Chinese Journal of Chemical Engineering 23 (2015) 1610–1619

Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

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

Separation Science and Engineering

Biosorption of basic violet 10 onto activated *Gossypium hirsutum* seeds: Batch and fixed-bed column studies

N. Sivarajasekar *, R. Baskar

Department of Chemical Engineering, Kongu Engineering College, Perundurai, Erode 638052, Tamil Nadu, India

ARTICLE INFO

Article history:
Received 30 June 2014
Received in revised form 13 May 2015
Accepted 17 June 2015
Available online 31 August 2015

Keywords:
Gossypium hirsutum seed
Isotherm
Kinetic
Fixed-bed
Mass transfer

ABSTRACT

Sulphuric acid activated immature *Gossypium hirsutum* seed (AIGHS) was prepared to biosorbe basic violet 10 (BV10) from aqueous solutions. Methylene blue number, iodine number and Brunauer–Emmett–Teller surface analysis indicated that the AIGHS were hetero-porous. Boehm titrations and Fourier-transform infrared spectra demonstrated the chemical heterogeneity of the AIGHS surface. Batch biosorption studies were used to examine the effects of process parameters in the following range: pH 2–12, temperature 293–313 K, contact time 1–5 h and initial concentration 200–600 mg·L^{-1}. The matching of equilibrium data with the Langmuir–Freundlich form of isotherms indicated that the BV10 was adsorbed *via* chemisorption and pore diffusion. Kinetic investigation indicated multiple order chemisorption through an Avrami kinetic model. Film diffusion controlled the rate of BV10 biosorption onto AIGHS. The spontaneous and endothermic nature of sorption was corroborated by thermodynamic study. Continuous biosorption experiments were performed using a fixed-bed column and the influence of operating parameters was explored for different ranges of initial concentration 100–300 mg·L^{-1}, bed height 5–10 cm, and flow rate 2.5–4.5 ml·min^{-1}. A dose response model accurately described the fixed-bed biosorption data. An external mass transfer correlation was formulated explaining BV10-AIGHS sorption.

1. Introduction

Treatment of colour bearing effluents is a growing need at the present time. Chemical industries are extensively using more than 10000 synthetic dyes in their processes. Among the variety of dyes used, basic violet 10 was widely employed for acrylic, wool, nylon and silk dyeing because of its favourable characteristics of bright colour, high solubility in water and low-energy consumption [1]. This cationic dye decomposes into carcinogenic aromatic amines under anaerobic conditions; therefore discharge of effluents bearing this dye into water bodies can cause harmful effects such as allergic dermatitis, skin irritation, mutations and cancer [2–5]. Therefore, strict discharge standards are being enforced to control the release of coloured wastewater into the environment. Hence, there is an urgent need for development of effective methods for removal of dyes. Different physicochemical methods including coagulation [6], ozonation [7], chemical oxidation [8], solvent extraction [9], ion exchange [10], photo-catalytic degradation [11], and adsorption [12–14] have been tried by many researchers for the treatment of dye contaminated water. Among the aforementioned methods, adsorption is an effective and eco-friendly process due to its simple design, easy operation and its efficacy to remove a wide range of compounds [2,4,5,15,16]. Activated carbon is considered to be an effective adsorbent for removal of dyes from water. However, due to its cost, unconventional low-cost bio based adsorbents have attracted the attention of several investigators in recent years [3,4,15]. Our search for an efficient new biomass to treat BV10 drew attention to immature cotton seeds rejected by seed manufacturers. According to the USA agricultural data base, 85% of the world cotton production is shared by 10 countries, namely, China, USA, India, Pakistan, Uzbekistan, Brazil, Turkey, Australia, Greece and Syria. Among these, India is the third largest country which produced 5787 × 10^3 metric tonnes of un-ginned cotton in the 2012/2013 market year [17]. Immature cotton seeds unfit for germination and having poor oil content, are usually discarded as waste and only needs activation to transform them into cheap and high quality adsorbent. Although many agricultural and waste materials were used as biosorbents for the removal of colour, biosorbent derived from immature *Gossypium hirsutum* seed was never reported to the best of our knowledge. Design of the adsorption process requires insight into adsorption equilibrium, kinetics, rate limiting steps and the thermodynamics of adsorption which can be readily obtained from batch adsorption experiments. However, due to the limitations of batch processing, requiring treatment of small quantities of effluent and inconvenience for use on an industrial scale, continuous flow fixed-bed columns are often employed. The design of fixed-bed adsorption processes requires in-depth understanding of mass transfer and breakthrough curve dynamics in light of process modelling to facilitate scaling up of the processes.

The objective of this work was to investigate the suitability of immature *Gossypium hirsutum* seeds as a precursor for biosorbent and to examine the seeds' ability to take up of basic violet 10 from aqueous

* Corresponding author.
E-mail address: sivarajasekar@gmail.com (N. Sivarajasekar).

http://dx.doi.org/10.1016/j.cjche.2015.08.029
1004-9541/

solution *via* batch and continuous operation. Batch biosorption studies were carried out to analyse the effect of process parameters, isotherms and kinetics. The rate limiting step, thermodynamics and possible reaction mechanism of the biosorption were also examined. Fixed-bed column experiments were performed to investigate the effect of column parameters. The dynamic response of the fixed-bed column was explored *via* mathematical modelling and mass transfer correlations.

2. Materials and Methods

2.1. Chemicals

Basic violet 10 (also called Rhodamine B, molecular mass = 479.02, chemical formula $C_{28}H_{31}ClN_2O_3$ and $\lambda_{max} = 555$ nm) was obtained from S.D. Fine Chemicals Ltd, Mumbai. All other chemicals were obtained from Merck India Ltd, Mumbai.

2.2. Preparation of dye solution

Stock solutions were prepared by dissolving 1 g of BV10 in 1 L of deionised water. All working solutions were prepared by diluting the stock solution with deionised water to the desired concentration. Before addition of biosorbent, the initial pH of the working solution was adjusted to the desired experimental conditions by mixing appropriate quantities of 0.1 mol·L^{-1} HCl or 0.1 mol·L^{-1} NaOH solutions. The concentration of BV10 in the sample was analysed using a double beam UV–Vis spectrophotometer (ELICO-SL244, India) at a maximum wavelength of 555 nm.

2.3. Activated biomass preparation

Immature *Gossypium hirsutum* seeds were obtained from seed producers near Attur, Tamil Nadu, India. The seeds were washed thoroughly with deionised water twice to remove impurities and dried at 313 K in a temperature controlled oven for 3 days. The dried seeds were then soaked in concentrated sulphuric acid (98 wt%) with a mass ratio of 1:4. The acid soaked seeds were stirred periodically and kept for 12 h to facilitate effective activation. The resultant slurry was carefully washed with deionised water and 0.1 mol·L^{-1} sodium bicarbonate solution was used to remove traces of acid. The final material, activated immature *Gossypium hirsutum* seed (AIGHS) was dried at 313 K and finely ground to the size of 0.088 cm, and then stored in an airtight container for biosorption experiments.

2.4. Characterisation of AIGHS

Iodine number and methylene blue number were calculated based on the ASTM 4607-86 standards at 298 K. Specific surface area, pore volume and pore diameter were measured based on the adsorption–desorption isotherm of nitrogen at 77 K using a surface analyser (Micromeritics ASAP 2020) and the BJH method. Surface morphology was examined by using a scanning electron microscope (SEM: JSM-6390LV-JEOL Ltd., Japan). Surface functional groups were determined based on a Boehm titration method. A solid addition method was employed to determine the zero surface charge (pH_{pzc}). Fourier transmission infra-red (FTIR) analysis was performed using a Thermo Nicolet, Avatar 370 FTIR spectrometer over a spectral range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1}.

2.5. Batch biosorption

Batch biosorption experiments were conducted for the selected parameter ranges such as pH 2–12, temperature 293–313 K, initial concentration 200–600 mg·L^{-1} and contact time 1–5 h. A known amount of biosorbent was added to 200 ml of BV10 solution in Erlenmeyer flasks and agitated at 100 r·min^{-1} by a thermo-regulated shaker. Samples were collected at predetermined time intervals and were centrifuged and analysed for the residual dye concentration using a dual beam UV–Vis spectrophotometer. The percentage of dye removal (R/%) and the dye biosorption capacity (q_t/mg·g^{-1}) were calculated using the following equation:

$$R = \frac{C_i - C_0}{C_i} \times 100 \tag{1}$$

$$q_t = (C_i - C_t) \times \frac{V}{M} \tag{2}$$

where C_i (mg·L^{-1}) is the initial concentration of the dye, C_0 (mg·L^{-1}) is the final concentration of the dye, C_t (mg·L^{-1}) is the concentration of BV10 at any time t, V (L) is the volume of the dye solution, and M (g) is the mass of the AIGHS. Desorption studies were carried out using different solvents such as hot deionised water, 2 mol·L^{-1} sulphuric acid and 2 mol·L^{-1} acetic acid.

2.6. Column biosorption

The fixed-bed columns were made of PVC tubes with 1.5 cm internal diameter and with different heights (5–10 cm). AIGHS was loaded into columns containing glass beads and sieve plates fixed at the top and bottom to enhance uniform inlet flow. Initially, the columns were flushed out with deionised water for 24 h to remove air bubbles and then the bed porosity was measured using tracer experiments. The BV10 solution was pumped into the columns in a downward-flow mode. All of the column experiments were carried out in the ranges of 100–300 mg·L^{-1}, 2.5–4.5 ml·min^{-1}, pH 6.8 ± 0.5 and room temperature (301 ± 2) K. Following Eqs. (3)–(5) were utilised to evaluate the fixed-bed column parameters.

$$z_m = H\left(1 - \frac{t_b}{t_e}\right) \tag{3}$$

$$m_{ad} = \frac{C_i Q t}{1000} \tag{4}$$

$$R_c = \frac{Q}{m_{ad} \times 1000} \int_{t=0}^{t=t} C_t \times 100 \tag{5}$$

where Z_m (cm) is the length of the mass transfer zone, m_{ad} (mg) is the amount of BV10 sent into the column, R_c (%) is the BV10 removal percentage in the fixed-bed, t_b (min) is the breakthrough time, t_e (min) is the bed exhaustion time, H (cm) is the height of the column and Q is the volumetric flow rate (ml·min^{-1}).

2.7. Nonlinear regression analysis

Nonlinear regression analysis was preferred wherever required to determine the parameters of the equations due to its versatility and its accuracy for equations containing more than two parameters [17,18]. The error functions such as ERRSQ, HYBRID, MPSD, ARE, and EABS were selected for nonlinear regression analysis. Statistical-comparison values, such as the coefficient of determination (R^2) and root mean square error (RMSE), were utilised to gauge the goodness of the fit. For a meaningful comparison between parameter sets produced by these five different errors, a 'Sum of the Normalised Errors' (SNE) procedure was adopted [17–19]. High values of R^2 and small values of RMSE are the criteria to choose the best fit [17,18].