SYNTHESIS OF ACTIVATED CARBON FROM ORANGE PEEL FOR THE TREATMENT OF CASSAVA WASTEWATER

JOSHUA BABTUBDE, PATIENCE O. SEDEMOGUN
[1] Department of Chemical Engineering,
Federal University of Technology, Minna, Nigeria
E-Mail: pilalokhoin@futminna.edu.ng Phone No: +234-803-589-1521

Abstract

This research was based on the synthesis of activated carbon from Orange peel for the removal of contaminants (Cyanide) from Cassava wastewater. Fresh Orange peels were dried and impregnated with Phosphoric acid for activation and then carbonized in a Muffle furnace at 600 °C. The effect of impregnation volumes of the activation agent was investigated and the SEM images of the activated carbon showed that the development of the pores increased with increasing impregnation volume showing that the Phosphoric acid was efficient in the creation of well-developed pores. The removal of cyanide from the wastewater by batch adsorption was carried out with the effect of contact time (between 40 to 80 minutes) and adsorbent dosage experimented. Cyanide levels were removed to a considerable extent (up to 68 mg/L, about 22.82%) with the adsorption of cyanide increasing with maximum adsorption at 80 minutes contact time and 6 g adsorbent dosage. This shows that the orange peel activated carbon can be considered for adsorption treatment of cassava wastewater.

Keywords: Adsorption, Activated Carbon, Cassava wastewater, Orange peel, Cyanide.

Introduction

Cassava with scientific name *Manihot esculenta,* also called *manihot*, *manioc, yuca, mandioca, or Brazilian arrowroot*, is a very rich source of carbohydrate. It is a woody shrub originating from South America of the Spurge family, Euphorbiaceae. It is widely cultivated in the tropical and subtropical regions of the world as an annual crop for its starchy root tuber which is edible (IITA, 2018). Nigeria has been constantly rated as the world's largest producer of Cassava with a net production approximately 45 million tonnes as at 2009, nearly 19% of the world's net production (Kolawole, 2010). Cassava's root tuber has multipurpose uses ranging from use for Garri (a common food among the rich and poor in Nigeria), Fufu, Starch, feed for animals, and even production of Bio-fuel (Adekanye *et al.,* 2013).

Cassava is cultivated in Nigeria mainly on the subsistence level (Omotioma *et al.*, 2013). Processing of cassava into edible form involves various steps which include peeling of the tubers, washing of peeled tubers, grating, pressing, fermenting, sieving, roasting and drying of the flakes gotten from grinded tubers (FAO, 2004). The steps stated above particularly the washing of the tubers and pressing produces a huge amount of wastewater (Okunade and Adakalu, 2013; Oghenejoboh, 2015). The wastewater generated from washing of the Cassava tubers holds a huge quantity of inactive substances with low Chemical Oxygen Demand (COD) while that generated from the pressing of the cassava tubers has a high contaminating load of Biological Oxygen Demand(BOD) accompanied by a high cyanide content (Okunade and Adakalu, 2013; Oghenejobo, 2012). Plants, animals and the environment in general are exposed to danger resulting from this high cyanide concentration in the wastewater generated from Garri processing (Oghenejoboh, 2015).

Enough emphasis cannot be laid on the danger posed to human, animals and plants by industrial liquid (wastewater) and gaseous wastes (Adewumi *et al.*, 2016). Cassava processing in Nigeria is practiced mainly by local farmers who don't have the knowledge and expertise to effectively manage the wastewater generated from Garri wastewater; therefore, the wastewater is discharged liberally into drains, open channels, water bodies. This haphazard discharge of the wastewater impacts adversely on the environment as its organic content may contaminate ground water supply and cause excessive growth of Algae in water bodies called Eutrophication (Omotioma *et al.,* 2013).

Cyanide is the major constituent of the wastewater generated (Okafor J. O., 2008). It is in most cases present in cassava waste-water as Hydrocyanic acid and in the unbroken down Cyanogenic glycoside (Oghenejoboh 2012; Onwuka and Ogbogu, 2007). By-products from Garri processing especially the cassava peels contains high concentration of cyanogenic glycosides and free cyanide which is decomposed by rain water or dewdrops which when disposed on the soil leaches into the soil causing changes in soil properties such as Total solids(TS), total organic carbon, Nitrogen and Phosphorus (Okunade and Adakalu, 2013).

Presently, adsorption is extensively applied in environmental treatment applications all over the world which includes wastewater treatment. The capability of certain solids to specially trap specific substances from solutions on their surfaces is the basis of development of the Liquid-Solid adsorption systems. In recent years, research has been done extensively on the synthesis of inexpensive, high capacity adsorbents including several activated carbons. The process involved in the synthesis of activated carbon can be grouped into two: Chemical activation and Physical activation. Chemical activation is a single method of synthesis of activated carbon in the presence of chemical reagents. Physical activation includes carbonization of a carbonaceous substance and by activation of the char in the presence of CO_2 or steam.

An alternative solution to minimize the cost of synthesizing activated carbon is to use plentiful and inexpensive carbon source such as industrial or agricultural waste. Activated carbon synthesized from orange peel has been found with a large surface area and pore volume (Loriane *et al.*, 2017). Orange peel is an abundant source of protein, cellulose and lignin. Tonnes of orange peel are disposed as waste, therefore it becomes necessary to make use of it now that we live in a world where waste disposal is posing a problem. Activated carbon synthesized from Orange peel has emerged as a prospective substitute for the synthesis of activated carbon. (Loriane *et al.*, 2017).

Arami et al., studied the use of Orange Peel as Activated Carbon for the Adsorption of dyes. The effects of initial dye concentration, pH, mixing rate, quantity of Orange peel Activated carbon, contact time at room temperature was studied. The orange peel Activated Carbon had Adsorption capacity of 10.72mg/g and 21.05mg/g at an initial pH of 2 and contact time of 15 minutes for two types of dyes (direct red 23 and direct red 80) respectively. Loriane et al., used Orange peel Activated carbon to remove Phenol from wastewater.

This research entails the treatment of Cassava wastewater using activated carbon synthesized from orange peel for the removal of cyanide. The orange peel activated carbon is synthesized by chemical activation and characterized using Scanning Electron Microscope.

Materials and methods

Activated carbon synthesis

Sample and Reagent Preparation

Orange fruit was bought from a Fruit store opposite Federal University of Technology, Gidan Kwano campus, Minna, Niger State, Nigeria. The Orange fruits were peeled using a knife. The Orange peel was then sundried for 1 day before it was dried in a Gallenkamp Oven at 100^{o}C. The dried Orange peel was ground, after which it was sieved using a 1 mm Sieve. A 7 M solution of Phosphoric Acid was prepared from analytical grade stock solution (14.745 M) of Phosphoric Acid (Sait and Derya, 2015).

Activation

75 g of the sieved orange peel was weighed using an Electronic Weighing Balance and divided into 3 parts of 25 g each. It was then poured into conical flasks labeled A, B, C. 77 ml of 7 M Phosphoric acid was added to the orange peel in conical flask labeled A. 97 ml of 7 M Phosphoric acid was added to conical flask labeled B and 117 ml of 7 M Phosphoric acid was added to conical flask labeled C, for impregnation/activation. The mixture was stirred with a stirrer thoroughly and then transferred into a Hot Water Bath at 85^{o}C and agitation of 120 rpm for 6 hours. Impregnation continued at room temperature for another 24 hours. After impregnation, the samples were washed with water and then filtered using filter paper and funnel. The samples were then dried in an Oven at 110^{o}C for 24 hours (Sait and Derya, 2015).

Carbonization

The Samples A, B, C were divided equally into 2 parts each before carbonization, and thereafter labelled A_1, A_2, B_1, B_2, C_1, C_2. Samples A_1, B_1 and C_1 were placed into crucibles and carbonized at 600^{o}C for 35 minutes and samples A_2, B_2, and C_2 were placed in crucibles and carbonized at 600^{o}C for 45 minutes. The samples were allowed to cool after which they were washed with tap water then distilled water till their pH was between 6 and 7. The washed samples were then dried in the oven for 30 minutes.

Adsorption Process

The cassava wastewater was obtained from Garri Processing factory in Gwari Market, Minna, Niger State, Nigeria. Batch Adsorption method was employed. The effect of contact time and adsorbent dosage were measured. There are 5 samples: Control sample, samples A_1 (3 g and 40 minutes), sample A_2 (3 g and 80 minutes), sample B_1 (6 g and 40 minutes) and sample B_2 (6 g and 80 minutes).

Effect of contact time and adsorbent dosage

For sample A_1, 3 g of orange peel activated carbon was weighed and then mixed with 150 ml cassava wastewater in conical flask and agitated in a hot water bath at 40^{o}C and 120 rpm for 40 minutes. This was repeated for sample A_2 but for 80 minutes.

For sample B_1, 6 g of orange peel activated carbon was weighed and then mixed with 150 ml cassava wastewater in conical flask and agitated in a hot water bath at 40^{o}C and 120 rpm for 40 minutes. This was repeated for sample B_2 but for 80 minutes (Olaoye *et al.,* 2018).

Results and Discussion

3.1 SEM images showing pore structure

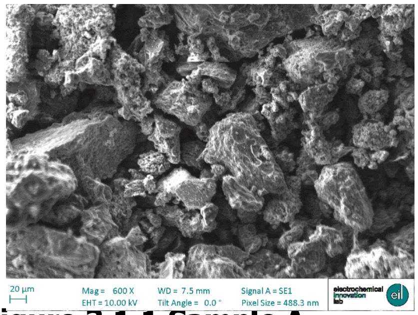


Figure 3.1.1 Sample A_1

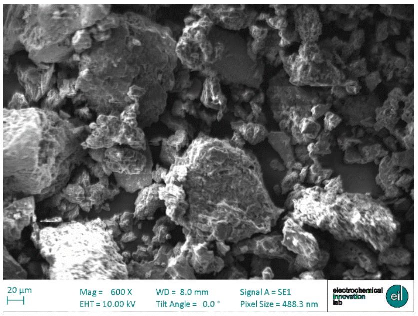


Figure 3.1.2 Sample A_2

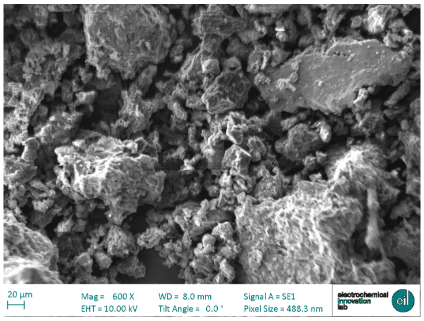


Figure 3.1.3 Sample B_1

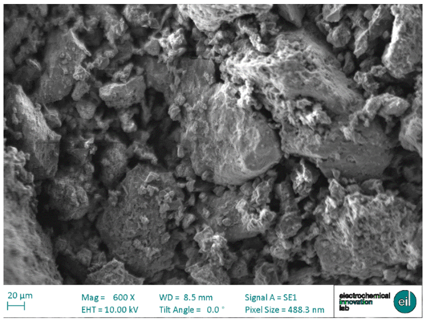


Figure 3.1.4 Sample B_2

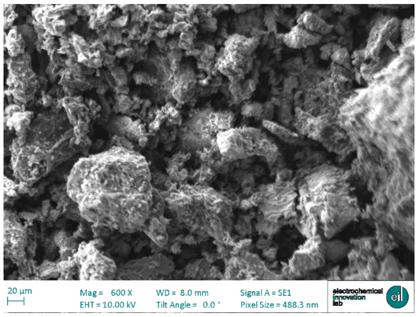


Figure 3.1.5: Sample C_1

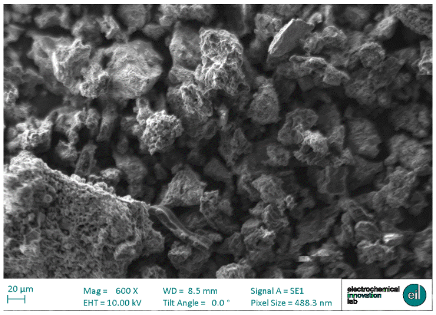


Figure 3.1.6 Sample C_2

SEM images of the orange peel activated carbon samples are shown in Figure 3.1.1 - 3.1.6. It is observed from the micrographs that the external surface of the activated carbons has cracks, crevices, and some grains of various sizes. It can be concluded from SEM images taken during experiments performed at a carbonization temperature of 600°C that porous structures were formed due to the fact that most of the organic volatiles were evolved, leaving behind ruptured surfaces of activated carbon with a number of pores.

The Phosphoric acid, impregnation volumes, activation temperature and carbonization time were effective for the creation of well-developed pores on the activated carbon surface. In the process of chemical activation, the pore diameter and pore volume increase and new pores are created due to the reaction between carbon and the activating agent. Upon increasing the impregnation volumes by 20 ml, the pore diameter enlarged and new micropores were generated. Figure 3.1.6 (sample C_2) had pores with more honeycomb-like structure than other samples on the carbon surface. This shows that formation of well-developed pores increased with impregnation volume and carbonization time no matter how small they are. Cafer (2012) and Sait and Derya (2015) obtained similar results with Phosphoric acid as activating agent.

Orange peel Activated Carbon Yield

The yield of activated carbon is given as a ratio of the activated carbon weight after the final steps of synthesis (washing, drying) to the weight of source material before chemical activation.

Orange peel activated carbon yield = $\frac{Weight\ of\ Activated\ Carbon}{Weight\ of\ Source\ material\ before\ activation}$

The corresponding activated carbon yields for the different impregnation volumes for chemical activation are given in the table below:

Table 3.1 Orange Peel Activated Carbon

S/No	Sample	Impregnation Volume (ml)	Yield (%)
1	A	77	49.28
2	B	97	48.80
3	C	117	46.00

Sample A had the highest activated carbon yield while sample C had the lowest. The yield is seen to decrease with increasing impregnation volume of H_3PO_4. This is due to the removal of volatile matter by H_3PO_4 during carbonization. This trend was also seen in literature (Sait and Derya, 2015). This shows that impregnation volume of 77ml is the best for Activated carbon yield.

The mean Orange peel activated carbon is 48.03%. This shows that a total of 51.97% of the source material was lost during Synthesis as volatile matter and ash. The mean orange peel activated carbon shows that orange peel a good source of Activated carbon and can be used as an abundant source of activated carbon.

Physico-chemical Properties of Cassava wastewater

Physico-chemical properties of the cassava wastewater before and after Treatment are shown in the Table 3.2

Table 3.2: Physico-chemical properties of Cassava wastewater

S/N	Sample	Contact time (minutes)	Chemical Oxygen Demand (mg/L)	Biological oxygen demand (mg/L)	Cyanide (mg/L)	Conductivity (µS/cm)	Total suspended Solid (mg/L)	Total dissolved solids (mg/L)
1	Raw	-	2,648	209	298	10,200	4,550	6,834
2	A_1	40	2015	163	272	9600	2550	6432
3	A_2	80	1987	159	246	9400	2375	6298
4	B_1	40	1877	141	239	9300	2225	6298
5	B_2	80	1802	139	230	9100	1825	6097

From the table above, it can be seen that there's a significant reduction in the Physico-chemical properties (BOD, COD, TDS, TSS, CN and Conductivity).

3.4 Cyanide Removal

The cyanide removal from the cassava wastewater ranged between 26 mg/L (8.73%) and 68 mg/L (22.82%). The cyanide level is very high in the raw sample (298mg/L). Burns *et al.,* (2012) discovered cyanide of about 262 mg/L in cassava. This high cyanide level is due to conversion of cyanogenic glucosides by the enzyme Limarase to Hydro Cyanide. The effect of contact time (between the adsorbent and the adsorbate) and adsorbent dosage were analyzed.

Table 3.4: Cyanide Removal

S/No	Sample	Mass of Adsorbent (g)	Contact time (minutes)	Amount of CN removed (mg/L)	Percentage of Cyanide Removed (%)	Adsorbent capacity, Qe (mg/g)
1	A1	3	40	26	8.73	1300
2	A2	3	80	52	17.45	2600
3	B1	6	40	59	19.80	1475
4	B2	6	80	68	22.82	1700

3.4.1 Effect of Contact time on Cyanide removal

The effect of contact time was analyzed for the adsorption of cyanide on orange peel activated carbon. Contact time used for analysis was 40 minutes and 80 minutes. For each dosage of 3 g and 6 g, the amount of cyanide adsorbed increased, that is, from time 40 minutes and time 80 minutes for both 3 g and 6 g dosage of adsorbent, the amount of cyanide reduced ranging from 26 mg/L and 59 mg/L for 40 minutes and 52 mg/L – 68 mg/L for 80 minutes runs.

This shows that adsorption of cyanide increased with increase in contact time. (Olaoye *et al.,*2018)

Figure 3.3: Effect of Contact time

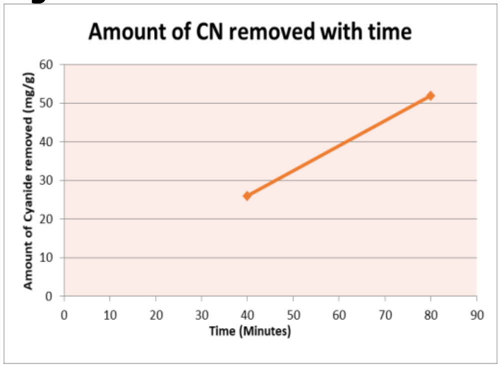
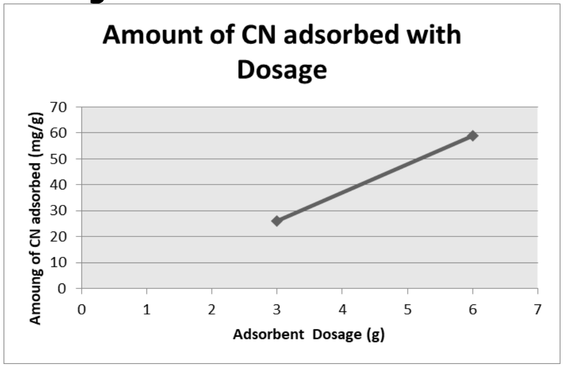


Figure 3.4: Effect of Adsorbent dosage



3.4.2 Effect of Adsorbent dosage on Cyanide removal

The effect of the adsorbent dosage was experimented for the adsorption of cyanide. The adsorbent dosage used for this analysis was 3 g and 6 g. The amount of cyanide adsorbed was seen to increase for each contact time from 40 minutes to 80 minutes. There is a significant increase in amount of cyanide adsorbed (from 3 g to 6 g) with an increase from 26 mg/L to 59 mg/L for 40 minutes and 52 mg/L to 68 mg/L for 80 minutes.

This shows that adsorption of cyanide increases with increase in adsorbent dosage as the adsorbent will have more surface area for adsorption of the cyanide molecules.

The table 3.4, shows the percentage of cyanide removed is seen to increase with increase in contact time and adsorbent dosage.

From the results gotten from the variations of adsorbent dosage and contact time, the highest adsorption of cyanide occurred at 6 g and 80 minutes showing that both contact time and Adsorbent dosage can simultaneously affect the extent of adsorption.

The capacity of the adsorbent which gives the amount of cyanide adsorbed per gram of activated carbon is also shown on table 3.4. Sample A_2 (3 g adsorbent dosage and 80 minutes contact time) had the highest adsorbent capacity.

Conclusion

Phosphoric acid was effective in the production of well-developed pores in the activated carbon samples as shown by the SEM images. The yield of the Orange Peel Activated Carbon reduced with increasing impregnation volume due to creation of more pores with increasing impregnation volume. Orange peel is an abundant, cheap and good source for the production of activated carbon for adsorption of cassava wastewater. Phosphoric acid is a good activating agent for chemical activation of orange peel activated carbon. Adsorption of cyanide took place, with the amount of cyanide removed reaching up to 68 mg/L (22.82% removal). Adsorption increased with increase in contact time. Adsorption increased with increases with increase in adsorbent dosage. This shows that orange peel activated carbon can be used as an adsorbent for the removal of cyanide from cassava processing wastewater although further work should be done by increasing contact time and adsorbent dosage to check the possibility of greater removal percentage.

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