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Tedi Hudaya
Department of Chemical Engineering, Faculty of Industrial Technology, Universitas Katolik Parahyangan, Bandung 40141, Indonesia, t.hudaya@unpar.ac.id

Velicia Rachmat
Department of Chemical Engineering, Faculty of Industrial Technology, Universitas Katolik Parahyangan, Bandung 40141, Indonesia

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Tedi Hudaya* and Velicia Rachmat

Department of Chemical Engineering, Faculty of Industrial Technology, Universitas Katolik Parahyangan, Bandung 40141, Indonesia

*e-mail: t.hudaya@unpar.ac.id

Abstract

Pollution caused by industrial wastewater containing heavy metals is a major issue, primarily due to its toxic nature. A cheap yet effective method to deal with such wastewater is activated carbon adsorption. The purpose of this research is to evaluate and design a fixed bed adsorber with granular activated carbon as an adsorbent to process wastewater-containing chromium hexavalent (Cr^{6+}). Experiments show that the Langmuir isotherm fits the equilibrium data as effectively as the Freundlich isotherm. Activated carbon used in this research is Jacobi 2000® derived from bituminous coal. The lab scale inlet volumetric flow is 100 mL/h with different Cr^{6+} concentration for each run, 20 and 35 ppm respectively. Based on scale-up calculation with Length of Unused Bed (LUB) method, for superficial flow of 400 $L.m^{-2}.min^{-1}$ and service time of six months, the column dimensions for inlet concentration of 20 ppm are 0.62 m diameter and 2.33 m height with 1.87 m carbon bed depth. Concurrently, a slightly bigger column (0.63 m diameter and 2.37 m height column with 1.89 m carbon bed) is necessary for treating inlet concentration of 35 ppm.

Abstrak

Perancangan Kolom Adsorpsi Karbon Aktif untuk Pengolahan Limbah Cair Cr(VI). Pencemaran akibat limbah cair industri yang mengandung logam berat merupakan masalah yang serius, karena logam berat bersifat beracun dan tidak dapat diuraikan. Metode pengolahan limbah yang cukup efektif dan murah untuk mengatasi limbah tersebut adalah adsorpsi karbon aktif. Tujuan dari penelitian ini adalah mengkaji dan merancang kolom adsorpsi karbon aktif untuk pengolahan limbah cair yang mengandung kromium heksavalen Cr^{6+}. Penelitian ini menunjukkan bahwa kesetimbangan adsorpsi dapat dideskripsikan dengan baik oleh model Langmuir *isotherm* atau Freundlich *isotherm*. Karbon aktif yang digunakan pada penelitian ini adalah Jacobi 2000® yang berasal dari *bituminous coal*. Laju alir volumetrik dalam eksperimen skala laboratorium adalah 100 mL/h dengan konsentrasi Cr^{6+} pada setiap *run* adalah 20 dan 35 ppm. Berdasarkan perhitungan *scale-up* (untuk skala industri) dengan metode *length of unused bed* (LUB), untuk laju alir superficial 400 $L.m^{-2}.min^{-1}$ dengan waktu servis selama 6 bulan, dimensi kolom adsorpsi untuk konsentrasi limbah 20 ppm yaitu 0,62 m diameter dan tinggi 2,33 m dengan tinggi unggun karbon 1,87 m. Kolom yang sedikit lebih besar (diameter kolom 0,63 m dan tinggi 2,37 m dengan tinggi unggun karbon 1.89 m) dibutuhkan untuk mengolah limbah berkonsentrasi 35 ppm.

Keywords: adsorption, activated carbon, fixed bed adsorbers, length of unused bed, scale-up

1. Introduction

In today's industrial and urbanization era, sometimes heavy metals are released into the environment and cause a severe pollution problem. Heavy metal is a non-biodegradable substance that harmfully impacts the environment. This research focuses on treating chromium hexavalent (Cr^{6+}) pollutant, which is normally produced by electroplating industries. Electroplating is a process of applying a metal coating to a different metal object by utilizing a DC electric current with an appropriate electrolyte solution, thereby forming a new characteristic on the surface [1]. The electrolyte used in this process is the chromium hexavalent solution, and wastewater contains 10–40 ppm chromium pollutant before entering a wastewater treatment system [2].

In Indonesia, there are laws regulating the concentration of effluent from the electroplating industry. All of the effluents of wastewater must meet the standards outlined under the Ministry of Environment and Forestry. The regulation states that the maximum chromium hexavalent concentration is 0.1 ppm and the maximum concentration of total chromium is 0.5 ppm [3].

The chromium hexavalent is our main concern because the Cr^{6+} can cause irritation, kidney failure, blindness, and even death, and chromium hexavalent is also confirmed to be a carcinogenic substance [4]. Moreover, there are still many traditional electroplating industries in Indonesia which do not treat their wastewaters, and thus cause further pollution in aquatic resources.

Adsorption process is a transport phenomenon process in which a solute migrates from a fluid phase to a solid phase [5]. There are two types of adsorption: physical adsorption and chemical adsorption. The physical adsorption process is a reversible process due to intermolecular forces (van der Waals). The chemical adsorption process, also known as chemisorption, usually occurs in solid catalysis. The chemical adsorption is the result of a chemical reaction (bonding) between the solid and the adsorbed substances [6].

In industrial wastewater treatment processes, we must utilize an efficient adsorbent characterized by high surface area with internal volume accessible to the adsorbed substances. Effective adsorbents must be porous solids; for example, carbon substances or inorganic substances made with a specific adsorption capability. In addition, the adsorbent must also have sufficient mechanical strength to be used in a fixed-bed structure [6].

Adsorption Equilibrium. Adsorption equilibrium is usually investigated in a stirred batch tank where the fluid concentration is uniform. In a reversible adsorption, molecules continue to accumulate on the surface of the adsorbent until the rate of adsorption equals the rate of desorption. When these two rates are equal to each other, the equilibrium has been reached and no further accumulation on the surface occurs. The adsorption isotherm represents the equilibrium distribution of the adsorbed material between solid and fluid phase. The adsorption isotherms considered in this investigation are the Langmuir isotherm and Freundlich isotherm models.

Langmuir Isotherm. The Langmuir isotherm is a semi-empirical equation that is widely used to describe adsorption equilibrium. This isotherm model was originally postulated for gas adsorption systems and later applied in liquid adsorption systems. The Langmuir isotherm assumes monolayer adsorption, which is expressed as [7]:

$$q = \frac{q_o\ c_e}{K_L + c_e} \quad (1)$$

The equation (1) can be expressed in linear equation form:

$$\frac{1}{q} = \frac{K_L}{q_o\ c_e} + \frac{1}{q_o} \quad (2)$$

where,

q = amount of Cr(VI) adsorbed at equilibrium (mg/g)
q_o = maximum adsorption capacity (mg/g)
K_L = Langmuir constant (mg/L)
c_e = Equilibrium concentration in fluid phase (mg/L)

The maximum adsorption capacity can be determined by creating a graph and plotting $\frac{1}{q}$ vs $\frac{1}{c_e}$, with slope $\frac{K_L}{q_o}$ and intercept $\frac{1}{q_o}$.

In the Langmuir isotherm model, there are essential characteristics expressed in terms of dimensionless equilibrium separation factor (R_L) which can be defined as follows:

$$R_L = \frac{1}{1 + (c_o/K_L)} \quad (3)$$

The R_L parameter is related to the shape of the isotherm according to these characteristics: $R_L > 1$ is unfavorable adsorption, $R_L = 1$ is linear relationship, and $0 < R_L < 1$ is favorable adsorption.

Freundlich Isotherm. The Freundlich isotherm is the second most commonly used model besides the Langmuir isotherm. This empirical model describes the adsorption equilibrium for non-ideal and reversible adsorption system. This model adapts an assumption about multilayer adsorption mechanisms which are caused by the heterogenous surface of the adsorbent [7]. The Freundlich isotherm equation is:

$$q = K_f\ c_e^n \quad (4)$$

The equation (4) can also be expressed in the linear equation below:

$$\ln q = \ln K_f + n\ \ln C_e$$

where,

q = amount of Cr(VI) adsorbed at equilibrium (mg/g)
K_f = Freundlich constant (mg/g)
c_e = Equilibrium concentration in fluid phase (mg/L)
n = Freundlich isotherm constants (dimensionless)

Fixed Bed Adsorption Process. Adsorption zones in the fixed bed adsorbent actually move downward through the bed. Imagine that the adsorbent moves rapidly upward through the column with countercurrent direction with

the fluid, fast enough so that the adsorption zone remains stationary in the column. This process is shown in Fig 1. In Fig 1(a), the solid leaving at the top of the column is in equilibrium with the fluid entering the column, and all solute is removed from the effluent fluid; this will require a tall column, but our concern will primarily be with the concentrations at the levels corresponding to the extremities of the adsorption zone [6].

The operating line over the entire column can be derived as:

$$G_s\,(Y_o - 0) = S_s\,(X_T - 0) \tag{5}$$

or it can be written as:

$$\frac{S_S}{G_S} = \frac{Y_O}{X_T} \tag{6}$$

Since the operating line passes through the origin in Fig 1(b), at any level in the column the concentrations of solute in the fluid Y and of adsorbate upon the adsorbent X can be related as:

$$G_s\,Y = S_s\,X \tag{7}$$

In Fig 2, if the mass transfer rate is considered infinitely rapid, the breakthrough curve can be idealized as θ_s, which can be estimated by making the shaded areas equal. The adsorption zone is then also idealized and reduced to a single plane. The bed length, *Z*, consists of the upstream of the plane at concentration X_T and the downstream (equal to the Length of Unused Bed). LUB can be defined as: [6]

$$LUB = Z - Zs = V(\theta_s - \theta_B) = \frac{Z}{\theta_s}\,(\theta_s - \theta_B) \tag{8}$$

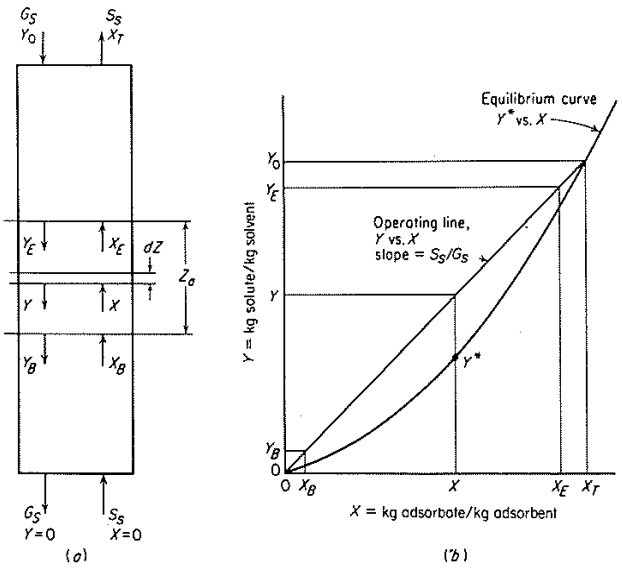

Figure 1. (a) Adsorption Zone (b) Operating line and Equilibrium curve [6]

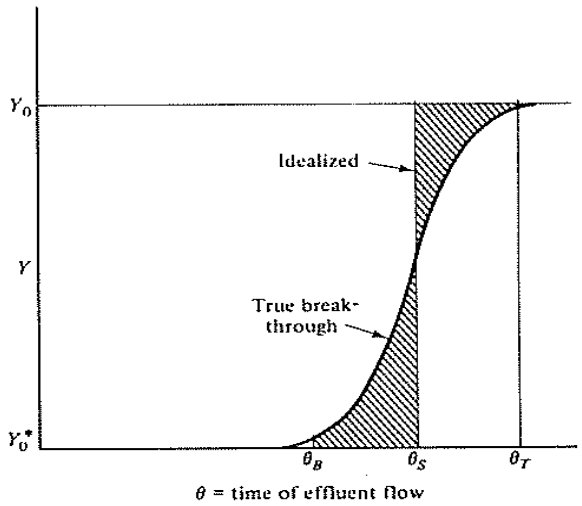

Figure 2. Idealized Breakthrough Curve [6]

The solute mass balance can be written as:

$$G_s\theta_B(Y_0 - Y_0^*) = Z_s\,\rho_s\,(X_T - X_0) \tag{9}$$

where Y_0^* is the solute equilibrium concentration at X_o.

In a carefully designed laboratory experiment (with the same G_s to be used on the industrial scale), the breakthrough curve can be measured with the equal areas determined between θ_s and θ_B, and the LUB is then calculated with equation (8). The LUB value should be the same on the industrial scale, as long as radial mixing or bed channeling are not significant. [6]

If θ_s in equation (8) is eliminated with equation (9), we can rearrange the LUB equation as:

$$LUB = Z - \frac{G_S\,\theta_B(Y_0 - Y_0^*)}{\rho_S\,(X_T - X_0)} \tag{10}$$

The length of the large-scale adsorbent bed (Z) can be determined by adding LUB with Z_s, defined as:

$$Z_S = \frac{G_S\,\theta_B(Y_0 - Y_0^*)}{\rho_S\,(X_T - X_0)} \tag{11}$$

When the initial adsorbate concentration in solid phase X_o is practically zero, thus $Y_0^* \approx 0$, we can determine the length of the column.

$$Z = LUB + \frac{G_S\,\theta_B Y_0}{\rho_S\,X_T} \tag{12}$$

2. Methods

Column Design and Scale-Up. In this research, we use the LUB method to calculate the specification of the applicable fixed bed adsorption process that may apply in the industrial sector. In this stage, several parameters needed for scale-up calculation are specified, namely fluid superficial flow rate (Gs), column specification for laboratory experimentation, and bed volume in the lab scale. The rule-of-thumb applied to adsorber design is summarized in Table 1.

Table 1. Summary of Rule-of-Thumb

No	Rule-of-Thumb	Reference
1	Z = 80% L	Towler, et al. [8]
2	L/D Ratio = 3	Towler, et al. [8] and Wallas, et al. [9]
3	Gs = 5–10 gpm/ft^2	Wallas, et al. [9]

Table 2. Lab Scale Column Specification

Variable	Specification	Unit
D	6	cm
L	18	cm
Column Material	Glass	

Table 3. Summary of Experiments for Scale-Up Calculations

No	Experimental Data	Experimental Procedure
1	X_T	Adsorption equilibrium
2	Z (height of column)	Lab scale column
3	$X_0 \sim 0$	Fresh carbon is used
4	ρ_s (bulk density)	Carbon bed
5	Effluent concentration per time	Continuous lab scale

where,
Z = length of the adsorbent bed
L = length of the adsorber column
D = diameter of the adsorber column
The lab scale column dimension is specified as follows (Table 2):

Based on equations (10) and (12), experiments must gather the data required for scale-up purposes. Table 3 summarizes the data to be collected/determined in the laboratory scale experiments.

Laboratory Experiments. In this research, all of the adsorptions are conducted at pH 1.7, which is the optimum pH for Cr(VI) adsorption onto activated carbon surface [10]. The feed solution is made by dissolving potassium dichromate ($K_2Cr_2O_7$) into reversed-osmosis (RO) water. To measure the concentration of Cr^{6+} ion, a complexing agent *1,5-diphenylcarbazide* (DPC) dissolved in Acetone with a concentration of 5000 ppm solution is used. All of the chemicals used in this research are pro-analysis grade from Merck®. The absorbance of the resulting solution is then measured at a wavelength of 540 nm with a UV-Vis spectrophotometer [11].

Activated carbon used in this research is Jacobi Aquasorb® 2000, originating from bituminous coal. The specification of this activated carbon is summarized in Table 4.
Adsorption isotherm studies are conducted with eight different initial concentrations: 10, 15, 20, 25, 30, 40, 50, and 60 ppm. The adsorption experiments are conducted in 250 mL Erlenmeyer flasks in which 250 mg activated carbon is used, and the mixture is shaken until equilibrium has been reached.

The continuous adsorption experiment is conducted for two different initial concentrations of Cr(VI), 20 ppm and 35 ppm. Based on Chiu et al., the wastewater produced by electroplating industries varies from 10 to 40 ppm [2]. The experiment is conducted in a glass column with 6 cm diameter and 18 cm of bed length, with feed flow of 100 mL/min. The column also uses two liquid distributors to prevent channeling. The continuous adsorption experimental set-up is shown in Figure 3.

Table 4. Activated Carbon Jacobi Aquasorb® 2000 Specification

SPECIFICATION			
Iodine adsorption	min.	1000	mg/g
Moisture content, as packed	max.	5	%
Total ash content	max.	13	%
Wettability	min.	97	%
Ball pan hardness		95	%
Particle diameter		-8 + 30	mesh
TYPICAL PROPERTIES			
Surface area		1050	m^2/g
Methylene blue adsorption		280	mg/g
Total pore volume		1.04	cm^3/g
Water-soluble ash		0.2	%
pH(I)		8–11	

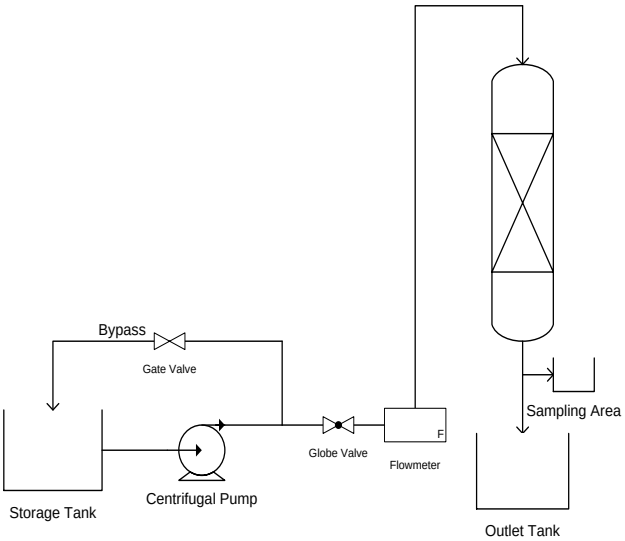

Figure 3. Continuous Fixed Bed Adsorber Set-Up

3. Results and Discussion

The standard curve for the spectrometry determination of Cr(VI) concentration is plotted in Figure 4. The curve

shows excellent linear trend, which follows the Lambert-Beer law.

Adsorption isotherm is determined by varying the initial concentration, and the equilibrium concentration of the solution is then measured. Figure 5 represents the linearized Langmuir isotherm, which is plotted according to equation (2).

Langmuir isotherm adsorption assumes that the adsorption process in the surface is a monolayer, and the other adsorbates only fill the remaining empty surface, so there is no collision between the adsorbate molecules [5].

The calculation of the separation Langmuir parameter (equation 3) also shows $0.583 < R_L < 0.201$ so that the adsorption process of Cr(VI) is favorable and suitable for the Langmuir isotherm. The adsorption capacity of chromium hexavalent based on the Langmuir isotherm is 0.06 mg Cr^{6+} /g activated carbon.

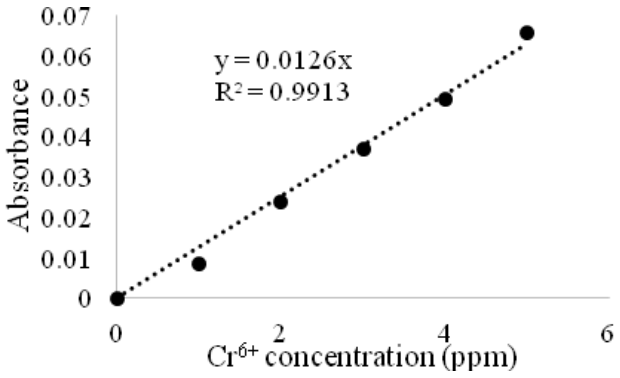

Figure 4. Standard Curve of Hexavalent Chromium

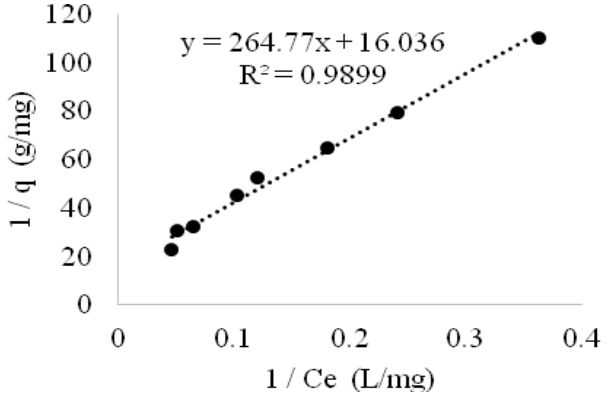

Figure 5. Langmuir Isotherm Curve

The Freundlich isotherm itself is an empirical equation, but Zeldowitch in 1935 states that the process of adsorption onto the solid surface could be multilayer due to the heterogeneous nature of the adsorbent surface itself, causing the adsorbate to collide and be adsorbed differently in the surface [12].

Linearized Freundlich isotherm is plotted in Figure 6 according to equation (3). Based on Figure 5 and 6, it appears that the Langmuir isotherm model fits the experiment almost as good as the Freundlich isotherm model.

Experiment 1. This experiment is conducted in a 6 cm diameter glass column with 18 cm height of adsorbent bed. The effluent is analyzed and then plotted. The initial concentration of this run is 20 ppm. Figure 7 is the breakthrough curve for this experiment.

This breakthrough curve is not as steep as usual, indicating that the adsorption zone is relatively wide, so the effluent concentration increases more slowly than usual. This also may occur due to the form of the chromium ion that changes in acidic environment. The chromium ions that exist in acidic solution are $Cr_2O_7^{2-}$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$, and $Cr_4O_{13}^{2-}$, in which $HCrO_4^-$ as the most dominant form. As the result of the varieties of ionic species, the adsorption in the continuous process is

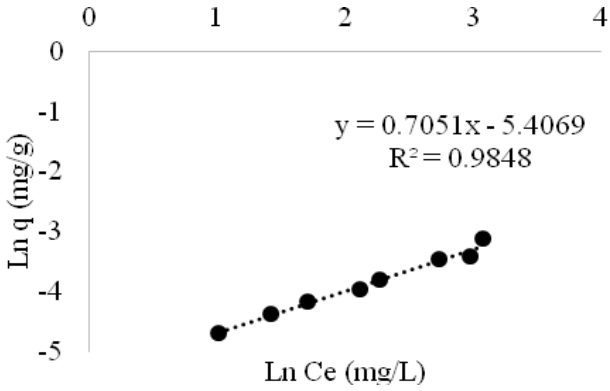

Figure 6. Freundlich Isotherm Curve

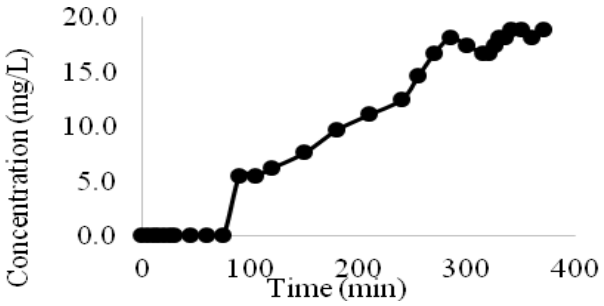

Figure 7. Breakthrough Curve for Experiment 1

not uniform in all adsorbent's surface as is suggested by the suitability of the adsorption equilibrium data to the Freundlich isotherm.

After the breakthrough curve is obtained, the scale-up calculation can be carried out. Table 5 shows the basis of the industrial scale calculation.

The scale-up calculation is divided into four main steps. The first step is to determine Yo (initial concentration), the Yb (breakthrough concentration), and Ye (exhausted concentration). The Yo, Yb, and Ye data are obtained from equilibrium experiment.

The second step is to then calculate the dimension of Zs using equation (11) with the help of calculation basis stated in Table 5. The third step is to determine the industrial scale bed length with equation (12). Lastly, the dimension of industrial scale fixed bed adsorbers is calculated with the Z/D and Z/L ratio stated in Table 5, to obtain the length as well as the diameter of the industrial scale column. Figure 8 presents an illustration of the industrial scale fixed bed adsorber. Ceramic balls at the top of the column function as a liquid distributor to prevent channeling.

The industrial scale fixed bed adsorber specifications for experiment 1 are shown in Table 6.

Table 5. Calculation Basis for Scale-Up Procedure

Description	Ratio/Basis Calculation
Gs (industrial flux rate)	400 L m^{-2} min^{-1}
Θb (industrial breakthrough/service time)	6 months
$\frac{Z}{D}$ Ratio	3
$\frac{Z}{L}$ Ratio	0.8

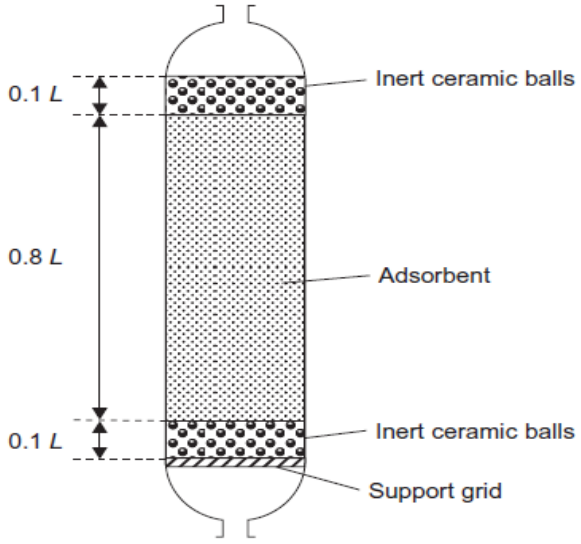

Figure 8. Industrial Scale Illustration

Table 6. Fixed Bed Adsorbers for $[Cr^{6+}]_o$= 20 ppm

Description		Unit
Z (carbon height)	1.87	m
L (column height)	2.33	m
D (column diameter)	0.62	m
A (surface area)	0.30	m^2
Mass flow	121.42	kg/h
Volumetric flow	121.78	L/h

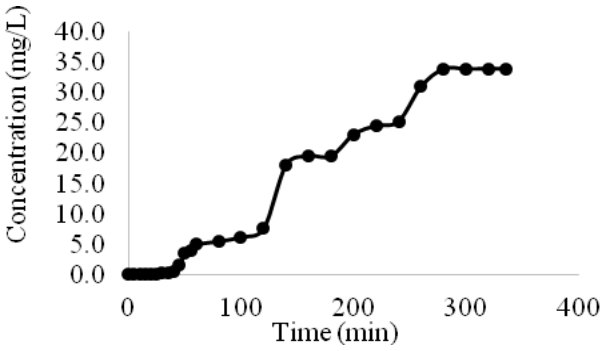

Figure 9. Breakthrough Curve for Experiment 2

Table 7. Fixed Bed Adsorbers for $[Cr^{6+}]_o$= 35 ppm

Description		Unit
Z (carbon height)	1.89	m
L (column height)	2.37	m
D (column diameter)	0.63	m
A (surface area)	0.31	m^2
Mass flow	125.02	kg/h
Volumetric flow	125.39	L/h

Experiment 2. This experiment is conducted in the same column as experiment 1. The initial concentration of Cr(VI) in this experiment is significantly higher than 35 ppm. The effluent is then analyzed and plotted to give the breakthrough curve as shown in Figure 9. Similar observations from previous experiments are also found.

Based on the scale-up calculation procedure as previously described, the large-scale fixed bed adsorber for feed concentration Cr (VI) of 35 ppm is summarized in Table 7.

4. Conclusion

Jacobi Aquasorb® 2000 can efficiently adsorb hexavalent chromium, with an adsorption capacity of 0.06 mg Cr(VI)/g activated carbon.

The adsorption isotherm demonstrates that the Langmuir isotherm fits the equilibrium data as good as the Freundlich isotherm. The breakthrough curve indicates that the adsorption zone is relatively wide due to various ionic Cr(VI) species.
Based on scale-up calculation, the dimension of a large-scale column for $[Cr^{6+}]_o$ = 20 ppm is 0.62 m diameter with

2.33 m height; for $[Cr^{6+}]_o$ = 35 ppm it is 0.63 m diameter with 2.37 m height.

Acknowledgement

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