DYE INDICATOR FOR THE EFFECTIVENESS OF TiO_2 WATER PURIFICATION

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ABSTRACT

The potential of an oxidation sensitive dye as a clear and real time indicator of the effectiveness of a titanium dioxide solar water purification system was explored with Indigo carmine selected as the best candidate. A pill created using food grade Methocel™ (hypromellose) as a binder was used for transport and controlled rate of release. Experiments were performed to determine the correlation between dye color change and bacterial destruction. The dye was found to be a conservative measure of bacterial destruction as full color change from blue to clear occurred well after the bacteria was destroyed in normal tests. Further there are no anticipated health effects due to the ingestion of these pills as the materials are FDA approved food additives. Additionally the binder does not support bacteria growth and does not degrade the TiO_2 film on the bottle. The pill cost of less than one cent makes it economical.

1. INTRODUCTION

Water is arguably the most important resource we have. Estimates are that more than 1.2 billion people in the world do not have access to clean water (UNDP, 2006). One approach to disinfection of drinking water is using plastic bottles and exposing water to the sun with the SODIS method (EAWAG, 1998). Recent work has involved using TiO2 as a photocatalyst to destroy in addition to bacteria (e.g., Maness et al., 1999), other contaminants such as pesticides and arsenic in plastic bottles with TiO2 (e.g., Litter et al., 2005; Heredia and Duffy, 2007). One potential drawback to these promising methods is the difficulty for the user to tell when the water is suitable to drink, particularly when solar irradiation is less than constant and at a high level.

The objective of this study is to develop a visual indicator that enables a user to test a bottle (or tank for that matter) for microbial destruction without time-consuming and potentially expensive biochemical testing of microbial kill rate. Steps to accomplish this objective included choosing a suitable dye that is safe, inexpensive, and relatively transparent in the UV range; developing a delivery mechanism for the dye; and testing its effectiveness.

Indigo carmine dye is a safe and economical chemical to use as a visual indicator. It is an ingredient used in food dye, and it is used in high school chemistry classes, making it an accessible substance and one that is relatively inexpensive. The dye is sensitive to the production of hydroxyl radicals, which are the byproduct of photolysis. It is similarly these radicals that are responsible for the destruction of organic compounds in water. Because both processes are dependent on the amount of hydroxyl radicals produced and not on the level of sunlight, the dye would be potentially a particularly good indicator. Photolysis will have a slow effect on the color change, while the photocatalytic reaction with titanium dioxide should have a much more rapid effect as the numbers of hydroxyl radicals created are increased. It is hypothesized that the only drawback the resistance the bacteria develops if the radicals created are removed for a time, as is common with cloud cover. Regardless, this should be a good indicator.

The advantage to using the visual indicator method for test development is that it eliminates the need to collect, use, and store bacteria-contaminated water.

The objective is a photocatalytic water purification design to maximize hydroxyl production, and this is what the dye measures. To establish a base line for the destruction of bacteria, laboratory samples of bacteria may be used or a calibration value can be determined to match the results to standardized data based on extrapolation.

The dye can provide a baseline understanding of the additional time required to purify the water due to turbidity and/or low and variable solar irradiation. The ratio added to the water can be calibrated, resulting in consistent results each time the experiment is performed.

2. WATER STANDARDS

To be considered clean, drinking water should not contain any microorganisms known to be pathogenic or any bacteria indicative of fecal contamination. According to the World Health Organization (WHO), the potential health consequences of microbial pollution are such that its control must always be paramount. Short-term peaks in pathogen occurrence may increase risk considerably, and may trigger outbreaks of waterborne disease. In general, the greatest microbial risks are associated with ingestion of water that is contaminated with human and animal feces. Verification of microbial quality of drinking water includes testing for Escherichia Coli (E. Coli) as an indicator organism since this indicates a fecal contaminate, which is of principal concern (WHO, 2004).

In practice, the detection of thermotolerant coliform bacteria can be an acceptable alternative (WHO, 2004). In addition to fecal born pathogens, other hazards like guinea worm, cyanobacteria and Legionella may be of concern in specific circumstances or geographic locations. The TiO_2 water purification method has been shown to be an effective system to treat several of these microbial contaminants as well as other organic contaminates. Examples of harmful contaminants, that research has shown photocatalytic reactors can destroy, include E Coli (Wei, 1994), arsenic (Ferguson, 2005), and many other organic compounds as indexed in a biography submitted by NREL (Blake, 2001).

The WHO suggests a system wide assessment to reduce the potential hazards of contamination by microbial contaminants. This includes monitoring to ensure the barriers within the system are functioning efficiently and the development of plans to describe proper action to take under both normal and incident conditions. The final system must have some control method to ensure the quality of the drinking water after purification. This is a difficult issue when using a photocatalytic system, as the sun's irradiance is variable from hour to hour.

The health risk due to toxic chemicals in drinking water arises primarily from prolonged periods of exposure. There are few chemicals constituents of water that can lead to health problems resulting from a single exposure, except through a massive accidental contamination of supply. In the case of massive contamination, the water generally becomes undrinkable because of its change in taste, odor, and appearance. Because of this, the WHO considers chemical contaminants a lower priority than microbial contaminants. It recommends efforts to find and remove the source of contamination rather than installing expensive drinking water treatment for its removal.

While many chemicals may occur in drinking water, only a few are of immediate health concern. Health concerns include exposure to high levels of the naturally occurring chemicals fluoride, arsenic, uranium and selenium. Another is the high levels of nitrates that may result from excessive application of fertilizers and which can cause methemoglobinemia in infants. Finally, but no less devastating, are the adverse neurological effects that may be inflicted on children by elevated lead levels in certain lead pipes and fittings.

The WHO recommends that a great effort be put into the protection of the water source to lessen the reliance on purification. Minimizing contamination from human waste, livestock, and other hazards will reduce microbial contamination. Control of chemical hazards may be placed primarily on initial screening of sources. Periodic screenings can be performed to ensure there has been no chemical contamination.

3. TITANIUM DIOXIDE PURIFICATION

The process of destroying biological contaminants using the sun occurs through the following process: When titanium dioxide is struck by a photon, an electron is "excited" and it is promoted from the valence band to the conduction band. An electron "hole" is reciprocally created on the surfaces of the TiO_2. This hole has the potential to break the bonds in water through recombination with the weaker hydrogen bond leaving a •OH radical. Similarly, this radical can recombine with the hydrogen from an organic substance since all organic substances are composed of a hydrogen carbon chain. This, in turn, will cause a breakdown of the organic substance into carbon dioxide and the water formed by this recombination. Since the titanium dioxide is not chemically changed in the reaction, it is considered a catalyst.

The photocatalytic effect requires ultraviolet radiation to strike titanium dioxide. Ultraviolet radiation is divided into three parts, UV-A, UV-B, and UV-C. UV-C radiation has powerful bactericidal effects and is the wavelength that is commonly used in water purification systems utilizing UV lamps. In these systems, UV lights are used to create this frequency irradiation, as UV-C radiation is almost entirely attenuated by the earth's atmosphere (Gibson, undated).

The advantage of TiO_2 systems is that UV radiation with a wavelength of less than 388 nm will result in the photocatalytic effect. Since some UV-A radiation from the sun penetrates the earth's atmosphere to reach the ground level, no artificial UV lights are necessary for a TiO_2 water purification system.

Much research has been conducted testing different variables that affect the TiO_2 photocatalytic process (Cho, 2005); however, there is no published data relating the time necessary to totally kill bacteria to a wide array of incident radiation levels. The data is instead measured in a UV dose which is independent of weather conditions. Most importantly, there is no definitive definition on the minimum level of irradiation necessary to keep the photocatalytic process going.

It has been shown that $400 W/m^2$ of sunlight can destroy $1x10^7$ CFU/ml of *E.Coli* bacteria in 30 minutes using a slurry mixture of TiO_2 (Rincon, 2003). However, periods of interrupted irradiation can allow the bacteria to recover by their self defense mechanism (Srinivasan, 2003). Therefore, it may be necessary for the samples to be subject to continued solar irradiance at these levels or higher. Surfaces coated with titanium dioxide have not yet proven as effective in detoxification as their slurry counterpart so longer or greater UV irradiation may be required. But a TiO_2 slurry would not be as easy to use in the field as a coating approach.

Two different media were used to host the TiO_2 coating. Glass rods used for the purposes of experimentation were made in the lab with the help of Christopher Lin in the spring of 2004. The type of TiO_2 used is a photocatalytic sol-gel solution STS-01 from Ishihara Corporation. This solution is listed to contain the following.

- TiO_2 – min 27%
- Nitric Acid – Max 2.5%
- Water

This procedure was adapted from a procedure detailed in a paper provided by Professor Dionysis Dionysiou (Balasubramanian et al., 2003, p. 74) and is explained in detail in Dubro (2007).

The bottles used for the purposes of experimentation were made in the lab by Manuel Heredia. The following was his procedure (Heredia, 2006):

> Recycled PET bottles of 500-600 ml were used, adapting the procedure stated by Litter at al (2005). Because this procedure should be repeated easily in isolated villages, the use of an ultrasonic bath has been left out of the procedure. The PET bottles were washed with deionized water, shaking vigorously several times and drying for 24 hours, to avoid the formation of residue from the drops of water. Later, 10 ml of coating film solution was introduced in each bottle, rolling the bottles until a uniform film was formed. The film must cover just half of the bottle. In the original procedure (Litter et al. 2005) the entire internal wall was covered but, in the experiments realized in Peru, this procedure slowed the disinfection rate, because thin upper TiO_2 film was able to absorb most of the UV radiation before it reached the water and the lower TiO_2 film. The excess of solution is drained, and the bottles are dried at room temperature for 24 hours. This procedure is repeated twice and, finally, the bottles are filled with water and shaken in order to eliminate loose particles.

4. OZONE SENSITIVE DYE

One article was located (Alsbury, 2003) in which it was demonstrated that indigo carmine can be used to measure photocatalytic activity. This finding was taken one step further and developed into a form that can be easily used to measure the effectiveness of a TiO_2 photocatalytic reactor.

Indigo carmine is used as a food colorant because of its deep blue color. Separately, it is used in the lab because of its pH indicator properties. Indigotindisulfonate sodium is the sodium salt form of indigo carmine used and has the following molecular formula $C_{16}H_8N_2Na_2O_8S_2$ and a molecular weight of 466.35. As a pH indicator, it is blue at pH 11.4 and yellow at 13.0. A common aqueous solution is 0.2%.

When ozone is produced, the double carbon bond in indigo carmine is broken. It is the end result of this reaction that is crucial for use of indigo carmine as an indicator: the once dark blue color fades and eventually disappears. Further study of the byproducts of this reaction will create the basis for a more thorough analysis of the health and safety of using indigo carmine as an indicator.

Adverse affects from ingestion of low doses of indigo carmine are not expected. Indigo carmine itself is used as a food colorant and is the major component of FD&C Blue Number 2. It can be toxic in high doses but should not be in the low levels used as a light blue dye.

Indigo carmine and hypromellose (Hydroxypropyl methylcellulose) were mixed together using an electric chopper/mixer. The resultant evenly distributed powder was poured into an herbal pill former and compacted into a pill form (Fig. 1). The pills were well formed with a speckled grayish color. They held up well to drop tests. Immediately upon contact with water, the pills became dark blue and slowly dissolved while they released a slow stream of blue dye over the course of several hours.

Two different pill batches were made using a measuring cup for the hypromellose and a very small measuring spoon. A gram per spoon measurement was made by weighing 22 spoonfuls and dividing out to find the average individual mass measurement. The mass measurements were taken with a Tangent 102 pocket scale with .1 gram precision. The batch that was later labeled medium blue was twice the amount of indigo carmine as the batch named light blue. A third batch, dark blue, was proposed which was twice the batch of the medium blue pills.

Fig. 1: Pill Maker

5. EXPERIMENTS

The experiments conducted for this research identify and quantify the color change of the dye versus the effectiveness of the photocatalytic process. Photocatalytic effectiveness was based on the kill rate of bacteria but correlated to the destruction of the indigo carmine dye. These experiments show the benefit of indigo carmine as a dye based indicator for photocatalytic water purification. Further the pill form shows promise as a disbursement method that allows bacteria to be destroyed by slow release of indigo carmine while providing a visible indication to verify the water purification process.

The WHO's guidelines for bacteriological quality of drinking water states that all water intended for drinking must have no detectable E. Coli or thermo-tolerant coliform bacteria in any 100 ml sample (WHO, 2004). There are many different disposable test kits with varied costs and reliability. A suitable method of testing must be chosen to accurately determine the safety of the drinking water.

In general, the testing for bacteria will involve incubating a sample of water in a broth to promote the growth of the bacteria of interest. Thereafter, some reaction that is characteristic of those organisms is observed. At different times during this study, a Presence/Absence test, a broth test, and a pectin-gel method were used.

The broth test involves adding samples diluted to various degrees to 10 or 15 tubes with a broth to enhance growth, followed by 24-48 hours of incubation. Gas production or cloudiness will be visible if the indicator organism (sulfur producing bacteria) is present. If replicates of the same dilution are used, a table based on the number of positive tubes is used to report results as Most Probable Number (MPN) per 100 mL of sample.

The Presence/Absence (P/A) test involves taking one sample, adding the testing broth, and incubating for 24-48 hours. Bacterial presence is denoted by color change in the water/broth mixture.

The pectin-gel test involves adding the water sample to a gel solution and putting it in a pretreated Petri dish. The sample forms a gel within 40 minutes and is incubated for 24 hours. Color changing dyes in the gel solution are digested by the bacteria and enable the colonies to be detected and counted.

Bacteria Test Kits were used from the Hach Company. A set of 15 prepared tryptic soy broth media tubes for the MPN test, and a set of 15 P/A tests were obtained. An additional 20 Coliscan Easygel pectin-gel tests from Micrology Labs were used later in testing bacteria destruction alongside indigo carmine dye color change.

Testing was done with toilet water containing fecal contaminates. The high level of contaminates served as a worst-case scenario. Tests indicated that water purification was achieved, on a small scale, within 3 hours given adequate sunlight or artificial UV irradiation.

The following experiments were undertaken with the objectives mentioned. Details of procedures are provided in Dubro (2007).

5.1 Experiment A: Bacteria destruction as a function of indigo carmine color change under natural sunlight

Objective: Determine the correlation between bacteria destruction and sample color change during photocatalytic water purification.

In this experiment, the contaminated water was colored with a light indigo carmine dye solution. The test tube that contained the solution also held a centered glass rod coated with titanium dioxide to serve as a photocatalytic reactor.

This was left in the sun for several hours during which samples of the water were taken.

Fig. 2 attempts to correlate the photosensitivity of the indigo carmine against bacterial destruction. The number of colonies was estimated for the initial cultures because the number of colonies were too many to count. It is interesting to note the linear behavior of the photosensitivity of the dye versus the logarithmic activity of the coliform destruction.

By the end of the test, there was still a bluish tint to the water despite the fact that the culture taken at the three hour mark showed no sign of coliforms. The test was a success because the dye remained through the purification process. However, a simple dye solution was not deemed effective because of the low initial concentration and purification time extended due to the potential of the indigo carmine to block light.

5.2 Experiment B: Bacteria destruction as a function of indigo carmine destruction under artificial UV light

Objective: Determine the correlation between bacteria destruction and sample color change while indigo carmine pill is dissolving. Verify that indigo carmine release in contaminated water does not skew results.

In this experiment, the indigo carmine pill that was developed was tested under black light in a test tube with a titanium dioxide rod. The light that was transmitted through the test tub was measured to gain an understanding of the amount of light transmitted to the sample during dye release.

In Fig. 3, the number of colonies is graphed along with the measured UVA light transmitted through the test tube.

In this case, with a dye pill, the amount of light transmitted through the test tube decreases as the pill dissolves from both the release of the indigo carmine and the hypromellose. The amount of light, however, that passed through the test tube when using the dye pill was consistently less than the initial time period when the indigo solution was added to the sample.

The dye pill provided an easily identifiable blue color when released into the water sample and maintained the blue color throughout the purification process. At the end of the test and a significant amount of time past total coliform destruction, the water was clear with only a small piece of pill residue. Consequently, the dye indicato appears to be conservative.

5.3 Experiment C: TiO_2-coated bottle test on cloudy day

Objective: Determine the usefulness of a indigo carmine pill when purifying water on a cloudy day.

Manuel Heredia (2006) tested the indigo carmine dye pill using the photocatalytic SODIS bottles made of PET plastic. The results of his tests evaluate the effectiveness of the indigo carmine indicator when used with a different photocatalytic reactor such as one that would be an effective resource in third world countries.

Manuel Heredia tested the medium blue pills using the TiO_2 coated SODIS bottles that he made. He used 3 bottles. One had a 0.02 g TiO_2 coating and the other had a 0.04 g coating and the third was a control with no coating. He placed them on a tilted black surface from 1:20 p.m. until 4:30 p.m. on a day of low irradiation of 150-230 W/m^2 with sporadic higher irradiation. The blue color did not disappear. It was determined that the purification process failed due to low irradiance or insufficient time of exposure. The water, had it been contaminated, would most likely not been safe to drink.

5.4 Experiment D: TiO_2-coated bottle test on partly sunny day

Objective: Determine the usefulness of an indigo carmine pill when purifying water on a sunny day.

Manuel Heredia tested the dye pill in PET bottles again starting at 10:45 a.m.. By 2:30 p.m., the bottle with higher TiO_2 concentration (0.04 g) was completely clear. The bottle with 0.02 g of TiO_2 was very light blue by 4:10 p.m.. The radiation was higher at around 300 W/m^2, although between 2:30 p.m. and 4:30 p.m. the irradiation was very low.

As demonstrated by the photo in Fig. 4, the difference in the color is easy to read and shows a successful test with the 0.04 gram TiO_2 coating. Manuel stored the bottles overnight in the dark. The bottle that was light blue the day before was also clear by morning. This suggests that there is still active oxidation occurring in the bottle, which is probably due to residual oxidative agents. Longevity tests have shown the natural decomposition of the indigo carmine dye over time but this generally occurs after several months if the bottle is stored in a dark location.

Fig. 4: Control bottle (left) next to bottles coated 0.02 g and 0.04 g TiO_2

6. COST AND USABILITY

The pill formulations in this section are based on pills found suitable for the amount of water in a 20 oz bottle such as the SODIS bottle used by Manuel Heredia in his experiments. The costs for indigo carmine are based on small 10g bottles since this can make thousands of pills. ($7.90 plus s/h). Similarly Methocel™ is priced by weight. The bottle of Methocel™ used for this evaluation was provided as a sample from Dow Chemicals. This is a food grade product, and it is suspected that this will have to be purchased in large quantity. The price used for economics is based on a generic hypromellose non-food grade product sold on eBay™. As in most cases, larger quantities can be purchased at a lower cost.

The medium blue pill was created by doubling the amount of indigo carmine added to the hypromellose binder. The material cost for 163 pills is around $1.25 or around 0.8 cents per pill. The medium pill is probably the most cost effective indicator that gives a blue tint result for the 1 liter bottles.

7. CONCLUSIONS

In general, this dye approach has the potential to make the photocatalyst method of water purification much more reliable, giving users direct feedback on the status of drinking water purification.

Use of photocatalytic dye in other methods of water purification, such as UV-water purification systems using UVC light, may be feasible. The effectiveness of this method using an ozonination purification process is probable since indigo carmine has been used to measure atmospheric ozone levels.

Soluble and non-soluble Methocel™ can be mixed together to increase the solubility and subsequently the dye release. For the purposes of the experiments conducted to this point, it was not necessary to change the reaction rate because it was desired that the pill release dye over an extended period. For the purposes of quicker tests, it may be desirable to lessen this time if it is shown that this still provides reliable testing. A similar result can be realized through larger concentration of indigo carmine to the hypromellose binder while reducing the pill size. However, a smaller pill will have less surface area which is also a factor in the release of the dye.

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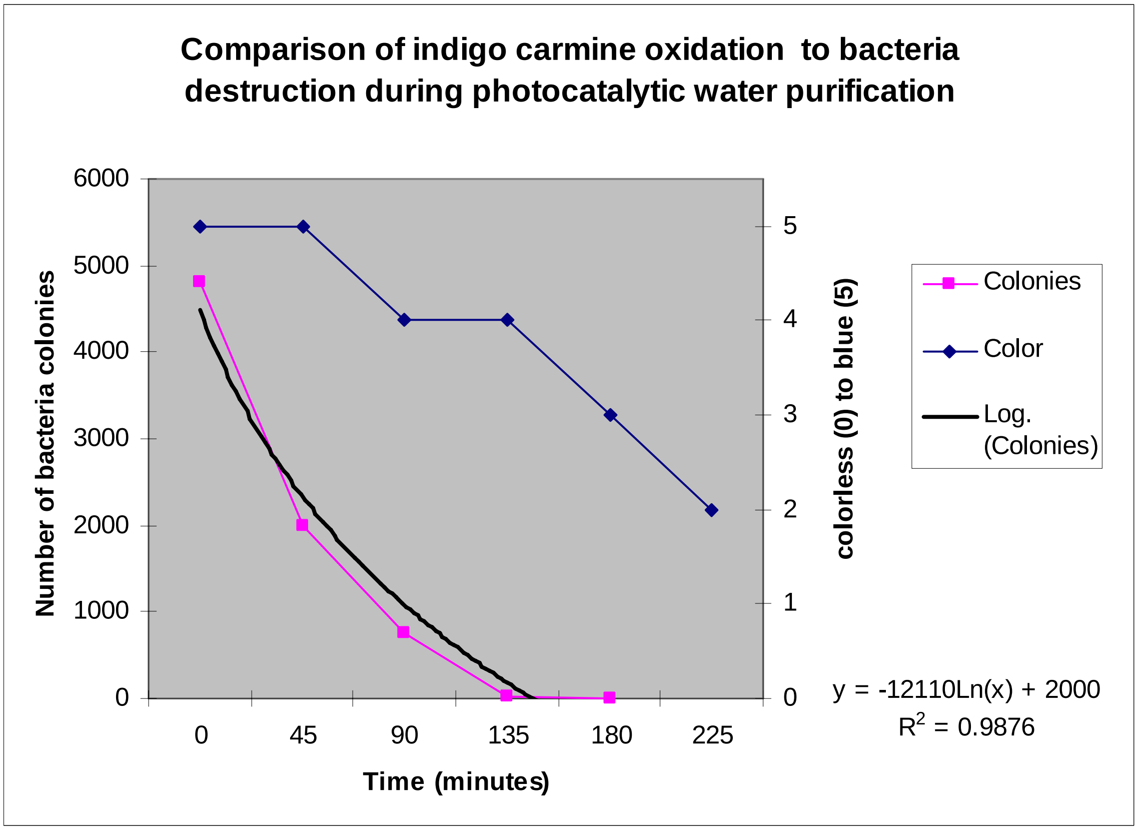

Fig. 2: Number of colonies versus color change

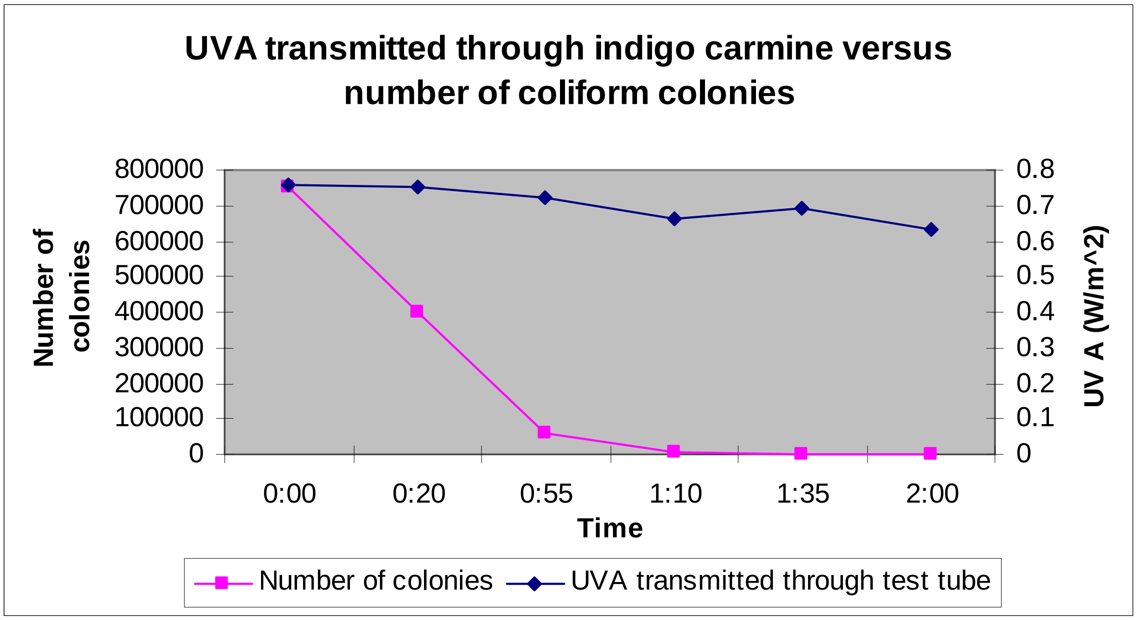

Fig. 3: Coliform colonies versus UVA transmittance