Adsorption of Cyanide from Cassava Wastewater Using Calcined and Activated Oyster Shell Ash

Oto-Obong P. Akpan* and B. R. Etuk

1Department of Chemical and Petroleum Engineering, University of Uyo, Uyo, Nigeria.

Authors’ contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

Article Information

DOI: 10.9734/JERR/2019/v6i116938

Received 09 April 2019
Accepted 21 June 2019
Published 29 June 2019

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 30oC. The effect of temperature on the adsorption process shows a small increase in the percent cyanide removal followed by a large decrease which suggests 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 cassava 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 ionized cyanide), depending on the prevailing pH and temperature of the environmental medium [7,8].

Adsorption process has been found to be an efficient and economic process to remove dyes, pigments, and other colourants [9]. In addition, it has 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 is 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 (Pb²⁺) from aqueous solution. They concluded that oyster shell was a good adsorbent for the removal of dextrin and Pb²⁺ from aqueous solution.

In Nigeria, high level of wastewater from processing of 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 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 on the adsorption of cyanide from cassava wastewater were also studied.

2. MATERIALS 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-phosphoric acid (H₃PO₄) solution and mixed thoroughly to form 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 (H₃PO₄), 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 (100 mg/L) and adsorbent doses (1 – 5 g/L). The pH value of the solution was maintained by measuring it intermittently 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 averaged were reported. In each case sample was filtered through a 0.45 µm membrane filter paper. Filtrate was analyzed for total cyanide ion concentration using picric acid method.

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 (0.5% picric acid and 2% sodium carbonate 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 prepared with potassium cyanide as standard from a range of 0.5 – 50 µg of cyanide. The percentage of the cyanide absorbed at equilibrium (% M) and the adsorption capacity of the adsorbent (qₑ) 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 C₀ is the initial concentration of the cyanide (mg/L), Cₑ 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).

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. |
3. RESULT AND DISCUSSION

3.1 Initial Properties of the Untreated Cassava Wastewater

The initial properties of the untreated cassava 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 cassava 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 ranges of the acceptable pH for most adsorption applications as reported by [19].

Bulk density determines the mass of carbon in a given solid capacity and also determines the amount of treated liquid that can be retained by the adsorbent [20]. 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 liquor 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]. The result shows that AOSA is a better adsorbent than COSA.

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

| Properties               | COSA   | AOSA   |
|--------------------------|--------|--------|
| Bulk density (g/cm³)     | 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 (cm³/g)      | 0.0897 | 0.0974 |
| Surface area (cm²/g)     | 883.8  | 903    |

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 Calcined Oyster Shell Ash (COSA) and Activated Oyster Shell Ash (AOSA)

3.3.1 Effect of pH on cyanide adsorption

The effect of pH on the removal of cyanide for adsorbents (COSA and AOSA) is shown in Fig. 1. From the result, percent removal of cyanide...
initially decreased 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].

3.3.2 Effect of adsorbent dosage on cyanide adsorption

The effect of adsorbent dosage on the removal of cyanide for adsorbents (COSA and AOSA) is shown in Fig. 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 Fig. 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.

3.3.3 Effect of contact time on cyanide adsorption

Fig. 3 represents the results of the effect of contact time on adsorption of cyanide onto COSA and AOSA. As illustrated in Fig. 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 Fig. 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 Fig. 4.4 depicts the temperature dependency on cyanide removal from industrial wastewater [27] 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.

3.3.5 Effect of Initial cyanide concentration on Cyanide adsorption

The result presented in Fig. 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 increase in 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 Fig. 5.
Fig. 1. Effect of pH on the adsorption of cyanide onto activated oyster shell ash (AOSA) and calcined oyster shell ash (COSA)

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

Fig. 3. Effect of contact time on the adsorption of cyanide onto activated oyster shell ash (AOSA) and calcined oyster shell ash (COSA)
4. 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 cassava 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.

Adsorption capacities of the adsorbents (COSA and AOSA) are observed to be affected by pH, contact time, adsorbent dosage, temperature and initial cyanide concentration. The highest percent cyanide removal for pH, contact time and temperature are found at pH 10, 80 minutes and 30°C respectively. The percent cyanide removal decreases with increase in initial cyanide concentration and increases with increase in adsorbent dosage. The percent cyanide increases to 30°C and then decreases with increase in temperature. This result indicates that the adsorption mechanism is chemical adsorption. The maximum percent cyanide removal from cassava wastewater onto COSA and AOSA were 93.22% and 91.05% respectively. The same percent
cyanide removal for AOSA at pH of 10, contact time of 80 minutes and adsorbent dosage of 5 g can also be obtained for COSA at pH, contact time and adsorbent dosage of pH 10.6, 93 minutes and 5.3 g respectively.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Dursun Ay, Calik A, Aksu Z. Degradation of ferrous(II) cyanide complex ions by Pseudomonas fluorescens. Journal of Process Biochemistry. 1999;34(9):901–908.
2. Tang P, Hseu YC, Chou HH, Huang KY, Chen SC. Proteomic analysis of the effect of cyanid on Klebsiella oxytoca. Current Microbiology. 2010;60(3):224-228.
3. Campos MG, Pereira P, Roseiro JC. Packed-bed reactor for the integrated biodegradation of cyanide and formamide by immobilised Fusarium oxysporum CCMI 876 and Methylobacterium sp. RXM CCMI 908. Enzyme Microbial Technology. 2006; 38(1):848–854.
4. Oliveira MA, Reis EM, Nozaki J. Biokinetic parameters investigation for biological treatment of cassava mill effluents. Water, Air and Soil Pollution. 2001;126(3):307-319.
5. Kaewkannetra P, Imai T, Garcia-Garcia FJ, Chiu TY. Cyanide removal from cassava mill wastewater using Azotobacter vinelandii TISTR 1094 with mixed microorganisms in activated sludge treatment system. Journal of Hazardous Materials. 2009;172(1):224–228.
6. Hosetti BB. Metabolic changes in the freshwater fish catlcatla, under copper cyanide intoxication. International Journal of Pharmaceutical and Biological Archives. 2011;2(3):874-879.
7. Ma J, Dasgupta PK, Blackledge W, Boss GR. Temperature dependence of Henry's law constant for hydrogen cyanide: generation of trace standard gaseous hydrogen cyanide. Environmental Science and Technology. 2010;44(8):3028-3034.
8. Smith A, Muddet T. The chemistry and treatment of cyanidation wastes. Mining Journal Books, London, UK. 1991:21-40.
9. Wang HL, Chen JL, Zhai ZC. Study on thermodynamics and kinetics of adsorption of p-toluidine from aqueous solution by hypercrosslinked polymeric adsorbents. Environmental Chemistry. 2004;23(2):188-192.
10. Garg VK, Amita M, Kumar R, Gupta R. Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: A timber industry waste. Dyes and Pigments. 2004; 63(3):243-250.
11. Adams MD. Removal of cyanide from solution using activated carbon. Mineral Engineering. 1994;9(7):1165–1177.
12. Maduka MC, Ibe SN. Bacteriological quality of fresh and smoke-dried oysters sold in creek road market, Port Harcourt, Nigeria. Scientia Africana. 2013;12(1):124-132.
13. Kamalu CIO, Oghome P, Nwaigwe KN, Anyanwu EE. Adsorption behaviour of dextrin onto activated oyster shell. International Journal of Research in Engineering and Technology. 2015;4(3):20-26.
14. Odoemelan SA, Eddy NO. Studies on the use of oyster, snail and periwinkle shells as adsorbents for the removal of Pb2+ from aqueous solution. E-Journal of Chemistry. 2009;6(1):213-222.
15. Ekpete OA, Horsfall M. Preparation and characterization of activated carbon derived from fluted pumpkin stem waste. Research Journal of Chemical Sciences. 2011;1(3):10-17.
16. Njoku VO, Hameed BH. Preparation and characterization of activated carbon from corncob by chemical activation with H3PO4 for 2,4-dichlorophenoxyacetic acid adsorption. Chemical Engineering Journal. 2001;173(2):391-399.
17. Onwuka GI, Ogbogu NJ. Effect of fermentation on the quality and physico-chemical properties of cassava based fufu products made from two cassava varieties NR8212 and Nwangbisi. Journal of Food Technology. 2007;5(3):261-264.
18. World Health Organisation. Maximum Allowable Concentration of Selected Water Quality Variables. Fourth Edition, Wiley Online Library. 2004;48–60.
19. Egwaikhide PA, Akporhonor EE, Okieimen A. Utilization of coconut fibre in the removal of soluble petroleum fraction from polluted water. International Journal of Physical Science. 2007;2(2):47-49.
20. Gumus RH, Okpetu I. Production of activated carbon and characterization from...
snail shell waste (*Helix pomatia*). Advance in Chemical Engineering and Science. 2015;5:51-61.

21. Ajayi OA, Olawale AS. A comparative study of thermal and chemical activation of Canarium schweinfurthii Nutshell. Journal of Applied Science Research. 2009;12(5): 2148-2152.

22. Naveen D, Chandrjit B, Prasenjit M. Study for the treatment of cyanide bearing wastewater using bio adsorbent prunus amygdalus (Almond shell): Effect of pH, adsorbent dose, contact time, temperature, and initial cyanide concentration. International Research Journal of Environmental Science. 2014;3(1):23–30.

23. Tsunatu DY, Azuaga IC, Tickson TS, Jirah EU. Development and characterization of shea butter seed husk carbon black for cyanide bearing wastewater treatment. Journal of Physical and Chemical Sciences. 2015;214:36-42.

24. Gergova K, Petrov N, Eser S. Adsorption properties and microstructure of activated carbons from agricultural by-products by stream pyrolysis. Carbon. 1994;32(4):693-702.

25. Mondal P, Majumder CB, Mohanty B. Effects of adsorbent dose, its particle size and initial arsenic concentration on the removal of arsenic, iron and manganese from simulated groundwater by Fe*3* impregnated activated carbon. Journal of Hazardous Materials. 2008;150(3):695–702.

26. Karthikeyan T, Rajgopal S, Miranda LR. Chromium (VI) adsorption from aqueous solution by Hevea brasiliensis sawdust activated carbon. Journal of Hazardous Material. 2005;124:192–199.

27. Gupta N, Majumder CB, Agarwal VK. Adsorptive treatment of cyanide-bearing wastewater: A prospect for sugar industry waste. Journal of Chemical Engineering. 2013;200:993–1007.

28. Dash RR, Gaur A, Majumder CB. Removal of cyanide from water and wastewater using granular activated carbon. Chemical Engineering Journal. 2009;146:408–413.

29. Katyal S, Thambimuthu K, Valix M. Carbonation of bagasse in a fixed bed reactor: Influence of process variables on char yield and characteristics. Renewable Energy. 2003;28(5):713–725.

© 2019 Akpan and Etuk This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.