CHARACTERIZATION OF ADSORBENT FROM OYSTER SHELL (*Crassostrea gigas*) USING PHYSICS AND CHEMICAL ACTIVATION WITH $ZnCl_2$ AND ITS APPLICATION FOR REMOVAL OF HEXAVALENT CHROMIUM

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Received : July 9, 2020 Accepted : December 20, 2020 Published : December 31, 2020

Abstract: Oyster shell waste has been investigated as a raw material for making adsorbents that will be activated. Physical activation uses temperatures of 500 ºC, 600 ºC, 700 ºC, 800 ºC, 900 ºC and chemical activation uses $ZnCl_2$ with a concentration of 1 %, 5 %, 10 % and 15 %. Based on the analysis of the characteristics that have been carried out for physically activated adsorbents, the oyster shell calcined at 800 ºC produces the best characteristics, it is a radius of 35.11 Å with a percentage of removal of 38.04 %, as well as the results of the FTIR, XRF and SEM analysis gives the best results among others. Whereas for chemically activated adsorbents, the use of activator $ZnCl_2$ 10% produces adsorbents with the best characteristics among others with a radius of 84.14 Å and removal percentage of 65.68 %, the best results for adsorbents activated using 10% $ZnCl_2$ are also supported by analysis results given by FTIR, XRF, and SEM.
Keywords: Adsorbent; BET; $Cr^{6+;}$ Oyster Shell Waste; XRF

Abstrak: Cangkang tiram (*Crassostrea gigas*) telah diteliti sebagai bahan baku pembuatan adsorben yang akan diaktivasi secara fisika dan kimia. Pembuatan adsorben dengan aktivasi secara fisika menggunakan variasi suhu 500 ºC, 600 ºC, 700 ºC, 800 ºC dan 900 ºC. sedangkan aktivasi kimia yaitu menggunakan aktivator $ZnCl_2$ menggunakan variasi konsentrasi 1 %, 5 %, 10% dan 15 %. Berdasarkan analisa karakteristik yang telah dilakukan untuk adsorben-adsorben yang telah diaktivasi secara fisika, cangkang tiram yang di kalsinasi pada suhu 800ºC menghasilkan karakteristik yang paling baik, yaitu radius pori-pori 35,11 Å dengan persentase penyisihan sebesar 38,04 %, begitu pula dengan hasil analisa FTIR, XRF dan SEM memberikan hasil terbaik diantara yang lain. sedangkan untuk adsorben-adsorben yang diaktivasi secara kimia, penggunaan aktivator $ZnCl_2$ 10% menghasilkan adsorben dengan karakteristik yang paling baik diantara lainnya dengan radius pori-pori 84,14 Å dan persentase penyisihan sebesar 65,68%, hasil terbaik untuk adsorben yang diaktivasi menggunakan $ZnCl_2$ 10 % juga didukung oleh hasil analisa dari FTIR, XRF dan SEM.
Kata kunci: Adsorben; BET; Cangkang Tiram; Cr^{6+}; XRF

DOI: 10.22373/ekw.v6i2.7333

Recommended APA Citation :

Handayani, L., Thaib, A., Nurhayati, Astuti, Y., & Darmawan. A. (2020). Characterization Of Adsorbent From Oyster Shell (*Crassostrea gigas*) Using Physics and Chemical Activation with $ZnCl_2$ and Its Application For Removal of Hexavalent Chromium. *Elkawnie*, *6*(2), 329-341. https://doi.org/10.22373/ekw.v6i2.7333

Introduction

Oyster shell waste which accumulates if not handled properly can pollute the environment as happened in Alue Naga Aceh Besar District, Indonesia as shown as in figure 1. Some of the problems caused by oyster shell waste include: increasing solid waste that disrupts environmental aesthetics, marine pollution that impacts on the destruction of marine ecosystems caused by illegal dumping of solid waste, causing the odour, higher management costs, demand for material (fertilizers etc.) of the recycled result of oyster shell waste is low. Oyster shell waste is potential for many purposes.

Figure 1. Oyster shell waste in Alue Naga Aceh Besar District, Indonesia (A) Empty oyster shell on the riverbank. (B), (C) The waste of oyster shells dumped by farmers.

Several studies on the use of shellfish shells continue to be developed, both as a source of calcium (Handayani & Syahputra, 2017) and as an adsorbent (Afranita, Anita, & Hanifah, 2014; Daud et al., 2017; Jung, Lee, Lee, Yoo, & Shon, 2007; Nasution & Iriany, 2015). Adsorbents originating from blood clam seashells (*Anadara granosa*) can absorb lead ions up to 53.113 % at a concentration of 30 ppm in an hour (Afranita et al., 2014). It contains 97 % calcium carbonate (Mohamed, Yousuf, & Maitra, 2012), so it has the potential to be an adsorbent in the absorption of heavy metals. The higher the level of shell hardness, the higher the level of calcium carbonate is (Surest, Wardani, & Fransiska, 2012). Calcium carbonate ($CaCO_3$) calcined at high temperature was decomposed into calcium oxide (CaO), at 900 ºC, calcium content of 56.77 % was obtained (Handayani & Syahputra, 2017). CaO is an activating compound that can function as an adsorbent for phosphate ions with a removal percentage of up to 80 % (Yuangsawad & Na-ranong, 2011). Therefore, it an be concluded that the oyster shell has excellent potential as an adsorbent.

Research on heavy metal removal from industrial waste continues to be developed. Still, for some types of heavy metals, the results obtained have not been maximized, especially research on efforts to eliminate metal chromium ions. Waste management that is applied in industries that produce bulky metal waste is by applying a deposition method using chemical compounds. But in the end, this method will produce other toxic compounds, so that the handling of waste will become complicated. Therefore the use of adsorption method is one of the alternative methods to be developed because it is considered more environmentally friendly. Adsorbents can be synthesized through the activation stage, both chemically and physically. Chemical activation is carried out using activators, such as $ZnCl_2$ (Hu, Zhou, He, Luo, & Cen, 2009; Wang et al., 2010) NaOH (Handayani, Rahmawati, Nurhayati, Astuti, & Darmawan, 2020) H_2SO_4 (Gimba, Ocholi, Egwaikhide, Muyiwa, & Akporhonor, 2009; Handayani et al., 2020). Many studies have stated that the use of $ZnCl_2$ activator will produce adsorbents with the best characteristics that are very effectively used as adsorbents (Pambayun, Yulianto, Rachimoellah, & Putri, 2013; Pitaloka, 2011).

The metal coating industry is one of the industries that produce high levels of chromium (Cr) ion waste. This is due to the use of chromium as a dye and coating. The chromium ion produced is in two oxidation conditions, namely Cr^{3+} and Cr^{6+}. Generally, in waters, chromium ions exist in their +3 oxidation state but can turn into +6 when oxidized. Cr^{6+} is toxic, so it needs to be treated so that the levels of the pollutant can decrease and not pollute the water sources. Elimination using adsorbents is known to be very useful for heavy metals such as Hg, Cu and Fe, but still very low for Cr metals. Therefore, the use of oyster shell waste as an adsorbent for Cr^{6+} heavy metal is essential to be developed, considering that oyster shell waste is one of shellfish waste that has not been widely used, in contrast to other shells which can be used as craft materials for making lamps ornamental and other souvenirs, while it can't be used as crafts or others. But it can be used as adsorbent due to high $CaCO_{3.}$ The use of oyster shell as an adsorbent is expected to increase the economic value of waste and can be an effective Cr^{6+} removal solution. The purpose of this study is to produce and characterize the adsorbent from oyster shells. Then it is used to adsorb Cr^{6+} heavy metals.

Experimental

Materials

The materials used in this study were oyster shells, $ZnCl_2$, sulphuric acid (H_2SO_4 98 %), Potassium dichromate ($K_2Cr_2O_7$) as a solution for Cr^{6+}, H_3PO_4, 1.5 diphenylcarbazide. Oyster shells used were collected from Alue Naga Aceh Besar District, Indonesia. *Crassostrea gigas* species were collected as the sample.

Preparation of adsorbent (Handayani *et al.*, 2020)

Oyster shells collected from landfills are washed thoroughly and dried for 5 days. After drying, the oyster shell is crushed to facilitate the smoothing using a planetary ball mill to turn into oyster shell flour and pass a 100 mesh sieve. This refined oyster shell flour is labelled as POS (Powdered Oyster Shell). Physically activated adsorbents are made by heating 100 grams each of oyster shell flour (POS) at different temperatures, namely 500 ºC, 600 ºC, 700 ºC, 800 ºC and 900 ºC for 3 hours. The adsorbent which has calcined at different temperatures is labelled COS-500 (Carbonized oyster shell at 500 ºC), COS-600, COS-700, COS-800, COS-900.

Besides, chemically activated adsorbents were made by soaking oyster shell flour (POS) that has been heated at 800 ºC for 3 hours with $ZnCl_2$ solutions of 1 %, 5 %, 10 % and 15 %. The procedure undertook as much as 30 grams of oyster shell flour (POS) which has been carbonized at 800 ºC was soaked in 90 ml of 1 % $ZnCl_2$ solution for 2 hours. Then it was filtered to separate the filtrate and residue. The residue is carbonized at 800 ºC for 1 hour. After the adsorbent reaches room temperature, it was washed using distilled water to neutralize it. Then it was dried at 105 ºC for 6 hours. The resulting adsorbent is labelled as Zn1-AOS. The same procedure was carried out for immersion using the 5 % $ZnCl_2$ activator (Zn5-AOS), $ZnCl_2$ 10 % (Zn10-AOS) dan $ZnCl_2$ 15 % (Zn15-AOS).

Characterization of oyster shell and adsorbent

The analysis of characterization conducted in this study is divided into 4 namely using Fourier transform infrared spectroscopy (FTIR), Surface area analyzer (SAA), X-ray fluorescence (XRF) and Scanning electron microscopy (SEM). Determination of functional groups is done by FTIR (Shimadzu) test equipment, chemical composition analysis using XRF (Bruker). The surface area and pore size were measured using the Brunaeur-Emmet-Teller (BET) and Barret-Joyner-Halenda (BJH) methods with the SSA instrument (NOVA Quantachrome 11.0 version). In contrast, the surface morphology of the adsorbent was analyzed using SEM (JEOL-6510 LA).

Adsorption of Cr^{6+}

Testing of Cr^{6+} adsorption was carried out by adding 1 g of adsorbent to the 30 ml/l Cr^{6+} test solution of 30 ml for 24 hours. Cr^{6+} test solution is made from 1,000 mg/L mother stock (stock solution). After 24 hours, the absorbance of Cr^{6+} was measured using a spectrophotometer (Biobase Model BK-UV1000.). The measurement follows the APHA procedure (APHA, 1985) where the Cr^{6+} solution was put into reaction with 1.5-diphenylcarbazide 0.5 % to form a purple complex, at a pH 2, in which the pH was adjusted using H_2SO_4 and H_3PO_4. Measurement of Cr^{6+} concentration before and after adsorption was analyzed using a spectrophotometer at a wavelength of 540 nm. The maximum wavelength is determined using a standard solution made from a 1,000 mg/l stock solution. The standard Cr^{6+} solution made to find the maximum wavelength is with concentrations ranging from 0.04 to 0.2 mg/l. The stock solution is made by dissolving 2.829 g $K_2Cr_2O_7$ in 1000 ml distilled water. The Cr^{+6} ions removal was determined using the equation below:

$$C\ (\%) = [C_0 - C_e / C_0] \times 100 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Results and Discussion

Analysis of FTIR

Oyster shell flour (POC) dan adsorbent (COS dan Zn-AOS) was characterized using FTIR to determine the functional groups contained therein. FTIR spectra of the samples obtained in this study are presented in Figure 2 below:

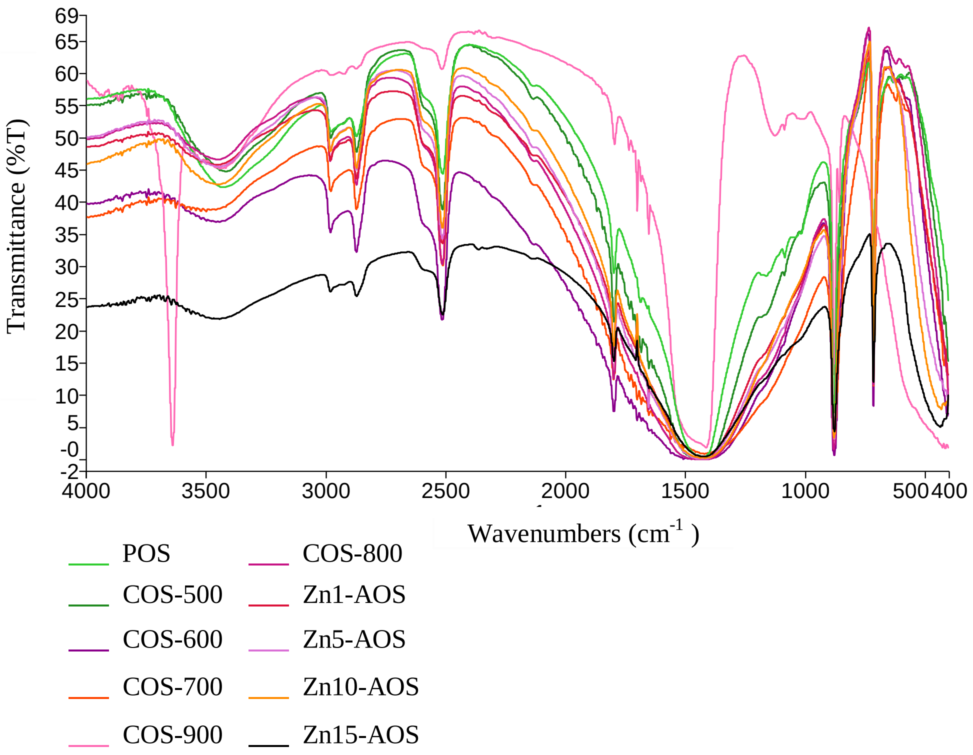

Figure 2. FTIR spectra of POS, COS and Zn-AOS

The peaks formed in the FTIR spectra produced by POS, COS and Zn-AOS are not much different. Intense peaks formed at wavenumbers 3466 - 3421 cm^{-1}, 2517 - 2513 cm^{-1}, 1799 – 1734 cm^{-1}, 1439 – 1411 cm^{-1}, 1084 – 1082 cm^{-1}, 877 – 712 cm^{-1}. It can be seen from Figure 2, that the peaks formed for POS are at wave number 3428.28 cm-1 indicating the presence of amine groups ($-NH_2$). Similar to the previous studies conducted, at the peak of 3363 cm^{-1} and 1639 cm^{-1}

(Ghafar, Hussein, & Zakaria, 2017) 3399 cm^{-1} and 1686.28 cm^{-1} (Handayani, Syahputra, & Astuti, 2018) representing the amine functional group, and all analyzed samples have absorption peaks due to amide (NH) and widening peaks which is caused by the O-H group at wave number 2517-2513 $cm^{-1.}$ But the COS-800 has the most typical and better amide absorption band compared to the others. While the COS-900 peak intensity of amide uptake has been greatly reduced, and it creates a very intense new uptake that is -OH at wave number 3643.62 cm^{-1}. The peaks at wave numbers 1422.03 cm^{-1} and 1083.97 cm^{-1} are characteristic of the calcium carbonate ($CaCO_3$) peak. (Hanura, Trilaksani, & Suptijah, 2017; Husna, Handayani, & Syahputra, 2020; Mondal, Mondal, Dey, & Mukhopadhyay, 2012) reported that the CO_3^{2-} group or carbonate group could be identified in the region between 1400 cm^{-1} – 1500 cm^{-1}. The amide group also functions to bind the adsorbate.

All analyzed samples have absorption peaks at wave numbers that indicate the presence of calcium carbonate (POS = 1422.03 cm^{-1}, 1083.97 cm^{-1} ; COS-500 = 1428.99 cm^{-1}; COS-600 = 1439.25 cm^{-1}; COS-700 = 1419.52 cm^{-1}; COS-800 = 1435.13 cm^{-1}; COS-900 = 1411.77 cm^{-1}; Zn1-AOS = 1429.75 cm^{-1}; Zn5-AOS = 1423.7 cm^{-1}; Zn10-AOS = 1417.26 cm^{-1}; Zn15-AOS = 1426.08 cm^{-1}). While the absorption peak caused by stretching C = O amide at wave number 1685 - 1635 cm^{-1} is shown by POS, COS-500, COS-600, COS-700, COS-900, Zn1-AOS and Zn5-AOS. Absorption peaks resulting from the presence of C = O groups in wave numbers 1799 - 1734 cm-1 are found in all samples. So the typical twin uptake by the carbonyl group (C = O) is produced by POS, COS-500, COS-600, COS-700, COS-900, Zn1-AOS and Zn5-AOS. The C = O group formed functions as a metal ion binder. Peaks of adsorbents similar to peaks of FTIR analysis from cockle shell (Ghafar et al., 2017). The samples analyzed all come from oyster shells containing silica, causing the formation of absorption peaks at wave numbers 877-712 cm^{-1}, this indicates that the SiO_2 contained in POS, COS and Zn-AOS has not been lost. Similar to previous studies conducted, at the peak of 871 cm^{-1}, there was an absorption caused by silica (Handayani et al., 2018). The silica content is one of the impurities for adsorbents that can fill the pores, so the ability of adsorption is reduced.

Surface area and pore size analysis

The analysis was carried out to determine the surface area and characteristics of the adsorbent pores produced because both are parameters that are near related to the ability of adsorption of the adsorbate. An adsorbent with a large surface area has a better adsorption ability because it has a broader contact area so that it will absorb more adsorbate. The surface area of an adsorbent will increase with the loss of impurities contained therein. These compounds can be released through the activation process, both physical activation using high temperatures, and chemical activation using an activator. The loss of these impurities will open the pores of the adsorbent so that it will cause an increase in surface area, pore size and volume. Data on surface area and pore characteristics of the adsorbent as the results of this study can be seen in Table 1.

Table 1. Surface area and pore characteristics of adsorbents

Sample adsorbent	**Physical properties**		
	Surface area (m^2/g)	**Pore radius (Å)**	**Pore volume (cc/g)**
POS	2.95	73.02	0.013
COS - 500	5.89	30.83	0.009
COS - 600	10.79	23.16	0.012
COS - 700	5.34	25.45	0.004
COS - 800	7.76	35.11	0.014
COS - 900	23.55	14.5	0.022
Zn1 - AOS	4.81	49.65	0.012
Zn5 - AOS	2.3	117.66	0.012
Zn10 - AOS	5.0	84.14	0.023
Zn15 - AOS	3.71	59.51	0.011

From Table 1, it can be seen that the oyster shell calcined at 800 ºC (COS-800) has better characteristics among the calcined oyster shells at different temperatures, so that this COS-800 is chosen for chemical reactivation using $ZnCl_2$ activator. COS-800 has better radius and volume than others. Physically activation at 850 ºC could increase surface area cockle shells from 1.56 m^2/g to 9.63 m^2/g (Rashidi, Mohamed, & Yusup, 2011). The quality of the adsorbent is not only seen from the surface area but also the radius and the volume. The COS-900 surface area is the highest, but the radius and volume pore has an unfavourable value, this is caused by damage to the carbon wall contained therein, which is caused by using high temperature. This causes the adsorbent has a low absorption too. Whereas POS, which has a high pore radius, does not have a good surface area and pore volume value. Chemically activated adsorbents have a higher pore radius, this is due to the loss of some impurities that cover the pores of the adsorbent (Pambudi, Prasetya, & Sumarni, 2014; Widihati, 2008). However, the adsorbent activated using $ZnCl_2$ 10 % (Zn10-AOS) is the best among others, this can be seen from the surface area, pore radius and pore volume better. Zn5-AOS has a larger pore radius, but the pore volume and surface area values are minimal. Physical activation or carbonization process purpose to the removal of non-carbon species and the production of a mass of fixed carbon (char) with a rudimentary porous structure and process chemical activation using $ZnCl_2$ produces activated carbons with larger porosity (Rodriguez-Reinoso & Silvestre-Albero, 2016).

XRF Analysis

This analysis is carried out to estimate the chemical composition of the adsorbent produced. The results of XRF POS, COS-800 and Zn-AOS analysis are presented in Table 2.

Table 2. Chemical analysis of POS, COS dan Zn-AOS

Adsorbent	**Chemical composition (%)**								
	Ca	**Cl**	**Al**	**Si**	**S**	**Fe**	**Sr**	**Ag**	**Zn**
POS	98.65	0.38	0.22	0.16	0.21	-	-	0.38	-
COS-800	97.23	0.74	0.27	0.37	0.26	0.45	0.32	0.36	-
Zn1-AOS	91.76	0.44	0.35	0.48	0.21	0.59	0.28	0.31	5.58
Zn5-AOS	81.77	0.49	0.34	0.44	0.18	0.48	0.24	0.35	15.71
Zn10-AOS	70.5	0.7	-	0.23	0.12	0.23	0.19	0.35	27.68
Zn15-AOS	64.29	0.79	-	0.33	0.13	0.24	0.16	0.38	33.68

Based on table 2 above, it can be seen that most of the adsorbent constituents analyzed were calcium (Ca), by the results of previous studies, namely calcined oyster shells at 900 ºC for 4 hours containing calcium levels of 57.77 % (Handayani & Syahputra, 2017). Ca is derived from CaO compounds formed from the decomposition of $CaCO_3$ at high temperatures. The most extensive chemical composition of the adsorbents is CaO, but also contains other components in small amounts such as POS (Al_2O_3, SiO_2, SO_3, Cl, Ag_2O). Whereas the COS-800, besides containing the same components as POS, also contains Fe_2O_3 and SrO, as reported by (Daud et al., 2017; Mohamad, Mohamad, & Jemaat, 2016; Nordin, Hamzah, Hashim, Kasim, & Abdullah, 2015). Likewise with Zn-AOS, the components that make it the same as COS-800 only have the addition of ZnO caused by the attachment of ZnO to the pore walls of the adsorbent. ZnO is caused by the $ZnCl_2$ activator used and the incomplete combustion of carbon with oxygen. Zn10-AOS and Zn-15-AOS are the lowest amounts of impurities, which do not contain Al_2O_3. Zn10-AOS has better characteristics than Zn15-AOS because it contains lower SiO_2 dan ZnO impurities. These impurities can cover the pores of the adsorbent so that it can inhibit adsorption. The high concentration of $ZnCl_2$ that is used can reduce the surface area of adsorbent due to pore-clogging. Some of the researchers in their studies was verified that the used of high concentration of activator could be pored clogging (Açikyildiz, Gürses, & Karaca, 2014; Marina Olivia Esterlita & Netti Herlina, 2015; Pitaloka, 2011; Xu, Liu, Oh, & Park, 2019; Yuangsawad & Na-ranong, 2011).

Surface morphologies (SEM Analysis)

Identification of the surface morphology of the adsorbents was carried out to determine the surface image and its pores. The analysis was carried out using

SEM instrument. The adsorbents analyzed for morphology are POS, COS-800 and Zn10-AOS. Based on the previous characterization, the best COS was adsorbent which was catalyzed at 800 ºC, while the adsorbent which was chemically activated, Zn10-AOS was the best namely adsorbent that used 10 % ZnCl activator. Then the morphological analysis results of the three adsorbents are presented in Figure 3.

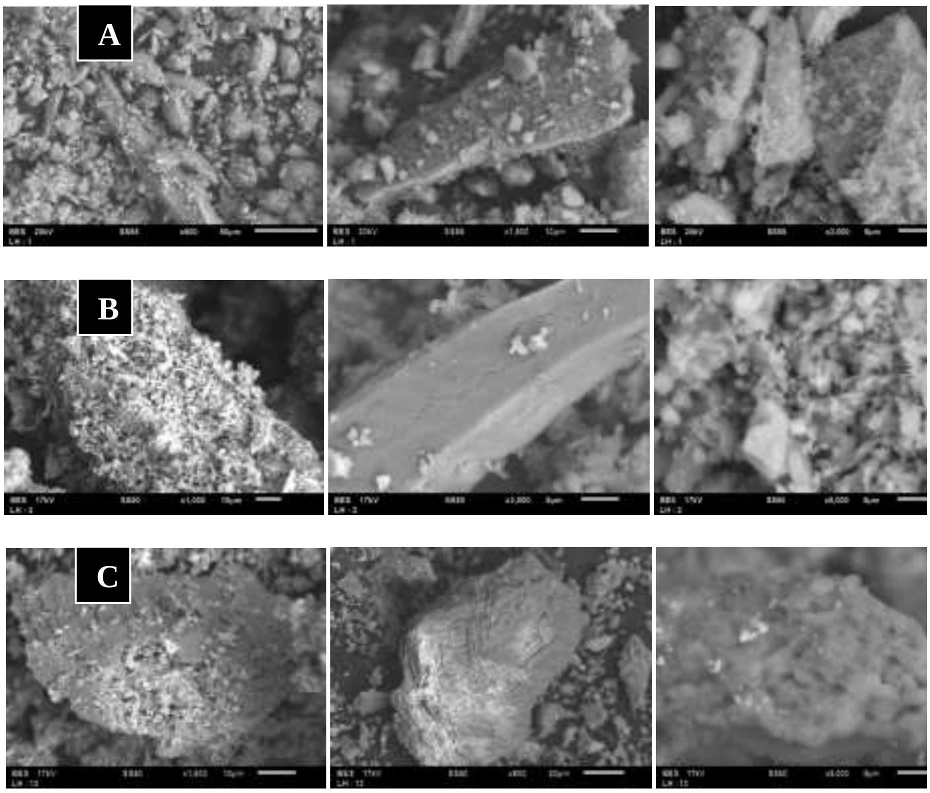

Figure 3. SEM Image of (A) POS (magnified: x500, x1500, x3000). (B) COS-800 (magnified: x1000, x3000, x5000). (C) Zn10-AOS (magnified: x1500, x800, x5000)

Based on the analysis presented in Figure 3, the surface morphology of the three adsorbents samples looks very different. POS has pores with a surface that is still covered by impurities because it still contains protein and fat (Handayani & Syahputra, 2017). Whereas COS-800, its pores look more open than POS, this is caused by the evaporation of organic compounds that fill the pores of adsorbents. Likewise, Zn10-AOS, which has a better surface morphology than COS-800, which is caused by some impurities that fill the pore walls, have disappeared by immersion using activator. If contaminants cover the pores of the adsorbent, it will decrease the adsorption power. The POS surface looks like irregular cotton beads, while the COS-800 and Zn10-AOS look smoother with more visible and relatively irregular pores. Similar to previous studies that at a higher calcination temperature of 800 ºC and 900 ºC The surface of calcined waste cockle shell presented much smoother surface and more uniform surface (Mohamad, Mohamad, & Jemaat, 2016; Nordin et al., 2015).

Adsorption hexavalent chromium (Cr^{6+})

The adsorbents that have been characterized are tested for their adsorption ability against Cr^{6+} heavy metal ions. The percentage of removal of adsorbents of these metal ions is presented in graphical form in Figure 4.

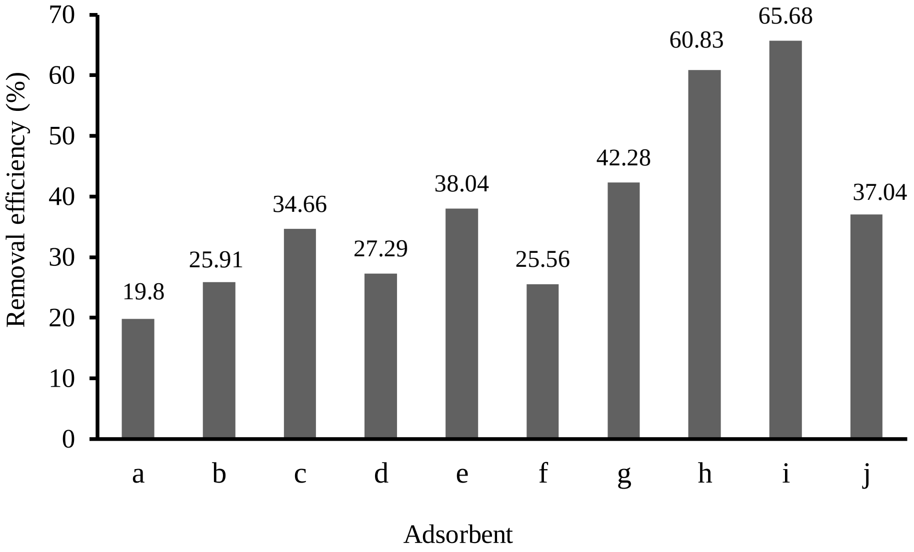

Figure 4. Removal efficiency of Cr^{6+} by (a) POS, (b) COS-500, (c) COS-600, (d) COS-700, (e) COS-800, (f) COS-900, (g) Zn1-AOS, (h) Zn5-AOS, (i) Zn10-AOS, (j) Zn15-AOS

Based on Figure 3, it appears that the Zn10-AOS adsorption ability is the best among others to reach 65.68 %, this is under its characteristics, namely having a good surface area, pores radius and pores volume. While the lowest adsorption ability is POC, which is only 19.8 %, this is because the POC has not undergone activation which can evaporate organic compounds and other impurities that cover the pores, so the POS pores have not been opened which causes the Cr^{6+} heavy metal ions cannot be absorbed by the adsorbent as reported by (Pambudi et al., 2014; Rashidi et al., 2011; Widihati, 2008).

Conclusions

Oyster shell waste can be used as Cr^{6+} heavy metal adsorbent. POSs are activated physically (using high temperatures) and can chemically open pores, thereby increasing the ability of adsorbent adsorption. Based on the results of FTIR, XRF, BET/Ads, SEM characterization and adsorption test for Cr^{6+} heavy metal, Zn10-AOS has the best value among other adsorbents. While the oyster shell is physically activated at various temperatures, it produces the best adsorbent with the calcination temperature of 800 °C (COS-800).

Acknowledgements

The authors are grateful to Abulyatama University and Ministry of Research, Technology and Higher Education of Republic of Indonesia for providing financial support (Contract No. 235/SP2H/LT/DRPM/2019; 099/L13/AKA/LT/2019; 12/HIBAH DIKTI/LPPM/IV/2019).

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