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The Efficacy of Banana Peel Activated Carbon in the Removal of Cyanide and Selected Metals from Cassava Processing Wastewater

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Authors' contributions

This work was carried out in collaboration between all authors. Author RAO designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors OIM and HGA performed the laboratory analysis and managed the analyses of the study. Author ODA managed the literature searches and final analysis of the study. All authors read and approved the final manuscript.

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ABSTRACT

The purpose of this study is to investigate the effectiveness of banana peel activated carbon as an adsorbent in the removal of cyanide and selected metals from fresh cassava wastewater collected from the discharge pit. Fresh banana peels were dried, adequately prepared and treated with 0.1 M HCl. Batch experiments were conducted by varying the adsorbent dose from 5 – 20 g and contact time between 10 – 360 minutes to determine the optimum percentage removal of cyanide - CN and selected metals (lead - Pb, chromium - Cr and cadmium - Cd) from the wastewater. Adsorption percentage was found to be proportional to contact time and dosage. Maximum removal percentage of the cyanide and metals at pH 7.2 was 96.45%, 15 g adsorbent in 300 minutes for CN, 98%, 20 g adsorbent in 240 minutes for Pb, 98%, 20 g adsorbent in 180 minutes for Cd while with 5 g adsorbent, initial traces of Cr in the wastewater was no longer detected. The effectiveness of the

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activated banana peel carbon increases with dosage at different contact time for cyanide and the selected metal removal. Thus, at 20 g adsorbent dose and contact time of 300 minutes cyanide and metal ions investigated could not be detected, indicating complete removal. Results indicated the best fitted model as the coefficient of determination (R^2) obtained for the adsorption capacity was 0.93, 0.98, 0.84 and 0.93 for CN, Pb, Cr and Cd respectively. Banana Peel Activated Carbon can efficiently treat cassava wastewater containing multi-ions.

Keywords: Cassava wastewater; heavy metal; adsorbent; banana peels; cyanide.

1. INTRODUCTION

The sustainable removal of cyanide and heavy metals from cassava wastewater has become a major challenge in developing countries. Cyanide is one of the undesirable compound discharged from cassava processing. Cassava wastewater is rich in cyanide and excess cyanide in water and food chain produces a significant toxic level to man, plant and aquatic life. Other heavy metals such as Cd, Pb, Ni, Cr, As, Cu, Fe etc. are continuously discharged from wastewater into the ecosystem, producing a significant toxic impact on man and the environment [1,2,3,4,5]. Some of the first indications of cyanide poisoning in man are rapid/deep breathing or shortness of breath, followed by convulsions (seizures) and loss of consciousness. These symptoms can occur rapidly, depending on the amount taken. The most toxic heavy metals are those that accumulate over time like Pb and Cd, hence requires removal [6]. Pb accumulates in human over time in bones and teeth leading to various diseases like anaemia, encephalopathy, hepatitis and nephritic syndrome [7,8]. Excessive intake of Pb often results in kidney damage, brain damage in fetal and appetite loss [9]. Cd results in kidney failure, carcinogenic or renal disorders [10].The health impact of excess Cr in water often result to a headache, nausea, vomiting and diarrhoea [11]. Cyanide, lead, chromium and cadmium should be kept as low as possible in wastewater before discharge into the environment.

Cassava (*Manihot esculenta Crantz)* is widely grown in the tropical parts of Africa. It was recorded that Nigeria is the largest producer of the cassava roots or tubers in the world with estimated production of about 35 million metric tons (MT) a year [12]. Presently, Cassava is primarily utilized in food products like; paste, biscuits, bread, flour, gari, chips, lafun, akpu, etc., in industrial products like; livestock ration, starch, baby food, jelly, gravies, custard powders, glucose, gum etc. [13]. By implication volume of cassava wastewater indiscriminately discharge per time is very significant.

The conventional methods for the treatment of heavy metals in wastewater include chemical precipitation, chemical oxidation, ion exchange, membrane separation, reverse osmosis, or electro dialysis. These methods are costly, energy intensive and often associated with the generation of toxic by-products. Thus, the adsorption technique has been investigated as a cost effective method for the removal of contaminants and heavy metals in wastewater. The technique has better advantages over others in terms of simplicity, low cost, high efficiency, flexibility and recovery of ions depending on target pollutant to be removed and adsorbent to be employed [1,14,15]. Different agro-wastes are used as adsorbents for heavy metal removal, such as orange peel, potato peel [3] rice straw [16], seaweed [17], wood and bark [18], tea-waste [19], maize corn cob, jatropha oil cake, sugarcane bagasse [20], tamarind hull [21], sawdust [22], rice husk [23], saltbush [24], marine algal biomass [25], olive pomace [26], activated sludge [27], sugar beet pulp [28], wool, olive cake, sawdust, pine needles, almond shells, cactus leaves, and charcoal [29], seafood processing waste sludge [30] and pine bark [31],and banana peel [2,14,32].

Studies have shown that banana peels are effective for the removal of heavy metals and contaminants [33, 34]. Banana peel adsorbent is very efficient and least selective for the removal of metals from multi-element aqueous solution [34]. Banana is a tropical common fruit grown in most countries of the world due to its vitality and sweetness. Globally, over 81.3 M tons is produced per year with the peel accounting to 25 – 30% of the dry matter constituting about 5 M tons of peels wasting per year [35]. The peels are rich in pectin, lignin, cellulose and hemicellulose with the pectin serving as a bonding agent in the adsorption process [35].

Banana peel powder without chemical or thermal activation was adopted as bio adsorbent to remove copper ion from aqueous water at different controlling parameter [1], it was used in the original form to remove copper and lead from synthetic aqueous solutions containing lead and copper in the range of 10-90 mg/L [14]. Another study employed the peels to remove lead ion from lead nitrate solution as well as utilized it to remove cadmium ion [36].

Banana peels were treated with sodium hydroxide NaOH pellets in hot distilled water to remove copper ions from an aqueous solution of water [32]. Several research had also compared the outcome of the treated and untreated peels in heavy metal removal as well as compare the chemically modified form with the non-modified to assess the removal efficiency of lead and copper at various conditions [37]. The efficiency of banana peel biomass was investigated for the removal of lead, copper, zinc and nickel under controlled condition [2]. Banana peel and pretreated fish scales had been used to treat pharmaceutical wastewater by varying the dose of the adsorbent from 1 - 3 g, optimum dose of the banana peel for the treatment was 3 g [38]. One of the most difficult metal to remove by the adsorbent is Arsenic (As), however, Arsenic was effectively removed with the banana peel at an adsorption percentage of ~37% [34]. Previous work revealed that the surface of conventional activated carbon is reactive, capable of oxidation by atmospheric oxygen, with varied surface area [39], however, production of activated carbons from agricultural byproducts has many advantages; the finer the particle size the better the access to the surface area and the faster the rate of adsorption kinetics.

The aim of this research is to determine the effectiveness of banana peel activated carbon in the removal of cyanide and selected metals from freshly collected cassava wastewater and not from prepared aqueous solution usually employed in the most study.

2. MATERIALS AND METHODS

2.1 Materials and Wastewater Collection

Fresh banana peels were collected as a waste product. Amidst the various items and equipment needed were, beakers, distilled water, muffle furnace (V-CLEAR 5 x /11008), crucible, measuring cylinders, filter papers, weighing balance, mortar and pestle, conical flask, spectrophotometer, Marham distillation apparatus, hot plate. The reagents used were of analytical grade. The equipment and instruments used were all calibrated to check their status before and in the middle of the experiments. Wastewater was obtained from disposal pit (Appendix A) of a cassava processing industry located on latitude: N 8°14'40.8668" and longitude: E 4°10'14.5154", in Iluju, Ikoyi- Ile, Oriire Local Government Area of Oyo state, Nigeria.

2.2 Wastewater Characterization

Collected cassava wastewater was characterized for cyanide (CN), lead (Pb), chromium (Cr) and cadmium (Cd). To evaluate the cyanogenic potential of the wastewater, the cyanogenic glycosides was measured using the titrimetric method. The choice of the technique was based on the result of the baseline test conducted. The titrimetric method is suitable for the determination of the concentration of ionic cyanide above 1 mg/L [40]. The procedure described by [41] was adapted accordingly.

The concentration of the selected metals was based on the calibration curve. For this purpose, stock solution (1000 mg/L) of each selected metal ion was prepared by dissolving calculated amounts of each metal salt in a litre of deionized water. For a 100 mg/L solution, 10 mL of standard solution was pipette into 100 mL flask and diluted with deionized water. Six standard solutions were prepared over a range of concentration suitable for each sample through serial dilution of each stock solution. For the wet digestion of sample, 10% of Nitric acid and 10% of Perchloric acid with sample were heated on a hot plate to boil until fumes cease and then allowed to cool and a known volume of distilled water was added to the digested residue before it was filtered. The volume of the filtrate was made up to mark with deionized water, following all procedure described by [42]. Calibration curve for each metal ion analyzed was prepared by plotting the absorbance as a function of metal ion standard concentration. The concentration of the metal ions present in the sample was determined by reading their absorbance using the Buck 200 Atomic Absorption Spectrophotometer (AAS) and comparing it on the respective standard calibration curve.

2.3 Activation of Banana Peels

The fresh banana peels obtained as agro waste was washed with distilled water to remove all dirt, cut into smaller sizes and air - dried to remove the free water before it was oven dried [1]. The dried peels were grinded to powder and sieved.

For the preliminary test, 350 g of the grinded dried banana peels was weighed and placed in a muffle furnace which had been pre-heated to 600°C for 1 hr. Appendix (b) – (d). After carbonization, the sample was allowed to cool to room temperature. 200 g of the carbonized sample was soaked in 200 mL of 0.1 M of HCl, for 24 hr after which the pH was taking with pH meter (SEARCHTEK). The concentration of hydrogen ion obtained was 4.5, indicating acidity. The carbonized activated sample was rinsed with deionized water until the pH of 7.2 was obtained. The wet neutralized activated carbon was finally dried in an oven at 105°C for 24 hr and allowed to cool before use. Similar procedure was adopted by [32,43,44,45,46].

2.4 Treatment of Cassava Effluent with Activated Carbon

Batch treatment method was employed. 1000 mL of cassava wastewater was filtrated into a beaker. 5 g of the activated carbon was added to 300 mL of wastewater, the solution was thoroughly shaken and stirred with a magnetic stirrer at a shaking speed of 150 rpm. The sample was filtered with Whatman filter paper and then concentrations were determined at a contact time of 10, 30, 60, 120, 180, 240, 300 and 360 minutes to determine the optimum adsorption of cyanide (CN) and the metals (Pb, Cr, Cd). The steps were repeated for 10 g, 15 g and 20 g at same time intervals and concentration using standard methods.

The amount of cyanide and metals adsorbed unto the adsorbent at equilibrium or adsorption capacity (q, in mg/g) in the wastewater was determined by using the mass balance equation [1, 2,14, 37,38] giving in equation 1;

$$\text{Cyanide and metal adsorbed } (q) = \frac{V(C_i - C_f)}{m} \quad (1)$$

Where, V is the volume of solution used in litre, m is the amount of adsorbent in g, C_i and C_f in mg/L are the initial and final cyanide/ metal concentrations in solution, respectively while the percentage removal (R_p) of the pollutants from wastewater was determined using equation 2 [1, 38];

$$R_P\ \% = 100 \times \frac{C_i - C_f}{C_i} \quad (2)$$

3. RESULTS AND DISCUSSION

3.1 Characterization of Cassava Wastewater

The initial concentration of cyanide and the selected metals in the collected cassava wastewater is presented in Table 1. From the table, the initial concentration of cyanide (CN) was 30.08 mg/L against the maximum permissible limit of 0.10 mg/L. The initial concentration of cyanide in cassava wastewater was reported to be 38 – 40 mg/L [47]. Cassava wastewater is rich in cyanide, biochemical oxygen demand (BOD), chemical oxygen demand (COD), dissolved and suspended matters amidst other polluting compounds. The concentration of lead (Pb) was 10.73 mg/L against the allowable value of 0.10 mg/L. Contrary to this research, a lower concentration of Pb as low as 0.01 – 0.05 mg/L was obtained at the point of collection in a study [47]. The concentration of Chromium (Cr) was lower (0.0004 mg/L) than the maximum permissible concentration of 0.10 mg/L. Cadmium (Cd) content (15.35 mg/L) was higher than the threshold value of 0.010 mg/L.

3.2 Efficiency of Treatment

The effect of adsorbent dose and contact time on the removal of cyanide and selected metals in

Table 1. Initial concentration of contaminants against disposal standard

Parameters (mg/L)	Initial concentration (mg/L)	*Highest desirable level	*Max. permissible	+LVs in wastewater discharge
Cyanide	30.08	0.05	0.10	
Lead	10.73	0.05	0.10	1
Chromium	0.0004	0.05	0.10	2
Cadmium	15.35	0.005	0.010	0.2

**Malaysian Environmental quality (industrial effluent) regulation, 2009. Applicable to discharge into waters within the catchment area.*

+Limit values (LV) of different parameters, stipulated by Decree-Law no. 236/98 of August 1, 1998 published in "Diário da República".7. (Portugal legislation of the LVs in wastewater discharge

the cassava wastewater was monitored, recorded and presented in Figs. 1 – 4. The concentration of the wastewater in each experiment was kept constant. The adsorbent dose was varied between 5 – 20 g at a contact time of 10, 30, 60, 120, 180, 240, 300 and 360 minutes. The mean concentration of cyanide, lead, chromium and cadmium at the start of the experiment were 30.08 mg/L, 10.73 mg/L, 0.0004 mg/L and 15.35 mg/L respectively. For an adsorbent dose of 5 g and contact time between 10 – 360 minutes, the average concentration of cyanide were reduced to 24.19, 24.09, 22.29, 18.28, 12.31, 7.75, 4.75 and 5.05 mg/L respectively. For lead, concentrations ranged between 2.36 – 8.48 mg/L. The initial concentration of chromium in the cassava wastewater was low. This indicates that the wastewater was within the recommended discharge standard for chromium. However, Cr ions were much more reduced with 5 g adsorbent dosage for the contact time of 10 -180 minutes, after which it was no longer detected. For the adsorbent dose of 5 g, the concentration of cadmium was reduced to 12.18, 11.43, 10.79, 7.9, 6.25, 2.04, 1.18 and 1.5 mg/L for the respective contact time of 10, 30, 60, 120, 180, 240, 300 and 360 minutes. At this initial dosage, the concentration of CN, Pb, Cr and Cd ion was 4.75 mg/L, 2.3 mg/L, 0.0 mg/L and 1.18 mg/L. This indicates that for the cassava wastewater, the longer the contact time the better the cyanide and heavy metal removal. The maximum permissible limit for discharge, however, was not attained at an adsorbent dose of 5 g and contact time between 10 - 360 minutes, except for chromium, as shown in Fig. 1. Traces of chromium in the wastewater was completely removed at a contact time of 240 minutes with 5 g adsorbent.

As the adsorbent dose was increased to 10 g, the maximum to the lowest concentration of cyanide obtained was 22.27 – 2.05 mg/L between 10 to 300 minutes respectively. Beyond 300 minutes the concentration tends to increase. For lead ion, the values recorded was between 5.8 –1.14 mg/L for the respective contact time of 10 – 360 minutes. Change of trend was also observed at a reaction time of 360 minutes while for cadmium the observed concentrations ranged between 10.01 – 0.95 mg/L for the selected contact time of 10 to 360 minutes as shown in Fig. 2. The concentrations of CN, Pb and Cd were 2.05, 1.14 and 0.95 mg/L respectively at an adsorbent dose of 10 g. At this contact time and adsorbent dose, the permissible threshold of 0.10, 0.10, and 0.001 for CN, Pb and Cd respectively were not attained. However, traces of chromium was completely removed at an adsorbent dose of 10 g and contact time of 120 minutes.

Fig. 3 shows the effect of 15 g adsorbent dose at contact time between 10 – 360 minutes. The concentrations of cyanide were further reduced from an initial value of 30.08 to 0.03 mg/L at a contact time of 300 minutes. For lead, the observed values ranged from 0.83 – 4.09 mg/L while for cadmium, the concentrations varied between 0.013 – 6.96 mg/L for the respective contact time. At this adsorbent dosage, chromium was not detected while the concentration of Pb was still above the permissible threshold for discharge, Cd ion was within the threshold for discharge limit at a contact time of 300 minutes.

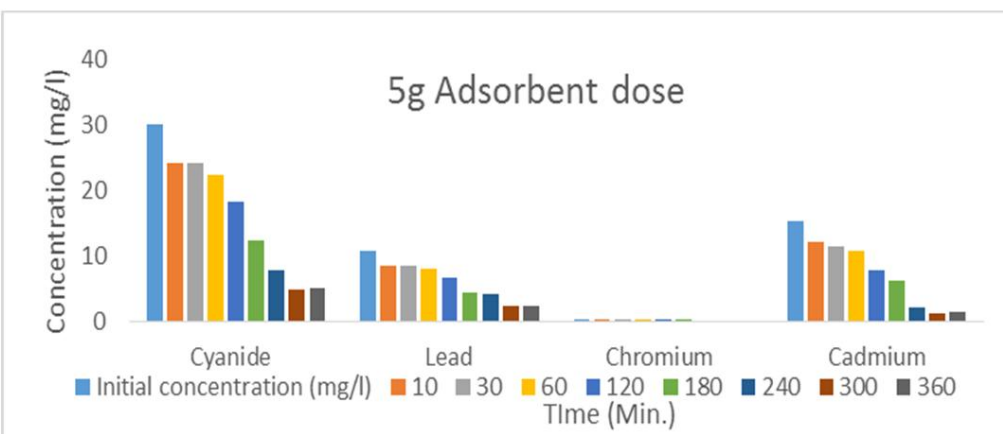

Fig. 1. Concentrations at adsorbent dose of 5 g

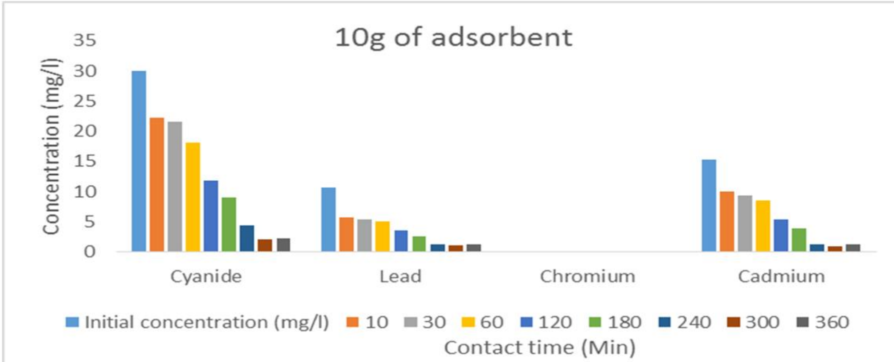

Fig. 2. Concentrations at adsorbent dose of 10 g

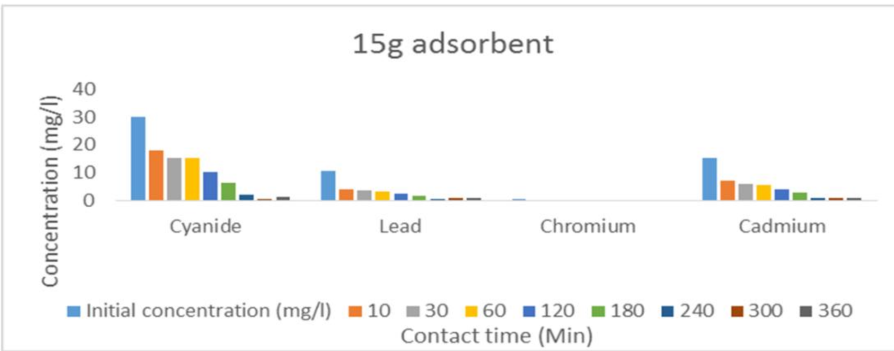

Fig. 3. Concentrations at adsorbent dose of 15 g

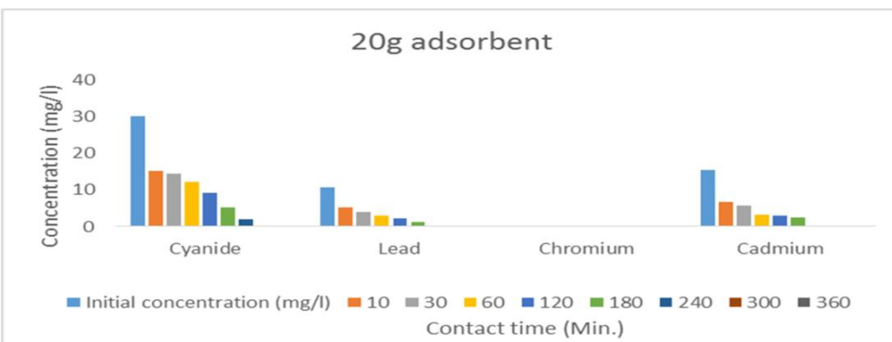

Fig. 4. Concentrations at adsorbent dose of 20 g

With further increase in the adsorbent dose to 20 g (Fig. 4), only traces of the contaminants could be detected. At a contact time of 300 minutes, the concentration of CN, Pb and Cd were 0.02, 0.03 and 0.01 mg/L respectively. Slight variance to the report by [48] where the maximum adsorption of Pb (II) was observed at pH = 7, contact time = 80 min., at adsorbent dose 0.5 g/100 mL and concentration = 10 ppm. Treatment and modification of adsorbent, wastewater type and collection technique often account for variation in the amount of metal adsorption per time. The result of the present research is in line with previous work which reported that the higher the amount of adsorbent the higher the elements' removal efficiency for most of the metals [48]. It is widely reported that banana peels are most efficient adsorbents for the removal of most of the metals and metalloids from multi-element solutions at pH above 2.0 as well as at pH of 5.5 [34].

3.3 Removal Efficiency

The percentage removal of cyanide and the selected metals are presented in Fig. 5. The percentage removal efficiency for cyanide at 5, 10 and 15 g of the adsorbent dose at a contact time of 10 – 360 minutes ranged between 19 – 84.21%, 25.95 – 93.18% and 40.45 – 96.45%, respectively. Cyanide removal increases with increase in adsorbent dosage and reaction time. The optimum removal efficiency for cyanide was 96. 45% at a contact time of 300 minutes for a dose of 15 g adsorbent.

The percentage removal of lead at an adsorbent dose of 5 g varied between 20.98 – 78.61%. At 10 g, removal efficiency ranged between 45.9 – 89.38% while at 15 g and 20g removal efficiency were between 61.9 – 94.43% and 50.61 – 98%, respectively. The higher the adsorbent dose, the higher the percentage removal of lead ion. Optimum percentage removal for the lead was 98% with 20 g absorbent dosage at a contact time of 240 minutes. Previous research reported percentage removal efficiency of 92.52% for lead ions at an experimental solution concentration of 150 mg/L [2]. In this study, lead ion concentrations were much lower than the earlier research reported. The percentage removal for lead using various adsorbents has been reported, adsorption efficiency for lead ion was 90% using dried water hyacinth stems and leaves [49], 21% using orange peel [50] and 8.7% using wheat bran [51].

Due to the low concentration of chromium, the trances of chromium was completed eliminated with an adsorbent dosage of 5 g at 240 minutes. Banana peel activated with 0.5 M H_2SO_4 for wastewater treatment was reported to show the percentage removal of chromium ion (88.9%) at a pH of 6 [52].

The removal efficiency of cadmium at 5, 10, 15 and 20g were between 20.64 – 92.35%, 34.8 – 93.79, 54.67 – 95.37 and 56.48 – 98.4%, respectively. Optimum removal of cadmium was observed at 98.4%. The percentage removal of cadmium using different adsorbents has been reported, maximum removal of 97 % was reported using smectitite clay particle [53], 65% by using cassava waste modified with thioglycolic acid [54] and 7% by using onion modified with HCl / H_2SO_4 [55].

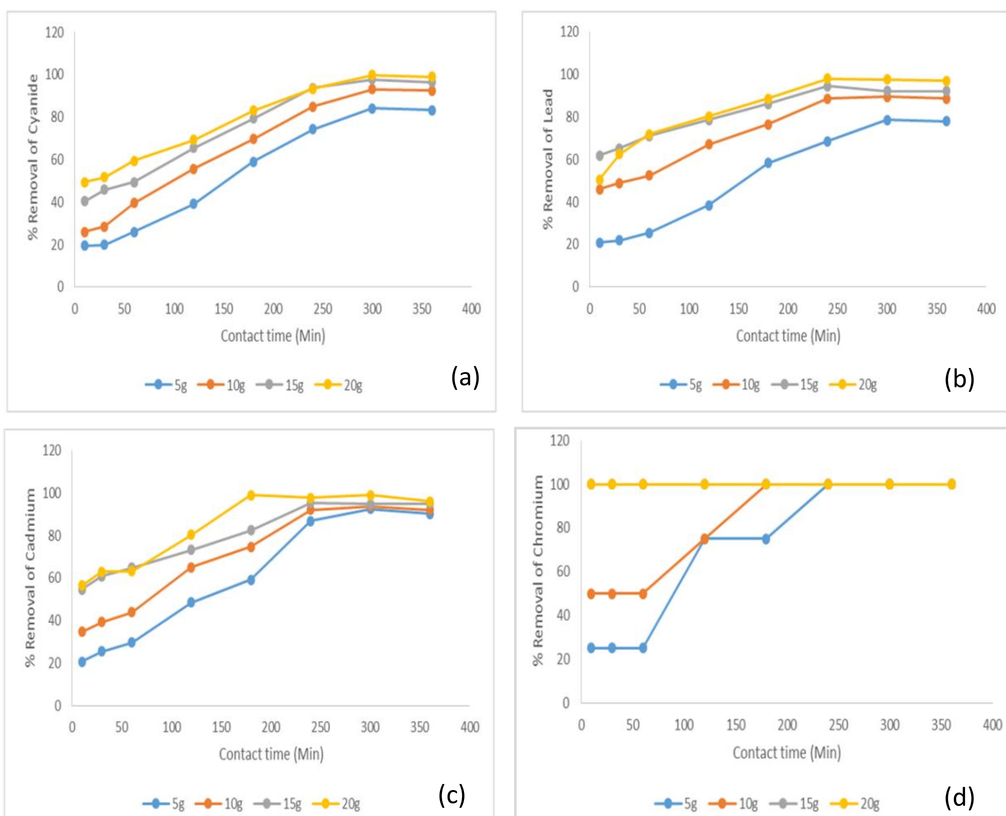

Fig. 5. Percentage removal of (a) Cyanide (b) Lead (c) Cadmium (d) Chromium

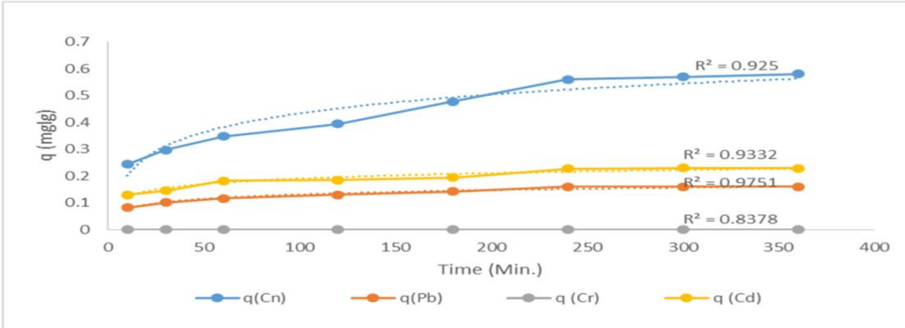

Fig. 6. Cyanide and metal uptake capacity

3.4 Adsorption Capacity

Cyanide and metal uptake capacities at varying time intervals is shown in Fig. 6. The curves were smooth and continuous indicating the formation of absorption of cyanide and metals at the surface of the adsorbent. The adsorption of cyanide, lead, chromium and cadmium increased with increasing contact time. The coefficient of determination (R^2) obtained for the adsorption processes were 0.93, 0.98, 0.84 and 0.93 for cyanide, lead, chromium and cadmium respectively which indicate the best fit for the data obtained.

4. CONCLUSION AND RECOMMENDATION

Banana peel activated carbon is a cheap and effective adsorbent for the adsorption of cyanide (CN) and the selected metals (Pb, Cr and Cd). The effectiveness of the activated carbon dose increases in the order of 20 g>15 g>10 g>5 g at different contact time for each metal removal. Adsorption percentage was found to be proportional to pH, contact time and dosage. Maximum removal percentage of the metals at pH 7.2 was 96.45%, 15 g adsorbent in 300 minutes for CN, 98%, 20 g adsorbent in 240 mins for Pb, 98%, 20 g adsorbent in 180 minutes for Cd while with a 5 g adsorbent, initial traces of Cr was no longer detected. Results obtained indicate best-fitted model as the coefficient of determination (R^2) obtained for the adsorption capacity were 0.93, 0.98, 0.84 and 0.93 for cyanide, lead, chromium and cadmium, respectively. To improve and protect public health, in developing countries, enforcement of law and regulations on cassava wastewater discharge is vital to controlling the level of toxic metals into the environment.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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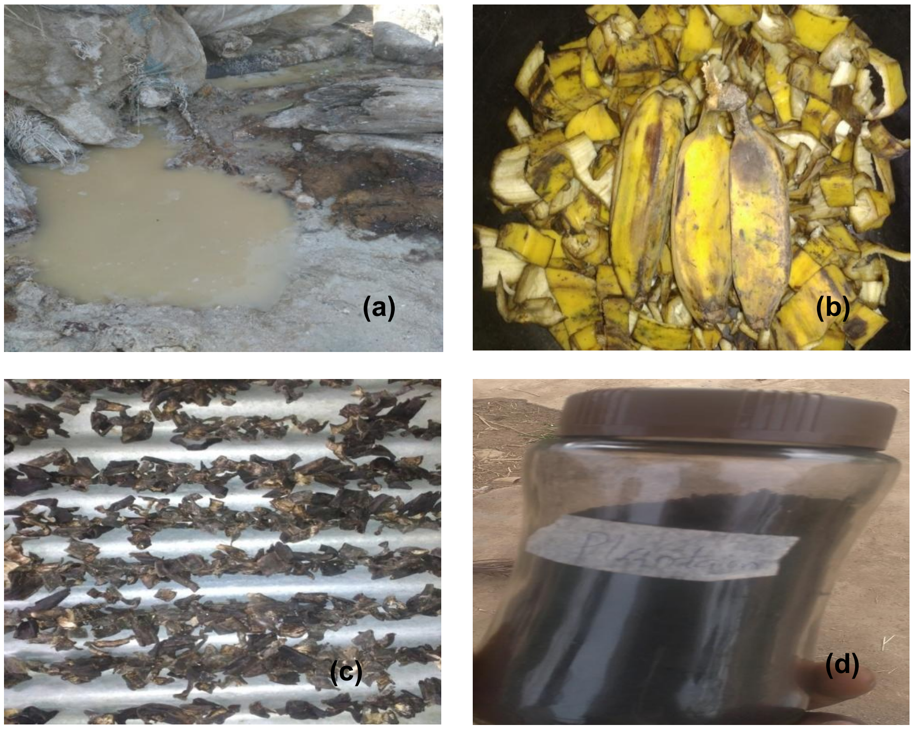
APPENDIX



(a) Cassava wastewater disposal pit (b) Fresh banana peel
(c) Dried banana peel (d) Activated banana peel

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