Characterization, Settling, and Recovery of Bismuth Phosphate Photocatalyst

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CHARACTERIZATION, SETTLING, AND RECOVERY OF BISMUTH PHOSPHATE PHOTOCATALYST

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Environmental Engineering

by
Kyle Charles Pohle
August 2017

Accepted by:
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Dr. David Ladner
Dr. Mark Schlautman
ABSTRACT

Photocatalysts have been increasing in popularity in recent years for the use of degrading contaminants in water treatment. Compared to other treatment methods, photocatalysts have the advantages of being reusable, being able to degrade contaminants of concern, and being relatively non-toxic. One major problem with implementing photocatalysts for water treatment on a large scale is their difficulty to recover after treatment. Although a significant amount of research success has been accomplished in degrading contaminants in a lab setting, few commercial treatment systems exist as a result of the recovery problem. One recently-discovered photocatalyst, BiPO₄, shows promise for overcoming the recovery issue due to its large particle sizes and high density. This work focuses on characterizing the size and settling behavior of BiPO₄ particles to determine whether gravity settling could be used to recover this material.

Particle size measurements were first conducted using a dynamic light scattering (DLS) instrument to estimate the expected settling velocity. An average size of 2.35 μm was measured which, according to Stokes’ Law, gives an expected settling velocity of approximately 1.60 \times 10^{-3} \text{ cm/s}. To verify this calculated settling velocity and determine the distribution of settling velocities in a sample of BiPO₄ particles, a column test was conducted using small, customized settling columns. A settling curve (C/C₀ vs. settling velocity) was obtained and the median settling velocity was determined to be 2.90 \times 10^{-3} \text{ cm/s}.

Using the calculated and measured settling velocities, a lab-scale rapid clarifier was designed and constructed to determine whether the BiPO₄ particles could be easily
removed from a water stream using gravity settling. The tank dimensions consisted of a length of 0.26 m, a width of 0.12 m, and a height of 0.33 m; the lab-scale clarifier was made from sheet acrylic with aluminum sheets to serve as the plate settlers. Various polyvinylchloride (PVC) fittings were altered for flow input and exit from the clarifier. Experiments were run using a BiPO₄ slurry fed to the lab-scale rapid clarifier by a 600 rpm Masterflex® pump; the flow rate was varied in order to determine the maximum overflow rate that would result in approximately 90% removal of the material. At an overflow rate of 0.4 m/h (0.011 cm/s), or 9.6 m³/m²·d, a removal percentage of 96% was measured.

Lastly, the design of the rapid clarifier was scaled up to determine if the overflow rate measured in the lab-scale experiments for BiPO₄ particle removal would be feasible at a large scale. Based on the experimental results, a design for a full-scale rapid clarifier was derived which is able to treat a flow rate of 131 m³/d to remove approximately 96% BiPO₄. Implementation on a large-scale would likely require multiple rapid clarifiers in parallel in order to treat a reasonable flow rate using BiPO₄ PAO technology.
DEDICATION

This work is dedicated to my family, who have supported me endlessly and given me the confidence to succeed in all my endeavors.
ACKNOWLEDGEMENTS

I would like to acknowledge my advisor, Dr. Ezra Cates, for providing guidance during this work as well as for his time in meeting each week and responding to countless emails. I would also like to acknowledge my thesis committee, Dr. David Freedman, Dr. David Ladner, and Dr. Mark Schlautman for each contributing in a unique way and for offering suggestions along the way. Additionally, this group has guided me through my studies at Clemson and taught me the engineering skills I have today.

Additionally, I must acknowledge members of the Cates’ Group, especially Sushant Sahu, who provided guidance on lab practices and offered advice. Also, I would like to acknowledge Dr. Brian Powell and Dr. Thompson Mefford for allowing me to use their DLS instruments for this work.
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<td>DDI</td>
<td>Distilled Deionized</td>
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<tr>
<td>DLS</td>
<td>Dynamic Light Scattering</td>
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<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
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<tr>
<td>Fr</td>
<td>Froude Number</td>
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<tr>
<td>MB</td>
<td>Methylene Blue</td>
</tr>
<tr>
<td>MGD</td>
<td>Million Gallons per Day</td>
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<tr>
<td>NTU</td>
<td>Nephelometric Turbidity Units</td>
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<tr>
<td>PAO</td>
<td>Photocatalytic Advanced Oxidation</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinylchloride</td>
</tr>
<tr>
<td>PDI</td>
<td>Polydispersity Index</td>
</tr>
<tr>
<td>PFAS</td>
<td>Perfluoroalkyl Substances</td>
</tr>
<tr>
<td>Re</td>
<td>Reynolds Number</td>
</tr>
<tr>
<td>rpm</td>
<td>Rotations per Minute</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
<tr>
<td>TSS</td>
<td>Total Suspended Solids</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>Z-ave</td>
<td>Average Particle Size</td>
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1. INTRODUCTION

New and innovative methods for removing contaminants in the drinking water supply are of particular interest to researchers with the goal of improving public health. Additionally, many organic contaminants have been found to be unaffected by conventional water treatment methods, indicating that new treatment methods are necessary to prevent public exposure [1, 2]. One relatively new method for degrading contaminants during water treatment is photocatalysis. This method involves irradiating a material (the photocatalyst) with ultraviolet (UV) light, causing an excited state of the material which acts as a catalyst for contaminant degradation in the water [3].

Advantages of photocatalysis compared to other novel water treatment strategies are the ability of the photocatalyst to be reused and the ability of photocatalysts to degrade recalcitrant compounds [4].

Although photocatalysts seem to be a promising prospect for water treatment, the materials have several downsides. Typical photocatalysts, such as TiO₂, are used at very small particle sizes of about 30 nm [5]. The use of particles this small make the recovery and reuse of the material more difficult for large-scale treatment applications. Additionally, typical photocatalysts are unable to degrade some of the most important emerging contaminants, such as flame retardants, under typical source water conditions [6]. TiO₂ may also be toxic to some freshwater organisms [7]. Progress should be made in these areas in order for the photocatalytic water treatment approach to become widespread.
One photocatalyst material that overcomes the challenges of recovery and ability to degrade recalcitrant compounds is BiPO₄ [8]. In preliminary experiments, BiPO₄ particles have been shown to degrade recalcitrant compounds such as 2,4-dichlorophenol [8]. Additionally, BiPO₄ particles are able to be synthesized at large particle sizes (> 2 μm), indicating they have the potential to be more easily recovered and reused than TiO₂. This project will focus on characterizing the settling behavior of BiPO₄ particles to show that gravity settling could be used to easily recover this material for reuse, indicating a significant advantage over other photocatalyst materials.
2. BACKGROUND

2.1. Photocatalysts

In the context of water treatment, a photocatalyst is a solid material which acts as a semiconductor, activated by light energy, to promote oxidative and reductive reactions which aid in the degradation of contaminants [9, 10]. The photocatalytic effect and its possible utilities were first discovered by Fujishima and Honda in 1972, when the researchers observed the splitting of water to hydrogen and oxygen by TiO$_2$ electrodes [11, 12]. Since, this technology has been applied to water treatment as a result of the ability of photocatalysts to destroy organic contaminants [12].

In general, photocatalysts work by absorbing energy from light which allows the excitation of an outer orbital electron from the valence band to the conduction band [3]. This process results in a hole in the valence band and a free electron in the conduction band which are available to participate in reactions with the water and contaminants in the water [3]. Figure 1 illustrates the process and subsequent reactions of photocatalysis on a TiO$_2$ particle [13].
As shown in Figure 1, reductive reactions occur at the conduction band as a result of the free electron and oxidative reactions at the valence band [13]. Free radical oxygen species are generated from these oxidation/reduction reactions which react with organic contaminants present in the water [3]. Equation (1) is a possible reaction at the valence band which results in the production of a hydroxyl radical, and Equation (2) is a possible reaction at the conduction band in which a superoxide free radical is formed [3].

\[
\begin{align*}
\text{h}^+ + \text{H}_2\text{O} & \rightarrow \text{H}^+ + \text{HO}^- \\
\text{O}_2 + \text{e}_{cb} & \rightarrow \text{O}_2^- 
\end{align*}
\]

These free radicals are then available to react with contaminants in the water resulting in their degradation. Additionally, contaminants may be degraded by direct oxidation/reduction reactions with the conduction band electrons and valence band holes.
The relative strength or reactivity of photocatalyst materials to promote oxidative/reductive reactions is given by the band edge potentials and resulting band gap [15, 16]. An evenly distributed band gap and band edge potentials indicate greater charge separation occurs and stronger oxidative/reductive reactions are possible [15, 16].

The most commonly used and widely studied photocatalyst for water treatment is titanium dioxide nanoparticles, or TiO₂ [9, 10, 17]. A good photocatalyst for degradation of contaminants in water treatment should be safe and non-toxic, inexpensive, stable, and highly photoreactive, all of which TiO₂ is [17]. One major advantage of photocatalyst technologies compared to other treatment methods is the ability to recover and reuse the material many times without significant loss of oxidation/reduction potential [18]. Typically, TiO₂ particles are added to the contaminated water in a slurry form and UV light is applied from the outside or within the reactor to encourage photocatalysis; although, other reactor types such as multiple tube and fluidized bed have also been used [19].

2.2. Reactor Design of TiO₂ Systems

TiO₂ nanoparticles have been incorporated into water treatment processes using a variety of designs. There are two main ways in which TiO₂ can be integrated into a water treatment process, which are immobilization on a support material and suspension in an aqueous solution [20]. A support material, such as glass or sand, could be used to more easily recover TiO₂ particles after reaction, but contaminant degradation in this type of reactor is typically lower [20]. Because of this trade-off, a significant amount of research
has been completed to determine the optimum method of implementation of photocatalyst materials to achieve the most contaminant degradation while maximizing recovery of TiO₂ nanoparticles.

In terms of reactor design for implementation of TiO₂ nanoparticles, four main types have been defined which are slurry, immersion, distributive, and external illumination reactors [21, 22]. A slurry reactor is one in which the photocatalyst particles are suspended in a fluid such as water, while immersion, distributive, and external illumination describe reactors with varying light (or UV) source implementation [22]. Each of these reactor designs must balance maximizing photon delivery to the photocatalyst while also maximizing mass transfer of the photocatalyst to the contaminants in solution [21]. Some examples of specific reactor designs that have been studied and incorporate the aforementioned qualities are suspension reactors, fluidized bed, and fiber optic cable among others [20, 23].

One of the few full-scale commercial TiO₂ treatment processes is the Photo-Cat® manufactured by Purifics. This system utilizes a slurry of P-25 TiO₂ with low-pressure mercury lamps to photocatalytically degrade contaminants in groundwater and process effluents [24, 25]. Figure 2 shows a full-scale 0.5 MGD Photo-Cat® system, while Figure 3 gives an overview of the individual components [25, 26]. As shown in Figure 3, water flows into the unit and is combined with the TiO₂ slurry, which then flows in a serpentine pattern through 3 mm channels around the low-pressure mercury lamps [25].
Figure 2. Full-scale 0.5 MGD Photo-Cat® system [26].

Figure 3. Diagram showing components and flow path for the Photo-Cat® system by Purifics [25].
After reaction, the slurry and treated water flow through ceramic microfiltration membranes (8 in Figure 3) which separate the TiO$_2$ from the treated water [25]. The nanoparticles are removed from the membranes by pulsation, which occurs intermittently and allows the TiO$_2$ to be recycled into the Photo-Cat® system while the treated water exits [25]. This system has been shown to degrade a number of problematic contaminants including pharmaceuticals, disinfection by-products, and recalcitrant organics [25, 27].

Although the Photo-Cat® system has been shown to be effective for degrading a variety of contaminants, it, and photocatalytic TiO$_2$ systems in general, have a number of operational issues. One issue is the recovery of the TiO$_2$ nanoparticles, which is difficult due to their very small size. The Photo-Cat® system has overcome this issue using ceramic microfiltration membranes, but membrane filtration requires significant energy input as well as creates the potential for fouling [3]. Additionally, scaling-up these systems to treat large flow rates may also be problematic due to their complexity and energy requirements. Thus, although photocatalytic treatment systems have been developed and researched extensively, there is still a need for advances in applying photocatalyst materials for contaminant degradation in water treatment.

2.3. BiPO$_4$ as a Photocatalyst

BiPO$_4$ is a relatively new photocatalyst which was first investigated by Pan and Zhu in 2010 [28]. This research group synthesized BiPO$_4$ using a hydrothermal method and investigated its ability to degrade methylene blue (MB) under UV light irradiation [28]. A hydrothermal method for chemical synthesis refers to a reaction that occurs at
temperature and pressure that are greater than ambient conditions, which, in this case, encourages formation of crystal BiPO$_4$ structures [28–30]. Pan and Zhu showed that BiPO$_4$ was more effective than TiO$_2$ at degrading MB under the same experimental conditions [28]. This is significant because, as previously mentioned, TiO$_2$ is currently the most widely used and studied photocatalyst for applications in water treatment [31].

Cates’ Research Group at Clemson University has been further investigating the photocatalytic capabilities of BiPO$_4$ due to its promising oxidation/reduction capacities compared to TiO$_2$ [28]. The unique ability of BiPO$_4$ to degrade organic compounds, such as 2,4-dichlorophenol as described by Liu et al., may possibly be attributed to the large band gap energy (3.5 to 4.6 eV) of BiPO$_4$ allowing for strong oxidative and reductive reactions [32].

In addition to BiPO$_4$’s ability to degrade important environmental contaminants, this material maintains its photocatalytic activity at large particle sizes (~2.0 μm) [28, 32]. This is a unique property because the surface area of particles typically has a significant effect on photocatalytic activity, and large particles have less surface area relative to smaller particles [28, 32]. For instance, a typical TiO$_2$ particle is on the order of 30 nm, while BiPO$_4$ particles of about 2.0 μm maintain good photocatalytic activity [5]. Figure 5 demonstrates the size of BiPO$_4$ particles synthesized at two pH values; images were compiled by members of the Cates’ Group.
Figure 4. Scanning electron microscopy (SEM) images showing morphology of BiPO$_4$ synthesized at pH 8 (left) and pH 11 (right).

These data indicate that larger particles of BiPO$_4$ can still provide effective treatment of recalcitrant compounds while these particles have the potential to be easily removed from water treatment processes through sedimentation or conventional filtration, a property not present in other photocatalysts. Additionally, BiPO$_4$ particles are quite dense, with a specific gravity of 6.32 (compared to 4.23 for TiO$_2$), which further enhances their potential to be recovered through sedimentation [33, 34]. These properties enable BiPO$_4$ to be more easily implemented into water treatment processes than other photocatalytic materials by utilizing simple, effective processes to remove the material from treated water.

2.4. BiPO$_4$ PAO System with Recovery

The motivation for this thesis is to experimentally show that BiPO$_4$ particles can be easily recovered through gravitational settling, giving this material a distinct advantage over other photocatalyst materials, like TiO$_2$. Eventually, a combined PAO
system with a photoreactor, rapid clarifier, and catalyst recycle will be built by the Cates’ Group to demonstrate the photocatalytic activity and ease of recovery for BiPO$_4$. This work will focus on the design and implementation of a rapid clarifier to recover BiPO$_4$ particles for reuse in a PAO system.

A rapid clarifier, in this text, refers to a sedimentation basin with inclined plates used for increasing the removal of particles from a water stream [3]. A conventional sedimentation basin is simply a large rectangular tank in which water flows horizontally through the unit; gravity acts upon solids in the water causing them to settle from the water to the bottom of the basin [3]. Clean water exits near the top of the basin while solids are periodically removed from the bottom [3]. In a rapid clarifier inclined plates are added in order to increase the surface area available for particles to settle on without increasing the size of the tank itself [35, 36]. A general schematic of a rapid clarifier is shown in Figure 6.

![Figure 5. Conceptual model of a rapid clarifier [35].](image)
Utilizing gravity settling for recovery of photocatalyst particles opposed to membrane filtration needed for TiO₂ recovery would decrease the complexity and energy use needed for an effective PAO system [37].

2.5. Plate Settlers and Their Function

Plate settlers are used in clarifiers and sedimentation basins in order to increase the area available for particles to settle, thus increasing the amount of particles removed from a water stream without increasing the size of the basin itself [36]. Another theoretical explanation is that inclined plates decrease the distance any given particle must settle before it is removed from the flow of water [3]. Once particles accumulate on the inclined plates they eventually slide to the bottom of the basin, or the sludge zone, where they can be removed [3]. Plate settlers have been used in upgrading sedimentation basins in water treatment, upgrading secondary clarifiers in wastewater treatment, and in various chemical engineering applications [35, 36, 38].

General conventions for implementing plate settlers have been developed over the course of research completed in the field. The angle of the plates is generally set between 45° and 60° from the horizontal axis; this ensures particles will eventually be removed from the plates due to gravity but still provide effective surface area for particles to land on [3, 36, 39]. Also, the first one-fourth of the length of the basin containing plate settlers is typically left free of plates allowing for flow conditions to develop more uniformly [3]. After water flows through the plates and solids have been collected, effluent water leaves at the top of the basin typically by launders [3, 36].
2.6. Design of a Rapid Clarifier

There are three typical configurations for a rapid clarifier with respect to the flow of water through the unit, which are countercurrent, cocurrent, and cross-flow [3, 36, 40]. Each configuration describes the direction of water flow through the plate settlers with respect to the downward settling of particles in the water [3, 36, 40]. For instance, in a countercurrent configuration water flows upward through the plates while the settling of particles is downward, but in a cocurrent configuration the direction of water flow and particle settling are both downward [40]. Figure 7 illustrates the flow of water and particle settling in each of the three clarifier configurations with respect to the plate settlers.

![Figure 7](image1)

**Figure 6.** Flow of water ($v_w$) and particles ($v_s$) in (a) countercurrent, (b) cocurrent, and (c) cross-flow configurations [3].

In this work, details will only be given on the design of a countercurrent system since this is the design that will ultimately be used in the final integrated PAO system. Countercurrent designs are typically used because this configuration avoids problems with flow distribution and sludge resuspension that typically occur in the other two designs [3].
The main design variable for a sedimentation basin or clarifier is the overflow rate, which is the flow rate into the basin divided by the tank surface area [3]. For a clarifier containing plate settlers, typical overflow rates may be from 17 to 40 m³/m²·d [40]. Particle removal in horizontal flow clarifiers without plate settlers is simply determined by the particle settling velocity, basin depth, and detention time; all particles with a settling velocity ($v_s$) greater than the basin depth divided by the detention time ($h_0/\tau$) will be removed from the water [3]. Particles with a settling velocity less than the overflow rate will be removed proportionately to their settling velocity divided by the overflow rate (or $h_0/\tau$) in the basin [40]. The terminal settling velocity of particles undergoing Type I (unhindered) settling in laminar flow can be estimated by Stokes’ Law, which is defined as:

$$v_s = \frac{g(\rho_p - \rho_w)d_p^2}{18\mu}$$

(3)

where $v_s$ is the particle settling velocity, $\rho_p$ and $\rho_w$ are the densities of the particle and the water, respectively, $d_p$ is the particle diameter, and $\mu$ is the dynamic viscosity of water [3]. It should be noted that a spherical particle shape is assumed in Stokes’ Law, while the BiPO₄ particles likely have a more hexagonal shape [3]. When plates are added, the particle removal based on settling velocity is dependent on plate length and spacing, as well as the fluid velocity which is represented by Equation (4):

$$v_s \geq \frac{v_{f\theta}d}{L_p \cos \theta + d \sin \theta}$$

(4)
where $v_s$ is the particle settling velocity, $v_{th}$ is the fluid velocity through the plates, $d$ is the plate spacing, $L_p$ is the plate length, and $\theta$ is the angle of the plates from horizontal [3, 36]. The fluid velocity through the plates is related to the overflow rate by Equation (5):

$$v_f \theta = \frac{Q}{A \sin \theta} = \frac{OR \sin \theta}{\sin \theta}$$

(5)

where $Q$ is the flow rate into the clarifier, $A$ is the surface area of the clarifier, and $OR$ is the overflow rate, Equation (6) is derived giving a design equation based on settling velocity [3].

$$v_s \geq \left[ \frac{d}{L_p \sin \theta \cos \theta + d \sin \theta} \right] \cdot \frac{Q}{A}$$

(6)

Two other important design variables for a rapid clarifier are the Reynolds number and the Froude number. The Reynolds number for a clarifier or sedimentation basin is defined as:

$$Re = \frac{v_f R_h}{v}$$

(7)

where $v_f$ is the horizontal fluid velocity, $R_h$ is the hydraulic radius (defined as the cross-sectional tank area divided by the wetted perimeter), and $v$ is the kinematic viscosity of the fluid [3, 40]. The Reynolds number describes turbulence of the flow of water through the basin; a Reynolds number of less than 20,000 should be maintained in the clarifier to avoid turbulent flow conditions [3, 40]. The Froude number for a clarifier or sedimentation basin is defined as:

$$Fr = \frac{v_f^2}{gR_h}$$

(8)
where \(v_f\) and \(R_h\) are still the horizontal fluid velocity and hydraulic radius, respectively, and \(g\) is the acceleration of gravity [3, 40]. This value describes the tendency of water to flow horizontally; a Froude number greater than \(10^{-5}\) should be maintained in order to prevent back-mixing in the tank [3, 40]. Additionally, the Reynolds number and Froude number should be less than 50 and greater than \(10^{-5}\), respectively, within the plates to ensure laminar flow [40]. The Reynolds number and Froude number are important design variables for a rapid clarifier to check that the flow of water encourages particle settling.

2.7. Wall Effects and Scale-Up

Scaling-up a lab-scale rapid clarifier should take into account differences that will inevitably occur as a result of drastically increasing the size and flow rate of a lab-scale unit. For example, one significant difference will be the “wall effects” from the clarifier on the flow of water and particle settling between the lab-scale and full-scale units [3]. These so-called wall effects are more dominant in small-scale than in large-scale units, thus a lab-scale unit large enough to neglect wall effects should be built or these effects should be taken into account in scale-up [41]. Two helpful variables in scale-up of any system involving fluid flow are the aforementioned Reynolds number and Froude number [42]. Since these values are dimensionless and depend on the geometry of, and fluid velocity in, the clarifier, they can be used to ensure that flow characteristics (and therefore particle settling behavior) will be similar between the small and large-scale units [3, 42].
The most important objective in scale-up is to ensure the BiPO₄ particles will be captured at the needed removal percentage. Thus, the most useful equation for scaling up a rapid clarifier containing plate settlers is Equation (6). Since the settling velocity for particle removal remains the same, the plate spacing and length along with the overflow rate can be altered according to the desired flow rate and dimensions to ensure that a given particle removal will be achieved.
RESEARCH OBJECTIVES

This project builds on work started by the Cates’ Group on the research of BiPO₄ and its implementation into a PAO system for degradation of recalcitrant contaminants. The main goal was to characterize the settling behavior of BiPO₄ particles and to show that this material can be easily recovered using gravity sedimentation. Specifically, the objectives were to:

1. **Determine the average BiPO₄ particle size using a dynamic light scattering (DLS) instrument.** Particle size was used to calculate the theoretical settling velocity of the material which was used for the preliminary clarifier design.

2. **Determine the settling velocity distribution (settling curve) of BiPO₄ particles using a settling column.** The settling column was fabricated in the lab to determine the particle settling velocity using small sample volumes.

3. **Design and construct a lab-scale rapid clarifier to determine the maximum overflow rate to achieve removal of BiPO₄ from the water.** This design could theoretically be scaled-up and implemented in full scale water treatment and will show that BiPO₄ particles may be recovered by gravity sedimentation.

4. **From the experimental results, scale-up the lab-scale rapid clarifier to determine the size of a full-scale unit needed for BiPO₄ particle removal based on an average water treatment plant flow rate.** These results show the size and design parameters of a full-scale unit that would be needed for implementation of the BiPO₄ PAO system.
3. MATERIALS AND METHODS

3.1. Synthesis of BiPO₄

BiPO₄ particles were synthesized according to the hydrothermal method used by Cates’ Group, which is based on that developed by Pan et al. [28]. Materials for the preparation of BiPO₄ photocatalyst particles included Bi(NO₃)·5H₂O (used as received, Sigma Aldrich), NH₄H₂PO₄ (used as received, Acros Organics), distilled-deionized (DDI) water, NH₄OH (used as received, BDH), and 100 mL stainless steel hydrothermal reactors containing Teflon inserts. Additionally, typical lab glassware such as graduated cylinders and an electronic balance and stir plate were also used.

The hydrothermal method for BiPO₄ synthesis is a technique that utilizes high temperature and pressure in order to synthesize and grow crystals [30]. First, a 3.22 mM solution of NH₄H₂PO₄ was made by adding 0.37 g to 35 mL DDI water. Also, a 3.22 mM solution of Bi(NO₃)·5H₂O was made by adding 1.562 g of the salt to 35 mL DDI water. Both solutions were stirred using magnetic stir bars for ten minutes in glass beakers, and the Bi(NO₃)·5H₂O solution was sonicated as needed since the material is less soluble in water. Once completely mixed, the NH₄H₂PO₄ solution was added drop-wise to the Bi(NO₃)·5H₂O solution while stirring until completion. The combined solution was then stirred for ten minutes and sonicated for five minutes. Next, the pH of the combined solution was raised to 11.0 by adding NH₄OH drop-wise and measuring with an electronic pH probe and meter. It should be noted that varying the pH, reaction time, and reaction temperature can change the morphology and size of the BiPO₄ particles produced [32]. The pH, reaction time and temperature described were chosen as the
particles obtained with these conditions were the largest in size while still maintaining
good photocatalytic activity as determined by members of the Cates’ Group. After the pH
was raised to 11.0, the combined solution was stirred for four hours to ensure
homogenous composition.

Next, the solution was poured into a 100 mL hydrothermal reactor Teflon insert to
a level of approximately 70 mL. The insert was placed in the stainless steel autoclave
reactor which was then tightly capped. The hydrothermal reactor was heated at 180°C in
a drying oven for 48 hours. After heating, the reactors were removed from the drying
oven and allowed to cool for at least one hour before opening. The solution was poured
from the reactors and centrifuged in 50 mL Falcon tubes at 5,000 rpm for five minutes,
then the supernatant was decanted to obtain the BiPO₄ particles. DDI water was used to
wash the material three times while centrifuging in between each wash to prevent particle
loss. The BiPO₄ particles were dried overnight in a drying oven at 82°C. This process
resulted in approximately 0.50 grams of BiPO₄ particles per 70 mL of initial solution.
This procedure was repeated numerous times in order to synthesize approximately twenty
grams of material used for the settling experiments in the lab-scale rapid clarifier and
settling column.

3.2. Dynamic Light Scattering (DLS) Measurements

DLS is a method used to quantify the particle size and size distribution of
materials in suspension by correlating the changes in light wavelength from a laser which
passes through a particle-containing solution [43]. For this work, the particle size of
BiPO$_4$ was of interest in order to calculate a theoretical settling velocity that could be used in the clarifier design. Additionally, DLS measurements were used to confirm particle size estimates made from SEM images of BiPO$_4$ particles.

A Malvern Zetasizer Nano was used to conduct the DLS measurements on the BiPO$_4$ particles. One important sample characteristic for DLS measurements is the concentration of particles in the sample; a concentration that is too high can cause multiple scattering, while a concentration that is too low may prevent a sufficient amount of light from being scattered for the instrument to take a reading [44]. Thus, a concentration study was first conducted with the BiPO$_4$ particles in which a range of concentrations was measured using the DLS instrument to determine the optimum concentration for measurement of the samples. From this experiment, the optimum particle concentration was determined to be 1,000 mg/L BiPO$_4$.

The samples were prepared by adding 0.10 g of BiPO$_4$ to 100 mL DDI water. This solution was stirred at approximately 800 rpm for five minutes and sonicated for five minutes. A 1 mL transfer pipette was used to transfer approximately 4 mL of the solution to plastic disposable cuvettes manufactured specifically for DLS measurements by Brookhaven Instruments. Zetasizer software installed on a desktop PC was used to set-up and run the measurements on the Malvern Zetasizer Nano. Figure 8 shows the instrument and software used to collect the DLS data.
The solvent was specified as water, the temperature as 25°C, and BiPO₄ was created as a material in the software. Of particular interest, the refractive index for BiPO₄ was set at 1.39, as recommended by Zhao et al., since this value represents the refractive index for LaPO₄ which has a similar crystal structure to BiPO₄ [45]. The samples contained in cuvettes were inverted several times and sonicated for approximately three minutes before measuring. The number of runs was reduced to six and the run duration was reduced to ten seconds in the software so that a single measurement would take one minute, in addition to thirty seconds of stabilization time. These adjustments were made as the particles were observed to aggregate and settle to the bottom of the cuvettes over time; reducing the measurement time ensured that a greater proportion of the BiPO₄ particles would be suspended in solution and detected by the DLS instrument.
3.3. Settling Column

A settling column was made in order to conduct experiments which describe the settling behavior of BiPO₄ particles. The settling column test is used in the design of conventional sedimentation basins to describe the expected particle removal at particular depths over time, which can be correlated to overflow rates in a real basin [3]. In this work, the settling column test was used to determine the distribution of settling velocities of the BiPO₄ particles.

3.3.1. Construction of a Settling Column

Because the BiPO₄ material takes 48 hours to make one batch, and one batch yields approximately 0.5 grams of material, it was desirable to reduce the consumption of the material as much as possible. Therefore, it was decided that custom settling columns should be made which reduce the volume of solution needed to conduct the experiment, and thus reduce the consumption of BiPO₄. The custom settling columns were made from 100 mL (2.7 cm diameter and 24.5 cm height) and 1,000 mL (6.0 cm diameter and 43.5 cm height) polypropylene graduated cylinders. Holes were drilled using a hand-held drill at intervals of 10 mL on the smaller column and intervals of 200 mL on the larger column. Butyl rubber septa were glued into the holes with clear silicone adhesive. Septa would allow for syringes with needles to be used to collect the solids samples without creating leaks. Silicone was again applied once the septa were secured to prevent leaks from occurring during experimentation. **Figure 9** shows the settling columns constructed for the experiments.
3.3.2. Procedure for Settling Column Experiments

The general procedure for the settling column test was adapted from *Water Treatment Unit Processes* by Hendricks, which was first developed by Camp in 1946 [46, 47]. This method assumes that particles settle discretely, or by Type I settling, meaning that settling occurs due to gravity and minimal interactions with other particles in the water occur [3, 46]. This was a reasonable assumption as a relatively low particle concentration was used in the settling column experiments, and no coagulant or settling aid was added to influence the settling behavior of the individual particles [40]. The experimental procedure for each settling column is described below.

**Figure 8.** 100 mL (left) and 1,000 mL (right) settling columns constructed for the settling experiments.
For the 100 mL column, 0.05 g of BiPO$_4$ was added to 100 mL DDI water to create a 500 mg/L suspension. DDI water was used to avoid any possible influences on particle settling from ions present in tap water. The suspension was stirred at 800 rpm for five minutes, sonicated for five minutes, and stirred until use. Sonication was used to disperse particle aggregates into discrete particles. Next, the suspension was added to the settling column and the top sealed with Parafilm before slowly inverting five times to ensure homogeneity. A timer was started once the column was placed on the lab bench and was allowed to sit quiescently. For each run, or time, five different samples of 1.0 mL were collected using a needle and syringe for five different column heights. Samples were analyzed for turbidity by diluting the 1 mL samples to 26 mL total volume. The turbidity of the diluted samples was measured using a Hach 2100N turbidimeter. Next, the diluted solutions were combined in a beaker and the BiPO$_4$ particles were allowed to settle for approximately thirty minutes. After this time, a pipette was used to collect the material from the bottom of the beaker to refill the settling column to the 100 mL level. This process was used so that minimal BiPO$_4$ material loss would occur and the initial concentration of BiPO$_4$ would be relatively constant throughout the various runs in the experiment. This process was repeated for five time points in order to collect enough data to create a plot of $C/C_0$ vs. settling velocity [46].

For the 1,000 mL settling column, TSS measurements were made in separate runs to confirm the results obtained using the turbidity measurements. First, 0.50 g of BiPO$_4$ was added to 1,000 mL DDI and stirred for five minutes, sonicated for five minutes, and stirred until use. The 500 mg/L suspension was poured into the 1,000 mL
column and inverted five times to ensure homogeneity. For these measurements, 10 mL samples were collected at five heights on the column for five time points using the same procedure already described. However, since the BiPO₄ material could not be returned to the column in this case since it would be dried on the glass fiber filter, a new initial solution was made for each time point, or run. These samples were dispensed into crucibles containing Whatman glass fiber filters under a vacuum and were allowed to dry at 105°C overnight. The next day, the masses of the crucibles, filters, and BiPO₄ material was recorded and the initial mass was subtracted to obtain the mass of BiPO₄ at a particular column height and time. The procedure for TSS measurements is explained in more detail in Section 3.5.1 and in Appendix C-2. Again, the goal was to create a plot of C/C₀ vs. settling velocity for determining an appropriate overflow rate for settling of BiPO₄ particles [46].

3.4. Clarifier Design and Construction

The construction of the lab-scale clarifier was based on the design of a conventional sedimentation basin with plate settlers added to increase particle removal. General conventions used in the design of sedimentation basins containing plate settlers were utilized from textbooks by Crittenden [3], Tchobanoglous [36], and Davis [40]. For the dimensions of the clarifier, a spreadsheet was created and utilized which takes the desired flow rate, overflow rate, and residence time as inputs and calculates the required dimensions in order to satisfy these inputs. For example, to calculate the required surface area (A) of the basin, the input flow rate (Q) was divided by the input overflow rate (OR):
\[ A = \frac{Q}{OR} \]  

Then, the volume of the basin \( V \) was set by multiplying the input flow rate by the residence time \( \tau \):

\[ V = Q \cdot \tau \]  

The depth of the basin \( D \) was set based on the required volume and surface area:

\[ D = \frac{V}{A} \]

Based on these values, the Reynolds and Froude Numbers were checked to ensure they are in the appropriate ranges of \(< 20,000 \) and \( > 10^{-5} \), respectively, for a classic rectangular sedimentation basin \([3, 40]\). Additionally, the Reynolds and Froude Numbers within the channels of the plate settlers were also checked to ensure values of \(< 50 \) and \( > 10^{-5} \), respectively \([40]\). The calculations for these values were described in Section 2.3. The spreadsheet utilized for these calculations and to determine the final design is shown in Appendix B.

The design of the lab-scale clarifier was based on a conventional sedimentation basin with plate settlers added in order to increase the overflow rate that could achieve a given percent removal of solids in the effluent. An example of a similar lab-scale clarifier is shown by Lee in *Environmental Engineering Research* \([48]\). AutoCAD was used to create a generalized sketch of the clarifier to use in the construction of the unit, which is shown in Figure 10. The final design incorporated the dimensions calculated from the design spreadsheet with the general layout shown in Figure 10.
The clarifier walls were cut from large sheets of clear, 3/8 inch-thick acrylic. A conventional table saw was used to cut the acrylic once the dimensions had been marked. Individual acrylic pieces were cut for the two side walls, front and back walls, base, and one baffle. The baffle was placed at one-fourth the length of the basin before the inclined plates in order to encourage ‘upflow’ of the water through the plates. The acrylic pieces were bonded together with Liquid Nails Fuze-It® multi-purpose adhesive. A single one-inch hole was drilled with a drill press in the front wall for flow entry, and two 1 ¼ inch holes were drilled in the back wall for flow exit. The holes were sanded and altered as needed with a Dremel rotary tool.

**Figure 9.** Generalized sketches of the upflow rapid clarifier showing A) front/back, B) horizontal cross-section, and C) plan view.
The flow distributor for the influent was constructed from a ¾ inch ‘T’ PVC piece. The ‘T’ was capped on both ends and a hose barb was glued to the inlet to allow hosing from the pump to be easily connected and disconnected. Eight holes of increasing diameter from the center of the ‘T’ to the edges were drilled to evenly distribute the inlet flow across the width of the clarifier as shown in Figure 11. This flow distributor was glued in the inlet to the clarifier with Fuze-It® adhesive.

![Figure 10](image1.png)  ![Figure 10](image2.png)

**Figure 10.** Inlet flow distributor for the lab-scale rapid clarifier.

The effluent collection channels were also constructed from PVC pieces. One-inch diameter PVC pipe was cut into two six inch pieces, which were then cut in half to obtain the collection channels. These pieces were slid into one-inch to ¾ inch adapters, which were connected into another adapter set with the acrylic wall between the pieces as shown in Figure 12. This was done to seal the space between the PVC pieces and the
acrylic in order to prevent leaks. Also, the entire effluent collection channel could be removed in order to remove and replace the plate settlers.

![Figure 11](image)

**Figure 11.** Effluent flow channels for the lab-scale rapid clarifier.

The plates for the clarifier were cut from 0.025 inch-thick aluminum sheet to the dimensions specified in the design using industrial scissors. These plates were designed to be removable in order to easily clean the clarifier after use and to alter the plate spacing. Angled tile spacers of thickness 3 mm were glued to the walls of the clarifier at an angle of 60° to evenly space and support the aluminum plates. Thin pieces of acrylic were glued under the bottom of the lower row of tile spacers to serve as a ledge for the plates to rest on and prevent flow from going around the edges of the plates during operation. The ledge and tile spacers allowed the plates to be easily added and removed as needed for the settling experiments. The completed clarifier is shown in **Figure 13.**
The calculations for the dimensions of the clarifier will be discussed in more detail in Section 4.3.

![Side view of the completed lab-scale rapid clarifier.](image)

**Figure 12.** Side view of the completed lab-scale rapid clarifier.

### 3.5. Settling Experiments with the Rapid Clarifier

The lab-scale rapid clarifier was constructed to determine the maximum overflow rate that could be used to remove a given percentage of BiPO$_4$. To accomplish this, a 600 rpm Masterflex® L/S pump was used to flow solution through the clarifier. Solids settle on the plates and in the collection zone of the clarifier, and effluent leaves at...
the top of the clarifier through the effluent flow channels. Turbidity and total suspended solids (TSS) measurements were used to determine the removal fraction of solids by comparing the values of the influent with the effluent values over time. Kaolinite clay was first used as the solid material in solution to characterize the effectiveness of the plates and to ensure the clarifier was functioning properly before using BiPO₄ as the solid material.

3.5.1. TSS Measurements

To conduct the TSS measurements, EPA Method 160.2 was generally followed [49]. In summary, Whatman type 934 AH glass fiber filters were seated in ceramic crucibles by applying a vacuum and adding several mL of DDI water. The crucibles were dried overnight in a drying oven at 105°C to evaporate any remaining moisture. The next day, the crucibles were removed from the drying oven and placed in a desiccator to cool. The mass of each dried crucible and glass fiber filter was recorded using an electronic balance to a precision of 0.1 mg. After weighing, the filters were reseated in the crucible by adding several mL of DDI water while applying a vacuum. During the settling experiments with the rapid clarifier, 10 mL of influent sample or 40 mL of effluent sample was poured into the crucible. Again, a vacuum was applied to force water through the glass fiber filter. After filtering, the crucibles were removed from the vacuum apparatus and placed in the drying oven set at 105°C and were allowed to dry overnight. The next day, the mass of each crucible plus glass fiber filter and suspended solids contained on the filter was recorded. Finally, the TSS for each measurement can be calculated by:
\[
TSS = (M_2 - M_1) \times \frac{1000 \text{ mg}}{V_{\text{sample}}} 
\]

where \( M_1 \) and \( M_2 \) are the initial and final recorded masses and \( V_{\text{sample}} \) is the volume of sample filtered during the experiment. The apparatus used to conduct the TSS measurements is shown in Figure 14.

Figure 13. Apparatus used for TSS measurements; rubber hose leads to a vacuum pump.

TSS measurements were used to characterize the solids removal by the clarifier by comparing the influent and effluent concentrations for the various solid materials and overflow rates.
3.5.2. Procedure for Clarifier Experiments

To run the clarifier experiments, BiPO$_4$ was dispersed in tap water contained in 20 L plastic buckets. For the preliminary experiments, the same procedure was followed except kaolinite clay and silt-sized sediment were used as the dispersed phases. Tap water was used since a large volume of water was needed to run the clarifier experiments and adverse effects from doing so were not expected. To ensure homogeneity, the solution was continuously stirred using a Lightnin® brand mechanical mixer. A concentration of 0.5 g/L BiPO$_4$ was selected; this is less than the 1.8 g/L concentration used in the photocatalysis experiments and was selected in order to run the clarifier for a longer period of time without having to make excess material. A Masterflex® L/S pump was used to transport the BiPO$_4$ solution through the clarifier. Flow rates of 200, 500, and 1,000 mL/min were used which correspond to overflow rates of 0.4, 1.0, and 2.0 m/h. Before pumping began, TSS samples of 10 mL were collected and filtered from the stirred influent solution. The pump was then set to the appropriate flow rate and started at time zero, and the mixer was set to 250 rpm. Over time, additional TSS samples of 40 mL were collected and filtered from the effluent flow channels. The TSS samples were filtered and dried according to the procedure described in Section 3.5.1. The resulting C/C$_0$ values calculated from the TSS data were plotted corresponding to the time at which the samples were taken. The settling and removal of BiPO$_4$ from the water was characterized by these experiments which related clarifier overflow rates to fractional removal.
3.6. Scale-Up of the Lab-Scale Clarifier

To scale-up the constructed clarifier to a full-scale application, the lab-scale conditions which achieve the desired percent particle removal were used along with the important design variables. Although there is little published information on the subject of scaling-up clarifiers for the use of particle removal, reasonable assumptions and design equations were used to determine a reasonable full-scale rapid clarifier design which achieves the desired particle removal. From the lab-scale experiments, a clarifier design which achieves a certain particle removal at a particular overflow rate was obtained, and these values were used as the inputs for the full-scale design.

Based on the overflow rate which gave at least 90% BiPO$_4$ particle removal in the lab-scale experiments, a corresponding particle settling velocity for removal at these conditions was calculated by Equation (6). Since this settling velocity remains the same for BiPO$_4$ regardless of the clarifier design, this settling velocity was used as a known variable in Equation (6). Additionally, the typical plate spacing in full-scale plate settler application is 50 mm, so this value was also used as a known variable [36]. Lastly, based on a typical tank depth of 5 m, the plate length could be no longer than 3 m, allowing Equation (6) to be solved for the maximum overflow rate that will achieve the needed capture velocity [3].

Since the depth of the tank should be approximately 5 m, the size of the lab-scale clarifier can be geometrically scaled-up by multiplying each dimension by a common factor. Once this was done, the surface area was set which allows for the overflow rate to be multiplied by the surface area, giving the maximum flow rate that
could be used based on the desired particle removal. This calculated flow rate and the scaled-up dimensions were then used to calculate the new Reynolds number and Froude number for the larger unit. Although Reynolds number and Froude number will not be exactly the same as the lab-scale unit using this method, if they lie in the same range as the lab-scale unit it is reasonable to expect that the flow will behave similarly in the larger unit.
4. RESULTS AND DISCUSSION

4.1. DLS Particle Size Measurements

First, the particle size of the BiPO$_4$ particles synthesized at pH 11 were analyzed using a DLS instrument. Before collecting final data on the size of the particles, a study relating the particle size of BiPO$_4$ relative to concentration in solution was conducted. This was done as the concentration of particles in solution has been shown to affect the particle size determined by DLS instruments; thus, a concentration range should be found where the particle size measured by the DLS instrument is relatively constant [43, 44]. Figure 15 shows the particle size data collected by the Malvern Zetasizer Nano over a range of BiPO$_4$ solution concentrations.

![Figure 14](image_url)

**Figure 14.** Particle size measured by a Malvern Zetasizer Nano DLS instrument relative to BiPO$_4$ concentration synthesized at pH 11.
Additionally, Table 1 shows the same data plotted in Figure 15 along with the polydispersity index measured for each sample.

Table 1. Particle size of BiPO$_4$ measured by a Malvern Zetasizer Nano DLS instrument at varying particle concentrations. Z-ave represents the average particle size, and PDI represents the polydispersity index.

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>Z-ave (nm)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,000</td>
<td>2,556</td>
<td>0.537</td>
</tr>
<tr>
<td>750</td>
<td>2,339</td>
<td>0.786</td>
</tr>
<tr>
<td>500</td>
<td>2,330</td>
<td>0.615</td>
</tr>
<tr>
<td>250</td>
<td>2,934</td>
<td>1.000</td>
</tr>
<tr>
<td>50</td>
<td>2,556</td>
<td>0.959</td>
</tr>
</tbody>
</table>

The data show that the BiPO$_4$ particle size (Z-ave) is relatively consistent over the measured concentrations of 50 to 1,000 mg/L. The Z-average is the approximate particle size measured by the instrument based on signal intensity and the assumption of a spherical particle shape and suspension of the particles in water [44]. The average particle size measured is 2,543 nm (or 2.54 μm), and the measured value which deviates the most is the 250 mg/L concentration at 15% difference from the average. However, the PDI values shown increase at lower concentrations. The PDI describes the heterogeneity of particle sizes detected in the sample by the instrument; a higher PDI value indicates a wider range of particle sizes detected, while a lower PDI indicates a more uniform distribution of particle sizes [44]. Since a lower PDI gives a more accurate average particle size, the highest concentration of 1,000 mg/L BiPO$_4$ was used for the final particle size measurements in order to obtain the most representative average particle size in the samples [44].
The final particle size measurements are shown in Table 2 along with measurements from a 2.1 μm particle size standard of polystyrene spheres.

**Table 2.** Final particle size of BiPO₄ measured by a Malvern Zetasizer Nano DLS instrument at a concentration of 1,000 mg/L in triplicate. Z-ave represents the average particle size, and PDI represents the polydispersity index. 2.1 μm std. represents a standard solution of polystyrene spheres of size 2,100 nm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Z-ave (nm)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 μm std. (1)</td>
<td>2,355</td>
<td>0.006</td>
</tr>
<tr>
<td>2.1 μm std. (2)</td>
<td>2,160</td>
<td>0.330</td>
</tr>
<tr>
<td>2.1 μm std. (3)</td>
<td>2,438</td>
<td>0.190</td>
</tr>
<tr>
<td>1,000 mg/L (1)</td>
<td>2,482</td>
<td>0.361</td>
</tr>
<tr>
<td>1,000 mg/L (2)</td>
<td>2,366</td>
<td>0.391</td>
</tr>
<tr>
<td>1,000 mg/L (3)</td>
<td>2,210</td>
<td>0.400</td>
</tr>
</tbody>
</table>

The 2.1 μm standard was measured to determine how accurately the Malvern DLS instrument could measure particles of this diameter, which is approximately the same size expected of the BiPO₄ particles. The average particle size of this standard was measured at 2,318 nm, or about 10% more than the 2.1 μm size expected. This deviation for the particle size measurements was deemed acceptable as these measurements were used to confirm particle-size approximations already made from SEM images of the material and to calculate the expected terminal settling velocity, to which a safety or correction factor could be easily applied. The average BiPO₄ particle size synthesized at pH 11 was measured to be 2,353 nm; incorporating a 10% correction factor gives a range of particle sizes from 2.12 to 2.59 μm. It should also be noted that the PDI values for these measurements fall in the acceptable range of less than 0.50 [44].

The purpose of conducting these particle size measurements was to calculate a terminal settling velocity for BiPO₄ particles which could be used to approximate the
overflow rate needed to achieve settling in the lab-scale clarifier. To calculate the approximate settling velocity of the particles, Type I settling was assumed allowing for the use of Stokes’ Law as shown in Equation (3) and described in Section 1.7. The specific gravity of BiPO$_4$ is 6.32, and constants for water were taken from Crittenden at a temperature of 20°C [3, 33].

\[
v_s = \frac{g(\rho_p - \rho_w)d_p^2}{18\mu}
\]

\[
= \frac{9.81 \frac{m}{s^2} \times (6,320 - 998) \frac{kg}{m^3} \times (2.35 \times 10^{-6} m)^2}{18 \times 0.001 \ Pa \cdot s} = 1.60 \times 10^{-5} m/s
\]

The lab-scale rapid clarifier could then be designed to remove particles with a mean settling velocity of 1.60·10$^{-5}$ m/s.

Several issues were encountered when conducting the DLS particle size measurements. One problem was that the particles were observed to aggregate in the cuvettes over time. In the time between pouring the solution into the cuvette and taking the particle size measurement, the BiPO$_4$ particles would settle to the bottom of the cuvette. When inverted to re-suspend the particles in the solution, the particles would be noticeably larger and quickly settle back to the bottom of the cuvette. This resulted in warnings from the Zetasizer software about the size and settling rate of the particles and measurements which were too scattered to perform particle size analysis on. To combat these issues, each sample contained in a polystyrene cuvette was sonicated for three minutes to suspend and disperse the particles in solution before performing the DLS measurements. Sonicating each sample improved consistency of the readings and the data.
quality. Additionally, the run time for each sample was reduced so that less time would be available for particles to settle and agglomerate. Even so, occasionally the software would still provide warnings such as ‘Detection of large or sedimenting particles’ during measurements. This is likely a result of the relatively large size and high specific gravity (or density) of BiPO₄. Although the BiPO₄ particle size is well within the 6.0 μm size limit on the Malvern DLS instrument, their high specific gravity and tendency to aggregate made accurate DLS measurements more difficult to obtain [44]. Additionally, the Z-ave value measured by the DLS is the equivalent diameter of a spherical particle measured by the instrument; since BiPO₄ particles have been shown to have a hexagonal shape, this assumption may provide a source of error [50]. Nevertheless, the final particle size data collected gave consistent results with low PDI values, indicating more uniform size measurements.

4.2. Settling Column Data

Experiments utilizing a settling column were used to determine the distribution of settling velocities of BiPO₄ particles synthesized at pH 11 and to confirm the estimated settling velocity calculated using Stokes’ Law. As mentioned previously, several methods were attempted in order to reduce the mass of BiPO₄ used for each settling column experiment while still obtaining representative data.

4.2.1. Turbidity Measurements and Data

Turbidity measurements were first used as a surrogate for BiPO₄ concentration in the settling column experiments since turbidity samples are able to be collected and
measured quickly. To correlate turbidity to BiPO$_4$ particle concentration, a standard curve was first made by varying the BiPO$_4$ particle concentration and measuring the turbidity at each concentration as shown in Figure 16.

![Figure 15](image-url)

**Figure 15.** Correlation between BiPO$_4$ concentration and measured turbidity for samples synthesized at pH 1 and pH 11. Linear trend-lines were fit to each data set and the equations shown correspond to the fitted trend-lines.

**Figure 16** shows that turbidity correlates well with BiPO$_4$ particle concentration for each of the samples. However, it should be noted that the slope of each fitted trend-line for the two samples synthesized at different pH values is quite different. This is most likely due to the difference in particle size between the two samples; particles synthesized at pH 1 (~0.5 μm) are smaller than those synthesized at pH 11 (~2.5 μm) based on SEM images of the samples. This same phenomenon has been shown in various studies in the literature; solutions containing smaller particles tend to have higher turbidities than
solutions containing the same material of larger particles at the same concentration [51, 52]. This fact would prove to be important in the following data.

The procedure described in Section 3.3.2 was used to collect and measure diluted turbidity samples from the settling column at various heights and times. The compiled data averaged for several runs is shown in Table 3 and plotted in Figure 17.
Table 3. Compiled data collected from settling column experiments utilizing a 100 mL graduated cylinder with sampling ports at various heights. C/\(C_0\) values were calculated from turbidity measurements.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Point</th>
<th>Height (cm)</th>
<th>(v_s) (cm/s)(^1)</th>
<th>C/(C_0)(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1.0</td>
<td>N/A(^3)</td>
<td>1.00</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>4.9</td>
<td>N/A</td>
<td>1.00</td>
</tr>
<tr>
<td>0</td>
<td>3</td>
<td>9.0</td>
<td>N/A</td>
<td>1.00</td>
</tr>
<tr>
<td>0</td>
<td>4</td>
<td>11.2</td>
<td>N/A</td>
<td>1.00</td>
</tr>
<tr>
<td>0</td>
<td>5</td>
<td>13.3</td>
<td>N/A</td>
<td>1.00</td>
</tr>
<tr>
<td>0</td>
<td>6</td>
<td>15.7</td>
<td>N/A</td>
<td>1.00</td>
</tr>
<tr>
<td>0</td>
<td>7</td>
<td>17.9</td>
<td>N/A</td>
<td>1.00</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1.0</td>
<td>0.008</td>
<td>0.65</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>4.9</td>
<td>0.041</td>
<td>0.60</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>9.0</td>
<td>0.075</td>
<td>0.51</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>11.2</td>
<td>0.093</td>
<td>0.85</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>13.3</td>
<td>0.111</td>
<td>0.49</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>15.7</td>
<td>0.131</td>
<td>0.95</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>17.9</td>
<td>0.149</td>
<td>0.63</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>11.2</td>
<td>0.037</td>
<td>0.82</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>15.7</td>
<td>0.052</td>
<td>0.89</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>1.0</td>
<td>0.002</td>
<td>0.24</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>4.9</td>
<td>0.008</td>
<td>0.31</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>9.0</td>
<td>0.015</td>
<td>0.39</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>13.3</td>
<td>0.022</td>
<td>0.42</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>17.9</td>
<td>0.030</td>
<td>0.30</td>
</tr>
<tr>
<td>30</td>
<td>1</td>
<td>2.9</td>
<td>0.002</td>
<td>0.12</td>
</tr>
<tr>
<td>30</td>
<td>2</td>
<td>4.9</td>
<td>0.003</td>
<td>0.14</td>
</tr>
<tr>
<td>30</td>
<td>3</td>
<td>9.0</td>
<td>0.005</td>
<td>0.26</td>
</tr>
<tr>
<td>30</td>
<td>4</td>
<td>13.3</td>
<td>0.007</td>
<td>0.20</td>
</tr>
<tr>
<td>30</td>
<td>5</td>
<td>17.9</td>
<td>0.010</td>
<td>0.18</td>
</tr>
<tr>
<td>60</td>
<td>1</td>
<td>2.9</td>
<td>0.001</td>
<td>0.14</td>
</tr>
<tr>
<td>60</td>
<td>2</td>
<td>4.9</td>
<td>0.001</td>
<td>0.07</td>
</tr>
<tr>
<td>60</td>
<td>3</td>
<td>9.0</td>
<td>0.003</td>
<td>0.19</td>
</tr>
<tr>
<td>60</td>
<td>4</td>
<td>13.3</td>
<td>0.004</td>
<td>0.26</td>
</tr>
<tr>
<td>60</td>
<td>5</td>
<td>17.9</td>
<td>0.005</td>
<td>0.26</td>
</tr>
</tbody>
</table>

\(^1\) \(v_s\) is the settling velocity calculated by dividing the sampling height by the time

\(^2\) C/\(C_0\) represents the measured concentration divided by the initial using turbidity measurements

\(^3\) N/A represents Not Applicable
As shown in Figure 17, the settling data utilizing turbidity measurements are relatively scattered, and the trend-line has a relatively low $R^2$ value of 0.80. Additionally, there was little consistency between individual runs of the experiment. One explanation for this may be the stratification of particle sizes that occurs in the column over the time of the experiments. Since larger particles have more mass they will settle more quickly than smaller particles, which results in smaller particles being present in higher concentrations at the top of the column over time. Since, as previously mentioned, smaller particles will produce a higher turbidity reading compared to the same concentration of larger particles, the turbidity did not decrease as much as expected [51, 52]. Slight variations in the concentration of smaller particles in the column may explain the problem of
reproducibility. Lastly, small sample sizes and the use of a small settling column may have also negatively influenced the results. To counteract these problems, a larger settling column was constructed and TSS measurements were conducted to characterize the change in particle concentration over time without the adverse impacts caused by different particle sizes.

4.2.2. TSS Measurements and Data

The 1,000 mL settling column was used to conduct the same settling column test while utilizing TSS measurements and larger sample sizes. The combined data are shown in Table 4 and are plotted in Figure 18 based on the sampling port.
Table 4. Compiled data collected from settling column experiments utilizing a 1,000 mL graduated cylinder with sampling ports at various heights. C/C₀ values were calculated from TSS measurements.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Point</th>
<th>Height (cm)</th>
<th>vₛ (cm/s)¹</th>
<th>C/C₀²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>1.6</td>
<td>N/A³</td>
<td>1.00</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
<td>9.1</td>
<td>N/A</td>
<td>1.00</td>
</tr>
<tr>
<td>0</td>
<td>3</td>
<td>16.6</td>
<td>N/A</td>
<td>1.00</td>
</tr>
<tr>
<td>0</td>
<td>4</td>
<td>24.6</td>
<td>N/A</td>
<td>1.00</td>
</tr>
<tr>
<td>0</td>
<td>5</td>
<td>32.8</td>
<td>N/A</td>
<td>1.00</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>1.6</td>
<td>0.0027</td>
<td>0.39</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>9.1</td>
<td>0.0152</td>
<td>0.94</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>16.6</td>
<td>0.0277</td>
<td>0.90</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td>24.6</td>
<td>0.0410</td>
<td>0.71</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>32.8</td>
<td>0.0547</td>
<td>0.92</td>
</tr>
<tr>
<td>12.5</td>
<td>1</td>
<td>1.6</td>
<td>0.0021</td>
<td>0.28</td>
</tr>
<tr>
<td>12.5</td>
<td>2</td>
<td>9.1</td>
<td>0.0013</td>
<td>1.00</td>
</tr>
<tr>
<td>12.5</td>
<td>3</td>
<td>16.6</td>
<td>0.0023</td>
<td>1.00</td>
</tr>
<tr>
<td>12.5</td>
<td>4</td>
<td>24.6</td>
<td>0.0034</td>
<td>1.00</td>
</tr>
<tr>
<td>12.5</td>
<td>5</td>
<td>32.8</td>
<td>0.0046</td>
<td>0.94</td>
</tr>
<tr>
<td>30</td>
<td>1</td>
<td>1.6</td>
<td>0.0009</td>
<td>0.16</td>
</tr>
<tr>
<td>30</td>
<td>2</td>
<td>9.1</td>
<td>0.0051</td>
<td>0.65</td>
</tr>
<tr>
<td>30</td>
<td>3</td>
<td>16.6</td>
<td>0.0092</td>
<td>0.76</td>
</tr>
<tr>
<td>30</td>
<td>4</td>
<td>24.6</td>
<td>0.0137</td>
<td>0.97</td>
</tr>
<tr>
<td>30</td>
<td>5</td>
<td>32.8</td>
<td>0.0182</td>
<td>0.88</td>
</tr>
<tr>
<td>60</td>
<td>1</td>
<td>1.6</td>
<td>0.0004</td>
<td>0.12</td>
</tr>
<tr>
<td>60</td>
<td>2</td>
<td>9.1</td>
<td>0.0025</td>
<td>0.30</td>
</tr>
<tr>
<td>60</td>
<td>3</td>
<td>16.6</td>
<td>0.0046</td>
<td>0.60</td>
</tr>
<tr>
<td>60</td>
<td>4</td>
<td>24.6</td>
<td>0.0068</td>
<td>0.74</td>
</tr>
<tr>
<td>60</td>
<td>5</td>
<td>32.8</td>
<td>0.0091</td>
<td>0.67</td>
</tr>
<tr>
<td>120</td>
<td>1</td>
<td>1.6</td>
<td>0.0002</td>
<td>0.07</td>
</tr>
<tr>
<td>120</td>
<td>2</td>
<td>9.1</td>
<td>0.0013</td>
<td>0.41</td>
</tr>
<tr>
<td>120</td>
<td>3</td>
<td>16.6</td>
<td>0.0023</td>
<td>0.44</td>
</tr>
<tr>
<td>120</td>
<td>4</td>
<td>24.6</td>
<td>0.0034</td>
<td>0.32</td>
</tr>
<tr>
<td>120</td>
<td>5</td>
<td>32.8</td>
<td>0.0046</td>
<td>0.28</td>
</tr>
</tbody>
</table>

¹ vₛ is the settling velocity calculated by dividing the sampling height by the time
² C/C₀ represents the measured concentration divided by the initial using TSS measurements
³ N/A represents Not Applicable
Figure 17. Relative concentration of BiPO₄ particles at varying settling velocities using the 1,000 mL settling column and TSS measurements. Port 1 represents the sampling port located closest to the top of the column, while Port 5 represents the sampling port located closest to the bottom.

Figure 18. Relative concentration of BiPO₄ particles at varying settling velocities using the 1,000 mL settling column and TSS measurements. The trend line is a fourth order polynomial fitted to the compiled data set.
Compared to the data shown in Figure 17, these measurements are much more consistent and fall along a common line. Additionally, since data from the various sampling ports fall along a common line, Type I (discrete) settling is most representative of the BiPO₄ particle settling over the depth of the column [47]. If flocculation of the particles was occurring, distinctly different trend lines would be seen for each sampling port since the particles would have greater settling velocities towards the bottom of the column than the near the top [47].

Table 4 shows that a settling velocity of approximately 0.0029 cm/s (2.9·10⁻³ cm/s) results in a C/C₀ value of about 0.50 (interpolated). This is greater than the settling velocity calculated from the average particle size DLS measurements of 1.60·10⁻³ cm/s. The increase in average settling velocity in the column test may be due to how the data is collected in the column test compared to the DLS measurements. In DLS measurements, the average particle size is based on the Z-average, or the laser signal intensity through the sample [44]. So, if there are more small particles relative to larger ones, the average size measurement will be skewed towards a smaller size. In the column test, the data are based on mass concentration of particles in which the larger particles will have more of an effect on the mass measured than smaller particles. This difference in concentration measurement may account for the difference between the theoretical settling velocity calculated with Stokes’ Law and that measured from the column test. Additionally, Stokes’ Law makes assumptions about the settling particles, such as a spherical shape, which is not true for the BiPO₄ particles [3]. These assumptions could further increase the difference in the calculated and measured particle settling velocities.
The data shown in Table 4 and Figure 19 can be used to estimate the fractional BiPO₄ particle removal based on a particular clarifier overflow rate. To do this, Equation (13) is needed, which relates the expected removal in a sedimentation basin to a given overflow rate based on the results of the column test assuming Type I settling [46].

\[
R = (1 - P_0) + \frac{1}{v_0} \int_{0}^{P_0} v_s \, dP
\]  

(13)

In the equation, \( R \) is the expected removal fraction, \( P_0 \) is the \( C/C_0 \) value at the overflow rate of interest from Figure 19, \( v_0 \) is the overflow rate of interest, and the integral represents the area above the curve in Figure 19 at the settling velocity that is equal to the overflow rate of interest. Table 5 gives calculated expected removal fractions based on applying Equation (13) to varying overflow rates.
Table 5. Calculated expected removal percentages for varying overflow rates in an ideal sedimentation basin based on data obtained from the column test.

<table>
<thead>
<tr>
<th>$v_0$ (m/hr)</th>
<th>$v_0$ (cm/s)</th>
<th>$\frac{1}{v_0} \int_0^{P_0} v_s , dP$</th>
<th>$\int_0^{P_0} v_s , dP$</th>
<th>$\frac{1}{v_0} \int_0^{P_0} v_s , dP$</th>
<th>$\int_0^{P_0} v_s , dP$</th>
<th>(1-$P_0$)</th>
<th>R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.001</td>
<td>0.0002</td>
<td>0.150</td>
<td>0.70</td>
<td>85.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.10</td>
<td>0.003</td>
<td>0.0006</td>
<td>0.200</td>
<td>0.40</td>
<td>80.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>0.007</td>
<td>0.0024</td>
<td>0.345</td>
<td>0.31</td>
<td>65.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>0.014</td>
<td>0.0064</td>
<td>0.459</td>
<td>0.09</td>
<td>54.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>0.021</td>
<td>0.0074</td>
<td>0.356</td>
<td>0.05</td>
<td>40.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\int$ values were estimated by calculating the area above the curve in Figure 19.

The data in Table 5 can be used to estimate the removal of BiPO$_4$ in a sedimentation basin with the given overflow rates. In the lab-scale clarifier, however, plate settlers have been added which will increase the expected removal for a given overflow rate.

4.3. Lab-Scale Clarifier Data

4.3.1. Selected Dimensions

The design process described in Section 1.7 was used to select the dimensions for the lab scale clarifier based on the settling velocity of the BiPO$_4$ particles calculated in
Section 4.1 and maintaining an appropriate Reynolds number and Froude number in the tank. Additionally, it was desirable to keep the size of the tank small to minimize material needed in the experiments and minimize materials needed to create the clarifier itself.

The dimensions were calculated using the design spreadsheet shown in Appendix B by iterating values of the flow rate, overflow rate, and residence time, which are shown in Table 6. The dimensions needed to achieve these values are shown in Table 7.

Table 6. Selected variables for the lab-scale rapid clarifier based on BiPO₄ particle settling velocity and achieving the Reynolds number and Froude number constraints.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>2.0 L/min</td>
</tr>
<tr>
<td>Overflow Rate</td>
<td>4.0 m/hr</td>
</tr>
<tr>
<td>Residence Time</td>
<td>5 min</td>
</tr>
</tbody>
</table>

Table 7. Dimensions calculated for the lab-scale rapid clarifier by iterating values of flow rate, overflow rate, and residence time in the design spreadsheet.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>10 L</td>
</tr>
<tr>
<td>Surface Area</td>
<td>0.030 m²</td>
</tr>
<tr>
<td>Depth</td>
<td>0.33 m</td>
</tr>
<tr>
<td>Width</td>
<td>0.12 m</td>
</tr>
<tr>
<td>Length</td>
<td>0.16 m</td>
</tr>
</tbody>
</table>

Additionally, the aluminum plate length and spacing in the basin were specified. The spacing was made as small as possible based on the idea that more plates would increase surface area available for particles to settle, which was set at 0.5 cm. The plate length was specified as 15 cm to occupy about one-third of the height of the basin. The dimensions of the clarifier are shown visually in Figure 20.
Figure 19. Dimensions of the lab-scale rapid clarifier, side view (left) and plan view (right).

For these dimensions and flow characteristics, the particle velocity for 100% recovery (Equation (3)) was calculated to be $8.09 \times 10^{-3}$ cm/s. Although this is slightly higher than the average settling velocity of the BiPO$_4$ particles calculated using their density and particle size, the overflow rate would ultimately be varied to experimentally determine the maximum overflow rate which still resulted in particle removal.

4.3.2. Preliminary Experiments

Preliminary data was collected using silt-sized sediment and kaolinite clay to approximate BiPO$_4$ particles to ensure the lab-scale rapid clarifier was functioning as expected before completing the final experiments with BiPO$_4$. First, silt-sized sediment was used as the solid phase and the solution was pumped through the clarifier at different flow rates resulting in varying overflow rates. The results from this experiment are shown
in Figure 21. Samples were collected after two residence times to allow steady-state conditions to develop.

![Figure 20](image)

**Figure 20.** Effluent turbidity of sediment measured after a 1.8 g/L solution was pumped through the lab-scale rapid clarifier at varying flow rates. Error bars represent the highest and lowest turbidity values measured after one residence time of pumping. No error bars are present for the 4.6 m/h overflow rate.

As expected, increasing overflow rates results in higher effluent turbidity readings in the effluent of the clarifier. As overflow rate increases, the time for particles to settle in the clarifier decreases and thus a greater concentration of particles is present in the effluent. This experiment showed quantitatively that the clarifier was functioning properly.

Next, kaolinite clay was used as the solid phase in solution to demonstrate how the clarifier functions with and without the plate settlers. Additionally, turbidity and TSS
measurements were compared to determine if the results obtained with both types of measurements were similar. The results from these experiments are shown in Figure 22.

**Figure 21.** Turbidity (left) and TSS (right) measurements made for the initial (feed) kaolinite clay solution of 1.8 g/L and in the effluent of the lab-scale rapid clarifier after two residence times at a flow rate of 1,000 mL/min with and without the plate settlers. Error bars represent the lowest and highest values measured for samples in triplicate.

In looking at the median values for each data set, the effluent values without plates and with plates for the turbidity measurements are very similar. In the TSS measurements, the median value for the run with plate settlers is noticeably lower than the effluent value measured without plate settlers. The reason for this is likely a result of the increased turbidity of small particles compared to larger particles as discussed previously [51, 52]. Although turbidity measurements were simpler to collect and give an indication of particle concentrations, TSS measurements were selected to be used in the remainder of the clarifier experiments as these give a more direct indication of particle mass removal.
In both data sets, the effluent concentration values measured with the plate settlers were more consistent than without plate settlers, as shown by the smaller error bars in both plots. Additionally, the TSS measurements show decreased effluent concentrations when the plate settlers were used. Since the plate settlers show increased clarifier performance when compared to runs without the plate settlers, the following experiments utilizing the clarifier were run with plate settlers.

4.3.3. Varying Overflow Rate with BiPO$_4$

The purpose of the following experiments was to determine the overflow rate in the lab-scale clarifier which gave at least 90% removal of BiPO$_4$ particles from the influent to the effluent. TSS measurements were used to quantify the effluent concentration over time while varying the flow rate (and hence the overflow rate) for each run. Steady-state effluent concentrations were achieved by allowing each run to continue for at least two residence times in the clarifier. Figure 23 shows the data compiled for $C/C_0$ values over time with varying overflow rates in the clarifier.
**Figure 22.** Effluent BiPO$_4$ concentrations relative to the initial concentration over time with varying overflow rates in the lab-scale rapid clarifier with plate settlers. Residence time represents the normalized tank volume divided by the flow rate.

The results from **Figure 23** show that decreasing the overflow rate (by decreasing the flow rate) in the lab-scale clarifier increases the removal of BiPO$_4$ particles from the influent to the effluent. An overflow rate of 0.4 m/h, which corresponds to a flow rate of 200 mL/min, gave a removal fraction of approximately 96% after reaching steady-state. Overflow rates of 1.0 and 2.0 m/h resulted in much lower BiPO$_4$ removal fractions of approximately 60% and 36%, respectively. These overflow rates were compared to the expected particle capture velocity at each corresponding flow rate using Equation (6) as shown in **Table 8**.
Table 8. Comparison between calculated particle capture velocities in a rapid clarifier using Equation (6) with the percent removal values obtained from the clarifier experiments.*

<table>
<thead>
<tr>
<th>Overflow Rate (m/h)</th>
<th>Calculated Capture Velocity (cm/s)</th>
<th>Experimental Percent Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>8.09·10^{-4}</td>
<td>96%</td>
</tr>
<tr>
<td>1.0</td>
<td>2.02·10^{-3}</td>
<td>60%</td>
</tr>
<tr>
<td>2.0</td>
<td>4.04·10^{-3}</td>
<td>36%</td>
</tr>
</tbody>
</table>

* The median particle settling velocity is 2.90·10^{-3} cm/s from the settling column data.

The data in Table 8 represent the particle settling velocity at which 100% removal would occur; for example, for 0.4 m/h the calculated particle settling velocity for 100% particle removal is 8.09·10^{-4} cm/s. Since the average BiPO₄ particle settling velocity is approximately 2.90·10^{-3} cm/s, about 50% removal should occur at the overflow rate which corresponds to that capture velocity. These data match well with the experimentally determined percent removals from the clarifier experiments. Since the capture velocity for 100% particle removal at 0.4 m/h is significantly less than the average BiPO₄ settling velocity of 2.90·10^{-3} cm/s, it is reasonable to expect that most particles would be captured at this overflow rate. Figure 24 shows the settling behavior of the particles over time at the 0.4 m/h overflow rate from start-up to steady-state conditions. A clear zone with a low particle concentration is visible above the plates for the duration of the experiment, indicating a high degree of particle settling which is confirmed by the TSS measurements.
Figure 23. BiPO₄ particle settling in the rapid clarifier over time (from top left to bottom right) at an overflow rate of 0.4 m/h.

4.4. Process Scale-Up

From the experimental results, the data from the overflow rate of 0.4 m/h was selected as this run gave a 96% removal of BiPO₄ from the influent to the effluent. From Equation (6) these parameters gave a capture velocity of 8.09·10⁻⁴ cm/s as shown below.

\[
v_s \geq \left[ \frac{d}{L_p \sin \theta \cos \theta + d \sin \theta} \right] \cdot \frac{Q}{A} \quad \text{(6)}
\]
\[ v_s \geq \left[ \frac{0.005 \, m}{(0.15 \, m) \sin 60 \cos 60 + (0.005 \, m) \sin 60} \right] \cdot \frac{0.4 \, m}{h} = 8.09 \cdot 10^{-4} \, cm/s \]

Regardless of the size of the clarifier, the calculated particle capture velocity should result in a similar percent removal of BiPO₄ particles. As a result, the calculated capture velocity was used in the same equation along with typical values for full-scale plate length (3 m) and spacing (50 mm) to determine the maximum overflow rate that could be used in a full-scale unit to achieve approximately 96% particle removal, as shown below [3, 36].

\[ 8.09 \cdot 10^{-4} \, cm/s \geq \left[ \frac{0.05 \, m}{(3.0 \, m) \sin 60 \cos 60 + (0.05 \, m) \sin 60} \right] \cdot \frac{Q}{A} \]

\[ \frac{Q}{A} \leq 0.78 \, m/hr \]

In order to obtain a tank depth of approximately 5 m, which is typical of basins containing plate settlers, a common factor of 15 was selected as the scale-up factor for each dimension of the lab-scale unit [3]. Multiplying each dimension by 15 results in a length of 3.9 m, a width of 1.8 m, and a depth of 5.0 m for the full-scale unit. Since the surface area is now set at 7.0 m², the maximum flow rate can be found by multiplying the overflow rate by the surface area.

\[ OR \cdot A = Q \]

\[ 0.78 \frac{m}{hr} \cdot 7.0 \, m^2 = 131 \, m^3/d \]
However, with a tank volume of 35 m$^3$ and a flow rate of 131 m$^3$/d, the detention time in the full-scale unit is in excess of 6 hours; this is much larger than the recommended detention time of 20 minutes in the plate settlers [3]. To decrease the overall detention time in the tank without changing the overflow rate, the volume can be reduced by decreasing the depth of the basin to 4.0 m. The dimensions and important variables of a scaled-up rapid clarifier that should result in approximately 96% BiPO$_4$ particle removal are shown in Table 9.

Table 9. Variables and design parameters for the full-scale clarifier based on the results from the lab-scale experiments. The flow rate is 131 m$^3$/d.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overflow Rate</td>
<td>0.78 m/hr</td>
</tr>
<tr>
<td>Depth</td>
<td>4.0 m</td>
</tr>
<tr>
<td>Length</td>
<td>3.9 m</td>
</tr>
<tr>
<td>Width</td>
<td>1.8 m</td>
</tr>
<tr>
<td>Plate Length</td>
<td>3.0 m</td>
</tr>
<tr>
<td>Plate Spacing</td>
<td>50 mm</td>
</tr>
<tr>
<td>Reynolds Number</td>
<td>154</td>
</tr>
<tr>
<td>Froude Number</td>
<td>$6.16 \cdot 10^{-9}$</td>
</tr>
</tbody>
</table>

As designed, the full-scale unit would be able to treat a flow rate of about 131 m$^3$/d, or 34,600 gal/d. Although this is small for typical water treatment applications, several tanks of this size could be built in parallel or a single unit could be made larger in order to drastically increase the flow rate that could be treated each day.
5. CONCLUSIONS AND FUTURE WORK

5.1. Conclusions

Overall, it seems that BiPO$_4$ recovery by gravity settling using a rapid clarifier in a slurry-type PAO system is plausible. Although nearly complete recovery of the material is possible, to do so requires a relatively low overflow rate which limits the flow rate of water that can be treated. The application is promising but may be limited to small-scale applications.

5.2. Assessment of Objectives

1. **Determine the average BiPO$_4$ particle size using a dynamic light scattering (DLS) instrument.** A concentration study was conducted to determine the optimal measurement concentration for the DLS instrument. At a concentration of 1,000 mg/L BiPO$_4$, the average particle size was measured to be 2.35 μm which gives a terminal settling velocity of 1.60·10$^{-3}$ cm/s calculated using Stokes’ Law.

2. **Determine the settling velocity distribution (settling curve) of BiPO$_4$ particles using a settling column.** Settling curve data was collected using turbidity and TSS measurements from two settling columns; TSS measurements were determined to be more representative of the mass concentrations at each port. A settling curve was made which describes the BiPO$_4$ settling velocity distribution. A median settling velocity of 2.90·10$^{-3}$ m/s was calculated from these data.

3. **Design and construct a lab-scale rapid clarifier to determine the maximum overflow rate to achieve removal of BiPO$_4$ from the water.** A lab-scale
clarifier was designed according to the spreadsheet in Appendix B and constructed using clear sheet acrylic. An overflow rate of 0.4 m/h (flow rate of 200 mL/min) resulted in 96% BiPO$_4$ particle removal.

4. **From the experimental results, scale up the lab-scale rapid clarifier to determine the size of a full-scale unit needed for BiPO$_4$ particle removal based on an average water treatment plant flow rate.** Based on the experimental results, the lab-scale clarifier was scaled up to a full-size unit of 28 m$^3$ that should result in approximately 96% recovery of BiPO$_4$ at a flow rate of 131 m$^3$/d.

5.3. Future Studies

One main area for future research should look at methods of increasing the settling velocity of BiPO$_4$ particles to increase the overflow rate that could be used to recover the material. Using a coagulant or polymer to increase the settling velocity could be one option, but these chemicals would need to be easily separated from the BiPO$_4$ particles. Also, varying water quality parameters could be studied to determine how individual parameters affect the particle settling characteristics. For instance, pH and calcium hardness could be varied individually and particle size and settling column measurements conducted to determine if changes in these parameters affect settling velocity. In addition, other methods for particle recovery could be attempted to determine if a higher flow rate could be used. One option for testing is a hydrocyclone, in which particles are separated from water in a solution by centrifugation [53]. Research on
increasing the settling velocity of BiPO₄ particles could increase ease of recovery of the material.

In addition, experiments could be conducted to determine if the lab-scale clarifier is functioning similarly to a full-size unit. It is possible that the smaller unit has issues which result in decreased particle removal, such as flow short-circuiting. Influent water to a sedimentation basin or clarifier at a real water treatment plant could be collected and tested in the lab-scale unit. The particle removal achieved in the lab-scale and full-size units could be compared to determine if the lab-scale unit functions similarly to a full-size clarifier. Based on the results, the lab-scale unit could be altered to function more like a full-size unit.

Another area for future work is the addition of a lab-scale photoreactor to the rapid clarifier. This will create a complete lab-scale PAO system which will be able to test the effectiveness of BiPO₄ to degrade contaminants while at the same time showing how the material is recovered and re-input to the system. A lab scale unit of this type is important to show that the entire process can function as expected and has benefits over other PAO systems.

Lastly, a cost analysis could be conducted to determine the feasibility of implementing a BiPO₄ PAO system on a large scale. Research should be completed on synthesizing BiPO₄ microparticles on a commercial scale and if making large quantities of this material would be cost effective compared to other photocatalysts, like TiO₂. Cost will play a major role in determining whether BiPO₄ PAO technology can succeed in large-scale treatment operations.
Appendix A – DLS Intensity Plots

Sample Name: Standard 1
SOP Name: KP - polystyrene std sop
File Name: KP - 6-23-17.dts
Record Number: 4
Material RI: 1.59
Material Absorption: 0.010
Dispersant Name: Water
Dispersant RI: 1.330
Viscosity (cP): 0.8872
Measurement Date and Time: Friday, June 23, 2017 10:58:29 AM
Temperature (°C): 25.0
Count Rate (kcps): 215.8
Cell Description: Disposable scirpt cuvette
Duration Used (s): 30
Measurement Position (mm): 1.05
Attenuator: 6
Size (d.nm): % Intensity: St Dev (d.nm):
Z-Average (d.nm): 2355
Peak 1: 2442 100.0 470.0
PdI: 0.006 Peak 2: 0.000 0.0 0.000
Intercept: 0.741 Peak 3: 0.000 0.0 0.000

Result quality: Refer to quality report

![Size Distribution by Intensity](image_url)

**Figure A - 1.** Intensity plot generated by the Malvern Zetasizer DLS instrument for sample one of the 2.1 μm polystyrene standard solution.
Figure A - 2. Intensity plot generated by the Malvern Zetasizer DLS instrument for sample two of the 2.1 μm polystyrene standard solution.
Figure A - 3. Intensity plot generated by the Malvern Zetasizer DLS instrument for sample three of the 2.1 μm polystyrene standard solution.
Figure A - 4. Intensity plot generated by the Malvern Zetasizer DLS instrument for sample one of the 1,000 mg/L BiPO₄ solution.
Figure A - 5. Intensity plot generated by the Malvern Zetasizer DLS instrument for sample two of the 1,000 mg/L BiPO4 solution.
**Figure A - 6.** Intensity plot generated by the Malvern Zetasizer DLS instrument for sample three of the 1,000 mg/L BiPO₄ solution.
## Appendix B – Clarifier Design Spreadsheet

**Figure B - 1.** Spreadsheet used in designing the lab-scale rapid clarifier.
Appendix C – Standard Operating Procedures (SOPs)

Appendix C-1: DLS Measurements

1. Turn on the Malvern Zetasizer DLS instrument and open the Zetasizer software on the PC; allow the system to warm-up for at least 30 minutes before measuring samples.

2. In the software under ‘Measurement’, select ‘Start SOP’ and select the SOP that matches the samples to be measured.

3. Dispense 4 mL of particle solution to a 4.5 mL disposable plastic cuvette.

4. Cap the cuvette and sonicate the sample for three minutes.

5. Wipe the cuvette with a lab tissue wipe to remove smudges before measuring.

6. Insert the cuvette into the DLS instrument and close the lid; select ‘Start’ to start the measurement.

7. The DLS instrument will beep when the measurement is completed.

8. Repeat steps 3-6 as needed.

Appendix C-2: Total Suspended Solids (TSS) Measurements

Total and Volatile Suspended Solids

1. Place a glass fiber filter (Φ=21 or 25 mm, depending on the size of the crucible used; Whatman 934AH or 984H) into a ceramic crucible used for filtering; either side is acceptable. Prepare a triplicate for each sample.

2. Record the number on the funnel. If there isn’t a number, you may use a pencil to label it. Do not label it with an ink marker, since the ink will be burned off in step 5.

3. Put the crucible in a rubber sleeve on a filter flask in Room 112. Connect the filter flask to the vacuum manifold.

4. Wet the filter paper in the funnel with DDI water. Turn on the vacuum pump for a few seconds to “seat” the filter.

5. Place the crucibles in the muffle furnace (550°C) in the Teaching Lab for 15 min. Alternatively, dry them overnight in the 105°C oven.
6. Transfer the crucibles to a desiccator. Allow them to cool to room temperature. **Caution: Use safety gloves and tongs when transferring due to high temperature in the furnace.**

7. Using tongs (to avoid the crucible picking up oil from your hands), transfer the crucibles to a 4-place scale; weigh and record the data (W1).

8. Using tongs, transfer the crucibles to the rubber funnels in the filter flasks in Room 112; once again, rinse the filter briefly with DDI water and turn on the vacuum to “seat” the filter.

9. Using a glass pipet, transfer 10.0 mL of a well-mixed MLSS sample or 40.0 mL of a well mixed effluent sample to the crucible. Rinse the pipet once with DDI water into the crucible. Turn off the vacuum pump after all of the free water has been pulled through the filter.

10. Transfer the crucibles to a 105°C oven in the Teaching Lab; dry overnight.

11. Transfer the crucibles from the oven to a desiccator using tongs; allow to cool to room temperature.

12. Weigh the crucibles on the same balance and record the data (W2).

13. Calculate the TSS concentration:

\[
TSS \text{ concentration} = \frac{(W2-W1 \ g) \times (1000 \ mg/g)}{\text{volume of the sample (L)}}
\]

14. Place the crucibles in the muffle furnace (550°C) in the Teaching Lab for 15 min; don’t go longer than that, since you may burn of fixed suspended solids (FSS).

15. Cool the crucibles for several minutes on the bench top; if you put them directly into the desiccator, you may pull a strong enough vacuum that you won’t be able to open the desiccator. After several minutes, but while the crucibles are still warm, put them into the desiccator to cool to room temperature. Weigh and record the data (W3).

16. Calculate the VSS concentration:

\[
VSS \text{ concentration} = \frac{(W2-W3 \ g) \times (1000 \ mg/g)}{\text{volume of the sample (L)}}
\]

---

**Appendix C-3: Turbidity Measurements**

1. Turn on the Hach 2100N turbidimeter and allow the bulb to warm for at least ten minutes before measuring samples.

2. Collect 1 mL of sample and dispense/pour into 30 mL glass sampling vial.
3. Using a 25 mL volumetric flask, dilute the sample 1:26 by adding 25 mL DDI water to the sample contained in the sampling vial.

4. Invert vial at least three times and wipe with a lab tissue wipe to remove smudges from the glass.

5. Insert vial into the turbidimeter and allow the reading to stabilize before recording the turbidity in NTU.

Appendix C-4: Settling Column Experiments [46]

100 mL Column and Turbidity Measurements

Procedure:
1. Add 0.05 g BiPO₄ and 100 ml DDI water to a 250 mL beaker.
2. Stir the solution for five minutes on a stir plate, sonicate for five minutes, and stir until use.
3. Measure the pH and conductivity to ensure each solution is approximately equal.
4. Fill column with 100 mL BiPO₄ solution.
5. Suspend the particles in the column by slowly inverting the column five times.
6. Start timer immediately after inverting the column.
7. Allow column to sit undisturbed while particles settle.
8. After the time of interest is reached, sample all ports from top to bottom using the needles and 3 mL syringes as quickly as possible.
9. Collect 1.0 mL at each port and store in a 30 mL turbidity vial.
10. Perform turbidity measurements by adding 25 mL DDI water to the 1.0 mL samples (1:26 dilution, as described in Turbidity Measurements section).
11. After turbidity measurements are taken, allow the BiPO₄ particles to settling in a 500 mL beaker and return the solid material to the column. 
   a. This is to maintain the original concentration of BiPO₄ in the column without having to make a new solution for each run.
12. Repeat steps 5-11 for five time points.
13. Turbidity will be recorded at each time and height to determine the fraction of the original concentration remaining at that point.
14. Data will be used to construct a plot of C/C₀ vs. vₛ and the removal for a particular overflow rate can be calculated by:

\[ R = (1 - P₀) + \int_0^{P₀} \frac{vₛ}{v₀} dP \]
1,000 mL Column and TSS Measurements

Procedure:
1. Add 0.50 g BiPO₄ and 1,000 ml DDI water to a 1 L media bottle.
2. Stir the solution for five minutes on a stir plate, sonicate for five minutes, and stir until use.
3. Measure the pH and conductivity to ensure each solution is approximately equal.
4. Fill column with 1,000 mL BiPO₄ solution.
5. Suspend the particles in the column by slowly inverting the column five times.
6. Start timer immediately after inverting the column.
7. Allow column to sit undisturbed while particles settle.
8. After the time of interest is reached, sample all ports from top to bottom using the needles and 3 mL syringes as quickly as possible.
9. Collect 10 mL at each port and store in a scintillation vial.
10. Repeat steps 1-9 for five time points.
11. Perform TSS measurements by filtering the 10 mL samples through Whatman glass fiber filters and drying overnight (described in TSS section).
12. TSS will be recorded at each time and height to determine the fraction of the original concentration remaining at that point.
13. Data will be used to construct a plot of C/C₀ vs. vₛ and the removal for a particular overflow rate can be calculated by:

\[ R = (1 - P₀) + \int_{0}^{P₀} \frac{vₛ}{v₀} dP \]

Appendix C-5: Clarifier Experiments

1. Add 6.0 g BiPO₄ to 12 L tap water in each of two five gallon plastic buckets to create two 0.5 g/L BiPO₄ solutions.
2. Fill the clarifier with tap water to begin the experiment with no BiPO₄ in the tank.
3. Use Masterflex L/S 35 tubing to connect the feed reservoir to the pump and to the inlet of the clarifier.
   a. Connect the effluent tubing to the launders and to an empty five gallon plastic bucket.
4. Stir the feed reservoir with a paint stirrer connected to a Lightnin® mechanical mixer at 250 rpm.
5. Take 10 mL samples from the stirred influent reservoirs using a pipette to conduct TSS measurements and obtain the influent concentration.
6. Start the Masterflex 600 rpm pump by setting the appropriate flow rate and pressing the ‘Start’ button.

7. Start timer immediately after starting the pump.

8. Over time, take 40 mL samples from the effluent tubing to conduct TSS measurements and determine effluent particle concentrations.

9. After approximately 2.5 residence times, stop the pump.

10. Use the TSS Measurements section to conduct the measurements.

11. Create a plot of C/C_0 vs. time to illustrate the removal at a particular flow rate after steady-state conditions have been reached.

12. Empty all BiPO_4 solution to two five gallon plastic buckets and allow to settle overnight in order to recover the material for the next run.
REFERENCES


[26] Purifics, “Purifics Photo-Cat AOP.”.


