
Iron (II) Removal Using Activated Silica/Lignin Composite: Kinetic and Equilibrium Studies

Atiek Rostika Noviyanti*, Yati B. Yuliyati, Ghaisani Nur Maulani, Irwan Kurnia

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran,
Jl. Raya Bandung – Sumedang Km. 21 Jatinangor, West Java, 45363

*Corresponding author: atiek.noviyanti@unpad.ac.id

Received: October 2021; Revision: November 2021; Accepted: April 2022; Available online: May 2022

Abstract

Recently, the Indonesian industry has been rapidly developed and affects the number of heavy metal ions waste such as iron (II). Iron (II) is dangerous to the environment because it is harmful to aquatic systems and carcinogenic. This research used activated silica/lignin to remove iron (II) in water. The activated silica/lignin was isolated from rice husk and activated by sodium periodate with a 10% weight of lignin in the range of pH of 2–5 at 55 °C. Then its specific surface area was analyzed with the methylene blue adsorption method. It is found that the condition in pH 2 showed the best isolation and activation condition to achieve the lowest impurity (cellulose and hemicellulose) in silica/lignin composite. Furthermore, the activated silica/lignin composite, isolated in pH 2, has a specific surface area of 366.6372 m²/g with the highest adsorption value of 1.1825 mg g⁻¹ for iron (II) ions solution (5 ppm) within a contact time of 90 minutes. Moreover, the adsorption kinetics followed the pseudo-second-order kinetic model, also the adsorption isotherm fitted with the Freundlich model. This research showed that activated silica/lignin could be used as an alternative of environmentally friendly material for iron (II) removal in water.

Keywords: Activated silica-lignin, adsorption, iron, rice husk, sodium periodate.

DOI: 10.15408/jkv.v8i1.22715

1. INTRODUCTION

The amount of industrial waste increased with the following industrial development in Indonesia. Industrial waste is heavy metal ions such as iron, cadmium, zinc, copper, nickel, mercury, and chromium, produced by the metal plating industry, mining, smelting, battery pesticide, and nuclear industries. The most common heavy metal ion waste is iron (II) (Nurhasni, 2014). The exceed of the iron content threshold in the waste will endanger the environment and the health of living things because the iron can accumulate in the body (Agus et al., 2017).

Several methods have been applied in order to remove the metal ions from industrial wastewater and soil, i.e., reverse osmosis, chemical precipitation, ultrafiltration, electrodialysis and ion exchange (Bratskaya et al., 2009; Borbely et al., 2009; Dbrowski et al.,

2004; Kravchenko et al., 2009;). Recently the adsorption process has been getting much attention, especially for natural-based or industrial waste-based adsorbents, due to their economical, environmentally friendly, and abundance (Qiu et al., 2009; Wu et al., 2008; Xiong et al., 2015). One of the natural materials that can be used as an adsorbent is rice husk (Gupta et al., 2009).

The high levels of silica and lignin, which are contained in rice husk, can be used as raw materials for adsorbents composite of the heavy metal ion. Silica/lignin composite material is expected to be superior to metal's mechanical properties and specific stiffness. Janekarn et al. (2020) have reported combining silica and carbon-based material as a composite to achieve a better mechanical property for dye removal application. Furthermore, silica/lignin composite has been

utilized as a heavy metal ion adsorbent for Ni (II), Cd (II), and Cr (IV) (Klapiszewski et al., 2015; Yuliyati et al., 2018). In addition, the activation of the adsorbent was carried out to increase the adsorption of heavy metal ion waste, such as physical or chemical activation. The physical activation can be accomplished by reducing the particle size and heating at high temperatures. In contrast, the chemical activation is carried out by adding a substance or chemical such as HCl (hydrochloric acid), NaOH (sodium hydroxide), ZnCl₂ (zinc chloride), and NaIO₄ (sodium periodate) (Handayani, 2010). This method is simple and produces no solid waste (Aidha, 2013). The chemical activation using sodium periodate will oxidize the guaiacyl group to ortho-quinone (Gosselink et al., 2011). The changing structure of the lignin monomer to ortho and para-quinone will add a carbonyl group, an active centre for heavy metal adsorption (Kozhevnikov et al., 2017). Febriyani (2018) reported silica/lignin composites from rice husk activated with an optimum 10% sodium periodate concentration at pH 5 for chromium metal ion adsorption.

In this study, rice husk is used as the raw material of activated silica/lignin composites. Rice husk was activated by a 10% sodium periodate in the range of pH 2–5 to modify the guaiacyl functional group of lignin to be ortho-quinone that will be the active centre of lignin for metal ion adsorption. Then, the specific surface area was analyzed by using methylene blue. Then, the adsorption performance of the silica/lignin composite was evaluated by the solution of iron (II) metal ions. The variation of iron (II) concentration and contact time were conducted to determine the adsorption mechanisms based on the isotherm and kinetic model for iron (II) removal investigation. Finally, the activated silica/lignin composite from rice husk can be utilized as an alternative economical and environmentally friendly adsorbent for heavy metal waste.

2. MATERIALS AND METHODS

Materials and Equipment

The raw material, rice husk, was collected from rice mills in Pancalang Village, Kuningan, West Java. Distilled water, hydrochloric acid (technical), sulfuric acid (p.a., Merck), iron (II) ammonium sulfate (p.a., Merck), and potassium thiocyanate (p.a., Merck), were used as chemicals. Glassware,

Buchner funnel (Normax), technical balance and analytical balance (Mettler Toledo AB104-S), shaker (Ika Labortechnik KS250 basic), and stopwatch, were used as equipment.

Preparation of Activated Silica/Lignin Composite from Rice Husk

The activated silica/lignin was isolated from rice husk and activated by 10% sodium periodate in the range of pH of 2–5. Initially, the rice husk was washed with distilled water and dried. Then, the rice husk was treated with 1 N hydrochloric acid to remove the metal impurities in the rice husk, then washed with distilled water until neutral and dried. Next, the obtained rice husks were ground and sieved with a molecular mesh number of 50 (<0.3 mm). Afterwards, the fine rice husk was put into a beaker and added 2 M sodium hydroxide with a ratio of 1:3 (w/v), then heated at 100 °C for 4 hours. After that, the mixture was filtered in a hot state using a Buchner funnel. The filtrate was put into a beaker and then heated at 90 °C. Then, sulfuric acid was added dropwise up to pH 5. Afterwards, sodium periodate was added with a 10% by weight of lignin at 55 °C (Gosselink et al., 2011). The variation of pH solutions of 2, 3, and 4 was conducted by adjusting sulfuric acid at 90 °C. The solution was agitated for 6 hours until a sol solution was obtained. The obtained sol solution was centrifuged and decanted. The precipitate was washed with distilled water and dried at 90 °C for 12 hours. Finally, these dried materials are denoted as activated silica/lignin composite (pH X), in which X represents the pH of the oxidation condition.

Determination of Silica/Lignin Content by Chesson Method

The content of lignin, cellulose and hemicellulose was analyzed followed the Chesson method (Datta, 1981). The sample was treated gradually with: (1) distilled water at 100 °C, (2) 1 N H₂SO₄ at 100 °C, (3) 72% H₂SO₄ at room temperature and (4) the final of dried residue was calcined in the furnace. The weight of dried sample was measured at the end of each treatment. Then, the composition of silica, lignin, cellulose and hemicellulose can be calculated with the equations of 1, 2, and 3 (Kurniaty *et al.*, 2017)

$$\% \text{ hemicellulose} = \frac{b-c}{a} \times 100\% \quad (1)$$

$$\% \text{ cellulose} = \frac{c-d}{a} \times 100\% \quad (2)$$

$$\% \text{ lignin} = \frac{d-e}{a} \times 100\% \quad (3)$$

where a is the initial of weight (g), b is the weight after DI water washing treatment (g), c is the weight after 1 N H_2SO_4 treatment (g), d is the weight after 72% H_2SO_4 treatment (g), and e is the weight of ash (g)

Determination of Specific Surface Area of Activated Silica/Lignin Composite

Specific surface area was analyzed based on methylene blue (MB) adsorption on the surface of material. The determination of surface area was calculated by using equation 4.

$$SSA = \frac{q_e \times N \times A}{M_{MB}} \quad (4)$$

where SSA is specific surface area (m^2/g), q_e is the adsorption amount at equilibrium of MB (mg g^{-1}), N is Avogadro's number ($6.023 \times 10^{23}/\text{mol}$), A is cross section of MB ($1.3 \times 10^{-16} \text{m}^2$) and M_{MB} is molecular weight of MB (319.86 g/mol)

Adsorption of Iron (II) with Activated Silica/Lignin Composite

In this study, the adsorption efficiency of iron (II) was observed by mixing activated silica/lignin composite (0.1 g) with 25 mL of iron (II) solution. Batch adsorption experiments were conducted at room temperature for 10 minutes. Further, the mixture was settled for 30 minutes and filtered. A similar procedure was applied with 20; 30; 60; 90; 120; 160; and 180 minutes for batch kinetic experiments. The equilibrium condition was determined when iron (II) adsorption on silica/lignin composite reached a saturated point ($t = 90 \text{ min}$). The resulting filtrate was analyzed with the UV-Visible light spectrophotometer (Genesys 10S, UV-Vis) to determine absorbed iron (II). The concentration of the adsorbed iron (II) solution can be calculated from the difference between the initial concentration and the final concentration of the iron (II) solution, as follows in equation 5.

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (5)$$

where C_e is the equilibrium concentration of adsorbate (mg L^{-1}), C_0 is the initial concentration of adsorbate (mg L^{-1}), V is the volume of solution (L) and M is the mass of the adsorbent (g).

For the determination of adsorption isotherm, a similar procedure as described above was conducted. The activated silica/lignin composite (pH 2) with 0.1 g was mixed with 25 mL of iron (II) solution with various concentrations, i.e., 2.5; 3.0; 3.5; 3.5; 4.0; 4.5; 5.0 ppm and shake with the optimum contact time (90 minutes). Then, the mixture was filtered and the filtrate was analyzed by a UV-Visible light spectrophotometer.

3. RESULTS AND DISCUSSION

The Composition of Lignin, Silica, Hemicellulose and Cellulose in the Activated Silica-Lignin Composites

Figure 1 shows that the activated silica/lignin composite, isolated at pH 2, has a higher silica and lignin composition than the isolation condition at pH 3, pH 4, and pH 5. Furthermore, the isolation condition of pH 2 can promote the cleavage of chemical bonding between cellulose and hemicellulose with lignin. Therefore, those activated silica/lignin composite has the lowest amount of impurities (cellulose and hemicellulose). It also minimises the involvement of the impurities in the metal adsorption. Moreover, based to Gosselink et al., 2011 and Kozhevnikov et al., 2017 works, the modified lignin functional group is the main active site to adsorb metal ions. According to the results, the activated silica/lignin composite (pH 2) was used as an adsorbent material for iron (II) ions.

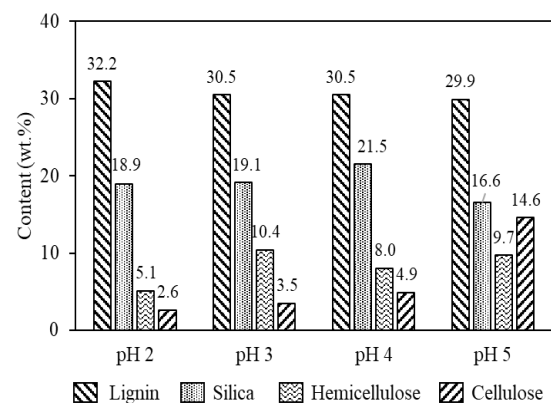


Figure 1. The composition of activated silica/lignin composite in the various of pH.

In this study, the oxidation process was conducted under a low concentration of NaIO₄ (10% by weight of lignin) for 10 minutes of immersion at 55°C (Gosselink et al., 2011). This oxidation process will change the guaiacyl functional group to form an ortho-quinone structure (Figure 2): The changing structure of the lignin monomer to ortho-quinone will add a carbonyl group active centre of lignin for metal adsorption (Kozhevnikov et al., 2017). The determination of specific surface area by methylene blue shows that the activated silica/lignin composite has a surface area of 366.6 m²/g.

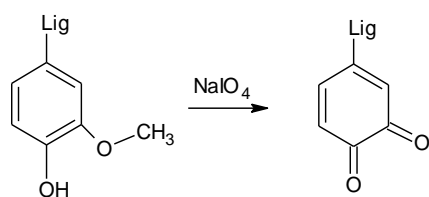


Figure 2. Oxidation reaction of guaiacyl to ortho-quinone (Kozhevnikov et al., 2017)

Adsorption Kinetic of Iron (II) by Activated Silica/lignin Composite

The adsorption kinetic research is primarily used to characterize the removal of the adsorbate from the adsorbent, which is useful for determining the control mechanism of adsorption. Two kinetic models (pseudo-first-order and pseudo-second-order) were used to fit the kinetic data to determine this study's adsorption process and mechanism. The linearized forms of pseudo-first-order and pseudo-second-order kinetic equations follow Equations 6 and 7, respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

where q_e and q_t (mg g⁻¹) are the amount of adsorbate at equilibrium and at time t , respectively; k_1 and k_2 (min⁻¹) are the pseudo first- order and the pseudo second-order rate constants, respectively.

The adsorption amount of iron (II) ion on activated silica/lignin composite (pH 2) increased with the extension of contact time. Initially, the q_t value rapidly increased for 60 minutes due to the sufficient adsorption sites for iron (II), and then the adsorption reached equilibrium after 90 minutes (1.1825 mg g⁻¹) (Figure 3). As shown in Figure 4 (B) and Table 1, the kinetics of iron (II) adsorption on activated silica/lignin composite (pH 2) follow a pseudo-second-order kinetics model with R² close to 1. Furthermore, the experimental q_e cal values similar to q_e exp values for the pseudo-second-order kinetics model.

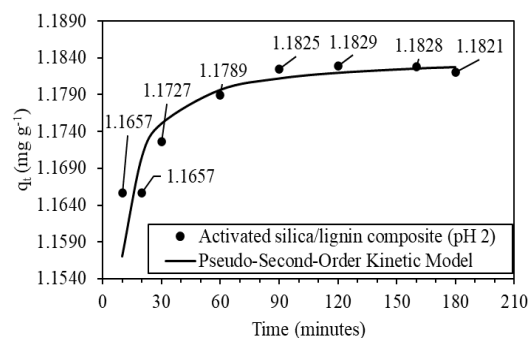


Figure 3. Adsorption profile of iron (II) ion on activated silica/lignin composite (pH 2).

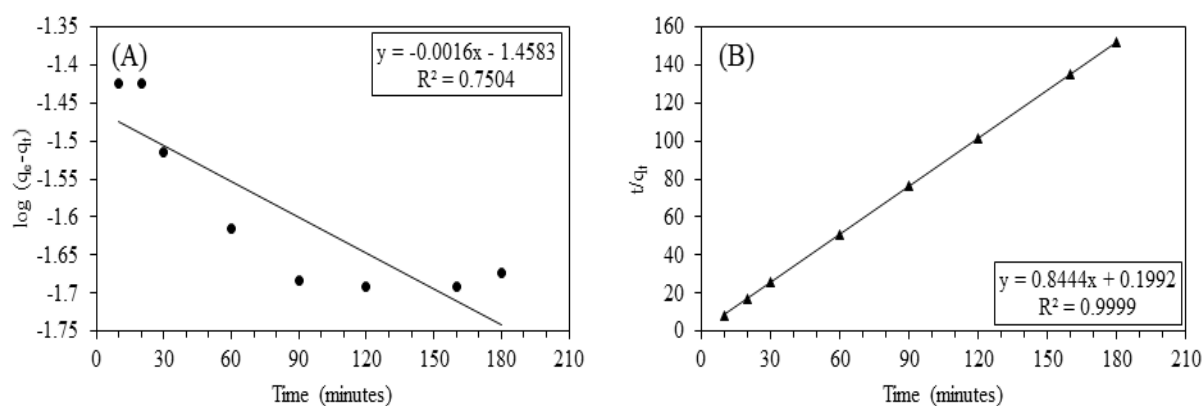


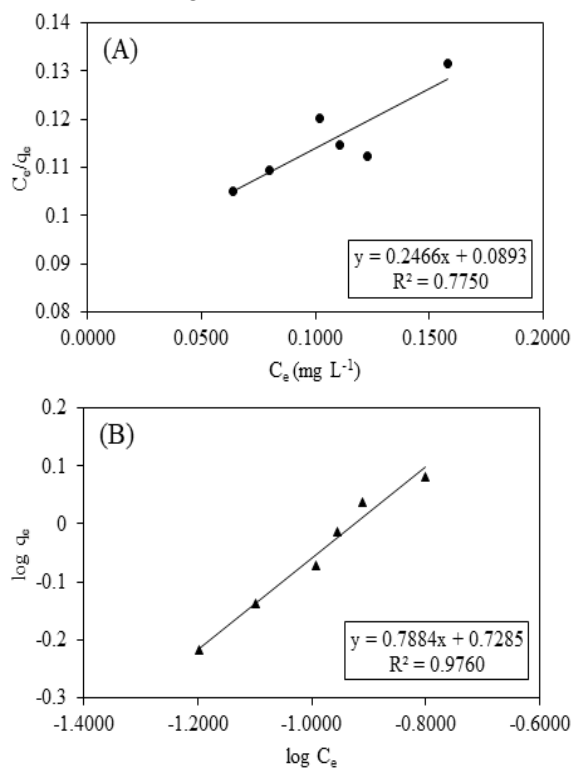
Figure 4. Adsorption kinetics model of activated silica/lignin composite (pH 2) on iron (II) ions. (A) pseudo-first-order model and (B) pseudo-second-order model.

Table 1. Pseudo-first-order and pseudo-second-order kinetics model parameters of activated silica/lignin (pH 2) on Iron (II) ions adsorption.

$q_{e \text{ exp}} (\text{mg g}^{-1})$	Pseudo-first-order			Pseudo-second-order		
	$q_{e \text{ cal}} (\text{mg g}^{-1})$	k_1	R^2	$q_{e \text{ cal}} (\text{mg g}^{-1})$	k_2	R^2
1.2032	0.0348	-0.0036	0.7504	1.1843	3.5787	0.9999

Adsorption Isotherm

Isothermal adsorption studies are important to understand the equilibrium relationship between the adsorbent and adsorbate. The adsorption mechanism and the affinity of the adsorbent are determined with the parameters obtained from different model fittings (Khaled et al., 2009). Here, two isothermal models, i.e., the Langmuir and the Freundlich models, were used to fit the isothermal data. The fitting calculation results are shown in Figure 5 and Table 2.

**Figure 5.** Adsorption isotherm model of activated silica/lignin composite (pH 2) on iron (II) ions. (A) Langmuir model and (B) Freundlich model.**Table 2.** Langmuir and Freundlich isotherm parameters and correlation coefficients

Langmuir Isotherm		
q_{max}	K_L	R^2
4.0554	2.7598	0.7750
Freundlich Isotherm		
$1/n$	K_F	R^2
0.7884	5.3521	0.9760

The Langmuir adsorption isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites, and there is no interaction between the adsorbates (Allen et al., 2003). The linear form of the Langmuir isotherm equation is given by the following Equation 8.

$$\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}K_L} + \frac{1}{q_{\text{max}}}C_e \quad (8)$$

where q_{max} is the amount of adsorbate adsorbed per gram of adsorbent, C_e is the equilibrium concentration, b is the adsorption capacity, and K_L is the equilibrium constant.

Meanwhile, The Freundlich isotherm proposes that multilayer adsorption occurs across a heterogeneous surface with a non-uniform distribution of adsorption heat (Anirudhan et al., 2008). The linear form of the Freundlich isotherm is given by the following Equation 9.

$$\log q_e = \log K_F + \frac{1}{n} \cdot \log C_e \quad (9)$$

where K_F is Freundlich constant correspond to the adsorption capacity and n is intensity of adsorption constants including the factors affecting the capacity of adsorption.

The adsorption model of activated silica/lignin composite (pH 2) is more suitable for the Freundlich model than the Langmuir model. It indicates that the surface modification of activated silica/lignin composite was not uniform. However, since the activated silica/lignin composite (pH 2) is an economical and environmentally friendly adsorbent, it can be used as an alternative for heavy metal waste, especially iron (II).

4. CONCLUSION

Activated silica lignin was used to remove iron (II) in water. The activated silica/lignin was successfully isolated from rice husk and activated by sodium periodate with a 10% by weight of lignin with the best isolation condition at pH 2 at 55 °C. Furthermore, the

activated silica/lignin composite (pH 2) has a specific surface area of 366.6372 m²/g with the highest adsorption value of 1.1825 mg g⁻¹ for iron (II) ions solution (5 ppm) within a contact time of 90 minutes. Moreover, the adsorption kinetic followed the pseudo-second-order kinetic model and the adsorption kinetic fitted with the Freundlich model. This research showed that activated silica/lignin could be used as an alternative of environmentally friendly material for iron (II) removal in water.

REFERENCES

- Aidha NN. 2013. Aktivasi Zeolit secara Fisika dan Kimia Untuk Menurunkan Kadar Kesadahan (Ca dan Mg) Dalam Air Tanah. *Jurnal Kimia Kemasan*. 35 (1): 58–64.
- Allen SJ, Gan Q, Matthews R, Johnson. 2003. Comparison of Optimised Isotherm Models for Basic Dye Adsorption by Kudzu. 88 (2): 143-152.
- Anirudhan TS, Radhakrishnan PG. 2008. Thermodynamics and Kinetics of Adsorption of Cu(II) from Aqueous Solutions onto A New Cation Exchanger Derived from Tamarind Fruit Shell. *The Journal of Chemical Thermodynamics*. 40 (4): 702-709.
- Bratskaya S, Pestov A, Yatlukb Y. 2009. Heavy Metals Removal by Occulation/Precipitation Using N-(2-carboxyethyl) Chitosans. *Colloids Surface A: Physicochemistry Engineering Aspect*. 339: 140-144.
- Borbely G, Nagy E. 2009. Removal of Zinc and Nickel Ions by Complexation-Membrane Filtration Process from Industrial Wastewater. *Desalination*. 240: 218-226.
- Datta R. 1981. Acidogenic Fermentation of Lignocellulose-Acid yield and Conversion of Components. *Exxon Research and Engineering Company*. 23: 60–64.
- Dbrowski A, Hubicki Z, Podkoscielny P, Robens E. 2004. Selective Removal of the Heavy Metal Ions from Waters and Industrial Wastewaters by Ion-Exchange Method. *Chemosphere* 56, 91-106.
- Febriyani SK. 2018. Pengaruh Natrium Periodat Pada Daya Serap Silika-Lignin Terhadap Kromium (VI). Thesis, Department of Chemistry, Universitas Padjadjaran
- Gosselink RJA, van Dam JEG, de Jong E, Gellerstedt G, Scott EL, Sanders JPM. 2011. Effect of Periodate on Lignin for Wood Adhesive Application. *De Gruyter*. 65(2): 155-162.
- Gupta VK, Suhas. 2009. Application of Low-Cost Adsorbents for Dye Removal – A Review. *Journal of Environmental Management*. 90 (8): 2313-2342.
- Handayani A. 2010. Penggunaan Selulosa Daun Nanas Sebagai Adsorben Logam Berat Cd (II). Thesis, Department of Chemistry, Universitas Sebelas Maret.
- Janekarn I, Hunt AJ, Ngernyen Y, Youngme S, Supanchaiyamat N. 2020 Graphitic Mesoporous Carbon-Silica Composites from Low-Value Sugarcane By-Products for The Removal of Toxic Dyes from Wastewaters. *R. Soc. Open Sci*. 7: 200438.
- Khairunnisa S. 2019. Komposisi Silika/Lignin Sekam Padi Teraktivasi Natrium Periodat pada Variasi pH. Thesis, Department of Chemistry, Universitas Padjadjaran.
- Khaled A, Nemr AE, El-Sikaily A, Abdelwahab O. 2009. Removal of Direct N Blue-106 from Artificial Textile Dye Effluent using Activated Carbon from Orange Peel: Adsorption Isotherm and Kinetic Studies. *Journal of Hazardous Material*. 165: 100–110.
- Klapiszewski L, Przemysław B, Marcin W, Marta J, Katarzyna K, Teofil J. 2015. Silica Conjugated with Kraft Lignin and Its Use as a Novel ‘Green’ Sorbent for Hazardous Metal Ions Removal. *Chemical Engineering Journal*. 260: 684-693.
- Kozhevnikov AY, Ul’yanovskaya SL, Semushina MP, Pokryshkin SA, Ladesov AV, Pikovskoi II, Kosyakov DS. 2017. Modification of Sulfate Lignin with Sodium Periodate to Obtain Sorbent of 1,1-Dimethylhydrazine. *Russian Journal of Applied Chemistry*. 90 (4): 416–422.
- Kravchenko TA, Polyanskiy LL, Krysanov VA, Zelensky ES, Kalinitchev A, Hoell W. 2009. Chemical Precipitation of Copper from Copper to Zinc Solutions onto Selective Sorbents. *Hydrometallurgy*. 95: 141-144.
- Nurhasni. 2014. Sekam Padi untuk Menyerap Ion Logam Tembaga dan Timbal dalam Air

- Limbah. *Jurnal Kimia Valensi*. 4(1): 36-44
- Qiu J, Wang Z, Li H, Xu L, Peng J, Zhai M, Yang C, Li J, Wei G. 2009. Adsorption of Cr(VI) Using Silica-based Adsorbent Prepared by Radiation-Induced Grafting. *Journal of Hazardous Materials*. 166: 270-276.
- Wibowo EAP, Hardyanti IS, Nurani I, HP DSH, Rizkita AD. 2017. Studi Penurunan Kadar Logam Besi (Fe) dan Logam Tembaga (Cu) pada Air Embung Menggunakan Adsorben Nanasilika. *Jurnal Ilmiah Sains*. 17 (2): 131-134.
- Wu Y, Zhang S, Guo X, Huang H. 2008. Adsorption of Chromium (III) on Lignin. *Bioresource Technology*. 99: 7709-7715.
- Xiong W, Yang D, Zhong R, Li Y, Zhou H, Qiu X. 2015. Preparation of Lignin-Based Silica Composite Submicron Particles from Alkali Lignin and Sodium Silicate in Aqueous Solution Using A Direct Precipitation Method. *Industrial Crops and Products*. 74: 285–292.
- Yuliyati YB, Listiani S, Solihudin S, Noviyanti AR. 2018. Isolation of Silica-Lignin Composites from Rice Husk and Their Adsorption to Cr (VI). *ALCHEMY Jurnal Penelitian Kimia*. 14 (2) 267-276.