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# Innovative use of pomegranate peels and chitosan as a bio-flocculant for heavy metal removal from wastewater

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This research explores the potential of using pomegranate peels and chitosan as a natural flocculant for pre-treating wastewater to enhance sand filtration and remove heavy metals ($Ni^{2+}$, $Cu^{2+}$, and $Zn^{2+}$) effectively. Active compounds like tannin are extracted and purified from the pomegranate peels, then chitosan and tannin are modified to create a novel flocculant. The synthesized flocculant is characterized and its performance is evaluated through laboratory experiments, analyzing factors such as dosage, pH, and heavy metal concentration. The results of this work can provide a safe, easy, eco-friendly and cheap method of wastewater treatment.

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*Keywords:* Wastewater treatment, Natural flocculant, Chitosan, Pomegranate peels, Eco-friendly

## 1. Introduction

Water is a vital resource that is essential for sustaining life and supporting various industrial processes. However, the rapid growth of industrialization and urbanization has led to a significant increase in the volume of wastewater, which is often contaminated with harmful pollutants, including heavy metals. Heavy metal pollution resulting from industrial activities in ferrous and nonferrous metallurgy and chemical industries poses a significant threat to the environment. The presence of heavy metals such as nickel ($Ni^{2+}$), copper ($Cu^{2+}$), and zinc ($Zn^{2+}$) in wastewater poses a serious threat to the environment, affecting ecosystems and human health [1]. To mitigate these challenges and promote sustainable water management, there is an urgent need for innovative and environmentally friendly wastewater treatment methods. Traditional treatment approaches often rely on chemical flocculants, which can be expensive and pose additional environmental problems [2].

Heavy metals such as chromium, copper, iron and lead are ubiquitous pollutants that, even in low concentrations, can cause serious damage to living organisms. Traditional methods of wastewater treatment often use inorganic and synthetic polymer flocculants, which can contain toxic and harmful chemical compounds that have a negative impact on the environment.

The use of iron and aluminum salts as inorganic coagulants in water and wastewater treatment has been widespread due to their effectiveness in pollutant removal, ease of mixing, user-friendly handling and storage, and cost-effectiveness [3]. However, despite their advantages, the usage of these coagulants is not without drawbacks, leading to certain concerns in water treatment processes. One of the main drawbacks associated with the use of iron and aluminum salts is the generation of a substantial volume of sludge during the treatment process. This sludge can pose challenges for disposal and can contribute to environmental concerns if not managed properly. Furthermore, the application of these coagulants often requires the addition of alkalinity

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and pH adjustment to achieve optimal treatment results. This additional step can increase the complexity of the treatment process and may result in increased operational costs. Another significant concern is the potential high concentration of residual metals, particularly aluminum, in the treated water or sludge. High levels of aluminum in water sources can have adverse effects on human health and the environment. Studies have raised concerns about the potential link between the neurotoxicity of aluminum found in wastewater sludge and the pathogenesis of Alzheimer's disease [4]. While the direct cause-effect relationship between aluminum exposure and Alzheimer's disease remains a subject of ongoing research, the potential risk underscores the need for careful consideration and monitoring of metal concentrations in treated water and sludge.

Plant-based coagulants have garnered significant attention in the field of water and wastewater treatment and have been the subject of frequent research. Some of the plant-based coagulants that have been extensively studied include Moringa oleifera (M. oleifera), Strychnos potatorum (nirmali), tannin, and cactus [5, 6].

The use of natural flocculants such as chitosan and tannin offer an environmentally friendly alternative to wastewater treatment. Recent research has shown the potential of cationic tannins as effective coagulants or flocculants for wastewater treatment. However, previous studies mainly focused on the removal of colloidal substances and the influence of heavy metals on hardness has not yet been fully studied. The structure of tannin is presented schematically in Figure 1.

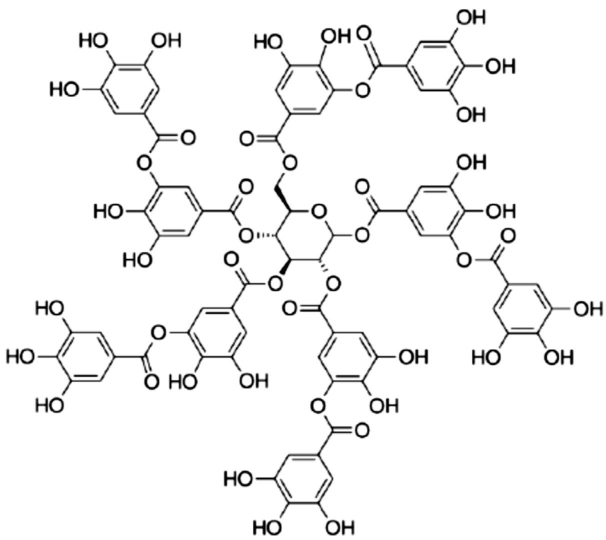

*Fig. 1. Structure of Tannin.*

Tannin extracted from various sources, such as valonia oak and Schinopsis balansae, has been applied in wastewater treatment for turbidity removal [7, 8].

Pomegranate peel, an abundant agricultural waste, has been found to contain active compounds such as tannin known for their flocculating properties [9]. By extracting and purifying these compounds, we can harness their potential for wastewater treatment. For over 4000 years, pomegranate (Punica granatum L.) has been cultivated by humans due to its medicinal and nutritional properties. This fruit holds significant cultural importance in ancient Mediterranean civilizations. In 2018 alone, California produced approximately 218,000 tons of pomegranates, making roughly 118,000 tons of pomegranate rind and seed waste. On a global scale, there are three-million tons of total pomegranate production, resulting in approximately 1.62 million tons of waste [10]. The sheer amount of waste that is produced for each edible percentage of pomegranate makes it important to look for proper methods of optimizing the nutritional and bioactive components of pomegranate waste and then convert this waste into value-added products to save energy, sustain resources, and protect the environment.

Chitosan, a biopolymer derived from chitin, complements the natural flocculating properties of pomegranate peel. Through modification, chitosan can be enhanced to further enhance its effectiveness as a flocculant, making it an ideal candidate for combination with tannin.

Chitosan, a non-toxic polysaccharide composed of repeating N-acetyl-D-glucosamine (GlcNAc) and D-glucosamine (GlcN) monomers, is widely used as a cationic coagulant pretreatment to assist in the removal of microbial and heavy metal contamination from drinking water. The structure of chitosan is presented schematically in Figure 2.

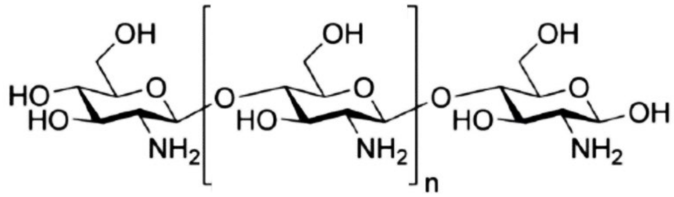

*Fig. 2. Structure of chitosan.*

Chitosan can neutralize the negative charges and also bridge the aggregate of destabilized particles. Chitosan can be produced locally as it is derived from the chitin found in the shells of shrimp and crustaceans, which are abundant in many resource-limited settings. This local production of chitosan presents a viable business opportunity for entrepreneurs in those regions. Presently, commercial production of chitin and chitosan is primarily conducted in several countries, including Japan, the United States, India, Poland, Australia, and Norway. Additionally, to a lesser extent, these materials are produced in Canada, Italy, Chile, and Brazil. The cost of chitosan manufacturing will vary depending on the specific region and the availability of feedstocks. According to Roberts, G., the average manufacturing cost of chitosan is estimated to be around \$11.5/kg [11].

Indeed, the urgent need to address the challenge of heavy metal removal from wastewater calls for the development of an efficient flocculant that can effectively treat such pollutants before conventional sand filtration. While natural coagulants have been extensively studied for water and wastewater treatment, the potential of chitosan modified with tannin as a natural coagulant remains unexplored. This presents a valuable opportunity for researchers to investigate the effectiveness and applicability of this novel coagulant in environmental remediation and sustainable water treatment practices. The study of chitosan modified tannin as a new flocculant holds great promise and may lead to significant advancements in wastewater treatment methodologies.

## 2. Experimental

Chitosan was is supplied by Merck (Sigma-Aldrich, USA, CAS N: 9012-76-4).

Tannin extract from pomegranate peels is obtained using the Soxhlet extraction method.

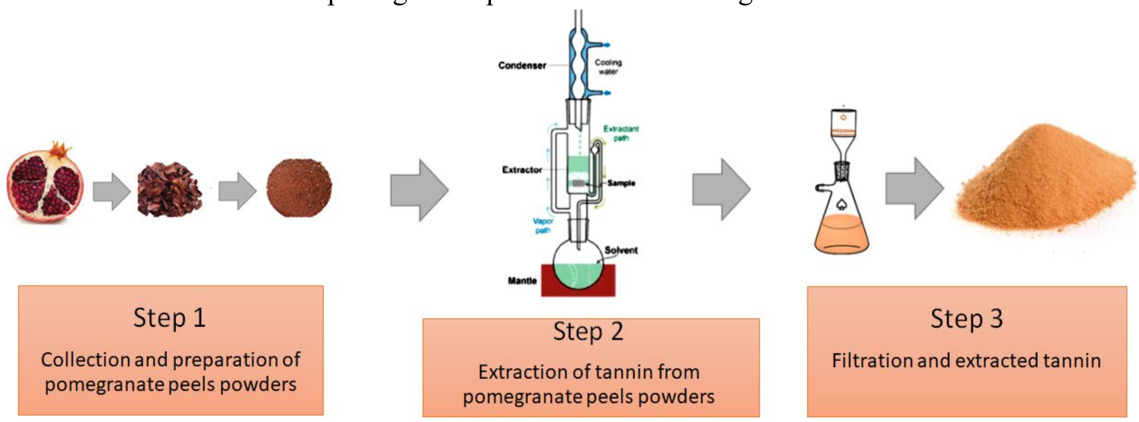


*Fig. 3. Soxhlet extraction of tannin.*

The Soxhlet extraction is a technique that involves continuously cycling a solvent (such as ethanol or water) through a sample material to extract desired compounds (Figure 3.). In this case, pomegranate peels are placed in a thimble and subjected to repeated solvent extraction and condensation cycles. This process allows for the efficient extraction of tannins from the peels, which can then be used as a coagulant in combination with chitosan for the pretreatment of wastewater and removal of heavy metals.

To extract tannin from pomegranate peels, the cleaned peels were first cut into pieces, thoroughly washed with distilled water, and then dried in an oven fora duration of 4 hours. Once dried, the peels were ground into a fine powder using a grinder. Subsequently, the powdered samples were sieved through a 40-mesh sieve to achieve a uniform particle size. To maximize tannin extraction, the process was carried out at elevated temperatures. This involved four rounds of extraction using a water-ethanol mixture (1:1) in a Soxhlet apparatus, following a known method [12]. The tannin extract obtained from the extraction process was collected in a ceramic bowl and further dried in a thermostat until its weight reached a stable state. To verify the presence of tannin in the pomegranate peel extract, a test was conducted. A mixture of 5 ml of the extract, 5 ml of distilled water, and 3-4 drops of 0.1%ferric chloride was prepared in a test tube. If tannin was present, a color change to blue would be observed in the reaction mixture, indicating the presence of tannin.

To analyze the chemical structure of the extracted tannin, was using the Fourier Transform Infrared (FTIR) spectroscopy (Shimadzu® Japan) within the wave range of 4000-500 $cm^{-1}$ in ± 60 seconds. This spectroscopic analysis allowed for the identification and characterization of the chemical bonds present in the obtained tannin, providing valuable insights into its molecular structure and properties.

Figure 4. shows that the spectrum of tannic acid where it can find a strong absorbtion around 3402 $cm^{-1}$. This band is assigned to the hydroxyl groups (-OH) H-bonded broad. At 1521-1517 a band due to the C-C aromatic compounds are observed. A weak signal at 1611 $cm^{-1}$ is related to carbonyl groups. Peaks determining during 1600-1400 $cm^{-1}$ are characteristics of aromatic compounds.

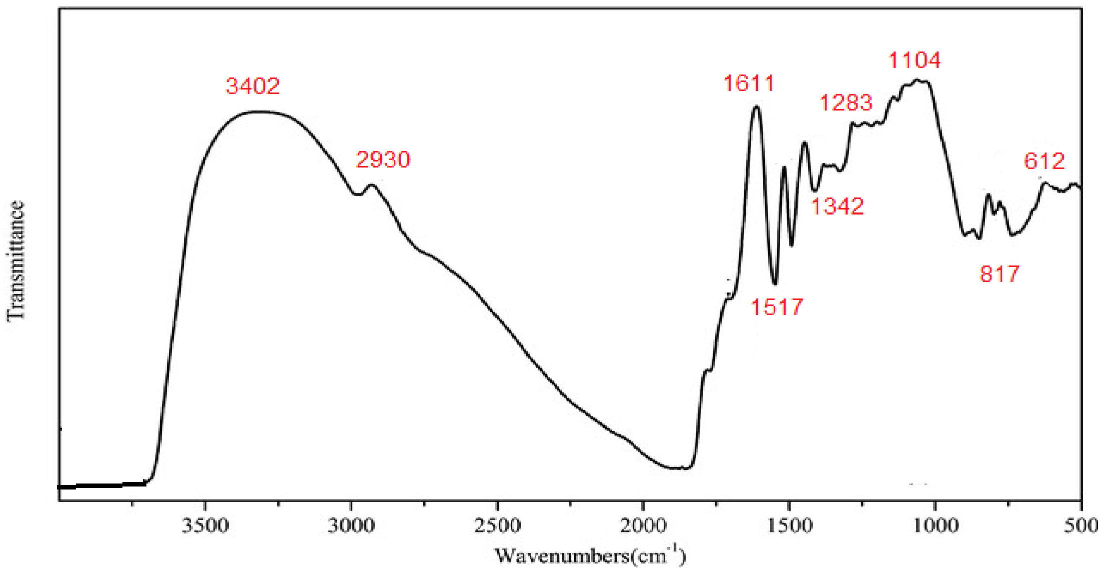


*Fig. 4. IR Fourier spectrum of tannin compound extracted from pomegranate peel.*

The composite utilized in the study in corporates a 25% glutaraldehyde or 1,5-pentanodial (OHC-$(CH_2)_3$-COH) compound, which is locally produced in Russia and serves as a binding agent in the composition. This compound is cost-effective and plays a significant role inaltering the properties of thepolymer through cross-linking via amino groups present in chitosan. Byutilizing 25% glutaraldehyde or 1,5-pentanodial in the composite, the researchers can create strong bonds between the chitosan molecules, enhancing the overall structural integrity and stability of the material. This cross-linking process results in improved properties such as increased mechanical strength, enhanced chemical resistance, and better tolerance to environmental conditions. The low cost and advantageous properties of this binding agent make ita suitable choice forthe synthesis of the composite, further supporting the development of a cost-effective and efficient flocculant for water and wastewater treatment applications.

### 2.1. Modification and blending of tannin and chitosan

In the experimental procedure, 4 g of chitosan was introduced into a 500 mL 2-neck round-bottom flask containing 1% acetic acid. The mixture was then stirred at a rate of 100 rpm using a magnetic stirrer for 1 hour. Concurrently, 4 g of tannin was added to25 ml of distilled water and mixed thoroughly. The two aqueous solutions were then combined and stirred together at a temperature of 25°C for a duration of 6 hours. Subsequently, 1 mL of glutaraldehyde (25%) was introduced into the suspended mixture. The stirring process continued initially at 25°C for 4 hours and then at an elevated temperature of 40°C for another 4 hours. Through out the experiment, the pH of the medium was maintained at 2 by the addition of hydrochloric acid. The resulting product was apale yellow material, which was then filtered, washed with distilled water, and dried in an oven at 40°C for 20 hours. Once dried, this modified tannin-chitosan composite was applied as apretreatment coagulant in wastewater treatment. By combining tannin and chitosan with the modification process, a synergistic coagulant mixture is created, offering improved capabilities for the efficient removal of heavy metals from wastewater. This innovative approachhas the potential to significantly enhance the overall efficiency and effectiveness of wastewater treatment procedures, contributing to a more sustainable and environmentally friendly water management system.

### 2.2. Collection of wastewater samples and analysis methods

Surface water was collected from Vilash river in the South of Azerbaijan on February 22, 2023 and was artificially contaminated with various metal solutions. The purpose of this approach was to examine the issue from a realistic perspective. The river water was treated immediately after collection. Metal concentration analysis was carried out by a spectrophotometric method. The characteristics of the raw water sample were analyzed following the APHA standard methods to assess both water and wastewater properties [13].

The treatment process involved the following steps: 1 liter of the turbid surface water was placed in a beaker. Approximately 20 ppm of metal was added, and the pH of the experiment was adjusted using a 1 M HCl solution and a saturated NaOH solution. The JAR-test procedure was performed using a VELP-Scientifica JLT4 apparatus. Subsequently, a specific dose of flocculant was added, the pH was readjusted, and the jar test procedure was repeated in the same manner. After 1 hour of settling, the loss in metal concentration was determined. Flocculation process at laboratory shown in Fugure 5.

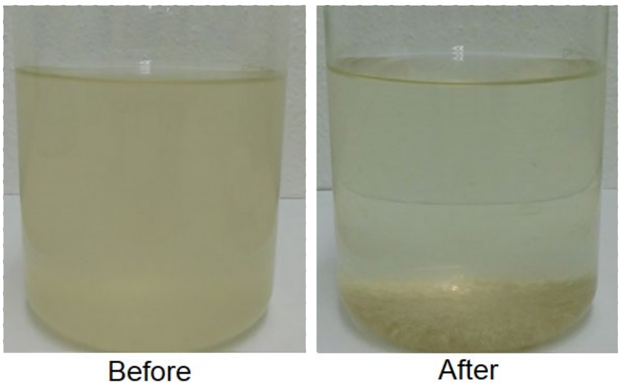


*Fig. 5. Flocculation process at laboratory.*

### 2.3. Chemical treatment and sand filtration

The schematic diagram of our proposed flocculation and sand filtration system consists of various components arranged in a sequential flow to purify water.

Firstly, coagulant adds to the wastewater. Coagulants help destabilize and aggregate small suspended particles in the water. Then the water with added coagulant enters the rapid mix tank. In this tank, high-speed mechanical mixing agitation is employed to promote the rapid and uniform mixing of the coagulant with the water. The detailed setup of the offer treatment filter system is shown in Figure 6.

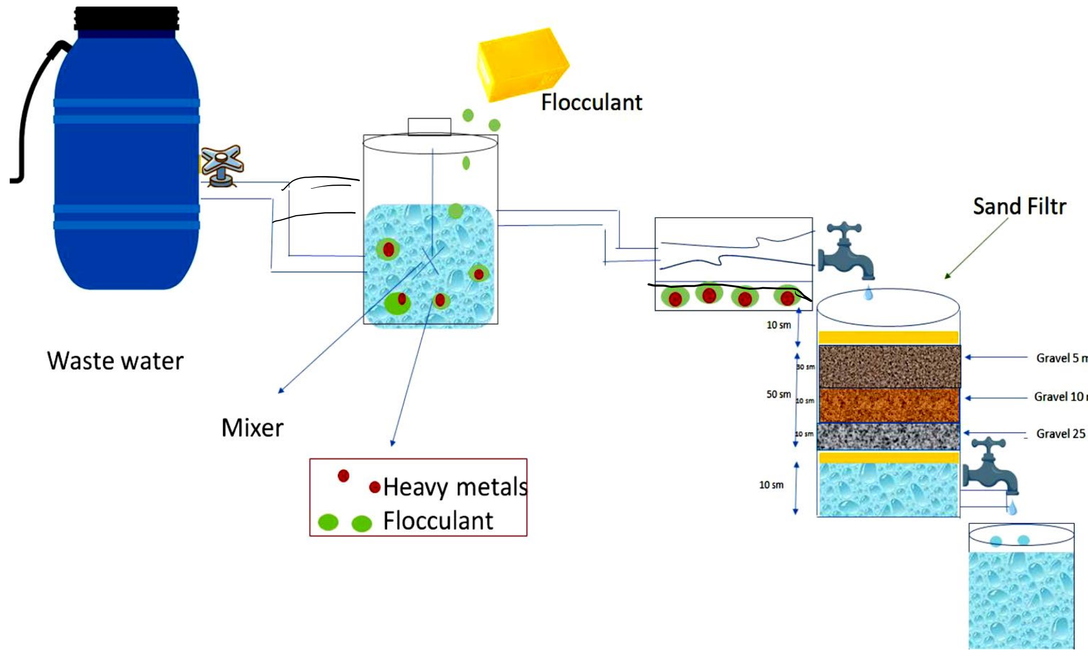


*Fig. 6. Schematic diagram of water treatment filtration system.*

As it clearly seen the water from the flocculation tank moves into the clarifier, which facilitates the settling of the larger floc particles. The clarifier is designed to provide a quiescent zone where the floc particles can settle under the force of gravity. The settled particles form a sludge layer at the bottom, while the clarified water moves on to the next stage. The clarified water then enters the sand filter, which consists of a bed of granular media. The sand acts as a physical barrier, trapping remaining suspended particles as well as some dissolved substances. The water percolates through the sand bed, allowing the clean water to pass through while retaining the contaminants.

## 3. Results and discussions

During the electroplating process, the wastewater generated can contain complex heavy metals, including $Cu^{2+}$, $Zn^{2+}$ and $Ni^{2+}$. These heavy metals pose significant risks to human health and the ecological environment if discharged without proper treatment [14-16]. The utilization of pomegranate peel extract and chitosan as a novel flocculant for wastewater pretreatment shows great potential in enhancing sand filtration and effectively removing heavy metals.

The combination of pomegranate peel extract tannin and chitosan as a flocculant offers several advantages, including being natural and eco-friendly. Application of this flocculant has successfully demonstrated the removal of heavy metals such as $Cu^{2+}$, $Zn^{2+}$, and $Ni^{2+}$ from wastewater, achieving significant reductions in metal concentrations, with $Cu^{2+}$ reduced by up to 90%, $Zn^{2+}$ by up to 75%, and $Ni^{2+}$ by up to 70%.

Figure 7 shows the removal of $Cu^{2+}$, $Zn^{2+}$, and $Ni^{2+}$ ions from water, depending on the dosage of the flocculant and the pH of the water.

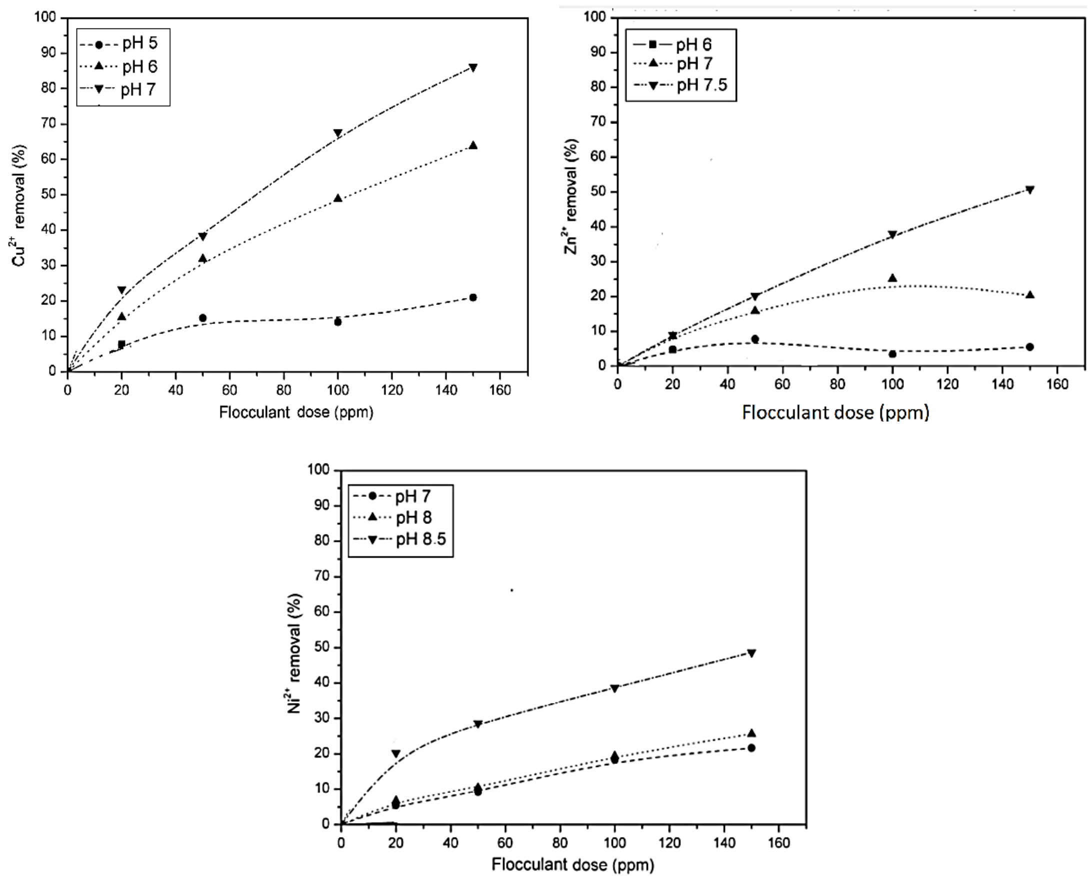


*Fig. 7. Removal of $Cu^{2+}$, $Zn^{2+}$, and $Ni^{2+}$ ions from water depending on the dosage of the flocculant and the pH of the water.*

The addition of the flocculant, along with proper pH adjustment, has improved the efficiency of the metal removal processes. pH was identified as a critical variable, with specific optimum values determined for different metals. Compared to traditional methods such as chemical precipitation and conventional coagulation-flocculation processes, the pomegranate peel-chitosan flocculant offers advantages due to its natural origin, ease of production, and simplified pH adjustment requirements. Further investigations are warranted to explore the efficacy of the pomegranate peel-chitosan flocculant with other challenging-to-remove metals using conventional methods.

## 4. Conclusion

The implemented wastewater treatment system, comprising of flocculation and sand filtration processes, effectively treated metal-ion-containing wastewater from a chemistry research laboratory, meeting the recommended discharge standards. The novel bioflocculant process significantly improved various water characterization parameters, including pH and turbidity. The application of bioflocculant successfully removed heavy metals such as $Cu^{2+}$, $Zn^{2+}$, and $Ni^{2+}$ from the wastewater, achieving substantial reductions in their concentrations, with $Cu^{2+}$ reduced by up to 90%, $Zn^{2+}$ by up to 75%, and $Ni^{2+}$ by up to 70%. The flocculation-sand filtration system offers a viable solution for treating wastewater with dissolved metal ions, operating at low pressures, and enabling environmentally safe discharge.

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