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Evaluation of kinetics adsorption models from Lampung ethnic textile industry wastewater for removal chromium onto modified activated sludge and zeolite adsorbent

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Abstract. The aim of this study to evaluate fifteen kinetic models by fitting the adsorption of chromium experimental data from aqueous solution on modified adsorbent from activated sludge and natural zeolite. All the fifteen kinetic models parameter were determined and ranked by sum of square errors (SSE). The results showed that intra-particle diffusion, power, Bangham, fractal exponential, fractal mixed 1.2 order, first order, fractal-like pseudo first order, fractal-like second order have a good fit to experimental data as their values of SSE 0.00057, 0.000617, 0.000617, 0.000621, 0.000624, 0.000639, 0.000639 and 0.000653 respectively. However the larger value of SSE was obtained for the pseudo first order, the pseudo second order, Avrami, exponential, Boyd, and mixed 1,2 model as their values of 0.002085, 0.001204, 0.002085, 0.00155, 0.004273, 0.00121

1. Introduction

Textile industries produce a large volume of wastewater that contains inorganic and organic pollutants such as cadmium, lead, chromium, suspended solids, BOD, COD. These pollutants especially heavy metal can cause a negative impact to human, other living organisms and environment when the pollutants do not treat effectively. One of the effective techniques for removing heavy metal from the textile industry is the adsorption process. Adsorption is the process by which one or more adsorbates are transferred to adsorbent by physical or chemical bonds [1]. The Adsorption process is better than other methods because of simple in design and operation, lower cost, energy efficiency [2]. The adsorbent generally used are clay minerals, agriculture waste, sludge, and zeolite. Natural zeolite is



abundant three-dimensional structure aluminosilicate minerals and consist of aluminum, silicon and oxygen atoms [3]. Sludge is a low-cost carbon-rich, renewable and abundant resources [4].

Many theoretical and numerical methods have been used for describing the kinetic model of chromium adsorption. The two of kinetic models have been widely proposed for many adsorption studies are pseudo-first-order and pseudo-second-order. The previous study about the adsorption of hexavalent chromium using polyethylenimine modified biochar fit well with the pseudo-second-order kinetic model [5]. The other study using modified zeolite with HDTMA-Br to adsorb Cr (VI) obeyed with the pseudo-second-order model [6]. However, the fitting between experimental data of Cr (VI) adsorption on modified red clay with HDTMA followed the first order kinetic model. The other study showed that adsorption of chromium on waste tire adsorbent was the best described by pseudo-first-order kinetic model [7]. This paper studies about chromium adsorption kinetic modeling by non-linear analysis on modified activated sludge and zeolite adsorbent, the determination of the kinetic parameters and finally choose the good model to fit the kinetics of experimental data.

2. Materials and methods

2.1. Data collection

The data of chromium adsorption was obtained from activated sludge/zeolite adsorbent modification experiment with ratio 3:2. The initial concentration of chromium obtained from the wastewater was 70 mg/l. The data from the experiment is shown in Table 1 and it was also used as an input for kinetic adsorption model simulation.

Table 1. The experimental data of chromium adsorption onto activated sludge/zeolite adsorbent with ratio 3:2.

Time (second)	Q data (mg/g)
30	0.221515
60	0.250756
90	0.299593
120	0.346822
150	0.346822

Source: [8]

2.2. Adsorption kinetic models

The kinetic model plays important role in adsorption process especially in the design of adsorption system. From the result of analysis kinetic model some important variables can be determined for example equilibrium time, mechanism of adsorption and the rate-determining step [9]. Fifteen kinetic models for this study were applied to analyze removal of chromium from aqueous solution that contained in the Lampung Ethnic Textile Industry (LETI) wastewater onto modified activated sludge/zeolite adsorbent.

The first-order model was proposed by [10] for investigating the removal of lead and chromium from aqueous solution by red mud. The first-order model consists of two-parameters and can be mathematically written in the form of:

$$q_t = q_e - \exp(-k_1 t) \quad (1)$$

where q_t is adsorption capacity (mg.g^{-1}), q_e is the adsorption capacity at equilibrium (mg.g^{-1}), t is time (min) and k_1 is the first order rate constant (min^{-1}).

The Ritchie second-order was used by [11] to investigate the adsorption of Cr (VI) by dead fungal biomass of *Aspergillus niger*. The second-order model can be written as follows:

$$q_t = \frac{q_e}{1 + q_e k_2 t} \quad (2)$$

where k_2 is the second-order rate constant (min^{-1}).

The pseudo-first and second order model is the most popular kinetic models for explaining the adsorption process with various adsorbent materials. These models calculate the rate of adsorption of adsorbate on the adsorbent. The pseudo-first-order model is used to describe the initial stage of adsorption, while the pseudo-second-order model depicts the whole range of adsorption stage [9]. The pseudo-first order model was proposed by [12], it can be expressed by the following equation:

$$q_t = q_e \left[1 - \exp(-k_p t) \right] \quad (3)$$

The pseudo-second-order can be expressed in the form:

$$q_t = \frac{k_{p2}q_e^2 t}{1 + k_{p2}q_e t} \quad (4)$$

where k_{p1} and k_{p2} are the pseudo-first and second order rate constant (min^{-1}).

The intra-particle diffusion model or pore diffusion mechanism describes the transportation of species from the surface to the interior pores of the particle [13]. The equation of this kinetic model can be estimated by the following equation:

$$q_t = k_{ip}\sqrt{t} + c_{ip} \quad (5)$$

where k_{ip} is diffusion coefficient ($\text{mg.g}^{-1}.\text{min}^{-1/2}$) and c_{ip} is intra-particle diffusion constant (mg.g^{-1}).

A power model was used by [11] can be written as follows:

$$q_t = k_p t^i \quad (6)$$

where k_p and i are the power constant of the power model.

The Avrami's model has been successful to describe adsorption methylene blue from aqueous solution [14] and it can be mathematically written by the following equation:

$$q_t = q_e \left[1 - \exp(-k_{av} t)^{n_{av}} \right] \quad (7)$$

where k_{av} is the Avrami rate constant (min^{-1}) and n_{av} is the Avrami dimensionless number.

The Bangham kinetic model was used by [15] to investigate the adsorption of anionic and cationic dyes on activated carbon and can be formulated as:

$$q_t = k_b t^{1/m} \quad (8)$$

where k_b is the rate constant of adsorption ($\text{mg.g}^{-1}.\text{min}^{-1}$) and m is the dimensionless number of adsorption intensity.

The mixed 1,2-order kinetic model is the combination between the pseudo-first-order and pseudo-second-order. This model was used by [16] to assess adsorption of methylene blue on mesoporous carbons. The formula of the model can be expressed as follows:

$$q_t = q_e \frac{1 - \exp(-kt)}{1 - f_2 \exp(-kt)} \quad (9)$$

where f_2 is the dimensionless coefficient of mixed 1,2 order and k is the adsorption rate constant ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$).

The exponential kinetic model describes adsorption kinetic at the solid/solution interface. This model can be used to homogenous and heterogeneous surfaces [17] and mathematically written as:

$$q_t = q_e \ln[2.72 - 1.72 \exp(-k_e t)] \quad (10)$$

where k_e is the exponential model constant ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$).

The fractal-like exponential model is used to assess adsorption on the heterogeneous surface. This model was proposed by [17] and can be expressed in the form of:

$$q_t = q_e \ln[2.72 - 1.72 \exp(-k_{fle} t)^\alpha] \quad (11)$$

where k_{fle} is the fractal-like exponential rate coefficient ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$) and α is the constants of the fractal-like model.

The fractal-like mixed 1,2-order model is a modification of the mixed 1,2-order model. It was proposed by [18] and expressed as:

$$q_t = q_e \frac{1 - \exp(-k_{ffs} t^\alpha)}{1 - f_2 \exp(-k_{ffs} t^\alpha)} \quad (12)$$

where k_{ffs} is coefficient of fractal-like mixed 1,2-order ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$) and α and f_2 are constants of fractal-like mixed 1,2-order model.

The fractal-like pseudo-first-order and pseudo-second-order models were proposed by [18]. These model are a modification of pseudo-first-order and pseudo-second-order model and can be written in the forms of:

$$q_t = q_e \left[1 - \exp(-k_{ffo} t^\alpha) \right] \quad (13)$$

$$q_t = \frac{k_{flso} q_e^2 t^\alpha}{1 + k_{flso} q_e t^\alpha} \quad (14)$$

where k_{ffo} and k_{flso} are coefficients of the fractal-like pseudo-first-order and fractal-like pseudo-second-order ($\text{mg.g}^{-1}.\text{min}^{-1}$), α is constant of the fractal-like pseudo-second-order.

Boyd's kinetic model considers that particle diffusion is the only rate-controlling process [19]. The equation of this model can be formulated as follows:

$$q_t = q_e \left[1 - \frac{6}{p^2} \exp(-Bt) \right] \quad (15)$$

where B is the Boyd number (min^{-1}).

2.3. Validation of adsorption kinetics

This study used a solver in excel to simulate and analyze experimental data of Cr adsorption on modified zeolite/sludge. The experimental data were fitted to the fifteen kinetic models and used the sum of square errors (SSE) to validate the simulation. The sum of squared errors (SSE) is calculated by the expression:

$$SSE = \sum_{i=1}^n (q_{exp} - q_{model})^2 \quad (16)$$

where q_{exp} is the experimental amount of adsorbed Cr onto modified adsorbent (mg.g^{-1}), q_{model} is the calculated amount of adsorbed Cr onto modified adsorbent (mg.g^{-1}), n is the number of data points.

3. Results and discussion

3.1. Adsorption of chromium on activated sludge/zeolite adsorbent

Calculated parameters of fifteen kinetic models and the validation of the model have been listed in Table 2. Low SSE indicates that models are good to describe the kinetics of chromium uptake onto activated sludge/zeolite adsorbent. From Table 1 shows that intra-particle diffusion, power, Bangham,

fractal exponential, fractal mixed 1.2 order, first order, fractal-like-pseudo-first order, fractal-like-second-order have a good fit to experimental data as their values of 0.00057, 0.000617, 0.000617, 0.000621, 0.000624, 0.000639, 0.000639 and 0.000653 respectively. However, the larger value of SSE obtained for the pseudo-first order, the pseudo-second order, Avrami, exponential, Boyd, and mixed 1,2 model as their values of 0.002085, 0.001204, 0.002085, 0.00155, 0.004273, 0.00121 suggesting that these models do not describe kinetics of Cr on activated sludge/zeolite adsorbent although q_e calculated is closer with q_e from experimental data by the value of 0.346 mg.g⁻¹.

The figure of experimental data and model curve fitting are shown in Figure 1 and Figure 2. Figure 1 is the best four of eight kinetic models which have lower SSE, while Figure 2 is the four of six kinetic models which have larger SSE. Based on the results from Table 1 and Figure 1, it indicates that the intra-particle diffusion model is better to describe the kinetic model for adsorption chromium onto activated sludge/zeolite.

Generally, the adsorption process of the adsorbate from the solution phase to the surface of the adsorbent is controlled by several factors. The overall adsorption process is taking place through one or more steps such as film or external surface diffusion, pore diffusion, surface diffusion and adsorption on the pore surface or a combination of more than one step [20]. The intra-particle diffusion model can be used to explore intra-particle diffusion resistant the in adsorption process. The value of c_{ip} in Eq. (5) gives an indication the thickness of the boundary layer, the larger value of c_{ip} the greater effect of the boundary layer [13]. To determine rate-limiting step in the adsorption process can be used the plot between q_t versus $t^{0.5}$. If the plot gives a straight line, intra-particle diffusion is the only rate-limiting step. However, if the plot gives multiple straight lines, the adsorption process is controlled by two or more steps [21]. For this experiment, the plot q_t versus $t^{0.5}$ can be seen in Figure 3.

Table 2. List of parameters from fifteen kinetic models.

Kinetic models	Value	Kinetic models	Value
First order		Avrami	
q_e calculated (mg.g ⁻¹)	1.18355	q_e calculated (mg.g ⁻¹)	0.34436
k_1 (min ⁻¹)	0.00131	k_{av} (min ⁻¹)	0.11760
SSE	0.000639	n_{av}	0.23519
Second order		SSE	0.002085
q_e calculated (mg.g ⁻¹)	0.21674	Mixed 1,2 order	
k_2 (min ⁻¹)	-0.01249	q_e calculated (mg.g ⁻¹)	0.40231
SSE	0.001434	k (mg.g ⁻¹ .min ⁻¹)	0.002332

Pseudo-first-order		f	0.92968
q_e calculated (mg.g ⁻¹)	0.34436	SSE	0.00121
k_{p1} (min ⁻¹)	0.02766	Fractal exponential	
SSE	0.002085	q_e calculated (mg.g ⁻¹)	6.53612
Pseudo-second-order		k_{fle} (mg.g ⁻¹ .min ⁻¹)	0.00646
q_e calculated (mg.g ⁻¹)	0.41622	α	0.32483
k_{p2} (min ⁻¹)	0.07738	SSE	0.000621
SSE	0.001204	Fractal like pseudo first	
Intra-particle diffusion		q_e calculated (mg.g ⁻¹)	1.05562
k_{ip} (mg.g ⁻¹ .min ^{-1/2})	0.02069	k_{ffo} (mg.g ⁻¹ .min ⁻¹)	0.06422
c_{ip} (mg.g ⁻¹)	0.10315	α	0.36862
SSE	0.00057	SSE	0.000639
Power model		Fractal like pseudo second	
K_p	0.07341	q_e calculated (mg.g ⁻¹)	1.25933
V_p	0.31406	k_{flso} (mg.g ⁻¹ .min ⁻¹)	0.04062
SSE	0.000617	α	0.40495
Bangham model		SSE	0.000653
k_b (mg.g ⁻¹ .min ⁻¹)	0.07341	Fractal mixed 1,2 order	
M	3.18378	q_e calculated (mg.g ⁻¹)	2.55411
SSE	0.000617	k_{flrs} (mg.g ⁻¹ .min ⁻¹)	0.02808
Exponential model		α	0.33305
q_e calculated (mg.g ⁻¹)	0.35543	f_2	0.001
k_e (mg.g ⁻¹ .min ⁻¹)	0.01905	SSE	0.000624
SSE	0.00155		
Boyd			
q_e calculated (mg.g ⁻¹)	0.32241		
B	0.05429		
SSE	0.004273		

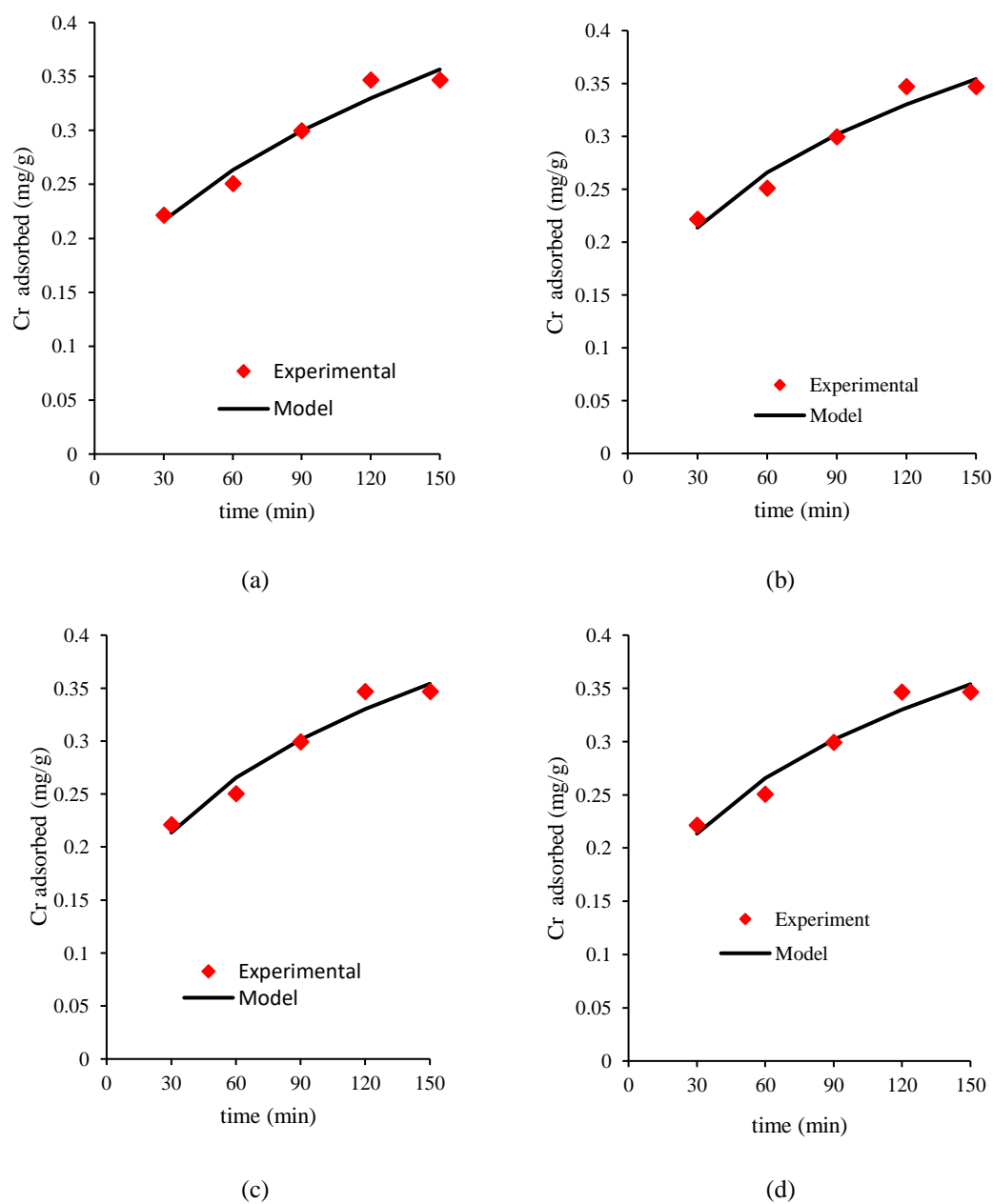


Figure 1. The curve of chromium adsorbed vs time on different kinetic model (a) intra-particle diffusion, (b) power, (c) Bangham, (d) fractal exponential.

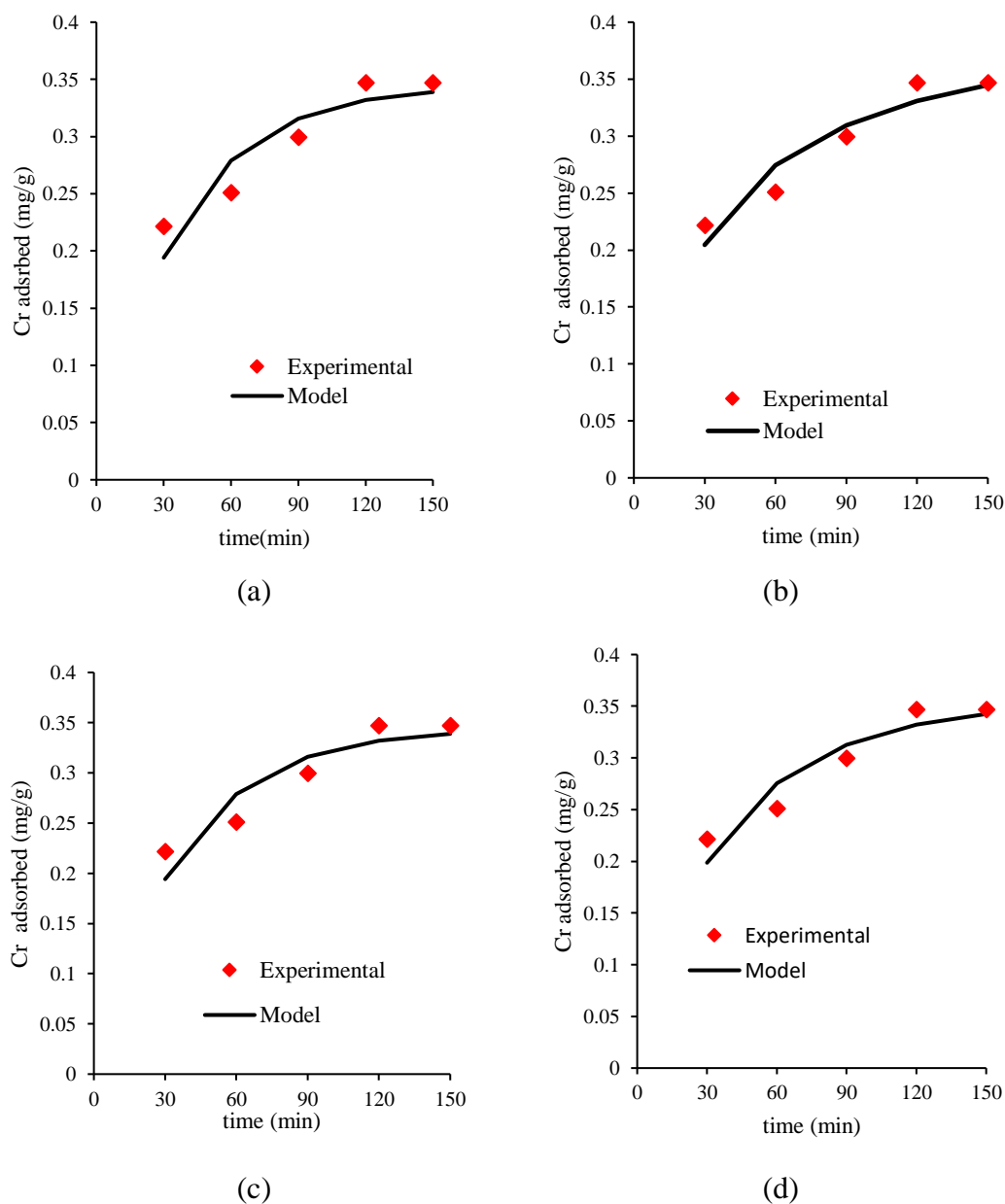


Figure 2. The curve of chromium adsorbed vs time on different kinetic model (a) the pseudo-first order, (b) the pseudo-second order, (c) Avrami, (d) exponential.

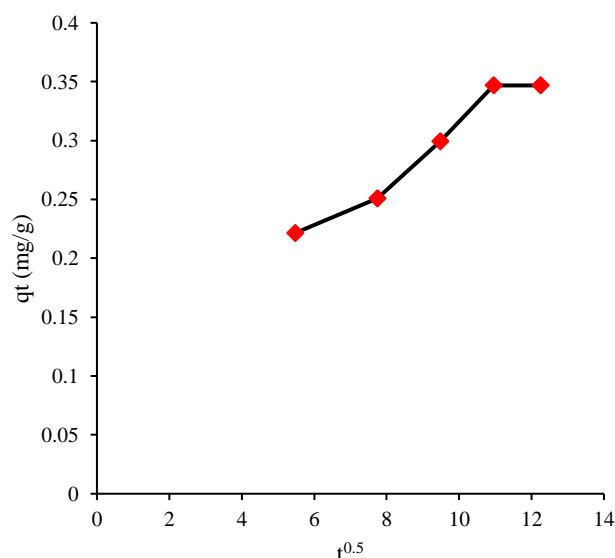


Figure 3. Intra-particle diffusion plot for removal chromium by activated sludge/zeolite.

It is shown from Figure 3 that there are three regions for adsorption of chromium by modified sludge/zeolite. The first region relates to the bulk diffusion or external surface diffusion, the second region describes the gradual stage of adsorption and the last region is the equilibrium step where adsorption becomes stable. Besides the intra-particle model, it can be seen that Bangham model has a good fit to the experimental data. This result shows that the adsorption is also affected by the pore diffusion.

4. Conclusions

The adsorption kinetics of chromium from aqueous solution on modified sludge and zeolite adsorbent can be described by intra-particle diffusion, power, Bangham, fractal-exponential, fractal-mixed-1.2 order, first order, fractal-like-pseudo-first order, fractal-like-second order.

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References

- [1] L. Largette and R. Pasquier 2016 *Chem. Eng. Res. Des.* **109** pp. 495–504.
- [2] G. Z. Kyzas, M. Kostoglou, N. K. Lazaridis, D. A. Lambropoulou, and D. N. Bikiaris 2013 *Chem. Eng. J.* **222**, pp. 248–258.

- [3] Q. Xie, J. Xie, Z. Wang, D. Wu, Z. Zhang, and H. Kong 2013 *Microporous Mesoporous Mater.* **179** pp. 144–150.
- [4] K. Björklund and L. Y. Li 2017 *J. Environ. Manage.* **197**, pp. 490–497.
- [5] Y. Ma, W. J. Liu, N. Zhang, Y. S. Li, H. Jiang, and G. P. Sheng 2014 *Bioresour. Technol.* **169**, pp. 403–408.
- [6] S. L. Hailu, B. U. Nair, M. Redi-Abshiro, I. Dlazi, and M. Tessema 2017 *J. Environ. Chem. Eng.* **5**, no. 4, pp. 3319–3329.
- [7] I. Ahmad, N. Ahmad, N. Iqbal, M. Zahid, and M. Iqbal 2017 *J. Environ. Chem. Eng.*, **5**, no. 3, pp. 2740–2751.
- [8] Darmansyah, S. br. Ginting, A. Sanjaya, F. Soraya, and D. Supriyadi 2018 (submitted) *Proc. of International conference on engineering, technologies, and applied sciences (ICETSAS)* (Bandar Lampung)
- [9] Y. H. Magdy and H. Altaher 2018 *J. Environ. Chem. Eng.* **6**, no. 1, pp. 834–841.
- [10] Gupta, V.K., Gupta, M., Sharma, S 2001 *Water Res.*, pp. 1125–1134.
- [11] Y. Khambhaty, K. Mody, S. Basha, and B. Jha 2009 *Chem. Eng. J.* **145**, no. 3, pp. 489–495.
- [12] B. K. S. S. Lagergren 1898 *R. Swed. Acad. Sci.Doc Band* **24**, pp. 1–13.
- [13] Y. Kismir and A. Z. Aroguz 2011 *Chem. Eng. J.* **172**, pp. 199–206.
- [14] B. Royer *et al.* 2009 *J. Hazard. Mater.*, vol. 164, no. 2–3, pp. 1213–1222.
- [15] A. Rodríguez, J. García, G. Ovejero, and M. Mestanza 2009 *J. Hazard. Mater.* **172**, no. 2–3, pp. 1311–1320.
- [16] A. W. Marczewski, “Application of mixed order rate equations to adsorption of methylene blue on mesoporous carbons 2010 *Appl. Surf. Sci.* **256**, no. 17, pp. 5145–5152.
- [17] M. Haerifar and S. Azizian 2013 *Chem. Eng. J.* **215–216**, pp. 65–71.
- [18] M. Haerifar and S. Azizian 2014 *The Journal of Physical Chemistry C* **118**(2),pp. 1129–1134.
- [19] R. M. C. Viegas, M. Campinas, H. Costa, and M. Joa 2014 *adsorption* **20** pp. 737–746.
- [20] R. Elmoubarki *et al.* 2015 *Water Resour. Ind.* **9**, pp. 16–29.
- [21] E. Alver and A. ü Metin 2012 *Chem. Eng. J.* **200–202**, pp. 59–67.