sensor that are connected in series. A mender sensor is based on five loops of coils. The interdigital sensor is designed based on a consecutive positive electrode and negative electrode.

A simulation using COMSOL Multiphysics 4.2 software has been carried out to evaluate the sensitivity of all configurations based on impedance changes. Hence, the best sensor in term of the highest sensitivity can be determined. The frequency for the simulation is varied from 1–24 MHz. Three parameters have been considered: conductivity σ, permittivity ε, and permeability μ. The results demonstrate that all configurations are sensitive to the material properties. Based on the simulation data, the best sensor that is highly sensitive to nitrate ions is the star configuration. Nor et al. [7] validated the simulation results through experiments. Both the simulation and experimental results are in good agreement.

Multivariate statistical tools associated with a planar electromagnetic sensor are useful for real-time measurement in estimating and classifying the nitrate concentration level in water. Such tools are independent component analysis (ICA) [19,69] and artificial neural networks (ANN) [7]. These tools enhance the capability of planar electromagnetic sensor to differentiate the nitrate contaminant level presence in water. Hence, the accuracy of the detection is improved. Generally, the indicator to determine the performance of ICA and ANN is based on the root mean square error (RMSE) value.

Yunus et al. [19] applied the ICA model for nitrate estimation in natural water. The proposed ICA model is tested using eight sets of samples that contain a mixture of ammonium nitrate (NH_4NO_3) and ammonium phosphate$(NH_4)_2HPO_4$. They proposed three components in the analysis: the fixed point algorithm, spectral matching and contamination calculation. A second derivative equation is applied to the output sensitivity of mixing samples in order to differentiate the sample's data trends significantly. Hence, the identification of nitrate based on concentration level can be easily carried out. The ICA model is able to detect nitrate contamination in distilled water as well as differentiate the concentration level with a correlation coefficient of 0.9921. A large error is observed when the concentration is less than 15.3 mg/L, while low error is obtained at high concentrations. This finding indicates that the ICA model is a trustworthy multivariate-statistical tool for nitrate estimation in water. On the other hand, the ICA model requires repeating measurements in order to obtain sufficient data for nitrate estimation. Hence, the estimation process of ICA is time-consuming as a number of measurements are compulsory.

Therefore, as an alternative, the ANN estimation tool has been introduced to overcome this problem.

The ANN approach has been used [7] to estimate nitrate contamination presences in water samples. The proposed ANN model is subjected to a nitrate sample in the form of KNO_3 and KNO_4. Nitrate concentrations vary from 5–114 mg and were dissolved in 1 L of distilled water. To confirm the estimation ability of the proposed ANN, seven sets of mixed KNO_3 and KNO_4 with different levels of concentrations dissolved in water were prepared and tested. The finding demonstrates that the proposed ANN model can detect and estimate the nitrate concentration in distilled water with an RMSE of 0.0132. To validate the capability of the ANN model in estimating nitrate concentration, the proposed ANN model is removed from the system and the output is observed. The result demonstrates that RMSE value increased significantly to 0.0977. Therefore, the application of proposed ANN model is beneficial and crucial for nitrate estimation in water.

b. Planar electromagnetic detection mechanism and equivalent circuit

PESA consists of a series-connected meander sensor and interdigital sensor [49]. The sensor array is fabricated in thin substrate such as printed circuit board (PCB) using a conventional PCB fabrication technique. The meander sensor consists of several loops or coils of electrodes and is designed to be spiral or square in shape. The interdigital sensor consists of positive and negative electrodes and is designed to be parallel between positive and negative electrode. The ground electrode is placed at the bottom of the interdigital sensor. The architecture of the electromagnetic sensor is illustrated in Figure 3.

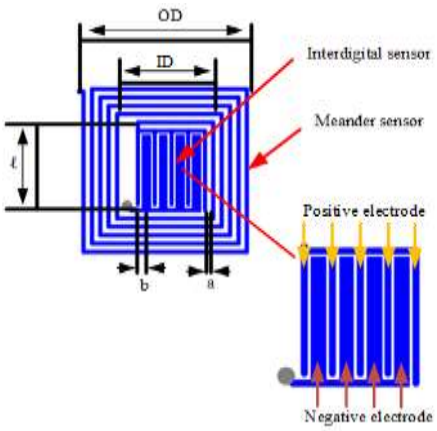

Figure 3: Electromagnetic sensor architecture

As reported in [48,50], the sensor's response in terms of strong current signal can be improved by widening the negative electrode dimension of the interdigital sensor [51]. Significant changes on impedance occurred by altering the shape and geometric parameters of the interdigital electrode. For example, [52] mentioned that the impedance of water bulk medium increases with the distance between the two electrodes and decreases by increasing the area of the electrode. Therefore, the total impedance of the sensor is increased as the wide distance configuration applies for the electrodes.

The inductance from a meander sensor could also influence the performance of the planar electromagnetic sensor. The inductance equation of the mender sensor can be expressed as [53,54]:

$$L = 1.39 \times 10^{-6}(OD + ID)N_L^{5/3}\log_{10}\left(4\frac{OD + ID}{OD - ID}\right) \quad (1)$$

Where L represents the inductance of a mender sensor (Unit: Henrys), and N_L is the number of inductor turns. OD and ID are the outer and inner diameters, respectively, of the inductor respectively (Unit: meters). A coil structure or inductive part in the planar electromagnetic sensor plays a very important role where it helps to weaken the capacitance of the measured medium. Hence, the capacitive impedance will definitely change to inductive impedance at high frequencies. Therefore, the measurement accuracy is improved as the capacitive part of the total impedance normally interferes with the measurement precision. Furthermore, weakening the capacitance caused by the inductance from coil structure will decrease the medium impedance. Hence, the current flow in the medium is increased as the total impedance decreases. As a result, the measuring error is reduced as the measuring current increases [53].

The measured resonant frequency and the zero reactance frequency from an experiment are very important to determine and estimate the real, imaginary, and complex permittivity of a medium. The resonant frequency is defined as the frequency in which the maximum impedance amplitude of the real part of a medium is observed. The zero reactance frequency is the frequency of the imaginary part of a medium where the impedance value is zero. On the other hand, these

frequencies change with the concentration of the measured medium, which in turn allows the calculation of concentration. Moreover, these frequencies are reported to be highly dependent on the inductance and capacitance of the planar electromagnetic sensor array [53].

An investigation on the relationship between capacitance and conductivity of a medium based on electromagnetic sensor configuration, coating layer and water solution has been carried out [54]. The protective layer known as the coating layer insulates the sensor surface from direct exposure to water solution. The protective layer protects the sensor surface from extreme chemical reaction that comes from contaminants. Hence, the use of a protective layer can avoid the sensor from being damaged. Moreover, a protective layer acts as a constant capacitance known as a double-layer capacitor, C_{dl}. C_{dl} is highly dependent on copper line surface area and the thickness of coating layer [54]. A charge transfer resistor, R_{ct} is the resistor that is present in the coating area. This resistor is connected in parallel with C_{dl} as illustrated in Figure 4. Psychochemical variables such as electrical potential and chemical potential have the ability to charge the interface and allow the transportation of reacting species between the water bulk solution and interfacial reaction zone. Therefore, the psychochemical variables make R_{ct} be influenced by their existence in the water bulk medium. R_E and C_E are the resistance and capacitance of water bulk, respectively.

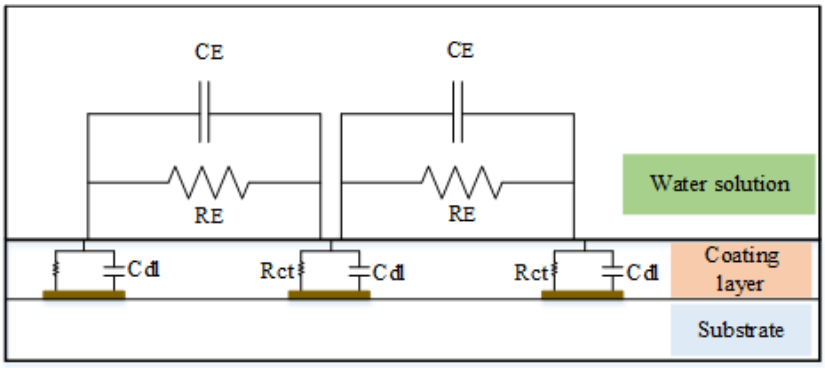

Figure 4: Physical representation based on planar electromagnetic sensor configuration

The dielectric properties of a water solution arise from the influence of an external electric field of planar electromagnetic sensor on the dielectric dipole and mobile ions. When the water solution is subjected to an external electric field, the neutralisation or polarisation process of dipoles occurs. As a result, the dipole is re-aligned by shifting its equilibrium positions, where a

positive charge is displaced toward the field of a negative charge and vice versa for a negative charge. Another significant dipole realignment is the formation of an internal electric field between the dipoles. This re-alignment process is different for different types of materials. Hence, the magnetic response of each material across the frequency spectrum is unique. The dipole re-alignment process is illustrated in Figure 5.

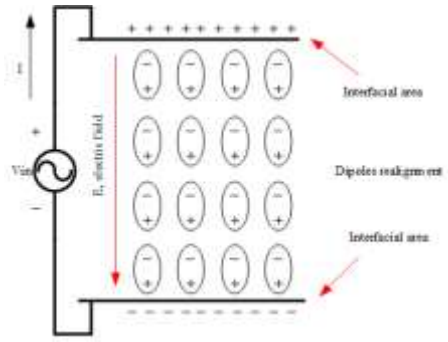

Figure 5: Dipole realignment process

Figure 5 shows the realignment process of dipoles. In the bulk liquid area, dipole re-alignment from the separation of charge in the monomers making up the material builds up capacitance C_E of the liquid solution. As a result, a charged surface is formed at the interfacial area. Hence, C_{dl} is formed in the interfacial area. This is known as an electrical double layer (EDL) [52].

Mobile ions must be considered as well. Mobile ions are present in water due to contamination. Conductive current movements in the water bulk area are based on the flow of mobile ions when subjected to an external electric field. Hence, the resistance of water bulk, R_E is highly dependent on the strength of the applied external electric field. Ion movement is dependent on the viscosity of the medium: it moves faster in the lower viscosity medium and moves slower in a higher viscosity medium. On the other hand, R_{ct} is based on the kinetics of absorbed or desorbed of mobile ions in the interfacial layer [52].

The equivalent circuit of the planar electromagnetic sensor based on a series-connected meander sensor and interdigital sensor is presented in Figure 12. The equivalent circuit shows the sensor's impedance, which consists of C_{dl}, R_{ct}, C_E and R_E. The constant parasitic capacitor is denoted as C_C. The equivalent circuit of PESA can be expressed as follows:

$$Z = j\omega L + \frac{\frac{1}{j\omega C_C}\left(\frac{R_E}{1+R_E j\omega C_E} + \frac{R_{ct}}{1+R_{ct} j\omega C_{dl}}\right)}{\frac{1}{j\omega C_C} + \left(\frac{R_E}{1+R_E j\omega C_E} + \frac{R_{ct}}{1+R_{ct} j\omega C_{dl}}\right)} \quad (2)$$

The relationship between the permittivity and conductivity with the sensor's geometrical constant will enable the calculation of the permittivity and conductivity of every water sample using a proper fitting function. Based on Equation (2), the real part of conductivity, σ can be estimated from Equation (3), while relative permittivity ε_r' is estimated from Equation (5) [53].

$$\sigma = \frac{1}{kR_E} \quad (3)$$

where k is the geometrically correlated constant of the interdigital sensor, which is defined as in Equation (4) [53], and R_E is the resistance of bulk liquid solution.

$$k = \frac{\ell(Nc-1)K[(1-(a/b)^2)]^{1/2}}{2K[a/b]} \quad (4)$$

Where ℓ, a, and b are the interdigital sensor dimensions as shown in Figure 3 while N_C is the number of interdigital electrodes.

$$\varepsilon_r' = \frac{C_E}{k\varepsilon_o} - \varepsilon_S \quad (5)$$

Where ε_o and ε_s are the free space permittivity and relative permittivity of substrate respectively. C_E is the capacitance of bulk liquid solution, calculated based on Equation (6) [52]:

$$C_E = \frac{\varepsilon_r' \varepsilon_o A}{d} \quad (6)$$

Where A is the electrode geometry of area A in which current is carried, and d is the thickness of the sample between electrodes. The imaginary part of complex permittivity of the medium, ε_r'' can be expressed as:

$$\varepsilon_r'' = \frac{1}{kR_E\omega\varepsilon_0} \quad (7)$$

Where ω is the radian frequency (Hz). The complex permittivity of a medium, ε_r'' shows an inverse relationship between R_E and ω. Therefore, increasing the radian frequency should decrease its complex permittivity.

c. Selective membrane for PESA detection improvement

Various methods have been introduced for water contamination treatment such as flocculation, floatation, ferric hydroxide and filtration. However, these conventional methods have their own drawbacks that restrict their applications, such as requiring pre-treatment process and reagent needing to be consumed during the operation. Furthermore, these methods are not economical for the treatment of large-scale samples with high concentration.

Currently, membrane technology has gained great attention in sensing technology. Most workers nowadays like to integrate membranes or known as conducting polymer, into their sensor system in order to improve the sensing performance [78]. Polymers have gained tremendous recognition in the field of liquid and gas sensing. This so called ‘an active layer’ has been introduced since 1980s. It is reported that the conducting polymer has various improved characteristic. Such characteristic are highly sensitive and short response time. Moreover, their fabrication process is not complicated which easy to synthesize via electrochemical process [79].

Yunus et al. [3] applied the membrane technology into a planar electromagnetic sensor array. The proposed membrane is inexpensive, as no additional reagent is required for the pre-treatment. Hence, this is an alternative method to save costs. The proposed membrane consists of a combination of polymer dope modified silica (polymer) and N-Methyl-2-pyrrolidone (NMP) (solvent). Poly-sulfone (PSF) and modified silica were selected to represent the polymer material in the membrane to enhance the selectivity towards nitrate ions. The organic compound NMP was employed as the main element of the membrane, where it has five-membered lactams.

This finding demonstrates that the average sensitivity of a planar electromagnetic sensor varied from 0.007–223 % via experiments using nitrate concentrations of 5 ppm, 25 ppm, and 100 ppm. The proposed membrane enhanced the sensor response in terms of sensitivity and selectivity towards nitrate ions.

IX. CONCLUSION

The aim of this study was to consider the various ways that the enhancements of knowledge and material sciences have played a prominent and relevant role in improving nitrate detection capability. The improvement may come from the introduction of a suitable membrane into a sensor system, sensor modification via design and configuration, system miniaturisation, the selection of electrode material for sensor development, techniques to improve bonding between membrane and sensor, and minimising the environmental impact during measurement.

The drawbacks of conventional methods such as system limitations have been highlighted. Even though most conventional methods provide sufficient results for nitrate ions detection, they are generally time-consuming, immobile (i.e. laboratory-based), and the measurement is not performed routinely.

In summary, planar electromagnetic sensors have become popular in pollutant determination due to their non-destructive measurement, low cost, high performance features such as fast response, and simple operation. Extensive research on membrane development is crucial in order to enhance the sensor performance in terms of selectivity and sensitivity.

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