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The Effect Of Citric Acid (*Acidum Citricum*) Addition on Chromium (Cr) Levels in Wastewater

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ABSTRACT

Chromium (Cr) is a heavy metal that contaminates the environment and poses severe risks to human health. Using citric acid as an eco-friendly complexing agent is a potential method to reduce chromium levels. Objective: This study aimed to determine the effect of varying citric acid concentrations on chromium (Cr) levels in wastewater. Research Method: A true experimental laboratory study with a post-test only control group design was conducted. Treatments consisted of a control group (0%), and citric acid concentrations of 0.5%, 1%, and 1.5% (w/v) with a contact time of 40 minutes and six replications each. Chromium levels were measured using a UV-Vis spectrophotometer at a wavelength of 540 nm and calculated using a standard linear regression curve. Results: The mean remaining chromium concentrations for 0%, 0.5%, 1%, and 1.5% treatments were 0.4803 ± 0.0086 mg/L, 0.1952 ± 0.0287 mg/L, 0.1916 ± 0.0162 mg/L, and 0.1890 ± 0.0145 mg/L, respectively. Statistical testing using the Kruskal-Wallis test yielded an Asymp. Sig. value of 0.631 ($p > 0.05$). Conclusions: Descriptive results indicate that citric acid addition reduces chromium levels, with the lowest remaining chromium observed at 1.5% concentration. However, increasing the concentration from 0.5% to 1.5% did not yield a statistically significant difference in percentage reduction.

INTRODUCTION

Water is an essential natural resource for human life and aquatic ecosystems. However, rapid industrialization, domestic practices, and mining activities have led to escalating water pollution. Heavy metals, such as lead (Pb), mercury (Hg), cadmium (Cd), and chromium (Cr), represent major aquatic pollutants due to their non-biodegradable nature, high toxicity, and tendency to bioaccumulate within food chains (Affifudin et al., 2023). Industrial effluents from electroplating, leather tanning, textile manufacturing, and metal fabrication frequently discharge chromium into environmental waters (Xie, 2024). Hexavalent chromium, Cr(VI), is particularly hazardous owing to its high solubility, mobility, strong oxidizing capacity, and carcinogenic effects on human biology (Worku et al., 2023). Chronic exposure leads to severe health consequences including skin damage, tubular renal necrosis, hepatic dysfunction, and respiratory malignancies (Jaishankar et al., 2014). Consequently, regulatory bodies limit total chromium in drinking water to 0.05 mg/L (Ministry of Health RI No. 492/2010).

Recent studies have explored diverse treatment methodologies to remove heavy metals from wastewater, including chemical precipitation, membrane filtration, ion exchange, and adsorption (Fu & Wang, 2011). Among these, organic chelating agents like citric acid have

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gained interest due to their eco-friendly, non-toxic, biodegradable nature and carboxyl functional groups capable of forming stable metal-ligand complexes (Qu et al., 2019). Prior research demonstrates that citric acid effectively mobilizes and chelates metal ions, thereby altering their speciation and facilitating precipitation or adsorption processes (Sari et al., 2018; Prasetyo & Lestari, 2020).

Despite existing remediation studies, there remains a need to establish specific operational parameters regarding how low-concentration organic acid additions affect chromium removal in domestic river systems spiked with Cr(VI) under controlled contact times. This study addresses this gap by investigating the impact of varying citric acid concentrations (0.5%, 1%, and 1.5% w/v) at a fixed 40-minute contact time on chromium levels in wastewater. It is hypothesized that adding citric acid significantly reduces chromium concentration in contaminated water.

MATERIALS/METHOD

Research Design and Sampling:
A True Experimental study using a Posttest-Only Control Group Design was employed. Grab sampling was used to collect river water samples in Mataram, which were spiked with 100 ppm Cr(VI) standard solution for 24 hours to simulate industrial wastewater. Based on Federer's formula $(t-1)(r-1) \geq 15$, four treatments ($t=4$) with six replications ($r=6$) yielded a total of 24 experimental units.

The treatments consisted of:

- **P0 (Control):** Wastewater + 0% citric acid (distilled water)
- **P1:** Wastewater + 0.5% (w/v) citric acid solution
- **P2:** Wastewater + 1.0% (w/v) citric acid solution
- **P3:** Wastewater + 1.5% (w/v) citric acid solution

For each unit, 10 mL of wastewater was mixed with 50 mL of the respective citric acid solution. A Jar Test apparatus was used for the coagulation process: rapid mixing at 100–150 rpm for 1–3 minutes, slow mixing (flocculation) at 30–60 rpm for 15–20 minutes, followed by sedimentation for 30–60 minutes. Supernatants were filtered through filter paper for chemical measurement.

Chromium Analysis:
Chromium concentrations before and after treatment were determined via UV-Vis Spectrophotometry using 1,5-diphenylcarbazide (DPC) as a chromogenic reagent. Absorbance was read at an optimum wavelength of 540 nm. Sample concentrations (x) were calculated using the standard calibration curve equation $y = ax + b$.

RESULTS AND DISCUSSION

Standard Calibration Curve and Initial Chromium Levels
The standard calibration curve yielded a linear regression equation of $y = 1.9487x - 0.2721$ with a coefficient of determination $R^2 = 0.901$. Initial chromium testing across six baseline

samples indicated an initial mean Cr concentration of 0.4803 ± 0.0086 mg/L (ranging from 0.4738 to 0.4844 mg/L).

Table 1. *Chromium Reduction at Various Citric Acid Concentrations*

Treatment	Concentration (w/v)	Contact Time	Mean Final Cr (mg/L)	Standard Deviation
P0 (Control)	0%	40 min	0.4803	0.0086
P1	0.5%	40 min	0.1952	0.0287
P2	1.0%	40 min	0.1916	0.0162
P3	1.5%	40 min	0.1890	0.0145

Effects of Citric Acid Addition:

As detailed in Table 1, adding citric acid led to a clear descriptive reduction in remaining chromium levels compared to the untreated control group (0.4803 mg/L). Addition of 0.5% citric acid reduced the mean Cr level to 0.1952 mg/L. Increasing the concentration to 1.0% and 1.5% further reduced the mean Cr levels to 0.1916 mg/L and 0.1890 mg/L, respectively. The 1.5% citric acid treatment produced the lowest remaining chromium concentration after 40 minutes of contact time.

This trend occurs because higher concentrations of citric acid supply more carboxyl groups (-COOH), increasing complexation capacity with heavy metal ions in aqueous solution. Citric acid acts as a chelating agent, forming stable complexes with Cr ions, thereby lowering free soluble chromium concentrations. These observations align with Wang et al. (2023) and Tan et al. (2022), who highlighted the chelating efficiency of low-molecular-weight organic acids during heavy metal remediation.

Statistical Analysis:

Data normality was evaluated using the Shapiro-Wilk test. The 1% concentration group violated the assumption of normal distribution ($p = 0.033 < 0.05$). Although Levene's test confirmed homogeneity of variance ($p = 0.169 > 0.05$), the non-normality required the use of the non-parametric Kruskal-Wallis test.

The Kruskal-Wallis test yielded $X^2 = 0.920$, $df = 2$, and an Asymp.Sig. = 0.631 ($p > 0.05$). Because $p > 0.05$, the null hypothesis (H_0) was accepted, indicating no statistically significant difference in chromium reduction percentage between the 0.5%, 1.0%, and 1.5% citric acid treatments.

While citric acid successfully lowered chromium concentrations from initial levels, increasing the dose within the 0.5%–1.5% range did not produce statistically significant incremental gains. Furthermore, the minimum achieved chromium level (0.1890 mg/L) remains above the regulatory drinking water standard of 0.05 mg/L. This indicates that while citric acid exhibits promising chelating potential, its application at these parameters should be paired with additional treatment stages (e.g., extended contact time, pH adjustment, or secondary bio-adsorbents) to achieve compliance with environmental discharge thresholds

CONCLUSIONS

Initial chromium levels in the evaluated wastewater averaged 0.4803 ± 0.0086 mg/L. Addition of citric acid at concentrations of 0.5%, 1%, and 1.5% reduced chromium levels to 0.1952 mg/L, 0.1916 mg/L, and 0.1890 mg/L, respectively. Although 1.5% citric acid achieved the maximum descriptive reduction, Kruskal-Wallis statistical analysis showed no significant difference among the 0.5%, 1%, and 1.5% treatment groups ($p = 0.631$). Future studies are recommended to investigate broader concentration ranges, varied pH conditions, and longer contact times to optimize chromium removal efficiency.

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