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Research Article

Removal of heavy metals from industrial paint effluent using coconut shell-derived activated carbon

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Abstract

This study evaluated the adsorption of heavy metals from paint industry effluent onto activated carbon produced from Coconut shells. The paint effluent samples were characterized before and after treatment via Atomic Absorption Spectroscopy (AAS) to identify the heavy metal ions present in the samples. The adsorption efficiency of the activated carbon and the effect of varying adsorbent particle size, impregnation ratio, and contact time were determined. The activated carbon from coconut shells was characterized via Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) to determine the surface morphology and surface-active functional group. The SEM revealed development in pore size after adding a chemical activator to create functional adsorption sites. The finding concluded that the smaller particle size of adsorbents, higher surface area, higher contact time, and higher impregnation ratio increase the efficiency of the adsorption process.

Introduction

Household wastes and Agricultural (biomass) can be very useful if properly recycled [1-5]. The increase in agricultural waste has endangered the lives of man and livestock. Environmental pollution can be of positive relevance if the waste can be recycled and re-used to ensure a healthier and cleaner environment [6,7].

Waste materials are one of the major components of solid organic waste that pollutes land. Inappropriate disposal of municipal waste (solid) not only affects land but is also a source of danger to both living and non-living things [8-10].

Solid waste has posed challenges of pollution in developing and developed countries where they are located in large

quantities due to industrialization, the difficulty in recycling all these wastes led to the nudging to delve into alternative ways of managing them [9,11-15].

The paint industry is one of the sectors responsible for water contamination as its effluent contains organic and inorganic pigments, solvents, emulsifying agents, anti-foaming agents, extenders, preservatives, and dye. Paint effluents include significant levels of heavy metals. These heavy metals, which are chromium, cadmium, mercury, copper, and lead, are nonbiodegradable; thus, their presence in lakes and streams causes bio-accumulation in living creatures, resulting in health issues in humans, plants, and animals [16].

The most effective physicochemical technique for the treatment of metal-bearing effluents has been studied to

be adsorption [17]. Compared to other heavy metal removal technologies, adsorption has several advantages, such as a low capital cost, the absence of sludge, and a simple design [16].

The most popular and oldest known adsorbent is activated carbon [18]. Because of its outstanding mechanical properties, presence of organic/inorganic functional groups, high porosity, high surface area, and low cost, activated carbon has gotten a lot of interest in industrial wastewater treatment. These characteristics found in activated carbon are affected by the technique of activation utilized in its preparation [19].

Materials and method

Materials collection

Coconut shells used in this project were gathered from fruit sellers in Ota, Nigeria. Samples of paint effluent were collected from President Paint Nigeria Limited, located in Ota, Ogun State, Nigeria.

Adsorbent preparation

Producing adsorbent from coconut shell-based activated carbon involves collecting the coconut shells, carbonization, activation, washing, drying, and sieving. The carbonization usually occurs at temperatures greater than 300 $^{\circ}$ C and lasts 4 - 7 hours.

Coconut shells were appropriately washed with distilled water to eliminate contaminants like dirt and grit. Properly washed samples were carbonized at 350 $^{\circ}\text{C}$ for about 5 hours – 7 hours until a constant weight was achieved to eliminate moisture. The dried samples were crushed and sieved (using a mesh size of 425 μm and 600 μm) and kept in a clean, dry container.

425 μ m and 600 μ m sieve sizes of coconut shells were carbonized in a muffle furnace at 450 °C in the absence of air to eliminate hydrocarbon. Thereafter, the carbonized samples were transferred into a desiccator to cool.

Carbonized coconut shells were accurately weighed and mixed with phosphoric acid at different impregnation ratios of 1:5 and 1:10. Samples and acid mixture were covered in aluminum foil and left for 24 hours for proper contact and surface area enhancement. Chemically activated product was filtered using Whatman filter paper and washed with distilled water until a pH of 6-7 was obtained to eliminate the acid on the product's surface. The samples were transferred into the oven to dry to a constant weight and were stored in an airtight polythene bag.

Adsorption experiment

1.25 g of prepared activated carbon samples were contacted with 50 ml of aqueous sample (paint effluent sample). The adsorbent-effluent solutions were agitated at a constant speed using a magnetic stirrer. The effect of contact time was studied as the solutions were agitated for 30 minutes and 60 minutes. Thereafter, the contacted solution was filtered with Whatman filter paper.

Adsorption/Removal efficiency

The estimated % metal ion removal efficiency was obtained using the formula below:

$$\frac{(\text{Co} - \text{Ce})}{\text{Co}} \times 100 \tag{1}$$

Where C_o = initial concentration before adsorption

Ce = final concentration after adsorption.

Results and discussions

Effect of particle size

The impact of particle size on adsorption efficiency was determined by varying the particle sizes of activated carbon prepared. 425 μ m and 600 μ m particle sizes of activated carbon were utilized. Based on the results obtained in Figures 1,2, the activated carbon with a smaller particle size (425 μ m) has better adsorption efficiency than activated carbon with a larger particle size (600 μ m) [20,21]. A relationship exists between surface area and particle size, as smaller particle sizes result in higher surface area, increasing adsorption efficiency [22–25].

Effect of contact time and impregnation ratio

The contact time utilized in the batch adsorption process was varied to assess the influence of contact time on adsorption efficiency. The contact time used in this study was 30 minutes and 60 minutes.

Figures 1,2 show the impact of contact time and impregnation ratio on iron, cadmium, and copper adsorption efficiency utilizing coconut shell-based activated carbon. The plotted findings revealed a linear relationship between contact time and adsorption/removal efficiency. The adsorption efficiency improved as the contact time increased from 30 to 60 minutes. The plot results also show an increase in adsorption efficiency when the impregnation ratio increased from 1:5 to

Scanning electron microscopy

Plate 1, shows the surface morphology of coconut shell-based activated carbon before and after activation, respectively. The surface morphology is relatively organized, with few pores before activation. After activation, it is visible that there are several significant, clear, and visible pores due to the loss of volatile matter after activation with phosphoric acid, resulting in the creation of pores on the surface of activated carbon, which gives more surface area. Numerous small pits can also be seen on the exterior surface, showing that the activating agent interacted with the carbonized shells, resulting in a product with a wide surface area and porous structure.

Before activation (Image A): The SEM image 15.0KV and 1000X magnification shows a rough texture with irregularly shaped pores or cavities. This pre-activation surface suggests a certain porosity level, typical for carbon materials like coconut shell-activated carbon.



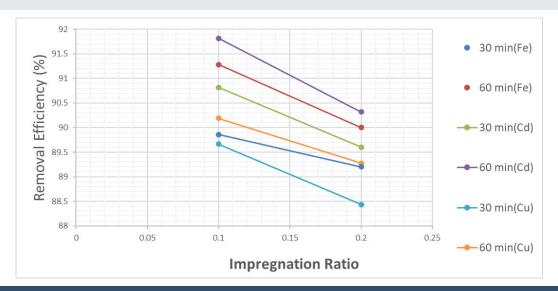


Figure 1: Removal efficiency of 600 μm coconut shell based on activated carbon.

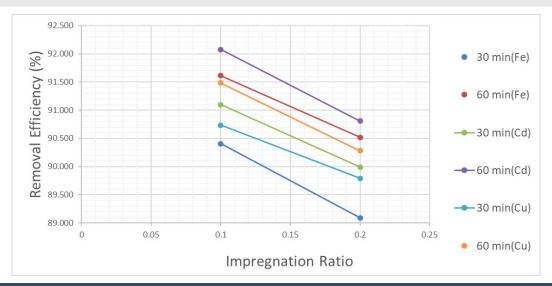


Figure 2: Removal efficiency of 425 µm coconut shell based on activated carbon.

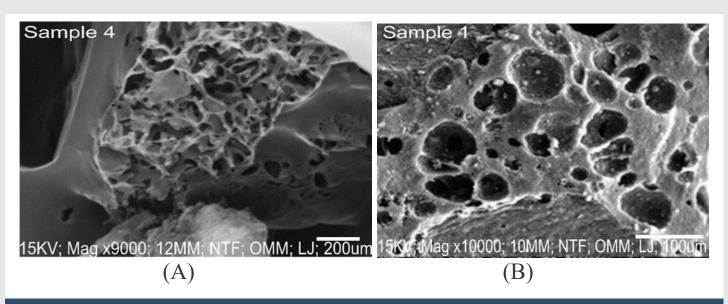


Plate 1: SEM images (A) before activation, and (B) after activation.

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After activation (Image B): The post-activation SEM image, also at 15.0KV but with a higher magnification of 1500X, reveals a more pronounced porous structure. There's a noticeable increase in the number and size of pores, which indicates the activation process's effectiveness in enhancing the material's surface area and porosity.

The activation process typically involves physical or chemical treatment to increase the adsorptive properties of materials like activated carbon. The SEM images provide visual evidence of these changes. The increased porosity seen in the post-activation image benefits applications such as filtration, where a larger surface area allows for better interaction with and adsorption of contaminants [26,27].

Fourier transform infrared spectroscopy

Table 1 shows a list of functional groups on the surface of coconut shell-based adsorbent before and after activation with phosphoric acid.

The absorption bands exhibited in Figures 3,4, and Table 1

revealed that the bond types had a carbon connected to most functional groups derived from the peaks, indicating that the adsorbent was naturally carbonaceous.

Before activation: A broad peak around 3779 cm^-1 indicates O-H stretching, typically associated with hydroxyl groups. Peaks at 1641.36 cm^-1 and 3460 cm^-1 suggest C=C stretching and O-H stretching respectively, which are common in organic compounds. The peak at 554.27 cm^-1 could be related to C-Br stretching, indicating the presence of bromine compounds.

After activation: New peaks appear at 4383 cm^-1 and 3423 cm^-1, indicating O-H stretching, suggesting increased hydroxyl groups after activation. The peak at 2401 cm^-1 could be associated with C=C stretching, showing changes in carbon double bonds. Notably, peaks at 1015 cm^-1 and 1108 cm^-1 indicate C-O stretching and C-O-C stretching, respectively, which might be due to the formation of ether or ester linkages.

The changes in the FTIR spectra reflect the chemical modifications that occur during the activation process.

Table 1: FTIR Spectra for coconut shell Activated Carbon before and after activation

IR Peak * 425µm	Bond type	IR Peak ** 425µm	Bond type	IR Peak * 600µm	Bond type	IR Peak ** 600µm	Bond type
1040.00	C-O Stretching	1101.00	C-O Stretching	722.27	C-H Bending	388.54	
1373.00	C-H Bending	1365.00	C-H Bending	1034.00	C-O Stretching	548.62	C-Br Stretching
1450.00	C-H Bending	1642.75	C-C Stretching	1375.54	C-H Bending	771.00	C-H Bending
1602.00		2109.00		1443.00		1027.45	C-O Stretching
1709.38	C=O Stretching	2393.00		1605.00		1633.25	C=C Stretching
2351.80		3428.00	0-H Stretching	1709.38	C=O Stretching	2373.66	
2918.00	O-H Stretching	4057.00		2351.80		2935.66	O-H Stretching
3390.00	N-H Stretching			2919.00	O-H Stretching	3433.00	O-H Stretching
3696.38	O-H Stretching			3368.00	O-H Stretching	3620.55	O-H Stretching
				3850.60		3687.00	O-H Stretching

*Before Activation (cm⁻¹), **After Activation (cm⁻¹).

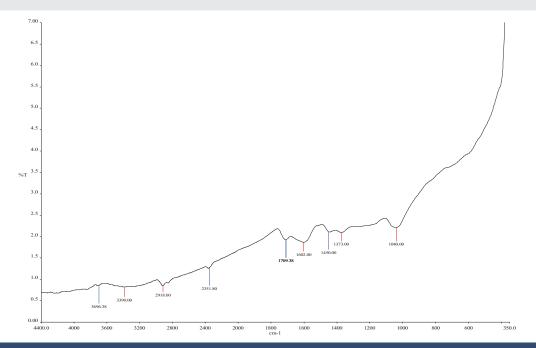


Figure 3: FTIR spectrum for carbonized coconut shells.

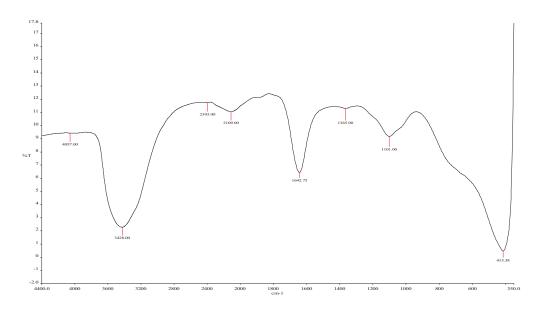


Figure 4: FTIR spectrum for activated coconut shells.

Activation typically increases the surface area and porosity of the carbon and introduces functional groups that enhance its adsorption capacity. The appearance of new peaks and the shift in the wavenumber of existing peaks can be attributed to the formation of new functional groups or the rearrangement of existing ones on the carbon surface [28].

Conclusion

The preparation of adsorbents with smaller particle sizes was found to be a better choice as it improves adsorption efficiency. A higher surface area of adsorbents also significantly impacts adsorption efficiency.

The quality of adsorption is significantly influenced by a higher impregnation ratio. A higher contact time yields better adsorption efficiency for coconut shell-based activated carbon.

Generally, this study showed that the adsorption mechanism using coconut shell-based activated carbon was environmentally friendly, cost-efficient, and effective adsorbent for removing heavy metals from paint wastewater.

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Author contributions

Conceptualization and original draft preparation, M.E; data curation and analysis T.R. and K.J; Proofreading, E.O. All authors have read and agreed to the published version of the manuscript.

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