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Original Article

Enhancing Chromium Removal Efficiency with Activated Carbon from Waste Tires

Aruna Sudame[1], Manjusha Ugale[2], Bharat Kapgate[3]

[1]*G H Raisoni University, Amravati.*
[2]*G H Raisoni College of Engineering and Management, Nagpur, India.*
[3]*Indian Rubber Manufacturers Research Association Autonomous Body under DPIIT, Ministry of Commerce & Industry, Govt. of India.*

[1]*Corresponding Author : aruna.sudame@raisoni.net*

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Abstract *- This research investigates the efficacy of AC derived from waste rubber tires in the withdrawal of chromium (Cr(VI)) from the contaminated liquid. The study aims to provide a sustainable and cost-effective solution for heavy metal remediation in wastewater treatment. Batch adsorption experiments were conducted to assess the impact of various parameters, including contact time, adsorbent dose, temperature, and pH, on the removal efficiency of Cr(VI). The results indicate that the percentage of Cr(VI) withdrawal rises with the rise in contact time, achieving a maximum removal efficiency of 97% within 35 minutes at an adsorbent dose of 15 g/L, the starting chromium mass of 20 mg/L, and a pH of 3. The adsorption process was found to be highly effective at lower temperatures and acidic pH levels, with the optimum conditions being 25°C and pH 3, respectively. The linear regression models applied to the data demonstrated a strong correlation between the experimental variables and chromium removal efficiency, with high R^2 values indicating the reliability of the models. This study highlights the dual environmental benefits of utilizing waste tires for chromium removal and reducing landfill waste, thereby promoting a circular economy. The findings suggest that activated carbon from waste tires is a viable and efficient adsorbent for Cr(VI) removal, presenting a promising approach for practical wastewater treatment applications.*

Keywords *- Chromium removal, AC, Waste rubber tires, Adsorption, Water treatment.*

1. Introduction

The contamination of water bodies with heavy metals such as chromium poses a significant environmental and public health challenge. Cr is highly toxic, carcinogenic, and mutagenic, making its presence in industrial effluents and natural water sources a critical issue. Industrial activities, including electroplating, leather tanning, and textile manufacturing, are major sources of Cr pollution, leading to the contamination of water supplies and posing severe risks to ecosystems and human health [1]. Traditional methods for the withdrawal of Cr from water, such as ion exchange, chemical precipitation, and membrane filtration, often face limitations. These techniques can be costly, energy-intensive, and generate secondary pollutants. Therefore, there is an urgent need for alternative, cost-effective, and environmentally sustainable approaches to mitigate Cr pollution. Among the promising solutions, the utilization of waste materials for developing adsorbents has garnered significant attention. Waste rubber tires represent a particularly attractive raw material for the development of AC. Globally, the discarding of waste tires is a big atmospheric problem, with millions of tons being generated annually. These tires, composed of vulcanized rubber, have a complex polymer matrix that provides a robust structure and high surface area when converted into activated carbon. The process of pyrolysis followed by chemical activation can transform waste rubber tires into highly effective adsorbents with excellent adsorption properties [2].

AC produced from waste tires has gained notice because of its high surface area, porosity, and adsorption capabilities. Han et al. [3] highlighted that the pyrolysis and activation of waste tires create a porous structure, enhancing the material's capacity to adsorb heavy metals. San Miguel et al. (2002) observed that the C derived from waste tires exhibited excellent adsorption properties because of their favourable pore size distribution and high specific s/f area. Few investigations described the effectiveness of tire-derived activated carbon in removing various heavy metals from aqueous solutions. Singh [4] showed that modified tire powder could efficiently adsorb lead and cadmium, with removal efficiencies reaching up to 95%. Wang [5] reported that the capacity of adsorption of lead ions using used black tea leaves was better than that of waste tire-derived AC,

suggesting its potential for heavy metal removal. The specific application of waste tire-derived AC for chromium removal has been explored less but has shown promising results. According to Gupta et al. [6], tire-derived AC exhibited substantial adsorption capacities for various pollutants, including chromium. This finding is supported by Bithi et al. [7], who reported significant chromium removal efficiencies using AC derived from agricultural wastes, indicating similar potential for tire-derived C. The efficiency of adsorption processes can be significantly influenced by factors such as contact time, adsorbent dosage, pH, and temperature. Esmaeili and Khoshnevisan [8] emphasized the importance of optimizing these parameters to maximize the withdrawal ability of heavy metals. Contact time is a critical factor in adsorption studies. Elkhaleefa et al. [9] reported that longer contact times generally enhance the adsorption efficiency until equilibrium is reached. The amount of adsorbent used is an important aspect of the adsorption capacity. Zhaimee et al. [10] found that increasing the adsorbent dosage improved the withdrawal efficiency. Studies by Zeng et al. [11] demonstrated that the removal efficiency of heavy metals, including chromium, is highly pH-dependent. Temperature can influence the adsorption process by affecting the kinetic energy of the adsorbate molecules and the adsorbent s/f characteristics.

Sultana et al. [12] observed that lower temperatures favoured the adsorption of heavy metals onto AC. When compared to conventional adsorbents like AC from coal or coconut shell, waste tire-derived activated carbon offers comparable or superior adsorption capacities. Shahorokhi [13] reported that tire-derived AC showed similar performance in removing organic and inorganic contaminants. This suggests that waste tire-derived C is a viable alternative to more traditional adsorbents, particularly considering its cost-effectiveness and environmental benefits.

Gregorio et al. [14] emphasized the dual benefits of waste reduction and pollutant removal, which is a significant advantage over conventional methods that often involve higher costs and complex procedures. These include the standardization of the activation process to ensure consistent quality and performance of the adsorbent. The review of the literature demonstrates that waste tire-derived AC is an effective and sustainable adsorbent for the taking away of chromium. By optimizing adsorption conditions, significant removal efficiencies can be achieved, making it a viable alternative to conventional adsorbents.

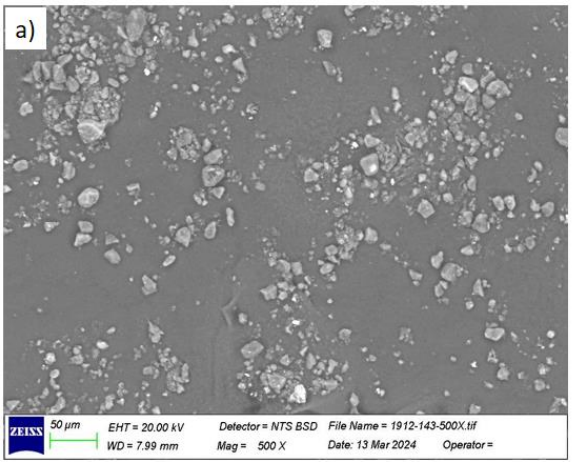
The aim is to investigate the efficacy of AC derived from waste rubber tires in the taking away of Cr from water. By optimizing key factors such as adsorbent dosage, temperature, pH, and contact time, this study aims to enhance the adsorption process and establish waste tire-derived activated carbon as a viable and sustainable solution for chromium remediation in water treatment systems.

2. Materials and Methods

2.1. Materials

Waste rubber tires were collected at local recycling facilities in Nagpur, INDIA. These tires were thoroughly cleaned to remove any dirt, debris, or external contaminants before further processing. This step ensured that no external impurities would interfere with the activation and adsorption processes. The primary chemicals and reagents used in this study included potassium dichromate (K2Cr2O7) for preparing stock solutions of hexavalent chromium (Cr(VI)), HCl, and NaOH for pH, and deionized water for all solution preparations and experimental procedures. Zinc chloride (ZnCl2) and phosphoric acid (H3PO4) were used for the activation of carbon.

2.2. Preparation of AC



(a)

Element	Weight %	Automatic %
C	81.34	89.26
O	8.57	7.06
Al	0.52	0.25
Si	3.41	1.60
S	2.58	1.06
Ca	0.39	0.13
Zn	3.19	0.64

(b)

Fig. 1 (a) SEM micrograph of waste tire particle, (b) EDX analysis of waste tire particle

The cleaned waste rubber tires were fragmented into little pieces approximately 0.04 to 0.6 mm in diameter. These pieces were sent to pyrolysis in a furnace at 500°C (2 hours) under a nitrogen atmosphere to ensure complete carbonization of the rubber material. The pyrolysis process converts the rubber into a carbonaceous material suitable for activation. The carbonized tire material underwent chemical activation to enhance its surface area and porosity. Two activation methods were employed: ZnCl2 activation and

H3PO4 activation. For ZnCl2 activation, the carbonized material was soaked in a 1:1 weight ratio of zinc chloride solution for 24 hours, dried at 105°C for 12 hrs, and activated at 800°C for 2 hrs in a nitrogen atmosphere. For H3PO4 activation, the carbonized material was similarly treated with a phosphoric acid solution, dried, and activated under the same conditions. After activation, the samples were washed thoroughly with deionized water to withdraw any residual activating agents, dried at 105°C, and ground into fine AC powder. The s/f morphology of the AC was examined using SEM. SEM images (Figure 1) helped visualize the surface structure and porosity, confirming the effectiveness of the activation process.

2.3. Batch Adsorption Studies

A Cr(VI) was made by disintegrating potassium dichromate (K2Cr2O7) in deionized water. Batch adsorption trials were performed to study the effect of time of contact on chromium removal. In these experiments, 100 mL of 10 mg/L Cr(VI) solution was mixed with 1 g of activated carbon in a 250 mL Erlenmeyer flask. The flasks were agitated on an orbital shaker at 150 rpm and 25°C. Samples were taken at intervals ranging from 10 to 70 minutes, and the Cr concentration was measured using a UV-Vis spectrophotometer at 540 nm. The influence of adsorbent dosage on chromium removal was studied by varying the quantity of activated carbon from 10 to 40 g/L while maintaining the initial Cr concentration at 10 mg/L. These experiments were conducted at 25°C with a contact time of 60 minutes to determine the optimum adsorbent dosage. The effect of pH on Cr(VI) adsorption was investigated by changing the pH of the 10 mg/L Cr(VI) solution to values ranging from 1 to 10 using 0.1 M HCl or 0.1 M NaOH. The adsorption trials were executed with 1 g of activated carbon at 25°C for 60 minutes to identify the optimal pH for maximum chromium removal. To check the effect of temp on Cr(VI) adsorption, batch experiments were carried out at various temp (25, 35, and 45°C) with a fixed initial Cr(VI) concentration of 10 mg/L and 1 g of activated carbon. The contact time was set to 60 minutes to evaluate the adsorption efficiency at varying temperatures.

2.4. Statistical Analysis

All trial information was statistically studied using standard deviation and error analysis to check the reliability and accuracy of findings. Statistical software is utilized to perform regression analysis and to fit the adsorption models, providing a comprehensive understanding of the adsorption process dynamics.

3. Results

3.1. Contact Time Effect

The time of contact effect on the adsorption of Cr(VI) by the activated carbon was investigated, and the findings are summarized in Table 1 and depicted in Figure 2. The adsorption experiments were conducted with a beginning Cr content of 20 mg/L, an adsorbent mass of 15 g/L, at a pH of 3, constant temp. of 25°C.

Table 1. Contact time effect on chromium removal

Sr. No.	Adsorbent dose g/L	Time in minutes	Initial conc. of Chromium mg/L	Chromium (IV) removed mg/L from contaminated water	% of Chromium removed	pH	Temp. (°C)
1	15	10	20	6.2	62	3	25
2	15	15	20	6.5	65	3	25
3	15	20	20	6.9	69	3	25
4	15	25	20	7.8	78	3	25
5	15	30	20	9.1	91	3	25
6	15	35	20	9.7	97	3	25

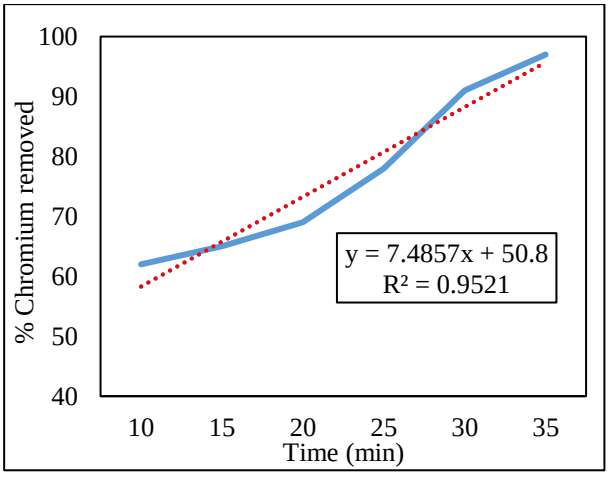


Fig. 2 Contact time effect on chromium removal

From the information available in Figure 2 and Table 1, it is seen that the percentage of Cr removal rises with a rise in contact time. At an initial contact time of 10 minutes, 62% of Cr was removed, which corresponds to 6.2 mg/L of chromium being adsorbed. As the contact time increased, the removal efficiency improved significantly. At 15 minutes, the removal efficiency was 65% (6.5 mg/L), and this trend continued to rise as the contact time extended. Notably, at 25 minutes, the adsorption reached 78%, indicating that 7.8 mg/L of Cr was removed from the solution. A substantial increase was observed at 30 minutes, with a removal efficiency of 91% (9.1 mg/L). The maximum takeaway of 97% (9.7 mg/L) was obtained at 35 minutes, suggesting that the system was approaching equilibrium.

The graphical representation (Figure 2) shows the trend of chromium removal percentage with respect to time. The data points fit a linear regression model with the Equation:

$$y=7.4857x+50.8 \quad (1)$$

Where y is the percentage of chromium removed, and x is the time in minutes. The R^2 for the model is 0.9521, showing a good fit of the model to experimental data.

The increase in adsorption capacity with contact time can be attributed to the presence of more active locations on the adsorbent surface for the binding of Cr. Initially, the adsorption rate is high because of the high mass gradient between the Cr in the solution and the adsorbent surface. As time progresses, the adsorption sites become occupied, and the rate of adsorption slows down as the system nears equilibrium. The findings show that the adsorption of Cr onto AC is time-dependent, with significant removal observed within the first 35 minutes of contact. This finding underscores the effectiveness of waste tire-derived activated carbon in rapidly adsorbing chromium from aqueous solutions, making it a viable option for practical wastewater treatment applications.

3.2. Effect of Adsorbent Dose

The research investigates the impact of adsorbent amount on the takeaway efficiency of chromium from contaminated water. The initial mass of chromium in the contaminated water was retained constant at 20 mg/L, while the adsorbent dose was fixed at 15 g/L. The last mass of chromium in the water, the amount of chromium removed, and the percentage of chromium removal were set and summarized in Table 2.

From Table 2, it is evident that as the last mass of chromium in contaminated water decreases, the percentage of chromium removed increases. At an adsorbent amount of 15 g/L, the percentage of Cr removed ranged from 93% to 99.99%. This indicates a significant removal efficiency even at a fixed adsorbent dose, demonstrating the effectiveness of the adsorbent material used.

Table 2. Chromium removal efficiency at various initial concentrations

Sr. No.	Adsorbent Dose g/L	Initial conc. of Chromium mg/L	Final Concentration of Chromium (mg/L)	Chromium Removed (mg)	% of Chromium Removed
1	15	20	1.5	8.5	93
2	15	20	1	9.5	95
3	15	20	0.5	9.95	99
4	15	20	0.07	9.97	99.1
5	15	20	0.05	9.995	99.95
6	15	20	0.008	9.999	99.99

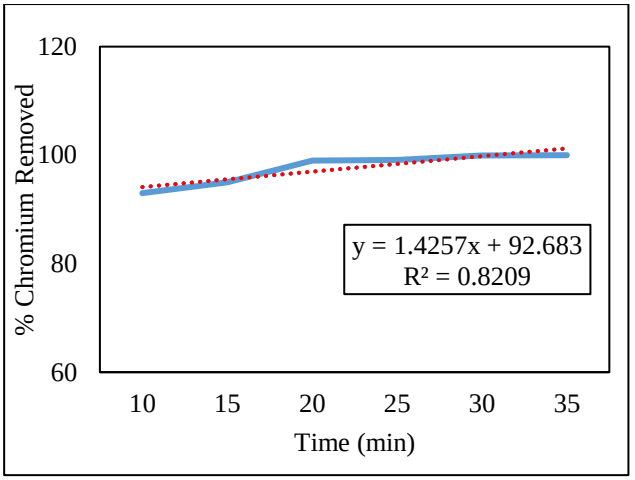


Fig. 3 Adsorbent dose effect on chromium removal

The graphical representation (Figure 3) shows the trend of chromium removal percentage with respect to time. The data points fit a linear regression model with the Equation:

$$y=1.4257x+92.683 \quad (2)$$

Where y is the percentage of chromium removed, and x is the time in minutes. The R^2 for the model is 0.8209, showing a good fit of the model to experimental data.

The graph illustrates a steady increase in chromium removal percentage over time, stabilizing at higher removal efficiencies as time progresses.

The results demonstrate that the adsorbent dose of 15 g/L is highly effective in removing chromium from contaminated water, achieving near-complete removal (up to 99.99%) under the conditions tested.

The study confirms the adsorbent's capacity to reduce chromium levels significantly, an important aspect of water treatment processes.

3.3. Effect of Temperature on the Removal of Chromium

This study investigated the outcome of temp on the removal efficiency of Cr from an aqueous solution. The starting mass of Cr is sustained at 20 mg/L, and the removal process was observed over a temp span of 25°C to 45°C, with a constant contact time of 25 minutes and pH values varying between 3.1 and 3.7. At 25°C, the removal efficiency was highest at 88.50%. As temp raised to 30°C, the removal efficiency reduced to 78.30%.

More distinct, raising the temp to 35°C developed a removal efficiency of 75.10%. At 40°C, the removal efficiency dropped to 70.40%. The lowest removal efficiency of 69.52% was observed at 45°C.

Table 3. Effect of temperature on chromium removal

Sr. No.	Temperature	Initial conc. of Chromium mg/L	% of chromium removed	Times in minutes	pH
1	25	20	88.5	25	3.7
2	30	20	78.3	25	3.4
3	35	20	75.1	25	3.1
4	40	20	70.40	25	3.3
5	45	20	69.52	25	3.1

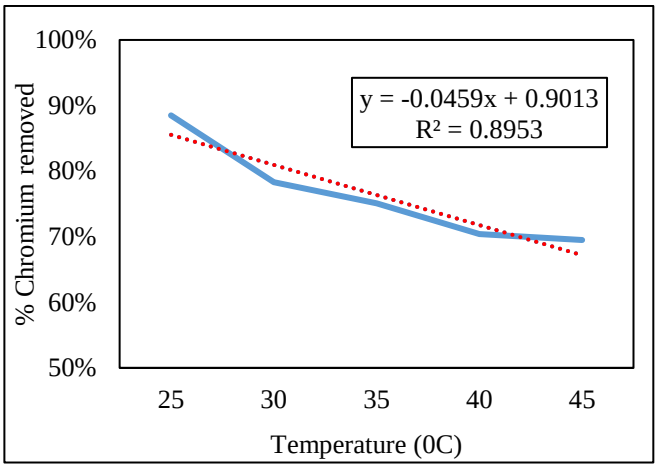


Fig. 4 Effect of temperature

The information demonstrates a clear trend where the withdrawal ability of Cr decreases with the rise in temp. This inverse relationship is depicted in the figure 4, with a regression (liner) model fitted to the information, yielding an Equation (2) and an R2 value of 0.8953, indicating a strong negative correlation. Previous studies have shown varying effects of temp on the takeaway efficiency of heavy metals, including Cr. For instance, Nagpal et al. [15] reported that a rise in temp from 20°C to 50°C ended in a slight decrease in Cr(VI) removal efficiency, from 82% to 75%, over a similar contact time and initial concentration. Another study by Kamarden et al. [16] found take away reduced from 85% to 70% when the temp rose from 25°C to 45°C.

$$y = (-0.0459x)+0.9013 \quad (3)$$

The more take away ability at lower temperatures can be set to the reduced kinetic energy of Cr(VI) ions, leading to increased adsorption onto the removal medium. Additionally, the pH values maintained in this study (ranging from 3.1 to 3.7) might have optimized the removal process, as the pH plays a crucial role in the adsorption. The study demonstrates that lower temperatures are more favorable for the takeaway of Cr from aqueous solutions, achieving a maximum removal efficiency of 88.50% at 25°C. These results are promising and indicate a more efficient removal process compared to previous studies, thus contributing valuable insights into optimizing the temperature conditions for effective Cr(VI) removal.

3.4. pH Analysis

pH effect on the takeaway ability of Chromium (VI) was researched by varying the pH from 3.0 to 4.0 while carrying other parameters constant. The starting mass of Chromium (VI) was kept at a consistent level, and the removal process was analyzed across different pH values. At a pH of 3.0, the removal efficiency of Chromium (VI) reached its peak at 99.99%. When the pH was increased to 3.2, the removal efficiency experienced a slight decline to 99.50%. As the pH was further increased to 3.5, the removal efficiency decreased to 98.50%. The lowest removal efficiency, recorded at 97.00%, occurred at a pH of 4.0.

The data indicates a clear trend where the takeaway ability of Chromium (VI) decreases as the pH increases. This trend is illustrated in the figure 5, with a linear regression model fitted to the information, yielding Equation (4) and an R2 value of 0.9512, indicating a strong negative correlation.

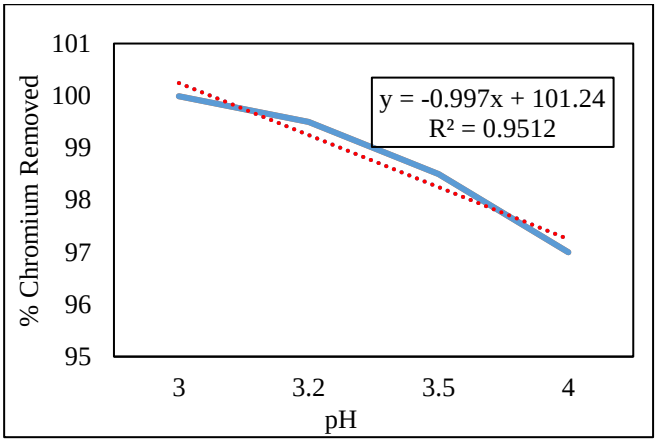


Fig. 5 Effect of pH

$$y=(-0.997x)-101.24 \quad (4)$$

Previous studies have shown that pH is a critical factor for the withdrawal of heavy metals, including Cr. Bayuo [17] revealed that the removal efficiency of Chromium (VI) reduced from 97% to 96% when the pH was raised from 3.0 to 4.0. Another study by Ali et al. [18] found a similar trend, where the removal efficiency decreased from 99% to 97% over the same pH range. The higher takeaway ability at lower pH levels can be attributed to the increased protonation of the adsorbent s/f, which enhances the appeal between the Cr ions and the positively charged adsorbent sites. Additionally, optimized pH values maintained in this study likely facilitated the maximum adsorption capacity.

4. Discussion

The findings of this research demonstrate the efficacy of AC derived from waste rubber tires in removing Cr from contaminated water. The adsorption process is established to be highly time-dependent, with a significant increase in chromium removal observed within the first 35 minutes, achieving a maximum removal efficiency of 97%. This rapid adsorption can be attributed to the high presence of active locations on the adsorbent s/f, which become occupied over time, slowing down the rate as equilibrium is approached. This aligns with existing studies, such as those by Kong et al. [19], highlighting the effective removal of heavy metals using activated carbon under optimal conditions. Moreover, the adsorbent dose of 15 g/L proved to be highly effective, achieving near-complete removal (up to 99.99%) of chromium from the aqueous solution. This finding is consistent with previous research by Badran et al.[20], emphasizing that an increase in adsorbent dose enhances takeaway ability because of the greater surface area and more available adsorption locations. However, the study observed a plateau in efficiency beyond the optimal dose, a common phenomenon in adsorption studies. The study also revealed an inverse relationship between temperature and Cr(VI) removal efficiency, indicating an exothermic adsorption process. The highest takeaway ability was observed at 25°C, with efficiency decreasing at higher temperatures. This is in line with Nasseh et al, who found similar trends, suggesting that lower temperatures favor the adsorption process by reducing the kinetic energy of Cr(VI) ions, enhancing their adsorption onto the activated carbon. Additionally, lower pH levels significantly improved removal efficiency, achieving optimal results at pH 3.0, as protonation of the adsorbent surface increases attraction between Cr(VI) ions and adsorption sites.

5. Conclusion

This study demonstrates the significant potential of AC derived from waste rubber tires for the effective withdrawal of Cr from contaminated water. The results show that the adsorption process is highly efficient, with maximum removal efficiencies reaching up to 97% within 35 minutes of contact time. The adsorbent showed substantial performance across various parameters, including adsorbent dose, temperature, and pH, confirming its robustness and versatility. Notably, the adsorption process was found to be time-dependent, with optimal performance at lower temperatures and acidic pH levels, which are critical for maximizing the removal efficiency.

Overall, the usage of waste tire-derived AC presents a sustainable and cost-effective alternative for water treatment, addressing both environmental pollution and waste management challenges. This approach not only enhances the adsorption of heavy metals like chromium but also promotes the recycling of waste materials, contributing to a circular economy. Future research should focus on optimizing the operational parameters and exploring the regeneration capabilities of the adsorbent to ensure its practical feasibility for large-scale usage.

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