

ADSORPTION OF CYANIDE FROM CASSAVA WASTEWATER USING CALCINED AND ACTIVATED OYSTER SHELL ASH

ABSTRACT

Calcined ash and activated ash adsorbents were prepared from oyster shell. The physico-chemical properties of the prepared calcined oyster shell ash (COSA) and activated oyster shell ash (AOSA) were obtained using ASTM standards and Sears method. The results show that AOSA is a better adsorbent for removal of cyanide from cassava wastewater than COSA. The adsorption of cyanide from cassava wastewater onto adsorbents (COSA and AOSA) was investigated as a function of pH, adsorbent dosage, contact time, temperature and initial cyanide concentration. The batch study reveals that the adsorption process is strongly pH dependent and maximum cyanide removal is found to occur at pH of 10. The highest percent removal of cyanide from cassava wastewater was found at contact time of 80 minutes and 30°C. The effect of temperature on the adsorption process shows a small increase in the percent cyanide removal followed by a large **decreased** which suggest physical adsorption as the adsorption mechanism. The percent cyanide removal efficiency decreases with increase in initial cyanide concentration and increases with increase in adsorbent dosage.

Keywords: Oyster shell; cassava wastewater; adsorbent; cyanide.

1. INTRODUCTION

Cyanide in form of free cyanide (HCN and **ionized cyanide**) is very harmful to humans and aquatic organisms [1]. A short-term exposure to cyanide causes rapid breathing, tremors and other neurological effects and long-term exposure cause weight loss, thyroid effects, nerve damage and death [2]. The presence of cyanide in effluents can attain considerable concentrations and occur both naturally (biogenes by plants and microorganisms) and from human activities (waste from metal plating, ore leaching, production of synthetic fibres, plastics, pharmaceuticals, coal gasification, metal extraction and cyanogenic crops plants like cassava plants), which forms the major source of contamination of natural water by this compound [3].

The cassava wastewater is highly acidic and has a pH of 2.6. A combined wastewater had been reported as ranging between pH of 3.5 and 5.2 [4]. The cyanide content of cassava plants ranges from 75 to 1000 **mg/kg of CN** depending on the plant variety and soil condition. A large amount of natural

cyanogenic glycosides found in cassava are released during the production of starch from cassava tubers [5]. Cyanide is toxic to most aquatic life and humans even in low concentration [6]. Free cyanide occurs as two species (hydrogen cyanide and **cyanide ionized**), depending on the prevailing pH and temperature of the environmental medium [7;8].

Adsorption process **had** been found to be an efficient and economic process to remove dyes, pigments, and other colourants [9]. In addition, it **had** been found to be superior to other techniques of wastewater treatment in terms of cost, simplicity of design, ease of operation, and insensitivity to toxic substances [10]. Adsorbents such as activated carbon, peat, chitin, clay, and others had been used for adsorption processes [9]. Activated carbon **was** known to be effective for the adsorption of cyanide from industrial and domestic wastewater [4]. Activated carbon acted both as an adsorbent and as a catalyst for the adsorption of cyanide [11].

An oyster is a soft-bodied invertebrate that is found in a shallow water of the sea. It has a

rough irregularly shaped shell. Many oysters are used for food. The oyster creates its own environment by secreting a shell composed of 95% of calcium carbonate. The remainder of the shell is made up of organic material and trace amounts of manganese, aluminium, iron, sulphate and magnesium [12]. [13] investigated the adsorption behaviour of dextrin onto activated oyster shell. [14] studied the use of oyster shells as adsorbents for the removal of lead ion (Pb^{2+}) from aqueous solution. They concluded that oyster shell was a good adsorbent for the removal of dextrin and Pb^{2+} from aqueous solution.

In Nigeria, high level of wastewater from processing cassava is released to the immediate environment and little effort is made to channel and collect the wastewater for proper disposal. It results in the loss of aquatic

2. MATERIAL AND METHODS

2.1 Materials

The oyster shell was gotten from a dump site near Ikot Ekpene main market, Ikot Ekpene, Akwa Ibom State. The tuber of cassava (bitter, TMT 101) was obtained from Michael Okpara University of Agriculture, Umudike, Abia State, Nigeria.

2.2 Methods

2.2.1 Preparation of Carbonized and Activated Carbon from Oyster Shell

The shell was washed thoroughly with distilled water, dried and pulverized. The pulverized shell was sieved with 106 μm standard Tyler sieve. Carbonization was done by using the method of [15] with modifications. A sample (15 g) of the pulverized sample was placed in a Gallenkamp muffle furnace (serial number 1B2613B) which allows limited supply of air at a temperature of 600°C for 3 hours. The carbonized sample was activated using the method of [16] with modifications. In the method, twenty five grams of the charred sample was soaked in 250 mL of 0.5M ortho-

life because it is toxic. Cassava wastewater is a liquid residue which shows high biochemical oxygen demand (BOD), cyanide and mineral contents. Due to increase in seafood consumption, enormous amount of oyster shells are discarded each year from oyster farms, restaurants and various homes. Oyster shells are non-biodegradable and pollute the land and water when discarded indiscriminately. This study aimed at investigating the potential of low cost adsorbent prepared from oyster shell waste in the adsorption of cyanide from cassava wastewater. The physicochemical properties of the adsorbents and adsorbate (cyanide) were studied. The effect of the adsorption parameters such as pH, adsorbent dose, contact time, temperature and initial cyanide concentration were also studied.

phosphoric acid (H_3PO_4) solution. The mixture was thoroughly mixed until it formed a paste. The paste was then transferred to an evaporating dish which was placed in a Gallenkamp Muffler Furnace (serial number 1B2613B) and heated at 700°C. It was allowed to cool and then washed with distilled water to remove the residual ortho-phosphoric acid (H_3SO_4), oven dried at 105°C and stored in air-tight plastic container. The activated oyster shell ash (AOSA) and calcined oyster shell ash (COSA) were characterized.

2.2.2 Batch Experiment

Batch experiments were carried out in a 250 ml conical flask at 30°C in a shaker at 50 rpm using 100 ml of cyanide solution of known concentration and adsorbent doses. The solutions pH were maintained by measuring it intermittently each hour and controlled by drop wise addition of HCl or NaOH solutions. Ranges of operating parameters for various experiments are shown in table 1. All experiments were performed in triplicate and the results average was reported. In each case sample was filtered through a 0.45 μm membrane filter. Filtrate was analyzed for total cyanide ion concentration using picric acid method.

Table 1: Ranges of operating parameters for pH, adsorbent dosage, contact time, temperature and initial cyanide concentration.

Objective of experiment	Operating parameters
To study the effect of pH on cyanide removal	Adsorbent dosage: 3 g/L; contact time: 80 minutes; temperature: 30°C; initial cyanide concentration: 100 mg/L; pH: 2 – 12.

To study the effect of contact time on cyanide removal	Adsorbent dosage: 3 g/L; contact time: 80 – 100 minutes; temperature: 30°C; initial cyanide concentration: 100 mg/L; pH: 10.
To study the effect of adsorbent dosage on cyanide removal	Adsorbent dosage: 1 - 5 g/L; contact time: 80 minutes; temperature: 30°C; initial cyanide concentration: 100 mg/L; pH: 10.
To study the effect of temperature on cyanide removal	Adsorbent dosage: 3 g/L; contact time: 80 minutes; temperature: 25° - 45°C; initial cyanide concentration: 100 mg/L; pH: 10.
To study the effect of initial cyanide concentration on cyanide removal	Adsorbent dosage: 3 g/L; contact time: 80 minutes; temperature: 30°C; initial cyanide concentration: 60 - 140 mg/L; pH: 10.

2.2.3 Procedure for Cyanide Content Determination

To 2 mL of the sample extract (cassava wastewater) in a corked test tube, 4 mL of alkaline picrate solution was added. It was incubated in a water bath at 95°C for 5 minutes. Upon cooling to room temperature, the absorbance of the orange-red colour solution formed was read in a UV/VIS spectrophotometer (model T60) at 490 nm. The cyanide concentration was extrapolated from a standard curve previously prepared with potassium cyanide as standard. The percentage of the cyanide absorbed at equilibrium (% M) and the adsorption capacity of the adsorbent (q_e) can be calculated from Equation 1 and 2 respectively [17].

$$M (\%) = \frac{C_o - C_e}{C_o} \times 100$$

$$q_e = \frac{V}{M}(C_o - C_e)$$

Where C_o is the initial concentration of the cyanide (mg/L), C_e is the concentration of the cyanide at equilibrium (mg/L), V is the volume of the cyanide in contact with the adsorbent and M is the mass of the adsorbent in (g).

3. RESULT AND DISCUSSION

3.1 Initial Properties of the Untreated Wastewater

The initial properties of the untreated wastewater are presented in Table 2. The result shows that the initial concentration of cyanide content in the wastewater falls above the permissible limit of 0.2 mg/L [18]. From this result, it is important to treat the wastewater before disposing it to the environment. The value of the pH of the wastewater shows that the wastewater is acidic.

Table: 2 Physico-chemical properties of the untreated wastewater.

Properties	Values
pH	4.8
Cyanide Concentration in wastewater (mg/L)	100

3.2 Physico-Chemical Properties of Calcined Oyster Shell Ash (COSA) and Activated Oyster Shell Ash (AOSA).

The physico-chemical properties of COSA and AOSA are presented in Table 3. From the results, the pH of COSA and AOSA are closed to neutral. The pH of both adsorbents falls between the range of the acceptable pH for most adsorption applications as reported by [19].

Table 3: Properties of calcined oyster shell ash (COSA) and activated oyster shell ash (AOSA).

Properties	COSA	AOSA
Bulk density (g/cm ³)	0.676	0.704
Iodine number (mg/g)	384.95	401.87
Ash content (%)	2.8	2.4
Moisture content (%)	6.3	5.1
pH	6.8	6.6
Porosity (%)	78.7	85.4
Pore volume (cm ³ /g)	0.0897	0.0974
Surface area (cm ² /g)	883.8	903

Bulk density determines the mass of carbon that can be contained in a given solids capacity and the amount of treated liquid that can be retained by the adsorbent. From the results, AOSA with bulk density of 0.704 g/cm³ compare to that of COSA with 0.676 g/cm³ will be able adsorbed more liquour volume before available pore space is filled better than COSA.

The surface area of AOSA is higher than that of COSA as shown in Table 3. A greater surface area of an adsorbent gives a greater adsorption capacity [20]. Therefore, AOSA adsorption capacity is slightly greater than that of COSA. This is expected because chemical activation normally develops more porosity and gives high surface area than thermal activation [21].

Ash content reduces the overall activity of an adsorbent. The lower the ash content, the better the adsorbent used [22]. From the results, the ash content value of AOSA is lower than that of COSA. Therefore, AOSA is a better adsorbent than COSA.

Porosity describes the number of pores present in a sample and enhances adsorption capacity of the adsorbent [23]. From the results, porosity value of AOSA is higher than that of COSA. Therefore, AOSA has a better adsorption capacity than COSA. Moisture content dilutes the carbon and increases the weight during treatment process. Thus, the lower the moisture contents, the better the adsorbent [23]. Therefore, AOSA with the lower moisture content is better than COSA.

3.3.2 Effect of adsorbent dosage on Cyanide Adsorption

Iodine number is a measure of the micropore content of the adsorbent which are responsible for the large surface area of the adsorbent [24]. From the results, the value of iodine number obtained for AOSA is higher than the value obtained for COSA. The result shows that AOSA has a larger surface area than COSA. Pore volume supports the result of the porosity of the adsorbents as shown in Table 3. Larger pore volumes are advantageous in removing larger molecules from aqueous media [20]. Therefore, AOSA shows better potentials of removing larger molecules from aqueous solution than COSA.

3.3 Effect of Adsorption Parameters on the Adsorption of Cyanide onto Calcine Oyster Shell Ash (COSA) and Activated Oyster Shell Ash (AOSA).

3.3.1 Effect of pH on Cyanide Adsorption

The effect of solution pH on the removal of cyanide for adsorbents (COSA and AOSA) is shown in Figure 1. From the result, percent removal of cyanide initially decreases with pH to a minimum of pH 4 and increases above this pH value until a maximum percent cyanide removal is obtained at a pH value of 10, after which the percent cyanide removal increases again. The highest cyanide removal of 91.48% and 89.38% are observed at pH 10 for AOSA and COSA respectively. This result is in agreement with the study by [23]. Based on the above observation, it can be concluded that the surface charges on adsorbent and behaviour of cyanide in water influence the percent removal of cyanide in wastewater [22]. The effect of adsorbent dosage on the removal of cyanide for adsorbents (COSA and AOSA) is shown in Figure 2. From the results, the percent removal of cyanide increases from a dosage of 1 g/100 mL to 5 g/100 mL for both

adsorbent. The highest percent cyanide removal for both adsorbent occurs at adsorbent dosage of 5 g. The above observations can be explained by the fact that with the increase in adsorbent dose, the number of active sites in unit volume of solution increases, which leads to an increase in the percent removal of cyanide in wastewater [25]. From Figure 2, it is observed that the isotherm of AOSA lies above that of COSA. This indicates that AOSA is a better adsorbent than COSA. However, both

adsorbents are proficient for treating cyanide-laden wastewaters. From the results, the same cyanide removal of 89% using AOSA can also be achieved by using COSA if the adsorbent dosage is increased from 4.7 g/100 mL to 4.9 g/100 mL. Since the difference in adsorbent dosage between the two adsorbent is small, COSA is preferred because of the extra cost of activation.

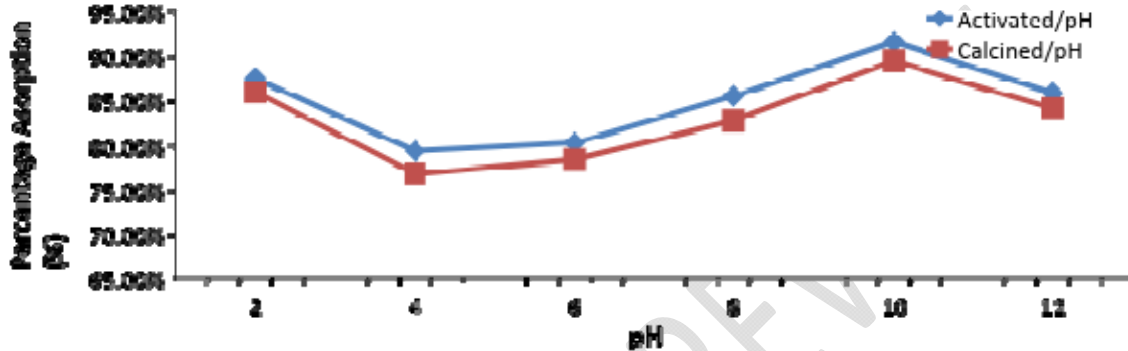


Figure 1: Effect of pH on the adsorption of cyanide onto activated oyster shell ash (AOSA) and calcined oyster shell ash (COSA)

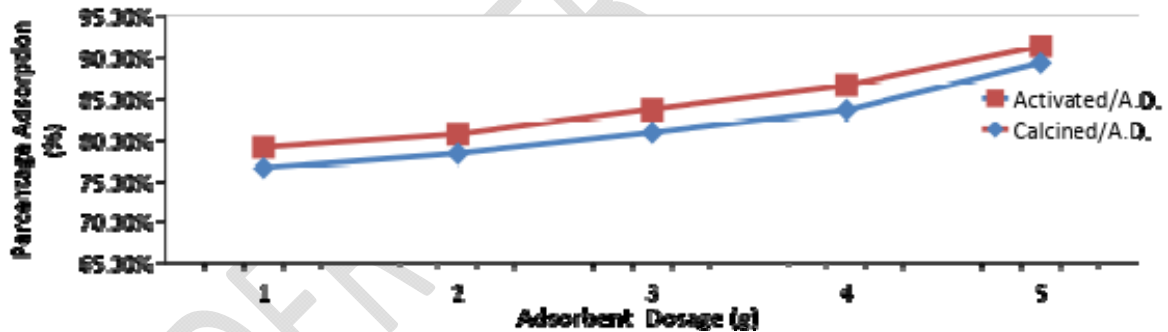


Figure 2: Effect of adsorbent dosage on the adsorption of cyanide onto activated oyster shell ash (AOSA) and calcined oyster shell ash (COSA)

3.3.3 Effect of Contact Time on Cyanide Adsorption

Figure 3 represents the results of the effect of contact time on adsorption of cyanide onto COSA and AOSA. As illustrated in Figure 3, the maximum adsorption is reached at 80 minutes with percent removal efficiencies of 91.13% and 93.33% for COSA and AOSA respectively. AOSA has a better percent cyanide removal than COSA. From the results, it is clear that increasing the contact time

beyond 80 minutes decreases the adsorption performance of both adsorbents. The slow adsorption rate at contact time beyond 80 minutes can be due to the electrostatic hindrance caused by already adsorbed adsorbate species (cyanide) [26]. This result implies high affinity and thus favourability of COSA and AOSA for adsorbing cyanide from industrial wastewater. Above contact time of 80 minutes, percent cyanide removal decreases below 90% for COSA.

3.3.4 Effect of Temperature on Cyanide Adsorption

As presented in Figure 4, the percent removal of cyanide slightly increased from 25°C to 30°C and decreased beyond 30°C which suggest that physical adsorption is the adsorption mechanism. From the results, the

maximum percent cyanide removal of 91.23% and 90.38% for AOSA and COSA respectively were established at 30°C. The rate of adsorption in most adsorption cases decrease with increase in temperature [27]. From the results, the decrease in percent removal of cyanide at temperature higher than 30°C may be due to the fact that at higher temperatures

there is a possibility of desorption of cyanide. This is confirmed by [28,22]. Result in Figure 4.4 depicts the temperature dependency on cyanide removal from industrial wastewater and the adsorption process was exothermic in nature. The percent removal of cyanide for AOSA is higher than that for COSA, as shown by the higher isotherm of AOSA.

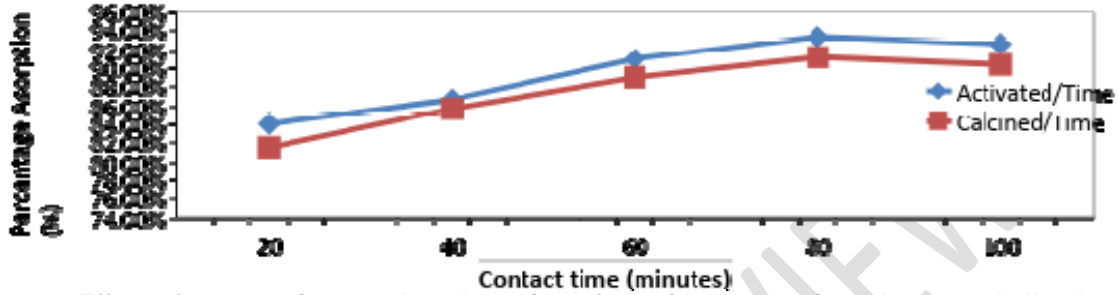


Figure 3: Effect of contact time on the adsorption of cyanide onto activated oyster shell ash (AOSA) and calcined oyster shell ash (COSA)

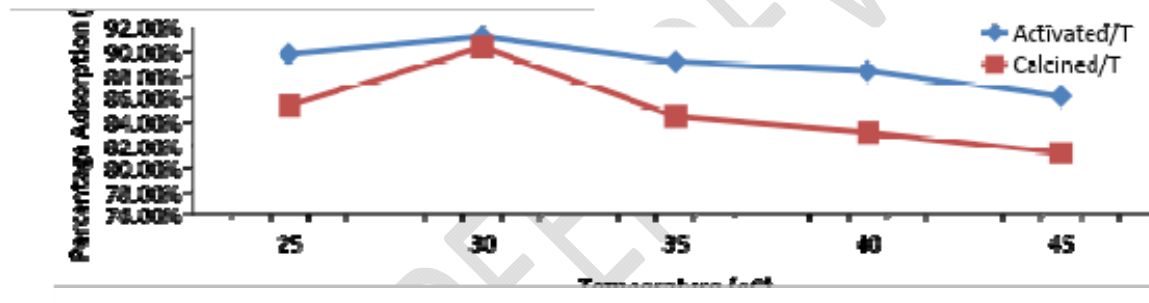


Figure 4: Effect of temperature on the adsorption of cyanide onto activated oyster shell ash (AOSA) and calcined oyster shell ash (COSA)

3.3.5 Effect of Initial Cyanide Concentration on Cyanide Adsorption

The result presented in Figure 5 shows that the percent cyanide removal increases with decrease in initial concentration of the adsorbate (cyanide). The reduction of cyanide removal with respect to increased initial concentration can be explained by the restriction of available free sites for adsorption of cyanide with increased cyanide

concentration in bulk solution for a fixed mass of adsorbent [29]. This result is consistent with other reports [28,22]. From the results, the percent cyanide removal due to initial concentration shows that AOSA is a better adsorbent for cyanide removal in industrial wastewater than COSA, as depicted in the isotherm of AOSA which lies above that of COSA in Figure 5.

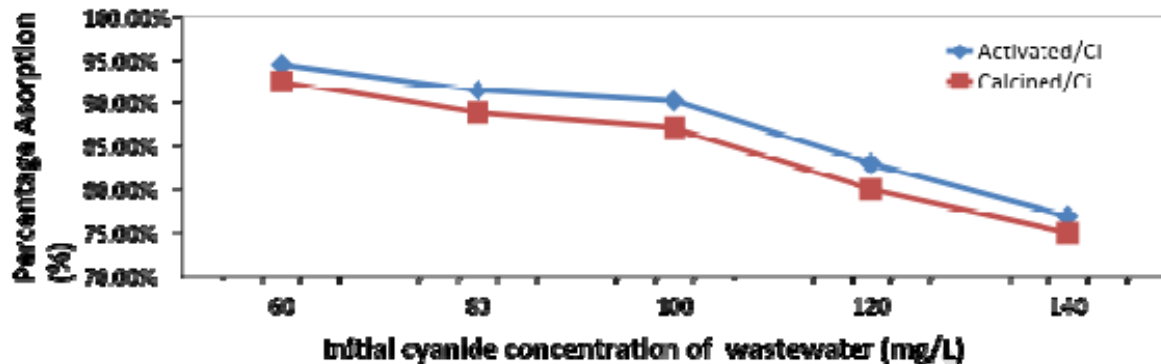


Figure 4: Effect of initial cyanide concentration on the adsorption of cyanide onto activated oyster shell ash (AOSA) and calcined oyster shell ash (COSA)

5. CONCLUSION

Based on the results obtained from the study and subsequent discussion made, the following conclusion can be established.

- i. The results of the initial properties of the **untreated wastewater** shows the concentration of the wastewater is above the permissible limit of 0.2 mg/L and also acidic. Therefore the wastewater should be treated before disposing it to the surroundings.
- ii. The results of the physico-chemical properties of calcined oyster shell ash (COSA) and activated oyster shell ash (AOSA) show that both adsorbents have the potential to remove cyanide from cassava wastewater. The surface area and porosity of AOSA were higher than that of COSA which indicate that AOSA is a better adsorbent than COSA for this adsorption process.
- iii. Adsorption capacities of the adsorbents (COSA and AOSA) are

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