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Detection of Copper (II) Ion on Chitosan Film Using Microstrip Ring Resonator

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ABSTRACT

The detection of copper (II) ion (Cu^{2+}), using chitosan film and ring resonator is presented in this paper. Chitosan has the ability to adsorb metal ion due to abundant reactive amino and hydroxyl groups. The adsorption amount is confirmed using Atomic Absorption Spectroscopy and the mechanism of ion conduction in the film, due to adsorption of Cu^{2+} ion was examined using impedance spectroscopy. The film was then introduced to ring resonator to detect the presence of Cu^{2+} ion at a frequency of 5 GHz. Results show that the film can adsorb Cu^{2+} ion at low concentration of 1 mg/l and the ring resonator together with chitosan film is able to detect the presence and changes in Cu^{2+} ion concentration from the shift in the resonance frequency. This shift in the resonance frequency was then used to calculate the Q factor and effective permittivity of the chitosan film.

Keywords: Chitosan Film, Copper (II) Ion, Ring Resonator.

1. INTRODUCTION

Unethical modern activities such as improper disposal of electrical goods, unsustainable mining activities as well as poor industrial waste management have led to copper contamination into the environment [1-2]. Copper is moderately soluble in water and binds easily to sediments and organic, making it a threat to aquatic ecosystems. Low concentration copper, which is also found naturally in aquatic systems, is an essential nutrient to the aquatic life. However, the higher copper concentration can affect the reproduction and metabolism, which lead to mortality. Cupric ion (Cu^{2+}) is the most toxic form of copper and it is also non-biodegradable [3]. Due to the severe threats that copper pollution poses to the environment, it is important to be able to detect and remove the contaminant.

Adsorption is the widely used process for removal of the metal ion contaminant as it offers low cost with high efficiency [4]. Chitosan is one of the adsorbent materials used for removal as it has the ability to form complexes with metals. It exhibits a higher adsorption capacity for metal ion due to the presence of very reactive amino ($-NH_2$) and hydroxyl (-OH) group in its backbone, as shown in Figure 1 [5]. Chitosan chelates with metal ion by releasing hydrogen ion and metal ion will bind to the amine group between the free electron pairs [6].

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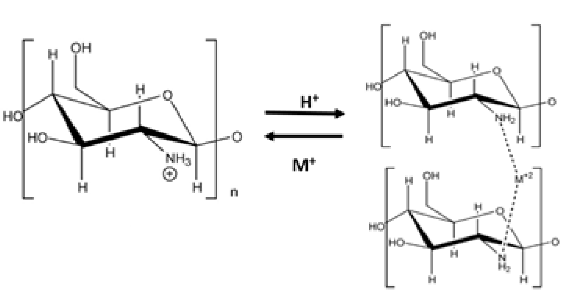

Figure 1. Mechanism of chelation process of chitosan.

Chitosan, with high nitrogen content (6.89 %) and subsequent amine linking, is notable for its ability to bind with metal ion [7]. It does not take up alkaline and alkaline earth metal ion but collects transition and post-transition metal only. Several parameters affect the chelation of metal ion onto chitosan. These include parameters such as pH, concentration, contact time and affinity level towards metal ion. The adsorption process of chitosan is partially reversible and attributed to the protonation of NH2 groups [8]. Chitosan chelates with metal ion by releasing hydrogen ion and the metal ion will bind to the amine group as described by the mechanism presented in Figure 1 [9]. At low pH, the high numbers of hydrogen (H+) ion attributed to the protonation of the amino sites. Hence there is competition for the binding sites of the basic NH2 groups between the H+ ion and the metal ion [10].

Ring resonator is made up of an integral multiple of the guided wavelength to force resonance and a resonance peak is produced at the fundamental frequency and at every multiple of the frequency [11]. From the series of resonance peaks, the dielectric permittivity and loss of the sample under test can be obtained. Ring circuit has been extensively used in the microwave region for a variety of purposed. It has been used as a narrowband antenna, made into miniature filter and widely used for material characterization [12-14]. For material characterization, the ring has been used in the characterization of printed wiring board, meat quality evaluation and soil moisture detection [15-17].

This paper will focus on the use of the ring resonator as a sensor with chitosan film to detect Cu^{2+} ion. Even though chitosan film has been used in conjunction with other detection techniques, there is no report on the use of chitosan film with ring resonator as part of a sensor element at microwave frequency region.

2. MATERIALS AND METHODS

The process of making the film starts with preparing the chitosan solution. Chitosan solution was prepared by dissolving 1.0 g of medium molecular chitosan flakes into 100 ml of 1% (v/v) acetic acid. The chitosan solution was stirred for 24 hours to obtain a homogeneous solution. The prepared solution was then poured into prepared mould [18] and left on a flat surface to dry at room temperature to produce smooth and even membrane. The dried film was removed from the mould, soaked in the deionized water for 30 minutes to remove any impurities before been cut to the required size.

For this work, chitosan film was cut into individual 1.6 cm×2 cm piece. Each film was dipped into 20 ml solution of Cu^{2+} at different concentration for 20 minutes. The film was then removed and keeps in individual petri dish while the discard Cu^{2+} solution was examined using Atomic Absorption Spectroscopy (AAS) to check for the percentage of adsorption.

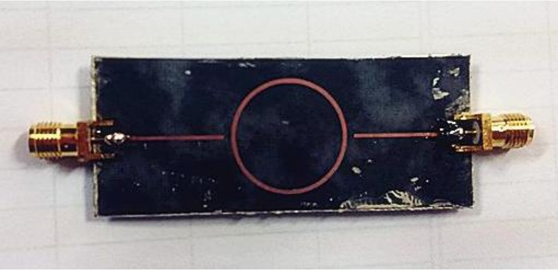

Figure 2. Fabricated ring resonator on Duroid substrate.

The ring resonator, as shown in Figure 2, was fabricated on RT/Duroid 5880 with a substrate thickness of 254 um and a relative permittivity of 2.2. The ring and the feed lines were designed to have characteristic impedances of 50 Ω, based on the thickness and permittivity of the dielectric materials. The ring resonator was measured with an HP8510C VNA and the system was calibrated prior to measurement to eliminate any system errors. Caution was taken to ensure no air gap exists between the film and the ring. The measurement was done in the frequency range between 4 GHz to 6 GHz. The unloaded resonance frequency of the ring was measured at 5.22 GHz with insertion loss of -23.02 dB. $Q_{D,1}$ for the ring was calculated to be 2500, based on the value of tanδ (0.0004) obtained from the Rt/Duroid 5880 data sheet. The ring resonator was used to characterize the material in a multilayer configuration, where in this configuration, the chitosan film is inserted onto the ring resonator as part of the ring sturucture.

3. RESULTS AND DISCUSSION

Table 1 Adsorption for chitosan film dipped in Cu (II) solution

Film	Initial Cu^{2+} solution (mg/l)	Amount of Cu^{2+} adsorbed (mg/l)	Percentage of adsorption (%)
Control	0	0	0
A	1	0.3339	33.39
B	5	2.1487	42.957
C	10	4.541	45.41
D	50	27.705	55.41

The amount of adsorbed absorption of each film is shown in Table 1. Results indicate that the percentage of absorption increases as the initial concentration of Cu^{2+} increased. As the concentration of Cu^{2+} solution increase, more ion is available for chelation process [19]. However, the rate of absorption will start to slow down when the number of available amine groups decreased before the film reaches its saturation [20]. Saturation will occur when the reaction reached equilibrium phase as many of the available amimne group have been occupied by Cu^{2+} ion.

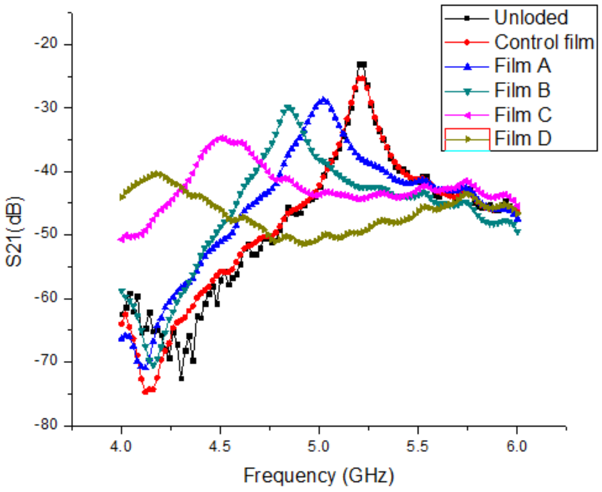

Figure 3. Measured insertion loss versus frequency for various adsorption rate of the Cu^{2+} ion on chitosan film.

Figure 3 shows the measured insertion loss response for the ring resonator when films A to D were introduced as part of the resonance ring structure. The resonance frequency for unloaded and loaded ring with a control sample (0 mg/l) shows that both have the same resonance frequency, but control sample produces a lower insertion loss. Film A with the lowest Cu^{2+} ion absorption shows 220 MHZ while film D shows 1.04 GHz shift in the resonance frequency. It is also apparent that the resonance frequency shifted towards the lower frequency with higher adsorbed Cu^{2+} film introduced. Table 3 below summarizes the value of insertion loss and resonance frequency for all films.

Table 3 Resonance frequency and insertion loss value of different film

Film	**Resonance frequency (*GHz*)**	***Insertion loss (dB)***
Control	5.22	-25.384
A	5.0	-28.799
B	4.84	-29.921
C	4.5	-34.778
D	4.18	-40.406

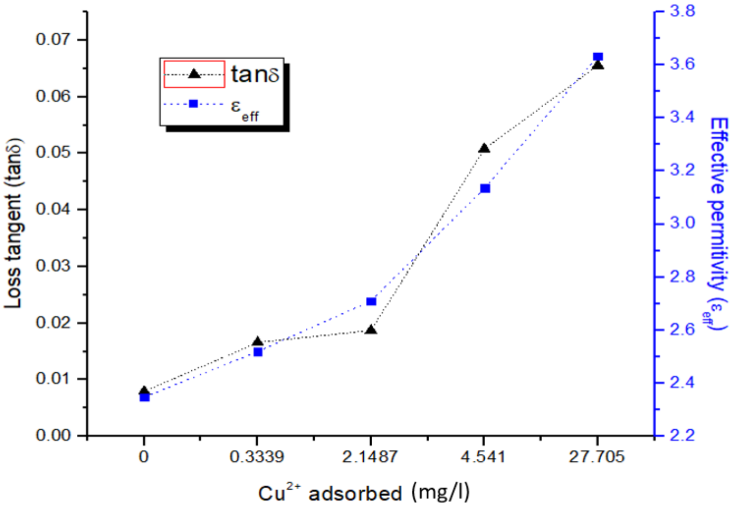

Figure 4. The calculated value of effective permittivity (ε_{eff}) and loss tangent (tanδ).

The shift in the resonance frequency, before and after the MUT is inserted, is directly related to the change in effective permittivity of the film [21]. Figure 4 shows the computed ε_{eff} and tanδ values for each film adsorption. With more Cu^{2+} ion being adsorbed, the film, which initially a dielectric start to change into dielectric-conductor composite having higher conduction and lower resistance value, cause the permittivity to increased [22]. The change in behaviour also increases the tanδ value.

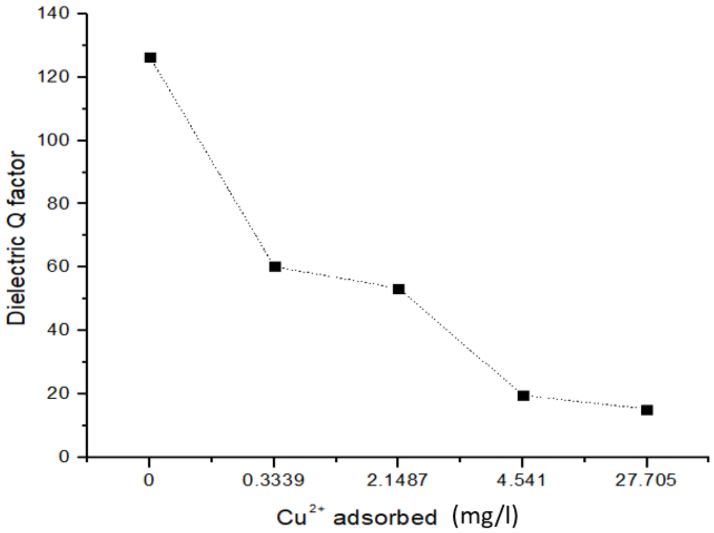

Figure 5. Q_D value for different films, calculated from measured insertion loss response.

The increment in tanδ related directly to the Q factor of the film. The change in resonance frequency and the 3dB bandwidth in figure 3 was used to compute the dielectric Q factor (Q_D) of each film sample. Figure 5 shows the calculated Q_D value for different Cu^{2+} adsorbed films. The Q_D of the corresponding films shows a decreasing trend as more amount of ion adsorbed on the film increased. This is consistent with the lost in the ability of the film to store charges as it becomes more conductive and corresponds to higher dispersion in the film [23]. This is in agreement that the film changing its characteristic towards metallic behaviour and become more conductive.

4. CONCLUSION

The present of Cu^{2+} ion adsorbed by chitosan film was able to be detected using the chitosan film. Ring resonator incorporating chitosan film was shown to be able to detect the presence of Cu^{2+} ion adsorbed on the film from concentration lower than 1 mg/l. The increase in film conductivity as more ion adsorbed allow the detection to be made through change in the resonance frequency of the ring. The obtained Q factor of the dielectric, effective permittivity and loss tangent from the resonance frequency further confirmed the change in ion absorption of each film and be used for detection purposed. The result will be a good basis for the development of complete sensor system for detection of Cu^{2+} ion in aqueous solution using ring resonator at microwave frequency.

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