Journal of Environmental Chemical Engineering 4 (2016) 1685–1697

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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

Process analysis of mercury adsorption onto chemically modified rice straw in a fixed-bed adsorber

Shiow-Tien Song[a], Ying-Fong Hau[a], Norasikin Saman[a], Khairiraihanna Johari[b], Siew-Chin Cheu[a], Helen Kong[a], Hanapi Mat[a,c,*]

[a] Advanced Materials and Process Engineering Laboratory, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia
[b] Department of Chemical Engineering, Faculty of Engineering, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia
[c] Advanced Material and Separation Technologies (AMSET) Research Group, Health and Wellness Research Alliance, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

ARTICLE INFO

Article history:
Received 24 November 2015
Received in revised form 25 February 2016
Accepted 27 February 2016
Available online 2 March 2016

Keywords:
Rice straw
Mercaptans
Adsorption
Mercury ion
Fixed-bed adsorber

ABSTRACT

The potential application of chemically modified rice straw (RSGM) was investigated in a fixed-bed adsorber as an extension of our previous batch adsorption studies. The effect of flow rates (2 mL/min, 4 mL/min and 8 mL/min), Hg(II) concentrations (50 mg/L, 100 mg/L, and 200 mg/L), and bed heights (1.5–4.5 cm) on the breakthrough characteristics of the fixed-bed adsorber was investigated. The adsorption isotherm data were best fitted to the Langmuir isotherm model, while the breakthrough data were found to be in good agreement with the Thomas and Yoon–Nelson models. The adsorbent bed regeneration results indicate a good adsorption–desorption reversibility with retaining adsorption performance of more than 90% after four cycles. The process design of the fixed-bed adsorber was demonstrated using the height of an equivalent transfer unit (HETU) method. The prediction of breakthrough curve was successfully carried out by scaling-up the Yoon–Nelson constants obtained from empty bed contact time (EBCT) plots.

1. Introduction

The use of mercury in many processes has significantly increased as a result of the industrial revolution of the 19th century. According to the United States Environmental Protection Agency (USEPA), the tolerance discharge limit of wastewater for mercury is 0.01 mg/L; meanwhile the World Health Organization (WHO) sets the permitted mercury concentration in drinking water as low as 0.001 mg/L [1]. This indicates that the reduction of mercury to an acceptable level is necessary because it can cause a severe hazard to human health as well as the ecosystem. The current methods for heavy metal removal such as chemical precipitation, chemical oxidation, ion exchange, liquid extraction and membrane process are however non-economical and possess several disadvantages such as incomplete metal removal particularly at low concentration, high reagent and energy requirements [2].

Adsorption has been found to be economically appealing for the removal of toxic metals from wastewaters. It offers some advantages such as a simple adsorbent regeneration, cost effectiveness, no additional nutrient requirement, and efficient even at low concentration [3]. The choice of any adsorptive separation process is however directly dependent on the adsorbent characteristics and ultimately on the process cost effectiveness. Thus, there has been a continuous improvement in the development of effective noble adsorbents, especially towards the applications of low-cost agricultural by-products which, in developing countries, are often under-utilized [4,5]. For instance, rice straw is one of the good sources of raw materials for natural adsorbent precursors because it is abundantly available and relatively cheap. The rice straw may offer better alternative to the existing adsorbent, it is however still under-utilised as adsorbents especially for the application in removing mercury ions from wastewater [6].

Our previous research on the Hg(II) adsorption by chemically modified rice straw in batch adsorption studies indicated its potential application in produced water treatment [7]. Under optimized conditions, the percentage of Hg(II) removal process by mercapto-grafted rice straw was over 90%, indicating that the

* Corresponding author at: Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia.
Fax: +60 7 5581463.
E-mail address: hbmat@cheme.utm.my (H. Mat).

http://dx.doi.org/10.1016/j.jece.2016.02.033
2213-3437/

Nomenclature

A	Area under the breakthrough curve
A_b	Cross-sectional area of the bed (cm^2)
C_0	Inlet Hg(II) feed concentration (mg/L)
C_t	Outlet Hg(II) concentration (mg/L)
C_b	Outlet breakthrough Hg(II) concentration (or limit effluent concentration) (mg/L)
F_v	Adsorbate feed solution volumetric flow rate (mL/min)
H_b	Adsorber bed height (cm)
I.D	Adsorber internal diameter (cm)
K_B	BDST model rate constant (L/mg min)
K_{BA}	Bohart–Adams model kinetic constant (L/mg min)
K_{Th}	Thomas model kinetic constant (mL/mg min)
K_{YN}	Yoon and Nelson model kinetic constant (L/min)
K_L	Langmuir constant (L/mg)
K_F	Freundlich adsorption constant ((mg/g)(mg/L)n)
N	Freundlich adsorption constant
N_o	Adams–Bohart model saturation concentration (mg/L)
N_s	Adsorption capacity per unit volume of bed (g/L)
m_a	Mass of adsorbent (mg)
m_{total}	Total amount of Hg(II) entering adsorber (mg)
N_b	Number of bed volumes of adsorbate effluent solution to breakthrough
Q_t	Total amount of Hg(II) adsorbed up to time t (mg)
q_t	Hg(II) adsorption capacity at saturation time
q_e	Equilibrium Hg(II) uptake per g of adsorbent in the adsorber
q_{max}	Maximum adsorption capacity (mg/g)
R	Maximum flow rate (L/m^3 h)
R_p	Permeability of the porous media
t	Flow time (min)
$t_{0.5}$	Time required for 50% adsorbate breakthrough (min)
t_b	Breakthrough time (min)
t_s	Exhaustion/saturation time (min)
V_o	Superficial velocity (cm/min)
V_b	Adsorbent bed volume (L)
V_s	Volume of adsorbate feed solution treated at breakthrough (L)
V_{eff}	Effluent volume (mL)
ε	Bed void fraction
r_a	Adsorbent density (g/mL)
μ	Fluid viscosity (Pa s)

modified rice straw is, in fact, an attractive adsorbent for mercury removal process. This result motivates us to further our studies on the continuous adsorption process which is more applicable as compared to batch process in real water treatment processes due to its low operating cost and ability of adsorbers to adapt to versatile processes. The use of a continuous adsorption process for practical applications requires the analyzing of both equilibrium and kinetics data obtained from the laboratory investigation of the continuous adsorption system such as fixed-bed or fluidized-bed adsorbers. The dynamic adsorption of metal ions can be interpreted by analyzing the shape and position of the breakthrough curves which are able to quantitatively predict the performance of a fixed-bed adsorber [8,9]. This makes the fixed-bed operation one of the most effective methods to study the adsorption–desorption cycles for a better efficiency in the adsorbent use [10]. Besides, if the breakthrough curves can be reliably predicted using laboratory measurements, studies at pilot plant scale before the industrial applications could be obviated and thus saving time and resources.

Therefore, the applicability of the modified rice straw was studied using a fixed-bed adsorber to evaluate the effects of adsorbate feed solution flow rate (F_v), bed height (H_b) and initial feed concentration (C_0) on breakthrough time (t_b) and adsorbent bed adsorption capacity (ABAC) followed by the breakthrough data analysis using the existing kinetic breakthrough models. In addition, the regeneration characteristics of an exhausted RSGM (rice straw grafted with 3-mercaptopropyltriethoxysilane) were also examined. Finally, the design and scale-up of the adsorber and the breakthrough data analysis based on the lab-scale results were demonstrated.

2. Material and methods

2.1. Preparation of adsorbent

The preparation of adsorbent was carried out according to our previous study [7]. The raw rice straw was first ground and sieved into 60–130 μm, washed with distilled water and dried in an oven at 50° C until a constant weight was obtained. For modification of adsorbent, 1.5% (v/v) 3-mercaptopropyltriethoxysilane (MPTES) was added to a medium (50/50 v/v ethanol/water, pH 4.5) and stirred for 2 h to pre-hydrolyze the MPTES. After that, 3 g of rice straw was immersed in the solution and stirred for 3 h. This was followed by drying at 65° C to allow covalent bonding between the rice straw and silanol groups via condensation. The dried-sample was then washed with the same medium for several times to eliminate excess organosilane and then dried at 50 °C until a constant weight was obtained. The treated adsorbent was designated as RSGM. A detailed discussion on the characterization of the adsorbent is available in our previous study [7].

2.2. Fixed-bed adsorption studies

The continuous adsorption studies were conducted in a glass adsorber with an internal diameter of 1.0 cm and length of 40 cm. A known quantity (0.25–0.75 g) of RSGM was placed in the adsorber to yield the desired adsorbent bed height (1.5–4.5 cm). A mercury nitrate solution of known concentration (50–200 mg/L) was then channeled into the adsorber using a peristaltic pump in a down flow manner at the desired flow rates (2 mL/min, 4 mL/min and 8 mL/min). Sampling of adsorber effluent was done at specified time intervals in order to investigate the breakthrough point of adsorber service time and the shape of breakthrough curve. The concentration of Hg(II) ions was determined using an atomic absorption spectrophotometer (AAS). The operation of the adsorber was stopped when $C_t/C_0 > 0.9$.

The desorption curves obtained for the displacement of the Hg (II) were obtained in a dynamic system, using the same flow rate held for the adsorption. The amount of eluted metal (q_{el}) was calculated by integrating the elution curves. The area under the curve, multiplied by the feed flow rate per gram of RSGM leads to the amount of metal desorbed [11].

2.3. Analytical methods

The concentration of Hg(II) in the samples was determined by the AAS (Model PerkinElmer-HGA 900) using an air-acetylene flame method (F-AAS). A mercury electrodeless discharge lamp (EDL) was employed as the radiation source (current: 86 mA, wavelength: 253.7 nm, spectral bandwidth: 0.2 nm). The minimum mercury detection limit was 0.3 ppm as provided by the manufacturer. Three standard solutions in the linear range of the instrument were used to construct each calibration curve.