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Effective Treatment of Industrial Wastewater Contaminated with Mn and Pb using Mesoporous Silica from Yogyakarta Beach

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ABSTRACT

The research was investigated using Yogyakarta beach sand as the main material to synthesize mesoporous silica (MS). The MS usage in the environmental field is mainly to overcome water pollution, contaminated from chemical waste used in industrial productions. In the sol-gel method, the silica from beach sand was extracted and synthesized into MS using a dodecyl amine (DDA) template. MS is used as an adsorbent for manganese (Mn) and lead (Pb) printing liquid waste. MS produced was analyzed with FTIR and surface area analyzer (SAA). The process of waste adsorption used MS weight variables of 1 gr, 2 gr, and 3 gr. The MS was mixed in the waste and stirred with a rotation speed of 120 rpm for 2 hours. The solution was left for 24 hours until separated from the adsorbent. AAS analyzed the resulting liquid, and the adsorbent was dried at 100 °C for 24 hours and analyzed by SEM-EDX. The synthesized MS was characterized. It has a surface area of 122.78 m^2/gr and a pore diameter of 4.65 nm. The AAS analysis results showed that the wastewater contains Ni <0.076 mg/L and Pb <0.415 mg/L. The SEM-EDX analysis showed that the adsorbent used contains 0.01% Mn, 0.01% Pb, and 0.39% Cu. The research showed that the liquid printing waste analyzed contains nickel, lead, and copper.

1. Introduction

As a natural resource containing the elements Si and O, Silica sand is abundantly available in the earth's crust. It has long been considered economic value for industrial applications [1]. To improve its function, one way is to engineer the pore size, which increases the surface area of the material to form mesoporous silica (MS). MS is of great interest to researchers because of its unique material characteristics: a structured pore structure and high specific surface area [2]. MS has unique material characteristics and can be formed with various morphological bases, such as long cylindrical rods, powders, slabs, and others.

Due to its uniqueness, MS can be designed for various applications and uncover development opportunities related to industrial-scale mass production, which has shifted the focus of lab-scale research to the applicable research stage. Nowadays, MS is widely applied in wastewater treatment [3]– [6], air and gas purification [7], [8], catalysts [4,9], [10], food industry [11], and health industry [11]– [15].

The use of MS in the environmental field is mainly to overcome water pollution contaminated with waste from industrial production processes that use chemicals [5], [6], [16], [17]. Previous studies have shown that the pore structure and surface material of MS are effective in absorbing dye waste produced by the dye industry [18], [19]. In addition, the application of MS in previous studies

was also aimed at dealing with heavy metal contaminants produced by industry [20]. Industrial waste containing heavy metals and discharged into the environment without prior treatment threatens the environment and human health. For this reason, many efforts to overcome heavy metals from industrial waste in previous studies have used porous silica material technology [21-25].

Due to its simplicity, economy, and low handling costs, heavy metal adsorption by MS is more advantageous than other methods [2]. In this study, MS was used to study the reduction of heavy metal contamination levels in the liquid waste of the printing industry, one of the industries containing heavy metal contamination. The printing industry can be a contributor to heavy metal contamination in the environment. For this reason, it needs to be managed seriously [26]– [28].

2. Research Methodology

2.1. Materials

Research Materials consist of beach sand materials Parangtritis Bantul, HCl, (HCl 37%, Mallinckrodt), sodium hydroxide (NaOH, PA VWR Chemicals), silver nitrate ($AgNO_3$), pyridine (Sigma Aldrich), dodecyl amine ($C_{12}H_{27}N$), fisher scientific, aquabidest, and printing waste taken from a printing house in Yogyakarta.

2.2. Procedures

2.2.1. Extraction of silica from beach sand

Silica is extracted from beach sand containing SiO_2 compounds and synthesized by washing the beach sand from dirt and iron (Fe) and Cl content using *aquadest*. Sand with a size of 100 mesh was refluxed with 6 M HCl solution at a constant temperature of 90 °C for 4 hours, then filtered and washed with *aquadest* until the filtrate pH was 7. The separated sand is placed in an oven at a temperature of 120 for 2 hours. The sand is refluxed with 6 M NaOH at a constant temperature of 80 °C for 4 hours, then filtered and washed. The concentrated 6 M HCl is added to the filtrate dropwise until pH 8, and the solution becomes milky white. The solution is stored for 24 hours to form a gel. The gel is separated and washed until the filtrate is free from Cl. Silica formed is dried in the oven at 120 °C for 4 hours [4].

2.2.2. Mesoporous silica synthesis

The synthesis of mesoporous silica adsorbent was conducted using the Sol-Gel method [1]. First, Mix 0.25 g of DDA (*dodecyl amine*) with 50 ml of distilled water solvent : ethanol (1:1), stirred for 30 minutes at 40 °C. The mixture was added with 6 M HCl to pH 4, and a white gel was formed. Then, Na_2SiO_3 solution was added to the DDA solution dropwise and stirred for 2 hours. The solution was allowed to stand at room temperature for 18 hours. The MS formed was filtered and washed with aquabidest until the pH of the filtrate was free from Cl^{-1}. MS dried at 50 °C for 4 hours and calcined at 600 °C for 5 hours. The resulting products were characterized by FT-IR, SAA *(Surface Area Analyzer)* [4].

2.2.3. Adsorption of Mn^{2-} and Pb metal in printing waste

MS was used as an adsorbent with a weight of 1, 2, and 3 grams and denoted as MS1, MS2, and MS3. Mix 100 ml of printing waste and the adsorbent into a 250 ml beaker glass. Stir the mixture using a *magnetic stirrer* for 120 minutes with a stirring speed of 120 rpm. The solution was allowed to stand for 24 hours. Filter the resulting products with filter paper, measure the volume, and analyze it using AAS. The adsorbent was dried at 100 °C for 4 hours and analyzed with SEM-EDX to determine the adsorbed metal.

3. Results and Discussion

3.1. Mesoporous Silica character

This study used MS made from beach sand using the sol gel method explained on method section. FTIR analyzed the synthesized mesoporous silica, and the results are shown in Figure 1.

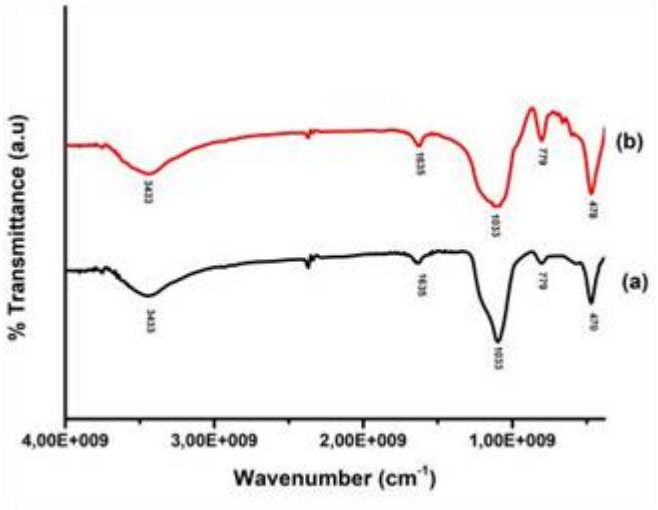

Fig.1. (a) MS from beach sand, (b) MS from standard silica

The regional wavenumber at the 478 cm^{-1} spectra signifies the vibration stretching of Si-O-Si asymmetry [19]. At 1095 cm^{-1} has a strong and sharp absorption and signifies a vibration stretching Si-O-Si asymmetry. The emergence of wavenumbers around 1635 cm^{-1} indicates the presence of a group bending of Si-OH, which indicates the presence of a water-bound molecule. [4] stated that the wavenumber in region 450-1300 cm^{-1} is identified as typical silica adsorption. Vibration at wavenumber 3441 cm^{-1} indicates the Si-OH stretching group. It occurs due to the OH group from silanol interacting with water on the silica surface through hydrogen bonds, a Si-O-Si asymmetric stretching vibration [19], [29]. These results indicate mesoporous silica (MS) synthesized from beach sand silica using the sol-gel method is formed.

3.2. Mesoporous silica characterization with GSA

The mesoporous silica (MS) synthesized in this study was characterized using Gas Sorption Analyzer (GSA). The GSA characterization ensures the synthesized MS has a pore size that matches the mesoporous character and provides information about the formation of pores, size distribution (diameter), pore-volume, and specific surface area of MS. The specific surface area analysis and the pore volume analysis of MS were conducted using N2 gas adsorption isotherm data on the MS surface based on the BET and BJH methods, respectively. The results of MS characterization are shown in Table 1.

Table 1. Mesoporous silica characterization

Mesoporous Silica Sample	Surface area (m^2/g)	Total volume pore (cc/g)	Pore diameter (nm)
Silica	54.43	0.006	3.13
Standard silica	162.36	0.682	16.80
Mesoporous Silica (MS)	122.78	0.136	4.65

Table 1 shows that the surface area of mesoporous silica from beach sand is 122.78 m2/gr, larger than silica but smaller than standard silica. This happens probably due to the purity of beach sand silica being less than the standard silica. According to [4], silica obtained from beach sand has 21.19% silica content, 34.22% carbon, 34.22% oxygen, and impurities, such as Br and Na. While standard silica contains 54.43% silica and 40.91% oxygen without any impurity. The diameter of mesoporous silica is 4.65 nm. This is in accordance with the pore size range of the mesoporous material of 2-50 nm [3,4]. These results showed mesoporous silica used has mesoporous characteristics and could be used as an adsorbent. The distribution of pore in MS can be seen in Figure 2 below:

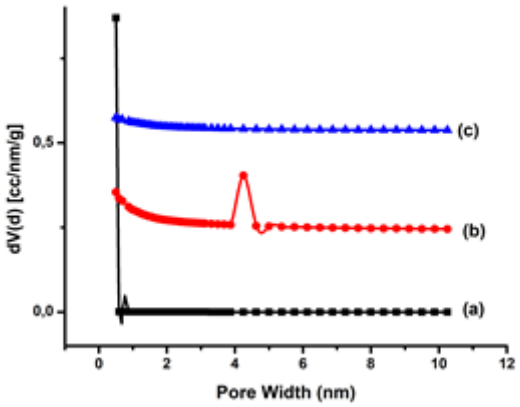

Fig.2. The pore distribution of a) silica from sand, b) standard silica, and c) Mesoporous silica

Beach sand silica, standard silica, and MS have non-uniform pore distributions. Based on pore size distribution from the DFT approach, there is a striking difference where the pores are smaller in silica sand. The pore size distribution of standard silica is dominated by the size diameter (one large peak at 3, 4, and 5 nm). In comparison, MS has a very wide pore distribution.

3.3. Waste adsorption results

The MS, as a porous material, can be used as an adsorbent for metal-containing waste of the printing industry, such as manganese (Mn) and lead (Pb). The adsorption process of printing waste occurred for 24 hours and was then filtered. AAS analyzed the adsorbed filtrate, and the results are shown in Figures 3, 4, and 2. SEM-EDX analyzed the used adsorbate. The adsorption has experimented with several materials shown in Figure 3. The clearest solution is the solution using standard silica as an adsorbent. It is possible due to its larger surface area and even pore distribution compared to sand silica and mesoporous silica [2], [17], [29].

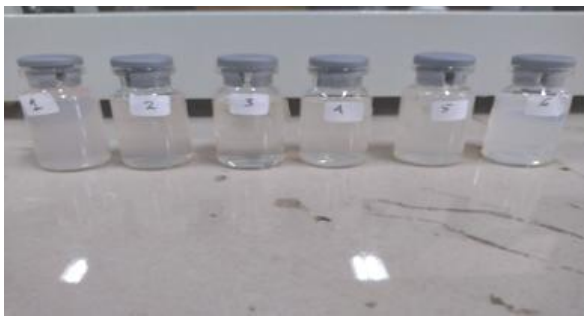

Fig.3. Adsorption of wastewater process: (1) printing waste, (2) adsorption silica, (3) standard silica, (4) MS 1 gr, (5), MS 2 gr, and (6) MS 3 gr

Fig.4. Adsorbate after adsorption

The content of Mn and Pb in printing waste were <0.076 mg/L and < 0.415 mg/L, respectively. The Pb content increased after the adsorption process to 0.431 mg/L and 0.541 mg/L using silica sand and standard silica as adsorbents. This is due to the surface area of the adsorbent material. The larger the surface area of the material, the higher the adsorption capacity [2], [29]. The more MS adsorbent used, the adsorbed Pb metal did not show a significant increase. This is due to the possible condition of the MS solution being saturated [31].

Table 2. The content of Mn and Pb in wastewater

Type of Materials	Metal Contents	
	[Mn] mg/L	*[Pb], mg/L*
Waste	<0.076	< 0.415
Beach sand silica (SP)	<0.076	0.431
Standard silica (STD)	<0.076	0.541
MS1	<0.076	< 0.415
MS2	<0.076	< 0.415
MS3	<0.076	< 0.415

3.4. Results of adsorbent analysis using Scanning Electron Microscopy (SEM-EDX)

SEM-EDX analysis was conducted to determine the morphology of mesoporous silica after the adsorption of printing waste. SEM-EDX images are needed to ensure that the mesoporous silica has a pore gap in accordance with the results of the GAS analysis conducted and the adsorbed metal contained. The adsorbed metal contents are shown in table 3, and the SEM-EDX image is shown in Figure 5.

Table 3. Data from SEM-EDX analysis of elements contained in adsorbate after adsorption

Element (%)	Material				
	SP	***S std***	***MS1***	***MS2***	***MS3***
C	11.89	15.09	17.98	17.17	29.83
O	62,80	61.05	58.20	60.08	55.40
Na	2.61	0.06	0.62	0.82	0.52
Al	0.85	-	0.88	0.88	0.61
Si	20.89	22.76	21.81	20.59	13.63
Cl	1.02	0	0	0	0
Ca	0	0.5	0.12	0	0
Mn	0	0	0.02	0.01	0.02
Cu	0.29	0.41	0.30	0.39	0.33
Pb	0	0.12	0.01	0.06	0.02

Data shown in Table 3 implied the metals adsorbed from the waste are manganese (Mn), lead (Pb), and copper (Cu) with quite large Cu content. The phenomenon of the ability of silica material to adsorb heavy metal components was also described in previous studies [20], [24]. Silica material from sand can adsorb 0.29 (%) of the elements contained in the material. The Cu and Pb metals were adsorbed optimally on standard silica and MS2. This is probably due to the characteristics of the materials, which have a large surface area and even pore distribution [29].

3.5. The SEM images of adsorbent after the adsorption of the printing waste

The image of mesoporous silica after adsorption is shown in Figure 5 where the silica appears to be blocked in some parts. In standard silica, where the Cu and Pb metals are more adsorbed, white lumps developed. There was also white color blocking in several locations in MS1, MS2, and MS3 that made the surface of the MS look like white coral, which was originally a wormhole. This matter indicated the adsorbed metal was attached to the surface of MS. It is in accordance with research [31].

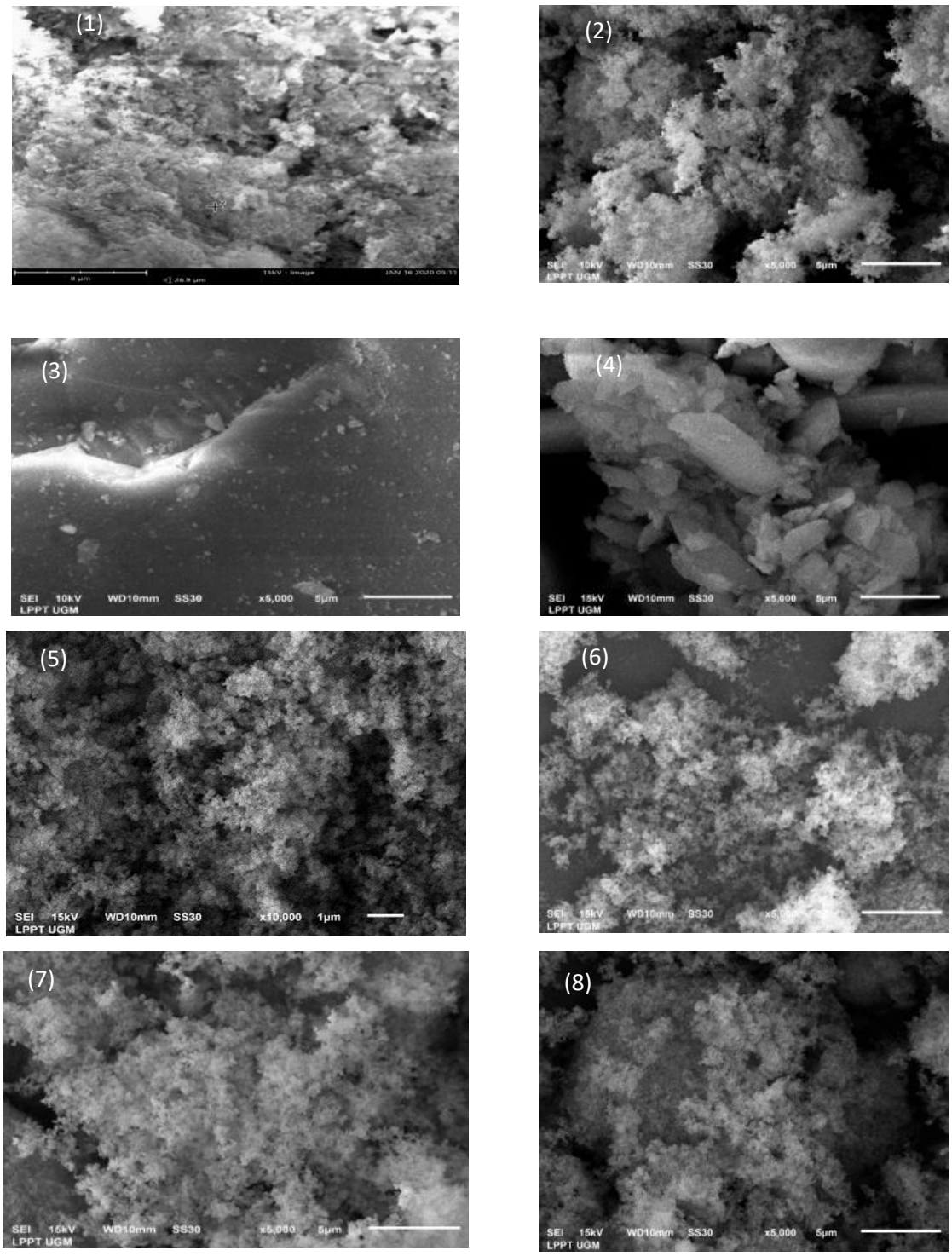

Fig.5. The surface morphology of SEM images: Silica before (1) and after (2) adsorption, Standard silica before (3) and after (4) adsorption, Mesoporous silica (MS1) before (5) and after (6) adsorption, (7) MS2 after adsorption, and (8) MS3 after adsorption

4. Conclusion

It is concluded that the mesoporous silica (MS) synthesized from beach sand has a surface area of 122 m^2/g and a pore diameter of 4.6 nm. The wastewater from the printing industry used in this study contained nickel, lead, and copper. The results of the AAS analysis showed that the printing waste had Ni <0.076 mg/L and Pb <0.415 mg/L. The synthesized MS adsorbed <0.076 mg/L of Ni and <0.415 mg/L of Pb. The results of the SEM-EDX analysis showed the adsorbents used in the adsorption process contained 0.01% of Mn, 0.01% of Pb, and 0.39% of Cu.

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