ORIGINAL PAPER



# **Biosorption of Cd(II) from synthetic wastewater using dry biofilms from biotrickling filters**

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Abstract Biofilms wasted from biotrickling filters was dried and used as biosorbent for Cd(II) removal from aqueous solutions. The adsorption condition and effect, adsorption isotherms and kinetics of Cd(II) removal were investigated, and the effects of competitive metal ions on Cd(II) removal were also examined. Results showed that the dry waste biofilms reached the maximum adsorption capacity of 42 mg/g of Cd(II) at 25 °C for 120 min when the initial concentration of Cd(II) and their pH were 50 mg/ L and 6.0, respectively. Under these conditions, the removal efficiency of Cd(II) reached to 89.3% when the biosorbent dosage was 2.0 g/L. The Langmuir isotherm model correlated with the isotherm data better than the Freundlich isotherm model, and the pseudo-second-order model fitted the kinetic data better than the pseudo-firstorder model. These results indicated that the adsorption was monolayer accompanied with chemical adsorption. In the presence of other metal ions, divalent metal ions of Ca and Zn inhibited the performance of Cd(II) biosorption

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significantly, while Na(I), K(I) and Fe(III) which had a higher or lower valence than Ca(II) affected slightly when containing 50 mg/L Cd(II), 0.5 g/L adsorbent dosage and pH 6.0. The analyses of scanning electron microscopy and Fourier transform infrared spectroscopy illuminated that the biosorbent had porous structures and the amide group was the majorly responsible for Cd(II) removal. Dry biofilms were novel sorbents for effective removal Cd(II), and it could be reused and recycled if necessary.

Keywords Biosorption  $\cdot$  Cd  $\cdot$  Heavy metal  $\cdot$  Mechanism  $\cdot$  Biofilm

#### Introduction

Although trace heavy metals are essential for human health, an excess amount of heavy metals can have negative effects (Chowdhury et al. 2016). Heavy metals such as cadmium (Cd), cuprum (Cu), lead (Pb) and arsenic (As) discharged in environment may pose a potential threat to nature environment communities. This result is caused by the characteristics of those heavy metals, namely long biological half-lives, nonbiodegradability and the potential for bioaccumulation (Achary et al. 2016). Cd is one of the massive hazardous metals which were discharged by metallurgy, machinery, mining and electroplating and can do harm to the growth and reproduction of plants and animals (Fan et al. 2008). When reached the threshold concentration in kidney of human, Cd can induce kidney injury and lead to osteoporosis, misshapen bones and even cancer (Bilal et al. 2016). As a consequence, it is very important to remove Cd ions from wastewater. The current methods for removing Cd ions include chemical precipitation, ion exchange, electrodialysis and membrane separations



(Sadeghalvad and Azadmehr 2015). Nevertheless, these methods have some disadvantages, such as high operating cost, incomplete removal, secondary contamination or the production of residual sludge (Aziz et al. 2008).

Recently, adsorption has some advantages over some other methods for heavy metal removal which include high adsorption capacity and flexible operation (Abedi et al. 2016). For now, a great deal of effort has been taken to explore new adsorbent, such as carbon composite, biomass adsorbents and nano-adsorbents (Wang et al. 2013; Jain et al. 2016). In particular, biosorbents including fungi, algae, waste sludge are extensively investigated (Fan et al. 2008; Wang and Chen 2009; Yang et al. 2010), because they have lots of active functional groups with high adsorption capacity of heavy metals (Cheng et al. 2016b). Besides, the biosorbents are also applied to Cd(II) removal in aqueous solution, such as agricultural wastes, Typha domingensis, fungi (Frutos et al. 2016; Fawzy et al. 2016). For the removal of heavy metal, the advantage of dead wasted biofilms is well established compared to living organism in some adverse environmental conditions, because living organism may be lost the adsorption ability in some unfavorable environment (Cheng et al. 2016a). Hence, dead waste biofilms can be considered as efficient and low-cost biosorbents for Cd(II) removal in comparison with other adsorbent materials (Bulgariu and Bulgariu 2016).

Gas biotrickling biofiltration is an established and competitive technology for volatile organic compounds (VOC) removal attractive because of its low operation and maintenance costs, high removal efficiency and environmentally friendliness (Cheng et al. 2016c). In biotrickling filters, biofilms containing many microorganisms play a major role in the biodegradation of VOC. However, excess microorganisms accumulated in biotrickling filters are frequently removed and usually discharged directly. These microorganisms contain many active functional groups, such as specific proteins and polysaccharides, which have many binding possibilities for pollutant removal. Wasted biomass which was taken from biotrickling filters for the removal of *n*-hexane as biosorbent for Pb(II) removal was studied (Cheng et al. 2016a). However, information about other heavy metals removal by wasted biofilms and the influence of competitive metal ions has not been reported.

In this study, the waste biofilms which are taken from biotrickling filters for ethylbenzene removal are used as biosorbents to treat Cd(II) from aqueous solutions. The adsorption operational conditions including solution pH, adsorption time, initial Cd(II) concentration and adsorbent dosage are examined and optimized. And also, the adsorption isotherms and kinetics are evaluated the adsorption mechanism. Furthermore, the influence of competitive metal ions such as Na(I), K(I), Ca(II), Zn(II) and Fe(III) is also investigated in the Cd(II) removal.

## Materials and methods

#### **Chemical reagents**

The chemical reagents used in the experiments, including  $Cd(NO_3)_2 \cdot 4H_2O$ , NaNO<sub>3</sub>, KNO<sub>3</sub>, Ca(NO<sub>3</sub>)\_2 \cdot 4H\_2O, Zn(NO<sub>3</sub>)\_2 \cdot 6H\_2O, FeCl<sub>3</sub> · 6H<sub>2</sub>O, HNO<sub>3</sub>, NaOH, were all of analytic grade purchased from Sinopharm Chemical Reagent Company in China. The stock solution of Cd(II) (1000 mg/L) was prepared by dissolving Cd(NO<sub>3</sub>)\_2 \cdot 4H\_2O in ultrapure water. The preparation of five competitive metal ions including Na(I), K(I), Ca(II), Zn(II) and Fe(III) used the same method, and also the metal ion concentrations were all 1000 mg/L.

At the beginning of the experiments, all chemical reagents were prepared in analytic grade and dissolved by ultrapure water. All glassware should be soaked in 10% (v/ v) HNO<sub>3</sub> for a whole day, then washed three times by ultrapure water and dried at 105 °C.

## Preparation and characterization of biosorbent

The dry waste biofilms were taken from a biotrickling filter which was used to remove ethylbenzene. After experiments, polyurethane sponge packing where microorganism attached and grew was taken out from the biotrickling filter and then put into water and washed. The production of waste biofilms could be 10 g per every washing time. After this process, waste biofilms which dropped from packing to water were filtrated and dried at 80 °C to constant weight (Cheng et al. 2016a). In order to increase contact between the biosorbent and Cd(II) in the synthetic wastewater, combined with the existing study (Yang et al. 2010), the dry waste biofilms were ground to powder until the particle size was smaller than 250  $\mu$ m. Then the dry biofilms were placed in a dryer and were further used as the biosorbents in the experiments.

The surface morphology of the biosorbent was measured by a scanning electron microscopy (SEM) (FEI QuANTA 200, USA). Fourier transform infrared spectrometer (FT-IR) (Infinity-1, Shimadzu, Japan) was used to identify the functional groups of the unloaded biosorbent and Cd(II) loaded biosorbent in the range of 400–4000 cm<sup>-1</sup>.

#### **Batch biosorption procedure**

In the biosorption experiments, different concentrations of heavy metal simulation wastewater were diluted by the stock solution. The batch experiments which used the dry



waste biofilms as biosorbent evaluated Cd(II) adsorption. Experiments were carried out in 150-mL Erlenmeyer flasks containing 50 mL solution with various metal concentrations. Then the solution pH was adjusted by adding different concentrations of HNO<sub>3</sub> or NaOH. After that, the dry waste biofilms with different dosages were added to the solutions. After these prepared steps, flasks were put into a Thermo Forma orbital shaker ZP-96F (Suzhou Will Test Products Co., Ltd., Jiangsu, China) at 150 r/min, contact time and setting temperature to obtain Cd(II) adsorption parameters. The samples taken from flasks after adsorption were filtered with 0.45-µm nylon syringe filter (Anpel Inc., China), and the Cd(II) concentrations in the filtrate were determined using a PerkinElmer A Analyst 700 atomic absorption spectrometer (AAS) (Waltham, Massachusetts).

When the influence of competitive metal ions on the Cd(II) adsorption was evaluated, the stock solutions of different competitive metal ions were added in 150-mL Erlenmeyer flasks containing Cd(II) solution. Then the concentrations of metal solutions were diluted to setting value by ultrapure water. The other experiment parameters were set as 50 mg/L Cd(II), 0.5 g/L biosorbent, 120 min contact time at pH 6.0 and temperature 25 °C. The remaining Cd(II) concentration after adsorption was measured by the above method.

All adsorption experiments were conducted in triplicates, and the average values were used for analyzing the results. Control experiments were also carried out through all experiments.

The adsorption capacity (Eq. 1) and removal rate (Eq. 2) of Cd(II) by the dry waste biofilms are calculated as follows:

$$Q_{\rm e} = \frac{(C_0 - C_i)V}{M} \tag{1}$$

$$W = \frac{C_0 - C_i}{C_0} \times 100\%,$$
 (2)

where  $Q_e$  is the adsorption capacity of Cd(II) (mg/g), *W* the removal rate of Cd(II) (100%),  $C_0$  the initial concentration of Cd(II) solution (mg/L),  $C_i$  the final concentration of Cd(II) solution (mg/L), *V* the solution volume (L) and *M* the amount of adsorbent (g).

## **Results and discussion**

# Effect of solution pH on Cd(II) adsorption

It is well known that the solution pH has significant impact on the adsorption of heavy metals (Wang and Chen 2006). Figure 1 illustrates that the variation of Cd(II) adsorption capacity onto 0.5 g/L adsorbent was influenced by solution

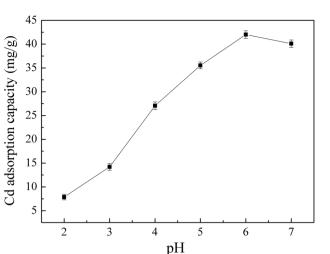


Fig. 1 Influence of pH on Cd(II) adsorption [initial Cd(II) concentration 50 mg/L, adsorption time 180 min, adsorbent dosage 0.5 g/L, temperature 25 °C, solution volume 50 mL]

pH. It was obvious that the adsorption capacity of Cd(II) dramatically increased from 7.86 to 42.01 mg/g when pH rose from 2.0 to 6.0. However, the adsorption capacity decreased to 40.1 mg/g with increasing to pH 7.0. At pH 6.0, the adsorption capacity reached a plateau. Similar trends had been reported for other types of biosorbents (Mathivanan et al. 2016). The experiments were not carried out as pH above 7.0 because of the Cd(II) precipitation. Hence, pH 6.0 was used for the following biosorption experiments in this study.

The results showed that the Cd(II) adsorption ability of the dry waste biofilms was low at pH 2.0. The reason could be that there were mass of protons existing in solution which led to the adsorbent protonated (King et al. 2008). Besides, the amide and hydroxide groups were the two main factors composing the waste biofilms, and the adsorption capacity of these groups was suppressed at low pH (Cheng et al. 2016a). As pH increased, the adsorption surface would be deprotonated, which could led to the increase in Cd(II) adsorption capacity (King et al. 2008; Karthik and Meenakshi 2016).

#### Effect of time on Cd(II) biosorption and its kinetics

The experiments on adsorbing Cd(II) by dry waste biofilms as a function of time were studied, and the results are shown in Fig. 2. Figure 2 shows that Cd(II) adsorption capacity increased from 26.64 to 41.91 mg/g when the adsorption time increased from 5 to 120 min. It was obviously that the adsorption capacity increased fast during the first 20 min of the metal-biosorbent contact. The reasons could be that this adsorption was a fast adsorption process, and the most readily available adsorbing sites of



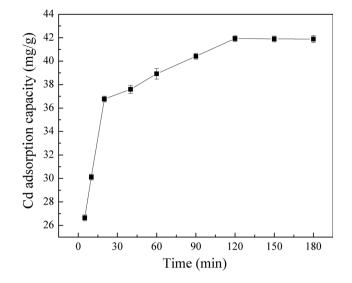


Fig. 2 Influence of time on Cd(II) adsorption [initial Cd(II) concentration 50 mg/L, pH 6.0, adsorbent dosage 0.5 g/L, temperature 25 °C, solution volume 50 mL]

the adsorbent surface were utilized instantaneously (Yang et al. 2010). With the increase in contact time, the adsorption equilibrium of Cd(II) was achieved at 120 min. Therefore, the Cd(II) equilibrium adsorption capacity  $Q_e$  (mg/g) and the concentration of the unadsorbed Cd(II)  $C_e$  (mg/L) were given at the end of 120 min. The biosorption time of following experiments was conducted at 120 min.

To better understand the adsorption kinetics of Cd(II) onto the dry waste biofilms, Lagergren's pseudo-first-order (PFO), pseudo-second-order (PSO) and Webber–Morris (W–M) models are applied to analyze the adsorption behavior of adsorbents which may be the most widely used models for the metal adsorption of a solute from a liquid solution. The pseudo-first-order model is based on the assumption that the adsorption process is a rapid initial phase, while the pseudo-second-order model is based on the assumption that the adsorption is rate-controlling (Aksu 2001; Karthik and Meenakshi 2016). The Webber–Morris kinetic model was usually applied to explain the diffusion mechanisms in adsorption process (Baraka 2015). The three equations are given as follows.

PFO model:

$$\log(Q_{\rm e} - Q_t) = \frac{k_1 t}{2.303} + \log Q_{\rm e}$$
(3)

PSO model:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t$$
(4)

W-M model:

$$q_t = K_i t^{0.5} + C, (5)$$

where  $k_1$  (1/min) and  $k_2$  (g/(mg min)) are the PFO and PSO constants,  $Q_e$  and  $Q_t$  (mg/g) are the adsorption capacities at equilibrium and at time t (min), respectively,  $k_1$  can be determined from the slope of the linear plot of  $\log(Q_e-Q_t)$  against time t (min) and  $k_2$  can be determined by the intercept of the linear plot  $t/Q_t$  against t (min),  $K_i$  (mg/ (g min<sup>-0.5</sup>)) is the diffusion rate constant which can be calculated from the slope of the linear plot and C is the thickness of the boundary layer.

The fitting figures of three kinetic models which were used to analyze the experimental data are shown in Fig. 3a-c, and the relevant kinetic parameters are demonstrated in Table 1. In the table, the correlation coefficient  $(R^2)$  was calculated by the equation through the data fitting automatically. Theoretically, if the whole adsorption processes could be explained by some model, the points of experiment data should be nearly in a straight line and the correlation coefficient  $(R^2)$  should be approximately 1.0 (Wang et al. 2016). As shown in Table 1, the experimental correlation coefficient  $(R^2)$  of the PFO and PSO was 0.8587 and 0.99993, respectively, which demonstrated that PSO correlated with the experimental data much better. The consequence indicated that the PSO model was more fitted to the Cd(II) adsorption process onto the dry waste biofilms. And it illuminated that the adsorption was mainly chemical adsorption. This result was also similar to the study by Ding et al. (2012). Figure 3c shows the intraparticle diffusion for Cd(II) ions. It was apparent that two diffusion process involved in the adsorption of Cd(II) ions onto the biosorbent. The first linear portion of the curve was attributed to the film diffusion, and this was a rapid process. The second fitting curve ascribed to the diffusion of Cd(II) into the inside pores of the biosorbent, which was a slow process.

## Effect of temperature and adsorption isotherms

The effects of temperature on the biosorption of Cd(II) by the waste biofilms were investigated when the temperature ranged from 15 to 45 °C, and the results are shown in Fig. 4. Figure 4 shows that Cd(II) adsorption capacity increased with the increase in temperature which indicated the adsorption was a endothermic process.

The adsorption isotherm is important for the description of how the adsorbate will interact with the adsorbent and it gives an idea of the adsorption capacity of the adsorbent (Zhong et al. 2013). The adsorption isotherms of the adsorbing Cd(II) onto the waste biofilms at 25 °C were analyzed by Langmuir and Freundlich models which may be the most widely used isotherms for the metal adsorption of a solute from a liquid solution.



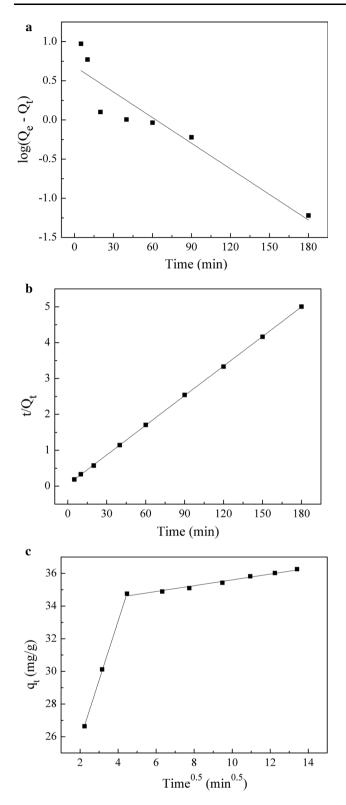


Fig. 3 Adsorption kinetics of Cd(II) onto the dry biofilms [initial Cd(II) concentration 50 mg/L, adsorbent dosage 0.5 g/L, pH 6.0, temperature 25 °C]: a pseudo-first-order model, b pseudo-second-order model, c Webber–Morris model

The Langmuir isotherm theory assumes that the adsorption is monolayer sorption and adsorbate was adsorbed on a homogeneous surface of adsorbent (Dil et al. 2017). The Freundlich model is an empirical equation which adsorption is a heterogeneous process accompanying by interactions between adsorbed molecules (Dil et al. 2017). The two models are described by the following equations.

The linearization of Langmuir isotherm model:

$$\frac{C_{\rm e}}{Q_{\rm e}} = \frac{C_{\rm e}}{Q_{\rm max}} + \frac{1}{bQ_{\rm max}}.$$
(6)

The linearization of Freundlich isotherm model:

$$\ln Q_{\rm e} = \ln K_f + \frac{1}{n} \ln C_{\rm e},\tag{7}$$

where  $C_e$  is the equilibrium Cd(II) concentration in the solution (mg/L),  $Q_e$  the equilibrium Cd(II) adsorption capacity of the adsorbent (mg/g),  $Q_{max}$  the maximum Cd(II) adsorption capacity of the adsorbent (mg/g), *b* Langmuir affinity constant (L/mg), which is related to adsorption energy, and  $K_f$  (mg/g) and *n* (g/L) are the Freundlich constants. The adsorption isotherms of Cd(II) by the dry waste biofilms are shown in Fig. 5, and the relevant constants of two isotherm models are presented in Table 2.

The adsorption isotherm is used to study the adsorption properties of adsorbent at adsorption equilibrium condition from the thermodynamics. From Fig. 5a and Table 2, the theoretical maximum adsorption capacity from the Langmuir isotherm was 34.71 mg/g which was close to the experimental result. Besides the correlation coefficient of Langmuir isotherm ( $R^2 = 0.995$ ) was closer to 1.0 than that of Freundlich isotherm ( $R^2 = 0.913$ ). The results indicated that the Langmuir isotherm model was more suitable to describe the adsorption process of Cd(II) onto the dry waste biofilms than the Freundlich isotherm model. And also the study illustrated that the Cd(II) adsorption came up on a homogeneous surface by monolayer sorption.

Similar results were acquired by Fan et al. (2008), who used *Penicillium simplicissimum* as biosorbent to adsorb Cd(II), Zn(II) and Pb(II). The Cd(II) adsorption isotherm process followed the Langmuir isotherm model, the calculated maximum monolayer adsorption capacity for Cd(II) was 61.35 mg/g at 20 °C and the Cd(II) adsorption capacity (21.5 mg/g) of *Penicillium simplicissimum* was lower than that (42 mg/g) of the dry waste biofilms in this study which could be due to the different adsorbents.

#### Effect of adsorbent dosage on Cd(II) adsorption

The effects of dosage on Cd(II) adsorption by the waste biofilms were studied with the dosage ranging from 0.3 to



Table 1 Adsorption kinetic equations and corresponding parameters of Cd(II)

Experiment parameter		PFO model		PSO model		W–B model	
Cd(II) (mg/L)	$Q_{\rm e} ~({\rm mg/g})$	$K_1$ (1/min)	$R^2$	$K_2$ (g/(mg min))	$R^2$	$\overline{K_i \;(\mathrm{mg/(g \; min^{-0.5})})}$	$R^2$
50	41.91	0.25	0.8587	0.516	0.99993	3.625	0.987

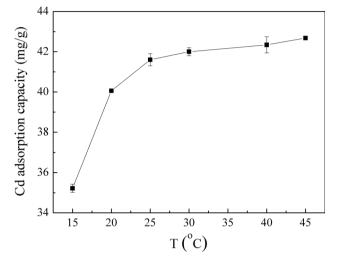


Fig. 4 Influence of temperature on Cd(II) adsorption [initial Cd(II) concentration 50 mg/L, pH 6.0, adsorption time 120 min, adsorbent dosage 0.5 g/L, solution volume 50 mL]

2.0 g/L at pH 6.0 and adsorption time of 120 min. The results are shown in Fig. 6. Figure 6 shows that the Cd(II) removal efficiency increased with the increase in adsorbent dosage. However, the Cd(II) adsorbent capacity decreased with the increase in the adsorbent dosage. The reasons might be that, on the one hand, the increase in adsorbent dosage resulted in a greater adsorption sites, so that the Cd(II) removal rate increased. On the other hand, the effectiveness of Cd(II) adsorption was decreased at abundant adsorbent, and some adsorption sites were not involved in the adsorption effectively when there existed only a small number of adsorbates, so the Cd(II) adsorbent capacity decreased (Utgikar et al. 2000). From Fig. 6, when the dosage was increased to 2.0 g/L, the Cd(II) removal rate reached to 89.3%. It showed that the waste biofilms as biosorbents were efficient in treating Cd(II) wastewater.

# Effects of competitive ions on Cd(II) adsorption

As is known to all, both industrial wastewater and agriculture wastewater contain plenty of metal ions which

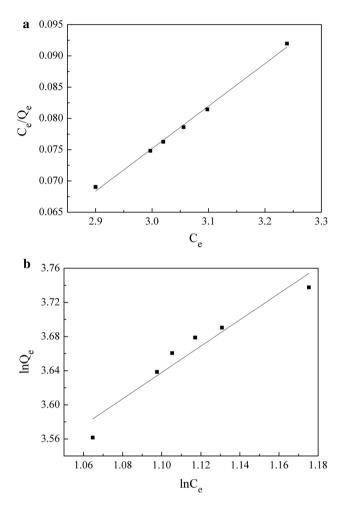
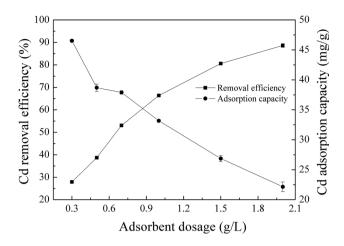


Fig. 5 Adsorption isotherms of Cd(II) onto dry waste biofilms (biosorbent dosage 0.5 g/L, pH 6.0, adsorption time 120 min, temperature 25 °C): a Langmuir isotherm, b Freundlich isotherm

Table 2 Langmuir and Freundlich isotherm constants for the adsorption of Cd(II)

Langmuir isot	herm	Freundlich isotherm			
$Q_{\rm max}$ (mg/g)	b (L/mg)	$R^2$	$K_f (mg/g)$	n (g/L)	$R^2$
34.71	0.224	0.995	6.96	0.648	0.913





**Fig. 6** Influence of adsorbent dosage on Cd(II) adsorption [initial Cd(II) concentration 50 mg/L, pH 6.0, adsorption time 120 min, temperature 25 °C, solution volume 50 mL]

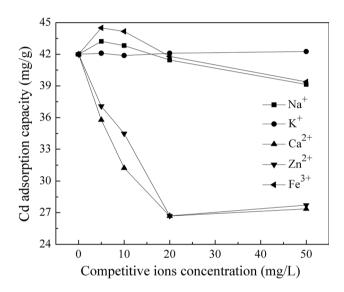


Fig. 7 Influence of competitive ions on Cd(II) adsorption [initial Cd(II) concentration 50 mg/L, pH 6.0, adsorption time 120 min, adsorbent dosage 0.5 g/L, temperature 25  $^{\circ}$ C, solution volume 50 mL]

could affect sorption on adsorbent. In this study, five competitive ions including Na(I), K(I), Ca(II), Zn(II) or Fe(III) were used to investigate the effect of Cd(II) removal by the dry waste biofilms as the competitive ions concentration ranging from 0 to 50 mg/L. The results are shown in Fig. 7.

Figure 7 illustrates that the Cd(II) adsorption capacity by the dry waste biofilms decreased as the existence of

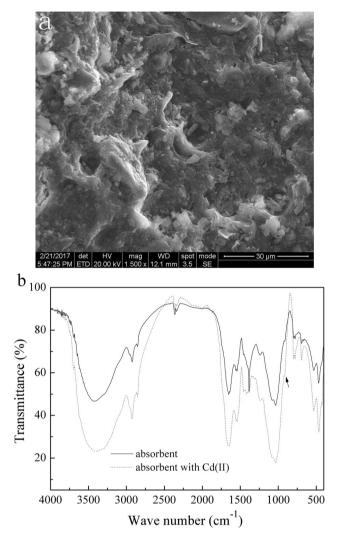


Fig. 8 Characterization of biosorbent: a SEM micrograph, b FT-IR spectra

Ca(II) or Zn(II), and the trend decreased more with the increase in the two ions concentration. However, the existence of Na(I), K(I) and Fe(III) had almost no effect on the adsorption of Cd(II) even as the increase in the three ions concentration. The reason could be that the same valence of metal ions had the same coordination number, similar diamagnetism and charge which competed the same adsorption sites of dry waste biofilms with each other, and that led to the decrease in Cd(II) adsorption capacity (Mahamadi and Nharingo 2010). On the contrary, the adsorption of different valence of metal ions (i.e., Na(I), K(I) or Fe(III)) took place in different adsorption sites



because of the different physicochemical properties of ions, so the Cd(II) adsorption was not affected (Deng et al. 2008). This phenomenon clearly showed that the Cd(II) adsorbent process remained favorable even at high concentration of Na(I), K(I) or Fe(III) compared with the present of Ca(II) or Zn(II).

Similar results were acquired by the researchers (Deng et al. 2008; Mahamadi and Nharingo 2010; Hossain et al. 2014). Hossain et al. (2014) studied that the presence of Zn(II) or Pb(II) greatly decreased the uptake of Cd(II) adsorbed on the cabbage, and the Cd(II) adsorption capacity reduced for 2.02 mg/g with the 10 mg/L Zn(II) existed. Deng et al. (2008) illuminated that Na(I) or K(I) had little effect on the adsorption of Cd(II) by *Cladophora fascicularis*, and the Ca(II) or Mg(II) inhibited the Cd(II) adsorption.

#### Characterization of biosorbent

The characterization of the biosorbent is shown in Fig. 8. As shown in SEM image (Fig. 8a), the particles had rough surface with a porous structure, which could be used as an efficient absorbent for the removal of Cd(II) from aqueous solution. FT-IR spectral analysis of unadsorbed and Cd(II) adsorbed biosorbent is shown in Fig. 8b. In the biosorbent without Cd(II), peaks appearing 3421.72, 1654.92 and 1543.05  $\text{cm}^{-1}$  were caused by the stretching vibration of – NH and -OH (Cheng et al. 2016a). The adsorption bands at 2924.09, 2852.72 and 1384.89  $\text{cm}^{-1}$  could be attributed to the asymmetric or symmetric vibration of -CH. The adsorption band around 1033 cm<sup>-1</sup> corresponded to the vibration of -C-O-C. After adsorption of Cd(II) onto biosorbent, it showed that the peaks appearing at 3421.72  $1384.89 \text{ cm}^{-1}$ had slightly shifts (3398.57, and 1417.68  $\text{cm}^{-1}$ ), and a new absorbance peak was found at 916.19  $\text{cm}^{-1}$ , which indicated that these shifts were caused by the interaction of Cd(II) with -NH and -OH groups of the biosorbent. Moreover, it also considered that surface complexes could be formed by Cd(II) and these functional groups which increased the adsorption of Cd(II) onto the dried biofilms.

## Conclusions

In this study, biofilms wasted from a gas biotrickling filter which treated ethylbenzene were selected as a low-cost biosorbent, and effectively removed Cd(II) from aqueous solutions. The biosorbent showed the strong adsorption capacity of Cd(II). Under the optimal conditions (pH 6.0, 25 °C, and contact time of 120 min), the maximum adsorption capacity of dry waste biofilms for Cd(II) was 42 mg/g when the initial Cd(II) concentration was 50 mg/ L.

Biosorption equilibrium data fitted very well to the Langmuir model, and the kinetic studies showed that the Cd(II) adsorption by the dry waste biofilms followed the pseudo-second-order model. These results demonstrated that the adsorption process was monolayer adsorption and mainly the presence of chemical ion exchange process.

The interference of five metal ions on the Cd(II) adsorption was shown that the divalent metal ions of Ca(II) and Zn(II) would badly inhibit Cd(II) adsorption onto the dry waste biofilms, while those with higher or lower valence such as Na(I), K(I) or Fe(III) affected slightly. The analyses of SEM and FT-IR illuminated that the biosorbent had porous structures and the –NH and –OH groups were majorly responsible for Cd(II) removal.

Unlike another commonly used adsorbent (activated carbon, adsorption resin), this biosorbent which was taken out from biotrickling filters was usually discharged directly, and it was one kind of biowastes, so it could be used as inexpensive and effective biosorbents for Cd(II) removal from aqueous solutions. In order to reduce the second pollution of the waste biofilms adsorbed Cd(II), the Cd(II) ions could be desorbed and removed from the biofilms by acid solution, and the regenerative biofilms could be reused.

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