Ammonia adsorption kinetics on substituted phthalocyanine thin film

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ABSTRACT

The sensing performance of 2(3),9(10),16(17),23(24)- tetrakis-[4-nitro-2-(octyloxy)phenoxy]phthalocyaninato zinc(II) thin film towards ammonia and the influence of relative humidity on it were studied. The results show that the exposure to ammonia gas leads to an increase in sensor current, which is unexpected because of the strong electron donating character of ammonia and p-type semiconductivity of phthalocyanine. This unexpected behavior is related to the change in electronic band structure of the Pc molecule. It was observed that relative humidity enhances the ammonia adsorption. Several adsorption kinetics model were employed to represent the ammonia adsorption on the sensor surface. Analysis of the experimental data indicated that a simple adsorption model can be used to represent our adsorption system.

Keywords: ammonia sensor, adsorption kinetics, response time

Substitute ftalosiyanin yüzeyinde amonyak adsorpsiyon kinetiği

ÖZ

2(3),9(10),16(17),23(24)- tetrakis-[4-nitro-2-(octyloxy)phenoxy]phthalocyaninato zinc(II) ince filmin amonyak algılama performansı ve nisbi nemin amonyak algılama özellikleri üzerindeki etkisi incelenmiştir. Sonuçlar filmin amonyak gazına maruz bırakılması durumunda, amonyak'ın kuvvetli bir elektron verici ve ftalosiyanin bileşiklerinin de p-tip yarıiletken özellik göstermelerine rağmen, beklenmedik bir şekilde iletkenliğinin arttığını göstermiştir. Ortamdaki nisbi nem oranının amonyak adsorpsiyonunu iyileştirdiği gözlemlenmiştir. Sensör yüzeyindeki amonyak adsorpsiyonunu temsil etmek üzere birkaç farklı kinetik model test edilmiş ve, adsorpsiyon sistemini temsil etmek üzere basit bir adsorpsiyon modelinin kullanılabileceği görülmüştür.

Anahtar kelimeler: amonyak sensörü, adsorpsiyon kinetiği, cevap süresi.

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1. INTRODUCTION

Because of its importance in formation of air pollutant aerosols and high toxic nature, the detection of low level concentrations of ammonia (NH_3) gas is crucial in many fields [1,2]. Due to their suitability for nano sized production and high sensitivity metal-oxide semiconductors such as, CuO [3], ZnO [4], and WO_3 [5] are considered to be the best sensing element for NH_3 sensor applications. Although significant improvement in sensing performance of metal-oxide based sensors have been achieved, the operating temperature of these sensors is still high, which limits their gas sensing application [6-8]. The development and synthesis of novel materials for ammonia gas detection at room temperature is therefore urgent.

More recently, it has been indicated that molecular materials have a good potential as an alternate to the inorganic counterparts in many fields, especially for sensing applications [9, 10]. In this regard, the use of organic material in sensing device seems to be promising for achieving significant device performance at low temperatures. This has opened a new opportunity of replacing conventional inorganic sensing layers by the organic ones. As an organic compound, phthalocyanines (Pcs) and their substituted derivatives has gained more attention in gas sensing devices because of their chemical stability, various possible synthetic modifications, and unique electrical properties [11-13]. It is well established that their gas sensing properties are extremely sensitive to the presence and position of substituent groups [14,15]. Relative humidity is one of the most important factor in reliable sensor design because it can interact both the sensor surface and analyte molecules. Although the sensing capability of Pc compounds have intensely been studied, related work especially the influence of relative humidity (RH) on ammonia sensing abilities of phthalocyanine has been relatively few [16].

In this work, the determination of the ammonia sensing properties and the influence of RH on the adsorption kinetics onto periperally substituted zincphthalocyanine (ZnPc) thin film were aimed. Ammonia adsorption onto the Pc compound was analysed using various adsorption kinetic models including Elovich equation, Ritchie's equation, first-order equation and an adsorption–desorption model.

2. EXPERIMENTAL (DENEYSEL)

2(3),9(10),16(17),23(24)-   tetrakis-[4-nitro-2-(octyloxy)phenoxy]phthalocyaninato zinc(II) (**1**) (Fig. 1) was selected as ammonia sensing layer. The synthesis details of the sensing layer can be found in [17]. Briefly, a mixture of 0.168 g *4-(4-nitro-2-(octyloxy)phenoxy)phthalonitrile*, 0.094 g $Zn(CH_3COO)_2$ and 4 mL of dimethylformamide (DMF) was stirred at 180 ºC for 6 h under nitrogen atmosphere. After adding 5 mL of methanol at room temperature, the product was filtered off and then washed several times, first with methanol, then with acetonitrile and acetone. The crude product was isolated by silica gel column chromatography with chloroform as the eluent. Column chromotography was used for purification of the complexes. The compound was characterized by FT-IR, UV/Vis, NMR and mass spectra. In ammonia sensing experiment, photolithographically patterned interdigital Au micro electrodes was used as transducer. Thin film of the sensing layer was prepared on the transducer surface by spin coating method. The spin coating procesess was carried out by spinnig of 0.2 mL tetrahydrofouran (THF) solution of **1** at 1500 rpm for 100 s. In order to be sure that the residual solvent completely removed the film was dried at 90 °C for 75 min. The ammonia sensing properties of the film was examined by measuring sensor current as the concentration of the ammonia gas in the nitrogen carrier gas was increased from 300 ppm to 2000 ppm at room temperature. The sensing experiments were carried out by exposing the sensor to ammonia gas for 20 min, followed by nitrogen purge for another 20 min.
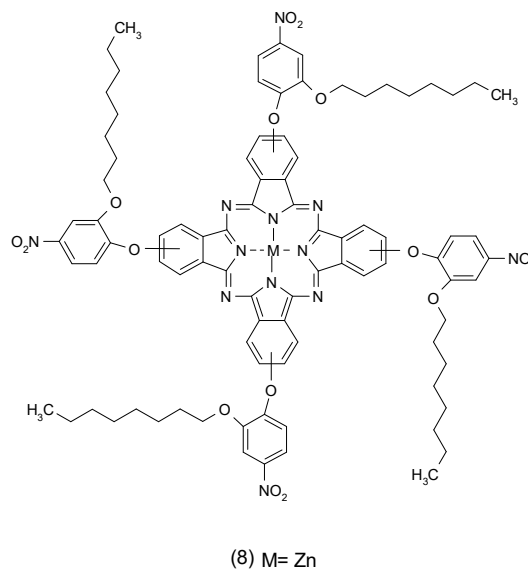

(8) M= Zn

Figure 1. The chemical structure of the studied zinc(II) phthalocyanine (İncelenen Çinko (II) ftalosiyaninin moleküler yapısı

3. RESULTS and DISCUSSION (SONUÇLAR VE TARTIŞMA)

3.1. Effect of RH on Ammonia Sensing (RH'nin Amonyak Algılamaya Etkisi)

It is well known for a long time that the interaction between a gas molecule and the surface of a solid results in detectable changes in physical properties of the solid. It is also well known that the kinetics of these interactions strongly depend on the nature of the solis surface and the the chemistry of the gas. The ammonia sensing performance of the **1** coated sensor was examined by measuring the changes in sensor current as function of exposure time for different concentrations of ammonia gas between 300 - 2000 ppm and in various RH levels. It was found that the exposure to ammonia gas leads to an increase in sensor current (Fig. 2), which indicate that charge transfer take place between Pc and ammonia gas molecules. Fig. 2 also shows that the increase in sensor current is reversible, when the sensor surface purged with dry nitrogen the sensor current was returned its initial value. It should be mentioned here that the observed response characteristic, increase in sensor current in ammonia, is not an expected behavior because of the well known p-type semiconducting character of the metallophthalocyanines [18,19] and good electron donating character of ammonia. Actually, the interactions mechanism between the gas and Pc

molecules is very complex phenomena and contains many physico-chemical processes. The molecular orbital structure of the Pc molecule is the most critical parameter in determining the nature of the interaction mechanism. The presence of the conjugated π-electron system and the metal ion within the Pc framework play roles in the position of HOMO and LUMO levels and the adsorption procesess. In the case of substituted phthalocyanine, as in our case, the substituents acts another adsorption site for analyte molecules.

For enhanced p-type conductivity of the Pc film, an electron transfer from Pc ring to ammonia gas should take place when the ammonia molecules adsorbed onto the sensing layer. Due to the above mentioned reason, it seems that the transfer of an electron from the Pc to ammonia is more difficult. Therefore, it can be concluded that electron withdrawing functional 4-nitro-2-(octyloxy)phenoxy groups are responsible for the observed increase in sensor current. The obssewed ammonia response of the sensor can be attributed to the drastic change in electronic band structure of the Pc molecule with the addition of 4-nitro-2-(octyloxy)phenoxy groups, leading to n-type semiconductor behavior of the Pc investigated. This inversion of the conduction type affects the interaction and the charge transfer mechanisms. This conclusion is in agreement with the earlier studies on molecular orbital structure and gas sensing properties of organic compounds [20, 21].

The effect of the RH level on the sensing performance of the **1** coated sensor was explored to sensitivity, response and recovery times. As usually used in sensor literature, the sensitivity, S, of the sensor was defined as

$$S = \frac{(I_g - I_N)}{I_N} \qquad (1)$$

where I_g is the current in the presence of gas , I_N stands for the sensor current in carrier gas. The effect of the ammonia concentration on the sensor sensitivity at different RH levels is shown in Fig.3. It is clear that the sensitivity increses with increasing ammonia concentration. An increase in sensitivity with increasing RH level is also clear. It was found that the sensitivity at 60% RH level is 3.3 and is almost approximately 8 order of magnitude higher than that of the sensitivity at 0% RH for the same concentration of ammonia (2000 ppm). From the analysis of the slopes of the sensitivity-concentration curves (the equation of the curves after linear fitting is shown inset of the Fig.3), it was found that for RH levels ≥ 20% the slopes of the curves remain in the same range whatever the RH level is.
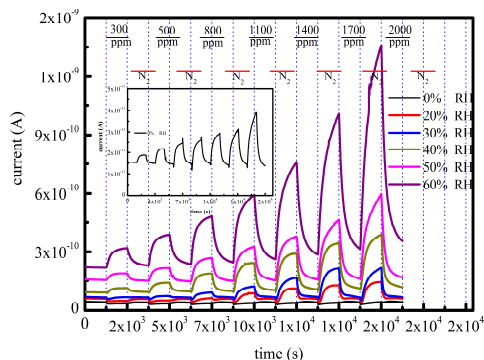

Figure 2. Time dependence of the sensor current exposed to various concentration of ammonia at indicated RH levels. Inset shows the response-recovery characterstic of the sensor at 0% RH (Sensörün ,gösterilen RH koşullarında, farklı konsantrasyonlardaki amonyak buharına tutulması durumunda akımn zamanla değişimi)
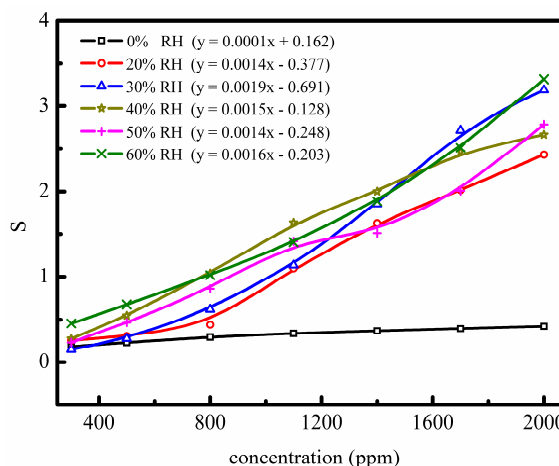

Figure 3. Sensor sensitivity as function of ammonia concentration for various RH levels (Değişik RH koşullarında sensör duyarlığının amonyak konsantrasyonu ile değişimi)

From the close analysis of the Fig. 2, how the RH level effect the baseline current and sensing performance of the sensor will be clear. At a first glance, Fig. 2 shows that the RH leads to an increase in base line current and the sensitivity of the coating material. It reveals that more attention should be paid to interpret the effect of RH on the sensing behavior. It should be outlined that the adsorption of water molecules on an organic surface is based mainly on the formation of hydrogen bonded bridges between the water molecules and the surface functional groups of the adsorbent. The adsorbed water molecules in the film can also effect the surface roughness by occupying voids. The combined influence of these effects lead to formation of more ordered film with high charge carrier mobility and higher base line current in RH atmosphere.

In order to make clear the effect of the RH on the ammonia sensing performance of the Pc film, response and recovery times were evaluated from the measured response and recovery characteristic of the sensor. The variation of the response time, which is defined as it passed the sensor current to reach 90% of its maximum in the presence of ammonia gas, with ammonia concentration at indicated RH levels is shown in Fig. 4 (a). The recovery time is defined as the time require the sensor current return to 10% below its base line value after exposure carrier gas and its concentration dependence is shown in Fig. 4 (b). The lowest value of the response time was observed for 500 ppm ammonia at 50% RH level. In general, it was observed that the response time is an incresing function of ammonia concentration. On the other hand, the reovery time is a decreasing function of ammonia concentration. The sensor showed the quickest recovery for 2000 ppm ammonia at 40% RH. On a close analysis of the response and recovery time plots, it becomes clear that there is no considerable effect

of the RH on the response time. But, the recovery time of the sensor strongly depend on the RH level, it shortened significantly with increasing RH level.
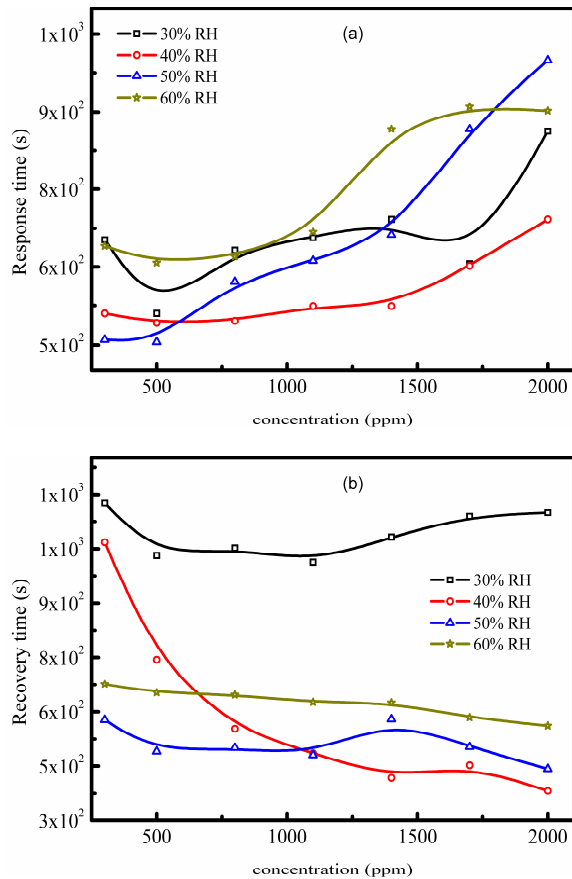

Figure 4. Concentration dependence of the response and recovery times at selected RH levels (Gösterilen RH koşullarında, cevap ve geri dönüşüm sürelerinin konsantrasyona bağlılığı)

3.2. Kinetics of Ammonia Adsorption (Amonyak Adsorpsiyon Kinetiği)

Adsorption kinetics describe the intensiy of the adsorption procesess. The modelling of the adsorption data, either by theoretical or empirical equations, is essential for the practical design and operation of adsorption systems. Elovich empirical equation and first-order rate equation of Lagergren are commonly used to describe in adsorption system with heterogenous solid surface. In this study, in addition to above mentioned kinetics models a simple adsorption-desorption model were employed in order to analyse ammonia adsorption data. Correlation coefficients (R^2) were used as an indicator of the applicability of the models.

3.2.1. Elovich Model (Elovich Modeli)

In Elovich model multilayer adsorption is assumed. It is the earliest one developed to investigate the adsorption mechanism onto heterogeneous solid. The differential form of this model is given by [22]

$$\frac{dC}{dt} = \alpha \exp(-\beta C) \qquad (2)$$

where C is the amount of adsorption at time t, α and β are the adsorption rate and desorption rate, respectively. If the Eq. (2) is intergated with the boundary conditions of ; C = 0 at t = 0 , and C = C at t = t, it becames

$$C = \frac{1}{\beta} \ln [\, \alpha\beta t + 1] \qquad (3)$$

As suggested by Chien and Clayton [23], with the assumption of $\alpha\beta t \gg 1$, then Eq. (3) can be rewritten as,

$$C = \frac{1}{\beta} \ln(t) + \frac{1}{\beta} \ln(\alpha\beta) \qquad (4)$$

It seems that to relate the increase in sensor current to amount of adsorption (C) is reasonable. In this case Eq. (4) becames,

$$I(t) = \frac{1}{\beta} \ln(t) + \frac{1}{\beta} \ln(\alpha\beta) \qquad (5)$$

where I (t) represent time dependence of the sensor current during ammonia exposure. Eq. (5) suggests that the I(t) - ln (t) plots should give a line with single slope, without deviation linearity.

The applicability of Eq. (5) to our data were checked under constant RH level and constant concentration conditions. Fig. 5 (a) shows Elovich plots for various concentrations of ammonia at constant RH level (60% RH). Extracted values of correlation coefficients (shown inset of Fig. 5 (a)) was found in the range of 0.907–0.955, which means bad correlation. In Fig. 5 (b) we presented Elovich plots for a constant ammonia concentration (2000 ppm) at selected RH levels in order to see the effect of the RH level on the Elovich kinetics model. As is clear from Fig. 5 (b), the overall variation of the correlation coefficient reveals that Elovich equation is not an appropriate model to represent our adsorption system.
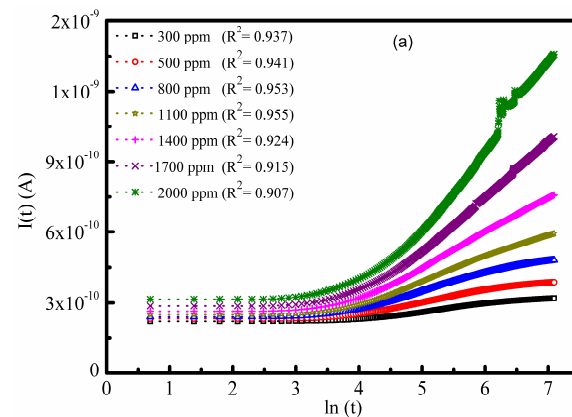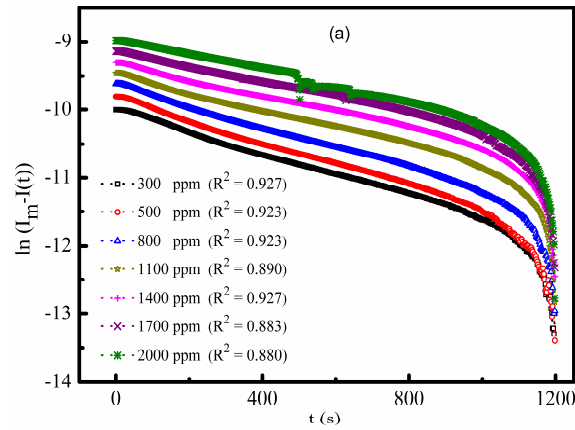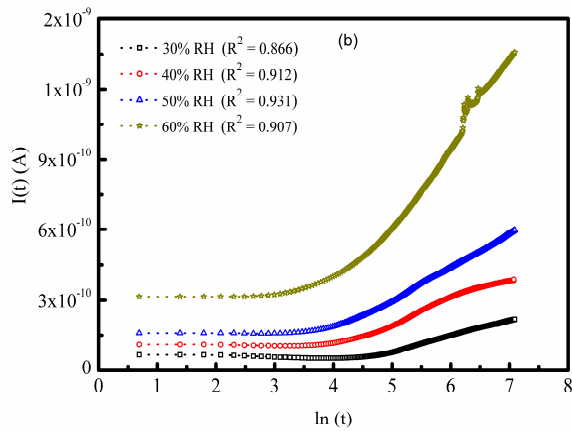
Figure 5. Elovich plots for constant RH (a) and constant ammonia concentration (b) ((a) Sabit RH ve (b) sabit amonyak konsantrasyonu için Elovich çizimleri)

3.2.2. First Order Model (I. Derece Model)

In firs order model, the rate occupation of active adsorption centre is assumed proportional to the number of unoccupied sites. The expression for the first order model in differantial form can be given as [23],

$$\frac{dC_t}{dt} = h_a(C_e - C_t) \qquad (6)$$

where C_e and C_t are the amounts of analyte vapor adsorbed at equilibrium and at any time t, respectively. h_a is the adsorption rate constant. When the Eq. (6) linearized with the appropriate boundary conditions, the following equation is obtained

$$\ln(C_e - C_t) = \ln(C_e) - \frac{h_a}{2.303}t \qquad (7)$$

By assuming that the sensor current is proportional to the amounts of adsorbed toluene, Eq. (7) can be rewritten as,

$$\ln(I_m - I(t)) = \ln(I_m) - \frac{h_a}{2.303}t \qquad (8)$$

where I_m stands the maximum steady-state sensor response. According to the Eq. (8), if the ammonia adsorption processes follow pseudo first order model, the plots of $\ln(I_m - I(t))$ versus t should yield straight lines. Figure 6 (a) and 6 (b) shows a plot of the first-order model for various concentrations of ammonia between 300-2000 ppm at 60% RH level and for constant concentration (2000 ppm) of ammonia at different RH levels, respectively.
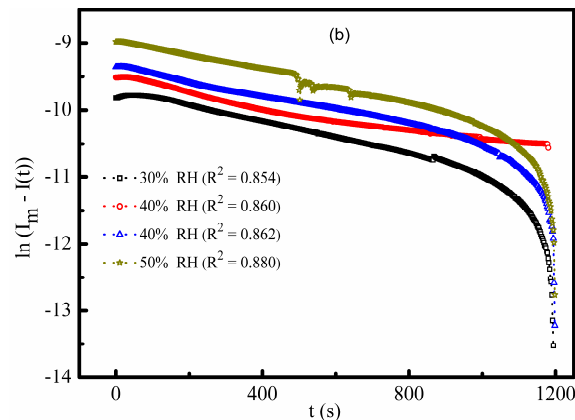

Figure 6. Pseudo-first order sorption kinetics of ammonia at 60% RH (a) for 2000 ppm ammonia at indicated RH levels (b) ((a) %60 RH koşullarında (b) Gösterilen RH koşullarında 2000ppm pseudo I. Derece amonyak adsorpsiyon kinetiği)

3.2.3. Simple Adsorption Model (Basit Adsorpsiyon Modeli)

A simple adsorption model was proposed by Liu et al.[24]in order to determine the NO_2 adsorption kinetics onto PbPc film. In this model it was asummed that there is only one type of adsorption site on the film surface. This model predicts that during adsorption stage the surface concentration of analyte molecules changes according to following equation

$$\frac{d\theta(t)}{dt} = k_a\theta_0 n - [k_a\theta_0 + k_d]\theta(t) \qquad (9)$$

where k_a and k_d are the rate constant for adsorption and desorption, respectively, θ_0 represents the gas phase analyte concentration, n the total number of adsorption sites. If we assume that the change in sensor current is proportional to the adsorbed analyte molecules, θ, then the Eq. (9) becomes,

$$\frac{di(t)}{dt} = k_a\theta_0 n - [k_a\theta_0 + k_d]i(t) \qquad (10)$$

The applicability of Eq. (10) can now be checked by the plot of $\frac{di}{dt}$ vs. i (t). A set of $\frac{di}{dt}$ - i (t) plots for room temperature

adsorption of ammonia at 60% RH level and 2000 ppm ammonia adsorption at various RH levels are shown in Figs. 7 (a) and (b), respectively. As can be seen from the Figs. 7 that $\dfrac{di}{dt}$ - i (t) plots is linear in nature. It was found from the Fig. 7 that the calculated values of the correlation coefficient varies between 0.977 and 0.991. This confirms that simple adsorption–desorption model can be used to interpret the ammonia adsorption on the film of **1**.
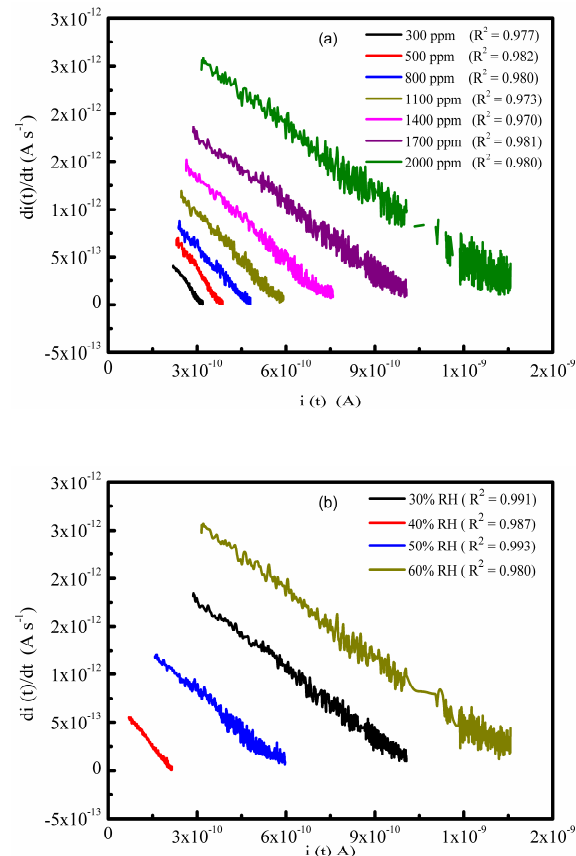

Figure 7. Simple adsorption plots for various concentration of ammonia at constant RH level 60% (a) and for different RH levels at constant concentrations (2000 ppm) (b) ((a) Sabit %60 RH koşullarında farklı konsantrasyonlardaki amonyak adsorpsiyonunun basit modele göre çizimi (b) Sabit konsantrasyondaki amonyak adsorpsiyonunu farklı RH koşullarındaki çizimi)

4. CONCLUSION (SONUÇLAR)

This studie has focused on relatively less discussed aspects of the adsorption kinetics on organic film surface. Ammonia adsorption kinetics on substituted Pc film were studied for various concentration of ammonia. The effect of yhe RH on the sensor performance and adsorption kinetics were also investigated. It was shown that the RH improves the ammonia sensitivity of the sensor. Three different kinetics models including Elovich model, first order rate equation and a simple adsorptio-desorption model were examined to fit experimental data. Results showed that the RH has a neglible effect on the sensor sensitivity for ≥ 20% RH level. Analysis of the adsorption data indicated that the ammonia adsorption kinetics follows a simple adsorption-desorption procesess irrespective of RH level.

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