

## THE CHARACTERIZATION OF OYSTER SHELL (*Crassostrea gigas*) AS ADSORBENT IN THE REMOVAL OF Cr(VI) IONS. A STUDY OF NaOH AND H<sub>2</sub>SO<sub>4</sub> ACTIVATION EFFECT

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Received: November 15, 2019 Accepted: May 12, 2020 Published: June 30, 2020

**Abstract** : Oyster shell as one of the highest bio-waste in Alue Naga Aceh Besar District, Indonesia, was used as an adsorbent to remove a heavy metal Cr (VI) ion. The study was started by calcinating oyster shells at a high temperature of 800 °C for 3 hours. The effect of various acid (H<sub>2</sub>SO<sub>4</sub>) and base (NaOH) activator was studied using characterization and adsorption experiments. The characterization obtained the sample activated by 10% NaOH (Na10-ACT) and 10% H<sub>2</sub>SO<sub>4</sub> (H10-ACT) had the highest surface area which had 14.23 m<sup>2</sup>/g, 10.77 m<sup>2</sup>/g, respectively. Furthermore, the adsorption experiments confirmed the highest surface area by showing the highest Cr (IV) ion removal of 57.66%, 70.7%, respectively. The further investigation using X-ray fluorescence (XRF) determined that the Na10-ACT adsorbent has a better composition compared to the H10-ACT due to its high purities.

**Keywords** : Adsorbent, BET, Chromium, Oyster Shells, XRF

**Abstrak** : Cangkang tiram sebagai salah satu bio-limbah padat di Desa Alue Naga Kabupaten Aceh Besar, digunakan sebagai adsorben untuk menghilangkan ion logam berat Cr (IV). Penelitian ini diawali dengan mengkalsinasi cangkang tiram pada temperatur tinggi 800°C selama tiga jam. Pengaruh penambahan aktivator asam (H<sub>2</sub>SO<sub>4</sub>) dan basa (NaOH) juga dipelajari melalui karakterisasi dan pengujian adsorpsi. Hasil karakterisasi menunjukkan sampel yang diaktivasi dengan 10% NaOH (Na10-ACT) dan 10% H<sub>2</sub>SO<sub>4</sub> (H10-ACT) memiliki luas permukaan tertinggi yaitu 14,23 m<sup>2</sup>/g, 10,77 m<sup>2</sup>/g, masing-masing. Lebih lanjut, pengujian adsorpsi juga mendukung luas permukaan yang tinggi dengan menghilangkan ion Cr (IV) sebesar 57,66%, 70,7%, masing-masing. Investigasi melalui analisa XRF menyimpulkan bahwa Na10-ACT memiliki komposisi yang lebih baik dibanding H10-ACT karena memiliki kemurnian yang tinggi.

**Kata kunci** : Adsorben, BET, Cangkang Tiram, Kromium, XRF

## Introduction

The presence of oyster shells in the environment can be one of the environmental problems due to its characteristic as bio-waste. Several common problems are increasing the solid waste that disrupts environmental aesthetics, contributing to marine pollution which has an impact on damage to marine ecosystems, providing a bad smell, having higher management costs, etc.

In Syiah Kuala sub-district, Aceh Besar, most of the coastal communities, work as oyster farmers in which the oyster shells are produced after peeling the oyster. Most of the oyster shells are just thrown away to the environment and contribute to environmental pollution. It is getting worse since the accumulation of bio-waste in the local surroundings such as water bodies, rivers, and ditches which potentially affect environmental quality.

Several studies have been reported in the utilization of oyster shells as the source of Calcium (Handayani & Syahputra, 2017) and Chitosan (Handayani, Syahputra, & Astuti, 2018) or converting as adsorbent (Afranita, Anita, & Hanifah, 2014; Daud et al., 2017; Jung, Lee, Lee, Yoo, & Shon, 2007; Nasution & Iriany, 2015). Afranita (2014) reported the adsorption capacity of clams shells in which it can absorb 53.11% of 30 ppm per hour of Tin ions (Afranita et al., 2014). The deep investigation found that Calcium Carbonate (CaCO<sub>3</sub>) played the main role in determining the adsorption capacity of any shell-based adsorbent (Mohamed, Yousuf, & Maitra, 2012). The hardness of shell differentiated the amount of CaCO<sub>3</sub> (Surest, Wardani, & Fransiska, 2012). However, CaCO<sub>3</sub> would decompose to Calcium Oxide (CaO) in the high temperature (> 900°C) where the Calcium containing in the CaCO<sub>3</sub> turned to 56.77% (Handayani & Syahputra, 2017). Moreover, CaO is reported as the activation component which also has adsorption performance. Yuangsawad (2011) reported the adsorption of phosphate ion using CaO based adsorbent (Yuangsawad & Na-ranong, 2011). Thus, oyster shells are potentially used as adsorbents, since oyster shells contain 56.77% of CaO (Handayani & Syahputra, 2017).

The research on industrial waste and wastewater treatment has continuously developed to improve the removal capacity of any pollutants including heavy metal. However, most of the obtained process provides high technology and relatively shows lower capacity. Most industrial waste and wastewater treatment used the coagulation process to remove the heavy metal which contains in their waste and wastewater. However, this method is generating the secondary pollutant which has more toxicity compared to un-treated waste and wastewater. Thus, the adsorption process can be an alternative process to remove heavy metal in waste and wastewater. It is supported by a comprehensive study which found that the adsorption process is relatively safe, cheap, and easy to handle. The preparation of adsorbent began with the activation process. The activation process can be achieved using the physical and chemical process. In the

chemical process, the activator agent such as H<sub>3</sub>PO<sub>4</sub>, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, HCl, CaCl<sub>2</sub>, Ca(OH)<sub>2</sub>, NaCl, HNO<sub>3</sub>, MgCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub> are used to adsorb water in the pore, resulting in higher surface area. Therefore, the mineral elements of the activator initiate the pores and open the closed or clogged surface. Moreover, the calcination is used to support the activation by providing additional energy to release the impurities. The high purities and higher surface area enhance adsorption capacities. A strong acid solution tends to clean organic contaminants. It is well known in the preparation of adsorbent, black carbon, and silica from rice hulk (Meliyana, Rahmawati, & Handayani, 2019).

The metal coating industry is one of the industries that produce waste with high levels of chromium (Cr) ions due to the use of chromium as the color substance and coating. The chromium ions produced under two oxidation conditions are Cr (III) and Cr (VI) ions. However, Cr (III) ions easily transform to Cr (VI) ions which have higher toxicity due to the oxidation process. Several studies have reported the high efficiency of adsorbent in heavy metal removals such as Hg, Cu and Fe. However, there is a limited number of adsorbents which have successfully removed ion Cr (IV) in the water bodies. Therefore, the use of oyster shell waste as an adsorbent for Cr (VI) ions removal is very important to develop since the fact that oyster shells are one of the most underused shells compared to other shellfish shells. The use of oyster shells as adsorbents is expected to increase its economic value as bio-waste and can be an effective process in the Cr (VI) ions removal.

In this study, there are two main activator components used which are NaOH and H<sub>2</sub>SO<sub>4</sub>. The study aims to investigate the performance of prepared adsorbent activated by acid and base solution which correlated to its surface area. To be more specific, the study would characterize each prepared sample using Brunauer-Emmett-Teller (BET) analysis to see how activator components enhance the surface area. Furthermore, the adsorption experiment is designed to confirm the correlation between surface area and adsorption capacity of each prepared sample.

## **Experimental method**

### **Materials and Tools**

All the chemicals used in this study have high purities (E-Merck) and did not need any further purification process. The main material was oyster shells obtained from Alue Naga sub-district, Syiah Kuala Sub-district, Banda Aceh City. The chemical used in this study were H<sub>2</sub>SO<sub>4</sub> 1%, 5%, 10%, 15%, NaOH 1%, 5%, 10% and 15%, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, H<sub>3</sub>PO<sub>4</sub>, and 1.5 diphenylcarbazide.

Several tools used in this study were glassware including funnel, stirring bar, beaker glass, volumetric flask, pipette, volumetric glass, distilled water, pH meter, Whatman filter paper, Surface Area Analyzer (NOVA Quantachrome 11.0

version), X-ray fluorescence (Bruker), and spectrophotometer (Biobase Model BK-UV1000).

### **Preparation of Oyster Shells Powder**

The preparation technique was referred to and modified from the previous experiment reported by Handayani (2017). In this experiment, the adsorbent has 100 mesh of fineness obtained by treating on Planetary Ball Mill for 8 hours. The obtained powder is further noticed as CT.

### **Preparation of Adsorbent**

The obtained CT was calcinated at 800°C for 3 hours and marked as CCT. The CCT was then activated using the acid solution of H<sub>2</sub>SO<sub>4</sub> and base solution of NaOH in various concentrations (1%, 5%, 10%, and 15%) to see the effect of acid and base concentration. 30 grams of CCT were immersed in acid and base solution in each concentration for 2 hours and filtered. The obtained residue was then calcinated at 800°C for 1 hour. After the calcinated, the obtained powder was washed several times until neutral pH achieved and dried at 105°C for 6 hours. The obtained adsorbent was then characterized using Brunauer-Emmett-Teller (BET) analysis.

### **Adsorption Experiment**

The adsorption experiment was conducted using a batch process. 1 gram of adsorbent was mixed with 30 mL of 25 mg/L of Cr(IV) ions and rest for 24 hours. After 24 hours, the concentration of Cr(IV) ions was controlled using a spectrophotometer (Biobase Model BK-UV1000). The concentration measurement followed the APHA measurement standard (APHA, 1985) which mixed the Cr(IV) ions solution with 1.5-diphenylcarbazide 0.5% to obtain a purple based solution. A mixture of H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> was used as a buffer to stabilize the color. The concentration measurement was conducted at a specific wavelength of 540 nm. The Cr(IV) ions removal was determined using the equation below.

$$C (\%) = \frac{C_0 - C_e}{C_0} \times 100 \dots\dots\dots(1)$$

Where C (%): % Cr(IV) removal; C<sub>0</sub> = initial concentration; C<sub>e</sub>: obtained concentration after treatment

## **Results and Discussion**

### **Surface area measurement using Brunauer-Emmett-Teller (BET) analysis**

The analysis of BET was used to calculate the surface area and pore characteristics of the prepared adsorbent. Both information determined the adsorption capacity of the prepared adsorbent. An adsorbent with a high surface area would have a better adsorption capacity because it had a higher contact area

as a place in conversion of the adsorbate. Moreover, the high surface area was determined by the material purities. The existence of impurities clogged the material surface and reduced the material surface area. The impurities could be removed by the activation process. The activation process could be conducted through physical activation using a calcination process or chemical activation using several activator compounds. The removal of impurities opened the clogged surface area and enhanced the material surface area. Table 1 showed the surface area of each prepared sample.

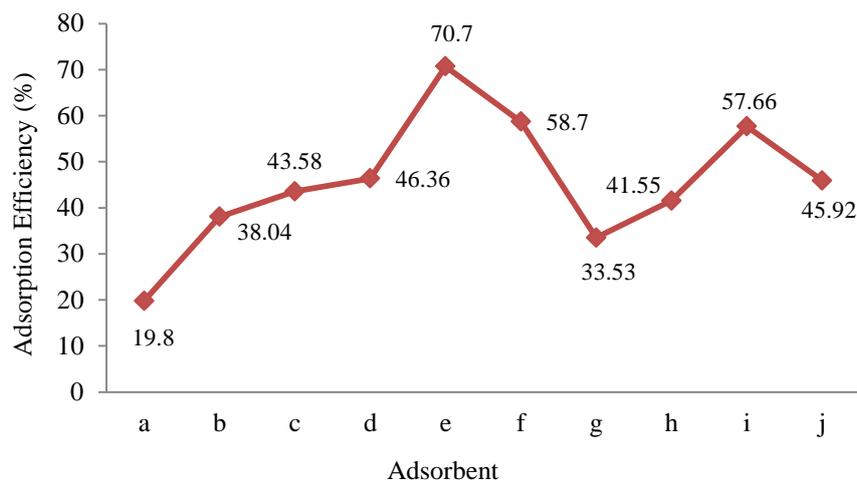
**Table 1.** Sample surface area

Sample	Physical Characterization	
	Surface area (m <sup>2</sup> /g)	Micropore surface area (m <sup>2</sup> /g)
CT	2.95	5.7
CCT	7.75	9.5
H1-ACT	1.11	1.56
H5-ACT	3.49	4.77
H10-ACT	10.77	14.78
H15-ACT	8.75	9.28
Na1-ACT	2.17	2.72
Na5-ACT	2.61	3.63
Na10-ACT	14.23	15.98
Na15-ACT	12.78	14.34

Table 1 showed that CCT had a higher surface area compared to the CT sample. It was because the CCT had lower moisture content after the calcination process. However, the chemical activation process using acid and base solution enhanced specifically prepared sample such as the one activated by 10% H<sub>2</sub>SO<sub>4</sub> (H10-ACT), and 10% and 15% NaOH (Na10-ACT and Na15-ACT). There would be many speculations to answer the phenomenon. Moreover, the possible reason was that only those concentrations could effectively remove the impurities and enhance the surface area. The low concentration of acid or base solution had low performance resulting in higher contamination of acid and based solution in the material surface. Besides, the higher concentration of an acid solution (>10%) resulted in the breakage of the surface due to a strong acid solution. In this study, 10% of acid and base solutions were found as the optimum condition to obtain the high surface area of the adsorbent.

### Adsorption of Cr(VI) ion

The adsorption experiment was used to see the correlation between the surface area and adsorption capacities. Figure 1 showed the result of the adsorption experiment using the prepared sample.



**Figure 1.** The percentages of Cr(VI) ions removal using (a) CT, (b) CCT, (c) H1-ACT, (d) H5-ACT, (e) H10-ACT, (f) H15-ACT, (g) Na1-ACT, (h) Na5-ACT, (i) Na10-ACT, and (j) Na15-ACT.

Figure 1 showed that the adsorbent activated using 10% H<sub>2</sub>SO<sub>4</sub> had the highest Cr(VI) removal followed by the one activated by 10% NaOH which approximately removed 70.7% and 57.66% of Cr(VI) ions, respectively. However, the percentage of absorption was still low. It was because there were no stirring and heating processes during the adsorption experiment. The chemical reaction rate was influenced by several factors including the concentration of adsorbate and adsorbent, pH, time, temperature, stirring (mechanical), and catalyst. It could be seen that the stirring process affected the adsorption capacity process. Thus, resting the adsorbent with adsorbate without any stirring process reduced the possibilities of physical interaction between adsorbent and adsorbate, resulting in lower adsorption percentage. Moreover, the further investigation confirmed that our prepared sample relatively had a low surface area compared to the other sample prepared by previous studies. Nasution (2015) reported that seashell shell which had the similar amount of CaCO<sub>3</sub> with oyster shell (approximately 97%) activated by calcination at 800°C had 803.82 m<sup>2</sup>/g of surface area (as comparison Na10-ACT as the highest surface area of 14.23 m<sup>2</sup>/g). The result found that the prepared sample obtained in this study had a low surface area. It was because of the calcination process was not optimum due to the short period (3 hours) of calcination. In this study, the ineffective calcination process generated a lower surface area.

Further analysis found that the existence of ion H<sup>+</sup> in the system played a more important role compared to the surface area. The result of the BET analysis found that Na10-ACT had higher surface area compared to H10-ACT. However, H10-ACT provided higher adsorption capacity compared to Na10-ACT. It was because the adsorbent activated by acid solution had higher H<sup>+</sup> ions in the pores resulting in high possibilities of physical interaction between adsorbent and

adsorbate. Besides, the high H<sup>+</sup> ions in the adsorbent surface reduce the oxidation number of Cr ion from +6 to +3 as the equation below (Shevla, 1982). The other reason was that the heavy metal ion removal was easy in acid solution to compare to neutral of base environment solution.



### X-Ray Fluorescence (XRF) Analysis

XRF analysis was used to confirm the chemical substance and impurities of H10-ACT, Na10-ACT, and CT as control. It was important since both H10-ACT and Na10-ACT providing the highest surface area and adsorption capacities in each activation process. The result of the XRF analysis was shown in table 2.

**Table 2.** Chemical composition of H10-ACT, Na10-ACT, and CT

No	Sample	Chemical Composition (%)							
		Ca	Cl	Al	Si	S	Fe	Sr	Ag
1	H10-ACT	67.23	0.40	0.47	0.27	30.38	0.34	0.20	0.24
2	Na10-ACT	97.83	0.24	0.32	0.41	0.16	0.44	0.31	0.28
3	CT (Control)	98.65	0.38	0.22	0.16	0.21	-	-	-

In table 2, each sample was consist of calcium as the main compound which following the previous result which reported that the oyster shell had similar calcium properties with clams shell (Handayani, L & Syahputra, F. 2018). The calcium compound was derived from the CaO compound formed from the decomposition of CaCO<sub>3</sub> at high temperatures during the physical calcination process. The result confirmed CaO as the main compound containing in each prepared sample. Several compounds in the small amount also detected such as Cl ion, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and SO<sub>3</sub>, Fe<sub>2</sub>O, SrO, and Ag<sub>2</sub>O. To be more specific, several compounds obtained inactivated samples were not found in control samples such as Fe<sub>2</sub>O, SrO, and Ag<sub>2</sub>O. It indicated that the activation process possibly contributed to high impurities. As we could see in table 2, CT has the highest purities compared to H10-ACT and Na10-ACT. Besides, the high amount of Calcium element in CT was not obtained from CaO, but coming from CaCO<sub>3</sub>. Moreover, the high adsorption capacity of H10-ACT was also because of the high purity of H10-ACT compared to Na10-ACT which had high impurities. It was well known that impurities giving an additional effect in determining adsorption capacities in adsorbent material.

### Conclusions

The characterization of adsorbent obtained from oyster shells was differentiated by the calcination process. The calcination process affected the surface area and impurities. Both parameters had a positive correlation to adsorption capacity. The characterization obtained the sample activated by 10%

NaOH (Na10-ACT) and 10% H<sub>2</sub>SO<sub>4</sub> (H10-ACT) had the highest surface area which had 14.23 m<sup>2</sup>/g, 10.77 m<sup>2</sup>/g, respectively. Furthermore, the adsorption experiments confirmed the highest surface area by showing the highest Cr (IV) ion removal of 57.66%, 70.7%, respectively.

### Acknowledgement

The authors acknowledge the Ministry of Research and Higher Education of Republic Indonesia for financial support in the scheme of Penelitian Kerjasama Antar Perguruan Tinggi 2019 with the specific grand number of 235/SP2H/LT/DRPM/2019; 099/L13/AKA/LT/2019; 12/HIBAH DIKTI/LPPM/IV/2019.

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