Accepted Manuscript

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PII: S0269-7491(18)32684-8

DOI: <https://doi.org/10.1016/j.envpol.2019.02.040>

Reference: ENPO 12209

To appear in: *Environmental Pollution*

Received Date: 14 June 2018

Revised Date: 15 November 2018

Accepted Date: 14 February 2019

Please cite this article as: Zhao, M., Wang, S., Wang, H., Qin, P., Yang, D., Sun, Y., Kong, F., Application of sodium titanate nanofibers as constructed wetland fillers for efficient removal of heavy metal ions from wastewater, *Environmental Pollution* (2019), doi: <https://doi.org/10.1016/j.envpol.2019.02.040>.

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Equilibrium adsorption experiment

Proposed adsorption mechanisms

Application of sodium titanate nanofibers as constructed wetland**fillers for efficient removal of heavy metal ions from wastewater**

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Abstract

Constructed wetlands are an environmentally friendly and economically efficient sewage treatment technology, with filler playing an important role in treatment processes. However, traditional wetland fillers (e.g. zeolite) are known to be imperfect because of their low adsorption capacity. In this paper, the adsorbent sodium titanate nano fillers (T3-F) was synthesized as an alternative to traditional filler with sodium titanate nanofibers (T3) as the raw material, epoxy adhesive as the adhesive agent and NH_4HCO_3 as the pore-making agent. The properties of T3-F were characterized by powder X-ray diffraction (XRD), scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX), porosity. The effect of different parameters such as pH, co-existing ions, contact time, initial metal ion concentrations and temperature was investigated for heavy metal adsorption. The results showed that the adsorption of heavy metal by T3-F followed the pseudo-second-order kinetic and Langmuir isotherm models. The maximum adsorption capacities for Cu^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} were about 1.5-1.98 mmol/g, which are 4~5 times that of zeolite, the traditional commonly used filler. Moreover, T3-F could entrap toxic ions irreversibly and maintain structural stability in the adsorption process, which solved the issue of secondary pollution. In the presence of competing ions, the adsorption efficiency for Pb^{2+} was not reduced significantly. Adsorption was strongest at high pH. From the results and characterization, an adsorption mechanism was suggested. This study lays a foundation for the practical application of T3-F as a constructed wetland filler in the future.

Capsule: The filler can effectively adsorb heavy metal ions and permanently trap toxic cations in the fiber.

Keywords: Constructed wetland; Titanate nanofillers; Adsorption; Heavy metal removal

1. Introduction

The problem of water pollution by heavy metal ions is of great concern. Heavy metal ions in water are bioavailable and accumulate through food chains (Suanon et al., 2016; Gao et al., 2013), posing a threat to the aquatic ecosystem and human health. Industries such as electroplating, battery, printed circuit board, and metal surface coating treatment are the main sources of wastewater containing heavy metal ions (Cheng et al., 2012). There are many different heavy metal ions often present in these polluted waters, the most common being Cu^{2+} , Pb^{2+} , Zn^{2+} and Cd^{2+} . Many methods have been used for treating wastewater containing heavy metal ions, such as chemical precipitation, electrolysis and membrane separation method. These methods are efficient for removing heavy metals in most cases. However, chemical precipitation produces large amount of sludge, which requires secondary treatment. In addition, the efficiency in removing heavy metal ions in trace concentration are poor. Electrolysis method has the disadvantages of high energy consumption, complex maintenance and side reactions. Membrane separation method is relatively high-cost and has complicated operation process.

Constructed wetlands are increasingly used to treat wastewater containing heavy metal ions (Liu et al., 2015) due to their environmental friendliness, especially for

non-point source pollution, such as highway runoff (Tromp et al., 2012), river sewage (Gao et al., 2015), municipal sewage (De la Varga et al., 2013). The main mechanisms by which constructed wetlands treat wastewater containing heavy metal ions include physical retention, adsorption and precipitation of filler, and plant adsorption and microbial biosorption processes (Yadav et al., 2010). However, the research on heavy metal ion removal by constructed wetlands has some limitations: (1) More attention has been paid to the role of diverse plants in constructed wetlands (Yeh et al., 2009; Galletti et al., 2010), ignoring the adsorption of filler materials. Actually, the adsorption and accumulation of metal by plants are limited, accounting for only 0.5%~2% of inputs (Galletti et al., 2010). The physical and chemical processes attributed to fillers are considered to be the main ways to treat heavy metals (Vymazal et al., 2016); (2) The fillers examined to date have been limited to soil, gravel, limestone and other traditional natural fillers (Allende et al., 2011) and industrial wastes (Hua et al., 2015). These fillers generally have low adsorption capacities and the heavy metal ions adsorbed by these fillers are easily eluted, resulting in secondary pollution problems (Yadav et al., 2010), which limits the development of constructed wetlands for treatment of wastewater containing heavy metals.

In recent years, the development of advanced materials provides a new possibility for effective removal of heavy metals from sewage by constructed wetlands. Among them, nanomaterials have attracted more and more attention because of their outstanding sorption performance. Studies show that titanate

nanofibers could adsorb heavy metals with a high and irreversible adsorption capacity through ion exchange with cations existing between the layers (Yang et al., 2010; Yang et al., 2008a; Yang et al., 2008b). If this nanomaterial is used as a filler, it could solve the problems of low adsorption capacity of traditional fillers and secondary pollution caused by desorption. However, the high dispersion of nanomaterial has limited the application of titanate nanofibers as fillers in constructed wetlands. Therefore, it is very important to find an appropriate method to best utilize these nanomaterials.

Herein, sodium titanate nano fillers (T3-F) were prepared by a simple method and applied as potential constructed wetland fillers for efficient removal of the heavy metal ions of Cu^{2+} , Pb^{2+} , Zn^{2+} and Cd^{2+} from wastewater. T3-F were formed by adding a certain proportion of sodium titanate nanofibers ($\text{Na}_2\text{Ti}_3\text{O}_7$), epoxy adhesive and NH_4HCO_3 powder, followed by mixing, molding and drying. Epoxy adhesive is semi-solid state at room temperature and solid state at high temperature (110 °C), is applied as the adhesive agent. NH_4HCO_3 is used as the pore-making agent and affects the specific surface area and porosity of the fillers (Chang et al., 2017; Wang et al., 2016). The adsorption performance of T3-F for heavy metal ions was studied by static adsorption experiments, and the adsorption data were fitted by kinetic and isotherm models. The interaction between M^{2+} and adsorbents was investigated. The effects of pH, temperature and some co-existing cations were also studied.

2. Experimental section

2.1. Materials and chemical

All chemical reagents were of analytical grade and used without further purification or treatment. Distilled water was used in all experiments. All glassware and polyvinyl acetate plastic bottles were soaked in 10% HNO₃ solution for 24 h, then washed with distilled water and dried. The standard solutions of Cu²⁺, Pb²⁺, Zn²⁺ and Cd²⁺ were purchased from National Center for analysis and testing of non-ferrous metals and electronic materials (Beijing, China). The stock solution (10 mmol/L) was prepared and stored in polyethylene bottles. Working solutions were prepared by diluting the stock solution. The pH of the working solution was regulated by 0.1 mol/L HNO₃ or NaOH. Epoxy adhesive was purchased from Kunshan Wanzhao Electronic Materials Company Limited (Jiangsu, China) and directly used without purification. Its main ingredients are bisphenol A epoxy resin as the adhesive agent and dicyandianide as the curing agent.

2.2. Preparation of sodium titanate nanofibers and T3-F

Sodium titanate nanofibers (Na₂Ti₃O₇) were synthesized by a reaction between NaOH solution and a titanium compound under hydrothermal conditions (Yang et.al., 2008a). Specifically, a solution of 10.7 g of TiOSO₄ · xH₂O (98%, from Fluka) in 80 mL of water was mixed with 200 mL of 15 M NaOH solution. The mixture was then autoclaved at 473 K for 2 days (hydrothermal reaction). The solid in the autoclaved mixture was recovered and washed with deionized water. After drying at 353 K for 6 h, the white powder product was sodium titanate nanofibers. Then, the fibers were used to synthesize T3-F by the following simple method. A slurry was formed by adding a certain proportion of sodium titanate nanofibers, epoxy adhesive and

NH₄HCO₃ powder. The optimal mass ratio of Na₂Ti₃O₇, epoxy adhesive and NH₄HCO₃ (1:1:0.5) screened out by our previous experiments was used in this study. Finally, the mixture was extruded through mould and dried in a oven at 110 °C for 4 h to ensure that NH₄HCO₃ was decomposed completely.

2.3. Characterization methods of T3-F

Scanning electron microscopy (SEM) images were taken with an JSM-7100F electron microscope. The composition of samples was determined by energy dispersive X-ray spectroscopy (EDX) under the same microscope. XRD pattern of the sample powder was recorded in a Bruker D8 Advance diffractometer equipped with Cu K α radiation and fixed power sources (30 mA and 40 kV). The data were collected over a 2 θ range from 5 to 90° at a scanning rate of 3°/min. The specific surface area and pore size distribution were determined by N₂ adsorption/desorption experiment at 77 K performed on a specific surface area and porosity analyzer (Tristar-3000, Micromeritics Instruments Corporation). Fourier Transform Infrared Spectroscopy (FTIR) spectra of T3-F were analyzed on a nexu-670 spectrometer (Thermal Nicolet Co., USA) from 400 to 4000 cm⁻¹. The sample was mixed with potassium bromide with a mass ratio of 1:10 and pressed into a thin slice for analysis.

2.4. Batch adsorption experiments

The adsorption behavior of heavy metal ions by T3-F was studied by batch experiments. The adsorption process was initiated by adding 30 mg of T3-F into 100 mL of heavy metal ion solution in a conical flask. Then, the flask was placed into a water bath constant temperature oscillator (SHZ-82) at a preset temperature and a

speed of 200 rpm. After adsorption, the mixture was filtrated and the filtrate was collected for determining the concentration of heavy metal ions, which was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin Elmer optima 8000). The effects of important parameters such as pH (from 2.0 to 6.0), co-existing ions (Na^+ , Ca^{2+} , Mg^{2+}), temperature (5, 15, 25 °C), contact time and initial concentration of heavy metal ions (from 0.3 to 1.5 mmol/L) were studied. All the experiments were duplicated. The maximum deviation of the experimental data was less than $\pm 5\%$. The adsorption capacity q_t (mg/g) at time t (min) and the adsorption capacity q_e (mg/g) at equilibrium were calculated as follows:

$$q_t = \frac{(C_o - C_t)V}{m} \quad (1)$$

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

where C_o (mg/L), C_t (mg/L) and C_e (mg/L) are the initial concentration, concentration at time t and concentration at equilibrium, respectively, V (mL) is the solution volume of heavy metal ion and m (mg) is the total mass of T3-F added.

2.5. Desorption efficiency

Desorption experiments were carried out in aqueous solutions with different pH. Before desorption experiments, the T3-F with heavy metal ions were obtained by adding 30 mg of T3-F into 100 mL of heavy metal ion (1.5 mmol/L) solution. Then, T3-F with heavy metal ions were filtrated out, and then added into 100 mL of the acid solution with different pH (4, 5, 6, 7) for desorption. The mixture was oscillated at 200 rpm for 24 h at 25 °C. T3-F were filtrated out from the solution by 0.45 μm filter

membrane and the amount of heavy metal ions desorbed into solution was monitored by ICP-OES.

3. Result and discussion

3.1. Physical characterization of T3-F

Scheme. 1 shows the synthesis and adsorption process of T3-F. In the preparation process, the main components react to form polymer material, which was crosslinked with nanofibers (Scheme. 1a). NH_4HCO_3 was used as the pore forming agent. After moulding and drying, hemispheric T3-F with a diameter of about 17 mm were formed (Scheme. 1b). The SEM image of T3-F is showed in Fig. S1a. The fiber morphology still existed and the fibers oriented randomly, indicating that mixing and drying had little effect on the fiber morphology. Moreover, fibers were bonded together under the action of epoxy adhesive. The specific surface area of T3 and T3-F were about 20 m^2/g and 2.48 m^2/g . The reason for the decrease of surface area was caused by the introduction of epoxy adhesive. The porosity of T3-F was about 42%. High porosity can improve the hydraulic and mechanical properties of filters and provide more space for microorganism adhesion, enhancing the pollutant removal capacity of the system (Lu et al., 2016). The structure stability of T3-F during adsorption process was presented in Scheme.1c, d. After adsorption of 36 h in an oscillator at a speed of 200 rpm, T3-F still remained the hemispherical structure and the aqueous solution was clean. Furthermore, we checked titanium content in solution experimentally by ICP-OES. The results showed that concentration of titanium was below the detection limit. Therefore, the structure stability could avoid the loss of adsorbents in practical

use and T3-F were appropriate to be used as fillers in constructed wetlands.

The FT-IR spectra of $\text{Na}_2\text{Ti}_3\text{O}_7$ and T3-F are shown in Fig. S2. For $\text{Na}_2\text{Ti}_3\text{O}_7$, the absorption peaks at 3133cm^{-1} and 1632cm^{-1} corresponded to the stretching vibration of O-H and the bending vibration of H-O-H. The absorption peaks at 907cm^{-1} and 472cm^{-1} were caused by Ti-O stretching vibration (Xiong et al., 2011) and symmetric vibration of TiO_6 (octahedron) bond (Chen et al., 2010; Zhu et al., 2018). Compared with $\text{Na}_2\text{Ti}_3\text{O}_7$, the apparent additional peaks of T3-F at 2188cm^{-1} and 1508cm^{-1} corresponded to $\text{C}\equiv\text{N}$ bond and stretching vibration of benzene ring skeleton, indicating the epoxy adhesive was successfully introduced. In addition, we found that there was no absorption peak corresponding to N-H, which was located at 3411cm^{-1} (Yang et al., 2018) (the N-H bond in the curing agent was disappeared after the curing reaction represented in the supplementary material). This phenomenon suggested that NH_4HCO_3 was completely decomposed in the heating process. The result was consistent with the yield results (77.0%).

3.2. Effect of pH, co-existing on adsorption

Solution pH is an important factor influencing heavy metal ion adsorption (Li et al., 2011). Fig. 1a shows the effect of pH on adsorption of heavy metal ions by T3-F. For Cu^{2+} , Pb^{2+} , Zn^{2+} and Cd^{2+} , the adsorption capacity increased with the increase of pH from 2 to 6. When the pH was 2, the adsorption capacity was the lowest due to the fact that H^+ ions would compete with heavy metal ions for adsorption sites (Yang et al., 2011) and the protonation of the adsorbent surface. A sharp increase of adsorption capacity was observed because of the decrease of H^+ ions and the deprotonation

effect.

Some inorganic ions are usually present in actual wastewater samples and they might interfere with heavy metal ion adsorption. Therefore, the effects of common co-existing cations (Na^+ , Mg^{2+} and Ca^{2+}) on Pb^{2+} uptake were investigated separately. As Fig. 1b shows, all co-existing ions show a little effect on Pb^{2+} adsorption. When the concentration of Na^+ increased from 0 to 50 mmol/L (50 times as high as Pb^{2+}), the Pb^{2+} uptake decreased slightly from 237.33 to 214.28 mg/g (by 9.7%). The presence of 50 mmol/L of bivalent Mg^{2+} and Ca^{2+} ions reduced Pb^{2+} uptake by 13% and 14.2%, respectively. Compared with Na^+ , Mg^{2+} and Ca^{2+} , Pb^{2+} has a lower hydration energy and is a softer Lewis acid. According to the size exclusion effect and the Pearson's hard soft-acid base principle, T3-F show high affinity and selectivity toward Pb^{2+} (Liu et al., 2014).

3.3. Effect of contact time and adsorption kinetics

Fig. 2 displays the effect of contact time on heavy metal ion adsorption at two different initial concentrations. Four types of heavy metal ions had the similar trend with the extension of time at two concentrations. The adsorbed amount of heavy metal ions increased dramatically in the first 2 h and gradually reached equilibrium. It also can be seen from Fig. 2 that the adsorption capacity increases with the increase of initial concentration, which would provide higher potential for the migration of heavy metal ions from the aqueous solution to T3-F.

In order to better understand the adsorption process, the adsorption data as a function of time were analyzed using pseudo-first order and pseudo-second order

kinetic models.

The pseudo-first order equation is based on the solid capacity (Di Bitonto et al., 2017) and expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

where q_t (mg/g) and q_e (mg/g) are the adsorption capacities at time t and at equilibrium, respectively, k_1 (1/min) is the pseudo-first order rate constants. The linear relationship between $\ln(q_e - q_t)$ and t can determine k_1 and the correlation coefficient (r^2).

The pseudo-second order model (Eq.(4)) predicts the behavior of the entire adsorption range, which is consistent with the rate controlling step of the chemical adsorption mechanism (Ho and McKay, 1999). It is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where k_2 (g/min/mg) is the pseudo-second order rate constant and h can be defined as initial specific adsorption rate, $h = k_2 \cdot q_e^2$. q_e , h and r^2 can be identified from the linear relationship between t/q_t and t .

Kinetic parameters calculated through two models are listed in Table 1. The values of R^2 calculated by pseudo-second order are higher than that by pseudo-first order model, suggesting that the adsorption was controlled by chemical adsorption (Ho and McKay, 1999). Moreover, lower k_2 values for adsorption of heavy metal ions suggested the slower kinetics (Liu et al., 2014).

3.4. Adsorption isotherms and thermodynamics

Adsorption isotherm shows the relationship between metal equilibrium concentration

in solution and the amount of metal adsorbed on a specific adsorbent under the condition of constant temperature (Rahman and Islam, 2009) and plays a vital role in optimizing the use of adsorbent. It can reveal the adsorption capacity of adsorbent and the interaction between adsorbent and adsorbate. Fig. 3 shows the adsorption isotherms of Cu^{2+} , Pb^{2+} , Zn^{2+} and Cd^{2+} at different temperatures. It can be seen that the adsorption capacity of heavy metal ions gradually increased and tended to be stable with the increase of the initial concentration from 0.3 mmol/L to 2 mmol/L. In the case of low concentration, heavy metal ions were absorbed by specific adsorption sites, while with the increase of heavy metal ions concentration, the specific adsorption sites were saturated and exchangeable sites were filled (Rahman and Islam, 2009). Moreover, the adsorption capacity increased with the increase of temperature and the experimental maximum saturation capacities of T3-F for Cu^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} were 103.07, 411, 101.7 and 181 mg/g at 25 °C, respectively. To explore the adsorption properties of T3-F on heavy metals, Langmuir and Freundlich isotherms were applied to explain the adsorption behavior (Tang et al., 2017).

The linear formula of the Langmuir isotherm (Langmuir, 1918) is written as:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m K_L} \quad (5)$$

and the linear formula of Freundlich isotherm (Freundlich, 1906) is expressed as:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (6)$$

where C_e (mg/L) is the aqueous equilibrium concentration of heavy metal ions, q_e (mg/g) is the uptake of heavy metal ions at equilibrium, Q_m (mg/g) is the maximum Langmuir adsorption capacity and K_L (L/mg) is the Langmuir affinity constant related

to free energy of adsorption. The linear plot of C_e/q_e against C_e , allows q_m and K_L and the determination coefficient (R^2) to be determined. K_F ($\text{mg}^{1-1/n} \text{L}^{1/n}/\text{g}$) is the Freundlich capacity constant, and n indicates the adsorption intensity. Based on the Langmuir model, the adsorption strength was evaluated by a dimensionless constant (Ma et al., 2017), which is called separation factor (R_L):

$$R_L = \frac{1}{1 + K_L C_o} \quad (7)$$

where C_o (mg/L) is the initial heavy metal ions concentration. Correspondingly, adsorption can be divided into irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) and unfavorable ($R_L > 1$).

The corresponding fitting parameters of two models are listed in Table 2. Langmuir model gives higher correlation coefficient (R^2) than Freundlich model, indicating that the adsorption is a monolayer coverage. The basic characteristics of Langmuir isotherm can be expressed by the dimensionless constant separation factor (R_L). For Cu^{2+} , the R_L value is within the range of 0.012 and 0.118 ($0 < R_L < 1$), which means that the adsorption process is favorable. For Pb^{2+} , Zn^{2+} and Cd^{2+} , the value of R_L is within the range of 0.00013~0.1383, 0.0033~0.3887 and 0.0103~0.0904, respectively. The R_L values are close to zero, which proves that the adsorption is irreversible (Gupta and Babu, 2009) and the equilibrium concentration of heavy metal ions maintains at a low level. The maximum monolayer adsorption capacity of Cu^{2+} , Pb^{2+} , Zn^{2+} and Cd^{2+} are 104.167, 400, 101, 181.8 mg/g at 25 °C, respectively. Natural zeolite had maximum adsorption capacities of 44.7 mg/g , 261.22 mg/g , 35.88 mg/g and 98.10 mg/g for Cu^{2+} , Pb^{2+} , Zn^{2+} and Cd^{2+} ions, respectively (Andrejkovičová et

al., 2016). And the maximum adsorption capacities of mordenite zeolite for Cu^{2+} , Pb^{2+} and Cd^{2+} were 32 mg/g, 151.11 mg/g and 61.6 mg/g, respectively (Nakamoto et al., 2017). A comparison of adsorption capacity of various adsorbents (Table S1) showed that T3-F had outstanding adsorption capacity for heavy metal ions.

The thermodynamic parameters, such as free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were calculated by Eqs (S1)-(S3) (Shi et al., 2009) and are listed in Table S2. It can be seen that each of ΔG values was negative, indicating that the adsorption process was spontaneous in nature. While with the increase of temperature, the decrease of ΔG values means that the adsorption of heavy metal ions on T3-F is more favorable at higher temperature (Xu et al., 2016). The positive values of enthalpy (ΔH) suggest that the adsorption process is endothermic. The positive entropy (ΔS) also indicates that the adsorption of heavy metal ions on T3-F is a spontaneous chemical adsorption process with high affinity.

3.5. Desorption experiment

The desorption properties of fillers are very important parameters in practical application. In wetlands, solution pH in the actual water is usually at a mild condition. So acid solutions with pH=4, 5, 6, 7 were chosen as desorption agents. Our purpose of desorption experiments was to study whether the adsorbed heavy metal ions in T3-f could be released to the wetland and recontaminate the purified water. The metal-loaded T3-F were eluted by HCl solutions and distilled water as the control (Bitonto et al., 2017; Ma et al., 2017). As Fig. S3 shows, heavy metal ions were not detected in the solution when distilled water was used as the desorption agent,

suggesting that heavy metal ions adsorbed by T3-F could not be desorbed in neutral environment. When pH were 4, 5 and 6, Pb^{2+} and Cd^{2+} could not be desorbed. The desorption rate of Cu^{2+} was about 4% when the pH of the solution was 4, and there was no desorption at other pH. The desorption rate of Zn^{2+} was about 3.76%, 0.86%, 0.47% when pH was 4, 5, 6, respectively. Thus, heavy metal ions adsorbed into T3-F could not be easily desorbed into aqueous solution, which avoided the secondary pollution.

3.6. SEM-EDX and crystal phase

The representative SEM images and EDX spectra of T3-F after adsorption of M^{2+} ions (T3-F_M) were showed in the Fig. 4. The sodium titanate in T3-F maintains fibril morphology after adsorption. EDX mapping analysis of T3-F indicated the presence of C, Si, Ti, Na and O atom (Fig. S1). After adsorption, the content of Na^+ decreased obviously, indicating that ion exchange between Na^+ and heavy metal ions might take place in the adsorption process. Moreover, we found that the molar ratios of released Na^+ ions to adsorbed Cu^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} ions were 1:1.19, 1:1.26, 1:1.21, 1:1.25, respectively. The number of heavy metal ions adsorbed was a little larger than that of Na^+ ions released, suggesting the possible existence of physical adsorption. Overall, adsorption mechanisms involved ion exchange and physical adsorption and ion exchange mechanism played a dominant role in the whole adsorption process.

Fig. 5 showed the XRD analysis of T3-F and T3-F_M. T3-F_M,1 represented T3-F with M^{2+} initial concentration of 0.3 mmol/L, and T3-F_M,2 of 1.5 mmol/L. The peak changes of T3-F_M,1 and T3-F_M,2 were almost the same, indicating that

T3-F adsorbed M^{2+} of different concentrations based on the same principle. The ion exchange between M^{2+} and Na^+ (Fig. 6) induced substantial changes of the crystal structure of T3-F. The interlayer spacing calculated by d_{100} spacing (Fig. 5a,c) decreased from 0.859 to 0.834 nm after adsorption of Cu^{2+} and Zn^{2+} and decreased to 0.817 and 0.828 nm when Na^+ ions were replaced by Pb^{2+} (Fig. 5b) and Cd^{2+} ions (Fig. 5d). In addition, The ion exchange between M^{2+} and Na^+ led to structure deformations, which were confirmed by the serious losses of diffraction intensity of d_{003} . The significant contraction of the interlayer spacing and the structure deformation suggested the strong interactions between M^{2+} and the negatively charged layer of T3-F (Yang et al., 2008b). Thus, T3-F would trap the toxic cation in the fiber steady.

4. Conclusion

Wetland fillers T3-F were synthesized for heavy metal ion removal and showed high adsorption capacity of 103.07, 411, 101.7 and 181 mg/g for Cu^{2+} , Pb^{2+} , Zn^{2+} and Cd^{2+} , respectively, which is superior to the conventional fillers. When pH was increased from 2 to 6, the adsorption capacity increased dramatically due to the decrease of competitive adsorption of H^+ ions and the deprotonation of adsorbent. In the presence of co-existing ions (Na^+ , Ca^{2+} , Mg^{2+}), the adsorption efficiency for Pb^{2+} was not declined significantly. Compared with other fillers, the most important property of T3-F was non-desorption, which could not cause secondary pollution in practical application. Thus, T3-F are suitable for the application of constructed wetland in treating heavy metal wastewater. This study lays a foundation for practical application of nanomaterials as fillers of constructed wetlands.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 41771098, 51473081, 51672143 and 51808303), Taishan Scholars Program, Outstanding Youth of Natural Science in Shandong Province (JQ201713).

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502

Figure captions

Scheme 1. Schematic illustration for the synthesis and adsorption M^{2+} of T3-F.

Fig. 1. (a) Effect of pH on adsorption of four different heavy metal ions. (b) Effect of Na^+ , Ca^{2+} , and Mg^{2+} on the adsorption of Pb^{2+} on T3-F (Experimental conditions: material dosage=0.3 g/L, concentration of co-existing ions=0.01-0.1 mol/L C_0 =1 mmol/L, 298 K, 36 h, 200 rpm).

Fig. 2. Effect of contact time on Cu^{2+} , Pb^{2+} , Zn^{2+} and Cd^{2+} adsorption (Adsorbent dosage=0.3 g/L, pH=5.2 $\pm$ 0.2, 298 K, 200 rpm).

Fig. 3. Equilibrium adsorption isotherms of Cu^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} at different temperatures (Experimental conditions: Adsorbent=30 mg, material dosage=0.3 g/L, C_0 =0.3~2 mmol/L, pH= 5.2 $\pm$ 0.2, 36 h, 200 rpm).

Fig. 4. SEM images and EDX spectra of T3-F after adsorption of M^{2+} ions (T3-F_Cu, T3-F_Pb, T3-F_Zn, T3-F_Cd).

Fig. 5. The XRD patterns of the T3-F before and after adsorption of M^{2+} ions.

Fig. 6. Adsorption mechanism diagram.

FIGURES

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TABLES

Table 1 Kinetic parameters and coefficients of determination (R^2) for adsorption of four different heavy metal ions with two initial concentrations.

Heavy metals	Initial concentration	$q_{e,exp}(mg/g)$	Pseudo-first order			Pseudo-second order			
			$K_1(1/min)$	$q_{e,cal}(mg/g)$	R^2	$K_2(g/min/mg)$	$h(mg/min/g)$	$q_{e,cal}(mg/g)$	R^2
Cu^{2+}	34	67.90	0.0081	23.113	0.9308	0.00100	4.8876	68.498	1.0000
	74	92.55	0.0013	45.550	0.9573	0.00009	0.7986	94.339	0.9944
Pb^{2+}	103	335.85	0.0018	120.550	0.9708	0.00006	7.0423	333.333	0.9990
	260	345.33	0.0020	133.647	0.9769	0.00006	6.5963	344.831	0.9987
Zn^{2+}	37	84.47	0.0013	28.386	0.9516	0.00023	1.5939	83.330	0.9982
	70	92.23	0.0017	40.354	0.9098	0.00019	1.4691	86.960	0.9895
Cd^{2+}	83	225.23	0.0012	103.049	0.8919	0.00005	2.6947	222.220	0.9972
	157	201.77	0.0018	103.409	0.9032	0.00007	2.7137	188.679	0.9862

Table 2 Langmuir and Freundlich constants and the coefficients of determination(r^2) for adsorption of four different heavy metal ions.

Heavy metals	Temperature($^{\circ}\text{C}$)	Langmuir			Freundlich		
		$q_m(\text{mg/g})$	$K_L(\text{L/mg})$	r_L^2	$K_F(\text{mg}^{1-1/n}\text{L}^{1/n}/\text{g})$	n	r_F^2
Cu^{2+}	5	88.49	0.2989	0.9968	54.77	9.91	0.9458
	15	93.46	0.3962	0.9986	59.66	10.36	0.9596
	25	104.17	0.6358	0.9994	76.87	15.11	0.9754
Pb^{2+}	5	344.83	0.1457	0.9959	178.23	8.06	0.9427
	15	384.61	0.1048	0.9805	205.12	9.12	0.5705
	25	400.00	25.0000	0.9989	334.42	26.88	0.686
Zn^{2+}	5	84.75	0.1356	0.9561	19.34	2.99	0.6033
	15	93.46	0.1210	0.9470	19.67	2.85	0.6859
	25	101.01	2.6053	0.9994	82.76	20.75	0.7335
Cd^{2+}	5	156.25	0.4476	0.9986	122.11	21.19	0.8718
	15	169.49	0.4917	0.9984	120.65	14.84	0.6841
	25	181.82	0.4135	0.9991	122.95	12.56	0.9227

Highlights:

- A new constructed wetland fillers was prepared by sodium titanate nanofibers.
- Fillers show excellent adsorption ability towards Cu^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} ions.
- Adsorption occurs through ion exchange mechanism.
- Fillers could entrap toxic ions irreversibly.