

Cypress fruit: A sustainable source of activated carbon for removal of Zn^{2+} , Cu^{2+} , and Ni^{2+}

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Abstract

In this study, Cypress fruit-based-activated carbon (ACCF) was employed to investigate the removal of Zn^{2+} , Cu^{2+} , and Ni^{2+} from aqueous solutions. The efficacy of adsorbent removal was studied concerning adsorption characteristics such as pH, dose of adsorbent, temperature, initial ion concentration, and contact time. The adsorption of metal ions on the ACCF surface was verified through Fourier transform infrared, scanning electron microscopy, and energy-dispersive X-ray spectroscopy analysis. Results revealed the best adsorption efficiencies for the investigated metal ions were attained in acidic to neutral medium for Zn^{2+} and Ni^{2+} , and neutral for Cu^{2+} , with an adsorbent dose of 0.04 for Zn^{2+} and Cu^{2+} , and 0.08 for Ni^{2+} . The most effective initial concentration for each of the three metal ions was 30 mg/L. Equilibrium was reached in 40 min for Zn^{2+} and in 100 min for both Cu^{2+} and Ni^{2+} . When removing the ions simultaneously, equilibrium was achieved in 40 min. Kinetic studies revealed a pseudo-second-order adsorption mechanism for all investigated heavy metal ions. The equilibrium data were best described by the Freundlich isotherm model. The maximum adsorption capacities were: Zn^{2+} (239.23 mg.g^{-1}), Cu^{2+} (134.95 mg.g^{-1}), and Ni^{2+} (45.93 mg.g^{-1}). Thermodynamic analysis suggests these adsorption processes to be endothermic and

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spontaneous. Cypress fruit-based activated carbon demonstrated high efficiency in removing Zn, Cu, and Ni metal ions from aqueous solutions.

Keywords

Activated carbon, adsorption, cypress fruit, metal ions, kinetics, thermodynamic, and isotherms

Introduction

Water quality is crucial for life and resources. Heavy metals pollute water, are toxic, bioaccumulate, and degrade slowly.¹ Heavy metals can bind to cellular proteins, leading to harmful effects. This affects the survival, growth, and reproduction of aquatic life. Chronic exposure to sublethal contamination can be ecologically devastating. Heavy metals enter the water through industrial discharge, urban runoff, and agricultural drainage.² Human activities such as mining, releasing industrial waste and sewage, and using agricultural and household products that contain heavy metals have increased environmental levels of these pollutants.³ This study concerns the removal of zinc, copper, and nickel ions from water. These heavy metals are at moderate to low pollution levels and can have toxic effects on the aquatic environment. For zinc (Zn), the threshold hardness theory suggests that its toxicity is due to interference with calcium uptake and/or toxicity resulting from Zn's high affinity for soft ligands such as sulfide, especially at low water hardness. However, at moderate water hardness, the inhibition of Ca uptake is protected by competitive water effects and the formation of less toxic carbonate complexes. The toxic response to Zn exposure is typical of an essential metal, where disruption of homeostasis occurs before mortality.⁴ Copper metal is unique compared to other metals because its toxicity can be critical in soft water because of the high bioavailability of the free ion. However, the activity of the copper-free ion decreases as water hardness increases because of the competition from other cations, which leads to reduced toxicity.⁵ Nickel is considered toxic to aquatic organisms encompasses algae, crustaceans, and fish.⁶ Several studies have proved that nickel can obstruct the growth and photosynthesis of aquatic plants, as well as disrupt the reproduction and development of aquatic invertebrates.⁷ Moreover, the biomagnification of nickel elements through the food chain can influence human health by consuming contaminated seafood, as it can accumulate in the tissues of aquatic organisms.⁸ Different treatment methods and technologies have been employed to remove hazardous elements from water. These methods and technologies consist of flotation, electrochemical methods, coagulation, filtration, precipitation, adsorption, ion exchanges, reverse osmosis, and membrane technologies.⁹ One of the most widely recognized and effective methods for the removal of heavy metals from water is adsorption. This process is generally easy to design and operate, and they are proficient in removing a diverse array of contaminants from polluted water, including heavy metals, even at low concentrations.¹⁰ The availability and affordability of adsorbents, such as activated carbon, make adsorption a feasible solution for water treatment. Furthermore, the reversibility of adsorption enables the

potential recovery and reuse of the adsorbent, rendering it a more environmentally sustainable approach than other techniques used for similar purposes.¹¹ Numerous researchers provided great efforts to produce more effective, cheaper, and environmentally friendly activated carbons. Therefore, various precursors, such as agricultural and agroindustrial by-product materials, have been utilized as precursor materials for activated carbon production by using various physical and chemical activation processes.¹² In this study, the cypress fruit-derived activated carbon (ACCF) was selected as an adsorbent for removing Zn, Cu, and Ni ions from water due to its abundance, renewability, and minimal competing uses, making it a cost-effective and environmentally sustainable material. Cypress fruit contains natural precursors for carbonization, enabling the development of porous structures and functional groups ideal for adsorption (Gan, 2021).¹³

The research emphasizes optimizing adsorption parameters to maximize the removal efficiency of heavy metals both individually and simultaneously, offering a cost-effective and sustainable solution to mitigate water contamination.

Materials and methods

Chemicals

All chemicals used in this study; Zinc (II) nitrate, $\text{Zn}(\text{NO}_3)_2$ (99.5%), copper (II) nitrate dihydrate, $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (95%), nickel (II) nitrate, $\text{Ni}(\text{NO}_3)_2$ (98%), Sodium hydroxide, NaOH, (97%), and hydrochloric acid (HCl) were purchased from Sigma Aldrich. All solutions were prepared using double-distilled water.

Preparation of solutions

A 500 ppm stock solutions of $\text{Zn}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, and $\text{Ni}(\text{NO}_3)_2$. Each solution was separately prepared in a 500 mL volumetric flask using double-distilled water to confirm purity. Afterward, these stock solutions were diluted further with doubled distilled water to attain the desired final concentrations for each metal ion according to the conducted experiments. For the simultaneous experiments, a mixture encompassing all three metal ions was prepared by combining calculated aliquots of the diluted stock solution. The pH of solutions was adjusted using solutions of 0.1 M NaOH and HCl to attain the desired experimental conditions.

Adsorbent preparation and characterization

The cypress fruit was obtained from the Isra University campus in Jordan. Afterward, the cypress fruits underwent washing and were then dried at a temperature of 100 °C for 48 h. They were subsequently ground, impregnated with 98% phosphoric acid, heated to a temperature of 450 °C, and finally washed with 1.0 M NaOH solution to attain neutralization.¹⁴ The Prepared cypress fruit-based activated carbon (ACCF) underwent a process that encompassed crushing and sieving, resulting in a particle size of 180 µm

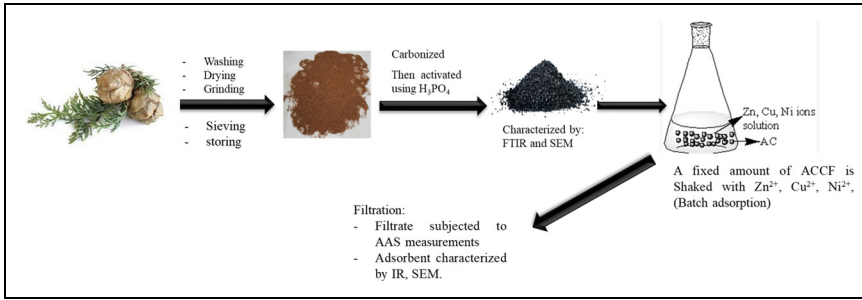


Figure 1. Preparation of ACCF and batch adsorption.

(Figure 1). Fourier transform infrared (FTIR, TENSOR 27 model from BRUKER) was used to assign the functional groups at the ACCF surface. The scanning electron microscope (SEM; Apreo 2 S LoVac, USA) was used to confirm the adsorption process.

Adsorption batch experiment

Solutions of each metal ion with different concentrations were shaken with a stated mass of ACCF for a set time. The study inspected adsorption parameters such as ACCF dosage (20–10 mg), initial metal ion concentration (20–120 mg L⁻¹), pH, shaking time (3–11), and temperature (298, 308, and 318 K). Further experiments were performed using a solution of the three metal ions to investigate the simultaneous adsorption process. The concentrations of the metal ions were determined using an atomic absorption spectrometer (ContraAA 800 from Analytik Jenna, Germany). The amount of adsorbed metal ions (q_e in mg g⁻¹) was calculated based on Equation 1 in which C_i and C_{eq} (mg L⁻¹) are the initial and equilibrium concentrations, respectively:

$$q_e = \frac{(C_i - C_{eq})V}{w} \quad (1)$$

where v and w are the volume (L) and weight of ACCF adsorbent (g), respectively. The percentage of removal was also calculated based on Equation (2):

$$\% \text{ Removal} = \frac{(C_i - C_{eq})}{C_{eq}} \times 100 \quad (2)$$

Regeneration of ACCF adsorbent

A chemical regeneration was employed. The adsorbent of ACCF was washed with 0.1 M HCl solution to remove residual adsorbates, followed by drying at 60 °C for 6 h. The regeneration efficiency was assessed by comparing the adsorption capacity of regenerated ACCF with fresh ACCF over 5 cycles.

Results and discussion

Characterization of adsorbent

Fourier transform infrared. The FTIR spectroscopy results (Table 1) offered valuable insights into the functional groups present in the ACCF adsorbent and their role in the adsorption of metal ions. The presence of a variety of functional groups on the ACCF surface is verified by the distinct peaks observed in the spectra. It is essential to comprehend these functional groups to elucidate the adsorption properties of ACCF and its potential applications in the removal of metal ions. It is important to note that the ACCF surface has a successful interaction with Zn^{2+} , Cu^{2+} , and Ni^{2+} ions, as evidenced by the observed variations in absorbance and intensity during metal ion adsorption. The emergence of new peaks in the $400\text{--}600\text{ cm}^{-1}$ region is particularly noteworthy. This spectral range frequently corresponds to metal–oxygen bond vibrations, which implies the formation of coordination bonds between the oxygen atoms present on the ACCF surface and the adsorbed metal ions (Zn^{2+} , Cu^{2+} , and Ni^{2+}). The effective adsorption of the metal ions onto the ACCF material is strongly supported by these findings. The FTIR spectra are depicted in Figure 2 both before and after adsorption.

Scanning electron microscope and energy-dispersive X-ray spectroscopy. SEM analysis (Figure 3) provides compelling evidence for the successful adsorption of Zn^{2+} , Cu^{2+} , and Ni^{2+} and a mixture of these metal ions onto the ACCF adsorbent. Figure 3(a) illustrates the unaltered ACCF, showcasing a highly porous architecture with multiple pores dispersed over its surface, which is optimal for effective pollutant capture. Figure 3(b) to (e) present the SEM image of the ACCF surface after metal ion adsorption. These images reveal a significant reduction in pore visibility, strongly suggesting the successful occupation and covering of surface pores by the adsorbed Zn^{2+} , Cu^{2+} , Ni^{2+} , and the mixed metal ion species. This visual confirmation reinforces the adsorption process.

Energy-dispersive X-ray spectroscopy (EDS) analysis (Figure 4) identified various elements in the synthesized ACCF adsorbent, including carbon, oxygen, phosphorus, sodium, and potassium. EDS confirmed the presence of adsorbed metal ions. As shown in Table 2, the weight percentages of Zn^{2+} , Cu^{2+} , and Ni^{2+} on the ACCF framework

Table 1. Fourier transform infrared (FTIR) results of ACCF, ACCF-zn, ACCF-cu, and ACCF-Ni, ACCF-mix.

	Absorbance (cm^{-1})				
	ACCF	ACCF-Zn	ACCF-Cu	ACCF-Ni	ACCF-Mix
Hydroxyl (O–H) stretching	3696	3367	3369	3365	3377
Aliphatic (CH, CH_2)	2781	2679	2687	2682	2951
Carbonyl (C=O) stretching	1723	1756	1754	1727	1756
Aromatic (C=C)	1545	1588,1452	1598,1456	1593,1458	1597, 1474
Aromatic (C=C–C)	2357	2314	2287	2334	2354
Metal ion – O stretching	-	494,476	447, 481	477, 501	449, 511,546

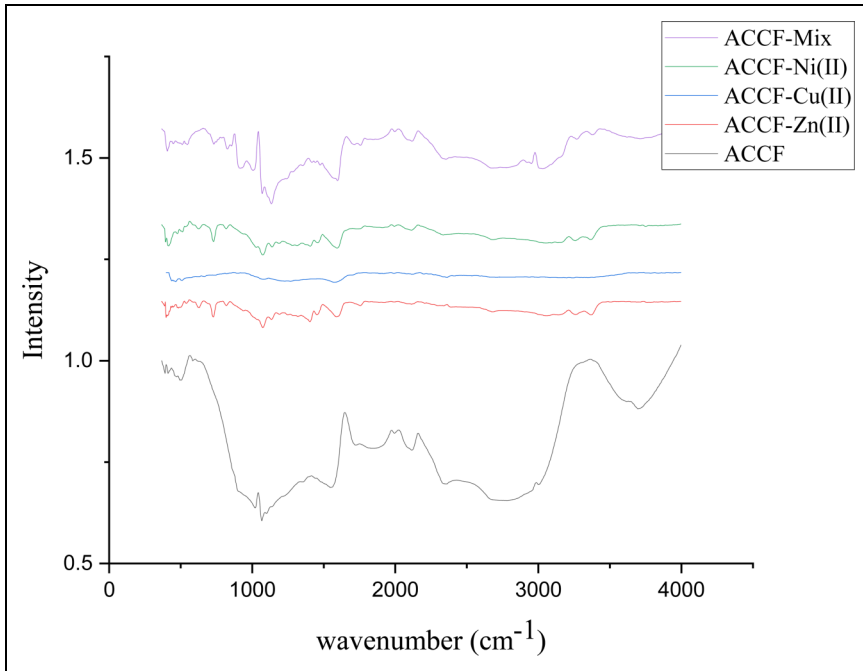


Figure 2. Fourier transform infrared (FTIR) spectra for the adsorbent (ACCF) before and after adsorption.

were 9.16%, 5.15%, and 12.72%, respectively, indicating their successful attachment to the adsorbent's active sites. Interestingly, for the mixed metal ion sample, EDS analysis at a specific surface point revealed a higher affinity of ACCF towards copper (13.33%) compared to zinc (5.10%) and nickel (4.49%).

Batch adsorption

Influence of adsorbent amount. This study inspected the influence of ACCF dosage on the adsorption of Zn^{2+} , Cu^{2+} , and Ni^{2+} . The experiments employed varying ACCF amounts (20–100 mg) at a constant temperature (298 ± 1 K). As illustrated in Figure 5(a), the best dosage for each metal ion was identified: 40 mg for both Zn^{2+} and Cu^{2+} and 80 mg for Ni^{2+} . Importantly, the mixed metal ion simultaneous removal (Figure 5(b)) achieved a maximum of 60 mg of ACCF. This optimal dosage maximizes the availability of easily accessible active sites for adsorption, leading to a significant increase in metal ion uptake. However, as the system approaches equilibrium, adsorption capacity diminishes.

Influence of ions initial concentration. This study explored the influence of initial metal ion concentration (30–120 mg/L) on their adsorption onto ACCF at a constant temperature

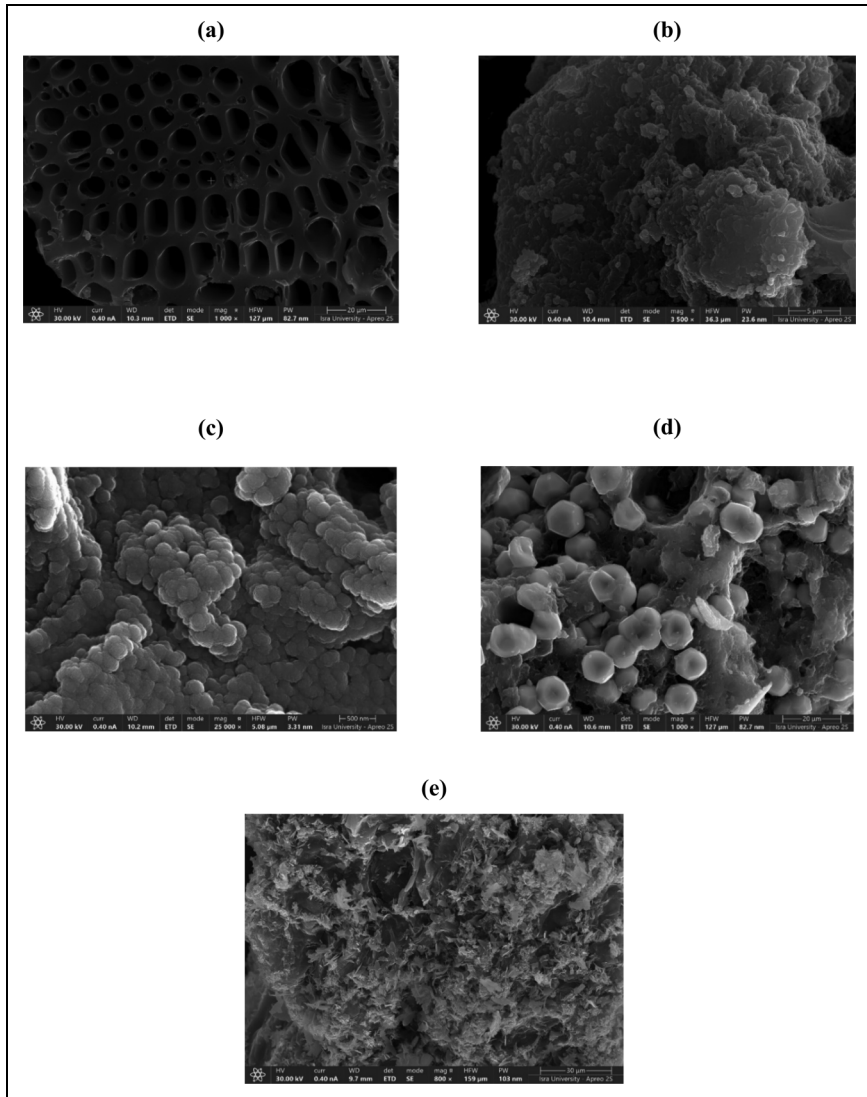


Figure 3. Scanning electron microscopy (SEM) analysis of (a) ACCF, (b) ACCF- Zn^{2+} , (c) ACCF- Cu^{2+} , (d) ACCF- Ni^{2+} , (e) ACCF-mix.

(298 ± 1 K). Figure 6 reveals a clear correlation between initial concentration and adsorption for each metal ion and the mixture. Notably, exceptional uptake percentages of 81.36% (Zn^{2+}), 88.03% (Cu^{2+}), and 94.98% (Ni^{2+}) were achieved using optimized ACCF dosages (40 mg for Zn^{2+} and Cu^{2+} , and 80 mg for Ni^{2+}). The best initial concentration for all scenarios (single ions in Figure 6(a) and the mixture in Figure 6(b)) was

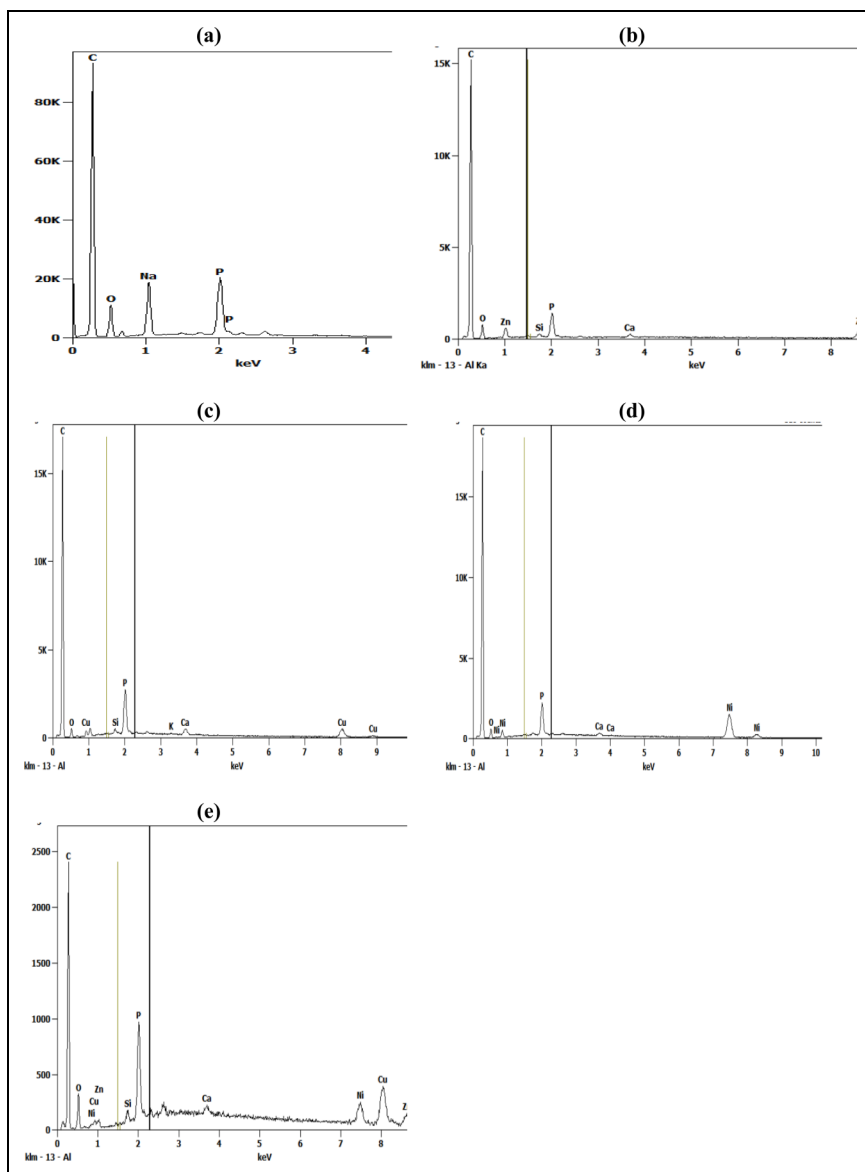


Figure 4. Energy-dispersive X-ray spectroscopy (EDS) analysis of (a) ACCF, (b) ACCF-Zn²⁺, (c) ACCF-Cu²⁺, (d) ACCF-Ni²⁺, and (e) ACCF-mix.

determined to be 30 mg/L. At this concentration, a sufficient number of active sites on the ACCF surface were readily available, leading to a significant increase in metal ion uptake. However, as the concentration increased, these sites became saturated, resulting in a decline in adsorption efficiency as the system approached equilibriums.

Table 2. Energy-dispersive X-ray spectroscopy (EDS) analysis of ACCF before and after adsorption.

Element	Sample									
	ACCF		ACCF-Zn ²⁺		ACCF-Cu ²⁺		ACCF-Ni ²⁺		ACCF-Mix	
	%w	% atom	%w	% atom	%w	% atom	%w	% atom	%w	% atom
C	67.99	76.36	76.18	86.92	81.64	80.85	67.15	78.97	56.55	76.97
O	21.14	17.83	11.36	9.73	5.61	4.69	6.95	6.08	12.95	13.23
Ca	7.17	4.21	0.46	0.16	1.04	0.35	0.41	0.14	0.70	0.28
P	3.69	1.61	2.53	1.12	4.79	2.07	3.32	1.50	5.80	3.06
Zn	0.0	0.0	9.16	1.92	0.0	0.0	0.0	0.0	5.10	1.28
Cu	0.0	0.0	0.0	0.0	5.15	1.08	0.0	0.0	13.33	3.43
Ni	0.0	0.0	0.0	0.0	0.0	0.0	12.72	3.03	4.94	1.38

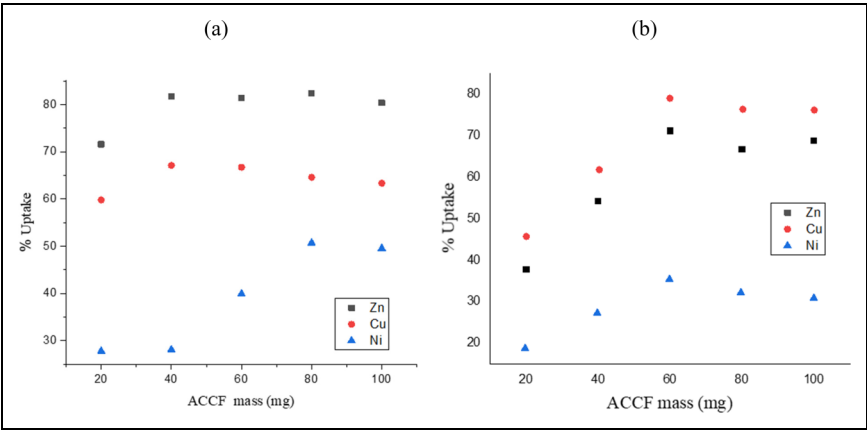


Figure 5. Influence of ACCF mass on the adsorption of (a) Zn²⁺, Cu²⁺, & Ni²⁺ and (b) ion mixture.

Influence of adsorption contact time. To determine the perfect contact time required for maximum adsorption onto ACCF, triplicate batch adsorption experiments were conducted for each metal ion. The experiments involved shaking 40 mg ACCF with separate solutions of 30 mg L⁻¹ Zn²⁺ and Cu²⁺ and 80 mg ACCF with 30 mg L⁻¹ Ni²⁺ at a constant temperature (298 ± 1 K) for varying durations (30–120 min). As illustrated in Figure 7(a), the optimal contact time for Zn²⁺ was 60 min, while both Cu²⁺ and Ni²⁺ achieved maximum uptake after 100 min. Furthermore, an experiment investigating the simultaneous adsorption of all three metal ions was conducted by shaking 40 mg of ACCF with a 30 mg L⁻¹ mixture. Figure 7(b) reveals that only 40 min were necessary to reach equilibrium in this scenario.

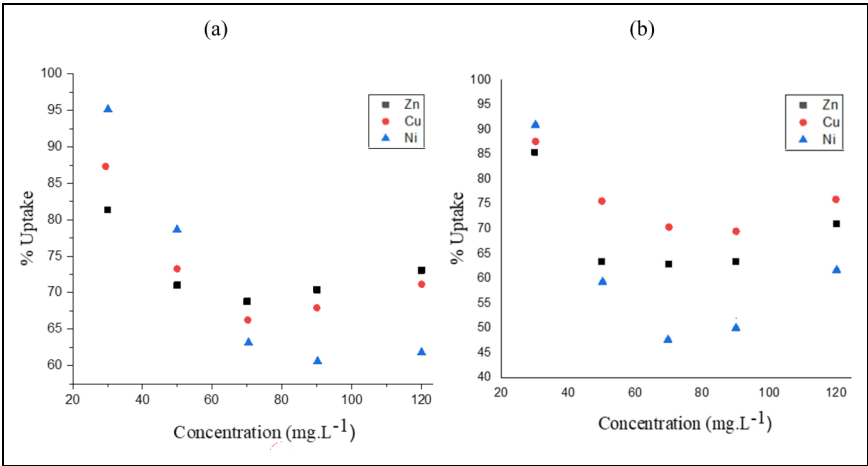


Figure 6. Influence of the initial concentration on the adsorption for (a) individual ion and (b) mixture ions.

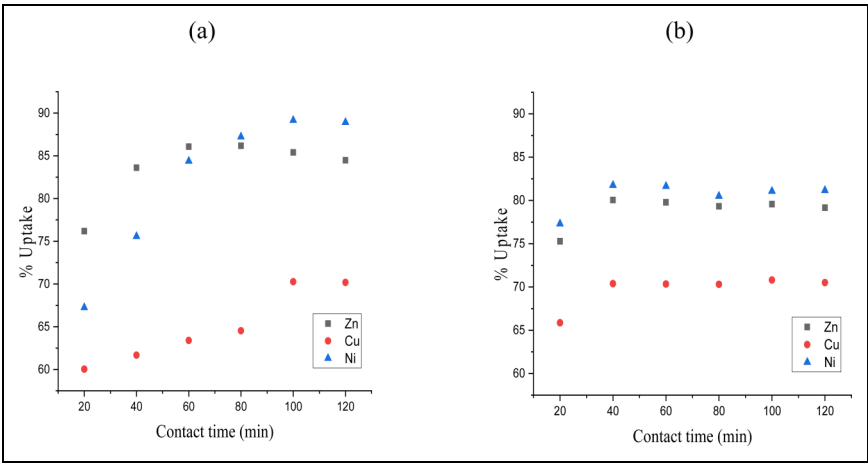


Figure 7. Influence of adsorption contact time for (a) individual metal ion and (b) simultaneous uptake of metal ions.

Influence of PH. The pH_{pzc} of the ACCF surface was reported as 7.0 by.¹⁵ This study investigated the influence of solution pH (3–11) on the adsorption of Zn²⁺, Cu²⁺, Ni²⁺, and a mixture of all three onto ACCF. Batch adsorption experiments were conducted at a constant temperature (298 ± 1 K) using optimized conditions. A 50 mL of metal ion solution was shaken with a predetermined amount of ACCF as follows: 30.0 mg L⁻¹ of Zn²⁺ solution with 40 mg ACCF for 60 min, 30.0 mg L⁻¹ of Cu²⁺ solution with 40 mg ACCF for 100 min, 30.0 mg L⁻¹ of Ni²⁺ solution with 80 mg ACCF for 100 min, and 30.0 mg L⁻¹ of the three metal ions with 60 mg ACCF for 40 min. Figure 8(a) reveals a distinct trend for

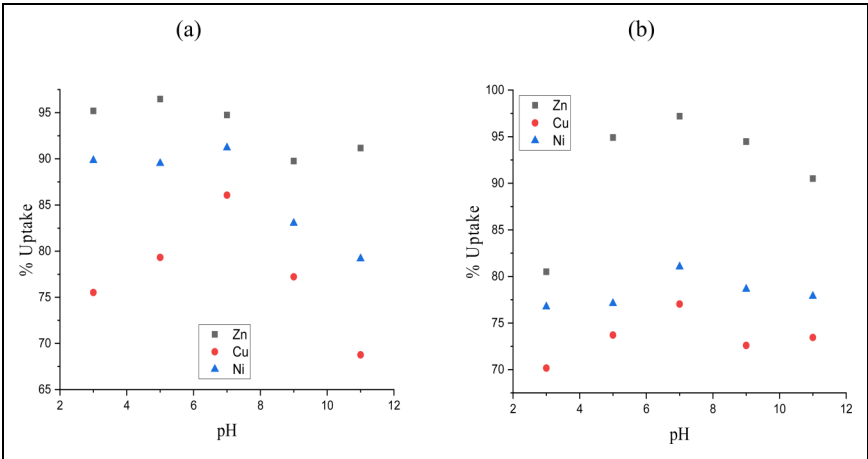


Figure 8. Impact of pH on the uptake of (a) individual metal ions and (b) mixture by ACCF.

Table 3. Kinetics models equations.

Kinetic model	Linear	Non-linear	Parameters
PFO	$\log (q_e - q_t) = \log (q_e) - \left(\frac{k_1}{2.303}\right) t$	$q_t = q_e(1 - e^{-k_1 t})$	q_e : the amount of metal ion (mg g^{-1}) at equilibrium. q_t : the amount of metal ion (mg g^{-1}). k_1 : the rate constant in min^{-1} .
PSO	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} - \frac{1}{q_e} t$	$q_t = \frac{q_e^2 k_2 t}{q_e k_2 t + 1}$	k_2 : the rate constant in $\text{g mg}^{-1} \cdot \text{min}^{-1}$.
IPD	$q_t = K_{id} t^{\frac{1}{2}} + C$	$q_t = K_{id} t^{\frac{1}{2}}$	K_{id} : the rate constant ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-0.5}$). $t^{\frac{1}{2}}$: the square root of time ($\text{min}^{0.5}$).

PFO: pseudo-first order; PSO: pseudo-second order; IPD: intra-particle diffusion.

single metal ion adsorption. Notably, Zn^{2+} displayed superior uptake in an acidic medium, with the optimal pH being 7. Conversely, both Cu^{2+} and Ni^{2+} achieved optimal adsorption in neutral pH conditions. Interestingly, the mixed metal ion experiment (Figure 8(b)) also showed neutral pH to be the most favorable for the simultaneous removal of all three ions.

Kinetics and mechanism

To understand the mechanisms controlling the adsorption of Zn^{2+} , Cu^{2+} , and Ni^{2+} onto ACCF, this study employed both linear and non-linear kinetic models. Pseudo-first-order (PFO), pseudo-second-order (PSO), and intra-particle diffusion (IPD) models were used

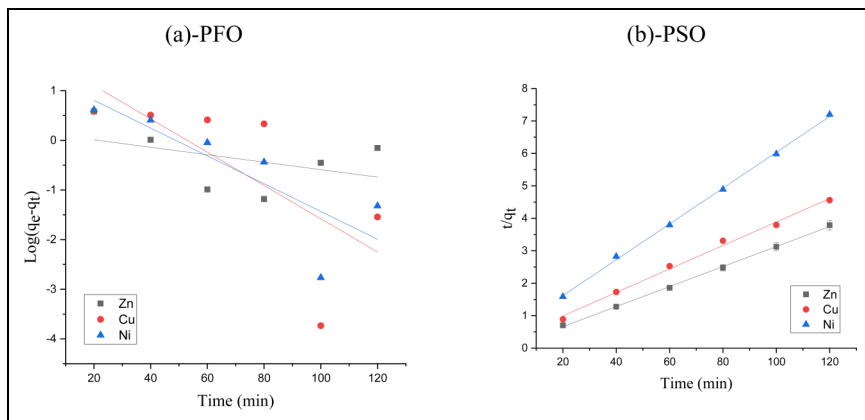


Figure 9. Linear kinetics studies of the adsorption of the metal ions on ACCF (a) PFO and (b) PSO. PFO: pseudo-first order; PSO: pseudo-second order.

to analyze the adsorption process. PFO and PSO denote the quantity of functional groups necessary for the biosorption of metal ions, whereas IPD offers insights into the role of elementary diffusion processes in the biosorption process.¹⁶ The relevant equations, presented in Table 3, quantified the adsorption behavior of these heavy metal ions on ACCF.

Figures 9 and 10 provide compelling evidence that the PSO kinetic model best describes the adsorption behavior of Zn^{2+} , Cu^{2+} , and Ni^{2+} onto ACCF for both the individual and the simultaneous removing. This finding is further supported by the strong agreement between the non-linear and linear model results, as detailed in Table 4.

The contribution of IPD to the adsorption mechanism of heavy metal ions onto ACCF was evaluated using the equations presented in Table 3.

The IPD model suggests that the rate-limiting step depends on the value of the intercept (C) obtained from the model fitting (refer to Table 3 for the equations). When C is zero, IPD is the sole factor controlling the adsorption rate. However, a non-zero C indicates that surface adsorption also plays a role alongside IPD in determining the overall rate. Based on Figure 11, surface adsorption appears to be the rate-limiting step for Zn^{2+} and Ni^{2+} adsorption, meaning it governs the overall speed of the process. In contrast, for Cu^{2+} adsorption, both surface adsorption and IPD seem to contribute to limiting the rate.

The values of R^2 and constants for all kinetics models were summarized in Table 4.

Adsorption isotherms

To understand the nature and characteristics of the adsorption process for Zn^{2+} , Cu^{2+} , and Ni^{2+} onto ACCF, various adsorption isotherm models were employed. These models, including Langmuir, Freundlich, and Temkin (refer to Table 5 for details), helped assess the interaction between the adsorbent (ACCF) and the adsorbates (metal ions). By

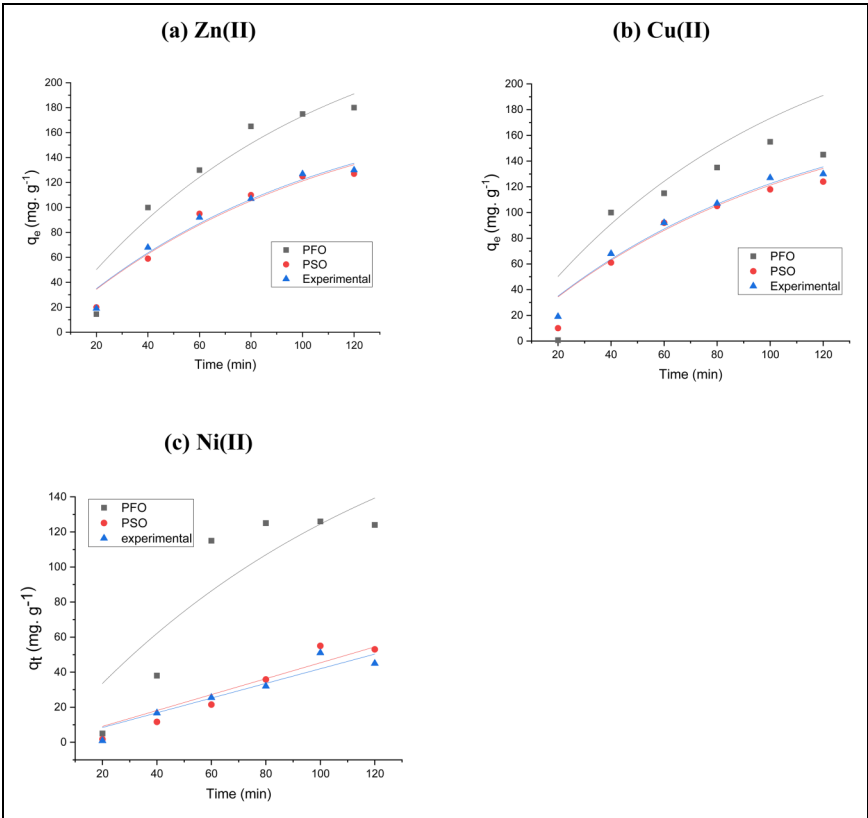


Figure 10. Non-linear kinetics studies of the adsorption of metal ions on ACCF for (a) Zn²⁺, (b) Cu²⁺, and (c) Ni²⁺.

analyzing the fit of these models, insights could be gained into whether the adsorption process is primarily physical or chemical in nature.

The linear forms of the three isotherm models (Langmuir, Freundlich, and Temkin) are presented in Figure 12(a) to (c) for visual analysis. Table 6 summarizes the key parameters obtained from these plots, including correlation coefficients (R^2) and relevant constants. Notably, the Freundlich isotherm exhibited the highest R^2 values for Zn²⁺ (0.9727), Cu²⁺ (0.9522), and Ni²⁺ (0.9884) adsorption onto ACCF. These high R^2 values suggest a good fit for the Freundlich model, indicating a non-uniform ACCF surface with heterogeneous adsorption sites for these metal ions. All adsorption processes are favorable at high metal ion concentrations (chemical interactions occur), as shown by the Freundlich model n parameter values greater than unit (Table 6). Table 6 shows that these data are valid regardless of the metal ion or biosorbent, indicating that all biosorption processes use comparable principles (Ciobanu et al., 2024Click or tap here to enter text.). The values of Temkin constant values, B (38.96, 26.53, & 6.56 for Zn²⁺, Cu²⁺, and

Table 4. Results of kinetics studies for the adsorption of Zn^{2+} , Cu^{2+} , Ni^{2+} , and mixture of metal ions onto ACCF.

Kinetic model	Linear models			
	R^2		Related constants	
	Individual	Mixture	Individual	Mixture
PFO	Zn^{2+}	0.015	$K_1 = 7.50 \times 10^{-3} \text{ (min}^{-1}\text{)}$	$K_1 = 3.00 \times 10^{-3} \text{ (min}^{-1}\text{)}$
	Cu^{2+}	0.5012	$K_1 = 3.85 \times 10^{-2} \text{ (min}^{-1}\text{)}$	$K_1 = 1.37 \times 10^{-2} \text{ (min}^{-1}\text{)}$
	Ni^{2+}	0.0673	$K_1 = 2.80 \times 10^{-2} \text{ (min}^{-1}\text{)}$	$K_1 = 1.05 \times 10^{-2} \text{ (min}^{-1}\text{)}$
PSO	Zn^{2+}	0.9998	$K_2 = 3.09 \times 10^{-2} \text{ (g mg}^{-1} \text{ min}^{-1}\text{)}$	$K_2 = 3.34 \times 10^{-2} \text{ (g mg}^{-1} \text{ min}^{-1}\text{)}$
	Cu^{2+}	0.9999	$K_2 = 3.62 \times 10^{-2} \text{ (g mg}^{-1} \text{ min}^{-1}\text{)}$	$K_2 = 3.74 \times 10^{-2} \text{ (g mg}^{-1} \text{ min}^{-1}\text{)}$
	Ni^{2+}	0.9998	$K_2 = 5.52 \times 10^{-2} \text{ (g mg}^{-1} \text{ min}^{-1}\text{)}$	$K_2 = 6.55 \times 10^{-2} \text{ (g mg}^{-1} \text{ min}^{-1}\text{)}$
IPD	Zn^{2+}	0.8430	$K_{id} = 0.4687 \text{ (mg g}^{-1} \text{ min}^{-0.5}\text{)}$	
	Cu^{2+}	0.4622	$K_{id} = 0.7779 \text{ (mg g}^{-1} \text{ min}^{-0.5}\text{)}$	
	Ni^{2+}	0.8873	$K_{id} = 5.4366 \text{ (mg g}^{-1} \text{ min}^{-0.5}\text{)}$	

PFO: pseudo-first order; PSO: pseudo-second order; IPD: intra-particle diffusion.

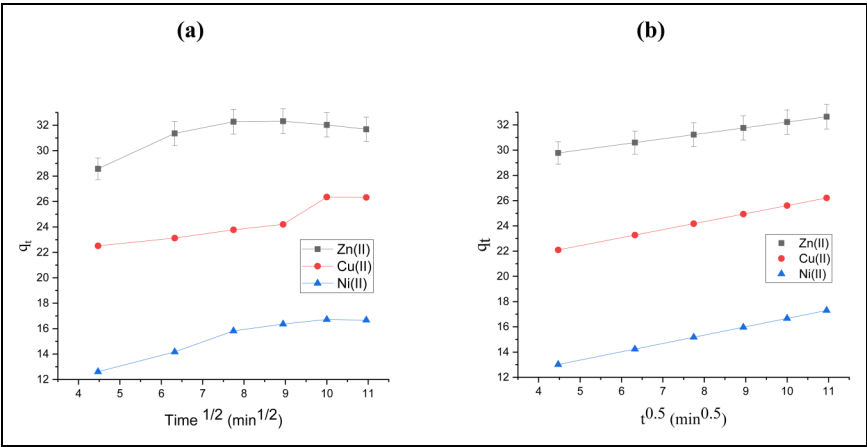


Figure 11. (A) Linear and (b) Nonlinear intra-particle model for the adsorption of the Zn²⁺, Cu²⁺, & Ni²⁺ on ACCF.

Table 5. Linear and non-linear isotherms model equations.

Isothermal model	Linear equation	Parameters
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	q_e : is the equilibrium quantity of the adsorbate (mg g ⁻¹). C_e : is the equilibrium concentration of the adsorbate (mg. L ⁻¹). K_L : the constant of Langmuir isotherm. q_m : is the adsorption capacity (mg. g ⁻¹).
Freundlich	$\log q_e = \log K_f + \frac{1}{n} \log C_e$	K_f : the Freundlich isotherm constant, measured in units of mg g ⁻¹ . n : denotes the adsorption intensity.
Temkin	$q_e = B \ln A + B \ln C_e$	A : the binding constant (g ⁻¹) when the system is at equilibrium. B : the adsorption heat.

Ni²⁺, respectively) indicate a significant interaction between the metal ion and the ACCF adsorbent.¹⁷

Thermodynamics

To further understand the effectiveness of metal ion removal by ACCF, thermodynamic parameters were measured under controlled conditions. Experiments were carried out at three constant temperatures (298 ± 1.0 K, 308 ± 1.0 K, and 318 ± 1.0 K) with continuous agitation (1.0 h). Key thermodynamic parameters (ΔG⁰, ΔH⁰, and ΔS⁰) were calculated to

Table 6. Isotherms model constants.

Isotherm	Related isotherms constants	Metal ion		
		Zn ²⁺	Cu ²⁺	Ni ²⁺
Langmuir	R_L^2	0.3903	0.6246	0.8525
	K_L	0.0193	0.0513	0.1228
	q_m (mg g ⁻¹)	239.23	134.95	45.93
Freundlich	R_F^2	0.9727	0.9522	0.9884
	K_F (mg g ⁻¹)	2.69	3.01	3.33
	N	2.0	2.0	5.0
Temkin	R^2	0.7677	0.6882	0.6909
	B	38.96	26.53	6.56
	A	0.0654	0.446	80.89

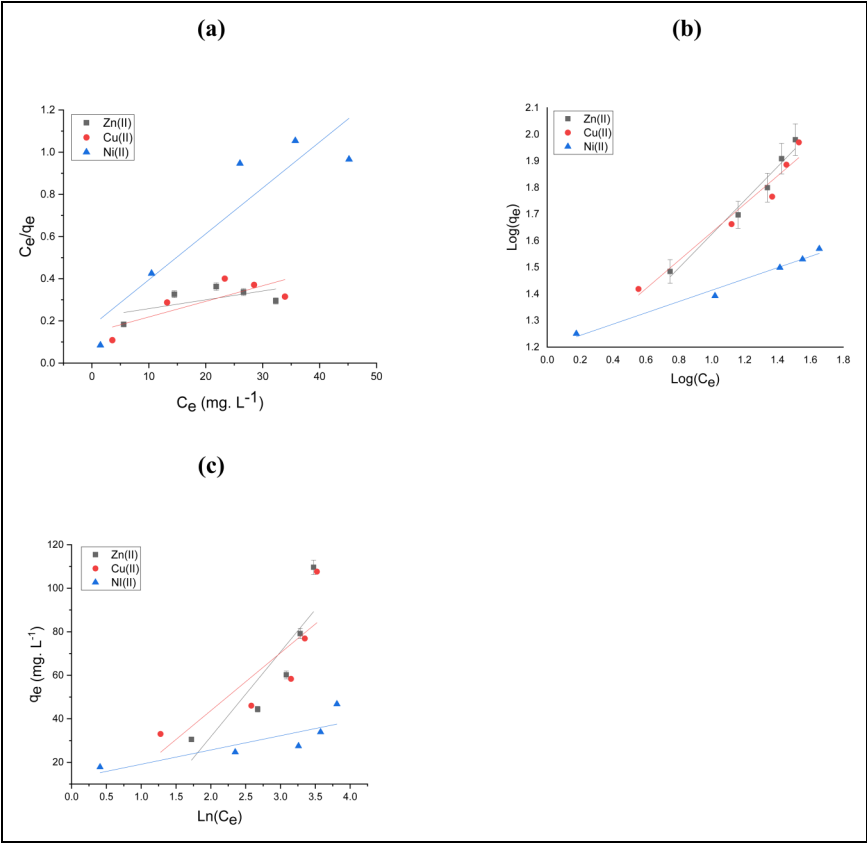


Figure 12. The linear isotherms of (a) Langmuir, (b) Freundlich, and (c) Temkin of Zn²⁺, Cu²⁺, and Ni²⁺ removal by ACCF.

Table 7. Thermodynamic parameters of metal ion removal by ACCF.

Metal ion	T (K)	Thermodynamic parameters					
		ΔG° (KJ mol ⁻¹)		ΔH° (KJ mol ⁻¹)		ΔS° (KJ K ⁻¹ mol ⁻¹)	
		Individual	Simultaneous	Individual	Simultaneous	Individual	Simultaneous
Zn	298	-1.212	-29.90	23.639	12.106	0.075	0.050
	308	-0.459	-3.496				
	318	-0.293	-4.002				
Cu	298	-0.320	-2.572	31.622	18.179	0.107	0.069
	308	-1.391	-3.268				
	318	-2.462	-3.964				
Ni	298	-6.730	2.956	71.817	86.765	0.263	0.281
	308	-9.365	0.1451				
	318	-11.999	-2.666				

Table 8. Comparison of ACCF Uptake capacity with other adsorbents.

Adsorbent	$q_{\max}$ (mg g ⁻¹)
Oak Cupules AC ²¹	89.21 Cu ²⁺ , 67.5 Ni ²⁺
Date stones AC ²²	12.19 Zn ²⁺ , 18.68 Cu ²⁺ , 16.12 Ni ²⁺
Olive stone waste AC ²³	16.95 Zn ²⁺ , 25.38 Cu ²⁺ , 14.65 Ni ²⁺
Macadamia Nutshell Waste AC ²⁴	95.92 Zn ²⁺ , 67.41 Cu ²⁺
Kashmiri Walnut Shell AC ²⁵	36.0 Zn ²⁺ , 50.0 Cu ²⁺
Cypress fruit ACCF (present study)	239.23 Zn ²⁺ , 134.95 Cu ²⁺ , 45.92 Ni ²⁺

reveal the nature of the adsorption process. The results are presented in Table 5. The standard Gibbs free energy change (ΔG°) was calculated using $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$. Vant Hoff equation was used to determine the enthalpy change (ΔH°) and entropy change (ΔS°) from the slope and intercept of a plot of $\ln(K)$ vs. $1/T$:

$$\ln(K) = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{T} \left(\frac{1}{T} \right)$$

K corresponds to the adsorption equilibrium constant according to the best-fitted model, and R is the universal constant of ideal gases, 8.314 J K⁻¹ mol⁻¹. The negative ΔG° value (Table 7) indicates that ACCF adsorbs metal ions spontaneously for both individual and simultaneous removal. The positive ΔH° value (Table 7) indicates the endothermic nature of the ions.¹⁸ Adsorbent affinity and irregularities in the adsorbate/adsorbent interface are implied by the positive value of ΔS° .¹⁹

Regeneration of ACCF adsorbent

After conducting numerous experiments, it was determined that 0.1 M HCl acid is an appropriate candidate for the recovery investigation. The adsorption process was carried

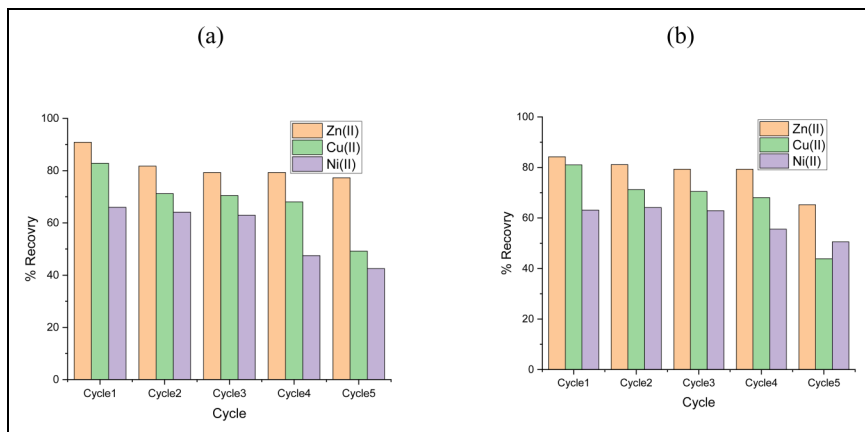


Figure 13. Regeneration of ACCF adsorbent.

out under the effectiveness parameters, after which the adsorbed heavy metal ions were desorbed by shaking the ACCF in a 0.1 M HCl solution. The ACCF was then dried and the adsorption/desorption process was repeated multiple times to evaluate its reusability. Atomic absorption analysis was conducted on metal ions of Zn^{2+} , Cu^{2+} , and Ni^{2+} that were eluted from ACCF. The subsequent equation was employed to determine the percentage of recovery:²⁰

$$\% \text{Recovery} = \frac{C_{\text{de}}}{C_{\text{ad}}} \times 100$$

C_{ad} represents the adsorbed concentration of metal ions and C_{de} represents the desorbed concentration. The adsorption/desorption performance of Zn^{2+} , Cu^{2+} , and Ni^{2+} ions using ACCF was evaluated over five cycles, as shown in Figure 13. The results demonstrate a decreasing trend in recovery efficiency with each successive cycle for all three metal ions. Among the metals, Cu^{2+} consistently exhibited the highest recovery efficiency across all cycles, which suggests a stronger affinity of ACCF for copper ions. Conversely, Ni^{2+} displayed the lowest recovery percentages, indicating comparatively weaker interaction with the adsorbent. Zn^{2+} recovery efficiency remained intermediate but showed a similar decreasing trend with repeated cycles. Figure 13(a) demonstrates that the recovery of metal ions decreased, going from 90.83.29% to 77.25% for Zn^{2+} , from 82.80% to 49.19% for Cu^{2+} , and from 65.98 to 42.50 for Ni^{2+} . This suggests that ACCF can be utilized again and again. For the combination of the three metal ions, similar outcomes were attained (Figure 13(b)).

Comparison with other adsorbents

The maximum uptake of heavy metal ions by ACCF was compared to other activated carbon adsorbent. (Table 8). The comparison shows that ACCF has satisfied adsorption capacity, which is better than other adsorbents.

Conclusion

This study demonstrates the efficacy of cypress fruit-based activated carbon (ACCF) for removing Zn^{2+} , Cu^{2+} , and Ni^{2+} from aqueous solutions using a batch adsorption process. The experiments definitively identified the effectiveness parameters for maximizing the removal efficiency of these metal ions using ACCF. The experimental results indicate that the best conditions for Zn^{2+} , Cu^{2+} , and Ni^{2+} individual removal using ACCF are as follows: 60 min of agitation for Zn^{2+} , 100 min for Cu^{2+} and Ni^{2+} , 0.04 g for Zn^{2+} and Cu^{2+} , and 0.08 for Ni^{2+} . Furthermore, it was found that acidic solutions are more effective in removing Zn^{2+} and Ni^{2+} than neutral solutions. However, for Cu^{2+} , the neutral solution demonstrated superior performance. It was discovered that the following were ideal for the simultaneous removal of Zn^{2+} , Cu^{2+} , and Ni^{2+} : Agitated for 40 min, with 0.06 g of adsorbent. In addition, the adsorption process works better with neutral solutions. ACCF exhibited a stronger attraction for Zn^{2+} ions compared to Cu^{2+} and Ni^{2+} . Kinetic and isothermal analyses revealed a strong fit between the adsorption of Zn^{2+} , Cu^{2+} , and Ni^{2+} by ACCF and both the Freundlich isothermal model and the PSO kinetic model. ACCF removes heavy metal ions from the environment using an endothermic and presumably spontaneous process, according to thermodynamic research. Results revealed 239.23 mg g^{-1} uptake capacity of Zn^{2+} , 134.95 mg g^{-1} for Cu^{2+} , and 45.93 mg g^{-1} for Ni^{2+} . After five regeneration cycles, ACCF may lose effectiveness yet remain functioning. Future studies will investigate surface modifications of ACCF to improve selectivity, alongside exploring strategies for scaling up its utilization.

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Ethical considerations

We confirm that this work is original and has not been published elsewhere nor is it currently under consideration for publication elsewhere.

Author contributions

All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by all authors. The first draft of the manuscript was written by Alaa Mahmoud Al-Ma'abreh and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability statement

The article contains the data that substantiates the results of this investigation.

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