Kinetic model for the immobilised biosorbents: Uptake of cationic dyes

Nityanand Singh Maurya [a], Atul Kumar Mittal [b],*

[a] Department of Civil Engineering, National Institute of Technology Patna, 800 005, India
[b] Department of Civil Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110 016, India

HIGHLIGHTS

- A kinetic model has been developed using the concept of Chemically Active Available Binding Sites.
- It has been validated using immobilized F. carnea in polyvinyl alcohol (PVA) matrix and two cationic dyes.
- It is compared with first order kinetic, Pore diffusion, single resistance and pseudo second order kinetic models.
- Effect of temperature, mixing speed and sorbent dose has shown applicability of the model.

ARTICLE INFO

ABSTRACT

A sorption kinetic model has been developed using concept of Chemically Active Available Binding Sites (CAABS). Dead "*Fomitopsis carnea*" immobilized on polyvinyl alcohol (PVA) matrix has been employed as the immobilized sorbent. Safranin O and Alcian Blue are the representative sorbates. Results indicate that CAABS model described the kinetics with high degree of correlation coefficient ($R^2 \geqslant 0.99$) for under different environmental conditions, viz., mixing speed (60, 200 and 500 revolutions per minutes), and biosorbent doses. Student's t-test also revealed that the predicted data using Chemically Active Available Binding Sites (CAABS) model were significantly correlated with the experimental data. The CAABS model was also compared with well known kinetic models such as Lagergren's model (first order kinetic model), Single resistance model, Pore diffusion model, and Pseudo-second order kinetic model. The comparative study of these models also confirmed high efficacy of the CAABS model to depict the experimental data.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Biosorption of inorganic [1–4] and organic species [5–7] has been extensively reported in the literature. However, field application of the biosorptive processes remained very limited. It may be due to poor engineering properties of the biosorbents. Immobilisation process has been quoted to improve the improve engineering properties of virgin biomass [8].

To design and/or to evaluation a biosorption system, suitable sorption kinetic model is warranted, which could simulate actual biosorption kinetics efficiently. Therefore, various sorption kinetic models have been proposed, i.e., Lagergrn's model (first order kinetic model) [9], Single resistance model [10,11], Pore diffusion model [12] and Pseudo-second order model [13]. These models were developed for metal surfaces, different types of coals and activated carbons. Physical and chemical characteristics of a biosorbent differ from the activated carbon. Surface of a biosorbent generally consists of biopolymers studded with a number of complex functional groups. Many researchers have indicated that the biosorptive processes involve chemical complexation, ion exchange, covalent and hydrogen bonds, and physio-sorption, besides involving oxidation–reduction and micro precipitation etc. The kinetic model proposed by Mittal [14] is based on virgin biomass without considering immobilization process. Immobilisation of a biomass may affect the surface of the biosorbent and its morphology. There is no study available in the literature which has specifically developed a sorption kinetic model for the immobilized biosorbent.

This paper reports a sorption kinetic model which is based on the basic principles of chemi-sorption and physi-sorption. Data generated from sorption kinetic experiments, employing immobilized biomass of a dead macro fungus namely "*Fomitopsis carnea*" in polyvinyl alcohol (PVA) matrix as a biosorbent and two cationic dyes namely Safranin O and Alcian Blue as sorbate under various environmental conditions viz., mixing speed and bisorbent dose, have been used to validate the developed kinetic model.

* Corresponding author. Tel.: +91 11 25691239.
  E-mail addresses: nsmaurya@nitp.ac.in (N.S. Maurya), akmittal@civil.iitd.ac.in (A.K. Mittal).

Glossary

CAABS	Chemically Active Available Binding Sites	N_t	Number of Chemically Active Available Binding Sites, CAABS present on the surface of the biosorbent
Q_e	Quantity of dye transferred (mg g^{-1}) onto the biosorbent at equilibrium condition	Kpm	Kinetic coefficient, (L g^{-1} h^{-1})
M	Dose of the biosorbent (g L^{-1})	$K_{pm\ max}$	Maximum possible mass transfer rate per unit time per unit weight of the biosorbent
C_0	Initial liquid phase concentration (mg L^{-1}) of the sorbate	E	Model constant related to the mixing speed
C_e	Liquid phase concentration (mg L^{-1}) of the sorbate (dye) at equilibrium,	F	Model constant related to the dose of the biosorbent
C_t	Sorbate concentration (mg L^{-1}) in bulk solution at time t	N	Mixing speed in rpm
Q_t	Solid phase concentration (mg g^{-1}) of the dye (sorbate) at time t	$K_{pm\ min}$	Minimum possible mass transfer rate coefficient per unit time per unit weight of biosorbent

2. Materials and methods

2.1. Biosorbent preparation

Dried powdered biomass of *F. carnea* – a macro fungus, was immobilized as per the method described elsewhere [15,16]. 5.0 g PVA (average molecular weight 89,000–98,000, Aldrich, USA) was dissolved in 50 mL distilled water at 80 ± 2 °C. After 16 h of stirring, pre-determined powder biomass was added to the cooled PVA solution. The completely mixed solution of PVA and biomass was extruded in the liquid nitrogen. As soon as solution drop came in contact with liquid nitrogen, instantly bead was formed. Beads were kept in liquid nitrogen overnight, and then were frozen and thawed for four cycles. Beads were kept at 40 ± 2 °C till the difference in weight between two consecutive days became negligible.

2.2. Sorbate

Cationic dye namely Safranin O (Basic Red 2, CI 50240) and Alcian Blue (C.I. No. 74240) were used as sorbate. Aqueous solution having dye concentration of 100 mg/L were used in all the experiments.

2.3. Batch biosorption kinetic experiments

Kinetic experiments were carried out in an acrylic vessel having 140.0 mm internal diameter and 180.0 mm height as described elsewhere [17]. At predetermined time intervals, samples were withdrawn from the adsorber and were analysed for residual dye concentration. Mass of dye transferred from the aqueous phase to the sorbent was determined by applying the mass balance on the reaction vessel as follows:

$$Q_e{}^*M = (C_0 - C_e) \tag{1}$$

$$\text{or } Q_e = (C_0 - C_e)/M \tag{2}$$

where Q_e is quantity of sorbate transferred (mg g^{-1}) onto the biosorbent (or solid phase sorbate concentration) at equilibrium condition, C_0 and C_e are initial and equilibrium liquid phase sorbate concentration (mg L^{-1}) respectively and M is dose of the biosorbent (g L^{-1}).

2.3.1. Effect of mixing speed

A number of kinetic experiments were undertaken at various mixing speeds, i.e., 60, 200 and 500 rpm. Biosorbent doses were 1.05 and 5.00 g L^{-1} for Safranin O and for Alcian Blue respectively.

2.3.2. Effect of dose

Biosorbent doses were 0.50, 1.05, 1.50 g L^{-1} for Safranin O and 2.00, 5.00, 9.24 g L^{-1} for Alcian Blue. Mixing speed in all these experiments was 500 rpm.

3. Model development

Biosorption could be considered as a result of unbalance forces acting upon the sorbate molecule. The unbalance forces may arise due to (1) liquid phase concentration gradient at the time of equilibrium, and (2) presence of Chemically Active Available Binding Sites (CAABS) on the outer surface of immobilised biomass and within the pores (micro and macro) of the biosorbent. Finally, the attachment of the sorbate occurs at these Chemically Active Sites (CAABS). So, biosorption rate for a specific sorbatan can be considered as a combined effect of the concentration gradient and CAABS. Graphically, this concept is presented in Fig. 1.

The total dye uptake by the sorbent can be considered as a result of (1) physi-sorption which is a function of liquid phase concentration gradient of the sorbate, and (2) chemi-sorption which is assumed to be the function of CAABS. Surface of the immobilised biosorbent can be considered as studded with CAABS, graphically shown in Fig. 1. Chemi-sorption including chemical complexation, ion exchange, electrical forces, and different types of chemical bonding occurs at the CAABS.

3.1. Physi-sorption

Rate of change in concentration of the sorbate on the solid phase (biosorbent) is directly proportional to the liquid phase concentration difference, which is assumed as the first order reaction. Mathematically, it can be represented as follows:
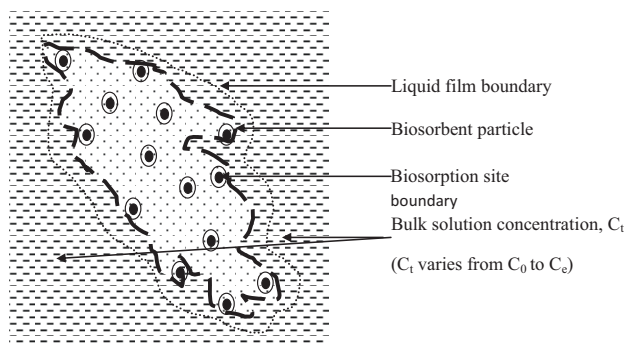

Fig. 1. Conceptual diagram for sorbate transport and attachment on to the sorbent particle.