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Adsorption of Organic Compounds in Leachate using Precipitated Calcium Carbonate (PCC) from Ale-Ale Shells

Adsorpsi Senyawa Organik Pada Lindi Menggunakan *Precipitated Calcium Carbonate* (PCC) dari Cangkang Kerang Ale-Ale

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ABSTRACT

Leachate waste from piles of garbage in the landfill (TPA) has a high concentration of Chemical Oxygen Demand (COD). High COD concentrations can cause a decrease in dissolved oxygen concentrations in the waters. Simple leachate treatment is carried out using the adsorption method with adsorbents derived from food waste. This research used Precipitated Calcium Carbonate (PCC) adsorbent from ale-ale shells. This study aims to evaluate the effect of particle size and calcination temperature variations on PCC yield and analyze the adsorption ability of PCC adsorbents in reducing COD concentrations. In addition, PCC was characterized using an infrared spectrophotometer (FTIR) and an X-ray diffractometer (XRD). Determination of COD concentration was carried out by permanganometric titration. The optimum PCC yield of 57.75% was obtained from Ale-ale shells with a particle size of 40 mesh with a calcination temperature of 800°C. The functional groups in PCC are C-O at wave numbers 1403 cm^{-1}, 873 cm^{-1}, and 713 cm^{-1}. XRD characterization showed the presence of a calcite phase with a high peak intensity at 2θ = 29.38°. The adsorption of organic matter on leachate by PCC (4.5 g/50 mL) with a stirring speed of 200 rpm for 240 minutes reduced the COD concentration of leachate from 1131.28 mg/L to 456.94 mg/L with an adsorption efficiency of 59.61%.

Keywords: adsorption, ale-ale shells, COD, leachate, PCC.

ABSTRAK

Limbah air lindi dari tumpukan sampah yang terdapat di Tempat Pembuangan Akhir (TPA) memiliki konsentrasi Chemical Oxygen Demand (COD) yang tinggi. Dampak yang ditimbulkan dari tinggi nya konsentrasi COD tersebut adalah terjadi penurunan konsentrasi oksigen terlarut dalam perairan. Pengolahan lindi secara sederhana dilakukan menggunakan metode adsorpsi dengan adsorben yang berasal dari limbah makanan. Pada penelitian ini digunakan adsorben Precipitated Calcium Carbonate (PCC) dari cangkang kerang ale-ale. Tujuan penelitian ini untuk mengetahui pengaruh variasi ukuran partikel dan suhu kalsinasi dalam pembuatan PCC terhadap rendemen yang dihasilkan serta mengetahui kemampuan adsorpsi adsorben PCC dalam menurunkan konsentrasi COD. PCC yang dihasilkan dikarakterisasi menggunakan spekrofotometer infra merah (FTIR) dan difraktometer sinar-X (XRD). Penentuan konsentrasi COD dilakukan secara titrasi permanganometri. Rendemen optimum PCC sebesar 57,75% diperoleh dari cangkang kerang ale-ale ukuran partikel 40 mesh dengan suhu kalsinasi 800°C. PCC memiliki gugus fungsi C-O yang terdapat pada bilangan gelombang 1403 cm^{-1}, 873 cm^{-1}, dan 713 cm^{-1}. Karakterisasi XRD menunjukan adanya fasa kalsit dengan intensitas puncak yang tinggi pada 2θ = 29,38°. Adsorpsi bahan organik pada lindi oleh PCC (4,5 g/50 mL) dengan kecepatan pengadukan 200 rpm selama 240 menit mampu menurunkan konsentrasi COD lindi dari 1131,28 mg/L menjadi 456,94 mg/L dengan efisiensi adsorpsi 59,61%.

Kata Kunci: adsorpsi, cangkang kerang ale-ale, COD, lindi, PCC.

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1. INTRODUCTION

The leachate from TPA Batu Layang, Pontianak, West Kalimantan has a high concentration of COD. It indicates that many organic compounds decomposed chemically in water using dissolved oxygen. The more organic compounds that decomposed chemically, the lower the dissolved oxygen concentration, which can impact the water quality (Sumantri and Cordova, 2011). Leachate is wastewater resulting from the dissolution of dissolved matter caused by external water entry into the waste pile (Peraturan Menteri Pekerjaan Umum RI, 2013). Therefore, leachate must be treated to reduce its COD concentration.

The leachate treatment system that has been carried out is to accommodate the leachate temporarily. It is feared that if the garbage pile rosts, it will become a breeding ground for bacteria and disease (Sarwono et al., 2017). In addition, there is a biological leachate treatment using aerobic and anaerobic bacteria to carry out the decomposition process of the leachate. However, this biological leachate treatment produces methane gas and residual sludge that requires further treatment (Said and Hartaja, 2015). Another alternative for leachate treatment is physicochemical treatment employing the adsorption method (Indrayani and Rahmah, 2018).

Adsorption is the removal of dissolved components in a fluid that occurs on the surface of the adsorbent (Setianingsih, 2018). The adsorption process is simple and does not generate new pollutants. The adsorbent used in this study was Precipitated Calcium Carbonate (PCC) from ale-ale shells (*Meretrix meretrix*) from Suka Bangun Village, Ketapang Regency, West Kalimantan. PCC results from a chemical reaction involving $CaCO_3$-containing materials (Jamarun et al., 2007). PCC has a greater degree of purity than other $CaCO_3$-containing materials because it is produced through chemical reaction stages (Erdogan and Eken, 2017). PCC is produced through calcination, hydration, and carbonation. It is believed that PCC adsorbent from ale-ale shells reduces the COD concentration of leachate. Research conducted by Elystia et al. (2016) using PCC from blood clam shells showed that the adsorbent reduced the concentration of organic compounds in peat water with an adsorption efficiency of 99.86% at a composition of 5 g with a stirring speed of 150 rpm for 30 minutes.

This research used PCC adsorbent from ale-ale shells. PCC adsorbents were prepared with variations in particle size and calcination temperature. The adsorption process was carried out in batches on an adsorbent mass of 4.5 g/50 mL with a stirring speed of 200 rpm for 240 minutes. This study aims to determine the variation of particle size and optimum calcination temperature on PCC yield in the adsorption of organic compounds in leachate from TPA Batu Layang.

2. MATERIALS AND METHODS

2.1. Materials

The materials used were nitric acid (Merck), oxalic acid (Merck), sulfuric acid (Merck), potassium permanganate (Merck), sodium carbonate (Smart-Lab), and ale-ale shells waste from Suka Bangun Village, Ketapang Regency, West Kalimantan.

The tools used were various types of beakers, 40, 60, 80, and 100 mesh sieves, hotplate, hammer mill, magnetic stirrer, analytical balance, oven, Fourier Transform Infra-Red spectrophotometer (FTIR) (Frontier Perkin Elmer FT-IR), UV-Vis spectrophotometer (UV-2600 Shimadzu), thermometer up to 110°C, and X-Ray Diffraction (XRD) (XPERT PRO PANalytical PW30/40).

2.2. Synthesis of Precipitated Calcium Carbonate (PCC) (Azkiya et al., 2016)

Ale-ale shells were washed, dried with various particle sizes of 40 mesh, 60 mesh, and 80 mesh, and calcined at a temperature of 800°C for 4 hours. A total of 5.6 g of each calcined product was added to a beaker glass and added with 20 mL of 6 M HNO_3 and distilled water until the volume reached 200 mL, then stirred using a magnetic stirrer at 700 rpm 65°C for 30 minutes. After that, it was filtered to separate the filtrate and added with 150 mL of 1.5 M Na_2CO_3 solution slowly at a flow rate of 2.5 mL/minute for 60 minutes. The precipitate formed was filtered and washed with distilled water to pH 7 and then dried in an oven at 105°C for 3 hours. The same steps were carried out for variations in calcination temperature of 900°C and 1000°C. The yield of $CaCO_3$

obtained was then calculated using the following equation:

$$\% \, yield = \frac{mass\ of\ product\ obtained}{theory\ mass} x\ 100\% \quad (1)$$

2.3. Adsorbent Characterization

The adsorbent was characterized using XRD instruments to determine the crystalline phase and FTIR to determine the functional groups in the adsorbent.

2.4. Leachate Characterization

The COD concentration of leachate before and after adsorption was analyzed based on SNI 06-6989.22-2004.

2.5. Organic Compound Adsorption in Leachate Using PCC Adsorbent

Adsorption was carried out on 50 mL leachate using 4.5 g of PCC adsorbent. The adsorption process was carried out in batches at 200 rpm for 240 minutes. The resulting filtrate was measured for its COD concentration to determine the efficiency of removing organic compounds from leachate based on Equation (2).

$$\%R = \frac{C_{in} - C_{out}}{C_{in}} x100\% \quad (2)$$

3. RESULTS AND DISCUSSION

The preparation of PCC begins with a calcination process that aims to release CO_2 gas and decompose organic components contained in ale-ale shells to initiate the decomposition of $CaCO_3$ into CaO (Cahyaningrum et al., 2017). The mass of calcined ale-ale shells decreased from their original state due to releasing CO_2 gas after the calcination process (Amin and Kurniasih, 2016). CaO obtained from the calcination is hygroscopic, which can absorb moisture from the air after being removed from the furnace (Khaira, 2011). The mass loss after the calcination is presented in Table 1. The reactions that occur in the calcination process follow Equation 3.

$$CaCO_{3(s)} \leftrightarrow CaO_{(s)} + CO_{2(g)} \quad (3)$$

Based on Table 1, the percentage reduction in the mass of ale-ale shells produced was not significantly different because the time required for the calcination process for 4 hours was sufficient to decompose $CaCO_3$. It is evidenced in Fig. 1b. The XRD diffractogram produces peaks of CaO and $Ca(OH)_2$ according to ICDD 98-002-6959 for CaO and ICDD 98-020-2228 for $Ca(OH)_2$. The presence of $Ca(OH)_2$ occurs because the hygroscopic CaO has absorbed water vapor from the air. Based on the XRD characterization, the calcination process at 800°C has completely decomposed $CaCO_3$ into CaO, which is indicated by the absence of $CaCO_3$ minerals.

The utilization of HNO_3 as a solvent in the preparation of PCC is a modification of the PCC preparation using the caustic soda method by Azkiya et al. (2016). Modification with acidic solvents could increase the solubility of CaO compared to hydration with H_2O alone. Research by Zikri et al. (2015) in the PCC preparation using HNO_3 as a solvent found that the PCC yield was higher than that of other acid solvents such as HCl and CH_3COOH. Arief dan Jamarun (2009) tested various types of acids (HCl, HNO_3, and $HClO_4$) and found that the highest PCC yield was obtained from using HNO_3. The dissolution of CaO with HNO_3 will produce $Ca(NO_3)_2$ salt, which has a high solubility level to increase the yield of PCC produced (Meilianti, 2017). The reaction that occurs follows Equation 4.

$$CaO_{(s)} + 2HNO_{3(aq)} \leftrightarrow Ca(NO_3)_{2(aq)} + H_2O_{(l)} \quad (4)$$

When Na_2CO_3 solution is added to the $Ca(NO_3)_2$ filtrate, the solution gradually becomes cloudy, and the turbidity increases as more Na_2CO_3 solution is added. It indicates the process of crystallization of $CaCO_3$ in a supersaturated solution condition. The reactions that occur are:

$$Ca(NO_3)_{2(aq)} + Na_2CO_{3(aq)} \rightarrow CaCO_3\downarrow_{(s)} + NaNO_{3(aq)} \quad (5)$$

Based on Reaction (5), the $CaCO_3$ product resulting from the precipitation process was the PCC. This study produced PCC with a pH of 12, so it must be washed with distilled water to achieve a neutral pH. $CaCO_3$ was washed with distilled water because the solubility of $CaCO_3$ in water is very small (Perry, 1984). After the pH of $CaCO_3$ was neutral, it was filtered using filter paper whose mass was known to separate the $CaCO_3$. The yield of $CaCO_3$ obtained as PCC is presented in Table 2.

Table 1. Percentage of mass loss

Particle size	Calcination temperature		
	800°C	900°C	1000°C
40 mesh	43.93%	44.36%	44.54%
60 mesh	43.91%	44.30%	44.48%
80 mesh	43.84%	44.16%	44.24%

Table 2. Yield of PCC

Particle size	Calcination temperature		
	800°C	900°C	1000°C
40 mesh	57.75%	57.51%	57.87%
60 mesh	58.20%	57.04%	56.98%
80 mesh	57.70%	58.12%	56.87%

Based on Table 2, the yield of PCC produced is not significantly different from the influence of particle size and calcination temperature. Therefore, the characterization and adsorbents production was carried out on PCC produced from 40 mesh ale-ale shells with a calcination temperature of 800°C. Based on the diffractogram in Fig. 1c, PCC has a peak of $CaCO_3$ (calcite). It is in accordance with research by Malia (2018) that the crystal phase formed in PCC is calcite. Typical characteristics of calcite based on ICDD 01-076-2712 have a high peak intensity ranging from 2θ = 29.39°.

The resulting PCC has a C-O functional group with wave numbers of 1403 cm^{-1}, 873 cm^{-1}, and 713 cm^{-1}, which is in accordance with the interpretation of the functional group in Table 4. C-O at wave numbers 1420 cm^{-1}, 872 cm^{-1}, and 710 cm^{-1}. Based on Fig. 2b, the resulting PCC has a higher degree of purity than the ale-ale shells, indicated by a sharper peak. PCC in this study functions as an adsorbent due to the attractive force generated by the C-O group. It occurs because of the difference in electronegativity between C and O atoms. Atom O has a greater electronegativity (Atkins et al., 2010). Due to the polarity of the C-O group on PCC, the polar adsorbate will be strongly bound (Hasyim, 2015).

The initial COD concentration of the Batu Layang TPA leachate was 1131.28 mg/L. The decrease in COD concentration using PCC adsorbent resulted in an adsorption efficiency of 59.61% with a COD concentration of 456.94 mg/L, followed by an insignificant decrease in color intensity, as shown in Figure 3. The change in color intensity was based on the physicochemical activation process on the PCC adsorbent. According to Rahimawati et al. (2019), there was a decrease in the color intensity of drilled well water using physicochemical activated blood clam shell adsorbents because it can remove impurities that cover the pores of the adsorbent.

Changes in color intensity after adsorption using PCC adsorbent were measured at the maximum wavelength using a UV-Vis spectrophotometer. The maximum wavelength of leachate before adsorption was 254.6 nm, and after adsorption was 241.8 nm (Fig. 4). Based on this, there is a hypochromic shift with a smaller maximum wavelength because there is no auxochrome bound to the chromophore to form hydrogen bonds (Suhartati, 2013).

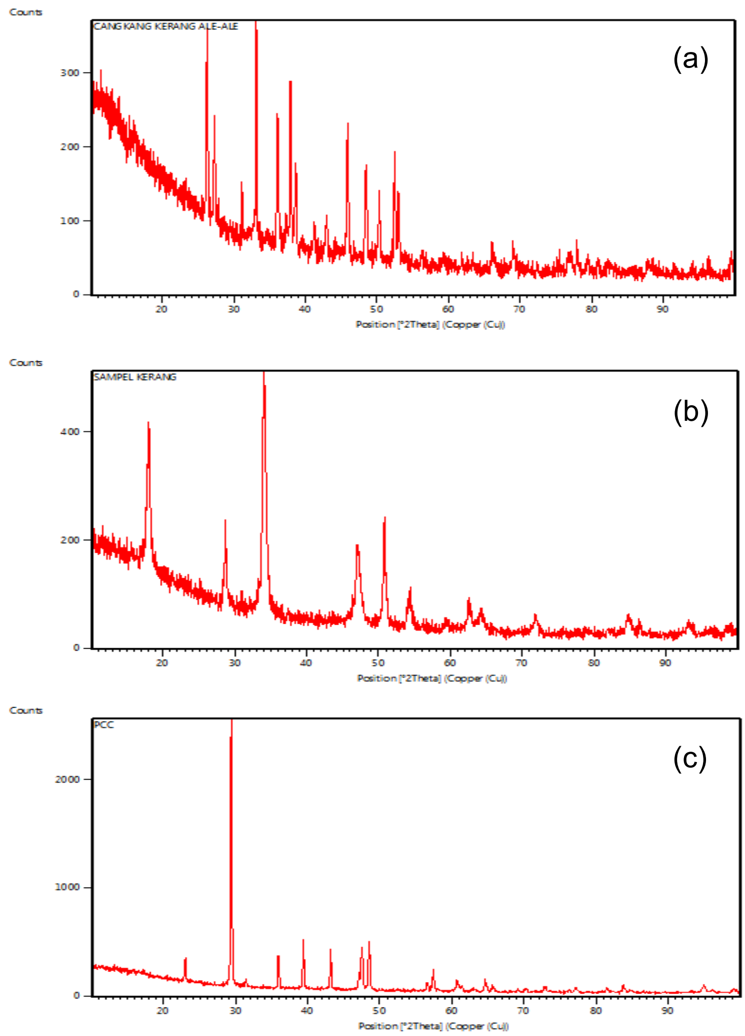

Figure 1. XRD diffractogram (a) ale-ale shells, (b) 40 mesh ale-ale shells after calcination at 800°C, and (c) PCC from 40 mesh ale-ale shells and 800°C calcination temperature

Table 3. Crystal phase interpretation

Sample	Crystal phase	2θ
Shells of ale-ale	Aragonit ($CaCO_3$)	26.18°, 27.22°, 33.12°, 36.10°, 45.87°, 48.41°, and 52.42°
Shell of ale-ale after calcining	Portlandite ($Ca(OH)_2$)	17.97°; 28.66°, 34.06°, 47.08°, 50.77°, 59.37°, 62.44°, 71.90°, and 84.60°
	Lime (CaO)	54.38° and 64.18°
PCC	Calcite ($CaCO_3$)	22.99°, 29.38°, 35.95°, 39.39°, 43.14°, 47.52°, 48.50°, 57.39°, and 64.65°

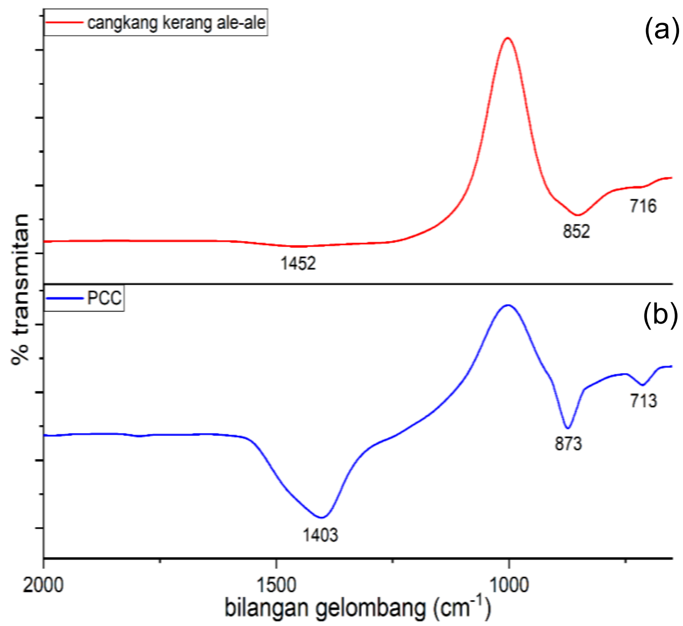

Figure 2. FTIR spectra of (a) ale-ale shells and (b) PCC

Table 4. Functional group interpretation

Sample	Wave number (cm^{-1})	Functional group	Reference
Ale-ale shells	1452	C-O	Kamba, et al., 2013 Ramasary, et al., 2017
	852	C-O	
	716	C-O	
PCC	1403	C-O	Barhoum, et al., 2014 Munawaroh, et al., 2019
	873	C-O	
	713	C-O	

(a) (b)

Figure 3. Leachate (a) before adsorption and (b) after adsorption using PCC

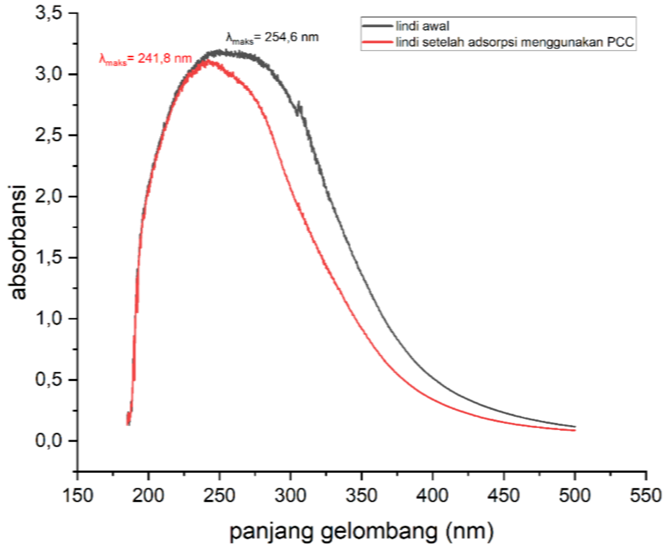

Figure 4. UV-Vis spectra of leachate before and after adsorption

4. CONCLUSIONS

PCC yields resulting from each variation in particle size and calcination temperature were not significantly different. The optimal yield at a particle size of 40 mesh with a calcination temperature of 800°C was 57.75%. The resulting PCC had a C-O functional group and a calcite crystal phase based on the characterization results. PCC adsorbent with a mass of 4.5 g with a stirring speed of 200 rpm for 240 minutes was able to reduce the COD concentration of 50 mL leachate to 456.94 mg/L with an adsorption efficiency of 59.61%. The COD concentration decreased due to the polar adsorbate binding by the polar C-O group on the PCC adsorbent.

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