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To cite this article: Chariztya Anggita Maharani *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **546** 042021

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Preparation and Characterization of Silica-Carrageenan Adsorbent for Pb^{2+} and Cd^{2+} as Interfering Ion

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Abstract. Pb^{2+} and Cd^{2+} are poisonous heavy metal ions produced by industrial waste. Waste processing is always required before such material is released into the environment. A safe biomaterial such as silica-carrageenan was designed for the heavy metal adsorbent. The objectives of this research were to prepare and characterize silica-carrageenan adsorbent as well as testing them in some applications, by thin layer chromatography as well as in batch methods. Adsorption profiles of the two heavy metal ions were expected. The result showed that this material contained 1.10 g/cm³ density, 2.10% moisture level, 81.70% ash level, and iodine adsorption value of 21.80%. SEM pictures showed the homogeneous structures with globular particle shape below 100 nm dimension. FT-IR spectra showed the presence of the siloxane groups ($\equiv Si-O\equiv$), silanols ($\equiv Si-OH-$), and -OH groups from carrageenan. Both ions could not be eluted by all of the organic eluents on TLC plates of the material, but less than 50% of Pb(II) can be separated. This adsorption value decreased in the presence of Cd(II) in the silica-carrageenan system in batch method.

Keywords: Adsorption, biosilica, carrageenan, Pb(II) ion, Cd(II) ion.

1. Introduction

Adsorption is one of many alternative methods to reduce heavy metals, which process is relatively simple, inexpensive, and works at low concentration. One most widely used adsorbent so far is silica gel. In this study, a modification of silica with carrageenan was prepared for Pb(II) and Cd(II) adsorption. The separation of Pb(II) and Cd(II) by thin layer plates were checked and adsorption of Pb(II) in the batch system was also tested.

The silica was obtained from the extraction of rice husk ash. In rice plants, silica is bio-accumulated and stored mostly in rice husks. Naturally, some organic materials also exist but it was destroyed during the burning to get the minerals including silica as the largest portion [1]. Rice husk ash was chosen because it has a very high silica content at around 89-91% [2]. In addition, silica from rice husk ash has active sites in the form of silanol (Si-OH) and siloxane (Si-O-Si) to give characters on its surface.

In previous studies, cellulose was used as a modification to the silica [3,4]. However, in this study carrageenan was used to be incorporated into the silica to alter the material's characters. Carrageenan has different properties compared to cellulose as it is easier to swell and act as a binder. Cellulose also



swells to a certain extent but does not bind to polar surfaces. The addition of carrageenan changes the polarity of the adsorbent. They form new material and this incorporation can be made occurred during gelling of the silica. When silica tends to be very absorbing, the presence of carrageenan makes the surface less polar. This property is good for adsorbents as well as chemical releasers [4,5].

Carrageenan used in this study was kappa-carrageenan. Kappa carrageenan was usually put as a thickening agent, water binder, and gelling inducer [6–8]. Kappa-carrageenan was chosen due to its small viscosity, to be able to mix easily with silica, and to get into the pore system during gelling. This act also avoided too much swelling of the carrageenan. The second important thing was the uniformity of adsorbent's pore system, which was related to the distance taken by molecules during the adsorption process. If the distance was different for the same analyte molecules, each will travel in different distances [9]. This leads to peak broadening in the chromatographic system. The sulfate groups in carrageenan were negatively charged along the polymer chain and its hydrophilic properties allowed carrageenan to be used as a binder [10]. It was chosen to maximize the adsorption on silica. The ability of oxygen atoms in the silanol groups in binding heavy metal ions is relatively small. In this case, a metal ion binder such as carrageenan might help.

In this study, Pb(II) was used as they possess properties that are harmful to human health. Lead ion in a large portion would accumulate in the kidney, liver, and some would be released through the digestive tract. This study also involved other heavy metal ions, Cd²⁺ as an interfering ion. Cd²⁺ was selected as interfering ion could come from waste, such as in tannery waste, in which both Pb²⁺ and Cd²⁺ present together. Cd²⁺ has the same charge as Pb²⁺ and both ions are harmful. Adsorption of Pb(II) and Cd(II) as interfering ion, studied using the batch method was then by the aid of Atomic Absorption Spectroscopy. A thin layer plate was also made using the new material, compared with commercial silica TLC plates, to evaluate the ability of both heavy metal ions elution as well as to study the separation of both ions.

Separation chemistry is based on the dynamics in the interfaces [9]. In porous media, it can be a solid-liquid or solid-gas interface, so that adsorption and desorption occur simultaneously according to the equilibrium constant of each adsorbate. The mechanism that governs separation actually depends on this balance and this is the basis of separation by chromatography. The dynamics of small particles on the surface have actually been thoroughly studied with the help of relaxation and diffusion of NMR long before [11,12]. More experiments on the surface with other methods actually describe the role of water in adsorption systems [13,14] by Raman spectroscopy, infrared, as well as computational chemistry.

2. Materials and Methods

2.1. Chemicals and Instrumentation

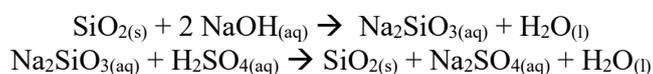
The chemicals were mostly obtained from Sigma Aldrich and E.Merck and all bench-activities were used pyrex glassware. Cd(NO)₂ and Pb(NO)₂ were used to study the dynamic of the silica-carrageenan surface, while the *R_f* study was used to examine the effectiveness of the material as a stationary phase to separate both heavy metal ions. Methanol and ethanol were used as a mobile phase for TLC. Kappa carrageenan was obtained from Merck.

Laboratory instrumentations used for this study were Thermolyne furnace for preparation of rice husk ash, magnetic stirrer of NESCO LAB MS-H280-Pro or Thermoscientific Cimarec for gelling reactions, EYELA oven type WFO-450ND, IR-*Prestige-21* (SHIMADZU), centrifuge type Kokusan H-130n, shaker IKA Ks 260 Basic type, SEM (Scanning Electron Microscopy) type FEI Inspect S50 and AAS (Atomic Absorption Spectrophotometry) Shimadzu Merck AA 240 type (hollow cathode lamp of Pb = 283.3 nm).

2.2. Material Preparation and Characterization

First, rice husk powder was heated to 350°C to get the ash as the source of silica [15,16]. The ash was heated again in the furnace for 1 hour prior to alkaline addition. The ash then dissolved in NaOH solution and stirred using a magnetic stirrer. Then, the solution was allowed to stand overnight and filtered off. The filtrate containing silica, in the form of sodium silicate (Na_2SiO_3), then used to make silica-carrageenan adsorbent.

Preparation of carrageenan colloid was done by adding the kappa-carrageenan powder to H_2SO_4 solution accompanied by stirring them in magnetic stirrer to form of a yellowish gel. The filtrate from the extraction of silica was combined to the carrageenan colloid until the gel started to form. The mixture was added with a solution of concentrated NH_4OH until pH rose slowly. The formed gel was filtered off, washed and finally dried in an oven. The dry residue was pulverized to obtain silica-carrageenan powder which ready to be used as an adsorbent for Pb^{2+} ion. The overall reaction of silica isolation can be seen in the equations below:



The silica matrix was also characterized (density, moisture level, ash level, and the iodine adsorption value). Identification of surface topography and functional groups of this adsorbent were done with SEM and FT-IR. For adsorption test, the silica-carrageenan was used in batch adsorption, with the adsorbate volume of 25 mL and contact time of 20 minutes. Furthermore, the supernatant was analyzed using AAS. After the batch process, the calculation of Pb^{2+} concentration before and after adsorption was carried out through their respective linear regression equations, then the percentage of adsorption was determined. Adsorption of Pb^{2+} and Cd^{2+} as interfering ion was carried out by batch method with the same treatment.

The material was also used in the TLC method. Adsorbents were added by CaSO_4 and 30 drops of distilled water and then stirred until homogeneous. The result was poured on top of a clean glass slide and dried and flattened to have the same thickness. The plates were dried by the oven and allowed to stand at room temperature. The separation process using TLC plate coated adsorbent began with a spotted mixture Pb^{2+} and Cd^{2+} in a solution of nitrate salt at a distance of 0.5 cm from the bottom edge of the TLC plate. Furthermore, the TLC chamber was prepared, the eluent was inserted into the chamber containing fine filter paper and covered with glass. If all the fine filter paper surface has been wetted by the eluent, the TLC chamber was surely saturated. The TLC plate containing Pb^{2+} and Cd^{2+} and mixture was put into each chamber and covered with glass to elute. The elution process was stopped when the eluent has reached a distance of 2.5 mm from the top edge of the TLC plate. TLC plate then aerated to dry, stain formed sprayed with KI and CS_2 reagents. spotting process and elution procedure were repeated for the separation using the commercial plate.

3. Result and Discussion

3.1 Silica-Carrageenan Material Characterization

Adsorbent characterization tests were carried out, including density test, moisture level, ash level, iodine adsorption value, Scanning Electron Microscopy (SEM), and Fourier-Transformed Infrared (FT-IR). The moisture level of the silica-carrageenan was low. The ash level of silica-carrageenan was very high due to silica itself. The absorption of iodine in silica-carrageenan was quite high too, indicating that the adsorbent's surface is full of active sites. The physical characterization of the material can be seen in Table 1.

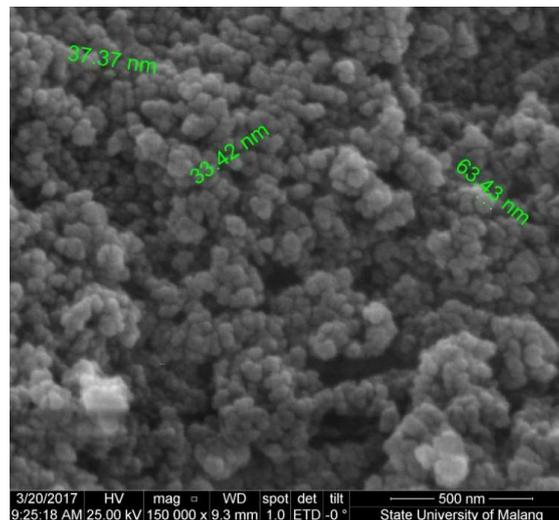
Table 1. Physical Characterization of Silica-Carrageenan.

Adsorbent	Density (g/cm ³)	Moisture level (%)	Ash level (%)	Iodine Adsorption Value (%)
Silica-Carrageenan	1.10	2.10	81.80	21.80

Physical characterization by SEM instrument can be seen in Figure 1. Characterization of the surface structure of the adsorbent using SEM was also carried out to determine the shape of the surface topology of the adsorbent. The image of silica-carrageenan with 150.000 times magnification showed the structure of the uneven silica-carrageenan surface with globular particle shape indicating pores on the surface of silica-carrageenan. The presence of pores on the surface would surely increase the surface area.

The FT-IR analysis aimed to identify the functional groups on the adsorbent, which spectra are presented in Figure 2. The comparison of silica, carrageenan, and silica-carrageenan spectrum can be observed. There was a wavelength shift occurred, indicating different functional groups in the new material.

The absorption patterns that appear generally are siloxane groups ($\equiv\text{Si-O}\equiv\text{Si}$) and silanol groups ($\equiv\text{Si-OH}$) contained in silica gel. The absorption band at wavenumber 457.13 cm^{-1} and 466.77 cm^{-1} are bending vibration of the siloxane group. The area at $820\text{-}600\text{ cm}^{-1}$ shows the stretching vibration of Si-O symmetry in siloxane ($\equiv\text{Si-O}\equiv\text{Si}$) and the absorption band $3200\text{-}3600\text{ cm}^{-1}$ is the O-H stretching vibration of carrageenan O-H in silanol. In the absorption area of $1220\text{-}1270\text{ cm}^{-1}$, there was a S=O bond in the sulfate ester in carrageenan. The $840\text{-}850\text{ cm}^{-1}$ spectrum identified the presence of galactose-4-sulfate group on kappa-carrageenan. The similarity of this spectra indicated that only physical interaction occurs on the two material, there was no indication of new chemical bonds on silica-carrageenan.

**Figure 1.** The SEM image of Silica-Carrageenan

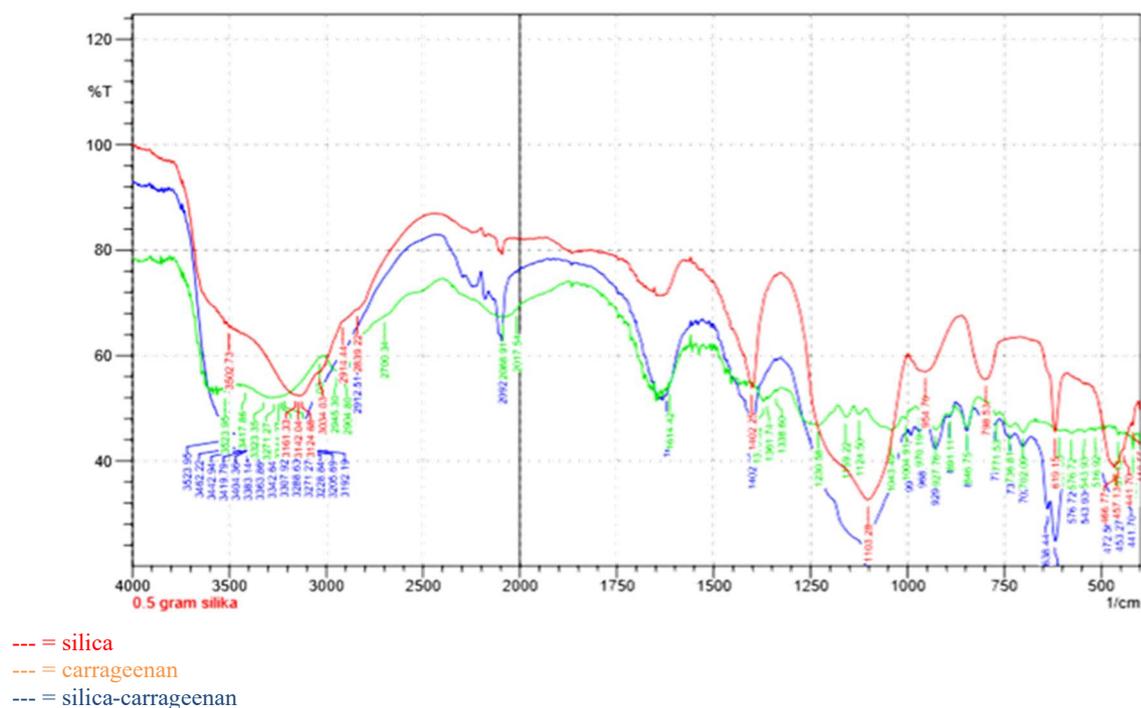


Figure 2. Spectrum IR of Silica-Carrageenan

3.2 Adsorption Applications using Thin Layer Chromatography (TLC) Method

Adsorption of heavy metal ions in the thin layer method was used to determine the migration of Cd^{2+} and Pb^{2+} by suitable solvents. The adsorbates were polar so that eluents were also polar. First, the elution process carried out on a commercial silica plate as standard, and the first metal ion used Pb^{2+} . The use of commercial silica plate aimed to determine the appropriate eluent for use. Furthermore, the TLC process uses preparative plates coated with silica-carrageenan. The results are presented in Table 2.

Table 2. The R_f of Pb^{2+} and Cd^{2+} and their mixture in different solvent.

R_f Systems	Solvents	Pb^{2+}	Cd^{2+}	The mixture of Pb^{2+} and Cd^{2+}
Commercial silica thin layer	Water	0.30	0	0
	Ethanol	0.24	0	0
	Methanol	0.26	0	0
	Methanol: Water 2:1	0.34	0	0
Silica-carrageenan preparative plates	Water	0	0	0
	Ethanol	0	0	0
	Methanol	0	0	0
	Methanol: Water 2:1	0	0	0

The result showed that elution of Pb^{2+} with eluent water, ethanol, methanol, and methanol: water 2:1 as eluents on a commercial plate gave R_f values <0.50 . Furthermore, the process TLC process used preparative plates coated with silica-carrageenan. In this study Pb^{2+} can be eluted in commercial silica with water, ethanol, methanol, and methanol: water 2:1 as eluents, but the same ion could not be eluted using the same eluents on silica-carrageenan. This was presumably because the stationary phase so tightly bound the Pb^{2+} ion or the eluent movement was blocked by the swelling carrageenan. This also

happens to Cd^{2+} ions and mixtures of Cd^{2+} and Pb^{2+} . The dynamics of solvent molecules and the tortuosity of the porous system can play a particular role as described previously [3–5,9,17–19].

However, TLC results of metal ion Cd^{2+} and a mixture of Cd^{2+} and Pb^{2+} showed there is no migration of these ions in the commercial silica or silica-carrageenan. R_f obtained was zero. It is assumed that Cd^{2+} and Pb^{2+} ions very strong interaction with the adsorbent and they were unable to elute. Cadmium ion behaved differently compared to lead ion.

3.3 Adsorption of Pb^{2+} on Silica-Carrageenan Adsorbent

Charts of the relationship between the concentration and percent adsorption of Pb^{2+} ions are presented in Figure 3. Percentage of Pb^{2+} adsorption increased with increasing concentration, even though the percentage was less than 50%. Carrageenan is an organic compound that is not easy to tie the charged ion, and moreover, this can block the surface of silica. In addition, the ions can actually be physically trapped in the pore system, as indicated in the SEM results.

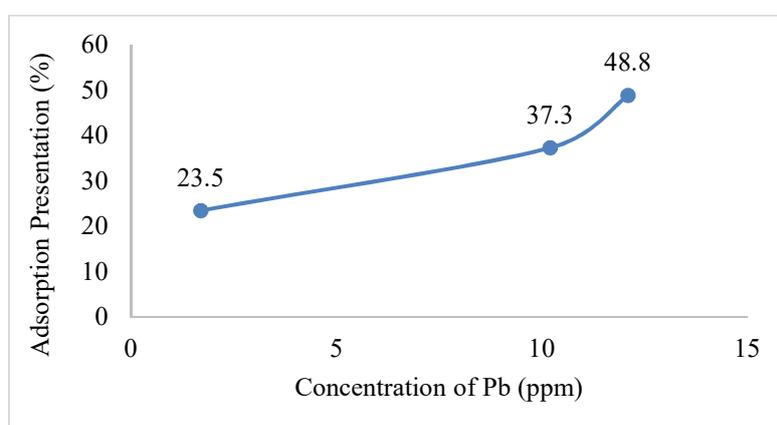


Figure 3. Relationships between Percent Adsorption curve Pb^{2+} at Different Concentration Variation

In this study, the adsorbed Pb^{2+} was desorbed back to the solvent during washing. This indicates that the physical adsorption occurs because the intermolecular attractive forces between the adsorbate with an adsorbent were weak so that the ion and solvent molecules can be released again. This phenomenon can be seen in Table 3 below.

Table 3. The result of Pb^{2+} desorption.

Concentration of Pb^{2+} (ppm)	Concentration of Pb^{2+} (ppm)		% Result of desorption
	Residual adsorption	Result of desorption	
12.10	6.20	0.10	0.017

3.4 Adsorption of Pb^{2+} on Silica-Carrageenan Adsorbent and Cd^{2+} as Interfering Ion

Adsorption of Pb^{2+} and Cd^{2+} as interfering ion was also done with the batch method. This analysis was conducted to determine the effect of interfering ion on the concentration of Pb^{2+} in the silica-carrageenan adsorbent. In fact, on the presence of Cd^{2+} , Pb^{2+} concentration decreased. The initial concentration of the mixed solution prepared in the ratio of 1:1. The data provided information that the presence of Cd^{2+} as interfering ion able to decrease the amount of Pb^{2+} adsorption to below 50%.

In Table 4, the concentration of Pb^{2+} in the mixture after adsorption by the silica-carrageenan adsorbent decreased to a value below 50%, which is 39.50% on the silica-carrageenan adsorbent. This data shows that in the adsorption process of Pb^{2+} and Cd^{2+} competition for the active side of the adsorbent.

Table 4. The measurement results of the concentration of Pb^{2+} and Cd^{2+} as interfering ion.

Concentration of $Pb^{2+} : Cd^{2+}$ (ppm)	Type of Adsorbent	Concentration of Pb^{2+} (ppm)		% Adsorption
		Before (ppm)	After (ppm)	
20:20	Silica-Carrageenan	15.20	9.20	39.50

The fact showed the competition of Pb^{2+} and Cd^{2+} on the surface of silica as well as silica-carrageenan. The radius of Pb^{2+} ions is greater than the Cd^{2+} ($Pb^{2+}= 119$ r.pm and $Cd^{2+}= 95$ r.pm). The large ionic radius causes a small electrostatic force so that the ion's ability to attract water molecules is weak. If the ion's ability to attract water molecules is weak, then the radius of the ion's hydration is small. The smaller the radius of hydration of the mobility of the ions in the water will be higher so it is easier to get to the surface of the adsorbent.

In addition, the adsorption percentage decrease is caused by competition between NO_3^- from both lead and cadmium salts, and water molecules in interacting with the silica-carrageenan. It means that with the increasing number of competitors to bind to the adsorbent, Pb^{2+} will be inhibited to be absorbed into the surface of the adsorbent. This explained that the adsorption process was influenced by the character other than the adsorbent only.

4. Conclusion

In this experiment, the silica-carrageenan material was made, it has a low density, low moisture level, very high ash content, and high iodine absorption. Characterization test of silica-carrageenan adsorbent using SEM showed that the structure of the adsorbent was uneven with the shape of globular particles, the pores were uniformly present. The FT-IR spectra showed siloxane and silanol groups contained as well as $-OH$ groups from carrageenan. Silica, carrageenan, and silica-carrageenan have similar spectra so that physical interactions occur between them. The mixture of Pb^{2+} and Cd^{2+} could not be eluted on TLC plate of silica-carrageenan system, the percentage adsorption Pb^{2+} decreased to below 50% on the silica-carrageenan adsorbent, and the presence of Cd^{2+} as interfering ion reduced the absorption of Pb^{2+} on the adsorbent.

Acknowledgment

Part of this research was funded by the Ministry of Research and Technology and Higher Education, Fundamental Research Scheme, 2016.

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