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Adsorption of thallium ion (Tl^{+3}) from aqueous solutions by rice husk in a fixed-bed column: Experiment and prediction of breakthrough curves

Hayder A. Alalwan [a,b,*], Mohammad N. Abbas [c], Zaidun N. Abudi [c], Alaa H. Alminshid [d,e,**]

[a] Department of Chemical and Biochemical Engineering, University of Iowa, Iowa City, IA 52242, USA
[b] Kut Technical Institute, Middle Technical University, Kut, Wassit, Iraq
[c] Mustansiriyah University, Collage of Engineering, Environmental Engineering Department, Baghdad, Iraq
[d] Department of Chemistry, University of Iowa, Iowa City, IA 52242, USA
[e] Department of Chemistry, Wasit University, Kut, Wasit, Iraq

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ABSTRACT

This study examined the use of rice husk, an inexpensive biosorbent material, for removing thallium ions (Tl^{+3}) from aqueous solutions in a continuous fixed-bed adsorption column. The impact of adsorbent bed height (from 1 to 7 cm), influent flow rate (from 0.4×10^{-3} to 1×10^{-3} m^3/min), Tl^{+3} concentration (from 10 to 40 g/m^3), solution pH (from 5 to 12), and influent temperature (278 to 308 K) on breakthrough curves was analyzed. To identify the design parameters needed to scale up the system, the results were compared to three models, namely, Thomas, Yoon–Nelson, and Bed Depth Service Time (BDST). The experimental results were found to be well described by these kinetic models. The results confirmed the dependence of the breakthrough and saturation points on the examined variables. The system displayed excellent efficiency, achieving full (100%) removal of Tl^{+3} in the first 20 min at optimum conditions. The results show that increasing the bed depth and decreasing the influent flow rate as well as the initial Tl^{+3} concentration improves removal efficiency. Increasing the pH to an optimal value of ten was found to increase Tl^{+3} uptake, after which any further increase of the pH inhibited adsorption due to the precipitation of Tl^{+3} as a salt. Increasing the solution temperature from 278 to 298 K was found to enhance the removal percentage which indicates that the adsorption is endothermic. However, further increasing of the temperature to 308 K was found to increase the solubility of Tl^{+3} in the solution which inhibits its adsorption on the adsorbent surface.

1. Introduction

The removal of thallium (Tl) compounds from wastewater has drawn considerable attention due to their high toxicity for human and aquatic organisms (Huangfu et al., 2017; Tatsi et al., 2015). Tl has been identified as more toxic than many materials, including lead, cadmium, and mercury (Campanella et al., 2016). Tl is widely used in the manufacture of optical lenses, alloys, dyes, rodenticides, semiconductors, and pigments (Li et al., 2017). According to the World Health Organization

* Correspondence to: 4131 Seamans Center, Iowa City, IA 52242, USA.
** Correspondence to: University of Iowa, W115 Chemistry Building, Iowa City, IA 52242, USA.
E-mail addresses: hayderabdulkhaleq-alalwan@uiowa.edu (H.A. Alalwan), alaahaninaser-alminshid@uiowa.edu (A.H. Alminshid).

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(WHO), a Tl level below 5 mg/m^3 is unlikely has adverse human health effects (Kazantzis, 2000). Several techniques including ion exchange, extraction, membranes, adsorption, and precipitation have been suggested for Tl removal (Chen et al., 2017; Hassanien et al., 2017; Liu et al., 2014; Cankara et al., 2016; Yang et al., 2017). Among these removal techniques, adsorption is widely used due to its ease of use and low cost (Ungureanu et al., 2015). Fixed beds with different absorbents such as activated carbon, titanium dioxides, titanium peroxide, manganese dioxides, and copper (II) ferrocyanide, are very efficient in the removal of Tl (Zhang et al., 2018; Sangvanich et al., 2010; Birungi and Chirwa, 2015; Zhang et al., 2009), but the high cost of these materials has motivated researchers to look for less expensive alternatives.

Agriculture by-products have attracted researchers as adsorbent materials due to their very low cost and the absence of the need for regeneration processes (Bartczak et al., 2017; Kumari et al., 2016). Numerous biomass materials have been evaluated for Tl removal (Khavidaki et al., 2013; Long et al., 2017, 2016). However, rice husk has been shown to have promising adsorption activity in heavy metal removal from water due to its high surface area and granular structure (Alexander et al., 2017; Qu et al., 2018). Rice husk consists of 50% cellulose, 25%–30% lignin (polar functional groups), and 15%–20% silica, which are the main active sites for chemical sorption (Kumar and Porkodi, 2006; Ummah et al., 2015). Successful design and operation of a fixed-bed adsorption system requires identifying its adsorption equilibrium and dynamics (Lakshmipathy and Sarada, 2015; Knox et al., 2016). Thus, determining the breakthrough and saturation points under operating conditions is of high priority to provide fundamental data for the design and scale-up of a continuous adsorption system. Specifically, the ability to predict the breakthrough point, which is identified by observing the adsorbed material in the effluent stream in a concentration higher than a proposed acceptable limit, is essential to scalp up to the adsorption system successfully. The shape of the breakthrough curve is determined by the shape of the equilibrium isotherm and it is impacted by several operational variables such as the adsorbent bed height, solution initial concentration, influent flow rate, and solution pH. Testing the validity of kinetic models that fit the real-time data can help with efforts to scale up the system to the industrial level. These models can help to predict the breakthrough and saturation points before they have been reached and therefore enable the appropriate action to be taken to guarantee high system efficiency.

In this investigation, rice husk was evaluated as an innovative adsorbent material for Tl^{+3} removal from aqueous solutions in a continuous fixed-bed column at room temperature. Consequently, the effect of operating parameters such as adsorbent bed height, influent flow rate, initial Tl^{+3} concentration, the pH of the Tl^{+3} solution, and influent temperature were identified. Column dynamic was examined using three mathematical models, namely Thomas, Yoon–Nelson, and Bed Depth Service Time (BDST). The value of the correlation coefficient, R^2, was used to validate the compatibility of the kinetic models with the real-time data. The analysis of these models confirmed their applicability to our system. Collectively, our work identifies an inexpensive adsorption material, rice husk, that has a promising sorption capability of Tl^{+3} from wastewater in a technique that can be used at the industrial level

2. Experimental work

2.1. Rice husk preparation and characterization

The rice husk residue used in this investigation was obtained from a local farm. After washing the rice husk with distilled water three times to remove any impurities, it was dried at 378 K for 24 h. Then, the surface area and pore volume were specified using the Brunauer–Emmett–Teller (BET) adsorption isotherm method, in which material was first degassed for two hours at 378 K. A seven-point and 13-points BET isotherm was used to calculate the surface area and pore volume, respectively, using N_2 (g) as the adsorbate. The surface area was found to be 1.75 m^2/g, while the pore volume was found to be 3 ($\pm$ 0.5) $\times$ 10^{-3} cm^3/g with average pore radius 36 ($\pm$1) nm. X-ray diffraction (XRD; Bruker D8 Advance 206112) and scanning electron microscopy (SEM; Hitachi S-4800) were used to characterize the fresh rice husk (Fig. 1). XRD analysis revealed that the primary component of rice husk is cellulose-I which was characterized by the three peaks at $2\theta = 16.5^\circ$, 22.0° and 34.5° which represent 110, 200, and 004 planes, respectively (Kumar et al., 2012; Johar et al., 2012). The high intensity peak at $2\theta = 22.0^\circ$ revealed the dominant of SiO_2 in the rice husk structure. Elemental mapping with a Hitachi S-3400N Scanning Electron Microscope (3.0 nm resolution under high vacuum mode) with a Bruker EDS detector was used to confirm the elemental composition of the rice husk (Fig. 2). The results showed the dominance of Si elemental composition (25.75%) in good agreement with the XRD results. In addition, trace percentages of other elements were detected as shown in Table 1. Furthermore, the EDS analysis showed that Si is concentrated on the exterior shell of the fresh rice husk which has different pattern than the interior surface, as shown in SEM images (Fig. 1).

2.2. Stock solution

A simulated synthetic aqueous solution (SSAS) was prepared in the laboratory with different Tl^{+3} concentrations to avoid contamination by other elements that might exist in real wastewater. The Tl^{+3} stock solution with 1000 g/m^3 was prepared by dissolving 500 mg of thallium nitrate $Tl(NO_3)_3.3H_2O$ (Alfa Aesar, 99.5%) in one liter of distilled water. This stock solution was used after dilution with distilled water to the desired concentration. The solution pH was altered by adding 0.1 N of potassium hydroxide (KOH) (Alfa Aesar) and 0.1 N of hydrochloric acid (HCl) (Sigma Aldrich) to achieve the desired pH value. A Shimadzu Atomic Absorption (AA-7000) instrument was used to measure the Tl^{+3} concentration in the influent and effluent solution.