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ARGAN SHELL - DERIVED CARBON MATERIAL AS AN EFFICIENT SORBENT FOR TOXIC METAL REMOVAL FROM WATER SAMPLES

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ABSTRACT

Carbon - based materials derived from waste biomass have attracted attention in water treatment applications due to their porous structure, high surface area, and sustainability. In this study, an activated carbon produced from argan shell biomass, an abundant, low - cost byproduct of the Moroccan Argania spinosa tree, was evaluated for the removal of toxic heavy metals from wastewater. Batch adsorption experiments demonstrated that solution pH was an important parameter governing uptake performance. Near - neutral conditions enabled simultaneous and efficient removal of Pb (II), Zn (II), and Cu (II), achieving metal ions sorption of about 90 - 100 % within contact time of 40 min. Under strong acidic conditions (pH 1), metal uptake was inhibited due to surface protonation and competition from excess H^+ ions. At mildly alkaline conditions (pH 9), Pb (II) removal remained consistently high, whereas Zn (II) and Cu (II) removal decreased significantly. These findings identify pH 7.0 as the optimized operational parameter for effective and simultaneous removal of Pb (II), Zn (II), and Cu (II).

Keywords: carbon - based material, argan shell, toxic metals, water treatment.

INTRODUCTION

Ensuring access to clean water is a global priority due to the persistence of toxic heavy metals in surface and groundwater arising from mining, electroplating, battery, and fertilizer industries [1, 2]. Heavy metals are non - biodegradable, bioaccumulative, and can cause severe neurological, renal, and carcinogenic effects even at trace concentrations, necessitating robust removal technologies that meet increasingly strict drinking - water standards [1, 3]. The conventional treatments methods, such as precipitation, ion exchange, membrane filtration, and coagulation/flocculation are effective but often suffer from high chemical or energy demands, sludge generation, sensitivity to water chemistry, and limited selectivity in complex matrices [1, 4]. By contrast, adsorption stands out for its operational simplicity, scalability, low energy footprint, and high efficiency at low concentrations, making it particularly suitable for applications focused on heavy metals removal [1, 4, 5].

Porous carbon materials are among the most widely used adsorbents, valued for their high specific surface area, tunable mesoporosity, chemical stability, and ease of regeneration [5, 6]. The adsorption of heavy metals onto carbonaceous sorbents arises from multiple mechanisms, including electrostatic attraction, surface complexation with oxygenated and heteroatom functional groups, cation-π interactions, ion exchange, whose contributions depend on pH, ionic strength, and the sorbent's surface chemistry and pore structure [5 - 8]. There is therefore motivation to develop sustainable, high - performance carbons whose surface functionalities and pore structures can be engineered to target specific metal ions in real waters [9].

Biomass - derived carbons from lignocellulosic wastes align with circular economy and low - carbon manufacturing principles while reducing costs relative to fossil - based precursors [6, 10, 11]. Activation strategies, physical (CO_2, steam) and chemical (KOH, H_3PO_4, $ZnCl_2$), allow tailoring the porosity and the introduction of surface oxygen/phosphorus functionalities, which enhance metal - binding via complexation as well facilitate intraparticle diffusion [6, 9]. KOH activation typically yields ultra microporous carbons with very high BET surface areas, favourable for small, hydrated ions, whereas H_3PO_4 tends to preserve mesoporosity and can introduce phosphate moieties that provide additional complexation sites for metal ions [9, 12]. Post - synthesis modification, such as nitrogen or sulfur heteroatom doping and oxidation, further increases the density and strength of metal - binding sites and can improve selectivity in competitive conditions [8, 9].

Argan (*Argania spinosa*) is endemic to southwestern Morocco and supports a well - developed industrial chain centered on argan oil. This sector generates large amounts of by - products, notably argan shells, which are typically underutilized [13, 14]. Argan shells are dense, lignocellulosic materials with high fixed - carbon content and low ash, characteristics favourable for producing high - yield activated carbons [15 - 17]. Prior studies on argan shell -derived carbons and related nut - shell precursors have demonstrated successful preparation via both physical and chemical activation, producing materials with high surface areas and abundant oxygenated functionalities [18]. However, the structure - property - performance relationships governing heavy - metal uptake, specifically, how activation conditions control pore size distributions, surface acidity/basicity, point of zero charge, and heteroatom speciation that in turn dictate kinetics, capacity, and selectivity across metals, remain insufficiently resolved for argan shell carbons.

There are remaining fields of research for practical application: efficiency under competitive conditions (coexistence of cations/anions and natural organic matter), efficiency at realistic pH and ionic strength values, regeneration, and cyclic stability [5 - 7].

In this study we integrate a rich lignocellulose raw material, such as argan Schell biomass, with specific carbonization process using appropriate carbonization temperature and specific activation conditions via impregnation with alkaline hydroxides KOH. The resulting microporous activated carbon is characterized with larger surface area, narrow pore size and pronounced content of nitrogen. The aim of this work is to investigate the adsorption efficiency of the prepared argan shell - derived activated carbon for toxic metals removal. By clarifying the relationships among precursor properties, processing parameters, and adsorption conditions, it provides practical issues for developing efficient and sustainable sorbents from argan shell waste for water treatment targeting heavy metal removal.

EXPERIMENTAL

Instruments, material and methods

Material

Argan hard shells were sourced from the southern region of Morocco. The raw shells were washed thoroughly with distilled water, oven - dried at 100°C for 24 h, then mechanically crushed and sieved to collect the 1 - 3 mm fraction. This fraction was used directly for carbonization. Carbonization of the clean and dried shell fraction proceeded under a continuous N_2 flow at 700°C for 1 h, followed by cooling to room temperature under flowing N_2. The carbonized product is referred to as Argan Shell Biochar (ASB). The carbonized product particles in the 500 - 1000 μm range were subjected to chemical activation using 1.4 M solution of potassium hydroxide via impregnation. Then the sample was subsequently heat - treated under flowing nitrogen. For post - activation the solids were washed with 5 mol L^{-1} HCl to remove inorganic residues, rinsed repeatedly with distilled water to neutral pH, and dried overnight at 110°C [19]. The resulting materials is denoted activated - Argan Shell Biochar (a - ASB).

Characterization study

Thermogravimetric analysis (TGA) was conducted on the raw shells using a PerkinElmer Pyris STA 6000 under nitrogen to determine the selection of carbonization temperature. Elemental composition was assessed by energy - dispersive X - ray spectroscopy (EDX) with a Bruker Nano XFlash Detector 430 - M. Surface functional groups were examined by FT-IR spectroscopy (JASCO 410). Morphology was investigated by scanning electron microscopy (SEM, model SH - 4000 M) operated at 15 kV. Crystallographic features were analyzed by X - ray diffraction (XRD) using a Bruker D8 Advance diffractometer. The degree of graphitization and structural disorder were evaluated by Raman spectroscopy (LabRAM HR) [19]. BET surface area (S_{BET}) was evaluated using the Brunauer-Emmett-Teller (BET) method [20].

Sorption procedure

Batch adsorption experiments were conducted using a - ASB. For each run, 50 mg of sorbent was weighed directly into a clean polypropylene centrifuge tube. An aqueous multi - element solution containing Pb (II), Zn (II), and Cu (II) (Sigma - Aldrich, nanoelement standard solution, 1000 ppm) at an initial concentration of 10 mg L^{-1} for each metal ion was then added to the tube to initiate sorption. The tubes were agitated on a mechanical shaker (LCD Digital Linear Shaker Labtex Biotech China Co., Ltd.) for 40 min to ensure adequate contact between the sorbent and the solution. Following contact, the suspensions were centrifuged at 6000 rpm (Centrafuge Neya 8, Remi, India). The supernatant was subsequently filtered through membrane filters with a pore size of 0.45 µm to remove any residual particulates. The filtrates were analysed by microwave plasma-optical emission spectrometry (MP - OES 4210, Agilent Technologies, USA) to determine the residual concentrations of Pb (II), Zn (II), and Cu (II) after adsorption. All experiments were performed in triplicate to ensure reproducibility, and the results are reported as mean values ± standard deviation.

Removal efficiency is calculated from the difference between initial and final concentrations.

Eq. (1) was used for calculation of sorption efficiency:

$$R = \frac{C_{initial} - C_{final}}{C_{initial}} x\ 100 \tag{1}$$

where R is the removal efficiency in %, $C_{initial}$ is the initial concentration of M (II) (mg L^{-1}) and C_{final} is the concentration after sorption (mg L^{-1}).

RESULTS AND DISCUSSION

Material characterization

The thermogravimetric analysis (TGA) profile of argan shells revealed distinct loss of the weight with the temperature rising, providing insights for selecting the optimal carbonization temperature. The TGA profile indicated that the material achieved thermal stabilization above 700 °C, with negligible further weight loss. This observation justified the selection of 700°C as the carbonization temperature for char production, ensuring maximum carbon yield and structural integrity of the resulting material.

The morphology obtained by Scanning Electron Microscopy (SEM) analysis revealed a rough microstructure of both the carbonized precursor and the activated carbon.

Energy Dispersive X-ray (EDX) elemental analysis indicated that ASB is primarily composed of Carbon and Oxygen. Minor amounts of Nitrogen, Potassium, and Calcium were also detected (Table 1).

X - ray diffraction (XRD) revealed that the carbonized precursor ASB exhibits an amorphous carbon pattern with no sharp crystalline peaks, showing only two broad features corresponding to two graphitic planes. After activation, these graphitic signatures broaden and diminish markedly, becoming barely visible for a - ASB, indicating disruption of graphitic order and formation of disordered, thin carbon domains along with

Table 1. Elemental composition of carbonized material (ASB), %.

	C	O	N	K	Ca
ASB	84.05	11.19	2.95	1.01	0.80

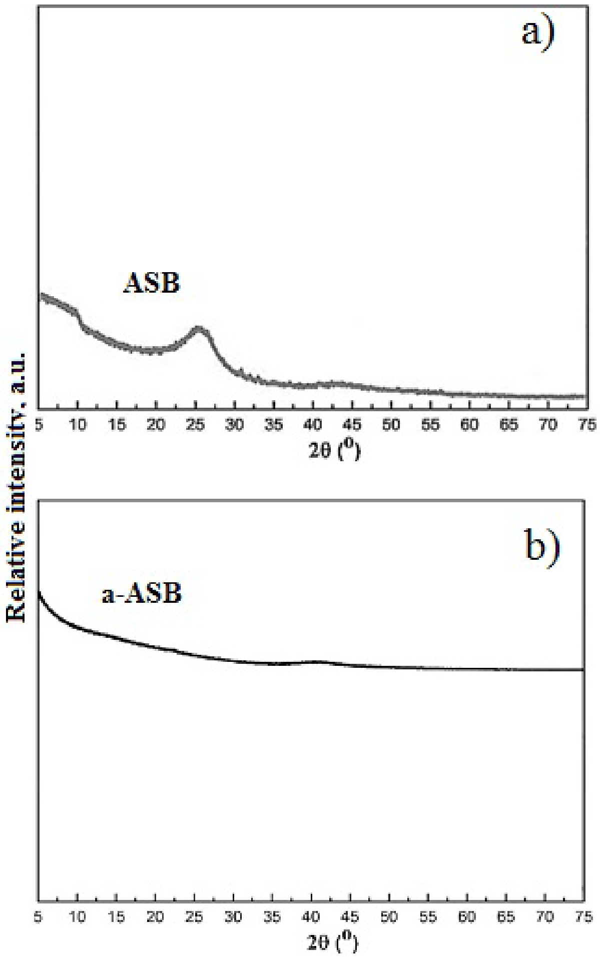

Fig. 1. X - ray diffraction of (a) the carbonized precursor (ASB) and (b) the resulting activated carbon (a - ASB).

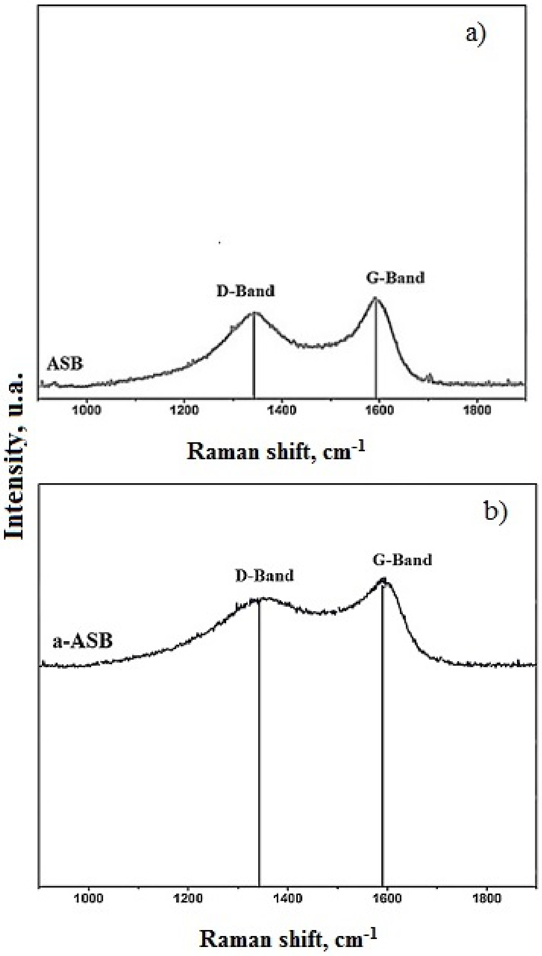

Fig. 2. Raman spectra of (a) the carbonized precursor (ASB) and (b) the prepared activated carbon (a - ASB)

significant porosity development.

Raman spectra of the carbon samples, including the carbonized precursor and activated carbon, display two characteristic peaks at approximately 1350 cm^{-1} and 1580 cm^{-1}. The intensity ratio of the peaks serves as an indicator of the material's graphitization degree. The rise in intensity ratio for the activated carbon relative to carbonized precursor ranging from 0.70 to 0.86 indicates a reduced degree of graphitization. This suggests that the activation process disrupted the ordered crystalline structure present in the ASB precursor, leading to a more disordered carbon framework.

The impregnation process with a potassium hydroxide solution resulted in a BET surface area of 1889.63 m^2 g^{-1} [19].

Sorption ability of the activated carbon. Effect of pH

The sorption performance of a - ASB for Pb (II), Zn (II) and Cu (II) ions was evaluated at three pH values: 1, 7, and 9 and is demonstrated at Fig. 3. The carbonization and activation process, involving high - temperature treatment under nitrogen and chemical activation with KOH, is known to enhance the surface area, porosity, and the abundance of functional groups, all of which are influence the metal ion adsorption [21 - 23]. Samsuri et al. compared oil palm and rice husk biochars for heavy - metal adsorption and found that oil palm biochar, despite its lower surface area, showed greater adsorption, indicating that oxygen - containing functional groups were more influential than surface area [24].

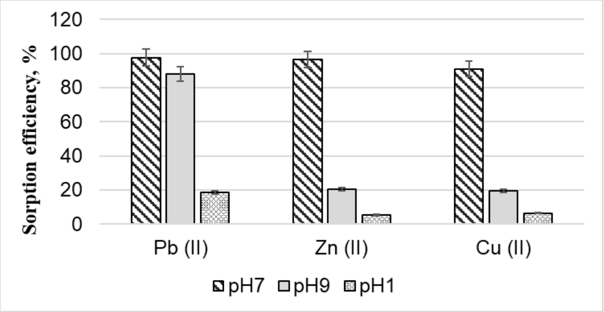

Fig. 3. Effect of pH on Pb (II), Zn (II), and Cu (II) sorption efficiency (Sorbent mass: 50 mg, metal concentration: 10 mg L^{-1}, agitation time: 40 min).

At pH 1, the sorption efficiency is low, 18.7 ± 1.3 %, 5.3 ± 1.5 %, 6.5 ± 1.0 %, for Pb (II), Zn (II) and Cu (II), respectively, as shown in the chart.

The reported values represent mean ± standard deviation from triplicate measurements, indicating good experimental reproducibility (relative error < 2 %).

At strongly acidic pH, several effects work together to suppress metal uptake by the activated carbon. The oxygen - containing groups available on the activated carbon surface (carboxyl, phenolic, hydroxyl, carbonyl) become protonated at low pH. Protonated functional groups are far less able to complex or ion - exchange with Pb^{2+}, Zn^{2+}, and Cu^{2+}. In effect, H^+ competes the metal ions for the same binding sites. Additionally, due to the low pH, the surface of the carbon is protonated, resulting in a positive surface charge that repels the positively charged metal ions, further inhibiting their adsorption.

At pH 7, the sorption efficiency for Pb (II), Zn (II), and Cu (II) is maximal, with Pb (II) and Zn (II) showing nearly complete removal (97.6 % ± 0.8 % and 96.6 % ± 1.0 %, respectively). The copper ions Cu (II) also exhibits high uptake with 91.0 % ± 1.3 %.

Statistical comparison (ANOVA, $p < 0.05$) confirms a significant difference between the adsorption efficiencies at neutral pH and those at acidic or alkaline conditions.

At this pH, the surface of the activated carbon is less protonated, and the competition from H^+ ions is minimized, allowing for more effective interaction between the metal ions and the functional groups present on the carbon surface. The high sorption degree at this pH is consistent with literature reports for KOH - activated carbons and other biochars, where optimal metal uptake is typically observed near neutral pH [5].

At pH 9, the sorption efficiency decreases compared to pH 7 but remains higher than at pH 1. In alkaline conditions, the surface of the activated carbon becomes more negatively charged, which can enhance the electrostatic attraction of metal cations. However, at higher pH values, metal ions begin to hydrolyse and form insoluble hydroxide precipitates, which are not adsorbed but rather removed from solution by precipitation. For Pb (II), the formation of Pb(OH) is less pronounced at pH 9, which may explain its relatively higher sorption compared to Zn (II) and Cu (II) at this pH [25, 26]. Under short - contact batch conditions (pH 9, 10 mg L^{-1}), Pb (II) is mainly present as labile Pb^{2+} and $PbOH^+$, with minimal precipitation of $Pb(OH)_2$, and these aqueous species continue to bind to deprotonated surface sites [27].

Besides pH, the sorption performance is also influenced by the surface chemistry and porosity of the activated carbon. The abundance of basic oxygen groups and the high specific surface area facilitate strong interactions via complexation and electrostatic attraction.

Variations in the distribution of micro- and mesopores further affect diffusion and accessibility of active sites.

CONCLUSIONS

This study confirms that argan shell is a sustainable and low - cost precursor for producing activated carbons with high adsorption capacity toward Pb(II), Zn(II), and Cu(II) in water. The two - step carbonization–activation process generated a micro/mesoporous structure with abundant oxygenated surface sites, verified through TGA, SEM/EDX, XRD, and Raman analyses.

The adsorption experiments highlighted pH as a key operational factor, with optimal metal removal achieved near neutrality. However, performance declined under strong acidity or alkalinity due to surface protonation, competition with H^+, and metal hydrolysis effects.

Despite its efficiency, the method presents potential challenges related sensitivity to environmental conditions, such as pH fluctuations, competing ions, and natural organic matter.

The regeneration capacity also requires systematic evaluation. Future research should focus on assessing reusability of the sorbent and implement selective surface modifications to improve affinity toward diverse contaminants.

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Authors' contributions

P.P., E.Ch., M.Ch.: Conceptualization; P.P., E.Ch., M.Ch., T.Ch.: Methodology; P.P., J.A., K.A., G.U.: Validation; P.P., J.A., K.A., G.U., T.Ch.: Formal Analysis; J.A., K.A., G.U., P.S., K.K.: Investigation; P.P., E.Ch., M.Ch.: Resources; J.A., K.A., G.U.: Data Curation; P.P., T.Ch.: Writing - Original Draft Preparation; M.Ch., P.S., K.K.: Writing - Review & Editing: E.Ch.

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