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Original Article

Effect of temperature and kinetic modelling of lignosulfonate adsorption onto powdered eggshell in batch systems

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Abstract

The sorption of lignosulfonate onto powdered eggshell under the influence of temperature has been studied. The rate of adsorption onto eggshell was investigated under a variety of adsorbent dosages. The kinetic data from these investigations were correlated to a number of adsorption models in an attempt to elucidate the mechanism of the adsorption processes. Thermodynamic parameter data indicated that the lignosulfonate sorption process was non-spontaneous and endothermic under the experimental conditions, with the Gibbs free energy (ΔG^o) in the range of 1.83-1.07 kJ mol^{-1}, enthalpy (ΔH^o) and entropy (ΔS^o) of 5.66 kJ mol^{-1} and 12.82 J mol^{-1}, respectively and the activation energy of 18.17 kJ mol^{-1}. The adsorption mechanism was found to follow a pseudo-second-order model, with the kinetic constants in the range of 0.689–1.430 g mg^{-1} min^{-1}. Both the intra-particle diffusion and Boyd kinetic models indicated that boundary layer/film diffusion was the main rate determining step in lignosulfonate adsorption process.

Keywords: adsorption, eggshell, kinetic, lignosulfonate

1. Introduction

Effluents from pulp and paper mills are highly toxic and a major source of aquatic pollution. Kraft Mills Process Effluent (KMPE) discharge a large volume of brown colored effluent due to the Kraft process used in the processing of wood and pulp. The brown color of the effluents results primarily from the presence of lignosulfonate and its degradation products, which are chemically stable, resistant to biological degradation (very high COD/BOD ratio), and intractable to separation by conventional treatment methods (Mohan and Karthikeyan, 1997). This wastewater causes three kinds of environmental impact i.e. high biological oxygen demand (BOD), toxicity and color (Diez *et al.*, 1999; Ali and Sreekrishnan, 2001).

At present, there are two kinds of method to remove color and toxicity from wastewater i.e. physical and chemical processes. Some of these processes are adsorption, coagulation, electro coagulation, flotation, oxidation, biosorption, biodegradation, UV photodecomposition and ultrafiltration. Most of these processes are expensive, ineffective and unfavorable economically. Adsorption has been found to be an efficient and economic method to remove dyes, pigments and other colorants and to control of the bio-chemical oxygen demand. The most widely used sorbent for industrial applications is activated carbon (Walker & Weatherley, 1997; Khalil and Girgis, 1998; Porter *et al.*, 1999). However, there are some problems associated with its use, i.e. the material is expensive, regeneration and reuse are complex and limited to the removal of non-polar materials (Oke *et al.*, 2008). This has led to a search for low-cost materials as alternative adsorbents in order to remove phenolic and lignin compounds (Bailey *et al.*, 1999).

Chicken eggs are used in enormous numbers by food manufacturers and restaurants and the shells are discarded

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as waste. Different investigations have been conducted to explore useful applications for eggshells. Such research has shown that eggshells may be used as a fertilizer and a feed additive for livestock and it appears to be able to effectively adsorb certain heavy metals and organic compounds (Kuh & Kim, 2000; Koumanova *et al.*, 2002; Chojnacka, 2005; Zulfikar *et al.*, 2012). The porous nature of eggshell makes it an attractive material to employ as an adsorbent. Each eggshell has been estimated to contain between 7000 and 17000 pores (William, 1995). In our previous work, we showed that the powdered eggshell could adsorb lignosulfonate compounds, and the percentage of adsorption depended on mixing time, pH and dosage of powdered eggshell (Zulfikar *et al.*, 2012).

The present study was aimed to examine the removal of lignosulfonate compound at various temperatures. In addition, the adsorption mechanism through various adsorption kinetics models was investigated.

2. Kinetic Modelling

2.1 Pseudo-first-order model.

In order to investigate the mechanism of adsorption, the pseudo-first-order adsorption, the pseudo-second-order adsorption and the intra-particle diffusion model were used to test dynamic experimental data. The pseudo-first-order rate expression of Lagergren (1898) is generally described by the following equation (Ho and McKay, 1998a, 1999; Chiou and Li, 2003; Jain and Sharma, 2002; Tseng *et al.*, 2003; Ugurlu *et al.*, 2005):

$$\log(q_e - q_t) = \log q_e - k/2.303.\ t \qquad (1)$$

where q_e and q_t are the amounts of organic compounds, (mg/g) adsorbed on sorbents at equilibrium and at time t, respectively, and k is the rate constant (min^{-1}). The rate k was obtained from slope of the linear plots of $\log(q_e - q_t)$ against t.

2.2 Pseudo-second-order model.

The pseudo-second-order model is based on the assumption that the rate-limiting step may be chemical sorption or chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate. It is assumed that the sorption capacity is proportional to the number of active sites occupied on the sorbent, then the kinetic rate law can be written as follows: (Ho and McKay, 1998b, 1998c, 2000; Ho, 2003; Ho and Chiang, 2001; Tseng *et al.*, 2003; Ugurlu *et al.*, 2005):

$$t/q_t = 1/k.q_e^{\,2} + \mathrm{t}/q_e \qquad (2)$$

where q_e and q_t are the amounts of organic compounds, (mg/g) adsorbed on sorbents at equilibrium and at time t, respectively, and k is the rate constant (g/mg.min^{-1}). If second-order kinetics are applicable, the plot of t/q_t against t of Eq. (2) should give a linear relationship from which the constants q_e and k can be determined.

2.3 Intra-particle diffusion model.

Intra-particle diffusion can be described by three consecutive steps (Ugurlu *et al.*, 2005):

(i) The transport of sorbate from bulk solution to outer surface of the sorbent by molecular diffusion, known as external (or) film diffusion.

(ii) Internal diffusion, the transport of sorbate from the particles surface into interior sites.

(iii) The sorption of the solute particles from the active sites into the interior surface of the pores.

The overall rate of the sorption process will be controlled by the slowest, rate-limiting step. The nature of the rate-limiting step in a batch system can be determined from the properties of the solute and sorbent. In adsorption systems where there is a possibility of intra-particle diffusion being the rate-limiting step, the intra-particle diffusion approach described by Weber and Morris (1963) is used. The rate constants, for intra-particle diffusion (k_i) are determined using equation given by Weber and Morris (1963). This equation can be written as follow: (Ho and McKay, 1998; Sivaraj *et al.*, 2001; Jain and Sharma, 2002; Basibuyuk and Forster, 2003 and Ugurlu *et al.*, 2005):

$$q_t = k.t^{0.5} + c \qquad (3)$$

where k and c are intra-particle diffusion rate constant (mg/g.min$^{0.5}$) and a constant, respectively. The k is the slope of straight-line portions of the plot of q_t vs. $t^{0.5}$. These plots generally have a dual nature i.e. an initial curved portion and a final linear portion. This is explained by the fact that the initial curved portion represents boundary layer diffusion effects. The final linear portions are a result of intra-particle diffusion effects (Ugurlu *et al.*, 2005). Extrapolating the linear portion of the plot yields the intercept (c) which is proportional to the extent of boundary layer thickness (Jain and Sharma, 2002).

2.4 Elovich model

The Elovich equation is one of the most useful models for describing chemisorption, which is given as (Ozacar & Sengil, 2005; Elkady *et al.*, 2011):

$$q_t = a + \ \ln t \qquad (4)$$

where α represents the initial sorption rate (mg/g min) and β is related to the extent of surface coverage and activation energy for chemisorption (g/mg). The parameters α and β can be computed from the slope and intercept of the linear plot of q_t versus ln t.

2.5 Boyd model

In order to determine the actual slow step involved in the dye sorption process, the kinetic data as obtained by the batch method were further analyzed using the Boyd model given by (Boyd *et al.*, 1947; Elkady *et al.*, 2011):

$$B_t = -0.4977 - \ln(1 - F) \tag{5}$$

F represents the fraction of solute adsorbed at any time, *t* (h), which is calculated as follows:

$$F = q_t / q_\alpha \tag{6}$$

where, q_α represents the amount sorbed (mg/g) at infinite time and B_t is a mathematical function of F. The B_t values at different contact times can be calculated using Eq. 5. The calculated B_t values were plotted against time *t* (h). The linearity of the plots can be used to identify control of sorption rate process, whether film diffusion or intra-particle diffusion (Ngah & Hanafiah, 2008).

3. Materials and Methods

3.1 Materials

Chicken eggshells collected from Balubur traditional market Bandung, Indonesia were washed with distilled water, air-dried, ground into powder with particle sizes of 150 µm and stored in desiccators. The characteristics of this eggshell were shown in our previous work (Zulfikar *et al.*, 2012). For adsorption studies lignosulfonate obtained from Aldrich was used as adsorbate. Water used was generated from a distillation system. All materials were used without further purification.

3.2 Methods

3.2.1 Sorption studies

Adsorption experiments were carried out in 100 mL flasks immersed in a thermostatic shaker bath at 25°C, 45°C, 65°C and 85°C for 15, 30, 45, 60, 75, 90 and 120 minutes. Chicken eggshell samples of 20 g were mixed with 100 mL lignosulfonate 500 mg/L. At the end of each adsorption period, the suspension was centrifuged. The concentrations of lignosulfonate compounds in the supernatant solutions after and before adsorption were determined spectrophotometrically, at the *l* of 290 nm.

3.2.2 Kinetic study

The kinetic study was investigated by varying the dosage of powdered eggshell (5, 10, 15 and 20 g) while other conditions were held constant at pH 7, particle size of 150 µm, temperature of 25°C and concentration lignosulfonate of 500 mg/L. The experimental data were calculated to determine the kinetics and mechanism using the pseudo-first-order, pseudo-second-order, intra-particle diffusion, Elovich and Boyd models.

4. Results and Discussion

4.1 Effect of temperature and contact time on lignosulfonate sorption

The effect of contact time on lignosulfonate sorption to eggshell at different temperatures is shown in Figure 1. It can be seen that a rapid initial uptake of lignosulfonate takes place at the beginning of the contact time and thereafter the sorption increases gradually with increasing contact time. The sorption of lignosulfonate reaches equilibrium after 75 minutes.

From Figure 1, it is clear that the amount of lignosulfonate adsorbed on eggshell is enhanced with increasing temperature. Increasing temperature is known to increase the diffusion rate of the lignosulfonate molecule across the external boundary layer and the internal pores of the adsorbent particles. Furthermore, increasing temperature may produce a swelling effect within the internal structure of the eggshell enabling large lignosulfonate to penetrate further (Mckay, 1982; Hiroyuki *et al.*, 1994a; Saker & Podar, 1994). The increasing adsorption of lignosulfonate with increasing temperature reported to be was due to more interaction between adsorbate and adsorbent (Pandey *et al.*, 1988; Hiroyuki *et al.*, 1994b).

4.2 Mechanism of adsorption

To explain the mechanism of adsorption of lignosulfonate compound onto eggshell as an adsorbent, a model of modified double-electric layer proposed by Grahame (1947) has been used. In this model, the Stern layer consists of two layers: an inner layer (IL) in which adsorbed molecules or ions connect with surface of eggshell directly and an outer layer (OL) in which adsorbed molecules or ions have a looser arrangement. When the eggshell powder is mixed with the solution, $CaCO_3$ contained in eggshell may partially dissolve and release Ca^{2+}, $CaHCO_3^+$, $CaOH^+$, HCO_3^-, CO_3^{2-} and OH^-

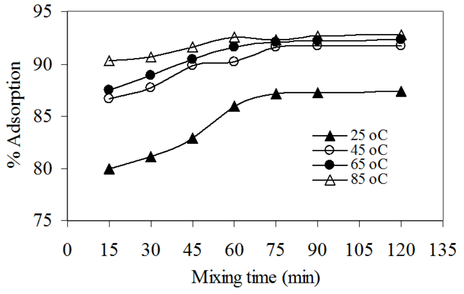

Figure 1. Effect of temperature on adsorption of lignosulfonate onto powdered eggshell.

ions (Pramanpol and Nitayapat, 2006; Arunlertaree *et al.*, 2007).

These ions may be adsorbed onto the surfaces of the eggshell particles and form a negative charge. Aside from the ions mentioned above, the solution also contains Na^+, Mg^{2+} and K^+ ions which originate from the eggshells. These ions may be adsorbed onto the surfaces of eggshell particles, forming an electrical double layer, with the surface of the eggshell particle acquiring a positive charge. Therefore, its Stern IL consists of positive ions and water dipole.

Lignin or lignosulfonate is a heterogeneous aromatic polymer which consists of many phenolic functional groups. It is known that the phenolic functional group may ionize in basic aqueous medium. Thus, phenolic compounds may acquire a negative charge in aqueous media. When lignosulfonate participates in competitive adsorption, lignosulfonate ion will be attracted to the surface of the adsorbent by electrostatic interaction, form a Stern OL and thus increase the adsorption rate of lignosulfonate.

4.3 Thermodynamic parameters

The thermodynamic parameters (DH°, DS° and DG°) for lignosulfonate sorption on eggshell are calculated from the temperature dependent sorption isotherms. The value enthalpy (DH^{o}) and entropy (DS^{o}) can be calculated from slope and intercept of the plot of ln K_L vs 1/T (Figure not show here):

$$\ln K_L = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{R.T} \qquad (7)$$

The Gibbs free energy change (ΔG°) is calculated as:

$$DG^{\circ} = DH^{\circ} - T.\, DS^{\circ} \qquad (8)$$

Where R (8.314 J/mol K) is the gas constant, T (K) absolute temperature and K_L (L/mg) is the Langmuir isotherm constant, which is obtained from Langmuir isotherm data.

The values obtained from Equations 7 and 8 are tabulated in Table 1. A positive value of the standard enthalpy change indicates that the sorption is endothermic. One possible explanation of this positive entropy is that adsorbent and lignosulfonate compound are dissolved well in water, and the hydration sheath of adsorbent and lignosulfonate have to be destroyed before the sorption process. This dehydration process needs energy, and it is favored at high temperature (Xie *et al.*, 2011). The enthalpy change (DH^{o}) for chemisorption is in the range 40-120 kJ/mol (Alkan *et al.*, 2004). Since the value of DH^{o} observed in the system is lower than 40 kJ/mol, the adsorption of lignosulfonate onto eggshell by physisorption.

The positive values of Gibbs free energy (DG^{o}) indicate the non-spontaneous nature of adsorption. The value of DG^{o} becomes more negative with the increase of temperature, which indicates that the reaction is more favorable at high temperatures. The positive value of entropy change (DS^{o}) implies some structural changes during the sorption process, which lead to an increase in the randomness at the solid-solution system (Xie *et al.*, 2011; Rahcamani *et al.*, 2011; Namasivayam & Sangeetha, 2006).

4.4 Adsorption kinetics

Kinetics of adsorption are an important parameter to evaluate adsorption dynamics. In order to examine the controlling mechanism of lignosulfonate adsorption process such as mass transfer and chemical reaction, the pseudo-first-order adsorption, the pseudo-second-order adsorption, the intra-particle diffusion, Elovich and Boyd models were used to test the experimental data. The validity of three kinetic models was checked and the models are depicted in Figures 2-6 and by the linear plots of log ($q_e - q_t$) against t, t/q_t against t and q_t against $t^{0.5}$, q_t against ln t and B_t against t, respectively. Figure 2 shows plots of log ($q_e - q_t$) against t at different adsorbent dosages. It was observed that the first-order kinetic model did not adequately fit the experimental values. Also from Table 2, it is indicated that the values of the correlation coefficients are not high for the different

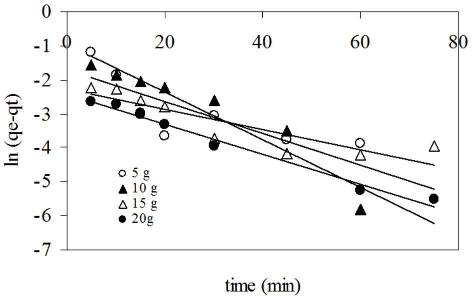

Figure 2. Pseudo-first-order plots for adsorption of lignosulfonate onto powdered eggshell.

Table 1. Thermodynamic parameters of adsorption process at different temperature.

Temperature (°C)	K_L (L/mg)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)	E_a (kJ/mol)
25	0.479	1.83	5.66	12.82	18.17
45	0.543	1.61			
65	0.610	1.39			
85	0.699	1.07			

Table 2. The pseudo-first-order and second-order kinetic parameters for lignosulfonate adsorption using eggshell powder.

Adsorbent Dosages (g)	Pseudo-first-order			Pseudo-second-order			
	k (min^{-1})	*qe*, cal (mg/g)	R^2	*k* (g mg^{-1} min^{-1})	*qe*, cal (mg/g)	R^2	*qe*, exp (mg/g)
5	0.047	0.179	0.795	0.689	8.696	1	8.682
10	0.070	0.390	0.914	0.459	4.523	1	4.498
15	0.030	0.103	0.790	0.971	3.055	1	3.051
20	0.102	0.004	0.982	1.430	2.294	1	2.286

adsorbent dosages. Furthermore, the estimated values of q_e calculated from the equation q_e differ substantially from those measured experimentally. That gives confirmation that the lignosulfonate sorption using eggshell did not obey the pseudo-first-order model.

In contrast, the pseudo-second-order rate equation for sorption of lignosulfonate compound onto eggshell agreed well with the data (Figure 3). The correlation coefficients calculated by using the pseudo-second-order model i.e. R^2, and the pseudo-second-order parameters i.e. k_2, q_e,exp and q_e,calc, are shown in Table 2.

As seen from Table 2, the calculated equilibrium sorption capacity for the pseudo-second-order model, q_e, calc, is close to the experimental value, q_e,exp, and the linear regression analysis of the pseudo-second-order rate equation gave a high R^2 value.

Figure 4 shows intra-particle diffusion plot at different adsorbent dosages. Referring to Figure 4, a linear relationship exists after a certain time but they do not pass through the origin. This is due to boundary layer effect. The larger the intercept effects the greater contribution of surface sorption is the rate determining step. Previous studies showed the same features of the plot which characterize different steps of adsorption process (Aksu & Aisoglu, 2005; Kamari *et al.*, 2009; Patil *et al.*, 2011). The intercepts (*C*) and k_d values of plots q_t against $t^{0.5}$ decrease with increasing of adsorbent dosage (Table 3). This was due to an increase in the overall rate of the lignosulfonate adsorption, which resulted in a rapid decrease in the lignosulfonate concentration and, thus, the driving force for intra-particle diffusion (Sun & Yang, 2003; Qada *et al.*, 2007). Moreover, this can also be attributed to the significance of the external diffusion and the reduction in the effect of intra-particle diffusion as the ratio of the adsorbent/adsorbate in the system increased (Mckay *et al.*, 1986; Qada *et al.*, 2007).

Figure 5 shows plots of the Elovich model at different adsorbent dosages. It is indicated from the estimated Elovich parameters (Table 4) that the R^2 values obtained from Elovich equation were in the range of 0.751-0.933 for the different adsorbent dosage. In order to determine the actual slow step

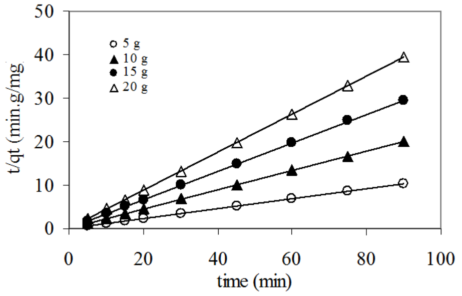

Figure 3. Pseudo-second-order plots for adsorption of lignosulfonate onto powdered eggshell.

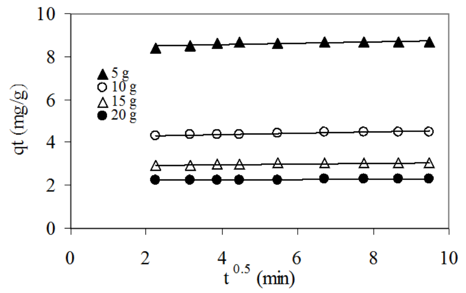

Figure 4. Intra-particle diffusion plots for adsorption of lignosulfonate onto powdered eggshell.

Table 3. Parameters of the intra-particle diffusion model for lignosulfonate adsorption using eggshell powder.

Adsorbent Dosages (g)	k_d (mg/g.min$^{0.5}$)	*C*	R^2
5	0.030	8.441	0.588
10	0.030	4.250	0.941
15	0.015	2.919	0.872
20	0.011	2.198	0.878

involved in the lignosulfonate adsorption process, the kinetic data as obtained by the batch method were further analyzed using the Boyd model, and the plot of B_t against t can be seen in Figure 6. The Boyd linear plots with high correlation coefficients R^2 (Table 4) indicate that boundary layer/ film diffusion mainly governs the lignosulfonate adsorption process.

From Figure 1, we can see that the amount of lignosulfonate adsorbed on eggshell is enhanced with increasing temperature. The other thermodynamic parameter, activation energy, E_a, was calculated using Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{R.T} \qquad (9)$$

where E_a is the activation energy (kJ/mol), A the Arrhenius factor, R the gas constant (8.314 J/mol K) and T is the absolute temperature (K). When ln *k* is plotted versus 1/T, a straight line with slope $-E_a/R$ is obtained (Figure 7). The magnitude of activation energy gives an idea about the type of diffusion path of sorption process which is mainly film or pore diffusion (Namasivayam & Sangeetha, 2006). Film diffusion typically has an activation energy of 17-21 kJ/mol and pore diffusion has an activation energy of 21-42 kJ/mol (Namasivayam & Sangeetha, 2006; Sparks, 1999).

The obtained value of activation energy (18.17 kJ/mol) in Table 1 confirms that the adsorption of lignosulfonate onto eggshell is film diffusion controlled.

4. Conclusions

The result from this work showed that the temperature has an important role in the adsorption of lignosulfonate compounds onto eggshell. Thermodynamic parameter data indicated that the lignosulfonate sorption process was non-spontaneous and endothermic under the experimental conditions, with the Gibbs free energy (ΔG^o) in the range of 1.83-1.07 kJ mol^{-1}, enthalpy (ΔH^o) and entropy (ΔS^o) of 5.66 kJ mol^{-1} and 12.82 J mol^{-1}, respectively, and the activation energy of 18.17 kJ mol^{-1}. The kinetic experimental data properly correlated with the pseudo-second-order kinetic model with a rate constant in the range of 0.689 –1.430 g mg^{-1} min^{-1}, while both the intra-particle diffusion and Boyd kinetic models and the value of activation energy indicated that boundary layer or film diffusion was the main rate determining step in lignosulfonate adsorption process.

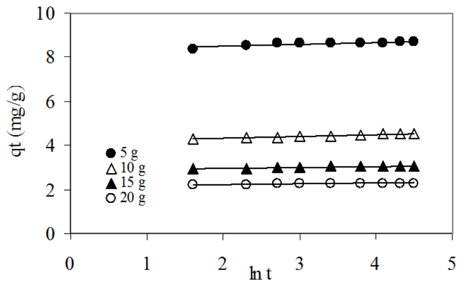

Figure 5. Elovich plots for adsorption of lignosulfonate onto powdered eggshell.

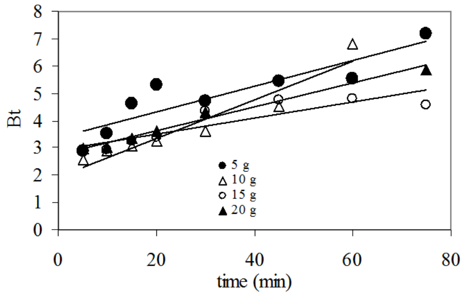

Figure 6. Boyd plots for adsorption of lignosulfonate onto powdered eggshell.

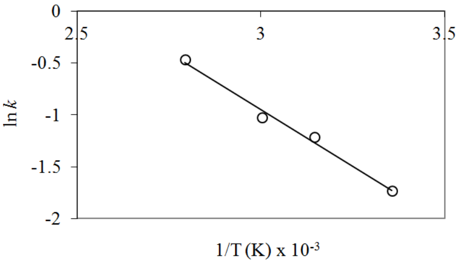

Figure 7. Arrhenius plots for adsorption of lignosulfonate onto powdered eggshell.

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Table 4. The Elovich and Boyd kinetic parameters for lignosulfonate adsorption using eggshell powder.

Adsorbent Dosages (g)	Elovich Model			Boyd Model
	α (mg/g.min)	β (g/mg)	R^2	R^2
5	8.325	0.087	0.751	0.795
10	4.160	0.078	0.989	0.914
15	2.873	0.040	0.930	0.790
20	2.165	0.028	0.933	0.982

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