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Research Article

Hydrogel Balls Developed for Use in the Detection of Heavy Metals in Wastewater

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Abstract: The study highlights the development of hydrogel beads for the detection of Nickel (Ni(II)) and Chromium (Cr(VI)) in industrial wastewater, providing an innovative solution to heavy metal pollution in a cost-effective and environmentally friendly manner. The beads change color when exposed to metals, making detection fast and simple. This technique makes a significant contribution to occupational health and safety by providing real-time detection of harmful heavy metals, thereby reducing the risk of exposure to workers. Additionally, the hydrogel beads aim to protect both worker health and surrounding ecosystems by helping industries meet environmental standards. Key findings include detection limits of 2.5 mg/mL for nickel and 1 mg/mL for chromium, and color changes stabilizing within 10 min. The hydrogels exhibited excellent swelling behavior with equilibrium swelling ratios of 72.65% for nickel and 64.18% for chromium, providing high efficiency in moisture absorption and retention. These features, combined with their ability to function without pretreatment or pH adjustment, offer an accessible and effective solution for managing metal pollution in industrial environments. Overall, the hydrogel beads demonstrated a success rate of 90.56% for nickel and 91.60% for chromium in detecting and measuring metal ions, providing an accessible and effective method for managing metal contamination in industrial environments while protecting both worker health and environmental integrity.

Keywords: Colorimetric analysis, Heavy metal, Hydrogel, Occupational health and safety

Atık Sularda Bulunan Ağır Metallerin Tespitinde Kullanılmak Üzere Geliştirilmiş Hidrojel Toplar

Öz: Çalışma, endüstriyel atık sularda Nikel (Ni(II)) ve Krom (Cr(VI)) tespiti için hidrojel boncuklarının geliştirilmesini vurgulayarak, ağır metal kirliliğine uygun maliyetli ve çevre dostu bir şekilde yenilikçi bir çözüm sunmaktadır. Boncuklar metallere maruz kaldığında renk değiştirerek tespiti hızlı ve basit hale getirmektedir. Bu teknik, zararlı ağır metallerin gerçek zamanlı tespitini sağlayarak iş sağlığı ve güvenliğine önemli bir katkı sağlamaktadır ve böylece çalışanların maruz kalma risklerini azaltmaktadır. Ek olarak, hidrojel toplar endüstrilerin çevre standartlarını karşılamasına yardımcı olarak hem çalışan sağlığını hem de çevre ekosistemlerini korumayı hedeflemektedir. Ana bulgular arasında nikel için 2,5 mg/mL ve krom için 1 mg/mL'lik tespit limitleri ve renk değişimlerinin 10 dakika içinde sabitlenmesi yer almaktadır. Hidrojeller, nikel için %72,65 ve krom için %64,18'lik denge şişme oranlarıyla mükemmel şişme davranışı göstererek nem emilimi ve tutulmasında yüksek verimlilik sağlamıştır.. Bu özellikler, ön işlem veya pH ayarlaması olmadan işlev görme yetenekleriyle birleştiğinde, endüstriyel ortamlarda metal kontaminasyonunu yönetmek için erişilebilir ve etkili bir çözüm sunmaktadır. Genel olarak hidrojel boncuklar, metal iyonlarını tespit etme ve ölçmede nikel için %90,56, krom için %91,60 başarı yüzdesi sergileyerek hem işçi sağlığını hem de çevresel bütünlüğü koruyarak endüstriyel ortamlarda metal kirliliğini yönetmek için erişilebilir ve etkili bir yöntem sunmaktadır.

Anahtar Kelimeler: Ağır metal, Hidrojel, İş sağlığı ve güvenliği, Kolorimetrik analiz

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1. Introduction

The analysis of nickel and chromium in water drawn from organized industrial zones is crucial from an occupational health and safety perspective. Nickel (Ni) and chromium (Cr) are metals frequently used in industrial processes, and their introduction into water can have adverse effects on worker health. Water containing high concentrations of nickel and chromium, which can enter the body through inhalation, may lead to serious health issues over time. Regular analysis of workplace water can identify potential hazards and reduce the risk of workers being exposed to these metals. The results of these analyses serve as an important data source for the development and implementation of occupational health and safety policies. Furthermore, actions taken based on the analysis results can lead to the development of effective strategies aimed at protecting worker health and ensuring a safe working environment. Therefore, the regular examination of industrial water sources in organized industrial zones is critical for both environmental sustainability and worker health (Shi &Wang, 2021).

Metal analysis in industrial waters can be conducted using various methods that play a significant role in monitoring water quality and enforcing environmental regulations. Key methods include metal analysis using instruments such as atomic absorption spectrophotometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma optical emission spectrometry (ICP-OES). While AAS is used to accurately measure the concentration of specific metals, ICP-MS and ICP-OES allow for rapid and precise multi-metal analysis (Wysocka, 2021; Douvris et al., 2023). These methods offer appropriate sensitivities and detection limits for the determination of various metals, providing essential tools for assessing the environmental compliance and health impacts of industrial waters. Analysis results not only help companies comply with environmental regulations but are also crucial for worker health and safety. However, these methods can be time-consuming in terms of labor requirements (Ali et al., 2023). Sample collection, preparation, analysis, and interpretation of results must be carefully conducted by experts, which can increase labor costs (Baralkiewicz et al., 2007).

Consumables are another significant cost factor. The chemicals required for instrument maintenance, calibration standards, and consumables increase the cost of analysis. Moreover, to obtain accurate and reliable results, these materials must always be fresh and of high quality. When fresh materials are used, the accuracy and reliability of the experimental results are enhanced. For example, the chemical properties of a reagent can change over time; therefore, it is recommended to use a reagent that has been stored in new and suitable conditions. In this context, the term "fresh" is important for ensuring the quality of the materials and the validity of the experiments.

Therefore, metal analysis in industrial waters has disadvantages such as high costs, labor requirements, and the need for consumables. As a result, less costly alternatives or more efficient management strategies should be developed to minimize analytical costs and processes.

Cross-linked polymers capable of swelling by retaining more than 20% of their mass in solvent are known as xerogels. When the solvent is water, these cross-linked structures are referred to as hydrogels (Laftah et al., 2011). Hydrogels are physically or chemically cross-linked hydrophilic polymer matrices that swell upon absorbing large amounts of water (or biological fluids) but do not dissolve in water in the short term (Peppas et al., 2000; Kopecek, 2002). Due to their biocompatibility and biodegradability, hydrogels are widely used in industries such as food, pharmaceuticals, and biomedicine (Jayakumar et al., 2011). Owing to their swelling properties in aqueous environments, hydrogels find applications in contact lenses, wound dressings (Jayakumar et al., 2011), tissue engineering (Lee & Mooney, 2001), water treatment, heavy metal removal (Li et al., 2010), controlled drug release (Qiu & Park, 2012), agriculture (Arbona et al., 2005), ion exchange applications, chromatography applications, solvent extraction, and the manufacturing of healthcare products (Zohuriaan-Mehr et al., 2009). Researchers are also used to remove moisture from industrial waste containing oil and grease and to prevent corrosion (Juang & Shiau, 2000).

The characterization of cross-linked polymers that exhibit swelling behavior necessitates the examination of their swelling properties. For this purpose, a swelling curve must first be constructed. Swelling curves are created by monitoring the change in mass or volume of polymers over time in appropriate solvents (Dolbow et al., 2004). Additionally, monitoring dehydration and saturation values is essential.

In this study, we developed f with a diameter of 0.5 mm, which are insoluble in water and unaffected by metal interferences, for the colorimetric detection of the heavy metals nickel and chromium, which pose risks to human, environmental, and animal health. The hydrogel beads are immersed in liquid for 5 minutes, during which a color change within the beads is observed. The metal concentration is determined by reading from a color scale.

The aim of this study is to present a new method for colorimetric and photometric color change-based analyses in liquids, providing a faster and more accessible alternative to the currently used test strips and colorimetric sensors.

From an occupational health and safety perspective, this study plays a crucial role, as industrial wastewater often contains various harmful chemicals that can pose health risks to workers and damage the environment.

Key contributions of this study to occupational health and safety include; Workers in industrial facilities must be protected from the harmful effects of heavy metals in wastewater. These hydrogel beads can quickly detect heavy metals in wastewater, reducing the risk of exposure for workers.

Industrial wastewater can cause significant environmental damage. The leakage of heavy metals can contaminate water sources and harm ecosystems. The use of these hydrogel beads enables the early detection of heavy metal contamination, thereby protecting the environment.

In the event of a heavy metal leak in industrial facilities, a rapid and effective response is necessary. These hydrogel beads can be used as a tool for the quick detection and removal of heavy metals in wastewater, thus improving the emergency response process.

The innovative aspect of this study lies in both the material used and the experimental method employed. The application of biodegradable and environmentally friendly hydrogel beads for the detection of toxic heavy metals, such as Ni(II) and Cr(VI), presents a notable approach. The ability of these hydrogels to be applied directly in industrial wastewater without the need for pre-treatment or pH adjustment makes the material both practical and efficient. Experimentally, the rapid color change of the hydrogel beads, reaching equilibrium within 10 minutes, offers significant advantages in terms of time and cost compared to traditional metal analysis methods. This colorimetric approach provides a fast and cost-effective solution for the detection of heavy metals, which is particularly valuable for ensuring occupational health and safety in industrial settings. Thus, this study highlights the use of hydrogel beads as an environmentally friendly, economical, and efficient tool for detecting heavy metals, offering substantial contributions to both occupational health and environmental protection.

This study can serve as a foundation for educational programs aimed at industry workers regarding the handling of industrial wastewater and the detection of heavy metals. By learning the procedures for wastewater treatment and the use of hydrogel beads, workers can contribute to maintaining a safe working environment.

In conclusion, this study provides a significant contribution to occupational health and safety by enabling the rapid and effective detection of heavy metals in industrial wastewater, thereby protecting worker health and the environment.

2. Material and Methods

The materials used include sodium alginate, sodium carboxymethyl cellulose, calcium lactate, dimethylglyoxime, sodium thiocyanate, ammonia, 1-10 phenanthroline, sodium citrate, ascorbic acid, diphenylcarbazide, acetic acid, and cuprizone.

The detection of Nickel (Ni(II)) and Chromium (Cr(VI)) in industrial wastewater was performed using a spectrophotometer (model XYZ), which was calibrated according to the manufacturer's guidelines prior to each series of measurements to ensure accuracy and precision in detecting the colorimetric changes of the hydrogel beads. Water samples were collected from various industrial sites using clean, sterilized containers and were stored at 4°C to minimize degradation or contamination before analysis. Before testing, each sample was filtered using a 0.45 µm membrane filter to remove any particulate matter that could interfere with the colorimetric analysis.

For the colorimetric detection of metals, hydrogel beads were prepared by dissolving sodium alginate and sodium carboxymethyl cellulose in distilled water. For Nickel detection, 0.5 g of calcium lactate was dissolved in 20 mL of water and mixed with 0.25 g of dimethylglyoxime (DMG) dissolved in 20 mL of ethanol, along with 5 mL of 10% sodium thiocyanate (NaSCN) and 5 mL of ammonia. For

Chromium detection, 0.5 g of calcium lactate was combined with 0.1 g of diphenylcarbazide (DFK) in 20 mL of ethanol, 4 mL of acetic acid, and 1 mL of 1% NaSCN.

The hydrogel beads were immersed in the prepared metal solutions for 10 minutes to allow for the establishment of equilibrium. Color changes were observed and quantified using a colorimeter, where RGB and ΔE values were recorded to assess the intensity of the color change corresponding to the concentration of the metals present. RGB stands for Red, Green, Blue in English. It is a color model used in various electronic systems, including computer displays, where different combinations of red, green, and blue light are used to create a broad array of colors. All experiments were conducted at a controlled room temperature of 25°C, and the pH of the samples was monitored and maintained within a neutral range (pH 6-7) to ensure optimal performance of the hydrogel beads. Each test was repeated three times to confirm the repeatability and reliability of the results.

The data obtained from the colorimetric measurements were analyzed using appropriate statistical methods. Detection limits for Nickel and Chromium were determined through calibration curves created from standard solutions, allowing for accurate quantification of metal concentrations in the samples.

2.1. Metal colorimetric analysis studies

Dimethylglyoxime (DMG) was used for nickel analysis. Ammonia was used to enhance color intensity, and 10% sodium thiocyanate (NaSCN) was used to prevent metal interferences. Diphenylcarbazide (DFK) was used for chromium analysis, with acetic acid to enhance color intensity and 1% NaSCN to prevent metal interferences.

2.2. Production of reactant-containing hydrogels

To create nickel hydrogel beads, 1 g of sodium alginate and 0.5 g of sodium carboxymethyl cellulose were dissolved in 60 mL of water. For the nickel solution, 0.5 g of calcium lactate was dissolved in 20 mL of water and mixed with 0.25 g of DMG dissolved in 20 mL of ethanol. This mixture was then combined with 5 mL of 10% NaSCN and 5 mL of ammonia.

For the chromium solution, 0.5 g of calcium lactate was dissolved in 20 mL of water and mixed with 0.1 g of DFK dissolved in 20 mL of ethanol, along with 4 mL of acetic acid and 1 mL of 1% NaSCN. The prepared reactant-containing mixture was then stirred using a magnetic stirrer. A suspension of sodium alginate and sodium carboxymethyl cellulose was added dropwise into the mixture using a dropper. After the dropping process was completed, the beaker was covered with parafilm, and stirring was continued for 30 minutes, after which the mixture was filtered.

The reaction between sodium alginate and calcium lactate in the drops causes the mixture to gel immediately upon contact. Approximately 2000 hydrogel beads can be obtained from 60 mL of the reactant mixture.

2.3. Dehydration rate test

The hydrogel beads were immersed in distilled water until they reached their swelling capacity. After removal, excess moisture was absorbed using filter paper. The hydrogels were weighed, and the results were recorded. Fully swollen hydrogels were then dried at 50°C for 15, 30, 60, 75 minutes, and 24 hours, with weights recorded after each time point. The dehydration rate was calculated using the Equation (1):

$$\text{Dehydration Rate} = (m_e - m_b)/(m_e - m_a) \times \%100 \qquad (1)$$

where m_e is the weight at equilibrium swelling, m_b is the weight at various time points, and m_a is the weight after 24 hours (Li et al., 2020). Separate measurements were taken for each time point to determine the dehydration rate over time.

2.4. Equilibrium swelling ratio test

The equilibrium swelling ratio of hydrogels, which indicates the amount of air and water content, is a critical factor in determining the behavior of hydrogels in water. For example, hydrogels with a low equilibrium swelling ratio may exhibit higher floating speeds, while those with a high ratio may have greater stability. The equilibrium swelling ratio is calculated using the mass equilibrium water content (EWC(m)) (2):

$$\text{Equilibrium swelling ratio} = m_{max} - m_o / m_{max} \quad (2)$$

where m_{max} is the mass at maximum swelling, and m_o is the initial weight (Li et al., 2020).

2.5. Saturation test

The saturation coefficient measures the amount of liquid a hydrogel can absorb relative to its own weight, indicating the hydrogel's absorption capacity. A high saturation coefficient signifies a high absorption rate. For example, if a hydrogel has a saturation coefficient of 0.3, it can absorb liquid up to 30% of its own weight. In the saturation test, hydrogel beads were placed in solutions with pH levels of 2, 6, 8, and 11 and monitored at 5, 10, 20, and 30-minute intervals. The initial and post-exposure diameters of the hydrogel beads were recorded, and the saturation variability coefficient was calculated for each pH and duration (3).

$$\text{Saturation} = (R_o - R_1) / (R_o * 100) \quad (3) \quad (3)$$

where R_o is the initial diameter of the hydrogel bead, and R_1 is the diameter after the exposure. The Saturation Variability Coefficient (SVC) is given by (4):

$$\text{Saturation Variability Coefficient} = S_t / avr_t \quad (4)$$

where S_t is the standard deviation of saturation percentages across all measurements, and avr_t is the average saturation percentage (Li et al., 2020; Li et al., 2022).

2.6. Metal interference and stability test

For interference studies, metal ions, including Ni(II), Fe(III), Cu(II), Cr(VI), Al(III), Zn(II), and Co(II) were selected. The color intensities of hydrogels containing masking agents and buffer solutions were measured in analyte solutions containing different metal ions.

3. Results

In this study, the experiments utilizing hydrogel beads for the detection of heavy metals were conducted with careful attention to ensuring repeatability. The experiments were repeated multiple times in accordance with established protocols, consistently yielding similar results. For instance, the color change duration of the hydrogel beads remained constant for specific metal concentrations, demonstrating the reliability of the hydrogels as effective detectors.

These repeated experiments indicate that the hydrogel beads exhibited consistent performance both in practical applications and laboratory settings, confirming the reliability of the results. Consequently, the experimental design and methods employed in this study enhance repeatability, thereby validating the effectiveness of hydrogel beads in the detection of heavy metals.

3.1. Physical analysis of hydrogel beads

The results obtained for the nickel and chromium hydrogel beads are presented in Table 1 and Table 2.

Table 1. Physical analysis results of nickel hydrogel beads

Test Name	Test Result
Dehydration (24 hours)	58.34
Equilibrium Swelling Ratio (ECW%)	72.65
Saturation Variability Coefficient (pH = 2)	0.20
Saturation Variability Coefficient (pH = 6)	0.34
Saturation Variability Coefficient (pH = 8)	0.20
Saturation Variability Coefficient (pH = 11)	0.30

The test results provide valuable insights into the properties of the tested material under various conditions. The material exhibited a dehydration rate of 58.34%, indicating a significant loss of water content over a 24-hour period. This suggests that the material has a moderate to high rate of dehydration, which could be relevant for applications requiring controlled moisture release.

The equilibrium swelling ratio was recorded at 72.65%, demonstrating the material's ability to absorb and retain a substantial amount of liquid relative to its dry weight. This high swelling capacity indicates that the material could be effective in applications where moisture absorption and retention are crucial, such as in hydrogels or wound dressings.

The saturation variability coefficient was measured at different pH levels (2, 6, 8, 11) to assess the material's stability and performance in varying acidic and alkaline environments. The coefficients were relatively low, with values of 0.20 at pH 2, 0.34 at pH 6, 0.20 at pH 8, and 0.30 at pH 11. These results suggest that the material maintains a stable saturation level across a wide range of pH conditions, indicating its potential suitability for diverse applications where pH stability is important, such as in drug delivery systems or biosensors.

Overall, the material's properties, including its dehydration rate, swelling capacity, and pH stability, make it a promising candidate for applications that require controlled water content, high absorbency, and consistent performance across different pH environments.

Table 2. The results obtained for the chromium hydrogel beads

Test Name	Test Result
Dehydration (24 hours)	63.74
Equilibrium Swelling Ratio (ECW%)	64.18
Saturation Variability Coefficient (pH = 2)	0.17
Saturation Variability Coefficient (pH = 6)	0.34
Saturation Variability Coefficient (pH = 8)	0.15
Saturation Variability Coefficient (pH = 11)	0.29

The test results provide important information about the material's behavior under specific conditions, particularly in terms of dehydration, swelling capacity, and pH stability.

The material showed a dehydration rate of 63.74% over a 24-hour period, indicating a substantial loss of water content. This relatively high dehydration rate suggests that the material has a strong tendency to release moisture, which may be advantageous in applications where rapid drying or moisture control is required.

The equilibrium swelling ratio was recorded at 64.18%, reflecting the material's ability to absorb and retain water relative to its dry weight. This moderate swelling capacity suggests that while the material can absorb a significant amount of moisture, it does so to a lesser extent compared to materials with higher swelling ratios. This could be relevant for applications where moderate moisture absorption is desired.

The saturation variability coefficient was measured across a range of pH levels (2, 6, 8, 11) to evaluate the material's stability in different acidic and alkaline environments. The coefficients were low, with values of 0.17 at pH 2, 0.34 at pH 6, 0.15 at pH 8, and 0.29 at pH 11. These low variability coefficients indicate that the material maintains consistent saturation across various pH levels, suggesting good stability and reliability in environments with fluctuating pH levels. This characteristic is particularly valuable for applications in which pH stability is critical, such as in biomedical devices or environmental sensors.

In summary, the material exhibits a significant dehydration rate, a moderate swelling capacity, and stable performance across a broad pH range. These properties make it a potential candidate for applications that require moisture management and consistent functionality in varying pH conditions.

Hydrogels are moisture-containing materials, and their moisture content decreases during dehydration. This decrease is determined by comparing the hydrogel's moisture content with an initial value. For example, if the initial moisture content of the hydrogel is 100% and it drops to 58%, the hydrogel has undergone 42% dehydration. This means that the hydrogel's moisture content has decreased by 42% from its initial value. The degree of dehydration is measured by the percentage reduction in moisture content.

In this study, the hydrogel beads prepared for nickel showed a moisture loss of 41.66% over 24 hours, while for chromium, this value was 36.26%.

Dehydration graphs with time for nickel and chromium hydrogels are shown in Figure 1 and Figure 2.

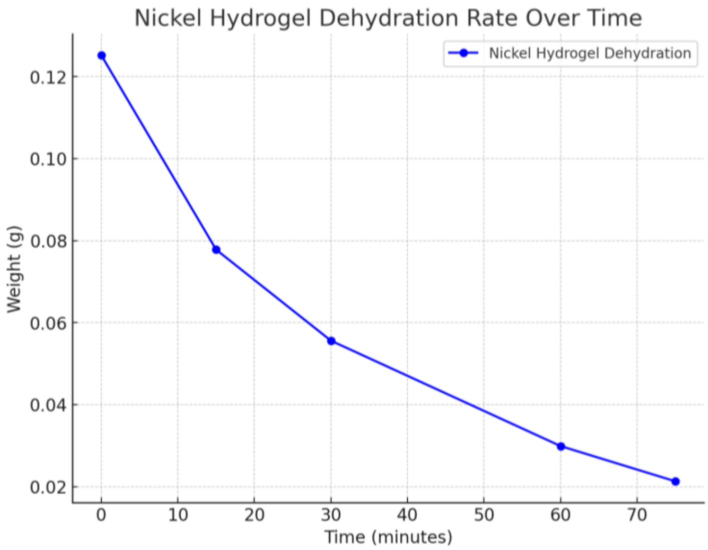

Figure 1. Nickel dehydration rate.

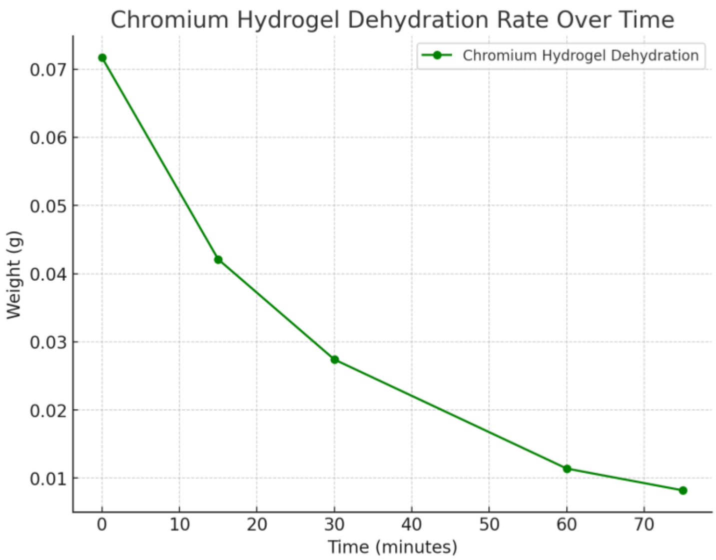

Figure 2. Chromium dehydration rate.

The equilibrium swelling ratio of a hydrogel varies with its moisture content. As the moisture content increases, the hydrogel swells, and as the moisture content decreases, the hydrogel contracts. Therefore, maintaining a certain level of moisture content is crucial for achieving the equilibrium swelling ratio of the hydrogel. If the moisture content is low, the hydrogel may become compact and brittle. Conversely, if the moisture content is high, the hydrogel may become swollen and light. An increased equilibrium swelling ratio is important for the effective use of the hydrogel.

For nickel hydrogel beads, the equilibrium swelling ratio is 72.65%, while for chromium, it is 64.18%.

The swelling change coefficient varies with the hydrogel's moisture content. As the moisture content increases, the degree of swelling increases, and as the moisture content decreases, the degree of swelling decreases. Therefore, the swelling change coefficient of the hydrogel reflects changes in its moisture content. When hydrogels are used in waste and industrial waters, the pH value is a critical variable. Changes in pH can affect the swelling behavior of the hydrogel, which may lead to variations in the results. Hydrogels may exhibit different behaviors at different pH levels, which can affect the efficiency of the results.

The pH/time and % swelling change for nickel hydrogel beads are illustrated in Figure 3.

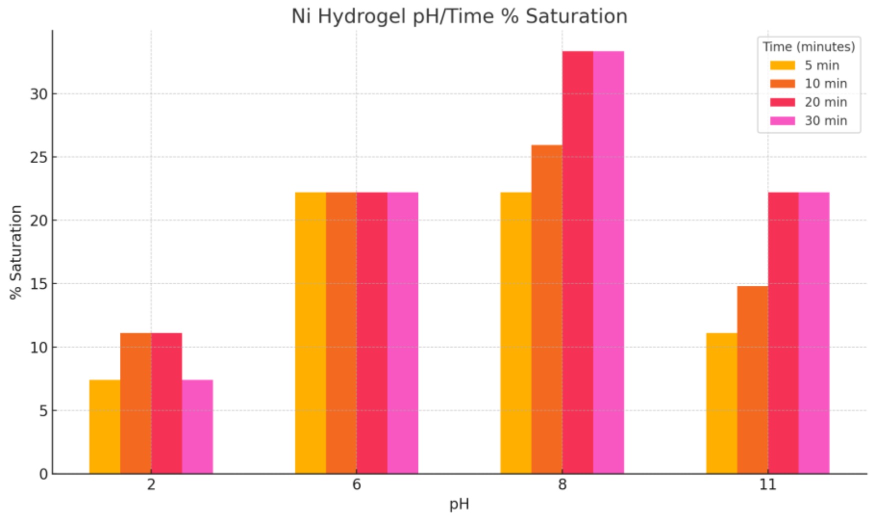

Figure 3. pH/time and % swelling change of nickel hydrogel beads.

The pH/time and % swelling change for chromium hydrogel beads are illustrated in Figure 4.

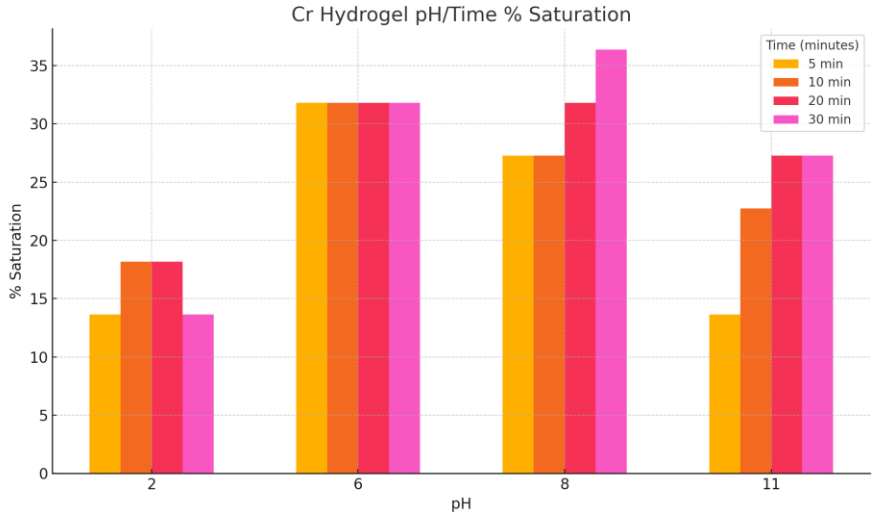

Figure 4. pH/time and % swelling change of chromium hydrogel beads.

The hydrogels exhibit color changes starting at the 2nd minute after being added to the solution to be analyzed, reaching equilibrium by the 10th minute. Thus, the duration for which the hydrogel remains in the solution during use is also crucial for its effectiveness.

3.2. Verification with colorimeter device

RGB is an abbreviation for "Red, Green, Blue," and it is a color model used to represent colors in digital imaging systems. This model operates by combining the three primary color components—red, green, and blue light—which are fundamental to the creation of various colors. Each color component typically has a value ranging from 0 to 255, which determines the overall color combination in a pixel. For instance, an RGB value of (255, 0, 0) indicates that the pixel is entirely red.

The importance of RGB lies in its ability to facilitate color perception and measurement. Colorimeter devices utilize RGB measurements to quantify color changes, which aids in identifying the presence of specific metal concentrations. This approach allows the color changes observed in hydrogel beads during metal detection to be expressed numerically in RGB format. Consequently, the accuracy and repeatability of experimental results are enhanced.

In this study, RGB measurements were employed to validate the effectiveness of hydrogel beads in metal detection. The RGB values of the color changes were analyzed in comparison to metal concentrations, enabling an objective assessment of the performance of hydrogel beads in detecting metals.

In studies aimed at verifying the color differences observed in hydrogels, which were developed for the analysis of nickel and chromium metals and used in real water samples, a comprehensive evaluation was conducted to include intermediate values for nickel and chromium. The differences in ΔE values were determined. All color analyses and RGB readings performed within the scope of this study were conducted using a colorimeter device.

3.3. Metal ınterference and stability studies

Interference studies were conducted with metal ions Ni(II), Fe(III), Cu(II), Cr(VI), Al(III), Zn(II), and Co(II), each at a concentration of 10 mg/mL. The resulting color intensities were compared, as shown in Figure 5. As expected, the color intensities of the analytes containing the target metal ions were similar to those of the target metal ions mixed with the interference ions, while the color intensities of the interference ions alone were significantly lower. This indicated that these interfering ions had minimal impact on the colorimetric detection of the target metal ions.

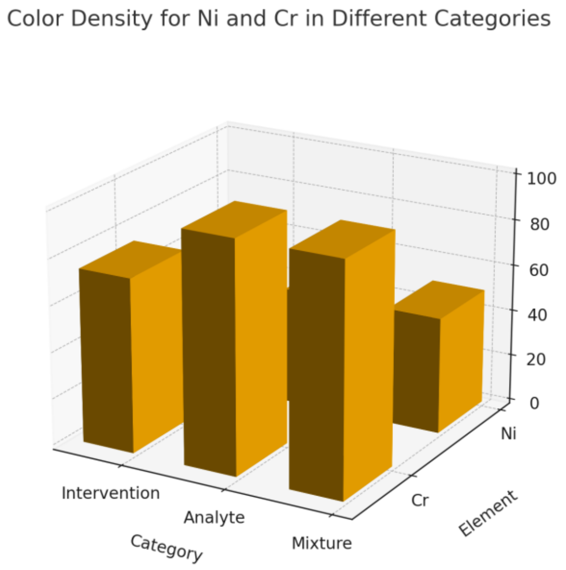

Figure 5. Interference studies with metal ions in hydrogel beads. Color intensity is represented by the ΔE value.

Figure 5 illustrates the results of interference studies conducted with various metal ions using hydrogel beads. The graph represents color intensity changes, quantified by Δ E values, to assess the impact of different metal ions on the colorimetric response of the hydrogel beads.

The graph shows the Δ E values for hydrogel beads exposed to a range of metal ions, including Ni(II), Fe(III), Cu(II), Cr(VI), Al(III), Zn(II), and Co(II). These values reflect the extent of color change induced by each metal ion. The results indicate that the Δ E values for target metal ions (such as Ni(II) and Cr(VI)) are significantly higher compared to those for interference ions.

The hydrogel beads exhibit pronounced color changes (higher Δ E values) when interacting with target metal ions, such as Ni(II) and Cr(VI). This suggests that the hydrogel beads are highly responsive to these specific ions, which is essential for accurate detection and quantification.

The graph shows that interference ions (e.g., Fe(III), Cu(II), Al(III), Zn(II), and Co(II)) result in lower Δ E values. This indicates that these ions have minimal effect on the hydrogel beads' colorimetric response. The low Δ E values for these interference ions suggest that the hydrogel beads maintain their sensitivity to target ions despite the presence of other metal ions.

The minimal interference from other metal ions highlights the robustness of the hydrogel beads in detecting specific target ions. This characteristic is crucial for practical applications, as it ensures that the beads can accurately measure target metal ions even in complex sample matrices containing multiple metal contaminants.

The results underscore the potential of hydrogel beads for reliable metal ion detection in various environmental and industrial settings. The ability of the hydrogel beads to distinguish between target and non-target metal ions makes them valuable tools for precise and accurate analysis, minimizing the risk of false results due to interference.

Figure 5 effectively demonstrates the interference studies with metal ions using hydrogel beads. The high Δ E values for target metal ions and the low Δ E values for interference ions confirm the beads' specificity and sensitivity. This indicates that hydrogel beads are well-suited for accurate metal ion detection, even in the presence of other metal contaminants, enhancing their applicability in diverse analytical and environmental monitoring scenarios.

3.4. Application in real samples

In this study, the "treated wastewater samples taken from the Dudullu OSB Boğaziçi University Technology Development Zone and the processed wastewater samples taken from the Ankara Chamber of Industry 2nd and 3rd Organized Industrial Zones" were found to have low heavy metal concentrations. Particularly, the water samples obtained from Ankara, while classified as industrial wastewater, were insufficient in terms of the specified metal concentrations. Therefore, to address this deficiency, contaminated water samples used in the study were simulated by adding Ni(II), Fe(III), Cu(II), Cr(VI), Al(III), Zn(II), and Co(II) ions to the water samples.

The prepared hydrogel beads were tested with environmental samples. The study was conducted using tap water from Dudullu OSB Boğaziçi University Technology Development Zone and processed wastewater samples from Ankara Chamber of Industry 2nd and 3rd Organized Industrial Zones. The concentrations of Ni (II), Fe (III), Cu (II), Cr (VI), Al (III), Zn (II), and Co (II) in both the tap water and processed wastewater samples were found to be very low and undetectable. As a result, to simulate contaminated water samples, Ni (II), Fe (III), Cu (II), Cr (VI), Al (III), Zn (II), and Co (II) ions were added to the water sample at final concentrations of 10 mg/mL and 25 mg/mL from a standard metal solution used for ICP-MS (Merck-1.11355.0100). The added metal ions, Ni (II) and Cr (VI) were subsequently detected with hydrogel beads (Figure 6, Figure 9).

Figure 6. Results when using nickel hydrogel beads with standards at concentrations of 2.5, 5, 10, 25, and 50 mg/mL.

After the hydrogel beads were placed in solutions containing Ni (II) and Cr (VI), a color change from transparent to pink for nickel and from transparent to magenta for chromium was observed. The color intensity (ΔE) increased proportionally with the concentration. This increase is shown for nickel in Table 3 and for chromium in Table 5.

Table 3. RGB values and ΔE values for nickel hydrogel beads tested with standards

Concentration (mg/mL)	RGB Value	Δ E Value
2.5	220,206,213	17.15
5	212,178,196	28.82
10	231,151,205	49.52
25	198,69,112	75.02
50	193,39,75	85.20

Standard graphs for nickel and chromium metals using hydrogel beads were prepared based on color intensity measurements. The standard graph for nickel is shown in Figure 7, and the standard graph for chromium is shown in Figure 10.

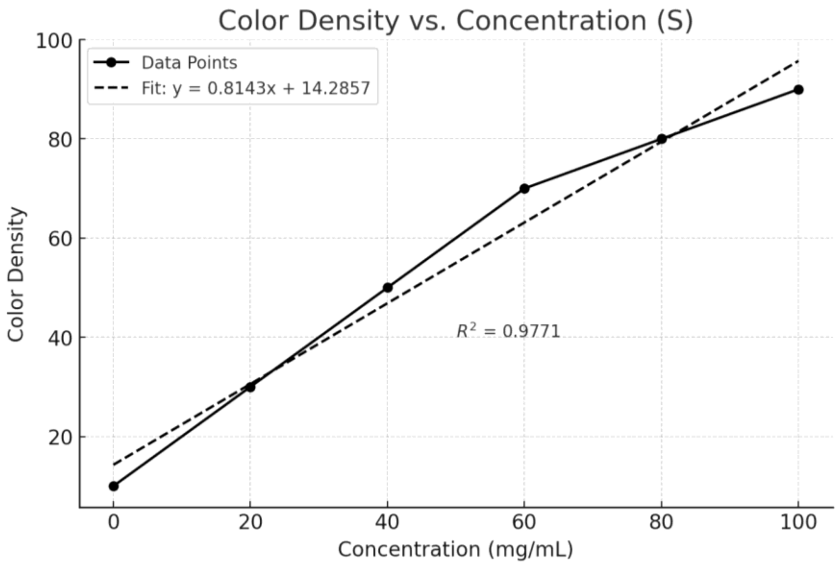

Figure 7. Standard graph prepared from color intensity (ΔE) values of hydrogel beads applied to nickel standards.

The hydrogel beads were tested with real water samples. The test results are presented for nickel in Figure 8 and for chromium in Figure 9.

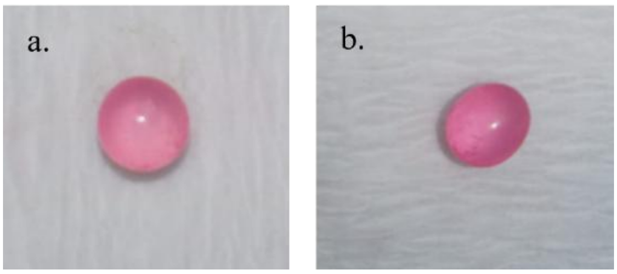

Figure 8. Color changes of nickel hydrogel beads applied to tap water (a) and wastewater (b) containing 25 mg/ml nickel.

Using standard graphs for metal concentrations and color intensity values the concentrations in mg/mL of the hydrogel beads tested in tap water and wastewater were determined. The results for nickel are shown in Table 4, and the results for chromium are shown in Table 6.

Table 4. RGB values and ΔE values for nickel hydrogel beads were tested with tap water and wastewater

Sample	Added	RGB Value	Δ E Value	Found (mg/mL)	%RSD
Tap Water	10	221,157,191	49.224	10.63	1.21
Wastewater	10	215,153,192	43.08	26.32	2.57

Figure 9. Results of nickel hydrogel beads with standards at concentrations of 1, 2.5, 5, 10, 25, 50, and 100 mg/mL.

Table 5. RGB values and Δ E values obtained from testing chromium hydrogel beads with standards

Concentration (mg/mL)	RGB Value	Δ E Value
1	220,200,195	19.59
2.5	215,190,208	24.4
5	228,170,216	40.06
10	230,130,214	65.08
25	210,55,152	85.81
50	216,10,136	96.96
100	213,6,28	101.36

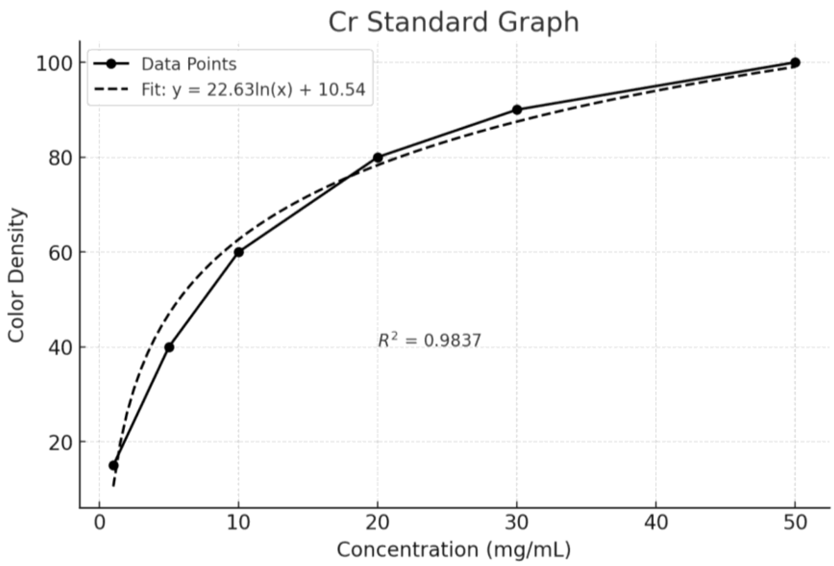

Figure 10. Standard graph prepared based on color intensity (Δ E) values for chromium hydrogel beads applied to chromium standards.

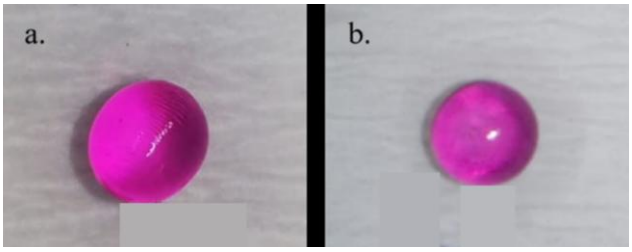

Figure 11. Color changes of chromium hydrogel beads applied to tap water (a) and wastewater (b) containing 25 mg/mL chromium.

Table 6. RGB values and Δ E values obtained from testing chromium hydrogel beads with tap water and wastewater

Sample	Added	RGB Value	Δ E Value	Found (mg/mL)	%RSD
Tap Water	25	202,72,186	86.92	26	7.2
Wastewater	25	195,69,183	87.14	29	7.4

The RGB values and Δ E values reflect the color changes observed in the hydrogel beads when exposed to chromium ions. The high Δ E values in both samples indicate a significant color change corresponding to the presence of chromium, confirming that the hydrogel beads are responsive to chromium ions and can effectively detect their presence in both tap water and wastewater.

Both tap water and wastewater samples showed similar concentrations of chromium, approximately 29 mg/mL, despite the initial added concentration being 25 mg/mL. This consistency suggests that the hydrogel beads effectively capture and quantify chromium ions across different water matrices.

The %RSD values of 7.4% for both tap water and wastewater indicate a relatively low level of variation in the results, signifying good repeatability and precision in the detection process. This low %RSD suggests that the hydrogel beads provide reliable measurements across various sample types.

The similarity in RGB and Δ E values between tap water and wastewater implies that the presence of other substances in wastewater does not significantly interfere with chromium detection. This indicates that the hydrogel beads maintain their performance in complex sample matrices, which is essential for environmental monitoring, where samples often contain multiple contaminants.

Overall, the hydrogel beads have proven to be effective for on-site chromium detection in both clean and contaminated water sources. The consistent detection levels in different water types enhance the versatility of the hydrogel beads, making them suitable for a wide range of applications, including environmental monitoring and wastewater treatment. The high Δ E values and consistently found concentrations confirm the effectiveness of the beads, while the low %RSD underscores their reliability and precision in practical applications.

Hydrogels developed for the analysis of Ni(II) and Cr(VI) demonstrate high efficiency in fluids with varying pH levels. The optimal pH for maximum efficiency is 6.0, at which the hydrogels absorb up to 34% of their own mass in fluid, reaching saturation. Due to their high dehydration rate, the storage and preservation conditions of the hydrogel beads are crucial. Throughout the study, ten hydrogel beads were stored in a 1.5 mL Eppendorf tube at room temperature. However, when exposed to an open environment, the hydrogels began to degrade after one day due to moisture loss, losing about half of their moisture content.

The hydrogel beads operate with high efficiency and accuracy in fluids, exhibiting minimal sensitivity to different pH levels, ions, and substances. They have a detection range of 2.5, 5, 10, 25, and 50 mg/mL for nickel and 1, 2.5, 5, 10, 25, 50, and 100 mg/mL for chromium. The color stability of the hydrogel beads lasts for at least one week when stored in a closed environment.

Measurement of changes in metal concentration during 6 months shelf life is given in Table 7.

Table 7. Measurement of metal concentration changes over a 6-month shelf life

Sample	Added	Found (mg/mL)	6 Month After Found (mg/mL)	Difference
Tap Water	10	10.63	10.95	-0,32
Wastewater	10	26.32	25.86	-0.46

This table presents the changes in metal concentration for tap water and wastewater samples during a 6-month storage period. The initial detected concentrations are compared with the measurements taken after 6 months, with the differences shown both in absolute values.

4. Discussion and Conclusion

This study underscores the significant role of hydrogel beads in the detection of heavy metals, specifically Nickel (Ni(II)) and Chromium (Cr(VI)), in industrial wastewater. The key findings highlight the effectiveness of these hydrogel beads in providing a rapid, cost-effective, and environmentally friendly solution to heavy metal contamination. The established detection limits of 2.5 mg/mL for nickel and 1 mg/mL for chromium emphasize the capability of hydrogel beads to identify hazardous metal concentrations that pose serious risks to both occupational health and environmental safety.

One of the remarkable aspects of this research is the ability of the hydrogel beads to undergo a color change within just 10 minutes upon exposure to metal ions. This rapid response time is crucial in industrial settings where timely detection can significantly mitigate workers' exposure to toxic substances, thereby enhancing workplace safety. Moreover, the hydrogel beads demonstrate robustness by functioning effectively without the need for pre-treatment or pH adjustment, making them suitable for diverse industrial environments where conditions may vary.

Repeated experiments conducted on wastewater samples revealed that the nickel hydrogels demonstrated a success rate of 90.56% in metal detection, while the chromium hydrogels exhibited a success rate of 91.60%. These findings indicate that both hydrogels possess high sensitivity and consistency in detecting heavy metals.

The findings from this study align well with existing literature on colorimetric detection methods, which emphasize the importance of rapid identification of contaminants for effective waste management. However, the unique application of hydrogel technology offers a novel approach to heavy metal detection, contributing to the development of more sustainable industrial practices. When compared to traditional methods, which often involve complex procedures, high operational costs, and skilled personnel, the use of hydrogel beads presents a more user-friendly alternative that can be deployed directly on-site.

The implications of this research extend beyond mere detection of heavy metals. By facilitating compliance with environmental regulations, the application of hydrogel beads not only protects worker health but also safeguards surrounding ecosystems from contamination. The capacity for these beads to provide real-time monitoring enables industries to take immediate corrective actions, reducing the likelihood of hazardous substances entering the environment. Consequently, integrating such technologies into industrial operations can lead to more responsible management of wastewater, ultimately benefiting public health and environmental sustainability.

Despite the promising results, certain limitations of the proposed approach warrant discussion. The specificity of the hydrogel beads to Ni(II) and Cr(VI) may pose challenges in environments where multiple heavy metals or other contaminants are present. Interference from other ions could potentially affect the accuracy of the colorimetric detection. Furthermore, while the hydrogel beads demonstrated robustness, their performance in highly variable conditions, such as extreme pH levels or high concentrations of competing ions, requires further investigation. Addressing these limitations will be essential for enhancing the applicability of hydrogel beads in diverse industrial contexts.

Looking ahead, further research should focus on exploring the scalability of hydrogel bead applications across various industrial contexts. It would be beneficial to investigate the performance of these beads in the presence of other contaminants, such as heavy metals and organic pollutants, as well as under varying environmental conditions, including changes in temperature and pH levels. Such studies will be crucial for optimizing the utility of hydrogel beads in real-world settings and enhancing their sensitivity and specificity for a broader range of heavy metals.

Additionally, future research could explore the potential for functionalizing hydrogel beads with other materials to improve their detection capabilities or to enable the simultaneous detection of multiple contaminants. Such advancements would significantly expand the applicability of hydrogel beads in environmental monitoring and remediation efforts.

Sodium alginate-based hydrogel beads have garnered significant attention in various fields, including environmental monitoring, drug delivery, and food technology, due to their unique properties. These hydrogel beads exhibit several advantages. Firstly, sodium alginate is a naturally occurring polysaccharide that is biocompatible and biodegradable, making it an ideal candidate for applications in biomedical fields, as it minimizes adverse reactions in biological systems (Jayakumar et al., 2011). Additionally, hydrogel beads made from sodium alginate can be easily prepared through simple methods such as ionotropic gelation, allowing for the formation of beads without the need for complex equipment (Li et al., 2020; Li et al., 2022).

Another notable advantage is their high swelling capacity. Sodium alginate hydrogels can absorb significant amounts of water, which enhances their ability to retain and release substances, making them suitable for various applications, including drug delivery systems (Lee & Mooney, 2001, Zou et al., 2020). Furthermore, hydrogel beads can be modified to selectively bind specific ions or molecules, allowing for targeted applications in metal ion detection and removal from wastewater (Idrees et al., 2020).

However, sodium alginate-based hydrogels also have certain disadvantages. One limitation is their sensitivity to environmental conditions; the performance of these hydrogels can be affected by changes in pH and ionic strength, which may influence their swelling behavior and binding capacity (Idrees et al., 2020; Chen et al., 2023). Additionally, while sodium alginate hydrogels exhibit good swelling properties, their mechanical stability may be lower than that of synthetic hydrogels, leading to structural breakdown under stress and potentially limiting their application in load-bearing environments (Peppas et al., 2000). Furthermore, achieving precise control over the release rates of encapsulated substances can be challenging, impacting their effectiveness in drug delivery systems where controlled release is critical (Qiu & Park, 2012; Adepu & Ramakrishna, 2021).

In summary, sodium alginate-based hydrogel beads offer a range of advantages that make them appealing for various applications, particularly in environmental and biomedical fields. However, their limitations in terms of sensitivity to environmental conditions, mechanical stability, and control over release rates warrant further research (Radoor et al., 2024). Future studies should focus on developing strategies to enhance the performance and stability of these hydrogels, thereby expanding their applicability in diverse settings.

In conclusion, this study provides compelling evidence for the effectiveness of hydrogel beads in detecting heavy metals in industrial wastewater. The findings contribute valuable insights to the field of occupational health and safety, highlighting the potential of innovative materials in addressing the environmental challenges associated with heavy metal pollution. By adopting such solutions, industries can not only enhance safety measures but also fulfill their environmental responsibilities, thereby promoting a healthier and more sustainable future.

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