International Journal For Technological Research In Engineering *ISSN (Online): 2347 - 4718*
REGIONAL CHEMICAL ENGINEERING UNDERGRADUATE CONGRESS (RCEUC) UNIVERSITY OF MALAYA, KUALA LUMPUR, MALAYSIA

INACTIVATION OF E.COLI IN GROUNDWATER USING SOLAR-ACTIVATED TiO_2-C_uO-SiO_2 PHOTOCATALYST COMPOSITE IMMOBILIZED IN WASTE POLYSTYRENE

Benjamin B. De Vera[1], Joshua G. Bullago[2], Imee A. Caw-is[3], Hannah Jenina Felice B. Ballesteros[4], Kendra D. Dao-wan[5], Alvin G. Benter[6], Jerry O. Dalapus[7], Trisha Mae B. Abaggue[8], Charlotte R. Hafalla[9], Robert Manuel S. Villarama Jr[10]
Department of Chemical Engineering, School of Engineering and Architecture
Saint Louis University, Baguio City, Philippines

Abstract: In the Philippines, an estimated 8.4 million rely on unsafe water sources where pathogens like E. coli thrive. Chlorination is conventionally used for disinfection; however, it produces carcinogenic disinfection by-products (DPBs). Thus, a solar-activated TiO2-CuO-SiO2 photocatalyst composite immobilized in waste polystyrene is proposed as an alternative for safely inactivating E. coli, the mandatory pathogen indicator, in water. The photocatalyst composite was prepared mainly by sonication and calcination then was immobilized in thin film form using waste polystyrene. In order to determine the efficiency of the photocatalyst in reducing E. coli concentration and to evaluate whether it is within the Philippine National Standards for Drinking Water (PNSDW) of 2017, the groundwater samples were characterized before and after 6 hours of solar irradiation. The highest photocatalytic inactivation was exhibited by PS-TiO2-CuO-SiO2 composite compared to PS-TiO2-CuO and PS-TiO2. PS-TiO2-CuO-SiO2 achieved almost 100 % reduction of E. coli concentration from 24,000 to <1.1 MPN E. coli per 100 mL. The results showed that the composite synergy between TiO2, CuO and SiO2, together with the homogeneous dispersion of the photocatalyst particles characterized by the EDS led to enhanced photocatalytic inactivation of E. coli. Furthermore, even if the pilot scale volumes were increased, the coliform concentrations were still reduced from 79 to <1.1 MPN per 100 mL, reaching almost 100%. The reusability of the catalyst was also studied. PS-TiO2-CuO-SiO2 can be reused for at most five times to reduce the coliform concentration in water to the PNSDW standard while retaining almost 100% efficiency. The entirety of the research is simple, efficient, environmental, sustainable and feasible for large-scale and point-of-use applications to convert non-potable water into safer drinking water without harmful DBPs.

Keywords: photocatalyst composite; E. coli; groundwater; titanium dioxide; solar irradiation

I. INTRODUCTION

Photocatalysis is a promising novel approach that can serve as an alternative or supplement in the treatment of water with respect to simultaneous disinfection and contaminant degradation. It is a catalytic reaction whereby a catalyst is produced through the absorption of light. In the process, usually using semiconductors as photocatalysts, electrons and electron holes generated act as strong reductants and oxidants participating in redox reactions produce highly reactive free radicals for the complete conversion of almost any harmful, even recalcitrant, substances into non-toxic ones such as water, carbon dioxide, inorganic ions, or small organic molecules. Furthermore, the free radicals are able to inactivate microbial cells by damaging their cell wall, cytoplasmic membrane and intracellular structures. (Batoev, Batoeva &Tsydenova, 2015; Brouwers, Hendrix & Lazaro, 2015; Ghosh & Oh, 2012; Reusch, 2013). Titanium dioxide (TiO2) is the most widely studied and used semiconductor photocatalyst for purification of air and water because of its low cost, good chemical and physical stability, non-toxicity to humans and the environment, and convenience in production. It is efficient in breaking down wide variety of organic and inorganic compounds. However, as a photocatalyst, it suffers from charge carrier recombination losses and its photocatalytic activity is limited only to the ultraviolet spectra of light. To compensate for these weaknesses, other semiconductors are incorporated forming a composite. The addition of cupric oxide (CuO) - an abundant, easily-processed, non-toxic material with good optical properties – can serve as a co-catalyst or photosensitizer in the composite extending absorption of light to the visible spectra, a large portion of solar radiation. Silica, which is inert, mechanically and thermally stable, cheap and porous, can act as a support providing good stability and longevity to the photocatalyst and adsorptive characteristics for more efficient degradation of pollutants in water (Alabi et al., 2013; Fujishima, Rao & Tryk, 2000; Hendrix & Lazaro, 2015; Marschall, 2014). Photocatalytic reactors may be narrowed down into two major classifications: (a) reactors whose photocatalysts are suspended in the reaction mixture (slurry photoreactors); and (b) reactors whose photocatalysts are fixed on a carrier or support material (immobilized photoreactors). Slurry photoreactors are advantageous in a way that photocatalytic degradation occurs at a greater efficiency relative to the second type because of greater contact surface area for reaction. However, suspension of photocatalysts, such as TiO2 nanoparticles, would require additional processes after

water treatment in order to separate the TiO2 particles from the treated water. This separation step is important to be able to recycle or reuse the catalyst. Overall, the added processes make slurry photoreactors more complex and costly to operate. Immobilized photoreactors, on the other hand, do not pose this kind of problem because instead of the photocatalyst particles being freely dispersed in the fluid, they are held securely by a different support media such as a polymer film. The immobilized photocatalysts are also easier to reuse, and they are deemed to be effective and do not need replacement as long as their photocatalytic activity remains high (Moiza, 2010). In this regard, this study immobilized the photocatalyst composite in polystyrene. In the Philippines, out of 101 million Filipinos, 8.4 million rely on unimproved, unsafe and unsustainable water sources. Of this, 2.3 million use untreated surface water for drinking and 6.1 million use unimproved drinking water sources such as dug wells (Ager, 2015). This makes people more vulnerable to waterborne diseases. Escherichia coli is a pathogen that is commonly found in water. It is also known as thermotolerant fecal coliform and it dominates the total coliform present in feces of humans and animals, thus it serves an indicator of the presence water-borne disease-causing pathogens. Being an indicator, it generally has a similar response to disinfection compared to other pathogens which may also be present in water. Furthermore, the Philippine National Standards for Drinking Water (PNSDW) of 2017 identifies E. coli as a mandatory microbiological parameter. According to the PNSDW of 2017, total coliform and fecal coliform should both be less than 1.1 MPN per 100 mL. Ingestion of excessive amounts of E. coli in water can lead to diseases such as amoebic dysentery, typhoid, polio, cholera, and hepatitis (Tayone, 2015). Chlorination, a process where chlorine is used to eliminate disease-causing pathogens in water, is one of the conventional methods employed in the Philippines. Furthermore, the process helps to make water more palatable (Gonzales, 2014). However, harmful disinfection by-products (DBPs), such as chloroform, are generated from chlorination. In chlorinated tap waters, over 600 DBP's are produced. These are synthesized from reactions between chlorine and specific organic substances in the water, and have been studied to cause liver, kidney, colon, and urinary bladder cancers upon consumption in the long run (Gonzales, 2014).

The objective of this study was to determine the feasibility of using PS-TiO2-CuO-SiO2 photocatalyst composite in the inactivation of E. coli in groundwater by knowing the following:

- The effect of introducing CuO and SiO_2 to the photocatalytic ability of TiO_2 to inactivate *E. coli*;
- The effect of varying the volume of groundwater to be treated on the reduction of *E. coli* in groundwater;
- The number of consecutive times a single photocatalyst film can be used to produce groundwater whose *E. coli* concentration is within the standard of the PNSDW of 2017; and

The acceptability of the treated water within the PNSDW of 2017.

II. METHODOLOGY

A. Research design

In order to assess the feasibility of PS-TiO_2-CuO-SiO_2 photocatalyst in the inactivation of total coliform, specifically fecal coliform (E. coli), in water and the possibility of reducing them to standard values of the PNSDW of 2017, this research utilized an experimental design. Natural groundwater sample was collected from South Sanitary Camp, Baguio City. The water samples were analyzed without modifications initially before treatment and after 6 hours (8:00 to 14:00) of treatment using PS-TiO_2_CuO-SiO_2 composite as photocatalyst.

B. Study site

The study was conducted within the vicinity of the Chemical Engineering Laboratory and Natural Sciences Research Unit of Saint Louis University, Baguio City. The solar shallow pond photocatalytic reactor (SSPPR) with PS-TiO_2-CuO-SiO_2 composite was operated at the Chemical Engineering Laboratory where there is sufficient sunlight. Samples for pre-characterization and post-characterization of the groundwater were sent to the Regional Standards Testing Laboratory (RSTL) of the Department of Science and Technology – Cordillera Administrative Region (DOST-CAR), which is accredited by PAB ISO/EIC 17025:2005 LA-2009-131B &132B.

C. Instrumentation

For safe handling, processing and disposal of chemicals, respective Materials Safety Data Sheets (MSDS's) were utilized. Proper aseptic techniques were observed since the experiment involved pathogens and is microbiologically sensitive. Personal protective equipment (PPE) such as masks, gloves and laboratory coats were used to ensure the safety and health of the researchers. Properly calibrated laboratory equipment and tools were used for the experimental proper to ensure the accuracy and integrity of the data gathered. The experiment was done in ambient pressure and temperature in the said vicinities unless otherwise specified in the procedure. The collected groundwater was used without modification and was collected within 6 hours prior to the experiment.

D. Materials and equipment

Titanium dioxide with high purity was purchased from Craftology Essentials^{TM} located in Metro Manila, Philippines. Silica was bought from the local hardware store. Cupric oxide, ethanol, and xylene were available with high purity in the Chemical Engineering Department of Saint Louis University. Waste polystyrene was obtained from the locality. Materials for the construction of the SSPPR system prototype, such as glass, recirculating pumps, storage tank and flexible hose were also purchased locally.

E. Collection and storage of groundwater

The groundwater samples were collected within 6 hours prior to solar irradiation from an artesian well in South Sanitary Camp, Baguio City. The opening of the well was first exposed to a lit alcohol lamp for several minutes then sufficient amount of water was pumped and stored in plastic bottles. The container of the groundwater samples were washed with soap and water first, before washing with dilute hydrochloric acid. The containers were tightly sealed by the bottle caps.

F. SSPPR system prototype design and operation

The SSPPR system prototype was constructed from glass, recirculating pumps, water storage and flexible hose. The rectangular transparent glass, with a thickness of 0.015 m, serving as the main reactor has dimensions of 0.3 m by width, 0.6 m by length, and 0.06 m by height. The flexible hose was used to connect the glass reactor and the storage tank which has a capacity of 6 to 8 liters. Recirculating submersible pumps were used to control the volumetric flow rate and ensure constant circulation of the water through the system. The operating conditions other than the variables under study were kept constant.

G. Synthesis of photocatalyst composite powder

Three photocatalyst were prepared namely, PS-TiO_2 (P1), PS-TiO_2-CuO (P2) and PS-TiO_2-CuO-SiO_2 (P3). A control group with no photocatalyst was also used in the study. SiO_2 used in the experiment was finely ground using a pulverizer. For P1, 16 g of TiO_2 was used. For P2, 16 g of TiO_2 and 1.392 g of CuO were mixed together. For P3, 16 g of TiO_2, 1.392 g of CuO and 16 g of SiO_2 were used. In the preparation of P2 and P3 composites, the desired amounts of TiO_2, SiO_2 and CuO were weighed and mixed with 60 mL of ethanol. The mixture was then sonicated for 1 hour in a sonicator bath. Sonication was followed by 12 hours of continuous magnetic stirring. The dispersed suspension was then transferred to an evaporating dish situated on a hot plate at 100^{o}C to evaporate the ethanol. The dried solid was then transferred to a clay container before it was sent to a muffle furnace for calcination at 500^{o}C for 6 hours. The product solid was collected and crushed in a mortar and pestle and stored in a weighing bottle.

H. Synthesis of photocatalyst film

To immobilize the photocatalyst composite, 50 g of thoroughly-washed polystyrene (PS) was dissolved in 175 mL of xylene. The solid photocatalyst was suspended in a separate 25 mL of xylene. This suspension was stirred vigorously in a magnetic stirrer for 5 hours. The PS solution was then added to the stirred suspension and has been stirred vigorously in a magnetic stirrer for 5 hours. The mixture was then sonicated for 1 hour. The resulting mixture was spread evenly throughout the bottom of the glass reactor. The reactor was kept in a dark storage room for 4 days to completely evaporate the xylene from the film.

Irradiation and coliform testing of groundwater

The irradiation of groundwater samples was from 8:00 in the morning to 14:00 in the afternoon, during which the intensity of sunlight is highest. The groundwater samples were sent to DOST-CAR for coliform testing (total coliform and fecal coliform) before and after 6 hours of the treatment process. The standard multiple tube fermentation technique was used for microbiological testing.

III. RESULTS AND DISCUSSION

A. Effect of introducing CuO and SiO_2 with TiO_2 in the reduction of E. coli

In order to study the effect of composites on the photocatalytic efficiency in reducing total and fecal coliform (E. coli) concentration in naturally contaminated groundwater, CuO and SiO_2 were added progressively to TiO_2. The same groundwater was used for all the set-ups and the E. coli concentration before irradiation was 24,000 MPN/100 ml. Table I shows that the control group, without photocatalyst, and P1, showed no significant decrease in the amount of E. coli. This shows that TiO_2 alone did not significantly decrease the E. coli concentration in groundwater. On the other hand, the data show that the presence of CuO as in P2 positively contributed to the overall photocatalytic activity and thus reduced the E. coli concentration in groundwater after 6 hours of solar irradiation. It was then able to reduce the E.coli concentration by almost 100% from 24,000 MPN/100 ml to 4.6 MPN E.coli /100 ml. The efficiency was further enhanced by the introduction of SiO_2 in the composite. This suggests that a composite of PS-TiO_2-CuO-SiO_2 (P3) created a synergistic effect that resulted to the highest photocatalytic activity as shown. It was able to reduce the E.coli concentration by almost 100% from 24,000 MPN/100 ml to <1.1 MPN E.coli /100 ml.

TABLE I.: COLIFORM CONCENTRATION BEFORE AND AFTER IRRADIATION

Set-Up	MPN coliform/100 ml before irradiation	MPN coliform/100 ml after irradiation
Control	24,000	> 8
PS-TiO_2 (P1)	24,000	> 8
PS-TiO_2-CuO (P2)	24,000	4.6
PS-TiO_2-CuO-SiO_2 (P3)	24,000	< 1.1

The coliform concentration before treatment (24,000 MPN coliform/100ml) with the following set-ups are significantly higher than the PNSDW 2017 standard of <1.1MPN/ 100ml. This makes it suitable for disinfection. Control, P1 and P2 set-ups do not pass the standard. However, adding CuO in the composite makes the final coliform concentration closer to the standard. Only PS-TiO_2-CuO-SiO_2 photocatalyst composite was able to reduce the coliform concentration well within the PNSDW standard.

B. Effect of volume of groundwater in reduction of coliform

The coliform concentration before treatment (24,000 MPN coliform/100ml) with the following set-ups are significantly higher than the PNSDW 2017 standard of <1.1MPN/ 100ml. This makes it suitable for disinfection. Control, P1 and P2 set-ups do not pass the standard. However, adding CuO in the composite makes the final coliform concentration closer to the standard. Only PS-TiO_2-CuO-SiO_2 photocatalyst composite was able to reduce the coliform concentration well within the PNSDW standard.

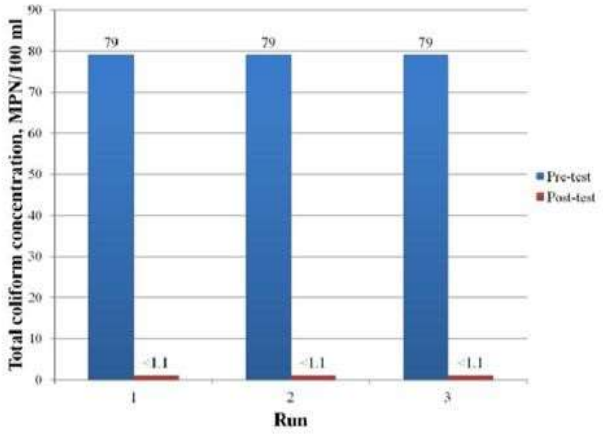

Figure 1. Total coliform concentration before and after solar irradiation with PS-TiO2-CuO-SiO2 when the volume of groundwater is varied

Increasing or decreasing the volume of water to be treated did not affect the efficiency of the photocatalyst as it was still able to reduce the coliform concentration well within the PNSDW of 2017 standard.

C. Reusability of PS-TiO2-CuO-SiO2 photocatalyst composite

The same photocatalyst was consecutively used for 7 times. The total coliforms and fecal coliforms have equal concentrations before treatment with PS-TiO2-CuO-SiO2 which means all coliforms in the sample are fecal coliforms. Before irradiation, a concentration of 79 MPN / 100ml coliform above the PNSDW 2017 standard was observed. After photocatalytic treatment, from runs 1 to 5, the coliform concentration was significantly reduced to <1.1 MPN / 100ml. An almost 100% decrease in coliform reduction was observed from these runs. However, from run 6 to 7, declines in coliform reduction were observed. From an almost 100% coliform reduction from runs 1 to 5, it decreased to around 96.71% on run 6 with a final concentration of 2.6 MPN / 100ml. Lastly, on run 7, the efficiency decreased to 89.87% with a final concentration of 8 MPN / 100ml. Beck et.al. as cited in Adishkumar et. al. (2015), stated two reasons for loss of activity throughout the consecutive reuse of photocatalysts. Accumulating adsorbed species on active sites and change of catalyst particle dimensions result to reduction of number of available active sites for photocatalysis.

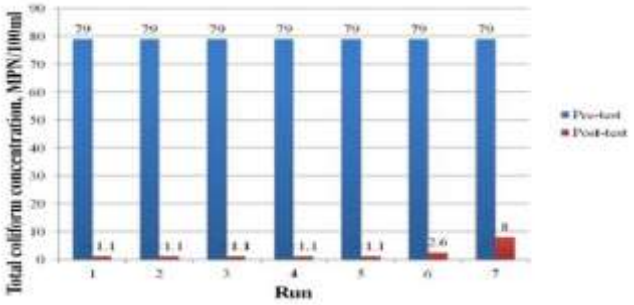

Figure 2. Total coliform concentration before and after solar irradiation after consecutive reuse of PS-TiO2-CuO-SiO2

Moreover, even if the photocatalyst was reused for five times as indicated from runs 1 to 5, the efficiency of the photocatalyst did not change and was still able to reduce the coliform concentration well within the PNSDW standard. However, after the fifth reuse, the coliform concentration is slightly above the PNSDW standard.

D. Discussion on efficiency of PS-TiO2-CuO-SiO2 photocatalyst composite

TiO2 alone did not significantly reduce the coliform concentration and is still above the PNSDW standard. This is because TiO2 is only limited to ultraviolet spectra, a small fraction, of sunlight and suffers from charge carrier recombination losses resulting to very low photocatalytic inactivation efficiency (Chen et al., 2011).

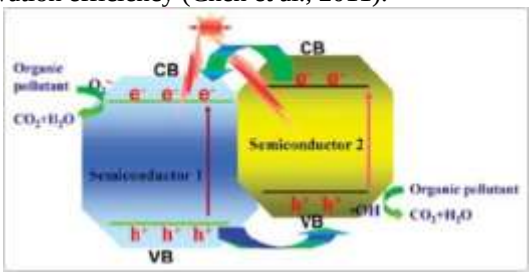

Figure 3. TiO2-CuO type II heterojunction

The addition of CuO, however, significantly increased the photocatalytic efficiency and showed dramatic reduction in coliform concentration under solar irradiation. Its introduction in the composite prevents charge carrier recombination losses and extends the photocatalytic activity in visible light spectra of the sunlight significantly increasing photocatalytic inactivation of E.coli. CuO has a band gap of 1.7 eV with its conduction band (CB) and valence band (VB) placed higher than TiO_2. Its narrow band gap can extend the absorption of the electromagnetic radiation in the visible light spectra. Specifically, since the solar radiation which is utilized in the study is largely comprised of visible spectra ranging from 400 to 800 nm, photocatalytic efficiency is optimized. Furthermore, because the CB and VB are placed higher than TiO_2, CuO can act as a co-catalyst following the mechanism of a type II heterojunction. This heterojunction prevents major charge carrier recombination losses (Marschall, 2014). All these effects contribute to a significant photocatalytic inactivation of coliform. The further optimization of efficiency is attributed to the

introduction of SiO_2 into the composite creating PS-TiO_2-CuO-SiO_2 photocatalyst. SiO_2 increases the adsorptive property of the composite film which is important for adsorption of water and pollutants which otherwise hardly adsorb to the film, a requisite for the generation of reactive oxygen species (ROS) and the inactivation of coliform itself. Since the study follows a heterogeneous photocatalysis, the pollutants and other necessary substances need to adsorb to the surface of the solid film before redox reactions occur that will result to the inactivation of the coliform. Silica, as an adsorbent, generates an "Adsorb & Shuttle" effect which adsorbs a reservoir of coliform to the solid film which can surface-diffuse near the photocatalyst particles which generate ROS (Paz, 2010).

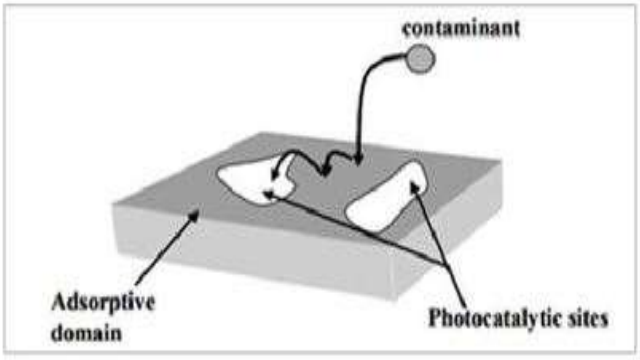

Figure 4. Concept of "Adsorb and Shuttle"

Despite all of the researches focusing on same concept of shallow pond photocatalysis and same manipulation of variables, Bajpai, Jotshi, Singh, Toor and Verma (2005) and Ray and Zhou (2003) both used TiO2 while this study uses a PS-TiO2–CuO–SiO2 composite photocatalyst. It has been agreed by several studies that composite photocatalysts are more efficient than their pristine counterparts. The overall success of the E.coli inactivation by photocatalyst composites can be well explained by the following reaction mechanism agreed upon by many proponents of photocatalysis:

$$\text{photocatalyst} + \text{light} \rightarrow \text{photocatalyst} + e^- + h^+ \quad [1]$$

$$OH^- + h^+ \rightarrow OH\bullet \quad [2]$$

$$H_2O \leftrightarrow OH^- + H^+ \quad [3]$$

$$O_2 + e^- \rightarrow O_2^- \quad [4]$$

$$O_2 + 2H_2O + 2e^- \rightarrow 2H_2O_2 \quad [5]$$

$$H_2O_2 + e^- \rightarrow OH^- + OH\bullet \quad [6]$$

Figure 5. Schematic view of the photocatalytic mechanism

This mechanism involves the following sequence: [1] generation of mobile charge carriers (electrons, e^- and electron holes, h^+) by photoexcitation using visible and UV spectra of sunlight; [2] charge carrier separation and diffusion to the photocatalyst surface enhanced by type II heterojunction between TiO2 and CuO; and [3] oxidation and reduction reaction on the catalyst surface to produce ROS which include hydroxyl radical (OH•), superoxide anion (O_2^-) and hydrogen peroxide (H_2O_2) (Marschall, 2014). OH• and O_2^- are the main agents for lipid peroxidation of E.coli. This results to loss of essential functions in the bacteria such as respiratory activity and bacterial lysis leading to bacterial death (Dalrymple, Stefanakos, Trotz, & Goswami, 2010). SiO2 supports the reaction mechanism [3] to create OH• by enhancing moisture adsorption of the composite.

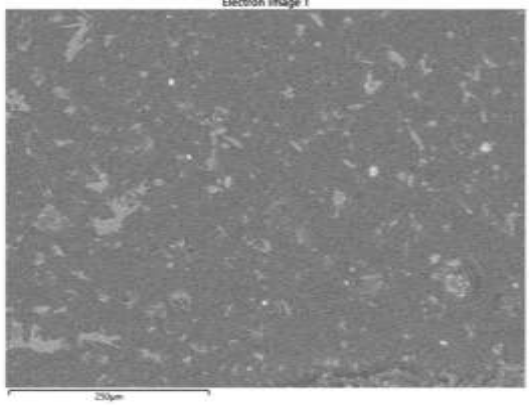

Figure 6. Microscopic state of the surface of the film taken by generating X-ray spectrum from the scan area using EDS

The elemental mapping show the distribution and relative proportion of each element over the area scanned. White "spots" seen on Figure 7 are areas in which oxygen and silicon atoms are more concentrated. Despite this, the four elements are relatively well distributed over the film which can be individually observed on Figure 7. The proper dispersion of the composite particles seen from the EDS elemental mapping is an evidence that simple indirect sonication is an effective method for homogeneous dispersion. The enhanced photocatalytic activity of the film could be attributed to this, since photocatalysis under the influence of visible light is increased with the presence of small and well dispersed particles of semiconductors, such as Ag2O and CuO (Duran-Alvarez, et al., 2017). This is because these particular conditions promote the lowering of the overall band gap of the CuO-TiO2 composite, enabling it to absorb and function well with solar light. Furthermore, simple sonication under suitable solvents which in this study, an ethanol solution with a pH around 7 was used since this pH is below the pH corresponding to the ZPC (9.5) of CuO while above the pH corresponding to the ZPC (around 6) of TiO2 ("point of zero charge," n.d.; Preo~anin & Kallay, n.d.). This concept is important to createan effective heterojunction between CuO and TiO2. This heterojunction which was discussed earlier is critical for an optimal photocatalytic inactivation of coliform.

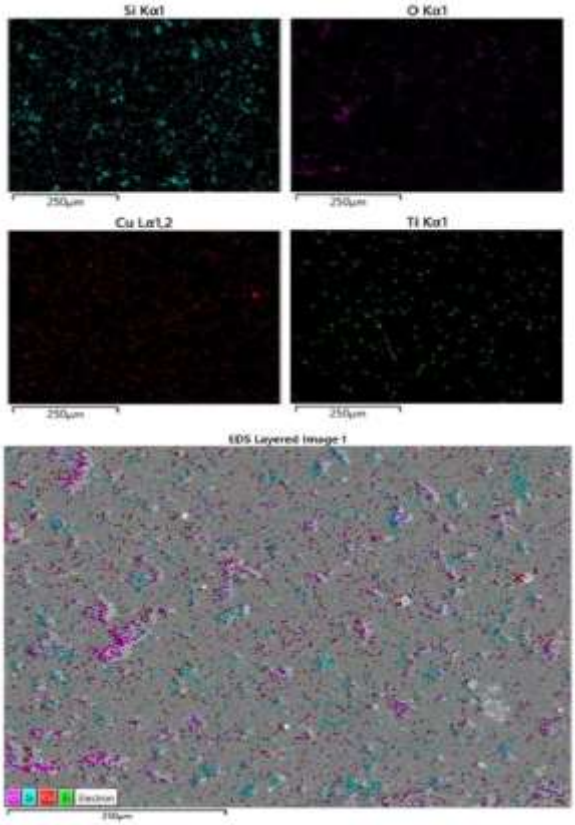

Figure 7. Elemental mapping (Si, O, Cu and Ti) over the area scanned using EDS

IV. CONCLUSION AND RECOMMENDATIONS

The results of this study showed that introducing CuO and SiO_2 to TiO_2 enhanced its photocatalytic ability in inactivating *E. coli* in water. The efficiency of this photocatalyst composite was also studied to be unaffected by increasing or decreasing the volume of water to be treated by it. With this, the composite has potential not only as a point-of-use water disinfection alternative but also for large-scale applications. Furthermore, the photocatalyst composite can be reused for a maximum of 5 consecutive times while maintaining almost 100% percent efficiency in inactivating *E. coli* in groundwater. Overall, the PS-TiO_2-CuO-SiO_2 photocatalyst composite is a potent disinfectant of *E. coli* in groundwater and can be used to convert naturally non-potable groundwater to safe drinking water without the risk of generating disinfection by-products.

ACKNOWLEDGMENT

This study was made possible with the help of the laboratory custodians and faculty members of the Chemical Engineering Department, Mining Engineering Department and Natural Sciences Research Unit of Saint Louis University – Baguio City, Philippines. We would also like to extend our gratitude to Engr. April Mae Patac of Mariano Marcos State University - Ilocos Norte for providing help in obtaining the characterization of the film used in the study. Lastly, we thank the Department of Science and Technology – Cordillera Administrative Region (DOST-CAR) for giving assistance for the testing of the water samples used in the study.

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