

Interference Study of Chlorine and Fluorine in Aqueous Medium Using Functionalized Carbon Nanotubes and Data Analysis through Principal Component Analysis

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Abstract

The presence of ions in water plays an important role which dramatically affects the properties of water. The presence of ions and their concentrations have been considered an important factor for water quality assessment. Due to their significant effects on the hardness, taste and suitability of water for a wide range of applications. The ions are present in the form of cations and anions, and their presence are essential up to their permissible limit. In this study, the 5 MHz AT-cut quartz crystal has been functionalized with Octadecyl Amine Carbon Nanotubes (ODA-SWCNTs) using spin coating technique to monitor the free chlorine and fluorine in aqueous medium at ppb level. The resonance frequency of quartz crystal is ultrasensitive to the mass changes on its surface. The solid powder of chloride and fluoride are decomposed into the water and changed into the chlorine and fluorine. Due to adsorption of free chlorine and fluorine onto the functionalized quartz surface, its resonance frequency decreases. The adsorbed quantity of anionic species was estimated through the change in a frequency of crystal. The resonance frequency of functionalized crystal was continuous monitor while the interaction of anionic species with sensing layer. The lowest detection limit of fluorine, chlorine was found to be 2 and 0.5 ppb, respectively. The natural polymer and cheap beeswax used to provide the stability to ODA-SWCNTs in aqueous medium which increases the sensitivity and reproducibility of ODA-SWCNTs sensing layer. Further the interference sensing was performed to observe the selectivity of sensing layer in the presence of fluorine for the chlorine and its vice versa. The obtained data was analyzed through clustering based principal components analysis algorithm, to discriminate between the similar kind of analytes based on their kinetics behavior.

Keywords: Piezoelectric; Quartz crystal; Chlorine; Fluorine; Resonance frequency

Introduction

The presence of some specific cationic and anionic species is important in the drinking water up to the permissible limit. In addition to heavy metal ions, anions are considering another class of hazardous pollutants because of their more reactive nature than cations [1]. Therefore, the presence of anion above permissible limit are more detrimental for human health and environmental. The weathering of rocks and minerals are natural resources of anions whereas anthropogenic sources having industrial discharges, agricultural runoff, and wastewater [2]. The fluorine and chlorine are vital anions for the healthy life up to the permissible limit. According to the WHO guide line, the safe limit of these anions are 1.5 mg/l (fluoride) and 5 mg/l (chlorine) in water [3]. Chlorine ion plays an important role in the disinfection

process, but palm sweating, hair loss and potentially damage of lungs are the side effect of excess chlorine. The small amounts of fluoride are commonly added to toothpaste and drinking water to reduce the effects of tooth decay, while excessive level of fluoride can lead to dental and skeletal fluorosis [4].

With increasing the popularity of nanotechnology has wide range of application in the areas of solar cell, wide range of sensors, water purifications, catalysis, flexible electronic device, drug delivery system etc. Where the carbon-based nanomaterials, in general Carbon Nanotubes (CNTs) have gained much attention due to their high Surface-to-Volume (S-V) ratio, functionalization with desired surfactants allows easy control over its physicochemical properties. CNTs has been used for the detection of wide range of analytes [5], such as Voltaic Organic

Compounds (VOC), gases, chemical sensor, ions where in the literature review, it has been reported that Single Walled Carbon Nanotubes (SWCNTs) are more sensitivity towards the anionic species [6]. Our research work deals with the monitoring of free chlorine and fluorine in aqueous medium using the thin film of ODA-SWCNTs. The aim of study was to investigate the behavior of piezo response of ODA-SWCNTs functionalized quartz crystal in the presence of fluorine, chlorine and their interference in aqueous medium. The findings of this research can help the water quality assessment industry to monitor anionic species in aqueous medium.

Experimental Work

Material

Octadecyl Amine functionalized Single Walled Carbon Nanotubes (ODA-SWCNTs) were purchased from carbon solution Inc. The Sodium Chloride (NaCl) and Sodium Fluoride (NaF) were purchased from Himedia Laboratories. The stock solution of ODA-SWCNTs was prepared in the chloroform solution with concentration of 0.1 mg/ml, after 15 min of ultrasonication a uniformly dispersed solution of ODASWCNTs was obtained. In a similar manner stock solution of beeswax was prepared having the concentration of 0.1 mg/ml. Deionized water obtained from a Milli-Q unit (Millipore, DQ-5), which had a resistivity of 18.2 MΩ-cm, was used throughout the experiment. The stock solution of NaCl and NaF were prepared in the ultrapure Milli-Q water with the concentration of 1 mg/ml. The known volume of stock solution of analytes was diluted into the Milli-Q water to prepared the testing solution of desired concentration.

Experimental Procedure

The QCM200 digital controller from SRS, USA sensing setup was used to detect the anion analytes in aqueous medium (Figure 1). Quartz crystal has piezoelectric property due to which it oscillates at its resonance frequency of 5 MHz. The resonance frequency of quartz is inversely proportional to its thickness. The oscillating frequency is ultrasensitive to changes in mass per unit surface area [7]; this feature of the crystal makes it useful for the sensing application of analytes even in the range of ppb. The mass changes per unit area (Δm) at the quartz electrode surface is calculated from the Sauerbrey relation, as stated in the equation 1. This equation is known as Sauerbrey equation, where C_f is sensitivity constant which depends on the property of the quartz crystal. The reported value of C_f for a 5 MHz AT-cut quartz crystal at room temperature is $56.6 \text{ Hz } \mu\text{g}^{-1} \text{ cm}^2$.

$$\Delta f = -C_f \Delta m \quad (1)$$

The surface of quartz crystal was cleaned through the standard method as mentioned in the literature [8]. The composite of ODA-SWCNTs and beeswax was mixed in the 10:1 ratio and employed for the deposition of thin film onto the quartz wafer using spin coating technique. The functional layer was deposited by spreading 30 μl solution of nanocomposite onto a rotating quartz having the speed of 1500 rpm. The quartz crystals were then placed in a vacuum desiccator to dry for 2-3 hours. Afterwards, the functionalized quartz crystal was fixed in the quartz holder and then immersed vertically into a beaker filled with ultrapure ion-free water and wait for 2-5 minutes to get stabilized its resonance frequency. It was then immersed in a diluted anionic

analyte solution where the complex interaction was formed between the analyte and ODA-SWCNTs sensing layer. Due to this interaction, mass on the surface of quartz crystal increases, and the resonance frequency of the crystal decreases. The change in resonance frequency (Δf) is proportional to the adsorbed concentration of the analyte on the quartz surface. The resonance frequency of crystal was continuously monitored for different concentrations of the analyte. The Sauerbrey relation was used to estimate adsorbed mass of analyte on quartz surface through Δf of crystal [9]. The sensing setup was specially prepared for detection of anions in Parts per Billion (ppb) range. The sensitivity was estimated from the linear fit of the calibration curve. The sensing was carried out at the constant room temperature due to crystal sensitive nature towards temperature.

Result and Discussion

The piezo response of ODA-SWCNTs functionalized quartz crystal was recorded for a given concentrations of fluorine and chlorine in aqueous medium. The stable frequency of functionalized quartz crystal in aqueous medium is considered as the reference. The chemical bonding between the cationic functional layer and anionic analytes, particularly the adsorption of ionic species due to electrostatic forces, reduces the frequency of crystal. The change in resonance frequency is estimated against the reference frequency, then the adsorbed mass on the crystal surface is calculated using the Sauerbrey relation (Equation 1). Finally, a calibration curve of the sensing response was plotted (Figure 2), where the y axis represents the change in mass and the concentration is plotted on the x axis. The linear regression fit was applied on the sensing response of chlorine and fluorine, where the change in slope with correlation coefficient was found to be, slope = $230.47 \pm 16.7 \text{ ng/cm}^2/\text{ppb}$, $R^2 = 0.96$ and Slope = $50.00 \pm 7.24 \text{ ng/cm}^2/\text{ppb}$, $R^2 = 0.90$ for chlorine and fluorine, respectively. The slope of calibration curve represents the sensitivity of sensing layer as reported in literature [10]. Chlorine response was recorded in the concentration range of 0.5 to 10 ppb and fluorine was recorded in the range of 2 to 10 ppb. From the piezo response of the sensor, the response and recovery time of the sensing layer were also estimated, where the change in frequency was plotted against the recorded time (Figure 3). The crystal frequency showed an exponential decrease followed by a decrease while responding to chlorine, with a time constant of $9.90 \pm 1.56 \text{ s}$, whereas the frequency was dropped sharply while responding to fluorine, with a time constant of $6.55 \pm 0.5 \text{ s}$. The sensor recovered with exponential growth of frequency with time constants of $8.16 \pm 1.21 \text{ s}$ for Cl^- and $4.09 \pm 0.51 \text{ s}$ for F^- . The protonated amine group in SWCNTs bundles provides the favorable electrostatic interaction to the anionic species. Whereas, our published work showed the electrochemical, spectroscopic and structural characterization of fluorine interaction with ODA-SWCNTs. That work revealed that F^- perturbs the π -electron system of the SWCNTs, consistent with a specific semi-covalent interaction between the fluoride and the carbon framework [11]. Whereas our present study analyzed the Cl^- and F^- response simultaneously to elucidate the role of physicochemical properties such as ionic size, charge density, polarizability, and hydration characteristics in the sensing response. The fluoride ion has a small ionic radius and high charge density; however, the strong hydration efficiency of F^- ions lower them impose to approach the sensing surface. Instead of this, weak hydration of

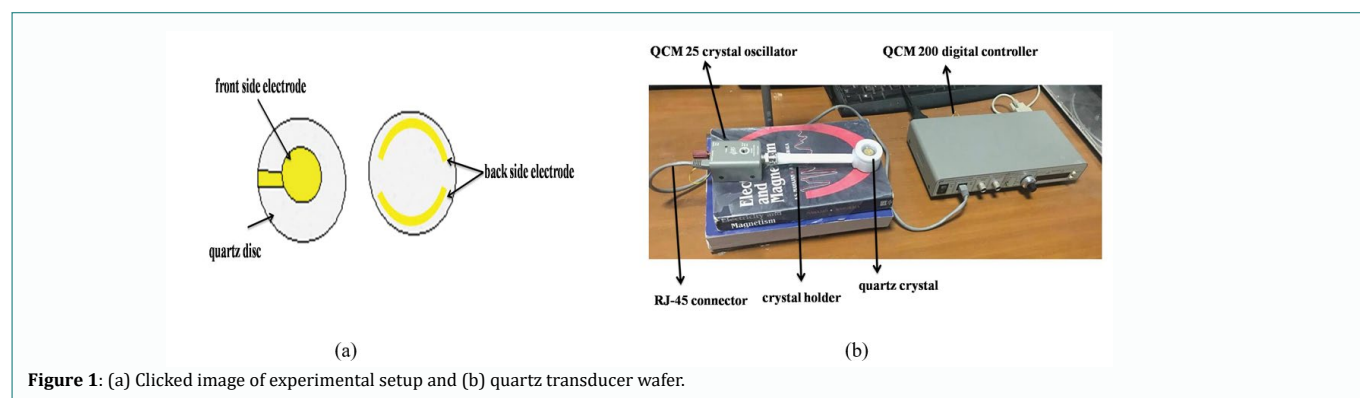


Figure 1: (a) Clicked image of experimental setup and (b) quartz transducer wafer.

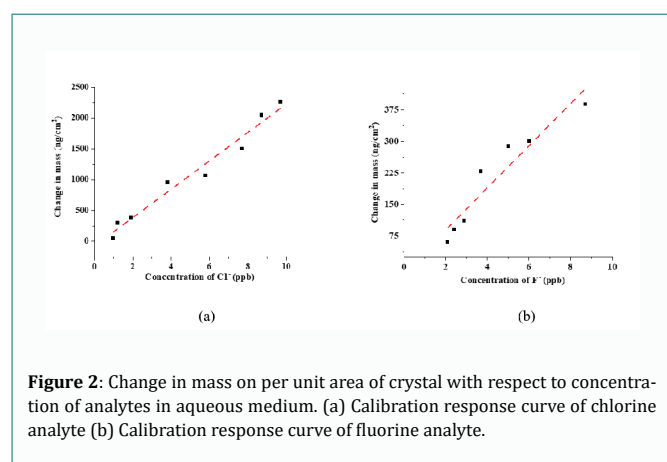


Figure 2: Change in mass on per unit area of crystal with respect to concentration of analytes in aqueous medium. (a) Calibration response curve of chlorine analyte (b) Calibration response curve of fluorine analyte.

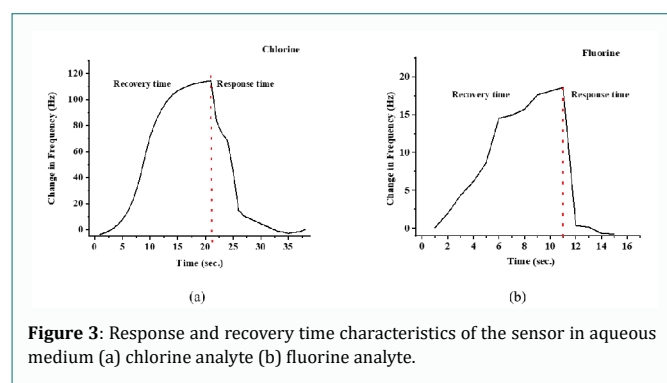


Figure 3: Response and recovery time characteristics of the sensor in aqueous medium (a) chlorine analyte (b) fluorine analyte.

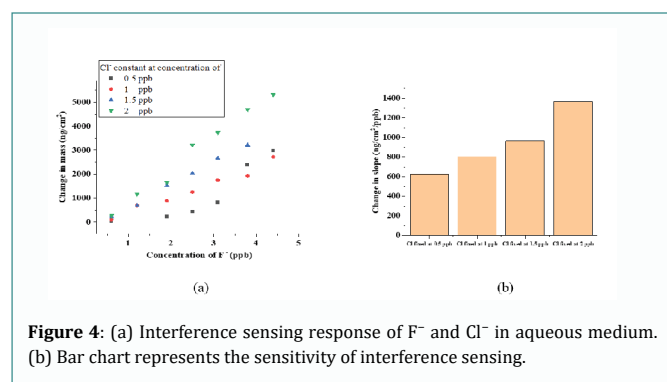


Figure 4: (a) Interference sensing response of F^- and Cl^- in aqueous medium. (b) Bar chart represents the sensitivity of interference sensing.

Cl^- ions allowing easier approach to the interfacial protonated adsorption sites, even with lower charge density and large ionic radius. Due to this, the sensitivity of fluorine was found to be lower than that of chlorine. Consequently, the LOD and sensitivity

for fluorine are higher and lower, respectively, compared to those of chlorine.

Based on that, composite sensing has been performed where the trend of piezo responses was observed as the chlorine concentration increased from 0.5 to 2 ppb in steps of 0.5 ppb for the concentration range of fluorine from 0.5 to 5 ppb. For the same concentration range of F^- , the sensitivity systematically increased with increasing concentrations of Cl^- as shown in the Figure 4 bar chart. As the concentration of chlorine is increases, the straight behavior of slope increases. The interference sensing response of F^- and Cl^- represents that chlorine sensing dominates that of fluorine because of weak hydration and high polarizability. The slope and correlation coefficient behavior is tabular summarized in Table 1. The PCA plot depicts that for the higher concentration of Cl^- the sensing behavior is resembled therefore the PCs data points are clustered in the same region (Figures 5-7).

Table 1: Depicts the slope and correlation behavior of F^- - Cl^- composite sensing.

Cl^- ion is constant, for concentration range of fluorine 0.5 ppb to 5 ppb	Slope (ng/cm ² /ppb)	Correlation Coefficient (R^2)
Cl^- constant at 0.5 ppb	628.87 ± 48.4	0.75
Cl^- constant at 1 ppb	807.05 ± 20.5	0.96
Cl^- constant at 1.5 ppb	963 ± 28.4	0.99
Cl^- constant at 2 ppb	1364 ± 74.01	0.98

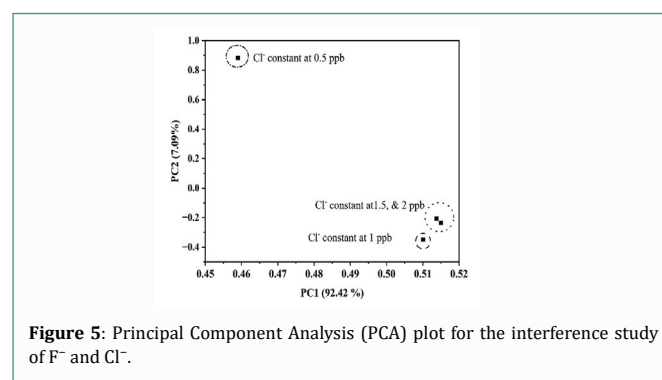


Figure 5: Principal Component Analysis (PCA) plot for the interference study of F^- and Cl^- .

Conclusion

We have demonstrated that spin coated film of ODA-SWCNTs can be used to detect the anionic species in aqueous medium. The beeswax was specially used to provide the stability to the sensing layer in aqueous medium. Where the ODA-SWCNTs and beeswax

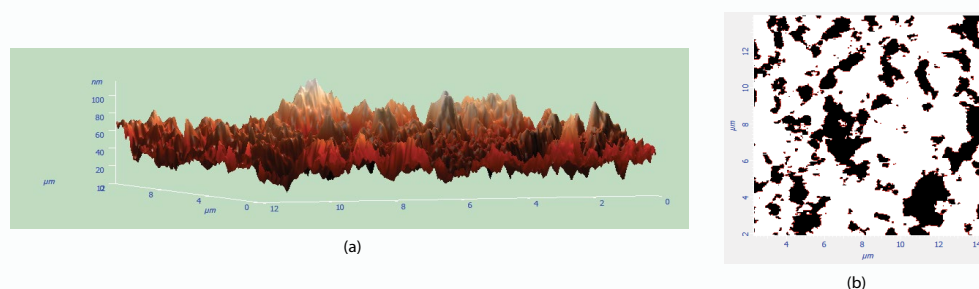


Figure 6: (a) 3D Topographic Atomic Force Microscope (AFM) image and (b) corresponding to grain size map, of beeswax functionalized quartz crystal surface.

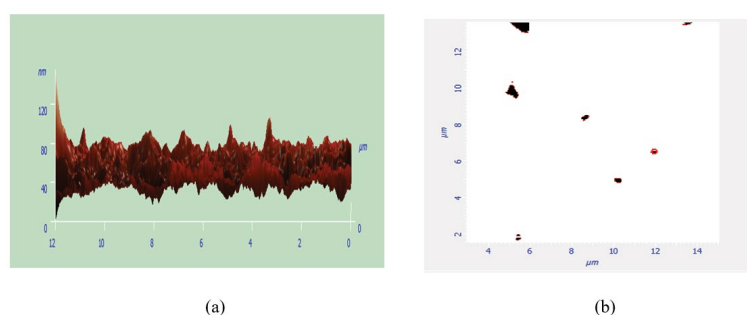


Figure 7: (a) 3D Topographic Atomic Force Microscope (AFM) image and (b) corresponding to grain size map, of nanocomposite of ODA-SWCNTs and beeswax functionalized quartz crystal surface.

composite was prepared in the ratio of 10:1. The interference sensing of fluorine and chlorine shows that the interaction of chlorine with the sensing layer is dominant than that of fluorine. The F^- possesses a higher charge density and can thus experience strong electrostatic attraction towards the protonated ODA sites, but its hydration is also significantly stronger compared to Cl^- . Consequently, more energy is required for dehydration prior to direct interaction with the sensing interface. In contrast, while Cl^- has a lower charge density, it exhibits weaker hydration and higher polarizability, making it easier to access and interact with the ODA-SWCNT interface. The sensing layer was recovery using the ultrapure ion free water. The response and recovery time of fluorine were found to be 6.55 ± 0.5 s and 4.09 ± 0.51 s, respectively, and for chlorine were 9.90 ± 1.56 s and 8.16 ± 1.21 s. The present work showed the comparative analysis of F^- and Cl^- anionic species but protonated cationic layer is able to respond to another anionic species also. Which we will show in our future work.

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