



## Preconcentration of Cr (VI) Using Ca-Alginate-EDTA Microcapsules in a Column System for UV-Vis Spectrophotometric Analysis

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**Abstract.** This study introduces optimized Ca-Alg-EDTA microcapsules specifically designed as a high-performance column filler for the preconcentration and sensitive detection of toxic Cr(VI) in aquatic systems. Monitoring Cr(VI) at trace levels is critical due to its high toxicity and environmental persistence. Unlike previous alginate-based sorbents, this work focuses on a synergistic EDTA integration within a column-switching framework to enhance retention efficiency (74.73 %) and capacity (0.3995 mg/g). Analytical validation using UV-Vis spectrophotometry demonstrated excellent linearity ( $R^2 = 0.9995$ ) with a low detection limit of 0.014 mg/L, ensuring reliability for samples with minimal analyte concentrations. The method's robustness was confirmed through Mahakam River water analysis, yielding a 93.05 % recovery in compliance with AOAC 2002 standards. This optimized microencapsulation approach provides a cost-effective and sustainable solution for routine environmental monitoring of heavy metal contamination.

**Keywords:** Ca-Alg-EDTA, Cr(VI), microcapsules, preconcentration, UV-Vis Spectrophotometry

**Abstrak.** Penelitian ini memperkenalkan mikrokapsul Ca-Alg-EDTA teroptimasi yang dirancang khusus sebagai pengisi kolom berkinerja tinggi untuk prakonsentrasi dan deteksi sensitif Cr(VI) yang beracun dalam sistem perairan. Pemantauan Cr(VI) pada level runtu sangat krusial karena toksisitasnya yang tinggi dan persistensinya di lingkungan. Berbeda dengan sorben berbasis alginat sebelumnya, penelitian ini berfokus pada integrasi sinergis EDTA dalam kerangka sistem kolom untuk meningkatkan efisiensi retensi (74,73 %) dan kapasitas (0,3995 mg/g). Validasi analitik menggunakan spektrofotometri UV-Vis menunjukkan linearitas yang sangat baik ( $R^2 = 0,9995$ ) dengan limit deteksi rendah sebesar 0.014 mg/L, memastikan keandalan untuk sampel dengan konsentrasi analit minimal. Ketangguhan metode ini dikonfirmasi melalui analisis air Sungai Mahakam, menghasilkan perolehan kembali sebesar 93,05 % yang sesuai dengan standar AOAC 2002. Pendekatan mikrokapsul teroptimasi ini memberikan solusi yang hemat biaya dan berkelanjutan untuk pemantauan rutin kontaminasi logam berat di lingkungan.

**Kata kunci:** Ca-Alg-EDTA, Cr(VI), mikrokapsul, prakonsentrasi, spektrofotometri UV-Vis

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### INTRODUCTION

Chromium exists primarily as trivalent Cr(III) and the highly toxic, carcinogenic hexavalent Cr(VI). Monitoring Cr(VI) at

ultratrace levels (0.1 – 0.5  $\mu\text{g/L}$ ) is challenging as it often falls below the detection limits of standard UV-Vis spectrophotometry. Thus, an efficient preconcentration step is essential to enhance sensitivity and minimize matrix

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interferences (Makosim et al., 2020; Pratiwi et al., 2020).

Among various techniques, column-based solid-phase extraction using biopolymer sorbents is preferred for its low cost and high recovery. Recent studies highlight that chemically functionalized alginate-based hydrogels are leading sustainable materials for heavy metal adsorption due to their tunable porosity and high site density (He et al., 2024). While alginate forms stable, non-toxic Ca-alginate gels, its pristine form lacks sufficient selectivity (Indriyani et al., 2023). Modification using chelating agents like EDTA (Ethylenediaminetetraacetic acid) is a promising strategy, as EDTA introduces powerful polydentate ligands that form stable complexes with metal ions within the alginate matrix (Wang et al., 2019).

Previous research has utilized modified Ca-alginate for capturing metals such as Cd, Mn, Cu, and Pb (Sari et al., 2016; Yantiana et al., 2018). Specifically, magnetite-alginate (MNPs-ALG) microcapsules have shown significant potential for Cu(II) analysis, proving that functionalized alginate can enhance analytical performance (Lianasari et al., 2024). However, a research gap remains regarding the synergistic effect of Ca-Alg-EDTA for Cr(VI) preconcentration in continuous column systems. Most Cr(VI) studies rely on expensive resins or acid-activated alumina (Panggabean et al., 2014), which lack the sustainability of microencapsulated biopolymers. Furthermore, specialized chelating resins remain a key strategy for flow-based trace metal analysis in river water (Amran et al., 2011).

This study introduces an optimized synthesis of Ca-Alg-EDTA microcapsules designed as a high-performance column filler.

The novelty of this work lies in the systematic validation of this hybrid material, which addresses the sensitivity gap of UV-Vis spectrophotometry for trace Cr(VI) analysis. By evaluating the retention capacity and applying the method to Mahakam River water samples, this research provides a robust and eco-friendly framework for routine environmental monitoring of toxic chromium.

## MATERIALS AND METHODS

### Materials

The chemicals used were of analytical grade, including  $K_2Cr_2O_7$ , 1,5-diphenylcarbazide (DPC),  $CaCl_2$ , sodium alginate, EDTA, HCl,  $H_3PO_4$ ,  $H_2SO_4$ , acetone, and deionized water. Real samples were collected from the Mahakam River (Tenggarong Seberang).

### Instrumentation

Instrumentation included an Orion AquaMate 8100 UV-Vis Spectrophotometer for Cr(VI) quantification at  $\lambda_{max}$ , a Bruker Alpha II FT-IR for functional group characterization, and a specialized glass column system for preconcentration.

### Procedure

#### Preparation of standard Cr(VI)

A 100 mg/L stock solution was prepared from  $K_2Cr_2O_7$ . Working standards (0.01 – 0.5 mg/L) were prepared by serial dilution.

#### Preparation of colorimetric reagent

0.5% 1,5-diphenylcarbazide was dissolved in acetone.

#### pH Adjustment

All solutions were adjusted to pH  $2 \pm 0.5$  using  $H_2SO_4$  and  $H_3PO_4$  to facilitate the formation of the Cr(VI)-DPC complex.

Absorbance was measured after 5 – 10 minutes of color development.

### **Synthesis of Ca-Alg-EDTA microcapsules**

Microcapsules were synthesized via the extrusive dripping method. Sodium alginate solution (0.5 – 3%) was mixed with varying masses of EDTA (0.5 – 3 g). This mixture was added dropwise through a syringe into a  $\text{CaCl}_2$  solution (0.1 – 2 M) under constant magnetic stirring (300 rpm). The resulting beads were filtered and air-dried at a controlled room temperature for 48 hours to ensure consistency in particle size and porosity (Figure 1).



**Figure 1.** Ca-Alg-EDTA microcapsules

### **Preconcentration and column procedure**

A glass column (internal diameter: 1 cm) was packed with 0.3 g of optimized Ca-Alg-EDTA resin (bed height: approx. 1 cm). To investigate the preconcentration efficiency, 10 mL of 0.5 mg/L Cr(VI) was passed through the column at a controlled flow rate of 1.0 mL/min. The retained Cr(VI) was eluted using 0.1 M HCl. The effect of eluent volume (3 – 10 mL) and contact time (10 – 120 min) was systematically evaluated. After each cycle, the resin was washed with deionized water for regeneration and reusability tests.

### **Validation and statistical analysis**

The method was validated for linearity, Limit of Detection (LoD), and Limit of Quantitation (LoQ) based on the standard deviation of the intercept and the slope of the calibration curve. Precision was expressed as Relative Standard Deviation (% RSD) from ten replicates, while accuracy was evaluated through a spike-recovery test (0.5 mg/L addition) on Mahakam River samples, following AOAC 2002 benchmarks.

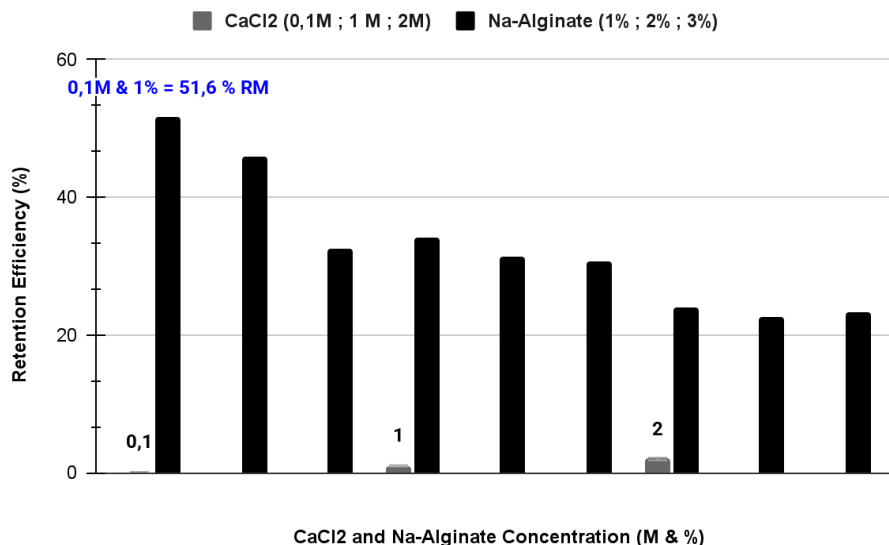
## **RESULTS AND DISCUSSION**

### **Optimization of Ca-Alg-EDTA Microcapsule Synthesis**

#### **Effect of varying $\text{CaCl}_2$ and Na-alginate concentrations**

The optimization of  $\text{CaCl}_2$  and Na-alginate concentrations was evaluated using a batch system to identify the most effective matrix for Cr(VI) retention (Figure 2). The highest retention efficiency (51.6 %) was achieved using a combination of 0.1 M  $\text{CaCl}_2$  and 1% Na-alginate.

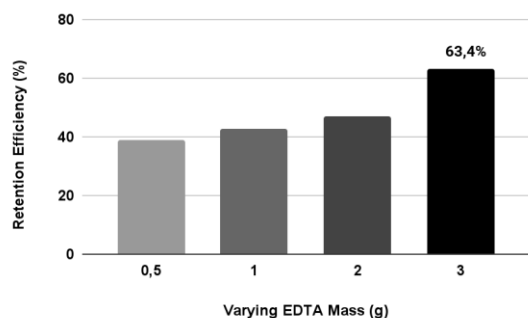
Statistically significant decreases in efficiency were observed as concentrations increased to 2 M  $\text{CaCl}_2$  and 3 % alginate. This phenomenon occurs because higher concentrations of  $\text{Ca}^{2+}$  and alginate increase the cross-linking density, creating a rigid and compact "egg-box" structure. Such high density restricts the internal diffusion of Cr(VI) ions into the microcapsule core, thereby reducing the available effective surface area (Indriyani et al., 2023; Wang et al., 2019). The 0.1 M/1 % combination was selected as it provided an optimal balance between structural stability and matrix porosity.



**Figure 2.** Effect of concentration variation on retention efficiency

### Effect of EDTA mass

The influence of EDTA mass on the retention efficiency of Cr(VI) is illustrated in Figure 3. The data shows a progressive increase in efficiency from 39.12 % (at 0.5 g EDTA) to a peak of 63.4 % (at 3 g EDTA).



**Figure 3.** Effect of varying EDTA mass on retention efficiency.

This linear enhancement is directly related to the density of active binding sites within the Ca-alginate matrix. This is consistent with the analytical performance observed in MNPs-ALG systems, where the integration of active components into the alginate structure leads to superior retention for heavy metal ions compared to pristine alginate (Lianasari, 2024).

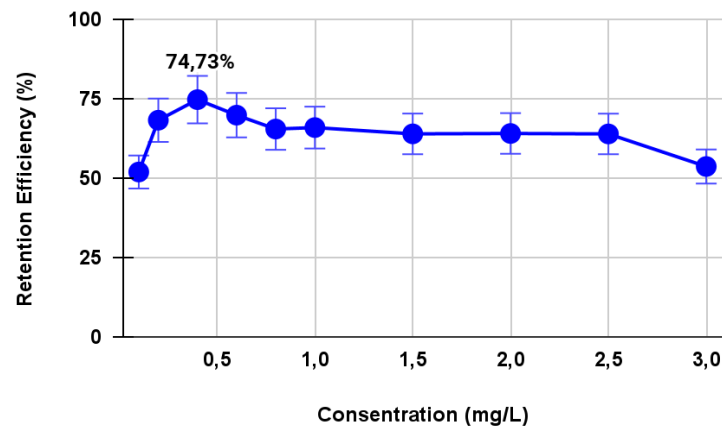
EDTA acts as a powerful hexadentate chelating agent, introducing additional carboxyl (-COOH) and amine (-NH<sub>2</sub>) groups into the polymer network. At a mass of 3 g, the ratio of EDTA to the alginate backbone provides the maximum availability of these functional groups, which effectively "trap" Cr(VI) ions through coordination bonding. The significant jump in efficiency at 3 g suggests that the microcapsules have reached an optimal surface-to-ligand ratio, allowing for better accessibility of the analyte to the internal pores of the resin. While higher masses might theoretically provide even more sites, 3 g was selected as the optimum to maintain the structural integrity of the microcapsule, as excessive EDTA can sometimes weaken the Ca-alginate cross-linking, leading to a more fragile gel (Pratiwi et al., 2020; Wang et al., 2019).

### Determination of Retention Efficiency and Capacity

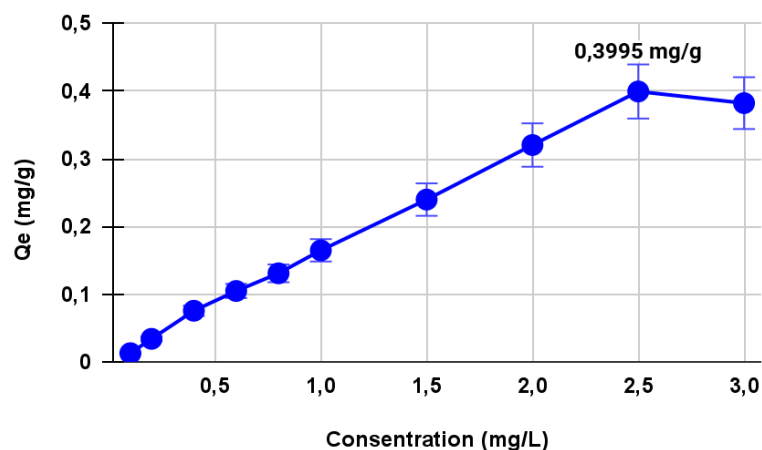
The adsorption performance of Ca-Alg-EDTA microcapsules across varying initial Cr(VI) concentrations is presented in Figures 4

and 5. The highest retention efficiency reached 74.73 % at an initial concentration of 0.4 mg/L, while the maximum retention capacity (q)

peaked at 0.3995 mg/g when the concentration was increased to 2.5 mg/L.



**Figure 4.** Effect of initial Cr(VI) concentration on the retention efficiency of Ca-Alg-EDTA microcapsules (n=3, pH  $2 \pm 0.5$ , contact time 24 h).



**Figure 5.** Effect of initial Cr(VI) concentration on the retention capacity of Ca-Alg-EDTA microcapsules (n=3, pH  $2 \pm 0.5$ , contact time 24 h).

As the concentration of Cr(VI) increases beyond 0.4 mg/L, the retention efficiency begins to decline despite the increase in the total mass of metal adsorbed per gram of resin (retention capacity). This plateau in capacity at 2.5 mg/L signifies a saturation point. Based on adsorption theory, this behavior indicates that the active functional groups on the surface and within the pores of the microcapsules have been fully occupied by Cr(VI) ions. Once these

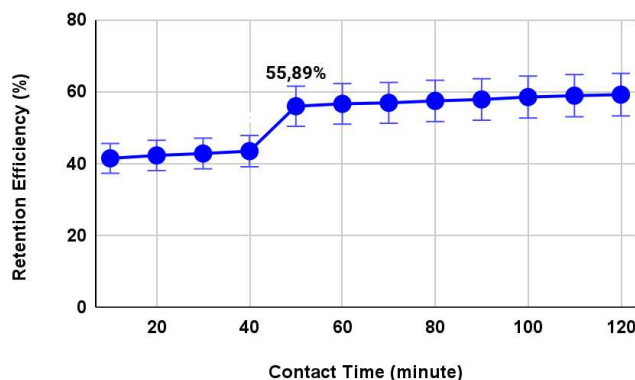
sites reach equilibrium, a "competitive effect" occurs among the remaining free ions in the solution, preventing further adsorption due to the limited number of specific coordination sites (Pratiwi et al., 2020; Wang et al., 2019). The steady capacity value at higher concentrations confirms that the Ca-Alg-EDTA matrix operates via a site-specific binding mechanism, which is ideal for preconcentration purposes where high selectivity at trace levels is required.

## Preconcentration Optimization in Column System

### Effect of contact time

The influence of contact time on Cr(VI) adsorption was evaluated to determine the

kinetic equilibrium within the column packing (Figure 6). The retention efficiency increased steadily and reached an optimum of 55.89 % at 50 minutes.



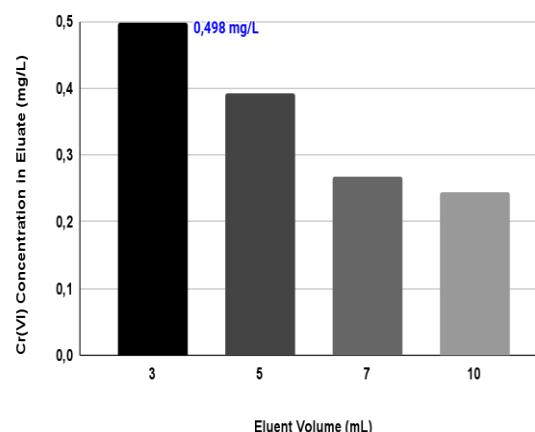
**Figure 6.** Effect of contact time

Mechanistically, this behavior is governed by mass transfer from the bulk solution to the surface of the Ca-Alg-EDTA microcapsules. During the initial stages (10 – 40 minutes), there is an abundance of vacant EDTA coordination sites, leading to a rapid uptake of Cr(VI). As time progresses to 50 minutes, the system approaches a breakthrough point where the rate of adsorption equals the rate of desorption, signifying that the active sites are nearing equilibrium. Beyond 60 minutes, the efficiency tends to stabilize, suggesting that the "mass transfer zone" has moved through the entire bed height of the column, and additional contact time no longer significantly improves retention (Pratiwi et al., 2020). This optimization strategy in column-packed systems is crucial to balance the interaction time and the flow rate, ensuring maximum uptake of metal ions as previously demonstrated in other preconcentration studies using inorganic-filled columns (Simanjuntak et al., 2020). This equilibrium behavior aligns with the fundamental mass transfer principles of alginate-based systems, where the rate-limiting

step transitions from surface diffusion to site saturation as the coordination capacity of the modified ligands is reached (He et al., 2024).

### Effect of eluent volume

The elution process is critical for the recovery of preconcentrated analytes. As shown in Figure 7, the optimum eluent volume was found to be 3 mL, yielding the highest concentration of 0.498 mg/L.



**Figure 7.** Effect of varying eluent volume

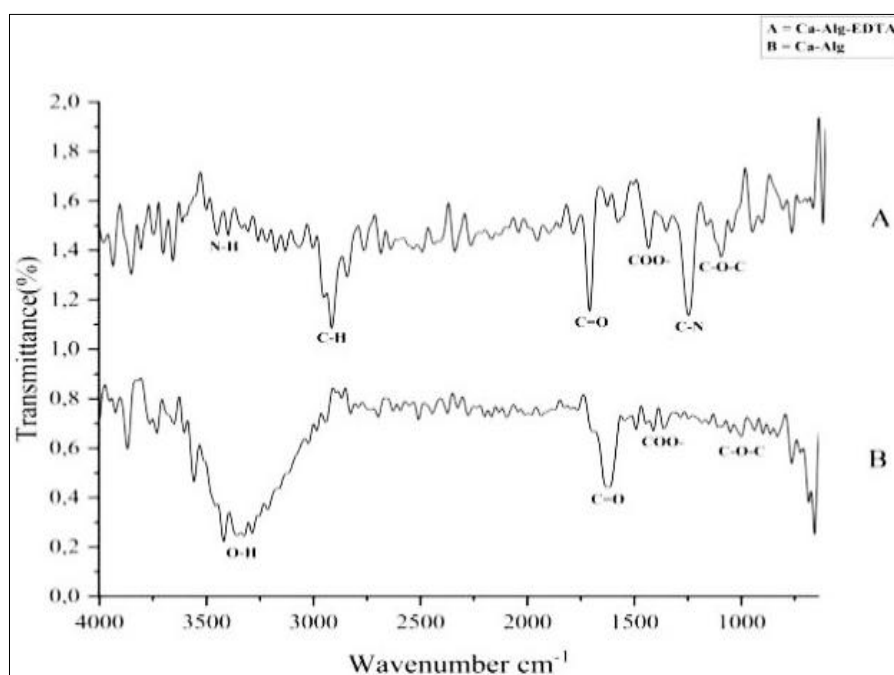
The use of 0.1 M HCl as an eluent promotes the desorption of Cr(VI) through a protonation mechanism. At low pH, the high concentration of H<sup>+</sup> ions competes with the metal ions for the binding sites on the EDTA ligands and the alginate carboxyl groups. The protonation of these functional groups weakens the coordination bonds, effectively releasing the Cr(VI) ions into the mobile phase (Panggabean et al., 2020). The choice of a small eluent volume 3 mL, is essential to achieve a high Preconcentration Factor (PF). According to Turan et al. (2022), an ideal elution process should recover the maximum amount of analyte in the smallest possible volume to ensure the highest sensitivity for subsequent detection by UV-Vis spectrophotometry. Increasing the eluent volume beyond 3 mL resulted in a decrease in the measured concentration due to the dilution effect, where the total mass of the desorbed metal is distributed across a larger volume of liquid (Wang et al., 2019; Pratiwi et al., 2020). This efficiency in using a small volume of eluent

underscores the cost-effectiveness and environmental friendliness of the Ca-Alg-EDTA system.

### Characterization Results using FT-IR Spectroscopy

The functional groups of Ca-Alg and Ca-Alg-EDTA microcapsules were identified using FT-IR spectroscopy to confirm the successful modification of the alginate matrix (Figure 8 and Table 1).

The FT-IR spectrum of Ca-Alg displays characteristic peaks at 3422.76 cm<sup>-1</sup> (O-H), 1613.18 cm<sup>-1</sup> (asymmetric COO<sup>-</sup> stretching), 1411.55 cm<sup>-1</sup> (symmetric COO<sup>-</sup> stretching), and 1003.54 cm<sup>-1</sup> (C-O-C glycosidic bond). These bands are consistent with the established structure of calcium-crosslinked alginate (Yantyana et al., 2018). The presence of these functional groups is typical for alginate biopolymers extracted from seaweed, which are characterized by a high density of carboxyl and hydroxyl sites as the primary points for metal binding (Kamisyah et al., 2020)



**Figure 8.** FT-IR characterization of (A) Ca-Alg microcapsules and (B) Ca-Alg-EDTA microcapsules

**Table 1.** Comparison of Ca-Alg and Ca-Alg-EDTA Microcapsule Spectra

Functional Group	Reference Wave Number Range (cm <sup>-1</sup> )	Literature	Identified Results	
			Ca-Alg	Ca-Alg-EDTA
O-H	3412.08	Yantiana <i>et al.</i> , 2018	3422.76	-
C=O	1608.63		1613.18	1733.02
C-O-C	1100-1000		1003.54	1013.84
COO-	1406.11	Wang <i>et al.</i> , 2019	1411.55	1463.07
C-H	2930		-	2926.14
N-H	3400-3300		-	3428.72
C-N	1300-1200		-	1273.49

Significant spectral shifts and new absorption bands were observed following the incorporation of EDTA. The emergence of a sharp peak at 1733.02 cm<sup>-1</sup> is attributed to the C=O stretching of the carboxylic acid or ester/amide groups from the EDTA molecule. The shift of the COO<sup>-</sup> band from 1411.55 cm<sup>-1</sup> to 1463.07 cm<sup>-1</sup> indicates a change in the chemical environment of the carboxylate groups, suggesting strong interaction or intercalation between the EDTA ligands and the alginate backbone (Wang et al., 2019). Furthermore, the disappearance of the broad O-H band and the appearance of a new band at 3428.72 cm<sup>-1</sup> (N-H stretching), coupled with the C-N stretching at 1273.49 cm<sup>-1</sup>, confirms the formation of amide linkages. This indicates that the amino groups of EDTA reacted with the carboxylate groups of the alginate via a condensation-like mechanism during the microencapsulation process. These spectral changes provide robust evidence for the successful synthesis of the Ca-Alg-EDTA hybrid material, where the EDTA ligands are not merely trapped but are chemically

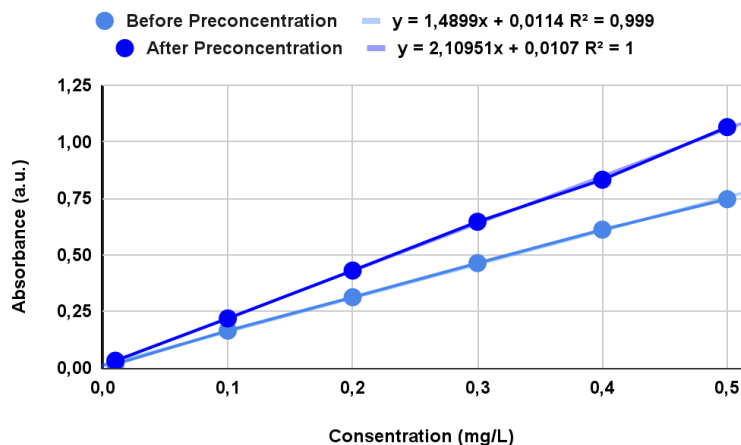
integrated into the polymer matrix, providing the necessary active sites for Cr(VI) chelation.

### Validation of Analytical Method

#### Linearity, LoD, and LoQ

The calibration curve for Cr(VI) quantification was established both before and after the preconcentration step (Figure 9). The linear range was observed between 0.01 and 0.5 mg/L. Before Preconcentration:  $y = 1.4899x + 0.0114$  ( $R^2 = 0.9993$ ) and After Preconcentration:  $y = 2.0951x + 0.0107$  ( $R^2 = 0.9995$ ).

The increase in the slope (sensitivity) after preconcentration demonstrates the effectiveness of the Ca-Alg-EDTA column in enriching the analyte. The  $R^2$  values exceeding 0.999 indicate excellent linearity according to Riyanto (2014). As shown in Table 2, the LoD was 0.014 mg/L, and the LoQ was 0.046 mg/L. These low values confirm that the method is sufficiently sensitive to monitor trace levels of Cr(VI) in environmental waters that typically fall below the direct detection limit of UV-Vis spectrophotometry.



**Figure 9.** Determination of Cr(VI) standard solution calibration curve

**Table 2.** LoD and LoQ test results

Calculation	Result
$\Sigma(y - y_i)^2$	$2,63 \cdot 10^{-4}$
Standard Deviation (SD)	$8,1 \cdot 10^{-3}$
LOD	0,014 mg/L
LOQ	0,046 mg/L

### Precision and accuracy

The precision was evaluated using the Relative Standard Deviation (%RSD) from ten replicates. As presented in Table 3, the % RSD values (0.096 % – 5.74 %) were all lower than

the Horwitz CV (predicted % RSD based on concentration). This indicates that the method is highly reproducible even at the lowest tested concentration (0.01 mg/L).

**Table 3.** Precision test results

Standard (mg/L)	$\bar{x}$	%RSD	Horwitz CV
0.01	$3.691 \cdot 10^{-3}$	5.74	6.22%
0.3	0.2617	0.29	5.22%
0.5	0.4912	0.096	5.13%

Horwitz CV represents the maximum allowable precision limit for a given concentration level; values below this limit indicate acceptable method reproducibility.

Accuracy was assessed through a spike-recovery test across three concentration levels (Table 4). The results yielded recoveries

between 85.6 % and 93.94 %, which comply with the AOAC (2002) acceptance criteria of 80–110 %. This confirms that the Ca-Alg-EDTA microcapsules do not introduce significant systematic errors during the adsorption-elution process.

**Table 4.** Accuracy test results

Standard (mg/L)	$\underline{y}$	$\underline{y}^i$	$\underline{x}$ Recovery
0.01	0.154	0.0955	85.6%
0.3	0.555	0.3646	92.53%
0.5	0.841	0.5567	93.94%

### Real sample application and matrix effects

The developed method was applied to Mahakam River water samples. The detected Cr(VI) concentration was 0.0877 mg/L (Table

5). To evaluate potential matrix effects—such as interference from other dissolved ions ( $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ , or organic matter) in the river water—a spike of 0.5 mg/L Cr(VI) was added.

**Table 5.** Results of Cr(VI) concentration determination in a real sample

Sample	$C_i$ (mg/L)	C Eluat (mg/L)	% Recovery
Mahakam River Water	0.0877	0.1246	93.05

The recovery for the real sample was 93.05 %, which is well within the acceptable range. This high recovery suggests that the Ca-Alg-EDTA microcapsules possess excellent selectivity for Cr(VI), effectively isolating the target analyte from the complex river water matrix before spectrophotometric measurement. This effectiveness in trace metal enrichment from river water samples is consistent with the performance of chelating systems reported in earlier preconcentration studies (Amran et al., 2011).

### CONCLUSION

This study successfully developed a sensitive and eco-friendly preconcentration method for trace Cr(VI) analysis using optimized Ca-Alg-EDTA microcapsules. The integration of EDTA into the alginate matrix significantly enhanced the available coordination sites, achieving a maximum retention capacity of 0.3995 mg/g and an efficiency of 74.73 %. The method proved highly reliable for environmental monitoring, as demonstrated by the low detection limit (0.014

mg/L and excellent recovery (93.05 %) in complex Mahakam River water samples.

The novelty of this work lies in the synergetic use of biopolymer-based microencapsulation within a column system to bridge the sensitivity gap of standard UV-Vis spectrophotometry. However, this study has limitations, particularly the absence of long-term reusability assessments and detailed kinetic modeling to fully understand the adsorption rate. Furthermore, while the material is cost-effective, a direct performance comparison with commercial ion-exchange resins remains to be explored.

Future research should focus on Scanning Electron Microscopy (SEM) for surface morphology analysis, adsorption isotherm modeling to clarify the energetic distribution of binding sites, and testing the resin's stability over multiple adsorption-desorption cycles. Ultimately, these Ca-Alg-EDTA microcapsules offer a promising, sustainable alternative for the routine detection of toxic heavy metals in natural water systems.

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