



Effect of Sodium Periodate on the Adsorption Capacity of Silica-Lignin from Rice Husk on Chromium(VI)

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Abstract

Reactive groups such as silanol, hydroxyl, and carbonyl groups in silica-lignin composites play a role in binding to chromium(VI) ions. The activation of functional groups in silica-lignin can be increased by the addition of an activator such as sodium periodate, which can also oxidize the lignin monomer (guaiasil) to ortho-quinone. This study aimed to obtain silica-lignin composites from rice husks activated by sodium periodate with a high surface area. Composite absorption was tested on chromium(VI) adsorption. Silica-lignin isolation was carried out by using the sol-gel method at concentrations of sodium hydroxide 5, 10, 15, and 20% (b/b). Silica-lignin activated with sodium periodate 10% (b/b) had the smallest particle size of about $8\mu\text{m}$, with a surface area of $14.0888\text{ m}^2\cdot\text{g}^{-1}$ and followed Halsey isotherm adsorption model, with an adsorption capacity of $0.3054\text{ mg}\cdot\text{g}^{-1}$.

1. Introduction

Efforts to overcome metal contamination in aqueous systems can be accomplished by applying several methods, including adsorption [1], chemical precipitation [2], solution extraction [3], ion exchange [4], membrane filtration [5], flocculation [6], and reverse osmosis [7]. However, the adsorption method is more widely used because it has several advantages, the most effective and economical [8].

Silica-lignin can be used as a heavy metal adsorbent in nickel(II) ions, cadmium(II) ions, and lead(II) ions, with high adsorption capacity. Based on previous research [9], silica-lignin can be produced from the isolation of rice husks through a sol-gel process using sodium hydroxide. Rice husk is used as a precursor because it has a lignin component of 19.8% and silica 18.7%. Silica-lignin from rice husk has mesopore with a size of about 60 nm with a surface area of $471.7\text{ m}^2/\text{g}$.

Yuliyati *et.al.* [10] isolated silica-lignin from rice husks using a potassium carbonate solvent, and its absorption capacity was tested on chromium(VI) ions,

with $0.3410\text{ mg}\cdot\text{g}^{-1}$. Based on the absorption test, this composite did not fulfill the requirements as an effective adsorbent; it was possible that the active group was less reactive. One effort to increase the active group was by adding an activator to lignin [11]. Sodium periodate has been shown to increase the adsorption capacity of lignin in organic dyes because sodium periodate can convert hydroxyl groups into carboxyl groups. Based on this, the use of sodium periodate as an activator in silica-lignin composites can increase its absorption when applied as an adsorbent.

Silica is formed from elements of silicon and oxygen, through strong covalent bonds. Nanoporous silica is widely used in wastewater treatment because of its high surface area and has a reactive group on its surface [12]. Similarly, lignin is a natural polymer that is present in plants that are firmly bound to cellulose and hemicellulose. The lignin-forming monomers are listed in Figure 1. Lignin has a complex three-dimensional structure chemically and physically, making it difficult to isolate from plants. Generally, strong alkaline or acidic solutions can be used to depolymerize macromolecules

and break the chemical structure of lignin at high temperatures. The presence of oxygen-containing groups in large quantities in lignin allows physical absorption, hydrogen bonds, coordination bonds, and covalent bonds so that they can interact with other acidic compounds [13].

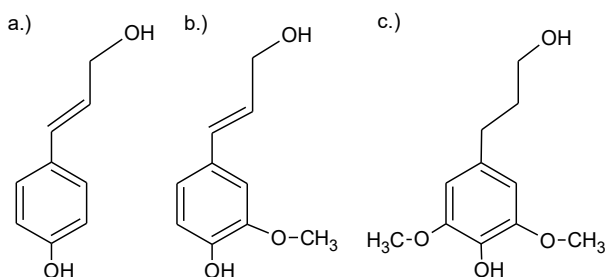


Figure 1. Lignin monomers: (a) p-kumaryl alcohol, (b) coniferyl alcohol (guaiasil) and (c) alcoholic alcohol [14].

As an adsorbent, lignin has been extensively studied to remove metals in wastewater (for example, from electroplating plants) by absorption and precipitation methods. However, during wastewater treatment, the pH value of wastewater dramatically affects the performance of the adsorbent and the solubility of lignin. To increase the absorption capacity of lignin, it is necessary to adjust the pH and thermal stability [12]. The addition of silica to the lignin adsorbent makes the oxygen functional group on the silica surface interact with lignin to increase its stabilization. Silica hybridization with lignin is accompanied by more active side formation on the surface of hybrid materials, which increases the ability of lignin to absorb heavy metal ions, organic compounds, and other pollutants [13].

The absorption capacity of lignin in heavy metal ions can be increased by adding oxidizing agents so that the active side of lignin, such as carbonyl groups, increases [11]. Oxidation occurs in guaiasil monomers to form ortho-quinone structures, as shown in Figure 2.

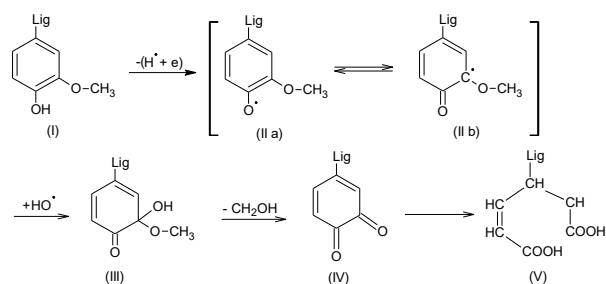


Figure 2. The mechanism of the oxidation reaction in guaiasil (lignin monomer) becomes ortho-quinone [15].

The first stage of periodic attacking the guaiasil and producing mesomeric radicals (II a), followed by mesomeric tautomer (II b). Then a reaction occurs with hydroxyl radicals producing hemiacetal (III). At this stage, methanol is released to form ortho-quinone (IV). Higher levels of lignin oxidation (50% sodium periodate) cause ring-opening, especially in C-3 and C-4, which lead to the formation of muconic acid (V). The structure of muconic acid increases the carbonyl group and increases the acidity of lignin [16]

2. Methodology

2.1. Isolation and Activation of Silica-Lignin from Rice Husks

Clean and dry rice husks are washed with 1 N hydrochloric acid while heated to remove metal oxide in rice husks [17]. Then they were rewashed with distilled water to neutral pH and dried, mashed to size 50 mesh (Retsch, ASTM). Fine rice husks were dissolved in a sodium hydroxide (p.a. Merck) 2 M with a ratio of 1: 3 (b/v), then heated at 100°C for 4 hours, and the filtrate and residue were then separated [9]. The filtrate was heated at 90°C while stirring, and sulfuric acid (p. A. Merck) was added dropwise to pH 5, then periodic sodium of 5% w / w was added by weight of lignin at 55°C [16]. Sulfuric acid was added back to pH 2 while heated at 90°C; then, the solution was allowed to stand for 6 hours until the precipitate was formed, then centrifuged to separate it from the supernatant. The precipitate was washed with distilled water then dried at 90°C for 12 hours. The above steps were repeated with the addition of different concentrations of periodic sodium (10%, 15%, and 20% and without the addition of periodic sodium as standard). Each sample was marked as SL5 (with added NaIO₄ 5%(b/b), SL10 (with added NaIO₄ 10%(b/b), SL15 (with added NaIO₄ 15%(b/b), SL20 (with added NaIO₄ 20%(b/b), and SL0 (without NaIO₄). Based on previous research [10], the samples obtained from this step were silica-lignin composites.

2.2. Characterization of silica-lignin composite

The surface bonding of the silica-lignin composite was characterized by FTIR (One Perkin Elmer), while the surface morphology was characterized by SEM (JED-2200 JEOL), and the composition was tested with EDX. The prediction of surface area was carried out through the absorption of methylene blue. The silica-lignin with the highest surface area was then tested with BET (Nova Touch LX4) to determine specific surface area, total pore volume, and average pore diameter.

2.3. Optimal Contact Time

Silica-lignin weighing as much as 0.1000 g was put into shake bottles containing 50 mL of 1 ppm chromium(VI) solution and shaken for 10 minutes. The same procedure was carried out for time variations of 15; 20; 30; 60; 90; 120 and 180 minutes. Diphenylcarbazide (IV) concentrations using a spectrophotometer (Genesys 10 S UV-Vis). The concentration of chromium(VI) adsorbed was calculated from the difference in initial and final concentrations. The optimum contact time was chosen based on the time when the concentration of chromium(VI) was not re-adsorbed (saturation point). The above process was repeated by changing the adsorbent (silica-lignin) with silica-lignin 10% activation, 15% activation, 20% activation, and blank as a standard.

2.4. Determination of Silica-Lignin Adsorption Types

Silica-lignin from 5% activation weighing as much as 0.1000 g, was put into shake bottles containing

chromium(VI) sample solution with a variation of 0.05 concentration; 0,1; 0.25; 0.5; 0.75; 1; 1.25; 1.5; 1.75; 2 and 2.25 ppm. The mixture was shaken for optimum contact time, allowed to stand for 30 minutes, and filtered. The filtrate was added with diphenylcarbazide, and its concentration was determined by a visible light spectrophotometer. The adsorption model was determined by the Halsey equation. The Halsey isotherm adsorption model was used for the evaluation of multilayer adsorption systems for adsorption of adsorbate at relatively large distances from the surface. Halsey isotherm adsorption equation was as per equation 1 [18].

$$\ln q_e = \left[\left(\frac{1}{m_H} \right) \ln K_H \right] - \left(\frac{1}{m_H} \right) \ln \frac{1}{C_e} \quad (1)$$

where:

K_H = Halsey's constant

m_H = Halsey equation exponent

Experimental data at high concentrations treated with this equation determine the heterogeneous pore distribution properties of adsorbents. The equation well presents adsorption data about isotherms similar to type II, which appears in hetero pore solids [19].

The steps above were repeated by changing the adsorbent with silica-lignin without activation as a comparison.

2.5. Brunauer–Emmett–Teller (BET) Theory

BET was a model for multilayer adsorption. Molecules occupy positions above other molecules to form various types of multilayers. The BET equation was listed in equation 2 [20].

$$\frac{C_e}{q_e(C_S - C_e)} = \frac{1}{q_S C_{BET}} + \left(\frac{C_{BET} - 1}{q_S C_{BET}} \right) \left(\frac{C_e}{C_S} \right) \quad (2)$$

Where:

C_e = equilibrium concentration (mg/L)

C_S = adsorbate monolayer saturation concentration (mg/L)

C_{BET} = BET adsorption isotherm relating to the energy of surface interaction (L/mg)

BET theory explains the phenomenon of adsorption of gas molecules on the surface of solids (absorption of gas molecules on the surface of solids). The number of gas molecules adsorbed depends on the surface area of the adsorbent; therefore, BET can determine the surface area, and determine its porosity.

3. Results and Discussions

3.1. Characterization of Silica-Lignin

Comparison of silica-lignin FTIR spectra with and without sodium periodic activation, at various concentrations (b/b) 5%, 10%, 15% and 20% (Figure 3).

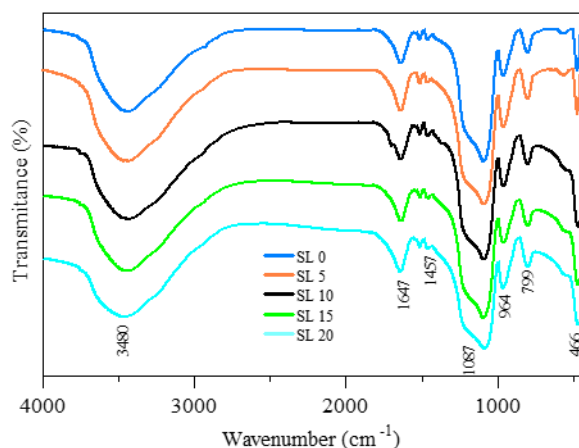


Figure 3. FTIR-spectra of SLO, SL5, SL10, SL15, and SL20.

Table 1. Comparison of silica-lignin functional group assignment between this work and reference.

No	Wavenumber (cm ⁻¹) (this work)	Wavenumber (cm ⁻¹) (reference)	Vibrational Assignment	Phase(s) assignment
1	466	476	Si-O bending	Silica
2	799	809	Si-O asymmetric stretching	Silica
3	964	856	Aromatic C-H (guaiacyl unit)	Lignin
4	1087	1085	C-O stretching	Lignin
5	1457	1467	C-H(CH ₃ +CH ₂) bending	Lignin
6	1647	1637	C=O stretching	Lignin
7	3480	3434	O-H stretching	Silica+Lignin

The functional groups attached in the structure were examined using FTIR and showed in Table 1. All silica-lignin spectra with and without sodium periodic activation with concentration variations showed very similar absorption characters. Characteristic uptake of silica-lignin occurs at 3480 cm⁻¹ from the stretching vibration of the OH group, at 1457cm⁻¹ from the C-H(CH₃+CH₂) bending, at 1420 cm⁻¹ from CH deformation and vibration of the aromatic ring, at 1647 cm⁻¹ from stretching of C=O conjugate, at 1200-1050 cm⁻¹ from the symmetrical stretch of Si-O-Si, at 799 cm⁻¹ of the asymmetry. Besides, absorption at 964 cm⁻¹ from Si-OH stretching and bending Si-O bending vibration appeared at 466 cm⁻¹. There is broadband that overlaps at 1250-1150 cm⁻¹ due to the stretching vibrations of C-O, C-O (H), and CO (Ar) (phenol groups and ether bonds), which are consequential types of bonds in lignin. The characteristic peaks in the FTIR spectra of silica-lignin composite derived from rice husk with and without sodium periodic activation are similar to the typical peak of the FTIR spectra of silica-lignin in the previous studies [21, 22]. The presence of C-O-C ether bonds is indicated by the bands corresponding to the stretching vibration at 1087 cm⁻¹. Silica-lignin FTIR uptake of insulation results in accordance with the literature. The addition of periodic sodium did not significantly influence the silica-lignin functional group, but it slightly affected the transmittance of OH and C=O (

Table 2).

Table 2. Transmittance(T) of OH and C = O groups in silica-lignin composites

Sample	OH-Group		C=O Group	
	%T	Ratio (Sample:SL0)	%T	Ratio (Sample:SL0)
SL0	44.1	1.00	75.7	1.00
SL5	39.2	0.88	71.2	0.94
SL10	41.5	0.94	73.5	0.97
SL15	37.1	0.84	75.3	0.99
SL20	33.9	0.77	65.7	0.87

The SL5 and SL10 samples had higher C = O and O-H transmittance among the samples. Referring to the FTIR results, the SL5 and SL10 samples were then determined for their surface morphology because they were considered to be the best as adsorbents.

3.2. Silica-lignin morphology

The surface morphology of the SL0, SL5, and SL10 samples is shown in Figure 4, with a magnification of 650 × and a 50 μm scale.

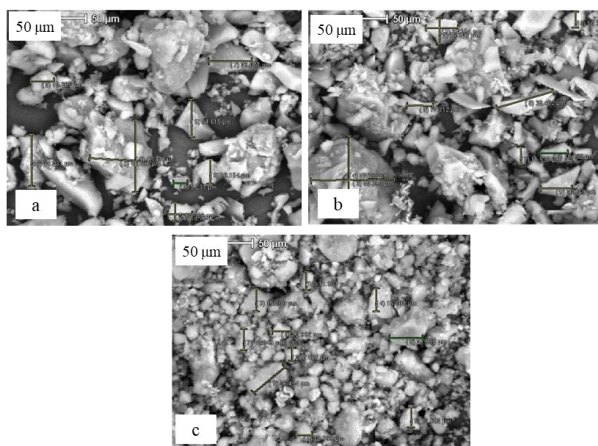


Figure 4. Micrograph SEM of (a) SL0, (b) SL5 and (c) SL10.

Surface morphology of SL0, heterogeneous, formed agglomeration and has a particle size of about 9 - 47 μm, while SL5 has a size of 10 - 55.3 μm with non-uniform particle shape, almost the same as SL0. Unlike SL10, the particle shape tends to be uniform, round, with a particle size of about 9 μm. This means that the addition of sodium periodate affects the shape of the silica-lignin composite particles, the higher the sodium periodate concentration, the smaller the size and the homogeneous shape of the particles. Also, the element composition in the SL0, SL5, and SL10 samples characterized by EDAX is shown in Table.

Table 3. The element composition in the SL0, SL5 and SL10 samples

Sample	Percentage of mass composition		
	Si	O	C
SL0	44.48	50.68	4.84
SL5	44.60	50.81	4.59
SL10	44.71	50.93	4.36

Each sample contains three main elements, namely silicon, oxygen, and carbon, for the three samples, the composition was very similar. This means that silica-lignin activation with sodium periodate does not affect the composition of the constituent elements.

The mapping of elements in the composite sample was carried out to prove the formation of silica-lignin composites. The color box on the edge of the picture shows the level of the element. The top color shows the highest level.

Mapping on SL0 samples shows the spread of silicon and oxygen, which was dominant in each particle, while lignin (characterized by carbon elements) was little. This means that silica dominates at SL0. Following the results of a previous study [23], silica acts as a matrix (skeleton), while lignin as a filler. The location of the three elements in the SL0 sample (yellow circle) was the same, which indicates that the three elements combined to form silica-lignin composites. Mapping of SL5 and SL10 samples showed the same results as SL0, which means that these two samples formed silica-lignin composites.

3.3. Lignin Silica-Lignin Surface Area

Silica-lignin adsorption of methylene blue was done to determine the absorption capacity of organic dyes, also to estimate its surface area. Blue methylene(MB) has a large size with a surface area of about 130 Å so that the absorption process occurs in the micropore. The calculation of the specific surface area is as per equation 3. The results are listed in Table .

$$LPS = \frac{q_e \times N \times A_{MB}}{M_{MB} \times 1000} \tag{3}$$

Where:

LPS = specific surface area (m²/g)

q_e = MB absorption (mg/g)

N = Avogadro number (6,023 × 10²³/mol)

A_{MB} = cross sectional area of MB (1,3 × 10⁻¹⁶ m²)

M_{BM} = molecular weight of MB (319,86 mg/mol)

1000 = conversion factor between g and mg

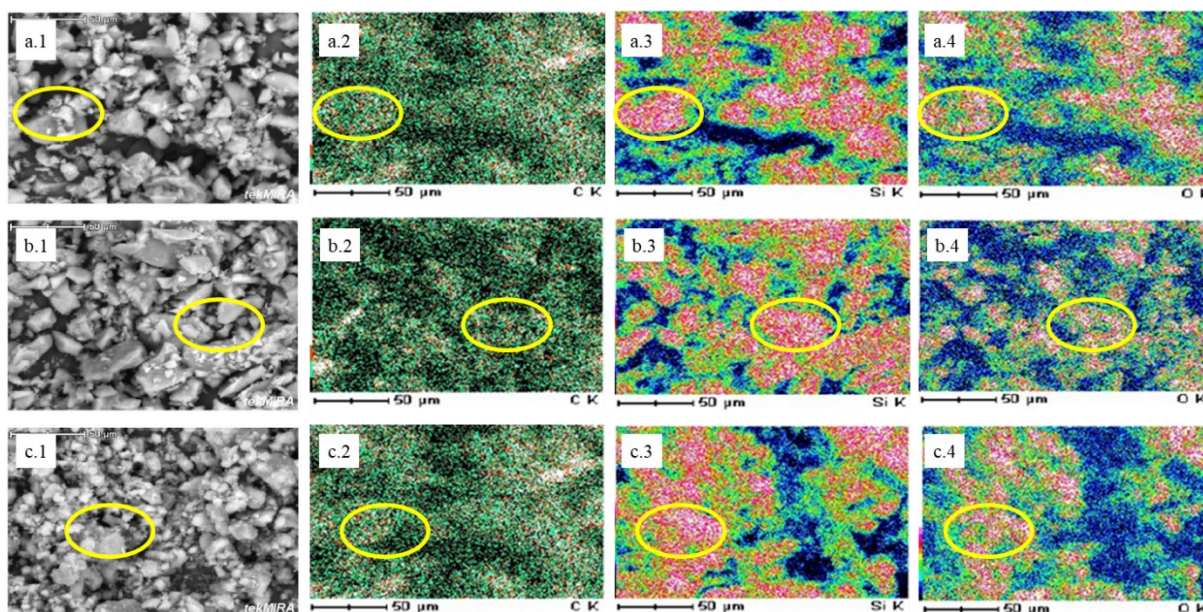


Figure 5. Mapping of (a.1) SL0, (b.2) SL5, and (c.1) SL10, whereas a.2, a.3, and a.4 is mapping for carbon, silica, and oxygen respectively in the sample SL0, b.2, b.3, and b.4 for carbon, silica, and oxygen respectively in SL5 and c.2 samples, c.3, and c.4 for carbon, silica, and oxygen respectively in the SL10 sample.

Table 4. Adsorption capacity of SL0, SL5 and SL10 to methylene blue

Sample	Adsorption capacity (mg/g)	Specific surface area (m ² /g)
SL0	5.6011	13.7109
SL5	5.6199	13.7569
SL10	5.7554	14.0888

SL10 sample had the highest surface area because the smallest particle size refers to the characterization by SEM. Measurement of surface area with BET, total pore volume, and pore diameter of SL10 are summarized in Table .

Table 5. Surface and pore characteristics of SL0 and SL10

Sample	Surface area m ² /g ⁻¹	Total pore volume / cm ³ .g ⁻¹	Average pore diameter/nm
SL0	407.575	0.82012	9.4011
SL10	424.068	0.66352	3.5988

The surface area of SL10 is 424,068 m².g⁻¹ higher than that SL0; however, it was smaller than that of Qu *et.al.* [9], i.e., 471,7 m².g⁻¹. The pore shape of both samples was mesopore, where the pore diameter was between 2-50 nm.

3.4. Silica-Lignin absorption capacity to Chromium (VI)

The absorption capacity of silica-lignin composite adsorbents in chromium(VI) with variations in contact time shown in Figure 6.

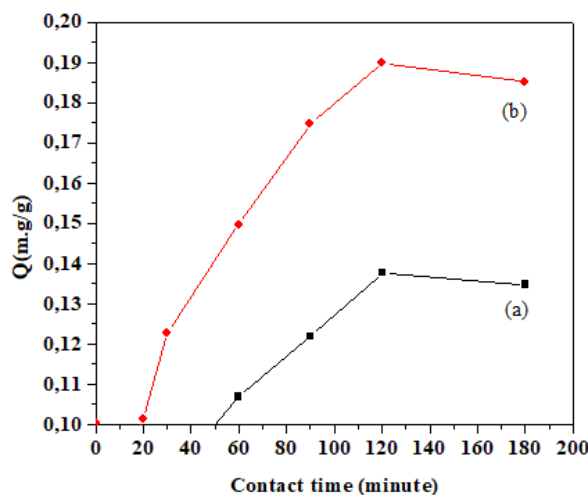


Figure 6. Contact time variations of (a) SL0, and (b) SL10 to chromium(VI).

Based on Figure 6, SL10 had a larger surface area than SL0. Determination of the optimum contact time, obtained when there was a constant saturation point, showed no increase in absorption. There is a saturation point in both samples, which is occurred between 120-180 minutes interval, and there is no process of decreased absorption, which indicates the occurrence of desorption. The optimum contact times of SL0 and SL10 were 87 and 86 minutes, respectively, close to 90 minutes, with absorbances of 0.1220 mg.g⁻¹ and 0.1747 mg.g⁻¹, respectively. The contact time in this study was close to the optimum contact time of activated lignin adsorption to chromium(VI) (1), i.e., 80 minutes.

The determination of the type of adsorption isotherm of SL0 and SL10 to chromium(VI) was carried out at various concentrations of chromium(VI) (Figure 7).

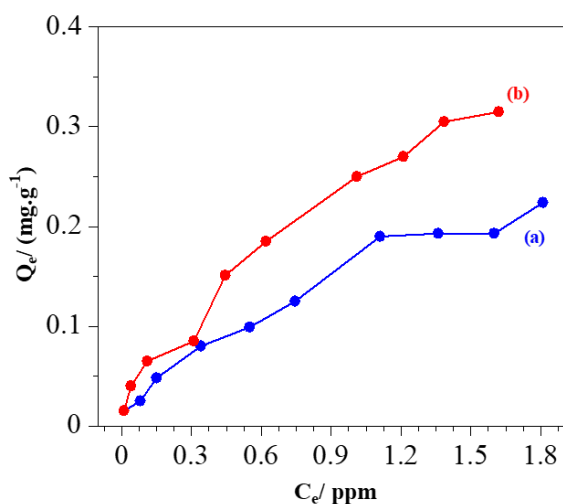


Figure 7. Graph of equilibrium concentration (Ce) to adsorption capacity (Qe) on adsorption of (a) SLO, and (b) SL10.

It is seen that the SLO absorption capacity increased (Figure 6.) as the chromium(VI) concentration increased. This happened because, at high concentrations, the collision between adsorbent and adsorbate increased so that the amount of adsorbate absorbed increased. However, there were several saturation points at concentrations of 0.65 and 1.2–1.6 ppm, which indicated the occurrence of multilayer adsorption processes. SLO adsorption capacity on chromium(VI) 2 ppm was 0.1944 mg. g⁻¹.

The same result happened at SL10, and it appeared that some saturation points occurred at 0.4; 1.25 and 1.7 ppm, which indicated multilayer formation. SL10 capacity in chromium(VI) with a concentration of 2 ppm was 0.3054 mg.g⁻¹. Based on its absorption, SL10 was higher than that SLO. This also proves that sodium periodate activator can increase silica-lignin absorption to chromium(VI). This result was slightly lower than that of previous research, which is 0.3410 mg. g⁻¹ [10].

Determination of the isotherm adsorption model, as in Figure 8, for multilayer adsorption, two parameters were used using the linear regression method of the Halsey equation (Equation 1). Based on the regression equation, the coefficient of determination (R²) is obtained. An acceptable R² value in determining the isotherm adsorption model is 95 0.95. The determination of the adsorption of SLO and SL10 isotherms is shown in Figure 8.

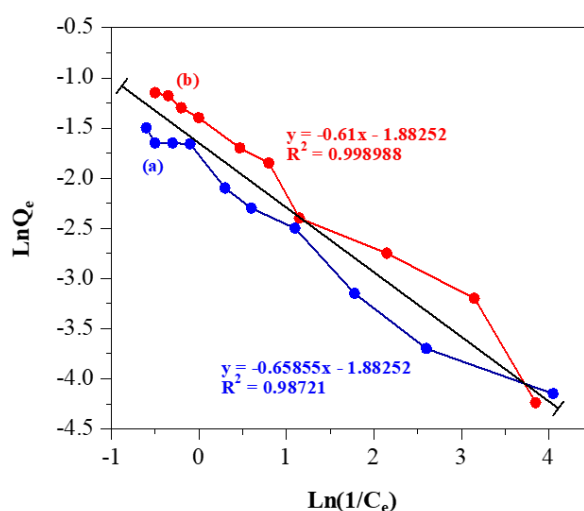


Figure 8. Isotherm adsorption curve of (a) SLO and (b) SL10 obtained by the Halsey equation.

SLO and SL10 have R², respectively 0.98721 and 0.98988, meaning that the isotherm adsorption model for chromium (VI) satisfies the Halsey equation because the R² value is close to 1. Thus, the adsorption process that occurs was a multilayer adsorption system, besides heterogeneous pore distribution at high concentrations (19). The surface morphology of SLO and SL10 after adsorption is shown in Figure 9.

The SL10 surface after adsorption (Figure 9c dan d) looks smoother than that SLO (Figure 9b dan d), which indicates chromium(VI), which binds more physically to silica-lignin. Based on the results of SEM, chromium (VI) cannot be distinguished because the particles were tiny and entered the silica-lignin pores. The results of SEM SLO and SL10 at 1000 × magnification (Figure 9b and d) show heterogeneous surface morphology with various pore sizes, which reinforces the result of the assumption that this adsorption is included in Halsey's isotherm.

The presence of chromium in SLO and SL10 particles is shown by EDX results (Figure 10). Both samples contained elements of silicon, oxygen, carbon, and chromium. Chromium contained in SL10 and SLO was small, each at 0.62% and 0.45%.

The determination of chemical interactions between SLO and SL10 with adsorbate was observed with FTIR (Figure 11). SLO and SL10 FTIR spectra showed a new band at 1511 cm⁻¹, which indicated the presence of a C-OH group in the plane, indicating the presence of chromium bonds with lignin through nucleophilic addition reactions. Besides, there was a significant shift in the transmittance intensity of the SL10, thought to have an induction effect of chromium as an electron driver, thus increasing the absorption frequency. Therefore, the chromium (VI) adsorption process by SLO and SL10 mostly occurs due to chemical interactions.

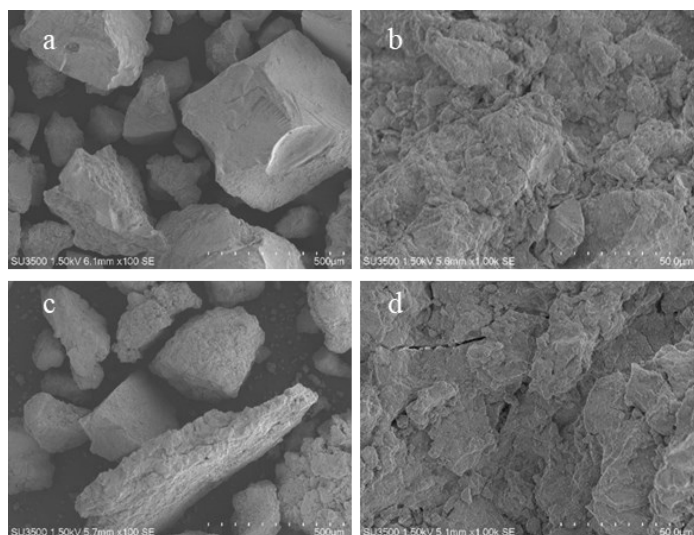


Figure 9. Micrograph SEM of SL0: (a) 100 × magnification, (b) 1000 × magnification; and SL10: (c) 100 × magnification, and (d) 1000 × magnification.

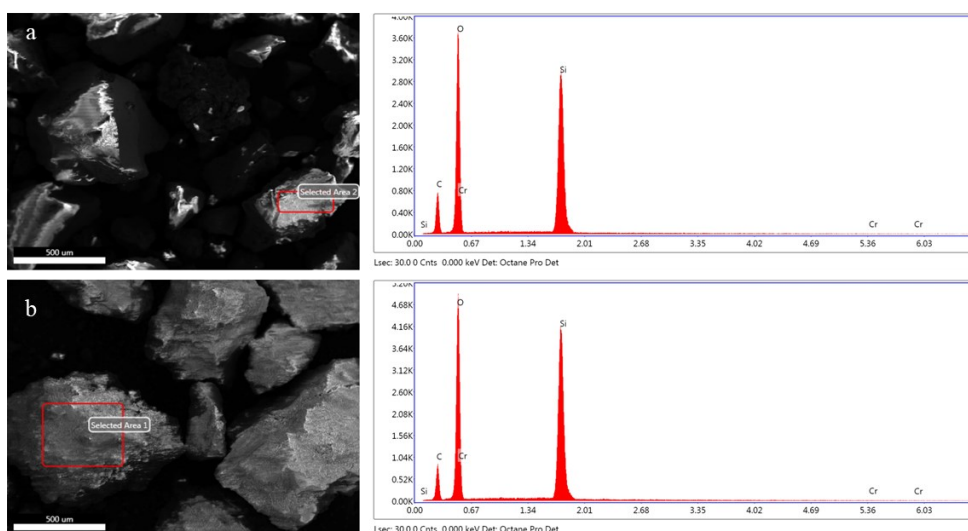


Figure 10. Morphology of SEM and EDAX (a) SL0, and (b) SL10.

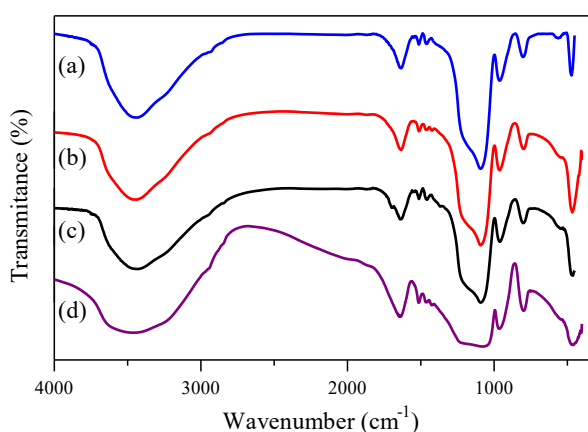


Figure 11. FTIR spectra (a) SL0 before adsorption, (b) SL0 after adsorption, (c) SL10 before adsorption, and (d) SL10 after adsorption.

4. Conclusion

In conclusion, sodium periodate activator has been shown to increase the capacity of silica-lignin adsorption, because it increases its surface area. The

highest surface area of adsorbent, which is 14.0888 m² g⁻¹, is obtained in silica-lignin with the addition of sodium periodate 10%. The silica-lignin isotherm adsorption model for chromium(VI), is the Halsey model.

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