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Effects of crude oil contaminated-soil on the germination and growth of cowpea *Vigna unguiculata* (L.) Walp

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Abstract

A greenhouse experiment was conducted to investigate the germination and growth response of cowpea (*Vigna unguiculata* (L.) Walp) to soils contaminated at different concentrations of crude oil. This was done with a view to access the impact of crude oil pollution on growth and nutrient content after harvest. The contaminated crude oil polluted soils were prepared at different concentrations of 0.0, 10.0, 20.0, 30.0, 40.0 and 50.0 (w/v) on 5 kg each of air-dried soil collected from the Obafemi Awolowo University Biological Garden rich in organic matter. Each treatment was replicated three times and arranged in complete randomized design. The following parameters, leaf length, breadth and leaf number, N and protein were determined. Results showed that leaf length, breadth and leaf number were significantly higher (p<0.05) recorded in the control pots. The least % N and protein were recorded in the pots with highest crude oil concentration (50.0 ml). The results also showed that increasing crude oil concentration, posed higher risk of edibility of the test-plant and no detectable amount of petroleum hydrocarbon was found in the soils at the end of the experiment. The study concluded that although cowpea germinated and grew well in crude oil-contaminated soils, its nutrient content was impaired and edibility not guaranteed.

Keywords: Crude oil; cowpea; germination; growth response; hydrocarbon.

Introduction

Crude oil exploration and exploitation in Nigeria have evolved through a long history [1]. Oil exploration and exploitation despite its economic importance has however, resulted in the contamination of a significant number of sites with crude oil and petroleum bye-products [2]. United Nations for Environmental Protection (UNEP) report on oil pollution in Ogoni shows that the Niger Delta Area of Nigeria has experienced several contaminated sites with petroleum hydrocarbon, metals pesticides, salts and other related contaminants [3]. Heavy human consumption of crude oil extract such as petroleum, kerosene, gasoline requires deep intense researches into some of accompanied crises which may arise during its exploration.

Petroleum is used in manufacturing a wide range of materials, and it is estimated that the world consumes about 90 million barrels each day [4]. Petroleum industry as an economic sector of Nigeria has created an economy boom for the nation; Nigeria ranks the Africa's largest producer of crude oil and the sixth largest oil producing country in the world with a maximum crude oil production of 2.5 million barrels per day [5]. The consequences and negative impacts caused by crude oil exploration and exploitation have resulted into a global environmental crisis like pollution of the environment and youth restiveness in such polluted area. Pollution is the process of contaminating the earth and atmosphere to such an extent that normal environmental processes are adversely affected [6]. The effects of crude oil on the growth and performance of plants have been reported in many researches. These effects have been observed to occur due to the interference of the plant uptake of nutrients by crude oil and the unfavorable soil conditions due to pollution with crude oil [7-9].

Despite the exploration of crude oil and its importance to the economy of many nations where they are found, the exploration has impacted negatively on the destruction of flora and fauna of such ecosystem. The destruction of food crops, farmlands, fish lakes and subsequent restiveness that follows the unsustainable processes of crude oil exploration in the Niger Delta region requires urgent attention by all and sundry. Various researchers have worked on testing different plants for crude oil or spent engine oil remediation processes [10-12]. However, little work have been done and reported on edible crops grown on or around crude-oil-polluted sites, hence, the need for this study. In Africa, cowpea is the most popular legume and the largest part of world production originates from the Africa continent. Cowpea has been reported by various researchers because of its adaptability to stressful environments where other crops either fail or do not perform well. Cowpea (*V. unguiculata* (L.) Walp.) was chosen as the test plant due to its nitrogen fixing ability, also, as a follow-up on some of the literature reviewed where several reports abound about its potential to surviving polluted soils.

Materials and methods

Seed viability test was done on the seeds to determine the seed viability efficiency which was ascertained to be 90% viable. The procedure for seed viability test followed [13]. This was done by soaking ten (10) viable seeds of cowpea in distilled water containing cotton wool. After 48 hours, nine (9) seeds germinated out of 10 placed in the petri-dish. The experiment was carried out in the greenhouse of the Faculty of Agriculture, Obafemi Awolowo University (OAU), Ile Ife, Nigeria. Surface soil from the OAU Biological Garden was collected and air-dried for 7 days and then sieved using a 2 mm mesh to remove debris. Air-dried and sieved soil (5 kg) was weighed into each of 18 plastic bowls measuring 30 cm by 18 cm (diameter by depth) and perforated at the base to drain water and increase soil aeration [11]. Crude oil obtained from the Nigerian National Petroleum Corporation (NNPC), Eleme, Rivers State, Nigeria with a concentration of 155.88 ppm/L was used as the contaminant.

There were six treatments and each was replicated 3 times. The treatments included: 0.0, 10.0, 20.0, 30.0, 40.0 and 50.0 ml of crude oil and were randomly assigned to bowls arranged in a completely randomized design [14]. The contaminated-soil was watered regularly for a week to allow penetration of the crude oil. Three viable seeds of cowpea (04k-339-1) collected from the seed bank of International Institute of Tropical Agriculture (IITA), Ibadan, Oyo State, Nigeria, were planted in each of the eighteen bowls of the 5 kg soil already polluted with known concentration of crude oil. The experiment was left for one week to establish, thereafter, pruned to two seedlings per pot before the commencement of data collection. Germination results were taken one week after planting (WAP) the seeds, the number of seeds that germinated from each pot was summed up after seven (7) days. Plants were watered regularly and the pots were maintained weed-free.

Plate 1. Experimental pots at one week after planting.

Measurement of germination and growth performance

Germination results were taken one week after planting the seeds, the number of seeds that germinated from each pot was summed up after seven (7) days. The percentage of germination in each treatment was calculated using the formula below [15-17].

Percentage germination:

$$= \frac{\text{Number of seeds that germinated}}{\text{Number of seeds sown}} \times 100$$

Growth performance such as plant height (cm) was measured from the base of the plant to the terminal bud; leaf length (cm) was measured from the base of the leaf to the leaf apex; leaf breadth (cm) was measured at its widest, and number of leaves were measured starting from the second week after planting (2WAP) on a weekly basis using non-destructive sampling method. Also, the number and weight (g) of seeds harvested were also measured by counting and using weighing balance respectively. Thinning of the plants to two plants per pot was done 1WAP to enable limited competition for nutrient by the plants [18]. The plastic pots were perforated at the bottom to allow for aeration. Watering of the plants was done evenly and at regular intervals and also leaching of soil nutrients was avoided by adding water to carrying capacity of the polluted soil. All removed-weeds were returned to the pot for nutrient return. All measurement and readings starts from the lowest pollution level to highest level to avoid contamination.

Proximate composition and heavy metals analysis

The proximate chemical compositions of the seeds were analyzed after drying at 70°C in an oven to constant weight according to standard [19] methods, while heavy metals were analyzed using Atomic Spectrophotometer (Buck 2.0) for the seeds in International Institute of Tropical Agriculture (IITA), Ibadan. Analyses done on the dried harvested seeds include the moisture, nitrogen and ash contents, crude fiber, protein, fat and carbohydrate. Heavy metals such as iron, zinc, copper, lead and nickel were determined in the harvested seeds.

Statistical analysis

A statistical comparison of means of different treatments was carried out using one way analysis of variance and treatment means were separated using the Duncan Multiple Range Test. Significance level was set at $p<0.05$. The data analysis was done using SPSS version 13.0 for Windows.

Results

Percentage germination of seeds

The percentage germination of seeds one week after planting were; 100%, 83.33%, 66.67%, 58.33%, 58.33% and 58.33% in the 0.0 ml, 10.0 ml, 20.0 ml, 30.0 ml, 40.0 ml and 50.0 ml respectively. There was a significant difference ($p<0.05$) in the germination rate of the cowpea seeds compared to the control. The control (0.0 ml) had the highest number of germinated seedlings while 30.0 ml, 40.0 ml and 50.0 ml had equal number of germinated seedlings (Figure 1).

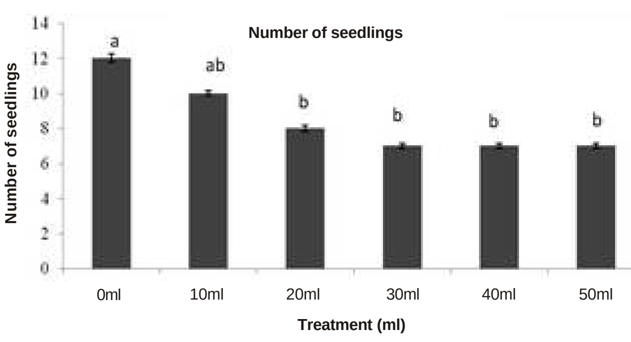

Figure 1. Effect of crude oil-treated soil on the germination of cowpea seeds. Means with the same superscript are not significantly different ($p<0.05$). Each value is a mean of three readings ± standard error.

Leaf length

The result on leaf lengths showed that there was significant difference ($p<0.05$) between the various treatments when compared with the control. The result for the leaf lengths indicated that there was a progressive increase from 1WAP to 9WAP, the leaf length ranged from 3.24 ± 0.34 cm to 10.27 ± 0.05 cm. A sharp decrease in the leaf length occurred from 9WAP to 11WAP, with the leaf length ranging from 10.27 ± 0.05 to 6.32 ± 0.06. The result also showed that there were significant difference ($p<0.05$) between the polluted plants and the control plants as influenced by the crude oil treatments except in the 6WAP and 11WAP with 50 ml having the highest negative effect on the plants' leaf length. No significant differences ($p<0.05$) were observed between 20.0 ml and 30.0 ml at 11WAP as well as 30.0 ml and 40.0 ml at 11WAP (Figure 2).

Plate 2. Experimental pots at ninth week after planting.

Plate 3(a&b). Germination of cowpea in 40 ml polluted soil at three and seven weeks after planting.

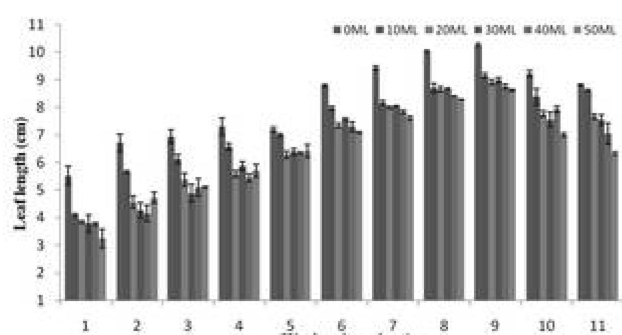

Figure 2. Effect of crude oil-treated soil on the leaf length of cowpea over the study period. Each value is a mean of readings ± standard error.

Leaf breadth

The results show that there was a significant difference ($p<0.05$) in the leaf breadths among the various concentrations of crude oil used compared to the control plants. It should however be noted that the differences were not ($p<0.05$) between 30.0 ml, 40.0 ml and 50.0 ml concentrations except at 10WAP and 11WAP. There was a rapid increase in the leaf breadth from the 1WAP to 9WAP and a significant reduction was observed from 9WAP to 11WAP as shown (Table 1).

Number of leaves

The number of leaves show that there was a significant difference ($p<0.05$) between the various concentrations compared to the control (Figure 3). There was a significant difference ($p<0.05$) at 5WAP to 8WAP. A rapid increase was observed in the number of leaves from 5WAP week to the 10WAP and this was followed by a reduction during the last week of the study, where the most reduced leaves were observed in the pots with 50.0 ml concentration. The effect was less pronounced from 1WAP to 4WAP (Figure 3).

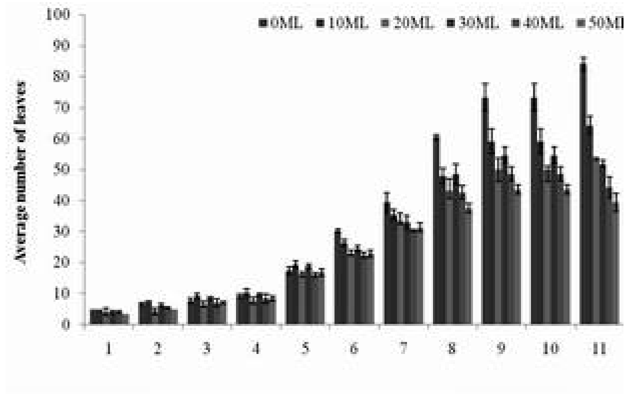

Figure 3. Effect of crude oil-treated soil on the number of leaves of cowpea over the study-period. Each value is a mean of three readings ± standard error.

Plant height

There was no significant difference ($p<0.05$) in the plant heights recorded across the various treatment levels when compared with the control plots in this study (Table 2). Although, there was rapid increase in the plants' heights from the 4WAP to the 9WAP as recorded in the 0.0 ml, 10.0 ml and 20.0 ml treatments.

Table 1. Effect of crude oil treated soil on the leaf breadth of cowpea over the study-period. Each value is a mean of mean three readings ± standard error.

Concentration	Week										
	1	2	3	4	5	6	7	8	9	10	11
0 ml	5.52± 0.34	6.71± 0.32	6.94± 0.24	7.30± 0.31	7.20± 0.09	8.78± 0.05	9.43÷ 0.06	10.03± +0.04	10.27 ÷0.05	9.22± 0.12	8.82± 0.03
10 ml	4.10± 0.04	5.65± 0.04	6.13± 0.17	6.57± 0.13	6.99± 0.05	7.97± 0.07	8.16÷ 0.09	8.70± 0.16	9.15÷ 0.09	8.38± 0.29	8.61± 0.03
20 ml	3.84± 0.05	4.55± 0.23	5.37± 0.23	5.57± 0.16	6.28± 0.14	7.34± 0.08	7.99÷ 0.04	8.65± 0.09	8.91÷ 0.10	7.76± 0.10	7.66± 0.10
30 ml	3.79± 0.32	4.26± 0.28	4.89± 0.29	5.87± 0.16	6.38± 0.11	7.57± 0.06	8.04÷ 0.03	8.66± 0.03	8.99÷ 0.10	7.55± 0.28	7.54± 0.19
40 ml	3.79± 0.05	4.15± 0.29	5.09± 0.32	5.45± 0.15	6.34± 0.05	7.30± 0.18	7.84÷ 0.06	8.40± 0.01	8.76÷ 0.07	7.93± 0.10	7.04± 0.38
50 ml	3.24± 0.34	4.72± 0.21	5.09± 0.03	5.71± 0.24	6.41± 0.24	7.08± 0.04	7.62÷ 0.07	8.29± 0.01	8.62÷ 0.04	6.99± 0.07	6.32± 0.06

Table 2. Effect of crude oil treated soil on the plant height of cowpea over the study-period. Each value is a mean of three readings ± standard error.

Duration	**Treatment**					
	0 ml	10 ml	20 ml	30 ml	40 ml	50 ml
Week 1	20.30±0.75	16.28±2.22	11.07±3.13	14.20±2.67	15.28±1.83	11.10±6.52
Week 2	23.42±1.05	20.63±1.70	12.15±3.02	15.05±2.72	16.37±4.80	13.40±5.63
Week 3	24.38±2.05	23.32±5.28	13.42±4.35	18.45±6.12	17.53±5.57	16.92±7.75
Week 4	26.80±1.30	24.67±5.32	14.48±4.15	19.95±6.49	19.00±5.83	18.33±8.11
Week 5	33.04±0.08	28.38±0.25	18.32±0.35	23.52±0.46	22.03±0.45	21.73±0.56
Week 6	34.28±0.08	30.20±0.35	20.95±0.64	25.60±1.07	22.77±0.79	23.72±0.52
Week 7	35.80±0.22	31.87±0.50	23.43±0.73	27.13±0.85	26.13±0.93	25.72±0.75
Week 8	38.65±0.27	34.33±0.61	25.45±0.53	30.18±0.70	27.47±0.93	27.42±0.92
Week 9	41.22±0.17	36.72±0.43	28.17±o0.64	31.90±0.82	28.75±0.84	29.80±0.96
Week 10	42.78±0.38	38.60±0.45	29.72±0.83	33.33±0.86	30.67±0.84	31.17±0.92
Week 11	43.02±0.52	39.08±0.74	30.37±0.95	33.62±0.93	30.95±0.91	31.87±0.63

However, significant reduction occurred from the 9th week to the end of the study duration with 20.0 ml having the highest negative effect on the plant height followed by 50.0 ml, whereas the highest plant height was recorded in the control followed by the 10.0 ml. There were no significant difference (p<0.05) between 30.0 ml and 40.0 ml as well as between 40.0 ml and 50.0 ml (Table 2).

Number and weight of seeds harvested as influenced by crude oil

Results show that a significant difference (p<0.05) exists between the various treatments compared with the control, where the 50 ml treatment had the lowest number of harvested seeds as shown in the (Figure 4). The 50.0 ml concentration also recorded the least number of harvested seeds. However, there is no significant difference between the 20.0 ml and 40.0 ml treatments at (p<0.05) (Figure 5). The result of weight of harvested seeds as influenced by the different levels of crude oil treatments show that there was significant difference (p<0.05) between the various treatments and the control (Figure 5).

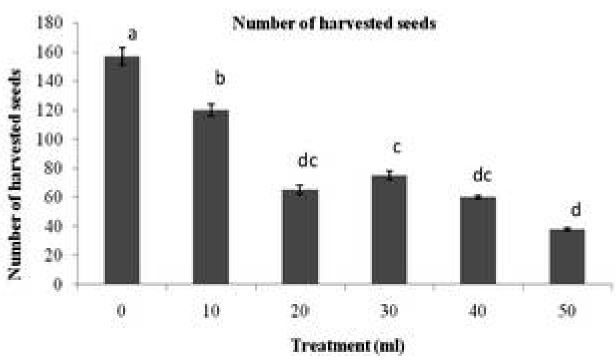

Figure 4. Effect of crude oil-treated soil on the number of harvested seeds of cowpea. Means with the same superscript are not significantly different (p<0.05), Each value is a mean of three readings ± standard error.

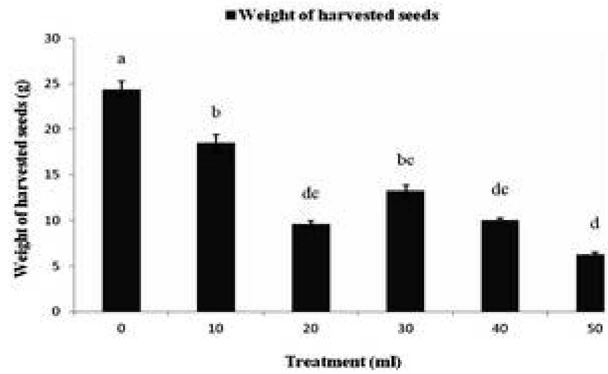

Figure 5. Effect of crude oil-treated soil on the weight of harvested seeds of cowpea Means with the same superscript are not significantly different (p<0.05). Each value is a mean of three readings ± standard error.

Percentage composition of nutrients in the cowpea seeds

The percentage N and protein stored in the cowpea seeds are found to be significantly different (p<0.05) between the various treatments and the control, where the lowest amount of nitrogen and protein contents stored in the seed was lowest in the 50.0 ml concentration. However, there were no significant differences (p<0.05) in the percentage moisture content % M.C, % Ash, % Fat, % Crude fiber and Carbohydrate (% CHO) between the treatments compared with the control, the highest percentage of moisture content % M.C and % Crude fiber were recorded in the 20.0 ml concentration (Table 3). The lowest % M.C, % Ash, % Fat and the highest % crude fiber and % were observed in 30.0 ml concentration treatment, while 20.0 ml had the lowest % CHO (Table 3). It was also observed that the highest amount of stored nitrogen, protein, moisture, ash and CHO were observed in the lowest treatment levels (10.0 ml and 20.0 ml) (Table 3).

Table 3. Effect of crude oil-treated soil on percentage nutrient composition of cowpea seeds over the study-period. Each value is a mean of mean three readings ± standard error.

Treatment	% N	% Protein	% M.C	% Ash	% Fat	% Crude fiber	% CHO
Pre-seed sample	$4.9^{a} \pm 0.1$	$30.5^{a} \pm 0.6$	$7.9^{a} \pm 0.3$	$9.1^{b} \pm 0.4$	$1.9^{b} \pm 0.2$	$3.6^{a} \pm 0.4$	$47.4^{a} \pm 1.1$
0 ml	$4.9^{a} \pm 0.2$	$30.6^{a} \pm 1.1$	$8.0^{a} \pm 0.5$	$10.4^{c} \pm 0.5$	$1.5^{c} \pm 0.1$	$3.7^{a} \pm 0.3$	$46.0^{a} \pm 1.3$
10 ml	$4.9^{a} \pm 0.2$	$30.1^{b} \pm 1.4$	$7.3^{a} \pm 0.4$	$9.9^{a} \pm 0.2$	$1.5^{a} \pm 0.1$	$4.3^{a} \pm 0.2$	$45.0^{a} \pm 2.8$
20 ml	$5.7^{b} \pm 0.2$	$35.2^{b} \pm 0.5$	$8.4^{b} \pm 0.5$	$9.6^{a} \pm 0.5$	$1.5^{a} \pm 0.3$	$4.7^{a} \pm 0.4$	$40.1^{b} \pm 1.1$
30 ml	$5.0^{a} \pm 0.1$	$31.2^{a} \pm 0.4$	$7.1^{c} \pm 0.2$	$8.5^{c} \pm 0.6$	$1.0^{c} \pm 0.1$	$4.7^{a} \pm 0.8$	$46.8^{a} \pm 0.3$
40 ml	$4.9^{a} \pm 0.1$	$30.2^{a} \pm 0.8$	$8.0^{a} \pm 0.2$	$9.3^{b} \pm 0.2$	$1.2^{c} \pm 0.1$	$4.6^{a} \pm 1.1$	$45.4^{a} \pm 1.5$
50 ml	$4.7^{a} \pm 0.4$	$29.6^{a} \pm 0.9$	$7.4^{a} \pm 0.6$	$9.5^{a} \pm 0.3$	$1.7^{b} \pm 0.1$	$4.5^{a} \pm 0.8$	$45.6^{a} \pm 1.4$
p-value	**0.017**	**0.010**	**0.217**	**0.071**	**0.079**	**0.685**	**0.097**

Means in the same column having the same letter(s) are not significantly different (p< 0.05). Each value is a mean of three readings ± standard error. N = Nitrogen, M.C = Moisture Content and CHO = Carbohydrate.

Discussion

Effect of crude oil treated-soil on the germination of cowpea

The pattern of higher percentage emergence of cowpea at one week after planting (WAP) in the lower concentration treatments indicated that crude oil had negative effect on the germination of the cowpea seeds. The negative effect observed on the cowpea seed may possibly be as a result of blockage of the cotyledon by the crude oil thereby inhibiting its growth. Also, the interaction of the crude oil with the soil may result into making the soil so compact that air may not freely diffuse through the soil. This finding is in line with that of [20-22] who all have reported low germination rate caused by crude oil contaminants in the soil and blockage of soil air pores by crude oil with their different test crop. Clarkson and Hanson [20] attributed the low emergence rate to insufficient aeration which results from the decrease in air-filled space and an increase in demand for oxygen by oil decomposing microorganism. Adams and Duncan [23] have also observed that the low germination rate of seeds in crude oil polluted soil could be due to the physical barrier caused by the crude oil enveloping the seed, preventing oxygen and moisture availability to the seeds.

Effect of crude oil treated-soil on the growth performance

The highest growth performance, leaf length, leaf breadth, and number of leaves of cowpea seeds recorded in the control compared to other treatments in this experiment might be as a result of the activity of the crude oil in the soil which may likely hinder the uptake of nutrients by the plants in the crude oil treated soils. This finding is consistent with the results of [24], who observed a significant reduction in the leaf length and number of leaves for all levels of crude oil treatment relative to the control. Ogbuchi *et al* [25], Ekpo *et al* [26] reported a significant reduction in the plant growth (number of leaves) of soybeans cultivated on crude oil. Akpan *et al* [22] has pointed out that plant nutrition is not only based on the presence of mineral elements in the soil but their availability for uptake by the plant. It has also been postulated that the presence of hydrocarbons in the soil can change the fertility of the soil, thereby leading to a nutritional imbalance which may ultimately cause lower growth and biomass production [27]. Adenipekun *et al* [28] who worked on *C. olitorius* in soil contaminated with oil also reported a lower number of leaves and reduced leaf area compared to those in the uncontaminated-soil.

The results of a sharp increase in the leaf length, breadth, and number of leaves across the treatments from 1WAP to 9WAP could be due to the tolerance and adaptive ability of cowpea to extreme conditions and its ability to fix atmospheric nitrogen through the interaction with nitrogen fixing bacteria in its root nodules. This finding is supported by [29] who suggested that, plants may tolerate sites polluted with petroleum by creating a soil environment rich in microbial activity that can change the availability of organic contaminants or enhance their degradation.

However, the reduction in leaf length, leaf breadth and leaf area observed across all the treatment levels including the control from 9WAP to 11WAP for number of leaves could be as a result of flowering where nutrients stored in the leaves are been translocated to the buds, flowers and subsequent fruiting. [30] has also pointed out that aging tissues (especially senescing leaves) being triggered by ethylene is associated with fruit ripening, flower wilting and leaf fall.

The lack of significant difference in the plant height, recorded between the various treatments relative to the control throughout this study period could be attributed to the fact that as the plant continued to grow on the crude oil treated soil, the activeness or toxicity level of the crude oil in the soil continue to decrease while the tolerance and adaptive ability of plants in the treated soils increases, thus enhancing the height of the plants. Also, cowpea being a leguminous plant is able to fix atmospheric nitrogen through the interaction with nitrogen fixing bacteria in its root nodules as a substantial number of nodules were found in the root region after harvest. [31] has reported that activities of nitrogen fixing microorganisms may enhance the soil condition and thereby improving productivity.

Effect of crude oil-treated soil on the nutritive content and weight of harvested seeds

The higher amount of stored nitrogen, protein, moisture, ash and carbohydrate in the cowpea seeds after harvest at lower treatment levels (10.0 ml and 20.0 ml) could be due to the ability of cowpea to tolerate or resist the effect of the crude oil at minimal level. This result is in agreement with the reports of [31], who opined that plants may tolerate sites polluted with petroleum by creating a soil environment rich in microbial activity that can change the availability of organic contaminants or enhance their degradation.

However, reduced stored nutrients in the harvested seeds of cowpea at higher treatment levels could be attributed to the fact that crude oil has inhibitory effect on nutrient mobilization or uptake by the plants and as the concentration increases tolerance ability reduces. The reduced number and weight of harvested seeds recorded in this study across the treatments could also be attributed to the reduced availability or absorption of nutrients and water from the soil due to the inhibitory conditions caused by crude oil in the treated soils. This finding is in line with the observation of [32], who suggested that oil level seem to exert the greatest influence on plant growth and yield.

Conclusion

The study concludes that cowpea can adapt minimally to crude oil polluted sites but as crude oil concentration increases, the tolerance ability reduces. Although, the plant reached flowering stage and fruiting even at high concentration but the harvested weight of cowpea was adversely affected. Furthermore, the nutrient content in the harvested seeds in relation to the control was also high in that cowpea was able to produce more protein content at lower treatment levels than in the control as observed in the nutrient composition table. However, it is necessary to note that cowpea can take up heavy metal elements such as Fe, Zn, Cu, Pb and Ni from crude oil polluted soils leading to heavy metal accumulation in the seeds of the plant thereby posing threat to lives of humans and other livestock that feed on it.

Finally, it is strongly advised that cowpea should not be consumed if planted in crude oil polluted soil because the excessive uptake of metals by the plant may produce toxicity in human nutrition.

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Kinetic studies of thiocyanate ions removal from aqueous solution using carbonaceous guinea-corn

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Abstract

Thiocyanate is one of the toxic and hazardous substances which is often discharged into the environment through several industrial processes. The adsorption kinetics study of the removal of thiocyanate in aqueous solution onto carbonaceous biomass which was primed from guinea-corn waste was investigated using UV-spectrophotometer. The effects of operational parameters such as contact time, initial concentration of thiocyanate ions, carbonaceous concentration, pH, foreign ions and temperature were evaluated in a batch adsorption process. The optimum conditions for thiocyanate removal were estimated to be contact time of 60 mins, thiocyanante initial concentration of 50 mg/L, biomass concentration of 5 g, temperature of 60°C and solution pH of 2.0. The kinetic results correlated well with both first and second order models. Thermodynamic parameters such as free energy change and enthalpy change showed that the adsorption process is spontaneous and endothermic in nature. FT-IR analysis revealed the involvement of functional groups such as –OH, -NH, C=O, C=C and COOH in the adsorption process. Thus, carbonaceous guinea-corn waste can be used as a cheap adsorbent for the removal of thiocyanate ions from aqueous solution.

Keywords: Adsorption; carbonaceous; guinea-corn; kinetics; thiocyanate.

Nomenclature

CGC carbonaceous guinea corn. CGC-500ºC carbonaceous guinea corn calcined at 500ºC. CGC-550ºC carbonaceous guinea corn calcined at 550ºC. CGC-600ºC carbonaceous guinea corn calcined at 600ºC. C_o initial concentration of thiocyanate ions (mgL^{-1}). C_e equilibrium concentration of thiocyanate ions (mgL^{-1}). q_e amount of thiocyanate ions adsorbed at equilibrium (mg/g). q_t amount of thiocyanate ions adsorbed at time t (mg/g). k_1 rate constant of pseudo-first-order (min^{-1}). k_2 rate constant of pseudo-second-order ($gmg^{-1}min^{-1}$). ΔG Gibbs free energy change of adsorption ($kJmol^{-1}$). ΔH enthalpy change of adsorption ($kJmol^{-1}$). ΔS entropy energy change of adsorption ($kJmol^{-1}$). R universal gas constant (8.314 $kJmol^{-1}$). R^2 correlation coefficient.

Introduction

The development of textile, printing, and tanning industries has lead to the production of large amounts of wastewater [1, 2]. The discharge of toxic effluents from various industries adversely affects water resources, soil fertility, aquatic organisms and ecosystem integrity. Appearance of colour in discharges from various industries is one of the major problems encountered in the textile industry [3]. Thiocyanate is widely used in several industrial processes such as metallurgical operations, dyeing, fibres production, photo-finishing, herbicide and insecticide production, electroplating and a wide range of other applications [3, 5, 6]. Wastewater from the mining of gold and silver also has been reported to contained thiocyanate [6]. Although, thiocyanate which is known to play very important role in the biosynthesis of hypothiocyanate through lactoperoxidase, is also known to be a very potent and competitive inhibitor of the thyroid sodium-iodine sympoter and since the presence of thiocyanate decreases the transportation of iodine to the thyroid follicular cell, the quantity of thyroxine produce via the thyroid gland will reduced [7, 8]. Thiocyanate toxicity could results in fatigue, anorexia and can as well altered mental behaviour such as psychosis, tinnitus, weakness, seizures and hyperreflexia, nausea and abdominal pain [6, 9, 10]. It is thus imperative to properly treat and remove thiocyanate containing substances from industrial effluent before releasing such into the water body.

Several studies have reported the degradation of thiocyanate using different chemical methods such as ion-exchange, coagulation/flouculation, complexation, advance oxidation and precipitation [11-13]. Some of these methods however appears to be expensive, require longer time of residence, generation of slugged, while others are not efficient in the removal of thiocyanate from contaminated environment [6, 13]. Thus, the use of waste of biological origin has been proposed as an alternative. Bioremediation is a waste management technique that involves the use of organisms (either *in situ* or *ex situ*) to neutralize contaminations from a contaminated site. Some of the adsorbents which have been employed in the decontamination of cyanide from wastewater include calcined hydrolalcite [6], activated charcoal [14], powdered activated carbon [15], *Acremonium strictum* [16]. The aim of this study is to evaluate the feasibility of carbonaceous biomass material primed from guinea corn waste as an alternative adsorbent for the removal of thiocyanate ions from aqueous solution. Kinetic study of the adsorption data of thiocyanate onto the carbonaceous biomass was also evaluated.

Materials and methods

Preparation of adsorbent

Raw biomass of guinea-corn (GC) waste were obtained from a local cereal miller in Ifo Local Government Area of Ogun State, Nigeria, and washed severally with distilled – deionized water and sun-dried for 21 days and this was later dried in an oven at 80ºC for 3 hours. The biomass was thereafter turned into powdered with the aids of a mechanical grinder. The resulted sample was then calcined at 500, 550 and 600 ºC for 4 hours. The samples were removed from the furnace and allowed to cool down and the biomasses were denoted as carbonaceous-500ºC (CGC-500ºC), carbonaceous-550ºC (CGC-550ºC) and carbonaceous-600ºC (CGC-600ºC).

Characterization of carbonaceous guinea-corn biomass

The physico-chemical characterization of carbonaceous guinea-corn biomass was done before and after the adsorption SCN^-. The pH determination of the biomasses was achieved by adding each biomass to distilled-deionized water, and the pH of the solution was then recorded. The percentage abundance of C and N was evaluated using A G. Vario EL analyzer (Germany), while, O was estimated by mass difference, i.e., 100% (% of C+N). Surface area and pore size analyzer (A Quantachrome NOVA 2200C, USA) was used in the analysis of surface area, pore volume, and pore size. Fourier Transform Infrared Spectroscopy (Bruker Optics, TENSOR 27 series FT-IR spectromete) was used to identify the various functional groups present in the biomass. Pellets were formed using 0.1 g of each biomass which was mixed with 0.3 g of KBr and pressed at 6 to 8 bar pressure. X-ray diffraction (XRD) was recorded using PANalytical (X'Pert PRO, Netherland). The diffraction patterns were collected over a range of 2θ = 10-60° with an incremental step size of 0.02 using CuKα (γ = 1.54178 °A) radiation.

Batch adsorption experiments

The method described by Qian *et al* [2] was modified and adopted. Briefly, about 5 g of the carbonaceous guinea-corn waste and 50 mL of thiocyanate solution was agitated at a speed of 200 rpm on a rotator shaker contained in a 250 mL flask for 1 hour to attained equilibrium. At the end of the sorption study, the solid biomass was separated by centrifugation, while the remaining concentration of thiocyanate ions was determined using UV-visible spectrophotometer (Shimadzu, UV-160) at a wavelength of 480 nm. For the kinetic study, the content of thiocyanate was taking at different time interval from the solution, spinned and analyzed for thiocyanate ions contents:

$$q_e = \frac{C_0 - C_e}{C_0} \times V \quad \text{. . . . (i)}$$

$$\%\ \text{removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad \text{. . . . (ii)}$$

Regenaration of thiocyanate-loaded with CGC

The regeneration of the thiocyante-loaded CGC was investigated in 15 mL 0.1M HCl and agitated on a rotator orbital shaker. After 60 minutes of contact, the $[SCN]^-$ desorbed was analyzed using UV-visible spectrophotometer (Shimadzu, UV-160). The ratio of the value of amount adsorbed (q_{ei}) and after desorption (q_{eaft}) gives the amount of thiocyanate ion concentration regenerated and the biomass was reconstituted for subsequent desorption experiment as shown in equation (iii):

$$\% \text{ desorption } = \frac{M_d}{M_a} \times 100 \quad \text{. . . . (iii)}$$

Results and discussion

Characterization of coconut shaft

Table 1. Physico-chemical parameters of carbonaceous guinea-corn biomass.

Parameters	CGC-500ºC	CGC-550ºC	CGC-600ºC
pH	6.10	5.70	5.20
Bulky density (g/mol)	0.63	0.74	0.86
Moisture content (%)	4.59	3.21	1.94
Ash content (%)	2.01	3.22	3.95
Surface area (m^2/g)	40.2	63.7	86.4
Average pore size (nm)	4.21	7.50	11.22
% C	67.23	71.32	75.24
% N	5.63	4.92	6.53
% O	27.14	23.76	18.23

The physico-chemical properties of CGC were evaluated and the results are as presented in Table 1. The results obtained from surface area and pore volume analysis indicated the high surface area and porous nature of the biomasses with the CGC-600ºC having the highest values followed by CGC-550ºC and CGC-500ºC had the least values. Elemental analysis showed the composition of untreated CGC-500ºC as C (67.23%), N (5.63%), O (27.14%), CGC-550ºC as C (71.32%), N (4.92%), O (23.76%) and CGC-600ºC as C (75.24%), N (6.53%), and O (18.23%). FT-IR spectra of GC are presented in Figure 1 which showed the various functional groups that are present in the cell walls of the biomass. The band observed at 3421 cm^{-1} corresponds to the stretching of –OH and –NH groups. The peaks at 2850 and 2920 cm^{-1} are characteristics vibration of methyl and methylene groups (C-H bond).

The peak at 1,735 cm^{-1} is a characteristic of C=O bonds in aldehydes, ketones, or carboxylic acids, while the band at 1,635 cm^{-1} is attributed to C=C indicating the presence of unsaturated compounds. The band appearing at 115 cm^{-1} is a vibration stretching corresponding to C-N bond, while the peak at 1049 cm^{-1} is assigned to the stretching of C-O bond in alcohols, ether, ester or carboxylic acids. These functional groups on the surface of GC such as –OH, -NH, C=O, C=C and COOH are potential adsorption sites for the entrapment of thiocyanide ions onto the surface of the biomass.

Thus, the mechanism of SCN^- bonding on GC waste occurs by surface complexation. The phase purity of the biomass was evaluated by X-ray diffraction which showed a pattern for cellulose type I with main peaks at about 2θ = 16.4°, 18.1° and 21.7º as presented in Figure 2. The diffraction peaks at 2è = 16.4° and 21.7º correspond to the (101) and (200) planes for cellulose [17, 18].

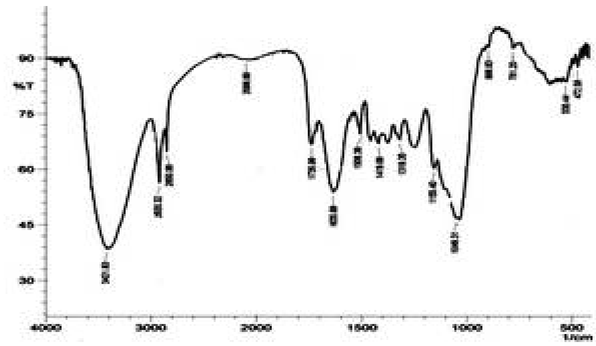

Figure 1. FT-IR spectra of carbonaceous guinea-corn waste calcined at 600ºC.

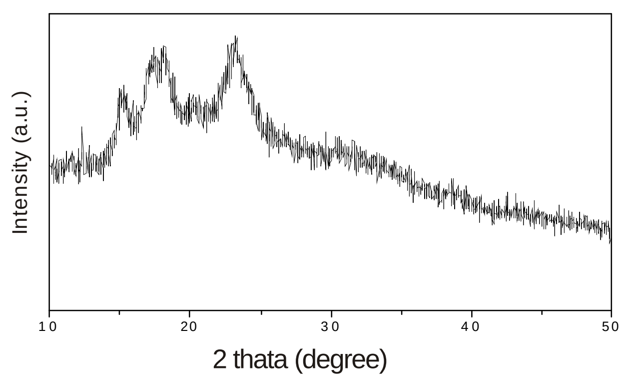

Figure 2. XRD pattern of carbonaceous guinea-corn waste calcined at 600ºC.

Effect of contact time and thiocyanate concentration

The effects of contact time and thioycanate concentration are as shown in Figure 3. It was observed that the adsorption of thiocyanate ions onto the biomass was rapid at the initial period (i.e. 5 to 60 mins.) and becomes uniform as the reaction reaches equilibrium stage. The results showed that the adsorption capacity increased with the contact time. The contact time required to attained adsorption equilibrium stage was 60 mins. The effect of initial $[SCN]^-$ on the adsorption was also evaluated at different thiocyanate concentrations (10, 15, 25, 35, 40 and 50 mg/L). As shown in Figure 3, the amount of thiocyanate ions adsorbed increased with the increase in thiocyanate concentration.

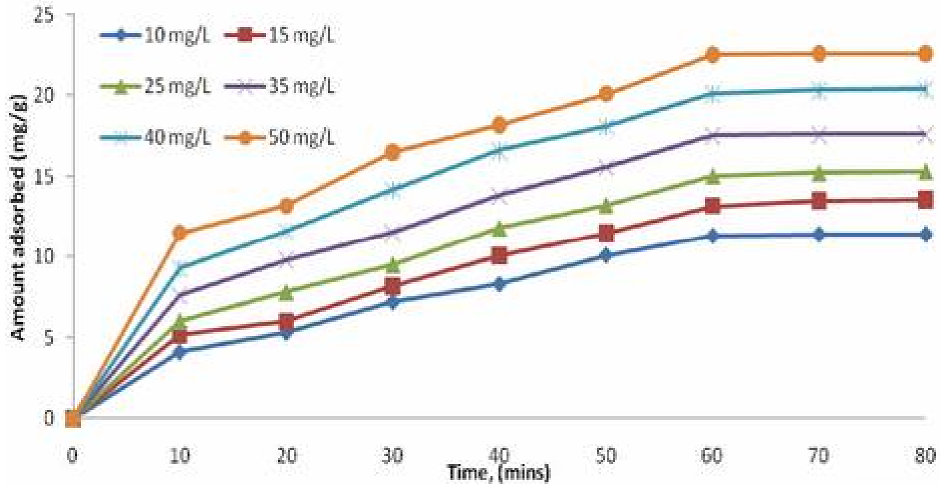

Figure 3. Effect of conctact time and concentration on the adsorption removal of thiocyanate ions at pH = 2.0, temperature = 60ºC and biomass dose = 5 g.

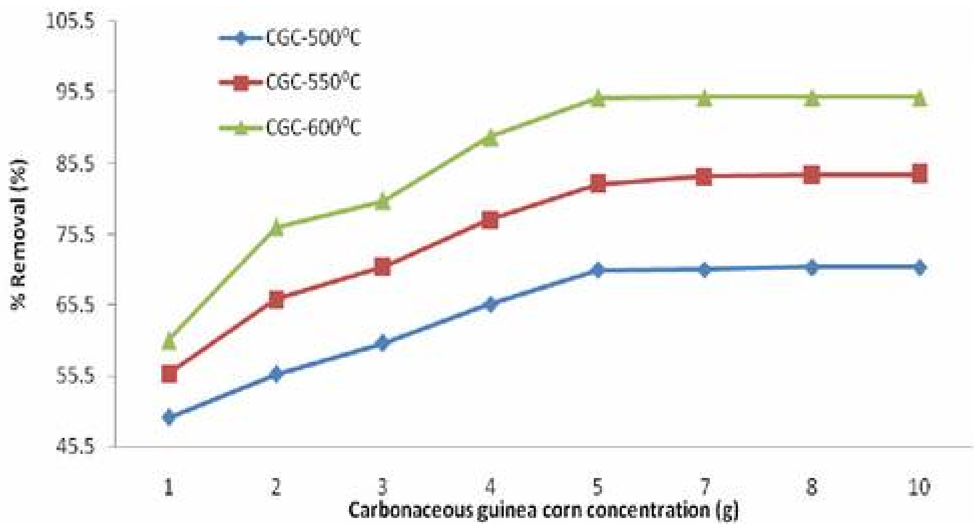

Figure 4. Effect of carbonaceous guinea-corn concentration on the adsorption removal of thiocyanate ions at contact time = 60 mins, inintial thiocyanate concentration = 50 mg/L, pH = 2.0 and temperature = 60°C.

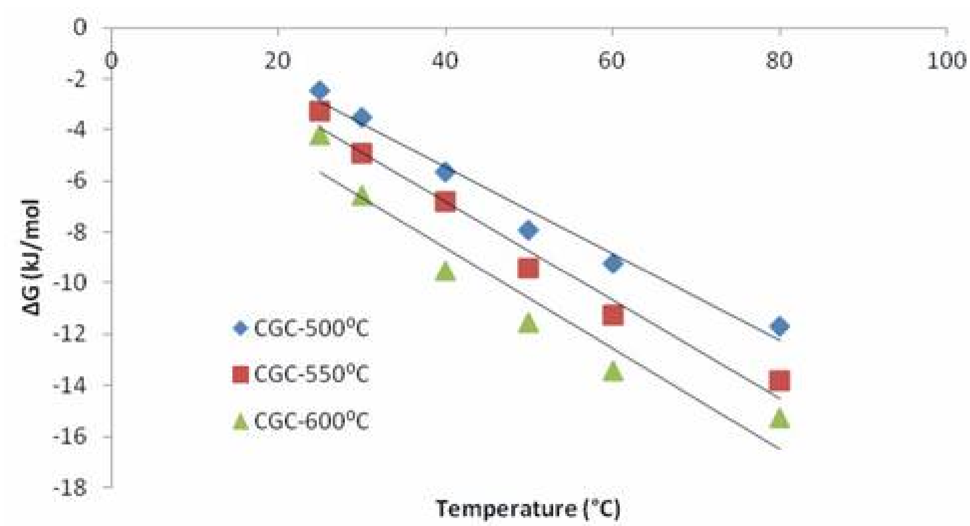

Figure 5. Effect of temperature on the adsorption removal of thiocyanate ions at contact time = 60 mins., inintial thiocyanate concentration = 50 mg/L, pH = 2.0 and biomass dose = 5 g.

The amount of $[SCN]^-$ adsorbed at equilibrium increased from 4.1 to 11.5 mg/g at 10 minutes and from 11.3 to 22.5 mg/g when the contact time was adjusted to 60 mins. According to Aksu and Tezer [19], resistance to mass flow can be easily overcome as a result of the driving forces at higher initial concentration of the adsorbate. The results showed good agreement with the findings of Reza *et al* [20].

Effect of carbonaceous guinea-corn concentration

Varied concentrations of CGC biomass (1, 2, 3, 4, 5, 7, 8 and 10 g) on the removal of thiocyanate ions were investigated and the results are as shown in Figure 4. As illustrated in the graph, the percentage removal of thiocyanate increases with increase in adsorbent dose until it reaches 5 g before showing a uniform adsorption on the surface of the adsorbent. The percentage removal increases from 49.6 to 70.9, 57.8 to 83.8 and from 60.5 to 94.9% for CGC-500, CGC-550 and CGC-600ºC respectively. The increase in percentage removal of the thiocyanate with adsorbent dose may be due to large vacant site on the surface of the adsorbent at the initial stage of the reaction which gradually becomes saturated as the concentration of the adsorbent increases, thereby leading to a decrease or constant adsorption of $[SCN]^-$ ions by the biomass. The result in this study is in good relation with previous findings [20, 21].

Effect of temperature

The sorption of thiocyanate ions was monitored at different temperature (25, 30, 40, 50, 60 and 100ºC) and the result is as shown in Figure 5. The effect of temperature greatly influenced the sorption behaviour of thiocyanante ions by the biomasses. The percentage removal was found to increase with an increase in the temperature and almost at a temperature above 60ºC. Thermodynamic parameters such as standard free energy change ΔGº, standard enthalpy change ΔHº and standard entropy change ΔSº were evaluated according the equation [21]:

$$\Delta G^{\theta} = -RTInK_0 \qquad \text{. . . . (iv)}$$

Where K_o is the equilibrium constant, ΔGº is the standard free energy change in kJ mol^{-1}, T is the temperature in Kelvin and R is the molar gas constant in kJ mol^{-1}.

The values of ΔHº and ΔS º were estimated from the relation:

$$\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta} \qquad \text{. . . . (v)}$$

Their values were estimate from the slopes and intercepts of the plots of ΔGº against T as shown in Figure 4, where their physical parameters are as shown in Table 2. The negative values of ΔGº shows the spontaneous nature of thiocyanate adsorption onto various CGC biomasses, the positive values of ΔHº is an indication that the reaction is endothermic in nature, while positive values of ΔSº revealed the increase in the degree of randomness during the adsorption of thiocyanate ions.

Table 2. Thermodynamic parameters of the adsorption of $[SCN]^-$ ions by CGC biomasses.

Temperature ºC	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol)
	CGC-500ºC		
25	-2.48	7.29	
30	-3.52	10.44	4.90×10^{-2}
40	-5.64	12.68	
60	-7.91	15.14	8.51×10^{-2}
	CGC-550ºC		
25	-3.28	9.22	
30	-4.94	12.45	4.97×10^{-2}
40	-6.83	15.32	
60	-9.90	18.65	7.77×10^{-2}
	CGC-600ºC		
25	-4.22	11.24	
30	-6.57	14.58	1.20×10^{-1}
40	-9.52	16.94	
60	-11.29	20.88	1.18×10^{-1}

Effects of pH

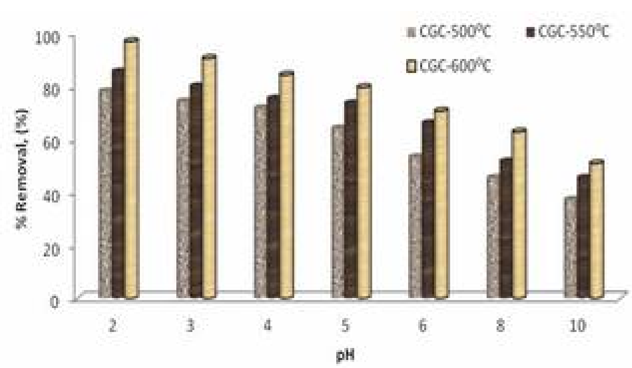

Figure 6. Effect of pH on the adsorption removal of thiocyanate ions at contact time = 60 mins, inintial thiocyanate concentration = 50 mg/L, temperature = 60ºC, biomass dose = 5 g.

In adsorption study of contaminant removal from aqueous solution, the influence of pH is one of the most important operational parameters which influence the surface state of biomass and the state of ionization of the adsorbabte. The data in Figure 6 indicate that when the pH was increased from 2 to 10, the percentage removal of $[SCN]^-$ decreased from 78.3 to 37.4% for CGC-500ºC, 85.7 to 45.6% for CGC-550ºC and from 96.9 to 50.80% for CGC-600ºC. This implies that the optimum adsorption of SCN^- was achieved in an acidic pH of 2.0, while a large decrease in adsorption capacity of thiocyanate ions was observed under basic conditions. Similar pH solution behaviour for contaminants removal via adsorption has been reported in literature [5, 20, 23, 24]. The decrease in the adsorption percentage at higher pH may be due to weakening of the electrostatic forces between the positively charged adsorbent and the negatively charged adsorbate [23, 25]. At lower pH, the surface of the CGC is positively charged and this may enhanced the uptake of the negatively charged SCN^- from the aqueous solution. At higher pH, the surface of the biomass becomes modified with hydroxyl ions which decrease the adsorption of the $[SCN]^-$ onto the surface of CGC as a result of the repulsion between OH^- and anionic $[SCN]^-$ species.

Effect of foreign ions

Apart from thiocyanate ions in industrial effluents, there are other anions with great affinity for the adsorbent for the sorption process. These anions may compete with the sorption of SCN^- onto the surface of the carbonaceous guinea-corn biomass which may affect the adsorption pattern of thiocyanate ions. In this study, the effects of anions such as PO_4^{3-}, SO_4^{2-}, NO_3^-, and Cl^- on the sorption of SCN^- are presented in Figure 7. As depicted in the graph, the percentage removal of SCN^- remain almost constant till 25 mg/L of sulphate concentration and latter showed a decrease to 33.4% at a higher sulphate concentration of 50 mg/L. The percentage removal of thiocyanate showed a gradual decrease from 83.6 to 42.5% when the concentration of phosphate was increased from 10 to 50 mg/L. For nitrate, the adsorption of thiocyanate was uniform up to 35 mg/L before showing a decrease to 50.8% at a higher nitrate concentration of 50 mg/L.

The percentage removal of thiocyanate remains constant throughout at different concentrations of chloride which indicated that chloride ion had no or little effect on thiocyanate ion removal. The adsorption of thiocyanate onto the surface of CGC was affected by foreign ions in this order: $PO_4^{3-} > SO_4^{2-} > NO_3^- > Cl^-$. The results from this study is similar to previous reports in literature [5, 6, 26].

Sorption kinetics investigation

In other to evaluate the kinetic behaviour of the adsorption of SCN^- onto the surface of carbonaceous guinea corn biomass, the adsorption data were incorporated into the Lagergren-pseudo-first order and Ho's pseudo-second order equation as described in equations [22, 27, 28]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad \text{. . . . (vi)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{e^2}} + \frac{1}{q_e}t \qquad \text{. . . . (vii)}$$

Where q_e and qt are the uptake concentrations of SCN^- in mg/g at equilibrium and SCN^- concentration at time t in mg/g, k_1 and k_2 are the rate constants for first and second order in min^{-1} and $gmg^{-1}min^{-1}$ respectively. The values of the rate constants as well as the equilibrium concentrations were estimated from the slopes and intercepts of the two curves in Figure 8 and 9 respectively. The plots of log $(q_e - q_t)$ against t is shown in Figure 8 which represent the curve for a first-order kinetic equation, while the physical parameters are

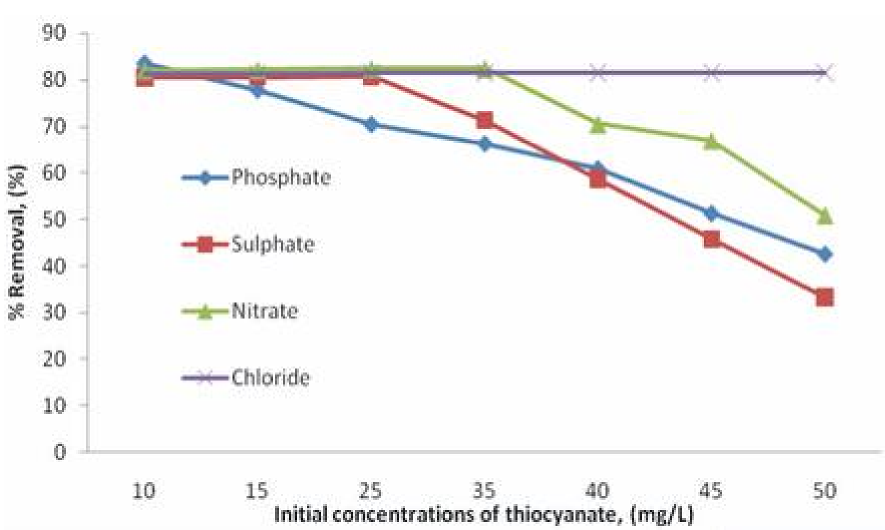

Figure 7. Effect of foreign ions on percentage adsorption removal.

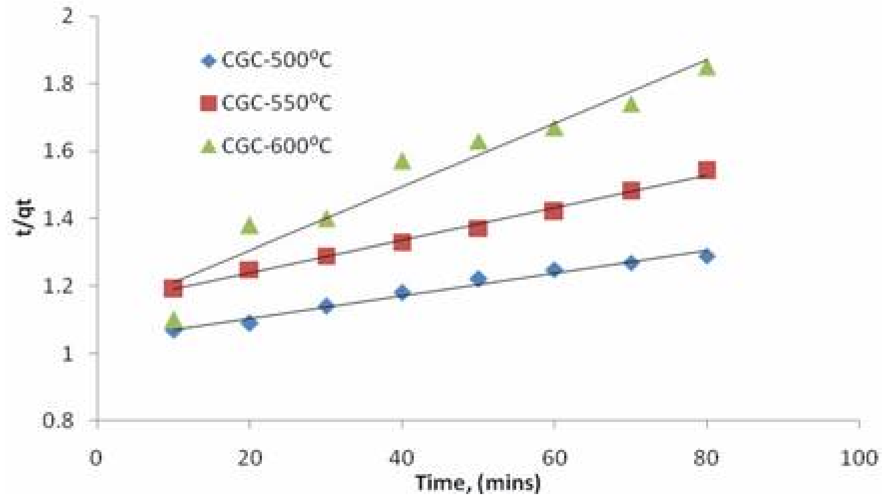

Figure 8. Largergren's first-order kinetic model for the adsorption of SCN^-.

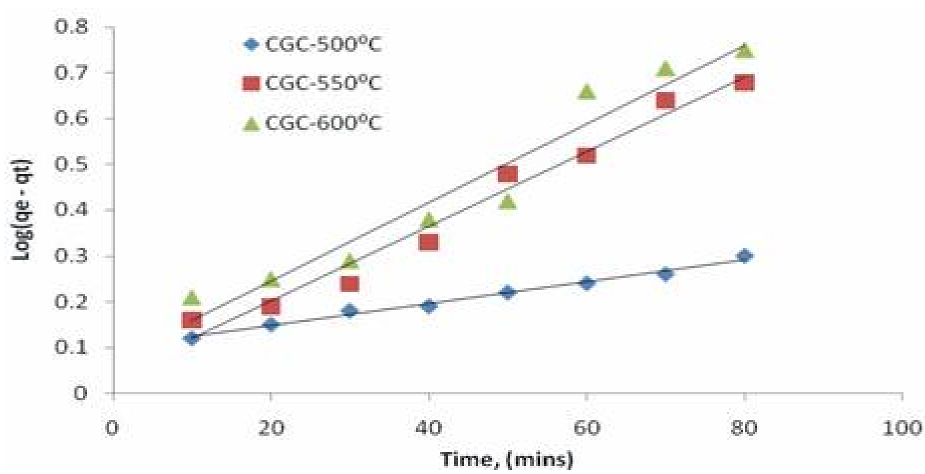

Figure 9. Ho's pseudo-second-order kinetic model for the adsorption of SCN^-.

Table 3. Kinetics parameters of the adsorption of SCN^- ions by CGC biomasses.

	First order model				Second order model			
Biomasses	**k_1 (min^{-1})**	**q_e (mgg^{-1})**	**R^2**	**X^2**	**k_2 ($gmg^{-1}min^{-1}$)**	**q_e (mg/g)**	**R^2**	**X^2**
CGC-500ºC at 30 mg/L	0.014	8.22	0.96	0.08	0.06	4.15	0.88	0.56
50 mg/L	0.026	10.14	0.98	0.10	0.08	6.63	0.86	0.63
CGC-550ºC at 30 mg/L	0.047	13.53	0.94	1.26	0.14	10.22	0.97	0.05
50 mg/L	0.049	14.62	0.86	2.43	0.36	11.58	0.99	0.03
CGC-600ºC at 30 mg/L	0.062	16.35	0.98	0.02	0.52	13.22	0.89	0.79
50 mg/L	0.085	18.22	0.98	0.05	0.73	15.68	0.94	0.88

presented in Table 3. For the second-order kinetic equation, the plots of *t/qt* against *t* is shown in Figure 9, while the physical parameters are as presented in Table 3.

Test of kinetics fitness

$$x^2 = \sum \frac{(q_e - q_{em})^2}{q_{em}} \quad \ldots . (viii)$$

As indicated in Table 3, the values of correlation coefficient (R^2) from the first-order kinetic model for CGC-500 and 600ºC as well as that of the CGC-550ºC from second-order kinetic model were close to unity. These implies that the adsorption of SCN^- by CGC-500 and 600ºC were governed by first order kinetic model, while that of 550ºC was governed by second-order kinetic model. This was further affirmed by the lower value from the test of kinetics fitness of first order for CGC-500 and 600ºC as well as that of the CGC-550ºC from second-order kinetic model. The smaller the value the better the fitness.

Regeneration study

The regeneration ability of CGC was performed since it's very important in the treatment of wastewater to ensure cost effectiveness [29]. The CGC-loaded with SCN^- was deployed in the evaluation of the regeneration using 0.1M of HCl as the eluting agent and the results are as presented in Figure 10. When CGC-500ºC was used, the percentage desorption increases from 58.4 to 70.2%, 61.5 to 75.6% for CGC-550ºC and 66.7 to 80.4% for CGC-600ºC when the number of reusability was increased from 1 to 3 and almost constant above three cycles. The results indicated that the carbonaceous biomass with the largest surface area (CGC-600ºC, 86.4m²/g) had the highest desorption capacity.

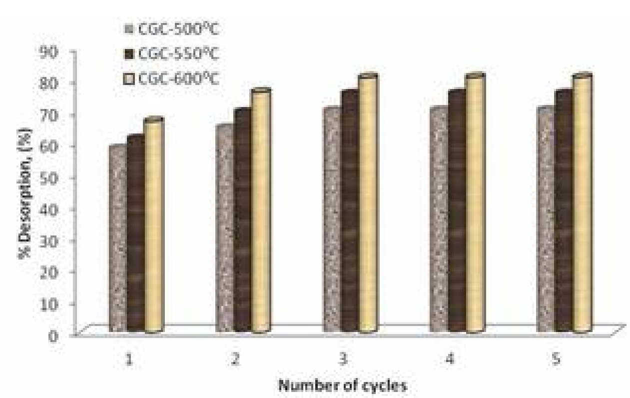

Figure 10. Plots of percentage desorption at different number of usage.

Conclusion

This study shows that carbonaceous biomass primed from guinea-corn waste could be effectively employed as adsorbent for the removal of thiocyanate ions from aqueous solutions. The adsorption of thiocyanate ions by the CGC biomass however depend on factors such as solution pH, biomass dose, initial concentration of thiocyanate, contact time and temperature. Among the selected physical parameters, pH was the most effective on SCN^- removal with 96.9% removal in acidic medium of 2.0. The adsorption of thiocyanate ions was greater in CGC-600ºC due to the large surface area provided by the active sites of carbonaceous biomass. The Lagergren pseudo-first-order model gave a better fit for CGC-500ºC and CGC-600ºC, while Ho's pseudo-second-order model described better adsorption patter for CGC-550ºC.

The negative and positive values of free energy change and enthalpy change from thermodynamic studies revealed that the adsorption process of thiocyanate is spontaneous and endothermic in nature. Desorption of thiocyanate from the CGC biomaterial was achieved with 0.1M HCl acid. Thus, base on the information provided by this research work, carbonaceous guinea corn can be considered as an effective, environmentally friendly and low-cost adsorbent for the decontamination of thiocyanante ions in aqueous solution.

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