International Journal of
INTELLIGENT SYSTEMS AND APPLICATIONS IN ENGINEERING
ISSN:2147-6799 www.ijisae.org Original Research Paper

Experimental Investigation of Graphene Derivatives Based Moisture Sensor Transfer Characteristics for Agriculture Applications

[1]Neema Amish Ukani, [2]Dr. Shelej Khera, [3]Saurabh S. Chakole

Submitted: 20/08/2023 **Revised**: 10/10/2023 **Accepted**: 21/10/2023

Abstract: In this work, we have fabricated the sensor to detect the water content in the soil using two graphene derivatives as the sensing material. In this work, we have considered two different graphene derivatives viz "graphene oxide" (GO) and reduced "graphene oxide" (rGO) with three different concentration i.e 0.1 mg, 1 mg and 10 mg dispersed in the 1 ml ethanol, which illustrates the novelty of this work. Further, we have fabricated the interdigitated electrodes (IDEs) on the printed circuit board (PCB), where the aforementioned concentration is drop casted. Further, we studied the sensor transfer characteristics such as the sensitivity, selectivity, hysteresis and stability. From the experimental investigation we have found that 1 mg/1ml (ethanol) concentration outperform when compared with 0.1 mg/1ml (ethanol) and 10 mg/1ml (ethanol) for the both the graphene derivatives used in this work.

Keywords*: Capacitive soil moisture sensor, multi-sensing points, IoT enabled moisture sensor, Field deployments, in-situ agriculture applications*

1. Introduction

In today's era, to feed the human, it is now important to make the agriculture sustainable and enhance the cultivation of the crops. It has now become mandate that besides increasing the crop yield, it is also pivotal to have crops with high quality. To ensure the high-quality crops with improved yield, maintaining soil water content within a field is one of the widely used method reported in the literature [1]. Soil water content defines the availability of the water molecule in the soil matrix and to measure the soil water content in the field soil moisture sensors are widely used [2]. For precise irrigation the water content in the soil needs to be maintained between the field capacity and permanent wilting point. For this purpose, considering the availability of various fertilizers, nutrients and chemicals, the sensors deployed in the field should be accurate and selective to the water molecule. Further, considering the diversity of the soil type in the agriculture field, the sensor should perform the reliable operation and needs to be cost-effective for the farmers working in the developing countries.

To measure the soil water content have reported various methods, which are used for the both lab as well as field measurements. The widely used lab methods includes the gravimetric method, which is considered as the golden standard for the soil moisture measurements. This method is more accurate, however the time taken (typically 24 hours) to get the results hinder its usage for the field applications [3, 4]. Thus, researchers have explored the rapid in-situ detection of the soil moisture sensor with the help of various methods like, time domain reflectometry, neutron probe frequency domain reflectometry [3, 4]. These methods are very accurate and offers very fast response time. But the cost of these methods are not affordable for the marginal of poor farmers. Thus, considering the affordability, researchers have introduced the resistive/capacitive, galvanic based, and heat pulse-based methods as one of the potential methods for the in-situ soil moisture measurements. Even though these methods are affordable but it needs a frequent calibrations and temperature variations effects the sensor performance [3, 4].

Further, to have an accurate acreage information, it is important to deploy plethora of sensors in the field and considering the cost of the accurate soil moisture measurements systems this becomes an expensive process. To abate this, researches have focused on developing the affordable sensor systems by using the micro-fabrication process. The micro-fabrication of the sensors for the agriculture applications has opened up the avenues not only to build affordable sensors but also accurate and fast response time agriculture sensors. For micro-sensors used for the soil moisture sensors, the sensing film plays a pivotal role considering the sensitivity and selectivity. Researchers have explored various sensing films such as "PEDOT: PSS and polyaniline polymers" [5-7]. However, the stability of these polymers hinders its use for the in-situ soil moisture sensing applications. Thus, to improve the stability, researchers have focused on various nanomaterials such as "graphene derivatives, MoS_2" etc. [8-10].

[1]*Lovely Professional University, Punjab,*
https://orcid.org/0000-0001-6262-9005
neema.ukani@gmail.com
[2]*SEEE, LPU, Punjab*
shelej.22390@lpu.co.in
[3]*Lovely Professional University, Punjab*
saurabhchakole89@gmail.com

In this work we have selected the “graphene derivative “graphene oxide”” (GO) and reduced “graphene oxide” (rGO) [11-12]. The rationale for selective graphene derivatives over other derivatives is the stability, selectivity and sensitivity offered by this nanomaterial. For any sensing film the concentration of the nano-material drop casted on the sensor plays an important role. For this purpose, it is important to study the effect of concentration on the sensor sensing properties. The reported work in the literature have performed the measurements with the fixed concentration and have not explored the effect of the various concentration on the “soil moisture sensing properties” of the graphene derivatives. This has motivated us to study the effect of various concentration of graphene derivatives and its performance on the “soil moisture sensing properties”. Another objective is to identify the best concentration of graphene derivatives considering the sensitivity. Thus, in this work, we have selected the “graphene oxide” (GO) with three different concentrations viz 0.1 mg/ 1 ml (ethanol), 1 mg1 ml (ethanol), and 10 mg 1 ml (ethanol), which are labelled as GO1, GO2 and GO3, respectively, henceforth in the further sections. Likewise, we have selected another graphene derivative i.e reduced “graphene oxide” (rGO) with different concentration viz 0.1 mg/ 1 ml (ethanol), 1 mg1 ml (ethanol), and 10 mg 1 ml (ethanol), which are labelled as rGO1, rGO2 and rGO3, respectively, henceforth in the further sections.

This work is organized as following, first we have fabricated the sensors on the “printed circuit board” (PCB) which comprise of interdigitated electrodes (IDEs). Further, the prepared GO and rGO samples with different concentration are drop casted on the fabricated sensors. Subsequently, we have prepared the soil samples with different soil water content and studied the fabricated sensor transfer function such as “sensitivity, selectivity, hysteresis and stability”. Further, we have explained the plausible sensing mechanism of the fabricated sensor, which has different concentration of GO and rGO as the sensing film.

2. Materials and Methods

A. Sensor fabrication on the PCB

For sensor fabrication we have used the printed circuit board technology (PCB) considering the affordability when compared with the MEMS fabrication process. We have used the PCB, which has copper thin plate on both the side of PCB as shown in Fig. 1 (a-c). For this purpose, first we have designed the interdigitated electrodes (IDEs) using the Inkscape software. IDEs has length and breadth of about 1.8 cm and 0.7 cm, respectively. The width of the fingers in IDEs is about 1 mm with spacing of about 2 mm. The contact pads of the IDEs is about 0.3 cm. Further, pattern this form factor of IDEs on the butter paper as depicted in Fig. 1 (d).

Transfer of the IDE pattern on the PCB is achieved with the application of the hot iron on the PCB. Mask the IDEs pattern with the help of thick marker. Then insert the PCB on $FeCl_2$ solution for about 15 minutes and stir the PCB as shown in Fig. 1 (e). This step will help in removing the unmasked copper on the PCB and IDEs pattern will remain on the PCB. Further, wash the PCB with the help of DI water as depicted in Fig. 1 (f). Finally, the IDEs on the PCB is printed as shown in Fig. 1 (g).

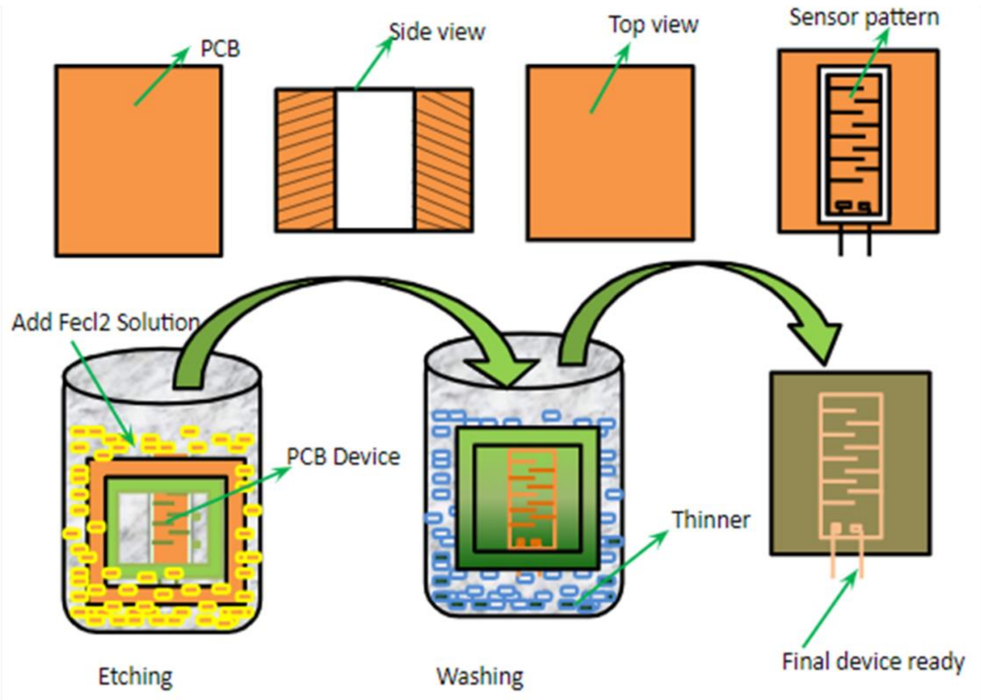

Fig. 1 Fabrication process of the IDEs on the PCB

B. Graphene derivatives sample preparation

In this work, we have studied effect of graphene derivative concentration on its "soil moisture sensing properties". For this purpose, we have selected the "graphene oxide" (GO) and reduced "graphene oxide" (rGO) with different concentration as depicted in Fig. 2. For GO, we have selected the three concentration 0.1 mg (named as GO1), 1 mg (named as GO2) and 10 mg GO (named as GO3) dispersed in the 1 ml ethanol as shown in Fig 2 (a), Fig. 2 (b) and Fig. 2 (c), respectively. Likewise, we have taken three different concentrations of rGO viz. concentration 0.1 mg (named as rGO1), 1 mg (named as rGO2) and 10 mg GO (named as rGO3) dispersed in the 1 ml ethanol as shown in Fig 2 (d), Fig. 2 (e) and Fig. 2 (f), respectively. For this purpose, first the 0.1 mg, 1mg and 10 mg GO is taken in the test tube and 1 ml ethanol is added into it. Further, these samples are kept in the ultra-sound sonicator for 20 minutes. Subsequently, these samples are drop casted on the fabricated IDEs on the PCB. Similar procedure is followed for the rGO sample preparation and drop-casted on the PCB with IDEs patterned on it.

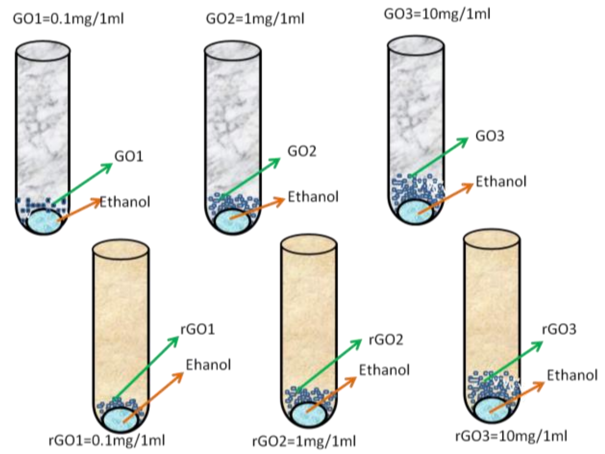

Fig. 2 GO and rGO sample preparation with different concentration

C. Soil sample preparation

Soil sample preparation is one of the important steps for this study. It is mandate to prepare the soil sample with utmost care and follow the steps as reported in [4] as depicted in Fig. 3. First, soil samples are collected from the agriculture field, which are brought to the lab and oven dried for 24 hours at about 105 ^{0}C. This step is followed to remove the soil water from the sample and make the sample complete dry. Next step is to crush the soil samples and collect 100 grams of the soil sample in the mould. Then add the desired water on the sample. For example, to make 10 % water content soil sample, add 10 ml water in 100 gm dry soil sample. Further, mix the soil sample for 15-20 minutes and keep it for the maturing for about 24 hours. This step ensures the proper distribution of the water molecule within the soil matrix. Then, soil sample are kept in the hot air oven and "gravimetric water content" (GWC) is measured. Once the GWC is measured then soil samples is considered to be ready for the measurements.

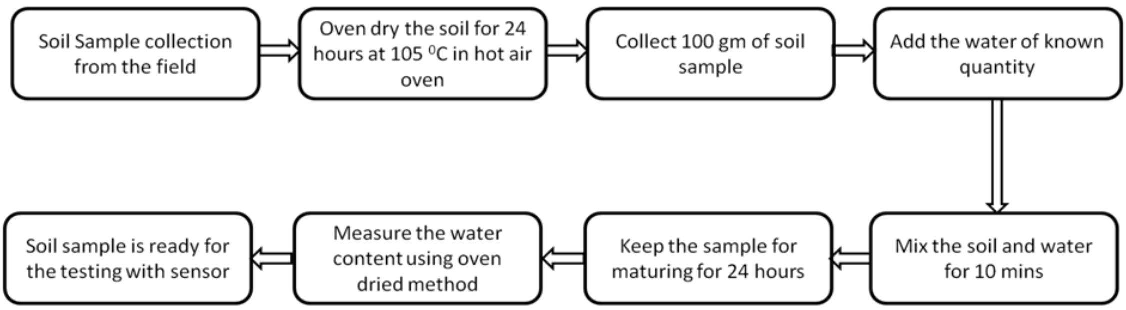

Fig. 3 Flow for the soil sample preparation, which are collected from the agriculture field

D. Experimental setup

Fig. 4 shows the measurement set-up used in this work, which has been reported in the earlier work [4]. First the fabricated PCB sensor is taken as depicted in Fig. 4 (a). The electrical contacts are taken out from the fabricated PCB and then applied the silicon glue on the contacts. Then, as prepared GO/rGO samples with different concentration are drop casted on the fabricated sensor as shown in Fig 4 (b). Then, sensor is connected to the "LCR meter" as shown in Fig 4 (c), which measures the change in the sensor capacitance when exposed to different soil water content. During the measurement it has been ensured that the excitation voltage from the LCR meter is limited to the 1 Vpp to abate the impact of electrolysis of water. Further, the soil sample with different water content is drop casted on the sensor and subsequently change in the sensor capacitance is recorded as depicted in Fig. 4 (d).

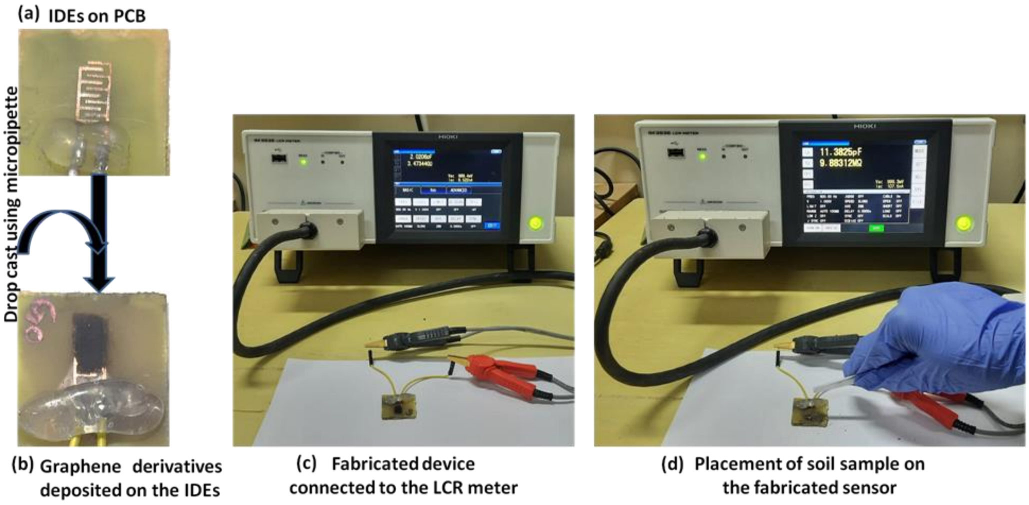

Fig. 4 Experiment set-up

3. Result and Discussion

A) Change in the sensor capacitance with soil water content

Fig. 5 shows the frequency characteristics of the fabricated with respect to different GWC ranging from 1 %, to 17 %. For the GO and rGO with different concentration. From Fig. 5 it is evident that the sensor capacitance decreases with increase in the frequency. From Fig. 5 (a-c), we can observe that fabricated sensor offers the capacitance of about 500 pF, 600 pF and 480 pF for GO1, GO2 and GO3, respectively at 500 Hz and 17 % GWC. Likewise, for rGO the maximum capacitance is about 450 pF, 1000 pF and 1100 pf for rGO1, rGO2 and rGO3, respectively at 500 Hz and 17 % GWC. From Fig. 5 it is also evident that fabricated sensor capacitance increases exponentially with increase in the soil water content, which is in agreement with [13]. Further, it is delightful that the fabricated sensor shows the monotonic behavior for all the graphene derivative samples with different concentration. For GO1, GO2 and GO3 the maximum ΔC is 516.822 pF, 637.602pF and 482.792 pF, respectively, when the GWC is varied from 1 % to 17 % GWC. Likewise, for rGO1, rGO2 and rGO3 the maximum ΔC is 456.587 pf, 986.481 pf and 1152 pF, respectively, when the GWC is varied from 1 % to 17 % GWC.

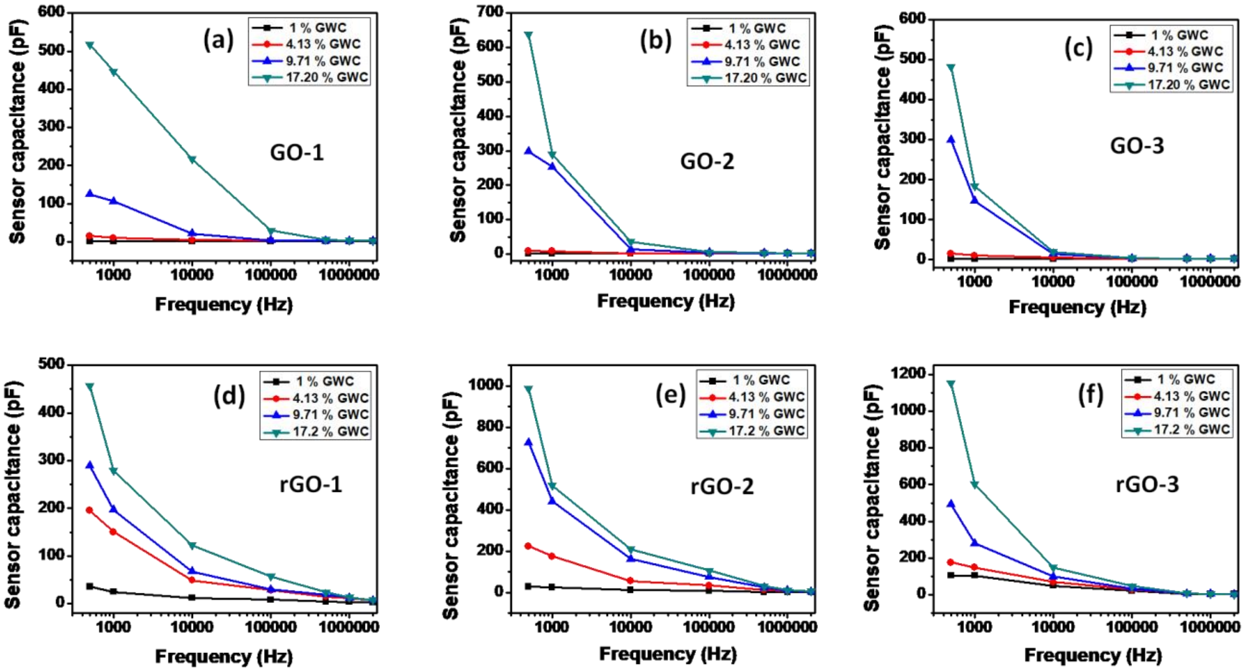

Fig. 5 Effect of frequency and soil moisture on the fabricated sensor with GO and rGO as the sensing film, and with different concentration.

B. Response of the fabricated sensor with soil water content

For any soil moisture sensor, it is pivotal to understand the response of the sensor when exposed to the different soil moisture. From Fig. 6 (a-c), it can be inferred that the sensor response for the GO1, GO2 and GO3 at 500 Hz is about 30212.14%, 37296.01 % and 22630%, respectively, at 500 Hz. Thus, it is evident that GO2 (1mg/1ml) concentration is highly sensitive to the soil moisture followed by the GO1 (0.1 mg/ml) and GO3 (10 mg/ml). Likewise, for rGO from Fig. 6 (d-f), we can observe that sensor response is about 1166 %, 3277 % and 995 % for rGO 1, rGO 2 and rGO 3, respectively. Thus, it can be concluded that for rGO1 is more responsive to the GWC followed by rGO 1 and rGO3.

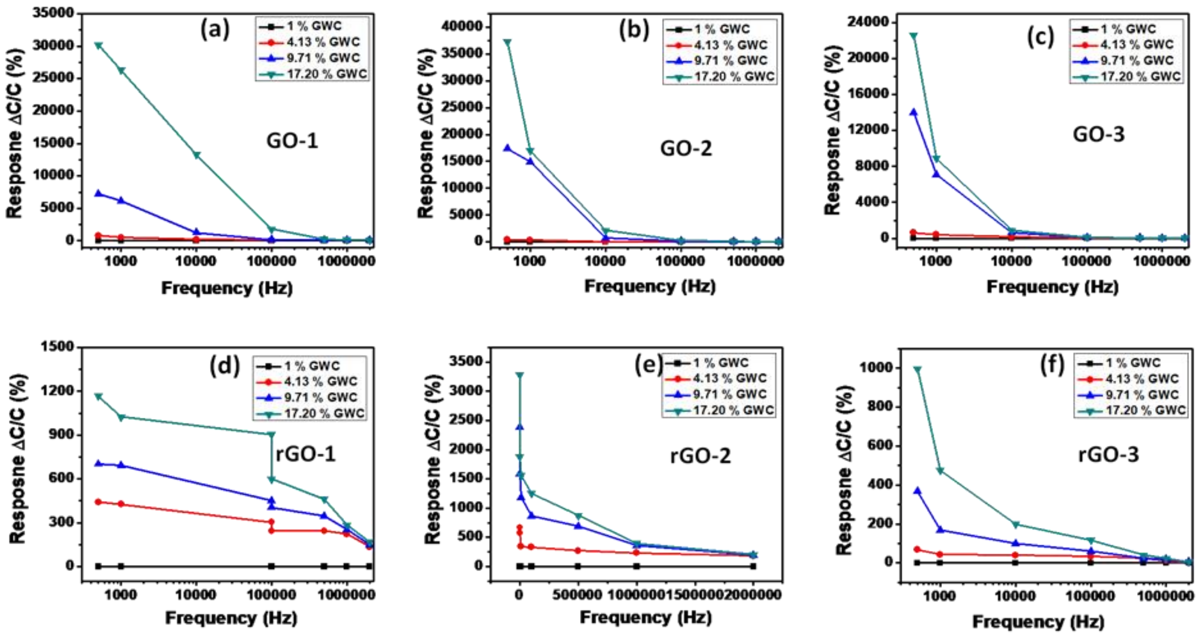

Fig. 6 Response of the soil moisture on the fabricated sensor with GO and rGO as the sensing film, and with different concentration.

Fig. 7 (a) shows the response of the GO with different concentration i.e GO2 (1mg/ml) GO1(0.1mg/ml) & GO2(10mg/ml). From Fig. 7 (a) it is evident that GO2 offers the highest response when the soil water content is varied from 1 % to 17% and followed by GO1 and GO3.

Similarly, Fig. 7 (b) depicts the response of the rGO with three different concentrations. From Fig. 7 (b) it can be inferred that rGO2 (1mg/ml) is more responsive when compared with rGO1 (0.1mg/ml) & rGO3 (10mg/ml).

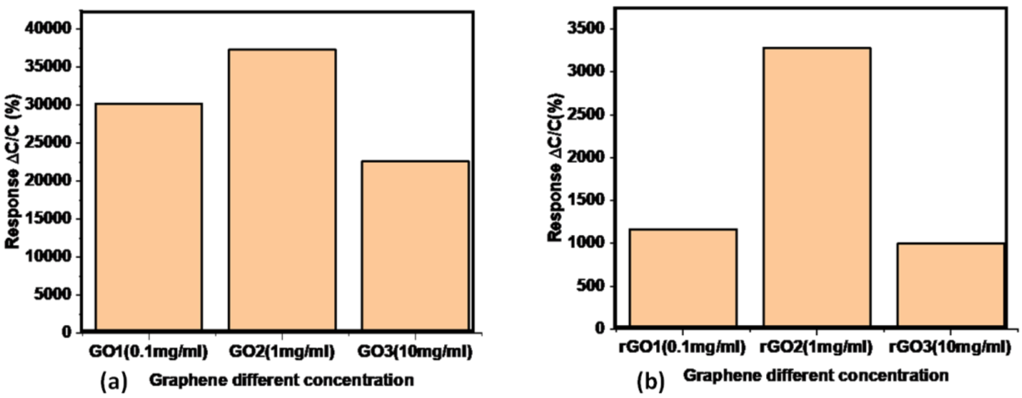

Fig. 7 Response of the fabricated sensor with GO and rGO as the sensing film, and with different concentration.

C) Selectivity of the fabricated sensor

Selectivity of the sensor is an ability to capture the target analytes in the presence of various ions present in the soil samples. To study the selectivity of the sensor, we have taken four dry soil samples and added 5 mg of cadmium chloride (Cd), cupric chloride (Cu), potassium chloride (K) and sodium chloride (Na). Subsequently, one more sample is prepared where 5 ml water is added in the dry soil. Fig. 8 shows the selectivity offered by the fabricated sensor when exposed to various ions present in the soil sample. From Fig, 8 it can be inferred that for all the graphene derivatives, the fabricated sensor shows higher selectivity towards water molecules when compared with Cd, Cu, K and Na.

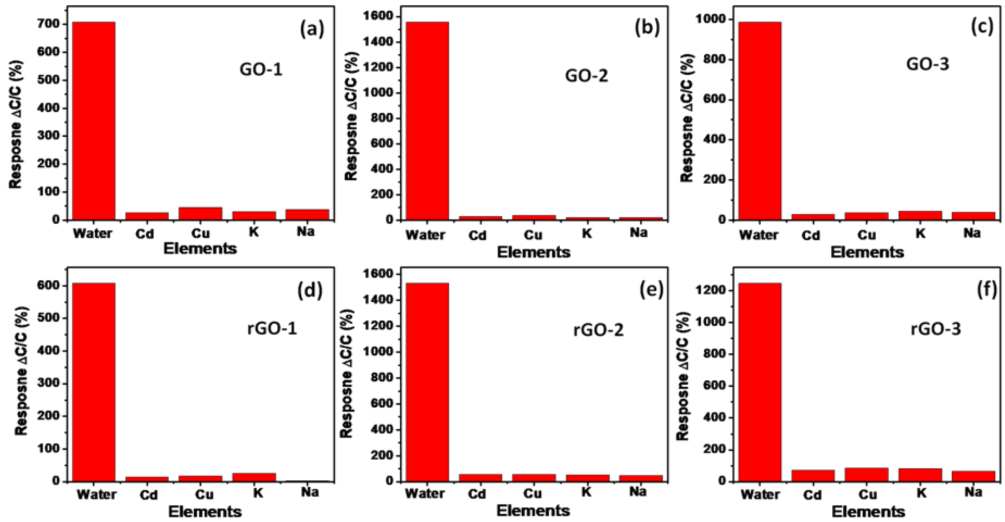

Fig. 8 Selectivity of the fabricated sensor with GO and rGO as the sensing film, and with different concentration.

D) Hysteresis of the fabricated sensor

Under in-situ condition, we observe the wetting and drying cycle due to variation in the environmental factors such as temperature. Thus, it is important to understand and analyze the hysteresis offered by the fabricated sensor. For this purpose, first we have deployed the sensor with the increase in the water content. Subsequently, the sensor is deployed in the soil where water content is decreased and sensor capacitance is recorded. From Fig. 9 (a-c), we can infer that the maximum hysteresis is about ± 2.5 % GWC for GO samples. Whereas, for the rGO samples maximum hysteresis observed is around ± 2.5 % GWC as depicted in Fig 9 (d-f).

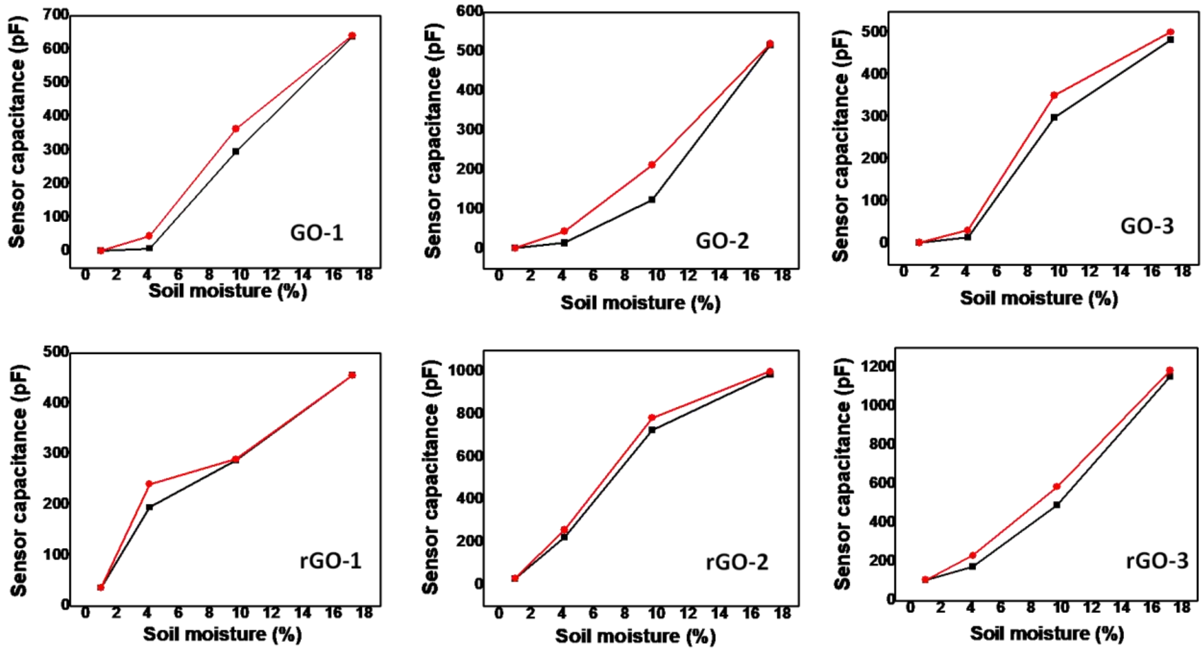

Fig. 9 Hysteresis of the fabricated sensor with GO and rGO as the sensing film, and with different concentration.

E) Stability of the fabricated sensor

Stability is a crucial factor for in-situ soil moisture sensors that are utilized in field deployments. The degradation in sensor performance can result in inaccurate measurements. Thus, in this work, we have studied the stability of the sensor where sensor capacitance is measured for about 4 months at 1 % GWC and 17 % GWC. Fig. 10 the fabricated sensor exhibits a high degree of stability for about 4 months. Fig. 10 (a-c) shows the stability of the GO sample with different concentration. From Fig. 10 (a-c) it is inferred that the standard deviation for sample GO1, GO2 and GO3 at 1 % GWC is 0.06 pF, 0.15 pF and 0.4 pF, respectively. Whereas at 17 % GWC the standard deviation for GO1, GO2 and GO3 is 30 pF, 18 pF abd 9 pF, respectively. Likewise, for the rGO the standard deviation at 1 % GWC for rGO1, rGO2 and rGO3 is about 2.2 pf, 2.16 pf and 2.07 pf, respectively. Subsequently, for the standard deviation for the rGO1, rGO2 and rGO3 at 17 % GWC is 14 pf, 53 pf and 17 pF, respectively.

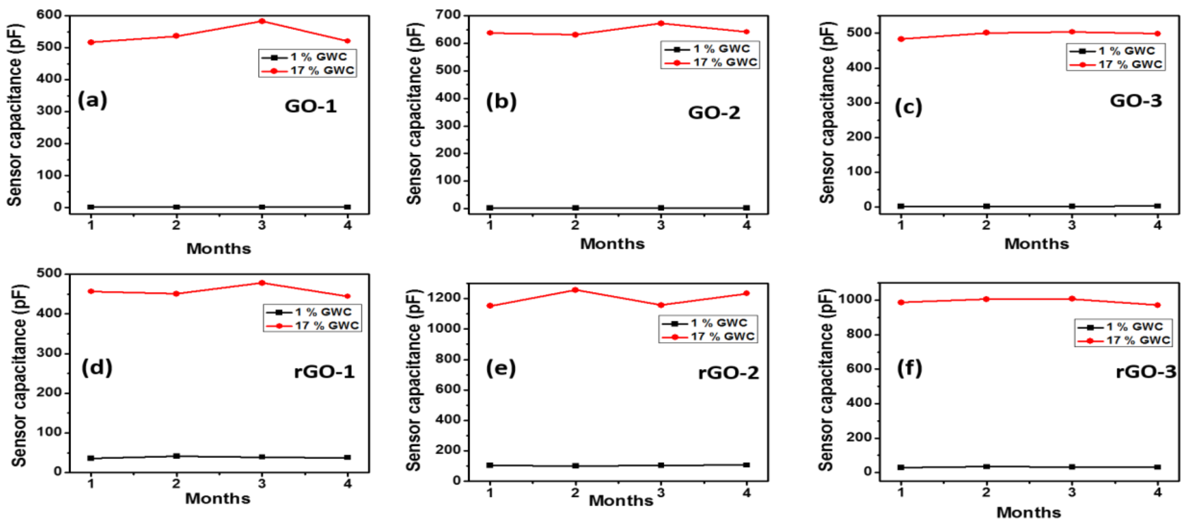

Fig. 10 Hysteresis of the fabricated sensor with GO and rGO as the sensing film, and with different concentration studied for 4 months

F) Sensing mechanism

Fig. 11 shows the sensing phenomenon of the graphene derivatives with the soil moisture, which has been reported in [13]. As discussed in the [13], the graphene comprises of various oxygen functional groups, which plays a pivotal for the soil moisture sensing. The –OH functional groups make the double hydrogen bonding with the H ions in the water molecule, which is termed as "first physisorbed layer". Further, when soil moisture increases then water molecule increases and this hydrogen bonding increase, which is termed as the second physisorbed layer. More binding of the water molecule on the graphene surface effectively increases the dielectric constant of the medium, thus capacitance increase with increase in the water molecule.

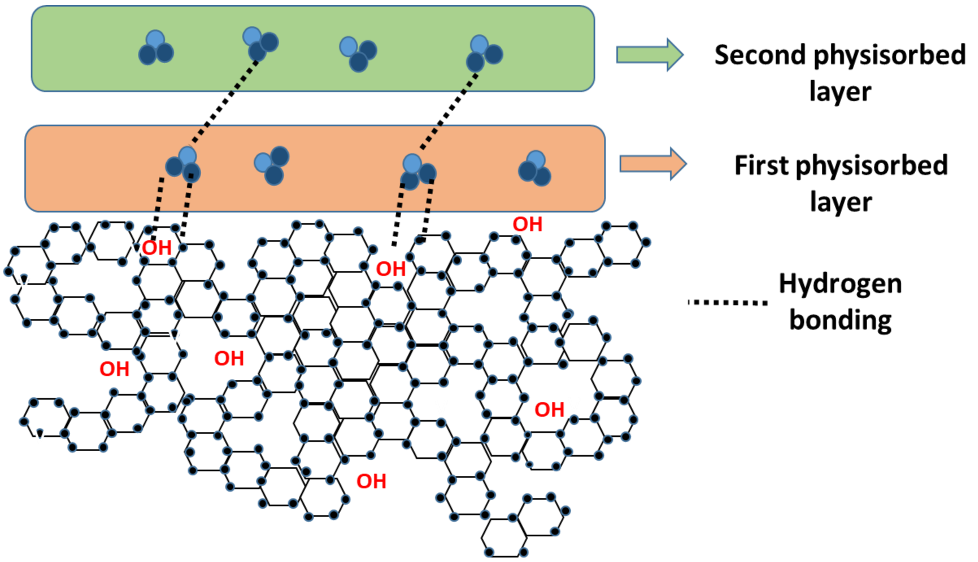

Fig. 11 sensing mechanism of the soil moisture with graphene derivatives

Table 1 and 2 tabulates the response of each ion introduced in the soil sample for various concentration of GO and rGO, respectively. From Table 1 and 2, it is evident that response of the fabricated sensor towards the water molecule is about 10 times more than the other ions such as Cd, Cu, K and Na for both GO and rGO, respectively. This, illustrates the potential use of the fabricated sensor for in-situ soil moisture sensing.

Table 1: Selectivity offered by the GO for three different concentrations

Material	Water (%)	Cd (%)	Cu (%)	K (%)	Na (%)
GO1	707.7	26.8	44.7	30.4	37.8
GO2	1556.3	30.4	36.6	21	21.4
GO3	986.9	29.6	35.7	45.1	37.8

Table 2: Selectivity offered by the rGO for three different concentrations

Material	Water (%)	Cd (%)	Cu (%)	K (%)	Na (%)
rGO1	607.1	13.9	17	24.9	2.5
rGO2	1530.8	56.5	55.4	49.5	47.5
rGO3	1245	71.9	83.8	82.3	64.9

4. Conclusion

In this study, a sensor has been developed for the purpose of detecting soil moisture levels. The sensing material employed in this sensor consists of two derivatives of graphene. In this study, we have examined two distinct derivatives of graphene viz “graphene oxide” (GO) and reduced “graphene oxide” (rGO) with three different concentration i.e 0.1 mg, 1 mg and 10 mg dispersed in the 1 ml ethanol, which illustrates the novelty of this work. Further, we have fabricated the interdigitated electrodes (IDEs) on the “printed circuit board” (PCB), where the aforementioned concentration is drop casted. Further, we studied the “sensor transfer characteristics” such as the “sensitivity, selectivity, hysteresis and stability”. From the experimental investigation we have found that 1 mg/1ml (ethanol) concentration outperform when compared with 0.1 mg/1ml (ethanol) and 10 mg/1ml (ethanol) for the both the graphene derivatives used in this work.

References:

[1] F. Veihmeyer, et. al., The moisture equivalent as a m easure of the field capacity of soils, Soil Science, 32 , (1931) 181-94.

[2] V. S. Palaparthy et. al., Review of polymer-based se nsors for agriculture-related applications. Emerging Materials Research, 2(4), (2013), 166-180.

[3] S.L. Su, et. al., A critical review of soil moisture me asurement, Measurement, 54, (2014) 92-105.

[4] S. G. Surya, et. al., “An in-field integrated capacitiv e sensor for rapid detection and quantification of soi l moisture” Sensors and Actuators B: Chemical, 321 , (2020), 128542.

[5] S.J. Patil, et. al., An ultra-sensitive piezoresistive po lymer nano-composite microcantilever platform for humidity and soil moisture detection, Sensors and A ctuators B: Chemical, 203, (2014) 165-73.

[6] T. Jackson, et. al., Measuring soil temperature and m oisture using wireless MEMS sensors, Measurement , 41, (2008) 381-90.

[7] J. Liu, et. al., Polymer-based microsensor for soil m oisture measurement, Sensors and Actuators B: Che mical, 129, (2008) 599-604.

[8] H. Kalita, et. al., “Graphene quantum dot soil moist ure sensor.” Sensors and Actuators B: Chemical, 23 3, (2016) 582-90.

[9] V.S. Palaparthy, et. al., “graphene oxide”-based soil moisture microsensor for in situ agriculture applicat ions, Sensors and Actuators B: Chemical, 273, (201 8) 1660-9.

[10] N. Kumar, et. al. Highly Sensitive Hierarchical MoS 2 Nanoflowers for In-Situ Soil Moisture Sensing. Se nsors and Actuators B: Chemical, (2022) 132572.

[11] V. S. Palaparthy, et. al., “graphene oxide”-based soi l moisture microsensor for in situ agriculture applica tions. Sensors and Actuators B: Chemical, 273, (201 8), pp. 1660-1669.

[12] K. S. Patle, et. al. Reduced “graphene oxide” Soil M oisture Sensor with Improved Stability and Testing on Vadose Zone Soils. In Artificial Intelligence Dri ven Circuits and Systems (2022), pp. 115-123. Sprin ger, Singapore.

[13] H. Bi, et. al., Ultrahigh humidity sensitivity of “grap hene oxide”, Sci. Rep., 3, (2013), 2714.

[14] P, R. H. ., B, S. D. ., M, D. K. ., Sooda, K. ., & B, K . R. . (2023). Transfer Learning based Automated E ssay Summarization. International Journal on Recen t and Innovation Trends in Computing and Commun ication, 11(1), 20–25. https://doi.org/10.17762/ijritc c.v11i1.5983

[15] Anthony Thompson, Anthony Walker, Luis Pérez , Luis Gonzalez, Andrés González. Machine Learnin g-based Recommender Systems for Educational Res ources. Kuwait Journal of Machine Learning, 2(2). Retrieved from http://kuwaitjournals.com/index.php /kjml/article/view/181