

Efficient and low-cost removal of heavy metals from aqueous solution using eco-friendly adsorbent

Nino Giorgadze^{1*}, Elizaveta Tskhakaia^{1,3}, Natela Ananiashvili¹, Tamaz Marsagishvili¹ and Ketevan Tavamaishvili²

¹ *Iv. Javakhishvili Tbilisi State University, R. Agladze Institute of Inorganic Chemistry and Electrochemistry, Mindeli str. 11, 0186 Tbilisi, Georgia*

² *Georgian American University, Merab Aleksidze str. 10, 0160 Tbilisi, Georgia*

³ *Tbilisi State Medical University, V. Pshavela ave.33, 0186, Tbilisi, Georgia*

*Corresponding author: nino.giorgadze718@ens.tsu.edu.ge

Abstract

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Heavy metal contamination of water by ions such as Pb^{2+} , Co^{2+} , Cd^{2+} , and Cu^{2+} poses significant environmental and public health risks. Adsorption is a widely accepted method for metal removal due to its efficiency, simplicity, and cost-effectiveness. This study investigates the adsorption potential of activated carbon derived from walnut (*Juglans regia* L.) shells, an agricultural waste material with high lignin and cellulose content. A novel, one-step activation method, developed at Ivane Javakhishvili Tbilisi State University was employed, to synthesize the sorbent using only water as the activating agent and without chemical additives. The process is energy-efficient and environmentally friendly, utilizing carbonization gases as an internal energy source. Physicochemical characterization showed a high surface area and well-developed porous structure suitable for adsorption. Batch adsorption experiments were conducted using model solutions of Pb^{2+} , Co^{2+} , Cd^{2+} , and Cu^{2+} at various concentrations. Adsorption performance was evaluated in static conditions at 25 °C using atomic absorption spectroscopy. The results showed outstanding removal efficiency, especially at lower concentrations (0.0025 M), with metal uptake following both Langmuir and Freundlich isotherm models ($R^2 > 0.90$), indicative of monolayer and heterogeneous surface adsorption. The maximum sorption capacities and removal efficiencies confirmed the effectiveness of walnut shell-derived carbon as a means of treating heavy-metal-contaminated water. This biosorbent provides a low-cost, sustainable, and efficient alternative for water purification, with potential scalability for industrial applications.

Keywords: heavy metals; adsorption; eco-friendly adsorbent; carbon material; wastewater treatment

Introduction

Heavy metal contamination of water by ions such as Pb^{2+} , Co^{2+} , Cd^{2+} , and Cu^{2+} is a critical environmental and health problem, exhibiting neurotoxicity, along with organ damage (Qasem et al., 2021). Adsorption is commonly regarded as an effective method for removing heavy metals because it is simple, versatile, and highly effective in reducing metal bioavailability in wastewater (Abiodun et al., 2023). Over the

past few years, low-cost agricultural waste-based biosorbents have received growing interest. Among them, walnut (*Juglans regia* L.) shells have been extensively researched due to their high abundance and beneficial properties. Walnut shells have high lignin and cellulose content, and can undergo treatment to convert them into activated carbon with superior chemical stability, high surface area, and low ash content (Albatrni et al., 2022). Since Albatrni et al. (2022) elaborated, walnut shell-derived carbon materials are endowed with high surface

area and dense functional groups, hence suitable precursors for water treatment adsorbents. Different reviews have highlighted the success of walnut-shell adsorbents in removing diverse contaminants, including heavy metal ions (Jahanban-Esfahlan et al., 2020; Karić et al., 2022).

Biomass-derived carbon materials typically exhibit highly porous structures and rich surface chemistry that enhance sorption. Activation processes (chemical or physical) enhance porosity and introduce oxygen-containing functional groups (e.g., $-\text{COOH}$, $-\text{OH}$), which are capable of complexing metal ions. Importantly, the adsorption capacity depends on both adsorbent characteristics and solution conditions (Albatrni et al., 2022). Key performance-controlling factors are: *Adsorbent properties*: Pore size distribution, surface area, and surface chemistry (Albatrni et al., 2022); *Solution conditions*: pH, temperature, ionic strength, and background solutes, which determine ion speciation and surface charge (Albatrni et al., 2022).

These factors jointly determine metal uptake. For example, oxygen-containing groups on carbon surfaces can complex metal ions, while micropores provide extensive surface area for adsorption. Optimization of activation methods can tailor these characteristics, as reported for various biomass carbons (Albatrni et al., 2022; Qasem et al., 2021).

Walnut-shell-based adsorbents have been used to adsorb several heavy metal ions from aqueous solution. Previous studies have shown that such adsorbents are effective in sorption of Pb^{2+} , Cd^{2+} , Co^{2+} , and Cu^{2+} under specific conditions (Jahanban-Esfahlan et al., 2020; Albatrni et al., 2022). Adsorption experiments have, for example, revealed efficient capture of: *Lead (Pb^{2+})*: Pb (II) ions bind strongly to activated walnut carbon. Studies on biosorbents report high Pb (II) removal efficiencies with walnut shell-derived adsorbents (Cheng et al., 2016; Hu et al., 2023); *Cadmium (Cd^{2+})*: Cd (II) is also efficiently removed by both raw and chemically treated walnut shell carbons (Mohseni et al., 2024; Gondhalekar et al., 2015); *Cobalt (Co^{2+})*: Cobalt adsorption has been achieved using acid-activated walnut shell carbon, which creates more binding sites for Co(II) ions (Irshad et al., 2023); *Copper (Cu^{2+})*: Cu(II) removal is typically high, especially with composite or modified walnut-shell carbons. For instance, porous composites combining walnut shell carbon with chitosan or other polymers show strong Cu (II) adsorption (Bamisaye et al., 2023).

Each of these metals is toxic at elevated concentrations, and their affinity for bio sorbent surfaces is influenced by ionic radius, hydration energy, and solution chemistry. Many studies fit equilibrium and kinetic data for these metal ions using standard adsorption models, confirming that walnut-based adsorbents are effective for multi-metal uptake (Abiodun et al., 2023; Feizi and Jalali, 2015).

To quantify sorption performance, equilibrium adsorption isotherm models are routinely applied. The Langmuir isotherm assumes a monolayer adsorption on a homogeneous surface with a fixed number of identical sites (Al-Ghouti and Da'ana, 2020). In contrast, the Freundlich isotherm describes adsorption on a heterogeneous surface with a spectrum of binding energies (Al-Ghouti and Da'ana, 2020). These models yield parameters such as maximum sorption capacity (Langmuir) and intensity or heterogeneity factors (Freundlich), which facilitate comparison of adsorbents. For heavy metal adsorption, it is common to fit experimental data to both models. Many studies report good agreement with one or both isotherms depending on surface uniformity and concentration range (Chakraborty et al., 2020; Abiodun et al., 2023). In this work, Langmuir and Freundlich analyses are used to characterize the Pb^{2+} , Co^{2+} , Cd^{2+} , and Cu^{2+} adsorption behavior of the novel walnut shell-derived carbon.

Carbon materials are of great interest in this regard. Their application areas are constantly growing in the direction of solving ecological problems caused by water factors (infectious and non-infectious diseases, etc.), due to their high porosity, developed surface, mechanical strength, antimicrobial, good sorption properties, and low cost (Ethaib et al., 2022).

Materials and Methods

The primary raw material utilized was walnut shells (*Juglans regia* L.), a lignocellulosic agricultural byproduct known for its high carbon content and low ash composition, and as a result, an excellent precursor in activated carbon production (Li et al., 2020; Beri et al., 2021). These shells were provided from local walnut processing facilities in Georgia. Prior to processing, the shells were thoroughly washed with distilled water to remove adhering impurities and then dried at 110 °C for 24 hours in order to remove moisture content, following standard preparation protocols (Beri et al., 2021).

The sorbent was synthesized using a proprietary one-step activation technology (Marsagishvili et al., 2021), developed in the Institute of Inorganic Chemistry and Electrochemistry of Ivane Javakhishvili Tbilisi State University. This method involves direct carbonization and activation of the raw walnut shells without the need for chemical activating agents, thereby minimizing environmental impact and operating expenses (Nowicki et al., 2024). This process employs water as the sole reagent, whereas gases developed in the course of carbonization are utilized as an internal energy source (Marsagishvili et al., 2021; Khusidman et al., 2016), which further contributes to the process sustainability. Notably, the stainless-steel reactor body serves as a catalyst, facilitating the activation process (Nowicki et al., 2024).

The technology is also flexible and has been successfully applied with various cellulose-containing raw materials, including sawdust and other nut shells without pretreatment. The resulting carbonaceous materials are highly porous with excellent adsorption capacities and are amenable to application in wastewater treatment applications (Li et al., 2020; Beri et al., 2021).

Based on laboratory-scale experiments, a large-scale laboratory reactor was designed to optimize the production process. The reactor is equipped with an automatic control system that allows one to exactly control the most important parameters, such as temperature, heating rate, and water vapor flow rate. This level of control ensures reproducibility of performance and the quality of adsorbents obtained (Nowicki et al., 2024).

The reactor’s design makes it possible to achieve a one-step activation process, without the need for separate carbonization and activation processes as individual steps. The one-step process, besides saving energy, also simplifies the overall production process, and this is in line with sustainable manufacturing concepts (Nowicki et al., 2024). The reactor body (stainless steel) acts as a catalyst (Fig. 1). Through the utilization of the technology outlined, the carbonaceous materials from cellulose-containing wastes are economically feasible.

The physicochemical properties of the carbonaceous material were determined by N₂ adsorption at a temperature of -196 °C in Surface Area Analyzer (Micromeritics Gemini VII 2390T). Before starting the experiments, the samples were degassed at a temperature of 300 °C. Specific surface area (SBET), total pore volume (VTOTAL) and pore size distribution were measured. The chemical composition and morphology were studied with a scanning electron microscope (SEM), with Bruker’s QUANTAX energy dispersive X-ray spectrometry system (EDS) HITACHI TM 3030 Plus). The measurement results are shown in Tables 1 and 2.

Experiments were conducted to study the effect of concentration on the adsorption process. The observation was made under static conditions at a constant temperature of 2 °C, adsorbates were 100 – 100 mL of 0.0025 – 0.02 M model solutions of Pb²⁺; Co²⁺; Cd²⁺; Cu²⁺ and the sorbent mass

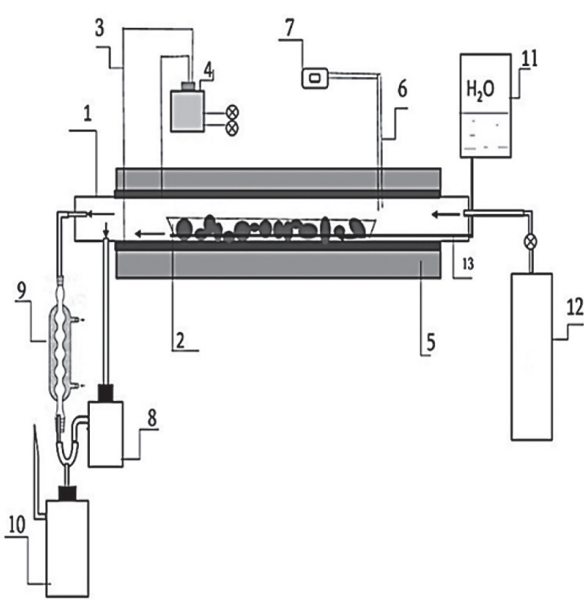


Fig. 1. Reactor construction: 1 – Reactor; 2 – Research sample storage volume; 3 – Nichrome heater; 4 – Laboratory autotransformer; 5 – Thermal insulation; 6 – Thermocouple; 7 – Multivoltmeter; 8 – Liquid fraction collector; 9 – Water cooler; 10 – Gas fraction condensate collector; 11 – Water supply system; 12 – CO₂ gas
Source: Authors’ own elaboration

(fraction size = 40 μm) was 1 g. After filtering the solution, the concentration of heavy metal ions was determined on an atomic absorption spectrophotometer AAS (ANALYST 200-1004 TAM; Perkin-Elmer). The amount of adsorbed heavy metal ions was determined by the following formula (Rehman et al., 2013):

$$q = \frac{(C_0 - C_e)V}{W}, \text{ eq.}$$

(1)

where *q* is the adsorption value, mg/g; *V* is the volume of solution, L; *C*₀, *C*_{*e*}, are initial and equilibrium concentrations, mg/L; *W* is the mass of adsorbent, g.

Table 1. Physical characteristics of walnut shell carbon material

Sample	BET surface area, m ² /g	Micropores area, m ² /g	Micropores volume, sm ³ /g
Walnut shell carbon material	499.00	380.26	0.16

Source: Authors’ own elaboration

Table 2. Chemical composition of walnut shell carbon material

Sample	Chemical composition of samples % (averaged)												
	C	O	Ca	K	Si	S	Fe	Ni	Cu	Zn	Al	F	Pb
Walnut shell carbon material	89.5	7.4	0.8	1.4	0.0	0.4	0.15	0.04	0.2	0.1	–	–	–

Source: Authors’ own elaboration

The rate of extraction (S , %) of heavy metal ions by the sorbent was calculated by the formula (Rehman et al., 2013):

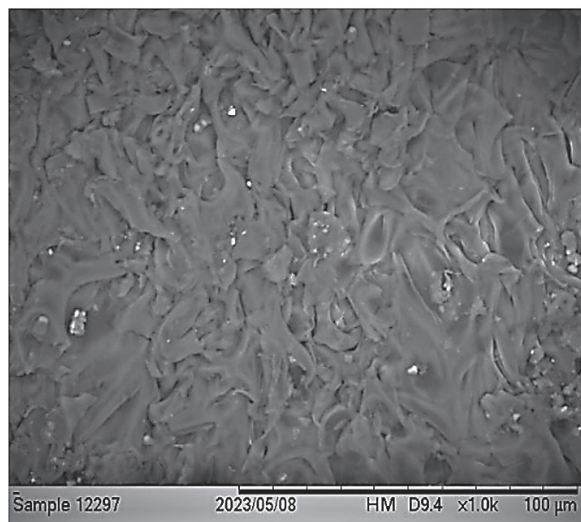
$$S = \frac{(C_0 - C_e)}{C_0} \times 100\%, \text{ eq.} \quad (2)$$

where S is rate of extraction, %; C_0 , C_e , are initial and equilibrium concentrations, mg/L.

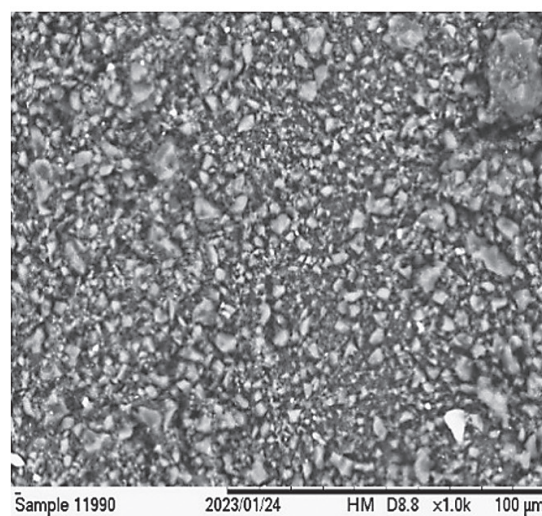
Results and Discussion

In the adsorption process, the porous structure of activated carbon is of great importance, the diameter and volume of the pores are larger than the size of heavy metal ions. The adsorption capacity of carbonaceous materials is related to chemical and structural characteristics. Therefore, the abundance of well-developed pores is very important. The values of structural parameters (BET surface area, micropores area and micropores volume) of the obtained carbon material are given in Table 1.

The Scanning Electron Microscopy (SEM) images of raw walnut shells and obtained carbon material shown in Fig. 2 A and B, respectively. Before treatment, the raw materials show a bulk structure with thick and large crystals as displayed in Fig. 2A. Powder produced after thermal treatment and grinding shows discrete sheets and carbon structures with enhanced surface area (Fig. 2B). The Chemical composition of the obtained carbon material is given in Table 2. Therefore, the developed structure is favorable for adsorption.



A)



B)

Fig. 2. Structure of (A) raw walnut shell and (B) carbonaceous material obtained from walnut shell

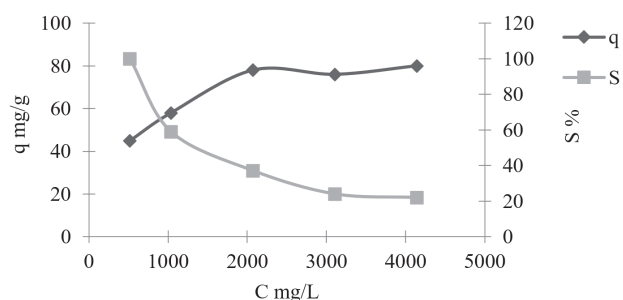
Source: Authors' own elaboration

Effect of concentration and adsorption isotherms

The influence of the initial concentrations of metal ion adsorbates on adsorption was studied and the upper limit of the adsorbent's adsorption capacity for Pb^{2+} , Cd^{2+} , Co^{2+} and Cu^{2+} ions in solution was determined. The behavior of the carbon adsorbent in relation to the concentration of metal ions is shown in Graph 1, 2, 3 and 4.

Studies of solutions of different concentrations of various metals have shown that the best adsorption and removal rate of all three ions are achieved at a solution concentration of 0.0025 M for 30 minutes.

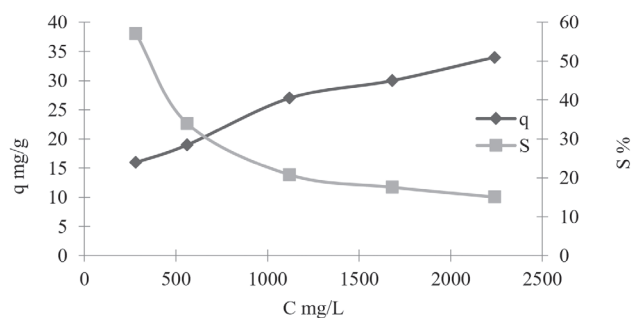
In the studied solutions, the efficiency of purification from various metal ions reaches 46–100% in the case of low



Graph. 1. Effect of initial Pb^{2+} concentrations on the adsorption value and extraction rate of carbon material obtained from walnut shells. Experimental conditions:

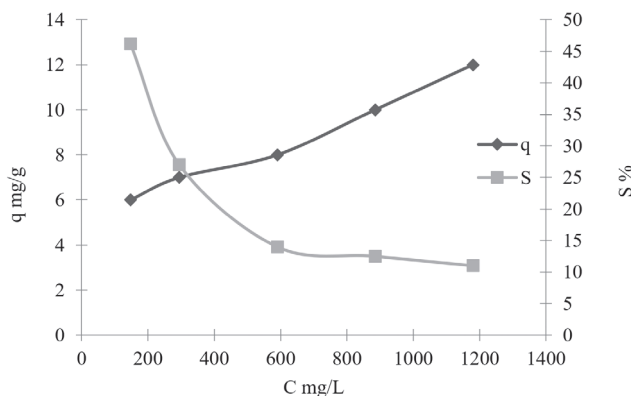
Temperature – 25°C, m_{ad} – 1 g, time – 5 min,
V – 100 mL, particle size – 40–20 μm

Source: Authors' own elaboration



Graph. 2. Effect of initial Cd^{2+} concentrations on the adsorption value and extraction rate of the carbon material obtained from walnut shells. Experimental conditions: Temperature – 25°C , $m_{\text{ad}} = 1\text{ g}$, time – 5 min, $V = 100\text{ mL}$, particle size – $40\text{--}20\text{ }\mu\text{m}$

Source: Authors' own elaboration

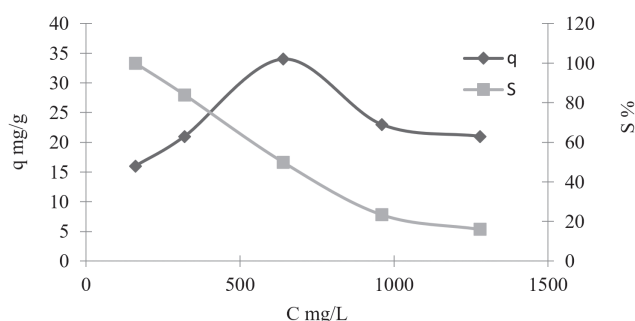


Graph. 3. Effect of initial Co^{2+} concentrations on the adsorption value and extraction rate of the carbon material obtained from walnut shells. Experimental conditions: Temperature – 25°C , $m_{\text{ad}} = 1\text{ g}$, time – 5 min, $V = 100\text{ mL}$, particle size – $40\text{--}20\text{ }\mu\text{m}$

Source: Authors' own elaboration

concentration solutions. To purify high concentration solutions, it will be necessary to increase the amount of adsorbent. As can be seen from the graphs, the amount of metal ions adsorbed increased with the increase in concentration, however, in terms of percentage removal, with the increase in concentration, the percentage removal of absorption by the samples decreased steadily.

In order to determine the removal of heavy metal ions (Pb^{2+} , Cd^{2+} , Co^{2+} , Cu^{2+}) from aqueous solutions by carbon adsorbent, it is necessary to study the adsorption mechanisms of these materials. It is known that ions and molecules, both in liquid and gaseous form, can be adsorbed on the surface of certain adsorbents (Reed and Matsumoto, 1993; Malik, 2004).



Graph. 4. Effect of initial Cu^{2+} concentrations on the adsorption value and extraction rate of the carbon material obtained from walnut shells. Experimental conditions: Temperature – 25°C , $m_{\text{ad}} = 1\text{ g}$, time – 5 min, $V = 100\text{ mL}$, particle size – $40\text{--}20\text{ }\mu\text{m}$

Source: Authors' own elaboration

The most likely mechanism by which carbonaceous materials absorb metal ions from aqueous solutions, is the formation of mono layers of adsorbed particles on their surface. Adsorption is usually described by isotherms, i.e. functions relating the amount of adsorbed by the adsorbent. The distribution of metal ions between the liquid and solid phases can be expressed by a number of isotherm models, such as the Langmuir and Freundlich isotherms.

The Langmuir isotherm assumes monolayer adsorption on a surface containing a finite number of adsorption sites with homogeneous sites, without transmigration across the adsorbed layer (Hameed et al., 2007). Once an adsorption site is occupied, no more sorption can occur at that site, indicating that the surface reaches a saturation point where maximum surface adsorption is achieved.

The results obtained during the study of the influence of concentrations were used to obtain Langmuir and Freundlich adsorption isotherms using known liquid isotherm equations. The linear model of Langmuir isotherm and Freundlich isotherm are shown in Equations (3) and (4), respectively (Hameed et al., 2007).

$$C_e/q_e = C_e/q_m + 1/K_L q_m \quad \text{eq.} \quad (3)$$

$$\ln q = \ln(K_F) + \ln C_e/n. \quad \text{eq.} \quad (4)$$

where: q_e (mg/g) is the quantity adsorbed on the adsorbent at equilibrium, C_e (mg L^{-1}) is the concentration at equilibrium, q_m (mg g^{-1}) is the maximum sorption capacity relative to complete monolayer capacity, K_L (L mg^{-1}) is Langmuir constant, K_F (mg g^{-1}) is distribution coefficient showing the amount of metal adsorbed on sorbent for unit equilibrium concentration, and “n” is the adsorption intensity.

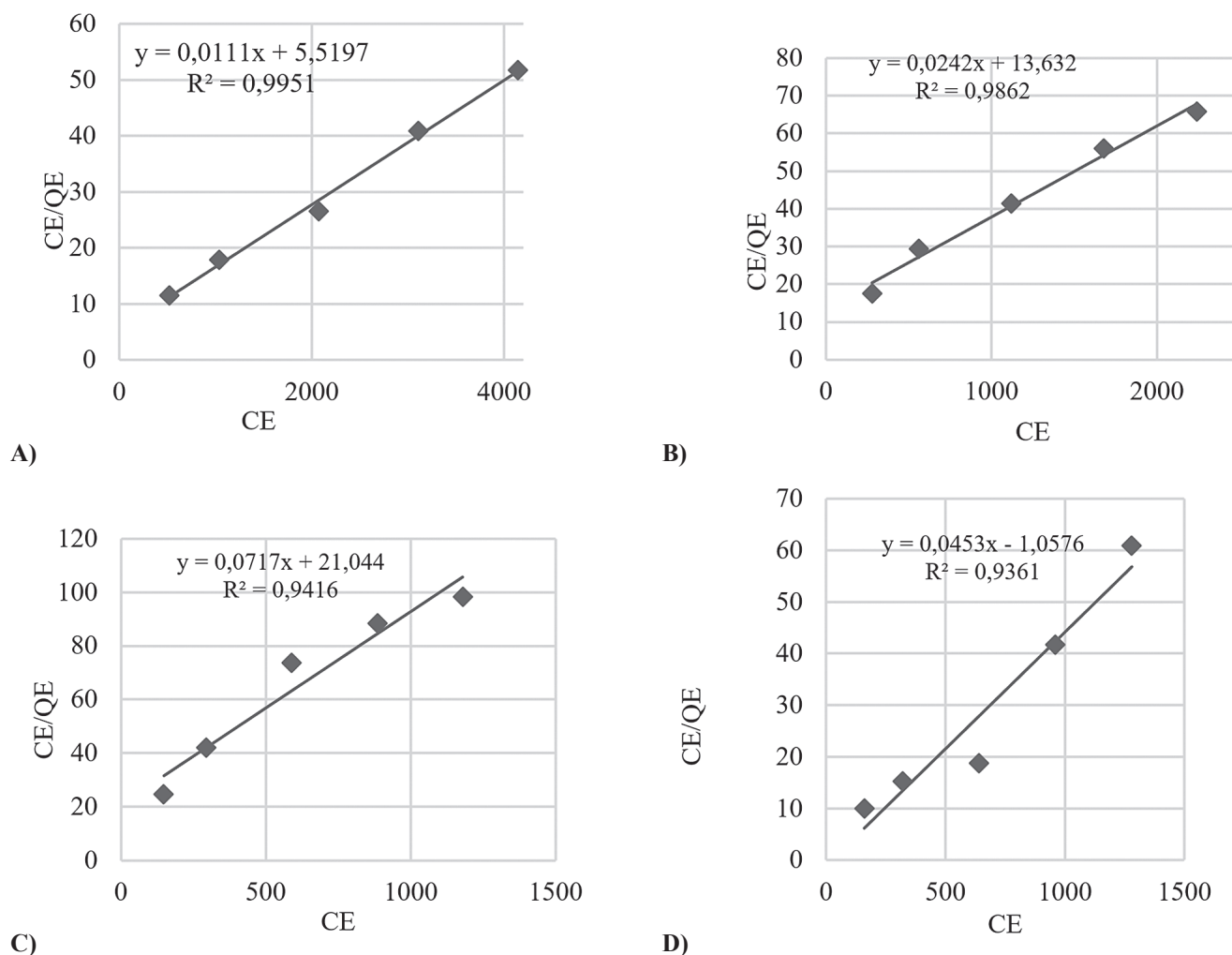
The adsorption isotherms relate the amount of heavy metal ions adsorbed at equilibrium q_e (mg g⁻¹) to the metal ions concentration at equilibrium, C_e (mg L⁻¹), the plots are given in Graph. 1, 2, 3 and 4. The Langmuir isotherm of Pb²⁺ Cd²⁺ Co²⁺ Cu²⁺ adsorption is shown in Graph. 5 A, B, C and D, and Freundlich isotherm in Graph. 6 A, B, C and D.

As it is shown on Graph. 5 (A, B, C, D) and Graph. 6 (A, B, C, D), the coefficients of correlation obtained are higher than 0.90 for the studied models. This suggests that the equilibrium of the adsorption of Pb²⁺ Cd²⁺ Co²⁺ and Cu²⁺ on the carbonaceous material from walnut shell is adequately represented by the models of Langmuir and Freundlich.

The Langmuir and Freundlich isotherm constants were

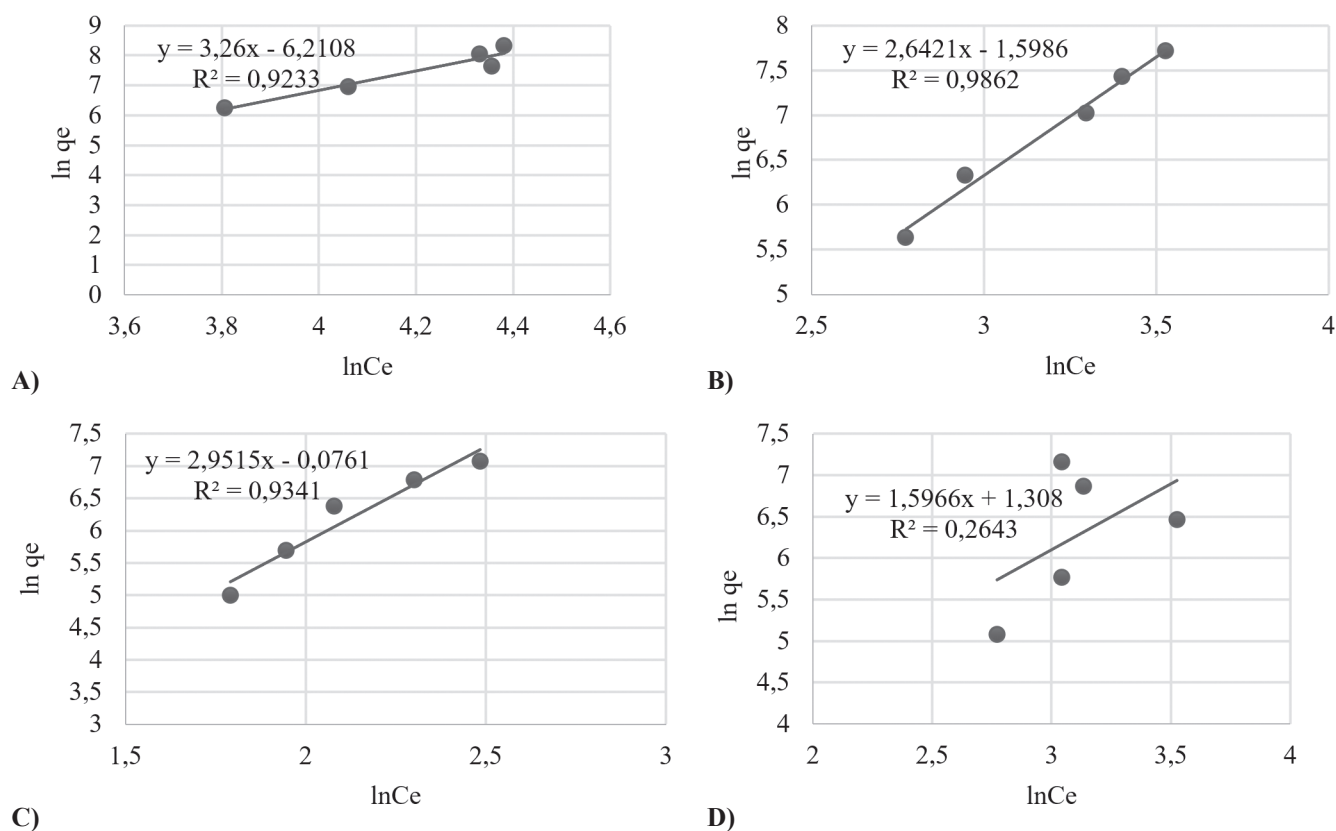
calculated from the slope and intercept of the corresponding linearized plots and are presented in Tables 3 and 4.

Linear regression analysis of the Langmuir isotherm demonstrated a strong correlation with the experimental data for most metal ions ($R^2 = 0.92\text{--}0.99$), including Pb²⁺, Co²⁺, and Cd²⁺. The walnut shell-derived carbon material exhibited high maximum adsorption capacities (q_m) for Pb²⁺ and Cd²⁺ ions, indicating its high potential for heavy metal removal. The relatively low K_L values suggest weaker interactions between some metal ions and the adsorbent surface; however, the adsorption mechanism cannot be determined from the Langmuir constant alone. In the case of Cu²⁺, the Langmuir model showed a poorer fit, suggesting more com-



Graph. 5. Adsorbent equilibrium of heavy metal ions ((A) – Pb²⁺; (B) – Cd²⁺; (C) – Co²⁺ (D)–Cu²⁺) on carbonaceous material obtained from walnut shell, Langmuir isotherm

Source: Authors' own elaboration



Graph. 6. Adsorbent equilibrium of heavy metal ions ((A) – Pb²⁺; (B) – Cd²⁺; (C) – Co²⁺ (D)–Cu²⁺) on carbonaceous material obtained from walnut shell Freundlich isotherm

Source: Authors' own elaboration

Table 3. Lengmiur Isotherm parameters for adsorption of metal ions onto walnut shell carbon material

Heavy metal	R ²	q _m mg/g	K _L Lmg ⁻¹
Pb ⁺⁺	0.99	90.09	0.002
Cd ⁺⁺	0.98	41.32	0.0017
Co ⁺⁺	0.94	13.95	0.0034
Cu ⁺⁺	0.93	22.08	-0.0428

Source: Authors' own elaboration

Table 4. Freundlich Isotherm parameters for adsorption of metal ions onto walnut shell carbon material

Heavy metal	R ²	n	K _f
Pb ⁺⁺	0.92	0.306	0.0020
Cd ⁺⁺	0.98	0.379	0.0202
Co ⁺⁺	0.93	0.339	0.926
Cu ⁺⁺	0.26	0.627	3.69

Source: Authors' own elaboration

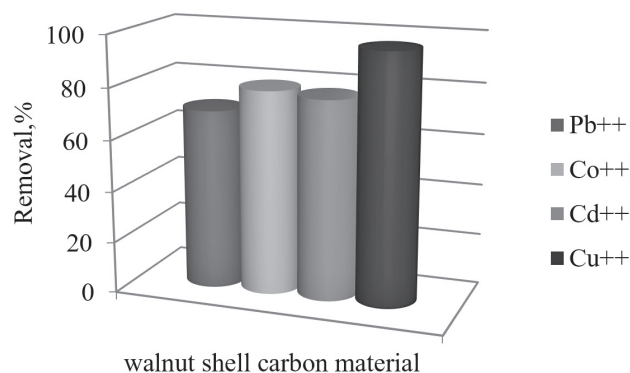
plex adsorption behaviour associated with the heterogeneous nature of the adsorbent surface.

The Freundlich isotherm analysis further confirmed the heterogeneous characteristics of the carbon material, with different adsorption capacities depending on the metal ion. The K_f and n values presented in Table 4 indicate differences in adsorption capacity and adsorption intensity among the investigated metal ions. Overall, the walnut shell-derived carbon material demonstrated selective adsorption behaviour toward different heavy metal ions, which can be attributed to differences in their physicochemical properties and interactions with the active sites on the adsorbent surface.

Walnut shell carbon material as adsorbent in multicomponent system

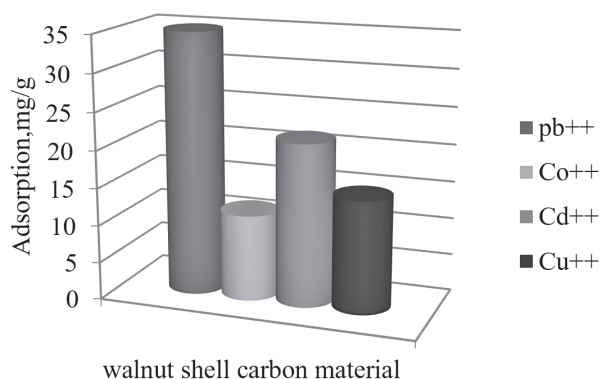
In general, multicomponent adsorption of heavy metals is adopted to evaluate the efficiency of an adsorbent. Selectivity is an important factor in understanding how an adsorbent will perform in real water systems, which is tested by adding vari-

ous concentrations of metal ions to the solution. Taking this into account, the next stage of the research was to determine the possibility of using our obtained adsorbents, namely walnut shell carbon material, in the simultaneous presence of the following ions (Pb (II), Cd (II), Co (II), Cu (II)) in solution. Walnut shell carbon material with a fraction size of 40–20 μm was used as an adsorbent. The delay time in the solution (with stirring) was $T = 30 \text{ min.}$, $m (\text{sorb.}) = 1 \text{ g.}$, $V (\text{res.}) = 100 \text{ ml}$, $T = 25^\circ\text{C}$, each metal concentration $C = 0.01 \text{ M}$. The results are given in graphs 7 and 8.



Graph. 7. Removal percentage of walnut shell carbon material for Pb(II), Cd(II), Co(II), Cu (II) each metals concentration 0.01M, $T = 30 \text{ min.}$, $m \text{ sorb.} = 1 \text{ g.}$, $V \text{ sol.} = 100 \text{ ml}$, $t = 25^\circ\text{C}$

Source: Authors' own elaboration

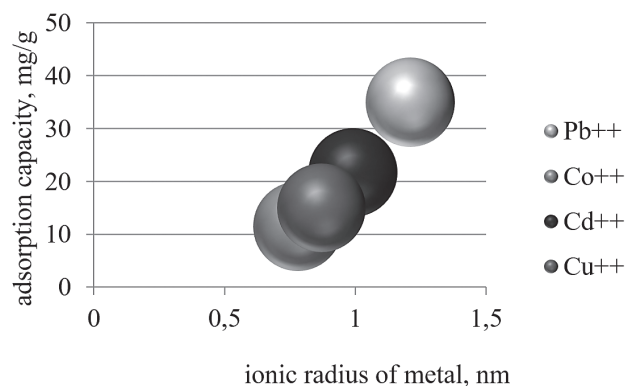


Graph. 8. Adsorption uptake of walnut shell carbon material for Pb(II), Cd(II), Co(II), Cu(II) each metals concentration 0.01M, $T = 30 \text{ min.}$, $m \text{ sorb.} = 1 \text{ g.}$, $V \text{ sol.} = 100 \text{ ml}$, $t = 25^\circ\text{C}$

Source: Authors' own elaboration

As can be seen from the graphs 7 and 8, the adsorption capacity of walnut shell material in relation to metal ions is characterized by the following sequence: $\text{Pb} > \text{Cd} > \text{Cu} > \text{Co}$.

The high adsorption capacity of lead compared to the other ions is likely influenced by several factors, including its relatively high electronegativity and large ionic radius. As shown in Graph 9, lead has the largest ionic radius (1.21 Å) and a relatively high electronegativity (2.33), both of which may contribute to its enhanced adsorption behavior. These characteristics increase the force of attraction between metal ions and the active centers of the sorbents, thus explaining the effectiveness of adsorption capacity of walnut shell carbon material towards these ions in solution (Lezcano et al., 2010; Ananiashvili et al., 2022).



Graph. 9. Bubble plot of adsorption capacity of walnut shell carbon material dependence on ionic radius of metal

Source: Authors' own elaboration

During the adsorption process, the removal of one pollutant from solution in a multicomponent system can be affected by the coexistence of other pollutants, as well as by the characteristics of the adsorbent, such as its surface charge, structure, size, porosity, and number of active centers (Guan et al., 2022; Liu et al., 2013; Girish, 2017). In a multi component system, the number of metal ions removed by the adsorbent can increase, decrease, or remain the same in the presence of other metal ions (Uwamariya et al., 2013).

To improve the competitive and simultaneous removal of more than one heavy metal ion in water systems, it is necessary to identify the types of interaction effects between heavy metals. In multicomponent systems, competitive adsorption typically occurs and three main types of effects are possible, including synergism, antagonism, and non-interaction (de Moraes França et al., 2021; Khalfa et al., 2016). The effect of ionic interactions in a sorption system is determined by the ratio of the maximum adsorption capacity of one heavy metal ion (q_{mix}) in a multicomponent system to the maximum adsorption of the same heavy metal in a single-component system (q_0) (Tovar-Gómez et al., 2014; Bayuo et al., 2023).

Mathematically, the interaction coefficient (R_{qe}) is expressed by the following formula:

$$R_{qe} = \frac{q_{mix}}{q_0},$$

where: q_{mix} is the multicomponent adsorption of a pollutant in a binary or multicomponent system, and q_0 is the adsorption of the same pollutant in a single-component system, under the same experimental conditions as a binary or multicomponent system. Under the same experimental conditions, the factor R_{qe} allows for a comparison of the efficiency of a multicomponent adsorbent with that of a single-component system (Tovar-Gómez et al., 2014; Bayuo et al., 2023).

Table 5 shows the types of interactive effects between heavy metal ions in a multicomponent adsorption system

(Touihri et al., 2021; Du et al., 2021; Girish, 2017; Bayuo et al., 2023).

The SEM images presented in Figure 3A and 3B reveal the morphological changes in the walnut shell material (5 μm) before and after the multisorption process involving Pb(II), Cd(II), Co(II), and Cu(II).

The results presented in Table 6 indicate that the ionic interaction effect for lead and copper ions is less than 1, suggesting that the presence of other ions in the multicomponent system significantly hinders the adsorption of individual heavy metal ions. In contrast, for cobalt and cadmium ions ionic interaction effect is greater than or equal to 1, implying that the presence of both cations in the multicomponent system does not influence the adsorption of the individual metal ions.

Table 5. The influence of ionic interactions on the adsorption process

$\frac{q_{mix}}{q_0} > 1$	Adsorptive removal of one heavy metal promotes the coexistence of other heavy metal ions in a multicomponent system, indicating synergism.
$\frac{q_{mix}}{q_0} = 1$	The presence of other cations and anions in the multicomponent system does not affect the individual deactivation of different heavy metal ions, indicating the absence of interactions.
$\frac{q_{mix}}{q_0} < 1$	The coexistence of other ions significantly inhibited the adsorptive removal of individual heavy metal ions from the multicomponent system, indicating antagonism.

Please note that the data presented in Table 5 are based on previously published literature. Therefore, the relevant literature reference should be:
Source: Authors' own elaboration

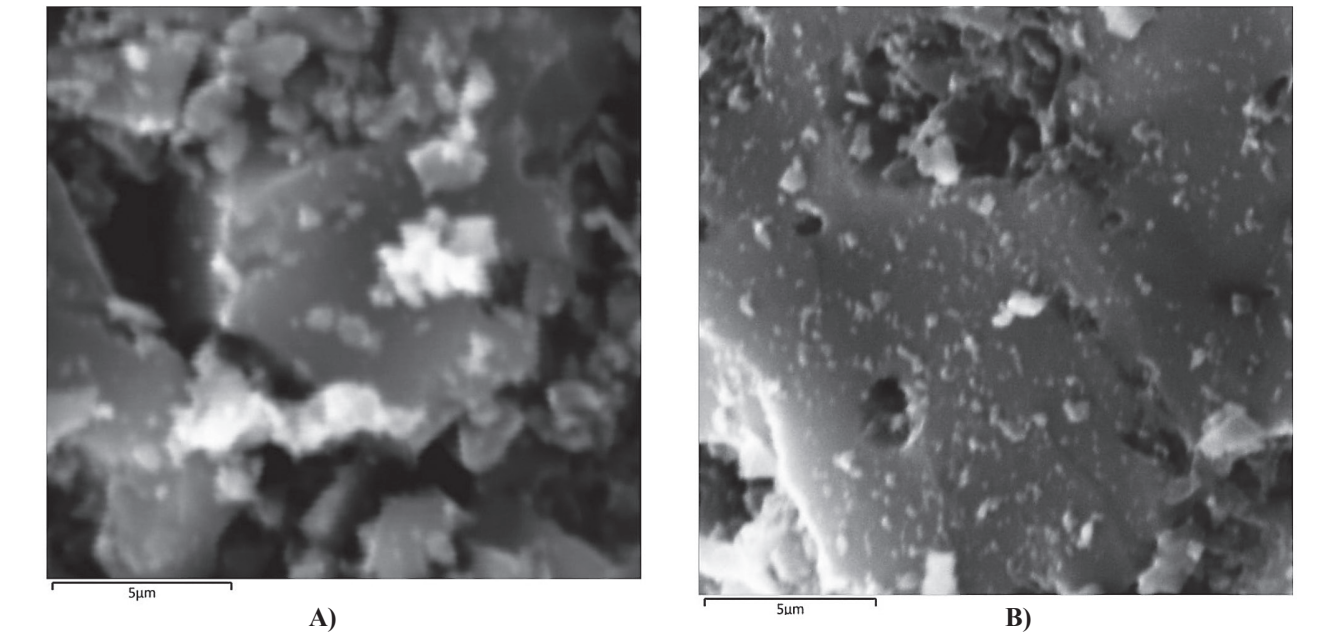


Fig. 3. (A) and (B) SEM images of walnut shell material (5 μm) before and after the multi-sorption process (Pb (II), Cd (II), Co (II), Cu (II))
Source: Authors' own elaboration

Table 6. Adsorption of heavy metals for single and multicomponent systems and the effect of ionic interactions for Pb²⁺, Co²⁺, Cd²⁺, Cu²⁺

Metal ion	Adsorption, mg/g in single-component system	Adsorption, mg/g in multi-component system	R _{qe} , Ionic interaction effect
Pb ⁺⁺	83	35	0.4
Co ⁺⁺	6	11.5	1.9
Cd ⁺⁺	21	21.7	1
Cu ⁺⁺	32	15	0.4

Source: Authors' own elaboration

Conclusions

Walnut shell carbon material obtained through new technology is an innovative and eco-friendly solution for removing heavy metals from aqueous solutions.

Research on walnut shell carbon material from solutions of various metal concentration has shown efficient adsorption of all four ions (Pb²⁺; Cd²⁺; Co²⁺; Cu²⁺). The removal efficiency amounts to 46 – 100%.

The walnut shell-derived carbon material demonstrated effective adsorption performance toward different heavy metal ions. The Langmuir model showed a strong correlation with the experimental data, indicating high adsorption capacities for the investigated metal ions. The Freundlich model confirmed the heterogeneous nature of the adsorbent surface and revealed ion-dependent adsorption behaviour. The variations in adsorption performance among metal ions were attributed to differences in their physicochemical properties and interactions with surface active sites. Overall, walnut shell-derived carbon material exhibited selective adsorption potential for heavy metal removal from aqueous systems.

The adsorption capacity of walnut shell material for metal ions is characterized by the following sequence: Pb > Cd > Cu > Co. The higher adsorption capacity of lead compared to other ions may be attributed to differences in their physicochemical properties, including ionic radius and electronegativity.

The ionic interaction effect for lead, cadmium, and copper ions is less than 1, indicating that the presence of other ions in the multicomponent system significantly inhibits the adsorption of the individual heavy metal ions. In contrast, for cobalt ions, the ionic interaction effect is equal to 1, indicating that the presence of cations and anions in the multicomponent system does not interfere with the adsorption of the individual metal ions.

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Conflict of interest

The authors declare that there is no conflict of interests regarding the publication of this article.

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