

# PREPARATION OF REUSABLE PVA-NANO TiO<sub>2</sub> FOAM FOR WASTEWATER TREATMENT

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## ABSTRACT

With increasing industrialization, rapid economic development, and an ever-growing population, the problem of water pollution and water scarcity is increasing at an alarming rate. It is estimated that more than 800,000 annual diarrheal deaths are attributed to unsafe water usage. Furthermore, traditional wastewater treatment technologies, such as adsorption, chlorination, and biochemical methods are difficult to utilize for treating wastewater at low concentration for they lead to high toxicity. However, Nano TiO<sub>2</sub>-based photocatalytic technology is a new high-efficiency and energy-saving alternative because NanoTiO<sub>2</sub> can degrade organic pollutants into non-toxic compounds such as CO<sub>2</sub> and H<sub>2</sub>O under the sunlight. Nonetheless, separating and recycling Nano TiO<sub>2</sub> from water remains to be a huge challenge. Therefore, we prepared PVA-Nano TiO<sub>2</sub> foam at high speed stirring, film laying, drying, and thermal crosslinking to embed in PVA for reuse and recycle. The morphology, structure, and photocatalytic performance of PVA-Nano TiO<sub>2</sub> foam were characterized in detail by SEM, TGA, FTIR, UV-Vis, and so on. The results show the cell size of the foam is about 0.2-0.5 mm, and the swelling degree of PVA-Nano TiO<sub>2</sub> foam is about 600%. The TiO<sub>2</sub> nanoparticles also have no effect on thermal crosslinking of PVA. Under sunlight, the PVA-Nano TiO<sub>2</sub> foam possesses photocatalytic activity that is higher than that of non-porous PVA-Nano TiO<sub>2</sub> film due to the higher permeability of water and impurity with higher porosity. In addition, the PVA-Nano TiO<sub>2</sub> foam exhibits good reusability under multi-cycle use. Thus, this novel design of PVA-Nano TiO<sub>2</sub> foam is simple, eco-friendly, and effective with potential practical application value.

## 1. INTRODUCTION

Water pollution and scarcity is a growing issue globally. In particular, water pollution in the form of plastics, toxic chemicals, and microorganisms causes harm to sea life in addition to limiting the supply of clean water for usage and drinking. It is estimated 1.5 billion people in developing countries are without safe drinking water (WHO 2014). Around 80% of wastewater is directly discharged into the ocean, river, or seas without any wastewater treatment, causing 1,000 children deaths each day due to preventable sanitation-related diarrheal diseases. The United Nations 6th sustainable development goal is to obtain access to clean water globally.

In order to combat these issues, an environmentally friendly and cost-effective solution to help treat water easily and efficiently has been sought. Currently, some methods used to provide clean drinking water are chlorination, ozone, and filtration [1]. National Drinking Water Clearinghouse provides the pros and cons of each method. Chlorination provides a relatively cheap disinfection method, but it is corrosive or toxic to humans. Ozone treatment is expensive, and filtration cannot get rid of all the dangerous viruses in our drinking water.

However, a new method to treat water involving the use of sunlight has been under consideration [2]. The treatment requires photocatalysts to harness the energy from the sun to react with harmful

microorganisms or harmful compounds. Titanium dioxide ( $\text{TiO}_2$ ), one of the most promising photocatalysts, has been widely used in the fields of air purification, sewage treatment, water splitting, reduction of  $\text{CO}_2$ , and dye sensitized solar cell, because of its low cost, nontoxicity, high photo stability and high photocatalytic activity [3]. The photocatalytic principle of  $\text{TiO}_2$  is shown in Figure 1. Under UV light, the electrons on the valence band of  $\text{TiO}_2$  are excited and transferred to the conduction band. Electron-hole pairs have strong redox abilities and can activate oxygen and water to produce reactive oxygen and hydroxyl radicals, which can react with and turn bacteria and other harmful pollutants into  $\text{CO}_2$ , water, etc [4].

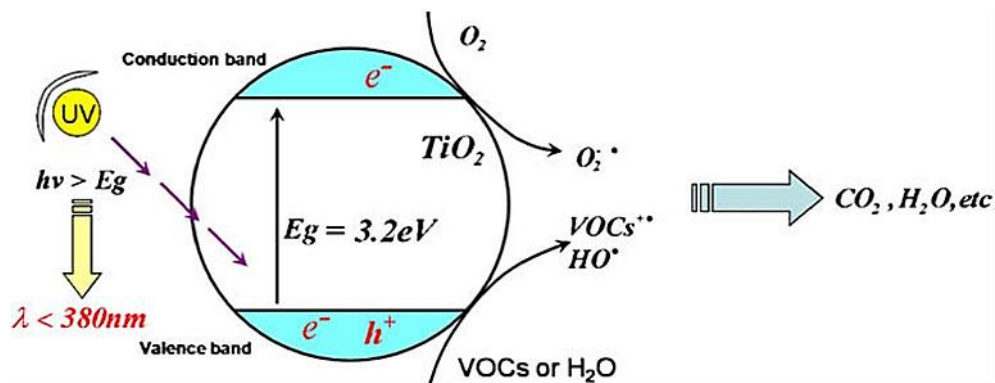


Fig. 1. schematic of the photocatalytic principle of  $\text{TiO}_2$

Nano  $\text{TiO}_2$  is even more efficient due to its higher surface area. However, it could not be collected from water afterwards, resulting in potentially threatening  $\text{TiO}_2$  residue. In order to use  $\text{TiO}_2$  photocatalyst, a reusable and recyclable method needs to be invented. Recently, substances such as glass, ceramics, Polypropylene, or PVA have been used to immobilize  $\text{TiO}_2$  [5]. Shang et al [6] coated  $\text{TiO}_2$  on the surface of stainless-steel wire meshes. Hashemizad et al [7] immersed  $\text{TiO}_2$  into polyester. Lei et al [8] prepared PVA-Nano  $\text{TiO}_2$  film and showed good results. Zhang et al [9] coated PVA/ $\text{TiO}_2$  on honeycomb ceramics and showed photocatalytic activity. However, using solids such as those limits accessibility of water impurity, thus lowering the efficacy. Thus, a large surface area and open structure are the basic requirements to facilitate the diffusion of the reactants from the solution to the surface of the photocatalyst. In order to test this further, Lee et al [10] prepared PVA/ $\text{TiO}_2$  by electrostatic spinning, and Nguyen et al [11] prepared a porous PVA/ $\text{TiO}_2$  by freeze-drying. However, there are still many challenges in developing a cheap and eco-friendly method for the preparation of efficient, recyclable, and reusable photocatalyst.

When mixing eggs or washing clothes, it can be observed that the high agitation and the high rotation of the respective machines for each task are able to bring air into the solutions and create aeration and more air bubbles. Thus, mimicking such actions, solutions of PVA- $\text{TiO}_2$  were stirred at a higher rate to inject more air into them. These air bubbles were able to increase the porosity of the PVA- $\text{TiO}_2$  film as well as the surface area of the resulting foam. The PVA-Nano  $\text{TiO}_2$  foam was prepared through high speed mixing, film laying, drying, and thermal crosslinking. The morphology, structure, and photocatalytic properties were then characterized in detail via SEM, TGA, FTIR, UV-Vis, and more. The resulting PVA-Nano  $\text{TiO}_2$  foam created showed photocatalytic performance under sunlight, proving a potential to purify water.

## 2. EXPERIMENTAL

### 2.1 Chemicals and Materials

- Three types of Polyvinyl Alcohol (PVA, from VWR) were used: Molecule Weight (MW) 31-50k with 98% hydrolyzed; MW 85-140k 98-99% hydrolyzed; MW 146-196k 99+% hydrolyzed
- TiO<sub>2</sub> 21nm with over 99.5% purity (Evonik)
- Methyl orange (dye content 99.9%, from VWR) was used as a model pollutant
- Sodium Lauryl Sulfate (SLS, from VWR) was used as a foaming agent

### 2.2. Preparation Of PVA-Nano TiO<sub>2</sub> Hybrid Foams

#### Step 1: PVA solution preparation

30g of PVA was added to a flask, and 370g deionized water was added. After leaving the mixture for an hour, the beaker was put in an oil bath and mixed at approximately at 300 r/min. The temperature was raised to 95°C, allowing the solution to dissolve for 3 hours into a transparent 7.5% PVA solution.

#### Step 2: PVA-Nano TiO<sub>2</sub> foam preparation

0.3g TiO<sub>2</sub> powder was put into a 150ml beaker with 5g deionized water. The solution was mixed with ultrasound for 10 minutes. Then, 40g 7.5% PVA solution was added. High-speed mechanical mixing at 1000r/min was utilized next for 10 minutes to introduce air in order to produce foam within the solution. Many bubbles that resulted possibly increased the contact area between titanium dioxide and pollutants, further enhancing the photocatalytic activity of the composite catalyst. We pour the PVA/TiO<sub>2</sub> solution on a horizontal Teflon plate, scrape it onto a thin film. After drying, we heated the foam inside a vacuumed oven at 140°C for 2 hours to get the cross-linked PVA/TiO<sub>2</sub> foam.

### 2.3. Characterization Of PVA/TiO<sub>2</sub> Foam (SEM, FTIR, TGA, UV-Vis, Et Al)

PVA/TiO<sub>2</sub> foam prepared above was characterized by SEM, FTIR, TGA, and UV-Vis. We used an FTIR machine to figure out the bonding and cross-linking in our foam by scanning for intramolecular bonding. A SEM was used in order to confirm the readings of the FTIR machine and to obtain pictures of the TiO<sub>2</sub> in the film before and after the foam formation. Originally, a scanning light microscope was used. However Nano TiO<sub>2</sub> was too small to be seen.

### 2.4. Evaluation of PVA-TiO<sub>2</sub> Foam's Photocatalyst Efficacy

Methyl orange was used as a model contaminant for studying the performance of PVA-TiO<sub>2</sub>. UV-3100 PC spectrophotometer VWR was used to measure the absorbance of the methyl orange solution in order to correlate the absorbance to the concentration of methyl orange. The change in concentration of methyl orange was monitored using absorbance at 465 nm with a UV-Vis. The formula for % degradation is as follows:  $\% \text{ degradation} = \frac{C_0 - C_t}{C_0} \times 100\%$ , where C<sub>0</sub> is the initial absorbance and C<sub>t</sub> is the absorbance of the contaminant solution at time t. The PVA-TiO<sub>2</sub> sample was then dried and re-measured in multiple trials.

### 3. RESULTS AND DISCUSSION

#### 3.1. PVA-TiO<sub>2</sub> Foam Showed Porosity / Bubbles And TiO<sub>2</sub> Nano Particles

Pictures, shown in Figure 2, were taken for pure PVA, PVA-TiO<sub>2</sub> film formed at low mixing rate, and PVA-TiO<sub>2</sub> foam formed at high mixing rate. Results show significant air trapped into the foam with high porosity.

To better visualize and confirm the air bubbles in PVA-TiO<sub>2</sub> foam, we took microscope images for B and C, shown in Figure 3. The microscope was able to capture the increased porosity of the PVA-TiO<sub>2</sub> foam. Both samples contain the TiO<sub>2</sub> photocatalyst. However, as seen in the second microscope picture, the size of the pores increased. This signifies that our process is able to increase porosity and therefore surface area. Results show the transformation of PVA between its pure form, with TiO<sub>2</sub> as a film, and with TiO<sub>2</sub> as a foam. The foam images clearly indicate the production of many pores that help increase porosity, thus allowing water/impurity permeation and increased surface area.

One of the instruments needed for our experiment was the Scanning Electron Microscope in order to capture what our Nano TiO<sub>2</sub> looked like before and after the PVA transformation. Furthermore, SEM images were taken for PVA-TiO<sub>2</sub> foam to confirm the embedded TiO<sub>2</sub>, shown in Figure 4 (A and B). As seen in this SEM image of our Nano-TiO<sub>2</sub> mixture, we can see the TiO<sub>2</sub> wedged into the foam. Thus, PVA-Nano TiO<sub>2</sub> can potentially be used well as a photocatalyst due to the foam containing the TiO<sub>2</sub> particles mixed throughout, as seen through our microscopic images. It should be able to perform its photocatalytic abilities because it has the Nano TiO<sub>2</sub> in the matrix and accessible.

#### 3.2. TGA And FTIR Indicates Cross-Linking Temperature Did Not Cause Samples Change

TGA (Thermal Gravimetric Analysis) was used to analyze the sample integrity, and the results in Figure 5 show that the pure PVA film, PVA-TiO<sub>2</sub> film, and PVA-TiO<sub>2</sub> foam were very similar during the experiment. However, at the end, only the PVA-TiO<sub>2</sub> film and PVA-TiO<sub>2</sub> foam were similar, as both contain the residue TiO<sub>2</sub>. FTIR results in Figure 6 further prove that PVA bonding did not get impacted by cross-linking and the addition of TiO<sub>2</sub> did not impact the PVA cross-linking either.

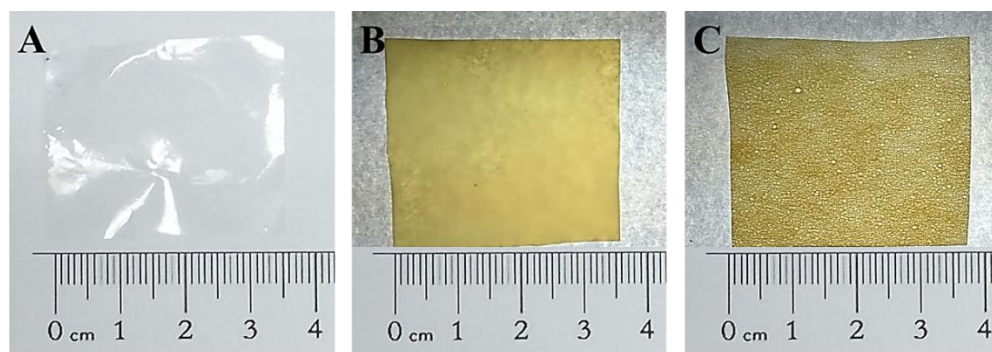


Fig. 2. Pictures of pure PVA (A), PVA-Nano TiO<sub>2</sub> film (B) and PVA-Nano TiO<sub>2</sub> foam

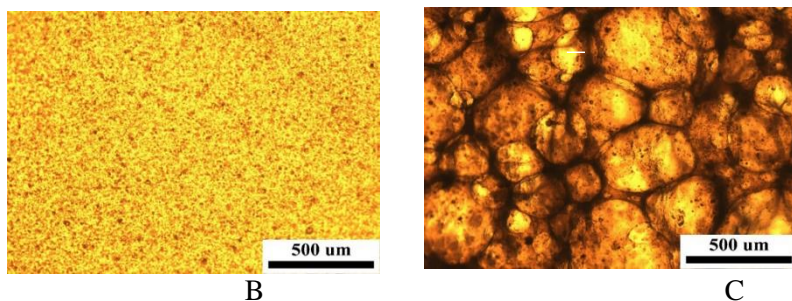


Fig. 3. Microscope images of PVA-Nano TiO<sub>2</sub> film (B) and PVA-Nano TiO<sub>2</sub> foam (C)

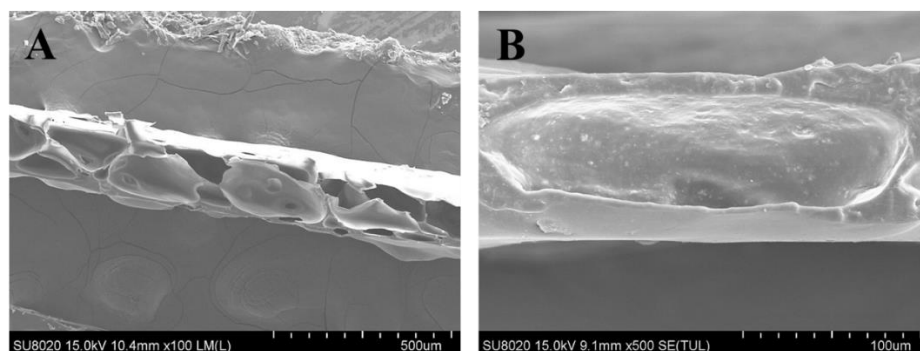


Fig. 4. Scanning Electron Microscope images of PVA-Nano TiO<sub>2</sub> foam (A and B)

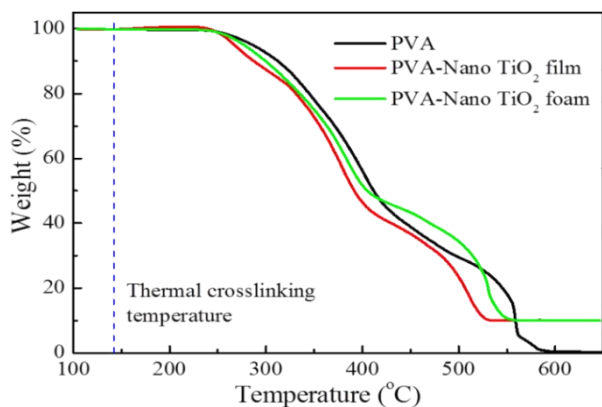


Fig. 5. TGA curves of pure PVA, PVA-Nano TiO<sub>2</sub> film and PVA-Nano TiO<sub>2</sub> foam

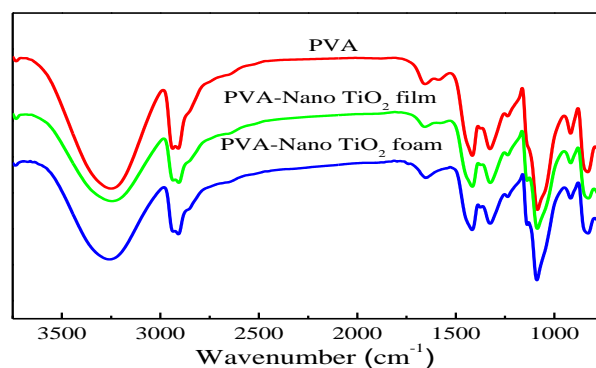


Fig. 6. FTIR spectra of pure PVA, PVA-Nano TiO<sub>2</sub> film and PVA-Nano TiO<sub>2</sub> foam

### 3.3. Swelling Degree And Sample Density Confirmed High Porosity In PVA-TiO<sub>2</sub> Foam

Swelling degree measurement on the sample was conducted by immersing it in water. The results in Table 1 show that PVA-TiO<sub>2</sub> foam has the higher porosity (lower density). We can see how the experimental process helps increase the surface area of the PVA-Nano TiO<sub>2</sub> mixture. We see that the swelling of the PVA and PVA-Nano TiO<sub>2</sub> foam change from 200% initially into 600% afterwards.

Table. 1. Swelling degree and density of the samples

Samples	PVA	PVA-Nano TiO <sub>2</sub> film	PVA-Nano TiO <sub>2</sub> foam
Swelling degree (%)	200	170	600
Density (g/cm <sup>3</sup> )	1.17	1.25	0.26

### 3.4. Proposed High Efficiency Method To Prepare PVA-TiO<sub>2</sub> Foam Show Success Via UV-Vis

Our PVA-Nano TiO<sub>2</sub> film was produced successfully so that the TiO<sub>2</sub> was trapped inside. After 21 experiments on how to create a better PVA-TiO<sub>2</sub> foam that is efficient and reusable, our method listed in the experimental part proved to be successful. In our data, it is clear that the PVA-TiO<sub>2</sub> foam is still able to treat the pollutants such as the methyl orange used in this scenario. In the solution of TiO<sub>2</sub> without PVA, we saw that the concentration of methyl orange decreased at a rate of 13 mg/L per hour, while the solution with the ideal PVA foam had a rate of around 4 mg/L per hour. This is because Polyvinyl alcohol (PVA) is a type of water-soluble polymer material that can hold TiO<sub>2</sub> due to its hydroxyl groups, its excellent film-forming, water-soluble, mechanical properties, and its biodegradability, making it the candidate for photocatalyst. Pure PVA film has no obvious absorption of UV and visible light and is very suitable for support Nano TiO<sub>2</sub>. However, due to the slow water permeability of PVA after cross-linking, the pollutants were not exposed to nano TiO<sub>2</sub> in time. Our data on photocatalytic measurement in Figure 7 show PVA-TiO<sub>2</sub> foam has higher photocatalyst performance than PVA-TiO<sub>2</sub> film does.

### 3.5. PVA-Nano TiO<sub>2</sub> Foam Was Easy To Recycle And Reuse

Our PVA-TiO<sub>2</sub> foam was reusable and recycled after being baked in the oven until dry again. After recharging the PVA-TiO<sub>2</sub> by using UV light and energy, the PVA-TiO<sub>2</sub> foam was ready to be utilized again. After reusing the same PVA-TiO<sub>2</sub> foam multiple times, we discovered that its performance remained approximately the same. Not only is PVA-TiO<sub>2</sub> foam able to effectively degrade highly concentrated pollutants, but it is recyclable.

As shown in Figure 8, PVA TiO<sub>2</sub> was unaffected by multiple trials, exhibiting the same performance in almost all 5 trials. The solution's bubbles helped increase the performance of the foam, allowing it to degrade more than 90% of the pollutant. The reusability of the PVA-TiO<sub>2</sub>, however, is much better than just using the nano-TiO<sub>2</sub> particles alone. With no difference in mass before and after the experiment, 100% of the PVA-TiO<sub>2</sub> foam's mass was retained, allowing us to use the foam again. Although a longer preparation time was required, methods discussed later can potentially reduce the time taken to reduce pollutants. The innovation of the product can expand the synergy of PVA and TiO<sub>2</sub>. After removing solid waste in water via filtration, freshwater can be turned into clean, safe, and drinkable water by using this product to remove pollutants that are in small concentrations but extremely toxic.

### 3.5. Optimization PVA-Nano TiO<sub>2</sub> Foam Efficacy Under Various Parameters And Conditions

To improve the performance of the invented PVA-Nano TiO<sub>2</sub>, we hypothesized that performance can be improved by increasing the permeability and the effective surface area. A few approaches were explored, and the results are shown in Figure 9 and Table 2.

#### 3.5.1. Lower PVA MW Results To Higher Efficacy

As PVA MW increases, it is possible that accessing TiO<sub>2</sub> will become more difficult. Three MW PVA were tested, and the lowest MW PVA had the best performance.

#### 3.5.2. Use foaming agent to increase the aeration

When foaming agent was used, it created more bubbles, thus increasing the foam porosity and potentially contributing to higher surface area and easier access. Less than 0.01% SLS was used, and results show increased performance. Figure 8 visibly shows pore sizes in the PVA foam. The foaming agent is much larger, meaning that the surface area of the foam will be larger and so will the photocatalytic ability of the foam. This is probably because when air is mixed in after adding a foaming agent, the surface tension of the liquid mixture was reduced. A foaming agent is able to align itself in such a way that the hydrophobic tails will be out of the liquid, while the polar heads will be in the liquid. Through such actions, the foaming agent is able to break intermolecular forces and interactions and reduce the surface tension. This decrease of interactions between the water molecules on the surface of the liquid allows for more air to be mixed in more easily. This is important because more air in the solution creates more bubbles and a higher surface area and thus, more effectiveness.

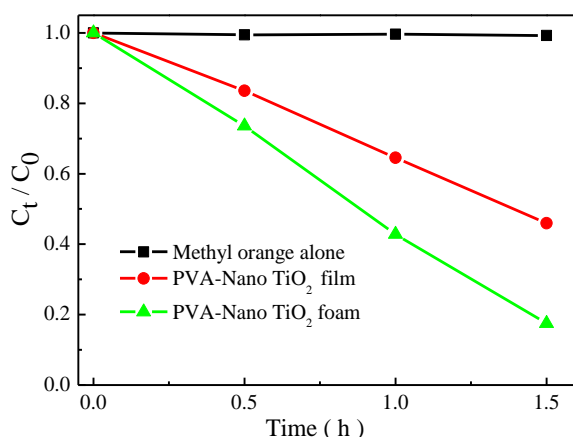


Fig. 7. Photocatalytic degradation of Methyl orange solution under simulated sun light

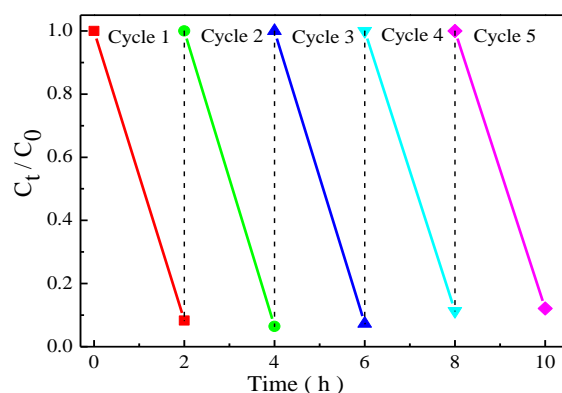


Fig. 8. Recycle photocatalytic performance test of PVA-Nano TiO<sub>2</sub> foam

#### 3.5.3. Lower The Drying Temperature To Optimize The Performance

With lower temperature, less bubbles collapse and less crosslinking degree, which can both potentially increase the access-ability and surface areas of the effective photocatalyst. We tested the experiment at 60°C instead of 140°C. It was discovered that by drying the foam at a lower temperature, it would be more effective.

### 3.5.4. Lower The Drying Time To Enhance The Performance

Similar mechanism to drying temperature impact, cross-linking for 30 minutes in the vacuum state instead of 2 hours, a higher performing PVA/TiO<sub>2</sub> foam was produced.

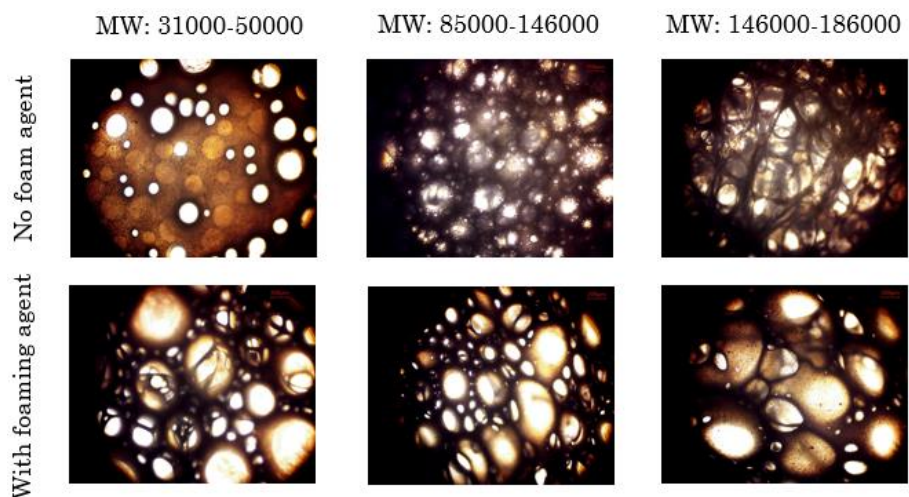


Fig. 9. Pictures of PVA-Nano TiO<sub>2</sub> foams: Different MW PVA and with/without foaming agent

Table 2. Photocatalyst performance of PVA-Nano TiO<sub>2</sub> at different conditions (vs. Base – PVA-Nano TiO<sub>2</sub> MW 31-50k, drying 2 hrs at 140°C without foaming agent)

Conditions	Performance index (vs Base)
PVA MW 31-50K	1.00
PVA MW 85-140K	0.87
PVA MW 146-196K	0.68
Addition of foaming agent	1.55
Drying at lower Temp. (60°C vs. 140°C)	3.10
Drying for shorter time (0.3 vs 2 hr)	1.32

The PVA-TiO<sub>2</sub> foam made in this project is more effective than other methods thanks to the addition of foaming agents, higher stirring rates, and finally the baking at lower temperatures. These 3 factors come together to create a better and more efficient version of the original reusuablenano foam. However, the reusability and recyclability of this improved version is unknown.



### **3.6. Broadened Applications Of PVA-Nano TiO<sub>2</sub> Foam**

This PVA-TiO<sub>2</sub> foam can be applied in many instances such as at water treatment plants, or communities without freshwater such as Flint, Michigan to purify water. It can also serve as self-cleaning products for cleaning wipes, textures, etc.

### **3.7. Recommendation For Industrialization**

In order to apply this to industrialization, we would need to apply this film into waste water plants as a final step. Although wastewater treatment normally involves the use of fluoride and chloride, our PVA-TiO<sub>2</sub> foam is able to do the same job and be reused many times without the need for repairment. By using our PVA-TiO<sub>2</sub> foam in such systems in third world countries, we can make a big difference in their availability of clean water.

## **4. CONCLUSION**

The PVA-TiO<sub>2</sub> foam was successfully synthesized using the procedures above at a very high stirring rate. The photocatalyst had improved capabilities and was able to be reused in multiple cycles. The higher surface area as a result of the stirring was enlarged by the increased number of pores, enabling the foam to perform more efficiently. In addition, the usage of a foaming agent, lower molecular weight PVA, lower drying time, and lower drying temperatures helped increase the porosity and permeability of the PVA foam; however, the integrity and re-usability under such conditions remain unknown and need be further studied and explored. The new formation method for the PVA-TiO<sub>2</sub> foam can be applied and used in water treatment plants or water pumps to provide more fresh water for the world's increasing population. While experimenting with methods of producing the PVA-TiO<sub>2</sub> foam, we also discovered new ways to improve upon the method for industrialization, such as using different molecular weights of PVA, baking at different temperatures, or mixing in a foaming agent. First, lower the molecular weight of the PVA, the faster the degradation rate of methyl orange. Afterwards, we tried testing out the baking temperature of the final PVA-TiO<sub>2</sub> foam. We found out that the lower the final baking temperature of the PVA-TiO<sub>2</sub> film before use, the higher the degradation rate of methyl orange. This PVA-TiO<sub>2</sub> foam is ideal for our purposes, because it was able to degrade large percentages of lowly-concentrated but highly-toxic products such as DDT or viruses. We were able to degrade a large percentage of these toxic particles with only 40mg of PVA-TiO<sub>2</sub>, and we were also able to conduct many experiments using the same film consecutively proving reusability. This shows that a product that can be mass-produced easily at a cheap price has been successfully prepared. Using our production method, we can create recycleable and reusable PVA-TiO<sub>2</sub> that can provide clean drinking water by degrading low-concentration toxins that may cause infections or deaths.

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