*Desalination and Water Treatment*
www.deswater.com

doi: 10.1080/19443994.2015.1098572

57 (2016) 19456–19465
September

Taylor & Francis
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# Hydrated ferric oxide (HFO)-encapsulated tea waste for enhanced lead(II), cadmium(II), and copper(II) removal from waters

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Received 26 March 2015; Accepted 12 September 2015

ABSTRACT

Hydrated ferric oxide (HFO) was impregnated successfully within tea waste by precipitation, and a novel hybrid adsorbent named HFO–TW was prepared. The sorption characteristics of HFO–TW toward Pb(II), Cd(II), and Cu(II) in aqueous solution were investigated. HFO–TW was characterized by X-ray diffraction and Fourier transform infrared analysis. Three heavy metals sorption onto HFO–TW is pH-dependent, and the higher pH value is more helpful for sorption at evaluated pH range. HFO–TW can exhibit strong sorption selectivity toward three metal ions, and the removal efficiencies fall only 21% for Pb(II), 34% for Cd(II), and 10% for Cu(II) in the presence of competing ions Ca(II), Mg(II), and Na(I) at concentration 50 times higher than target metal ions. The maximum sorption capacities calculated by Langmuir equation for Pb(II), Cd(II), and Cu(II) removal onto HFO–TW are 87.84, 26.01, and 22.97 mg/g, respectively. The sorption process of three heavy metals could approach equilibrium within 60 min. Both the sorption capacities and speed of three heavy metals by HFO–TW have improved significantly compared to the host tea waste. The kinetics curves could be fitted well by the pseudo-second model and the related coefficients were all higher than 0.97. In addition, the experiment results of initial concentration influence and column sorption runs further validated that HFO–TW was more appropriate for heavy metals removal of low concentration. All the results indicated that the modification of tea waste by loading HFO was a great promotion for tea waste application toward heavy metals removal.

*Keywords:* Hydrated ferric oxide; Heavy metal; Tea waste; Adsorption; Application

## 1. Introduction

Heavy metal contamination has gradually become a global environmental issue. Heavy metals like Pb(II), Cu(II), Hg(II), Cr(VI), Cd(II), Tl(I), etc. even at an extremely low concentration can cause many toxic effects towards human health, for example, hypertension, headache, abdominal pain, nausea, vomiting, inertness, and development defect [1]. To reduce heavy metals harmfulness toward human health, China government have set the permissible concentration of Pb(II), Cd(II), and Cu(II) in effluent as 1.0, 0.1, and 0.5 mg/L, respectively [2]. In general, heavy metals have been introduced into the environmental media as a result of the rapid increase

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in mining and industrial activities involving toxic metals [3].

In the past decades, many physical, chemical, or biological treatment methods like chemical precipitation [4,5], reverse osmosis and nano-filtration [6,7], solvent extraction [8,9], adsorption [10,11], and biological repair [12] have been developed in response to heavy metals contamination. Among these treatment technologies, adsorption has earned more and more attention due to its flexibility of design and ease of operation as well as the development of many novel sorbents. Recently, many agricultural byproducts have been constantly exploited for pollutants capture [13,14], and some waste materials like walnut shells [15], dry tree leaves [16], rice hulls [3], saw dust [17], and corn cobs [18] have also been developed for toxic metals capture. Several salient advantages such as easy availability, cheapness, and low pollution make these bio-adsorbents become the focus of research. However, a lot of fatal defects like low sorption capacity, slow sorption speed, and poor sorption selectivity have seriously hindered their practical application. In previous research, we selected tea waste as sorbent for heavy metals retention [19], owing to several functional groups such as amine groups, carboxyl, and phenolic hydroxyl fixed on the surface [20]. Usually, these groups can effectively form some stable interactions, for instance, inner-sphere complex formation or ion exchange with heavy metal ions [19,20]. However, the experimental results showed that Pb(II), Cd(II), and Cu(II) sorption capacities were relatively low, sorption process was slow, and the sorption selectivity was also not satisfactory. In order to enhance the practical application feasibility of heavy metals removal onto tea waste, it is necessary to improve its sorption capacity, speed, and selectivity by some modifications.

Hydrous metal oxides like hydrous Fe(III), Mn(IV), Sn(IV), Ti(II), Zr(IV), and Al(III) oxides have always been considered to be efficacious adsorbents for heavy metals retention because of their specific and stronger binding to target metal ion [21–24]. Hydrous ferric oxide (HFO) as the typical one has also attracted many concerns. Unfortunately, it cannot still be used for purifying practical wastewater of heavy metals owing to its fine or ultrafine particles, which can usually cause excessive pressure drop and difficulty of separation when applied in fixed-bed or any flow-through systems directly. To overcome these technical bottlenecks, some researchers had exploited various inorganic–organic hybrid adsorbents by loading HFO particles onto conventional porous materials. But the high cost of supporting materials has prevented the popularization and application of these hybrid adsorbents.

To simultaneously overcome the practical application flaws of tea waste and fine HFO particles for heavy metals removal, we prepared a novel hybrid sorbent by loading hydrous ferric oxide (HFO) within tea waste in the current study. Sorption behaviors of three toxic metal ions, lead, cadmium, and copper from aqueous solutions were investigated by evaluating the influence of solution pH, coexistence of competing ions, temperature, time, initial concentration of target ions and column sorption experiments.

## 2. Material and methods

### 2.1. Reagents

All chemicals used in the present study are of analytical grade or more pure and were purchased from Guoyao Reagent Station (Anhui, China). The stock solutions containing 1 g/L of the target metals were prepared by dissolving their corresponding nitrates in the deionized water.

### 2.2. Preparation of HFO–TW

The supported tea waste of HFO–TW was acquired from tea plants located in Green tea region in Huangshan, China. The pretreatment of host tea waste was reported in our previous research [19]. In brief, the procedures for HFO–TW preparation consist of the following steps: Firstly, 10.0 g tea waste was added into 40 g/L $FeCl_3$ solution and stirred continuously for 24 h. Subsequently, the filtered solid was dried under vacuum at 333 K for 2 h and then was added into binary NaCl–NaOH solution of concentration at around 7%, afterward, the solution was stirred continuously for 24 h. Finally, the obtained hybrid materials were washed with 0.001 M HCl and deionized water till the neutral pH, followed by desiccation under vacuum at 333 K until reaching a constant weight. The prepared HFO–TW was stored in sealed glass bottles for the following experiments.

### 2.3. Batch sorption experiments

20.0 mg of HFO–TW was added into 100-mL polyethylene Erlenmeyer flasks including 50 ml solution of the given concentration of target metals. A 1.0 M $HNO_3$ or NaOH solution was used to adjust the solution pH during the experiment when desired. Detailed parameters of the experiment systems are depicted in the corresponding figure captions. The flasks were then put into a Model G-25 incubator shaker with thermostat and vibrated at 180 rpm for 24 h at a desired temperature. The time was proved to be sufficient for ensuring apparent sorption equilibrium according to preliminary kinetic tests. For the kinetic experiment, 500 mL solution containing target metal ions was added into flask and a 0.5-mL aliquot was sampled at various time intervals, e.g. every 5 min for 0–30 min, every 10 min for 30–150 min, every 20 min for 150–210 min, and every 30 min for 210–240 min. The sample was then filtered to remove any fine sorbent particles and determined for the metal ion content. Removal of target metals was calculated with the mass balance before and after the sorption.

### 2.4. Fixed-bed column sorption

Column experiments were conducted using a polyethylene column (12 mm diameter and130 mm length) equipped with a water bath to maintain a constant temperature. A 5-mL aliquot of wet HFO–TW particles was filled into the column prior to operation. A constant flow rate was ensured by A Lange-580 pump (Baoding, China). The hydrodynamic parameters, i.e. a superficial liquid velocity (SLV) and an empty bed contact time (EBCT), were depicted in the caption of related figure.

### 2.5. Analyses

Concentrations of all the metal ions in aqueous solution were usually determined using atomic absorption spectroscope (Beijing Puxi Co. China), and the absorbance of the samples was read in triplicates. When the metal content was lower than 1 mg/L, it was determined by atomic fluorescence spectrophotometer with an online reducing unit (AF-640, China) containing $NaBH_4$ and HCl solution. The amount of encapsulated HFO within tea waste was determined by analyzing Fe content after digesting HFO–TW particles in $HNO_3$ solution. Fourier transform infrared (FT-IR) spectra of HFO–TW before and after metals sorption were obtained using a Nicolet 380 FT-IR spectrometer (USA) with a pellet of powered potassium bromide and adsorbent in the range 400–4,000 $cm^{-1}$. Speciation of HFO–TW was conducted by X-ray diffraction (XRD) analysis with a step size of 0.02° (D8 ADVANCE, Germany). The surface morphology of two sorbents was observed using a scanning electron microscope (S-3400N, Japan). $N_2$ adsorption–desorption test onto HFO–TW particles was conducted at 77 K to obtain specific surface area based on BET model and pore volume and pore size distribution based on BJH model using Micromeritics ASAP2020 (USA).

## 3. Results and discussion

### 3.1. Characterization of HFO–TW particles

HFO amount loaded within tea waste was 5.25 (w/w)% in Fe mass by determining the digestion solution, while there was no Fe existing in the original tea waste according to the controlled trial. This result indicated that HFO was capsulated within tea waste successfully. Moreover, the sorption band of 890 $cm^{-1}$ on FT-IR spectra of HFO–TW (Fig. 1) demonstrated that Fe–OH group presented in the surface of HFO–TW [25], which further indicated the successful loading of HFO particles. Fig. S1 describes the XRD pattern of the HFO–TW beads. As depicted, some diffraction peaks existed in the pattern, which implied that the most loaded HFO is amorphous in nature. SEM images of supported tea waste and HFO–TW are shown in Fig. 2. It could be discovered that a lot of wide pores existed in the surface of tea waste. However, the pores became dense and tiny for HFO–TW because of HFO particles loading. BET specific surface area and average pore diameter of the tested HFO–TW are around 1.21 $m^2/g$ and 2.74 nm, respectively, which is little different compared to the host tea waste, whose BET specific surface area is 0.86 $m^2/g$ and average pore diameter is 3.62 nm [19]. The higher BET specific surface area of HFO–TW was caused by the fine particles of HFO which possess larger surface areas than bulk tea waste, while the smaller average pore diameter resulted from the pore blockage because of the HFO impregnation.

### 3.2. Effect of solution pH

As an important environmental variable, solution pH can usually influence the sorption process through playing a role in the solubility of the target metal ions

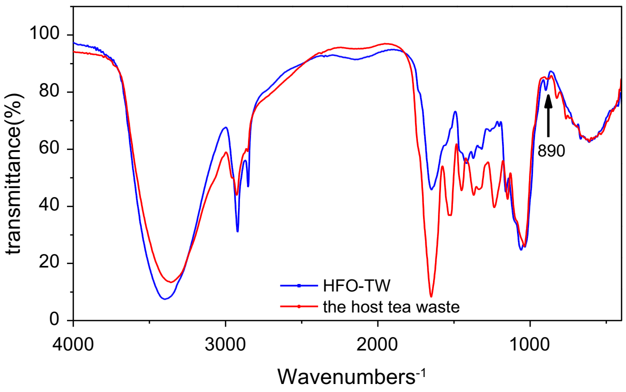
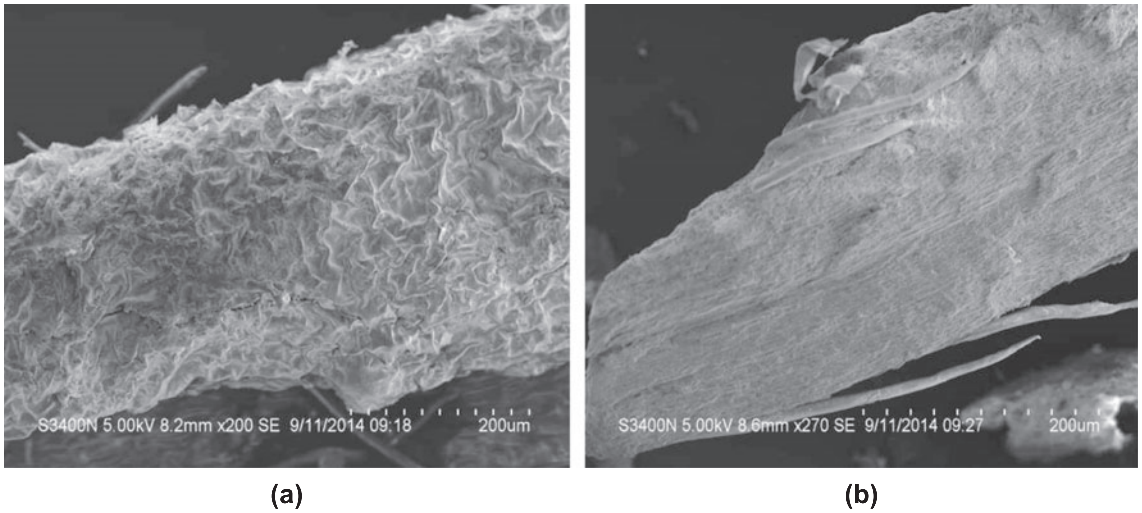


Fig. 1. FT-IR spectra of HFO–TW and the host tea waste.



(a)

(b)

Fig. 2. SEM images of the supporting tea waste and HFO–TW used in the present study: (a) tea waste and (b) HFO–TW.

and physicochemical properties of the surface functional groups of sorbent. Thus, the effect of solution pH vs. retention of Pb(II), Cd(II), and Cu(II) ions by HFO–TW was conducted, and the curves are exhibited in Fig. 3. As depicted, the more preferable sorption of three heavy metals onto HFO–TW has appeared in high solution pH range, and they were almost in linear relationship in the tested pH range 2–6.5. The results were similar to several heavy metals sorption onto other bio-adsorbents [3,16]. The pH-dependent mechanism could be reasonably interpreted by the ion-exchange process between target metal ions and HFO–TW. Specifically, for the host tea waste, the $H^+$-motivated ion-exchange mechanism between the surface carboxyl or phenolic hydroxyl groups and the heavy metal ions could contribute to above-mentioned phenomenon, which had been illustrated detailed in our previous research [19]. For loaded HFO, the surface hydroxyl groups can also capture heavy metal ions by forming inner-sphere complexes as [26,27].

$$-\text{Fe–OH}^{-} + \text{M}^{2+} \rightleftarrows -\text{Fe–O–M}^{+} + \text{H}^{+} \tag{1}$$

$$-\text{Fe–(OH)}_2^{-} + \text{M}^{2+} \rightleftarrows -\text{Fe–O–M} + 2\text{H}^{+} \tag{2}$$

Obviously, higher pH values are more helpful for heavy metals uptake by loaded HFO, which follows a same trend to the host tea waste only driven by a simple ion-exchange formation. The inner-sphere complexes of Fe–OH and heavy metal ions have been further confirmed by FT-IR spectroscopy depicted in Fig. S2 [25]. All the above mechanisms together lead to the pH-dependent results presented in Fig. 3. Besides, the Fe outflow from HFO–TW vs. solution pH is also depicted in Fig. 3. As shown, most Fe leached when solution pH was lower than 2, but little Fe leached when solution pH was higher than 2. This result verified that HFO–TW is stably applied in faintly acidic conditions.

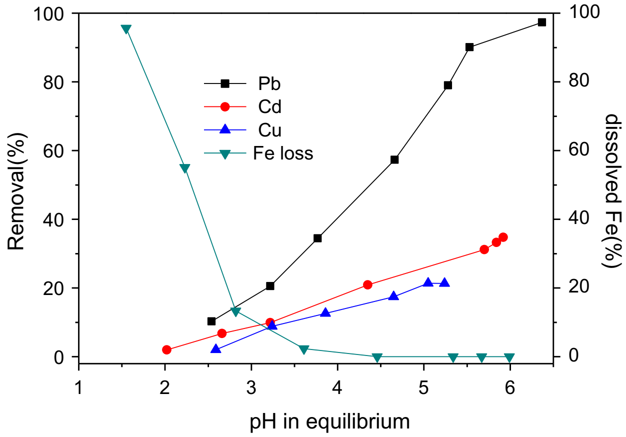


Fig. 3. Effect of pH value on the removal of heavy metal ions onto HFO–TW and Fe outflow from HFO–TW at 298 K (0.02 g HFO–TW was added into 50 mL solution with 30 mg/L of target metal).

### 3.3. *Effect of competing ions on sorption*

Generally, some alkali and alkaline-earth metal ions, for instance, Ca(II), Mg(II), Na(I), or K(I), which have similar physicochemical properties with target metal ions coexist with heavy metal ions in natural waters and industrial effluents at much higher levels.

The presence of these co-ions will be without doubt a great challenge for given sorbent to selectively capture target metal ion from practical wastewaters because of their strong competition toward the binding sites of sorbent. Thus, it is significantly important to evaluate the sorption selectivity of the given sorbent for practical application goals. In the current study, several typical cations like Ca(II), Mg(II), and Na(I) were selected as co-ions and their influence on the retention of Pb(II), Cd(II), and Cu(II) onto HFO–TW is illustrated in Fig. 4. The results showed that the added co-ions lead to varying degrees of decrease in retention of three heavy metals onto HFO–TW, but HFO–TW showed satisfactory sorption selectivity towards target metal. For example, increasing Ca(II) from 0 to 50 times of target metal ion only caused a removal efficiency drop of 21% for Pb(II), 34% for Cd(II), and 10% for Cu(II), respectively. The preferable sorption of HFO–TW mainly resulted from the encapsulated HFO within tea waste, which was proved to possess excellent sorption selectivity towards heavy metals in previous research [28,29]. Certainly, the Donnan membrane effect [29] which was caused by the non-diffusible functional groups of the host tea waste is also helpful for improving the sorption selectivity. Moreover, it is noteworthy that the competitive capability in the order of Ca(II) > Mg(II) > Na(I) mainly resulted from their different electric charges and Gibbs free energies of hydration. It is easy to understand that Ca(II) and Mg(II), divalent cations, have greater ion exchangeable capability than monovalent Na(I). The Gibbs free energies of hydration can usually act as an indicator of ion exchangeable capability, and the same valence cations possessing lower Gibbs free energies of hydration are generally more favorable for ion exchange among [30]. According to the professional reference, the Gibbs free energies of hydration of Ca(II) and Mg(II) are −1,656, −2,049 kJ/mol, respectively [31], indicating that competitive capability of two ions onto heavy metals sorption should follow the sequence Ca(II) > Mg(II).

To quantify the sorption selectivity of three metals onto HFO–TW, the distribution coefficient $K_d$ (L/g) was also introduced [32]:

$$K_d = \frac{C_o - C_e}{C_e} \times \frac{V}{m} \tag{3}$$

where $C_o$ (mg/L) is the initial heavy metal ion content of the solute, $C_e$ is the heavy metal ion concentration in the solution (mmol/L), $V$ (mL) is the volume of the solution, and $m$ (g) is the mass of the adsorbent. The $K_d$ values of three heavy metals sorption by HFO–TW

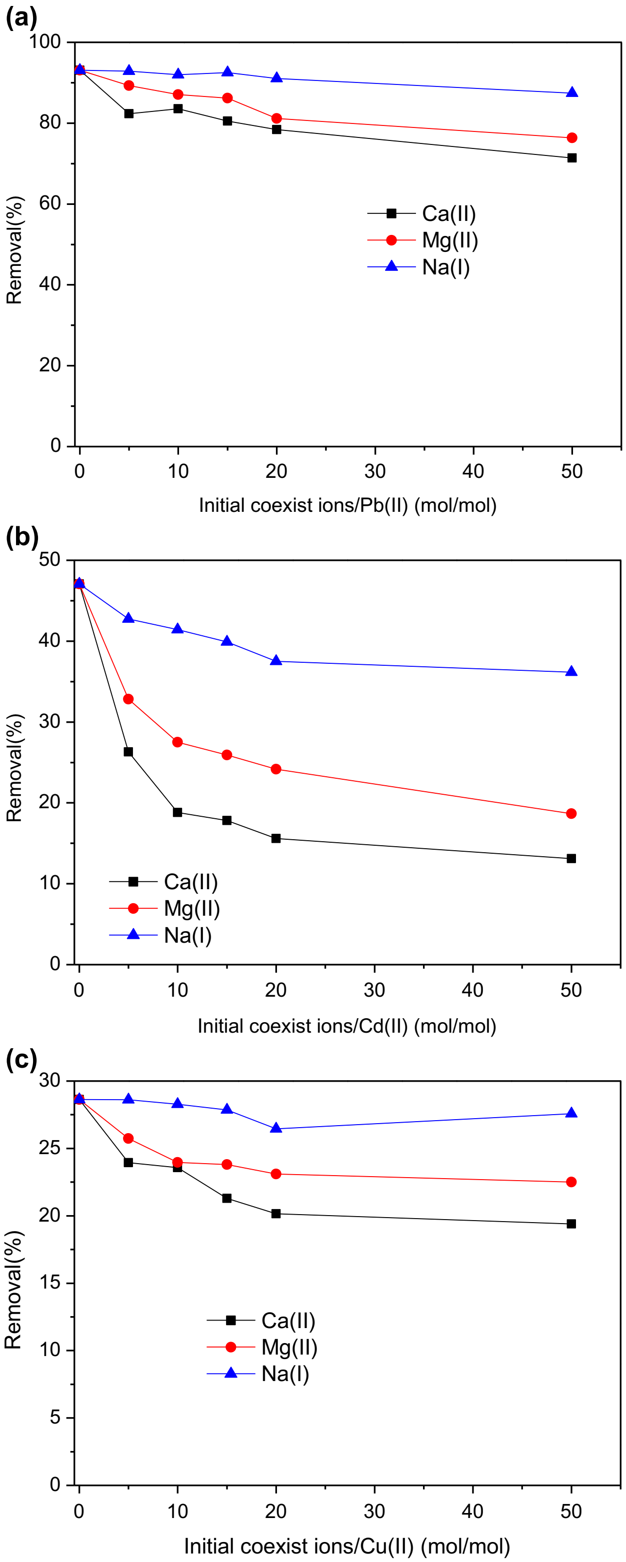


Fig. 4. Effect of competing ions Ca(II), Mg(II), Na(I) on the removal of (a) Pb(II), (b) Cd(II), and (c) Cu(II) onto HFO-TW at 298 K (pH 5.5 ± 0.2).

in the presence of different levels co-ions is illustrated in Fig. S3. As shown, the change in $K_d$ values was consistent with the results of Fig. 4. The high sorption selectivity of HFO–TW towards heavy metals implied that HFO–TW possesses wide application potential toward the practical heavy metal contaminated waters.

### 3.4. Sorption isotherms

Sorption isotherm experiments of Pb(II), Cd(II), and Cu(II) uptake by HFO–TW were conducted at 308 K, and the plots are illustrated in Fig. 5. In addition, the Langmuir and Freundlich models were introduced to fit the sorption isotherm of three heavy metal ions:

$$q_e = \frac{K_L q_m C_e}{K_L C_e + 1} \tag{4}$$

$$q_e = K_F C_e^{\frac{1}{n}} \tag{5}$$

where $C_e$ is the heavy metal concentration at equilibrium (mg/L), $q_e$ is the equilibrium sorption capacity (mg/g), $q_m$ is the maximal sorption capacity (mg/g), $K_L$ (L/mg) is a binding constant, and both of $K_F$ and n are the Freundlich constants. The fitted parameters are listed in Table 1, and the results implied that Pb(II) sorption process can be represented more appropriately by the Langmuir model than the Freundlich one, while it was opposite for Cd(II) and Cu(II) removal. The fitting results indicated that the effective binding sites on HFO–TW surface are heterogeneous for Cd(II) and Cu(II) sorption. The calculated $q_m$ values for Pb (II) and Cd(II) (87.84 mg/g for Pb(II), 26.01 mg/g for Cd(II)) based on the Langmuir model had great increase compared to the host tea waste (29.30 mg/g for Pb(II), 15.51 mg/g for Cd(II)), while that for Cu(II) sorption was also a little increase. In present study, the sorption capacities of Pb(II), Cd(II), and Cu(II) onto HFO–TW, the host tea waste, and several other bio-sorbents had been summarized, and the corresponding data are shown in Table 2. As illustrated, the sorption capacities of Pb(II), Cd(II), and Cu(II) onto HFO–TW were much greater than the host tea waste and other listed bio-sorbents, which indicated that the modification was a feasible pathway to improve the sorption capacities and practical application potential of biomass.

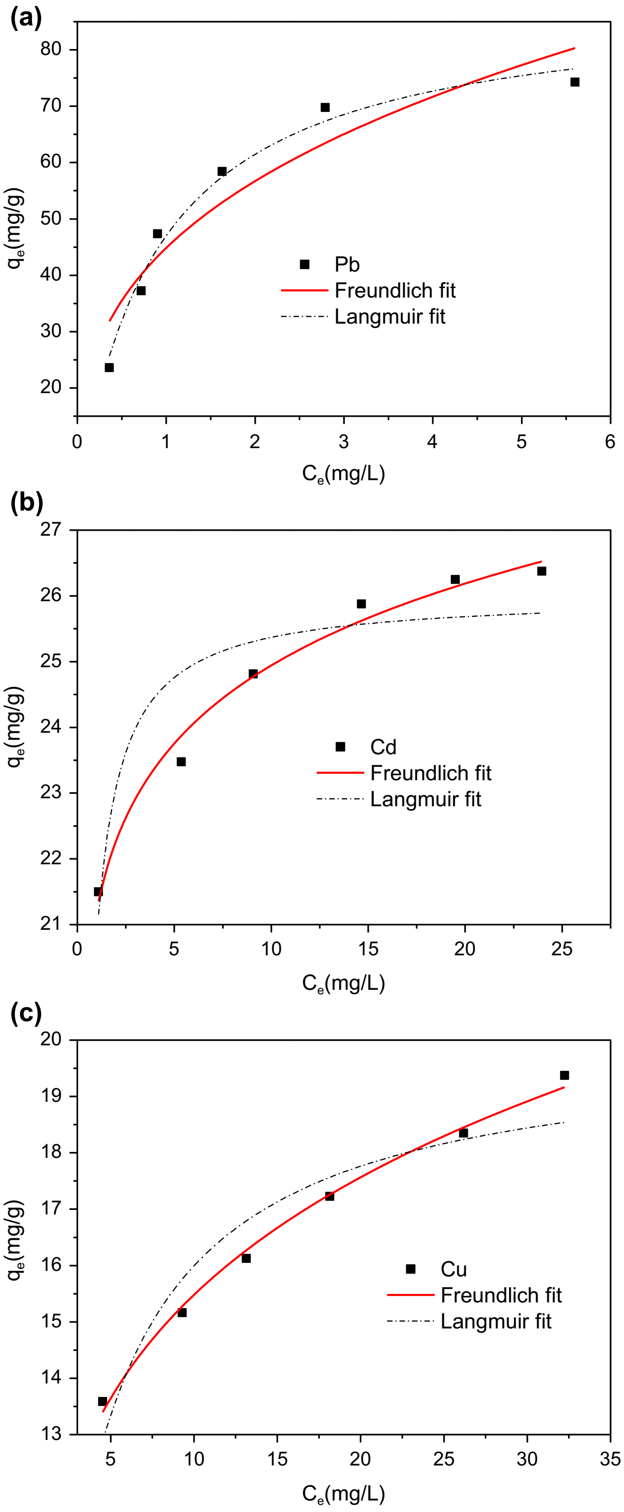


Fig. 5. Adsorption isotherms of (a) Pb(II), (b) Cd(II), and (c) Cu(II) onto HFO–TW at 308 K (pH 5.5 ± 0.2).

Another noteworthy conclusion drawn from Table 1 was that the sorption capacities of three heavy metals onto HFO–TW followed the sequence Pb(II) > Cd(II) > Cu(II). This conclusion could also be further confirmed by the competitive sorption experiment results in Fig. 4. The sorption capacity sequence was

Table 1
Isotherm parameters for three heavy metals uptake onto HFO–TW at 308 K

| | Freundlich model | | | Langmuir model | | |
|---|---|---|---|---|---|---|
| Heavy metals | $K_F$ (mg$^{1-n}$ L$^n$/g) | $n$ | $R^2$ | $K_L$ (L/mg) | $q_m$ (mg/g) | $R^2$ |
| Pb(II) | 44.87 | 0.34 | 0.869 | 1.12 | 87.84 | 0.984 |
| Cd(II) | 21.21 | 0.07 | 0.981 | 3.96 | 26.01 | 0.792 |
| Cu(II) | 10.17 | 0.18 | 0.993 | 0.40 | 22.97 | 0.883 |

mainly caused by the different Gibbs free energies of hydration of three metals. According to the professional reference, the Gibbs free energies of hydration of Pb(II), Cd(II), and Cu(II) are −1,504, −1,708, and −2,030 kJ/mol, respectively [31], which indicated that the binding of three ions onto HFO–TW should follow the sequence Pb(II) > Cd(II) > Cu(II), and it is also coherent with the observed experimental results.

### 3.5. Sorption kinetic

The adsorption rate is a crucial indicator to evaluate practical applicability of a given adsorbent because of its decisive role on initial investment such as the quantity and volume of adsorption devices. In the present study, the lead, cadmium, and copper removal onto HFO–TW vs. contact time were evaluated and the results are presented in Fig. 6. As depicted, the sorption speed was very quick for three heavy metals retention by HFO–TW. In detail, initial sorption from 0 to 30 min was faster, followed by a relatively slow sorption until approaching equilibrium within 60 min, noting that the sorption speed of three metals onto HFO–TW had improved significantly compared to the host tea waste. This probably resulted from the loaded HFO particles which usually have a very quick sorption speed toward heavy metals. Both the pseudo-first-order model and the pseudo-second-order model were provided to represent the kinetic data of three toxic metals:

$$q_t = (1 - 10^{-\frac{k_1}{2.303}t})q_e \tag{6}$$

$$q_t = \frac{k_2 q_e^2 t}{t k_2 q_e + 1} \tag{7}$$

where $q_e$ and $q_t$ are sorption capacities of heavy metal (mg/g) at equilibrium and at time $t$, respectively, $k_1$ and $k_2$ are the first-order and second-order sorption rate constants. The fitting parameters are shown in Table 3, and the higher correlation coefficients ($R^2$) for pseudo-second-order model implied that the sorption of Pb(II), Cd(II), and Cu(II) onto HFO–TW can be fitted more appropriately by this model. However, the calculated $q_e$ values based on pseudo-first-order model (63.40 mg/g for Pb(II), 25.92 mg/g for Cd(II),

Table 2
A comparison of the sorption capacities for HFO–TW, the host tea waste and several other biomass

| Sorbent | Pb(II) sorption capacity (mg/g) | Cd(II) sorption capacity (mg/g) | Cu(II) sorption capacity (mg/g) | Refs. |
|---|---|---|---|---|
| HFO–TW | 87.84 | 26.01 | 22.97 | Present study |
| The host tea waste | 33.49 | 16.87 | 21.02 | [19] |
| Wheat bran | 64 | – | 15 | [33] |
| Date leaves | 58.83 | | | [34] |
| Saw dust | 15.90 | 5.76 | 8.06 | [35] |
| Wheat straw | 3.11 | 9.96 | 4.48 | [18] |
| Soybean straw | 6.83 | 2.02 | 5.44 | [18] |
| Corn stalk | 6.00 | 5.15 | 3.78 | [18] |
| Corn cob | 3.93 | 10.75 | 2.18 | [18] |
| Oat straw | 18.84 | 4.70 | 5.18 | [18] |
| Fir sawdust | – | 0.56 | 2.18 | [18] |
| Poplar sawdust | – | 0.45 | 2.30 | [18] |
| Grape stalk waste | 49.89 | 27.78 | – | [18] |
| Kraft lignin | – | 4.26 | 2.62 | [18] |

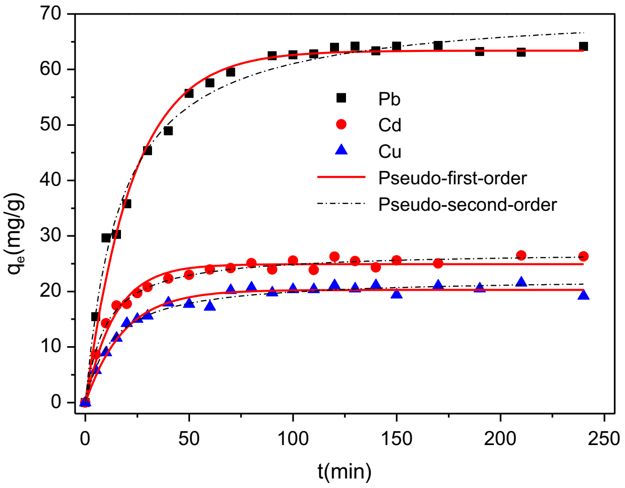


Fig. 6. Kinetics curves of heavy metal ions sorption onto HFO–TW at 298 K (0.20 g HFO–TW was added into 500 ml solution containing 50 mg/L of Pb(II), 35 mg/L of Cd(II) and 40 mg/L of Cu(II), respectively).

21.29 mg/g for Cu(II)) were closer to the experimental data (64.15 mg/g for Pb(II), 26.30 mg/g for Cd(II), 21.55 mg/g for Cu(II)).

### 3.6. Effect of initial heavy metal ions concentration

Effect of the initial metal ions concentration on removal and sorption amount of Pb(II), Cd(II), and Cu (II) by HFO–TW was carried out, and the curves are marked in Fig. 7. As depicted, the retention of three toxic metals decreased with the increase in the initial metal ions concentration, but the sorption amount is opposite. Similar conclusions had been drawn for heavy metal ions sorption onto other bio-sorbents like rice hulls [3], and tree leaves [16]. As for removal efficiency, the initial concentration-dependent trend might result from the fact that the surface coverage of heavy metal ions in solution is small at low concentration and hence almost all the available heavy metal ions are captured. However, at higher concentration, the chance for heavy metal ions to bind to sorption sites reduces significantly, and thus the removal efficiency is lower. For sorption amount, the initial concentration-dependent trend might be caused by the internal binding sites, which could not have played a role at high concentration. The initial concentration-dependent trend of removal implies that HFO–TW is more appropriate for heavy metals removal from slightly polluted waters.

### 3.7. Fix-bed column sorption

A complete effluent history of fixed-bed columns packed with HFO–TW for feeding solution containing target heavy metal ion is described in Fig. 8. As illustrated, the bed volume (BV) of $C_e/C_o$ approaching a unity on breakthrough curves for three heavy metals sorption on HFO–TW are around 1,300, 2,400, and 1,400 BV, respectively. The column sorption results display that HFO–TW is significantly effective for heavy metals removal in flow-through systems, further improving the feasibility of practical application.

### 3.8. Environmental implications

As a byproduct obtained from human daily consumption, tea waste is easily accessible and cheap. Selecting tea waste as the supporting materials of HFO–TW not only reduces the cost of sorbent but also overcomes the bottlenecks of practical application for fine HFO particles. Certainly, the successful loading of HFO also improved significantly the sorption capacity and speed of tea waste towards heavy metals. Usually, it is important for exploring the regeneration property of a given sorbent for practical application. But as a cheap sorbent, regeneration of the exhausted HFO–TW is no longer important as the expensive sorbents. The batch sorption–regeneration experiment revealed that the regeneration efficiencies of three metal ions were larger than 90% using a binary HCl and NaCl solution. However, it is unadvisable to regenerate the exhausted HFO–TW owing to the high operating cost of regeneration and further treatment of eluted heavy metals. Moreover, the subsequent treatments of eluted heavy metals will cause inevitably secondary

Table 3
Kinetic fitting results for three heavy metals retention onto HFO–TW at 298 K

| Heavy metals | Pseudo-first-order | | | Pseudo-second-order | | | Experiment |
|---|---|---|---|---|---|---|---|
| | $k_1$ ($10^{-3}$ min$^{-1}$) | $q_e$ (mg/g) | $R^2$ | $k_2$ ($10^{-3}$ min$^{-1}$) | $q_e$ (mg/g) | $R^2$ | $q_e$ (mg/g) |
| Pb(II) | 43.9 | 63.40 | 0.987 | 0.83 | 71.29 | 0.988 | 64.15 |
| Cd(II) | 70.5 | 25.92 | 0.984 | 3.8 | 27.22 | 0.990 | 26.30 |
| Cu(II) | 54.6 | 21.29 | 0.976 | 3.45 | 22.47 | 0.977 | 21.55 |

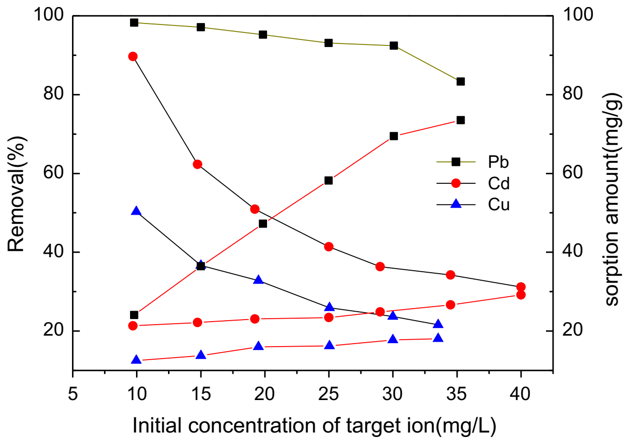


Fig. 7. Effect of initial concentration of three heavy metal ions onto removal efficiency and sorption amount of them by HFO–TW at 298 K and pH 5.5 ± 0.2 (black lines represent removal vs. initial concentration and red lines represent sorption amount vs. initial concentration).

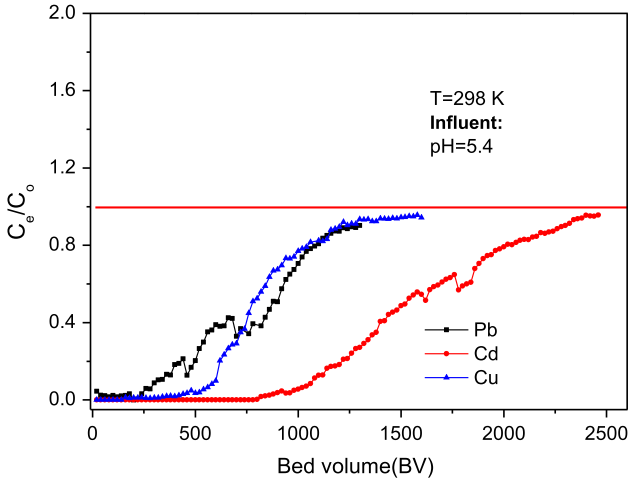


Fig. 8. Breakthrough curves of three heavy metal ions sorption of synthetic waters onto HFO–TW (for synthetic Pb(II)-polluted waters containing Pb(II) 9.8 mg/L, for Cd (II) 1.5 mg/L and for Cu(II) 3.7 mg/L. The SLV and the EBCT for three metals are all 1.50 m/h and 6.0 min, respectively).

pollution. Given all these, it might be a promising technology for solidifying the exhausted HFO–TW using impermeable material to prevent toxic metals released into the environment again. The related research about solidifying parameters is under way.

## 4. Conclusions

A novel bio-adsorbent HFO–TW was successfully prepared by impregnating hydrated ferric oxide (HFO) onto tea waste. Sorption of Pb(II), Cd(II), and Cu(II) onto HFO–TW is pH-dependent due to synergistic effects of the ion-exchange mechanism of the host tea waste and the inner-sphere complexes of impregnated HFO. HFO–TW still maintains strong sorption selectivity toward three heavy metal ions in the presence of competing ions at 50 times higher than target metals ion because of the loaded HFO. Besides, three heavy metals sorption capacities and speed by HFO–TW are higher when compared to the host tea waste. All these results demonstrate that HFO–TW is a potential candidate for removing heavy metals from contaminated water.

## Supplementary material

The supplementary material for this paper is available online at http://dx.doi.10.1080/19443994.2015.1098572.

## Acknowledgments

This work has been supported by the Science Foundation for Excellent Youth Scholars of Universities and Colleges of Anhui Province (2013SQRL091ZD), and Innovative Training of College Students of Huangshan University (AH2014103753123).

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