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Original Article

Adsorption of lignosulfonate compounds using powdered eggshell

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Abstract

Batch adsorption of lignosulfonates using untreated powdered eggshell under the influences of mixing time, pH, particle size and dose of powdered eggshell was investigated. Adsorption isotherms of lignosulfonates onto powder eggshell were also studied. Eggshells were collected from the Balubur traditional market in Bandung, Indonesia, washed with distilled water, air dried, and then ground into powder of different particle sizes. Kinetic studies found that equilibrium time was as high as 90 minutes. From experiments carried out at different pH, it was observed that pH plays an important role in the adsorption of lignosulfonate compounds. It was also observed that particles size has no significant effect on the adsorption of lignosulfonate compounds. The optimum dosage of powdered eggshell was 30 g/100 mL of 500 mg/L lignosulfonate solution. Adsorption isotherms studied through the use of graphical methods revealed that the adsorption of lignosulfonates onto powdered eggshell follows the Langmuir model.

Keywords: adsorption, eggshell, lignosulfonate

1. Introduction

Pulp and paper mills are a large industry that generates a significant amount of wastewater and is a major source of water pollution. Black liquor produced from Kraft processes contains a large volume of brown coloured effluent. The effluent colour is primarily due to lignosulfonates and their degraded products, which are chemically stable, resistant to biological degradation (very high COD/BOD ratio), and are intractable to separation by conventional treatment methods (Mohan and Karthikeyan, 1997). This wastewater causes three kinds of environmental impacts: high biological oxygen demand (BOD), toxicity and color (Diez *et al.*, 1999; Ali and Sreekrishnan, 2001).

Physical and chemical processes to remove colour and toxicity from wastewater were extensively studied. These processes include adsorption, coagulation, flotation, oxidation, biosorption, biodegradation, UV photodecomposition and ultrafiltration. Most of these processes are expensive and none of them are considered commercially viable by pulp and paper industries due to unfavorably high costs. Adsorption has been found to be an efficient and inexpensive method for removing dyes, pigments and other colorants and for controlling the bio-chemical oxygen demand. Activated carbon, inorganic oxides, mineral and natural adsorbents have been extensively used as adsorbents to treat wastewater (Al-Asheh *et al.*, 2003; Naseem and Tahir, 2001). Despite its prolific use in water and wastewater industries, commercial activated carbon remains an expensive material. In addition, three problems are associated with the use of carbon for the adsorption of pollutants, these are: (i) its relatively high cost, (ii) the fragility of present types of activated carbon makes the regeneration and reuse of activated carbon difficult, and (iii) activated carbon is limited to the removal of non-polar materials (Oke *et al.*, 2008). Therefore, there is a need to continue the search for materials that are more suitable than

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carbon for water treatment, be it for lower initial costs or the potentially greater ease of regeneration.

In recent years, numerous low cost natural materials such as activated charcoal (Mohan and Karthikeyan, 1997), wood ash (Tantemsapya *et al.*, 2004), sandstone (Grigg and Bai, 2004), limestone (Bai and Grigg, 2005), fly ash (Ugurlu *et al.*, 2005), sepiolite (Ugurlu *et al.*, 2005), dolomite (Bai *et al.*, 2009), hematite (Nanthakumar *et al.*, 2010) and other adsorbents (Ratinac *et al.*, 2004) have been used and investigated for removal and adsorption of lignin or lignosulfonates.

Meanwhile, eggshells are used in enormous quantities by food manufacturers, restaurants and household and the shells are disposed of as solid waste. Investigations have been conducted to explore the possibility of useful applications of eggshells, especially for wastewater. The porous nature of eggshells makes it an attractive material to be used as an adsorbent. Each eggshell is estimated to contain between 7000 and 17000 pores (Pramanpol and Nitayapat, 2006; Elkady *et al.*, 2011). Research has shown that eggshells and eggshell membrane may be used as an adsorbent for iron (Yeddou and Bensmaili, 2007), cadmium (Park *et al.*, 2007; Kuh and Kim, 2000), chromium (Chojnacka, 2005; Park *et al.*, 2007; Ghazy *et al.*, 2008; Rajendran and Mansiya, 2011; Liu and Huang, 2011), lead (Arunlertaree *et al.*, 2007; Park *et al.*, 2007), arsenic (Oka *et al.*, 2008), reactive dye (Pramanpol and Nitayapat, 2006; Ehrampoush *et al.*, 2011; Elkady *et al.*, 2011), cationic dye (Tsai *et al.*, 2006), azo dye (Tao, 2011) and malathion (Elwakeel *et al.*, 2010). However, there has so far been no study reported in academic literature related to the use of powdered eggshells as an adsorbent for removing lignosulfonates from black liquor. Therefore the main aim of this study was to investigate the possibility of using powdered eggshells as adsorbent material. Eggshells were chosen as adsorbent due to its reasonable cost and ease of regeneration. In addition, there has yet to be any study reported in literature related to the use of powdered eggshells as an adsorbent to remove lignosulfonates from black liquor. This would benefit not only mills by reducing the costs of lignosulfonate treatment, but also minimizing the impact of eggshell waste on the environment.

2. Materials and Methods

2.1 Materials

Chicken eggshells were collected from the Balubur traditional market in Bandung, Indonesia. The membranes were separated from the eggshells by hand. The eggshells were then washed with distilled water, air-dried, ground into powder with particle sizes of 50, 100 and 150 μm and stored in desiccators. Physical and chemical properties of the eggshells are listed in Table 1. Sodium hydroxide and hydrochloric acid used to adjust pH was purchased from Merck. For adsorption studies lignosulfonate obtained from Aldrich was used as adsorbate. The structure of lignosulfonate compounds can be seen in Figure 1. The water used was

Table 1. Physical and chemical properties of the eggshell sample

Component	Value
Real density (g/cm^3)	2.47[a]
pH (H_2O)	8.3[a]
Cation exchange capacity (meq/100 g)	9.52[a]
Particle porosity	0.0162[b]
Total pore volume (cm^3/g)	0.0065[b]
BET surface area (m^2/g)	3.23[c]
Content of soluble salts (ppm)[a]:	
K	12.0
Ca	50.2
Mg	12.0
Na	21.0
Organic matter (%)	5.36
Organic carbon (%)	3.11
$S - SO_4$ content (ppm)	39.0

[a] Freire and Holanda, 2006
[b] Tsai *et al.*, 2006
[c] Experiment

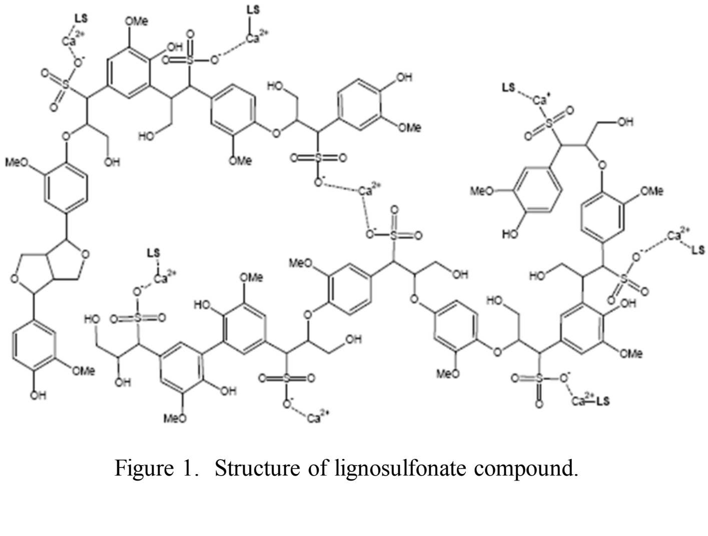

Figure 1. Structure of lignosulfonate compound.

generated from a distillation system. All materials were used without further purification.

2.2 Methods

2.2.1 Characterization of powdered eggshells

A scanning electron microscope (JEM-2010, JEOL) was used for the investigation of particle morphology of powdered eggshells. X-ray diffraction patterns were measured using RINT 2000 (Rigaku Instrument Corp.) with Cu Kα radiation for confirming the structure and mineral composition of powdered eggshells. The surface area of powdered eggshells was analyzed through nitrogen adsorption measurements at 77 K using Micromeritics Gemini 2370 equipment.

2.2.2 Sorption studies

Adsorption experiments were carried out in 100 mL flasks immersed in a thermostatic shaker bath at 25°C for 2, 5, 10, 15, 20, 25, 30, 45, 60, 75, 120, 180, 240 and 300 minutes. Chicken eggshell samples of 5, 10, 15 and 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 λ of 290 nm. The effect of pH on the adsorption of lignosulfonate compounds was studied by conducting equilibrium sorption tests at different suspension pH values (7.0, 9.0, 11.0 and 13.0) using 20 g of powdered eggshell for 15, 30, 45, 60, 75, and 90 minutes. The suspension pH was adjusted by using NaOH and HCl solutions. To determine the effect of powdered eggshell dosage, the experiments were carried out at seven different dosages (5, 10, 15 and 20, 25, 30 and 35 g) for 90 minutes and pH of 7. The effect of particle size was investigated by using three different particle-size: 50, 100 and 150 µm, of powdered chicken eggshells. The experiments were carried out using 20 g of powdered eggshell for 90 minutes.

2.2.3 Study of adsorption isoterm

The adsorption isotherm for determining of adsorbent advisability 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 lignosulfonate concentration of 500 mg/L. The experimental data were calculated to determine the adsorption isotherm by using the Langmuir and Freundlich models.

3. Results and Discussion

3.1 Characterization of powdered eggshells

In order to characterize the crystallinity of eggshells, XRD analysis was performed. The diffractogram in Figure 2

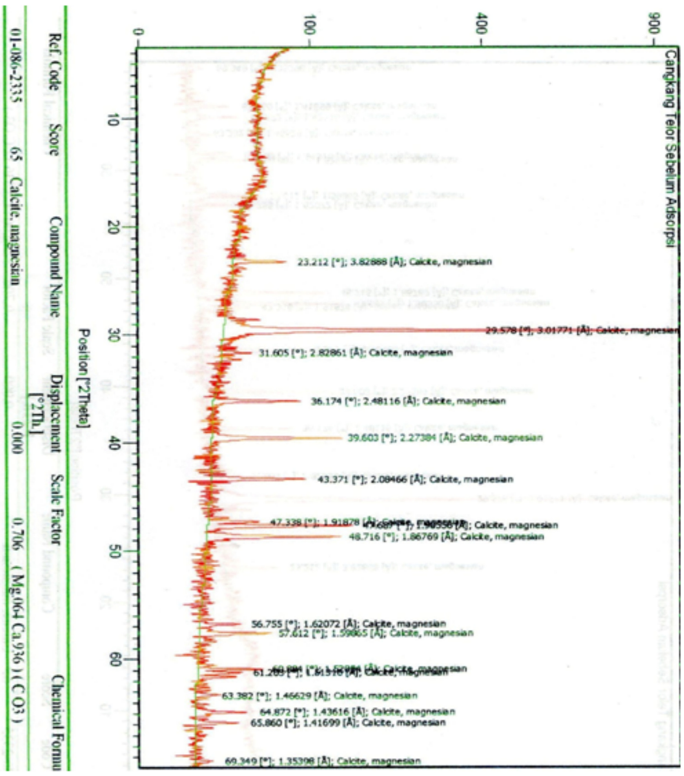

Figure 2. Diffractogram of powdered eggshell.

indicates that diffraction pattern of eggshell has calcite structure and is similarity to calcium carbonate mineral (Murakami and Rodrigues, 2007). SEM result at Figure 3 shows the morphology of powdered eggshell. It confirms the crystallinity of eggshell and the existence of pores in the structure. The surface area of powdered eggshells obtained from nitrogen adsorption measurement is 3.23 m^2/g.

3.2 Sorption studies

3.2.1 Effect of mixing time on sorption process

In order to obtain optimum adsorption with high efficiency, we need to obtain the optimum mixing time of adsorbent and lignosulfonate solution. Figure 4 shows the effect of mixing time on adsorption of lignosulfonate solution on powdered eggshell for different dosages. The adsorption of lignosulfonate solution reaches equilibrium after 90 minutes.

3.2.2 Effect of pH on sorption process

The effect of pH on the sorption lignosulfonate compounds is given in Figure 5. It is well known that adsorption processes depend highly on pH because of the high sensitivity of functional groups of the adsorbate.

A slight decrease in the amount of lignosulfonate compound adsorbed with increasing pH solution was observed (see Figure 5). The observed lower sorption capacities at the high pH can be attributed to the decrease in the adsorption ability of lignosulfonate compounds at high pH.

To explain the adsorption behavior of these lignosulfonate, a model of modified double-electric layer proposed by Grahame (1947) has been used. According to 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. It is well known that eggshells contain $CaCO_3$ as the major component (up to 95%). In the presence of water, calcium salts undergo displacement reaction (Oka *et al.*, 2008) and this reaction results in a basic solution that is also observed in this experiment. When the eggshell powder is mixed with the solution, calcium salts may partially dissolve and release Ca^{2+}, HCO_3^-, CO_3^{2-} and OH^- ions (Pramanpol and Nitayapat, 2006; Arunlertaree *et al.*, 2007), through the following reaction:

$$CaCO_3 + H_2O \rightleftarrows Ca^{2+} + HCO_3^- + OH^- + CO_3^{2-}$$

These ions may be adsorbed onto the surfaces of the eggshell particles and form a negative charge. Similar phenomena have also been reported by other researchers with calcite (Somasundaran and Agar, 1967). 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 through the following reaction:

$$\varnothing\text{-}OH + OH^- \leftrightarrow \varnothing\text{-}O^- + H_2O \quad (\varnothing = \text{phenyl group})$$

Thus, phenolic compounds may acquire a negative charge in aqueous media. When lignosulfonate is participated in competitive adsorption, lignosulfonat ion will be

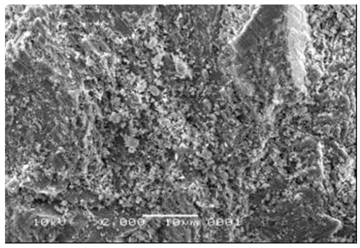

Figure 3. SEM micrographs of powdered eggshell.

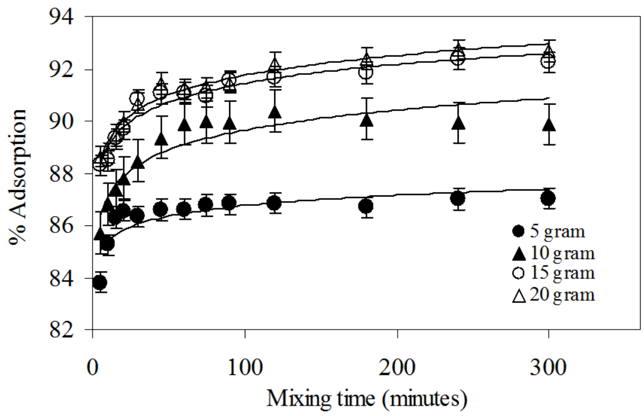

Figure 4. Effect of mixing time on adsorption of lignosulfonate onto powdered eggshell.

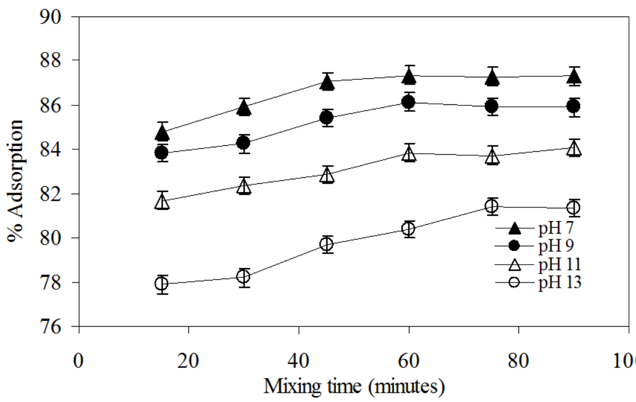

Figure 5. Effect of pH on adsorption of lignosulfonate onto powdered eggshell.

attracted to the surface of the adsorbent by electrostatic interaction, form a Stern OL and thus increase the adsorption rate of lignosulfonate. Besides that, at low pH, hydrogen ions are also present in the solution, giving the surface of the eggshell particle a positive charge, causing electrostatic interaction to occur between the adsorbent and the lignosulfonate compound. Meanwhile at high pH, more hydroxyl ions are present in the bulk solution and are adsorbed onto eggshell surface, so the surface charge is negative. This will reduce the electrostatic attraction between the eggshell particle surface and lignosulfonate compound because of the less positive or more negative surface charge. This decreases the adsorption rate of lignosulfonate.

3.2.3 Effect of particle size of powdered eggshells on sorption process

Determination of the effect of particle size on sorption was conducted using samples of three different average particle sizes: 50, 100 and 150 µm at pH 7 and temperature of 25°C for 90 minutes. The result is shown at Figure 6. As seen from Figure 6, variation of the particle size of powdered eggshells statisticaly has no significant effect on the adsorption of lignosulfonate compounds as indicated by 89 – 92%.

3.2.4 Effect of powdered eggshells dosage on sorption process

The effect of powdered eggshells dosage on sorption of lignosulfonate is shown in Figure 7. The amount of lignosulfonate compound adsorbed increased from 78.83% to 92.16% with an increase in adsorbent dosage from 5 g to 30 g at pH = 7. As explained above, when the eggshell powder is mixed with the solution, calcium salts may partially dissolve and release Ca^{2+}, HCO_3^-, CO_3^{2-} and OH^- ions causing the solution to become basic and forming negative charges of the surfaces of the eggshell particles. As the dosage of eggshell is increased, the solution becomes more basic and the surface area negative charge increases; thus, adsorption of ligno¢sulfonate is increased. A maximum removal of 92.16% was observed at an adsorbent dosage of 30 g per 100 mL of lignosulfonate solution.

3.2.5 Adsorption isoterm

1) Langmuir adsorption isoterm

The isotherm experimental data were fit to the Langmuir model using the equation below:

$$q_e = \frac{q_m.b.C_e}{1+b.C_e} \quad (1)$$

where q_e and q_m is the amount adsorbed at equilibrium and maximum mg/g, respectively, C_e is the equilibrium concentration (mg/L) and b is the Langmuir isotherm constant (L/mg). The result is shown in Figure 8 and Langmuir constants are tabulated in Table 1. From Figure 8, we can see that the adsorption curves were single, smooth, plateau, continuous,

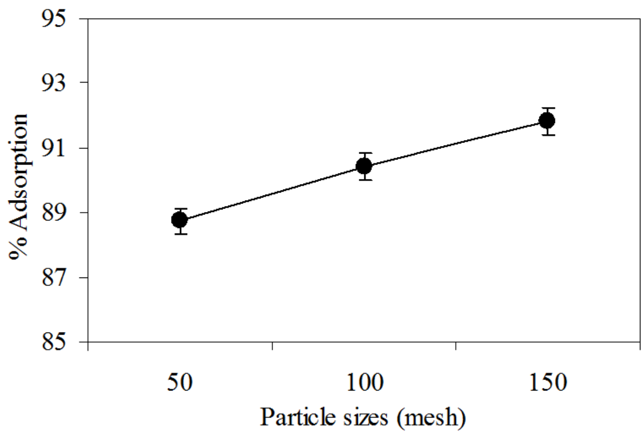

Figure 6. Effect of particle size on adsorption of lignosulfonate onto powdered eggshell.

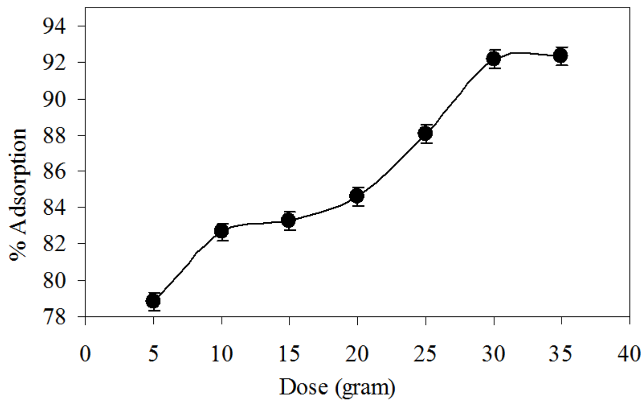

Figure 7. Effect of dosage on adsorption of lignosulfonate onto powdered eggshell.

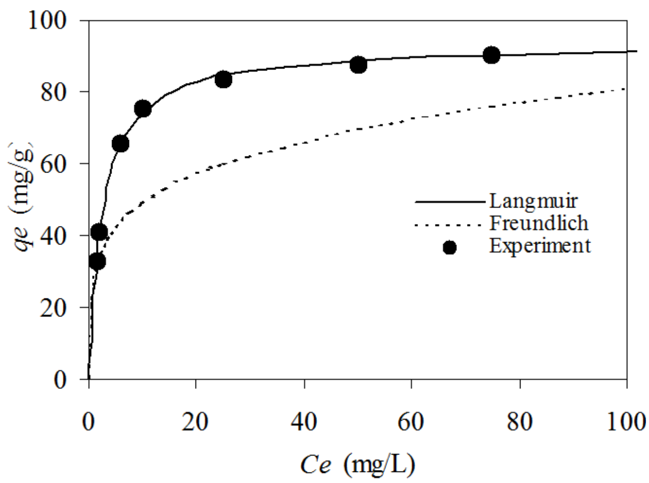

Figure 8. Fitting curve for both Langmuir and Freundlich isotherms.

leading to saturation, and this indicates the possible monolayer coverage on the surface of the adsorbent (Meski *et al.*, 2010; Ratinac *et al.*, 2004). To see whether the processes were chemi- or physical sorption, we also studied the effects of temperature on the sorption of lignosulfonate compound onto eggshells. Results indicated that the adsorption capacity of eggshells for the lignosulfonate increased with temperature (Figure not shown here). This suggests that the adsorption mechanism was chemisorption (Jadhav and Vanjara, 2004; Carvalho *et al.*, 2011). From the linearization plot of the Langmuir isotherm model, the value of q_m in our experiment was found to be 93.46 mg/g. However, when comparing b and q_m of the powdered eggshell (Table 1) to b and q_m of sephiolite for lignin adsorption, which were 0.44 L/mg and 233.1 mg/g (Ugurlu *et al.*, 2005), the adsorption pattern of the two materials were similar but sephiolite was better. This is due to the lower specific surface area of powdered eggshell (3.23 m^2/g) compared to sephiolite (200 - 276 m^2/g).

The effect of isotherm shape has been discussed with a view to predicting whether an adsorption system is favorable or unfavorable (Choi & Cho, 1996). The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L, which is defined by (Choi & Cho, 1996; Lin & Huang, 2002):

$$R_L = \frac{1}{1 + aCo} \quad (2)$$

Mamdouth *et al.* (2004) and Choi & Cho (1996) stated that R_L indicates the isotherm shape according to the following adsorption characteristics: $R_L > 1$ (unfavorable), $R_L = 1$ (linear adsorption), $R_L = 0$ (irreversible) and $0 < R_L < 1$ (favorable). The value of R_L in this study was found to be between zero and one. This suggests that adsorption of lignosulfonate by powdered eggshell is favorable.

2) Freundlich adsorption isotherm

The isotherm experimental data were fit to the Freundlich model by using the equation below:

$$q_e = K_f C_e^{1/n} \quad (3)$$

where C_e is the equilibrium concentration (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of absorbent (mg/g), K_f and n is Freundlich constants.

The resulting fitting curves from this isotherm are illustrated in Figure 8 and Freundlich constants are tabulated in Table 1. It was shown that the experimental data of lignosulfonate adsorption on powdered eggshell could not be fitted by this model. In our experimental range, the results of powdered eggshells are best described using the Langmuir model, as indicated by the well fitted curve lines.

3.2.6 Comparison of lignosulfonate adsorption with other adsorbents reported in the literature

It is also important to compare the value of maximum adsorption capacity obtained from this study with values from other reported adsorbents, since this will determine the applicability of powdered eggshells as a potential low-cost adsorbent in cleaning up lignosulfonate compounds. The values of lignosulfonate adsorption capacities of some adsorbents are shown in Table 2. Experimental data of the present investigation show different values from other reported values. Adsorption capacity varies and depends on the properties of the individual adsorbent, the extent of surface/surface modification, the initial concentration of the adsorbate (Mousavi and Seyedi, 2011), range of molecular size fraction of adsorbate and degree of ionization per unit weight of adsorbate (Garcia *et al.*, 1998).

4. Conclusions

Results from this research show that pH has an important role in the adsorption of lignosulfonate compounds. In addition, the particle size of powdered eggshell has no significant effect on the adsorption of lignosulfonate com-

Table 2. The Langmuir and Freundlich isoterms constant.

Langmuir Model		Freundlich Model	
q_m (mg/g)	b (L/mg)	n (g/L)	K_f (g/g)
93.46	0.27	0.37	0.01

Table 3. Comparison of adsorption capacity of various adsorbent for lignosulfonate adsorption

Adsorbent	q_m (mg/g)	Reference
Sepiolite (adsorbate is lignin)	233.1	Ugurlu *et al.*, 2005
Eggshell	93.46	This study
Limestone	1.646	Bai *et al.*, 2005
Dolomite	0.534	Bai *et al.*, 2009
Wood ash (adsorbate is lignin)	0.177	Tantemsapya *et al.*, 2004
Activated charcoal (adsorbate is lignin)	0.42	Mohan and Karthikeyan, 1997
Berea sandstone	6.08	Grigg and Bai, 2004

pounds. Sorption tends to attain equilibrium in nearly 90 minutes for these systems. The optimum dosage of powdered eggshell was 30 g of 500 mg/L lignosulfonate solution. The adsorption isotherm data could be fitted with the Langmuir model. The results of this study suggest that powdered eggshell, with its low cost and abundant availability, has a potential for being used as an adsorbent for contaminants, such as lignosulfonate compounds.

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