Journal of Environmental Chemical Engineering 4 (2016) 2243–2249

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Column adsorption of aniline by a surface modified jute fiber and its regeneration property

Qi Hu[a], Peng Wang[a,b,*], Jiping Jiang[a], Hongyu Pan[c], Da-Wen Gao[a,b]

[a] School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China
[b] State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China
[c] Harbin Drainage Group Co., Ltd., Harbin 150010, China

ARTICLE INFO

Article history:
Received 9 November 2015
Received in revised form 8 March 2016
Accepted 12 March 2016
Available online 14 March 2016

Keywords:
Wastewater
Jute fiber
Aniline adsorption
Adsorbent regeneration
Fixed-bed column
Biosorbent

ABSTRACT

Pyromellitic dianhydride (PMDA) modified jute fiber was prepared for aniline adsorption from aqueous solution in a fixed-bed column. A series of column tests were performed to determine the breakthrough characteristics, by varying bed depths (12–48 mm), influent flow rates (10–20 mL/min) and initial concentrations (50–200 mg/L). Results illustrated an encouraging performance for aniline adsorption, with an adsorption capacity of 91.5 mg/g, at an influent concentration of 200 mg/L and adsorbent bed depth of 24 mm. Dynamic adsorption behavior was satisfactory described by Thomas, Bed Depth Service Time (BDST) and Yoon-Nelson models. Dynamic modeling analysis revealed that the best predictions of breakthrough curves were obtained with the BDST model. The exhausted biosorbent could get an effective desorption with 0.5 M hydrochloric acid solution. After three regeneration cycles, above 95% adsorption capacity of the biosorbent was maintained. The findings reveal that the modified jute fiber is a potential adsorbent for aniline pollution remediation.

1. Introduction

A common problem for most industrial enterprises is the disposal of large volumes of wastewater containing potentially toxic organic solutes. The wastewater discharged from these industries has become a severe environmental problem. It is extremely toxic and has harmful influences on human health and aquatic life. Considering general safety and the ecological consequences of these solutes, their presence in wastewater requires treatment prior to disposal. Aniline and its derivatives, as essential raw materials, are commonly used in the dyestuff, pharmaceutical, explosive, rubber curing promoter and medicine sectors. Effluents containing aniline have brought a series of serious environmental problems because of its high toxicity and accumulation in the environment. Strict limits on the release of aniline have been set up. A number of technologies are available for removing aniline, such as advanced oxidation [1], membrane separation [2], biodegradation [3], adsorption [4–6] etc. From the technical and economic points of view, adsorption has been shown to be an effective method for aniline removal.

At present, the widely used adsorbents include activated carbon [7], carbon nanotubes [8] and so on. Although activated carbon is used in various cleaning procedures, it remains expensive. Their use is also restricted due to the difficulties associated with regeneration and disposal of the spent carbon. These constraints have rendered the search for alternative adsorbents from certain easily accessible low cost materials such as sugarcane bagasse, rice straw, sawdust, corncob etc [9]. These natural biosorbents contain a considerable amount of floristic fiber, protein, and some functional groups such as carboxyl, hydroxyl, and amidogen, which can form hydrogen bonds with organic compounds or bind organic compounds through the ion-exchange effect [10].

Jute fiber (JF), a highly abundant agricultural product mainly found in India, Bangladesh, Thailand and China, has extensively been used for making geotextiles and composites [11]. JF is mainly composed by the small units of cellulose. These small units are cemented together by lignin and hemi-cellulose, which demonstrate some ion-exchange and adsorption properties. However, the adsorption capacities of virgin JF aren't highly effective for biosorption because of its low density of active anchoring sites per unit surface area [11]. Modifications with graft polymerization could enhance the adsorption capacity of JF. However, the improved capability was generally investigated in batch processes [12,13] by evaluating the equilibrium adsorption capacity (q_e) of adsorbents for adsorbates present in aqueous phases, which had

* Corresponding author at: Harbin Institute of Technology, School of Municipal and Environmental Engineering, 73 Huanghe Road, Nangang District, Harbin 150090, China.
E-mail addresses: pwang73@vip.sina.com, pwang73@hit.edu.cn (P. Wang).

http://dx.doi.org/10.1016/j.jece.2016.03.022
2213-3437/

limitations for prediction of the performances in the practical treatment system. Column adsorption offers a more realistic simulation than the replicate investigation in batch mode. In industrial water treatment processes, the column tests are preferable to evaluate the applicability of an adsorbent [14]. For column operation, the adsorbent is continuously in contact with fresh wastewater and consequently, the concentration of the solution in contact with a given layer of the biosorbent changes very slowly [15]. The data obtained from fixed-bed columns allow more efficient utilization of the biosorbent capacity and result in a better quality of the effluent [16]. A fixed bed is also effective in cyclic adsorption/desorption, as it makes a good use of the concentration difference as the driving force.

The optimum operational design of the column could be decided based on the experimental study, but it is a time-consuming process. Mathematical modeling is one tool, which has been researched in adsorption processes. The modeling helps in understanding the process behavior prior to its commercial implementation [17]. The prediction by some mechanistic models can help to describe the process of adsorption. The Thomas, Bed Depth Service Time (BDST) and Yoon-Nelson models can estimate the parameters of fixed bed adsorber in practical applications [18]. These models have been widely applied in study the column adsorption performance of adsorbents under isothermal conditions [19–21].

The work is meant to remove aniline by the pyromellitic dianhydride modified jute fiber (PMJF) from aqueous solution using a fixed-bed column. The bed depth, influent flow rate and initial aniline concentration were chosen as variable factors. The breakthrough curves were analyzed using the Thomas, BDST and Yoon-Nelson models. Finally, cyclic adsorption was conducted to verify the possibility of the bioadsorbent reutilization.

2. Materials and methods

2.1. Characteristics of the bioadsorbent

The Jute fiber used in the present study were treated with sodium hydroxide (5%) solution for 2 h, and then reacted with pyromellitic dianhydride (PMDA) in the *N*,*N*-dimethyl formamide (DMF) solvent assisted by microwave for 25 min (EXCEL Microwave Reaction System, Preekem Scientific Instruments Co., Ltd., China). The reaction temperature was kept at 123 °C [13]. The maximum adsorption capacity of the pyromellitic dianhydride modified jute fiber (PMJF) is estimated to be 104–169 mg/g. The BET surface area was 0.54 m^2/g, and the average pore diameter was about 2.66 nm.

2.2. Column experiments

Continuous flow adsorption experiments were conducted in a Perspex glass column with 30 cm in height and 2.0 cm in internal diameter. The top and bottom of the PMJF bed were covered by a layer of pre-equilibrated glass wool in order to avoid the loss of adsorbent, and also to ensure a closely packed arrangement. A variable speed peristaltic pump was used to inject influent aniline solution at a fixed and controlled discharge rate upward through the column. The water flowed through the adsorbent bed, and the aniline was adsorbed by PMJF. Breakthrough curves showed the performance of the column. The variable parameters investigated were bed depth (Z), influent flow rate (Q) and influent aniline concentration (C_0).

First, the adsorbent with four separate bed depths of 12, 24, 36 and 48 mm was prepared by correspondingly packing with 1.0, 2.0, 3.0 and 4.0 g of PMJF in the column. Water sample (initial aniline concentration: 100 mg/L) was allowed to flow through the bed with an influent flow rate of 15 mL/min. Effluent was collected at regular time intervals to determine the concentration of aniline until there was no further adsorption. Then, a series of experiments was conducted to study the effect of inlet flow rate (10, 15 and 20 mL/min) at a bed depth of 24 mm with an initial aniline concentration of 100 mg/L. Finally, experiments were conducted to study the effects of initial aniline concentration (50, 100 and 200 mg/L) at a bed depth of 24 mm with a fixed influent flow rate of 15.0 mL/min.

2.3. Column data analysis

The concentration of aniline solution was determined by a UV–vis dual-beam spectrophotometer (T6, China) at a maximum wavelength of 545 nm according to the *N*-(1-naphthyl) echylenediamine spectrophotometer method (GB 11889-89, Standards of China). All the experiments were carried out in duplicates, and average values were given. C_t and C_0 are the concentration of aniline in the effluent and influent, respectively. The breakthrough curves were expressed by C_t/C_0 as a function of time of the effluent for a given bed depth. Experimental data acquired from breakthrough curves were analyzed to determine the various types of column parameters. For a given flow rate and influent concentration, the value of the total mass of aniline adsorbed, q_{total} (mg), can be calculated from the area under the breakthrough curve:

$$q_{\mathrm{total}} = \frac{Q}{1000}\int_{t=0}^{t=\mathrm{total}} C_{\mathrm{ad}}\,dt = \frac{Q}{1000}\int_{t=0}^{t=\mathrm{total}} (C_0 - C_t)\,dt \quad (1)$$

where Q is the volumetric flow rate (mL/min), and t_{total} is the time (min) when the C_t/C_0 is equal to 0.95. $C_{ad} = C_0 - C_t$ is the concentration of aniline removal (mg/L). The equilibrium column capacity, q_{eq}(mg/g), is calculated as following:

$$q_{\mathrm{eq}} = \frac{q_{\mathrm{total}}}{m} \quad (2)$$

where m is the dry weight of MJF in the column (g).

2.4. Chemical regeneration by HCl

A desorption process, which was conducted in a 24 mm bed depth, was used to regenerate the aniline loaded adsorbent. The exhausted adsorbent was rinsed with 0.5 mol/L hydrochloric acid solution until the aniline concentration in effluent is nearly unchanged, and then it was rinsed with deionized water until a near-neutral pH was reached at the outlet. The diluted hydrochloric acid and deionized water were fed on the fixed-bed at a flow rate of 15 mL/min. The regeneration procedure was repeated three times, and four breakthrough curves were plotted.

3. Results and discussion

3.1. Column adsorption of aniline by the pyromellitic dianhydride modified jute fiber (PMJF)

3.1.1. Effect of bed depth

PMJF adsorption in a fixed-bed column system was associated with the quantity of adsorbent in the column. In order to get breakthrough curves at different bed depths, the column was packed with 1.0, 2.0, 3.0 and 4.0 g of PMJF to provide bed depths (Z) of 12, 24 and 36–48 mm, respectively. Adsorption experiments were conducted using 100 mg/L aniline solutions. Typical breakthrough curves, obtained at a constant flow rate and influent concentration, were given with the dimensionless concentration (C_t/C_0) plotted versus the service time (t) (Fig. 1). A typical S-shaped curve was gotten as the bed depth grew larger. As the bed depth increased, the breakthrough and exhaustion time also