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TREATMENT OF INDUSTRIAL ANIMAL FEED PROCESSING WASTEWATER USING FUNCTIONALIZED NANO-ADSORBENT

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ABSTRACT

This study was carried out to address the growing concern for treatment of animal feed processing industry wastewater using a developed nano-adsorbent. In this study, nano-adsorbent was produced from carbon nanotube via chemical catalytic vapour deposition method. This was further purified and functionalized using multi-step purification techniques to give purified carbon nanotube (P-CNTs). The obtained nano-adsorbent were characterized by high resolution scanning electron microscopy (HRSEM), dynamic light scattering (DLS), and the Braunauer-Emmett-Teller (BET) method. Clear different morphological features were displayed by HRSEM, HRTEM while crystallinity and mineralogical phases were observed by XRD. The length and diameter of the adsorbent was revealed by nanozetasizer analysis to be 4.20 nm and 35 nm respectively, with an aspect ratio of 3200. The BET analysis showed the surface area of the nano-adsorbent to be 227.639 m^2/g and pore size to be 3.156. Furthermore, there were high percentage reduction of some physicochemical parameter and heavy metal content present in the wastewater. The TSS, BOD and COD was reduced by 98%, 82% and 76% respectively, while the removal of selected heavy metals (Mn, Fe, Ni, Cu and As) from animal feed wastewater revealed a removal efficiency as follow: 92% of As, 70% of Ni, 66% of Fe, 65% of Cu and 60% of Mn. Conclusively, it can be deduced that the nano-adsorbent is unique and has potential ability, large surface area and greater chemical reactivity for the treatment of animal feed processing wastewater. Hence, the treated wastewater can be re-used for industrial application and irrigation.

Introduction

Industries are often considered as a major tool for economic growth of any nation [1]. The production of useful consumer products is the indicators of this growth. One of such industries is the animal feed processing industry which utilizes raw agricultural ingredients such as corn, wheat, forages, vitamins and minerals to formulates a nutritious feed, which serve to provide highly nutritional diets that both maintain the health of the animal and increase the quality of end products such as meat, milk or eggs as the case maybe. However, the environmental concern is related to the volume of water used during the operational processes such as washing of raw materials and products, cleaning of machines, containers or flushing of the working floor, thereby generating large quantity of wastewater [2].

Due to increase in industrialization in developing countries, wastewater disposal has become a major threat [3]. The major challenge is how to deal with the manner in which the water is being discharged into the water body, as most processing industries (especially animal feed industries) do not have wastewater treatment technology, and where they exist, they are non-functional or inefficient. Consequently, all these challenges resulted into serious environmental degradation and health problems [4].

The adverse environmental effects associated with indiscriminate discharged of animal feed processing industrial wastewater, have been of great concern [5]. Effect of exposure to high organic loads (such as biochemical oxygen demand, chemical oxygen demand and total suspended solid) and inorganic pollutants (such as Fe, Cu, Ni, Mn and As) present in animal feed processing wastewater affect the lakes and reservoirs, caused the death of plants and trees, increased number of dead aquatic animals and affect humans within their food chain [6], [7]. However, most of the wastewater released from the animal feed industries are toxic to the environment and require cost effective and a comprehensive advanced sustainable treatment techniques [8]. Of the wide diversity of pollutants affecting water resources, organic loads and inorganic pollutants are of particular interest due to their strong toxicity (heavy metals) even at low concentration. They have also been reported to cause development of chronic diseases such as cholera, hepatitis B, diarrhoea, fever ad typhoid [6].

Several conventional methods (such as filtration, sedimentation, floatation, flocculation, membrane separation, and coagulation and precipitation) for wastewater treatment have been employed, yet, most of these techniques are generally ineffective and often very expensive [9], [10]. Also, some are prone to fouling and generate chemical sludge. On this note, adsorption method when combined with nanotechnology is a logical options for appropriate and a comprehensive sustainable treatment techniques. However, the use of carbon nanotubes as adsorbent exhibit exceptional potency via adsorption mechanism compared to activated charcoal. This occurred through physical adsorption and interaction of specific chemical functionality with the graphite like carbon lattice [11]. Adsorption to the surface of CNTs especially for larger compounds will be the primary site of interaction. In an aggregated form, CNTs will also present internal meso and micro pore adsorption sites, suitable for smaller species to interact with [12]. Moreso, adsorption capacity of CNTs is usually linked to the available high surface area, aspect ratio and surface chemical functional group that are generated during purification and functionalization of CNTs [13], [14]. Another attractive property of CNTs as adsorbent for wastewater treatment technologies is their increased capacity to remove heavy metals from aqueous solution [15], [16]. Therefore, this present study is focused on production of carbon nanotubes via chemical catalytic vapour deposition method as adsorbent for the treatment of industrial animal feed processing wastewater through batch adsorption process.

Materials and Methods

Materials

All the chemical reagents used in this study are of analytical grade with percentage purity in the range 96-99.9%. The chemicals were obtained from Sigma Aldrich and used without further purification. The animal feed processing wastewater was collected from Olam Nigeria Limited, Ilorin Kwara State, Nigeria.

Methods

Preparation of Bi-metallic Catalyst

By employing wet impregnation method, the preparation of bi-metallic catalyst (Fe-Co) supported on $CaCO_3$ substrate was used to grow carbon nanotube according to Bankole *et al*. [17] with slight modification. In this study, 10 wt% of the catalyst which contains equal proportion by weight, 5 wt% each of Fe $(NO_3)_2$. $9H_2O$ and Co $(NO_3)_2$. $6H_20$ were weighed and dissolved in 50 cm^3 of distilled H_2O followed by the addition of 10 g of $CaCO_3$ under continous stirring at 2000 rpm for 60 min. The stirring continues until a reddish brown colouration was formed. The resulting slurry was then allowed to dry at room temperature and later dried in an oven at 120 ^oC for 12 h cooled to room temperature, ground and finally screened through a 150 μm sieve. The final powder was then calcined at 400 ^oC for 16 h. The dried catalyst was ground to avoid agglomeration. The yield of bi-metallic catalyst prepared was calculated after drying and after calcination using the equation 1 and 2.

$$Percentage\ Yield\ (Y\%)_{(Pre-calcined)} = \frac{Mass\ of\ Catalyst\ after\ Drying}{Initial\ mass\ of\ mixture} \times 100\% \quad (1)$$

$$Percentage\ Yield\ (Y\%)_{(Post\ calcined)} = \frac{Mass\ of\ Catalyst\ after\ Calcination}{Mass\ after\ Drying} \times 100\% \quad (2)$$

Production of Carbon nanotubes

The procedure described by Bankole *et al*. [18] was adopted to produced CNTs. CNTs were synthesized by the decomposition of acetylene in a CVD reactor. A known weight (1 g) of the prepared Fe-Co Catalyst on $CaCO_3$ substrate was placed in the ceramic boat. The furnace was heated at rate of 30 cm^3/min for 90 min to purge the system of air before the commencement of the reaction. Once the reaction temperature was attained at 700 ^oC, the argon flow rate was adjusted to the required flow of 30 cm^3/min and acetylene gas was introduced at its required flow rate (190 cm^3/min). The reaction process was allowed to proceed until the reaction time 45 min was reached, thereafter the flow of acetylene was stopped and the flow of argon was reduced to 30 cm^3/min and waited until the system of the furnace cooled to room temperature. The ceramic boat was then removed and weighed to determine the quantity of CNTs produced. Percentage of CNTs yield was calculated using the relationship provided by Taleshi [19] as presented in equation 3.

$$CNTs\ Yield\ (\%) = \frac{M_{Total} - M_{Catalyst}}{M_{Catalyst}ure} \times 100\% \quad (3)$$

Where M_{Total} is the total mass of the final catalyst and carbon products after CVD reaction process and $M_{Catalyst}$ is the initial mass of Fe-Co/$CaCO_3$ catalyst.

Purification of Carbon Nanotubes

The purification of the produced CNTs was achieved via an acid treatment with mixture of concentrated HNO_3 and H_2SO_4 acid in the ratio 1 to 3 (v/v), to remove residual metallic impurities (such as Fe, Co) and amorphous carbon introduced into the sample during the catalyst production. De-ionized water was added to the mixture and thereafter ultrasonicated for 3 h at 40 ^{o}C. The mixture was then refluxed and washed with distilled water until a pH of 7 was achieved. The mixture was later filtered out to obtain the wet CNT residue, which was further oven-dried at 80 ^{o}C for 8 h to give purified CNTs (P-CNTs).

Characterization of P-CNTs

A purified CNTs sample was characterized for its morphologies, particle size and specific surface area by Zeiss Auriga High Resolution Scanning and Transmission Electron Microscope (HRSEM and HRTEM), Malvern Dynamic Light Scattering (Malvern Nano-zetasizer) and NOVA 4200e Braunauer-Emmett-Teller (BET) analysis.

Characterization and Batch Adsorption Experiment of the Wastewater

All the analyses carried out on the collected industrial animal feed processing wastewater were determined using American Public Health Association (APHA) method. Batch adsorption experiment: effect of contact time was carried out on the wastewater (0.01 g of P-CNTs was shaken in 50 cm^3 of the wastewater at different time of 10, 20, 30, 40, 50, 60, 70, and 80 min).

Results and Discussion

In this study, the nano-adsorbent is characterized to be able to know their adsorptive properties and capacities for the specific usage. The morphology, surface area and particle size of the adsorbent are considered necessary for an effective adsorption processes. The morphological features (size, shape and purity) of the produced P-CNTs were investigated via HRSEM as shown in the micrograph (see Figure 1 a and b).

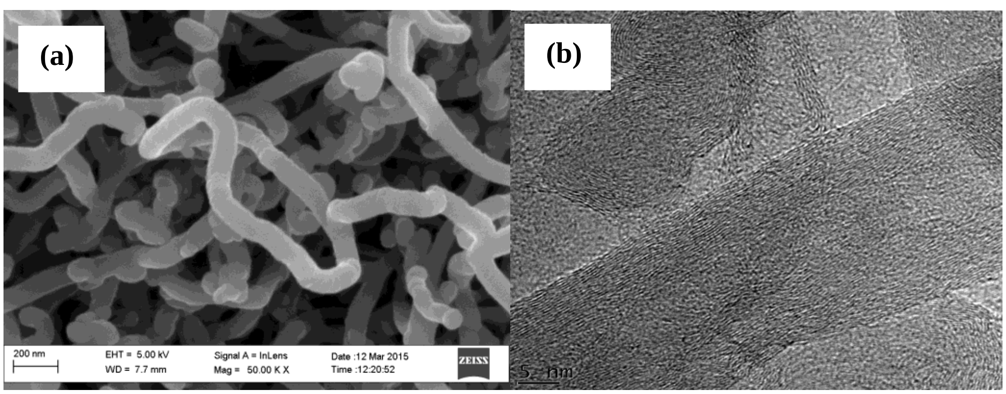

Figure 1: (a) High Resolution Scanning Electron Microscope (HRSEM) Image of Purified Carbon Nanotubes (P-CNTs) (b) High Resolution Transmission Electron Microscope (HRTEM) Image of Purified Carbon Nanotubes (P-CNTs)

The HRSEM image of P-CNTs (Figure 1a) showed bundles of interwoven tube-like structures with shiny tips depicting and confirming the nanotube structure of P-CNTs. Also, the observed morphologies may be related to the purification procedure adopted during production. However, the purification of CNTs with oxidative acid treatment introduces the presence of functional groups such as COOH, OH along the edges of the CNTs and around the openings. These act as a linkage to the binding sites of the CNTs for better adsorptive property.

In Figure 1b, the HRTEM image of the P-CNTs depicts the multiple graphitic layers multi-wall structure (MWCNTs) with the hollow inner diameter of 5.5 nm and defective etching at outer edges wall was observed. The graphitic wall denotes its crystallinity, an essential ingredient for favourable adsorption process.

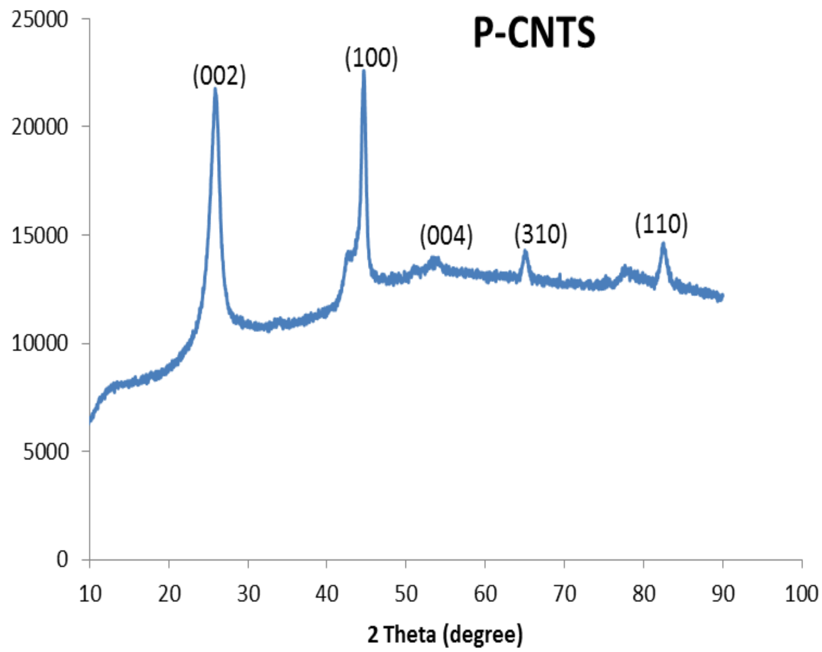

Figure 2: X-ray Diffraction (XRD) patterns of the P-CNTs

The mineralogical phases and extent of crystallinity of the P-CNTs was investigated using X-ray diffraction (XRD) as presented in Figure 2. In Figure 2, the sharp and intense diffraction peaks observed at 2 theta value of 25.9^o and 44.67^0 with a crystal plane of (002) and (100) represent a typical graphitic multi-walled CNT structure which is in agreement with the HRTEM result of Figure 2.

Table 1 DLS (Nanozeta-sizer) of the Purified Carbon Nanotubes

Adsorbent	Z-Average (D_h)	Polydispersity (Đ) Index	Length (μm)	Diameter (nm)	Aspect Ratio
P-CNTs	832.1	0.410	4.20	35	3200

A dynamic Light Scattering (DLS) technique was used to obtain the particle size of the P-CNTs in terms of length and diameter as shown in Table 1. The length and diameter of the produced P-CNT was found to be 4.20 μm and 35 nm. A correlation chart for length, diameter and aspect ratio of the nano-adsorbent was reported according to IUPAC that when polydispersity index Đ = 0, it means that there is uniformity of size and shape within the sample (monodisperse), when Đ is within the range 0.1-0.4, it is moderately polydispersed while for Đ > 0.4, is broadly polydispersed. The produced P-CNTs sample was found to be 0.410, indicating that the sample is broadly polydispersed and has aspect ratio of 3200, which depict an essential property for the development of nano-adsorbents during the adsorption process [20].

Table 2 Brunauer-Emmett-Teller (BET) Analysis of the Purified Carbon Nanotubes

Adsorbent	Specific Surface Area (m^2/g)	Total Surface Area (m^2)	Pore Volume (cm^3/g)	Pore Radius (nm)
P-CNTs	227.637	100.16	0.0827	3.156

Surface area analysis was carried out on the produced P-CNTs using BET method. It was observed from Table 2 that the specific surface area and porosity of the P-CNTs was found to be 227.637 mg/g and 3.156 nm respectively. According to IUPAC, it was reported that samples with pore size in the range of 2-50 nm are classified as mesoporous material [21]. Thus, the pore size implies that the developed nano-adsorbent is mesoporous in nature.

Industrial Animal Feed Processing Wastewater Treatments

Prior to the treatment of industrial animal feed processing wastewater, selected physicochemical parameters and heavy metals content of the wastewater were analyzed and the results after contact time (10 min) treatment of the adsorption process are presented in Table 3.

Table 3: The mean concentration of selected physicochemical parameters and heavy metals content in industrial animal feed processing wastewater (before and after treatment)

Physicochemical parameters	Raw Value	P-CNTs Treated	WHO/EPA Permissible Limits	NIS Permissible Limits
TSS (mg/L)	120	2.00	0.75	0.75
COD (mg/L)	320	77.00	40	-
BOD (mg/L)	84.9	15.40	10/5-7	6
Copper (mg/L)	1.143	0.40	1.0	1.0
Nickel (mg/L)	0.611	0.184	3.0	-
Iron (mg/L)	0.979	0.329	0.5	0.3
Manganese (mg/L)	0.747	0.302	1.0	-
Arsenic (mg/L)	0.037	0.003	0.1	-

Key: TSS = Total Suspended Solid, COD = Chemical Oxygen Demand, BOD = Biochemical Oxygen Demand, WHO (2008) = World Health Organization, EPA (2007) = Environmental Protection Agency and NIS (2007) = Nigerian Industrial Standard

The results presented in Table 3, indicate that the level of total suspended solid (TSS) was 120 mg/L and reduced drastically after treatment to 2 mg/L. The standard limits of wastewater containing TSS are set to be 0.75 mg/L according to WHO/EPA [22, 23] and NIS [24] from Table 3. It was observed that the concentration of chemical oxygen demand (COD), in animal feed processing wastewater is 320 mg/L and after treatment with the P-CNTs adsorbent, the value fall to 77.00 mg/L. The permissible limit in wastewater according to NIS [24] is < 40 mg/L. According to the results in Table 3, the biochemical oxygen demand (BOD) value of animal feed processing wastewater is 84.9 mg/L, which is far above the maximum allowable concentration set by WHO/EPA [22, 23] and NIS [24]. However, after the treatment process with the produced P-CNTs adsorbent, it was able to remove 82% of BOD concentration from the animal feed processing wastewater.

Acute exposure of Cu causes gastro-intestinal effect such as nausea, vomiting and diarrhoea, which can lead to death [25]. Table 3 shows Cu concentration to be 1.143 mg/L, while after treatment, reduced to 0.404 mg/L (65% removal). Thus, the P-CNTs adsorbent has significant effect on the removal of Cu. The Ni content at pretreatment was 0.611 mg/L and after treatment, the Ni concentration was reduced to 0.184 mg/L. However, before and after treatment, the Ni concentration falls within the maximum permissible limits of 3 mg/L. Furthermore, the amount of Fe concentration in Table 3 is 0.979 mg/L. According to standard limits set by WHO/EPA [22, 23] and NIS [24], 0.5 mg/L and 0.3 mg/L respectively, is the allowable concentration for safe water. Also, in Table 3, it was noticed that the amount of manganese in the wastewater is 0.747 mg/L and reduced to 0.302 mg/L. This indicates that the prepared P-CNTs were able to remove 60% of Mn from the animal feed processing wastewater. More so, As concentration prior to treatment was 0.037 mg/L and at post treatment is 0.003 mg/L. Both the pretreatment and post treatment results fit into the maximum permissible limit of As in water. However, it can be deduced from the results obtained that the P-CNTs adsorbent is suitable for the treatment of industrial animal feed processing wastewater.

The high capacity of P-CNTs in the adsorption of the pollutants may be linked to availability of more binding sites, adsorbent surface area (see Table 2), crystallinity nature (see Figure 1 and 2), and electrostatic attraction of P-CNTs to the wastewater.

Conclusion

In summary, the study focused on the production, purification and characterization of carbon nanotubes as adsorbent for removal of selected physicochemical parameters and heavy metals from animal feed processing wastewater. Based on the results of the study, HRSEM analysis of the P-CNTs showed formation of a clear morphology with less degree of aggregation. The BET results gave enhanced surface area and porosity of the CNTs on purification. However, the DLS Nano-zetasizer shows that the P-CNTs adsorbent is broadly polydispersed with high aspect ratio. The study revealed the maximum percentage removal efficiency of the physicochemical parameters from animal feed processing wastewater by the P-CNTs to be in the order: TSS (98%), BOD (82%) and COD (76%) while heavy metal removal efficiency from the animal feed processing water are as follow, As (92%), Ni (70%), Fe (66%), Cu (65%) and Mn (60%). From this study, it can be concluded that the P-CNTs nano adsorbent have unique and high potential adsorptive capabilities for the treatment of industrial animal feed processing wastewater.

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