



SYNTHESIS AND ADSORBENT APPLICATIONS BASED ON SILICA FROM VULCANIC ASH SINABUNG FOR HEAVY METAL ADSORPTION OF Cd (II)

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ABSTRACT

Synthesis of silica gel has been done by utilizing the volcanic ash Sinabung Mountain taken Berastepu Village, Simpang Empat, Karo within 1,5 km from the top of the Sinabung Mountain. Volcanic ash is one of the biggest source of silica, potentially as materials for synthesis of silica gel. Synthesis of silica gel in this study conducted by sol-gel method. Volcanic ash in the destruction carried out with NaOH 4M solution and establishment of gel with HCl 3M solution. The result of synthesis of silica was characterized with AAS, FTIR, and XRD. The levels of silica obtained in this study amounted to 17,85%. Based on the results of analysis by FTIR pointed to the existence of the siloxane (Si-O-Si) and silanol (Si-OH) functional groups stating that the silica adsorbent was successfully formed. The XRD analysis showed amorphous structure of silica. The silica gel was result of synthesis used as adsorbent to adsorbs heavy metal Cd(II). The method used in interaction adsorbent with a solution is batch method. The determination of the optimum mass of silica adsorbent was carried out on variations (0.1, 0.15, 0.2, 0.25, 0.3) g. Data obtained using AAS showed that optimum absorption was obtained at 0.1 gram of silica with adsorption capacity of 17.95 mg/g.

Keywords: *volcanic ash sinabung, silica gel, sol-gel, adsorption, batch, Ion Cd(II).*

INTRODUCTION

Sinabung's mountain is one of the active volcanoes which is located in North Sumatra province-Indonesia. Its coordinates are 03^o 10' LU dan 98^o 23' BT with the highest peak of 2,460 meters from sea level. This mountain is very interesting due to it has erupted since 2010 until now ¹. It is constantly erupting and expelling millions of cubic volcanic ash materials. The abundance of mountain volcanic ash material as a result of the eruption of Mount Sinabung is an interesting thing to be studied and utilized further.

Several studies have shown that volcanic ash volcanoes contain mainly silica material (Sudaryo and Sutjipto, 2009)². Zuarida reported that amount silica oxide (SiO₂) on Kelud volcanic mountain's ash is 45,9%,³ Merapi volcanic mountain's ash is 56,39%⁴,



Sinabung volcanic mountain's ash is 58,10%⁵. It means the ash is Sinabung mountain's higher than others and very potential as a raw material to produce adsorbent base on silica. Silica is a giant molecule and usage as an adsorbent. It is possible because its large pore and have both silanol group (-Si-OH) and siloksan (-Si-O-Si-) as an active site. There are four oxygen atoms on Si; it may be used as an active site to bind metal namely chemical bonding between Si-Metal⁶.

Heavy metal pollutants cause direct toxicity both to humans and other living beings. Heavy metals do not degrade with time and become bio-accumulative in living tissues which can cause death or serious health threats. Cadmium, is considered among three most toxic metals, the other two being lead and mercury^{7,8}. Industrial effluents from metallurgical plants, plating works, plants manufacturing cadmium pigments, textile operations, cadmium-stabilized plastics, or nickel-cadmium batteries, or the effluents from sewage treatment plants are the main source of water pollution by cadmium⁹. Adverse health effects due to cadmium poisoning are well documented¹⁰. Cadmium can be removed from wastewater by precipitation, ion exchange, electrolytic and evaporative recovery processes etc.¹¹. Most of the studies were done in batch mode with only a few in column mode. In the present paper adsorptive removal of cadmium from synthetic wastewater using fly ash as the adsorbent has been studied in column mode. The adsorption process of heavy metals using silica gel adsorbent from rice husk ash and coal fly ash has been done in both batch and column systems by different researchers¹²⁻¹⁹. But the use of volcanic ash as an adsorbent to bind heavy metals has not been widely used. There are only a few studies that have used volcanic ash as an adsorbent²⁰⁻²¹. Base on the recent situation, In the present paper adsorptive removal of cadmium from synthetic wastewater using silica gel prepared from mount Sinabung fly ash as the adsorbent has been studied in batch mode.

MATERIALS AND METHODS

Materials

The silica gel used is the result of synthesis of volcanic ash that has been done in previous research²¹. The silica gel has been used as the adsorbent material in the present study.

Reagents and Chemicals

Analytical (AR) grade chemicals (MERCK) were used for preparation of all the reagents. To prepare the stock cadmium solution (1000 mg/l), 1,951 gram CdCl₂.2H₂O (Cadmium chloride dihydrate) was dissolved in double distilled (DD) water and diluted to 1000 ml. The pH of the stock solution was kept around 2.00 by adding 1 ml of concentrated HNO₃(nitric acid) to it for preservation. Standard cadmium solutions of various concentrations as required during the experiments were prepared by diluting the stock.



Instrumentations

Equipment includes: analytic balance, mortar, 200 mesh sieve, desiccator, filter paper whatman 42, Magnetic stirrer, universal indicator, buchner funnel, glassware and equipment Plastic. The concentration of cadmium and other metals were measured using an atomic absorption spectrometer (AAS) made Hitachi Z2000.

Experimental Methodology

Batch Adsorption Studies of Cd(II)

Silica gel that had synthesized then used as adsorbent using batch method. The respective amount of silica adsorbent was added to a container that filled with 30 mL of respective concentration of Cd(II) cation. The adsorption capacity was measured to determine the optimal amount of adsorbent weight

RESULTS AND DISCUSSION

Formation of Silica Gel

First of all, the volcanic ash of Sinabung Mountain was characterized with XRF. The data is shown at Table 1.²²

Table 1. Composition of Sinabung Mountain's volcanic ash

Volcanic ash components	Amount (%)
Si	91,4 ± 0,1
K	3,09 ± 0,02
Ca	2,60 ± 0,02
Cr	0,086 ± 0,003
Mn	0,19 ± 0,03
Fe	0,54 ± 0,01
Ni	1,09 ± 0,02
Cu	0,18 ± 0,003
Zn	0,32 ± 0,01
Ga	0,090 ± 0,003
Eu	0,2 ± 0,02
Re	0,3 ± 0,03

Physically, the volcanic ash is smooth powder and its color is gray. Table 1 show that the volcanic ash components are heterogeneous. The main component of volcanic ash is SiO₂ (42,65%). It means the volcanic ash has a cement pozzolant material with high concentrate, those are SiO₂.

The mechanism reaction is shown in Figure 1. Formation of silica gel is started by

reacting between volcanic ash and NaOH 4M at $T = 500\text{ }^{\circ}\text{C}$. Sodium hydroxide is dissociated at that temperature to form sodium and hydroxide ions. At SiO_2 , electro negativity of oxygen is higher than silica (Si), so Si is such more electropositive and form intermediate $[\text{SiO}_2\text{OH}]^-$ which it is unstable and dehydrogenation occur. Ion Na^+ will react with SiO_3^{2-} to form sodium silica (Na_2SiO_3).

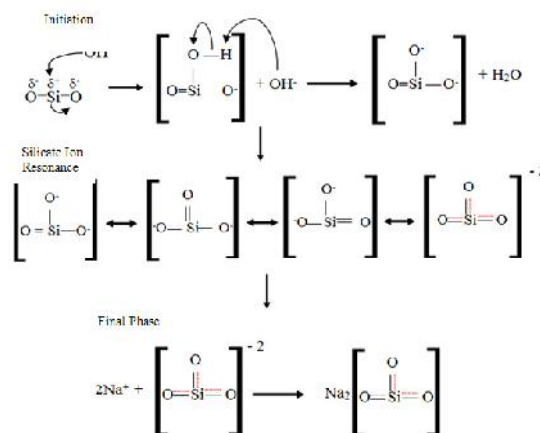


Figure 1. Mechanism reaction of Sodium Silicate formation ²³

Silica gel was formed by using sol-gel preparation method using hydrochloric acid. The addition of hydrochloric acid caused the ionic exchange between H^+ and Na^+ to form silicic acid which did not dissolve in the solution. ²⁴

The formation of silica precipitates was observed at pH 14, however the gel precipitates started to form at pH 8 to 10. And the addition of hydrochloric acid was stopped at pH 7. In the formation of silica gel, the silicic acid which formed from reaction between hydrochloric acid and sodium silicate solution exhibited water polycondensation to form dimers, trimers, and polymers of silicic acid thus releasing water molecule in the process ²⁵.

Silica gel synthesis was characterized by using FTIR and XRD. FTIR data showed The broad peak of 3433.29 cm^{-1} is a specific peak for hydroxyl functional group ($-\text{OH}$). Normally, $-\text{OH}$ group should be appear at 3500 cm^{-1} . It means there is an interaction between electropositive substances and $-\text{OH}$, namely Si-OH (2862.36 and 2927.94 cm^{-1}). XRD data also shows that the silica is amorphous which it is possible be applied as adsorbent ²³.

Determination of the Optimal Adsorbent Weight

The variation of silica gel used was 0.1; 0.15; 0.2; 0.25; and 0.3 grams. The concentration of Cd(II) solution used was 60 ppm and the contact time was 30 minutes. The measured adsorption capacity for each variation of adsorbent weight is shown in figure 2.

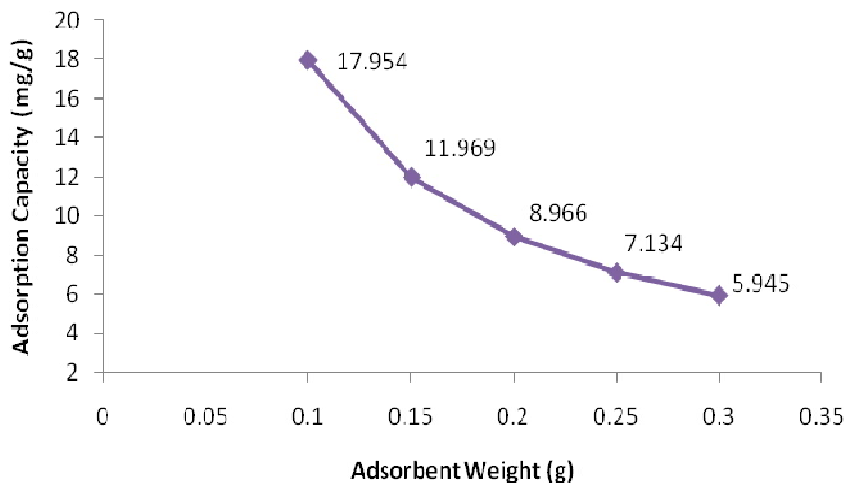


Figure 2. Adsorption Capacity Cd(II) from each Variation of Adsorbent Weight

The figure 2 shows that the highest amount of adsorption capacity is at adsorbent weight 0.1 grams. The increased amount of adsorbent used does not correlate with the amount of adsorption capacity. This is due to the structural form of silica gel which has irregular distribution pattern of siloxane (-Si-O-Si-) and silanol (-Si-OH) group. The adsorption ability of silica gel is determined from the amount of silanol group which presents for each surface amount of silica gel²⁶.

CONCLUSION

The silica gel is successfully synthesized by using volcanic ash base on Sinabung Mountain. The silica gel consists of -OH from Si-OH and Si-O from Si-O-Si. Silica gel. XRD data also shows that the silica is amorphous which it is possible to be applied as adsorbent. The optimum adsorption capacity of silica gel to metal ion of Cd (II) by Batch method is 0.1 g with the amount of Cd (II) metal ion adsorbed by 17,954 mg / g.

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REFERENCES

- [1] Global Volcanism Program, Sinabung, <http://www.volcano.si.edu.com> (2008)
- [2] Sudaryo dan Sucipto, Identifikasi dan Penentuan Logam Berat pada Tanah Vulkanik di Daerah Cangkringan, Kabupaten Sleman dengan Metode Analisis Aktivasi Neutron Cepat, *Seminar Nasional V SDM Teknologi*, Yogyakarta(2009).
- [3] Zuraida, *Penggunaan abu volkan sebagai amelioran pada tanah gambut dan pengaruhnya terhadap sifat kimia tanah dan pertumbuhan jagung*. Thesis, Bogor, Pascasarjana, Institut Pertanian Bogor(1999)
- [4] Anda, M., dan Sarwani, M., Mineralogical, Chemical Composition and Dissolution of Fresh Ash Eruption: New Potential Source of Nutrients, *Soil Science Society of America Journal* **76**:733-747(2012)
- [5] Nakada, S., dan Yoshimoto, M., Eruptive Activity of Sinabung Volcano in 2013 and 2014, *Earthquake Research Institute*, The University of Tokyo(2014)
- [6] Rapierna, A., *Sintesis dan Pemanfaatan Membran Kitosan-Silika Sebagai Membran Pemisah Ion Logam Zn^{2+} dan Fe^{2+}* , Tugas Akhir II, FMIPA, UNNES, Semarang(2012)
- [7] Occupational Safety & Health Administration (OSHA), An extensive report on the health effects of exposure to cadmium. U.S. Department of Labor. (2001)
- [8] G.M. Naja, B. Volesky, Toxicity and sources of Pb, Cd, Hg, Cr, As, and radionuclides in the environment, in *Heavy metals in the environment*, ed. by L.K. Wang, J.P. Chen, Y.T. Hung, N.K. Shamma (CRC Press, Boca Raton, 2009)
- [9] M. Fleischer, A.F. Sarofim, D.W. Fassett, P. Hammond, H.T. Shacklette, I.C. Nisbet, S. Epstein, Environmental impact of cadmium: a review by the panel on hazardous trace substances. *Environ. Health Perspect.* **7**, 253–323 (1974)
- [10] World Health Organization (WHO), Environmental health criteria for cadmium (WHO, Geneva, 1974)
- [11] W.W. Eckenfelder Jr, *Industrial water pollution control*, International edn. (McGraw-Hill Book Company, New York, 1989)
- [12] A. Papandreou, C.J. Stouraras, D. Panias, Copper and cadmium adsorption on pellets made from fired coal fly ash. *J. Hazard. Mater.* **B148**, 538–547 (2007)
- [13] S. Mohan, R. Gandhimathi, Removal of heavy metal ions from municipal solid waste leachate using coal fly ash as an adsorbent. *J. Hazard. Mater.* **169**, 351–359 (2009)
- [14] M. Visa, C. Bogatu, A. Duta, Simultaneous adsorption of dyes and heavy metals from multicomponent solutions using fly ash. *Appl. Surf. Sci.* **256**(17), 5486–5491 (2010)
- [15] M. Visa, R.A. Carcel, L. Andronic, A. Duta, Advanced treatment of wastewater with methyl orange and heavy metals on TiO₂ fly ash and their mixtures. *Catal. Today* **144**(1–2), 137–142 (2009)
- [16] B. Thakur, A. K. Misra, M. Biswas, K. Bandyopadhyay, Fixed bed column adsorption studies using fly ash for removal of cadmium from aqueous solution, *J. Inst. Eng. India Ser. A*, **94**(3):161–168, (August–October 2013)
- [17] Lisnawaty Simatupang, Narsito, Nuryono, Interaksi simultan antara Mg(II), Zn(II), Ni(II), Cd(II) dan 3-aminopropiltrimetoksisilan yang diimobilisasikan pada silika melalui proses sol-gel, Thesis, Departemen of Chemistry, Universitas Gadjah Mada.



- [18] Lisnawaty Simatupang, S. R. Dewi, and N. Susanti. "Pengembangan Metode Alir Menggunakan Silika Gel Dari Sekam Padi Untuk Mengatasi Limbah Cair Industri Logam." *Laporan Akhir Research Grant Unimed* (2011).
- [19] Lisnawaty Simatupang, Ratna Sari Dewi, Boston Sidabutar, Optimalisasi pH untuk meningkatkan efektifitas dan selektifitas adsorben hibrid silika pada simultan ion logam divalent Zn(II) dan Cd(II) dengan metode ekstraksi fase padat
- [20] Fadjri, Martina Safitri, *Adsorpsi Zat Warna Methyl Orange Menggunakan Pasir Vulkanik Gunung Merapi*. Skripsi. Yogyakarta: FMIPA Universitas Yogyakarta(2012)
- [21] Lisnawaty Simatupang, Devi Putri Octavia, Maryati Doloksaribu, The adsorption of heavy metal Pb(II) by silica based adsorbent from volcanic ash of mount sinabung, *Jurnal Pendidikan Kimia*, Vol 9, No 2 (2017)
- [22] Lisnawaty Simatupang, Devi Putri Octavia, The preparation and characterization of Sinabung volcanic ash as silica based adsorbent, *Jurnal Pendidikan Kimia*,8(3), 9-13(2016)
- [23] Trivana, L., Sugiarti, S., Rohaeti, E., Sintesis dan Karakterisasi Natrium Silikat (Na₂SiO₃) dari Sekam Padi, *Jurnal Sains dan Teknologi Lingkungan*, 7(2), 66-75(2015)
- [24] Mori, H., Extraction of Silicon Dioxide from Waste Colored Glasses by Alkali Fusion Using Sodium Hydroxide, *Journal of the Ceramic Society of Japan* **111(6)**: 376-381(2003)
- [25] Kalapathy, U., Proctor, A., dan Shultz, J., A Simple Method for Production of Pure Silica From Rice Hull Ash, *Bioresource Technology* **73**: 257-262(2000)
- [26] Oscik, J., *Adsorption*, John Wiley and Sons, New York (1982),