Proceedings of the World Congress on Engineering and Computer Science 2007
WCECS 2007, October 24-26, 2007, San Francisco, USA

The Study of Adsorption Breakthrough Curves of Cr(VI) on Bagasse Fly Ash (BFA)

Chandra W. Purnomo, and Agus Prasetya

Abstract— **The breakthrough curves of Cr(VI) on bagasse fly ash (BFA) at room temperature were measured in a fixed-bed apparatus. It has been tried to fit the experimental data to fixed-bed model for breakthrough curve. Then. the effective diffusivity of hexavalent chrome ion was obtained. The effective diffusivity can be used to predict breakthrough curves at other adsorption conditions. The material characterizations have been conducted before the adsorption experiments.**

Index Terms— **Adsorption model, Breakthrough curve, Effective diffusivity.**

I. Introduction

In developing countries, the heavy metal contained wastewaters have been produced by electroplating and leather tanning industries, which are mostly categorized as small and medium scale industries. Unfortunately, these small scale industries in the region have a lack of capital for installing an appropriate wastewater treatment unit. This condition led the industries to release their waste directly without any pretreatment to the environment.

In the case of Indonesia, on the other hand there are many sugar cane plant which produce bagasse fly ash (BFA) in a huge amount annually. Considering such an abundantly available solid waste, thus the usage of fly ash for heavy-metal contained wastewater treatment will create multiple benefits. The fly ash adsorption will be low cost method, which maybe economically affordable to be applied in small and medium scale industries of Indonesia.

Research on fly ash application for heavy metal removal from wastewater has been carried out widely [1-4]. There are also numbers of other technologies available for removing heavy metal ions from industrial wastewater, among them is adsorption process which is found to be an effective method. Investigations on heavy metals ions adsorption by various type of adsorbent have been carried out [5-6].

Although a number of studies as mentioned above have been performed, fundamental studies on adsorption kinetics were rarely undertaken thoroughly. Understanding the characteristic and capacity of adsorption through breakthrough curve will enable us to better design continuous wastewater treatment units. In this paper, breakthrough curves of hexavalent chrome ions (Cr(VI)) into BFA is studied and simulated.

Manuscript received July 20, 2007. This work was supported by Japan International Cooperation Agency (JICA) through Hi-Link Research Grant.

C. W. Purnomo and A. Prasetya are with Department of Chemical Engineering, Gadjah Mada University, Grafika Street no.2 Yogyakarta 55281 Indonesia. (phone: 62 274 902171; fax: 62 274 902170; e-mail: chandra@ chemeng.ugm.ac.id).

II. Experimental

A. Material

Fly ash used in the present study was bagasse fly ash generated from a furnace unit of PT. Madukismo, a nearby local sugar cane industry located in the city of Yogyakarta, Indonesia. The bulk fly ash was washed by distilled water to remove surface dust and then had been oven dried at 120^{o}C for 3 hours. Dry flyash was then sieved. The fly ash of the size range from 20 mesh to 30 mesh was collected and activated by putting it into 10 ml solution of 3 N HCl per gram dry-flyash under thorough mixing for 2 hrs. The flyash was then filtered, washed by distilled water and oven dried at 120^{o}C for 3 hours.

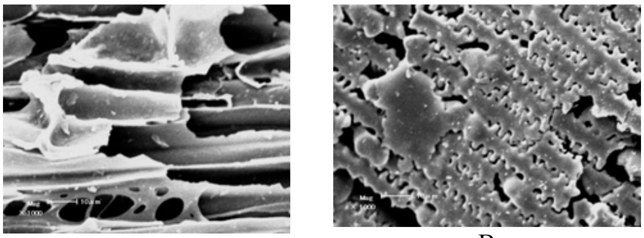
The composition of each material has been measured by X-ray Fluorescence (XRF), for non activated and activated BFA. The table below summarized all the composition data obtained for BFA before activation.

Table 1. Composition of BFA from XRF analysis

Element	% weight
SiO_2	49.98
Al_2O_3	2.2
CaO	2.78
MgO	1.645
FeO	1.218
K2O	3.97
Carbon	36.5

From the above composition table, BFA has a significant amount of unburnt carbon. The carbon content will provide large effective sites for adsorption. The silica and alumina content of BFA also give a unique contribution to adsorption process.

SEM coupled with EDX analysis of the materials has been conducted as well. The results have revealed a unique characteristic of BFA particles. There are two types of grains, the first is porous particles which contain a large unburnt carbon and the other is dense particles which are rich with silica but low of carbon content. The two types are described in the following figures.



A B

Figure 1. SEM images of BFA: A. carbon rich grain. B. silica rich grain of BFA

B. Experiment

Breakthrough curve has been obtained by the continuous adsorption experiment using two different columns filled by fly ash as the adsorbent. The bed porosity of the both column is similar at 0.44. The first column has a 42 cm of height of the bed and contain of 65 g of fly ash. The second column height is 21.5cm and packed with 10 grams of fly ash. Cr(VI) solution flows continuously upward the column at velocity of 0.1 cm/s. The equipment layout is shown in the following figure.

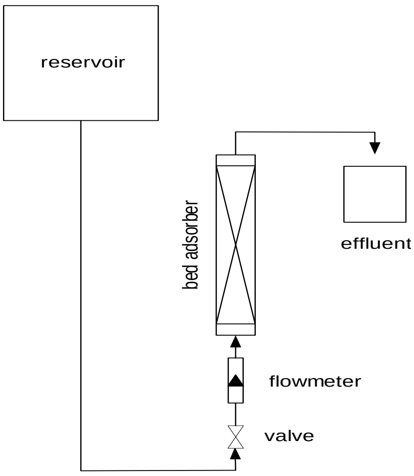


Figure 2. Experimental apparatus for measuring breakthrough curves.

In the experiment, the flow of Cr(IV) solution was utilizing gravity flow. The flowrate was adjusted by the valve and was maintained in the desired value indicated by flowmeter. The effluent was collected and sampled periodically for measuring concentration of Cr(VI).

III. FIXED BED ADSORPTION MODEL

A. Mass balance on an element of column

The model is developed from mass balance on the solute for the flow of solution through a differential adsorption-bed length, dZ over a differential time duration, dt. Thus, the generated equation gives the concentration of solute in the bulk fluid as a function of time and location in the bed.

$$-D_L\frac{\partial^2 c}{\partial Z^2}+\frac{\partial(uc)}{\partial Z}+\frac{\partial c}{\partial t}+\frac{(1-\varepsilon_b)}{\varepsilon_b}\frac{\partial q}{\partial t}=0 \tag{1}$$

In Eq. (1) the first term represents the axial dispersion with eddy diffusivity D_L, the second term accounts an axial variation in fluid velocity, and the fourth term that is based on q, the mass-average adsorbate loading per unit mass accounts for the variation of q throughout the adsorbent particle.

The analytical solution of a simplified form of Eq. (1), in which constant fluid velocity u, negligible axial dispersion, and the linear driving force mass-transfer model were assumed, was provided by Klinkenberg [7]. An adopted approximate solution is represented below:

$$\frac{c}{c_F}\approx\frac{1}{2}\left[1+erf\left(\sqrt{\tau}-\sqrt{\xi}+\frac{1}{8\sqrt{\tau}}+\frac{1}{8\sqrt{\xi}}\right)\right] \tag{2}$$

where $\xi=(kKZ/u)((1-\varepsilon_b)/\varepsilon_b)$ is dimensionless distance coordinate, $\tau=k(t-(Z/u))$ the dimensionless time coordinate and erf(x) is the error function.

B. Relationship for the coefficients

For estimating several variables, the value can be obtained by employing the two following equations [8].

$$\frac{1}{kK}=\frac{R_p}{3k_c}+\frac{R_p^2}{15D_e} \tag{3}$$

where kc is the external mass-transfer coefficient in cm·s^{-1}, De is effective diffusivity in cm^2/s and Rp is adsorbent particle radius in cm. Meanwhile, k is overall mass-transfer coefficient (s^{-1}) and K is adsorption equilibrium constant for Cr(VI) in a linear adsorption isotherm.

The first term in Eq. (3) is the overall mass-transfer resistances, the second and third term is external one and internal one, respectively. The external transport coefficient of particles in a fixed-bed column can be correlated by [8]:

$$Sh = 2 + 1.1Re^{0.6}Sc^{1/3} \tag{4}$$

where Sh = Shrewood number = kcDp/Di, Re =Reynolds number =Dp.G/μ, and Sc = Schmidt number =$\mu/\rho Di$. By Eq. (4), external mass-transfer coefficient kc can be estimated from Sh.

The fitting method between experiment and calculation data was using numerical method of error minimization by sum of square error (SSE) principle. The chosen numerical method was multi variables minimization. Firstly the value of k and ξ were guessed and then iterated to get lowest SSE. The best obtained value of the both variables can be used to determine De by Eqs. (3) and (4).

IV. RESULT

Fig 3. show the adsorption breakthrough curve of ion Cr(VI) carrying in the first column. The breakthrough time is in a τ range of 20 to 50. The value is significantly above the value that being produced by second column length as depicted in Fig. 3. This figure is mainly because a larger column contains more adsorbent to be filled by Cr(VI) ions first before a breakthrough taking place.

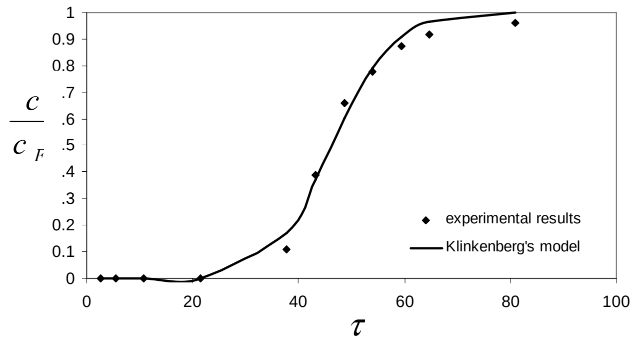


Figure 3. Breakthrough curve in 42 cm fly ash bed column

From the Fig 3 and 4, the saturated time of the two columns is also different. The first column is completely saturated at above 70 while the shorter column is already saturated at 50.

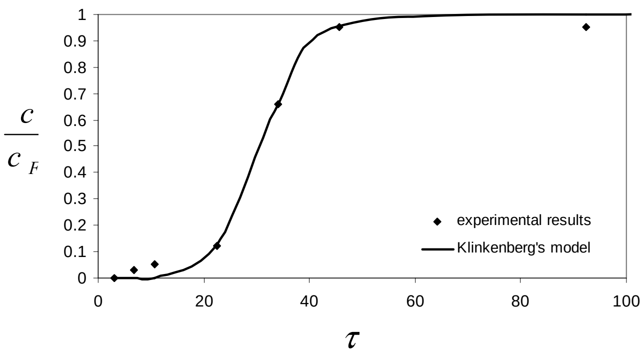


Figure 4. Breakthrough curve in 21.5 cm fly ash bed column

From the figures, it can be concluded that the method can fit the experiment data satisfactorily. The value of k, ξ dan calculated *De* are listed in Table 1.

Table 2. Summary of the calculated variables

Column length (cm)	k (s^{-1})	ξ	*De* ($cm^2 \cdot s^{-1}$ x 10^6)
42	0.0032	47.8227	4.0283
21.5	0.0031	27.4919	4.0195

The two experiments were conducted in the same temperature, using the same effective velocity *u*. Therefore, the value of *De* and k must remain constant.

V. CONCLUSION

If the value of *De* and k can be obtained, it will allow an easily prediction of the behavior of breakthrough curves in a specific adsorption operating conditions and column dimensions without doing any adsorption equilibrium experiments.

APPENDIX

- c : concentration of Cr(IV) ($mol \cdot cm^{-3}$)
- c_F : concentration of Cr(VI) in feed solution ($mol \cdot cm^{-3}$)
- Di : molecular diffusivity ($cm^2 \cdot s^{-1}$)
- Dp : diameter of adsorbent (cm)
- G : mass velocity of liquid ($g \cdot m^{-2} \cdot s^{-1}$)
- k : overall mass-transfer coefficient (s^{-1})
- kc : external mass-transfer coefficient ($cm \cdot s^{-1}$)
- K : adsorption equilibrium constant for Cr(VI) in a linear adsorption isotherm
- u : effective velocity of Cr(VI) ($cm \cdot s^{-1}$)

REFERENCES

[1] Weng, C. H. and C. P. Huang, "Treatment of Metal Industrial Wastewater by Fly Ash and Cement Fixation", *J. Envir. Engrg.*, **120** (6), pp.1470-1487 (1994).

[2] Lin, C. J., J. E. Chang, M. C. Lu, "Application of fly ashes in the removal of metal ions from wastewater", R'99 Congress on Recovery, Recycling, Re-integration (1999).

[3] Woolard, C.D., K. Petrus and M. van der Horst, "The use of a modified fly ash as an adsorbent for lead", Water SA, **26**(4), pp.531-536 (2000).

[4] Narendran, R, K.C.Gowri Shankar, S.Senthil Kumar, "Flyash based zeolite-A: A suitable sorbent for lead removal", Chemcon-2005, New Delhi (2005).

[5] Zhang, Y. S., "Development of Heavy Metal Adsorbed by Granulation of Natural Zeolite", 18th World Congress of Soil Science, Philadelphia, PA, USA (2006).

[6] Erdem, E., N. Karapinar, R. Donat, "The removal of heavy metal cations by natural zeolites", J. Coll. Inter. Sci., 280, pp.309-314 (2004).

[7] K. Adriaan, "Numerical evaluation of equations describing transient heat and mass transfer in packed solids", *Ind. Eng. Chem*. 40 (10) (1948) 1992–1994.

[8] J.D. Seader, E.J. Henley, " Separation Process Principles", John Wiley & Sons, Inc., 2002, p. 814.