Ligand-modified eggshells for rapid naked-eye detection and removal of trace level Ni$^{2+}$ ions

P. Rosaih, S. Vadivel, Kalaivani Dayanidhi, Mohammad Rezaul Karim, Ibrahim A. Alnaser, Sambasivam Sangaraju, M. Dhananjaya and Sang Woo Joo*

The global disposal of approximately 8 million tons of eggshell waste each year poses a significant environmental challenge. Nevertheless, this waste can be transformed into novel materials with various industrial applications. Herein, we have prepared a sustainable composite material modified with a ligand dimethyl glyoxime (DMG) by simple immobilization on a porous eggshell surface. The proposed composite material (DMG@ES) demonstrated remarkable Ni$^{2+}$ ion visual detection by the naked eye with a detection limit as low as 1.7 µg L$^{-1}$, while also boasting a swift response time. Importantly, the composite was highly selective towards the detection of Ni$^{2+}$ ions due to strong affinity between Ni$^{2+}$ ions and the ligand-modified composite material. This stable composite presents a straightforward, efficient, and cost-effective method for sensitive, rapid, and specific optical detection of a wide range of concentrations of Ni$^{2+}$ ions. Hence, the prepared composite material with tested practical applicability can potentially be up-scaled for commercial purposes, particularly in the field of environmental monitoring.

1. Introduction

Nickel (Ni), a transition metal, stands as one of the ten most prevalent elements. This metal ion finds versatile applications in various industries, such as electroplating, battery production, medical instrument manufacturing, and food processing equipment manufacturing. It is also utilized as a catalyst in multiple industrial processes. Additionally, nickel plays a substantial role in various biological functions, encompassing treatment of anaemia, red blood cell regeneration, and stimulation of insulin secretion. Nickel can enter the environment through industrial activities, and hence it is regarded as a pollutant. Elevated concentrations of nickel in soil, water, and air can negatively impact both ecosystems and human health. Ingesting or inhaling substantial amounts of soluble nickel compounds can result in acute toxicity, manifesting symptoms like nausea, vomiting, diarrhoea, headaches, and dizziness. Skin contact with Ni$^{2+}$ can induce skin disorders like nickel-eczema and dermatitis. Furthermore, certain aquatic organisms have the capacity to accumulate nickel within their tissues. This accumulation is detrimental to the organisms themselves and to the creatures that consume them, potentially posing health risks to humans who consume seafood contaminated with elevated nickel levels. Ni compounds have been categorized as carcinogenic by the International Agency for Research on Cancer (IARC), whereas World Health Organization (WHO) has set a limit of 20 ng mL$^{-1}$ for nickel contamination in drinking water. Therefore, it is of utmost importance to identify and eliminate the Ni$^{2+}$ ion pollutant. Typically, the traditional techniques employed for the identification and removal of this metal ion encompass chemical precipitation, membrane filtration, ion exchange processes, adsorption onto activated carbons, precipitative softening, hydroxide co-precipitation, and coagulation and flocculation. Nonetheless, these conventional methods have notable drawbacks, including the use of costly materials, the potential for secondary pollution, limited efficiency, and lack of selectivity, which have hindered their continuous application. Furthermore, traditional instrumental methods like online pre-concentration, voltammetry, polarography and ion-selective electrode potentiometry are characterized by their expensive and time-consuming nature,
complexity, and sophistication. Consequently, there is an urgent need to develop economical and competent materials and techniques.

Recent research trends are leaning toward colorimetric analysis due to its simplicity. Many researchers have reported the successful detection of Ni$^{2+}$ ions by this approach, with oxime compounds being extensively utilized reagents for selective detection of Ni$^{2+}$ ions. Also, choosing an appropriate carrier material is of utmost significance for the detection of metal ions for various reasons, including factors such as sensitivity, selectivity, adsorption capability, stability, durability, consistency, cost-effectiveness, and ease of use. Specifically, materials typically regarded as wastes, resulting from agricultural and industrial activities, have been explored as potential materials for removal of harmful metals from water. Utilizing these waste materials to purify polluted water offers an appealing and a hopeful solution, presenting two key benefits such as reducing waste generation and reclaiming valuable substances to eliminate toxic metals.

Eggshells, a common solid waste generated by the food industry, are frequently disposed of in substantial amounts in waste disposal sites, adding to ecological contamination. Recently, there has been growing interest among researchers to explore potential applications that can add value to this eggshell waste. Eggshells primarily consist of calcium carbonate, comprising about 94–96% of their composition, and their abundant availability at low cost, coupled with their porous nature, has led to extensive investigation into their use as both an adsorbent and a catalyst. Researchers have explored various applications of this readily available bio-waste, including its potential for sorption of organic and inorganic pollutants from water, as well as its use as a support material for creating adsorbents designed to remove dyes and aromatic compounds.

In this context, we have fabricated a composite material based on the dimethylglyoxime (DMG) ligand and eggshell carrier. This composite enables a straightforward and rapid process for both detecting and removing Ni$^{2+}$ ions in just a matter of seconds. In our previous research, the diverse uses of eggshells were highlighted. Hence, herein, we have prepared a simple composite material that immobilizes the DMG ligand for selective and sensitive detection and removal of Ni$^{2+}$ ions. The carrier material made from eggshells and the composite incorporating the dimethylglyoxime ligand were characterized using various analytical methods. In addition, the visual detection and digital image analysis, focusing on the RGB components, were successfully explored. Furthermore, to investigate the practical usability, the developed composite was utilized for identifying ultra-trace nickel in actual water samples. This work provides a straightforward and rapid method devoid of the need for any sample treatment.

2. Experimental

2.1. Materials

Local restaurants provided the eggshells, which were cleaned with double distilled water. They were then subjected to a 3 h drying process at 110 °C in a hot air oven, followed by mechanical pulverization within a scientific lab grinder and subsequent screening through a 100-mesh sieve. The resulting micron-sized eggshell (ES) powder was carefully preserved in a dehydrating container for future utilization. For this study, we sourced nickel sulphate and dimethylglyoxime (DMG) from Merck Ltd, India.

2.2. Fabrication of the DMG@ES composite

The DMG@ES (dimethylglyoxime@eggshell) composite was fabricated using a straightforward direct immobilization approach. To outline the process briefly, we dispersed the ES (100 g L$^{-1}$) in an ethanol solution containing DMG (1 g L$^{-1}$) and stirred it for 24 hours to ensure optimal immobilization. Subsequently, we filtered the suspension and gently rinsed it with ethanol until there was no further elution of DMG. Afterward, the composite was thoroughly dehydrated using a convection oven for approximately 1 hour at around 100 °C. Finally, the DMG@ES composite was preserved in an airtight box for later examination and utilization.

2.3. Detection of Ni$^{2+}$ ions

Colorimetric detection of Ni$^{2+}$ ions using the DMG@ES composite was conducted across a wide range of Ni$^{2+}$ ion concentrations to analyse its sensitivity towards Ni detection. To initiate the process, an aqueous solution of Ni$^{2+}$ ions with different concentrations at a neutral pH of 7.0 was prepared, and approximately 10 mg of the DMG@ES composite was added at a constant whole volume (50 mL). Subsequently, the solution was allowed to settle, resulting in noticeable changes in color and saturation of the signal of the absorbance pattern. The DMG@ES composite containing Ni$^{2+}$ ions was then collected through filtration using a filter paper perforated into circular discs of 1.0-cm diameter. The color of the collected sample was assessed visually using a digital camera and analytically through DRS UV-vis spectrometry. Furthermore, in order to evaluate the selectivity of the composite, aqueous solutions of various other metal ions were prepared with a concentration of 10 ppm and the detection was carried out with the DMG@ES composite and analysed as described earlier. In addition, to examine the practical applicability of the composite, real-time analysis was done by adding three different concentrations (25, 50 and 100 ppm) of Ni$^{2+}$ ions into water samples (tap water was collected from our laboratory and drinking water was collected from a supermarket) and the recovery percentage was evaluated.

2.4. Characterization

The materials were investigated by various characterization techniques. UV-visible diffuse reflectance spectroscopy (DRS) was performed using dehydrated BaSO$_4$ as a reference standard, within the wavelength range of 200 to 800 nm on a UV 2600 Shimadzu instrument. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectra were recorded for the samples at 4.0 cm$^{-1}$ resolution within the range of 4000 to 500 cm$^{-1}$ (JASCO, FT/IR-6300). Thermogravimetric analysis
(TGA) was conducted with a thermo-balance (NETZSCH STA 2500), covering the temperature range between 30 and 1000 °C with a heating rate of 10 °C per minute. To obtain morphology images, the materials were subjected to gold sputter coating (JEC 3000, JEOL) and were then examined using a scanning electron microscope (SEM) from ZEISS. X-ray diffraction (XRD) was employed to examine both the crystal structure and impurities. This analysis utilized the Bruker USA D8 Advance instrument with Cu Kα radiation, characterized by a wavelength of $\lambda = 1.540 \text{ Å}$. The scanning array from 10 degrees to 80 degrees ($2\theta$).

3. Results and discussion

3.1. Characterization of the DMG@ES composite

Fig. 1 presents the FT-IR spectra for comparing the chemical compositions of the ES and DMG@ES. In these spectra, we can identify two major peaks at 1400 and 867 cm$^{-1}$, associated with the existence of calcium carbonate in the eggshell matrix. These peaks are associated with the vibrational modes of carbonate ions, including unequal stretching, bending in planes, and bending out of planes at 1400, 867, and 711 cm$^{-1}$, respectively. There is also a minor, low-intensity peak at 3304 cm$^{-1}$, which can be linked to the –OH stretching vibrations caused by the eggshell’s capacity to absorb moisture as described by Mosaddegh et al. A noteworthy observation is the increased intensity and slight shift in peak positions for DMG@ES, from 1400 to 1401 cm$^{-1}$ and from 867 to 874 cm$^{-1}$. These changes may be linked to the immobilization of the DMG ligand within the porous eggshell structure, providing supporting evidence for DMG ligand immobilization on the surface of the ES. Furthermore, the existence of a more significant peak at 989 cm$^{-1}$ for DMG@ES compared to the ES suggests that carbonyl groups in the eggshell are involved in complexation with the DMG ligand. This finding aligns with observations made by Zhang, Shaoqing, et al., who reported similar minute peak shifts in IR spectra when loading DMG molecules during zeolite modification.

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Fig. 2 shows SEM images captured at 2 µm resolution. These images revealed that the eggshell surface (Fig. 2a) displayed an
uneven crystal arrangement with a multitude of randomly scattered pores, consistent with the findings of several published studies.\textsuperscript{35,44,45} Notably, in Fig. 2b, it can be observed that the porous structure is somewhat reduced following the immobilization of the DMG ligand. To evaluate the heat resistance of the ES and DMG@ES, we performed thermogravimetric testing. As depicted in Fig. 3, the thermogram of the ES revealed three distinct degradation stages. The initial stage, occurring between temperatures of 21 °C and 130 °C, is related to the removal of adhered or physically adsorbed water. The second phase, spanning temperatures from 130 °C to 662 °C, represents the degradation of residual organic content, while the last phase, taking place between 662 °C and 840 °C, involves the transformation of carbonates into CO\textsubscript{2} and CaO. Notably, these findings align with previous research.\textsuperscript{46,47} The thermogram of DMG@ES exhibited the following degradation pattern, albeit with small alterations in the temperature ranges: (28–146) °C, (193–635) °C, and (635–753) °C, as related to the ES. These changes could be attributed to the dehydration of DMG molecules and the vaporization of anhydrous DMG, in line with previous literature observations.\textsuperscript{43} Of particular interest, the percentages of the remaining mass observed at 999 °C were found to be 53.21% for the ES and 49.71% for DMG@ES, indicating that loading of DMG onto the DMG@ES composite was approximately 3.5%.

![Scheme 1](image1.png)

**Scheme 1** Complex formation between Ni\textsuperscript{2+} ions and dimethylglyoxime.

Fig. 4 displays the powder XRD patterns of the ES and DMG@ES, covering the 2θ range of 10° to 80°. The peaks at 2θ with the corresponding crystal planes (hkl) of 23.0° (012), 29.3° (104), 31.5° (006), 36.1° (110), 39.4° (113), 43.2° (202), 47.6° (018), 48.6° (116), and 57.5° (122), respectively, are related to one of the stable phases of CaCO\textsubscript{3}, specifically calcite, as denoted by JCPDS File #47-1743. The presence of distinct and clear peaks signifies the ordered atomic structure of the substance and evidently indicates the absence of impurities in the eggshell structure.\textsuperscript{48} Notably, even after immobilizing the DMG ligand, only a slight decrease in peak intensities was observed for the eggshell structure.

### 3.2. Selective and sensitive detection and removal of Ni\textsuperscript{2+} ions

The extensive examination of the colored complex formation between Ni\textsuperscript{2+} and dimethylglyoxime has been a focal point in colorimetric methods for nickel determination. In this context, the dimethylglyoxime molecule donates electron pairs to Ni\textsuperscript{2+} ions through its nitrogen atoms, contrary to the common expectation of oxygen atom involvement. Furthermore, each dimethylglyoxime molecule loses one proton from the oxime group. The introduction of OH\textsuperscript{-} anions facilitates the formation of metal–chelate complexes, a process that takes place quantitatively within a pH range of 5 to 9. The complex formation is presented in Scheme 1.\textsuperscript{49}

Quantitative determination of the Ni\textsuperscript{2+} ions was achieved through colorimetric studies using DRS UV-vis spectroscopy. This was done by examining the changes in the absorption spectra of the composite upon the inclusion of Ni\textsuperscript{2+} ions at an optimum pH of 7.0 as depicted in Fig. 5a. A clear decline in the absorption spectral peak at 544 nm with decrease in concentration reveals the good sensitivity of the composite material towards Ni\textsuperscript{2+} detection and visual detection by the naked eye up to 100 ppb Ni\textsuperscript{2+} is achieved as shown in Fig. 5b. The absorption spectra of the [Ni(DMG)\textsubscript{2}] complex reveal that the nitrogen group of the DMG ligand binds to the Ni\textsuperscript{2+} ion, forming a colored complex [Ni(DMG)\textsubscript{2}]. The color intensity of this complex at a particular wavelength exhibited a linear relationship with the concentration of Ni\textsuperscript{2+} ions, up to a peak value, which could be considered as the saturation point. This relationship was validated through the standardization plots (Fig. 6) of the DMG@ES detection framework. As seen in the inset figure, linear fitting was observed with a regression coefficient of $R^2 = 0.9245$. The detection limit was calculated to be 1.72 μg L\textsuperscript{-1} according to the following equation (eqn (1)):

$$\text{Limit of detection (L_D) = } \frac{KS_b}{m}$$  \hfill (1)
where $K$ is a constant and $S_b$ and $m$ are the standard deviation and slope, respectively, obtained from Fig. 6.

Furthermore, the selectivity of the DMG@ES composite towards Ni$^{2+}$ was determined by addition of several other interfering ions (Cr$^{2+}$, Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Pb$^{2+}$, and Cd$^{2+}$).

The primary interferents in nickel detection using DMG are Cu$^{2+}$, Fe$^{2+}$ and Co$^{2+}$, which form stable complexes with the organic reagent. Other than these three aforementioned interfering ions, the selectivity study, as depicted in Fig. 5c, revealed that no tremendous change in the absorption intensity was observed for other metal ions (10 ppm). Hence, we presumed that most of the metal ions would not interfere significantly in the detection of Ni$^{2+}$ ions. In addition, Table 1 displays the comparison of Ni$^{2+}$ detection using several other composites in the literature, which indicates that DMG@ES would be a better material for nickel detection.

To digitally assess the image attributes of the RGB digital pictures of the colored DMG@ES composite captured with an iPhone 11, we employed the Adobe Photoshop software, as previously documented in the literature. The software meticulously scanned all the pixels within the chosen section of the image. This analysis aimed to retrieve the RGB average values and standard deviations of saturation for primary colors in the image: red, green and blue for each individual pixel. In the RGB system, each color is represented as a combination of pure colors red, green, and blue, with the influence of every component being quantified by its intensity, typically ranging from 0–255 for each of the three primary colors. Fig. 7 displays a series of digital images depicting the DMG@ES composite at various concentrations of Ni$^{2+}$ ions.

Fig. 8 reveals the intensity differences of the DMG@ES composite, which are directly related to the Ni$^{2+}$ ion concentrations. As Ni$^{2+}$ ion concentration increased, the color became intense, and the average numerical value for every RGB component declined. As seen in Fig. 8, green component’s intensity within the DMG@ES composite was reduced as the concentration of Ni$^{2+}$ ion raised, while the intensities of the blue and red components experienced smaller decreases when compared to the green component. This phenomenon can be attributed to the complementary relationship between green
wherein an elevated absorbance of the green color is anticipated when the speculative reference color is red.

### 3.3. Real sample analysis

To evaluate the practical applicability and feasibility of the DG@ES composite to detect nickel ions in real samples, real water samples were spiked with three different concentrations of Ni$^{2+}$ solution. The accuracy of real-time analysis was checked by determining the recovery percentage of the water samples using eqn (2).\(^5\)

\[
\text{Recovery} \% = \frac{C_{\text{found}}}{C_{\text{added}}} \times 100
\]

where \(C_{\text{found}}\) and \(C_{\text{added}}\) are the concentrations of analyte (Ni$^{2+}$) found and added in real samples. As shown in Table 2, good recovery percentages of 93.24–103.5% for both tap water and drinking water were obtained. These results suggest that the prepared DMG@ES composite can be a potential material for detection and removal of Ni$^{2+}$ ions in real-time practical applications.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added (ppm)</th>
<th>Found (ppm)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water</td>
<td>25</td>
<td>25.64</td>
<td>102.56</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>51.75</td>
<td>103.50</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>101.91</td>
<td>101.91</td>
</tr>
<tr>
<td>Drinking water</td>
<td>25</td>
<td>24.80</td>
<td>99.20</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>49.35</td>
<td>98.70</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>93.24</td>
<td>93.24</td>
</tr>
</tbody>
</table>

### Table 1 Comparison of different composite materials and methods for the detection of Ni$^{2+}$

<table>
<thead>
<tr>
<th>Composite material</th>
<th>Method of detection</th>
<th>Detection range (µg L$^{-1}$)</th>
<th>Limit of detection (µg L$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. DMG@N-GQDs</td>
<td>RLS intensity</td>
<td>50–200</td>
<td>20.0</td>
<td>50</td>
</tr>
<tr>
<td>2. DMG@MSNs</td>
<td>Colorimetry</td>
<td>0.5–100</td>
<td>0.22</td>
<td>19</td>
</tr>
<tr>
<td>3. NGr–DMG-GCE</td>
<td>Adsorptive cathodic stripping voltammetry</td>
<td>2–20</td>
<td>1.5</td>
<td>49</td>
</tr>
<tr>
<td>4. 3Ds-CM/DMG</td>
<td>Square-wave cathodic adsorptive stripping voltammetry</td>
<td>5–100</td>
<td>1.693</td>
<td>51</td>
</tr>
<tr>
<td>5. MOR/G/DMG-GCE</td>
<td>Electrochemical</td>
<td>0.57–15.75</td>
<td>0.18</td>
<td>52</td>
</tr>
<tr>
<td>6. DMG@ES</td>
<td>Colorimetry</td>
<td>0.1–100</td>
<td>1.72</td>
<td>This work</td>
</tr>
</tbody>
</table>

Fig. 7 Visually detected colors of the DMG@ES composite with various concentrations of Ni$^{2+}$ ions after filtration using filter paper no. 1 punched into 1.0 cm diameter circular discs.

Fig. 8 Correlation between Ni$^{2+}$ ion concentrations and the average integer values of RGB component intensities.
3.4. Regeneration studies

Assessing the efficacy of the constructed material involves considering reusability as a key parameter. Successful reusability was achieved through the use of a 0.01 M HCl eluent, which effectively eliminated the adsorbed Ni^{2+} ions from the DMG@ES composite. The procedure involved immersing the composite in 0.01 M HCl for 4 hours, followed by washing with water. This regeneration process was repeated multiple times to release the Ni^{2+} ions. Despite undergoing five successive regeneration cycles the DMG@ES composite exhibited a minimal impact on sensitivity for Ni^{2+} detection, and also the recovery time of Ni^{2+} from the DMG ligand increased slightly after the fifth regeneration cycle.

3.5. Stability of the DMG@ES composite

The remarkable, long-lasting efficiency of the composite holds great promise in terms of its technological applications. To assess its durability over an extended period, the composite’s long-term stability was investigated during storage spanning several months. Interestingly, even without the use of a surface modifier and through the direct incorporation of the DMG ligand into the ES, this composite effectively managed to minimize potential leaching issues when stored. The data revealed minimal changes in the optical density, particularly the “absorption spectra” of the ligand, even after moderately extended storage periods, specifically equal to or exceeding 3 months, all within a dark container and under optimal temperature conditions. This robust storage stability can be primarily attributed to the application of the ES framework with its unobstructed pores and the assembly of the DMG ligand within these pores. In contrast to other designs relying on surface alteration that entails robust electrostatic interactions between the ligand molecule and electrically charged surface, this solid sensor demonstrates considerably greater stability with respect to its shelf-life.

4. Conclusion

In summary, the innovative composite, achieved through the simple immobilization of the DMG ligand onto the surface of eggshells, offers a straightforward and effective monitoring pathway characterized by its sensitivity, selectivity and stability. When the Ni^{2+} ions were introduced into the DMG@ES composite, a pronounced color change due to the increased linkage of the DMG ligand was witnessed. This approach enabled the rapid and cost-effective naked-eye detection and elimination of Ni^{2+} ions. The detection limit was calculated to be 1.7 μg L⁻¹ with a linear regression value of R² = 0.9245. Moreover, the real sample analysis conducted with tap and drinking water proves the real-time practical applicability of the DMG@ES composite towards the detection and elimination of Ni^{2+} ions from the environment.

Conflicts of interest

There are no conflicts to declare.

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