Electrochemical sensing of malathion using doped MOFs

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Abstract Coordination polymerization produces a variety of metal–organic frameworks (MOFs), each with its own set of physical & chemical properties. Making MOFs suitably conductive in nature, is one of the hurdles faced to be utilized its potential practical applications. To explore the electrical conductivity’s features of MOFs, NH₂-Al-MOF, ZnQ@ZIF-8 and Al-MIL-53 MOF have been treated with NaOH, H₂SO₄, and HCl. Acid/Alkaline doped MOFs have been utilized to prepare conducting thin films on indium tin oxide (ITO) slides using drop-casted method. Electrical feature analysis has indicated reduction in overall resistance of NH₂-Al-MOF < ZnQ@ZIF-8 < Al-MIL-53. The prepared MOF thin films have been used for malathion detection. We have found limit of detection (LOD) i.e., 1.668 mg/L 2.386 mg/L and 2.397 mg/L for malathion using doped MOFs, respectively.

Keywords: NH₂-Al-MOF, ZnQ@ZIF-8, Al-MOF electrochemical sensors, Organophosphate Pesticides

1. Introduction

In present literature, electrochemical sensors are widely popular in diverse application including environmental nursing, food production process regulator systems, and biotic investigation. It is due to their disposing quick response output, better sensitivity with cheaper price [1–4]. As like, pesticide electrochemical sensors has shown greater accessibility as a sensitive sensor for pesticides especially organophosphate pesticide (OPPs) determination. Basically, OPPs are widely employed in farming, profitable, and suburban applications. Importantly, they have terrible health and environmental adversely affect. As a result, the detection of OPPs has find out wide attention [5–7]. In present literature, insufficient/limited stability, sensitivity character loss, improper transduction methods and many more are matter of concern for OPPs sensing in real world application [8]. To counter these concern use of novel and advanced materials for pesticides sensors have shown great results [9]. For examples, AuNPs tinted graphene nanosheets (GNs) on glassy carbon electrode for enzymeless OPPs sensing. Au nanoparticle-decorated graphene hybrid nanosheet was demonstrated for rapid and, unpretentious of methyl parathion. The better sensitivity with linearity range 0.2-1.0
g mL\(^{-1}\) and limit of detection (LOD) 0.6 ng mL\(^{-1}\) was reported via stripping voltammetric performances to capture the MP [3].

Here, we utilized doped metal organic framework (MOFs) for malathion sensing. Basically, MOFs are intriguing nano-structured materials made up of metallic ions with organic linker at certain experimental conditions [10,11]. Basically, they have comprising tunability behaviour, high surface area, excellent chemical and thermal features [12,13]. Surpassing interior MOFs surface area; they are greatly explored for gas adsorbent, electrochemical sensor with an establishment of H\(_2\), CO\(_2\), N\(_2\) and methane [14-17]. We have synthesized ZnQ@ZIF-8, Al-MIL (53), and NH\(_2\)-Al-MIL as per reported in literature [18,19].

Afterward, the drop casting method was used for deposition of above said MOFs on ITO glass slides. Alkaline/acidic doping of NaOH, H\(_2\)SO\(_4\), and HCl on synthesised MOFs was performed. Morphological and conductive analysis was performed at each stage confirm analytical changes. In order to sense the selected OPPs i.e., Malathion, linear sweep voltammetry (LSV) was performed using current range (100mA – 10nA).

2. Experimental Details

2.1 Materials Used
Aluminium nitrate, Dimethyl formamide (DMF), terephthalic acid, 2-methyl imidazole, zinc acetate, triethylamine (TEA), 8-HQ (hydroquinidine), NH\(_2\)H\(_2\)BDC (2-aminoterephthalic acid), AlCl\(_3\)·6H\(_2\)O (aluminium chloride hexahydrate), sodium hydroxide (NaOH), Indium Tin oxide (ITO) slides, Ethanol (EtOH), H\(_2\)SO\(_4\) (sulfuric acid), HCl (hydrochloride), malathion were of analytical reagent grade and used without further purification. All solution was prepared and diluted in deionized water.

2.2 Synthesis of MOFs
To synthesis of NH\(_2\)-Al-MOF, ZnQ@ZIF-8 and Al-MIL-53 MOF have been performed as per literature (Sánchez et al., 2015; Chaudhari et al., 2016).

2.3 MOF@Thin Film Preparation
After analysis, thin film of lab synthesized NH\(_2\)-Al-MIL ZnQ@ZIF-8, and Al-MIL (53) MOF was prepared on ITO using drop casting technique. A 10 mg/ml denser conjugated stock solution of lab synthesised MOFs in ethanol was prepared. The homogenously stock solution was well mixed before the drop casting. Drop casting of the prepared stock solution was poured using a pipette drop wise over the ITO, simultaneously. This was then allowed to air dry for 10-15 minutes for the drop casting and analysed.

2.4 Alkaline/Acidic Doping @ MOF
0.1 M solution of sodium hydroxide (NaOH), sulphuric acid (H\(_2\)SO\(_4\)) and hydrochloric acid (HCl) was prepared in distilled water. Afterward, NaOH, H\(_2\)SO\(_4\), and HCl are doped to each NH\(_2\)-Al-MIL ZnQ@ZIF-8, and Al-MIL (53) sample independently on ITO slide. We have used doped NH\(_2\)-Al-MIL ZnQ@ZIF-8, and Al-MIL (53) for pesticides sensing. Importantly; the electrical features were measured using electrochemical workstation.
2.5 Linear sweep voltammetry

Linear sweep voltammetry (LSV) protocol has been introduced to measure the current (I) versus voltage (V) linearity (I-V) graph. LSV was used to measure the resistance of blank ITO in the current range (100mA – 10nA).

2.6 Malathion sensing

The different dilution ranges (5ppm – 0.001ppm) solutions have been prepared in ethanol for malathion sensing. All dilutions were used for IV analysis using doped MOFs@ITO. The resistance was analysed over doped surfaces to measure the all-investigative alteration of analyte.

3. Results and Discussion

3.1 Morphological and spectroscopic analysis

NH$_2$-Al-MIL ZnQ@ZIF-8, and Al-MIL (53) were synthesized as per reported literature. Selection of above said MOFs was made due to and Metal based reversible and multi-electron transfer characters. Basically, the drop casting technique was used for the thin film deposition on ITO slides. Afterwards, 0.1 M solution of NaOH, H$_2$SO$_4$, and HCl were used for doping of ZnQ@ZIF-8, Al-MIL (53), and NH$_2$-Al-MIL. The morphological and spectroscopic techniques was utilized for undoped and doped MOFs analysis.

The SEM analysis shows nine images of Blank ITO lab synthesized undoped and doped NH$_2$-Al-MIL ZnQ@ZIF-8, and Al-MIL (53) thin film, respectively (Figure 1A, D & G). The morphological analysis specifies the pure crystalline pristine MOFs with rhombic dodecahedral (ZnQ@ZIF-8), irregular shape (Al-MIL (53)), microneedles and nanorods (NH$_2$-Al-MIL (53)) with estimated crystal size, respectively (Figure 1. B, E & H). Afterward, significant changes in morphological of doped MOFs were find out and confirmed through SEM analysis (Figure 1. C, F & I).
Figure 1. SEM Analysis on undoped and doped MOFs on ITO: Blank ITO (A, D & G), lab synthesized undoped (B, E & H) and doped ZnQ@ZIF-8, Al-MIL (53), and NH$_2$-Al-MIL thin film, respectively (C, F & I).

The voltametric analysis was performed using LSV technique. Swept linearity was measured with respect to time when in absence of potential between the reference electrode (RE) and working electrode (WE). Basically, the redox behaviour was observed in the current range (100mA – 10nA).

Figure 2 (A & B). Current–voltage (I-V) curve to resistance analysis of undoped and doped NH$_2$-Al MOF, AL-MOF and ZnQ@ZiF-8 at constant temperature using two probe techniques.
Figure 2 present the current–voltage (I-V) features of MOFs film developed on ITO. The data analysis with the linear visuality of I-V peaks achieved by performing LSV with scan rate of 21 sec⁻¹. All analysis was considered to following power law (IxV) dependency at constant temperature. This I-V peak allows measuring the outflow of resistance over the doped and undoped materials. A power scaling mechanism can be predicted with the effect of SCL (space-based charge limited) to show conduction modal and power-law $V^2\propto I$ efficacy [20,22]. The conduction nature was shown by the doped MOFs surface which was Ohmic resistivity ($V_{\text{Ohm}} = aI$) expression accompanied in series, i.e., $V=aI+bI^{0.5}$. Finally, we find out that NH$_2$Al-MOF washave excellent conductive due to conjugated π orbital and bridging the dimeric aluminium subunits in MOF. It allows first-rate continuous conducting electrons path to support electron transfer [21-24]. The resistance values recorded was measured for undoped and doped MOFs (Table 1).

### Table 1. Resistance (Ω) variations analysis undoped and doped MOF on ITO surfaces

| Description     | Undoped MOF Resistance (Ω) | Doped MOF Resistance (Ω) | $H_2SO_4$ | HCl | NaOH |
|-----------------|----------------------------|--------------------------|-----------|-----|------|
| ITO – Blank     | 140.231                    |                          | -         | -   | -    |
| NH$_2$-Al-MOF   | 184.759                    | 128.046                  | 136.908   | 158.746 |
| ZnQ@ZiF-8       | 242.814                    | 134.059                  | 150.104   | 166.069 |
| Al-MOF          | 288.908                    | 149.945                  | 174.532   | 196.822 |

Our results indicate that the resistance level i.e., NH$_2$-Al -MOF< ZnQ@ZIF8 < Al-MIL (53), respectively. On comparing norms, the conductivity of undoped MOF has given a evidential exposure to show the efficacy of the doped MOFs. It is clearly observed from the given data in Table 1.1, treatment with alkaline and acidic medium, i.e., NaOH, H$_2$SO$_4$, and HCl has caused increase in surface conductivity on applying potential range of -0.6 V to +0.6 V. The conductivity scale implies as. H$_2$SO$_4$>HCl> NaOH, means the hydrogen sulphide drags a more conductive behaviour than other doping solvents. These outcomes have proved that the doping of H$_2$SO$_4$, HCl and NaOH implies a conductive surface.

### 3.2 Malathion Sensing

The different concentration levels of malathion i.e., 1 ppb -5 ppm was made to explore the sensing application of doped MOFs. The current–voltage (I-V) data for malathion (with concentrations; 1 ppb, 10 ppb, 100 ppb, 500 ppb, 1 ppm, 2ppm, 5 ppm), with different doped MOFs have been shown
in Figure 3, 4 and 5, Basically, interaction between doped MOFs and malathion sensing was noted through decreases in the resistance with respect to increasing concentration of malathion. Basically, doped MOF have p-moieties which allowing them to interact with analyte and provide a transport channel. The delocalization of charge caused due to donor/acceptor interactions between analyte and MOFs[25].

![Figure 3](image3.png)

**Figure 3.** Current–voltage (I-V) curve to resistance analysis between H$_2$SO$_4$ doped ZnQ@ZIF-8 and different concentration of malathion.

![Figure 4](image4.png)

**Figure 4.** Current–voltage (I-V) curve to resistance analysis between H$_2$SO$_4$ doped Al-MIL (53) and different concentration of malathion.
Interestingly, poor analyte interaction was found with Al-MIL-53 than ZnQ@ZIF-8 and NH₂-Al-MOF, respectively. The change in resistance during the interaction with all different pesticides concentration is shown in Table 2. Interaction comparison of analyte and doped MOFs clearly revealed that NH₂-Al-MOF performs better over ZnQ@ZIF-8 and NH₂-Al-MOF for malathion sensing. Finally, our results indicate limit of detection (LOD) i.e., 1.668 mg/L, 2.386 mg/L and 2.397 mg/L, for malathion using doped NH₂-Al-MOF < ZnQ@ZIF-8 < Al-MIL-53, respectively.

**Figure 5.** Current–voltage (I-V) curve to resistance analysis between H₂SO₄doped NH₂-Al-MOF and different concentration of malathion.
Table 2. Interaction comparison on resistance ($\chi$) variations between malathion and doped MOFs

| Sr. No. | NH$_2$-Al-MOF | ZnQ@ZIF-8 | Al-MIL (53) |
|---------|---------------|------------|-------------|
|         | $H_2SO_4$    | $HCl$      | $NaOH$      | $H_2SO_4$    | $HCl$      | $NaOH$      | $H_2SO_4$    | $HCl$      | $NaOH$      |
| 1       | 100 ppb       | 120.32     | 134.01      | 157.34      | 127.54      | 135.63      | 173.73      | 143.31      | 177.94      | 193.28      |
| 2       | 10 ppb        | 131.48     | 141.40      | 164.29      | 135.42      | 144.53      | 182.48      | 161.65      | 185.39      | 161.17      |
| 3       | 100 ppb       | 139.33     | 145.19      | 169.08      | 143.45      | 151.63      | 190.13      | 191.23      | 194.05      | 191.23      |
| 4       | 500 ppb       | 151.28     | 153.01      | 180.09      | 149.16      | 159.28      | 200.87      | 198.71      | 201.65      | 198.26      |
| 5       | 1 ppm         | 160.91     | 162.34      | 188.42      | 157.88      | 163.91      | 206.19      | 220.72      | 213.03      | 214.85      |
| 6       | 2 ppm         | 168.64     | 167.10      | 197.20      | 166.63      | 179.86      | 218.46      | 235.25      | 218.02      | 225.68      |
| 7       | 3 ppm         | 178.29     | 177.73      | 205.71      | 174.70      | 188.35      | 226.29      | 243.26      | 232.29      | 238.12      |
| 8       | 5 ppm         | 218.03     | 186.93      | 213.31      | 183.45      | 218.56      | 238.03      | 256.60      | 239.12      | 245.25      |

4. Conclusion

In this model study, we have performed the acid and alkaline doping of lab synthesized NH$_2$-Al-MOF, ZnQ@ZIF-8, and Al-MIL-53. Our results indicated that electrical features of MOFs have sustainably improved after doping of NaOH, $H_2SO_4$, and HCl. More importantly, we explore doped MOFs for pesticide sensing and find out suitable for the same. Interestingly, our comparison study indicated that $H_2SO_4$ doped NH$_2$-Al-MOF is most suitable doped MOFs for malathion sensing with limit of detection (LOD) i.e., 1.668 mg/L. We are exploring more possibility on electrochemical sensing based doped MOFs for organophosphate pesticides (OPPs) detection. Hopefully, we will present more good results in near future.

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