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Effects of different activation methods on the capacity of an agro-waste adsorbent in the removal of organochlorine pesticides and heavy metals contaminants from wastewater

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Abstract

In the present study, the effects of different activation methods on the capacity of an agro-waste adsorbent in the removal of multi-component contaminants from wastewater were investigated. The adsorbents were treated using sodium hydroxide (NaOH), dichloromethane (DCM), distilled water, sulphuric acid (H_2SO_4), n-hexane, and nitric acid (HNO_3), and the eluted effluents were analyzed for the levels of organochlorine pesticides and heavy metals using Gas Chromatography-Mass Spectrometer (GC-MS) and Atomic Absorption Spectrometer (AAS), respectively. The percentage recoveries of the organochlorine pesticides (87 - 98%) indicated that the precision, reliability, and reproducibility of the adopted procedure were acceptable. The results of the study showed that DCM-treated adsorbents exhibited the highest removal efficiency for the organochlorine pesticides with 100%, 99.64%, and 91.89% of chlorinated benzenes, dichlorodiphenylethanes, and cyclodienes respectively, being removed while distilled water-treated adsorbents exhibited the lowest removal efficiency. In contrast, the H_2SO_4-, HNO_3-, and NaOH-treated adsorbents exhibited significant removal (>80%) of Cd, Cu, and Pb from the wastewater. The removal of pesticide congeners by organic solvents was ascribed to the theory that similarities are easily solvable in each other while the removal of metal ions by inorganic acids was attributed to the creation of more acidic functional groups on the adsorbent's surface. The economic feasibility and eco-friendliness of the process pave way for further research and development into the optimization of reaction conditions for the complete removal of these contaminants.

***Keywords*:** Adsorption; Agrowaste; Heavy metals; Organochlorine pesticides; Wastewater

Introduction

The increasing human population coupled with the ever-growing industrialization has made satisfying the global food requirements a cumbersome task (Ishtiaq *et al.,* 2020). Despite the surge in human population, agricultural farmlands on which food crops are propagated do not tend to experience the same increase and yet there is the need to increase crop yield and productivity (Suo *et al.,* 2019; Vigneshwaran *et al.,* 2019). One of such measure to increase crop yield and productivity is the application of protective agents called pesticides, which serve the purpose of controlling plant pests and diseases (Qamar *et al.,* 2017). The production of these chemicals has increased in many folds (Parveen *et al.,* 2020), and despite their many advantages, their continuous application is fast becoming a global environmental menace (Iqbal *et al.,* 2019).

Over the years, there has been a surge in the pollution of water resources emanating from the inadvertent addition of synthesized chemical pesticides into the atmospheric, surface, and groundwater resources (Des Ligneris *et al.,* 2018). As a result of the various stresses exerted by these chemicals on the environment, the Stockholm Convention called for the classification of these chemicals as Persistent Organic Pollutants (POPs) and went ahead to ban and/or restrict their use globally (UNEP, 2022). This group of chemicals called POPs comprises several pollutants such as polycyclic aromatic hydrocarbons, polybrominated flame retardants, organophosphate pesticides, polychlorinated biphenyls, and organochlorine pesticides (Des Ligneris *et al.,* 2018). The direct and/or indirect introduction of these pollutants into the environment is associated with toxicity concerns for biotic and environmental health as a whole (Rashed *et al.,* 2013; WHO 2022).

Owing to their partial degradability in water resources, the chemical oxygen demand of water is affected resulting in a significant depletion of available oxygen at a faster rate than its replenishment (Rashed *et al.,* 2013; Des Ligneris *et al.,* 2018). Some of the by-products formed upon the reaction of these chemicals with water are even relatively more toxic. For instance, heptachlor epoxide, a product of the reaction of heptachlor with water, poses more threats to human life than its parent compound (WHO, 2004). One of the many other concerns associated with persistent organic pollutants is their long-range transportability (Bigot *et al.,* 2016). Also, several POPs are semi-volatile compounds and as such are capable of mobility among soil, water, and the atmosphere (Breivik *et al.,* 2016).

In addition, heavy metals are components of the wastewaters emanating from industrial activities such as pesticides, tanneries, refining ores, paper, and mining industries (Alalwan *et al.,* 2018; Aguilar-Rosero *et al.,* 2022). The predominant heavy metals occurring in wastewaters include zinc, lead, chromium, vanadium, selenium, iron, cobalt, copper, cadmium, and nickel, and their removal from wastewaters is important for both the elimination of toxicity and the recovery of precious metals (Alalwan *et al.,* 2020). They pose adverse health threats such as mutagenesis, carcinogenesis, and endocrine disruption, even at trace levels (Ngambia *et al.,* 2019; Pesqueira *et al.,* 2020) due to their ability to bind to nucleic acids and proteins in living organisms (Almomani *et al.,* 2020).

The removal of the aforementioned pollutants from water resources is of utmost interest to researchers all over the world in a bid to increase access to clean water and sanitation as one of the sustainable development goals. Many technologies including phytoremediation (Rissato *et al.,* 2015), constructed wetlands (Yang *et al.,* 2022), adsorption (Sahmarani *et al.,* 2021), supercritical oxidation (Xu *et al.,* 2015), ozonation (Bourgin *et al.,* 2013) and so on, have been adopted to remove organochlorine pesticides from environmental matrices. Advanced oxidation processes have particularly shown high efficiency in the remediation of organochlorine pesticides. However, increased toxicity of the resulting effluents after treatment is widely associated with these techniques (Des Ligneris *et al.,* 2018). Nevertheless, the available evidence in the literature has revealed that adsorption can be a viable alternative for the abatement of organochlorine pesticides owing to its simplicity, non-toxicity, and easy operation (Wekoye *et al.,* 2020). Among other factors, the efficiency of adsorption processes is largely dependent on the choice of adsorbents as well as the method used in treating the adsorbent (Enaime *et al.,* 2017; Barjasteh-Askari *et al.,* 2021; Adeola *et al.,* 2022). While many studies have investigated the use of different adsorbents in the remediation of both organic and inorganic pollutants, there is a rarity of studies focused on the treatment methods of adsorbents used in the removal of organochlorine pesticides and heavy metals.

No doubt, wastewaters often contain multiple contaminants simultaneously which may largely fall under heavy metals and trace organics. The present study was therefore designed to investigate the effects of different activation methods on the capacity of an agro-waste adsorbent in the simultaneous removal of organochlorine pesticides (OCPs) and heavy metals (HMs) from wastewater.

Materials and Methods

Sample collection and preparation

Fresh unripe plantain peels were the precursors used for activated carbon production. Fresh unripe plantain peels were collected from a plantain flour processing industry at Iyin, Ekiti. The unripe plantain peels were sundried, rinsed with distilled water, and carbonized by subjecting the precursors to incomplete combustion by heating in a covered earthenware pot at high temperatures (≈ 550^{o}C). The covering was done to prevent complete combustion and well-formed highly amorphous carbon. The contents of the pot were stirred occasionally to ensure uniformity of temperature and the consequent transformation of the peels into well-formed charcoal. The pot and its content were allowed to cool to ambient temperature, while the carbonized material was subsequently allowed to cool in a desiccator. Later, the carbonized materials were grounded with an agate mortar and pestle. The charcoal was sieved with a 250 µm (microns) pore size sieve [Endocotts (Test Sieves) LTD, London, England] to achieve a uniform particle size and increased surface area for adsorption. Then, the sieved carbonized materials were heated to a constant weight at 105^{o}C in a Gallenkamp oven (Model Ov-160 England) overnight and then stored in an airtight (polyethylene zip-lock) container in readiness for further use. Activation of the untreated charcoal was done by soaking six equal portions separately in 0.2 M sulphuric acid, 0.2 M nitric acid, 0.2 M NaOH, distilled water, dichloromethane (DCM), n-hexane, and stirred. The mixture was allowed to stand for 24 hours and then filtered. The charcoals treated with sulphuric acid, nitric acid, NaOH, and distilled water were further washed thoroughly with doubly distilled water while still in the filter funnel and washing continued until the filtrate was neutral. Those treated with DCM and n-hexane were similarly treated with more DCM and n-hexane until the colourless filtrate was obtained. The treated charcoal samples were then dried overnight to constant weights in an oven at 105°C, after which they were stored in a desiccator.

Chemical reagents used and their sources

The chemicals and reagents used in the present study include dichloromethane (BDH Chemical Limited, England), n-hexane (BDH Chemical Limited, England), sodium hydroxide (M&B Laboratory Chemicals, Dagenham, England), silica gel (Loba Chemie Pvt. Ltd., India), glass wool (Loba Chemie Pvt. Ltd., India), nitric acid (GFS Chemicals Inc., Columbus), acetic acid (GFS Chemicals Inc., Columbus), sodium acetate (M&B Laboratory Chemicals, Dagenham, England), hydrochloric acid (GFS Chemicals Inc., Columbus), perchloric acid (GFS Chemicals Inc., Columbus), sulphuric acid (GFS Chemicals Inc., Columbus), and anhydrous sodium sulphate (M&B Laboratory Chemicals, Dagenham, England).

Preparation of OCPs- and HMs-containing synthetic wastewater

The OCPs synthetic wastewater was prepared from six different commercial pesticide products, namely: Paraforce, Weedoff, Perfect killer, Cyper force, DD force, and Weed crusher. These commercial pesticide products have been reported to contain some traces of OCPs (Abdulkareem, 2020). From each, 5 mL was measured and added together into a 2 L standard flask, diluted with distilled water to the mark, and shaken thoroughly. Then 500 mL of the 2 L OCPs synthetic wastewater was measured into another 2 L standard flask. A solution mixture (100 mL) of soluble salts of Cd, Cu, Pb, and Zn containing a calculated amount of 0.4 ppm of the metals was added to the OCPs-containing wastewater, diluted with distilled water to the mark, and shaken thoroughly. This was covered and allowed to equilibrate.

Column Adsorption Experiments

The adsorbent packed column (flow through packed bed) experiment was carried out at room temperature, using a glass column with a height of ≈ 20 cm and an internal diameter of 2 cm. A little quantity of decontaminated glass wool was used to plug the lower end of the column and 10 g of the activated carbon was added into the column, while another decontaminated glass wool was placed on top of the adsorbent to prevent floating of the adsorbent particles. Thereafter, water-soluble components of the adsorbent material were removed by flushing distilled water through the adsorbent. Having set up the flow through the packed bed (adsorbent packed column), the adsorption experiments were performed by flushing about 120 mL of the synthetic pesticide wastewater through the column from which 100 mL was collected for liquid-liquid extraction and subsequent determination of the level of OCPs using GC-MS. For the heavy metal determination, a similar experiment was performed but using decontaminated cotton wool to plug the lower end of the column while another decontaminated cotton wool was placed on top of the adsorbent in the column.

Extraction protocols for OCPs

For the determination of levels of OCPs in raw synthetic wastewater, 100 mL of the synthetic wastewater was obtained using a measuring cylinder. This was quantitatively transferred into a 250 mL separatory funnel and about 1 g sodium chloride was added and thoroughly shaken together. This was extracted with 3 x 10 mL in triplicates 1:2:2 Acetone-Dichloromethane-Ethanol. The extracts were pooled together into an amber-colored vial and stored at 4^oC in readiness for clean-up. Also, 100 mL of the wastewater taken through the treated adsorbents in the adsorption column was quantitatively transferred into a 250 mL separatory funnel and extracted as done with the raw synthetic wastewater. The extracts were equally pooled together into amber-colored vials and stored at 4^oC in readiness for clean-up

Clean-up Procedure

The clean-up procedure used the principle of chromatography which involved a stationary phase (silica gel) and a mobile phase (1:2:2 Acetone-Dichloromethane-Ethanol) mixture. A little quantity of glass wool was used as a plug to prevent the loss of the stationary phase at the bottom before the addition of silica gel. Anhydrous sodium sulphate was then added on top of the silica gel. The solvent mixture was first introduced into the packed column to prevent any interference by contaminants. The clean-up stage is essential to remove or reduce all forms of impurities which might be present in the eluate. The recovered eluate was left to dry completely and then reconstituted with 1 mL of n-hexane and stored in amber-coloured vials prior to GC-MS determination.

Recovery experiment

During the course of this study, no certified pesticide reference materials were available; hence, recovery analysis was performed in order to evaluate the precision and efficiency of the analytical procedures using standard addition method. Accurately measured 200-mL sample of the synthetic wastewater was measured using a measuring cylinder. This was divided into two equal halves (A and B); portion A was spiked with 10 mL of the 10 µg/mL standard mixture consisting of some of the available organochlorine insecticides of interest, namely: Aldrin, Chlordane, Dieldrin, Heptachlor and Endrin, while the second portion B was left unspiked. Each portion was taken through the extraction and clean-up protocols as earlier itemized. Also, 10 mL of the standard 10 µg/mL mixture of the OCPs, in spectra grade n-hexane, was put into a clean, oven-dried sample bottle. This was dried at ambient temperature by passing a stream of nitrogen gas through it, and the residue reconstituted using 1 mL n-hexane. Along with the extracts obtained from the samples, these were taken for GC-MS analysis and percentage recoveries (%R) were evaluated from the relationship:

$$\%R = \frac{A-B}{C} \times 100$$

(1)

where A is the amount of an OCP in the spiked sample, B is the amount of the OCP in the unspiked sample and C is the amount of OCP used for spiking.

Gas Chromatographic Analysis

The determination of OCPs in the extracts was performed by Gas Chromatograph (Agilent Model 7890B) coupled with Pegasus 4D Mass Spectrometer (GC-MS). The features and operating conditions were as follows: a GC column Restek Rtx-CL pesticides 2 capillary column, 30 m × 0.25 mm id × 0.25 µm film thickness at 340°C. The GC operating conditions were: splitless injection, injector temperature 250°C, helium carrier gas (99.99% purity) at a flow rate of 0.9 mLmin^{-1} with column head pressure 7.4 psi, the oven temperature was kept at 70°C for 2 min, and then programmed to rise to 130°C at 25°C min^{-1}, afterwards rise to 220°C at 2°C min^{-1}, and then finally set to 280°C at 10°C min^{-1}. This temperature was maintained for 4.6 min. The sample (1 µL) was injected in splitless modes. The Mass spectrometer was set as follows: electron impact ionization mode with70eV electron energy, scan mass range 100 - 400 at 0.62 sec/cycle, ion source temperature 230°C, MS quad temperature 150°C, EM voltage 1450, and solvent delay 4 min. The MS system was routinely operated in selective ion monitoring (SIM) mode with electron ionization. The OCPs compounds were identified based on a comparison of the retention times of peaks with those of standard OCPs compounds. Thereafter, an internal standard method was used for OCPs quantification.

Sample Digestion

Accurately measured 10 mL of the untreated multi-component sample was poured inside a Teflon beaker. About 5 mL of HNO_3 was added and covered with a watch glass. The beaker (and its content) was placed on a thermostated hot plate maintained at about 120^{o}C for a period of 1 hour. Concentrated nitric acid was added to the mixture at intervals to prevent total dryness. Thereafter, 1 mL of perchloric acid was added to the solution and digested further for 30 minutes. After this, the beaker was brought down to simmer. The solution was quantitatively transferred into a 25 mL volumetric flask and it was made up with distilled water. The solution was shaken vigorously and poured into a plastic vial. Similarly, 10 mL of the treated multi-component sample was subjected to digestion protocol as enumerated above. The digested samples of untreated and treated wastewater were then analyzed using Atomic Absorption Spectrophotometer (AAS).

Results and Discussion

Validation of analytical procedure

The adopted analytical procedures in the present study were validated in terms of recovery. The percentage recoveries of the organochlorine pesticides ranged from 87% to 98% (Table 1). These values are in good agreement with the EU (1999) acceptable range for recovery (70-110%), suggesting that the analytical method yielded good recovery values. This indicated that the method is reliable, sensitive, reproducible, and sensitive.

Table 1: Retention time, Response factor, Limit of Detection, and %Recovery for OCPs

OCPs	Retention Time (min)	Response Factor (RF)	% Recovery	Limit of Detection
Aldrin	6.16	1.075	91.89	1.18
Heptachlor	5.58	0.979	88.23	3.37
o,p′-DDE	12.28	0.629	92.75	3.53
o,p′- DDD	14.06	0.957	91.37	3.47
o,p′-DDT	15.05	1.090	91.64	3.29
Heptachlor epoxide	8.12	1.061	94.83	2.63
Chlordane	9.89	1.085	94.34	3.51
α-Endosulfan	11.18	1.010	89.99	2.22
Dieldrin	12.58	0.987	98.40	2.38
o,p′- methoxychlor	17.75	0.972	87.64	2.64

Levels (mg/L) of organochlorine pesticides in eluted effluents

The synthetic wastewater was treated using adsorbents modified with NaOH, DCM, distilled water, H_2SO_4, n-hexane, and HNO_3, and the levels of the OCPs in the eluted effluents are presented in Table S1 (supplementary material). The representative chromatogram of the OCPs-containing wastewater treated using the different adsorbents is shown in Figure S1 (supplementary material). The identified OCPs were grouped into three classes comprising chlorinated benzenes, dichlorodiphenylethanes, and cyclodienes, and the removal efficiency of the OCPs by the adsorbents is shown in Figure 1. It was observed that the DCM-treated adsorbent exhibited the highest removal efficiency for the chlorinated benzenes, dichlorodiphenylethanes, and cyclodienes while the distilled water-treated adsorbent exhibited the least removal efficiency. For the chlorinated benzenes, the removal efficiency followed the order: DCM-treated adsorbent (100%) > n-hexane-treated adsorbent (85.99%) > H_2SO_4-treated adsorbent (70.61%) > NaOH-treated adsorbent (67.35%) > HNO_3-treated adsorbent (65.77%) > distilled water-treated adsorbent (62.03%) while it followed the order: DCM-treated adsorbent (99.64%) > n-hexane-treated adsorbent (97.87%) > NaOH-treated adsorbent (86.61%) > H_2SO_4-treated adsorbent (79.71%) > HNO_3-treated adsorbent (65.48%) > distilled water-treated adsorbent (65.42%) for the dichlorodiphenylethanes. The removal efficiency of the cyclodienes by the adsorbents followed the order: DCM-treated adsorbent (91.89%) > NaOH-treated adsorbent (87.28%) > H_2SO_4-treated adsorbent (84.72%) > HNO_3-treated adsorbent (84.62%) > n-hexane-treated adsorbent (84.35%) > distilled water-treated adsorbent (83.79%). The relatively high efficiency exhibited by DCM-treated adsorbents as opposed to n-hexane-treated adsorbents can be explained in terms of their polarity indices. Dichloromethane (3.4) has a relatively higher polarity index than n-hexane (0.06), indicating that the weakly polar organochlorine pesticides have relatively better dispersibility in dichloromethane as opposed to n-hexane. This allows the adsorbent to easily adsorb the organochlorine pesticides. This is consistent with the solubility theory that similarities can be easily solvable in each other (Du *et al.,* 2013). The interaction between the adsorbents and organochlorine pesticides depends mainly on the binding forces between each class of organochlorine pesticides and the adsorbent. Generally, dichlorodiphenylethanes are hydrophobic compounds with a symmetrical chlorobenzene ring that can easily bind with the functional moieties of the adsorbent whereas the more chlorinated congeners of cyclodienes and chlorinated benzenes are more difficult to permeate the adsorbent's cavity owing to steric hindrance effect (Mahpishanian and Sereshti, 2017). Single-factor analysis of variance (Table S2, supplementary material) indicated that there was a significant difference ($p < 0.05$) in the levels of OCPs except for γ-BHC in the raw synthetic wastewater and the eluted effluents, suggesting that the adsorbents exhibited significantly high efficiency in the removal of the OCPs.

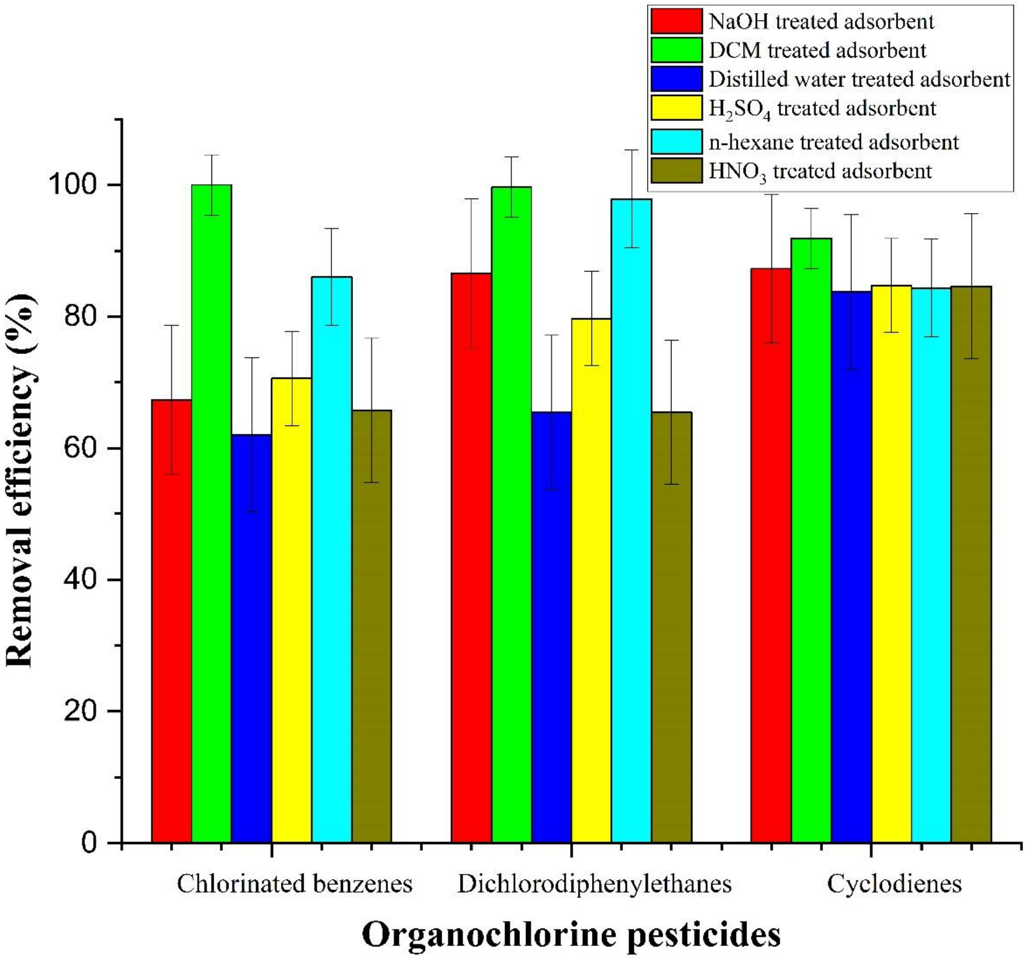

Figure 1: Removal efficiency of organochlorine pesticides using different treatment methods of adsorbent

Levels (mg/L) of heavy metals in eluted effluents

The levels of heavy metals in the synthetic wastewater and eluted effluents are presented in Table S3 (supplementary material) while the removal efficiency of the heavy metals by the adsorbents is shown in Figure 2. There were variations in the removal efficiency of metals exhibited by the various adsorbents. For Cd, the removal efficiency followed the order: H_2SO_4-treated adsorbent (88.23%) > HNO_3-treated adsorbent (85.29%) > NaOH-treated adsorbent (82.35%) > DCM-treated adsorbent (79.41%) = n-hexane-treated adsorbent (79.41%) > distilled water-treated adsorbent (76.47%)

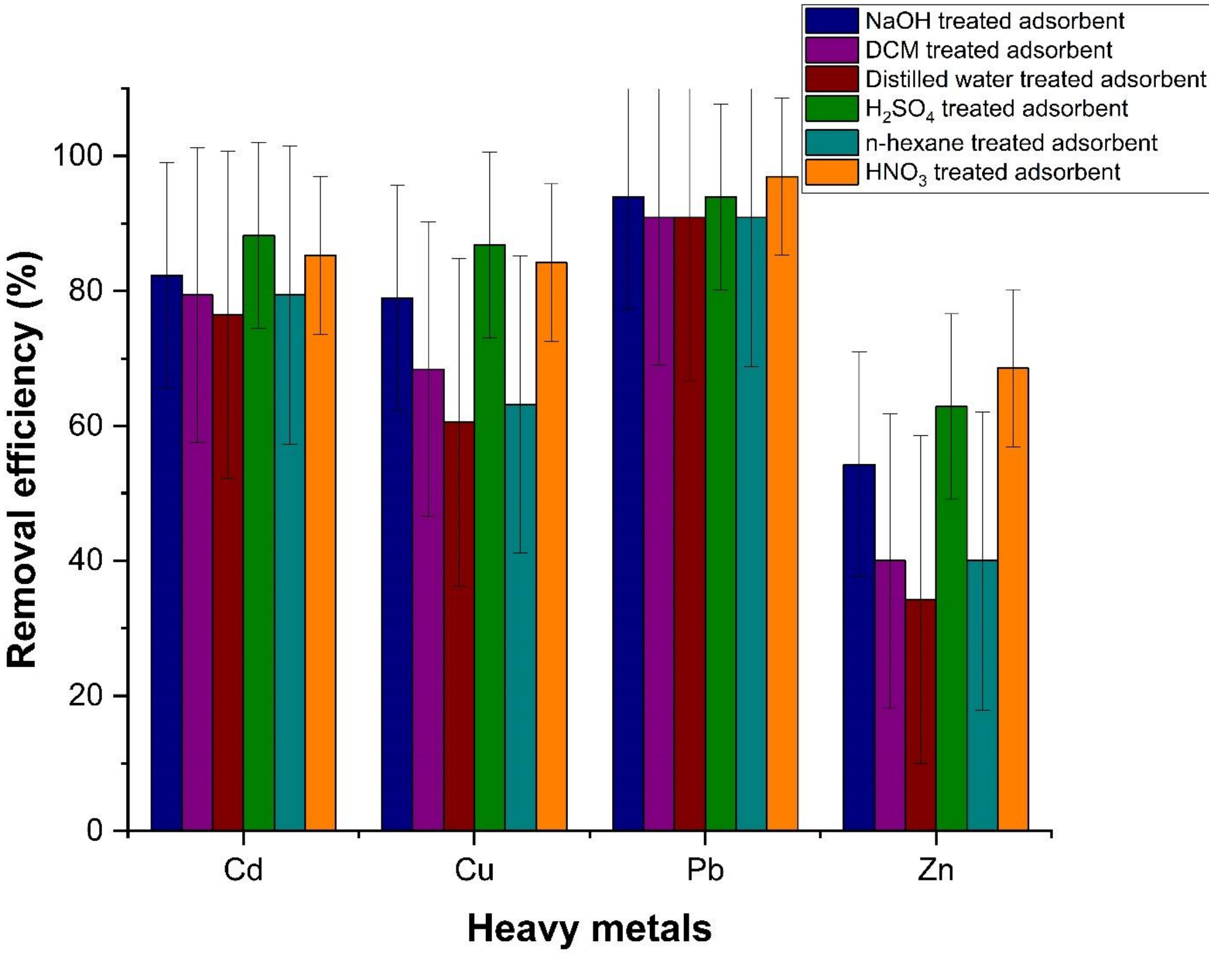

Figure 2: Removal efficiency of heavy metals using different treatment methods of adsorbent

The removal efficiency of Cu followed the order: H_2SO_4-treated adsorbent (86.84%) > HNO_3-treated adsorbent (84.21%) > NaOH-treated adsorbent (78.94%) > DCM-treated adsorbent (68.42%) > n-hexane-treated adsorbent (63.15%) > distilled water-treated adsorbent (60.52%), while for Pb, the order was: HNO_3-treated adsorbent (96.96%) > NaOH-treated adsorbent (93.94%) = H_2SO_4-treated adsorbent (93.94%) > DCM-treated adsorbent (90.91%) = distilled water-treated adsorbent (90.91%) = n-hexane-treated adsorbent (90.91%) whereas it followed the order: HNO_3-treated adsorbent (68.57%) >H_2SO_4-treated adsorbent (62.85%) > NaOH-treated adsorbent (54.28%) > DCM-treated adsorbent (40%) = n-hexane-treated adsorbent (40%) > distilled water-treated adsorbent

(34.28%) for Zn. The inorganic acids treated adsorbents (HNO_3 and H_2SO_4) exhibited relatively higher removal of the studied metals in the wastewater. There are two possibilities for this observation. One, it could be due to the creation of more acidic functional groups on the adsorbent's surface (Shah *et al.,* 2011). Also, it might be due to the ability of the acids to leach out metals, salts, and other inorganic matters from the adsorbents thereby creating more adsorption sites on the surface of the adsorbent such that their extraction efficiency is enhanced in many folds. This is consistent with previous studies which reported that inorganic acids cause sufficient changes in the adsorbent's chemical composition, making it effective in the remediation of metal ions (Schwantes *et al.,* 2016). In consonance with existing literature, the method of activation largely influences the sorption properties of adsorbents (Pietrzak *et al.,* 2014). This was reflected in the higher removal efficiency of Cd and Cu exhibited by H_2SO_4 as opposed to HNO_3. This is not surprising because H_2SO_4 is a strong modifier solution capable of extracting metallic elements from the matrices of environmental samples (Schwantes *et al.,* 2016). The removal efficiencies of Cd, Cu, and Pb by NaOH-treated adsorbent were 82.35%, 78.94%, and 93.94% respectively. The high removal efficiency exhibited due to the influence of NaOH can be ascribed to the enlargement of adsorptive pores resulting from oxidative modification which enhances the degradation of graphitic layers in the adsorbent. Cavities of various dimensions are created on the surface of the treated adsorbent, providing more suitable channels for the penetration of metal ions into the carbon structure (Pezoti *et al.,* 2016). As shown in equations (2) and (3), the removal mechanism by NaOH occurs via the reaction of NaOH with carbon to produce Na_2CO_3 which in turn decomposes to produce carbon dioxide, resulting in the production of wider holes on the adsorbent's surface (Singh *et al.,* 2019). Single-factor analysis of variance (Table S4, supplementary material) showed that there was a significant difference ($p < 0.05$) in the levels of heavy metals in the synthetic wastewater and eluted effluents, indicating the efficiency of the adsorbents in removing the metal ions.

$$6NaOH + 2C \rightarrow 2Na + 2Na_2CO_3 + 3H_2 \qquad (2)$$

$$Na_2CO_3 \rightarrow Na_2O + CO_2 \qquad (3)$$

Conclusions

The present study investigated the efficiency of adsorbents from the same precursor that were subjected to different activation methods for the simultaneous removal of organochlorine pesticides and heavy metals from synthetic wastewater. The results of the study showed that plantain peels can be a good and cheap precursor for the production of activated carbon which can be used in the remediation of multi-component contaminants from wastewater. The different classes of organochlorine pesticides exhibited variation in their sorption to the adsorbents, a phenomenon attributed to the varying hydrophobic behaviour of the pesticide congeners. The efficiency of the adsorption process was heavily reliant on the activation method of activated carbon. The adsorbents treated with dichloromethane showed the highest removal efficiency for organochlorine pesticides while the adsorbents treated with sulphuric and nitric acids exhibited very high reclamation of metal ions. The alkaline treatment of adsorbents was equally characterized by relatively high sorption capacity for the metals. The findings of the present study are attractive as it allows for the conversion of agricultural wastes into environmental-friendly useful products for the remediation of multi-component contaminants. Further studies should be carried out to optimize the reaction conditions for the optimum removal of both organic and inorganic pollutants from wastewater using low-cost agricultural wastes.

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Conflict of Interest

The authors declare that there is no conflict of interest.

References

Abdulkareem, M. (2020). Group warns against use of dangerous herbicide in Nigeria. https://www.premiumtimesng.com/agriculture/431315-group-warns-against-use-of-dangerous-herbicide-in-nigeria.html. Accessed 16 September, 2022.

Adeola, A. O., Ore, O. T., Fapohunda, O., Adewole, A. H., Akerele, D. D., Akingboye, A. S. and Oloye, F. F. (2022). Psychotropic drugs of emerging concerns in aquatic systems: ecotoxicology and remediation approaches. *Chemistry Africa*, 5(3): 481-508.

Aguilar-Rosero, J., Urbina-López, M. E., Rodríguez-González, B. E., León-Villegas, S. X., Luna-Cruz, I. E., and Cárdenas-Chávez, D. L. (2022). Development and characterization of bioadsorbents derived from different agricultural wastes for water reclamation: A review. *Applied Sciences*, 12(5): 2740.

Alalwan, H. A., Abbas, M. N., Abudi, Z. N. and Alminshid, A. H. (2018). Adsorption of thallium ion (Tl+ 3) from aqueous solutions by rice husk in a fixed-bed column: experiment and prediction of breakthrough curves. *Environmental Technology & Innovation*, 12: 1-13.

Alalwan, H. A., Kadhom, M. A. and Alminshid, A. H. (2020). Removal of heavy metals from wastewater using agricultural byproducts. *Journal of Water Supply: Research and Technology-Aqua*, 69(2): 99-112.

Almomani, F., Bhosale, R., Khraisheh, M. and Almomani, T. (2020). Heavy metal ions removal from industrial wastewater using magnetic nanoparticles (MNP). *Applied Surface Science*, 506:144924.

Barjasteh-Askari, F., Davoudi, M., Dolatabadi, M. and Ahmadzadeh, S. (2021). Iron-modified activated carbon derived from agro-waste for enhanced dye removal from aqueous solutions. *Heliyon*, 7(6): e07191.

Bigot, M., Muir, D. C., Hawker, D. W., Cropp, R., Dachs, J., Teixeira, C. F. and Bengtson Nash, S. (2016). Air–seawater exchange of organochlorine pesticides in the southern ocean between Australia and Antarctica. *Environmental Science & Technology*, 50(15): 8001-8009.

Bourgin, M., Albet, J. and Violleau, F. (2013). Study of the degradation of pesticides on loaded seeds by ozonation. *Journal of Environmental Chemical Engineering*, 1(4): 1004-1012.

Breivik, K., Armitage, J. M., Wania, F., Sweetman, A. J., and Jones, K. C. (2016). Tracking the global distribution of persistent organic pollutants accounting for e-waste exports to developing regions. *Environmental science & technology*, 50(2: 798-805.

Des Ligneris, E., Dumée, L. F. and Kong, L. (2018). Nanofiber-based materials for persistent organic pollutants in water remediation by adsorption. *Applied Sciences*, 8(2): 166.

Du, Z., Liu, M. and Li, G. (2013). Novel magnetic SPE method based on carbon nanotubes filled with cobalt ferrite for the analysis of organochlorine pesticides in honey and tea. *Journal of Separation Science*, 36(20): 3387-3394.

Enaime, G., Ennaciri, K., Ounas, A., Baçaoui, A., Seffen, M., Selmi, T., and Yaacoubi, A. (2017). Preparation and characterization of activated carbons from olive wastes by physical and chemical activation: application to Indigo carmine adsorption. *Journal of Materials and Environmental Sciences*, 8(11: 4125-4137.

Iqbal, M., Abbas, M., Nisar, J., Nazir, A. and Qamar, A. (2019). Bioassays based on higher plants as excellent dosimeters for ecotoxicity monitoring: a review. *Chemistry International*, 5(1): 1-80.

Ishtiaq, F., Bhatti, H. N., Khan, A., Iqbal, M. and Kausar, A. (2020). Polypyrole, polyaniline and sodium alginate biocomposites and adsorption-desorption efficiency for imidacloprid insecticide. *International Journal of Biological Macromolecules,* 147: 217-232.

Mahpishanian, S. and Sereshti, H. (2017). One-step green synthesis of β-cyclodextrin/iron oxide-reduced graphene oxide nanocomposite with high supramolecular recognition capability: Application for vortex-assisted magnetic solid phase extraction of organochlorine pesticides residue from honey samples. *Journal of Chromatography A*, 1485: 32-43.

Ngambia, A., Ifthikar, J., Shahib, I. I., Jawad, A., Shahzad, A., Zhao, M., and Chen, Z. (2019). Adsorptive purification of heavy metal contaminated wastewater with sewage sludge derived carbon-supported Mg (II) composite. *Science of the Total Environment*, 691: 306-321.

Parveen, S., Bhatti, I. A., Ashar, A., Javed, T., Mohsin, M., Hussain, M. T. and Iqbal, M. (2020). Synthesis, characterization and photocatalytic performance of iron molybdate (Fe_2 (MoO_4) $_3$) for the degradation of endosulfan pesticide. *Materials Research Express*, 7(3): 035016.

Pesqueira, J. F., Pereira, M. F. R. and Silva, A. M. (2020). Environmental impact assessment of advanced urban wastewater treatment technologies for the removal of priority substances and contaminants of emerging concern: a review. *Journal of Cleaner Production*, 261: 121078.

Pezoti, O., Cazetta, A. L., Bedin, K. C., Souza, L. S., Martins, A. C., Silva, T. L. and Almeida, V. C. (2016). NaOH-activated carbon of high surface area produced from guava seeds as a high-efficiency adsorbent for amoxicillin removal: Kinetic, isotherm and thermodynamic studies. *Chemical Engineering Journal*, 288: 778-788.

Pietrzak, R., Nowicki, P., Kaźmierczak, J., Kuszyńska, I., Goscianska, J. and Przepiórski, J. (2014). Comparison of the effects of different chemical activation methods on properties of carbonaceous adsorbents obtained from cherry stones. *Chemical Engineering Research and Design*, 92(6): 1187-1191.

Qamar, A., Asi, R., Iqbal, M., Nazir, A. and Arif, K. (2017). Survey of Residual Pesticides in Various Fresh Fruit Crops: A Case Study. *Polish Journal of Environmental Studies*, 26(6): 2703-2709.

Rashed, M. N. (2013). Adsorption technique for the removal of organic pollutants from water and wastewater. *Organic Pollutants-Monitoring, Risk and Treatment*, *7:* 167-194.

Rissato, S. R., Galhiane, M. S., Fernandes, J. R., Gerenutti, M., Gomes, H. M., Ribeiro, R., and Almeida, M. V. D. (2015). Evaluation of Ricinus communis L. for the phytoremediation of polluted soil with organochlorine pesticides. *BioMed Research International*, 549863. https://doi.org/10.1155/2015/549863

Sahmarani, R., Net, S., Chbib, C., Baroudi, M. and Ouddane, B. (2021). Elimination of organochlorine pesticides from water by a new activated carbon prepared from Phoenix dactylifera date stones. *Environmental Science and Pollution Research*, 28(8): 10140-10154.

Schwantes, D., Gonçalves, A. C., Coelho, G. F., Campagnolo, M. A., Dragunski, D. C., Tarley, C. R. T. and Leismann, E. A. V. (2016). Chemical modifications of cassava peel as adsorbent material for metals ions from wastewater. *Journal of Chemistry*. 3694174. https://doi.org/10.1155/2016/3694174

Shah, J., Jan, M. R., ul Haq, A., and Sadia, M. (2011). Biosorption of cadmium from aqueous solution using mulberry wood sawdust: equilibrium and kinetic studies. *Separation Science and Technology*, 46(10): 1631-1637.

Singh, J., Basu, S. and Bhunia, H. (2019). CO2 capture by modified porous carbon adsorbents: Effect of various activating agents. *Journal of the Taiwan Institute of Chemical Engineers*, 102: 438-447.

Suo, F., Liu, X., Li, C., Yuan, M., Zhang, B., Wang, J.and Ji, M. (2019). Mesoporous activated carbon from starch for superior rapid pesticides removal. *International*

Journal of Biological Macromolecules, 121: 806-813.

United Nations Environment Programme.(2022) Stockholm Convention. Available online: http://chm.pops.int/ (accessed on 4 September 2022).

Vigneshwaran, S., Preethi, J. and Meenakshi, S. (2019). Removal of chlorpyrifos, an insecticide using metal free heterogeneous graphitic carbon nitride (g-C3N4) incorporated chitosan as catalyst: Photocatalytic and adsorption studies. *International Journal of Biological Macromolecules*, 132: 289-299.

Wekoye, J. N., Wanyonyi, W. C., Wangila, P. T. and Tonui, M. K. (2020). Kinetic and equilibrium studies of Congo red dye adsorption on cabbage waste powder. *Environmental Chemistry and Ecotoxicology*, 2: 24-31.

World Health Organization (2022). Persistent Organic Pollutants (POPs). Available online:http://www.who.int/foodsafety/areas_work/chemical-risks/pops/en/ (accessed on 5 September 2022).

World Health Organization. (2004). *Heptachlor and heptachlor epoxide in drinking water. Background document for development of WHO Guidelines for Drinking-Water Quality*. WHO/SDE/WSH/03.04/99. WHO, Geneva.

Xu, D., Wang, S., Zhang, J., Tang, X., Guo, Y. and Huang, C. (2015). Supercritical water oxidation of a pesticide wastewater. *Chemical Engineering Research and Design*, 94: 396-406.

Yang, C., Wang, B., Wang, H., He, Z., Pi, Y., Zhou, J. and Fu, T. (2022). Removal of organochlorine pesticides and metagenomic analysis by multi-stage constructed wetland treating landfill leachate. *Chemosphere*, 301: 134761.

Table S1: Concentration (mg/L) of OCPs remaining in the synthetic wastewater and eluted effluent

OCPs	Raw	A	B	C	D	E	F
α-BHC	ND	ND	ND	ND	ND	ND	ND
β-BHC	7.01	2.56	ND	3.01	2.98	1.21	2.63
Heptachlor	3.91	1.05	ND	1.25	0.59	1.11	0.92
Aldrin	5.03	0.91	0.52	2.03	1.32	0.09	0.98
γ-BHC	1.21	0.75	ND	0.61	ND	0.11	0.51
δ-BHC	1.92	ND	ND	0.23	ND	0.10	0.33
Heptachlor epoxide	2.01	0.25	ND	0.09	0.55	ND	0.92
Endosulfan I	ND	ND	ND	ND	ND	ND	ND
P, p'- DDE	8.92	1.22	0.06	3.15	1.31	0.21	2.96
Dieldrin	ND	ND	ND	ND	ND	ND	ND
Endrin	10.52	0.52	1.22	0.11	0.82	2.16	0.48
P, p'- DDD	ND	ND	ND	ND	ND	ND	ND
Endosulfan II	ND	ND	ND	ND	ND	ND	ND
P, p'- DDT	ND	ND	ND	ND	ND	ND	ND
Endrin aldehyde	ND	ND	ND	ND	ND	ND	ND
Endosulfan sulfate	ND	ND	ND	ND	ND	ND	ND
Methoxychlor	8.03	1.05	ND	2.71	2.13	0.15	2.89
Total	48.56	8.31	1.80	13.19	9.70	5.14	12.62

A = NaOH-treated adsorbent, B = DCM-treated adsorbent, C = Distilled water-treated adsorbent, D = H_2SO_4-treated adsorbent, E = n-hexane-treated adsorbent, F = HNO_3-treated adsorbent, ND = Not detected

Table S2: Single factor analysis of variance of OCPs in synthetic wastewater and eluted effluents

OCPs	Sum of Squares	df	Mean Square	F	Sig.

α-BHC	Between Groups	.000	1	.000	.	.
	Within Groups	.000	5	.000		
	Total	.000	6			
β-BHC	Between Groups	20.960	1	20.960	14.376	.013
	Within Groups	7.290	5	1.458		
	Total	28.249	6			
Heptachlor	Between Groups	8.184	1	8.184	38.706	.002
	Within Groups	1.057	5	.211		
	Total	9.241	6			
Aldrin	Between Groups	14.094	1	14.094	31.650	.002
	Within Groups	2.227	5	.445		
	Total	16.321	6			
γ-BHC	Between Groups	.664	1	.664	5.997	.058
	Within Groups	.553	5	.111		
	Total	1.217	6			
δ-BHC	Between Groups	2.808	1	2.808	141.537	.000
	Within Groups	.099	5	.020		
	Total	2.907	6			
Heptachlor epoxide	Between Groups	2.501	1	2.501	18.571	.008
	Within Groups	.673	5	.135		
	Total	3.175	6			
Endosulfan I	Between Groups	.000	1	.000	.	.
	Within Groups	.000	5	.000		
	Total	.000	6			
P, p'- DDE	Between Groups	47.382	1	47.382	27.216	.003
	Within Groups	8.705	5	1.741		
	Total	56.087	6			
Dieldrin	Between Groups	.000	1	.000	.	.
	Within Groups	.000	5	.000		
	Total	.000	6			
Endrin	Between Groups	79.571	1	79.571	150.706	.000
	Within Groups	2.640	5	.528		
	Total	82.211	6			
P, p'- DDD	Between Groups	.000	1	.000	.	.
	Within Groups	.000	5	.000		
	Total	.000	6			
Endosulfan II	Between Groups	.000	1	.000	.	.
	Within Groups	.000	5	.000		
	Total	.000	6			
P, p'- DDT	Between Groups	.000	1	.000	.	.
	Within Groups	.000	5	.000		
	Total	.000	6			
Endrin aldehyde	Between Groups	.000	1	.000	.	.
	Within Groups	.000	5	.000		
	Total	.000	6			
Endosulfan sulfate	Between Groups	.000	1	.000	.	.
	Within Groups	.000	5	.000		
	Total	.000	6			

Methoxychlor	Between Groups	36.680	1	36.680	22.734	.005
	Within Groups	8.067	5	1.613		
	Total	44.747	6			

Table S3: Concentration (mg/L) of metals remaining in the eluted effluent

Metals	**Raw**	**A**	**B**	**C**	**D**	**E**	**F**
Cd	0.34	0.06	0.07	0.08	0.04	0.07	0.05
Cu	0.38	0.08	0.12	0.15	0.05	0.14	0.06
Pb	0.33	0.02	0.03	0.03	0.02	0.03	0.01
Zn	0.35	0.16	0.21	0.23	0.13	0.21	0.11
Total	1.40	0.32	0.43	0.49	0.24	0.45	0.23

A = NaOH-treated adsorbent, B = DCM-treated adsorbent, C = Distilled water-treated adsorbent, D = H_2SO_4-treated adsorbent, E = n-hexane-treated adsorbent, F = HNO_3-treated adsorbent

Table S4: Single factor analysis of variance of heavy metals in synthetic wastewater and eluted effluents

Metals		**Sum of Squares**	**df**	**Mean Square**	**F**	**Sig.**
Cd	Between Groups	.066	1	.066	306.473	.000
	Within Groups	.001	5	.000		
	Total	.067	6			
Cu	Between Groups	.067	1	.067	37.333	.002
	Within Groups	.009	5	.002		
	Total	.076	6			
Pb	Between Groups	.081	1	.081	1209.143	.000
	Within Groups	.000	5	.000		
	Total	.081	6			
Zn	Between Groups	.026	1	.026	10.983	.021
	Within Groups	.012	5	.002		
	Total	.038	6			