Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2017, 9(5):289-293

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Accurate Breakthrough Curve Prediction of Hexavalent Chromium Biosorption Using a Deactivation Based Reaction Model

Masoud Samadi*

Faculty of Chemical, Petroleum and Gas Engineering, Hakim Sabzevari University, Sabzevar, Iran

---

ABSTRACT

A modeling approach for prediction of the breakthrough curve in adsorption of hexavalent chromium on sawdust in a fixed bed column is presented. The model was introduced by Zhang and Cheng and benefit from geometrical dimensions of the bed that is useful if an industrial scale up will be needed. Validation with experimental data and a comparison with well-known Thomas model, the pore diffusion and the solid diffusion models were performed. The results showed that Zhang and Cheng model has better output than Thomas and the pore diffusion models and almost near to the solid diffusion model.

Keywords: Fixed bed reactor; Chromium; Adsorption model; Breakthrough; Sawdust

---

INTRODUCTION

Finding a model with appropriate assumptions to describe the manner of a system or a process is an important step in each scientific research. Breakthrough curve is a graph which shows the dynamic variation of outlet concentration with respect to time in a continuous adsorption column. When the effluent flow concentration reaches to the inlet concentration, it means the adsorption column is saturated and no more adsorption is happening. Breakthrough time (the time of stopping the operation in industry) is usually applied for a time that effluent concentration becomes about 5 to 10% of the influent concentration, or depending to its process something about these limitations. Trivalent chromium is essential to mammalian systems, while hexavalent chromium [Cr (VI)] is more toxic than the trivalent form [1]. In this paper, adsorption modeling of Cr (VI) has been considered. With growing technology progressions and industrialization, Cr (VI) is continuously liberated into the environment and makes a serious threat to community because of its toxicity, collects in the food chain and perseveres in nature [2]. In many compounds that have vast industrial applications and used in different industries Cr (VI) is present. Such as rubber, glass, ceramics, fertilizers, fungicides, mining, tanning, metallurgical, dyes and pigments, film and photography [3], etc. Concentration of Cr (VI) present in industrial effluent streams are in the range of 50-200 mg L^{-1}, and the allowed limit of Cr (VI) in potable water is 0.05 mgL^{-1} [4]. In order to obey from the permissible limit, it is necessary that industries treat their effluents to decrease the Cr (VI) concentration in water and wastewater to the tolerable levels before its disposal into the environment. The removal of chromium from wastewaters is mostly achieved by methods such as filtration, chemical precipitation, adsorption, ion exchange, evaporative recovery and electrodeposition [1]. Adsorption is proved to be an efficient and cost effective method for the elimination of Cr (VI). Recently, biosorption has emerged as a treatment technology alternative to the conventionally used ones for pollution control [5]. Different low cost natural and waste materials have received growing attention among the environmental communities as an innovative and economical technology in removing chromium instead of the costly conventional methods. Lignocellulosic materials, including both wood residues and agricultural residues, have desired chromium sorption capacity comparable to that of other natural or waste sorbents, as well as, they have the advantage of a very low or no cost at all, great availability and simple operational process [6]. The adsorption study of Cr (VI) from

aqueous solutions on sawdust was carried out by few researchers. Gupta and Babu [4], Memon et al. [7], Gode et al. [8], and Yu et al. [9] performed some experiments and showed the ability of sawdust in adsorption of chromium. The breakthrough time and the shape of the breakthrough curve are important characteristics for determining the operation and the dynamics of a column. Mathematical models for this purpose which are frequently used in literatures are usually, Thomas model, Bohart and Adams or BDST (bed depth service time) model, Yoon and Nelson model and Clark model which among these models Thomas model has been more applied. All of these models are derived from mass balance (continuity) equation and a kinetic equation along with an isotherm model such as Langmuir or Freundlich isotherms. Above models are discussed and investigated clearly with their basis and consumption in [6,10]. Zhang and Cheng [11] proposed a model to describe the removal of cyanogen chloride (CNCL) from a gas stream passing through a bed packed with activated carbon impregnated with copper, chromium and silver. The model is based on the assumption that the uptake process follows two independent approaches: physical adsorption of CNCL by activated carbon and a first-order catalytic deactivation reaction of the toxic gas. The term of catalytic deactivation in this model is new rather than other mentioned models. So, the present paper aims to explore the applicability of this model for the simulation and prediction of experimental biosorption breakthrough curves in comparison with well-known Thomas model and pore diffusion and solid diffusion models which Gupta and Babu [4] used in their research article for modeling of Cr (VI) adsorption on sawdust. Experimental data are also extracted from [4].

EXPERIMENTAL SECTION

Mathematical Model

Zhang and Cheng:

Zhang and Cheng proposed a model on the basis of the catalytic hydrolysis reaction of cyanogen chloride in a fixed carbon bed adsorber. Here, this model will be examined in the application of Cr (VI) adsorption on sawdust. It was assumed that physical adsorption and catalytic self-deactivation reaction occurred at the same time. The active sites of adsorbent are covered by reaction products. A first-order deactivation reaction is assumed and the deactivation rate equation is:

$$\frac{\partial \emptyset}{\partial t} = K_d . \emptyset \quad (1)$$

Where, t, is time (min), $\emptyset$ is the deactivation function (dimensionless), and K_d (min^{-1}) is the deactivation rate constant. Given the initial condition, when t = 0, then $\emptyset$ = 1, and taking the derivative, Eq. (2) is obtained for the deactivation function. The solution below is true for separable deactivation kinetics resulting from contact with a catalyst poison at a constant inlet concentration and no spatial variation [12].

$$\emptyset = e^{-K_d t} \quad (2)$$

The chemical reaction obeys a first-order reaction as Eq. (3).

$$R = K . C . \emptyset = K . C . e^{-K_d t} \quad (3)$$

Where, R is the reaction rate, K is the reaction rate constant (min^{-1}), C is the adsorbate concentration in the stream (mg/kg). Assuming an ideal plug flow with no axial dispersion for bed dynamics and isothermal conditions, then the superficial fluid velocity is kept constant and the continuity equation of the fixed bed adsorber is as follow:

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x} + \frac{1-\varepsilon}{\varepsilon}\rho\frac{\partial q}{\partial t} + R = 0 \quad (4)$$

Where, u, is superficial velocity (cm/min), x, is the distance from the bed inlet (cm), ε is bed porosity (dimensionless), q is the adsorbate concentration in the carbon (mg adsorbate/mg sawdust), and ρ is the bulk density of the sawdust (gr/cm^3). The physical adsorption is described by a linear isotherm as at small concentrations, the Langmuir isotherm is linear [12].

$$q = K_i . C \quad (5)$$

Derivation with respect to time gives Eq. (6).

$$\frac{\partial q}{\partial t} = K_i \frac{\partial C}{\partial t} \quad (6)$$

Where, K_i, is the adsorption constant in (kg flow/mg sawdust). Using the streamline method and the boundary conditions of at, x = 0, t > 0, C = C_0 and at, t = 0, x > 0, C = 0 the following solution of the partial differential Eq. (4) was done by Zhang and Cheng.

$$lnln\frac{C_0}{C} = ln\frac{K}{[1+\frac{K_i\rho(1-\varepsilon)}{\varepsilon}]K_d} - K_d t + \ln(e^{\frac{K_d L\left[1+\frac{K_i\rho(1-\varepsilon)}{\varepsilon}\right]}{u}} - 1) \quad (7)$$

The above equation can be linearized and written also as:

$$lnln\frac{C_0}{C} = a - K_d t \quad (8)$$

Where

$$a = ln\frac{K}{\propto K_d} + \ln(e^{\frac{K_d \propto L}{u}} - 1) \quad (9)$$

And

$$\propto = 1 + \frac{K_i \rho (1-\varepsilon)}{\varepsilon} \quad (10)$$

Where, L is the length of the bed. If the model works properly, it will be expected that a linear relationship by plotting [LnLn (C_0/C)] versus (t), fit the experimental data. It worked as shown in Figure 1 and from this method, a, K_d and K will be determined. The value of K_i that is the Langmuir isotherm adsorption constant must be specified from saturation adsorption capacity and equilibrium concentration; Gupta and Babu [4] determined it 0.43 mL/mg for this case.

Other Models:

Thomas model is discussed and investigated clearly with its basis and consumptions in [10,11] and pore diffusion and solid diffusion models are explained in detail in [4]. For conciseness, only the breakthrough curves which are generated from these models are shown and compared with Zhang and Cheng model.

RESULTS AND DISCUSSION

Model Investigation

Figure 1 shows that lnln (C_0/C) has a linear relationship with respect to time and this fact proves that Zhang and Cheng model can properly comply with experimental data. Comparison among different models is illustrated in Figure 2. It is clearly seen that Thomas model and the pore diffusion model have not precision of Zhang and Solid diffusion models. If the breakthrough curve in Figure 2, divide into two regions, i.e., low and high concentration zones, it will be deduced that Zhang and solid diffusion models have similar trending in the low concentration region but different in the high concentration zone, or, it can be said that Zhang model comply better in the second half of the breakthrough curve and totally in both zones and Zhang and Cheng model is more suitable for explaining the dynamic behavior of breakthrough curve. Beside this, working with Zhang model is easier than solving solid diffusion model equations and as well as because of applying some dimensions such as length and flow rate, Zhang and Cheng model can be an appropriate model for scale-up purpose. This indicates that the Zhang and Cheng model has the correct mechanisms included in the governing equations to represent the adsorption behavior of Cr (VI) on sawdust. Parameters in modeling for Figure 2 are summarized in Table 1 and Figure 3. Shows prediction for changing at the inlet flow rate just by changing the number of flow rate in Zhang model without varying other parameters which were tuned for Q=15 ml min^{-1}, and the result showed an acceptable trend in comparison with experimental data.

Table 1: Summary of Zhang-Cheng model and column parameters related to figure 2

K_i (mL/mg)	0.43
K_d (min^{-1})	0.0032
K (min^{-1})	15.5
Flow rate (mL/min)	10
Length (cm)	14.2
Cross section area (cm^2)	1.76
Porosity	0.254
C_0 (mg/L)	50

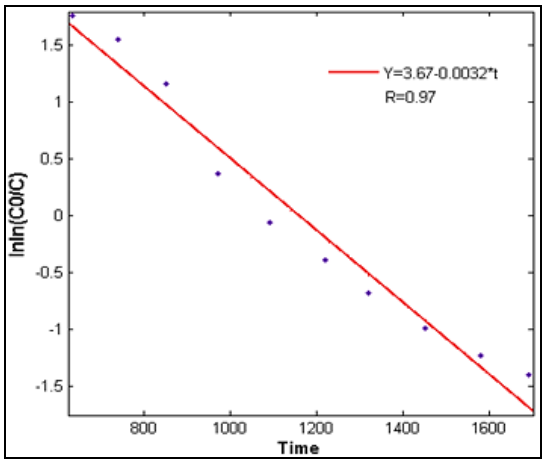

Figure 1: Experimental data fitting for determining of (k_d) and (a) in equation 8

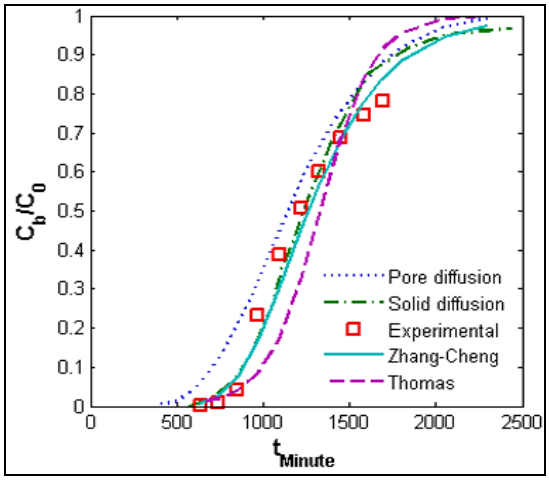

Figure 2: Comparison between experimental breakthrough curve and different models.(Q=10 mL min^{-1}, L=14.2 cm and C_0=50 mg L^{-1})

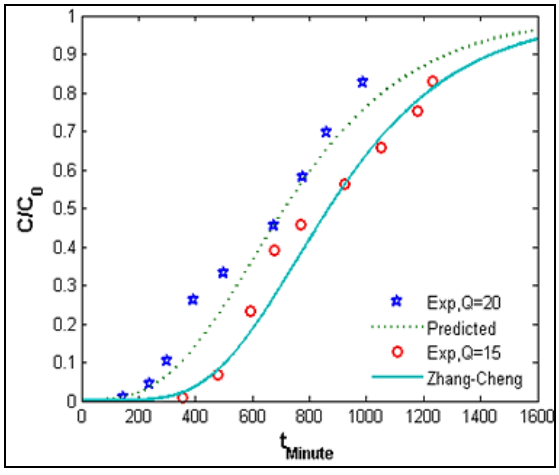

Figure 3: Prediction of inlet flow rate varying on breakthrough curve

CONCLUSION

A simplified modelling approach to simulate the operation of a fixed bed biosorption column has been presented and validated with data from selected cases reported in the literature. This study has analyzed and compared the capabilities and limitations of four methods for the modeling of breakthrough curves of Cr (VI) adsorption on sawdust. Results showed that the Zhang-Cheng model, obeying the Lungmuir isotherm has the best affinity to the experimental data and its performance depends on the tuning of its parameters. The solid diffusion model is acceptable too, but working with Zhang and Cheng model is more comfortable than the solid diffusion model. The concept of the Thomas model is not suitable for chromium adsorption pattern on sawdust. On the other hand, the consumptions of Zhang –Cheng model such as a first-order deactivation reaction and a first-order reaction rate model are compatible with the Cr (VI) adsorption. From the Zhang and Cheng model it was deduced that, if the ratio of length to superficial velocity stay constant, it will be possible to select scale up length, flow rate and cross section with similar breakthrough curve pattern to the desired one for industrial purposes. It is also possible to see the effect of varying of length and flow rate on breakthrough curve shape using Zhang-Cheng model.

REFERENCES

[1] YX Li; Y Wang; FJ Zhao. *Biotechnol Biotech Eq*. **2015**, 29, 498-505.
[2] SS Ahluwalia. *Int J Current Microbiol Appl Sci*. **2014**, 3, 383-398.
[3] Y Wang; Y Li; FJ Zhao. *Biotechnol Biotech Eq*. **2014**, 28, 259-265.
[4] S Gupta; BV Babu. *Bioresource Technol*. **2009**, 100, 5633-5640.
[5] U Farooq; M Athar; MA Khan; JA Kozinski. *Environ Monit Assess*. **2013**, 185, 845-854.
[6] L Tofan; C Paduraru; C Teodosiu; O Toma. *Celloluse Chem Technol*. **2015**, 49, 219-229.
[7] SQ Memon; MI Bhanger; MY Khuhawar. *Anal Bioanalytical Chem*. **2005**, 383, 619-624.
[8] F Gode; ED Atalay; E Pehlivan. *J Hazardous Mat*. **2008**, 152, 1201-1207.
[9] LJ Yu; SS Shukla; KL Dorris; A Shukla; JL Margrave. *J Hazardous Mat*. **2003**, 100, 53-63
[10] Z Xu; JG Cai; BC Pan. *J Zhejiang U Sci A*. **2013**, 14, 155-176.
[11] H Zhang; D Cheng. *Carbon*. **2000**, 38, 877-880.
[12] HS Fogler. Elem chem eng, 3rd Edition Prentice-Hall Inc, Englewood Cliffs, **2004**, 450-451.