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Cite as: AIP Conference Proceedings **2353**, 030123 (2021); https://doi.org/10.1063/5.0052808
Published Online: 25 May 2021

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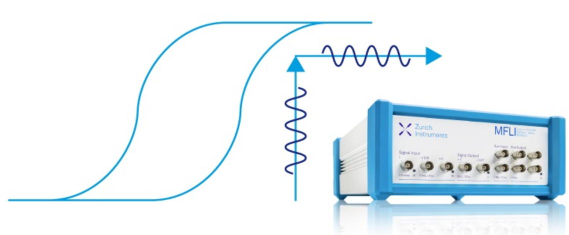

The Application of Silica-Cellulose Material as Heavy Metal Adsorbent on Laboratory Wastewater

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Abstract. Environmental pollution is a complex problem because waste is generated in all areas of life. If not handled properly, laboratory waste can pollute and endanger the environment. Laboratory waste containing heavy metals such as Cadmium, Chromium, Nickel, and Zinc is hazardous if it pollutes the environment. An easy and inexpensive method of treating heavy metal waste is adsorption. This research applies silica-cellulose material as heavy metal adsorbent in laboratory waste. Variations in contact time were used to measure the adsorbent capacity and adsorbent effectiveness on heavy metals Cadmium, Chromium, Nickel, and Zinc. The results showed that the contact time affected the adsorption capacity and the adsorption effectiveness of silica-cellulose on heavy metal content in laboratory waste. For Cd and Zn metals, the highest adsorption capacity at the contact time of 1 h with adsorption effectiveness values above 90%. Whereas for Cr and Ni metals, the highest adsorption capacity was at the contact time of 3 h with different values of adsorption effectiveness. For Cr metal, almost entirely can be absorbed well, while Ni metal is only half of the total metal can be absorbed.

INTRODUCTION

The demand of the working world that is so complex has required universities to equip their graduates with adequate skills including lab practices which play a significant role in skill development. On the other hand, the activity also makes a considerable contribution to environmental pollution. Extensive use of chemical substances in lab practices or research activities will undeniably produce wastes [1]. Expired chemicals, disposable chemicals, wastes from lab activities, the remaining chemicals from lab practices that are no longer used, as well as the residual samples from previous analyses are highly dangerous to the environment [2].

Chemicals that contain heavy metals are among those considered harmful in the laboratories. Heavy metals are highly toxic and readily accumulate, thus, requiring further treatment before disposal. Several heavy metals that have been given particular attention in wastewater treatment are nickel, zinc, copper, mercury, cadmium, lead, and chromium [3]. Inside the human body, heavy metals may cause carcinogenicity, mutagenicity and reproductive system damage [4].

Environmental pollution is an occurrence where pollutants are entering water, air or soil, leading to poisoning and the death of living organisms in a polluted environment [5]. Heavy metals are among those pollutants that have become a serious threat to the environment due to their non-degradable and long-term accumulative properties [6]. Heavy metal wastes on low concentrations between 0.001 - 0.1 ppm may endanger and poison the organisms. Those pollutants accumulate in the body of animals and humans through the food chain cycle, which may lead to carcinogenicity, mutagenicity, and reproduction system damage [4].

International Conference on Life Sciences and Technology (ICoLiST 2020)
AIP Conf. Proc. 2353, 030123-1–030123-7; https://doi.org/10.1063/5.0052808
Published by AIP Publishing. 978-0-7354-4096-8/$30.00

Several attempts have been made to decrease heavy metal pollution in the aquatic environment using the following methods; evaporation, ion-exchange, physical and chemical precipitation, membrane-filtration, reserve osmosis and adsorption [7]. Adsorption is one of the most widely developed methods due to its simplicity, inexpensive and high success rate [8,9]. The adsorptions of heavy metal are performed with various types of adsorbent, including activated carbon, zeolite biosorbents and lignocellulosic fibers [10]. In this research, the removal of heavy metal was conducted with a modified silica-cellulose material. Silica obtained from rice husk wastes was modified with the cellulose of Nata de Coco through the sol-gel method.

The modification of silica with cellulose gives rise to a globular, and homogenous new material which has been proven to increase the size of the porosity and absorbency of the silica surfaces. A number of researches have reported the use of silica-cellulose as an adsorbent for textile colouring with significant results [11,12]. The ability of silica-cellulose to separate chemical substances on the plate of thin-layer chromatography has also been noted [13]. Another research reported that silica-cellulose could also be used as the immobilization media of bacteria, such as *zymomonas mobilis* and *pseudomonas fluorescence* [14,15].

According to the researches mentioned above, silica-cellulose has been proven to have the potential as a suitable adsorbent. However, the material has never been used as the adsorbent of wastes containing a more complex and varying composition. This research applied silica-cellulose material as an adsorbent for heavy metal-containing laboratory wastewater with variations in contact time to determine the effectiveness and adsorption capacity of the material in laboratory wastewater.

EXPERIMENTAL DETAILS

Reagents and Instrumentation

All chemical reagents were of pro-analysis quality, purchased from Merck and the glassware were of Iwaki Pyrex. This research used the following instruments to support with data collection; atomic absorption microscopy (AAS) Varian AA240, scanning electron microscopy (SEM) Hitachi TM 3000 Tabletop Microscope in LSIH Universitas Brawijaya, furnace XD-1700 M and Nabertherm.

Preparation and Morphological Determination of Silica Cellulose Material

5 g rice husks were heated in a furnace for several hours. The ash was then introduced into the strong base solution and stirred for 8 h. The resulting filtrate was mixed with the cellulose of *Nata de Coco* and stirred until the pH turned acidic. In this research *Nata de Coco* were produced by biology department of Muhamadiyah Malang University. Afterwards, a strong base was added to the solution to turn the pH to basic, thus gradually forming silica-cellulose. To see the details of making cellulose silica, this procedure has been patented on February 14th, 2018 under Indonesia trademark number IDP000049626 [11]. After that, the obtained silica-cellulose material underwent morphological study using SEM (Scanning Electron Microscopy) to determine the porosity and particle distribution of the material.

Preparation of Laboratory Wastewater and Determination of Heavy Metal Content

Laboratory wastewater was prepared using wet digestion before undergoing further treatment. 1 L of laboratory wastewater was added with 100 mL of concentrated nitric acid and subsequently heated until the volume reduced to 100 mL. The solution was then filtered using Whatman filter paper No. 21. The obtained filtrate would be the sample of laboratory wastewater that will be taken to further treatment. 5 g of silica-cellulose matrices were transferred into an erlenmeyer flask 250 mL and added with 100 mL of wastewater sample, which has been prepared in advance. The mixture was homogenized for 1, 3, 6, 12 and 24 h on the shaker at a constant speed of 150 rpm. Samples were subsequently filtered with Whatman filter paper No. 21 and analysed to determine Cd, Cr, Ni, and Zn content using atomic absorption spectroscopy (AAS).

Determination of Effectiveness and Adsorption Capacity of the Material

The adsorption capacity of silica-cellulose was determined with the following Equation 1 [16]:

$$q = \frac{(C_{inisial} - C_{final})}{M} V \quad (1)$$

where :

q	: Adsorption capacity (mg/g)
$C_{initial}$	: The concentration of heavy metal before treatment (mg/L)
C_{final}	: The concentration of heavy metal after treatment (mg/L)
V	: Waste volume (L)
M	: Mass of adsorbent (g)

Whereas, to determine the effectiveness of the adsorption process, the following equation was applied [17]:

$$Effectiveness\ of\ Adsorption\ (\%) = \frac{C_{inisial} - C_{final}}{C_{inisial}} 100\% \quad (2)$$

RESULTS AND DISCUSSION

Characterization of Silica-Cellulose

The formation of silica-cellulose material from rice husks and Nata de Coco yielded white powder material. Preparation of silica-cellulose was divided into three parts; the heating of rice husks as the source of silica, drying of Nata de Coco sheets as the source of cellulose, and the preparation of silica-cellulose adsorbent. These steps of preparing silica-cellulose material have been patented under Indonesia trademark number IDP000049626 [15].

(a) (b)

FIGURE 1. (a) Matrix Silica-cellulose (b) SEM image of cellulose silica with magnification 80.000x

The characterization of silica-cellulose was carried out by examining the morphology of the material surfaces through SEM. The particles were observed as roundish gel granules as the homogeneity of sol-gel has ensured a well-distributed pore size. Silica-cellulose particles were not easily differentiated and exhibited a good interaction between silica and cellulose. Based on the result of SEM imagery with 80,000 times magnification, the morphology of silica-cellulose (Figure 1) appears to be globular particles with uneven surfaces and particle size under 100 nm. Uneven surfaces on globular-shaped material indicate the formation of porosity on the surface of silica-cellulose. The presence of pores on material surfaces expands the surface area of the adsorbent as well as a small size of particles which also provides a greater surface area, indicating the potential of the material as a good adsorbent. These characteristics are a must for an adsorbent used for separation [18]. The image shows the porosity of the material ranges from 100 - 500 nm.

The Effect of Contact Time on the Reduction of Heavy Metal Content

Sample preparation before use was carried out through wet digestion of laboratory waste. This process was performed by adding concentrated acid and heating laboratory waste before undergoing filtration. The purpose of the preparation was to dissolve all heavy metal content and eliminate organic matter contained in laboratory waste samples. After wet digestion treatment, the color of the sample turned to yellowish clear. Determination of heavy metal content on laboratory waste was carried out for cadmium, chromium, nickel and zinc. Measurements were performed on samples before and after the addition of silica-cellulose.

TABLE 1. Heavy metal content on laboratory waste (n = 3)

Contact Time (hour)	Heavy Metal (ppm)			
	Cd	Cr	Ni	Zn
0	8.15 ± 0.00	5.53 ± 0.00	9.38 ± 0.00	6.00 ± 0.00
1	0.64 ± 0.08	2.28 ± 0.04	0.51 ± 0.03	0.47 ± 0.04
3	0.40 ± 0.02	2.48 ± 0.07	0.58 ± 0.03	0.15 ± 0.01
6	3.48 ± 0.03	3.45 ± 0.05	2.39 ± 0.47	2.64 ± 0.04
12	3.29 ± 0.07	3.30 ± 0.05	1.92 ± 0.11	2.60 ± 0.38
24	1.92 ± 0.06	4.13 ± 0.09	2.55 ± 0.06	4.95 ± 0.04

The result of the application of silica cellulose as heavy metal adsorbent on laboratory waste is detailed on Table 1. Table 1 shows that the initial concentration of cadmium, chromium, nickel and zinc in laboratory waste is 8.15, 5.53, 9.38, and 6 ppm, respectively. These concentrations are considered high and very dangerous if the wastewater is not properly treated, as those levels of heavy metals can pollute the surrounding environment and are harmful to humans. In the process, this research employed a batch method with variations in contact time; 1, 3, 6, 12, and 24 hours, with the addition of 5 g silica-cellulose material. The batch method was used to determine the correlation between concentration and adsorption percentage of heavy metal ions with the use of contact time as treatment variation. During the process, samples were stirred at 150 rpm to help heavy metal ions interact with the surface of silica-cellulose material, thus increasing the absorption of the ions. Tests for the reduction of heavy metal levels in laboratory waste by the silica cellulose matrix using AAS with 3 times repeated readings. The data on the reduction of heavy metal levels by the cellulose silica matrix were tested using the ANOVA test with a significance value of sig ≤ 0.05. The calculation results show the significance value is less than 0.05 then the results of the Turkey test show a significant difference in data for each treatment.

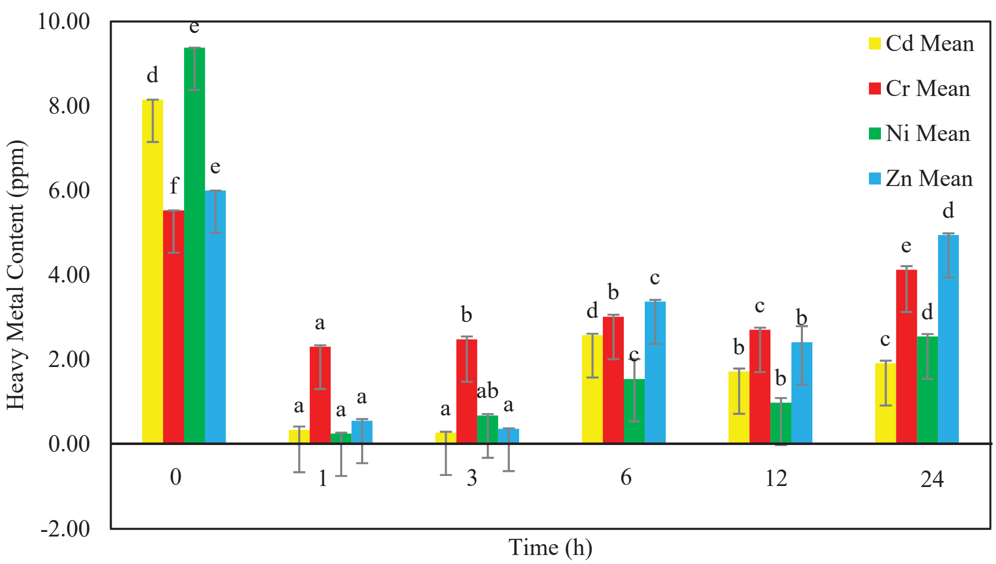

FIGURE 2. The effect of contact time on the heavy metal content of laboratory wastewater (sig. 0.05 n = 3)

The table and graph above demonstrate that after 1-hour contact time, the concentration of Cr and Ni exhibit the most prominent decrease, while the reduction of Cd and Zn reaches optimum only after 3-hour contact time. The difference in optimum contact time could be because 1 hour is not sufficient for the function group of silica-cellulose to interact with Cd and Zn ions. At 3-hour contact time, the more Cd and Zn ions get adsorbed by the function group of the adsorbent. In the table, it can be seen that for all heavy metals, both Cd, Cr, Ni, and Zn, at the contact time for 6 hours, heavy metals undergo desorption or re-release. Then when the contact time was 12 hours for all metals there was no change in the amount of adsorption or desorption. And for 24 hours treatment, more metal was released because the system was saturated. So, it can be concluded that the contact time for 3 hours is the optimum contact time for the silica cellulose matrix as an adsorbent. Generally, the adsorption of heavy metals by silica-cellulose involves the silanol group (–SiOH) from silica whose active site is enhanced with the addition hydroxyl group (–OH) from cellulose. Improvement of the active site of the hydroxyl group –OH on the surface of the adsorbent will increase the adsorption capacity of the adsorbent [19]. This causes the adsorbent to interact less optimally with Cd and Zn ions in one hour and the more ions get adsorbed after 3-hour contact time [20].

Effectiveness and Adsorption Capacity of Silica-Cellulose Material towards Heavy Metal Ions of Laboratory Waste

The efficiency and adsorption capacity of the adsorbent can be used as the reference of the ability and effectiveness of the adsorbent. Adsorption capacity is the ability of an adsorbent to absorb or adsorb adsorbates. In order to determine the correlation between adsorption capacity and concentration of the solution, a graph of adsorption (mg/g) versus the initial concentration (Co) was constructed.

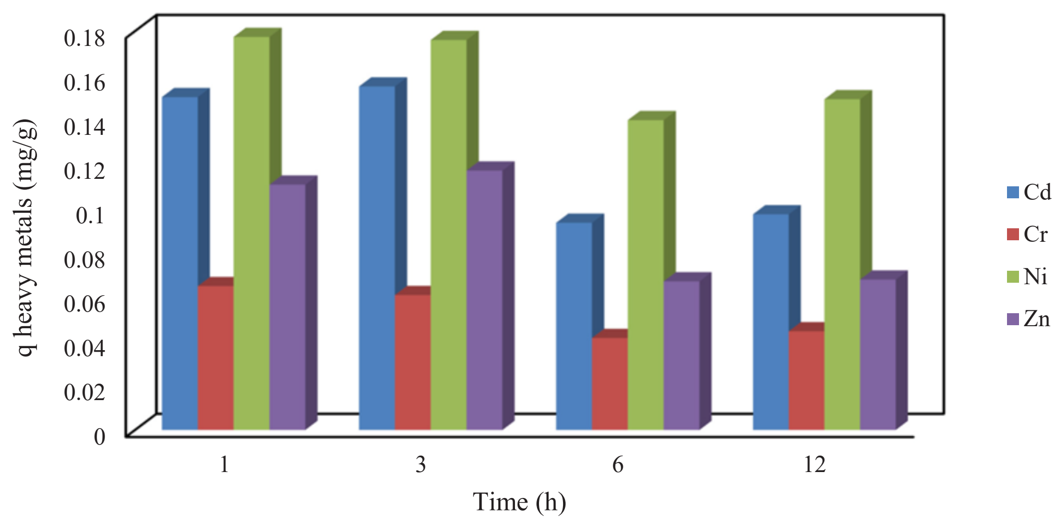

FIGURE 3. The adsorption capacity of silica-cellulose

The data above show that the highest adsorption capacity of the material was obtained after 3-hour contact time which can be concluded that the optimum contact time for the use of silica-cellulose for the adsorbent of heavy metals in laboratory wastewater is 3 hours. From the data above, it can be seen that when the contact time is less than 3 hours, the amount of heavy metal absorbed is still increasing, while at the contact time of more than 3 hours the heavy metal will experience desorption or release of metal ions by the adsorbent because the optimum point has been reached. The data also demonstrate that the adsorption capacity of silica cellulose is proportional to the level of heavy metal contained in laboratory waste [21].

The effectiveness of heavy metal adsorption on waste samples was analyzed by calculating the reduction effectivity in which the difference of the initial and final heavy metal content divided by the initial heavy metal content [22]. Several factors are affecting the adsorption process, including the stirring process, the characteristic of the adsorbent and its solubility [23]. In this study, stirring was performed during the process at a constant speed of 150 rpm. Appropriate stirring speed could increase the adsorption of heavy metals ions contained in laboratory waste by silica-cellulose material.

Calculation results on the reduction effectivity of heavy metal content in the waste sample by silica-cellulose demonstrates that the material exhibits high effectiveness of reducing Cd, Ni, and Zn up to above 90%, as depicted in Figure 4. This is caused by the influence of Cd, Ni and Zn concentration within waste samples, which is proportional to the number of adsorbates that could be adsorbed to the surface of the material [24].

Silica-cellulose is a material resulting from the modification of silica from rice husks with cellulose from Nata de Coco which provides many advantages, especially as an adsorbent [12,13,15]. Silanol (Si-OH) and siloxane (Si-O-Si) functional groups from silica are modified with organic groups to improve the function of the material [25]. One of the organic compounds that can be used for modification of silica is cellulose that has molecular formula $(C_6H_{10}O_5)n$ and belongs to the group of organic compounds that can form polymers. Cellulose has many oxygen atoms due to the presence of hydroxyl and ether functional groups which give cellulose its polar characteristic.

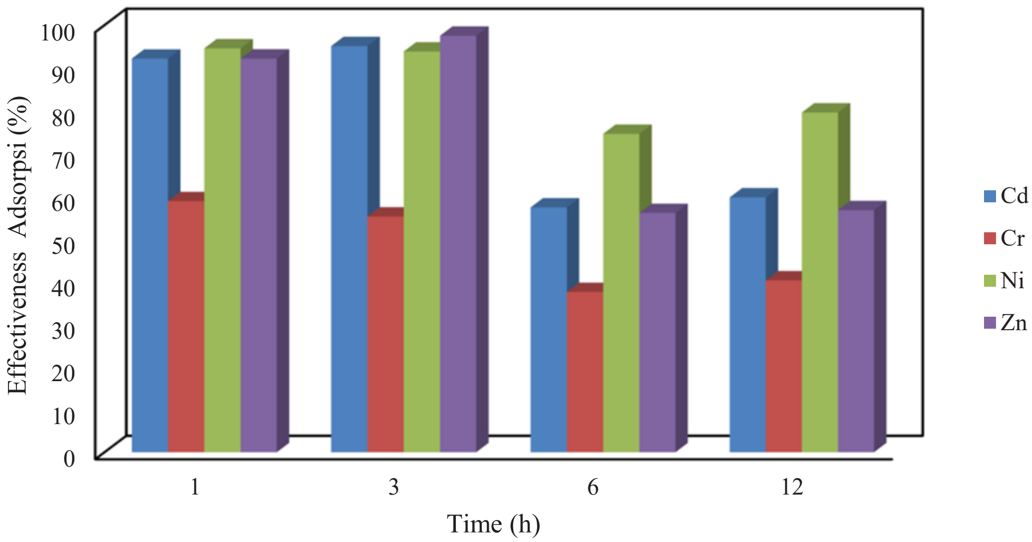

FIGURE 4. Adsorption effectivity of silica-cellulose

SUMMARY

In this research, silica-cellulose as the material was successfully synthesized and used as an adsorbent for heavy metals, cadmium, chromium, nickel and zinc in laboratory waste. The results of physical characterization using SEM showed identical results with previous studies with an even surface with a range of approximately 50 nm. The percentages of remediation were 95.09 % for cadmium metal, 58.77% for chromium metal, 94.56 % for nickel metal, and 97.50 % for zinc metal, respectively. The optimum time for chromium and nickel is 1 h, while for cadmium and zinc, the optimum time is 3 h.

ACKNOWLEDGMENTS

This research was funded by the Directorate of Research and Civil Service, Ministry of Education and Culture under Magister Research Grant, entitled (Immobilization of Pseudomonas Fluorescence Bacteria using Silica Cellulose Matrix for Heavy Metal Remediation, contract number 10.3.55/UN32.14.1/LT/2020.

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