



Sorption Characteristics of Halogenated Acetonitriles (HANs) in Surface Water onto Activated Carbon Prepared from Walnut Shell

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Authors' contributions

This work was carried out in collaboration among all authors. Author AAO designed the study, wrote the protocol, and wrote the first draft of the manuscript. Author RMAA collected the data and performed the statistical analysis, and managed the analyses of the study with author AAO. Author KNA managed the literature searches and attended to the reviewers' comments. All authors read and approved the final manuscript.

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ABSTRACT

Sorption efficiencies of activated carbon prepared from walnut shell for the removal of Halogenated Acetonitriles (HANs) from surface water was investigated in this study, as an ethically sound-way of utilizing this unexploited abundant natural resource, and was also compared with burgoyne commercial activated carbon (BCAC). Major HANs created during the disinfection process consist of dichloroacetonitrile (DCAN) and bromoacetonitrile, (BCAN). Physicochemical properties of both raw and chlorinated water were determined using standard methods, and concentration of DCAN were determined from water treatment plant at different stages of treatment using High Performance liquid Chromatography (HPLC). Recovery experiments were carried out to validate experimental procedure. Batch adsorption experiments were carried out and different parameters such as adsorbent dosage (0.2, 0.4, 0.8 g), contact time (30, 60, 90 minutes), pH (5, 7, 9), and concentration (0.006 mg/L, 0.009 mg/L and 0.012 mg/L) were optimized for removal of DCAN using

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walnut shell activated carbon (WSAC). Experimental sorption data from different initial concentrations of DCAN were used to test conformity with Freundlich and Langmuir adsorption isotherms. Percentage recovery from experimental procedure is 86.01 ± 0.62 to 100.0 ± 0.00 for DCAN. Mean percentage adsorption efficiencies for simulation experiment is 16.670 ± 0.467 to 41.67 ± 1.103 for DCAN. Optimum conditions for DCAN were 0.8g adsorbent dosage, 60 minutes contact time, pH 9 and 0.012 mg/L initial concentration. Optimum values of these parameters used for adsorption of DCAN in raw and chlorinated water serving the treatment plant gave an adsorption efficiency of $69.00 \pm 1.43\%$ and 79.00 ± 0.03 respectively. Adsorption efficiency of BCAC gave 94.4 ± 0.42 and 98.00 ± 1.41 for raw and chlorinated water respectively, with a total decrease in all physicochemical parameters examined after adsorption experiment. Adsorption isotherm studies indicated that Langmuir model was more suitable for the experimental data than Freundlich isotherm model. Conclusively, the effective adsorbent properties displayed by WSAC in the removal of DCAN indicate its potentials in treatment of water contaminations.

Keywords: Acetonitriles; activated carbon; HPLC; walnut shell; water; Nigeria.

1. INTRODUCTION

Chlorination of water is among the most significant general well-being advances of the twentieth century, its presentation in the US, dispensing with cholera rates by 90%, typhoid by 80%, and amoebic diarrhea by half [1]. However, the formation of a variety of disinfection by-products (DBPs) due to interaction of chlorine with organic matter is a significant health hazard and adversely affecting the ecosystem [2]. Many drinking water utilities have changed their purification practices, and the essential disinfectant has changed from chlorine to supposed elective disinfectants, including ozone, chloride dioxide, UV, and chloramines [3,4]. However, the degrees of many rising DBPs are expanded by elective disinfectants (principally ozone or chloramines) compared to chlorination, and many emerging DBPs are more genotoxic than some of the regulated DBPs [3].

Nonetheless, to successfully control and expel the rising nitrogen-containing (halogenated acetonitriles) DBPs has been of extraordinary criticalness, and the exploration of developing DBPs will keep on being a hot territory of drinking water at home and abroad. It has been estimated in a few event contemplates that major halogenated acetonitriles (HANs) created during the disinfection process consist of dichloroacetonitrile (DCAN), bromoacetonitrile, (BCAN), and trichloroacetonitrile (TCAN) [5,6]. It has also been accounted for that HANs are exceptionally poisonous, and when enters the body it promptly responds with the gastric corrosive to form frail acidic hydrogen cyanide, which can wreck the film and deaden the tissue respiratory focus of the cerebrum, only a couple of milligrams can cause individuals' demise [7].

The wellbeing impacts of HANs may not be dismissed as a result of their higher poison levels. This, therefore, necessitates their removal from aqueous systems and the environments.

Agricultural waste is a biomass by-product that outcomes from the agricultural processes which may include stalks, leaves, seeds, shells, peels, husks, and straws [8,9]. Agricultural waste also includes livestock and poultry waste. They are characterized by a wide range of sources and large quantities. Due to their quantity and lack of proper waste disposal system, the wastes always constitute pollution to the environment [9,10]. As of late, some agricultural waste items, biomass, and different solid substances have been developed into activated carbon as alternative cheap adsorbents to remove DBPs [11-13]. Such products for example includes biochar and activated carbon/biochar have been reported to be produced from different agricultural wastes and they find application for various uses for example, in water and wastewater treatment, along these lines turning into another monetary asset for agriculturists.

Walnut (*Tetracarpidium conophorum*) species is usually cultivated by small subsistence farmers in the hot and humid zones of tropical Africa in compound gardens and backyards just for the family and local market consumption. Consequently the utilization of adsorbent delivered from plant and creature biomass in water and wastewater treatment has been given an expanding thought and at present offer an alluring strategy for contamination remediation [14]. Likewise, water treatment is essential in this time of prospering human populace, and appeal for water assets and water reuse has surfaced in both urban and country territories [15].

Convenient water is turning into a scant ware, and the treatment of accessible water with disinfectant for residential water flexibly now and again leaves disinfectant by-products, such as Halogenated Acetonitriles.

Out of the numerous methods of HANs removal such as Ultraviolet degradation, Hydrolysis which can not but leave disinfection by-products, adsorption has demonstrated to be an increasingly proficient and financially savvy technique for evacuating numerous contaminations [9]. Different agricultural wastes have been used as adsorbent in the removal of pollutants. The agricultural wastes used include straw [16], wheat straw [17], bagasse [18], banana skin [19], walnut shell [20], and coconut shell [21,14]. This study hence looks to determine the concentration of halogenated acetonitriles (dichloroacetonitriles) present in the water supply, evaluate the adsorption efficiency of Walnut shell activated carbon for the removal of dichloroacetonitriles, and compare the efficiencies of walnut shell and Burgoyne commercial activated carbon.

2. MATERIALS AND METHODS

2.1 Preparation and Carbonization of Sample

The Walnut Shells (WS) were collected from a local market (Oja Oba) in Osogbo, Nigeria. The WS were first thoroughly washed in a running tap water to remove debris and dust and then with deionized water, sun-dried to a constant weight, crushed and pulverized to increase the surface area for activated carbon production. The pulverized walnut shell of 456 g was then placed in a weighed clean-dried crucible, and put into a muffle furnace [Carbolite 12/65 tube furnace ESSEN (Germany)] at 700°C [22] for 1 hour and sieved to <150 μm particle size [23- 26].

2.2 Chemical Activation of the Carbon

The method is as outlined in [23,25]. One hundred grams (100 g) of the pulverized WS was soaked in 1% H_3PO_4 (v/v) for 24 hours, filtered using Whatman filter paper No.1, and placed in an oven at a temperature of 120°C for 24 h. After cooling, it was washed with freshly distilled water to remove the residual acids until the solution reaches a pH of 7 and then air-dried. The activated carbon sample was then screened to particle size fraction of 150 microns before being

stored in an experimental bag and used as an adsorbent.

2.3 Characterization of the Activated Carbon

The elemental composition and the surface morphological characteristics of the activated carbon were determined based on the dry combustion method using a scanning electron microscope coupled with energy dispersive X-ray analyzer (high-resolution SEM/EDX, Carl Zeiss). Structural chemical functional groups in the activated carbon were determined using the Fourier transform infrared technique (FTIR, Spectrum 100, Perkin Elmer) [23,25,26].

2.3.1 Preparation of samples for SEM/EDX analysis

The Walnut Shell activated carbon (WSAC) sample was placed on the aluminum holder stub using a double sticky carbon tape. Insulating samples were located with carbon and electrically grounded. Also, silver paint was used to electrically ground the samples. Then, the samples were completely dried in the drying oven at 60°C for about 3 hours and were left overnight in the drying oven. The samples were loaded in the scanning electron microscope (SEM) holder, and the SEM machine was switched on. The SEM instrument then placed the samples in a relative high-pressure chamber where the working distance is short, and the electron optical column is differentially pumped to keep vacuum adequately low at the electron gun. Imaging was then acquired.

The energy dispersive X-ray acceleration voltage was then set to 20 kV with a working distance of 14 mm, and the detector was moved to 45 mm by rotating the knob, the samples were focused, and the X-ray spectrum was collected and saved in .pgt file [25].

2.3.2 Preparation of samples for FTIR analysis

The samples were analyzed using the FTIR KBr method. A drop of the liquid was placed on the face of a highly polished KBr plate. A second plate was placed on top of the first plate so as to spread the liquid in a thin layer between the plates and clamped together. Liquid on the edge of the plate was wiped after which the sample plate was mounted onto a sample holder connected to a recording device and analyzed [25].

2.4 Sampling and Physicochemical Analysis of Water Samples

Amber bottles of 2.5 L sizes used for water sampling was pre-cleaned following the standard procedure for organic contaminant sampling [27-29,25]. The bottles were allowed to air dried for about 24 hours and covered with aluminium foil to prevent further contamination till the time of sampling. Water samples were collected from two sampling points (the influent raw and chlorination stage) in triplicate from water the treatment plant. Parameters such as temperature, pH, electrical conductivity, turbidity and total dissolved solids of the water samples were determined in-situ. The water samples were properly labelled, acidified with concentrated H_2SO_4 and put in ice boxes and then transferred to the laboratory immediately for further analysis. The water samples were characterized for the presence of HANs (DCAN) residue in the raw and chlorinated water using High Performance Liquid Chromatography Analysis. Other physiochemical parameters such as total suspended solids, total organic carbon, turbidity, alkalinity, nitrite, nitrate, sulphate, chloride, acidity, dissolved oxygen, biological oxygen demand, and chemical oxygen demand of the water were determined following the standard procedures by [30,28,29].

2.5 Batch Adsorption Experiment of Simulated Polluted Water

The batch adsorption experiments were carried out according to the method described in [31, 25]. HANs polluted water was simulated in the laboratory by preparing a stock solution of DCAN and diluted to varying degrees of concentrations (0.006 mg/L, 0.009 mg/L and 0.012 mg/L). Batch adsorption studies were carried out using 0.2, 0.4, and 0.8 g of the adsorbent made from WSAC and 50 ml of the simulated solution of HANs (DCAN) polluted water in a conical flask with constant shaking using a shaker operated at 120 osc/min. The parameters such as adsorbent dosage, contact time, pH and initial HANs (DCAN) concentration were optimized for successful adsorption. The batch adsorptions were followed by filtration using Whatman filter paper (No. 1). The filtrates containing the residual concentration of the HANs under study were determined using High Performance Liquid Chromatography (HPLC). The data obtained were subjected to paired-sample *T*-test and one-way analysis of variance.

2.6 Extraction of DCAN

Each filtrate from the batch adsorption and 10 ml solvent of dichloromethane (DCM) were mixed in a 250 ml capacity separating funnel (DURAN, Germany) and was shaken by mixing well for about 10 min and then were allowed to stand for 10 – 15 min for clear separation [25,26]. The organic solvent layer was collected in a test tube. The aqueous layer was re-extracted by adding another 10 ml of DCM following same procedure. The organic solvent layers were added together and 2 g of anhydrous sodium sulphate (Merck, Germany) was added to remove the residual water. The collected extract was then concentrated to dryness under room temperature of 29°C. The concentrates were then reconstituted with DCM to a 1.5 ml in HPLC vials for analysis [25,26].

2.7 High Performance Liquid Chromatography Analysis

The LC-2000 plus series High Performance Liquid Chromatography (HPLC) was used to for determining DCAN, and identification, quantification and resolution was based on the retention time. This experiment uses reverse-phase chromatography, where the stationary phase employed is C18 hydrocarbon groups bounded to 3- μ m silica particles, while mobile phase (an aqueous buffer with a polar organic modifier) added to vary its elution strength. The operation of Gel Permeation columns was programmed at ambient temperature of 40 to 60°C for 5 min and increased at the rate of 60°C to 120°C, held for 5 min, and then continued at a rate of 20°C/min to 250°C and held for 5 min [32] so as to enhance good resolution at different boiling points. The injection was done on a splitless mode injector at 250°C, and the run time was 45.75 minutes.

2.8 Recovery Experiment for the Extraction Process and Determination of DCAN

Liquid/liquid extraction method (LLE) described by [33,25] was adopted for the extraction of water samples. Acidified raw and chlorinated water (100 ml) were spiked separately with 50 ml of 0.006 mg/L of DCAN concentration of the standard mixture was extracted with 10 ml of dichloromethane (DCM). Anhydrous sodium sulphate (2 g) (Merck, Germany) was added to the collected extracts to remove the residual water. The collected extract was then

concentrated to about 2 ml at room temperature for HPLC analysis according to the method of [33,25]. Recovery of DCAN standard were also investigated by spiking deionized water sample to check on the effect of matrix on extraction efficiencies. The equation of recovery experiment residual concentration is shown as follows [34,25]:

$$(\%) \text{ Recovery} = \frac{\text{spike concentration} - \text{Unspike Concentration}}{\text{spiked concentration}} \times 100 \quad (25)$$

2.9 Adsorption Efficiency

The percentage of DCAN adsorbed (adsorption efficiency %) per unit mass of the adsorbent was calculated by using the following percentage balance equation: [35,25,26].

$$\text{Adsorption Efficiency} = \frac{(C_0 - C_1)}{C_0} \times 100\% \quad [35,26].$$

Where:

C_0 is the initial concentration of DCAN before adsorption (mg/L)

C_1 is the final concentration of DCAN solution (mg/L) in the filtrate after adsorption.

2.10 Adsorption Isotherm

The sorption ability of WSAC as natural adsorbent was evaluated through determination of sorption isotherm of DCAN sorption system. Equilibrium models and sorption isotherms were used to explore how an adsorbate interacts with an adsorbent. Common equilibrium models used to describe isotherms of DCAN sorption on WSAC include Langmuir and Freundlich which are applied in this study.

3. RESULTS AND DISCUSSION

3.1 Carbon Yield of Charred Walnut Shell

The result of carbon yield of WSAC is as shown in Table 1. Table 1 shows the percentage yield of carbon from the charred Walnut Shell (WS). WS produced 32.40% of carbon from 456 g of powdered walnut shell charred.

3.2 Characterization of Activated Carbon

The results of the physicochemical parameters (the ash content, carbon yield, pH, and moisture content) of WSAC are presented in Table 2. The

high rate carbon yield from WSAC acquired makes it an advantage contrasted with other rural squanders and non-renewable energy source sources [36] with low ash content since it can fill in as one of the salary wellsprings of agro-based businesses. High carbon yield and low ash content give better attributes of pore structures and this prompted the built up reality that high carbon yield of agricultural is demonstrative of acceptable adsorption. Additionally from Table 2, the mean pH of 6.5 ± 0.00 is demonstrative of an acidic substrate. Activated carbon is typically amphoteric in nature and it suggests it could be positively or negatively charged relying upon the arrangement pH; for this situation, the solution pH will be positively charged. Fascination between enacted carbon and anionic or cationic adsorbate is for the most part identified with the surface qualities. All the more positively charged surfaces are obtained at lower pH value and this favors the uptake of increasingly anionic gatherings because of expanded electrostatic fascination among anions and the outside of the activated carbon [37].

3.3 Elemental Composition of the Activated Carbon before and after Adsorption

The WSAC was analyzed using scanning electron microscope coupled with energy dispersive X-ray analyzer (SEM/EDX) (high-resolution SEM/EDX, Carl Zeiss) to determine its elemental composition both before and after adsorption experiment (Table 3). The result shows carbon to be the highest of all the element present before and after adsorption with percentage composition of 70.00% and 70.09%, followed by Hydrogen (H) of 15.56% and 10.85%, Oxygen (O) 9.27% and 15.66%, Sulphur 3.70% and 3.40% and Iron (Fe) 1.48% for raw and chlorinated water respectively after the adsorption experiment. This makes the WSAC suitable for adsorption [38,25].

3.4 Surface Morphology of WASC before and after Adsorption Experiment

The surface morphological characteristic of the adsorbent is shown by the scanning electron micrograph. Fig. 1(A) shows the surface morphology of the activated carbon (adsorbent) before and Fig. 1 B and C after adsorption process of chlorinated and raw water. This clarifies the mass of particle and the surface

morphology of the adsorbent. The surface of the adsorbent before adsorption shows wavy-like curves with impeccable pore sizes which empower access into the internal pores.

Nonetheless, after adsorption, it was seen that the pores were at that point stopped up with the DCAN contaminants adsorbed on the activated carbon demonstrating adsorption had occurred.

Table 1. Carbon yield of charred walnut shell

Powdered walnut shell		
Weight before charring (g)	Weight after charring (g)	Percentage yield (%)
456 ±0.00	145±2.64	32.00

Table 2. Physicochemical parameters of Walnut Shell activated carbon

Parameters	Unit	Walnut Husk Activated Carbon (WSAC)
Ash content	(%)	3.42±0.55
Carbon yield	(%)	79.20±0.07
pH	-	6.5±0.00
Moisture content	(%)	7.3±0.41

Table 3. Percentage composition of the elements in Walnut shell activated carbon (WSAC)

Elements (%)	Before adsorption amount (%)	Raw water after adsorption amount (%)	Chlorinated after adsorption (%)
S	12.0	3.70	3.40
O	23.0	9.27	15.66
C	62.0	70.00	70.09
Si	3.0	-	-
H	-	15.55	10.85
Fe	-	1.48	-

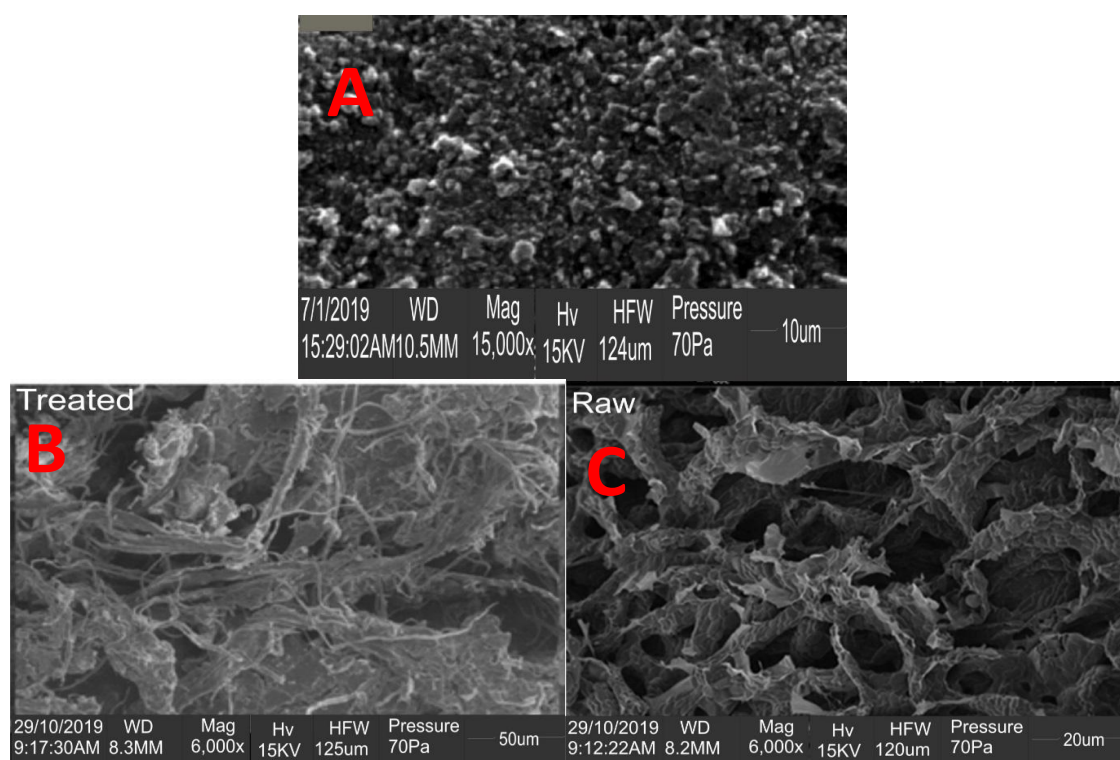


Fig. 1. SEM micrographs of WSAC (A) before adsorption (B) after adsorption (Treated) (C) after adsorption (Raw)

3.5 Functional Groups of *Moringa oleifera* Seed Husk Activated Carbon

The functional groups of the Walnut shell activated carbon (WSAC) were determined using Fourier transform-infrared spectroscopy (SHIMADZU-FTIR- 8400S). Fig. 2 shows the functional groups present in the activated carbon of Walnut Shell. Each one of the band groups on the FTIR represents a particular functional group which empowers adsorption. The band at 3450 cm^{-1} is attributed to (O-H) vibrations in hydroxyl groups. The band appearing at 1770.71 cm^{-1} is attributed to carbonyl (C=O) groups. The olefinic (C=C) absorptions cause the band at about 1637.62 cm^{-1} , while the skeletal C=C vibrations in aromatic rings cause another band at about 1384 cm^{-1} . The appearance of band at 1143 cm^{-1} can be assigned to C-O stretching vibrations. The peak at around 889.21 and 669.32 cm^{-1} is ascribed to the aromatic C-H out of-plane vibrations.

3.6 Physicochemical Parameters of Water Samples before and after Adsorption

The physicochemical parameters of raw surface and chlorinated water samples were investigated to determine the range of values of contaminants both before and after the adsorption processes. All the parameters falls within the World Health Organization (WHO) limits after the adsorption

experiment (Table 4). This is in agreement with the work of Okoya et al. [25] who worked on efficacy of *Moringa oleifera* seed husk as adsorptive agent for Trihalomethanes from a water treatment plant in southwestern, Nigeria. The study concludes that *Moringa oleifera* seed husk activated carbon showed excellent result for the removal of Trihalomethanes and organic contaminants present in water, and the quality parameters of water treated with the activated carbon met most of the Nigerian standard for drinking water quality. The results are presented in Table 4 and demonstrated that parameters such as temperature, conductivity, turbidity, SO_4^{2-} , DO, TSS, TDS, TOC, BOD, and alkalinity decreased in concentration after adsorption for both raw and chlorinated water while pH, NO_3^- , Cl^- and acidity decreased for raw water sample and increased for treated water. The trend observed for the conductivity and SO_4^{2-} particles is expected since conductivity ordinarily correlates with major ions and total dissolved solids. It is likewise an indication that the Cl^- and SO_4^{2-} are in the solution. It is in order to observe TOC and BOD following a similar pattern as indicated by logical guidelines that both TOC and BOD are legitimately relative to one another, and a decrease in BOD implies that adsorption process has an impact on the organic matter by implication, and consequently the Halogenated Acetonitriles which are formed by the reaction of organic matter and chlorine in water.

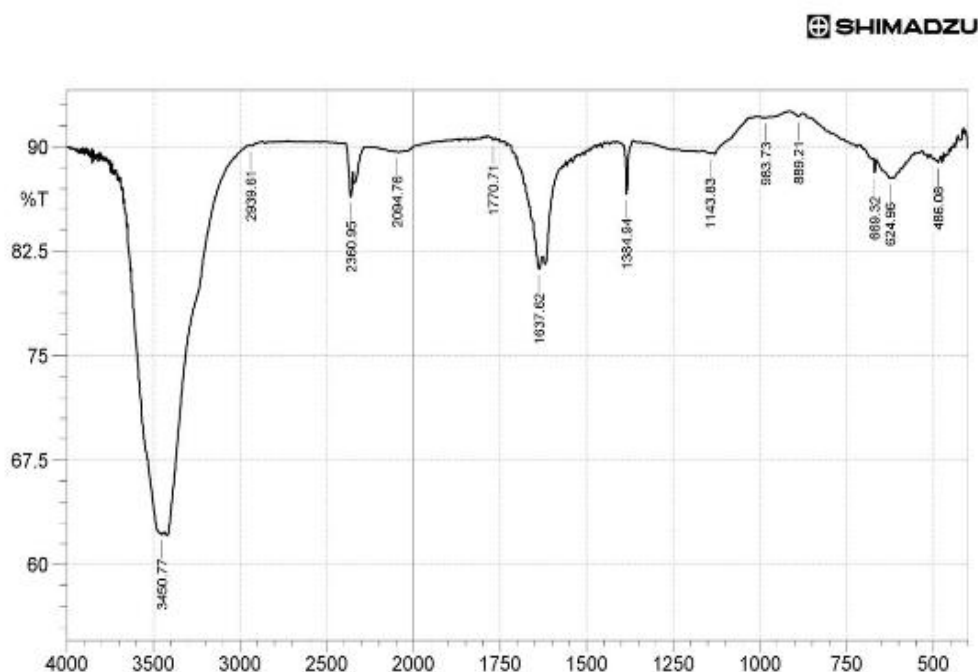


Fig. 2. FTIR spectrum of Walnut shell activated carbon

Table 4. Physicochemical analysis of influent raw and chlorinated water before and after adsorption

S/N	Parameters	Units	Raw water before adsorption	Chlorinated water before adsorption	Raw water after adsorption	Chlorinated water after adsorption	World Health Organization standards guideline values
1	Temperature	°C	27.7±0.14	27.15±0.07	25.75±0.00	26.09±0.24	25 – 32
2	pH	-	6.80±0.00	5.64±0.12	6.50±0.14	6.05±0.21	6.5 – 8.5
3	Conductivity	µS/cm	104.5±3.54	108.5±0.71	101.9±0.00	105.4±0.14	2500
4	Turbidity	NTU	9.76±0.03	1.89±0.24	3.97±0.00	0.57±0.00	5.00
5	TDS	mg/L	63.00±11.31	64.50±0.70	61.8±0.00	62.7±0.00	500 – 2000
6	TSS	mg/L	2.87±0.00	1.67±0.00	2.01±0.00	1.52±0.00	100
7	Acidity	mg/L CaCO ₃	5.85±0.07	0.23±0.08	3.23±0.00	0.72±0.21	5.5
8	Alkalinity	mg/L	71.88±0.30	52.02±7.07	41.62±0.00	35.76±0.00	50
9	TOC	mg/L	5.78±0.00	4.33±0.08	0.56±0.01	0.39±0.00	25
10	COD	mg/L	20.25±0.00	3.24±0.00	17.58±0.00	2.46±0.15	250
11	BOD	mg/L	34.07±0.00	4.79±0.31	14.92±0.18	3.17±0.08	30
12	DO	mg/L	9.03±0.01	2.31±0.01	0.00±0.00	0.00±0.00	4-7
13	NO ₃ ⁻	mg/L	0.78±0.00	0.27±0.00	0.45±0.00	0.47±0.00	10.00
14	NO ₂ ⁻	mg/L	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00
15	SO ₄ ²⁻	mg/L	5.48±0.01	0.31±0.01	4.35±0.04	0.23±0.00	400
16	Cl ⁻	mg/L	9.61±0.23	7.26±0.41	10.90±0.16	2.20±0.02	250 – 1000
17	DCAN (Walnut shell using HPLC)	mg/L	9.06×10 ⁻⁴ ±8.27×10 ⁵	8.41×10 ⁻⁴ ±3.75×10 ⁵	2.81×10 ⁻⁴ ±1.34×10 ⁵	1.77×10 ⁻⁴ ±4.60×10 ⁵	0.009
18	DCAN (CAC using HPLC)	mg/L	9.06×10 ⁻⁴ ±8.27×10 ⁵	8.41×10 ⁻⁴ ±3.75×10 ⁵	0.051±07.07	0.02±0.00	0.009

3.7 Batch Adsorption Studies on Simulated Solution of Dichloroacetonitrile (DCAN) Using Walnut Shell Activated Carbon (WSAC) as Adsorbent

The efficiency of WSAC as adsorbent for the adsorption of DCAN was examined. The parameters such as concentrations, pH, adsorbent dosage and contact time affecting the adsorption were studied using the WSAC. The results of the effects of each of the parameters are presented as follows:

3.7.1 Effect of initial concentration on adsorption of dichloroacetonitrile (DCAN) in simulated experiment

The initial analyte concentration is an important parameter in biosorption technology, which influences the adsorption of analyte to the biomass surface. The results obtained from the investigation of adsorption of DCAN using WSAC with the varied initial concentrations of 0.006, 0.009 and 0.012 mg/L (while other conditions were kept constant) are presented in Fig. 3. The results in this study indicated that DCAN biosorption was increased with increasing DCAN concentration of up to 0.012 mg/L. The adsorption efficiency took the trend of 16.67% at 0.006 mg/L, 20.00% at 0.009 mg/L and 41.67% at 0.012 mg/L initial concentration respectively. This is in agreement with the study of Akhtar et al. [31] and Yu et al. [39].

3.7.2 Effect of pH on adsorption of Dichloroacetonitrile (DCAN) in simulated experiment

The results of the investigation of the adsorption of DCAN on WSAC with varied pH 5, 7 and 9 are presented in Fig. 4 while other conditions such as adsorbent dosage, contact time and concentration were kept constant. The result shows that adsorption efficiency increased with an increase in pH of DCAN solution. The highest adsorption efficiency of 41.76% was observed at

pH of 9 while the least adsorption efficiency of 24.60% was observed at pH of 5 and 33.33% at the pH of 7 shows an adsorption efficiency of 34.61%. This trend may be due to the presence of hydroxyl (O-H) and carbonyl (C=O) bonds on the adsorbent as shown in the FTIR result. This is in line with the study of [25,23].

3.7.3 Effect of adsorbent dosage on adsorption of Dichloroacetonitrile (DCAN) in simulated experiment

The results obtained from the investigation of adsorption of DCAN using WSAC with the varied adsorbent dosages of 0.2, 0.4 and 0.8 g is presented in Fig. 5 while all other conditions (contact time, concentration and pH) were kept constant. The result shows that adsorbent dosage had a significant effect on the adsorption of DCAN using WSAC. The percentage adsorption efficiency increased from 53.37% to 60.11% and 61.1% as the adsorbent dosage was increased from 0.2 g to 0.4 and 0.8 g respectively. This is due to the fact that the increase in adsorbent dose enhances the free sorption surface and adsorption site, thereby adsorbing more of DCAN [11,25]. Adsorbent dose of 0.8 g gave the highest adsorption efficiency for the study. From the economic perspective however, adsorbent dosage of 0.2 g could be considered as best dosage of adsorbent for this study.

3.7.4 Effect of contact time on adsorption of Dichloroacetonitrile (DCAN) in simulated experiment

The results of the adsorption of DCAN using WSAC with varied contact time (30, 60 and 90 minutes) are presented in Fig. 6 while other conditions (concentration, adsorbent dosage and pH) were kept constant. The result shows that equilibrium adsorption capacity was established at contact time of 60 minutes since it has highest adsorption efficiency of 47.50% compare to 30 minutes contact time that has 38.33% and 60 min that has 45.00% adsorption efficiency. This might be due to the initial availability of vacant

Table 5. Adsorption efficiency of WSAC on raw and treated water samples

Contaminant	Adsorbent	Adsorption efficiency (%)	
		Raw water	Chlorinated water
DCAN	WSAC	69.00±1.43	79.00±0.03
	CAC	94.4±0.42	98.00±1.41

Confidence level = 0.05; *Sig. value =0.537

KEY: DCAN: Dichloroacetonitrile, WSAC: Walnut Shell Activated Carbon, CAC: Commercial Activated Carbon.

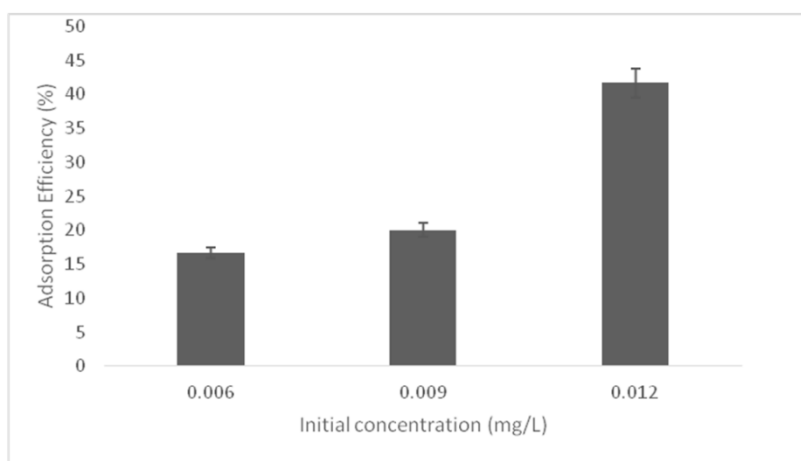


Fig. 3. Effect of Initial Concentration on DCAN Adsorption in Simulated Experiment

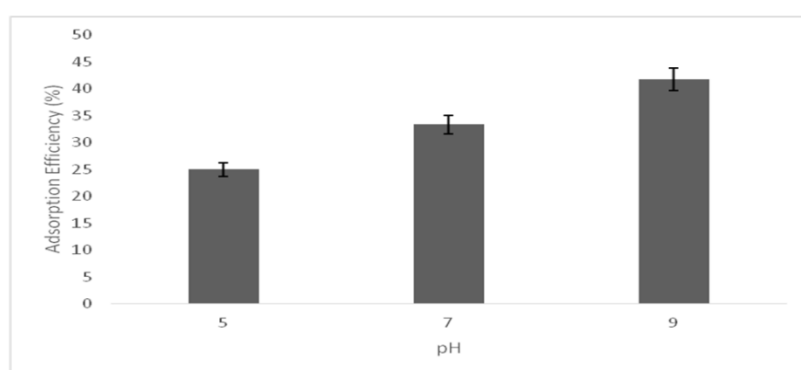


Fig. 4. Effect of pH on DCAN adsorption in simulated experiment

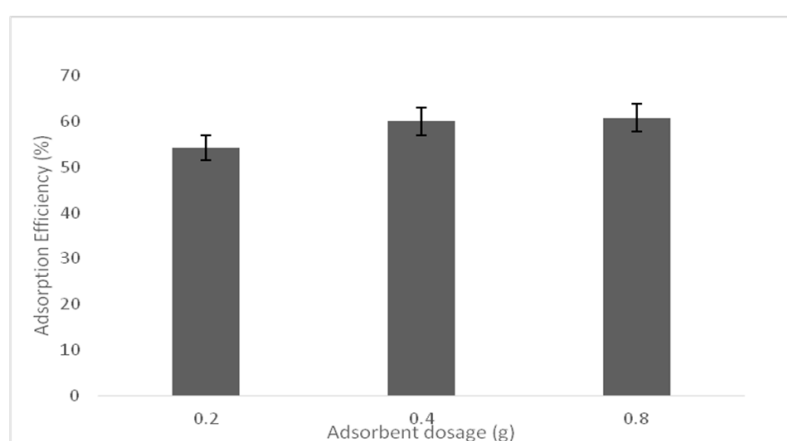


Fig. 5. Effect of adsorbent dosage on DCAN adsorption in simulated experiment

sites for the adsorption, the dynamic increment in adsorption and consequently the attainment of equilibrium adsorption which might also be due to the limited transfer of DCAN molecules from the bulk solution to the surface of the adsorbent [39,25,26].

3.8 Adsorption Study on Influent Raw Water and Treated Water Using WSAC and BCAC

Adsorption studies were conducted on raw and chlorinated water from the water treatment plant

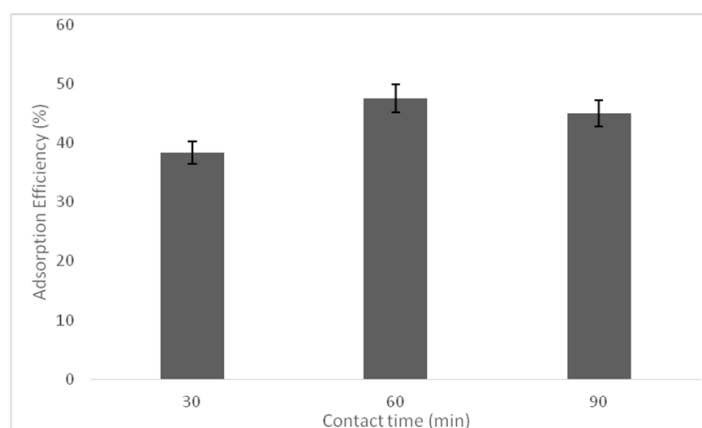


Fig. 6. Effect of contact time on DCAN adsorption in simulated experiment

using WSAC as adsorbent and compared with Burgoyne commercial activated carbon (BCAC) with the optimized conditions (pH 9, adsorbent dosage 0.8, and 60-minute contact time) from simulated experiments. DCAN concentrations of raw and chlorinated water samples were determined using High Performance Liquid Chromatography (HPLC) with the concentrations of $9.06 \times 10^{-4} \pm 8.27 \times 10^{-5}$ and $8.41 \times 10^{-4} \pm 3.75 \times 10^{-5}$ mg/L in raw and chlorinated water samples respectively. The result showed that the removal efficiency of WSAC for the adsorption of DCAN gave $2.81 \times 10^{-4} \pm 1.34 \times 10^{-5}$ and $1.77 \times 10^{-4} \pm 4.60 \times 10^{-5}$ mg/L in the raw and chlorinated water samples respectively (as presented in Table 5) which gave 69.00 ± 1.43 and 79.00 ± 0.03 (%) adsorption efficiency, while the removal efficiency of BCAC for the adsorption of DCAN result showed 0.051 ± 0.07 and 0.02 ± 0.00 mg/L with 94.4 ± 0.42 and 98.00 ± 1.41 (%) adsorption efficiency for both raw and treated water samples respectively (as presented in Table 2).

3.9 Recovery Experiment for the Extraction Process and Determination of DCAN

The result for the recovery experiment for the extraction process and determination of DCAN are presented in Table 6. The percentage

recoveries for the extraction of DCAN from raw and chlorinated water sample were $84.91 \pm 1.38\%$ and $86.01 \pm 0.62\%$ for raw and chlorinated water respectively. However, in order to validate the extraction procedure, deionized water was used as blank sample, was also spiked with a known concentration of DCAN, and the recovery percentages after the extraction process was $100 \pm 0.00\%$ respectively. According to Okoya et al. [25], recovery percentage yields of 100 and 90% are considered to be qualitative and excellent yield, 50–80% are considered to be good yield while 40% below are considered to be poor yield.

3.10 Adsorption Isotherms

The results of the sorption ability of Walnut Shell Activated Carbon (WSAC) as a natural adsorbent was evaluated through determination of adsorption isotherm of Dichloroacetonitrile (DCAN) sorption system and presented in Fig. 7a (Langmuir adsorption isotherm) shows the plot of C_e/q_e against q_e and Fig. 7b (Freundlich adsorption isotherm) shows the plot of $\ln q_e$ against $\ln C_e$, while Table 7 shows the coefficients of these isotherms (Langmuir and Freundlich adsorption Isotherms). The results show that the adsorption process is suitable well with Langmuir than Freundlich isotherms.

Table 6. Mean Percentage (%) recoveries of Dichloroacetonitrile (DCAN) from raw, chlorinated and blank water samples after extraction with dichloromethane

Sample ID	Unspiked concentration (mg/l)	Spiked concentration (mg/l)	% recovery
Raw Water Sample	9.06×10^{-4}	0.006	84.91 ± 1.38
Treated Water Sample	8.41×10^{-4}	0.006	86.01 ± 0.62
Blank Water Sample	0.000	0.006	100 ± 0.00

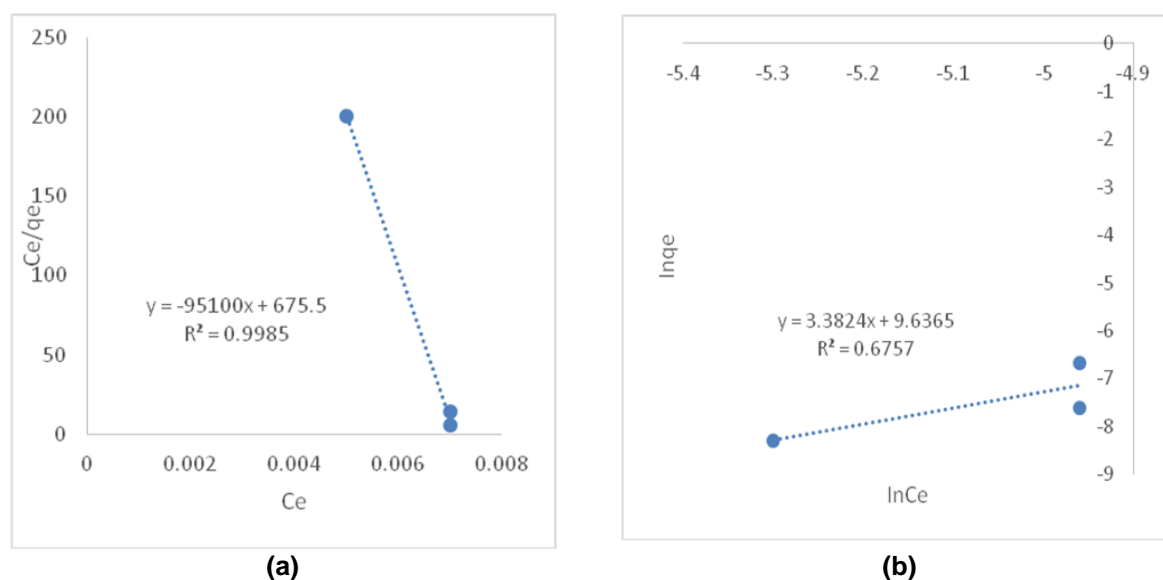


Fig. 7. Langmuir (a) and freundlich (b) adsorption isotherm for the adsorption of dichloroacetonitrile by walnut shell activated carbon

Table 7. Langmuir and Freundlich constants for the adsorption of Dichloroacetonitrile (DCAN) using Walnut Shell Activated Carbon (WSAC)

Adsorbent	Langmuir constants			Freundlich constants		
	$q_m(\text{mg/g})$	$K_a(\text{L/mg})$	R^2_L	$K_f(\text{mg/g(L/mg)})^{1/n}$	$1/n$	R^2_F
WSAC	-1.05×10^{-5}	-140.78	0.9985	15313.65	3.3824	0.6757

$R^2 = \text{correlation coefficient}$

4. CONCLUSION

The study demonstrated that the newly developed adsorbent from walnut shell has the potential application for DCAN removal from aqueous solution. The study concluded that the concentration of 9.06 and 8.41 mg/L of Dichloroacetonitrile (DCAN) were present in the raw and chlorinated water, respectively, from the water treatment plant. The Walnut Shell activated Carbon (WSAC) produced in a one stage simple procedure at 700°C has a strong affinity for the removal of DCAN in this study with 0.012 mg/L concentration, adsorbent dosage of 0.8 g, contact time of 60 minutes and pH of 9. Adsorption capacity of WSAC was very good compare to the commercial activated carbon. This adsorbent can therefore serve as a cheap and ecofriendly material for the remediation of DCAN from aqueous solution.

5. RECOMMENDATION

Treatment of drinking water with agricultural wastes should complement the conventional

treatment for efficient removal of Halogenated Acetonitriles (Dichloroacetonitriles). Water supply and treatment plants should take advantage of adsorption technologies by developing these natural adsorbents for water treatment purposes.

CONSENT

It is not applicable.

ETHICAL APPROVAL

Authors have declared no ethical issues in the manuscript.

DATA AVAILABILITY

The data used to support the findings of this study are included within the article.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

- Orme J, Mullin CS, Ohanian E. Health effects of disinfectants and disinfection by-products: A regulatory perspective. *Water Chlorination*. 1990;6:75-86.
- Doyle TJ, Zheng W, Cerhan JR, Hong CP, Sellers TA, Kushi LH, Folsom AR. The association of drinking water source and chlorination by-products with cancer incidence among postmenopausal women in Iowa: A prospective cohort study. *American Journal of Public Health*. 1997; 87(7):1168-1176.
- Richardson SD, Plewa MJ, Wagner ED, Schoeny R, DeMarini DM. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. *Mutation Research/Reviews in Mutation Research*. 2007;636(1-3):178-242.
- Shah AD, Dotson AD, Linden KG, Mitch WA. Impact of UV disinfection combined with chlorination/chloramination on the formation of halonitromethanes and haloacetonitriles in drinking water. *Environmental Science & Technology*. 2011;45(8):3657-3664.
- Williams DT, LeBel GL, Benoit FM. Disinfection by-products in Canadian drinking water. *Chemosphere*. 1997;34(2): 299-316.
- McGuire MJ, McLain JL, Obolensky A. Information collection rule data analysis. *American Water Works Association*. 2003; 1583212736.
- Shen K, Xu B, Xia S, Gao N, Li D, Tian F. Progress on the formation and control of disinfection byproduct halogenated nitriles in drinking water chlorination. *Journal of Environmental Pollution & Control*. 2010;10.
- Sulyman M, Namiesnik J, Gierak A. Low-cost adsorbents derived from agricultural by-products/wastes for enhancing contaminant uptakes from wastewater: A review. *Polish Journal of Environmental Studies*. 2017;26(2):479–510.
- Dai Y, Sun Q, Wang W. Utilizations of agricultural waste as adsorbent for the removal of contaminants: A review. *Chemosphere*. 2018;211:235–253.
- Egila JN, Dauda BEN, Iyaka YA, Jimoh T. Agricultural waste as a low cost adsorbent for heavy metal removal from wastewater. *International Journal of the Physical Sciences*. 2017;6(8):2152–2157.
- Amuda O, Ibrahim A. Industrial wastewater treatment using natural material as adsorbent. *African Journal of Biotechnology*. 2006;5(16).
- Zheng W, Guo M, Chow T, Bennett DN, Rajagopalan N. Sorption properties of greenwaste biochar for two triazine pesticides. *Journal of Hazardous Materials*. 2010;181(1):121-126.
- Karakoyun N, Kubilay S, Aktas N, Turhan O, Kasimoglu M, Yilmaz S, et al. Hydrogel–biochar composites for effective organic contaminant removal from aqueous media. *Desalination*. 2011; 280(1-3):319-325.
- Okoya AA, Akinyele AB, Amuda OS, Ofoezie IE. Chitosan-grafted carbon for the sequestration of heavy metals in aqueous solution. *American Chemical Science Journal*. 2016;11(3):1-14.
- Standards Organisation of Nigeria (SON). Nigerian standard for drinking water quality. *Nigerian Industrial Standard NIS*. 2007;554.
- Salem NA, Yakoot SM. Non-steroidal anti-inflammatory drug, ibuprofen adsorption using rice straw based biochar. *International Journal of Pharmacology*. 2016;12(7):729–736.
- Shang Y, Zhang J, Wang X. Use of polyethyleneimine modified wheat straw for adsorption of Congo red from solution in batch mode. *Desalination and Water Treatment*, 2015;57(19):8872–8883.
- Rattanachueskul N, Saning A, Kaowphong S, Chumha N, Chuenchom L. Magnetic carbon composites with a hierarchical structure for adsorption of tetracycline, prepared from sugarcane bagasse via hydrothermal carbonization coupled with simple heat treatment process. *Bioresources Technology*. 2016;226:164–172.

19. Gupta H, Gupta B. Adsorption of polycyclic aromatic hydrocarbons on banana peel activated carbon. *Desalination and Water Treatment*. 2015;57(20):9498–9509.
20. Tang R, Dai C, Li C, Liu W, Gao S, Wang C. Removal of methylene blue from aqueous solution using agricultural residue walnut shell: equilibrium, kinetic, and thermodynamic studies. *Journal of Chemistry*. 2017;2017:10. Article ID 8404965.
21. Tang C, Shu Y, Zhang R. Comparison of the removal and adsorption mechanisms of cadmium and lead from aqueous solution by activated carbons prepared from *Typha angustifolia* and *Salix matsudana*. *RSC Advances*. 2017; 7(26):16092–16103.
22. Chen B, Zhou D, Zhu L. Transitional adsorption and partition of nonpolar and polar aromatic contaminants by biochars of pine needles with different pyrolytic temperatures. *Environmental Science & Technology*. 2008;42(14):5137-5143.
23. Nguyen TAH, Ngo HH, Guo WS. Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. *Bioresource Technology*. 2013;148:574–585.
24. Okoya AA, Olaiya OO, Akinyele AB, Ochor NO. Efficacy of *Moringa oleifera* seed husk as adsorptive agent for trihalomethanes from a water treatment plant in Southwestern, Nigeria. *Journal of Chemistry*. 2020a;2020:11. Article ID 3450954, Available:<https://doi.org/10.1155/2020/3450954>
25. Okoya AA, Adegbaolu OS, Akinola OE, Akinyele AB, Amuda OS. Comparative assessment of the efficiency of rice husk biochar and conventional water treatment method to remove chlorpyrifos from pesticide polluted water. *Current Journal of Applied Science and Technology*. 2020b; 39(2):1-11. Article no.CJAST.54205 ISSN: 2457-1024.
26. Hunt DTE, Wilson AL, Wilson A. The chemical analysis of water: General principles and techniques Royal Society of Chemistry. 1986;2:0851867979.
27. Ademoroti CM. Environmental chemistry and toxicology. Foludex Press Ltd., Ibadan, Nigeria; 1996.
28. American Public Health Association (APHA) Standard Methods for the Examination of Water and Wastewater; 2012.
29. Golterman HL, Clymo RS, Ohnstad MAM. Methods for physical and chemical analysis of freshwater. Scientific Publication, Oxford, Lord. 1978;1-243.
30. Akhtar M, Hasany SM, Bhangar M, Iqbal S. Low cost sorbents for the removal of methyl parathion pesticide from aqueous solutions. *Chemosphere*. 2007;66(10): 1829-1838.
31. Liu Y, Lee ML. Pressure liquid chromatography using elevated temperature. *Journal of Chromatography*. 2006;1104(1-2):198–202.
32. Fatoki OS, Awofolu OR. Methods for selective determination of persistent organochlorine pesticide residues in water and sediment by capillary gas chromatography and electron capture detector. *Journal of Chromatography A*. 2003;983(1-2):225–236.
33. Standardization and Industrial Research Institute Malaysia (SIRIM), Specification of Powdered Activated Carbon MS873, Standardization and Industrial Research Institute Malaysia (SIRIM), Kuala Lumpur, Malaysia; 1984.
34. Thuy PT, Moons K, Van Dijk J, Viet Anh N, Van der Bruggen B. To what extent are pesticides removed from surface water during coagulation–flocculation? *Water and Environment Journal*. 2008;22(3):217-223.
35. Shinogi Y, Kanri, Y. Pyrolysis of plant, animal and human waste: Physical and chemical characterization of the pyrolytic products. *Bioresource Technology*. 2003; 90(3):241-247.
36. Gokce Y, Aktas Z. Nitric acid modification of activated carbon produced from waste tea and adsorption of methylene blue and phenol. *Applied Surface Science*. 2014; 313:352–359.
37. Warhurst AM, McConnachie GL, Pollard SJT. Characterisation and applications of activated carbon produced from *Moringa oleifera* seed husks by single-step steam pyrolysis. *Water Research*. 1997;31(4): 759–766.
38. Yu Q, Li M, Ji X, Qiu Y, Zhu Y, Leng C. Characterization and methanol adsorption of walnut-shell activated carbon prepared by koh activation. *Journal of Wuhan University of Technology-Mater. Sci. Ed*. 2016;31(2):260-268.

39. Thuy PT, Anh NV, Van der Bruggen B. Evaluation of two low-cost–high-performance adsorbent materials in the waste-to-product approach for the removal of pesticides from drinking water. CLEAN–Soil, Air, Water. 2012;40(3):246-253.

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