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ADSORPTION KINETICS OF Cd^{2+} IONS ONTO MgPz THIN FILM

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ABSTRACT

A *(2,3,7,8,12,13,17,18-Octakis(4-tert-butylbenzylthio)-porphyrazinato)Mg(II)* functionalized quartz crystal microbalance sensor has been developed for the detection of trace Cd^{2+}ions in water samples. The quartz crystal microbalance results indicated that the MgPz coated sensor exhibited high sensitivity, stability and selectivity for the detection of Cd^{2+} in aqueous solution. The lowest detection limit can reach 10 μg/ml Cd^{2+} in aqueous solution, which resulted in the frequency shift of ~ 150 Hz. The observed adsorption data were analyzed using four adsorption kinetic models; the Elovich equation, Ritchie's equation, pseudo first- and second-order equations. Results show that the linear regression analysis with respect to pseudo-second-order rate equation generates a straight line that best fit to the data of adsorption of Cd^{2+} on Pz film.

Keywords: Adsorption kinetics, thin film, QCM

1. INTRODUCTION

Recently, pollution of water sources with heavy metal ions has become one of the most important problems all over the world [1]. Cadmium, which is widely used in paints, batteries, plastics, photoconductors and photovoltaic cells, is considered as the main pollutant because of its toxic and non biodegradable nature [2]. Its accumulation causes serious health problems such as hypertension, lung cancer and pulmonary [3]. Therefore, there is a demand for the development of sensitive and simple analytical tool for the detection of trace amount of Cd^{2+} ions in water samples [4,5]. Various traditional methods such as, inductively coupled plasma mass spectroscopy [6], atomic absorption spectrometry [7] and anodic stripping voltammetry [8] have extensively been applied for this purpose because of their well-known advantages [9]. However, all of these methods require sample collection, transportation to laboratories and long-term analysis process. In this respect, there is no need to conclude the importance of the development of novel sensors for on-line detection of Cd^{2+} ions in liquid media.

Gravimetric based methods such as quartz crystal resonator or quartz crystal microbalance (QCM) for the detection of various molecules in gas phase have been investigated in the last decade [10]. The QCM based sensor provides real-time analysis, low cost in instrumentation, and without requirement of expensive reagents. Although important advances have been made toward the detection of various gas and bio molecules with QCM based sensors [11-15], its reported use in liquid media is still rather limited despite of some promising results already obtained. The appropriate surface modification for sensitive and selective detection of analytes is essential for gravimetric based sensors. In this manner, tetraazaporphyrins suffer many advantages over phthalocyanine and porphyrins such as simple synthesis and isolation procedure, modification of the physical properties of the macrocycles with meso-substitution of nitrogen in tetraazaporphyrin. Recently, many applications, especially in the thin film form, such as solar cells, treatment of cancerous tissues and gas sensing for molecular materials based on tetraazaporphyrin units have been identified [16,17].

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Compared to the more intensely studied on the synthesis of porphyrazine and their metal complexes [18,19], related work on especially metal binding abilities of porphyrazine has been relatively few [17] and none on adsorption kinetics of heavy metal ions onto porphyrazine thin film. Therefore, in this work we have focused on the heavy metal ion sensing performance of the novel magnesium (II) porphyrazine substituted with eight (1-phenyl-1-propenylthio) groups on the peripheral positions (MgPz) thin film. We have also analyzed kinetics of Cd^{2+} ions adsorption onto this film using various kinetic models such as pseudo first-order and second-order equations, Ritchie's equation and the Elovich equation.

2. EXPERIMENTAL SECTION

Schematic representation of the sensing molecule is shown in Figure 1.

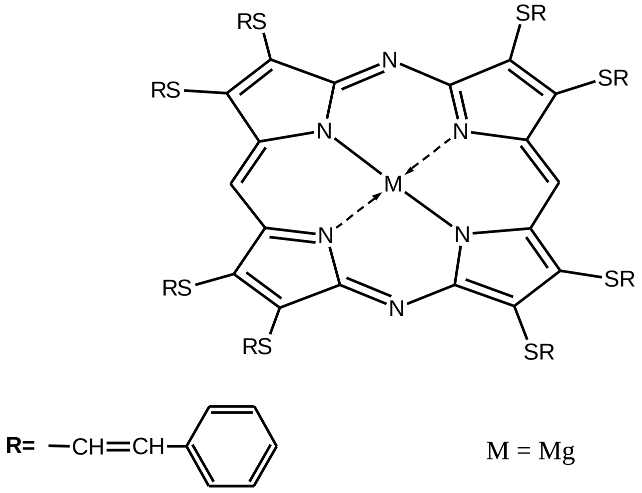

Figure 1. Schematic representation of *(2,3,7,8,12,13,17,18-Octakis(4-tert-butylbenzylthio)-porphyrazinato)Mg(II)*

The transducer used was AT-cut quartz crystals vibrating in the thickness shear mode with a fundamental resonant frequency of 10 MHz with Au electrodes. After surface cleaning, the Mg(II)Pz based sensitive layer was deposited onto the transducer using spray pyrolysis technique. For spraying processes, a solution of 2.5 mg Mg(II)Pz in a 6 ml chloroform was prepared and the solution was sprayed onto the one side of the QCM at a flow rate of 4 ml/min. During the sensitive layer deposition, the frequency shift of the quartz crystal was monitored on-line by using a programmable frequency counter (Keithley Model 776). The thickness of the sensing layer was determined from the measured frequency shift (Δf) by using Sauerbrey equation [20]

$$\Delta f = -\frac{\mathrm{C}\,\mathrm{f}_0^2}{A}\Delta m \tag{1}$$

where Δf is the frequency shift due to the added mass (Δm), C is a constant, f_0 is the fundamental frequency of the quartz crystal, and A is the electrode area. After the surface functionalization, the quartz crystal was fixed in a flow through cell attached to a peristaltic pump (Heidolph, 5201 Pump Drive) using teflon tubes. A flow rate of 0.3 μl/min was chosen as optimal. Typical measuring cycle consisted of repeated flow of target measurands through the flow cell and subsequent washing with de-ionized water (DI–water) to return the baseline. Millipore DirectQ–3 UV ultrapure water (18.2 MΩ cm) was used to prepare all solutions. Analytical grades of metal salts were used to prepare stock solutions. The stock solutions were always prepared freshly just before the measurements. All experiments were conducted at a cell temperature of 25 ± 0.5°C.

3. RESULTS AND DISCUSSION

3.1. Cd^{2+} Ion Sensing Behavior

Already established, the use of quartz crystals as transducer in sensors has its origins in the work of Sauerbrey [20]. According to Sauerbrey, the shift in the resonant frequency of an oscillating thickness shear mode quartz crystal is correlated with addition or removal of mass from the surface of the quartz crystal. This relation between the frequency shifts and addition or removal of mass is given by Equation (1).

The Cd^{2+} ion sensing performance of Mg(II)Pz functionalized QCM sensor was tested for various concentrations of Cd^{2+} ions in a background of DI - water. Typical responses-recovery behavior of the Mg(II)Pz modified QCM sensor to indicated concentrations of Cd^{2+} solution at 0.3 ml/min flow rate is shown in Figure 2. It is clear from Figure 2 that when the sensor surface is exposed to Cd^{2+} aqueous solution the resonance frequency decreases sharply in the initial stage of sorption, followed by a drift to the steady state value. The decrease in resonance frequency indicates the adsorption or complexation of Cd^{2+} ions onto the sensing layer. It was found that the 0.056 mg/ml Cd^{2+} ion solution can lead to the frequency shift of $\Delta f = 1.13 \times 10^5$ Hz.

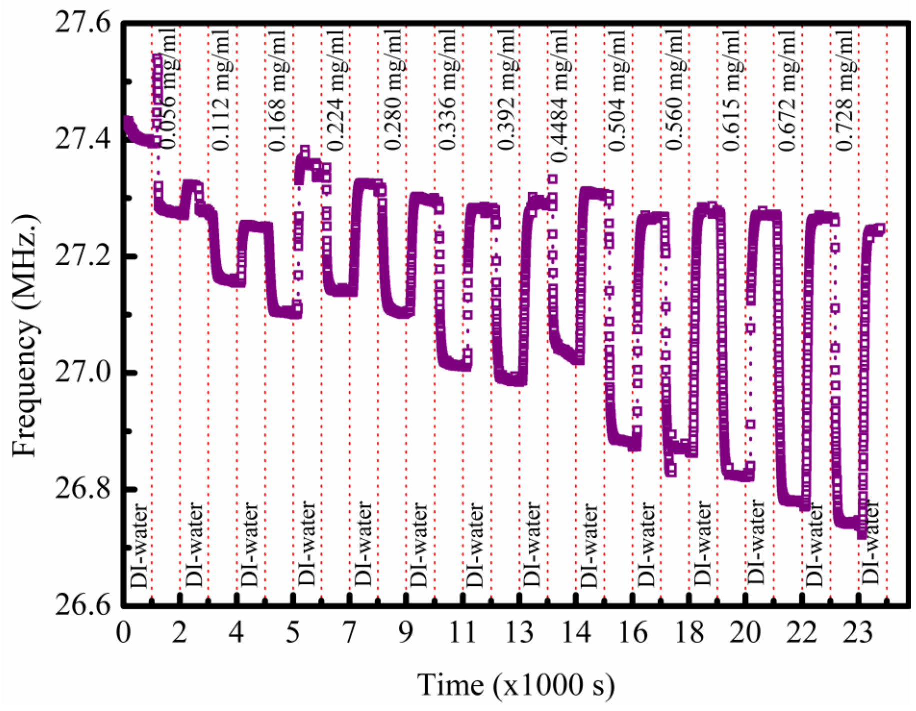

Figure 2. The shifts in resonance frequency of the sensor during exposure to aqueous solutions of Cd^{2+} ions with various concentrations

It is also clear from Figure 2 that when the sensor surface is washed with DI–water leads to an increase in resonance frequency and the resonance frequency reaches its initial value. This proves that the sorption or complexation processes is reversible. The effect of the Cd^{2+} ion concentration on the frequency response of the Mg(II)Pz coated QCM sensor was also investigated. Increasing the Cd^{2+} concentration resulted in more adsorption of Cd^{2+}, leading to the larger frequency shifts. A nearly linear increase of frequency shift was observed with increasing the Cd^{2+} concentration (Figure 3). It is well established that the heavy metal ion sensing behavior of a QCM based sensor depends strongly on several factors including the surface reactions, such as chemical components, surface modification and microstructures of sensing layer, coordination and size of the analyte. In this manner, a possible explanation for the observed frequency shift in resonance frequency may be given as follows; as known the Pz compound contains many sulfur (S) atoms in the side groups as electron donors, which can easily form complexes with heavy metal ions. The complexation of metal ions with sulfur atoms in the compound is the main driving force for the adsorption. Additionally, it is possible that the central metal atom in Pz compound participates in metal ion detection. We believe that better coordination and size of the Cd^{+2} ions also play role in sensing processes.

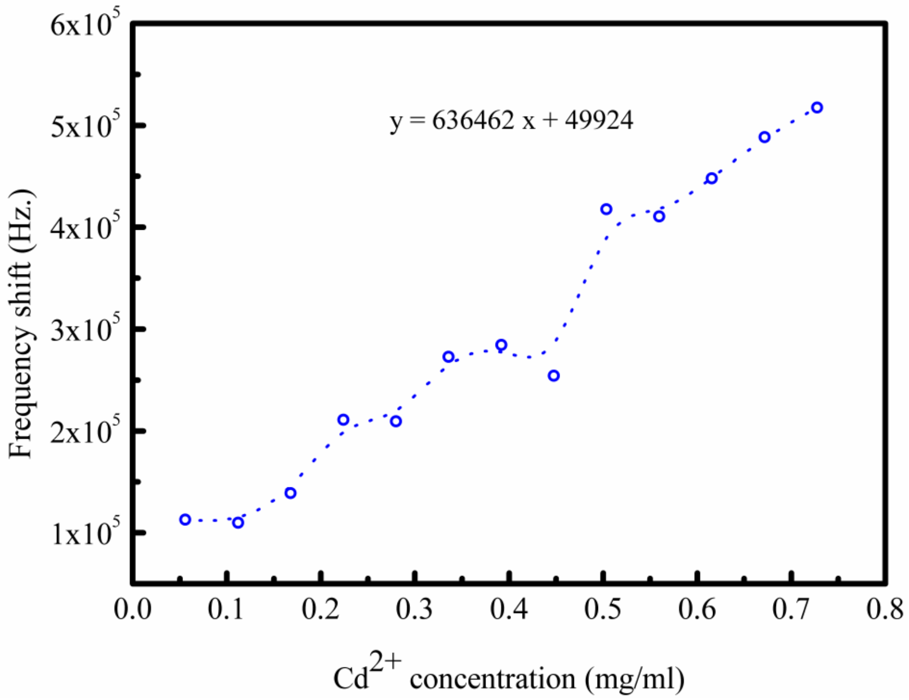

Figure 3. Concentration dependence of the frequency shifts for the data of Figure 2

To evaluate detection of the Cd^{+2} ions under competitive conditions, the sensor was saturated with Cd^{2+} ion followed serial replacement of the pure Cd^{2+} solution with mixed Cd^{2+}/Cu^{2+}, Cd^{2+}/Sn^{2+}, and Cd^{2+}/Co^{2+} solutions of progressively increasing interferant ion concentration. No noticeable additional frequency shift was observed for the low concentrations of interferant ions. The frequency shifts after 15 min. exposure to saturated Cd^{2+} solution was 5.18×10^5 Hz. At higher concentrations of interferant ions, although there was no systematic variation with interferant concentrations, an additional frequency shift of ~ 475 Hz. was observed. This additional shift in resonance frequency is less than those measured for the pure Cd^{2+} ion solution. It reveals that the selectivity of the sensor is good that detection of cadmium ion is practically unaffected by the interferants.

The Cd^{2+} ion sensing performance of the sensor investigated was also compared with its response (τ_{90}) and recovery time (τ_{10}). Response time of a sensor is defined as the time it takes for the sensor response to reach to 90% of the final response. Likewise, recovery time is defined as the time required in returning to 10% below its equilibrium value during washing cycle. The derived τ_{90} and τ_{10} values for various concentration of Cd^{2+} ion were given in Figure 4. It can be seen from Figure 4, both the response and recovery times of the sensor are a decreasing function for low concentration of the Cd^{2+} ion. On the other hand, τ_{90} and τ_{10} values remain nearly constant for high concentration of the Cd^{2+} ions.

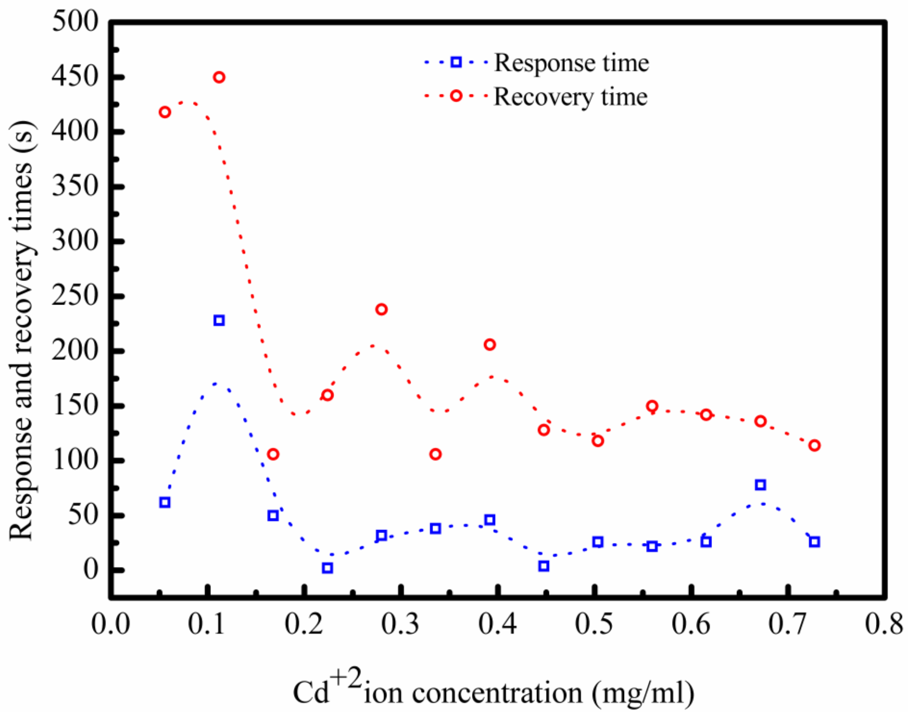

Figure 4. Variation of the response and recovery times with Cd^{2+} concentration

3.2. Adsorption Kinetics

Adsorption kinetics is an important characteristic in evaluating the efficiency of adsorption processes. In order to analyze the experimentally obtained adsorption data a suitable kinetic model is needed. Various kinetic models (such as Elovich kinetic model, Ritchie's equation, first-order rate equation of Lagergren and the pseudo-second-order rate equation) have been extensively applied to many adsorption systems. In this study, the adsorption of Cd^{2+} ions onto Mg(II)Pz thin film was modelled using these rate equations. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2).

3.2.1. Elovich model

The Elovich model is an empirical model that has found wide application in kinetic studies of sorption process, particularly in the field of chemisorption [21]. The linearized form of Elovich equation is given by [22,23].

$$f_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t) \tag{2}$$

where f_t is the amount of adsorbed Cd^{2+} during the time t, a is the initial sorption rate and b is the desorption constant. By assuming that the shift in the resonance frequency is proportional to the change in surface coverage, the applicability of the Elovich model to our adsorption data can now be checked by the plot of f_t vs. ln (t), according to Equation (2) this plot should be a straight line.

For room temperature the adsorption of Cd^{2+} ions with various concentrations on Mg(II)Pz surface are shown in Figure 5. As can be seen from the Figure 5 that the correlation coefficient is in the range of 0.902 - 0.955. It is obviously noticed that the linear regression analysis does not fit Elovich's equation, this confirms that Elovich equation is not appropriate to use as a model to predict the sorption kinetics of Cd^{2+} ions onto the compound of Mg(II)Pz for the entire adsorption period.

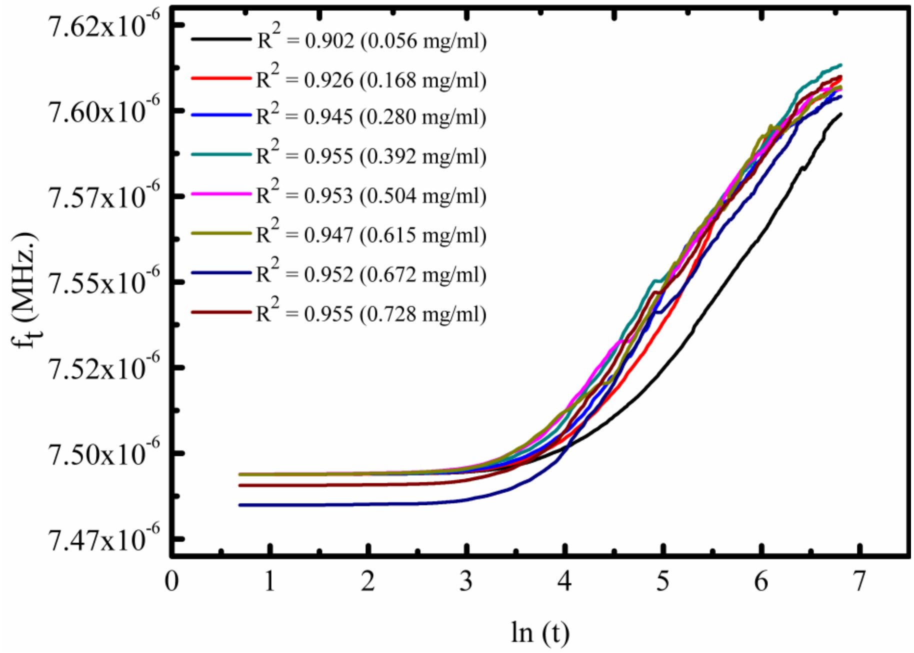

Figure 5. Plot f_t vs. ln (t) and its corresponding R^2 according to Elovich's equation

3.2.2. Ritchie equation

In 1977 [24], Ritchie reported a model for the adsorption of gaseous systems by assuming that the rate of adsorption depends solely on the fraction of unoccupied sites at time t. If we assume that metal ion adsorption is a second-order reaction, the linear form of the Ritchie' equation can be expressed as,

$$\frac{1}{f_t} = \frac{1}{\alpha f_e t} + \frac{1}{f_e} \tag{3}$$

where f_e and f_t are the amount of metal ion adsorbed at time t and after an infinite time, respectively. By assuming that the frequency shift is proportional to the amount of metal ions adsorbed, the plot of $1/f_t$ as a function of 1/t should give a linear relationship. Figure 6 shows ($1/f_t$) vs.1/t plot for various concentrations of Cd^{2+} ions at room temperature.

It is clear from the Figure 6 that for Ritchie model, the correlation coefficient is always less than 0.310 for all Cd^{2+} concentrations investigated, which is indicative of a bad correlation. This confirms that Ritchie equation is not appropriate to use as a model to predict the adsorption kinetics of Cd^{2+} onto the compound.

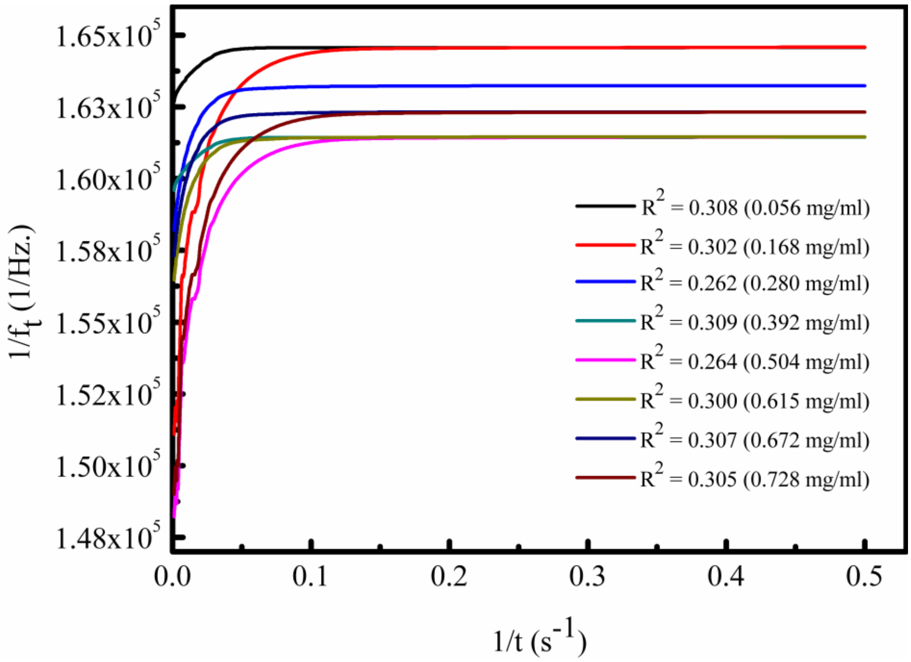

Figure 6. Plot of Ritchie' equation and its corresponding R^2 for sorption of Cd^{2+}

3.2.3. The Pseudo-first-order process

When adsorption is preceded by diffusion through a boundary, the kinetics in most cases follows the pseudo-first-order rate equation of Lagergren [25]. The pseudo-first-order model considers the rate of occupation of adsorption sites is directly proportional to the number of unoccupied sites and is generally expressed as follows:

$$\frac{df_t}{dt} = k_{ads}\left(f_e - f_t\right) \tag{4}$$

After integration and applying boundary conditions $f_t = 0$ at $t = 0$ and $f_t = f_t$ at $t = t$, Equation (2) becomes:

$$\log \frac{f_e}{f_e - f_t} = \frac{k_{ads}}{2.303} t \tag{5}$$

Equation (4) can be rearrangement to obtain a linear form:

$$\log\,(f_e - f_t) = \log\, f_e - \frac{k_{ads}}{2.303} t \tag{6}$$

where f_e and f_t are the amounts of metal ion adsorbed at equilibrium and at any time t, respectively, k_{ads} is the first-order adsorption rate constant. According to Equation (6) the plot of log (f_e - f_t) vs. t should be linear. Figure 7 shows a plot of linearized form of pseudo-first-order model for eight different concentrations of Cd^{2+}.

It is clear from the Figure 7 that the experimental data deviated considerably from the theoretical model. To quantify the applicability of the pseudo-first-order model the correlation coefficient was calculated from these plots. As seen in Figure 7, R^2 is in the range of 0.984 - 0.994. This suggests that pseudo-first-order equation is not suitable to describe Cd^{2+} sorption processes.

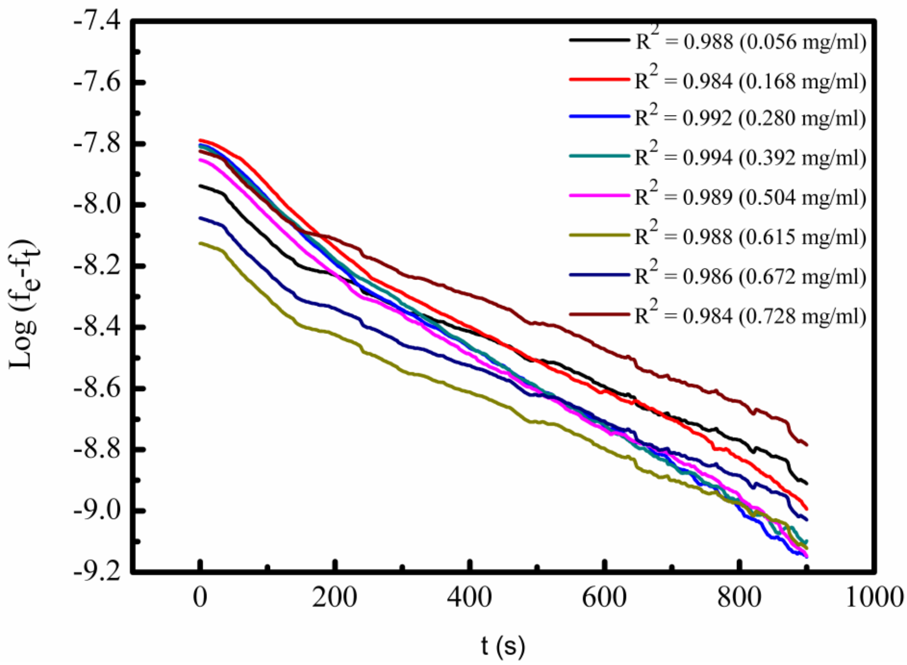

Figure 7. Pseudo-first-order sorption kinetics of Cd^{2+} ions onto the compound

3.2.4. The Pseudo-second-order equation

The adsorption kinetics may also be described by a pseudo-second-order equation. The rate of adsorption for pseudo-second-order model [26,27] can be given as

$$\frac{df_t}{dt} = k_2 (f_e - f_t)^2 \tag{7}$$

Integrating Equation (7) with the boundary conditions ($f_t = 0$ at $t = 0$; $f_t = f_t$ at $t = t$) yields the linearized form of the above equation

$$\frac{t}{f_t} = \frac{1}{k_2 f_e^2} + \frac{t}{f_e} \tag{8}$$

where k_2 is the rate constant of pseudo-second-order adsorption. According to Equation (8) the plot of t/f_t versus t should result in a straight line. The applicability of the pseudo-second-order model can be tested by linear fitting of (t/f_t) versus t plot. Figure 8 displays the variation of (t/f_t) with t for various concentration of Cd^{2+} investigated.

A detailed investigation of the Figure 8 shows that good correlation coefficients (R^2) were obtained by fitting the experimental data to pseudo-second-order kinetics than that for the pseudo-first-order kinetic model, Elovich equation and Ritchie’ equation.

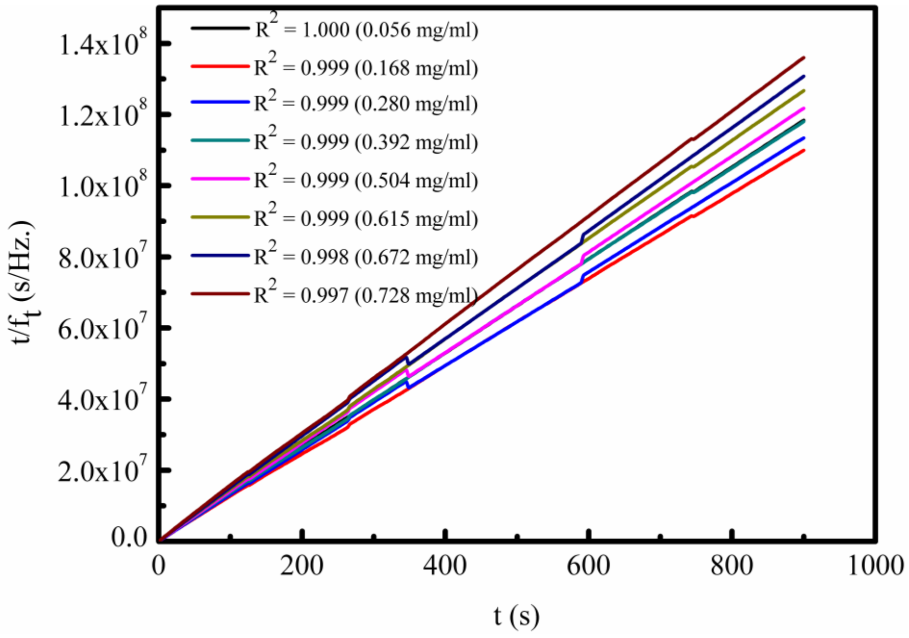

Figure 8. Second order plots for Cd^{2+}adsorption onto the MgPz

4. CONCLUSIONS

A novel *(2,3,7,8,12,13,17,18-Octakis(4-tert-butylbenzylthio)-porphyrazinato)Mg(II)* have been successfully synthesized. By using this compound as sensing materials, a flow type quartz crystal microbalance sensor was developed for the detection of small concentrations of Cd^{2+} ions. We have demonstrated in this study that the spray coated film of Mg(II)Pz is a promising metal ion sensing material in aqueous samples. A comparative study of the applicability of kinetic models of Elovich equation, Ritchie's equation, pseudo-first-order and pseudo-second-order equations to describe the experimental adsorption data of Cd^{2+} on Mg(II)Pz compound has been carried out. Comparing the regression coefficients R^2 shows that the second-order model best describes the experimental data on the adsorption of Cd^{2+} with studied samples at low and high concentrations of Cd^{2+} ions.

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