Investigation of Adsorption behaviour of Acetone Vapour towards a Surface Plasmon Resonance Sensing Layer using Adsorption Isotherm Models

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Abstract. Surface plasmon resonance (SPR) sensors are widely explored due their ultrasensitivity to even a minute alteration of refractive index. Knowledge of adsorption processes could be exploited to explain the performance and interaction mechanism of an SPR sensor. Herein, we report the fitting of the experimental SPR sensing data during the detection of low concentrations of acetone vapour (0.5-5 ppm) using the linearized and non-linearized format of the Langmuir and the Freundlich isotherm models. The sensing layer is made from a ternary composite material of doped polyaniline, reduced graphene oxide and chitosan. The objective is to find the best model, understand the interaction mechanism and investigate the performance of the sensing layer. Correlation factors and error values were used to determine the best fit. The results showed that the Freundlich model could fit the data better than the two formats of the Langmuir model. Also, the interaction mechanism was predicted to be the physical one due to the heterogeneity parameter value, n<1. In addition, the selectivity of the sensing toward acetone compared to water, methanol, ethanol and propanol vapours was explained in terms of proximity of solubility parameters. Moreover, the ternary based sensor was found to be reversible and stable.

Keywords: Surface plasmon resonance (SPR), Langmuir, Freundlich, Sensor, Acetone Vapour

1. Introduction
Surface plasmon resonance (SPR) sensors are widely explored for numerous applications such as environmental monitoring, drug discovery, and disease screening and monitoring due to their ultrasensitive detection of any material on the surface of their sensing layer [1, 2].
Adsorption of an analyte on the surface of SPR sensing layer varies the refractive index in the vicinity of the sensing layer [1, 3, 4]. This variation serves as the basis for the response of the SPR sensor. The adsorption strength is quantified using various adsorption parameters such as the binding affinity constant ($K_A$), dissociation constant ($K_D$) and Freundlich adsorption parameter ($K_F$). Based on these parameters, a measurable data on the interactions between an analyte and a sensing layer can be derived, which depicts the performance of an SPR sensor with regards to parameters such as sensitivity, stability, interaction mechanism, response, recovery and selectivity [3, 4].

The adsorption process is originally described by non-linear adsorption isotherm models. However, linear adsorption isotherm models are currently explored due their advantages such as simplicity, quantification of the adsorbates distribution, analysis of the adsorption system, and easy verification of the stability of theoretical assumptions of adsorption isotherm models. Unfortunately, inconsistency between the predictions and experimental data has been observed from linear based fittings of isotherm model. The aforementioned limitation necessitates the comparison and investigation of the applicability of linear or non-linear isotherm models in describing a number of adsorption system [3].

Acetone vapour sensing attracts attention especially due to its potential prediction of diabetes occurrence [5]. This work is aimed at comparing the applicability of the linear and the non-linear formats of Langmuir and Freundlich models in describing the adsorption process between acetone vapour and a ternary based SPR sensing layer comprising of doped polyaniline, reduced graphene oxide and chitosan. The best fits are judged in terms of least error and high correlation factor [6]. In addition, the interaction mechanism has been explained based on the adsorption studies. Finally, the repeatability, stability and the reversibility of the ternary sensing layer were also investigated.

2. Experiment

2.1. Experimental Data

In this work, the two widely explored isotherm models, Langmuir and Freundlich were used for the modelling. The experimental data was obtained during the experimental detection of low concentrations of acetone vapour using a ternary composite based SPR sensor. The ternary composite sensing layer comprises of doped polyaniline (PANI), reduced graphene oxide (RGO) and chitosan [7]. The details on the synthesis of the ternary composites, its characterisation and the information of the ternary composite based SPR sensor can be found in our previous works [2, 5, 7-11]. The main data used for the modelling is summarised in Table 1.

| Concentration of acetone vapour (ppm) | SPR shift due to acetone, $\Delta\theta$ (degree) |
|--------------------------------------|-----------------------------------------------|
| 0.5                                  | 0.4037                                        |
| 1                                    | 0.6161                                        |
| 2                                    | 1.3967                                        |
| 3                                    | 2.0453                                        |
| 4                                    | 2.6957                                        |
| 5                                    | 3.5256                                        |

2.2. Isotherm Modelling Equations

As mentioned earlier, the non-linear and linear formats of Langmuir and Freundlich isotherm equations for the description of the adsorption process, in which equations 1-4 were used for the evaluation, respectively.
\[ \Delta \theta = \frac{\Delta \theta_{\text{max}}}{K_D + C} \]  

(1)

\[ \frac{1}{\Delta \theta} = \left[ \frac{1}{\Delta \theta_{\text{max}} K_A} \right] \frac{1}{C} + \frac{1}{\Delta \theta_{\text{max}}} \]  

(2)

\[ \Delta \theta = K_F C^{\frac{1}{n}} \]  

(3)

\[ \ln(\Delta \theta) = \ln(K_F) + \frac{1}{n} \ln(C) \]  

(4)

Where, \( \Delta \theta \) is the SPR shift, \( \Delta \theta_{\text{max}} \) is the maximum SPR shift at the saturation, \( C \) is the concentration of the analyte, and \( K_D \) is the equilibrium dissociation constant. Affinity constant \( (K_A) \) is the reciprocal of \( K_D \). Where, \( 1/n \) is the heterogeneity factor [12, 13]. A variation in the slope \( (1/n) \) between 0 and 1 is associated with a chemisorption process. When a slope above 1 is observed then a physical absorption process is expected [14, 15]. \( K_F \) can be related to the strength of the adsorptive bond or adsorption capacity.

3. Results and Discussions

3.1. Adsorption study

To investigate the binding strength between the single layers ternary composite and acetone on the SPR sensor, the average SPR shifts versus acetone concentrations (Table 1), in the range of 0.5 ppm to 5 ppm were plotted and fitted to non-linear and linear formats of Langmuir and Freundlich isotherm models as shown in equations 1-4, respectively [13, 16]. The best fit was judged in terms of low error value and higher correlation factor [6, 17].

Figure 1 (a-d) show the graphs of the fittings for the non-linear Langmuir, linear Langmuir, non-linear Freundlich and linear Freundlich models, respectively and the result is summarised in Table 2.
Figure 1. Adsorption process between the ternary based SPR sensing layer and various acetone concentrations (0.5-5 ppm) fitted to (a) non-linear Langmuir, (b) linear Langmuir, (c) non-linear Freundlich and (d) linear Freundlich isotherms models.

Table 2. Binding parameters of acetone vapour towards single layer ternary composite based SPR sensor extracted from non-linear Langmuir, linear Langmuir, non-linear Freundlich and linear Freundlich fittings.

| Format       | Format     | Parameter       | Value   | Standard Error |
|--------------|------------|-----------------|---------|----------------|
| Langmuir     | Non-linear | $\Delta \theta_{max}$ | 3.288E+13 | 4.018E+19      |
|              |            | $1/K_A$         | 4.761E+13 | 5.847E+19      |
|              |            | Reduced chi-square | 0.005  | -              |
|              |            | Adj. $R^2$      | 0.997   | -              |
|              |            | $K_D$           | 2.100E-14 | -              |
|              |            | $K_D$           | 4.761E+13 | 5.847E+19      |
|              |            | Residual sum of squares | 0.097 | -          |
|              |            | Intercept       | 0.105   | 0.096          |
|              |            | Slope           | 1.244   | 0.100          |
|             | Linear     | Adj. $R^2$      | 0.968   | -              |
|             | Linear     | $\Delta \theta_{max}$ | 9.524  | -              |
|             | Linear     | $K_A$           | 0.084   | -              |
|             | Linear     | $K_D$           | 11.905  | -              |
|             | Linear     | $K_F$           | 0.665   | 0.035          |
|             | Linear     | $n$             | 0.973   | 0.036          |
|             | Linear     | Adj. $R^2$      | 0.997   | -              |
|             | Linear     | Reduced chi-square | 0.004 | -              |
|             | Linear     | Residual sum of squares | 0.033 | -          |
|             | Linear     | Intercept       | -0.339  | 0.049          |
|             | Linear     | Slope           | 0.963   | 0.046          |
|             | Linear     | $K_F$           | 0.791   | -              |
|             | Linear     | $n$             | 1.038   | -              |

The maximum SPR shift at the saturation ($\Delta \theta_{max}$) is measured in degrees, the affinity constant ($K_A$) is measured in ppm$^{-1}$ and both the equilibrium dissociation constant ($K_D$) and the adsorption capacity parameter ($K_F$) are measured in ppm [16, 18]. $1/n$ is the heterogeneity factor [12, 13] and a variation in the slope ($1/n$) between 0 and 1 is associated with a chemisorption process. When a slope above 1 is observed then a physical absorption process is expected [14, 15]. It could be observed from Table 2 that the non-linear format for both the Langmuir and Freundlich fittings show better correlation factor of
about 0.997. However, Langmuir model is hindered by its large error value. As such, fittings based on the non-linear Freundlich model can be considered as the most powerful description tool owing to its lower reduced chi-square value and lower standard error values for the $K_D$ and $n$, relatively. Additionally, both the linear and the non-linear Langmuir fitting formats showed the value of $\Delta \theta_{\text{max}}$ to be far away from the experimentally achieved value especially the non-linear format [7]. On the other hand, lowest error parameters are observed in the non-linear Freundlich fitting relatively (Table 2). Based on these, it could be concluded that the Freundlich model better fits the ternary based SPR acetone vapour sensor. This implies heterogeneity of the ternary sensing layer [13].

The values for the $K_F$ and $n$ are 0.665 ppm and 0.973, respectively. The $K_F$ value indicate the great affinity of the acetone vapour towards the ternary sensing layer [16]. In addition, physical adsorption could be expected since the slope $(1/n) > 1$ [14]. Therefore, the affinity could be attributed to the abundance of OH and amine functional groups as well as the possible solvation effect of the ternary sensing layer [19].

### 3.2. Interaction Mechanism and Selectivity

The adsorption study presented in section 3.1 predicts physisorption process to be the dominant mechanism for the ternary composite sensing layer in the detection of acetone vapour [14, 15]. But, it is worth noting that other interactions may also occur between the sensing layer and the acetone vapour. The high electronegativity of the oxygen in the C=O group of acetone is capable of forming a hydrogen bonding with N-H group of the ternary composite [20, 21]. Therefore, hydrogen bond formation is expected to be the dominant primary interaction. In addition, the RGO is expected to enhance the adsorption process [22].

The selective detection of acetone vapour against water vapour, propanol, methanol and ethanol vapours has been proven [7]. This could be achieved secondarily through swelling and solvation effects [21]. Normally, solubility is highly anticipated when the solubility parameters of two substances are similar or closer [21]. The highest response of the ternary composite based SPR sensor to acetone vapour compared to other vapours could be explained in terms of the proximity of the solubility parameters for the acetone and the polyaniline, which is the parent material in the ternary composite. The Hildebrand solubility parameter for all the vapours and the polyaniline is shown in Table 3. In addition, the variation among the alcohols and water vapour is also dependent on the proximity of the solubility parameters as well as the hindrance effect.

### Table 3. Hildebrand solubility parameter for the polyaniline and the analytes [21, 23, 24]

| Material   | Hildebrand solubility parameter $(\text{MPa}^{1/2})$ |
|------------|-----------------------------------------------|
| Water      | 47.9                                          |
| Acetone    | 20.1                                          |
| Propanol   | 23.8                                          |
| Methanol   | 29.7                                          |
| Ethanol    | 26.6                                          |
| Polyaniline| 22.2                                          |

### 3.3. Reversibility, Reversibility and Stability Test

The graph of SPR angle versus time for the single layer ternary composite based SPR sensor was obtained in order to investigate its response, recovery, repeatability, stability and reversibility [25]. The graph is shown in Figure 2 in which SPR angle is plotted against time [16, 26]. The SPR angle can only be measured at the interval of 3.5 minutes due to the requirement to control some components of our SPR device manually. As such, the exact values for the response time and the recovery time could not be determined. However, both could be estimated to be in the order of seconds each (Figure 2a and b).
The excellent repeatability and stability of the sensor has been observed from the small values of $\sigma$ and $COV$ as presented previously [7]. In addition, the two cycles of 5 ppm acetone vapour detection in Figure 2b also confirms the excellent repeatability and stability of the response of the SPR sensor. Moreover, the reversibility and the recovery of the sensor could also be observed when the supplies of the different concentrations of acetone vapour are turned off and replaced by the introduction of the synthetic or dry air (Figure 2a-b).

![Figure 2](image)

**Figure 2.** Measurement of the SPR angle versus time for the SPR sensor based on the single layer ternary composite showing the baseline in synthetic air and at different acetone vapour concentrations of (a) form 0.5 ppm to 5 ppm and (b) for two cycles at 5 ppm.

4. Conclusions

The adsorption process during interaction between acetone vapour and a ternary layer comprising of doped polyaniline, reduced graphene oxide and chitosan has been investigated using the linear and non-linear formats of the Langmuir and Freundlich isotherm modelling equations. The data is obtained during the detection of low concentrations of acetone vapour in the range of 0.5-5 ppm using a ternary based surface plasmon resonance (SPR) sensor. The fittings were conducted using Origin Pro 9 software. The results showed that the Freundlich model could fit the data better than the two formats of the Langmuir model, and the attained parameters were acceptable. The values for the $K_F$ and $n$ were 0.665 ppm and 0.973, respectively. In addition, physical adsorption process is expected due to observed $n$ value. This is important as it eases the description of the dominant interaction mechanism. Therefore, it can be concluded that, as for the adsorption of acetone vapour on the surface the ternary composite SPR sensing layer, the Freundlich isotherm model is more powerful and viable in describing the adsorption process. In addition to the excellent performance of the ternary sensing layer, it has also proven to be very selective to acetone vapour against water, methanol, ethanol and propanol vapours. Thus, the adsorption study can be employed to explain the sensing properties of materials.

5. References

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