Simultaneous detection of Lead and Cadmium using a composite of Zeolite Imidazole Framework and Reduced Graphene Oxide (ZIF-67/rGO) via electrochemical approach

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ABSTRACT

Present work reports the application of a composite of ZIF-67/rGO for the simultaneous detection of traces of lead and cadmium via square wave anodic stripping voltammetry (SWASV) technique. For this, grafoil sheets were modified with synthesized composite for the electrode fabrication [(ZIF-67/rGO)/Grafoil] for its use in sensing studies. The SWASV response of (ZIF-67/rGO)/Grafoil electrode was optimized against deposition potential (-1.0 V) and time (350 s), required for the accumulation of metal ions onto the sensor electrode. The performance of the sensing electrode was then evaluated for lead (Pb²⁺) and cadmium (Cd²⁺) ions at various concentrations. The sensor displayed linear response in a wide concentration range of 5-100 ppb. The peak current of the electrode was found to be shifted towards the higher potential at higher metal ion concentrations. Based on the response measured, the limit of detection (LOD) of the fabricated sensor has been estimated and found to be 5 and 2.93 ppb for Pb²⁺ and Cd²⁺ ions, respectively. The results obtained revealed good specificity of the proposed sensor towards Pb²⁺ and Cd²⁺ ions in the co-presence of several other ions. In addition, the sensor exhibited good reproducibility with a relative standard deviation (RSD) of ~2% for both Pb²⁺ and Cd²⁺ ions.

Keywords: Electrochemical, Heavy metals, Metal-organic framework, Sensor, Specificity

Graphical Abstract
1. Introduction

With the expansion of scientific and technological boundaries, the environment has become increasingly polluted with various contaminants, which in turn affect human life [1–5]. There are safety limits recommended by environmental monitoring agencies without suffering any health effects. In developing countries, where economic growth mostly depends on agricultural and industrial development have bypassed all the safety and acceptable guidelines. Heavy metal contamination is increasingly being recognized as dramatic in large parts of the developing countries of the world. Its concentration has increased rapidly over the past few decades [6–10]. Their toxicity is highly serious due to their solubility in water, non-biodegradability, extended high life and accumulation in the human body [11,12]. These are easily transferred to human beings through the food chain and other associated routes.

According to the research survey, various rivers of the world were found to be heavily polluted with toxic metal ions beyond the permissible limit [13,14]. This is alarming as the majority of the population is making use of water from rivers and lakes for their daily and necessary requirements like drinking and cooking without knowing its ill effects. Continuous intake of contaminated food and water containing heavy metal ions in turn causes various health related problems. Potential effects could include chronic poisoning, and damage to the gastrointestinal organ, immune, nervous, and reproductive systems. Long-term exposure to heavy metals can even cause cancer [15–18]. Their intake could even lead to death when the concentration of metal ions exceeds the maximum permissible limit. Hence, it is particularly incumbent to develop miniaturized, accurate, cost-effective, sensitive, and fast monitoring systems for the sensing of heavy metals in food, drinking water and other biological fluids.

Among the different analytical techniques that are widely used for the determination of metal ions are flame atomic absorption spectroscopy, electrothermal atomic absorption spectroscopy, inductively coupled plasma optical emission spectrometry, and inductively coupled plasma mass spectrometry. However, these types of equipment are complex, bulky, time-consuming, require trained personnel and are not suitable for real-time monitoring. Consequently, the development of low cost, rapid and sensitive analytical methods for the detection of heavy metals is of particular significance.

In the recent past, some interesting nanomaterials such as metal oxides, metal nanoparticles [19–21], graphene and its derivatives [20,22–25], carbon/carbon nanotubes [26–29] nanocomposites [30] and so on have been explored for the electrochemical detection of heavy metal ions. But these materials tend to feature low surface area and hence result in low sensitivity of the sensor. Metal-organic frameworks (MOFs) are evolving as a new class of ultra-high porous crystalline materials featuring a very high surface area, thus finding their way into many real-world applications [31–40]. However, the insulating nature of MOFs poses some limitations on their application for electronic sensing [41,42]. Hence, the development of MOF-based electrochemical sensors needs the creation of conduction pathways in the material. So, to take advantage of the unique properties of MOFs, these can be integrated with other conducting materials and the composite nanomaterials thus synthesized can be explored as sensing materials.

The present work reports the ZIF-67/rGO-based electrochemical sensor for the simultaneous detection of Pb^{2+} and Cd^{2+} ions. The SWASV technique has been preferred for the development of the sensing protocol owing to its important advantages over other electrochemical techniques. The composite material is prepared with the use of inexpensive chemicals and is easy to synthesize. In addition, the composite was found to possess excellent hydrophobicity which provided for the better adhesion of the sensory material on the electrode surface in the aqueous solutions, thus improving the durability and shelf life of the sensor for electrochemical applications.

2. Experimental

2.1. Materials and Equipment

Cobalt nitrate hexahydrate (Co(NO3)2·6H2O, ≥98%), 2-methyl imidazole (C2H5NIm, 99%), graphite flakes (repeating units of C), sulphuric acid (H2SO4, 98%), o-phosphoric acid (H3PO4, 85%), potassium permanganate (KMnO4, ≥99%), hydrogen peroxide (H2O2, 30% (w/w)), L-ascorbic acid (C6H8O6, 98%), sodium acetate salt (CH3COONa, ≥99%), glacial acetic acid (CH3COOH, ≥98.8% conc.), Ethanol (C2H6O, ≥99.9%) and stock solutions of cadmium, lead, zinc, selenium, nickel, and arsenic (1000 ppm) were purchased from Merck Sigma-Aldrich. All the solutions were prepared in de-ionized (DI) water (18.2 MΩ-cm). Graffoil was used as the working electrode. The acetate buffer solution (ABS) was used as a supporting electrolyte (detection buffer). The ABS solution was prepared by mixing an appropriate amount of sodium acetate and glacial acetic acid.

2.2. Synthesis of ZIF-67/rGO

The ZIF-67/rGO composite was synthesized via a hydrothermal route. Briefly, rGO sheets were first sonicated for 2 hrs in 20 ml DI water followed by the addition of 2-methyl imidazole. Cobalt nitrate hexahydrate was added to 3 ml DI water. Both the solutions were then mixed and stirred for 6 h at RT. A detailed description of the synthesis procedure is provided in our previous publication [43]. The navy-blue colored precipitates of the composite thus formed were used for its application in the simultaneous detection of Pb^{2+} and Cd^{2+} ions in water.

Further, the composite was characterized using several analytical techniques such as FT-IR, UV-Vis, XRD, BET, FE-SEM, HR-TEM and contact angle measurement which are discussed in detail in our earlier publication [43]. The fresh FE-SEM and HR-TEM micrographs of ZIF-67/rGO are also provided in the supplementary file [Fig. S1].

2.3. Fabrication of Electrode with ZIF-67/rGO

The Graffoil sheet of dimensions 30mm×10mm was used as a working electrode. The sheet was coated with ZIF-67/rGO (active area = 12mm×10mm) to prepare several identical batches of
(ZIF-67/rGO)/Grafoil electrodes. For this, a viscous slurry of ZIF-67/rGO was first prepared in ethanol (9:1, w/w). A known amount (i.e., 20 μL) of this slurry was then drop-casted onto each grafoil sheet electrode and was then dried at 60 °C overnight to ensure proper adhesion of the coating material onto the electrode surface.

2.4. Electrochemical Measurements

Electrochemical studies (SWASV) were performed using an electrochemical workstation (Potentiostat PGSTAT302N, AUTOLAB Metrohm, The Netherlands). All the experiments were conducted using a 3-electrode configuration at room temperature (RT, 25±2 °C) under ambient conditions. The studies were performed using ZIF-67/rGO modified grafoil [(ZIF-67/rGO)/Grafoil], platinum (Pt) and Ag/AgCl as working, counter/auxiliary, and reference electrodes, respectively.

The SWASV analysis for the simultaneous determination of Pb²⁺ and Cd²⁺ was carried out by pre-concentrating the metal ions present in the solution on the surface of (ZIF-67/rGO)/Grafoil electrode. The measurements were carried out at an optimized value of deposition potential and time in the presence of ABS of pH 5.0. It was then followed by the stripping cycle by scanning the potential from -1.0 to -0.1 V in a step of 0.005 V. The application of anodic stripping voltage by sweeping the potential from -1.0 to -0.1 V causes the metal ions deposited on the surface of the electrode to strip back into the solution, leading to a peak current response at a particular potential corresponding to a metal ion. During the experiments, the pulse amplitude, pulse width, and pulse period were maintained as 0.08 V, 0.04 s, and 0.2 s, respectively. The optimized conditions obtained are elaborated in the subsequent sub-sections.

During the process of detection of metal ions, the pre-concentrated ions are assumed to be bound by N- groups present in the imidazole linker and various surface functionalities such as hydroxyl, carboxyl, and epoxy functional groups/moieties present in rGO via adsorption or complex formation.

3. Results & Discussion

The confirmation of the synthesis of ZIF-67/rGO is already discussed in our earlier publication [43].

![Fig. 1. SWASV response of (ZIF-67/rGO)/Grafoil electrodes (a&b) Different deposition potentials keeping deposition time fixed as 350 s and 400 s for Pb²⁺ and Cd²⁺, respectively, (c&d) Different deposition times keeping fixed deposition potential of -1.0 V for Pb²⁺ and Cd²⁺ ions, respectively.](image-url)
3.1. Optimization Conditions for the Pre-concentration of Metal Ions

To establish ZIF-67/rGO as a sensing material and its utilization in the fabrication of chemical sensors for the simultaneous detection of Pb$^{2+}$ and Cd$^{2+}$, some parameters have been optimized by considering individual ions. These include deposition potential and deposition time required for the pre-concentration of metal ions onto the modified working electrode. These studies are elaborated in the following subsection:

3.1.1. With varying potentials and constant time

For recording the SWASV response of the electrode, a defined concentration of individual metal ion (Pb$^{2+}$ or Cd$^{2+}$) was added to the acetate buffer solution (pH 5.0) and the solution was stirred for the next 5 min. The (ZIF-67/rGO)/Grafoil electrode was then dipped into this buffer solution and metal ion species present in the solution were allowed to get adsorbed (pre-concentrate) onto the ZIF-67/rGO surface. This was performed by applying a varying deposition potential from -0.5 to -1.1 V for a fixed duration of 350 s [Fig. 1(a&b)]. After the completion of the deposition step, the ions accumulated on the electrode surface were stripped back into the solution by applying a sweeping potential from -1.0 to -0.1 V. Due to this, a peak current is observed, which increases with increasing negative potential till a certain value of the deposition potential (-0.5 to -1.0 V). Application of more negative potential beyond -1.0 V results in instability in the sensing material (ZIF-67/rGO), causing the film to peel off from the electrode surface. Therefore, a deposition potential of -1.0 V was used for further studies.

3.1.2. With varying deposition times and constant potential

Similarly, the time required for the pre-concentration of ions on the electrode surface was optimized by applying a constant deposition potential of -1.0 V with varying deposition time starting from 100 s and a further increase in steps of 50 s, till the film, remains stable or saturated response was obtained [Fig. 1(c&d)].

The data obtained suggest that the peak current of the electrode increases with an increase in deposition time up to a certain value. This is because, as the deposition time increases, more metal ions present in the aqueous solution can get adsorbed at the surface of the electrode, hence, resulting in increased peak current. Further increase in deposition time causes the electrode current to get saturated and also results in instability in the sensing film. The saturation time was found to be different for both the ions i.e. 350 and 400 s for Pb$^{2+}$ and Cd$^{2+}$ ions, respectively.

So, the optimized conditions of deposition potential and deposition time obtained for individual Pb$^{2+}$ and Cd$^{2+}$ ions are summarized in Table 1.

3.2. Stripping Voltammograms and Sensor Calibration

Based on the optimized deposition potential and deposition time conditions obtained for individual Pb$^{2+}$ and Cd$^{2+}$ metal ions, the sensor response was checked for the simultaneous detection of both these ions as shown in Fig. 2. For this, solutions of different concentrations having Pb$^{2+}$ and Cd$^{2+}$ ions (5–100 ppb) were taken for the analysis. The ions present in the solution were first allowed to deposit onto the (ZIF-67/rGO)/Grafoil electrode surface by applying a deposition potential of -1.0 V. The deposition time was kept to be 350 s. However, the optimized deposition time obtained for individual ions was 350 and 400 s for Pb$^{2+}$ and Cd$^{2+}$ ions, respectively. This was kept to avoid any sort of instability/peel-off of the sensing film from the electrode surface. The deposition step was followed by stripping back of deposited metal ions in the solution by sweeping the applied voltage from -1.0 to -0.1 V. The stripping current in both cases was found to increase with the increasing concentrations of Pb$^{2+}$ and Cd$^{2+}$.

In addition, peak shift was also observed towards positive potential with increasing concentration in the case of both metal ions. The shifting of the peak potential is governed by the Nernst equation. A higher concentration of ions leads to a higher potential. Further, the shift may be associated with the metal complex formation during the deposition step [44]. The shift also depends on the mass transport of metal ions towards the electrode surface. Some time-lapse is observed in the electrochemical to allow the diffusion of the target analyte species at the electrode surface. The presence of a high concentration of analyte can cause a disordered diffusion, which is otherwise not seen in the case of low

![Fig. 2. SWASV response of (ZIF-67/rGO)/Grafoil electrodes at different concentrations of mixture of Pb$^{2+}$ and Cd$^{2+}$ (5–100 ppb) ions.](image-url)

Table 1. Optimized Conditions of Deposition Potential and Deposition Time for Pb$^{2+}$ and Cd$^{2+}$ Ions

| S.No. | Metal Ions | Deposition Potential (V) | Deposition time (s) |
|-------|------------|--------------------------|---------------------|
| 1.    | Pb$^{2+}$  | -1.0                     | 350                 |
| 2.    | Cd$^{2+}$  | -1.0                     | 400                 |


analyte concentrations. This change in the diffusion process at high analyte concentrations disturbs the mass transport rate, which in turn causes a shift in the peak potential.

Also, it was noticed that there is more increase (linear) in the peak current response at low concentrations (5 to 50 ppb). Further increase in the ion concentration (60 to 100 ppb) causes slight increase in the stripping current response of the electrode. The is due to the attainment of the equilibrium for the deposition or the adsorption of Pb^{2+} and Cd^{2+} ions. The peak current values corresponding to each concentration of a mixture of Pb^{2+} and Cd^{2+} were plotted and fitted linearly and the calibration curves are shown in fig. 3. The linear fit equation of both the curve is expressed as Eq. (1).

\[ I_p = a + bx \]  

(1)

It can be seen in Fig. 3 that the calibration plots of Pb^{2+} and Cd^{2+} covered two linear ranges varying from 5 to 50 ppb and 60 to 100 ppb, demonstrating the good linearity in these two linear ranges. For Pb^{2+}, the correlation equations were fitted as \( I(A) = 1.81 \times 10^{-6}c \) (ppb) + 5.91 \times 10^{-4}, \( R^2 = 0.997 \), in the range of 5-50 ppb and as \( I(A) = 5.36 \times 10^{-7}c \) (ppb) + 6.55 \times 10^{-4} with a correlation coefficient of \( R^2 = 0.998 \) in the range of 60-100 ppb. In addition, the correlation equations for Cd^{2+} were calculated as \( I(A) = 1.31 \times 10^{-6}c \) (ppb) + 6.00 \times 10^{-4}, \( R^2 = 0.999 \), and \( I(A) = 4.85 \times 10^{-7}c \) (ppb) + 6.40 \times 10^{-4}, \( R^2 = 0.990 \), in the range of 5-50 ppb an 60-100 ppb, respectively. The limit of detection (LOD) of the sensor was calculated using the following expression as Eq. (2).

\[ LOD = 3.3 \times \frac{S.D.}{Slope} \]  

(2)

where S.D. is the standard deviation of the blank. The LOD value for the linear calibration range (5-100 ppb) is calculated and found to be 5 and 2.93 ppb for Pb^{2+} and Cd^{2+} ions, respectively. These values satisfy the global criteria for determining the safe limits of lead and cadmium in drinking water according to WHO and USEPA [45–48].

A comparison of the performance of the present sensor with respect to previously reported similar electrochemical sensors is summarized in Table 2.

3.3. Specificity & Reproducibility

For the specificity studies, the SWASV response of the electrode was checked in water containing 150 ppb (y) of other commonly

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Calibration plot of peak currents of (ZIF-76/rGO)/Grafoil sensor for (a&b) Pb^{2+} ions, (c&d) Cd^{2+} ions at 5–50 ppb and 60–100 ppb, respectively.}
\end{figure}
found ions (Ni\textsuperscript{2+},Se\textsuperscript{2+}/As\textsuperscript{2+}/Zn\textsuperscript{2+}) along with 30 ppb (x) of Pb\textsuperscript{2+} and Cd\textsuperscript{2+} ions each. The results obtained show no significant interference of the other ions, indicating the selectivity of the fabricated sensor towards Pb\textsuperscript{2+} and Cd\textsuperscript{2+} (Fig. 4a).

For the reproducibility studies, five (ZIF-67/rGO)/Grafoil electrodes were used for the adsorption of 30 ppb of the Pb\textsuperscript{2+} and Cd\textsuperscript{2+} concentration followed by the investigation of SWASV response. As can be seen from the data obtained (Fig. 4b), the peak current values of all the electrodes were found to be almost equal with a relative standard deviation of ~2% for both Pb\textsuperscript{2+} and Cd\textsuperscript{2+}.

### Table 2. Comparison of ZIF-67/rGO sensor for the simultaneous detection of Pb\textsuperscript{2+} and Cd\textsuperscript{2+} with some previously reported electrochemical sensors

| S.No | Sensing Material | Technique | Detecting Ions | Linear Range | LOD | Ref. |
|------|------------------|------------|----------------|--------------|-----|------|
| 1.   | Yb-BTC/GCE       | DPV        | Cd\textsuperscript{2+}  | 0-50 ppb     | 3 ppb | [49] |
|      |                  |            | Pb\textsuperscript{2+}  | 1.6 ppb      |      |      |
| 2.   | Glutathione@Fe\textsubscript{3}O\textsubscript{4} | SWASV | Cd\textsuperscript{2+}  | 0.5-100 ppb  | 0.172 ppb | [50] |
|      |                  |            | Pb\textsuperscript{2+}  | 0.182 ppb    |      |      |
| 3.   | Fe\textsubscript{3}O\textsubscript{4}/F-MWCNTs/GCE | SWASV | Cd\textsuperscript{2+}  | 56.2-3372 ppb | 5.62 ppb | [51] |
|      |                  |            | Pb\textsuperscript{2+}  | 103.6-6216 ppb | 16.58 ppb |      |
| 4.   | Nanoplate stacked Fe\textsubscript{3}O\textsubscript{4} | SWASV | Cd\textsuperscript{2+}  | 11.24-224.8 ppb | 17.53 ppb | [52] |
|      |                  |            | Pb\textsuperscript{2+}  | 8.3-870 ppb  | 3.15 ppb |      |
| 5.   | GA-UiO-66-NH\textsubscript{2}/GCE | DPASV | Cd\textsuperscript{2+}  | 6.745-337.2 ppb | 2.248 ppb | [53] |
|      |                  |            | Pb\textsuperscript{2+}  | 2.072 ppb-0.8288 ppm | 0.3108 ppb |      |
| 6.   | g-C\textsubscript{3}N\textsubscript{4}/CNT/NH\textsubscript{2}-MIL-88(Fe) | SWASV | Cd\textsuperscript{2+}  | 13.49 ppb-0.6745 ppm | 4.4515 ppb | [54] |
|      |                  |            | Pb\textsuperscript{2+}  | 4.144 ppb-1.2432 ppm | 1.5747 ppb |      |
| 7.   | Tapioca-derived carbon dots | DPV & CV | Cd\textsuperscript{2+}  | 0.01 to 0.27 ppm | 2.8 ppb | [55] |
|      |                  |            | Pb\textsuperscript{2+}  | 0.01 to 0.27 ppm | 4.2 ppb |      |
| 8.   | pg-C\textsubscript{3}N\textsubscript{4}/CoMn\textsubscript{2}O\textsubscript{4} | SWASV | Cd\textsuperscript{2+}  | 56.2-787 ppb | 2.36 ppb | [56] |
|      |                  |            | Pb\textsuperscript{2+}  | 41.44-912 ppb | 3 ppb |      |
| 9.   | MIL-100(Cr)      | SWASV      | Cd\textsuperscript{2+}  | 0 to 1.12 ppm | 4.946 ppb | [57] |
|      |                  |            | Pb\textsuperscript{2+}  | 0 to 2.07 ppm | 9.946 ppb |      |
| 10.  | ZIF-67/rGO       | SWASV      | Cd\textsuperscript{2+}  | 5-100 ppb    | 2.93 ppb | Present work |
|      |                  |            | Pb\textsuperscript{2+}  | 5 ppb        | 5 ppb |      |

GCE- Glassy carbon electrode; F-MWCNTs- Fluorinated multi-walled carbon nanotubes; g-C\textsubscript{3}N\textsubscript{4}- graphitic carbon nitride; g-C\textsubscript{3}N\textsubscript{4}-porous graphitic; carbon nitride

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For the reproducibility studies, five (ZIF-67/rGO)/Grafoil electrodes were used for the adsorption of 30 ppb of the Pb\textsuperscript{2+} and Cd\textsuperscript{2+} concentration followed by the investigation of SWASV response. As can be seen from the data obtained (Fig. 4b), the peak current values of all the electrodes were found to be almost equal with a relative standard deviation of ~2% for both Pb\textsuperscript{2+} and Cd\textsuperscript{2+}.

**Fig. 4.** SWASV response of (a) (ZIF-67/rGO)/Grafoil electrode towards Pb and Cd in co-presence of Arsenic (As\textsuperscript{2+}), Zinc (Zn\textsuperscript{2+}), Nickel (Ni\textsuperscript{2+}), Selenium (Se\textsuperscript{2+}) ions, (b) Five different (ZIF-67/rGO)/Grafoil electrodes under identical experimental conditions.
ions, confirming a satisfactory reproducibility of the sensor response.

4. Conclusion

The composite, ZIF-67/rGO, has been investigated as a sensory electrode material for the simple and selective electrochemical detection of Pb\(^{2+}\) and Cd\(^{2+}\) ions simultaneously. The target metal ions (mixture of Pb\(^{2+}\) and Cd\(^{2+}\)) were allowed to get adsorbed on the surface of (ZIF-67/rGO)/Grafoil by applying the optimized deposition potential of -1.0 V for 350s. This was followed by the SWASV signal collection by sweeping the voltage from -1.0 to -0.1 V. The performance of the developed electrochemical sensor was measured for various concentrations of Pb\(^{2+}\) and Cd\(^{2+}\). The results demonstrated a greater increase in peak current at low ion concentrations (5-50 ppb) as compared to higher concentrations (60–100 ppb) of Pb\(^{2+}\) and Cd\(^{2+}\) ions. This phenomenon can be attributed to the attainment of equilibrium for the adsorption of target metal ions such that further increase in ions concentration resulted in a very small increase in peak intensity. The proposed sensor facilitates the simultaneous determination of Pb\(^{2+}\) and Cd\(^{2+}\) in aqueous solutions to as low as 5 and 2.93 ppb concentrations, respectively. Apart from this, the sensor demonstrated good reproducibility (RSD = ~2%) and selective response towards Pb\(^{2+}\) and Cd\(^{2+}\) ions. The superior sensing performance of the sensor is attributed to the porous nature and high specific surface area of the active surface sites to allow the adsorption of Pb\(^{2+}\) and Cd\(^{2+}\) metal ions. Secondly, the interconnection of ZIF-67 with rGO nanosheets provided efficient electronic pathways for charge transfer across the material.

The significance of the proposed work is that the ZIF-67/rGO/Grafoil outperforms or competes well with many of the similar sensor systems for the simultaneous detection of Pb\(^{2+}\) and Cd\(^{2+}\) reported in the recent past. Furthermore, the sensor is prepared with the use of inexpensive chemicals, and it should allow the translation of the method into disposable options for the easy, sensitive, and simultaneous analysis of Pb\(^{2+}\) and Cd\(^{2+}\) ions in environmental samples.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contribution statement

N.G. Conceptualization, Methodology, Data curation, Data interpretation, Writing - original draft, Funding acquisition. A.D. Conceptualization, Analysis, Supervision, Reviewing & editing the draft. A.L.S. Conceptualization, Analysis, Supervision, Reviewing & editing the draft.

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