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CaO ADSORBENT FOR REDUCING METAL CONTENT OF Fe, Mn, AND Zn FROM PET-SET WASTE-WATER

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Abstract

Primary Effluent Treatment-Secondary Effluent Treatment (PET-SET) is refinery waste-water. PET-SET waste contains hazardous substances, namely Fe, Mn and Zn metal ions. The novelty of this research is that it looks at the CaO adsorbent to reduce the metal content of Fe, Mn, and Zn from PET-SET Waste-water. This research's aimed to reduce the metal content of Fe, Mn, and Zn using CaO adsorbent. CaO was prepared from the golden snail shell by previous researchers. Concentration of Fe, Mn, and Zn from PET-SET waste before treatment were 8.6 mg/L, 8.52 mg/L and 9.28 mg/L. This research was conducted through the adsorption method by variating the adsorbent mass and contact time to determine the optimum condition in the absorption of Fe, Mn, and Zn metal ions that analyzed using the ICP-OES instrument. This instrument was quite well used for multielement analysis. In this study, CaO was applied to adsorb previously treated PET-SET waste samples which previous reasearcher used CaO from golden snail shell as a catalyst for transesterification reaction. It was reported that the optimum condition to absorb Fe, Mn, and Zn metal ions was 0.2 g for 20 minutes with an absorption effectiveness of 100% .
Keywords: Adsorbent; CaO; ICP-OES; PET-SET; Waste-water.

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1. INTRODUCTION

Petroleum is processed to produce several products such as premium, pertalite, pertamax, diesel, avtur, asphalt, MFO, LPG, as well as Primary Effluent Treatment-Secondary Effluent Treatment (PET-SET) as by product (1). PET-SET waste contains various kinds of hazardous substances such as phenol, ammonia, sulfide, Chemical Oxygent Demand (COD), and heavy metals. Before being disposed, PET-SET waste was treated with an aeration process involving waste-decomposing bacteria, but metal contents were not decomposed by bacteria. Therefore, treated waste water must be re-analyzed to ensure that the metal content in PET-SET waste did not exceed the threshold according to Governor Regulation No. 8 of 2012 concerning Liquid Waste Quality Standards for Industrial, Hotel, Hospital, Domestic and Coal Mining Activities that the quality standard value for Mn metal is 2 mg/L, Fe and Zn metals are 5 mg/L. To reduce the metal content in waste, various methods can be used, one of which is the adsorption method. The adsorption method has several advantages, including the relatively simple process, relatively high effectiveness and efficiency and no side effects in the form of toxic substances. Several types of adsorbents to adsorb heavy metals are silica gel, zeolite, activated carbon, and CaO (2). CaO is often used as an adsorbent because of its high absorption effectiveness. As in previous studies that utilized CaO adsorbents to adsorb Fe, Pb, Zn, Cu and Sn metals in wastewater. The CaO used was taken from several sources such as blood clam shells, clam shells and crab shells and has an absorption effectiveness level of 98-100% (3). The adsorption product was then analyzed to determine the metal content. There are several methods to analyze such as the Neutron Activation Method, the method using the Atomic Absorption Spectrophotometry (AAS) instrument and the Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). The ICP-OES method is more often used because it has several advantages, namely, being able to measure several heavy metal parameters according to the multielement standard used, the ability to read metal elements at a concentration of parts per billion or ppb, a fairly low detection limit, and a high level of accuracy (4). Based on the literature study, a case study was conducted regarding the use of CaO adsorbent to adsorb Fe, Mn, and Zn metals in PET-SET waste. In previous studies CaO was used to adsorb metals on a lab scale using specific reagents, whereas in this case study CaO was applied directly to waste samples containing various metals.(5) In addition, the CaO used also comes from waste, namely gold snail shell waste that has been prepared by previous researchers (6). Thus, this case study has the concept of reducing waste with waste. The experiment was started by adding CaO adsorbent to 500 mL of PET-SET waste sample with a mass variation of 0.05mL of CaO; 0.1mL; 0.15mL; 0.2mL; 0.4mL; 0.8mL and variation of stirring time 20 and 40 minutes. Then the PET-SET waste sample was deposited, filtered, and analyzed using ICP-OES.

2. MATERIAL AND METHODS

Materials

The materials used included aquades, 65% HNO3 from Merck, standard multielement solution of metal containing Fe, Mg, Mn, and Zn 1000mg/L from Merck, CaO from golden snail shells that had been prepared by previous researchers, and samples of PET-SET waste.(6)

Tools

The equipment used included a Stuart floculator, glasswares from Pirex, Mettler Toledo analytical balance, and the Agilent 5800 ICP-OES instrument.

Methods

Sample Preparation

Sample preparation was carried out by adding 500 ml of PET-SET waste samples into 5 beakers for each that had been previously sterilized and then labeled.

Preparation of Fe, Mn, and Zn Standard Solutions

Multielement solution was used as standard solution of Fe, Mn, and Zn. Standard solution was prepared in concentration of 2 ppm, 5 ppm, 10 ppm, and 20ppm.

Adsorption of PET-SET using CaO

0.05 g, 0.10 g, 0.15 g, 0.20 g, 0.4 g, and 0.8 g of CaO was put into beaker glasses for each containing PET-SET waste then stirred using floculator for 20 minutes and leave it until a precipitate forms. Filtrate was added 0.5 mL of 65% HNO_3 then analyzed using ICP-OES with wavelengths of Fe, Mn, and Zn of 234,350 nm; 257,610 nm; and 202,548 nm respectively that repeated three times or triples. The same treatment was carried out at a contact time of 40 minutes.

3. RESULT AND DISCUSSION

PET-SET waste contains high phenol, ammonia, sulfide, metal and Chemical Oxygent Demand (COD) so that it was treated through an aeration process. The aeration process used waste-decomposing bacteria, but not all waste content was completely decomposed such as Fe, Mn, and Zn contaminants. These metal contaminants were reduced using CaO adsorbent from golden snail shells. In a previous study, the CaO adsorbent from *Anadara granosa* shells was able to absorb 98% of the Cu and Sn content in the wastewater (7). This proved that CaO had potency to absorb metal contaminants, so that in this study CaO was used to absorb Fe, Mn, and Zn contaminants in PET-SET wastewater. There are several factors that affect the adsorption process, namely the type of adsorbent, type of adsorbate, contact time, concentration of each substance, pressure, surface area, and coadsorption (4).

The analysis data showed that the standard deviation of each analysis had a value smaller than 0.3. According to the Indonesian National Standard (SNI) ISO 13528:2016 that the data can be said to be accurate if the standard deviation value is less than 0.3. This suggests that the repetition of the analysis in this study was acceptable.

The results of the analysis of Fe, Mn, and Zn metals were shown in Table 1,2,3

Table 1. Fe Contaminants Analysis

Mass (gr)	20 Minutes					40 Minutes				
	Concetration(ppm)			DS	$\overline{X}$	Concetration (ppm)			DS	$\overline{X}$
	1	2	3			1	2	3		
0.00	8.57	8.62	8.6	0.03	8.6	8.57	8.62	8.6	0.03	8.6
0.05	4.71	4.64	4.68	0.04	4.68	4.71	4.64	4.68	0.04	4.68
0.10	3.93	3.74	3.66	0.14	3.78	3.93	3.74	3.66	0.14	3.78
0.15	3.37	3.31	3.27	0.05	3.32	3.37	3.31	3.27	0.05	3.32
0.20	0.00	0.00	0.00	0.00	0.0	0.00	0.00	0.00	0.00	0.00
0.40	0.10	0.00	0.00	0.06	0.03	0.10	0.00	0.00	0.06	0.03
0.80	0.00	0.00	0.00	0.00	0.00	0.0	0.00	0.00	0.00	0.00

Note: DS : Deviation standard

X : Average

Table 2. Mn Contaminant Analysis

Mass (gr)	20 Minutes					40 Minutes				
	Concetration (ppm)			DS	$\overline{X}$	Concetration (ppm)			DS	$\overline{X}$
	1	2	3			1	2	3		
0.00	8.50	8.52	8.53	0.02	8.52	8.50	8.52	8.53	0.02	8.52
0.05	5.37	5.38	5.32	0.03	5.36	5.37	5.38	5.32	0.03	5.36
0.10	5.18	5.12	5.11	0.04	5.14	5.18	5.12	5.11	0.04	5.14
0.15	4.05	4.01	3.98	0.04	4.01	4.05	4.01	3.98	0.04	4.01
0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.40	0.10	0.10	0.10	0.00	0.10	0.10	0.10	0.10	0.00	0.10
0.80	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Note: DS : Deviation standard

X : Average

Table 3. Zn Contaminant Analysis

Mass (gr)	20 Minutes					40 Minutes				
	Concentration (ppm)			DS	$\overline{X}$	Concentration (ppm)			DS	$\overline{X}$
	1	2	3			1	2	3		
0.00	9.27	9.29	9.27	0.01	9.28	9.27	9.29	9.27	0.01	9.28
0.05	6.41	6.45	6.38	0.04	64.1	6.41	6.45	6.38	0.04	6.41
0.10	6.07	6.02	6.01	0.03	6.03	6.07	6.02	6.01	0.03	6.03
0.15	4.79	4.74	4.71	0.04	4.75	4.79	4.74	4.71	0.04	4.75
0.20	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.00	0.01
0.40	0.06	0.06	0.06	0.00	0.06	0.06	0.06	0.06	0.00	0.06
0.80	0.10	0.16	0.16	0.03	0.14	0.10	0.16	0.16	0.03	0.14

Note: DS : Deviation standard

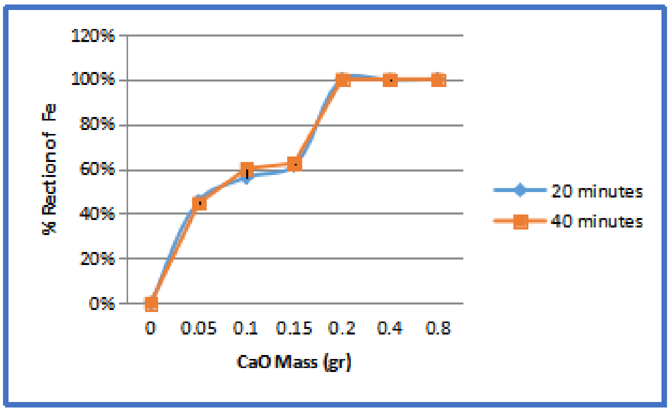
X : Average

Based on the table of analysis results of Fe, Mn, and Zn metals (Tabel 1, 2, 3), the decrease in metal content was directly proportional to the increase in mass of CaO. The more mass of CaO, the more metal was absorbed. This is due to the large number of

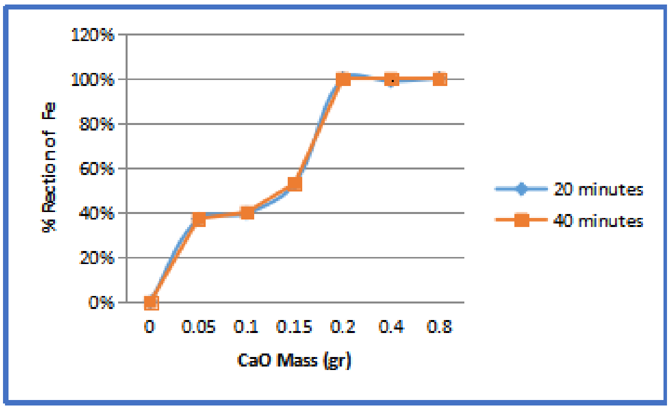
CaO active sites that absorb the adsorbate. This is in accordance with previous studies that used pineapple leaf adsorbents to absorb Fe metal whose absorption efficiency increased as the adsorbent mass increased (8).

In this study, an anomaly was found in the decrease in Zn metal content with a mass of CaO 0.4 and 0.8 grams. In the three analysis tables, it can be seen that the decrease in Zn metal content with a mass of 0.4 grams of CaO was higher than that of a mass of 0.8 grams of CaO. This can be caused by various possibilities, including the presence of the active side of the adsorbent which had not all bonded to the adsorbate and the presence of impurities that hinder the analysis process by ICP. In addition, anomalies can be caused by the state of the tool and human error.(8)

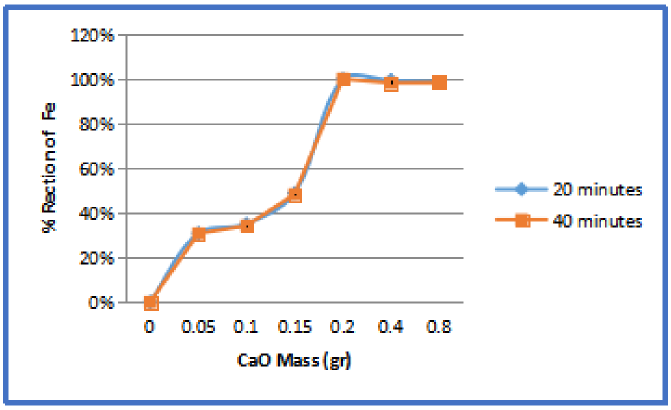
Contact time is one of the parameters that is also important to determine the optimum condition. The adsorption of Fe, Mn, and Zn metal content at contact time of 20 and 40 minutes was shown in graph 1,2,3, respectively.



Graph 1. % Reduction of Fe Metal Content on CaO mass and Variation of contact time



Graph 2. % Reduction of Mn Metal Content on CaO mass and Variation of contact time



Graph 3. % Reduction of Zn Metal Content on CaO mass and Variation of contact time

Based on the graph 1,2 and 3, it showed that the contact time of 40 minutes had a higher percentage of metal content reduction than the contact time of 20 minutes. The longer the contact time, the greater the interaction between CaO and metal ions, so that more metal ions were adsorbed by CaO (9).

The difference in the percentage reduction in metal content between 40 minutes of contact time and 20 minutes of contact time was not very significant. Within 20 and minutes the percentage reduction in Fe, Mn, and Zn metal content reached 100% at a mass of 0.2 grams of CaO. This is due to the possibility that there is no longer an active site that can absorb metal ions (8). This means that in this case study it only takes 20 minutes of contact time to get optimum results because it is more efficient. Then the optimal concentration data can be taken from 20 minutes of contact time, namely at a mass of 0.2 grams of CaO because on the graph curve the percentage decrease in the levels of Fe, Mn, and Zn metals in a mass of 0.2; 0.4; 0.8 grams of CaO was relatively stable because only in 0.2 grams of CaO the absorption effectiveness is 100% or called the optimum mass.

4. CONCLUSION

CaO from golden snail shells had a good performance as adsorbent of Fe, Mn, and Zn metals in PET-SET waste. The highest percent degradation obtained when degraded using 0.2 gram CaO for 20 minutes was 100%.

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