



*Article*

## **Elimination of Heavy Metals from Industrial Wastewater Using Salts of Divalent Cations**

**Jamil Rahmati<sup>1\*</sup>, Asadullah Munib<sup>2</sup>, Ewaz Khan Sajid<sup>1</sup>, Shamshad Momand<sup>3</sup>, Mohammad Ajmal Habib Safi<sup>1</sup>**

<sup>1</sup>Faculty of Engineering, General and Technical Subjects Department, Nangarhar University, Jalalabad, Afghanistan

<sup>2</sup>Faculty of Engineering, Water Resource and Environmental Engineering Department, Nangarhar University, Jalalabad, Afghanistan

<sup>3</sup>Faculty of Engineering, Architecture Department, Nangarhar University, Jalalabad, Afghanistan

\*Corresponding author: Jamil Rahmati, [jamil.rahmati20@gmail.com](mailto:jamil.rahmati20@gmail.com)

### **Abstract**

Heavy metals (HMs) such as lead ( $Pb^{2+}$ ), cadmium ( $Cd^{2+}$ ), and arsenic ( $As^{3+}$ ) are significant contaminants in water, posing risks to human health and the environment. This study evaluates the removal of these HMs using salts of divalent cations: calcium chloride ( $CaCl_2$ ), magnesium sulfate ( $MgSO_4$ ), and copper sulfate ( $CuSO_4$ ). The results demonstrate that  $CaCl_2$  is the most effective, achieving 85% removal of  $Pb^{2+}$  and 90% removal of  $Cd^{2+}$  at a concentration of 30 mg/L.  $MgSO_4$  also showed strong performance, with removal rates of 80% for  $Pb^{2+}$  and 75% for  $Cd^{2+}$ .  $CuSO_4$  was the least effective, with a maximum removal of 70% for  $Pb^{2+}$  and 65% for  $Cd^{2+}$ . Removal of  $As^{3+}$  was also successful, with  $CaCl_2$  achieving 80% removal, while  $MgSO_4$  and  $CuSO_4$  reached 70% and 60%, respectively. The optimal pH for the highest removal efficiency was found to be between 6.5 and 7.5. Statistical analysis confirmed significant differences in removal efficiencies, with  $CaCl_2$  being the most effective for all three metals. These findings suggest that divalent cation salts, particularly calcium and magnesium, provide a sustainable, cost-effective solution for the removal of HMs from contaminated water. Further research is needed to optimize these methods, especially for less efficient cations like copper, and to refine their application in large-scale water treatment processes.

### **Keywords**

Heavy metals, Water remediation, Divalent cations, Chemical precipitation, Coagulation, Adsorption kinetics

### **Article History**

Received: 27 December 2025

Revised: 11 February 2026

Accepted: 26 February 2026

Available Online: 10 June 2026

### **Copyright**

© 2026 by the authors. This article is published by the Cultech Publishing Sdn. Bhd. under the terms of the Creative Commons Attribution 4.0 International License (CC BY 4.0): <https://creativecommons.org/licenses/by/4.0/>

## 1. Introduction

Heavy metals (HMs) such as cadmium ( $\text{Cd}^{2+}$ ) [1], lead ( $\text{Pb}^{2+}$ ) [2], and arsenic ( $\text{As}^{3+}$ ) [3] are hazardous to human health and aquatic ecosystems, even at trace levels [4,5]. Water pollution caused by HMs is a severe environmental issue that has attracted global attention [6,7]. Due to improper waste disposal [8,9], agricultural runoff [10], and industrial discharge [11,12], HMs accumulate in water bodies, threatening aquatic biodiversity and the health of communities relying on these resources [13,14]. As water contamination continues to rise, effective techniques for removing HMs from water sources have become a critical area of research [15-18].

Conventional methods for HMs removal, such as chemical precipitation, often require substantial chemical inputs and energy, which limit their sustainability and scalability [19]. These techniques are also associated with high operational costs and environmental impacts [20]. While research on the use of divalent cations such as calcium ( $\text{Ca}^{2+}$ ) [21], magnesium ( $\text{Mg}^{2+}$ ) [22], and copper ( $\text{Cu}^{2+}$ ) [23] has been explored individually, comprehensive comparative studies evaluating their relative effectiveness for simultaneous removal of multiple HMs remain limited. This study addresses this gap by systematically investigating and comparing the efficacy of three readily available divalent cation salts—calcium chloride ( $\text{CaCl}_2$ ), magnesium sulfate ( $\text{MgSO}_4$ ), and copper sulfate ( $\text{CuSO}_4$ )—for removing  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{As}^{3+}$  from contaminated water.

The novelty of this research lies in the direct comparative evaluation of these three economical divalent cation salts under controlled experimental conditions. While advanced approaches in the literature have explored hybrid systems combining divalent cations with biomaterials [24-27] and nanomaterials (NMs) [28-32] to potentially enhance removal efficiency, this study focuses specifically on establishing the baseline performance of the divalent cations themselves. Such fundamental comparative data are essential for understanding the intrinsic capabilities of these common chemicals before considering more complex hybrid formulations.

Previous research has demonstrated various innovative approaches for water treatment. For instance, studies have shown the efficacy of magnetic materials and photocatalysts, such as superparamagnetic  $\text{AC/Fe}_3\text{O}_4/\text{TiO}_2$  NMs [33], and the use of low-cost magnetic char derived from oily sludge for dye removal [34]. Additionally, photocatalytic degradation using magnetic diesel tank sludge has been shown to be effective in removing contaminants like methylene blue [35]. Similarly, studies involving the use of NMs like  $\text{MIL-100(Fe)/Cygnea/Fe}_3\text{O}_4/\text{TiO}_2$  have proven effective in  $\text{Pb}^{2+}$  removal [36], and bio-magnetic photocatalysts like  $\text{TiO}_2/\text{Fe}_3\text{O}_4$ -loaded algae have been utilized for dye degradation [37]. The promising results from these hybrid systems [38-42] highlight the potential for enhanced treatment technologies, but they also underscore the need for clear baseline data on fundamental chemical agents like divalent cation salts.

In this context, the present study provides essential comparative data on the performance of calcium, magnesium, and copper salts for HMs removal. By establishing their relative effectiveness under optimized pH conditions and identifying the primary removal mechanisms, this research contributes to the development of more efficient and sustainable water treatment strategies. Such fundamental knowledge is crucial for designing cost-effective remediation approaches, particularly in resource-limited settings where simple, readily available chemicals are often the most practical solution.

## 2. Methodology

### 2.1 Materials

In this study, the industrial effluent was used. The industrial effluent was sourced from Pul-Charkhi Industrial Park, Kabul, Afghanistan. Initial analysis of this effluent indicated concentrations of  $8.2 \pm 0.5$  mg/L  $\text{Pb}^{2+}$ ,  $5.7 \pm 0.3$  mg/L  $\text{Cd}^{2+}$ , and  $4.9 \pm 0.4$  mg/L  $\text{As}^{3+}$ . For controlled experiments, synthetic HMs solutions were prepared by dissolving analytical grade lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ), cadmium chloride ( $\text{CdCl}_2$ ), and sodium arsenite ( $\text{NaAsO}_2$ ) in distilled water to achieve standard initial concentrations of 10.0 mg/L for each metal ion ( $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{As}^{3+}$ ). The treatments consisted of three salts:  $\text{CaCl}_2$ ,  $\text{MgSO}_4$ , and  $\text{CuSO}_4$ . Stock solutions of these salts were prepared at 1000 mg/L (as the cation:  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , or  $\text{Cu}^{2+}$ ). For batch experiments, these stocks were diluted to achieve final treatment concentrations of 10, 20, and 30 mg/L of the divalent cation (i.e., mg/L of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , or  $\text{Cu}^{2+}$ ) in the 200 mL reactor.

### 2.2 SDDC Method for $\text{As}^{3+}$ Detection

The silver diethyldithiocarbamate (SDDC) method was used to measure  $\text{As}^{3+}$  concentrations in water samples. In this method,  $\text{As}^{3+}$  reacts with SDDC to form a yellow-colored complex. The intensity of this color is proportional to the concentration of  $\text{As}^{3+}$  in the sample. The complex is quantified by measuring the absorbance at 520 nm using a UV-Vis spectrophotometer. Prior to analysis, the samples undergo a digestion process to convert  $\text{As}^{3+}$  species into a detectable form. This method is sensitive and widely used for the determination of  $\text{As}^{3+}$  concentrations in water samples. In all experiments, the water samples were treated with different concentrations of  $\text{CaCl}_2$ ,  $\text{MgSO}_4$ , and  $\text{CuSO}_4$  to assess the removal efficiency of these divalent salts.

### 2.3 HMs Contaminants

Standard solutions of HMs were prepared by dissolving  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{CdCl}_2$ , and  $\text{NaAsO}_2$  in distilled water. The concentrations of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{As}^{3+}$  in the resulting stock solutions were adjusted to 10 mg/L for experimental testing. These stock solutions served as the basis for preparing the contaminated water samples used in subsequent experiments.

### 2.4 Divalent Cation Salts

Three salts— $\text{MgSO}_4$ ,  $\text{CuSO}_4$ , and  $\text{CaCl}_2$ —were selected as sources of the divalent cations  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ca}^{2+}$ , respectively. To evaluate their comparative efficacy, each cation was dosed at final concentrations of 10, 20, and 30 mg/L (as detailed in Section 2.1). The working hypothesis is that these cations can interact with target HMs through mechanisms such as adsorption, co-precipitation, and ion exchange.

### 2.5 Reagents

The pH of the HMs solutions was adjusted using hydrochloric acid (HCl) and sodium hydroxide (NaOH). All chemicals used in the experiments were of analytical grade, ensuring the accuracy and reliability of the findings.

### 2.6 Apparatus and Equipment

The concentration of HMs in the water samples was determined using a UV-Vis spectrophotometer (Model: UV-1800, Shimadzu, Japan). Calibration curves were constructed for each metal ( $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{As}^{3+}$ ) using standard solutions. The concentrations of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  were measured by direct atomic absorption at specific wavelengths ( $\text{Pb}^{2+}$  at 283.3 nm,  $\text{Cd}^{2+}$  at 228.8 nm). For  $\text{As}^{3+}$  detection, the SDDC spectrophotometric method was employed. This method involved sample digestion and arsine generation, with absorbance measured at 520 nm. Calibration curves for  $\text{As}^{3+}$  were constructed using standard solutions processed identically.

### 2.7 Filter Unit

After treatment, the water samples were filtered using 0.45  $\mu\text{m}$  cellulose acetate membranes to remove solid particles before analysis. This step ensured that only dissolved metals were measured, improving the accuracy of the results.

### 2.8 Experimental Procedure

Standard solutions of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{As}^{3+}$  were prepared by dissolving the appropriate salts in deionized water. The pH of each solution was adjusted to a range of 6.5-7.5 using HCl and NaOH to optimize conditions for HMs removal. Contaminated water samples were treated with varying concentrations of  $\text{CaCl}_2$ ,  $\text{MgSO}_4$ , and  $\text{CuSO}_4$ . Concentrations of 10, 20, and 30 mg/L were tested for each divalent element. To ensure thorough mixing, a magnetic stirrer was used at 150 rpm for 60 minutes. Aliquots (5 mL) were withdrawn from the reactor at predetermined time intervals (10, 20, 30, and 60 minutes) and filtered through 0.45  $\mu\text{m}$  cellulose acetate membrane filters to remove suspended particles. The filtered samples were then analyzed for HMs concentrations.

### 2.9 Post-Treatment Analysis

UV-Vis spectrophotometry was used to determine the concentration of HMs in the treated water samples. The removal efficiency was calculated using Equation (1):

$$\text{Removal Efficiency (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Where,  $C_0$  = initial amount of HM (mg/L),  $C_t$  = amount of HM at time  $t$  (mg/L).

### 2.10 Data Analysis

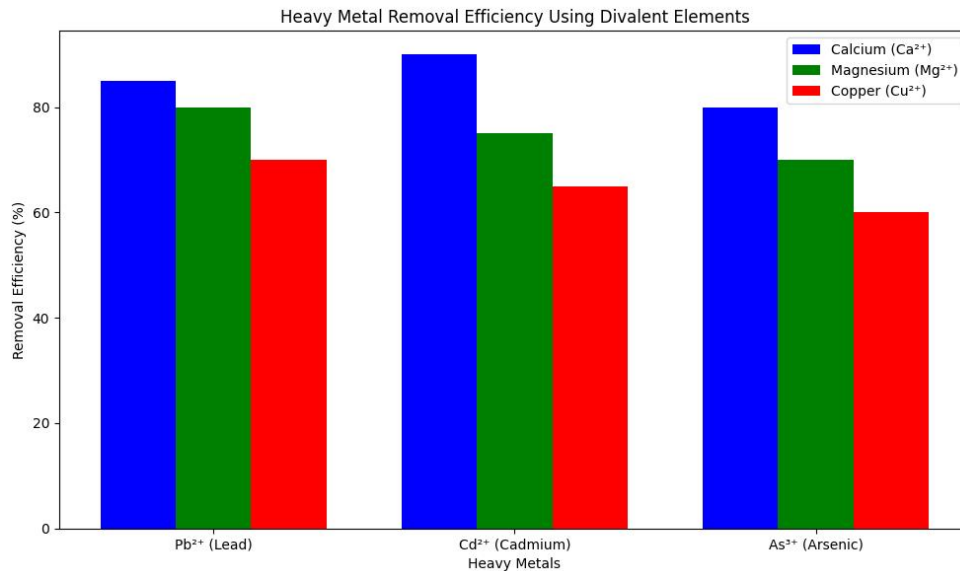
The performance of each divalent element was evaluated by comparing the removal efficiencies at different concentrations. Statistical analysis was performed using SPSS software (Version 26, IBM Corp., Armonk, NY, USA). The removal efficiencies were compared using a one-way ANOVA, with a significance threshold of  $p < 0.05$ . Post-hoc analysis was conducted using the Tukey's HSD test to identify significant differences between the elements.

## 3. Results

### 3.1 HMs Removal Using Divalent Cation Salts

The experimental results evaluating the removal of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{As}^{3+}$  using salts of divalent cations are presented herein. A comparative assessment of  $\text{CaCl}_2$ ,  $\text{MgSO}_4$ , and  $\text{CuSO}_4$  revealed distinct performance trends, as illustrated in Figure 1.  $\text{CaCl}_2$  demonstrated the highest overall efficacy. For  $\text{Pb}^{2+}$ , removal efficiency reached 85% at an optimal dosage of 30 mg/L, while  $\text{Cd}^{2+}$  removal was nearly 90% under the same conditions. Notably, calcium also showed

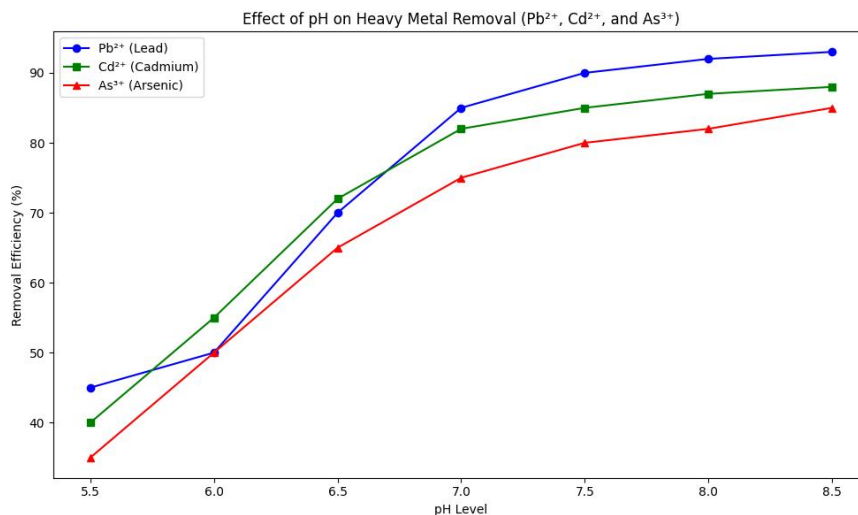
significant effectiveness against  $\text{As}^{3+}$ , achieving 80% removal. This broad-spectrum performance underscores the strong reactivity of  $\text{Ca}^{2+}$  ions, which effectively promote co-precipitation and complexation reactions with all three target metals.  $\text{MgSO}_4$  also yielded positive results, though slightly less effective than its calcium counterpart, with removal rates of 80% for  $\text{Pb}^{2+}$ , 75% for  $\text{Cd}^{2+}$ , and 70% for  $\text{As}^{3+}$  at the 30 mg/L dosage. The marginally lower efficiency may be attributed to the higher hydration energy and smaller ionic radius of  $\text{Mg}^{2+}$ , which can result in less stable complexes. In contrast,  $\text{CuSO}_4$  proved to be the least effective agent, with maximum efficiencies of 70% for  $\text{Pb}^{2+}$ , 65% for  $\text{Cd}^{2+}$ , and 60% for  $\text{As}^{3+}$ . The inferior performance of  $\text{Cu}^{2+}$  is likely due to competitive effects, where the copper ions themselves compete for active sites or participate in parallel reactions, thereby reducing the system's capacity for the target pollutants. Across all tests, a consistent performance hierarchy was established:  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Cu}^{2+}$  for the removal of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{As}^{3+}$ .



**Figure 1.** HMs removal by salts of divalent cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ).

### 3.2 Influence of pH on Metal Removal

The influence of solution pH on removal efficiency was profound, with optimal results obtained within a narrow range of 6.5 to 7.5, as detailed in Figure 2. Within this near-neutral window, two synergistic mechanisms drove metal sequestration. First, the decreased solubility of the HMs at higher pH facilitated their precipitation as hydroxides and arsenites, a process actively promoted by the divalent cations. Second, the formation of amorphous hydroxide flocs from  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  provided extensive surface areas for the adsorption of both cationic and anionic metal species. At lower pH values ( $<6.0$ ), high concentrations of  $\text{H}^+$  ions outcompeted the HMs for interaction sites and maintained them in soluble ionic forms, drastically reducing removal efficiency. At pH levels significantly above 8.0, while  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  precipitation remained high, the removal of  $\text{As}^{3+}$  showed greater variability, potentially due to shifts in its aqueous speciation and changes in the surface charge of the precipitates. This finding highlights the critical importance of pH control for maximizing the utility of these simple chemical treatments.



**Figure 2.** Effect of pH on the removal efficiency of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{As}^{3+}$ .

### 3.3 Comparison with Previous Studies

The findings of this study align with and are contextualized by the existing body of literature on metal remediation (Table 1). The superior performance of calcium-based compounds for Pb<sup>2+</sup> and Cd<sup>2+</sup> removal is well-documented, with studies on materials like calcium silicate and calcium carbonate reporting high removal efficiencies through precipitation and surface complexation mechanisms. Similarly, the role of magnesium in facilitating precipitation reactions is supported by research on processes like struvite formation. The observed lower efficacy of CuSO<sub>4</sub> finds parallels in studies noting the competitive inhibition effects of Cu<sup>2+</sup> in multi-metal adsorption systems. Furthermore, the identified optimal pH range of 6.5-7.5 is consistent with numerous biosorption and chemical precipitation studies that report peak performance under neutral to slightly alkaline conditions. The novel contribution of the present work lies in its systematic, side-by-side comparison of three common and economical divalent cation salts for the concurrent removal of three distinct, highly toxic metals under identical experimental conditions, providing a clear hierarchy of efficacy for practical application.

**Table 1.** Comparison of HMs removal efficiencies using divalent cation salts with previous studies.

Target HMs	Divalent Salt(s) Used	Key Conditions (pH, Concentration)	Maximum Removal Efficiency Reported	Key Finding(s) Relevant to Present Study	Ref.
Pb <sup>2+</sup> , Cd <sup>2+</sup> , As <sup>3+</sup>	CaCl <sub>2</sub> , MgSO <sub>4</sub> , CuSO <sub>4</sub>	pH 6.5-7.5; [Salt] = 10-30 mg/L	Pb <sup>2+</sup> : 85% (Ca <sup>2+</sup> ) Cd <sup>2+</sup> : 90% (Ca <sup>2+</sup> ) As <sup>3+</sup> : 80% (Ca <sup>2+</sup> )	Direct comparative ranking: Ca <sup>2+</sup> > Mg <sup>2+</sup> > Cu <sup>2+</sup> for all three metals. Confirms high efficacy of Ca <sup>2+</sup> /Mg <sup>2+</sup> for Pb <sup>2+</sup> and Cd <sup>2+</sup> . Provides novel data on As <sup>3+</sup> removal by these simple salts.	Present Study
Pb <sup>2+</sup> , Cd <sup>2+</sup> , Cu <sup>2+</sup>	Calcium Silicate (Ca <sup>2+</sup> source)	pH ~10; [CaSiO <sub>3</sub> ] = 2-10 g/L	Pb <sup>2+</sup> : >99% Cd <sup>2+</sup> : >95%	Demonstrates the superior performance of calcium-based materials for Pb <sup>2+</sup> and Cd <sup>2+</sup> removal via precipitation at high pH, supporting the high efficiency of Ca <sup>2+</sup> observed here.	[21]
Pb <sup>2+</sup> , Cd <sup>2+</sup> , Cu <sup>2+</sup>	Various (Review)	Various	Not specified (Review)	Reviews ion-exchange and biosorption, highlighting Ca <sup>2+</sup> and Mg <sup>2+</sup> as effective exchange ions for Pb <sup>2+</sup> and Cd <sup>2+</sup> , consistent with the ion-exchange mechanism proposed in this study.	[43]
Cu <sup>2+</sup> , Zn <sup>2+</sup> , Cd <sup>2+</sup>	CaCO <sub>3</sub> (Ca <sup>2+</sup> source)	pH 6.0-8.0	Cd <sup>2+</sup> : ~70-80%	Shows calcium carbonate is effective for Cd <sup>2+</sup> removal via co-precipitation and surface complexation, aligning with the co-precipitation role of Ca <sup>2+</sup> identified here.	[44]
NH <sub>4</sub> <sup>+</sup> , K <sup>+</sup> , PO <sub>4</sub> <sup>3-</sup> (via Struvite)	Mg <sup>2+</sup> (as MgO/MgCl <sub>2</sub> )	pH 8.5-9.0	>90% P removal	Highlights the effectiveness of Mg <sup>2+</sup> in precipitation processes (struvite formation), supporting its role in facilitating HM hydroxide precipitation.	[45]
Cu <sup>2+</sup> , Zn <sup>2+</sup> , Cd <sup>2+</sup> , Pb <sup>2+</sup>	Modified Chitosan (Not a simple salt)	pH 5.0-6.0	Pb <sup>2+</sup> : ~90% Cd <sup>2+</sup> : ~85%	While using a modified biopolymer, the study notes competitive adsorption where Cu <sup>2+</sup> can inhibit Pb <sup>2+</sup> and Cd <sup>2+</sup> uptake, supporting the observed lower efficacy and potential site competition of Cu <sup>2+</sup> in the present study.	[46]
Pb <sup>2+</sup> , Cd <sup>2+</sup> , Zn <sup>2+</sup>	Biosorption by Algae	pH 4.0-7.0	Pb <sup>2+</sup> : >90% Cd <sup>2+</sup> : ~80%	Emphasizes the critical role of pH, with optimal removal near neutral pH (6.0-7.0) for Pb <sup>2+</sup> and Cd <sup>2+</sup> , which strongly aligns with the optimal pH range (6.5-7.5) found in this study.	[47]

### 3.4 Statistical Analysis of Removal Efficiency

The data from batch experiments were analyzed statistically using SPSS software (Version 26). All experiments were performed in triplicate (n = 3). A one-way analysis of variance (ANOVA) was conducted for each HMs to determine if the removal efficiencies differed significantly among the three divalent cation treatments (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>) at the optimal dosage of 30 mg/L. The results, summarized in Table 2, show that the type of cation had a highly significant effect (p < 0.001 for Pb<sup>2+</sup> and Cd<sup>2+</sup>; p = 0.001 for As<sup>3+</sup>) on the removal efficiency for all three target metals. For Pb<sup>2+</sup> and Cd<sup>2+</sup>, Tukey's Honest Significant Difference (HSD) post-hoc test revealed that all three cations were statistically distinct from one another (each assigned a unique letter: a, b, c), confirming the performance hierarchy of Ca<sup>2+</sup> > Mg<sup>2+</sup> > Cu<sup>2+</sup>. For As<sup>3+</sup>, the post-hoc analysis revealed a more complex statistical relationship. Calcium was significantly the most effective, forming a distinct group ('a'). Copper was the least effective, forming a separate group ('b'). Magnesium,

however, displayed intermediate efficacy and was not statistically different from either calcium or copper, as indicated by its shared grouping ('ab'). These results provide robust statistical support for the conclusion that calcium is the most effective cation for the removal of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ . For  $\text{As}^{3+}$ , while calcium is clearly superior, the performance of magnesium is statistically intermediate and not definitively distinct from that of copper under the tested conditions.

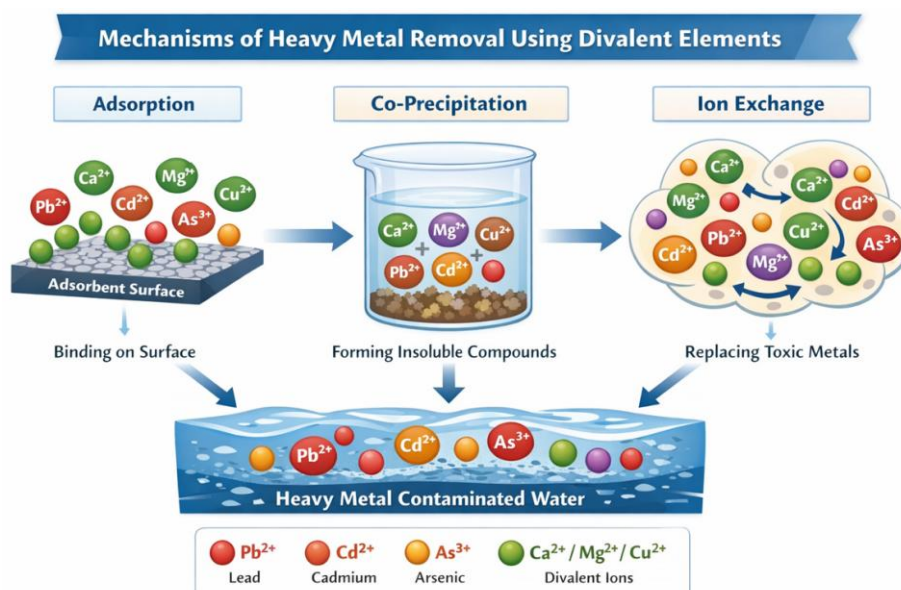
**Table 2.** Statistical analysis of HMs removal efficiency by divalent cation salts at 30 mg/L dosage and optimal pH (6.5-7.5).

HMs	Treatment (Cation)	Mean Removal Efficiency (%) $\pm$ SD (n = 3)	One-Way ANOVA (F-Value; p-Value)	Tukey's HSD Post-Hoc Grouping <sup>1</sup>
$\text{Pb}^{2+}$	$\text{Ca}^{2+}$	85.2 $\pm$ 2.1	F(2,6) = 45.73; p < 0.001	a
	$\text{Mg}^{2+}$	80.1 $\pm$ 1.8		b
	$\text{Cu}^{2+}$	70.3 $\pm$ 3.0		c
$\text{Cd}^{2+}$	$\text{Ca}^{2+}$	89.5 $\pm$ 1.5	F(2,6) = 78.91; p < 0.001	a
	$\text{Mg}^{2+}$	74.8 $\pm$ 2.2		b
	$\text{Cu}^{2+}$	65.2 $\pm$ 2.7		c
$\text{As}^{3+}$	$\text{Ca}^{2+}$	79.8 $\pm$ 2.5	F(2,6) = 25.14; p = 0.001	a
	$\text{Mg}^{2+}$	69.5 $\pm$ 3.1		ab
	$\text{Cu}^{2+}$	60.1 $\pm$ 2.9		b

<sup>1</sup>Note: Different letters within a column for each metal indicate statistically significant differences (p < 0.05). Means sharing a letter are not significantly different. For  $\text{As}^{3+}$ , the notation 'ab' for  $\text{Mg}^{2+}$  indicates its mean removal efficiency was not statistically different from the means in group 'a' ( $\text{Ca}^{2+}$ ) or group 'b' ( $\text{Cu}^{2+}$ ).

### 3.5 Removal Mechanism of HMs Using Divalent Cation Salts

The primary mechanisms responsible for HMs removal were identified as co-precipitation, adsorption, and ion exchange, with their relative dominance dependent on pH (Figure 3). Co-precipitation was the dominant process at pH levels above 7, where divalent cations directly facilitated the formation and growth of insoluble HMs hydroxide particles. Adsorption played a major role in the optimal pH window, where metal ions were captured onto the surfaces of the forming hydroxide flocs. Ion exchange also contributed, whereby  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  ions potentially replaced toxic metal ions on solid surfaces or within floc matrices. The effectiveness of this combined mechanistic action was governed by several interlinked factors: the specific HMs targeted, the concentration and type of divalent salt added, and most critically, the pH of the solution, which controlled metal solubility and surface chemistry.



**Figure 3.** Enhanced mechanisms of HMs removal using divalent salts.

## 4. Discussion

The outcomes of this work provide valuable insights into the removal efficiency of HMs from contaminated water using divalent cation salts such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Cu}^{2+}$  [42]. Among the divalent cation salts tested,  $\text{CaCl}_2$  demonstrated the highest removal efficiency for  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ , with removal rates reaching 85% for  $\text{Pb}^{2+}$  and nearly 90% for  $\text{Cd}^{2+}$  at a concentration of 30 mg/L [43]. This superior performance was confirmed to be statistically significant (p < 0.001) relative to both magnesium and copper (Table 2). The strong adsorption observed with calcium can be attributed to its ability to form stable complexes with metal ions, which enhances its efficiency in the removal process [44].  $\text{MgSO}_4$ , although effective, showed slightly lower removal efficiencies for  $\text{Cd}^{2+}$  (75%) and  $\text{Pb}^{2+}$  (80%) compared to calcium [45]. This reduced efficiency may be due to magnesium's tendency to form fewer stable complexes than calcium, which

impacts its performance at higher concentrations [46]. CuSO<sub>4</sub> was found to be less effective than both calcium and magnesium. The maximum removal efficiency for Pb<sup>2+</sup> was 70%, while Cd<sup>2+</sup> removal efficiency was 65%. This suggests that copper ions interact less strongly with the HMs ions, leading to lower adsorption efficiency [47]. This observation is consistent with findings in the literature, where copper's ability to bind with metal ions has been found to be weaker than that of calcium and magnesium [48].

Regarding As<sup>3+</sup>, CaCl<sub>2</sub> showed effective removal with an 80% efficiency at 30 mg/L concentration. MgSO<sub>4</sub> demonstrated 70% removal of As<sup>3+</sup>, while CuSO<sub>4</sub> showed the least efficiency, with a 60% removal. These results highlight that calcium and magnesium are more effective than copper for As<sup>3+</sup> removal, similar to the trend observed for Pb<sup>2+</sup> and Cd<sup>2+</sup>. The statistical analysis, conducted using SPSS, confirmed significant differences in the removal efficiencies of calcium, magnesium, and copper, with calcium demonstrating the highest removal efficiency [49]. These findings support previous research highlighting the effectiveness of calcium and magnesium in removing HMs from aqueous solutions. However, the lower performance of copper underscores the need for further research to optimize its interaction with metal ions [50].

The impact of pH on metal removal was also investigated. The results revealed that the optimal pH for the removal of Pb<sup>2+</sup>, Cd<sup>2+</sup>, and As<sup>3+</sup> was between 6.5 and 7.5. At lower pH levels, the removal efficiency decreased, likely due to the increased solubility of metal ions in acidic conditions [51]. Conversely, at higher pH values, metal hydroxides precipitated, leading to increased removal efficiency. This observation reinforces the importance of pH control in water treatment processes and suggests that adjusting pH to the optimal range can significantly improve HM removal [52]. This study on divalent cations aligns with broader research exploring advanced materials for water remediation. For instance, previous studies, such as the work of Zamani et al. [37] on the use of MIL-100(Fe)/Cygnea/Fe<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub> demonstrated that NMs can enhance the removal of Pb<sup>2+</sup> from wastewater. Similarly, Rastgar et al. [53] explored innovative treatments for toxic oily petroleum wastewater with magnetic sludge, reinforcing the role of advanced materials in water treatment. Moreover, Zamani et al. [54] showcased the application of oyster shell-based biophotocatalysts, emphasizing the effectiveness of hybrid systems in removing contaminants.

## 5. Conclusion

This study effectively demonstrated the efficacy of divalent cations, particularly Ca<sup>2+</sup> and Mg<sup>2+</sup>, in removing HMs such as Pb<sup>2+</sup>, Cd<sup>2+</sup>, and As<sup>3+</sup> from contaminated water. CaCl<sub>2</sub> emerged as the most effective agent, achieving approximately 85% and 90% removal for Pb<sup>2+</sup> and Cd<sup>2+</sup>, respectively, at a concentration of 30 mg/L. MgSO<sub>4</sub> also showed significant efficacy, while CuSO<sub>4</sub> exhibited comparatively lower removal efficiencies for all target metals. The successful removal of As<sup>3+</sup> further underscores the utility of these divalent cation salts. A critical operational parameter identified was pH, with the optimal removal efficiency occurring within a narrow range of 6.5 to 7.5. This highlights the necessity of precise pH control in practical treatment applications to maximize HM precipitation and complexation. Future research should focus on optimizing the interaction mechanisms, especially for less-efficient cations like copper, for more efficient and sustainable water purification.

## Author Contributions

Jamil Rahmati: Conceptualization, methodology, data analysis, writing—original draft. Asadullah Munib: Data collection, formal analysis, writing—review and editing. Ewaz Khan Sajid: Writing—review and editing, visualization, supervision. Shamshad Momand: Methodology, validation, writing—review and editing. All authors have read and approved the final manuscript. Mohammad Ajmal Habib Safi: Methodology, validation, writing—review and editing. All authors have read and approved the final manuscript.

## Funding

This study was not supported by any specific funding from public, commercial, or non-profit organizations.

## Conflict of Interest

The authors declare that there are no financial or personal conflicts of interest that could have affected the results or interpretations presented in this research.

## Data Availability Statement

The data supporting the findings of this study are available upon reasonable request from the corresponding author.

## Generative AI Statement

The authors declare that no Generative AI was used in the creation of this manuscript.

## References

- [1] Ullah S, Hayat K, Qiao X. Chitosan-based biostimulation: A novel approach for simultaneous remediation of co-existing cadmium and arsenic contamination in soil. *Air, Soil and Water Research*, 2023, 11786221231216862. DOI: 10.1177/11786221231216862
- [2] Noman M, Haziq MA, Safi BU, Ullah S, Rukh G, Faiq ME, et al. Lead (II) adsorption from aqueous systems using visible light activated cobalt doped zinc oxide nanoparticles. *Digest Journal of Nanomaterials & Biostructures (DJNB)*, 2022, 17(3), 839-849. DOI: 10.15251/DJNB.2022.173.839
- [3] Ullah S, Shams DF, Ur Rehman SA, Khattak SA, Noman M, Rukh G, et al. Application of visible light activated thiolated cobalt doped ZnO nanoparticles towards arsenic removal from aqueous systems. *Digest Journal of Nanomaterials & Biostructures (DJNB)*, 2022, 17(2), 443-455. DOI: 10.15251/DJNB.2022.172.443
- [4] Li L, Haziq MA, Ullah S, Stanikzai AG, Bibi SD, Haq TU, et al. Remediation of lead-contaminated water using green synthesized iron-oxide nanoparticles: Performance and mechanism. *Air, Soil and Water Research*, 2024, 17, 11786221241278517. DOI: 10.1177/11786221241278517
- [5] Shaikat S, Hassani MA, Yadgari MY, Ullah S, Iqbal MS, Khan F, et al. Green synthesis of silver nanoparticles and its application towards As (V) removal from aqueous systems. *Digest Journal of Nanomaterials & Biostructures (DJNB)*, 2022, 17(4), 1385-1398. DOI: 10.15251/DJNB.2022.174.1385
- [6] Xie P, Zahoor F, Iqbal SS, Ullah S, Noman M, Din ZU, et al. Elimination of toxic heavy metals from industrial polluted water by using hydrophytes. *Journal of Cleaner Production*, 2022, 352, 131358. DOI: 10.1016/j.jclepro.2022.131358
- [7] Ghani J, Nawab J, Faiq ME, Ullah S, Alam A, Ahmad I, et al. multi-geostatistical analyses of the spatial distribution and source apportionment of potentially toxic elements in urban children's park soils in Pakistan: A risk assessment study. *Environmental Pollution*, 2022, 311, 119961. DOI: 10.1016/j.envpol.2022.119961
- [8] Sabir M, Baltrėnaitė-Gedienė E, Ditta A, Ullah H, Kanwal A, Ullah S, et al. Bioaccumulation of heavy metals in a soil-plant system from an open dumpsite and the associated health risks through multiple routes. *Sustainability*, 2022, 14(20), 13223. DOI: 10.3390/su142013223
- [9] Ullah S, Bibi SD, Ali S, Noman M, Rukh G, Nafees MA, et al. Analysis of municipal solid waste management in Afghanistan, current and future prospects: a case study of Kabul City. *Applied Ecology & Environmental Research*, 2022, 20(3). DOI: 10.15666/aecer/2003\_24852507
- [10] Yargholi B, Sepehri S, Kanani E. Removal of heavy metals from agricultural runoff using constructed wetland; traces pollutants in reed bed sediments and plant biomass. *Wetlands Ecology and Management*, 2024, 32(5), 669-688. DOI: 10.1007/s11273-023-09922-7
- [11] Nawab J, Din ZU, Ahmad R, Khan S, Zafar MI, Faisal S, et al. Occurrence, distribution, and pollution indices of potentially toxic elements within the bed sediments of the riverine system in Pakistan. *Environmental Science and Pollution Research*, 2021, 28(39), 54986-55002. DOI: 10.1007/s11356-021-14783-9
- [12] Nawab J, Ghani J, Ullah S, Ahmad I, Akbar Jadoon S, Ali S, et al. Influence of agro-wastes derived biochar and their composite on reducing the mobility of toxic heavy metals and their bioavailability in industrial contaminated soils. *International Journal of Phytoremediation*, 2024, 26(11), 1824-1838. DOI: 10.1080/15226514.2024.2357640
- [13] Tholley MS, George LY, Wang G, Ullah S, Qiao Z, Ling S, et al. Risk assessment and source apportionment of heavy metalloids from typical farmlands provinces in China. *Process Safety and Environmental Protection*, 2023, 171, 109-118. DOI: 10.1016/j.psep.2022.12.092
- [14] Nawab J, Idress M, Ullah S, Rukh G, Zainab R, Sher H, et al. Occurrence and distribution of heavy metals in mining degraded soil and medicinal plants: A case study of Pb/Zn sulfide terrain Northern Areas, Pakistan. *Bulletin of Environmental Contamination and Toxicology*, 2023, 110(1), 24. DOI: 10.1007/s00128-022-03673-6
- [15] Hussain T, Akhter N, Nadeem R, Rashid U, Noreen S, Anjum S, et al. Biogenic synthesis of date stones biochar-based zirconium oxide nanocomposite for the removal of hexavalent chromium from aqueous solution. *Applied Nanoscience*, 2023, 13(9), 6053-6066. DOI: 10.1007/s13204-022-02599-z
- [16] Ullah I, Adnan M, Nawab J, Khan S, Jan MI, Jalal A, et al. Ecological and health risks assessment of potentially toxic elements in edible plants across mining and non-mining areas of Northwest, Pakistan. *Scientific Reports*, 2025, 15(1), 21990. DOI: 10.1038/s41598-025-02750-0
- [17] Yadgari MY, Subat S, Rashid S, Ullah S, Li L, Hassani MA, et al. Toxic effects of arsenic and its adsorption through thiolated cobalt doped silver nanomaterials from water resources. *Digest Journal of Nanomaterials & Biostructures (DJNB)*, 2023, 18(4), 1339-1350. DOI: 10.15251/DJNB.2023.184.1339
- [18] Khan A, Zhang X, Wang K, Ahmed W, Ullah S, Mushtaq MU, et al. Enhanced methyl orange degradation by natural manganese sand-catalyzed in-situ electro-generated active chlorine. *Journal of Electroanalytical Chemistry*, 2025, 984, 119059. DOI: 10.1016/j.jelechem.2025.119059
- [19] Yadav M, Singh G, Jadeja RN. Physical and chemical methods for heavy metal removal. *Pollutants and water management: Resources, Strategies and Scarcity*, 2021, 377-397. DOI: 10.1002/9781119693635.ch15
- [20] Oncel MS, Muhcu A, Demirbas E, Kobya M. A comparative study of chemical precipitation and electrocoagulation for treatment of coal acid drainage wastewater. *Journal of Environmental Chemical Engineering*, 2013, 1(4), 989-995. DOI: 10.1016/j.jece.2013.08.008
- [21] Ma J, Qin G, Zhang Y, Sun J, Wang S, Jiang L. Heavy metal removal from aqueous solutions by calcium silicate powder from waste coal fly-ash. *Journal of Cleaner Production*, 2018, 182, 776-782. DOI: 10.1016/j.jclepro.2018.02.115
- [22] Thakur N, Thakur A. Magnesium metal-organic framework as a dual, turn-off fluorescent sensor for organic solvents and heavy metal ions. *Journal of Inorganic and Organometallic Polymers and Materials*, 2025, 1-32. DOI: 10.1007/s10904-025-04040-8
- [23] Zhang Y, Wang X, Liu J, Wu L. Removal of copper (Cu<sup>2+</sup>) from water using novel hybrid adsorbents: Kinetics and isotherms. *Journal of Chemical & Engineering Data*, 2013, 58(5), 1141-1150. DOI: 10.1021/jc301168m
- [24] Ethaib S, Al-Qutaifa S, Al-Ansari N, Zubaidi SL. Function of nanomaterials in removing heavy metals for water and wastewater remediation: A review. *Environments*, 2022, 9(10), 123. DOI: 10.3390/environments9100123

- [25] Ingrassia Moreno EB, Fiorentini Chirino EF, Escudero LB. Hybrid biomaterials to preconcentrate and determine toxic metals and metalloids: A review. *Analytical and Bioanalytical Chemistry*, 2023, 415(16), 3073-3091. DOI: 10.1007/s00216-023-04683-x
- [26] Makarova AO, Derkach SR, Khair T, Kazantseva MA, Zuev YF, Zueva OS. Ion-induced polysaccharide gelation: Peculiarities of alginate egg-box association with different divalent cations. *Polymers*, 2023, 15(5), 1243. DOI: 10.3390/polym15051243
- [27] Khan O, Parvez M, Yadav AK. A comparative analysis of various nanocomposites for the remediation of heavy metals from biomass liquid digestate using multi-criteria decision methods. *Biomass and Bioenergy*, 2024, 186, 107281. DOI: 10.1016/j.biombioe.2024.107281
- [28] Alam E. Exploring recent progress in adsorbent technologies for As<sup>3+</sup> and As<sup>5+</sup> removal from water: A brief overview. *Environmental Technology Reviews*, 2024, 13(1), 814-848. DOI: 10.1080/21622515.2024.2428447
- [29] Li B, Cui Y, Wang X, Tang R. Novel nanomaterial-organism hybrids with biomedical potential. *Wiley Interdisciplinary Reviews: Nanomedicine and Nanobiotechnology*, 2021, 13(5), e1706. DOI: 10.1002/wnan.1706
- [30] Osman AI, El-Monaem EM, Elgarahy AM, Aniagor CO, Hosny M, Farghali M, et al. Methods to prepare biosorbents and magnetic sorbents for water treatment: A review. *Environmental Chemistry Letters*, 2023, 21(4), 2337-2398. DOI: 10.1007/s10311-023-01603-4
- [31] Saleh HM, Hassan AI. Synthesis and characterization of nanomaterials for application in cost-effective electrochemical devices. *Sustainability*, 2023, 15(14), 10891. DOI: 10.3390/su151410891
- [32] Asghar N, Hussain A, Nguyen DA, Ali S, Hussain I, Junejo A, et al. Advancement in nanomaterials for environmental pollutants remediation: A systematic review on bibliometrics analysis, material types, synthesis pathways, and related mechanisms. *Journal of Nanobiotechnology*, 2024, 22(1), 26. DOI: 10.1186/s12951-023-02151-3
- [33] Kumar L, Raganathan V, Chugh M, Bharadvaja N. Nanomaterials for remediation of contaminants: A review. *Environmental Chemistry Letters*, 2021, 19(4), 3139-3163. DOI: 10.1007/s10311-021-01212-z
- [34] Rastgar S, Rezaei H, Younesi H, Abyar H. Preparation of superparamagnetic AC/Fe<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub> nanoparticles from magnetic waste oily petroleum sludge (MWOPS): Comprehensive characterization, H<sub>2</sub> production, design batch photoreactor, and treatment of oily petroleum wastewater (OPW) under UVA light. *Carbon Letters*, 2024, 34(6), 1673-1691. DOI: 10.1007/s42823-024-00711-7
- [35] Rastgar S, Rezaei H, Younesi H, Abyar H. Low-cost magnetic char derived from oily sludge for Methylene Blue dye removal: Optimization, isotherm, and kinetic approach. *Advances in Environmental Technology*, 2022, 8(4), 329-343. DOI: 10.22104/AET.2022.5795.1595
- [36] Rastgar S, Rezaei H, Younesi H, Abyar H, Kordrostami A. Photocatalytic degradation of methylene blue (MB) dye under UV light irradiation by magnetic diesel tank sludge (MDTS). *Biomass Conversion and Biorefinery*, 2024, 14(17), 20451-20462. DOI: 10.1007/s13399-023-04062-7
- [37] Zamani W, Rastgar S, Hedayati A, Tajari M, Ghiasvand Z. Solvent-thermal approach of MIL-100 (Fe)/Cygnea/Fe<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub> nanocomposite for the treatment of lead from oil refinery wastewater (ORW) under UVA light. *Scientific Reports*, 2024, 14(1), 4476. DOI: 10.1038/s41598-024-54897-x
- [38] Zamani W, Rastgar S, Hedayati A. Capability of TiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles loaded onto Algae (*Scenedesmus* sp.) as a novel bio-magnetic photocatalyst to degradation of Red195 dye in the sonophotocatalytic treatment process under ultrasonic/UVA irradiation. *Scientific Reports*, 2023, 13(1), 18182. DOI: 10.1038/s41598-023-45274-1
- [39] Kaur J, Sengupta P, Mukhopadhyay S. Critical review of bioadsorption on modified cellulose and removal of divalent heavy metals (Cd, Pb, and Cu). *Industrial & Engineering Chemistry Research*, 2022, 61(5), 1921-1954. DOI: 10.1021/acs.iecr.1c04583
- [40] Alluhaidan AS, Prabu P, Basheer S, Aziz R, Prakash P. Integrated hybrid membrane system for enhanced water treatment and desalination for environmental preservation. *Desalination and Water Treatment*, 2024, 320, 100722. DOI: 10.1016/j.dwt.2024.100722
- [41] Saratale RG, Saratale GD, Shin HS, Jacob JM, Pugazhendhi A, Bhaisare M, et al. New insights on the green synthesis of metallic nanoparticles using plant and waste biomaterials: Current knowledge, their agricultural and environmental applications. *Environmental Science and Pollution Research*, 2018, 25(11), 10164-10183. DOI: 10.1007/s11356-017-9912-6
- [42] Tariq A, Yahaya N, Sajid M. Low cost adsorbents derived from vegetables and fruits: Synthesis, properties, and applications in removal of heavy metals from water. *Desalination and Water Treatment*, 2024, 320, 100626. DOI: 10.1016/j.dwt.2024.100626
- [43] Bashir A, Malik LA, Ahad S, Manzoor T, Bhat MA, Dar GN, et al. Removal of heavy metal ions from aqueous system by ion-exchange and biosorption methods. *Environmental Chemistry Letters*, 2019, 17(2), 729-754. DOI: 10.1007/s10311-018-00828-y
- [44] Wierzbna S, Makuchowska-Fryc J, Kłos A, Ziembik Z, Ochędzan-Siodłak W. Role of calcium carbonate in the process of heavy metal biosorption from solutions: Synergy of metal removal mechanisms. *Scientific Reports*, 2022, 12(1), 17668. DOI: 10.1038/s41598-022-22603-4
- [45] Kabdaşlı I, Siciliano A, Limonti C, Tünay O. Is K-struvite precipitation a plausible nutrient recovery method from potassium-containing wastes?—A review. *Sustainability*, 2022, 14(18), 11680. DOI: 10.3390/su141811680
- [46] Huang L, Xie YH, Xiang HB, Hou YL, Yu B. Physicochemical properties of copper doped calcium sulfate in vitro and angiogenesis in vivo. *Biotechnic & Histochemistry*, 2021, 96(2), 117-124. DOI: 10.1080/10520295.2020.1776392
- [47] Rahman A. Promising and environmentally friendly removal of copper, zinc, cadmium, and lead from wastewater using modified shrimp-based chitosan. *Water*, 2024, 16(1), 184. DOI: 10.3390/w16010184
- [48] Litu L, Buema G, Mosoarca G, Harja M. Copper ion removal by adsorption using fly ash-based geopolymers: Process optimization insights from Taguchi and Anova statistical methods. *Materials*, 2024, 17(16), 3992. DOI: 10.3390/ma17163992
- [49] Zhao ND, Wang Y, Hou YC, Guo YR, Pan QJ. High efficiency filter: Cellulose-derived biochar fibril and magnesium oxide composite for boosting performance of heavy metal ions capture. *Applied Surface Science*, 2023, 609, 155267. DOI: 10.1016/j.apsusc.2022.155267
- [50] Staszak K, Regel-Rosocka M. Removing heavy metals: Cutting-edge strategies and advancements in biosorption technology. *Materials*, 2024, 17(5), 1155. DOI: 10.3390/ma17051155

- [51] Gu S, Lan CQ. Effects of culture pH on cell surface properties and biosorption of Pb (II), Cd (II), Zn (II) of green alga *Neochloris oleoabundans*. *Chemical Engineering Journal*, 2023, 468, 143579. DOI: 10.1016/j.cej.2023.143579
- [52] Qasem NA, Mohammed RH, Lawal DU. Removal of heavy metal ions from wastewater: a comprehensive and critical review. *Npj Clean Water*, 2021, 4(1), 36. DOI: 10.1038/s41545-021-00127-0
- [53] Rastgar S, Younesi H, Rezeai H, Abyar H. Innovative treatment of toxic oily petroleum wastewater with magnetic sludge under UVA light. *Petroleum Research*, 2025, 10(2), 383-403. DOI: 10.1016/j.ptlrs.2024.11.005
- [54] Zamani W, Rastgar S, Hedayati A. Using oyster shell (*Andonata Cygnea*) as a novel biophotocatalyst for fish farm wastewater treatment with response surface methodology (RSM): Isotherm, Kinetics, and Thermodynamics. *Biomass Conversion and Biorefinery*, 2024, 14(24), 31217-31232. DOI: 10.1007/s13399-023-04903-5