

Research Journal of Environmental Sciences

ISSN 1819-3412



www.academicjournals.com

Research Journal of Environmental Sciences

ISSN 1819-3412 DOI: 10.3923/rjes.2023.1.11



Research Article Adsorptive Properties of Sawdust Activated Carbon for the 2,2-Dichlorovinyl-Dimethyl-Phosphate Removal from Agrochemical Industrial Wastewater

¹Aderonke Adetutu Okoya, ²Abimbola Bankole Akinyele and ¹Olusola Olufemi Farinde

¹Institute of Ecology and Environmental Studies, Obafemi Awolowo University, Ile-Ife, Nigeria ²Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University, Awka, Anambra, Nigeria

Abstract

Background and Objective: In the aquatic environment, pesticides are the most studied class of organic toxins but their management has received little attention. The efficacy of activated carbon formed from sawdust as an adsorbent for pesticide removal from industrial wastewater was investigated as well as the effectiveness of conventional wastewater treatment processes for pesticide removal. It also compared the adsorbent's efficiency to activated carbon that is commercially available. **Materials and Methods:** The SEM-EDX, FTIR and the brunauer-emmett-teller (BET) analyzer were used to analyze sawdust-activated carbon (SAC) made from locally available sawdust. Batch adsorption experiment on simulated solutions of 2,2-Dichlorovinyl-dimethyl-phoshate (DDVP) at varied concentrations (0.001, 0.005, 0.01, 0.1 and 0.5 mg L⁻¹) using SAC. Other variables including pH, adsorbent dose and contact time were optimized. **Results:** The pH was 7.2±0.14, ash content was 3.1 ± 0.00 , moisture content was $2.0\pm0.32\%$, Brunner Emmett Teller surface area was 736 ± 0.00 m² g⁻¹, micropore volume was 0.3131 ± 0.00 m³ g⁻¹ and bulk density was 0.55 ± 0.00 , according to the SAC. In the untreated and company-treated wastewater samples, the percentage recoveries for DDVP were 86 ± 0.71 and 88 ± 1.41 , respectively. In the adsorption of DDVP from industrial wastewater, the optimum parameters obtained during the simulation experiment were used. Sawdust activated carbon has higher adsorption efficiencies (89.06 ± 0.014 and 88.62 ± 0.962) than commercial activated carbon (80.94 ± 2.744 and 77.50 ± 0.410) for both untreated and company-treated wastewater, according to the findings. **Conclusion:** The sawdust-activated carbon for the removal of DDVP from wastewater.

Key words: Pesticide, sawdust, wastewater, agrochemical, activated-carbon, adsorption, industry

Citation: Okoya, A.A., A.B. Akinyele and O.O. Farinde, 2023. Adsorptive properties of sawdust activated carbon for the 2,2-dichlorovinyl-dimethyl-phosphate removal from agrochemical industrial wastewater. Res. J. Environ. Sci., 17: 1-11.

Corresponding Author: Aderonke Adetutu Okoya, Institute of Ecology and Environmental Studies, Obafemi Awolowo University, Ile-Ife, Nigeria

Copyright: © 2023 Aderonke Adetutu Okoya *et al.* This is an open access article distributed under the terms of the creative commons attribution License, which permits unrestricted use, distribution and reproduction in any medium, provided the original author and source are credited.

Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

In many parts of the world, increasing demands on water resources make the recovery and reuse of municipal and industrial wastewater a significant component of the water budget to meet these needs. One of the most common routes for anthropogenic organic and inorganic pollutants to enter the environment is through wastewater. Domestic and industrial wastewater are generally collected and treated separately due to their varied compositions and treatment requirements, allowing for more efficient source control and specific pollutant mitigation measures. Municipal wastewaters in developing countries, on the other hand are generally mixed and include both home and industrial wastewaters¹.

The majority of wastewater in underdeveloped nations is dumped into the environment either untreated or after only mechanical treatment. As a result of poor wastewater management procedures in developing countries, the organic load discharged into receiving waters is frequently very high and has a very complex chemical makeup². Moreover, certain categories of legally controlled contaminants classified wastewater as containing a large number of different specific organic constituents for which environmental quality standards have yet to be developed³. A growing number of studies on the prevalence of unregulated anthropogenic substances sometimes referred to as emergent organic pollutants, have raised concerns about their potential detrimental environmental implications in the last decade⁴.

Rivers have been highly polluted by industrial, mining and urban wastewaters as well as surface runoff from agricultural areas. Surface runoff from agricultural areas used to be the most prevalent source of pesticide pollution but wastewaters are now one of the most common routes for pesticide contamination into the environment in urban areas⁵. Because of non-agricultural usage, pesticides are mostly discovered in urban Wastewater Treatment Plants (WWTPs). Grass management (golf courses, educational plants, parks and cemeteries), industrial vegetation control (industrial facilities, electric utilities, roadways, railroads and pipelines), public health (mosquito-abatement districts, rodent-control areas and aquatic areas) and non-agricultural crops (commercial forestry, horticulture and plant nurseries as well as pesticides and chemical industries) are just a few examples⁶.

Even though pesticides are the most researched class of organic contaminants in the aquatic environment, little attention has been paid to their incidence and behaviour in WWTPs, presumably because these compounds have typically been associated with agricultural rather than urban sources⁷. Pesticides are relatively stable when they enter living bodies and can bioaccumulate. Because of their toxicity and carcinogenic qualities, they are also exceedingly harmful. Pesticides can be classified based on their chemical structure, target organism and physical state. Chemical structural categorization includes organophosphates, carbamates and organochlorines. Because organophosphates and carbamates inhibit the enzyme acetylcholinesterase, acetylcholine (a neurotransmitter) cannot be converted to choline and acetic acid, the neurological system is disrupted. As a result, nerve impulses are constantly transferred, causing symptoms such as weakness or paralysis. Organochlorines can bioaccumulate and remain in the environment for a long time³. As a result, which have a shorter lifetime in the environment and are more degradable.

Pesticides are a broad term that covers a wide range of compounds. Defoliants are chemicals that cause plants to lose their leaves or other foliage to harvest them. Desiccants help to dry live tissues like plant tips that are no longer needed. Insect growth regulators halt the reproduction of pests insects. Plant growth regulators influence the normal growth of plants (excluding fertilizers and other nutrients). Pesticide residues can pollute areas where pesticides are used if they persist in the soil. These leftovers might be swept into surface waters by rainwater. If they stay stable in the environment for a long time, bioaccumulation can be harmful to living creatures. Pesticides are now designed to be more biodegradable and less toxic to non-target organisms than in the past^{3,8}.

Despite these efforts, their concentrations in aquatic ecosystems are higher than the acceptable limit in a variety of situations. Pesticides are increasingly widely utilized and have a high level of stability, causing humans to offer solutions to the environmental damage they cause. A variety of solutions have been developed to solve this problem, including adsorption, improved oxidation, electrocoagulation and membrane approaches. One of the most frequent methods for eliminating hazardous substances from polluted water is adsorption. Activated carbon is the most popular material used to remove organic contaminants through adsorption, notwithstanding its high cost⁹. Recent research has focused on alternative adsorbents, namely low-cost adsorbents, which involve converting waste into adsorbents capable of extracting large amounts of various contaminants from aqueous waste. Biomass is an effective alternative sorbent for this purpose due to its great potential for removing contaminants from aqueous solutions¹⁰.

Many recent studies have examined how low-cost materials can be used as adsorbents to remove organic pollutants from aqueous solutions. Biomass in water

treatment is receiving more attention and it now appears to be a viable option for contaminant removal¹¹. For removing organic contaminants from wastewater, a variety of biomass has been employed. According to the literature, biosorption can be used alone or in combination with other strategies to increase removal efficiency. This biosorption, on the other hand, has precise requirements for capturing different pollutants from various wastewater sources. Hence, there is a need to develop adsorbents from sawdust and conditions must be optimized for optimal efficiency in the removal of 2,2-Dichlorovinyl-dimethyl-phoshate from agrochemical industrial wastewater.

MATERIALS AND METHODS

Study area: The study was carried out between 2018 and 2019 at SwWECh Laboratory, Institute of Ecology and Environmental Studies, Obafemi Awolowo University, Ile-Ife, Nigeria.

Collection and carbonization of the sawdust: Sawdust was obtained locally from a sawmill in Osogbo, Osun State, Nigeria, for this investigation. It was cleaned with distilled water and sun-dried to remove foreign contaminants before being used to make activated carbon. The washed-dried sawdust (200 g) was placed in a crucible that had been cleaned, dried and weighed before being placed in a muffle furnace (ESSEN Germany's Carbolite 12/65 tube furnace). To develop the char, the furnace was heated to 700°C for 2 hrs¹². The char was taken out of the oven, covered and left to cool to room temperature. The char was repeatedly cleaned with distilled water to remove tars before being air-dried until it reached a consistent weight. Subsequent laboratory studies at the SwWECh Laboratory and Research Unit, Institute of Ecology and Environment Studies, employed analytically graded reagents.

Activation of carbonized sawdust char: The sawdust char was impregnated with 1M KOH at a 1:1 (w/w) impregnation ratio. After that, the mixture was dehydrated in a 100°C oven for 4 hrs. The dry solid mixture was activated for 45 min at 500°C in a muffle furnace. It was then soaked overnight in dilute HNO₃ to remove any remaining alkali from the pores of the sawdust char. Then, it was rinsed with distilled water to eliminate any remaining acid and bring it back to a neutral pH. The activated sawdust char was then oven-dried at 110°C until it reached a consistent weight, then stored in a desiccator for future examination. **Characterization of sawdust activated carbon (SAC):** The surface morphological features and elemental composition of SAC were examined using a scanning electron microscope and energy dispersive X-ray (SEM/EDX). The Brunauer-Emmett-Teller (BET) Analyzer (VARIO EL III, Elementar, Germany) was used to determine the surface area of the activated carbon and the functional groups were determined using the Fourier Transform Infrared method (SHIMADZU-FTIR-8400S).

Preparation and sampling of wastewater: The water sampling bottles (2.5 L) were pre-cleaned according to standard methods for organic contamination sampling^{13,14}. To prevent further contamination, the bottles were allowed to air dry for 24 hrs and the mouthparts were wrapped in aluminium foil until sampling. Samples of wastewater were taken from an agrochemical plant in Lagos, Nigeria. In triplicates, wastewater samples were obtained from two sampling stations (the company-treated wastewater and the untreated wastewater). In situ measurements of temperature, electrical conductivity, total dissolved solids and pH were made on wastewater samples. The wastewater samples were properly labelled, acidified with concentrated H₂SO₄ and delivered to the SwWECh laboratory and Research Unit at the Institute of Ecology and Environmental Studies for further examination¹⁵. Other physicochemical characteristics of the wastewater, such as total suspended particles, alkalinity, total hardness and sulphates, were determined using Ademoroti's methodologies¹⁶.

Characterization of the wastewater: The concentration of 2, 2-Dichlorovinyl-Dimethyl-Phosphate (DDVP) in both the firm treated and untreated wastewater was evaluated using gas chromatography coupled with a Mass Spectrometer (GC-MS) after the wastewater samples were extracted with dichloromethane. Standard procedures were used to determine the physicochemical properties of the wastewater. This was done to aid in the variation of DDVP concentrations during the simulation experiment and to analyze the adsorbent's efficiency subsequently.

Extraction of DDVP in wastewater samples: The extraction of DDVP from wastewater samples was carried out using a modified Okoya *et al.*¹⁷ method. In a 250 mL capacity separating funnel (DURAN, Germany), dichloromethane (10 mL) was added to 50 mL of each of the wastewater samples and vigorously shaken for 10 min before being left to stand for another 10 min. The organic layer was collected in a test tube once the separating funnel was opened. By adding

another 10 mL of dichloromethane, the aqueous layer was re-extracted using the same technique. To eliminate any remaining water, anhydrous sodium sulphate (2 g) was added to the collected organic solvents. At room temperature, the dried extract was concentrated until it was completely dry. The concentrates were reconstituted in the same organic solvent and then analyzed in 1.5 mL GC/MS vials.

Gas chromatography analysis: The presence of DDVP in the wastewater samples was determined using an Agilent 7890 Series GC-MS. For operation, data processing and reporting, ChemStation software was installed on the GC-MS. A maximum length of 30 m, a diameter of 250 m and a film thickness of 0.25 m define the HP-5 fused silica capillary column. The GC-MS uses helium gas as a carrier gas to transport the solute through the column. The column temperature was programmed from 4°C for 2 min, then increased at a rate of 6°C/min to 120°C, held for 2 min and then continued at a rate of 20°C/min to 250°C, held for 5 min, to improve good resolution at varied boiling points Fatoki and Awofolu¹⁸. The oven temperature was 300°C with an equilibrium time of 0.25 min and a peak flow rate of 104.5 mL min⁻¹ at a pressure of 11.604 psi and a peak flow rate of 104.5 mL min⁻¹. The injection took 45.75 min and was performed at 250°C with a splitless mode injector.

Recovery experiment for the extraction process and determination of DDVP: The Liquid/Liquid Extraction method (LLE) described by Okoya *et al.*¹⁷ and Fatoki and Awofolu¹⁹ was used to extract DDVP from wastewater samples. Each of the acidified untreated and company-treated wastewater samples (100 L) was spiked with 50 mL of 0.5 mg L⁻¹ DDVP concentration and extracted with 15 mL dichloromethane, followed by 2 g of anhydrous sodium sulphate. The resultant extract was concentrated to approximately 2 mL at room temperature for chromatographic analysis (as in section above). By spiking a deionized water sample with the DDVP standard, the effect of the matrix on extraction efficiency was investigated. Equation 1 contains the recovery experiment equation:

$$Recovery (\%) = \frac{GC - MS \text{ spiked concentration} - GC - MS \text{ Unspiked concentration}}{GC - MS \text{ spiked concentration}} \times 100$$
(1)

Simulation of DDVP wastewater: In the laboratory, a 1 mg L⁻¹ stock solution of wastewater containing DDVP was simulated and then diluted with deionized water to concentrations of 0.001, 0.005, 0.01, 0.1 and 0.5 mg L⁻¹.

Adsorption experiment

Batch adsorption from simulated solutions: The SAC was used as the adsorbent in a batch adsorption experiment. Each of the simulated DDVP (50 mL) solutions of various concentrations (0.001, 0.005, 0.01, 0.1 and 0.5 mg L⁻¹) was combined with the adsorbent in a separate conical flask with constant shaking using an orbital shaker (Celtech KJ-201BD) set to 120 osc/min. For the adsorption efficiency of the produced SAC, parameters such as pH, adsorbent dosage, contact time and DDVP initial concentration were varied. After batch adsorption, Whatman filter paper was used for filtration (No.1). Following the procedures in sections above, the residual DDVP in the filtrate was collected and the concentration was measured. Equations 2 and 3 were used to calculate the amount of DDVP adsorbed by a unit mass of SAC (q) and the percentage of DDVP adsorbed (Adsorption efficiency percent) for each adsorption method^{20,21}:

$$q = \frac{v(C_i - C_f)}{m}$$
(2)

Where:

$$q = Amount of DDVP uptake per unit mass of SAC (g)$$

- v = Volume of the matrix sample (L)
- C_i = Initial concentration of the DDVP in the solution (mg L⁻¹)
- C_f = Final concentration of the DDVP in the filtrate (mg L⁻¹)
- m = Amount of SAC used (g)

Adsorption efficiency(%) =
$$\frac{(C_0 - C_1)}{C_0} \times 100$$
 (3)

Where:

 C_1 = Final concentration of DDVP in the filtrate after adsorption

Adsorption of DDVP from agrochemical wastewater: Using the prepared sawdust activated carbon and commercial activated carbon, the optimal adsorption conditions from the simulated solutions were applied to company-treated and untreated effluent from agrochemical industries.

Adsorption isotherms: Different constants were generated using the Langmuir and Freundlich equilibrium models to determine sorbent interaction with the adsorbate²²⁻²⁴.

Statistical analysis: The various data obtained from the study were subjected to statistical analysis using a Paired Sample t-test Analysis.

RESULTS AND DISCUSSION

Determination of carbon yield from sawdust: The result of the carbon yield of the char (136.8 \pm 0.56) from sawdust showed a percentage yield of 68.40 \pm 0.28 from 200 g of the stated sawdust.

Physicochemical Properties SAC: The results of the physicochemical parameters of SAC were presented in Table 1. The activated carbon product has a porous volume of 0.3131 cm³ g⁻¹ and a surface area of 736 m³ g⁻¹. These are characteristics of a good adsorbent²⁴.

Elemental composition of SAC: Carbon, oxygen and sulfur are among the components found in SAC before adsorption. Carbon has the highest percentage of all the elements detected (65.30%), followed by oxygen (20.10) and sulphur (14.30%). For both untreated and company-treated wastewater, the elemental compositions of SAC changed following adsorption with the addition of hydrogen and a change in carbon composition. In the SAC sample used for adsorption of company-treated wastewater, the percentage of carbon decreased from 65.30-65.24%, whereas, in the SAC sample of untreated wastewater, the percentage of carbon increased from 65.30-70.47%. This could be due to the presence of organic molecules in the untreated wastewater sample²⁵. Furthermore, hydrogen that was lacking from the activated carbon before adsorption was discovered to be

present after the adsorption process, 15.75 and 20.37% for untreated and company-treated wastewater, respectively. This could be due to the wastewater sample's anaerobic digestion (fermentation of cellulose and other organic debris) to produce biogas (methane, carbon dioxide, hydrogen sulphide, hydrogen and other components). This also means that the activated carbon made from sawdust using KOH is mostly microporous as hydrogen adsorption normally occurs in micropores²⁶.

FTIR analysis of SAC: The functional groups found in sawdustactivated carbon were depicted in Fig. 1. Each of the FTIR bands represents a different functional group that allows for adsorption. The presence of cellulose and hemicelluloses components of sawdust is indicated by the peak seen on the spectra at the broadband at 3398.69 cm⁻¹, which represents the O-H stretching vibration of hydroxyl functional groups in low concentrations. The stretching in the hydroxyl group is shown by the band at 3207.73 and 3049.56 cm⁻¹. The C=O stretching vibration in carbonyls such as carboxyl, aldehydes, lactones and ketones has a peak at 875.71 cm⁻¹. Ketonic and

Table 1: Physicochemical properties of SAC

Parameter	Sawdust activated carbon	
рН	7.2±0.14	
Ash content	3.1±0.00	
Moisture content (%)	2.0±0.32	
BET surface area (m ² g ^{-1})	736±0.00	
Micropore volume (cm ³ g ⁻¹)	0.3131±0.00	
Bulk density (g mL ⁻¹)	0.55±0.00	



Fig. 1: FTIR image of sawdust activated carbon



Fig. 2(a-c): SEM image of SAC (a) before adsorption and after adsorption of DDVP from (b) untreated and (c) company treated wastewater

	Concentrati		
	Unspiked	Spiked	Recovery (%)
Untreated	0.085	0.585	86±0.71
Company treated	0.080	0.580	88±1.41
Deionized water	0.000	0.500	100±0.00
±: Standard deviation	า		

Table 2: Recovery experiment for the extraction and determination of DDVP
$C_{\text{opcontration}}$ (mg $ -1\rangle$)

methoxy C=O extending frequencies may be responsible for the band at 2505.62 cm⁻¹. The band at 1577.82 cm⁻¹ was also attributed to C-O-H extension and -OH distortion, while the band at 584.45 cm⁻¹ was attributed to the metal-halogen link²⁴. The molecules with aromatic rings, ether and methoxy groups are responsible for the peaks found at 1139.97 and 2212.43 cm⁻¹, respectively.

SEM image of sawdust activated carbon: The scanning electron micrograph clearly showed the surface morphological characteristic of SAC. The surface morphology of the SAC before and after adsorption was shown in Fig. 2. The data in Fig. 2a depicted the particle mass and surface

morphology of SAC before adsorption, whereas, Fig. 2b-c depicted the surface morphology of SAC following adsorption of DDVP from untreated and company-treated wastewater samples, respectively. The adsorbent's surface has wavy-like curves with pores (Fig. 2a), allowing access to the inside pores. The wavy-like curves were discovered to be hidden in Fig. 2b and 2c. These could be a result of DDVP and other toxins found in untreated and treated water blocking the surface of the adsorbent.

Recovery experiment for the extraction and determination

of DDVP: A recovery experiment was carried out for the extraction procedure as well as the determination of DDVP. The final results were shown in Table 2. In the untreated and treated wastewater samples, the percentage recoveries for DDVP were 86 ± 0.71 and $88\pm1.41\%$, respectively. However, the recoveries of DDVP standard on deionized water samples were tested to check for matrix efficiencies. The percentage of recovery yielded a result of 100 ± 0.00 .

DDVP was found in both untreated and company-treated wastewater samples (0.085 ± 0.021 and 0.080 ± 0.028 mg L⁻¹, respectively) at concentrations greater than the pesticides' permitted limit of 0.05 mg L⁻¹ for wastewater set by the National Environmental Standard and Regulations Agency (NESREA). The DDVP concentrations in both the untreated and treated wastewater samples were reduced to 0.0093 ± 0.00 and 0.0091 ± 0.00 mg L⁻¹, respectively, after SAC treatment. These values were lower than the NESREA's acceptable standard limit. This confirmed that DDVP as well as other organic matter and dissolved elements present in the untreated and treated wastewater samples.

Optimization of parameters in batch adsorption of DDVP:

The effectiveness of SAC as an adsorbent for DDVP adsorption from wastewater was examined. The pH, adsorbent dosage, contact time and concentrations were all investigated as factors that could affect the rate of adsorption. The following were the results of the effects of each of the parameters.

Effect of pH on adsorption of DDVP from simulated solution:

The SAC has 50% adsorption efficiency for the removal of DDVP at pH 5 and 7 and 30% adsorption efficiency at pH 9 as depicted in Fig. 3. It was discovered that as pH rises, the efficacy of DDVP adsorption reduces from 50-30%. This trend may have occurred because, at pH 5, the adsorbent's surface is surrounded by hydronium ions (H₃O⁺), which may have increased the DDVP's interaction with binding sites $(C_4H_7C_{12}O_4P$, with lone pair of electrons on the oxygen atom) of the adsorbent by greater attractive forces, resulting in improved uptake on polar adsorbent²⁷. The increase in hydroxyl ions may explain the lower adsorption effectiveness seen at pH 9. The degree of dissociation of groups at the adsorbent surface is high at basic pH values and both the adsorbent and the solutes exist in their negatively charged forms. As a result of the electrostatic repulsion between the molecules and the surface of the adsorbent, adsorption is not favoured²⁸. This pattern is similar to what has been seen for other adsorbent systems²⁸⁻³⁰.

Effect of adsorbent dosage on adsorption of DDVP from simulated solution: The adsorbent dose, which is an important parameter in adsorption studies, determines the optimal dosage at which maximal adsorption occurs. The effect of SAC dosage on DDVP adsorption was shown in Fig. 4. The percentage removal of DDVP rose from 49-79% when the adsorbent dose increased from 0.2-0.8 g. The number of accessible adsorption sites and surface area increase as the



Fig. 3: Effect of pH on the adsorption DDVP



Fig. 4: Effect of adsorbent dosage on the adsorption DDVP

adsorbent dosage is raised, resulting in a rise in the number of pesticide adsorbed^{31,32}. The adsorbent dosage of 0.8g has the highest removal efficiency (79 %) in this investigation.

Effect of contact time on adsorption of DDVP from simulated solutions: While the effect of shaking duration on percentage sorption of DDVP onto SAC was examined during agitating times of 30, 60 and 90 min, other parameters such as pH, adsorbent dosage and starting concentration were kept constant. As the contact duration increased from 30-60 min, the adsorption efficiency of DDVP improved, increasing from 78-88% as shown in Fig. 5. The adsorption efficiency dropped to 85% after 60 min at a contact period of 90 min. During the early phases of the adsorption process, there may have been a large number of vacant surface sites available for adsorption but after 60 min, the number of available vacant sites dropped³³. As a result, at 60 min, the adsorption equilibrium period, the maximum removal of 88% was achieved. A similar

Table 3: Adsorption efficient	ncy of sawdust activated carbon and commercial activate	d carbon on untreated and treated wastev	vater
	Adsorbent	Adsorption efficiency (%)	
Contaminant		Untreated water	Company treated water
DDVP	Sawdust activated carbon	89.06±0.014	88.62±0.962
	Commercial activated carbon	80.94±2.744	77.50±0.410

Res. J. Environ. Sci., 17 (1): 1-11, 2023

Confidence level = 0.05, Significant value = 1.000 and \pm : Standard deviation



Fig. 5: Effect of contact time on the adsorption DDVP



Fig. 6: Effect of initial concentration on the adsorption DDVP

response was seen when the adsorptive activity of activated carbon derived from Hyphaene Thebaica nutshells was investigated for the removal of dichlorvos from wastewater³⁴.

Effect of initial concentration on adsorption of DDVP from simulated solution: As illustrated in Fig. 6, the removal of DDVP from SAC increased with an increase in initial DDVP concentration. At a DDVP concentration of 0.5 mg L⁻¹, the highest adsorption efficiency was 93%, while, the lowest was 62% at a starting concentration of 0.001 mg L⁻¹. The effect of

the rising concentration gradient, which is the fundamental driving force for the adsorption process, may be credited with this increase in adsorption efficiency as the initial concentration of DDVP increases. That is, by increasing the initial concentration of DDVP, the obstacle to mass transfer between the aqueous and solid phases has been overcome and the interaction between DDVP and the adsorbent has been increased^{28,35}. It is also worth noting that the adsorption efficiencies (above 60%) obtained with the prepared adsorbent (SAC) at extremely low concentrations (0.001 and 0.005 mg L^{-1}) are impressive.

Adsorption of DDVP from Agrochemical wastewater: The

removal of DDVP from both untreated and treated wastewater samples was investigated using both sawdust activated carbon and commercial activated carbon in an adsorption experiment. In the adsorption investigation, the optimum parameters found during the simulation experiment were taken into account. The results of the GC-MS analysis of untreated and treated wastewater samples after adsorption were shown in Table 3. In the adsorption of DDVP from wastewater, sawdust activated carbon has greater adsorption efficiency than commercial activated carbon, according to the findings. The paired sample t-test analysis, on the other hand, reveals that while there is no statistically significant difference between the two adsorbents for the untreated wastewater sample, there is a significant difference between the two adsorbents for the company-treated wastewater sample. The Sig. (2-Tailed) value for untreated wastewater is 0.150, which is greater than the confidence threshold of 0.05. There was no statistically significant difference between sawdust-activated carbon and commercial activated carbon, according to the results.

However, because the mean of the sawdust activated carbon was greater than the mean of the commercial activated carbon in the paired samples statistics, it can be concluded that the sawdust activated carbon is more effective than the commercial activated carbon in the treatment of the untreated wastewater sample.

Adsorption isotherms: The data in Fig. 7a and b showed the Langmuir and Freundlich adsorption isotherms for DDVP



Fig. 7a-b: (a) Langmuir and (b) Freundlich adsorption isotherm for the adsorption of DDVP with SAC

Table 4: Langmuir and Freundlich constants for the adsorption of DDVP with SAC

•
Values
-6.12×10 ⁻³
0.038
0.743
1.417
2.915
0.993

using sawdust-activated carbon as the adsorbent, whereas Table 4 presented the coefficients of these isotherms (Langmuir and Freundlich) for the different conditions. Both the Langmuir and Freundlich isotherms are suitable for the adsorption process, according to the data. Both model's correlation coefficients (R^2) are within 0< R^2 <1 (Fig. 7a and b and Table 4), indicating that they satisfactorily reflect the experimental data of DDVP sorption. The correlation coefficient (R²) of the Freundlich equation was always >0.95 as shown in Table 4, demonstrating the validity of the experimental isotherm. This finding explained how the DDVP molecule forms multilayer coverage on the sawdust-activated carbon's outer surface³⁶. The adsorption capacity of an adsorbent at equilibrium concentration in a solution is determined by the value of Kf (2.915) for DDVP³⁷. A greater Kf value, on the other hand, indicated a better adsorption capacity especially for biomass in water treatment in which adsorption is now a viable option for contaminant removal³⁸.

CONCLUSION

The adsorptive capacities of activated carbon generated from sawdust, an agricultural waste, for the removal of DDVP,

an organophosphate insecticide, from wastewater were examined in this study. At optimal conditions (neutral pH, 0.8 g of adsorbent, 60 min contact duration and a concentration of 0.5 mg L⁻¹), the wide surface area and well-developed pores enabled a very good uptake of the pesticide (93%). Furthermore, the effectiveness was good even at very low concentrations of 0.001 mg L⁻¹ (62%). In this study, the adsorption efficiency of sawdust-activated carbon was compared to that of commercial activated carbon utilizing effluent from the agrochemical sector. When compared to commercial activated carbon for the removal of DDVP from wastewater, the results showed that sawdust-activated carbon may be employed as a low-cost, high-performance and environment-friendly adsorbent (89.06% efficiency).

SIGNIFICANCE STATEMENT

The pollution of water resources with organic pollutants from untreated or partially treated wastewater has been of great concern to the environment. Removal of these pollutants from the environment using an effective and efficient adsorbent material has been of interest since the conventional methods are not environment-friendly and difficult, hence this study.

REFERENCES

 Kaštelan-Macan, M., M. Ahel, A.J.M. Horvat, D. Jabučar and P. Jovančić, 2007. Water resources and waste water management in Bosnia and Herzegovina, Croatia and the State Union of Serbia and Montenegro. Water Policy, 9: 319-343.

- 2. Daughton, C.G., 2004. Non-regulated water contaminants: Emerging research. Environ. Impact Assess. Rev., 24: 711-732.
- 3. Daughton, C.G. and T.A. Ternes, 1999. Pharmaceuticals and personal care products in the environment: Agents of subtle change? Environ. Health Perspect., 107: 907-938.
- 4. Fent, K., A.A. Weston and D. Caminada, 2006. Ecotoxicology of human pharmaceuticals. Aquat. Toxicol., 76: 122-159.
- Cahill, M.G., G. Caprioli, M. Stack, S. Vittori and K.J. James, 2011. Semi-automated liquid chromatography-mass spectrometry (LC-MS/MS) method for basic pesticides in wastewater effluents. Anal. Bioanal. Chem., 400: 587-594.
- Köck-Schulmeyer, M., M. Villagrasa, M.L. de Alda, R. Céspedes-Sánchez, F. Ventura and D. Barceló, 2013. Occurrence and behavior of pesticides in wastewater treatment plants and their environmental impact. Sci. Total Environ., 458-460: 466-476.
- Sarkar, S., J.D.B. Gil, J. Keeley and K. Jansen, 2021. The Use of Pesticides in Developing Countries and their Impact on Health and the Right to Food. 1st Edn., European Commission, Publications Office of the European Union, Luxembourg, ISBN: 9789284676736, Pages: 44.
- 8. Zolgharnein, J., A. Shahmoradi and J. Ghasemi, 2011. Pesticides removal using conventional and low-cost adsorbents: A review. CLEAN-Soil Air Water, 39: 1105-1119.
- Alade, A.O., O.S. Amuda, O.O. Ogunleye and A.A. Okoya, 2012. Evaluation of Interaction of carbonization temperatures and concentrations on the adsorption capacities and removal efficiencies of activated carbons using response surface methodology (RSM). J. Biorem. Biodegrad., Vol. 3. 10.4172/ 2155-6199.1000134.
- Anastopoulos, I., I. Pashalidis, A. Hosseini-Bandegharaei, D.A. Giannakoudakis and A. Robalds *et al.*, 2019. Agricultural biomass/waste as adsorbents for toxic metal decontamination of aqueous solutions. J. Mol. Liq., Vol. 295. 10.1016/j.molliq.2019.111684.
- 11. Okoya, A.A., A.B. Akinyele, O.S. Amuda and I.E. Ofoezie, 2016. Chitosan-grafted carbon for the sequestration of heavy metals in aqueous solution. Chem. Sci. Int. J., Vol. 11. 10.9734/ ACSJ/2016/21813.
- 12. Chen, H., M. Shao and Y. Li, 2008. The characteristics of soil water cycle and water balance on steep grassland under natural and simulated rainfall conditions in the Loess Plateau of China. J. Hydrol., 360: 242-251.
- 13. Okoya, A.A. and M.A. Elufowoju, 2020. Seasonal assessment of the physico-chemical properties of groundwater in some villages around an iron and steel recycling industry in Southwestern Nigeria. Am. J. Water Resour., 8: 164-172.
- Katsanou, K. and H.K. Karapanagioti, 2016. Water Supplies: Water Analysis. In: Encyclopedia of Food and Health, Caballero, B., P.M. Finglas and F. Toldrá (Eds.), Elsevier, Amsterdam, Netherlands, ISBN: 978-0-12-384953-3, pp: 463-469.

- 15. Demetillo, A.T., M.V. Japitana and E.B. Taboada, 2019. A system for monitoring water quality in a large aquatic area using wireless sensor network technology. Sustain. Environ. Res., Vol. 29. 10.1186/s42834-019-0009-4.
- Olasoji, S.O., N.O. Oyewole, B. Abiola and J.N. Edokpayi, 2019. Water quality assessment of surface and groundwater sources using a water quality index method: A case study of a peri-urban town in Southwest, Nigeria. Environments, Vol. 6. 10.3390/environments6020023.
- Okoya, A.A., A.O. Ogunfowokan, O.I. Asubiojo and N. Torto, 2013. Organochlorine pesticide residues in sediments and waters from cocoa producing areas of Ondo State, Southwestern Nigeria. Int. Scholarly Res. Not., Vol. 2013. 10.1155/2013/131647.
- Fatoki, O.S. and O.R. Awofolu, 2004. Levels of organochlorine pesticide residues in marine-, surface-, ground and drinking waters from the Eastern Cape Province of South Africa. J. Environ. Sci. Health Part B, 39: 101-114.
- 19. Fatoki, O.S. and R.O. Awofolu, 2003. Methods for selective determination of persistent organochlorine pesticide residues in water and sediments by capillary gas chromatography and electron-capture detection. J. Chromatogr. A, 983: 225-236.
- 20. Kyriakopoulos, G.G., A.A. Hourdakis and D.D. Doulia, 2003. Adsorption of pesticides on resins. J. Environ. Sci. Health Part B, 38: 157-168.
- Khan, A.R., H. Tahir, F. Uddin and U. Hameed, 2005. Adsorption of methylene blue from aqueous solution on the surface of wool fiber and cotton fiber. J. Appl. Sci. Environ. Manage., 9: 29-35.
- 22. Zenasni, M.A., B. Meroufel, A. Merlin and B. George, 2014. Adsorption of congo red from aqueous solution using CTAB-Kaolin from Bechar Algeria J. Eng. Mater. Adv. Technol., 4: 332-341.
- 23. Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc., 40: 1361-1403.
- 24. Ossman, M.E., M.A. Fatah and N.A. Taha, 2014. Fe(III) removal by activated carbon produced from Egyptian rice straw by chemical activation. Desalin. Water Treat., 52: 3159-3168.
- 25. Jaouadi, M., 2021. Characterization of activated carbon, wood sawdust and their application for boron adsorption from water. Int. Wood Prod. J., 12: 22-33.
- Vasiliev, L.L., L.E. Kanonchik, D.A. Mishkinis and M.I. Rabetsky, 2000. Adsorbed natural gas storage and transportation vessels. Int. J. Therm. Sci., 39: 1047-1055.
- 27. Memon, F.N., S. Memon, S. Memon and N. Memon, 2011. Synthesis and application of a new calix[4]arene based impregnated resin for the removal of endosulfan from aqueous environment. J. Chem. Eng. Data, 56: 3336-3345.
- 28. Tiwari, A. and A. Bind, 2014. Effective removal of pesticide (dichlorvos) by adsorption onto super paramagnetic poly (styrene-co-acrylic acid) hydrogel from water. Int. Res. J. Environ. Sci., 3: 41-46.

- 29. Tan, I.A.W., A.L. Ahmad and B.H. Hameed, 2008. Adsorption of basic dye using activated carbon prepared from oil palm shell: Batch and fixed bed studies. Desalination, 225: 13-28.
- Okoya, A.A., O.S. Adegbaju, O.E. Akinola, A.B. Akinyele and O.S. Amuda, 2020. Comparative assessment of the efficiency of rice husk biochar and conventional water treatment method to remove chlorpyrifos from pesticide polluted water. Curr. J. Appl. Sci. Technol., Vol. 39. 109734/CJAST/2020/ v39i230491.
- 31. Malik, R., D.S. Ramteke and S.R. Wate, 2007. Adsorption of malachite green on groundnut shell waste based powdered activated. Waste Manage., 27: 1129-1138.
- Okoya, A.A., O.O. Olaiya, A.B. Akinyele and N.O. Ochor, 2020. Efficacy of *Moringa oleifera* seed husk as adsorptive agent for trihalomethanes from a water treatment plant in Southwestern, Nigeria. J. Chem., Vol. 2020. 10.1155/2020/ 3450954.
- Ifeoma, A.O.O. and O.D. Onukwuli, 2013. Utilization of sawdust (*Gossweilerodendron balsamiferum*) as an adsorbent for the removal of total dissolved solid particles from wastewater. Int. J. Multi-Discip. Sci. Eng., 4: 45-53.

- Ogwuche, E.O., C.E. Gimba and E.S. Abechi, 2015. An evaluation of the adsorptive behaviour of activated carbon derived from *Hyphaene thebaica* nut shells for the removal of dichlorvos from wastewater. Int. J. Sci. Technol., 3: 274-285.
- 35. Chang, K.L., C.C. Chen, J.H. Lin, J.F. Hsien and Y. Wang *et al.*, 2014. Rice straw-derived activated carbons for the removal of carbofuran from an aqueous solution. New Carbon Mater., 29: 47-54.
- 36. Nguyen, T.A.H., H.H. Ngo, W.S. Guo, J. Zhang and S. Liang *et al.*, 2013. Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. Bioresour. Technol., 148: 574-585.
- 37. Sintakindi, A. and B. Ankamwar, 2020. Uptake of methylene blue from aqueous solution by naturally grown *Daedalea africana* and *Phellinus adamantinus* fungi. ACS Omega, 5: 12905-12914.
- Farombi, A.G., O.S. Amuda, A.O. Alade, A.A. Okoya and S.A. Adebisi, 2018. Central composite design for optimization of preparation conditions and characterization of hydroxyapatite produced from catfish bones. Beni-Suef Univ. J. Basic Appl. Sci., 7: 474-480.