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Production of New Activated Carbon from Agricultural Waste and its Use as an Eco-Friendly Solution for Removing Copper Ions from Industrial Effluents

Rajae Ghibate[1*], Meryem Ben Baaziz[2], Mohammed Chrachmy[2], Meryem Kerrou[1], Rachid Taouil[3] and Omar Senhaji[4]

[1] Laboratory of Physical Chemistry, Materials and Environment, Faculty of Sciences and Technologies, Moulay Ismail University of Meknes, 52000, Errachidia, Morocco

[2] Laboratory of Materials Engineering for the Environment and Natural Resources, Faculty of Sciences and Technologies, Moulay Ismail University of Meknes, 52000 Errachidia, Morocco

[3] Laboratory of Mechanics, Energetics, Automation, and Sustainable Development, Faculty of Sciences and Technologies, Moulay Ismail University of Meknes, 52000 Errachidia, Morocco

[4] Laboratory of Biomolecular and Macromolecular Chemistry, Faculty of Sciences, Moulay Ismail University of Meknes, 11201 Meknes, Morocco

* Corresponding author's e-mail: rajae.ghibate@gmail.com

ABSTRACT

This study explored the production of activated carbon from agricultural waste, specifically *Punica granatum* peel, and its application as an eco-friendly solution for removing copper (Cu^{2+}) ions from industrial effluents, particularly those from copper-plating industries. The Punica granatum peel was chemically activated using ortho-phosphoric acid to produce activated carbon. The activation process involved impregnation followed by thermal activation at 500 °C. The resultant activated carbon was characterized using FTIR, TGA/DTA, and adsorption tests at room temperature and pH 5, which demonstrated a Cu^{2+} ion retention rate exceeding 95% within the first 15 minutes. The adsorption kinetics were analyzed using pseudo-first-order and pseudo-second-order models, while the adsorption isotherms was examined using Langmuir and Freundlich models. The study demonstrated that the activated carbon derived from Punica granatum peel exhibits high adsorption efficiency for Cu^{2+} ions, with a maximum adsorption capacity of 19.62 mg/g. The adsorption process was best described by the pseudo-second-order kinetic model and the nonlinear Langmuir isotherm model. The newly developed activated carbon exhibits a markedly higher adsorption efficiency compared to existing activated carbons, highlighting its innovative potential for adsorbing Cu^{2+} ions. Consequently, its use proves to be a cost-effective and sustainable solution for treating copper-contaminated industrial effluents. In fact, this research offers a dual benefit by providing a sustainable waste management solution for agricultural residues and an effective method for treating industrial effluents. Incorporating this activated carbon in post-copper plating rinsing water treatment ensures regulatory compliance and facilitates water reuse. This approach also supports copper recovery and reuse in new plating baths, promoting cyclic material circulation within the industry.

Keywords: adsorption, copper-plating industry, new activated carbon, agricultural waste, copper ions removal, saving water.

INTRODUCTION

Amidst ongoing industrialization and ecosystem destruction caused by toxic substances, adopting clean technology (Cleantech) is essential for preserving environmental balance (Shakeel, 2021). In this context, protecting aquatic environments from heavy metals is crucial for minimizing negative impacts on ecosystems and human health (Singh et al., 2024). Copper-plating

is essential in many industries, such as automotive, aerospace, and electronics. This process uses specialized techniques to treat different surfaces, improving their appearance or functionality. It usually involves sequential treatment baths with intermittent rinse baths. The rinsing stage often produces a significant amount of harmful liquid waste containing chromium (Cr^{3+} and Cr^{6+}), copper (Cu^{2+}), zinc (Zn^{2+}), nickel (Ni^{2+}), and organic compounds from the treatment agents (Elboughdiri et al., 2024; Gündoğan et al., 2004). These substances can be extremely harmful to aquatic ecosystems. As a result, strict environmental standards regulate discharges of these liquids due to their content of hazardous substances, notably Cu^{2+} ions.

It cannot be denied that copper is an essential trace element critical for properly functioning various enzymatic processes within the human body (Więcek and Paprocka, 2024). It plays a pivotal role in the synthesis of red blood cells, the maintenance of bone health, as well as regulation of cardiovascular parameters such as heart rate and blood pressure (Alkhanjaf et al., 2024). However, copper levels must be stringently regulated to prevent excessive exposure, which can lead to neurological symptoms, gastrointestinal issues, as well as damage to the liver and kidneys (Rahimzadeh et al., 2024). In severe cases, copper toxicity has the potential to cause multiple organ failures and death (Lin et al., 2024). The individuals with Wilson's disease are particularly vulnerable to liver failure due to copper accumulation in their bodies (Cave et al., 2024).

Copper contamination in aqueous environments is a growing concern due to its ability to infiltrate surface and groundwater systems, thereby posing a threat to drinking water quality and public health. The increasing levels of Cu^{2+} pollution have been identified as a significant global issue, highlighting its status as a major heavy metal contaminant with considerable health risks (Liu et al., 2023; Saeed et al., 2024).

Regulatory agencies have established permissible effluent limits for Cu^{2+}, such as the United States Environmental Protection Agency's threshold of 1.3 mg/L and the World Health Organization's guideline of 1.5 mg/L for drinking water (Salman et al., 2023). Consequently, it is crucial to remove Cu^{2+} ions from industrial effluents before their discharge into surface waters. The presence of these toxic ions heightens environmental risks. To address these concerns, the development of sensitive and selective materials and methods for removing Cu^{2+} ions from contaminated water is essential to protect public health. Therefore, there is a growing demand for adopting cleantech to remediate Cu^{2+} ion water pollution.

In response to these challenges, several techniques for removing Cu^{2+} ions from effluents have been proposed, including chemical precipitation (Loughlaımı et al., 2024), adsorption (Kali et al., 2024), ion exchange (Zakaria et al., 2023), coagulation/flocculation (Ahmed et al., 2024; Baatache et al., 2024), electrodeposition (Duyen and Bac, 2024), reverse osmosis (Khan et al., 2023), cementation (Aâtach et al., 2024), and solvent extraction (Huang et al., 2024). Each method presents limitations in terms of cost, complexity, and generation of secondary waste. However, recent research studies have emphasized adsorption as a less expensive and easily applicable method suitable for industrial use. It is regarded as a promising and effective approach for removing Cu^{2+} ions.

In recent decades, the adsorption systems using activated carbon have gained significant importance in purification and separation processes, especially on an industrial scale (Assal et al., 2024; Packialakshmi et al., 2023). Activated carbon can be produced from various organic precursors, including agricultural wastes. Research into the preparation of activated carbon has identified these wastes as a potential source of high-performance carbons (Koli et al., 2024). Utilizing agricultural wastes for wastewater treatment offers dual benefits by converting waste into a valuable material and reducing disposal costs associated with on-site burning (Awogbemi and Von Kallon, 2023; Wu et al., 2020). There are two primary methods for preparing activated carbon: chemical activation and physical activation.

Chemical activation offers certain advantages over physical activation, primarily due to its higher yield and lower activation temperature (Gao et al., 2020), making it more economical. Various activating agents have been employed in the chemical preparation, including $ZnCl_2$, KOH, NaOH, $AlCl_3$, H_3PO_4, and $CaCl_2$. Among these agents, phosphoric acid has received particular attention recently due to its environmental, economic, and functional advantages (Grich et al., 2024; Tetteh et al., 2024). These considerations led to the adoption of a Cleantech approach by developing a new activated carbon that adheres to the principles of industrial ecology. The activated carbon was produced from *Punica granatum* peel, chosen for their availability and suitable

physical characteristics. The peel was activated using H_3PO_4 to create an adsorbent with a high retention capacity for Cu^{2+} ions, addressing the issue of liquid discharges from copper-plating activities on metal surfaces.

The purpose of the research was to develop a new, environmentally friendly adsorbent from *Punica granatum* peel, featuring high copper adsorption efficiency. This research aimed to ensure cost-effective and high-quality treatment of industrial wastewater while promoting the valuation of agricultural waste.

MATERIAL AND METHODS

Activated carbon preparation

The *Punica granatum* peel was thoroughly washed with water to remove any adhering impurities and dust particles, followed by a rinse with distilled water. Subsequently, they were air-dried until they attained a rigid texture. After drying, the peel was ground into a fine powder and washed with bi-distilled water to eliminate residual contaminants. The powder was then oven-dried until it reached a constant weight. Subsequently, the powdered *Punica granatum* peel was impregnated with ortho-phosphoric acid and thermally activated using a controlled heating rate to achieve the optimal carbonization temperature of 500 °C. Upon cooling, the precursor underwent multiple washings with bi-distilled water to remove excess acid. The resultant activated carbon was dried and kept in a desiccator until needed. The choice of activation agent was based on its environmental, economic, and functional advantages (Grich et al., 2024; Tetteh et al., 2024). The temperature of 500 °C was chosen for the treatment, as numerous studies have shown it to be the optimal activation temperature for biomasses in chemical activation processes (Khadem et al., 2023; Silva et al., 2024).

Characterization techniques

The Bruker Alpha II FTIR spectrometer, equipped with a Diamond Crystal ATR accessory, was utilized for analyzing both raw and activated *Punica granatum* peel to uncover the chemical activation-induced changes. Spectral data were systematically collected across the wavelength range of 400–4000 cm^{-1} with a resolution set to 4 cm^{-1}. Additionally, the thermal properties of the activated carbon were analyzed using TGA/DTA techniques. A LABSYS/evo TGA/DTA thermal analyzer was used to perform simultaneous thermal analysis in the presence of nitrogen. The sample underwent linear heating at a rate of 10 °C/min, covering a temperature range from room temperature to 700 °C. This thermal analysis provided insights into the stability and decomposition patterns of the activated carbon.

Adsorption process

Adsorption tests were conducted in a batch system at room temperature, employing 0.05 g of *Punica granatum* peel activated carbon in 50 mL of Cu^{2+} aqueous solution (10 mg/L). For each test, the pH of the solution was adjusted to 5 to prevent exceeding the copper precipitation threshold (Figure 1). Subsequently, the suspensions underwent filtration through a 0.45 µm membrane filter. Residual Cu^{2+} concentrations were measured using a Shimadzu AA-660 atomic absorption spectrometer at the specific wavelength of copper (324.8 nm) with an air/acetylene flame. The percentage of Cu^{2+} ions adsorption (R) and their adsorbed amount at time t (q_t) were determined utilizing Equations 1 and 2, respectively.

$$R(\%) = \frac{(C_0 - C_t)}{C_0} \cdot V \quad (1)$$

$$q_t\,(mg/g) = \frac{(C_0 - C_t)}{m_{AC}} \cdot V \quad (2)$$

where: C_0 – initial Cu^{2+} concentration (mg/L), C_e – Cu^{2+} concentration remaining after a given time t of adsorption (mg/L), m_{AC} – mass of activated carbon (g), V – volume of solution containing Cu^{2+} ions (L).

Kinetic study

The kinetic study was undertaken to gain a better understanding of the adsorption of Cu^{2+} ions onto the prepared activated carbon and to determine the optimum time necessary to achieve effective treatment results. In this context, two kinetic models were applied to the experimental data: the pseudo-first-order model (PFOM) and the pseudo-second-order model (PSOM), both in their nonlinear and linear forms (Table 1). These models describe the rate at which Cu^{2+} ions are adsorbed onto the activated carbon over time. PFOM assumes that the rate of occupation of adsorption sites is proportional to the number of unoccupied sites. In contrast, PSOM assumes that

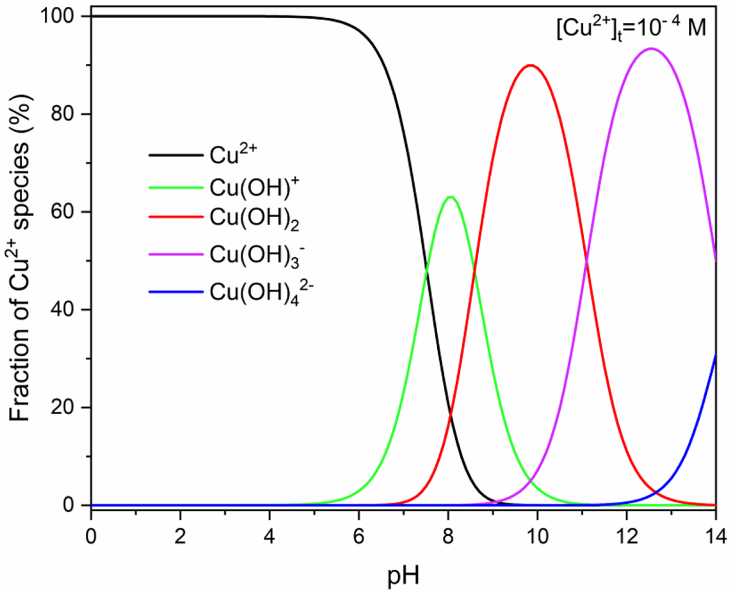

Figure 1. Distribution diagram of Cu^{2+} species based on pH levels

Table 1. Linear and nonlinear forms of applied kinetic models

Model	Nonlinear form	Linear form	Reference
PFOM	$q_t = q_e(1 - e^{-K_1 t})$	$ln(q_e - q_t) = ln(q_e) - K_1 t$	(Ouallal et al., 2023)
PSOM	$q_t = \frac{q_e^2 K_2 t}{q_e K_2 t + 1}$	$\frac{t}{q_t} = \frac{1}{q_e^2 K_2} + \frac{1}{q_e} t$	

Note: q_e – the amount of adsorption at equilibrium (mg/g), K_1 (min^{-1}) and K_2 (min.g/mg) – are the rate constants of PFOM and PSOM, respectively.

the adsorption rate is dependent on the square of the number of unoccupied sites. By fitting the experimental data to these models, the kinetic parameters were estimated, providing insights into the adsorption mechanism and efficiency of the activated carbon for Cu^{2+} ion removal.

Isotherm study

The isotherm study was conducted to gain deeper insight into the adsorption of Cu^{2+} ions onto the prepared activated carbon and to determine its adsorption capacity. To achieve this, equilibrium data were analyzed using both Langmuir and Freundlich models. These models were employed in both their linear and nonlinear forms (Table 2) to provide a comprehensive understanding of the adsorption behavior.

RESULTS AND DISCUSSION

Adsorbent characterization

The FTIR spectra of raw *Punica granatum* peel and its derivative activated carbon, as

Table 2. Linear and nonlinear forms of applied isotherm models

Model	Nonlinear form	Linear form	Reference
Langmuir	$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}}$	(Ghibate, Kerrou, et al., 2024)
Freundlich	$q_e = K_F C_e^{1/n}$	$lnq_e = lnK_F + \frac{1}{n} lnC_e$	

Note: C_e – the dye concentration that is still present at equilibrium (mg/L). q_{max} – the maximum adsorption capacity (mg/g). K_L – the Langmuir constant (L/mg). K_F – Freundlich coefficient linked to the adsorption capacity $(mg/g)(L/g)^n$, n – Freundlich's affinity coefficient (-).

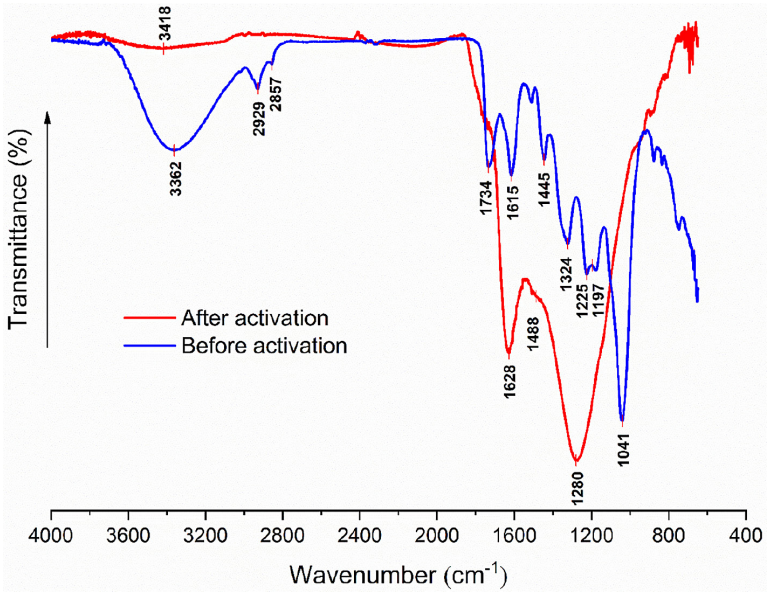

Figure 2. FTIR spectra of *Punica granatum* peel before and after activation

illustrated in Figure 2, show that the spectrum of the activated carbon exhibits fewer peaks compared to that of the raw *Punica granatum* peel. The spectra demonstrate some common absorption bands with variations, such as a decrease in intensity or the emergence and disappearance of specific bands. For instance, there is a significant reduction in the intensity of the band at 3362 cm^{-1}, which corresponds to the -OH stretching of carboxylic acids or phenolic groups (Ghibate, Ben Baaziz, et al., 2024; Mokti et al., 2021). Additionally, the peaks observed at 2929 and 2857 cm^{-1}, associated with asymmetric and symmetric C-H stretching, respectively, have also disappeared. Following the activation process with H_3PO_4, these bands, among others, are notably diminished or have disappeared, indicating the decomposition of organic matter. Furthermore, the formation of phosphate groups on the surface of the activated carbon is evidenced by the two peaks observed at 1628 cm^{-1} and 1280 cm^{-1} (Kan et al., 2017). This transformation underscores the structural and chemical changes induced by the activation process, which may enhance the adsorption properties of activated carbon.

The thermogravimetric curve of *Punica granatum* peel derived activated carbon (Figure 3) reveals two main mass losses during heating, occurring in two distinct stages. The first loss, starting around 50 °C and ending around 150 °C, is marked by a maximum endothermic peak on the DTA curve at 109 °C, with a mass loss percentage of 12.48%. This loss results from the evaporation of water adsorbed in the sample. The second loss, occurring between 250 °C and 650 °C, shows a maximum exothermic peak on the DTA curve at 471 °C, with a mass loss percentage of 29.56%. This loss is primarily due to the decomposition of organic components.

Retention of Cu^{2+} ions

Figure 4 illustrates the adsorption behavior of Cu^{2+} ions on the prepared activated carbon over time. The results indicate rapid adsorption of Cu^{2+}, with over 95% of the maximum adsorption occurring within the first 15 minutes, suggesting a high affinity for copper cations. Afterwards, there is no more significant change in the metal abatement. Furthermore, Table 3 demonstrates that the elaborated activated carbon exhibits a markedly higher adsorption efficiency compared to other activated carbons, indicating its considerable potential for adsorbing Cu^{2+} ions. Consequently, its use proves effective in purifying the Cu^{2+} ion-polluted effluents, enabling the recovery of high-quality water suitable for reuse in rinsing metal parts without compromising their quality.

Kinetic study

The adsorption kinetics data of Cu^{2+} ions on the studied activated carbon were modeled using both linear and nonlinear forms of the pseudo-first-order (PFOM) and pseudo-second-order (PSOM) models, as depicted in

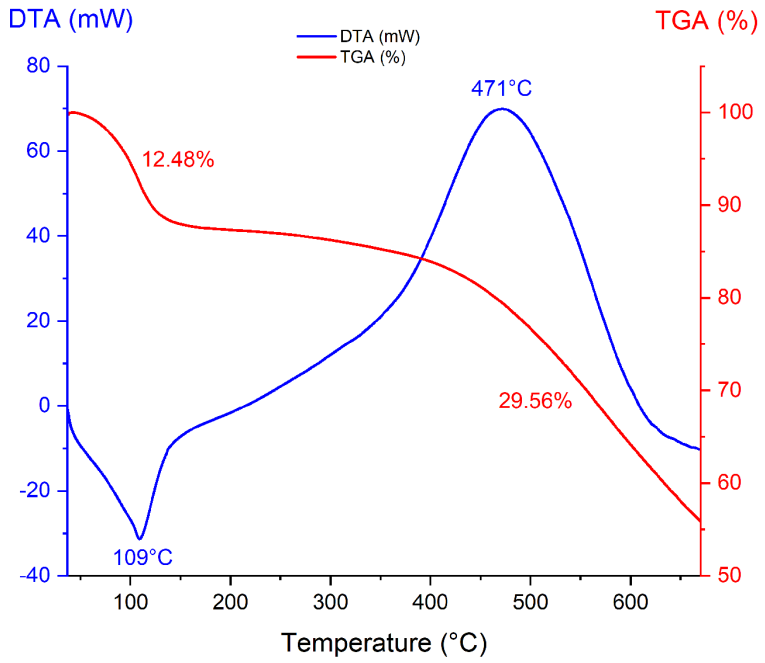

Figure 3. DTA and TGA curves of *Punica granatum* peel derived activated carbon

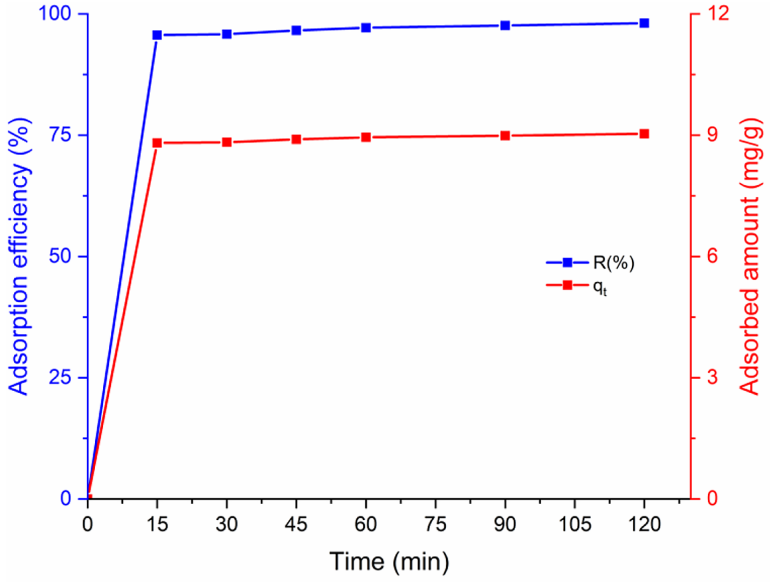

Figure 4. Retention of Cu^{2+} as function of contact time

Figure 5. The model parameters are presented in Table 4. The results reveal that the linear form of the PFOM poorly correlates with the experimental data. Additionally, the equilibrium adsorption quantity predicted by the nonlinear form of PFOM is significantly lower than the experimental value (q_{exp} = 9.014 mg/g), indicating that PFOM is unsuitable for describing the adsorption kinetics of Cu^{2+} ions on the studied activated carbon. Conversely, both the linear and nonlinear forms of PSOM show a better correlation with the experimental data, as indicated by the coefficient of determination analysis. Moreover, the equilibrium adsorption quantity predicted by the nonlinear form of PSOM closely matches the experimentally measured value. Thus, the nonlinear form of PSOM more accurately describes the adsorption behavior of Cu^{2+} ions on the synthesized activated carbon.

Table 3. Comparison of Cu^{2+} adsorption on activated carbons derived from different biomasses

Biomass	Activation method	Activation agent	Activation temperature (°C)	R(%)	pH	Reference
Corn husk	Chemical activation	H_3PO_4	500	57.42	4	(Silva et al., 2024)
Hazelnut shell	Pyrolysis under nitrogen	-	500	82.00	4	(Kaya et al., 2020)
Walnut shell	Pyrolysis under nitrogen	-	700	86.00	4	(Kaya et al., 2020)
Sunflower residue	Carbonization (900°C under nitrogen) and chemical modification	KOH	900	98.60	5	(Radenković et al., 2024)
Acacia Senegal waste	Pyrolysis	-	300	75.50	5	(Ali Babeker et al., 2024)
Acacia Senegal waste	Hydrothermal carbonization	-	180	18.25	5	(Ali Babeker et al., 2024)
Neem hull	Chemical activation	H_3PO_4	600	36	5	(Fita et al., 2023)
Hyphaene thebaica hull	Chemical activation	H_3PO_4	600	21	5	(Fita et al., 2023)
Oak Cupules	Chemical activation	H_3PO_4	450	60.00	5	(Khater et al., 2024)
Punica granatum peel	Chemical activation	H_3PO_4	500	97.15	5	This work

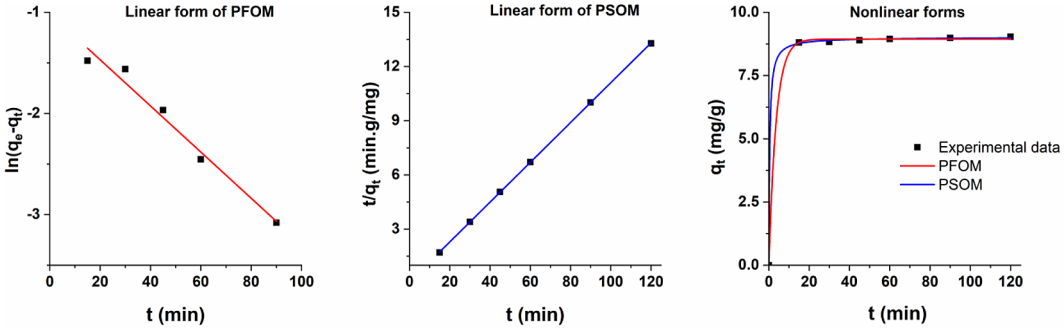

Figure 5. The plots of the linear and nonlinear forms of PFOM and PSOM

Table 4. Adsorption kinetic parameters for Cu^{2+}/activated carbon system

$q_{e,\,exp}$ (mg/g) = 9.034						
Model	Pseudo-first-order			Pseudo-second-order		
Parameters	$q_{e,cal}$ (mg/g)	K_1 (min^{-1})	R^2	$q_{e,cal}$ (mg/g)	K_2 (g/mg min)	R^2
Linear form	0.363	0.023	0.9749	9.076	0.145	0.9999
Nonlinear form	8.939	0.279	0.9996	9.014	0.264	0.9998

Isotherm study

Figure 6 displays the experimental data from the isotherm study alongside predictions made by both linear and nonlinear forms of the Freundlich and Langmuir models. The findings of this study are compiled in Table 5. On the basis of the R^2 analysis, the nonlinear Langmuir model appears to be the most appropriate choice for describing Cu^{2+} adsorption on the prepared activated carbon. This indicates that Cu^{2+} ions are adsorbed onto energetically similar sites, forming a monolayer without interaction among the adsorbed ions. The maximum adsorption capacity predicted by this model in its nonlinear form is 20.096 mg/g, which is very close to the value measured experimentally ($q_{max,\,exp}$ = 19.62 mg/g).

The Langmuir isotherm model has an important parameter called the separation factor R_L. This is a unitless number that depends on the equilibrium constant K_L of the Langmuir model and the initial concentration C_0 of the adsorbate. It is calculated according to the following equation:

$$R_L = \frac{1}{1+ K_L C_0} \quad (3)$$

The value of R_L is used to determine whether adsorption is favorable, linear, irreversible, or unfavorable (Ouallal et al., 2024): If $0 < R_L < 1$, adsorption is favorable. If $R_L \approx 1$, adsorption is linear. If $R_L = 0$, adsorption is irreversible, and if $R_L > 1$, adsorption is unfavorable. In the case studied, the values of R_L are between 0 and 1 (Table 5), indicating that the adsorption of Cu^{2+} ions on activated carbon is a favorable process.

Cleantech approach

Using *Punica granatum* peel as activated carbon represents a significant step towards a green economy. By incorporating this material in the treatment of rinsing water post-copper plating, companies can ensure regulatory compliance and facilitate the reuse of water in rinsing baths without compromising product quality. This closed-loop water circulation system results in substantial resource savings. The effectiveness of this Cleantech approach in meeting both economic and environmental standards highlights its essential role in maintaining competitiveness within the copper-plating sector. This approach involves the separate treatment of effluents from each surface treatment unit, ensuring selective adsorption and preventing competition among metal ions (Cu^{2+},

Table 5. Freundlich and Langmuir isotherm constants

$q_{max,\,exp}$ (mg/g) = 19.62					
Langmuir model			Freundlich model		
Parameters	Linear form	Nonlinear form	Parameters	Linear form	Nonlinear form
$q_{max,\,cal}$ (mg/g)	21.142	20.096	$q_{max,\,cal}$ (mg/g)	22.295	21.095
K_L (L/mg)	0.003	1.026	K_F (mg/g)	7.556	9.288
R_L	0.985–0.764	0.163–0.001	1/n	0.297	0.225
R^2	0.7078	0.9364	R^2	0.7868	0.8797

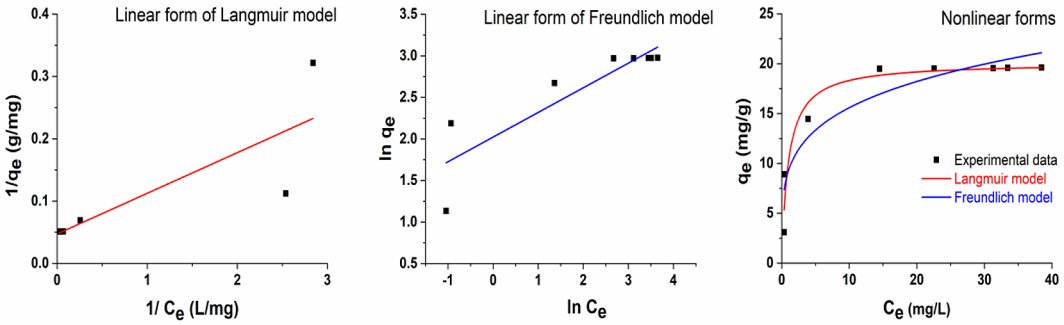

Figure 6. Cu^{2+}adsorption isotherm at 25 °C and their fitting through Freundlich and Langmuir models

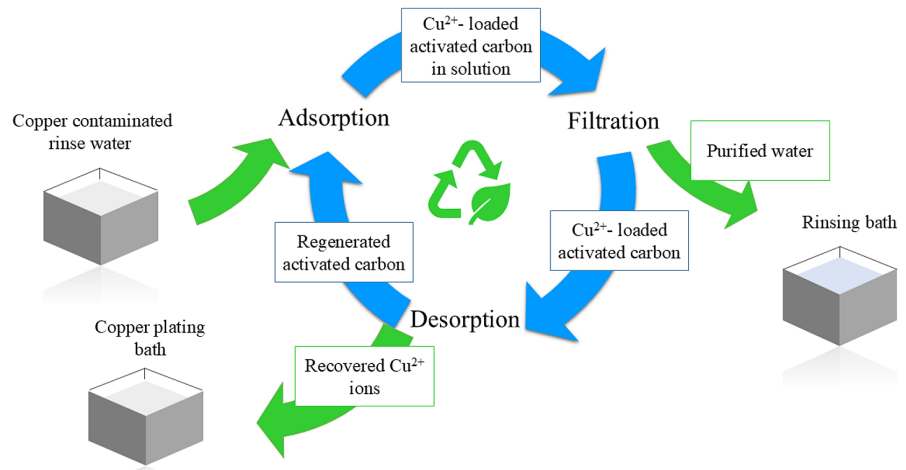

Figure 7. Cleantech approach proposed for the copper-plating industry

Ni^{2+}, Cr^{3+}) for active sites. This simplification of the treatment process allows for the recovery and reuse of copper in new copper-plating baths. Desorption is necessary to regenerate the activated carbons and recover the copper. These purification efforts for rinsing baths enable the metal surface copper-plating industry to achieve cyclic material circulation (Figure 7). The treated water can serve as a raw material for other treatment baths, promoting sustainable business development without harming the environment.

CONCLUSIONS

In conclusion, the Cleantech approach employing *Punica granatum* peel-derived activated carbon effectively addresses the sustainability and economic viability of the copper-plating industry while ensuring green competitiveness. This method demonstrates dual ecological benefits: recovering a waste product and purifying rinsing bath water. The characterization of the activated carbon, conducted using FTIR and TGA/DTA, provided insights into the structural and chemical changes as well as the mass variations induced after the activation process. The synthesized activated carbon efficiently removes Cu^{2+} ions, as evidenced by robust adsorption performance under optimal conditions (pH 5, 1 g/L activated carbon, 10 mg/L Cu^{2+} ions, 60 minutes contact time). Rapid adsorption kinetics and favorable R_L values confirm high affinity and effective removal capabilities. The adsorption data fit well with the nonlinear pseudo-second-order and Langmuir models. The close alignment of the predicted maximum adsorption capacity (20.096 mg/g) with the experimental value (19.62 mg/g) underscores the Langmuir model's reliability in describing the studied system. This indicates monolayer adsorption on uniform sites with no interaction between adsorbed ions. Ultimately, the use of activated *Punica granatum* peel provides a sustainable solution for managing industrial effluents containing Cu^{2+} ions, promoting the cyclical use of water and reducing freshwater consumption. Additionally, the recovered copper can be reintegrated into production processes after activated carbon regeneration, enhancing resource efficiency. This Cleantech approach exemplifies the potential for integrating waste valorization and environmental protection within industrial practices.

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