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Biosorption studies of Cu(II) onto Mansonia sawdust: Process design to minimize biosorbent dose and contact time

Augustine E. Ofomaja *

Department of Chemistry, Vaal University of Technology, P. Bag X021, Vanderbijlpark 1900, South Africa

A R T I C L E I N F O

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The aim of this paper is to examine the various operating processes and determine the overall biosorption rate and how each of the processes influences biosorption. The results revealed that external mass transfer, film diffusion and ion exchange were predominant at the initial 5 min of biosorption and their rate constants were measured. The pseudo-second order model rate constants were determined and the relationship between these constants and the biosorption performance such as the approaching equilibrium factor, R_w, the rate factor k_2q_e, the biosorption half-life ($t^{0.5}$) and the operating time (t_x) were determined. The pore and film diffusion coefficients decreased with increasing copper(II) concentration. The values of initial biosorption factor, R_i, for the biosorption process showed that for all initial copper(II) concentrations, initial biosorption was faster than intraparticle diffusion. The activation energies, enthalpies, entropies and free energies for each of the operating processes were determined and the results showed that film diffusion had the highest activation energy and may be the overall rate limiting step. Mathematical models for the optimization of multistage process for minimum biosorbent mass and contact time were also developed.

1. Introduction

There has been an increase in the demand for water treatment as well as reclamation and reuse of wastewater in recent times. This has lead to significant research activities in the area of biosorption which has been viewed as a promising alternative to some wastewater treatment technologies because of its simplicity, cost and possibility of regeneration and reuse [1,2].

To achieve effective design and scale-up procedures, a good theoretical understanding of both thermodynamics and kinetics of metal biosorption processes are required. For example, biosorption kinetics alone is insufficient to predict the overall rate of metal biosorption during the biosorption process, since biosorption onto a porous biosorbent solid can be described by (i) external mass transport, (ii) intraparticle diffusion and (iii) biosorption at the interior site. In biosorption systems, the mass transfer of metal ions onto and within the biosorbent particles directly affects biosorption rate. Therefore in the determination of the overall biosorption rate these processes most be taken into account.

Bulut and Tez [3] studied the biosorption of lead(II), cadmium(II) and nickel(II) ions from aqueous solutions by walnut sawdust. The authors concluded that metal biosorption followed two sections according to the intraparticle diffusion plots, indicating transport of metal ions from bulk solution to sawdust surface and into pores in the sawdust particles, as well surface biosorption are responsible for metal uptake from solution. They also suggested that because of the deviation from the origin of the straight line of the second section of the intraparticle diffusion curve, intraparticle diffusion is not the only rate limiting step and that the pseudo-second order kinetic model plots which give a straight line with a high correlation coefficient may be rate-determining. Semerjian [4] studying the removal of cadmium ions from aqueous solution using untreated *Pinus halepensis* sawdust observed that although the pseudo-second order model described the biosorption process for the whole biosorption period, intraparticle process was active in the rate-determining step especially in the second stage of the biosorption process. Li et al. [5] studied the biosorption of lead(II), chromium(III) and copper(II) by sawdust and modified peanut husk, the authors concluded that intraparticle diffusion was not rate controlling since the plot of amount biosorbed, q_t, versus square root of time, $t^{0.5}$, did not pass through the origin. But rather the pseudo-second order model which gave a straight line plot with high correlation coefficient, r^2, is rate controlling. In each of the above studies the authors agreed that ion-exchange mechanism is present and important in each of the biosorption processes.

These conclusions cannot be used to make accurate predictions about the mechanism and overall rate-determining steps of biosorption processes. The overall rates and mechanism can best be

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* Present address: Center of Material and Process Synthesis (COMPS), Department of Chemical Engineering, School of Chemical and Metallurgical Engineering, The University of the Witwatersrand, Johannesburg, South Africa. Tel.: +27 738126830/+2348029815034.

E-mail addresses: aus_ofomaja@yahoo.com, augustine@vut.ac.za, Augustine.Ofomaja@wits.ac.za

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ascertained by comparing results from both thermodynamics and kinetic data. Therefore, in this study, the overall biosorption rate of copper(II) ions onto Mansonia wood sawdust will be determined from kinetic data of the effect of copper(II) concentration and reaction temperature. Kinetic models such as pseudo-first and second, ion exchange and diffusion models such as intraparticle and external mass transfer will be used in the kinetic data analysis and parameters such as activation energies, free energies, enthalpy and entropy of these processes analyzed and based on these results an overall rate will be determined. Parameters of the pseudo-second order model which relates to biosorbent performance such as the R_w factor, the rate parameter k_2q_e and operating time, t_x, which are useful tools for scale up design will also be examined. Finally, the minimum biosorbent dose and contact time for a multi-stage optimized biosorption will also be reported. These results will be useful for the design and use of an biosorption system for copper(II) biosorption onto Mansonia sawdust.

2. Materials and methods

2.1. Materials

Mansonia sawdust used was obtained from a local sawmill in Benin City, Edo State of Nigeria. The sawdust was washed several times with distilled water to remove surface impurities, and this was followed by drying at 100 °C for 24 h. The sawdust was ground and sieved. Sawdust particles used was that retained between the set of sieves: 150–400 μm. The sieved sawdust was then stored in an airtight container.

Copper(II) nitrate ($Cu(NO_3)_2$) salt was used in the preparation of the salt solution. Stock solution of 1000 mg/dm^3 was prepared by dissolving the accurately weighed amounts of $Cu(NO_3)_2$ in 1000 ml distilled water. The experimental solution was prepared by diluting the stock solution with distilled water when necessary.

2.2. Methods

2.2.1. Iodine number

In this experiment, 25 ml of iodine solution of 0.05 mol dm^{-3} was added to eight flasks, which contained different amounts of Mansonia sawdust ranging from 0.031 to 0.500 g. The flasks were then shaken for 24 h to ensure equilibrium adsorption of iodine onto Mansonia sawdust. The iodine number (mg g^{-1}) (or adsorption capacity) was determined from the titration of the residual solution of 10 ml with 0.1 mol dm^{-3} sodium thiosulfate in the presence of 1 ml of 1 wt.% starch solution as an indicator. The iodine adsorption capacity was determined from the adsorbed iodine/unit mass of the adsorbent at the residual iodine concentration.

2.2.2. Effect of initial metal ion concentration

Batch biosorption experiments were conducted with different initial copper(II) concentrations from 60 to 140 mg/dm^3 respectively at a fixed time of contact, 90 min at pH 5.0 and Mansonia sawdust dose of 2.0 g dm^{-3} in 100 ml solution. Agitation was done at 200 rpm and temperature was maintained at 299 K. A portion of the sample was collected at regular intervals and centrifuged. Equilibrium concentration of copper(II) was determined by atomic absorption spectrophotometer.

2.2.3. Effect of biosorption temperature

Batch biosorption experiments were carried out by varying the temperatures (299, 309, 319 and 329 K) using 100 ml of 140 mg/dm^3 of copper(II) solutions respectively in contact with 0.2 g of Mansonia sawdust at a fixed time of contact, 90 min at pH 5. Agitation was done at 200 rpm and temperature was maintained at 299 K. A portion of the sample was collected at regular intervals and centrifuged. Equilibrium concentration of copper(II) was determined by atomic absorption spectrophotometer.

3. Result and discussion

3.1. Effect of initial copper(II) concentration on biosorption kinetics

3.1.1. Theory

In the case of sorption preceded by diffusion through a boundary, the kinetics most likely follows the pseudo-first-order equation of Lagergren [6]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{1}$$

where q_t and q_e are the amount sorbed at time t and at equilibrium and k_1 is the rate constant of the pseudo-first-order kinetic model. Plots of log $(q_e - q_t)$ versus t gives a straight line for pseudo-first-order kinetics, which allows computation of the biosorption rate constant, k_1 and the equilibrium capacity, q_e.

The pseudo-second-order chemisorption kinetics may be expressed as [7]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2}$$

and Eq. (2) integrated and rearranged to give Eq. (3) below:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t \tag{3}$$

On rearrangement Eq. (3) gives

$$q_t = \frac{k_2q_e^2t}{1 + k_2q_et} \tag{4}$$

were the initial sorption rate h, can be represented by

$$h = k_2q_e^2 \tag{5}$$

the constant can be determined experimentally by plotting of t/q_t against t.

The effect of initial copper(II) concentration, C_0, on the biosorption of copper(II) onto Mansonia sawdust surface was studied. The kinetic data obtained were plotted using both the pseudo-first and pseudo-second order kinetic models and the kinetic parameters were calculated and given in Table 1. Fig. 1 shows the plot of the experimental data of the amount of copper(II) ions biosorbed per unit mass of Mansonia sawdust against time along with the model values from the pseudo-first and pseudo-second order model. From Fig. 1 it will be observed that both model lines were quite close to the experimental data at the initial biosorption period. After the first 5 min of biosorption the model lines of the pseudo-first order kinetic model deviated substantially from the experimental points. The observed deviation from the experimental data has been attributed to the sharp fall in concentration gradient after the initial rapid uptake of copper(II) ions at the onset of the biosorption process due to large amount of vacant site for biosorption [1,8] Within this time period, it is believed that there is a switch between mass transfer diffusion control and pore diffusion control [1,8]. The pseudo-second order kinetic model lines on the order hand were found to be close to the experimental data all through the biosorption period.

The correlation coefficients, r^2, values for the biosorption process were higher for the pseudo-second order kinetic model than for the pseudo-first order model as can be seen in Table 1. The equilibrium capacity values for the pseudo-second order model were higher than for the pseudo-first order kinetic models and