Chlorine retention in drinking water with UiO66 metal–organic framework

SERGIO A SERRANO-PALAFOX[1,2,*] ⓘ, **FERNANDO ROMERO-ROMERO**[2],
VÍCTOR VARELA-GUERRERO[1,2] **and MARÍA F BALLESTEROS-RIVAS**[1,2]

[1] Sustainable Chemistry Research Joint Center UAEM-UNAM, Toluca de Lerdo, Mexico
[2] Faculty of Chemistry, Autonomous University of State of Mexico, 50120 Toluca de Lerdo, Mexico
*Author for correspondence (sserranop003@alumno.uaemex.mx)

Abstract. In this article, the chlorine retention performance of both UiO-66 and UiO-66@GO metal–organic frameworks has been highlighted. A 48×10^{-5} % solution of drinking water with sodium hypochlorite (H_2O-NaClO) was filtered on one hand with UiO-66 and on the other with UiO-66@GO. Using OTO reagent, it was determined their respective performance in terms of chlorine retention. It is worth to note that UiO-66@GO composite is a good material option to retain chlorine from drinking water.

Keywords. Metal–organic framework; graphene oxide; UiO-66; chlorine.

1. Introduction

Disinfection is of undoubtedly importance in the supply of safe drinking water. Disinfection is an effective barrier to many pathogens in drinking water treatment [1]. Destruction of pathogens is essential and pretty commonly involves the use of reactive chemical agents such as chlorine [2]. The disinfection goal is to eliminate or inactivate pathogenic micro-organisms to avoid waterborne diseases [3]. The first application of disinfection, as a continuous process in water treatment, took place back in the 1900s in Belgium, where chlorine was used as a disinfecting reagent.

Since the introduction of filtration and disinfection at water-treatment plants, waterborne diseases, like typhoid and cholera, have been practically eliminated.

For almost a century, chlorine gas or chlorine reagents (hypochlorite) were the most used disinfectants for drinking water production.

The primary use of chlorine is for disinfection [4]. Chlorine also works as an oxidizing agent for taste and odour control, it prevents algae growth, maintains a clear filter media, removes iron and manganese, destroys hydrogen sulphide, removes colour, maintains the quality of water at distribution systems and improves coagulation [5].

Back in 1974, researchers from Netherlands and USA demonstrated that trihalomethanes (THMs) were formed during chlorination.

In addition to THMs, disinfection byproducts (DBPs) have been shown to be carcinogenic, mutagenic, etc. Even if such health risks are negligible, they have to be taken seriously since there is a large population exposed.

When natural organic matter (NOM) reacts with free chlorine or free bromine, halogenated organic byproducts are formed.

Factors that affect the formation of halogenated DBPs include the concentration and type of natural organic matter, oxidant dose and type, time, the concentration of bromide ion, pH, temperature and organic nitrogen concentration.

When strong oxidants react with organic compounds found in water, non-halogenated DBPs are formed.

According to researchers, NOM is the principal precursor of organic DBP formation.

When chlorine reacts with NOM, they produce a variety of DBPs, including THMs, haloacetic acids (HAAs) and others.

Chlorine is extremely used as disinfectant for bacteria, highly disinfectant for viruses and less disinfectant for protozoa.

Nevertheless, chlorine is used to disinfect raw water when it is stored in tanks for water purification processes. Activated carbon is commonly used to remove chlorine from water in purification process equipment.

Activated carbon is very well recognized as a reliable and effective means of removing impurities. It has excellent adsorptive capacity, an affinity for dissolved organics and chlorine, and it has been employed for the purification of gases, removal of organic pollutants from water and in medical applications as well [6].

Activated carbon is usually produced from biomass materials. It can be synthesized from agricultural waste materials such as orange peel, palm kernels, rice husk, banana peel or pineapple leaf fibre. However, a cost-effective material to synthesize activated carbon is coconut shell [7,8]. Activated carbon from coconut shells has a mesoporous structure and a large surface area [9].

In water-treatment processes, activated carbon is used to remove chlorine, taste, colour and odour. Its surface's microporous can adsorb lightweight organic contaminants.

Through a chemical reaction, activated carbon can eliminate chlorine from water:

$$HOCl + C \rightarrow HCl + CO$$
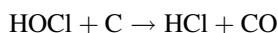
Free chlorine can be found in water as hypochlorous acid (HOCL) or as a hypochlorite ion (OCl^-) [10]. Both can react with activated carbon to produce a chloride ion (Cl^-), a proton (H^+) and carbon monoxide (CO). This last one can either get linked to the surface of carbon or can be dissolved in water as carbonic acid (H_2CO_3).

In addition, activated carbon can adsorb organic contaminants that provide tastes and odours to water or which can be harmful to humans (pesticides).

Metal–organic frameworks (MOFs) are porous materials with great flexibility in terms of pore size and resistance to temperature variation [11–14]. MOFs have a unique chemical versatility with a framework similar to that of zeolite with the advantage that both structural distribution and pore size can be controlled [15,16]. They act as a promising adsorbent that can accommodate guest molecules. MOFs have unique framework designs and efficient adsorption in contrast to conventional materials such as zeolite, silica, activated carbon and mesoporous alumina [17–19]. Interest in MOFs has mostly focused on synthesis routes, with a process to extend their pore size, increase their surface area and enhance the structural stability of the respective materials [20–23].

Metal–organic frameworks UiO-66 and UiO67 belong to the family of MOFs known as UiO (University of Oslo) [24]. UiO-66 presents good stability at high temperatures (540°C) and high pressure (up to 10 kg cm^{-2}) [25–28].

Recent work by Wang *et al* [31] showed that UiO-66, a Zr-based MOF, has remarkable stability in water [29–33]. UiO-66 is a porous material with an FCC crystal structure [34], which consists of octahedral cages with a diameter of 11 Å and tetrahedral cages with a diameter of 8 Å (figure 1). The mentioned cages are connected through narrow triangular windows with the size of 6 Å. When UiO-66 is prepared, $ZrCl_4$ is used as a metal precursor, which is later mixed with 1,4-benzenedicarboxylic (H_2BDC) as a linker. Zr^{4+} would then undergo a self-assembling process into hexanuclear $[Zr_6O_4(OH)_4]^{12+}$ clusters [35] connected to 12 dicarboxylate linkers to form an expanded cubic close-packed framework [29]. Its porosity is variable; it runs from 900 to 1,600 m^2 g^{-1} (BET surface area) [34].

Graphene oxide (GO) is a promising filler material in composite membranes for water purification. It is a two-dimensional carbon material with rich functional groups (carboxyl, hydroxyl and epoxy groups), large surface area, strong hydrophilicity [36] and an outstanding chemical stability [37,38].

There are some problems with GO, though. GO nanosheets can easily stack together due to the strong interactions among the neighbouring nanosheets. The narrowed interlayer space blocks the water flux. Therefore, there is a need to seek solutions to effectively avoid stacking and fully utilize the unique properties of GO nanosheets. According to Ma *et al* [37], MOFs may be
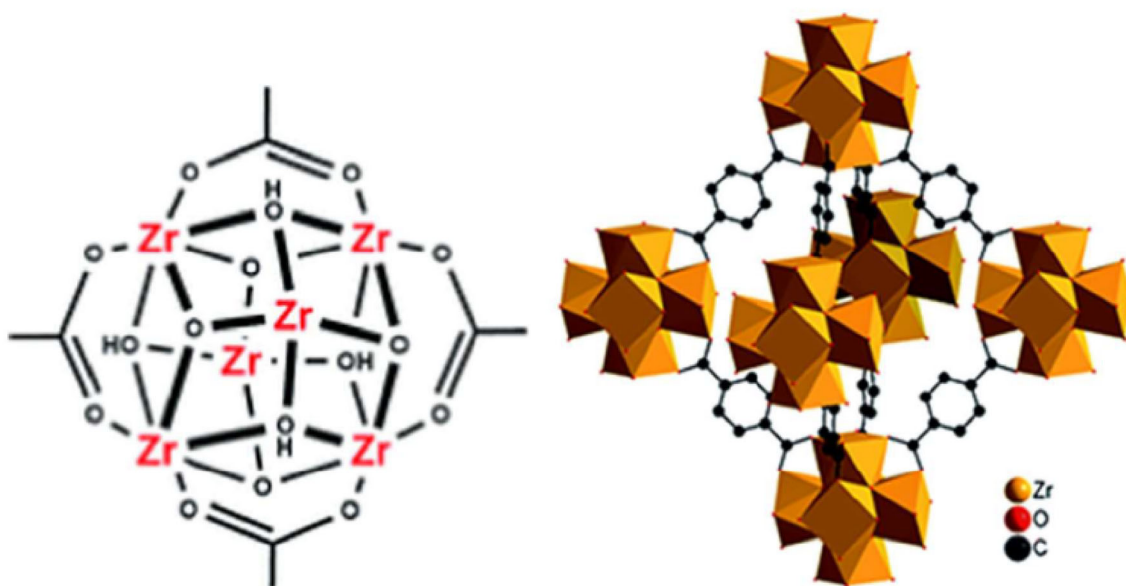

Figure 1.   UiO-66 structure [20].

promising candidates as modifiers for GO nanosheets due to their designable pore structure and tunable surface chemical properties.

Water purification equipment suppliers' recommendation about stored water (raw water) is to chlorine it. According to the original equipment user's manual, it is recommended to apply 5 ml of sodium hypochlorite (NaClO @ 13%) per every 1,000 l of water [39]. In practice, it is recommended to apply 12 ml of NaClO to a 2,500 l tank. Based on the aforementioned numbers, it is a NaClO-H_2O solution at 48×10^{-5} % to be considered in a tank of 2,500 l capacity.

In this study, a UiO-66@GO modified composite was synthesized and put together in order to filter water. UiO-66 was synthesized too. Later verified their capacity to retain chlorine from water.

2. Experimental

2.1 Motivation and strategy

There is no piece of information about both UiO-66 and UiO-66@GO performance to remove chlorine from water. In water purification, activated carbon is used to remove chlorine from water. The intention of utilizing both UiO-66 and UiO-66@GO to remove chlorine from water is to have another material option for this kind of operation.

2.2 Materials

Zirconium (IV) chloride (Cl4Zr ≥99.5%) from Sigma Aldrich, dimethylformamide (DMF) from Macron, graphene oxide (GO, 4 mg ml^{-1}, dispersion in H_2O) and terephthalic acid (H_2BDC, 99%) from Sigma Aldrich.

2.3 Synthesis of UiO-66

Firstly, 0.386 g (1.67 mmol) of $ZrCl_4$ and 0.276 g (1.67 mmol) of H_2BDC are to be dissolved in 37.5 ml of DMF; stir for 45 min. Secondly, the mixture is to be transferred into a 100 ml Teflon liner within a stainless-steel autoclave and kept at 120°C for 24 h. After the reaction, the product must be centrifuged and washed with fresh DMF and methanol three times. Then, the product must be filtered and, finally, it has to be dried at 50°C for 24 h in an oven.

2.4 Synthesis of UiO-66@GO

Firstly, 10 mg GO (2.5 ml of GO dispersion) to be dispersed into 37.5 ml DMF by sonication for 8 h. Secondly, GO solution is to be poured into $ZrCl_4$ (0.386 g, 1.67 mmol) and stirred at room temperature overnight.
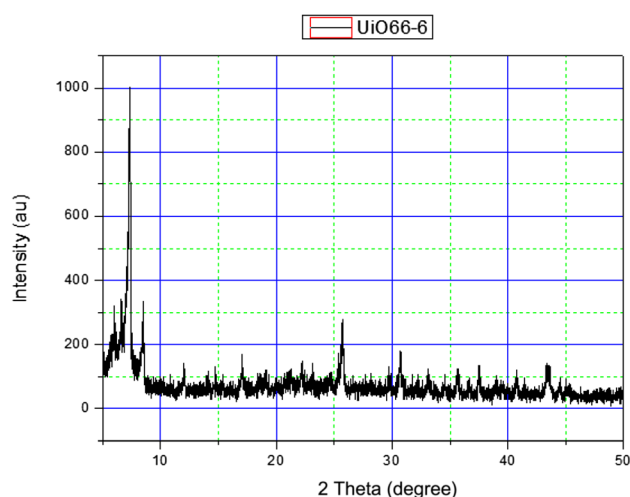

Figure 2. PXRD pattern of the synthesized UiO-66.

Afterwards, H_2BDC (0.276 g, 1.67 mmol) is to be added; stirred for 45 min. Run a solvothermal reaction at 120°C for 24 h. Afterwards, the resulting solution is to be centrifuged and washed with fresh DMF and methanol three times. Then, the solution must be filtered. Finally, the product must be dried at 50°C in an oven.

2.5 Characterization of UiO-66 and UiO-66@GO

Powder X-ray diffraction (PXRD) was performed and recorded in a Rigaku Ultima IV X-ray diffractometer in reflection mode using Cu Kα radiation ($\lambda = 1.5406$ Å). The 2θ range of 5° to 50° was scanned with a step size of 0.01°. Fourier transform infrared spectroscopy (FT-IR) was performed in a Shimadzu IRTracer-100 spectrophotometer. Scanning electron micrographs (SEM) analysis was performed in a Jeol JCM 6000 equipment.
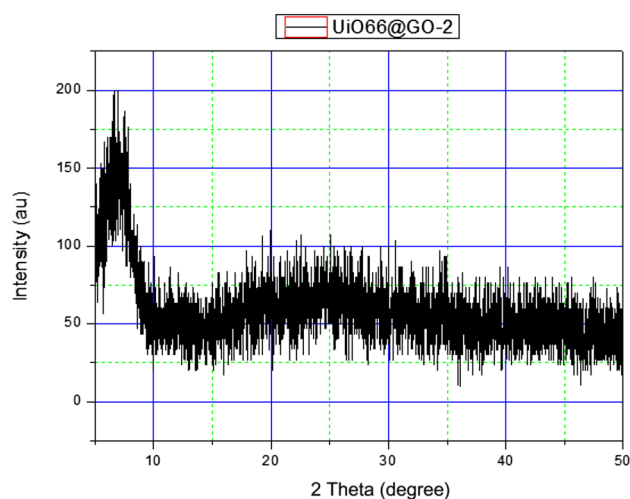

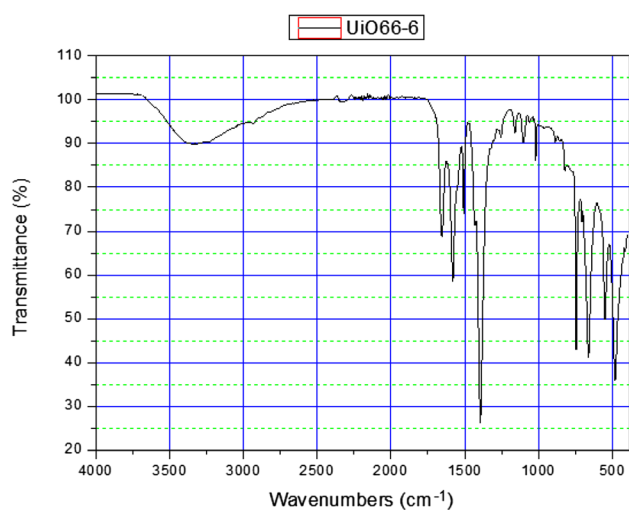**Figure 3.** PXRD pattern of the synthesized UiO-66@GO.

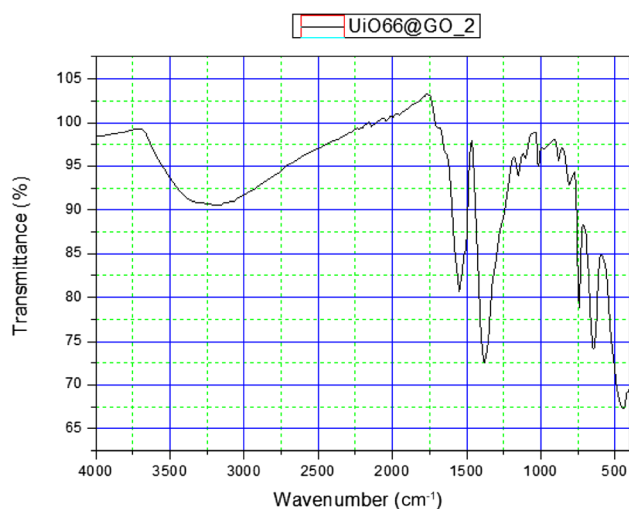**Figure 4.** FTIR analysis of UiO-66.

Figure 5. FTIR analysis of UiO-66@GO.

2.6   Chlorine detection

Analytic reagent to analyze chlorine presence in water, Orthotolidin (OTO) from Impulsora Química OAXXA, S.A. de C.V. In a vial, add 3ml of sample water to be tested and add 3 drops of OTO reagent. Close vial with its cap and shake well. Observe. If sample remains uncolored, there is no chlorine presence in sample. If sample turns yellow, determine the amount of chlorine's presence according to vial's colored-scale.

3.   Results and discussion

3.1   Characterization of UiO-66 and UiO-66@GO

Figures 2 and 3 show the PXRD diffractograms of UiO-66 and UiO-66@GO composites. The diffractogram of UiO-66 is in good agreement with that reported in the literature, therefore there is a successful synthesis [40]. The diffractogram of UiO-66@GO composite material (figure 3) shows how GO has occupied empty spaces within the UiO-66 structure. The characteristic peak at around 7° takes place in its diffractogram.

Figures 4 and 5 show the FT-IR spectra of UiO-66 and UiO-66@GO composites to characterize the functional groups. About UiO-66, the absorption peaks at wavenumbers 1655, 1580, 1506 and 1395 cm^{-1} represent the BDC's C=O symmetric stretching in the carboxylate group, the O–C–O asymmetric stretching in the BDC ligand and the C=C stretching of benzene ring, respectively. The spectrum of UiO-66@GO composite does not change much contrasted to UiO-66. About UiO-66@GO, the absorption peaks at 1550 and 1381 cm^{-1} may represent the groups on the GO layers, which are bonded to the metal sites of UiO-66.

The morphology of both UiO-66 and UiO-66@GO composites was analysed by SEM. Figure 6 shows how the UiO-66 crystal size is in the order of nanometres, while the UiO-66@GO composite aggregates are in the order of micrometres.

3.2   Water filtration with UiO-66

A quantity of 40 ml of H_2O-NaClO @ $48 \times 10^{-5}\%$ solution was filtered through UiO-66. After filtration, water was analysed with OTO reagent and it was noticed that chlorine was almost completely retained by UiO-66 (figure 7). According to the probe's scale, there is a chlorine presence in filtered water of 0.3 mg l^{-1}.

3.3   Water filtration with UiO-66@GO

A quantity of 40 ml of H_2O-NaClO @ $48 \times 10^{-5}\%$ solution was filtered through UiO-66@GO. After filtration,
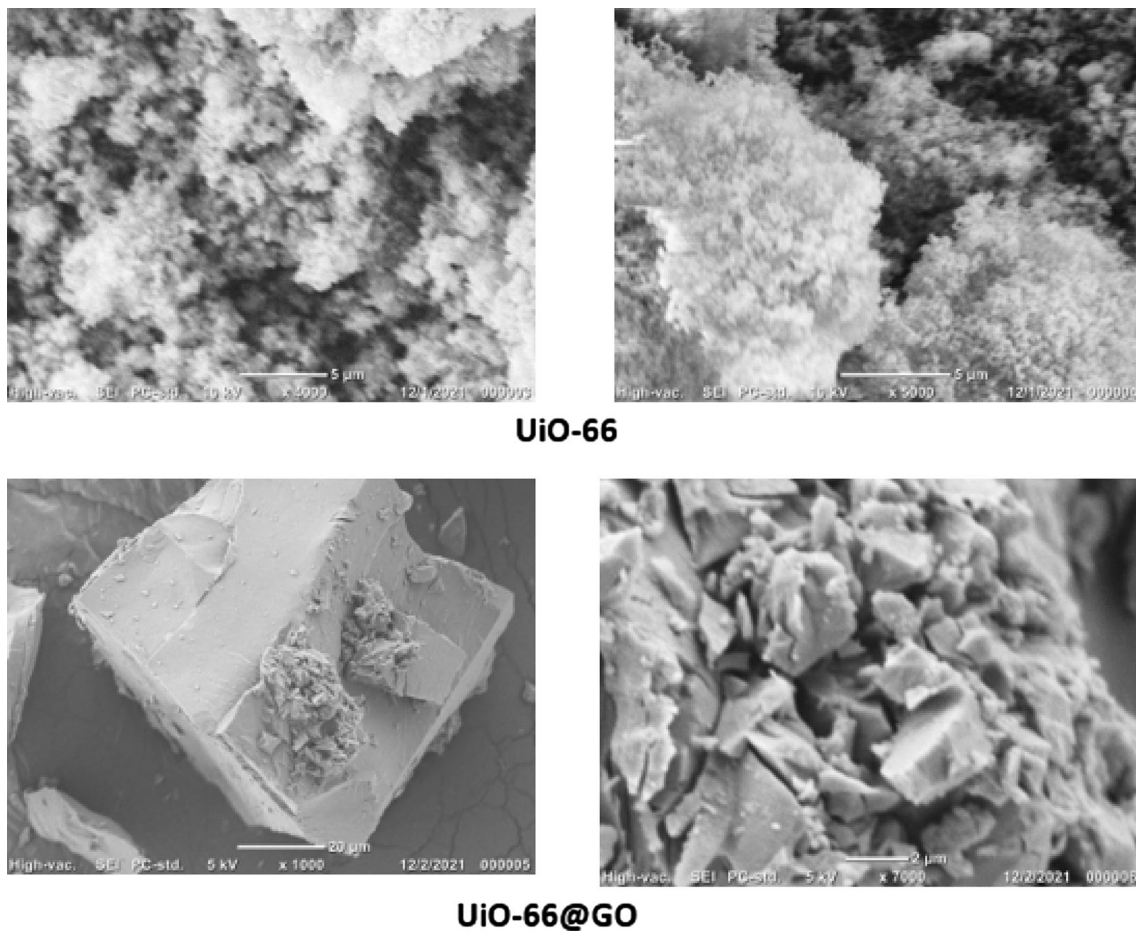
Figure 6.   Scanning electron microscopy images of UiO-66 and UiO-66@GO.

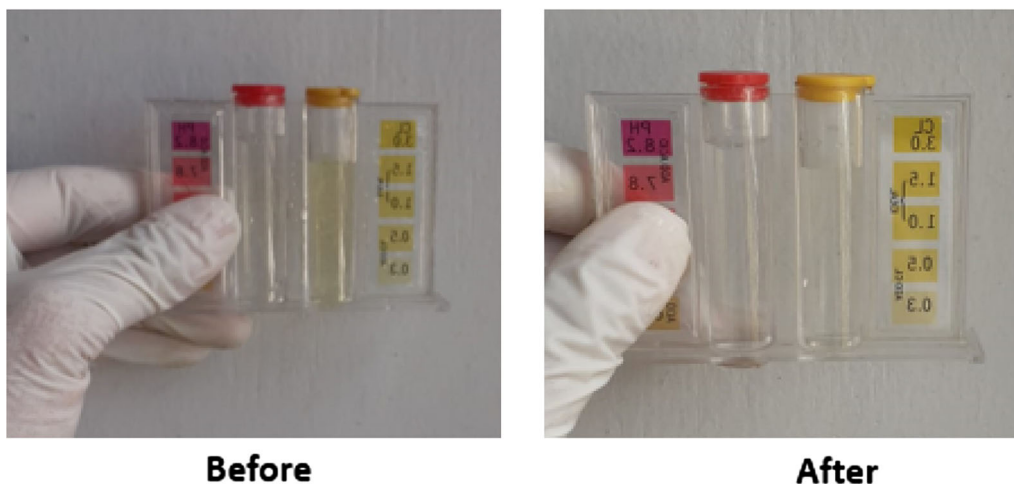**Figure 7.**   Images of chlorine retention with UiO-66.

Water filtration with UiO-66@GO

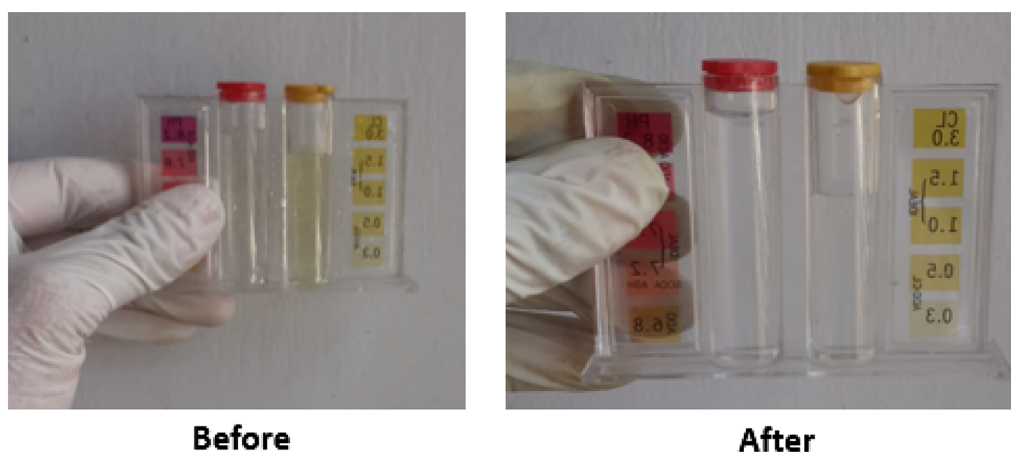**Before**   **After**

Figure 8.   Images of chlorine retention with UiO-66@GO.

water was analysed with OTO reagent and it was noticed that chlorine was completely retained by UiO-66@GO composite (figure 8). According to the probe's scale, there is a presence of chlorine in filtered water of 0 mg l^{-1}.

4.   Conclusions

In this study, it is highlighted that both UiO-66 and UiO-66@GO show successful performance in chlorine retention in the process of water filtering. UiO-66@GO has better chlorine retention than UiO-66. For solutions of H$_2$O-NaClO @ 48×10^{-5}%, UiO-66@GO performs better chlorine retention than UiO-66 alone.

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