

UV PHOTOCATALYSIS AND METAL DOPED TITANIUM DIOXIDE: ELIMINATION OF *E. COLI* AND *S. AUREUS* IN WATER

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Abstract: Photocatalysis has been widely used for water disinfection and wastewater treatment. UV photocatalysis induced bacteria photocatalytic disinfection, focusing on mechanisms in bacteria inactivation. The problem with industrial wastewater is that it generally contains a high concentration of toxic or non-biodegradable pollutants. The application of photocatalysis is mainly focused on the removal of microorganisms. Metal-doped TiO₂-based photocatalyst has a significant potential for the inactivation of harmful pathogens. In this research, the effect of different metal-doped on photocatalytic disinfection against *Escherichia coli* (*E. coli*) (gram-negative) and *Staphylococcus aureus* (*S. aureus*) (gram-positive) under UV light was investigated. TiO₂ was used and doped with various types of metal such as copper (Cu), cobalt (Co), and iron (Fe). The experiments were run under UV light with 1 g/L of selected metal-doped for up to 3 hours. A series of photocatalytic disinfection on *E. coli* and *S. aureus* were conducted on water contamination with 500 mL of trypticase soy broth (TSB) and 5 ml of bacteria. These results show that the UV photocatalyst with Cu doped-TiO₂ gives 99% of *E. coli* disinfection. While for *S. aureus* disinfection Co-doped-TiO₂ gives 96% of removal bacteria after 3 hours of treatment. In conclusion, a metal-doped TiO₂-based UV photocatalytic system is highly recommended for improving the water decontamination process.

Keywords: Metal-doped, titanium dioxide, UV photocatalysis, *Escherichia coli*, *Staphylococcus aureus*, disinfection.

Introduction

Water pollution is a major problem affecting current societies and can harm human health. Domestic, industrial and military activities create a large amount of organic and inorganic pollutants daily that inevitably end up in the environment (Haider *et al.*, 2017). Furthermore, viruses and bacteria are common contamination water resources of biological micropollutants that result from human activities. The biological micropollutants are the source of most waterborne diseases and remain the major cause of death globally (Gavrilescu *et al.*, 2015). The sources and pathways of those emerging pollutants are increasingly related to the waste and wastewaters from domestic, agricultural or industrial activities. Haider *et al.* (2017) stated that continuous exposure to those contaminants might result in various health issues, like

irritations and toxic effects, as well as other common respiratory and skin diseases. Chlorine, ozone, dioxide and chloramines are the common disinfectants which will produce carcinogenic disinfection by-products (DBPs). Pathogen inactivation can be desirous of environmental disinfection methods to reduce the formation of DBPs (Shang *et al.*, 2011). The pathogen inactivation demand in water can be utilised in various disinfection technologies. The chemical disinfectants could also be overused or misused; they can react with organic and inorganic precursors and cause the formation of DBPs which will cause adverse effects (Collivignarelli *et al.*, 2018). Most physicochemical techniques and usual cleaning procedures are inactive to eliminate the microbes.

E. coli and *S. aureus* are highly contagious pathogens that commonly cause gastrointestinal

diseases and contagious diseases in humans (Shang *et al.*, 2011). A growing concern for public health and environmental quality was created with great interest in developing and implementing varied materials and methods for disinfecting pathogenic bacteria in the water. Bacteria are established as a crucial source of pollution among all microbes. Among a large range of bacteria, an example, *E. coli* coliform is understood as an indicator of polluted water since its appearance indicates faecal water contamination generally (Laxma Reddy *et al.*, 2017).

Photocatalysis technology as energy-saving modern sewage and new high-efficiency treatment technology has many advantages in wastewater treatment. A photocatalyst is often used to decontaminate wastewater containing organic pollutants (Zhang *et al.*, 2019). This process uses a catalyst to speed up chemical reactions that need or consume light. The photocatalysis formation occurs when it is exposed to the light of the specified wavelength, then the energy of the photons is absorbed by an electron (e-) of the valence band and is exciting to the conduction band. The valence band will create a hole (h+). This will form the photo-excited state where the e- and h+ pair is generated (Byrne *et al.*, 2018). The excited electron is employed to reduce an acceptor, a hole used to oxidise donor molecules. This reaction will produce hydroxyl radicals ($\bullet\text{OH}$) and hydrogen ions (H+). The importance of photocatalysis is that a photocatalyst gives both the oxidation and reduction processes at the same time. Many semiconductor types like zinc oxide (ZnO), titanium dioxide (TiO_2), and tungsten oxide (WO_3) are utilised in such applications. The characteristic affects the production of electron-hole pairs, surface adsorption-desorption and the redox process by the photocatalytic activity of TiO_2 . There are influenced by the crystal structure, the surface area, size distribution, porosity, surface hydroxyl group density, etc. (Crişan *et al.*, 2018).

TiO_2 receives widespread attention among all semiconductor photocatalysts as a promising

photocatalyst due to its superior characteristics like non-toxicity, chemical stability, highly photocatalytic activity, and potential to be layered as a thin film on a substrate, eco-friendly (Tsang *et al.*, 2019). The main feature of TiO_2 is the oxidative power of hydroxyl radicals produced when the electrons are photoexcited by UV light absorption (Avilés-García *et al.*, 2018). It has been considered one of the ideal energy and environmental photocatalysis.

One of the modifications of photocatalyst known as doping is a process that decreases the band gap between the valence band and the conduction band by adding impurities to the pure semiconductor. Mathew *et al.* (2018) state that the efficient approach is the elemental doping to resolve the TiO_2 band gap by introducing new energy levels between the conduction band minima (CBM) and valence band maxima (VBM). Doping titanium with metallic and non-metallic elements is another way to boost the TiO_2 photocatalytic efficiency and alter the absorption toward the visible light region (Fiorenza *et al.*, 2018). In this regard, cationic dopants served to increase the visible light absorption and enhance the heat stability of the anatase phase TiO_2 . However, when employing a 'dopant,' it can alter the properties of the samples, including the structure, which can contribute to photocatalytic activity degradation (Byrne *et al.*, 2018).

According to Ameta *et al.* (2018), each dopant has its unique effect on the connection network. Material and non-metal contamination improve the photocatalyst's reaction to the visible region by creating a brand new level of energy between the valence band and conduction band. The excited electrons are shifted from the impurity state to the conduction band and these new levels decrease the band gap (Ameta *et al.*, 2018). The photocatalytic applications will improve effectively if doped TiO_2 to several transition metals like Fe, Cu, Ni, Cr and Co (Sadanandam *et al.*, 2013). Metal dopants enhance photocatalytic semiconductors electronic and magnetic properties, morphology, photocatalytic performance, and surface area.

Therefore, this work aims to research the photocatalytic disinfection of metal-doped TiO_2 . Among these metals, this research will study and evaluate metal-doped like Cu-doped TiO_2 , Co-doped TiO_2 , and Fe-doped TiO_2 . It also determines the photocatalytic disinfection efficiency of metal-doped TiO_2 against gram-positive and gram-negative bacteria in an aqueous environment.

Materials and Methods

Photocatalysts Synthesis

Four types of photocatalysts powder were synthesised as shown in Figure 1, which are Cu- TiO_2 , Co- TiO_2 and Fe- TiO_2 and TiO_2 blank. Photocatalysts were prepared using different methods and doped using different metal oxides. The dried samples were characterised with the analytical technique using X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM).



Figure 1: Photocatalyst powder (A) blank TiO_2 , (B) Fe- TiO_2 , (C) Cu- TiO_2 and (D) Co- TiO_2

Titanium Dioxide

The mixture of 0.34 mol titanium isopropoxide (Aldrich, 97%) and 2.72 mol isopropanol (Sigma-Aldrich, 99.5%) is mixed under constant stirring at room temperature. The mixture was stirred for 2 hours to undergo a hydrolysis process to form a homogeneous solution. Under constant stirring, the mixture of 0.374 mol distilled water and 0.017 mol acetic acid (Sigma-Aldrich, $\geq 99.7\%$) is added dropwise to the hydrolysed mixture. When the mixture has turned cloudy, 1.02 mol acetylacetone (Sigma-Aldrich, 99%) is

added and stirred for another 30 minutes. As a result, the stability of the mixture is increased and can last for a few months. The mixture is sealed and allowed to age for a minimum of 24 hours.

Copper-Titanium Dioxide

40 mL of titanium isopropoxide (TTIP) stirred in 200 mL of isopropanol for 15 minutes (Solution A). The required amount of copper sulphate was mixed with 200 mL of deionised water and the mixture was stirred for 15 minutes (Solution B). The ratio of both solvents was kept

constant. Then, solution B was added dropwise to solution A under vigorous stirring. After that, the mixture was kept for gelation for 2 hours at room temperature. The resulting gel was dried in an oven at 100 °C for 12 hours. The powder was then calcined at various temperatures of 650 at a ramp rate of 10 °C/min for 2 hours. Pure TiO₂ was also synthesised by the same procedure without adding copper sulphate and calcined at two different temperatures, 650 to obtain pristine anatase and rutile samples, respectively. These samples were used as a control for all further experiments.

Cobalt-Titanium Dioxide

A mixture of 20 mL titanium (IV) isopropoxide, Ti(OC₃H₇)₄, 20 mL ethanol and 1.62 mL acetylacetone was prepared and stirred for 30 minutes at room temperature. Then, a new mixture containing X mg CoCl₂·6H₂O (X: 800 mg), 80 mL ethanol and 2 mL H₂O was added to the first solution, leading to a coloured solution. This solution was moved into an autoclave and then heated to 240 °C at a ramping rate of about 2 °C/min. Finally, the temperature was retained at 240 °C for 6 hours. After cooling, the obtained solid was washed with ethanol and water and dried at 100 °C for 2 hours at room temperature.

Iron-Titanium Dioxide

The Fe doped TiO₂ nano-powder was prepared by sol-gel method using titanium (IV) isopropoxide

(TTIP) as a titanium precursor. Mixed 4.5 mL of TTIP, 21 mL of ethanol, 3.5 mL of distilled water and FeCl₃ with the molar ratio Fe/TTIP equal 10% (w/w). The obtaining sol was stirred at room temperature for 4 hours. The Fe-doped TiO₂ formed during the stirring. The nano-powder is obtained after the sample is filtered and desiccated overnight at room temperature. Finally, TiO₂-Fe powder was calcined at 500 °C for 1 hour.

Disinfection Experiments

The experiment was started by culturing the bacteria (*E. coli* and *S. aureus*) from the trypticase soy agar in the petri dish for 1-2 days. The bacteria were grown under aerobic conditions at 37 for 24 hours in a trypticase soy broth medium. 5 mL of cultured *E. coli* with an initial concentration of approximately 10⁹ CFU/mL was inoculated in the reactor containing autoclaved in a growth medium for 24 hours. After 24 hours on the orbital shaker, the solution must be centrifuged twice and rinsed with saline solution. The remaining solution was removed and the “pallet” was left in the tube. Next, the pallet that contained bacteria was added with the new solution of TSB and underwent the experimental process. The experiment was continued with the photocatalytic disinfection by using 100-200 pieces of TiO₂ with metal dopants under UVC light in Figure 2. The experiment was conducted for about 3 hrs.

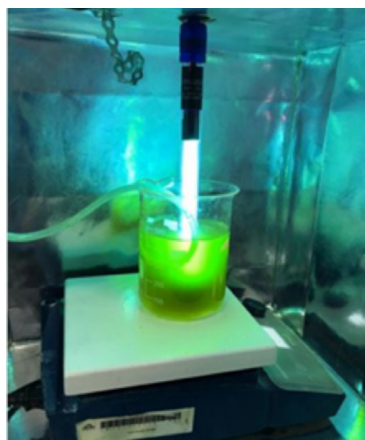


Figure 2: Photocatalytic under UVC light

Next, the sample was used to determine Colony Forming Unit (CFU) and cell viability by

plate count method, as shown in Figure 3. After detecting the CFU of bacteria, the efficiency of TiO_2 with metal dopants was determined.

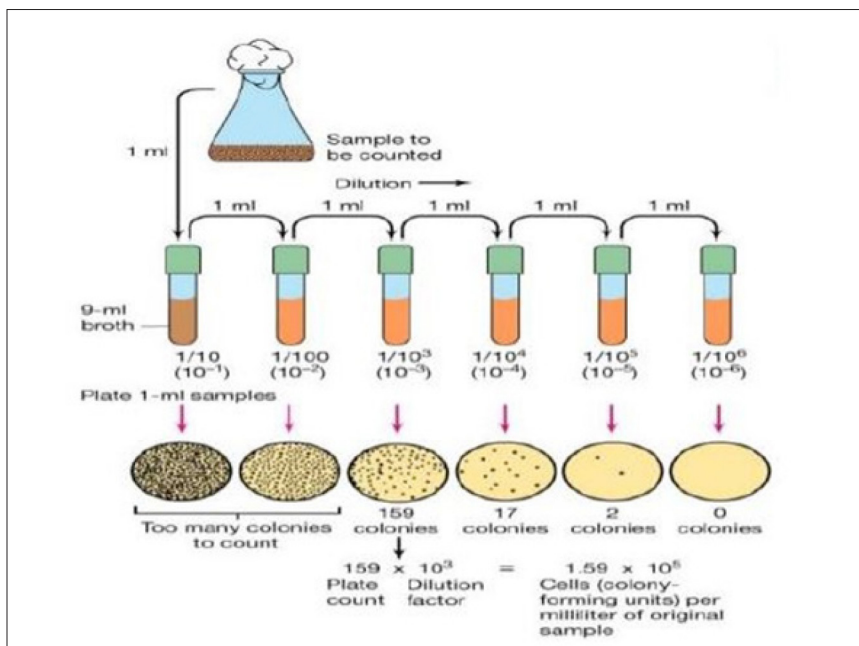


Figure 3: Serial dilution techniques & Plate count method

Results and Discussion

X-Ray Diffraction Analysis

X-ray diffraction analysis (XRD) was run to determine the preferred orientation, crystallographic structure and grain size of a crystalline materials and can be used to identify crystalline species in materials. The profile of the four samples is shown in Figure 4(a) for blank titanium, (b) for titanium doped copper, (c) for titanium doped cobalt and (d) for titanium doped iron. The profile for blank titanium in Figure 4(a) of 2θ at peak 25.4° approves the TiO_2 anatase structure. Furthermore, strong diffraction peaks at 25° and 48° indicate TiO_2 in the anatase phase. Furthermore, the profile for titanium

doped with copper in Figure 4.0(b) shows at a calcination temperature of 500°C and without diffraction peaks fit into the anatase phase. It can be expected that the anatase phase of TiO_2 completely converts to the rutile phase at 500°C . Next, XRD configurations titanium doped with cobalt in Figure 4.0(c) shows the characteristic peaks appeared in the 2θ angles of $25.4, 37.1, 37.8, 38.6, 48.2, 54.0, 55.1, 62.8, 68.9, 70.3,$ and 75.2 respectively and the results can be readily indexed to anatase phases. As shown in Figure 4.0(d), XRD profile titanium doped with ferum shows that there are no diffraction peaks of the rutile phase and iron-related crystal phase in the XRD pattern, which shows that the doping of Fe^{3+} does not alter the crystal structure of TiO_2 , and Fe^{3+} does not form a phase alone.

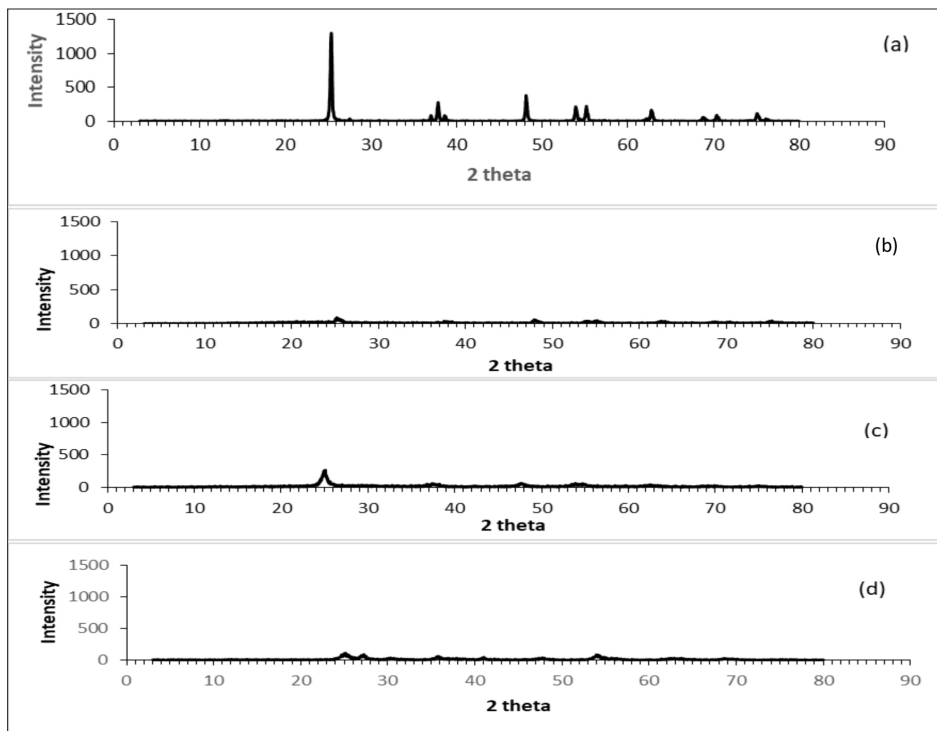


Figure 4: XRD profiles of (a) blank titanium, (b) titanium doped copper, (c) titanium doped cobalt, (d) titanium doped iron

Scanning Electron Microscope

SEM analysis was administered for two dimensions of 50 μm and 100 μm . Figure 5.0 shows SEM analysis for (a) blank titanium, (b) titanium doped with copper, (c) titanium doped with cobalt and (d) titanium doped with iron. SEM images show that each one of the samples is slightly agglomerated, which is more intense as regards the doped samples. SEM analysis of nano titanium oxide powder shows that the sample contained needle-like particles. The asymmetric particle size distribution verifies that

titanium powder comprises more grains, which retain their size less than the typical value. The titanium-doped copper samples appeared as agglomerates of smaller particles. Next, the morphology of the TiO_2 powder of titanium doped with cobalt showed that the agglomeration of particles creating large clusters could be seen in Co-doped samples. The tiny particles are agglomerated and bound to the spherical shape because of cobalt doping. For titanium doped with iron with this catalyst, iron oxide content can be observed in the combination of fine particles and bulk TiO_2 .

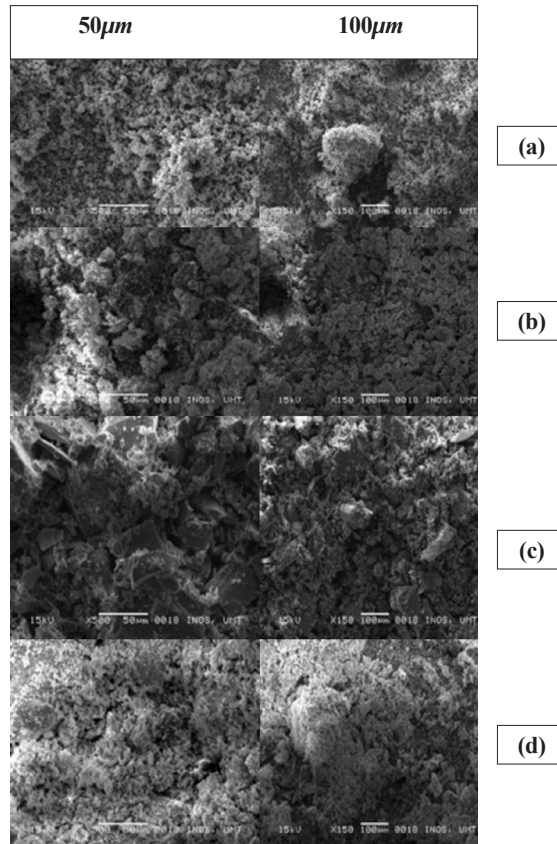


Figure 5: SEM images of (a) blank titanium, (b) titanium doped copper, (c) titanium doped cobalt, (d) titanium doped iron

Control Experiment

Figure 6 shows the graph of the *E.coli* control experiment with three different conditions: with catalyst without lamp, with lamp without

catalyst, and without the presence of both lamp and catalyst. In Figure 6, negative hours represent the bacteria of that condition are in the dark phase. The dark phase represents time without UVC light.

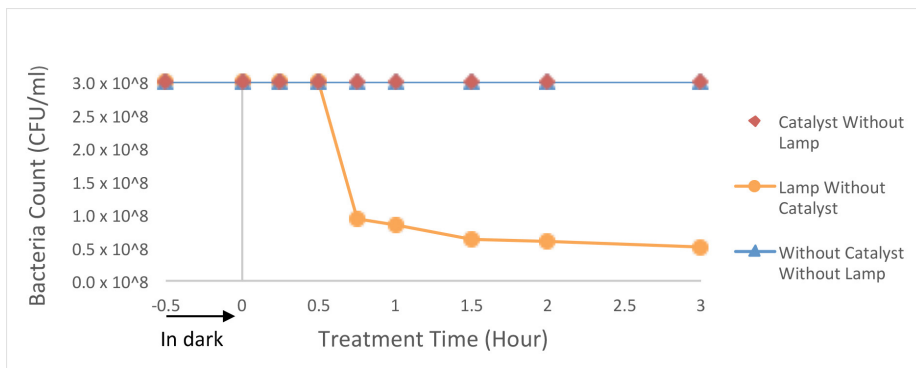


Figure 6: Bacteria Count (CFU/ml) vs Treatment Time (Hour) of *E.coli* control

Figure 6 shows no changes in bacteria numbers in the condition ‘with catalyst without lamp’ and ‘without catalyst without lamp’. Because the photocatalytic does not occur due to the absence of UVC light, there is no disinfection.

The condition of with lamp but without catalyst shows the decline as the time passed in 3 hours. It could be assumed that the bacteria were disinfected quickly when the UVC light was turned on after 30 minutes. The degradation of bacteria concentration could be seen in the first hour until the final hour when the results were obtained (3.0×10^8 cfu/ml) and decreased to (0.051×10^8 cfu/mL). UVC light causes the greatest inactivation of bacteria.

According to Yin *et al.* (2013), UVC light has the most effective potential to deactivate microorganisms because the wavelength of 250-270 nm is intensely and mostly absorbed by microbial cell nucleic acids and is, therefore, the most harmful wavelength range. It is due to the presence bactericidal mechanism of UVC that can cause damage to the RNA and DNA of bacteria. This may cause deformation of the DNA molecule which defects cell replicate and subsequently result in necrobiosis. UVC light damages DNA to induce pyrimidine dimers, deters cell propagation, causes apoptosis, and eventually induces necrobiosis. UVC light has the strongest bactericidal effects, mainly around 254 nm of UVC absorbed by DNA.

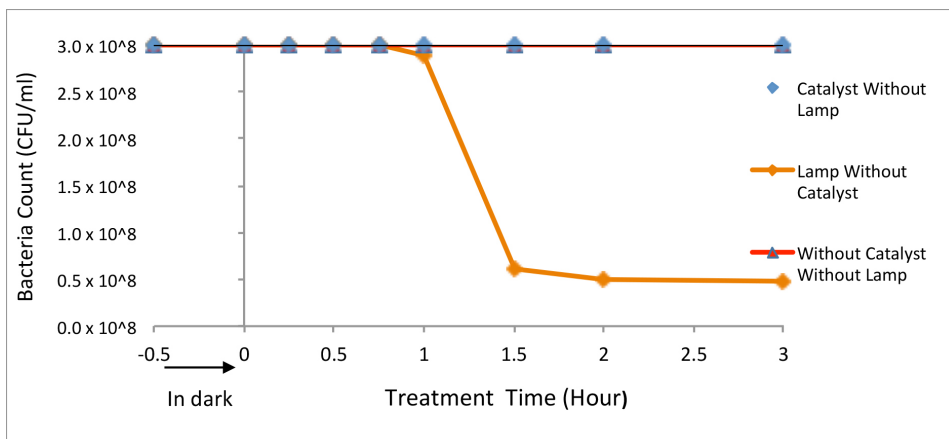


Figure 7: Bacteria Count (CFU/ml) vs Treatment Time (Hour) of *S. aureus* control

Three different conditions of *S. aureus* control were represented, with a result shown in Figure 7. The control conditions ‘with catalyst without lamp’ and ‘without lamp, without catalyst’ shows the consistent result at (3.0×10^8 cfu/mL). The absence of the UVC light caused the degradation of bacteria concentration not to occur.

The condition of ‘with lamp without catalyst’ declined as the time increased. It shows the degradation bacteria concentration in the final hour of treatment time because they were degraded from (3.0×10^8 cfu/mL) to (0.0048×10^8 cfu/mL).

These results show the importance of UV lamp in photocatalytic activity. According to Ibhaddon & Fitzpatrick (2013), the photoreaction is initiated by the light source and semiconductor material and the catalyst system simultaneously performs oxidation and reduction reactions using UV light. Studies show that UVC irradiation is extremely bactericidal, a significant advantage of using UVC as it can destroy resistant and pathogenic microorganisms way faster.

Photocatalytic Disinfection

This work aimed to determine the disinfection performance of titanium dioxide and TiO_2 on three different metal dopes: copper, cobalt and

iron, against gram-negative bacteria *E.coli*. The photocatalysis experiments were conducted to obtain the results. Through these performances, it can be seen how the effectiveness of the metal-doped for disinfection of the bacteria. Figure 8 showed that all metal-doped reacted with the bacteria during the photocatalysis experiment since the concentration of bacteria decreased as the time increased. From the observation,

the most effective metal-doped is copper-doped with titanium dioxide. From the Figure 8.0 the initial concentration at (3.0×10^8 cfu/mL) decreased to (0.001×10^8 cfu/mL). From the observation in Figure 9, titanium dioxide doped with copper shows the highest performance of killing bacteria which is 99%. This is because 95% of them were disinfected in 60 minutes and reached 99% removal efficiency during the third hour of treatment.

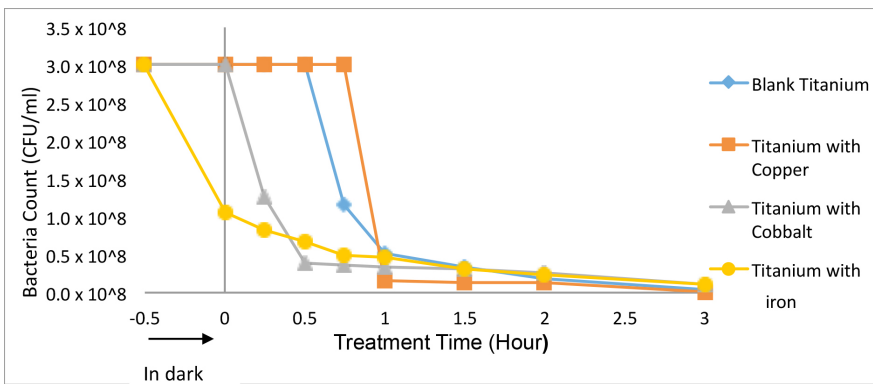


Figure 8: Bacteria Count (CFU/mL) vs Treatment Time of Disinfection *E. coli*

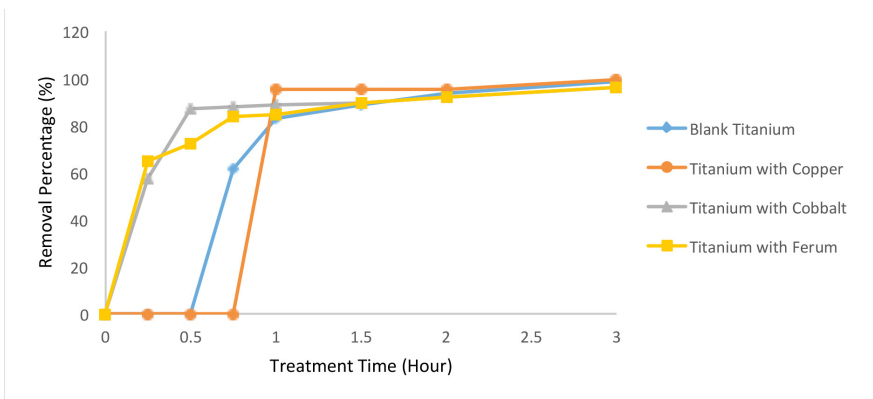


Figure 9: Removal Percentage (%) vs Treatment Time of Disinfection of *E.coli*

For removal percentage of Cu-TiO_2 at 180 minutes is 99.97%. However, the overall performance of blank titanium hits 98% of disinfection efficiency and could be assumed to be the second-highest performance disinfection of *E.coli*. The bacteria cells were disinfected when the initial concentration (3.0×10^8 cfu/mL) decreased to (0.004×10^8 cfu/mL).

Compared to Co-doped-TiO_2 , the disinfection efficiency was about 96% during the three hours treatment time. As the least effective metal dopes, bacteria concentration was degraded by about (0.011×10^8 cfu/mL). At the same time, Fe doped-TiO_2 performs similarly to cobalt metal. The bacterial with initial concentration (3.0×10^8 cfu/mL) decreased to (0.011×10^8 cfu/mL).

cfu/mL). The disinfection efficiency for Fe doped-TiO₂ was about 96% during the treatment time. Mostly, bacteria cells were destroyed by this photocatalytic activity for 180 minutes. Therefore, it considers Cu doped-TiO₂ as the effective metal for killing the *E.coli* bacteria.

According to Backhaus *et al.* (2010), the gram-negative pathogen was more sensitive to photocatalytic disinfection than the gram-positive pathogen. The disparities are because of dissimilar cell surface structures between gram-negative and gram-positive bacteria. The cell walls of gram-negative bacteria are thinner, around 12 nm but have triple-layered. Some studies reported that gram-negative bacteria are

more resilient than gram-positive bacteria to the antimicrobial effects of TiO₂ (Lopez de Dicastillo *et al.*, 2020). Furthermore, the relation between the ratio of deactivating bacteria or actual antimicrobial activity by TiO₂ is influenced by the initial bacterial concentration and bacterial population throughout inactivation (Wang & Xu, 2012). This is because when the initial bacteria population is high, many dead cells and mineralisation yields are produced throughout the reaction process, while when initial bacteria concentrations are low, the main disinfecting efficiency is reduced (Rincón & Pulgarin, 2004). Therefore, it considers Cu doped-TiO₂ is the effective metal for killing the *E.coli* bacteria.

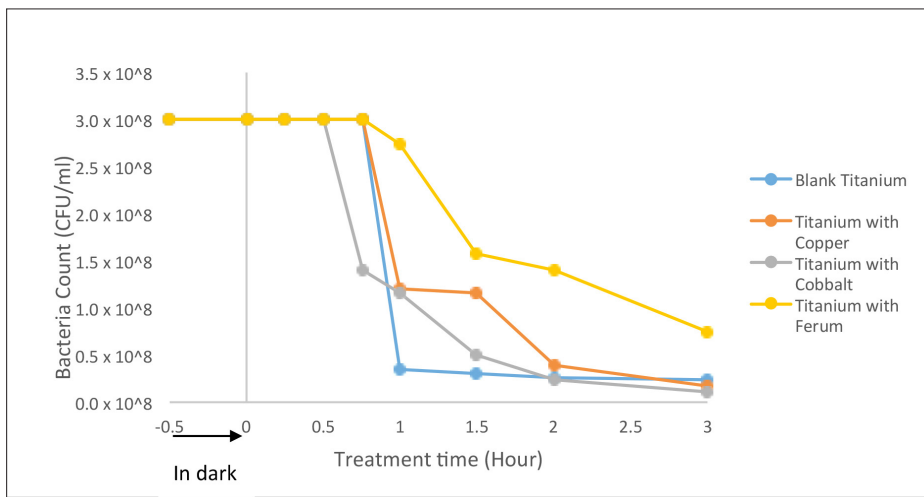


Figure 10: Removal Percentage (%) vs Treatment Time of Disinfection of *S. aureus*

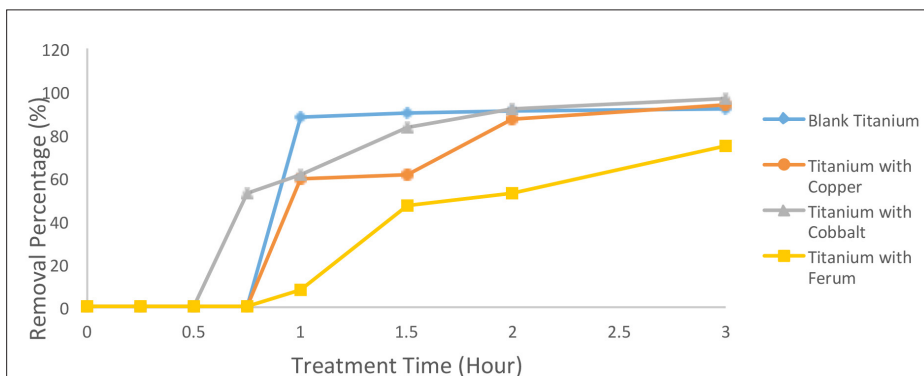


Figure 11: Bacteria Count (CFU/mL) vs Treatment Time of Disinfection *S. aureus*

Figure 10 shows the photocatalytic activity that occurred when the concentration of bacteria of *S. aureus* declined tremendously. While Figure 11 shows the percentage of bacteria with a treatment time of disinfection of *S. aureus*. Fe doped-TiO₂ decreased from (3.0 x 10⁸ cfu/mL) to (0.0075 x 10⁸ cfu/mL) which is about 75% of disinfection efficiency in 3 hours treatment time. Next, blank titanium shows the inclined of disinfection efficiency, which is 92% during the third hours period and bacteria concentration was degraded from (3.0 x 10⁸ cfu/mL) to (0.0023 x 10⁸cfu/mL). Besides, the metal-doped copper showed second highest of removal percentage bacteria with initial concentration (3.0 x 10⁸cfu/mL) decreased to (0.0017 x 10⁸ cfu/mL) and the final efficiency was 94%. However, Co-doped-TiO₂ showed the highest performance since the bacteria were killed 96% for 3 hours of treatment time. The result of final concentration recorded with (0.0011 x 10⁸ cfu/mL). According to Venieri *et al.* (2017), microbes play an important role in photocatalysis. Gram-positive bacteria *S.aureus* has a thick cell membrane comprising many layers of peptidoglycan and

teichoic acids, which successfully provides resistance during photocatalytic treatments and the generation of reactive oxygen species. Some studies also reported that the gram-positive bacteria were more sensitive than gram-negative bacteria (Barnes *et al.*, 2013). According to Laxma Reddy *et al.* (2017), metal doping can improve photocatalysis effectiveness by forming intermediate bands. The photocatalytic characteristics of TiO₂-based materials rely on improved light absorption as the formation of hydroxyl radicals (Laxma Reddy *et al.* 2017b).

Reduction of Bacteria

The photocatalyst treatment inactivation of *E.coli* cells was carried out in 180 minutes, as shown in Figure 12. The copper doped with TiO₂ shows the efficient killing of the bacterial raw condition of >300 colonies during 0 hour. During 1.5 hour, the reductions of total bacteria are 14 colonies. However, the experiment shows the highest degradation of bacteria within treatment time of 3 hours with the last hours of treatment showing only 1 colony detected, and Cu-doped TiO₂ showed the highest performance since the bacteria were killed by 99%.

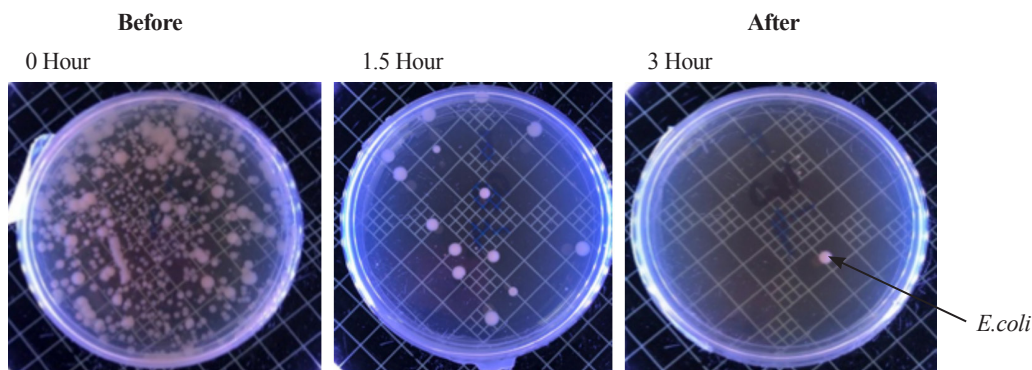


Figure 12: Reduction *E.coli* of Cu-TiO₂ after three hours of treatment time

The results showed the photocatalytic disinfection of *S. aureus* when it was doped with metals for 180 minutes. According to the results, the most effective catalyst, cobalt-doped TiO₂. It can be seen in the raw condition of the petri dish area showed that bacteria appeared mostly in more than 300 colonies. Figure 13 shows a

reduction of *S. aureus* of Co-TiO₂ after three hours of treatment. The 1.5-hour treatment time shows the reduction process with 50 colonies of *S.aureus*. During the process, the bacterial colonies slowly showed the degradation process until the end of treatment time, with the cobalt-doped giving the highest efficiency with 96% removal of bacteria.

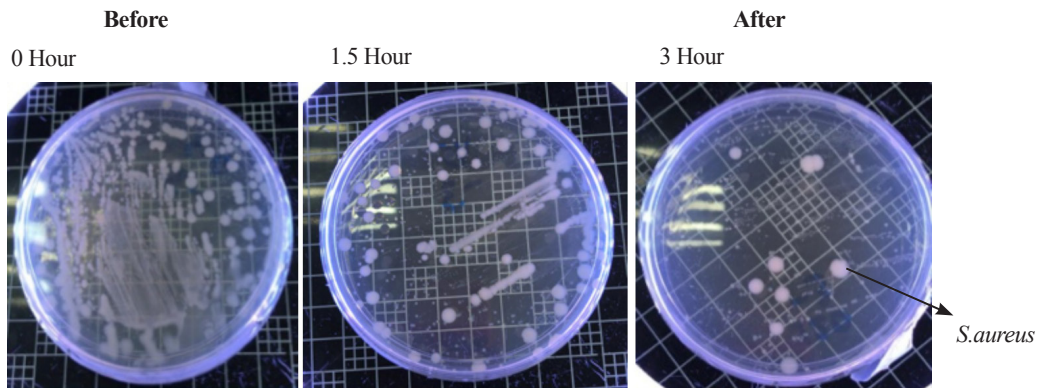


Figure 13: Reduction *S. aureus* of Co-TiO₂ after three hours of treatment time

Conclusion

It can be concluded that Gram-negative bacteria, which is *E. coli* were disinfected by the photocatalytic activity and shows the different effects of metals doped performances. It was shown that the Cu-doped TiO₂ produced the highest efficiency of photocatalytic disinfection since this metal doped photocatalyst killed approximately 99% of bacteria within three hours of treatment time. The photocatalytic disinfection efficiency of metal-doped TiO₂ against Gram-positive bacteria such as *S. aureus* were disinfected by the photocatalytic activity and showed the different effects of metal-doped performances. The highest photocatalytic disinfection efficiency was 96% produced by the performance of Co-doped TiO₂ for 180 minutes. In conclusion, a metal-doped TiO₂-based UV photocatalytic system is highly recommended to improve water decontamination.

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