Experimental study of the application of date palm trunk fiber as biosorbent for removal cadmium using a fixed bed column: investigation of the influence of particle size

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Received 6 September 2020; Accepted 12 February 2021

ABSTRACT

The adsorption capacity of date palm trunk fiber (DPTF) as an economic agricultural waste adsorbent was studied for the removal of cadmium from wastewater using a fixed-bed column. The DPTF has been used directly as an adsorbent and only subjected to washing, drying and sieving, without any further preparation steps. Breakthrough curves were obtained for size cuts ($250-355 \mu m$) and ($560-630 \mu m$) under identical conditions (flow rate = $10 \mu L/min$, initial pH = 6.05, Cd(II) concentration = 110 mg/L, mass of adsorbent = 4 g). Analysis of the experimental breakthrough curves using the Thomas model indicated that the smaller size adsorbent has a higher value of adsorption capacity to cadmium ions (20.9 mg/g) than the larger size adsorbent (19.4 mg/g). The 50% breakthrough time was estimated by applying Yoon–Nelson model. The 50% breakthrough time is 80.77 and 71.72 min for size cuts ($250-355 \mu m$) and ($560-630 \mu m$), respectively. This indicated that the smaller size adsorbent exhibits a better performance with larger service time. Wolborska's model is used to estimate the kinetic coefficient of the external mass transfer. The estimated values are 4.38 1/min for the adsorbent size ($250-355 \mu m$) and 1.98 1/min for the adsorbent size ($560-630 \mu m$).

Keywords: Adsorption; Breakthrough; Cadmium; Capacity; Date palm trunk fiber; Fixed bed column

1. Introduction

Contamination of industrial wastewater streams with heavy metal ions has been considered as a major environmental concern due to their toxicity and dangerous effects on human health [1–3]. Heavy metals can be accumulated in living things any time they are taken up and stored immediately. They are non-degradable and characterized by their stability in water for long periods [4]. The presence of heavy metals such as: copper, lithium, zinc, lead, cadmium and mercury in water even at very small concentrations (parts per million) can be a major cause of many diseases. Therefore, the contaminated wastewater must be treated to separate these hazardous substances prior to discharging to the larger water bodies [5].

Cadmium is a hazardous heavy metal that contaminates effluent water streams from several industries such

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as metallurgical processing, electroplating process, pigments, and batteries production factories [6,7]. Pollution of industrial wastewater and potable water with cadmium has become a serious issue and is considered as one of the most current environmental challenge [8]. Cadmium can be absorbed by numerous plants and water life animals. On the other hand, absorption of cadmium by the human body will lead to its accumulation in tissues for long periods due to its distinctive non-biodegradable property [9]. Accumulation of cadmium in the kidney tissues can be a reason of kidney destruction due to necrotic protein precipitations [10]. Also, the dangerous effects of cadmium on lever tissues has been reported [11]. Moreover, the adverse role of cadmium absorption in harming the lung tissues and related illnesses such as respiratory problems and weakening of immune systems has also been addressed [12]. Consequently, the developing of processes for the removal of cadmium from industrial effluent wastewaters as well as drinking water becomes crucial [13] as the limit of cadmium pollution levels set by FAO/WHO is to be under 0.005 mg/L.

There are a few well known conventional processes that have been utilized for the wastewater contaminated with heavy metal ions such as membrane based processes [14–17], chemical precipitation techniques [18], electrodialysis [19], ion exchange process [20], photocatalytic hydrogen evolution [21], methods based on flotation [22] coagulation/ flocculation process [23] and extraction [24].

Adsorption process was implemented as attractive, efficient and low-cost alternative for the separation of heavy metals from industrial wastewater streams [25]. Activated carbon is generally utilized as an adsorbent to separate heavy metals as well as many other pollutants from wastewater such as dyes, organic. Activated carbon has many advantages as adsorbent due to its adsorptive capacity and its structural properties such as high surface area, micro porous structure and chemical reactivity. However, the high cost of activated carbon and the additional cost of subsequent regeneration and reuse processes [26] are considered as restriction. Therefore it is more economic to apply lowcost and disposable adsorbent such as agricultural waste biomass. Several studies have discussed the potential of different agricultural waste biomass to adsorb Cd(II) as well as their efficiency to treat industrial wasters contaminated with heavy metals [27-29]. Most Agricultural wastes composed principally of organic compounds such as cellulose, pectins, lignins and terpenes. These compounds have -OH and -COOH functional groups which possess a high potential capacity to adsorb metal ions by ion exchange or chelating processes [30]. Date palm trunk fibers (DPTFs) are available in huge amounts as waste by product which was reported in previous investigations as a high potential and low cost biosorbent in treating wastewater contaminated with heavy metals [10,31-33]. However there is lack of experimental data of its application as adsorbent in continuous fixed bed columns.

In this work, trunk fibers obtained as agricultural wastes from date palm trees has been investigated as a low-cost adsorbent for Cd(II) removal from industrial wastewater in a continuous fixed-bed column. The influence of particle size was focused.

2. Experimental part

2.1. Apparatus

Fig. 1 illustrates the experimental apparatus which was uses to measure the continuous adsorption of Cd(II) on DPTF [25]. Breakthrough curves were measured by collecting effluent samples at regular periods. The prepared artificial cadmium contaminated aqueous solution was stored in a tightly sealed 20 L feed vessel. The adsorption column is a glass cylindrical tube with cross sectional area of 1 cm² and 50 cm length [25]. The DPTF was packed inside the column until the desired bed height and mass is obtained. The backed column was kept stable by fixing a fiber glass wool layer at the top and the bottom of the backing, to keep constant mass of adsorbent during the experiment. The solution was introduced into the column at a constant flow rate by a peristaltic pump (Heidolph, Germany) with the use of a valve and flowmeter fixed at the entrance to the column. The flow rate was controlled at 10 mL/min for all experiments with a superficial velocity of 10 cm/min. The effluent samples were collected at specified intervals and analyzed for the residual Cd(II) ion concentration using an atomic adsorption spectrophotometer. Column studies were terminated when the column reached exhaustion.

2.2. Materials

Synthetic Cd(II) stock aqueous solution at a concentration of 1,000 mg/L was prepared by dissolving cadmium nitrate Cd(NO₃)₂·4H₂O analytical grade (Merck p.a.) salt in double deionized water. The solution was then diluted to the required initial concentration of 110 mg/L. The pH of the prepared solution was 6.05.

The DPTFs used in this study as adsorbent were gathered from Yanbu Area in KSA which is the same type



Fig. 1. Experimental apparatus to measure the breakthrough curves for continuous adsorption of Cd(II) on DPTF [25].

DPTFs used previously for batch studies [31]. Fig. 2 presents Fourier-transform infrared spectroscopy spectral characteristics of DPTFs used. It contains the functional groups: –OH, aliphatic C–H groups and C–O groups. For the adsorption of cadmium on the same type DPTFs used in this study, scanning electron microscopy (SEM) analysis was already performed [31], Fig. 3, in order to understand the morphology and pore structure of DPTFs. The SEM photograph presented the availability of a wide variety of pores along with fibrous structure. SEM analyses proved that the adsorption takes place inside the pores. It is also seen that the cadmium deposits on the pores of the DPTFs.

2.3. Experimental

The fibers were washed several times with deionized water to remove all the solid particles. After confirming clean fibers, further washing with distilled water to ensure removal of all impurities or contaminants of the fibers. After washing the fibers were kept in an oven for 24 h at 100°C to produce dry and clean fibers. The fibers were then grinded and sieved. The samples were then sieved into two sizes: the size cuts (250–355 μ m) and (560–630 μ m) for



Fig. 2. Fourier-transform infrared spectral characteristics of the same type DPTFs used in this study. Reproduced from Al-Ghamdi et al. [31] Journal of Water Reuse and Desalination 3(1) 47–54, with permission from the copyright holders, IWA Publishing.



Fig. 3. SEM analysis of the same type DPTFs used in this study. Reproduced from Al-Ghamdi et al. [31] Journal of Water Reuse and Desalination 3(1) 47–54, with permission from the copyright holders, IWA Publishing.

DPTF adsorbent. For both size cuts, 4.0 g of DPTF were packed inside the column. The experimental conditions are summarized in Table 1.

3. Results and discussion

Measurements of breakthrough curves are typically used to determine the performance and the separation efficiency of the continuous column adsorption process. The trajectory of the breakthrough curve and the breakthrough time are significant design parameters of the adsorption column. Also finding a mathematical model which fits the experimental data is a design tool of the column.

In this research, experiments were conducted to estimate the operational factors for the adsorption process of Cd(II) onto DPTF adsorbent in a continuous fixed bed operation. The experimentally measured breakthrough curves for small size (250–355 μ m) and large size (560–630 μ m) DPTF are illustrated in Fig. 4.

The measured variation of the concentration reduction with time for both small and larger size adsorbents exhibit S type breakthrough curve. Therefore, it can be predicted that the adsorption process is controlled by bulk diffusion resistance and the bonding at the surface and inside the pores of the DPTF. Fig. 4 shows a faster exhaustion of the fixed bed for larger size fibers and time needed to start the breakthrough for the smaller size (250–355 μ m) adsorbent is 60 min however for the larger size (560–630 μ m) adsorbent is 45 min.

3.1. Modeling of fixed-bed breakthrough curves

3.1.1. Thomas model

Thomas model is typically applied to fit the experimental breakthrough curves and to estimate the performance of the fixed bed adsorption column. Furthermore, it evaluates the adsorption capacity of the adsorbent, which is a significant design parameter of a fixed bed adsorption column process. This model is based on the assumption that adsorption process follows Langmuir isotherm with no axial dispersion. The following equation represents the linear form of Thomas [34–37]:

$$\ln\left(\frac{C_0}{C} - 1\right) = -\frac{C_0 K_T}{F} V + \frac{MqK_T}{F}$$
(1)

where *F* is the volumetric feed flow rate (mL/min), K_{τ} is Thomas rate constant (L/min mg), *V* is the Volume of

Table 1 Experimental conditions

Column internal diameter, cm	1.1
Column height, cm	50
Bed mass, g	4
Flow rate, mL/min	10
Cd(II) initial feed concentration, mg/L	110
pH of the feed solution	6.05
DPTF size, µm	250-355 and 560-630

effluent wastewater (mL), q is the maximum adsorption capacity (mg/g). M is the adsorbent mass in the column (g).

Eq. (1) is an improvement of the Thomas model, which is frequently used to fit the experimental data for breakthrough curves in a fixed bed adsorption column. This modified model assumes an irreversible isotherm when solving the differential mass balance equation for a fixed bed column, and is mathematically equivalent to the Bohart–Adams model [38]. According to Eq. (1), the Thomas model parameters (K_T and q) can be estimated by the linear fitting of $\ln(C_0/C-1)$ vs. V (Fig. 5). The Thomas model parameters are listed in Table 2.

The results presented in Table 2 point to a greater adsorption capacity q for the adsorbent of smaller size however the value of Thomas constant K_T decreases for larger size adsorbent. This is due to the greater value of mass transfer driving force for the smaller adsorbent size. This is in agreement with the measured better column performance for the adsorbent with smaller size. The predicted break-through curves for both adsorbent sizes according to the Thomas model are displayed in Fig. 4. It is clear that Thomas model is remarkably smoothing the experimental break-through data in the earlier part while in the later part there is a minor deviation from the experimental data allowing the use of this model in column design.



Fig. 4. The measured breakthrough curves for the fixed bed adsorption of Cd(II) ions on the DPTF. (Flow rate = 10 mL/min; initial pH = 6.05; Cd(II) concentration = 110 mg/L).



Fig. 5. The plot of the measured breakthrough curves according to the linear form of Thomas model [Eq. (1)] for size cuts (250–355 μ m) and (560–630 μ m).

Table 2

Parameters of Thomas model, Yoon–Nelson model and Wolborska model using linear regression analysis of the experimental breakthrough curves

Kinetic model parameters	Adsorbent	
	250–355 μm	560–630 μm
Thomas model		
K_{T} (L/mg min)	2.22 × 10 ⁻³	1.93 × 10 ⁻³
<i>q</i> (mg/g)	20.93	19.48
R^2	0.9872	0.9662
Yoon–Nelson model		
$K_{\rm YN}$ (min ⁻¹)	0.2468	0.2017
τ (min)	80.77	71.72
<i>R</i> ²	0.9872	0.9655
Wolborska model		
β_a (1/min)	4.38	1.98
$N_0 (\mathrm{mg/L})$	2.345×10^{-3}	2.352×10^{-3}
R^2	0.95	0.95

3.1.2. Yoon-Nelson model

The Yoon–Nelson model based on assuming that the probability of adsorbate adsorption and adsorbate breakthrough on the adsorbent is proportional to the rate of decrease in the possibility of adsorption for each adsorbate molecule [39]. The linearized Yoon–Nelson equation is [40]:

$$\ln\left(\frac{C}{C_0 - C}\right) = K_{\rm YN}t - \tau K_{\rm YN}$$
⁽²⁾

where $K_{\rm YN}$ and τ are the rate constant (min⁻¹) and the time at 50% breakthrough (min), respectively. The value of $K_{\rm YN}$ depends on the column operating parameters such as initial feed concentration, height of the bed and feed flow rate. The values of $K_{\rm YN}$ and τ are estimated from the slopes and intercepts of the linear plot of $\ln(C/C_0-C)$ vs. *t* (Fig. 6) for the measured breakthrough curves. The evaluated Yoon–Nelson model parameters for both small and large size adsorbents are given in Table 2. It is noticeable that the smaller size adsorbent has the advantage of longer time (+9 min) than the larger size adsorbent to reach the 50% breakthrough which will affect the design and operation of the adsorption column.

Fig. 7 displays an evaluation of the degree of fitting of Yoon–Nelson model of the measured experimental breakthrough curves. It can be envisaged that the theoretical curves calculated by the Yoon–Nelson model fit exactly the measured experimental curves. Also, it is clear that the Yoon– Nelson model fits the experimental data to a higher degree than the Thomas model (Fig. 8).

3.1.3. Wolborska model

The experimental breakthrough curves are analyzed using Wolborska model [41] to get better understanding of



Fig. 6. The plot of the measured breakthrough curves according to the linear form of Yoon–Nelson model [Eq. (2)] for size cuts (250–355 μ m) and (560–630 μ m).



Fig. 7. Experimental and calculated from the Yoon–Nelson model breakthrough curves for the adsorption of Cd(II) ions on the DPTF for the size cuts (250–355 μ m) and (560–630 μ m).



Fig. 8. Comparing the calculated breakthrough curves using the Thomas model parameters (Table 2) and the measured experimental breakthrough data for the adsorption of Cd(II) ions on the DPTF for the size cuts (250–355 μ m) and (560–630 μ m).

the role of particle size on the mechanism of mass transfer. The linear form of this model is given by the equation:

$$\ln\left(\frac{C}{C_0}\right) = \frac{\beta_a C_0}{N_0} t - \frac{\beta_a H}{V_0}$$
(3)

where β_a is the external mass transfer kinetic coefficient of (1/min). N_0 is the bed volumetric capacity (mg/L). This model represents the diffusion mechanism in low concentration systems which derived from the general equation of mass transfer. Fig. 9 shows the linear fitting of the breakthrough



Fig. 9. The linear fitting of the breakthrough data as per (Wolborska model).

data as per equation 3 (Wolborska model) and the estimated Wolborska model parameters are listed in Table 2.

With referring to the Wolborska model perimeters listed in Table 2, it can be notices that the adsorbent size has minor effect on the volumetric bed capacity. The values of the bed capacity for the adsorbent size ranges 250–355 µm and 560–630 µm are 2,345.87 and 2,352.17, respectively. However, the coefficient of the external mass transfer (β_a) changes significantly by particle size. The adsorbent of smaller size has a higher external mass transfer kinetic coefficient (4.38 1/min) than larger size adsorbent (1.98 1/min). This result indicates an enhanced external mass transfer rate in the case of smaller size adsorbent which reflected on the improved performance of the fixed bed as can be concluded from the breakthrough data.

On the other hand, the internal mass transfer process is affected by the size of the adsorbent. It is well predictable that adsorbent with larger sizes has longer paths for diffusion thus the adsorbate will be subjected to higher resistance to be adsorbed to the active sites inside the pores. Moreover, the accessible surface area at the solid liquid interface is larger for smaller size. This will enhance the rate of adsorption process.

4. Conclusions

In this work, DPTF has been studied as an economic agricultural waste biosorbent to treat wastewater streams contaminated with cadmium. The benefit of this biosorbent is its availability in large amounts and converting it from solid waste to a potential and valuable adsorbent with no need to any process to prepare the adsorbent. It can be used as adsorbent directly after washing, drying, and crushing with no further costs. The column continuous operation is examined and exhibits an excellent performance with a high separation efficiency. This study showed that the DPTFs of small size can be used as a potential adsorbent as packed bed in the wastewater treatment processes. However further process parameters need to be studied for the design of a continuous adsorption process.

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