

Development and Application of Valorized Coffee Ground-Based Activated Carbon for Zinc Adsorption in Aqueous Solutions

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Heavy metals are still a problem in aquatic systems; for example, Zinc represents environmental and health risks due to its toxicity, persistence, and bio-accumulative character. This work focuses on a sustainable and cost-effective approach for the elimination of Zinc by activated carbon derived from coffee grounds (ACCG). The ACCG was chemically activated by phosphoric acid, which greatly improved its surface reactivity and porosity. The physicochemical characterization supports this by revealing a high specific surface area ($421 \text{ m}^2/\text{g}$), a pore volume of $0.35 \text{ cm}^3/\text{g}$ and the presence of functional groups ($-\text{COOH}$, $-\text{OH}$) favoring adsorption. The adsorption experiments achieved a maximum efficiency of 99.8% under optimal conditions. Kinetic studies have shown that the adsorption follows a pseudo-second order model, suggesting chemisorption dominance. The analysis of adsorption isotherms showed that the Langmuir model offers the best fit, indicating monomolecular adsorption on a homogeneous surface. Regeneration studies showed that ACCG maintained its effectiveness over three cycles before its performance gradually decreased, as observed in desorption experiments. These results confirm that ACCG is an economical and environmentally friendly adsorbent, making it a promising material for wastewater treatment and the removal of Zinc ions.

Keywords: Coffee grounds; activated carbon; zinc, adsorption; wastewater treatment

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Heavy metals, such as Zinc, are ubiquitous pollutants as a result of industrial, agricultural, and domestic activities that serve as double-edged swords in the environment [1]. Zinc is a crucial trace element present in minute amounts, but in excess in wastewaters renders it an injurious contributor, threatening aquatic environments and human lives [2]. Having originated from industries like mining, metallurgy, and electroplating, Zinc enters the environment in significant quantities with variable solubility and a propensity to bio-accumulate in soils, sediments, and organisms [3]. Its persistence due to chemical stability allows it to last in the environment for decades, amplifying its toxic effect [4].

In aquatic life, Zinc disrupts metabolic and reproductive functions, but in chronic human exposure, neurological and immune diseases have been linked [5,6]. To address this problem, adsorption is a preferred method of decontamination, valued for ease, low cost, and efficiency in trapping contaminants without yielding toxic byproducts [7]. Adsorption was selected over energy-intensive methods like oxidation or membrane filtration due to its simplicity, minimal generation of secondary pollutants, and the sustainability of using bio-sourced activated carbon from coffee grounds (ACCG), which valorizes agricultural waste and reduces environmental impact. As for processes like oxidation or membrane filtration, both being energy-intensive in terms of energy demand and

producing toxic byproducts, adsorption stands out particularly because of the breadth of applicability and lack of environmental impact [8]. Still, conventional adsorbates, derived from fossil-sourced materials, remain costly and non-environmentally friendly, with the incentive of driving research into bio-sourced analogs [9].

Coffee grounds step in as an abundant waste product of world coffee consumption, and as a potential solution [10]. With millions of tons produced annually, this carbon-based waste material-like lignocellulose offers an ideal raw material for the production of activated carbon [11]. The coffee grounds owe their adsorption ability to a unique chemical composition like cellulose, hemicellulose, and lignin, which when subjected to processing yield a porous texture [12]. Their surface, naturally bearing functional groups like phenols and carboxylates, allows interaction with Zinc ions, enhancing their effectiveness [13]. Available almost everywhere, and more often than not, without a cost, this residue presents an affordable solution over synthetic ones without compromising two key environmental problems: organic waste mitigation and controlling water pollution [14]. Literature has already proved that activated carbon produced from coffee grounds can sequester contaminating dyes and other heavy metals, giving us a foreboding for its use against Zinc too [15].

This work details the adsorption of Zinc from contaminated waters with activated carbon, realized through coffee grounds. While bringing the maximum adsorption capacity from the highly porous and reactive bio-sourced material by optimizing its preparation, substantial parameters defining the ability of the adsorbent were pH, initial concentration, and contact time. The outcomes of this research point toward the versatility of ACCG, in addition to giving it an economically affordable and ecological-friendly method to combat heavy metal blocks, using a waste as ammunition for the environmental conservation.

EXPERIMENTAL

Reagents and Materials

Arabica coffee grounds were collected from nearby cafeterias for the synthesis of activated carbon. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98%) was received from Sigma-Aldrich (USA) and served as a source of Zinc ions for adsorption. Chemical activation of the precursor used phosphoric acid (H_3PO_4 , 98%) that was received from Merck (Germany).

The sodium hydroxide (NaOH, 98%) and hydrochloric acid (HCl 37%) for pH adjustment were also bought from Merck. Ultrapure water was utilized for the preparation of all solutions.

Preparation of ACCG

Arabica coffee grounds were washed with distilled water to extract impurities and kept in the oven at 60°C for 24 h. The dried grounds were ground and sieved to obtain a uniform particle size of 100–200 μm . Chemical activation was carried out by soaking coffee grounds in phosphoric acid solution (H_3PO_4) at 1:1 mass ratio. The blend was kept in contact for 24 hours at room temperature for proper impregnation. Oven drying at 105°C for 12 hours was carried out just after impregnation, followed by carbonization in a muffle furnace, subject to 600°C for 2 hours under an inert atmosphere, at a heating rate of 10°C/min. The resulting ACCG was washed several times with distilled water until a neutral pH was achieved. Eventually, air-drying was performed, and the sample was stored pending further analyses. The 1:1 H_3PO_4 ratio was selected based on preliminary tests showing optimal surface area (421 m^2/g) and porosity, while H_3PO_4 was chosen for its ability to enhance pore development and introduce phosphate groups that improve Zinc adsorption.

Characterization of ACCG

The ACCG had its structural, textural, and morphological characteristics assessed by the application of some exquisite characterization methodologies. Working within the wavenumber

range of 600 to 4000 cm^{-1} , an FTIR spectrometer (Bruker Tensor 27, Germany) worked to identify chemical bonds and functional groups present on the surface of the material using a resolution of 4 cm^{-1} , 32 scans, and attenuated total reflectance (ATR) mode. The crystalline phases were identified, and the structural integrity of the ACCG was acknowledged through XRD analysis (PANalytical X'Pert Pro, Netherlands) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), a 2θ range of 10–80°, a step size of 0.02°, and a scan speed of 2°/min. Surface topography and pore development indicated possible adsorption sites on the material, characterized by SEM analysis (Hitachi TM-1000, Japan) at an accelerating voltage of 15 kV, magnifications up to 10,000 \times , and on gold-coated samples. In addition, the BET test (Micromeritics ASAP 2020, USA) performed on the samples would further give detailed accounts of specific surface area, total pore volume, and nitrogen adsorption/desorption pore size distribution done at 77 K, with samples degassed at 200°C for 6 hours under vacuum and a relative pressure range of 0.01–0.99, and the textural properties of the samples.

Adsorption Studies of Zinc on ACCG

Adsorption experiments were conducted to evaluate the removal of Zinc from aqueous solutions using ACCG. A stock solution of 1000 mg/L of $\text{Zn}(\text{NO}_3)_2$ was prepared and diluted to concentrations of 10, 20, 50, 100, and 200 mg/L. For each experiment, 50 mg of ACCG was added to 50 mL (100 mg/L) of Zinc solution followed by mixing at room temperature (~25°C) with an agitation rate of 150 rpm. After stirring, the solution was filtered and then measured by atomic absorption spectroscopy (AAS, PerkinElmer, Analyst 400).

For pH, adsorbent dosage, and kinetic studies, a Zinc concentration of 100 mg/L was used, selected for its optimal removal efficiency. The effects of pH, dosage, contact time, and initial concentration were studied. The optimal pH was determined at 8, but a natural pH (~6) was preferred for subsequent studies to reflect realistic wastewater treatment conditions. Optimized adsorption conditions were pH 8, 50 mg ACCG, and 60 minutes contact time.

Adsorption capacity, q_t (mg/g) and percentage removal were calculated using Equations (1) and (2). Pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models were applied. Isotherm studies were conducted with 50 mg of ACCG in 50 mL of Zinc solutions (10–200 mg/L) at pH ~6, with an agitation time of 60 minutes. The Langmuir and Freundlich models were applied.

$$q_t (\text{mg} / \text{g}) = \frac{c_i - c_f}{W} \times V \quad (1)$$

The percentage removal of Zinc was calculated using Equation (2):

$$\text{Adsorption (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

Where, C_i , C_t , and C_e (mg/L) are the initial, time t , and equilibrium Zinc concentrations, respectively; and V and W are the liquid's volume (L) and the weight of the adsorbent (g), respectively.

Adsorption Kinetics

The adsorption kinetics was studied using the PFO and PSO models to understand the adsorption mechanism [16]. The linear form of the PFO equation by Lagergren is expressed as:

$$\ln(q_e - q_t) = \ln q_e - k_f \times t \quad (3)$$

The linear form of the pseudo-second order rate equation is given as:

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{t}{q_e} \quad (4)$$

Where, q_t (mg/g) is the amount of adsorbate adsorbed at time t , q_e (mg/g) is the adsorption capacity at equilibrium, k_f (min^{-1}) is the rate constant of the PFO model, and t (min) is the time. K_s is the PSO adsorption rate constant ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$).

RESULTS AND DISCUSSION

Characterization of ACCG

FTIR Spectroscopy

The infrared spectrum of the ACCG is shown in Figure 1, which exhibits wide surface chemical

and functional features represented by absorption bands, evidence for which has been documented. Most of the broad peaks in the O-H stretching band at 3400 cm^{-1} are due to OH groups, coming from either absorbed water or the surface of the ACCG. For typical carbonaceous materials, this band shows that the surface is polar, thus making it advantageous to interact with polar molecules. Various typical distinctive bands within the range of the C=O stretching associated with the carbonyl and carboxyl functional groups appear in the spectral range of 1500 to 1700 cm^{-1} , with other prominent ones located at 1521 , 1567 , 1588 , and 1689 cm^{-1} of the spectral range. These functional groups appreciably contribute to controlling the adsorption characteristics of ACCG, wherein interactions might occur with particles of pollutants or desired analytes through hydrogen bonding or electrostatic attraction. In the spectral region of 1000 - 1300 cm^{-1} , C-O vibration modes of ether or ester functional types, which are mostly due to thermal degradation of the organic matter present in coffee grounds, are assigned. In addition, the presence of absorption bands near 1251 and 1100 cm^{-1} attributed to P=O and P-O-C vibration modes confirms the incorporation of phosphate groups upon chemical activation using H_3PO_4 . According to literature [13], raw coffee grounds exhibit significantly fewer surface functional groups, which further supports the enhancement provided by chemical activation. The phosphate species would possibly contribute to a significant alteration of the surface chemistry of the ACCG and thus contributes to a better interaction with different adsorbates. The ill-defined and broad bands highly indicative of amorphous materials confirm the ACCG's disordered nature. Thus, it passes clear evidence that ACCG possesses a complex surface chemistry with high functionalization and is therefore suitable for adsorption applications in water treatment and gas sequestration.

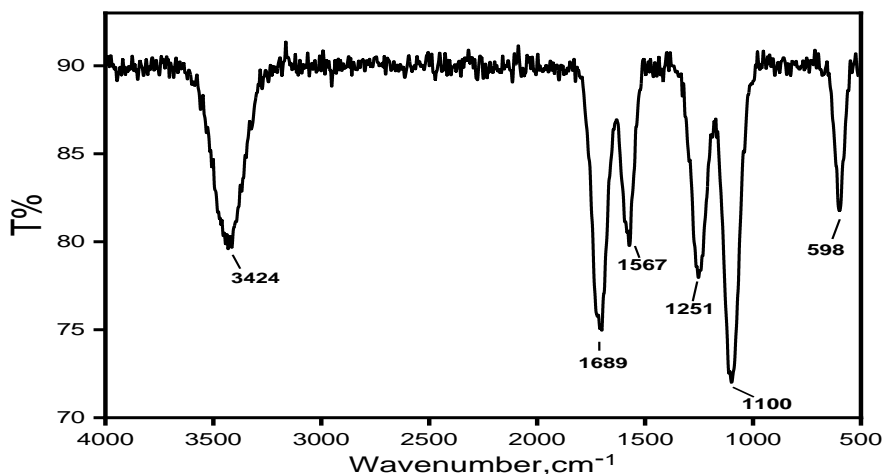


Figure 1. FT-IR spectrum of ACCG.

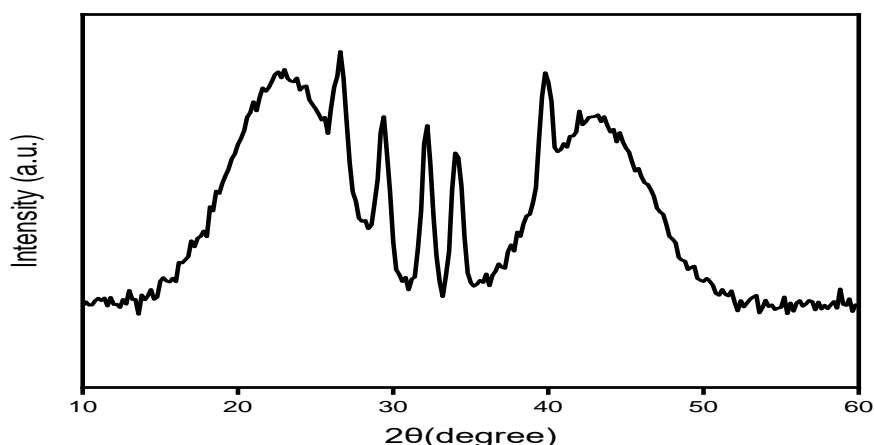


Figure 2. XRD pattern of ACCG.

XRD Analysis

As shown in Figure 2, the XRD pattern of the ACCG indicates the existence of sharp and broad peaks, verifying more or less an amorphous structure with crystalline domains. Two broad diffractions with centers at $2\theta \approx 22\text{--}30^\circ$ and $40\text{--}50^\circ$ are the characteristic features of disordered carbonaceous materials such as turbostratic carbon, in which the graphene sheets are arranged randomly. They are (002) and (100) graphitic carbon reflections of disordered graphitic domains. Some sharper peaks in the 2θ range $\approx 25^\circ$ to 40° are other laws for the presence of crystalline phases introduced by chemical activation with H_3PO_4 . Compared to raw coffee grounds, which typically lack crystalline phosphate phases and show minimal crystallinity [13], H_3PO_4 activation introduces these sharper reflections, confirming phosphate incorporation that enhances adsorption properties. Phosphorus activation creates phosphate structures, changing the texture and crystallinity of the material and influencing its adsorption properties directly. The occurrence of an intrinsic disordered structure, graphitic domains, and phosphate functionalities is accountable for the high surface area and complexity of functionality of the ACCG and thereby increases its potential application as an adsorbent for pollutants and gas storage materials.

BET analysis

The BET analysis provides valuable insights into the porous structure and adsorption capacity of the ACCG. The BET analysis reveals a specific surface area of $421\text{ m}^2/\text{g}$, a pore volume of $0.35\text{ cm}^3/\text{g}$, and an average pore diameter of $\approx 2.25\text{ nm}$, indicating a micro-/mesoporous structure. This high surface area

significantly increases the number of active sites available for interaction with Zinc ions, making the material highly suitable for water purification applications. The nitrogen adsorption–desorption isotherm (Figure 3) exhibits a Type IV shape with an H4 hysteresis loop, confirming the presence of slit-shaped pores typically found in biomass-derived activated carbon [17]. Such pore geometry is particularly efficient in trapping both organic and inorganic contaminants through physisorption and chemisorption mechanisms. Compared to raw coffee grounds, which exhibit negligible porosity [13], the ACCG shows a drastically enhanced porous network. The combination of large surface area, substantial pore volume, and an average pore diameter within the mesoporous range supports an efficient adsorption process. Although the average pore diameter reflects a dominant mesoporous fraction, the pore size distribution obtained from the BJH method (together with SEM observations) also reveals the presence of larger pores ($>50\text{ nm}$), characteristic of macropores. This confirms that the ACCG possesses a hierarchical pore structure combining micropores ($<2\text{ nm}$), mesopores ($2\text{--}50\text{ nm}$), and macropores ($>50\text{ nm}$), which facilitates Zinc ion transport through macropores towards mesopores and micropores, thereby enhancing the overall adsorption performance. Furthermore, the heterogeneous surface and the presence of macropores ($>50\text{ nm}$) are supported by both BET and SEM analyses, confirming a hierarchical pore structure [17] that promotes multi-scale accessibility to Zinc ions during adsorption. The activation process using phosphoric acid is therefore validated not only by the improved textural properties, but also by the favorable isotherm shape and hysteresis behavior observed, highlighting the efficiency of the synthesized ACCG for selective heavy metal removal in aqueous systems.

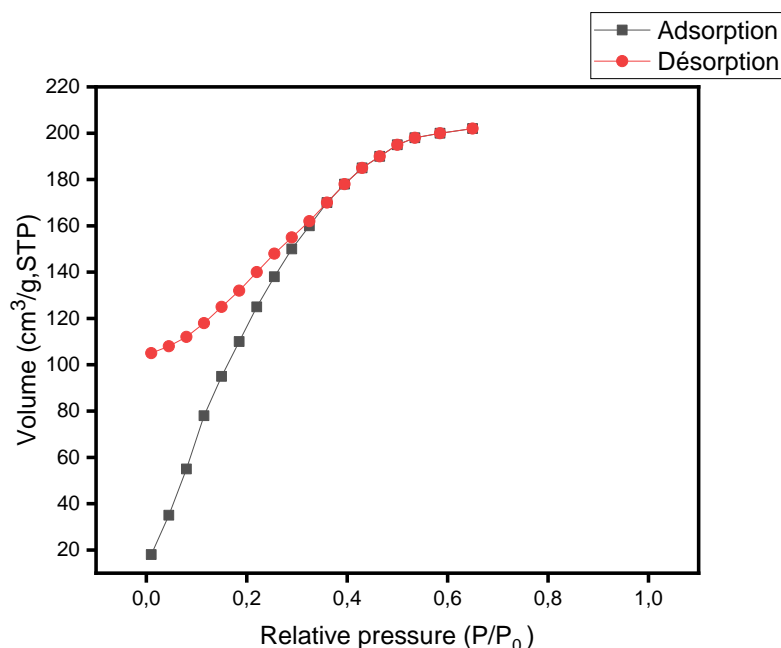


Figure 3. Nitrogen adsorption–desorption isotherm of ACCG.

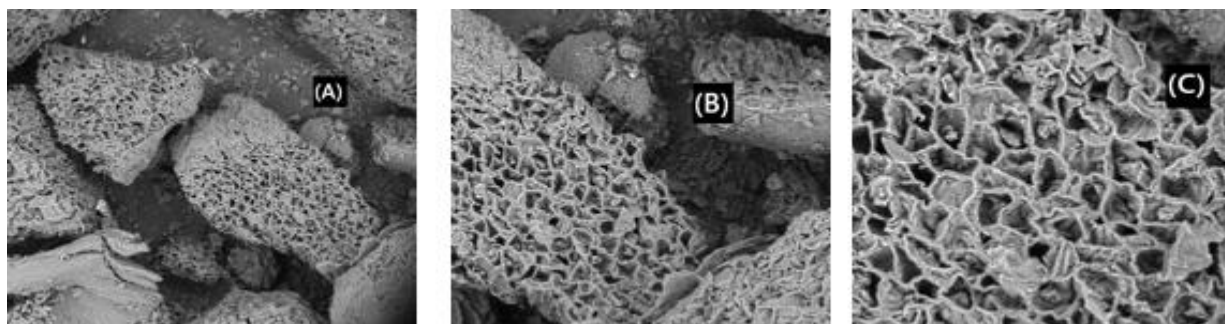


Figure 4. SEM images of ACCG: (A) 150×, (B) 250×, and (C) 500×.

Morphological Structure Characterization using SEM Analysis

SEM micrographs of the ACCG, at various magnification levels (150×, 250× and 500×), as demonstrated in Figure 4, show its porous nature to be quite complex, which is favorable for an adsorbent. The overview image (150×) depicts pore distribution and surface morphology and shows a heterogeneous surface with histological represented cavities. Those with higher magnification (250× and 500×) have a more intricate surface texture, composed of pores of medium to small size. This illustrates that there is an interconnecting network of pore systems; such a precise textural structure with surface roughness is probably highly favorable for molecule adsorption, independent of their size. The coexistence of macropores (>50 nm), mesopores (2–50 nm), and micropores (<2 nm) confirms a hierarchical structure,

and this hierarchical structure, confirmed by BET analysis, facilitates Zinc transport and adsorption [17]. Whereby, impurities are transmitted to the mesopores and micropores through the macropores, where the maximum adsorption occurs.

Adsorption Studies

Effects of pH

The effect of pH on Zinc adsorption was studied over 60 minutes using a Zinc concentration of 100 mg/L, 50 mg of ACCG, and an agitation speed of 150 rpm. This investigation was conducted over a pH range of 2 to 12 to assess the impact of pH on the adsorption capacity of ACCG for $\text{Zn}(\text{NO}_3)_2$. From the Figure 5, it can be observed that q_e increases as pH rises, attaining a peak of 6.36 mg/g with a percentage removal of 99.7% at pH=8, and then decreases afterwards.

When pH is less than 4.9, which is the point of zero charge (pH_{pzc}) of ACCG, the surface is positively charged due to the protonation of the functional groups. As a result, the adsorbent surface will repel Zinc ions, which are also positively charged. Therefore, adsorption will be minimal. As pH rises, the surface charge of the ACCG approaches negative and this results in favorable electrostatic forces with Zinc ions, thus increasing adsorption. This is also responsible for q_e increase, especially after $pH=6$ where more favorable conditions of adsorption are achieved. The ideal pH for Zinc adsorption is

$pH=8$, where maximum record of adsorption capacity occurs.

Nonetheless, q_e shows a decrease at a pH greater than 8. The drop is due to the precipitation of Zinc hydroxide ($Zn(OH)_2$). This precipitation occurs at highly basic (>10) conditions. Zinc ions do not remain in solution but instead precipitate as insoluble hydroxides. Rendering Zinc unable for adsorption onto the surface of ACCG because the value of the pH. Usually, pH level has considerable effects on the adsorption of Zinc, owing to the surface charge of ACCG.

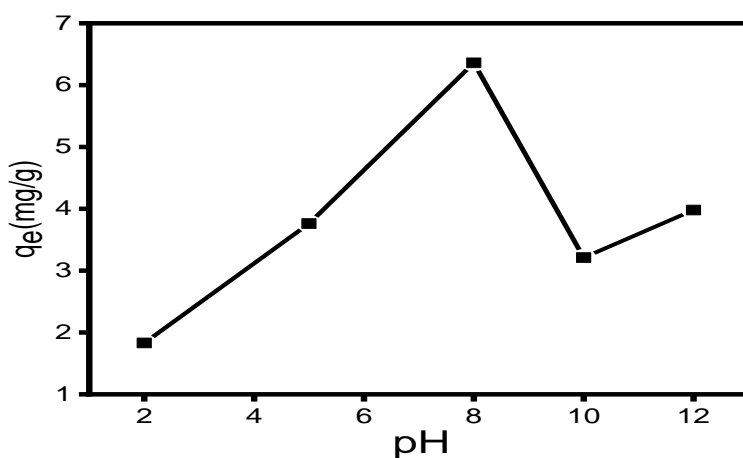


Figure 5. Adsorption of Zinc on ACCG as a function of pH.

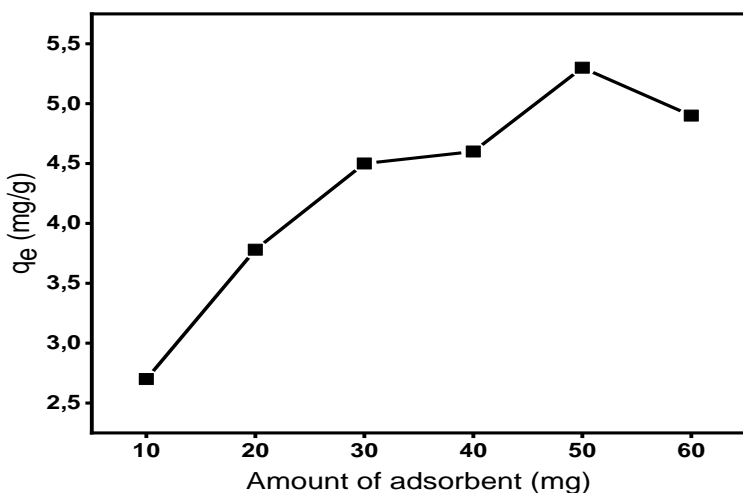


Figure 6. Adsorption of Zinc on ACCG as a function of adsorbent dosage.

Effects of Adsorbent Dose

The influence of adsorbent dosage on adsorption capacity was examined by varying the weight of ACCG between 10 to 60 mg in 50 mL of 100 mg/L Zinc solution at ~pH 6. The results indicate that the equilibrium adsorption capacity (q_e) enhances with adsorbent dosage to a maximum value of approximately 5.2 mg/g at 50 mg, with a percentage removal of 97.5%, confirming 50 mg as the optimal dosage. The reason being that with greater availability of active sites, Zinc adsorption is favored. Beyond 50 mg, no significant rise in adsorption capacity is observed, indicating the attainment of an optimum level. This can be explained on the basis of saturation of Zinc in solution: beyond a certain amount of adsorbent dose, all the available ions have already been adsorbed and excess adsorbent does not lead to any increase in adsorption. A dose of 50 mg is, therefore, considered to be optimum for maximum adsorption efficiency.

Kinetic Study

The effect of contact time on adsorption of Zinc onto ACCG was studied using the conditions of pH=6, 50 mg of ACCG, and 100 mg/L of Zinc. As per Figure 6, adsorption capacity for Zinc increases dramatically in the initial time period, and reaches a steady level at 60

minutes, with maximum capacity for adsorption of $q_{max} = 3.68$ mg/g. Figure 7 shows a maximum capacity of 5.85 mg/g at 60 minutes, with a percentage removal of 97.3%. This rapid initial uptake is attributed to the extremely high surface-active site density of the ACCG, allowing it to react instantly with Zinc ions in solution. After 60 minutes, the adsorption process stabilizes, as the maximum adsorption capacity $q_{max}=3.77$ mg/g is already reached. This is because the active sites are progressively saturated. Only the adsorption of Zinc ions that are capable of diffusing into the interior pores or binding to the remaining interior sites occurs here, which is a slower and less efficient process. To clearly understand the adsorption mechanism, the PFO and PSO models were chosen. The findings provided in the graphs in Figure 8 show that the PSO model is greater than the PFO model due to having a higher R^2 value. Thus, it can be concluded that the adsorption is primarily controlled by complexation and ion exchange driven by chemical interactions rather than simple diffusion. Also, the equilibrium adsorption capacity from the PSO ($q_e = 3.85$ mg/g) tallies with the experimentally determined value ($q_{ex} = 3.77$ mg/g) well. This implies that electrons are exchanged or shared between active sites in ACCG and Zinc, promoting complexation. Therefore, this study confirms that Zinc adsorption is primarily governed by chemical interactions rather than diffusive processes.

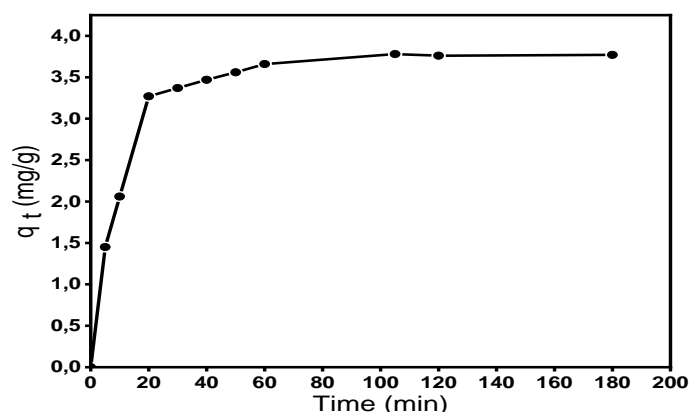


Figure 7. Adsorption of Zinc on ACCG as a function of time.

Table 1. PFO and PSO models for adsorption.

	Parameters	Value
Pseudo-first order	K_f, min^{-1}	0.04
	$q_e, \text{mg/g}$	4.12
	R^2	0.91
Pseudo-second order	$K_s, \text{g/mg} \cdot \text{min}^{-1}$	0.25
	$q_e, \text{mg/g}$	3.85
	$q_{ex}, \text{mg/g}$	3.77
	R^2	0.99

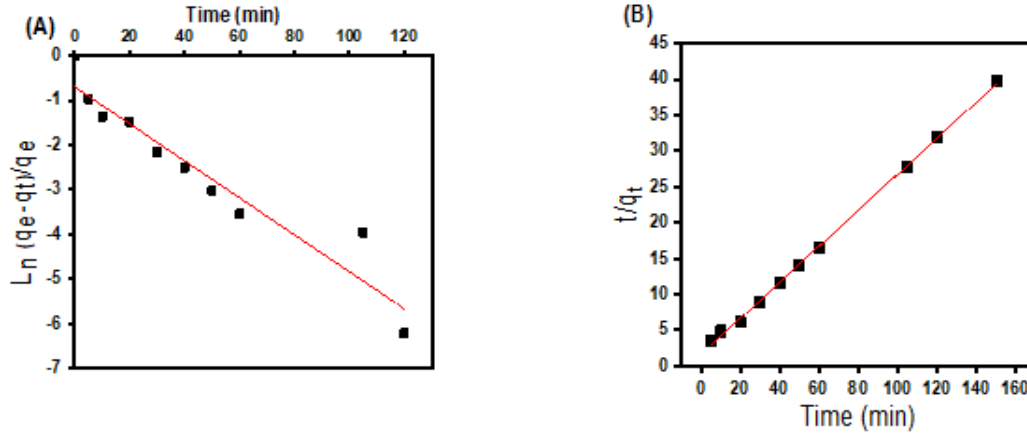


Figure 8. Kinetic model plots of (A) PFO and (B) PSO.

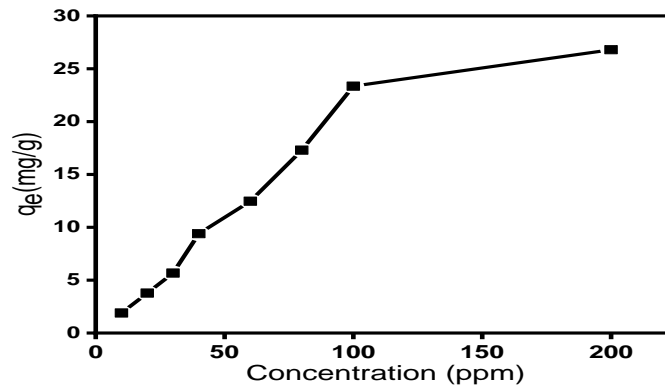


Figure 9. Adsorption of Zinc on ACCG as a function of concentration.

Effects of Initial Concentration of Zinc

As indicated by Figure 9, the Zinc adsorption onto ACCG rises steeply with initial concentration, indicating a high availability of active surface sites on the adsorbent. Beyond 100 ppm, adsorption slows down progressively due to the saturation of active sites on the ACCG, leading to a plateau in adsorption capacity. At higher concentrations of Zinc, the adsorption levels off, which indicates that most of the active sites have been saturated. The saturation phenomenon limits further adsorption even if a plenty of ions is available in the solution. This peculiar behavior of adsorption taking place on a heterogeneous surface confirms that the process follows a dynamic equilibrium in which the retention ability of the material is directly related to the availability of free active sites.

Adsorption Isotherms

The experimental data obtained have been analyzed using the Freundlich and Langmuir isotherm models

to gain a better understanding of the adsorption mechanism of ACCG. These models are crucial for characterizing the interactions between the adsorbent and the pollutants present in the aqueous solution [17].

Langmuir and Freundlich isotherms are represented by the following equations:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (5)$$

$$\ln q_e = \ln K_F + n \ln C_e \quad (6)$$

Where, C_e is the equilibrium concentration of Zinc (mg.L^{-1}), q_e is the amount of Zinc adsorbed on ACCG (mg/g), K_L is the Langmuir adsorption constant (L/mg), q_m is the maximum amount of Zinc that can be adsorbed by ACCG, K_F is the Freundlich adsorption constant, and n is a constant that indicates the capacity and intensity of the adsorption.

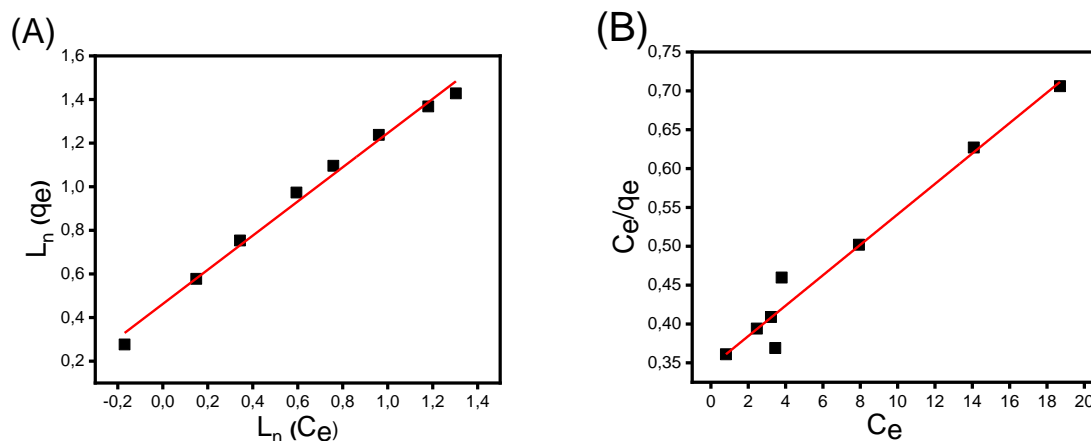


Figure 10. Isotherms plots for Zinc adsorption onto ACCG. (A) Freundlich and (B) Langmuir.

Experimental data revealed a linear relationship between q_e and $\ln(C_e)$, enabling the determination of constants. The results and the linearized plot of q_e against $\ln(C_e)$ are illustrated in Figure 10.

Some of the isotherm models like Freundlich and Langmuir have been modeled and plotted against experimental data, like in Figure 10. Table 2 shows that the Freundlich model provides the best fit ($R^2=0.99$), showing adsorption over a heterogeneous surface with multilayer interactions. The Freundlich

constant (K_F) was 2.90 and the intensity parameter ($1/n$) was 0.78, showing a good adsorption process. The Langmuir isotherm, with monolayer adsorption on a homogeneous surface, also gave a good fit ($R^2=0.96$). The q_{max} value was 2.90 mg/g and K_L value was 4.36 L/mg, which seems to show that the adsorbent and Zinc ions had intense interaction. It can be said that multilayer adsorption is dominant in the system due to the higher Freundlich correlation coefficient, which leads to the conclusion that surface heterogeneity has a significant influence for the adsorption process.

Table 2. Isotherm parameters for the adsorption of Zinc onto ACCG.

	$q_m(\text{exp.}), \text{mg/g}$	Langmuir isotherm	Freundlich isotherm
		$R^2 = 0.96$	$R^2 = 0.99$
Zinc	3.85	$q_m(\text{calc.}) = 2.9 \text{ mg/g}$	$K_F = 2.9$
		$K_L = 4.36 \text{ (L/mg)}$	$1/n = 0.78$

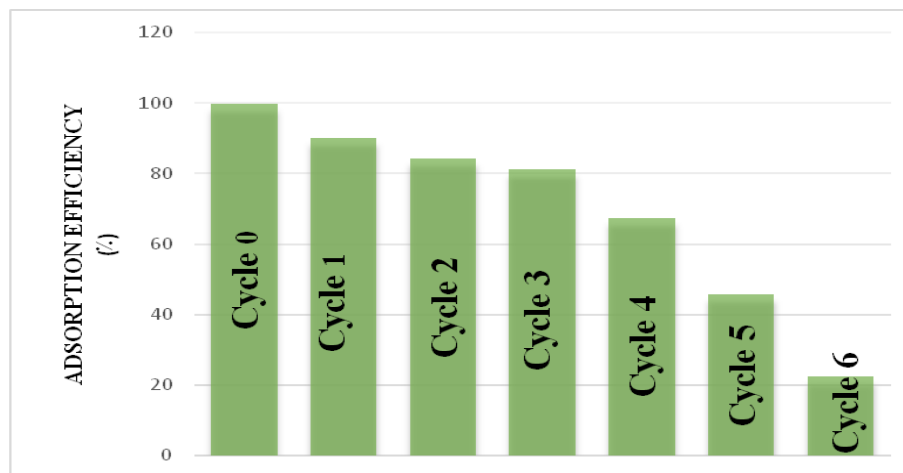


Figure 11. Regeneration studies of ACCG.

Adsorbent Regeneration

ACCG reusability was estimated from different cycles of adsorption-regeneration with optimized conditions. The material was recovered after each cycle; the regenerated ACCG was washed with distilled water to remove residual Zinc ions and dried, and reutilized. From Figure 10, adsorption efficiency reduced regularly through successive cycles. Initially, when the number of cycles was 0, the efficiency stood at 99.7% as a comparison reference. After the first regeneration (Cycle 1), it fell to 90.15%, then 84.3% for Cycle 2 and 81.13% for Cycle 3, indicating a steady but minimal decline in performance. A more pronounced

decline was observed from Cycle 4 (67.3%), which may be due to partial degradation of active sites. The decline was dramatic from Cycle 5 (45.7%) and Cycle 6 (22.32%), reflecting a significant loss of adsorption capacity. Although no substantial physical loss of the adsorbent was observed, the reduced performance after the third cycle is primarily attributed to the chemical deterioration of functional groups on the ACCG surface [17]. Despite this degradation, the results confirm that ACCG is effective for multiple cycles of reuse, particularly the initial three or four, making it a promising and cost-effective adsorbent, although material degradation cannot but limits its long-term effectiveness.

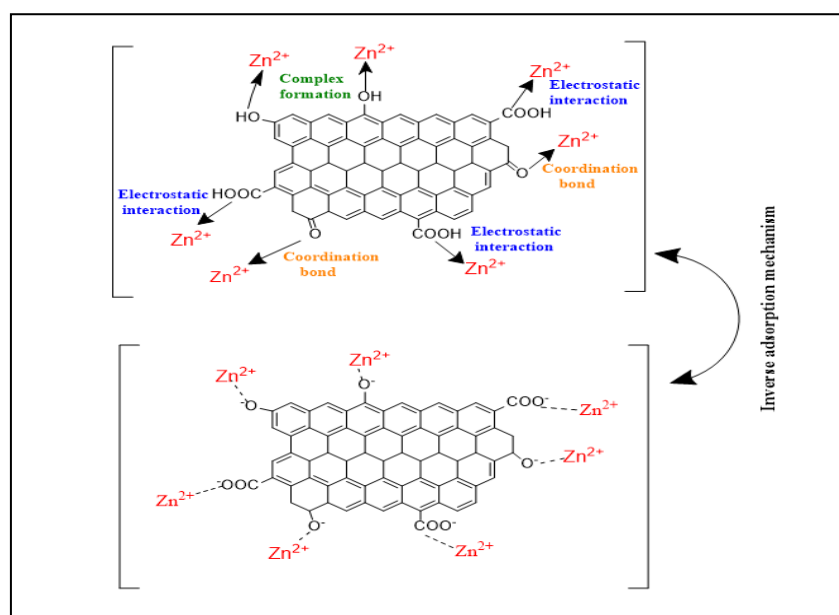


Figure 12. Proposed adsorption mechanism of Zinc onto ACCG.

Table 3. Comparison of the adsorption capacities of different adsorbates.

Adsorbent	Adsorption Capacity (%)	Conc. (mg/L)	Adsorption Isotherm	Optimum pH	Dosage (mg/mL)	Agitation Time(min)	Ref.
ACCG	99.8	100	Freundlich	8	2.0	60	This work
Activated Carbon from Ricinus	70.81	100	Langmuir	7	2.0	100	[18]
Activated Carbon from Bagasse	65.0	50	Freundlich	5	2.0	1440	[19]
Activated Carbon Cloth	60.0	10	Langmuir	7	3.0	1440	[20]
Biochar from Walnut Shells	85.0	50	Freundlich	6	1.0	120	[21]
Modified Chitosan	92.5	20	Langmuir	6	1.6	180	[22]
Modified Natural Zeolite	88.0	100	Langmuir	5	2.0	240	[23]
Hydroxyapatite from Eggshells	90.0	50	Freundlich	6	3.0	120	[24]

Mechanism of Adsorption

The process of adsorption of Zinc ions on ACCG involves several mechanisms of chemical interaction, as illustrated by Figure 12. In this figure, the term “inverse adsorption mechanism” refers to the fact that Zinc ions not only attach to the surface but also move into the pores of the material and bind to inner sites. This makes the adsorption more stable and not just based on surface attraction.

Before adsorption, the functional sites available for interaction on ACCG are carboxyl ($-\text{COOH}$), hydroxyl ($-\text{OH}$), and carbonyl ($\text{C}=\text{O}$) groups. The interaction of the Zinc ions with ACCG begins with an ion-exchange mechanism at the carboxyl sites with the release of H^+ , producing coordination bonds ($\text{COO}^- \text{Zinc}$). The complexation interactions occur simultaneously between the Zn^{2+} ions and the hydroxyl groups ($\text{O}^- \text{Zinc}$), while electrostatic interactions stabilize the adsorbed ions. The adsorption is reversible, in the sense that under some conditions such as pH adjustment, availability of competing ions, or use of complexing agents desorption of Zinc ions is feasible. Reversibility allows the recovery of adsorbent capacity to be possible, hence the potential for ACCG's reusability in a series of adsorption cycles and enhancing its efficiency in wastewater treatment.

Comparison with Different Adsorbents

The coffee ground-based activated carbon prepared in this work achieved the highest removal efficiency of 99.8% under the optimized conditions, which were $\text{pH}=8$, adsorbent dosage of 2 mg/mL, and relatively short contact time of 60 minutes. In contrast, other adsorbates, while being very effective (with relative removal efficiency $R\%$ between 60.0% and 92.5%), generally require larger amounts of adsorbent or much longer agitation times, in some cases even several hours. Activated carbon cloth, for instance, and bagasse-activated carbon achieved removal efficiencies of 60.0% and 65.0%, respectively, but required 24 hours contact time. Similarly, chemically modified chitosan and modified zeolite exhibited $>88\%$ adsorption capacities with higher dosage and longer equilibration time. Such data support ACCG's high performance superiority to endorse its efficacy as a proper, efficient, and inexpensive adsorbent for the separation of Zinc in wastewater treatment processes.

CONCLUSION

ACCG was, in this study, exhibited to be highly efficient and green adsorbent for Zinc removal from water. Phosphoric acid activation significantly enhanced porous volume and surface area ($421 \text{ m}^2/\text{g}$) and functionality, and hence provided maximum adsorption performance. Adsorption experiments determined 99.8% removal efficacy of Zinc at $\text{pH } 8$ in 60 minutes with predominance of chemisorption

and ion-exchange, as reflected in the PSO ($R^2=0.99$) and Freundlich isotherm ($R^2=0.99$). The adsorption capacity was determined to be 6.36 mg/g, where active site saturation was predominant of subsequent adsorption of Zinc. The regeneration experiments demonstrated that ACCG's efficiency is maintained to a point of three cycles before declining abruptly. While similar adsorption efficiencies were achieved using other adsorbates, such as modified chitosan and activated carbon from bagasse, ACCG was more effective at half the dosage used and 50% less contact time. Not only does this work indicate a sustainable way of Zinc removal that reduces the need for natural resources, but also promotes large-scale valorization of waste coffee grounds. Future research should include the testing of long-term material stability, functionality within real wastewater conditions, and removal of other heavy metals, further verifying its potential as an environmentally friendly solution.

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