Pomegranate Peel-Derived Carbon Quantum Dot Zinc Ferrite Nanocomposite (PPPCQD–$ZnFe_2O_4$) for Effective Uptake of Copper Ions from Aqueous Solutions

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Abstract

Pomegranate peel-based carbon quantum dots embedded with zinc ferrite (PPCQD–$ZnFe_2O_4$) is a novel nanocomposite that is synthesized, characterized, and used in two ways as an adsorbent for the removal of copper (Cu (II)) ions from aqueous solutions. Agro-waste was utilized to produce the green nanocomposite, which exhibited outstanding physicochemical properties, including magnetic recoverability, photoluminescence, and a large surface area. Batch adsorption tests demonstrated the optimum removal of copper at a pH close to neutral, a contact period of 70 minutes, and a dosage of 2.0 g/L. The highest adsorption capacity, as determined by Langmuir isotherm modeling, was 51.64 mg/g, indicating monolayer chemisorption. The process was found to be endothermic and spontaneous, as confirmed by thermodynamic analysis. Desorption tests indicated more than 80% reusability for a maximum of three cycles with EDTA. The results emphasize PPCQD–$ZnFe_2O_4$ as a cost-effective and sustainable nanomaterial for water remediation processes. Further research is suggested to confirm its field-scale usability and environmental stability.

Keywords: Green Synthesis, Nanocomposite, Adsorption Studies, thermodynamic analysis, water remediation.

I. INTRODUCTION

Water forms the pillars of life, maintaining agricultural yield, ecosystem health, and human health [1]. As they are coupled, degrading one will naturally harm the other. For example, soil heavy metals may leach into the nearby water body, leading to widespread ecological and public health issues [2]. That is why coupled remediation policies are necessary to safeguard both resources.

Heavy metals are especially hazardous because they are toxic, persistent, and non-biodegradable. They enter the environment through industrial effluents, agricultural runoff, and improper waste disposal, posing a significant threat to both human beings and aquatic organisms [3]. Copper (Cu), while it is biologically essential, is toxic at elevated concentrations and is capable of inducing liver and kidney damage, gastrointestinal disturbances, and neurological disorders. The World Health Organization (2017) recommends a maximum limit of 2.0 mg/L for copper in drinking water, thereby ensuring the health and well-being of all individuals [4].

Nanotechnology, a practical and eco-friendly approach, now facilitates the remediation of heavy metal contamination. Nanomaterials have increased surface area, reactivity, and tunability, which enhances the efficient adsorption and immobilization of pollutants [5]. The green synthesis of materials, particularly from crop waste, facilitates a circular economy by repurposing biowaste into functional nanomaterials [6].

Carbon quantum dots (CQDs) are zero-dimensional nanomaterials with excellent photoluminescence, water solubility, and surface functionalization [7]. Pomegranate peels, with their carbon and bioactive contents, are green precursors of choice for the synthesis of CQDs [8]. Alternatively, zinc ferrite ($ZnFe_2O_4$) is a magnetic nanoparticle with excellent thermal stability and a high sorption capacity for heavy metals [9].

The combination of zinc ferrite and CQDs enhances adsorption efficiency, magnetic recovery, and recyclability. The present work involves the preparation of a green nanocomposite from zinc ferrite and CQDs derived from pomegranate peel for the removal of copper (Cu^{2+}) from water.

II. MATERIALS and METHODS

A. Materials and chemicals

The experimental reagents used in the current work for the synthesis of zinc ferrite nanocomposite from pomegranate peel-derived carbon quantum dots include, sodium hydroxide (NaOH), zinc nitrate heptahydrate ($Zn\ (NO_3)_2{\cdot}6H_2O$), iron nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$), and hydrochloric acid (HCl). Sequential metal extraction requires precise chemicals, including magnesium chloride ($MgCl_2$), sodium acetate (NaOAc), acetic acid, hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$), nitric acid (HNO_3), hydrogen peroxide (H_2O_2), ammonium acetate (NH_4OAc), hydrochloric acid (HCl), and water.

B. Synthesis of PPCQD and PPCQD/ZnFe₂O₄

Pomegranate peel-derived carbon quantum dots (PPCQDs) were synthesized through hydrothermal route and then conjugated with zinc ferrite ($ZnFe_2O_4$) by the co-precipitation technique to prepare the PPCQD/$ZnFe_2O_4$ nanocomposite. In short, pomegranate peels were carbonized, hydrothermally processed to produce PPCQDs, and subsequently mixed with $Zn(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ precursors at a 1:2 mole ratio (Zn:Fe) in alkaline condition to produce the groundnut shell carbon quantum dots zinc ferrite nanocomposite (GSCQD/$ZnFe_2O_4$). The obtained material was rinsed extensively with water, dried, and reserved for utilization as an adsorbent in this work.

C. Characterization

Carbon quantum dots (CQDs) from pomegranate peel and their nanocomposites are characterized using PL, UV–vis, XRD, FE-SEM, and FT-IR to determine optical, structural, and surface properties. These techniques reveal crystallinity, morphology, and functional groups that govern metal interaction. Copper removal from water is primarily driven by adsorption, electrostatic attraction, and complexation with oxygenated surface groups, making CQD-based nanocomposites effective adsorbents.

D. Batch Adsorption Studies

The batch adsorption experiment was conducted as follows: 1.0 g of PPCQD/$ZnFe_2O_4$ adsorbent was placed in a 50-ml conical flask, along with 50 mL of a copper solution containing an initial concentration of 50 mg/L. The solution was agitated at a speed of 250 revolutions per minute on a magnetic stirrer.

The operating parameters were optimized using 1.0 g of PPCQD/$ZnFe_2O_4$ as adsorbent while considering a range of parameters, including contact time (CT) from 10 to 100 minutes, initial copper (II) concentration (IC) from 10 to 50 mg/L, pH from 1 to 10, and a dose of the adsorbent from 1.0 g/L to 4.0 g/L. The solution's stirring rate was maintained at 250 rpm. The pH of the solution was changed with either 0.1 M HCl or 0.1 M NaOH.

The percentage removal of copper (II) and adsorption capacity were calculated by using the following equations:

$$\%\ \mathrm{Removal}\ = (\mathrm{C_0} - \mathrm{C_e})\ \mathrm{X}\ 100\% \qquad (1)$$

$$\mathrm{Adsorption\ capacity} = (\mathrm{C_0} - \mathrm{C_e})\ \mathrm{X}\ \frac{\mathrm{M}}{\mathrm{V}} \qquad (2)$$

Where C_0 and C_e are the initial and final concentrations in mg/L, V is the total volume of the copper (II) solution in millilitres, and M is the mass of the synthesized adsorbent in grams.

E. Adsorption equilibrium constant

The study addresses the mechanism of chromium adsorption onto the PPCQD/Zn/$ZnFe_2O_4$ adsorbent using the Langmuir and the Freundlich isotherm models. According to the Langmuir model, the adsorbate can be chemically adsorbed at a finite number of well-defined positions, with each position capable of holding only one adsorbate species, and all adsorbate positions have the same energy. In contrast, interactions between the adsorbate species are neglected. Below is the Langmuir equation:

$$\mathrm{C_e/q_e} = (1/\mathrm{K_L q_m}) + \mathrm{C_e/q_m} \qquad (3)$$

where qe and qm are the equilibrium adsorption capacity (mg/g) and maximum adsorption capacity (mg/g) of PPCQD/$ZnFe_2O_4$, respectively, Ce is the adsorbed concentration (mg/L) of Cu (II), and K_L is the Langmuir constant. A plot of Ce/qe gives the value of qm and K_L.

On the other hand, the Freundlich isotherm assumes that as the concentration of adsorbate is increased, the concentration of adsorbate on the surface of the adsorbent is also increased. Essentially, this model of usage thinks that an infinite amount of adsorption can occur. Freundlich equation:

$$\log_{10} q_e = \log_{10}(k_f) + \left(\frac{1}{n}\right)\log_{10}(C_e) \qquad (4)$$

Where K_f and n are the Freundlich constants. The values K_f and n are determined by the graph of log q_e against log C_e.

F. Thermodynamics Study

Thermodynamic parameters such as enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) are of paramount importance in supplying information on the energy changes that result from the adsorption process. In this present study, several temperature conditions were tested, viz., 298 K, 308 K, and 318K for the adsorption of copper ions onto PPCQD/$ZnFe_2O_4$ adsorbent. The following equations were used to calculate the thermodynamic parameters:

$$lnK_d = \frac{\Delta S}{R} + \frac{\Delta H}{RT} \qquad (5)$$

$$K_d = q_e/C_e \qquad (6)$$

$$\Delta G = -RT lnK_d \qquad (7)$$

Where R and K_d represent the distribution coefficient and the universal molar constant (3.1416 J/kmol), and T is the temperature in degrees Kelvin. The ΔG, ΔH, and ΔS values were derived from the graph between lnK_d versus 1/T.

G. Preparation of Copper Stock Solution

A total of 3.929 grams of copper sulphate ($CuSO_4 \cdot 5H_2O$) was dissolved in 1 litre of distilled water to prepare a stock solution with a concentration of 1000 mg/L of copper.

III. RESULTS

A. UV and Luminescence Analysis

The UV–Visible absorption spectrum of the PPCQD (Fig. 1) sample exhibits characteristic peaks at 214 nm, 275 nm, and 358 nm. The 214–275 nm peaks are due to π → π transitions of aromatic carbon frameworks, whereas the 358 nm peak shows n → π transitions due to oxygen-containing functional groups on the carbon quantum dots' surface. The gradual decrease in absorbance with increasing wavelength is characteristic of carbon quantum dots and indicates the presence of different surface states and particle sizes [10].

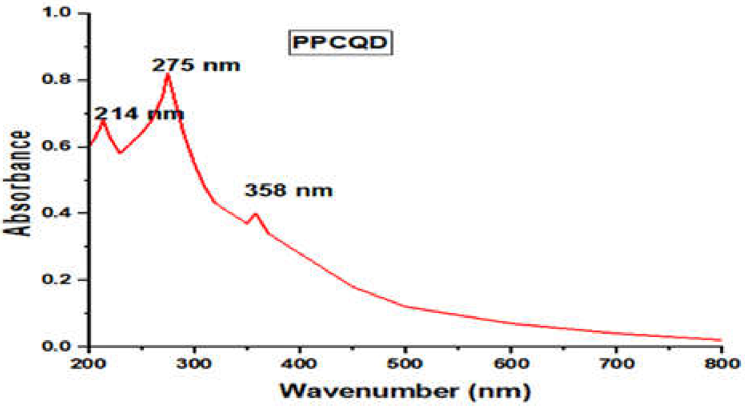

Fig.1: UV spectra of PPCQD

B. Fourier Transform Infrared Spectroscopy

The FTIR spectra of PPCQD (Fig. 2) and PPCQD/$ZnFe_2O_4$ (Fig. 3) were analyzed to identify functional groups and confirm nanocomposite formation. A strong absorption band at 3300–3500 cm^{-1} corresponds to O–H stretching vibrations. Peaks at 2975 cm^{-1} and 2932 cm^{-1} indicate aliphatic C–H stretching, while the peak at 1650 cm^{-1} represents C=O stretching .

Bands at 1380–1400 cm^{-1} indicate C=C bending vibrations, suggesting conjugated systems on CQD surfaces.

Peaks at 1087 cm^{-1} and 1044 cm^{-1} are associated with C–O stretching. Additionally, peaks at 542 cm^{1} and 467 cm^{1} point to Fe–O and Zn–O bonds, confirming the coordination modes of $ZnFe_2O_4$. These metal-oxygen bonds are visible in both the nanocomposite spectrum and the PPCQD spectrum, confirming the incorporation of zinc ferrite without significantly altering the primary functional groups in PPCQDs [11].

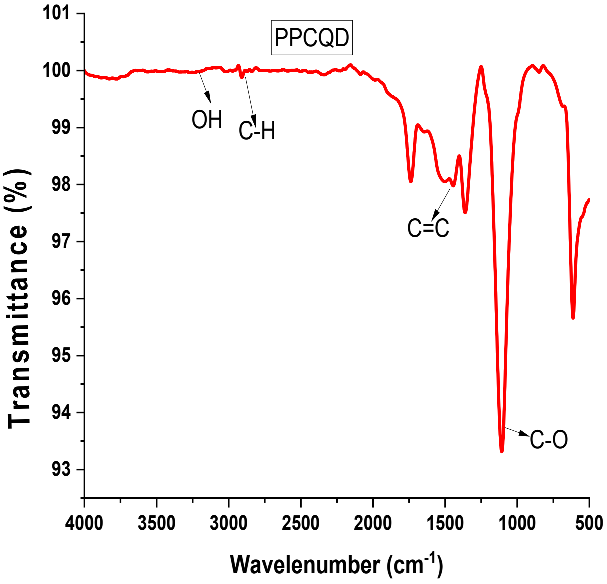

Fig. 2: FT-IR of PPCQD

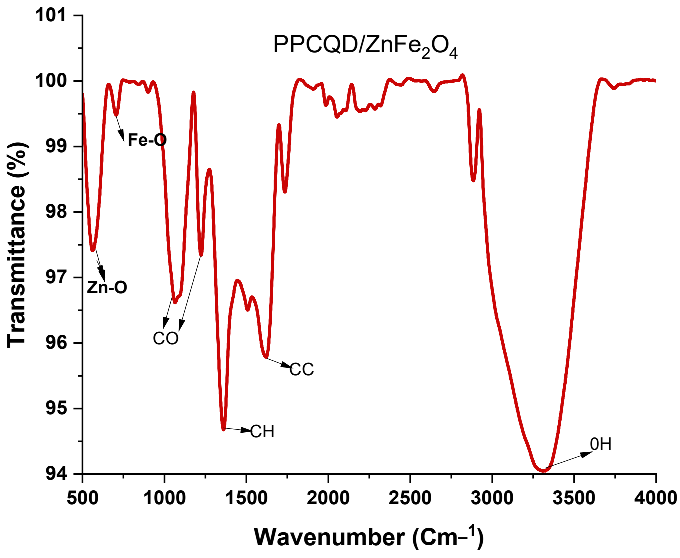

Fig. 3: FT-IR of PPCQD-$ZnFe_2O_4$

C. X-Ray Diffraction Analysis

The X-ray diffraction (XRD) analysis of PPCQD and the PPCQD/$ZnFe_2O_4$ nanocomposite reveals key structural information. PPCQD shows three peaks at 19.3363°, 32.3482°, and 38.9350°, indicating ordered structures. In contrast, the PPCQD/$ZnFe_2O_4$ nanocomposite exhibits a broader range of peaks at 21.4725°, 33.4617°, 34.9376°, and others, suggesting multiple crystallographic planes and successful incorporation of the $ZnFe_2O_4$ phase.

To determine the crystalline size, Scherrer's equation was used:

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad (8)$$

In the above equation, D = crystalline size, K is the Scherrer's constant, λ = wavelength given as 0.15406 nm, β = FWHM in radians, and θ = peak position in radians.

The crystallite size for PPCQD was calculated to be 16.55 nm, increasing to 18.02 nm upon combining it with $ZnFe_2O_4$. This slight increase indicates effective integration while maintaining nanoscale dimensions necessary for efficient adsorption applications.

D. Field Emission Scanning Electron Microscope

Figure 4 depicts the FE-SEM images of PPCQD and PPCQD-$ZnFe_2O_4$ nanocomposite. The scanning electron microscopy (SEM) images reveal that the PPCQD exhibits a dense and aggregated structure characterized by irregular particles. Conversely, the PPCQD-$ZnFe_2O_4$ nanocomposite demonstrates a porous morphology with distinct cavities, which indicates the successful integration of $ZnFe_2O_4$. This enhancement in structure contributes to an increased surface area, thereby improving the material's adsorption performance.

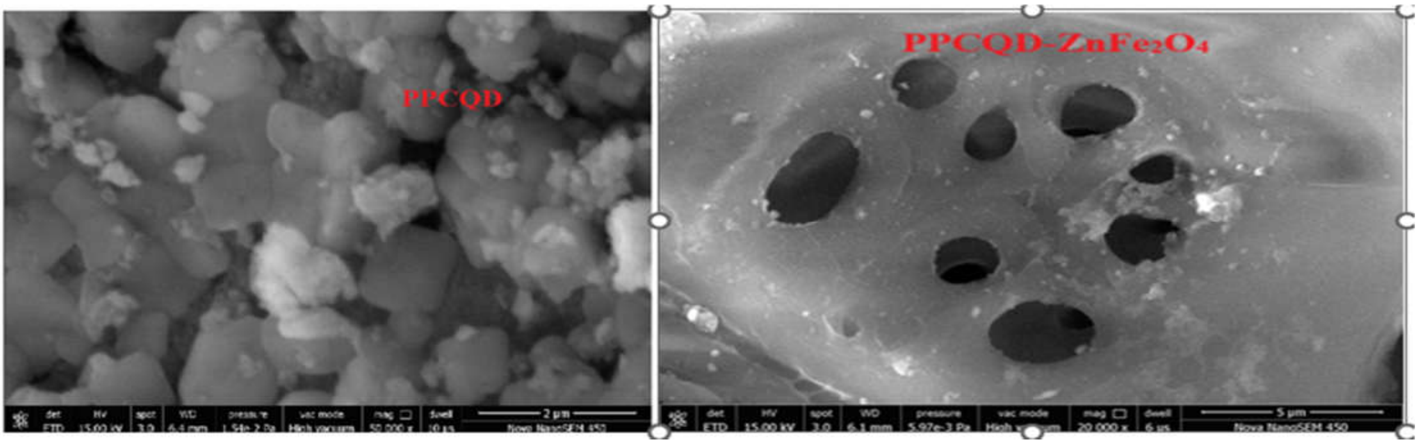

Fig. 4: FE-SEM images of PPPCQD and PPCQD-$ZnFe_2O_4$

E. The Effect of pH

With 1.0 g of adsorbent, a 10-minute contact time, and an initial Cu(II) concentration of 10 mg/L, Figure 5 shows the influence of pH on copper removal. Adsorption increased from about 25% at pH 1 to 88% above pH 6. Low uptake under acidic conditions results from proton competition and surface protonation, which reduce affinity for Cu^{2+}. As pH rises, decreased proton concentration and greater surface negativity enhance electrostatic attraction and complexation with Cu^{2+}. Removal efficiency levels off around pH 6, beyond which $Cu(OH)_2$ precipitation may also contribute. These results agree with previous findings that near-neutral pH favors Cu(II) adsorption due to deprotonated functional groups becoming more reactive toward metal ions [12].

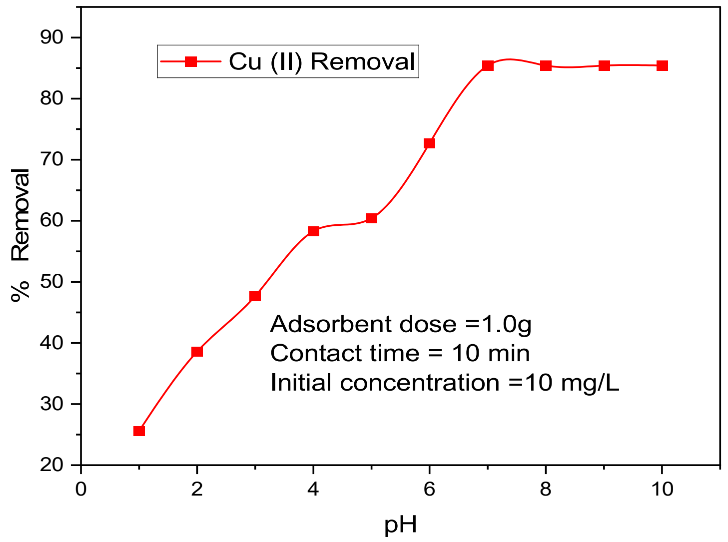

Fig. 5: Effect of pH

F. *Contact Time*

Figure 6 illustrates the relationship between contact time and the percentage removal of Cu (II) ions by an adsorbent under specific conditions: 1.0 g dosage, 10 mg/L initial concentration, and a pH of 7. The removal rate increases to about 88% at 70 minutes, after which it levels off, indicating that equilibrium has been reached. Initially, the removal was rapid due to the many active sites available in the adsorbent. As time progresses, these sites become occupied, leading to a slower removal rate.

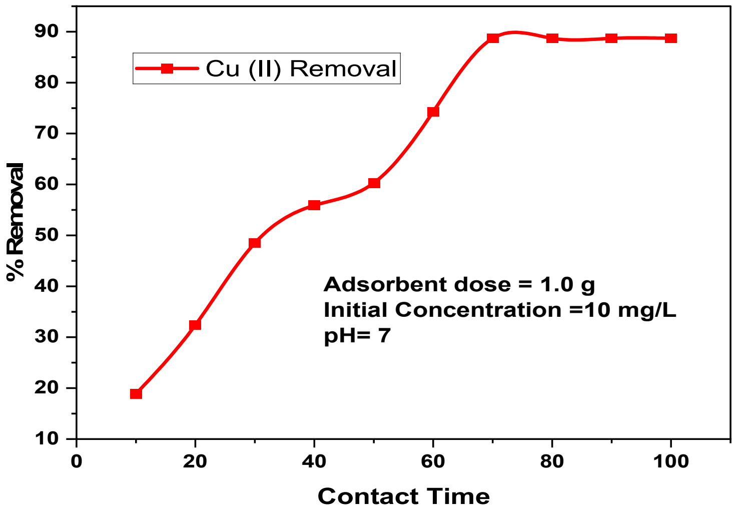

Fig. 6: Effect of contact time

G. Adsorbent dose

With an initial concentration of 10 mg/L, a contact time of 70 minutes, and a pH of 7, Figure 7 shows the effect of adsorbent dosage on the removal of Cu (II) ions from an aqueous solution. As the adsorbent dose increases from 1.0 g/L to 2.0 g/L, the removal efficiency rises to nearly 88%, indicating increased availability of active sites for adsorption. Beyond 2.0 g/L, the effectiveness plateaus, suggesting that excessive dosing can lead to particle agglomeration, which reduces the effective surface area and the number of available adsorption sites. Thus, the graph highlights the need to optimize adsorbent dosage for effective and efficient water treatment.

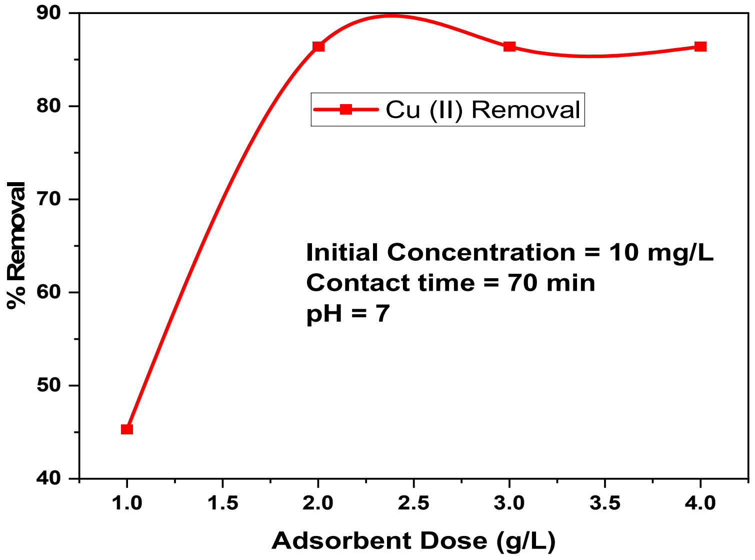

Fig. 7: Effect of adsorbent dosage

H. Initial Concentration

Figure 8 indicates the influence of initial copper ion concentration on percentage removal efficiency with a constant adsorbent dose of 2.0 g, contact time of 70 minutes, and pH 7. The removal efficiency decreases as the initial Cu (II) concentration ranges from 10 to 50 mg/L. This is due to the saturation of the available active sites on the adsorbent at high concentrations, where the metal ions exceed the adsorption capacity. Hence, it results in a low removal percentage. At low concentrations, the active sites are in excess, resulting in high adsorption efficiency.

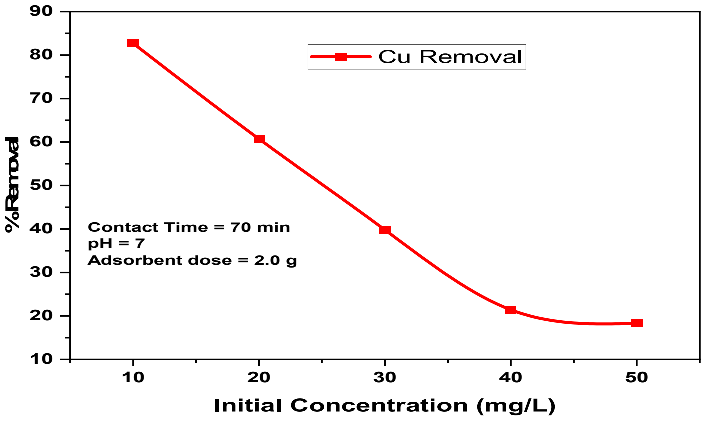

Fig. 8: Effect of initial concentration

I. Adsorption Isotherms

Figure 9 illustrates the adsorption isotherms of Cu (II) ion removal by PPCQD-$ZnFe_2O_4$ nanocomposite, correlating the experimental data with the Langmuir and Freundlich isotherm models. The Langmuir model ($R^2 = 0.976$) exhibits a better correlation with the experimental data compared to the Freundlich model ($R^2 = 0.6422$), indicating monolayer adsorption on a homogeneous surface. This response suggests that the adsorption process would likely occur at specific sites with uniform energies. The better fit of the Langmuir model validates reports by researchers such as [13] who found that Langmuir models tend to accurately describe metal ion adsorption onto nanocomposites due to saturation at active sites. The outcomes confirm the viability of PPCQD-$ZnFe_2O_4$ as a potential adsorbent for removing copper from water solutions.

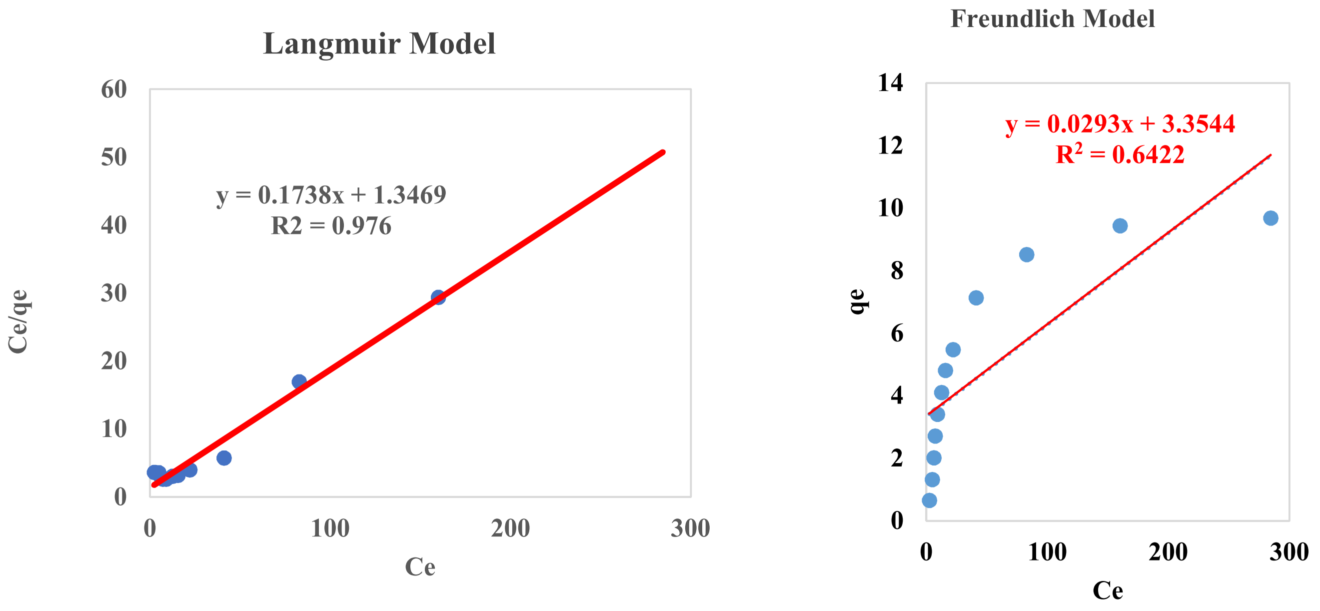

Fig. 9: Adsorption Isotherm Models

Table: 3

Langmuir	q_{max}(mg/g)	K_L (L/mg)	R^2	Freundlich	K_F (mg/g)	n	R^2
Cu (II)	51.64	0.41	0.976	Cu (II)	18.04	0.23	0.6422

J. Thermodynamic parameters

The table below lists thermodynamic parameters—Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°)—for Cu (II) ion adsorption by PPCQD-$ZnFe_2O_4$ at different temperatures (298 K, 308 K, and 318 K). The negative ΔG° values at all temperatures suggest that the adsorption process is spontaneous. As the temperature rises, more negative ΔG° values (-10.12 to -12.50 kJ/mol) indicate spontaneity at higher temperatures, which agrees with the endothermic behavior. The positive ΔH° value (+25.45 kJ/mol) also indicates that the adsorption is endothermic, involving a heat input. The positive ΔS° (+119.21 J/mol·K) means greater randomness at the solid–solution interface due to desolvation of Cu (II) ions and reorganization of water molecules upon adsorption. These findings are consistent with the literature regarding metal ion adsorption by carbon-based nanocomposites, which tend to be endothermic and entropy-driven in nature

Table 4 : Thermodynamic Parameters for Cu (II) Adsorption by PPCQD-$ZnFe_2O_4$

Pollutant	**Temperature (k)**	**ΔG° (kJ/mol)**	**ΔH° (kJ/mol)**	**ΔS° (J/mol·K)**	**Interpretation**
Copper (II)	298	-10.12	+25.45	+119.21	Spontaneous, endothermic, decreased disorder
	308	-11.31			
	318	-12.50			

K. Desorption Studies

After adsorption, desorption research was conducted on the PPCQD–$ZnFe_2O_4$ nanocomposite to extract copper ions Cu (II). The desorbing agent utilized in the investigation was 0.05 M ethylenediaminetetraacetic acid (EDTA). The procedure was carried out for two to three hours at a temperature of 30°C while rotating at 200 rpm. To facilitate regeneration, the material was thermally treated for five hours at 60°C following desorption. Throughout three consecutive cycles, the nanocomposite's reusability was evaluated. In these cycles, the respective desorption efficiencies were 84.55%, 82.8%, and 72.6%. The material's remarkable durability and reusability potential are demonstrated by these data, which show a high initial desorption efficiency with a steady reduction over several uses. In line with patterns seen in related nanocomposite desorption studies, the decrease in desorption performance may be caused by partial adsorbent surface degradation or incomplete copper ion desorption across several cycles.

IV. CONCLUSION

This research reports the successful synthesis of pomegranate peel carbon quantum dots conjugated with zinc ferrite, forming a durable nanocomposite called "pomegranate peel carbon quantum dots zinc ferrite nanocomposite (PPCQD-$ZnFe_2O_4$). The addition of pomegranate peel carbon quantum dots (PPCQDs) to zinc ferrite enhanced the nanocomposite's physicochemical properties, including surface area, functional group availability, and magnetic recoverability, all of which contributed to its outstanding adsorption performance. Batch adsorption experiments showed that Cu (II) ion removal efficiency was highest at near-neutral pH, moderate contact time, and an adsorbent dosage of 2.0 g/L. The Langmuir model, which matches the experimental data, indicates monolayer adsorption on a uniform surface. Thermodynamic analyses further confirmed that the adsorption process was entropy-driven, spontaneous, and endothermic—signs of favorable energy interactions at the solid-liquid interface. Overall, this study provides strong evidence that nanocomposites like PPCQD-$ZnFe_2O_4$ derived from agricultural waste offer a technically feasible, cost-effective, and environmentally friendly solution for remediating copper-contaminated environments. Future research should focus on field conditions, performance, and scalability of this method to support real-world applications and guide policy integration into environmental strategies.

ACKNOWLEDGEMENT

The authors extend their gratitude to Sharda University's Central Instrumentation and Facility for aiding in the absorbance readings. Special thanks to all contributors for their dedication and collaborative efforts, crucial to the success of this research.

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