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Research Article

Cyanide adsorption from cassava wastewater onto calcined periwinkle shell

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Abstract: Local cassava processing industries produce large quantities of wastewater containing cyanide which is toxic in nature with negative impacts on the environment when disposed of without treatment. In this study calcined periwinkle shell (CPS) was prepared, characterized and used to adsorb cyanide present in cassava wastewater. Equilibrium studies were conducted in batch set ups to investigate the influence of process variables such as adsorbent dosage, pH, temperature, contact time and initial cyanide concentration on the adsorption process. The highest removal rate of cyanide from cassava wastewater was found to be 78.34% with equilibrium reached at a fixed adsorbent dosage of 3.0 g at contact time of 80 minutes. Cyanide adsorption was also observed to be dependent on pH with the maximum adsorption of cyanide occurring at a pH 10. The percentage of cyanide removed decreased with increase in cyanide concentration. Results from the study confirm calcined periwinkle shell as low-cost and effective adsorbent which can be used for the removal of cyanide from cassava wastewater.

***Keywords**: adsorption, cassava, cyanide, periwinkle shell, wastewater*

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Introduction

Human industrial activities which leads to the generation of large quantities of wastewater (Behnamfard and Salarirad, 2009) has been on the increase, especially wastewater generated from local food processing industries (cassava processing mills) which has become an environmental challenge in developing countries where the processing of staple foods such as cassava is encouraged to provide both food and employment opportunities for the increasing populace (Eletta et al., 2016) . The processes involved in starch production from cassava (Kaewkannetra, 2009) and other allied products such as garri and fufu leads to the release of large quantities of natural occurring cyanoglycosides compounds present in cassava. The concentration of cyanide in cassava has been observed as 100 mg/100 g plant tissue (Onyesom and Okpokunu, 2008) though this may vary depending on the cassava variety (Balagopalan and Rajalekshmy, 1998). Cyanide refers to a compound with a chemical combination of one atom of carbon which is triple bonded to an atom of nitrogen and can be found in naturally occurring organic and inorganic compounds. Despite the toxic nature cyanide, it is found in a wide range of various life forms (Dubey and Holmes, 1995). There have been cases of cassava poisoning recorded in Nigeria with exposure of workers in contact with HCN for more than 5 years resulting in remarkable increase in symptoms which include headaches, throat irritations, body weakness, changes in taste and smell and in cases of severe intoxication could lead to loss of lives (Ifeabunike et al., 2017). Recently the reduction or total elimination of cyanide from wastewater containing large amounts of cyanide by adsorption making use of activated carbon has been considered since the activated carbon is known to act firstly as a sorbent and secondly as an oxidation catalyst of cyanide (Dash et al., 2009). Activated carbon is quite costly thus there is a need for a cheap substitute as a precursor from sea shell wastes. Periwinkles are small edible sea snails that are usually found in the Niger Delta region of southern Nigeria between Badagry in the west and Calabar in the east in lagoons and estuaries (Ejikeme et al., 2017). However, the large amounts of the periwinkle shells are disposed of as wastes and have accumulated over long periods constituting a nuisance in the environment (Badmus et al., 2007).

There is a need to preserve the immediate environment and water bodies where effluents from cassava processing industries which contain cyanide are usually released, since cassava wastewater tends to pollute the soil and subsequently contaminate groundwater (Ogundola and Liasu, 2007) with cyanide levels of root tubers cultivated in farmlands were cassava wastewater is being disposed of being found to increase significantly (Uhegbu et al., 2012). Therefore the effluents must be treated properly before being released into the environment.

In this present study, a low-cost adsorbent prepared from periwinkle shell by thermal activation is used in the adsorption of cyanide present in cassava wastewater. The physico-chemical properties of the prepared adsorbent were analysed. The influence of adsorption variables such as pH, contact time, adsorbent dosage, temperature and initial cyanide concentration were investigated to determine the propensity of the adsorption process.

Materials and Methods

Periwinkle shells were obtained from a dumpsite at a local market in Uyo, Akwa Ibom State. The bitter cassava variety (TMS98/0581) was obtained from the National Root Crop Research Institute, Umudike, Abia State, Nigeria. Analytical grade chemicals without purification were used in this study.

Preparation and calcination of periwinkle shell

The sourced periwinkle shells were properly washed with warm water to remove dirt and subsequently rinsed in distilled water before being sundried for a period of 48 hours. The periwinkle shells were then pulverized into powder using a hammer mill and sieved using a Tyler sieve of mesh size 100 µm. The powdered periwinkle shell was calcined using the method of (Verla et al., 2012) with slight modifications. The powdered periwinkle shells (200 g) was calcined using a Gallenkamp Muffle Furnace set at a temperature of 600°C for 2 hours in limited supply of oxygen and at the end of the completion time removed from the furnace and kept in a desiccator to cool down to room temperature before being stored in an airtight plastic bag. Characterization of the prepared calcined periwinkle shells was carried out to determine the physico-chemical properties.

Characterization of calcined periwinkle shell

Determination of the calcined periwinkle shell specific surface area was carried out using the sears method (Al-Qodah and Shawabkah, 2009). Physical properties of the calcined periwinkle shell such as pH, ash content, moisture content were determined using standard methods. The pH of the calcined periwinkle shell was determined following ASTM D3838-80 where 1 g of calcined periwinkle shell was introduced into 100 ml of distilled water in a 250 mL beaker and stirred continuously for 10 minutes (ASTM D3838, 2011), the calcined periwinkle shell was filtered and the pH of the filtrate solution was determined using a digital pH meter. The calcined periwinkle shell ash content was determined using ASTM D2866-96 method (ASTM D2866, 2011). Moisture content was determined using oven drying method ASTM D2867-09 (ASTM D2867, 2009). The method of Gumus and Okpeku, (2015) was used to determine the bulk density of the calcined periwinkle shell.

Preparation of cassava wastewater and cyanide content analysis

The cassava wastewater was prepared by crushing 100 g of the cassava tuber and soaking overnight in 500 mL of distilled water. The extract was filtered and the remaining solution added to the water used in washing the peeled cassava and stored in a dark container and put in a refrigerator to preserve the quality of the wastewater. The cyanide present in the cassava wastewater was determined using the method of (Onwuka and Ogbogu, 2007) with slight modifications. To 2 mL of cassava wastewater was added 4 ml of alkaline picrate solution, the solution was placed in a water bath at a temperature of 60°C for 5 minutes and allowed to cool. The orange-red colour solution formed was read using a U-V Spectrophotometer (model T60) at a wavelength of 490 nm and cyanide concentration extrapolated from a previously prepared potassium cyanide curve. A digital pH meter (Model 3510, Jenway) was used to measure the pH of the cassava wastewater.

Adsorption experiments

The investigation of the adsorption of cyanide onto the calcined periwinkle shell was conducted using batch techniques. The adsorption experiments were conducted in batches making use of labeled 250 ml Erlenmeyer flasks containing 50 ml of cassava wastewater. The batch units were agitated in an orbital shaker (Model 05-752, Optima) at 150 rpm and pH readings carried out using a digital pH meter (Model 3510, Jenway). The effect of different experiment parameters were conducted by varying pH (2, 4, 6, 8, 10, 12) adjusted using HCl and NaOH solutions, Contact Time (20, 40, 60, 100, 120 minutes), Adsorbent Dosage (2.0, 2.5, 3.0, 3.5, 4.0 g), Temperature (20, 25, 30, 35, 40 °C). The influence of Initial Cyanide Concentration was carried out by preparing stock solution of potassium cyanide solution and diluting the stock solution to get different concentrations (40, 60, 80, 100, 120 mg/L) from the stock solution. At equilibrium time the contents of the labeled 250 mL Erlenmeyer flasks were filtered using a Whatman filter (No 541) with the residue concentration of cyanide determined using a U-V Spectrophotometer. To calculate the adsorption capacity q_e, and the percentage removal efficiency E (%) the following equations were used (Eletta et al., 2016):

$$q_e = \frac{C_o - C_e}{M} \times V \tag{1}$$

$$E(\%) = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

Where :

M (g)	=	amount of calcined periwinkle shell adsorbent used
C_o (mg/L)	=	the initial cyanide concentration of the cassava wastewater
C_e (mg/L)	=	the final cyanide concentration of the cassava wastewater (mg/L)
q_e (mg/g)	=	the adsorption capacity per unit mass of calcined periwinkle shell
V (mL)	=	the volume of cassava wastewater in contact with the adsorbent

Each of the batch adsorption experiments was conducted in triplicates and the average values obtained from the samples were presented.

Results and Discussion

Characterization of untreated cassava wastewater

The results of the characterization of the untreated cassava wastewater are presented in Table 1. The results show that the pH of the cassava wastewater is acidic and within the expected ranges comparable to other studies where the pH of cassava mill wastewater ranges from 3.8-5.7 (Kaewkannetra et al., 2009). The average cyanide concentration of the cassava wastewater is observed to be quite high at 80 mg/L when compared to the statutory limit of 0.2 mg/L required by most countries for the safe discharge of cyanide bearing wastewater into the environment (Kaewkannetra et al., 2009).

Table 1. Cyanide content and pH value of cassava wastewater sample.

Parameter	Value
pH	5.6 ± 0.2
Cyanide Content (mg/L)	80 ± 0.5

Characterization of calcined periwinkle shell

The physico-chemical properties of the calcined periwinkle shell is presented in Table 2. From the results, it is observed that the specific surface area of the calcined periwinkle shell (CPS) is high at 779 m^2/g. The high surface area indicates a high adsorptive capacity for an adsorbent (Evbuomwan et al., 2013). The ash content is one property which is very important in determining the quality of an adsorbent with a good adsorbent having a low ash content as possible (<15%) according to (Sabino et al., 2016) since high ash content reduces the adsorptive capacity of the adsorbent and lowers specific surface area. The ash content of the calcined periwinkle shell is seen as 6.1% which is quite low.

The pH affects the rate of adsorption of an adsorbent. pH of the calcined periwinkle shell is close to neutral generally within acceptable limits of pH of 6-8 for general applications in the treatment of wastewater (Khadija et al., 2008). Bulk density refers to the weight of an adsorbent that can be held within a given volume under certain conditions. A high bulk density is indicative of a better adsorbent as a result of an increase in volume density with the bulk density of the calcined periwinkle shell at 0.58.

Table 2. Physico-chemical properties of calcined periwinkle shell (CPS).

Properties	CPS
Specific Surface Area (m^2/g)	779
Ash Content (%)	6.1
pH	6.8
Bulk Density (g/cm^3)	0.58
Moisture Content (%)	5.6

The moisture content of the calcined periwinkle shell is low at 5.6% which is an indication that the calcined periwinkle shell was properly handled since moisture content dilutes the adsorbent requiring the use of additional weight during the treatment process without affecting the adsorptive capacity (Sivakumar et al., 2012).

Influence of pH

The influence of the pH of the solution as a control parameter on the adsorption of cyanide from cassava wastewater using CPS is presented in Figure 1. The pH is known not only to affect the charges present on the adsorbent surface but also the ionization of species which are found in the solution (Nwoko et al., 2016). From Figure 1 it is seen that the amount of cyanide removed from the cassava wastewater increases with increase in pH. The maximum cyanide adsorbed from the cassava wastewater is seen to occur at pH of 10 with percentage adsorption at 69.03% from 40.05% at a pH of 2. This trend is comparable to the reports of many researchers on the higher rate of adsorption of cyanide at pH values of 9-11 (Agarwal et al., 2013).

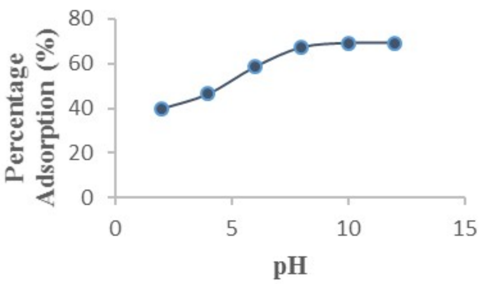

Figure 1. Effect of pH on the adsorption of cyanide onto calcined periwinkle shell (CPS).

It is likely that the surface charge of the calcined periwinkle shell at pH 10 is negative (Badmus and Audu, 2009) and since pKa value for hydrocyanic acid is at 9.4 this implies that in a situation where pH>Pka the HCN dissociates to its basic ionic form $CN^- + H^+$ (Stavropoulos et al., 2013). When the nucleophilic cyanide comes in close contact with a negatively charged adsorbent surface a binding occurs with the anionic functional groups present on the adsorbent surface which results in a significant improvement in the adsorption process. It is likely that the surface charge of the calcined periwinkle shell at pH 10 is negative (Badmus and Audu, 2009) and since pKa value for hydrocyanic acid is at 9.4 this implies that in a situation where pH>Pka the HCN dissociates to its basic ionic form $CN^- + H^+$ (Stavropoulos et al., 2013). When the nucleophilic cyanide comes in close contact with a negatively charged adsorbent surface a binding occurs with the anionic functional groups present on the adsorbent surface which results in a significant improvement in the adsorption process.

Influence of adsorbent dosage

The influence of adsorbent dosage on cyanide adsorption is presented in Figure 2. The results from Figure 2 show a steady rise in the percentage of cyanide removed from 68.16% at an adsorbent dosage of 2.0 g to 77.65% at an adsorbent dosage of 3.0 g. However, above 3.0 g the percentage of cyanide removed was observed to remain constant with minimal decreases in the percentage of cyanide removed. A plausible explanation for this observed trend could be due to the active sites on the calcined periwinkle shells being overlapped at higher dosages which in turn leads to a decrease in the surface areas available for adsorption (Asgari et al., 2012). Hence 3.0 g of adsorbent dosage was selected for subsequent adsorption experiments since heavy dosages might not be cost-effective.

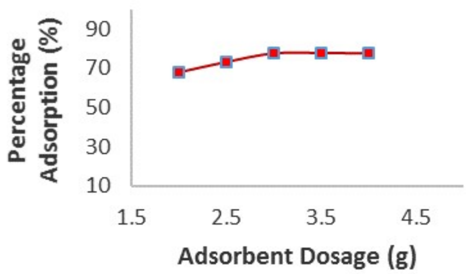

Figure 2. Effect of adsorbent dosage on adsorption of cyanide onto calcined periwinkle shell (CPS).

Influence of contact time

The investigation into the influence of contact time on the adsorption process is presented in Figure 3. From Figure 3 it is observed that the adsorption of cyanide onto calcined periwinkle shell is rapid from 20 minutes to about 80 minutes at which point equilibrium is reached with percentage cyanide adsorbed increasing from 65.99% to 78.34% at 80 minutes. The percentage of cyanide adsorbed after 80 minutes revealed no significant changes in the adsorption performance of CPS remaining at 78.09% and 78.15% at contact times of 100 minutes and 120 minutes. The implication of this phenomena is that the adsorption sites available for binding must have been saturated and exhausted at equilibrium time and probably a reason why more cyanide could not be adsorbed. Similar trends have been reported (Eletta et al., 2016).

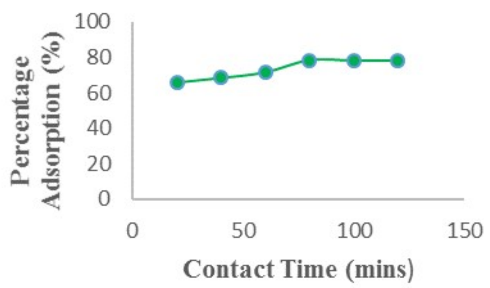

Figure 3. Effect of contact time on cyanide adsorption onto calcined periwinkle shell (CPS).

Influence of temperature

The influence of temperature on the adsorption process is presented in Figure 4. The percentage of cyanide absorbed rises with an increase in temperature from 65.58% to 86.05% at 20°C and 40°C respectively. An increase in cyanide adsorbed could be as a result of reduced solution viscosity due to temperature increase, which increases the diffusion rates of the adsorbates within the pores present in the adsorbent (Agarwal et al., 2013).

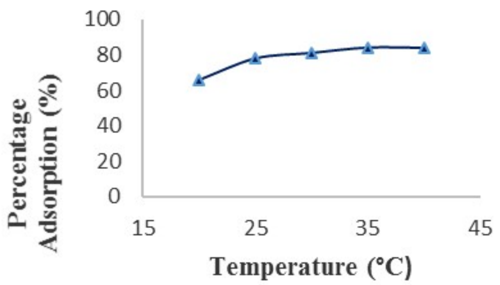

Figure 4. Effect of temperature on cyanide adsorption onto calcined periwinkle shell (CPS).

Influence of initial cyanide concentration

The influence of initial cyanide concentration in the adsorption process is presented in Figure 5. It is observed that at an initial cyanide concentration of 40 mg/L there is a considerable increase in cyanide removal of 76.00%. With increase in cyanide concentration from 40 mg/L to 120 mg/L it is observed that the percentage of cyanide removed at equilibrium decreased to 67.33% at cyanide concentration of 120 mg/L. The significant decrease observed in the percentage removal may be as a result of the surface saturation of the CPS as well as the limited availability of active sites for a fixed dosage. The trend observed is in agreement with other similar findings (Eletta et al., 2016; Nwoko et al., 2016) and shows that CPS can adsorb higher concentrations of cyanide within typical ranges found in cassava mill wastewater.

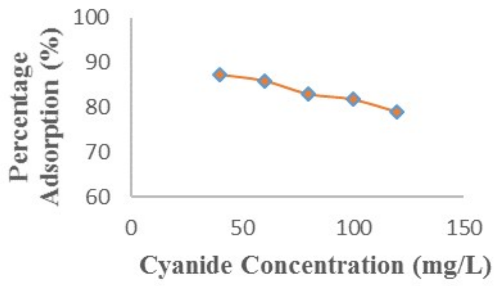

Figure 5. Effect of initial cyanide concentration on cyanide adsorption onto calcined periwinkle shell (CPS).

Conclusion

Calcined periwinkle shell was successfully prepared and used for the adsorption of cyanide present in cassava wastewater. The physico-chemical properties of the calcined periwinkle shell showed the adsorbent has the potential to remove cyanide from cassava wastewater. Investigations carried out on the influence of adsorption parameters reveal that maximum cyanide adsorption is strongly dependent on adsorbent dosage and contact time within a pH solution of 10 with maximum percentage of cyanide removed at 78.34%. The removal of cyanide was seen to increase with rise in temperature. Calcined periwinkle shell proved to be an effective low-cost adsorbent with the potential to adsorb cyanide present in cassava wastewater.

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