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Abstract. In this study, a modification of exopolysaccharide (EPS) from *Spirulina* sp. algae biomass with silica (HES) and exopolysaccharide from *Spirulina* sp. algae biomass with silica coated by magnetite particles (HESM) has been done successfully. A series of experiments with the batch method were conducted to test the ability of HESM adsorption of Pb(II) ions in solution. Identification of functional groups of HESM adsorbents was studied using infrared spectrometer (IR) while surface morphological analysis and composition of the constituent elements of HESM were performed using scanning electron microscope-energy (SEM). Concentration of Pb(II) ion in the adsorption process were analysed by inductively coupled plasma-atomic emission spectrometry (ICP-AES Adsorption of Pb(II) ions with HES and HESM is optimum at pH 7 and concentration at 25 ppm with the adsorption capacity on HES at 3.85 mg g^{-1} while on HESM at 272.63 mg g^{-1}, contact time of 15 min and it tends to follow second orde pseudo kinetic model and Langmuir adsorption isotherm model.

Keywords: Sol-gel, exopolysaccharide, adsorption, silica coated magnetite.

1. Introduction

Heavy metal pollution to the environment is closely related to the activities carried out by humans. Much of the heavy metal pollution is generated from agricultural activities such as making fertilizers and applying insecticides containing heavy metals, industrial factory activities, as well as ceramics and metal smelting activities. Heavy metal contamination activity which is carried out continuously every day will result in the accumulation of heavy metals in large quantities [1]. Heavy metals are usually present in the form of ions, either in the form of single ions or pair ions in the water [2].

Dangerous metal ions such as Cd, Pb, Zn, Hg, Cu, and Fe are elements that have high molecular weight types [3]. To reduce heavy metal contamination, many techniques have been used including coagulation, complexation, ion exchange and adsorption methods. Of all these methods, the adsorption method is the method most widely used to reduce the impact of heavy metal pollution [4]. This adsorption method has several advantages including, the process is very simple, the cost used is quite cheap, and it is environmentally friendly [5].

The adsorbents that are usual used in the adsorption process are activated carbon, silica gel, alumina, and zeolite. At this time starting to develop the use of alternative adsorbents derived from nature because it is more economical. One example of such adsorbent is algae biomass. Several types of algae have

received attention because of their high ability to adsorb ionic ion bound to biomass and the possibility of reusing biomass as a biosorbent that can be used for wastewater treatment in liquid form [6].

However, algae biomass has several disadvantages, low density, easily damaged due to degradation by other microorganisms and technical difficult to use in columns to be used as adsorbent [7]. This weakness is carried out by immobilization of algae biomass with a silica gel matrix through a sol-gel process which to homogenize the solution but does not damage its structure so that the immobilization process of algae biomass in the silica matrix is expected to maintain the activity of functional groups present in the adsorbent and increase ion-adsorption capacity. Metal ions, especially in heavy metals. One example of an adsorbent that can be used well in handling heavy metals is exopolysaccharides. Exopolysaccharides play a role in biosorption [8]. Exopolysaccharides can adsorb heavy metals because exopolysaccharides are negatively charged [9].

Exopolysaccharides are mobile because they are generally composed of organic materials such as monosaccharides and disaccharides [10]. The application of exopolysaccharides as heavy metal biosorbents has been carried out and the results showed that exopolysaccharides are good media for absorbing metal ions and have a high adsorption capacity for wastewater treatment containing lead, nickel, and zinc ions [11]. exopolysaccharides are water soluble. Therefore, in this research, an immobilization process was carried out with a silica gel matrix through the sol-gel process. The sol-gel technique is a colloidal suspension of silica particles that is glued to a solid form based on hydrolyzed molecular precursors, which are mostly metal alkoxides and semi metal. The application of this sol gel technique in the exopolysaccharide immobilization process will produce adsorbents that are homogeneous, well mixed in multi-component systems, the size, shape and properties of the particles can be controlled [13].

In this study, the synthesis of exopolysaccharide hybrids from the algae cultivation of *Spirulina* sp. with a silica-magnetite matrix and its application as an adsorbent of Pb(II) ion in solution. Adsorption data were analyzed to determine the kinetic model and adsorption isotherm of Pb(II) ion which was absorbed by the adsorbent. The exopolysaccharide-silica-magnetite hybrid material from the algae cultivated by *Spirulina* sp. effectively absorbs Pb(II) ions in solution.

2. Materials and Methods

2.1. Isolation of Exopolysaccharide

Microalgae *Spirulina* sp. ready to harvest separated by centrifuge at 8.500 rpm at 4ºC for 5 min, then the precipitate or gel was obtained from Spirulina sp. and the filtrate. Twice the volume of the filtrate, ethanol was added and left to stand for 4 h. Then it is deposited using a centrifuge at a speed of 8.500 rpm and a temperature of 4ºC for 5 min. Sediment of *Spirulina* sp. and the exopolysaccharide formed was washed using distilled water and dried using frezee dry. Biomass of *Sprirulina* sp. and the dry exopolysaccharide was characterized using an IR spectrometer.

2.2. Shynthesis of HESM

Solution A, as much as 5 mL of TEOS mixed with 2.5 mL of distilled water is put into a plastic glass, then added with magnetite with concentrations 50 mg, then add a few drops of 1 M HCl to pH 2. Stir with a stirrer magnet until the solution is homogeneous. Solution B, consisting of 5 mL of ethanol plus an optimum exopolysacride of 0.1 gram silica and stirred with a magnetic stirrer. The two solutions are mixed to form a gel. The wet gel that is formed is left to stand for 24 hours then washed with ethanol and distilled water to pH 7, dried using freeze dry, then crushed until smooth. The resulting material is used for the adsorption test.

2.3. Adsorption kinetics

The optimum dose of HES was included in 5 Erlenmeyers. Then 25 mL of 100 ppm Pb (II) ion solution with optimum pH was added to each Erlenmeyer. Solution was shaken using a stirrer with time variations from 5, 15, 30, 60, and 120 min and the filtrate was analyzed by ICP-AES.

2.4. Adsorption isotherm

An amount of 50 mg of HES and HESM adsorbents with optimum concentration was put into 5 different plastic containers. Then added 20 ml of solution with different concentrations (10, 25, 30, 100, 200, and 300 mg L^{-1}) with optimum stirring time. The optimum pH was made using citrate buffer solution with pH range of 3.0-6.0 for the acidic pH and the phosphate buffer solution with pH range of 7.0-9.0 for the alkaline pH. After stirring, the adsorbent and solution were separated using centrifugation. The concentrations of ion Pb(II) in the adsorption process were analyzed inductively coupled plasma-atomic emission spectrometry (ICP-AES).

3. Results and discussion

3.1. Characterization of adsorbent by IR spectrometer

From the synthesis that has been done in this practical work. A functional group analysis was performed on the materials of EPS, HES, and HESM which were varied by magnetite using an *IR* spectrophotometer. The spectra IR of the adsorbent material will be shown in (Figure 1) to identify the functional groups of the adsorbent material before and after being modified with magnetite. Spectra *IR* shows several peaks that the functional groups present in the sample both belong to the material and functional groups that are possible from impurities that cannot be cleaned completely. Characterization using an IR spectrophotometer shows a success from the synthesis that has been carried out.

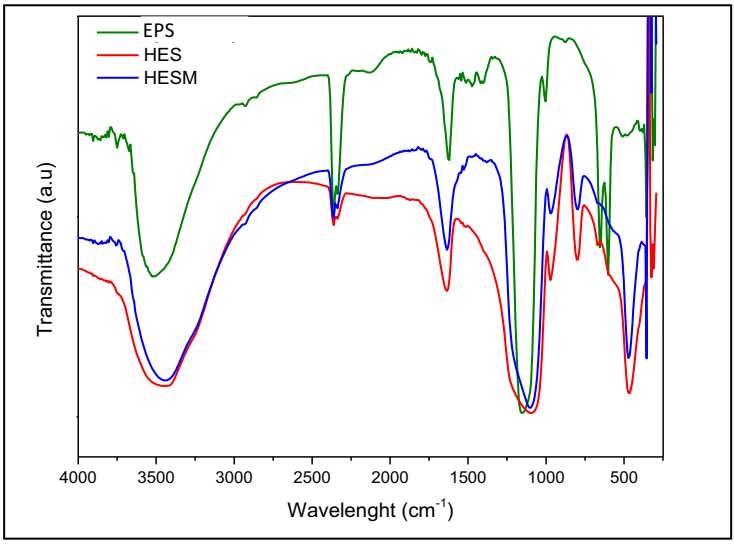

Figure 1. Spectra *IR* of EPS, HES, and HESM from algae *Spirulina* sp.

The IR spectra of EPS can be observed that the presence of a sharp peak in the absorption band 1149.57 cm^{-1} shows the characteristics of the polysaccharide, there is stretch vibration absorption from O–H and is strengthened by the presence of an absorption band at 1002.98 cm^{-1} which is a stretching vibration C–O (Figure 1). The absorption area of 1620.21 cm^{-1} shows asymmetric carbonyl. It was also found in the absorption of 1473.62 cm^{-1} of an asymmetric carbonyl. *IR* (HES) spectra in it can be observed that a sharp peak in the absorption band 1103.28 cm^{-1} shows the characteristics of the polysaccharide, then there is a change in the absorption band in the exopolysacride after being modified with silica gel especially in the absorption band at a frequency of around 470.63 cm^{-1}, it is the bending vibration absorption of O atoms from the siloxane functional group (Si–O–Si). The presence of siloxane functional groups is strengthened by the appearance of absorption bands in the area of 794.67 cm^{-1} which is the presence of Si–O (Si–O–Si) symmetric stretching vibrations.

In the absorption band around 3448.72 cm^{-1} is the stretching vibration of (–OH) from the silanol (Si–OH) group. In the area of wave number 2931.8 cm^{-1}, there is an absorption band originating from the (C–H) stretching vibration of ($–CH_2$) aliphatic. The frequency of the wave number 1635.64 cm^{-1}, it is an absorption that shows the OH vibration attached to the carbonyl group (–C=O) originating from the exopolysacride. Spectra *IR* (HESM) can be observed that there is a sharp peak in the absorption band 1103.57 cm^{-1} shows the characteristics of polysaccharides, then there is a change in the absorption band in the exopolysacride after being modified with silica gel with magnetite variations, especially in the absorption band at a frequency of around 470.63 cm^{-1}, which is the bending vibration absorption of O atoms from the siloxane (Si–O–Si) functional group.

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3.2. Characterization of adsorbent by SEM

The results of analysis by SEM to determine the morphology of HES and HESM (Figure 2). Can be seen that there are morphological differences between HES and HESM, the morphology of HES is more homogeneous because of the presence of gelatinous silica which acts as a supporting matrix for EPS. Silica gel is an inorganic solid which is used to enrich the surface of exopolysaccharide solids as adsorbent. Silica gel was chosen as the support matrix because it has a large surface area and active sites such as silanol (–Si–OH) and siloxane (Si–O–Si) which can bind chemically with the functional groups found in exopolysaccharides.

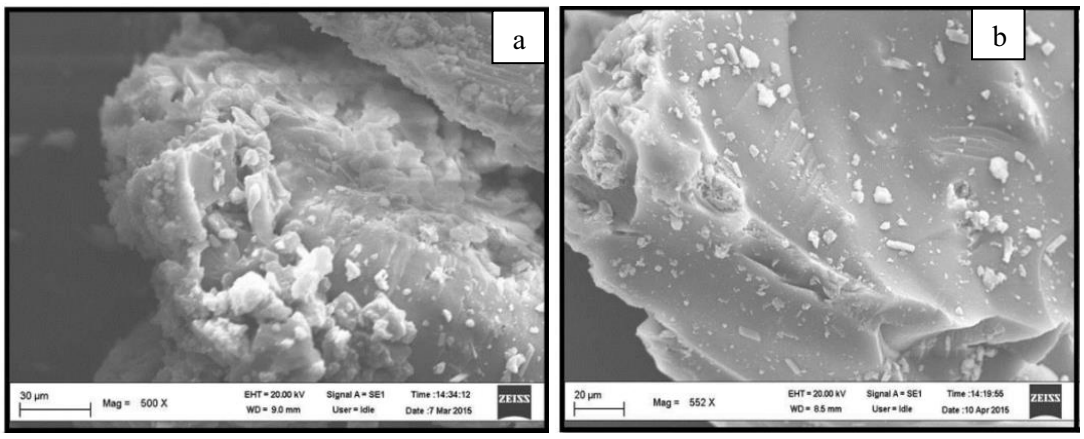

Figure 2. Scanning Electron Microscope (SEM) results (a) HES with 500x magnification and (b) HESM with 500x magnification.

From the results of this analysis it is in accordance with Figure 2. The largest element contained in HESM is Si. The results of HES and HESM characterization by SEM are compatible with the *IR* spectrophotometer characterization. In Figure 2, the different SEM results between HES and HESM are shown, in HESM there is Si obtained from the synthesis of exopolysaccharides with silica gel, indicating a more homogeneous surface morphology. Silica gel is an inorganic solid which is used to enrich the surface of exopolysaccharide solids as adsorbent.

3.3. Adsorption

3.3.1. Adsorption kinetics

The adsorption kinetics of metal ions in solution with the adsorbent can be determined by determining the adsorption rate. The adsorption rate between the adsorbent against metal ions plays a role in determining the optimum conditions for the interaction of metal ions from the solution and its equilibrium state to the adsorbent. The data in (Figure 3) were analyzed using the first-order pseudo and second-order pseudo equations with the kinetics of Pb(II) ion adsorption kinetics parameters. The results of the analysis show that the pseudo second order rate constant (k_2) of Pb(II) ions in HESM and HESM against Pb(II) ions is the greatest, this identify that HESM against Pb(II) ions has a greater adsorption rate than others. The data in this study shows that the HES and HESM adsorbents in this study tend to follow second-order pseudo kinetics because the R^2 values for HES and HESM for Pb(II) ions tend to be around 0.99 (Table 1).

Table 1. Second-order kinetic parameters on HES and HESM with respect to Pb(II) ion.

Adsorbent	*qe* (g mg^{-1})	K_2 (g mg^{-1})	R^2
HES	10.97	3.48	0.99
HESM	2.91×10^{-8}	0.34×10^{-8}	1

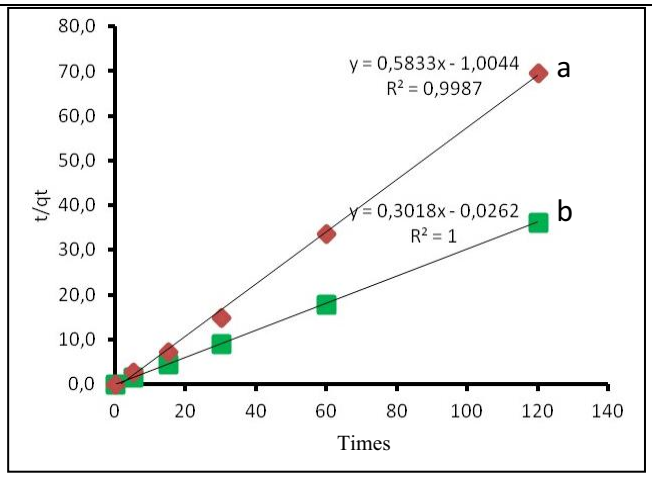

Figure 3. Kinetics of pseudo second-order Pb(II) ion on a. HES and b. HESM.

3.3.2. Adsorption isotherm

Adsorption isotherm can be used to determine the interaction between the amount of adsorbed substance (adsorbate) and the amount of adsorbent (adsorbent) and the optimum ability achieved by the adsorbent to adsorb metal ions.

The adsorption isotherm is a very important parameter in adsorption because it plays a role in determining the maximum conditions for optimal adsorption [15]. In this study, two forms of adsorption isotherm equation were used, namely the Langmuir and Freundlich adsorption isotherms to analyze the Pb(II) ion solution, presented on Table 2.

Table 2. Langmuir and Freundlich adsorption isotherm parameters.

Adsorbent	Langmuir			Freundlich		
	n_m (mg g^{-1})	K_L (L mol^{-1})	R^2	n (mol g^{-1})	K_F (mg g^{-1}) (L $mg^{-1})^{1/n}$	R^2
HES	3.85	39.39	0.86	1.098	2.55	0.63
HESM	272.63	99.99	0.96	1.101	1.15	0.77

In Figure 4 it can be seen that the adsorption isotherm model more closely follows the Langmuir adsorption isotherm model with an R^2 value of 0.9631 which is greater than the R^2 value in the Freundlich model. The adsorption capacity of the HESM adsorbent against Pb(II) was greater than the adsorption capacity of the HES adsorbent against Pb(II). The higher adsorption capacity indicates that the Pb(II) ion is more capable of making the site active and reliable. In the Langmuir isotherm, it explains that the adsorbent surface, namely HESM, has an active site which is proportional to the surface area of the adsorbent. Langmuir and Freundlich adsorption parameters including adsorption capacity and equilibrium constant seen in Table 2.

From the data analysis of adsorbent using Langmuir isotherm model which can be seen in Table 2, the adsorption capacities of HES and HESM for Pb(II) ions are 3.85 and 272.63 mg g^{-1}, respectively, K_L values (adsorption equilibrium constant) of 39.39 and 99.99 L mol^{-1}, respectively. The greater the K_L value, the greater the absorption affinity by the bio-sorbent can be seen in Figure 4.

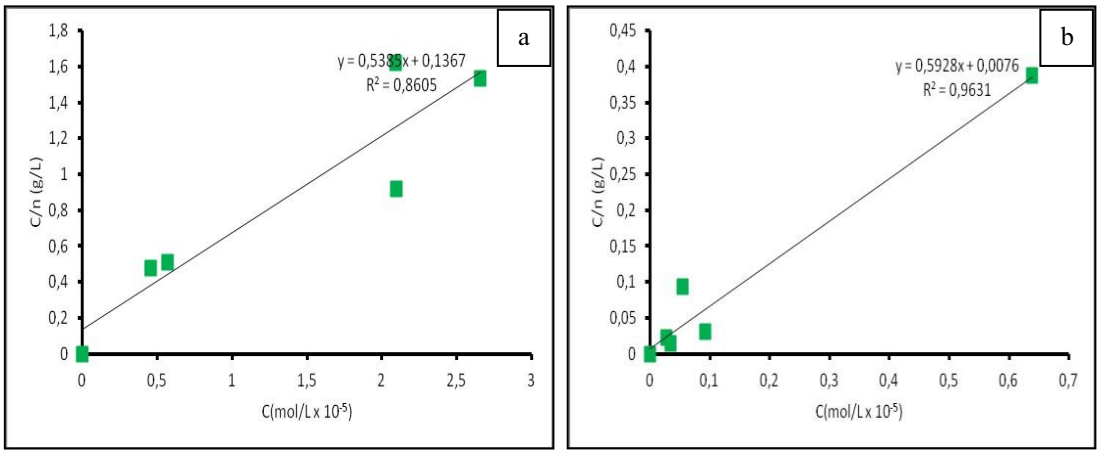

Figure 4. Adsorption isotherm curve of (a) Pb(II) ion in HES and (b) Pb(II) ion in HESM Langmuir model

Langmuir adsorption isotherm is an adsorption process that occurs because of the interaction between the adsorbate and the active sites on the adsorbent surface. The adsorption of metal ions by the adsorbent in this study tends to follow the Langmuir isotherm, so that the adsorption capacity can be determined directly using the Langmuir isotherm based on the slope value [16].

4. Conclusions

Adsorption of Pb(II) ion with HES and HESM is optimum at pH 7 and concentration at 25 ppm with the adsorption capacity on HES at 3.85 mg g^{-1} while on HESM at 272.63 mg g^{-1}, contact time of 15 min and it tends to follow second order pseudo kinetic model and Langmuir adsorption isotherm model. The HESM are effective adsorbents for removing heavy metals specifically Pb(II) ion in solution.

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References

[1]Kausar R A, Buhani & Suharso 2019 IOP Conference. Materials Science and Engineering. **857**.
[2]Seshadri S, Bishop P L,& Agha A M 1994 *Waste Manage*. **14** 127–137.
[3]Sen S & Demirer GN 2003 *J. Environt. Eng.* **129** 595-601.
[4]Buhani, Hariyanti F, Suharso, Rinawati, & Sumadi 2019 *Desalin Water Treat*. **142** 331–340.
[5]Buhani, Suharso, & Sumadi 2010 *Desalination*. **259** 140-146.
[6]Gupta SS& Bhattacharyya K G 2006 *J. Colloid. Interf. Sci*. **295** 21-32.
[7]Buhani, Suharso, Luziana F, Rilyanti M, & Sumadi 2019 *Desalin Water Treat*. **171** 281–293.
[8]Gupta V K, Nayak A, & Agarwal S 2015 *Environ. Eng. Res.* **20** 1–18.
[9]Celekli A, Atmaca, M Y,& Bozkurt H 2010 *J. Hazard. Mater*. **173** 123–129.
[10]Morillo P J A, García R R, & Quesada T 2008 *J.* of Microbiology & Biotechnology. **24** 2699–2704.
[11]Wei W, Wang Q, Li A, Yang J, Ma F, Pi S, & Wu D. 2016. *J. Scientific Reports*, **6** 1.
[12]Peng Q, Liu Y, Zeng G, Xu W, Yang C, & Zhang *J* 2010 *J. Hazard*. Mater. **177** 676-682.
[13]Liu Y, Zeng Y, Xu W,Yang C, & Zhang J 2010 *J. Hazard. Mater*. **177** 676-682.
[14]Buhani, Musrifatun, Pratama D S, Suharso, & Rinawati 2017 *Asian J. Chem*. **29** 2734-2739.
[15]Entezari MH & Bastami T R 2013*Mater. Res. Bull*. **48** 3149–3156.
[16]Buhani, Herasari D, Suharso, & Yuwono S. D 2017 *Orient. J. Chem.* **33** 418-429.