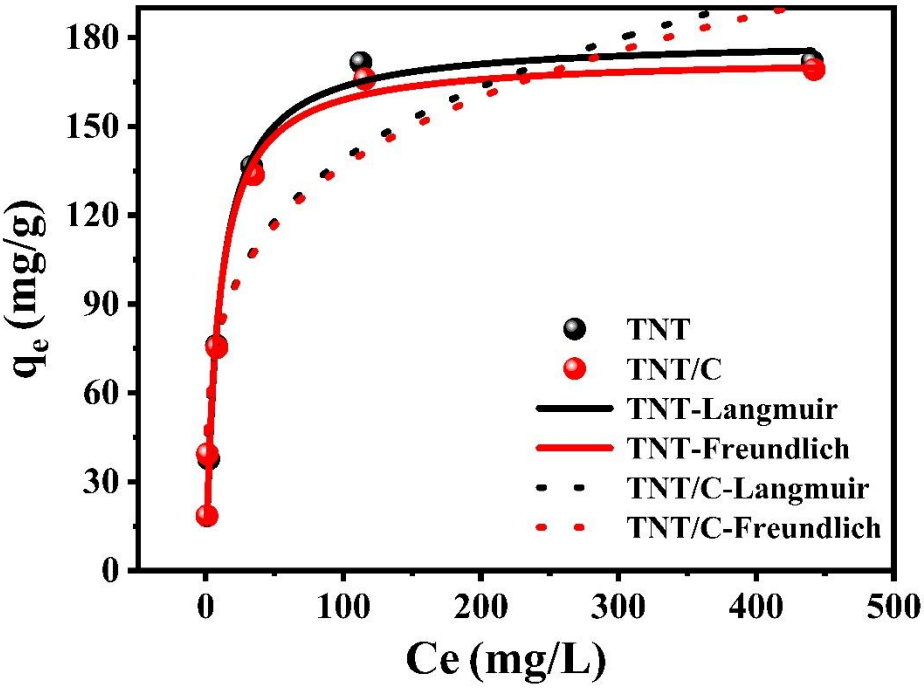


Fig. 7. Adsorption isotherm of Cd^{2+} on TNT and TNT/C

Table 2

Parameters of Langmuir and Freundlich isotherm models for the adsorption of Cd^{2+} on TNT, TNT@C.

Samples	Langmuir equation			Freundlish equation		
	q_m mg/g	K_L L/mg	R^2	K_F	$\frac{1}{n}$	R^2
TNT	179.37	0.1026	0.9951	47.0877	4.2597	0.8119
TNT/C	173.31	0.1109	0.9806	47.5353	4.3662	0.8375

3.5 Effects of ionic strength (Ca^{2+}, Mg^{2+})

Figure 8 shows the competition between coexisting cations and Cd^{2+} on TNT, TNT/C and TNT/HC. Generally, the adsorption capacity of Cd^{2+} will decrease in the

presence of Ca^{2+} or Mg^{2+} (Liu et al. 2013). This is due to the competition adsorption between Ca^{2+} or Mg^{2+} and Cd^{2+}. In this paper, the adsorption capacity of Cd^{2+} also decreases when Ca^{2+} or Mg^{2+} exists in the adsorption environment, but the adsorption capacity of TNT/C and TNT/HC exceeds that of Cd^{2+} absorbed by TNT due to the loading of carbon. When Ca^{2+} or Mg^{2+} exists in the adsorption environment, the order of the adsorption capacity of Cd2+ to different adsorption materials is TNT/HC>TNT/C>TNT. But the order of adsorption capacity is TNT>TNT/C>TNT/HC in the absence of Ca^{2+} or Mg^{2+}. It is also interesting to see that the anti-interference ability of TNT/HC prepared by hydrothermal method is improved after the carbon on the surface of TiO2 is oxidized by nitric acid (TNT/HC). The experimental results also show that when the concentration of Ca^{2+} or Mg^{2+} is high up to 0.1 mol/L, the adsorption capacity of TNT/HC on Cd^{2+} increases from 44.28 mg/L to 65.52 mg/L (in the presence of Ca^{2+}), and from 49.04 mg/L to 66.6 mg/L (in the presence of Mg^{2+}) compared with TNT. It is proved that TNT/HC is more promising than TNT as an adsorbent for the selective separation of Cd^{2+} from complex water conditions.

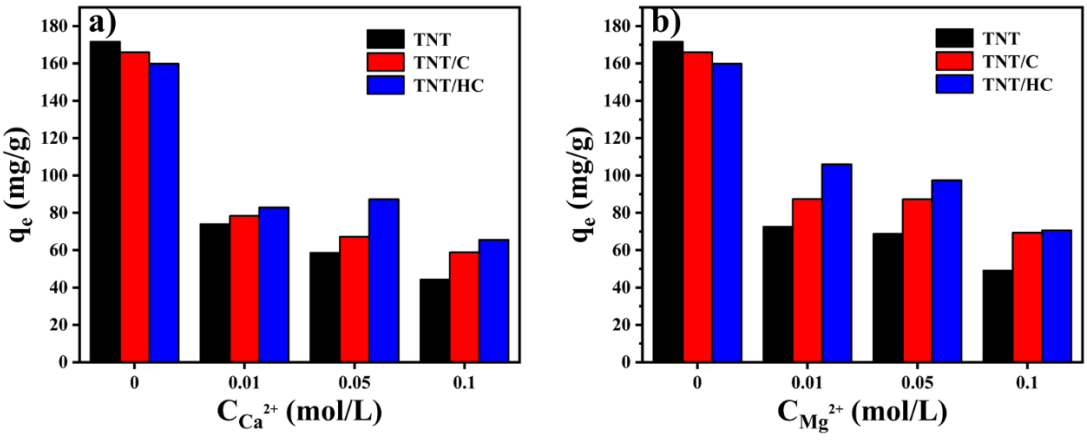
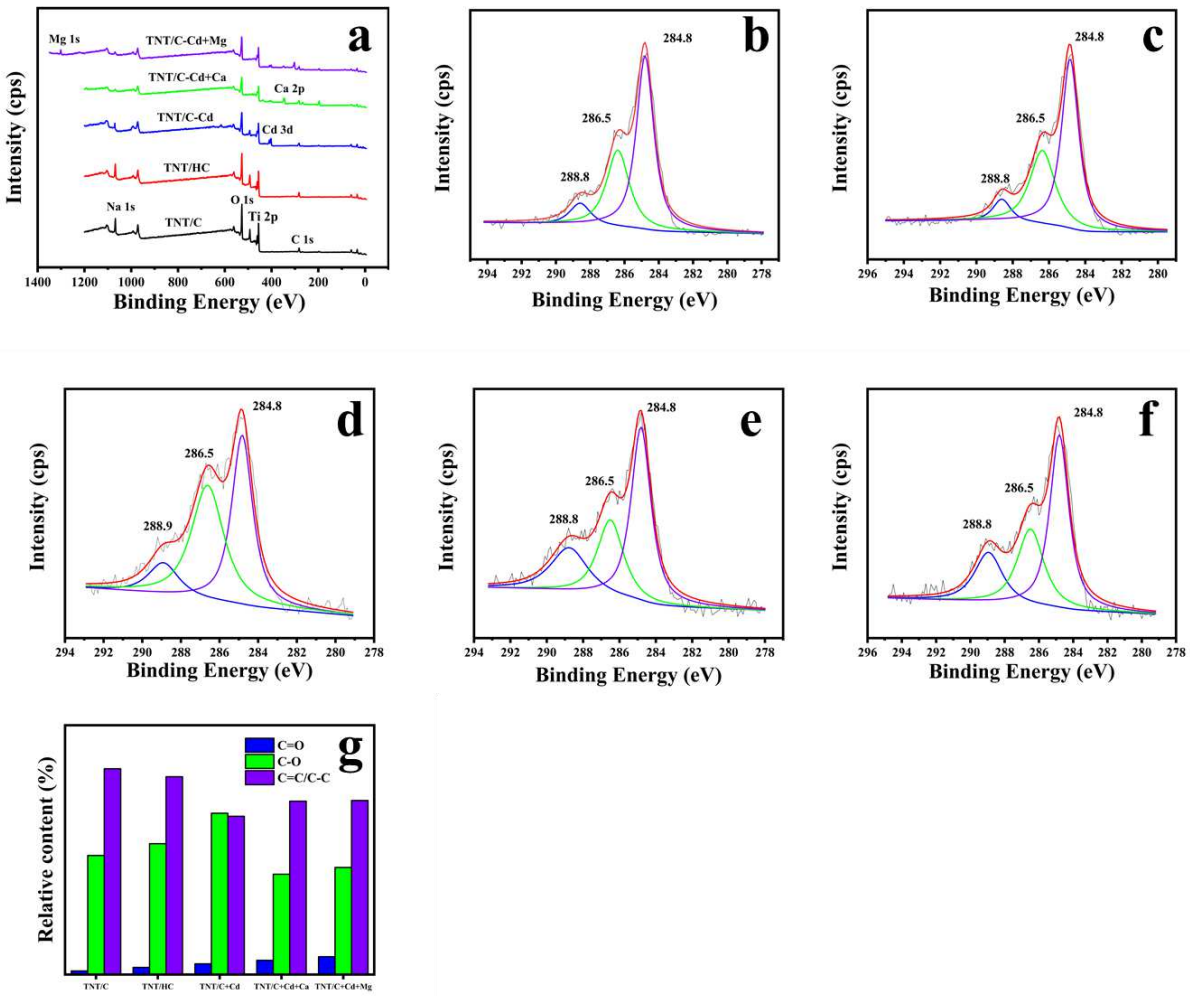


Fig. 8. The adsorption capacity of Cd^{2+} on TNTs, TNTs/C and TNTs/HC with or without the presence of Ca^{2+}(a) or Mg^{2+}(b).

3.6 Mechanisms of competitive adsorption

In order to reveal the competitive adsorption mechanism of TNT based adsorbents to metal ions, we tested the XPS spectra of adsorbents before and after adsorption. The experimental results are shown in the figure 9. In the wide-scan spectrum, after the adsorption of Cd^{2+}, Ca^{2+}, and Mg^{2+}, the peaks of sodium ions almost disappeared, and Cd^{2+}, Ca^{2+}, and Mg^{2+} peaks appeared, which indicates that the adsorption of Cd^{2+}, Ca^{2+}, and Mg^{2+} are achieved (Huang et al. 2020b). This reveals that the main adsorption mechanism is the sodium ion exchange with metal ions in the TNT layers. In the narrow sweep of C 1s, the peaks at 284.8, 286.5, and 288.8 eV represent C=C/C-C, C-O, and C=O, respectively (Yang et al. 2020). After the adsorption of Cd^{2+}, the C=C/C-C peak decreased (from 57.79% to 44.45%). This indicates that the cadmium ion-*p* effect supports the loading of Cd^{2+} on C. In the Cd^{2+}+Ca^{2+} and Cd^{2+}+Mg^{2+} systems, the C=C and C-O peak decreases after adsorption (Yuan et al. 2020). This can be explained by the theory of hard and soft acids and bases: $Ca^{2+}$and Mg^{2+} belong to the ranks of hard acids and C-O belongs to hard base, while Cd^{2+} is classified as soft acid. it is caused by the complexation of C-O to Ca^{2+} and Mg^{2+}, while C-O is not interested in Cd^{2+}. This is why the adsorption capacity of TNT/C is greater than that of neat TNT. And the experimental data shows that there is Ca^{2+} or Mg^{2+} in the water, the order of Cd^{2+} adsorption is TNT/HC>TNT/C>TNT, which is consistent with the order of C-O content.



405

406 Fig. 9. XPS wide-scan spectra (a); C1s XPS spectra off TNT/C(b), TNT/HC(c),
407 TNT/HC-Cd(d), TNT/C-Cd +Ca(e) and TNT/C-Cd +Mg(f); (g) the content of carbon-
408 containing functional groups in the adsorbent before and after adsorption.

409

410 ## 4.Conclusions

411 We successfully synthesized titanate nanotubes and compounded a layer of carbon
412 on the surface of titanate nanotubes in situ. A series of characterization of the
413 synthesized adsorbent were carried by SEM, TEM and XRD. The characterization
414 results show that the modification of carbon does not affect the formation of titanate
415 nanotubes. Through experiments, we have obtained the optimal pH value for Cd^{2+}
416 adsorption by TNT and TNT/C which is pH=6; the pseudo-second-order kinetic model

and Langmuir isotherm adsorption model are more suitable for the adsorption process, which means chemical adsorption and single-layer adsorption occurs during the adsorption of Cd^{2+} on TNT and TNT/C. However, the fact that Ca^{2+} and Mg^{2+} inhibit the adsorption of Cd^{2+} on titanate nanotubes is well known. We set out to solve this problem by loading a layer of carbon in situ on the surface of TNT and then activating it with strong acid. Experimental results show that this procedure improved the competitive adsorption of Cd^{2+} in the presence of Ca^{2+} or Mg^{2+}. Although the surface loading of a layer of carbon lowers the total adsorption capacity of titanate nanotubes for ions (the order of adsorption capacity is TNT>TNT/C >TNT/HC in the absence of Ca^{2+} or Mg^{2+}), it improves its ability of resist interference from Ca^{2+} and Mg^{2+} (the order of adsorption capacity of Cd^{2+} on different adsorption materials is TNT/HC >TNT/C >TNT in the presence of Ca^{2+} or Mg^{2+}). Although it is not the first time to pay attention to the influence of Ca^{2+} and Mg^{2+} on titanate nanotube adsorbent, as far as we know, this is the first time to try to solve this problem and get a positive response. This paper provides an idea for the research and development of heavy metal ion adsorbents.

Declarations

Ethics approval and consent to participate: Not applicable.

Consent for publication: Not applicable.

Availability of data and materials: All data generated or analysed during this study are included in this published article.

Conflicts of interest: The authors declare no conflict of interest.

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Author Contributions: This research was designed, implemented and written by Mr. Mingda Wu; the research was supervised by Ms. Tao Zhou. Mr. Yi Ma and Zhengsong Weng performed statistical analysis, Professor Linghong Lu provided laboratory support.

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