Photocatalytic degradation of Atrazine herbicide using nano-Hydroxyapatite from Cow Bone synthesized via Simulated Body Fluid

Rugi Vicente Rubi a*, Erison Roque a, Francis Dela Rosa b, Rey Martin Estoque, Gerald Olvido, Patricia Jane Perey, Jabin Sta. Teresa, May Anne Tesalona

a - Department of Chemical Engineering, Adamson University, Philippines
b - Department of Chemistry, Adamson University, Philippines

*ruyi.vicente.rubi@adamson.edu.ph

Abstract. The excessive usage of herbicide in agricultural industry has known to cause unexpected side effects both on human and environment. This present study investigates the viability of using nano-Hydroxyapatite as a catalyst in the photodegradation of the herbicide Atrazine. Nano-hydroxyapatite (nHAp) was synthesized using cow bone as the calcium source via simulated body fluid (SBF). Physical and morphological characterization was done using scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD). The SEM analysis results indicates the formation of globular precipitated nHAp with 22 to 114 nm particle diameter size. The FTIR and XRD results confirmed the presence of functional groups and crystal structure associated to presence of hydroxyapatite. The photodegradation of the Atrazine herbicide results showed a steady increase in efficiency with the increasing amount of catalyst and UV exposure time. The highest degradation efficiency of 52% was achieved with 0.7 g nHAp for 2.5 hrs exposure. This study showed that Atrazine herbicide can be effectively treated with the proposed method to reduce the environmental impact of the herbicide by converting it into potentially less dangerous by-products that can be less harmful.

Keywords. Biomimetic deposition, Photodegradation, Simulated body fluid, Atrazine, Cow Bones

1. INTRODUCTION

For the past few years, pesticides like Atrazine has been a prevailing problem for groundwater contamination. Different studies have been conducted in order to remove or prevent the influx of this harmful compound in the waterways system. In fact, potential health risk such as birth defects and other long term physical effects (Ochoa-Acuña, 2009) had lead scientists and researchers to extensively study on how to eliminate this persisting pollutant in the environment (Winchester et al., 2009).

Atrazine is a general herbicide from triazine group that is used to prevent unwanted weeds in crops like corn, sugarcane, and turf. It is widely used in the provinces of the Philippines but has
been banned in the UK for posing health problems such as low male fertility, low birth weight, increased hazard of miscarriage, increased possibilities of any birth defect, and higher frequency of abdominal defects (Rinsky et al., 2012). In addition, atrazine has been known to cause disruption to human endocrine which changes the natural hormonal systems in the human body.

Typical treatment of Atrazine containing wastewater is the incorporation of activated charcoal filters in some treatment facilities (Campos, Baudin, & Laine, 2000). The activated charcoal attached in the equipment adsorbed the pesticide particles present in the wastewater. The drawback is the persisting presence of the pesticide in the post-treatment facility. Another widely available industrial solution to counteract pesticides in water is via nano-filtration. However, atrazine and a wide variety of volatile organic compounds are incompatible with reverse osmosis separation. In addition, the high operating cost of reverse osmosis operation makes it a less favorable solution for the removal of the herbicide compounds.

One viable solution is via photodegradation which utilized photocatalyst in breaking down the harmful compound into less toxic components in the presence of ultraviolet light (UV). A typical example of a photocatalyst is hydroxyapatite (HAP), which can be easily synthesized via calcination method (Shariffuddin et al., 2013). In addition, producing HAP can lead to sustainable practice since raw materials can be chosen from any calcium based waste materials such as eggshells, seashells and animal bone (Chandrasekar et al., 2013).

In this study, nano-hydroxyapatite (nHAp) was synthesized via the simulated body fluid (SBF) method. SBF is an ionic solution that mimics blood plasma and contains calcium and phosphate ions suitable for hydroxyapatite formation. Unlike HAP synthesis via calcination which operates at a high-temperature condition, the SBF method requires low energy consumption which is favorable for industrial set-up. In addition, since hydroxyapatite exhibits very high biocompatibility, SBF can be used to nucleate HAP into nanoparticles thus producing a high surface area photocatalyst. The nanostructure of nHAp allowed larger active sites thus enhancing the degradation of atrazine (Suresh et al., 2017).

To the best of our knowledge, utilizing SBF in the synthesis of nHAp is still lacking in the literature. Also, the photodegradation of pesticides using nHAp has not been applied to atrazine, which is a widely used commercial herbicide. Lastly, the utilization of a cow bone as a replacement raw materials for calcium-based synthetic chemicals in the production of nHAp may contribute to sustainable practices.

2. MATERIAL AND METHODS

2.1 Materials and Reagents

2.1.1 Raw Material
Cow bones were collected from Mulanay Public Market in Mulanay, Quezon.

2.1.2 Reagents and Chemicals
The reagents and chemicals used in this study are 1M Hydrochloric acid (HCl, 37%), Sodium Hydroxide (NaOH, ≥97.0%), Disodium phosphate (Na$_2$HPO$_4$, ≥97.0%), Sodium chloride (NaCl, ≥97.0%), Potassium chloride (KCl, ≥97.0%), Magnesium chloride (MgCl$_2$, ≥97.0%), Calcium Chloride (CaCl$_2$, ≥97.0%), Sodium sulfate (Na$_2$SO$_4$, ≥97.0%), Sodium hydrogen
carbonate (NaHCO$_3$, ≥97.0%), Tris-hydroxymethylaminomethane ((CH$_2$OH)$_3$CNH$_2$) Tris, ≥98.0%)

The chemicals were purchased from DKL Laboratories Supplies in Sampaloc, Manila and Belman Laboratories in Quezon City. The commercially available atrazine was purchased from CyBERTH Philippines, Inc. in Los Baños, Laguna. Distilled water was used for the entire experiment.

2.2 Experimental Procedure

2.2.1. Calcination of Cow Bone
The cow bones were cleaned by boiling it with water at 180°C for 45 minutes. The boiling process was repeated five times and water was replaced for each repetition. Then the bones were mechanically scrubbed, to remove loose organic matter. After which, the cow bones were soaked in a 2.5 L of 4 M NaOH solution for 24 hours to remove the organic matters in bones completely. Thereafter, bones were oven-dried at 150°C for 4 hours. The dried bones were reduced to a smaller size using jaw crusher. Then, it was calcined in a furnace at 900°C for 8 hours. Calcium oxide was obtained and further crushing was employed using mortar and pestle to produce a fine and uniform particles size.

2.2.2 Conversion of CaO to CaCl$_2$
The CaO obtained from section 2.2.1 was mixed with 12 M HCl solution (10% excess) for about 1 hour to form a CaCl$_2$ precipitate. The CaCl$_2$ precipitate was collected by decantation and the remaining solid residue was dried using convection oven set to a temperature of 150°C for 3 hours.

2.2.3. Preparation of Simulated Body Fluid
The SBF was made based on the protocol discussed in the work of Cuneyt Tas (Tas, 2000). Seven hundred milliliters of distilled water was prepared in a 2L beaker at 37°C with constant stirring. Then the following chemicals were dissolved in succession in the distilled water: 6.547g NaCl, 2.268g NaHCO$_3$, 0.373g KCl, 0.141g Na$_2$HPO$_4$, 0.305g MgCl$_2$. The reagent was added after the preceding chemical was completely dissolved in order to avoid the occurrence of unnecessary reaction. Also, a buffer solution was added to keep the pH 7.0 by adding 1M HCl. After which the following reagents were dissolved in succession: 0.277g CaCl$_2$, 0.071g Na$_2$SO$_4$, and 6.057g Tris-buffer. Dissolution of the reagents was done in a very small amount to avoid a sudden increase in pH of the SBF solution. Again, 1M HCl buffer solution was added to keep the pH to 7.40. Then, continuous addition of distilled water was done during titration until the final volume equals to 1L. The SBF solution prepared was stored in the refrigerator at a temperature of 5°C.
2.2.4. Synthesis of Hydroxyapatite by Biomimetic Deposition
For a 1L of SBF solution, 0.4935g of Na$_2$HPO$_4$ was added to 980mL of SBF solution and 0.9695g of CaCl$_2$ obtained from cow bone was added to the remaining 20mL of SBF solution. The two obtained solutions were mixed together with constant stirring at 37 °C. The precipitate formed was allowed to settle for 1, 2, and 3 days. Then, the precipitate was separated from the solution via filtration. The wet precipitate was oven-dried at 80°C for 4 hours. The dried product was collected and powdered using mortar and pestle to obtain nano-hydroxyapatite (nHAp).

Finally, the nHAp samples from different soaking time (1, 2, and 3 days) in SBF solution were characterized via XRD, FTIR, and SEM.

2.2.5 Photocatalytic Degradation of Atrazine
Atrazine solution with a concentration of 70mg/L was prepared by diluting atrazine herbicide stock to distilled water. 0.3g of nano-hydroxyapatite was added to 50 mL of atrazine solution. Prior to UV illumination, the solution was continuously stirred for half an hour at dark to achieve adsorption-desorption equilibrium between atrazine and nHAp photocatalyst. Then, the stable aqueous atrazine suspension was exposed to UV illumination under constant stirring. Five millimeters of the sample was withdrawn after 30 minutes and subjected to filtration to separate out the nHAp photocatalyst. The same procedure was followed for UV light time exposure of 1 hr, 1.5 hr, 2 hrs, and 2.5 hrs to see the effect of time to degradation rate. The filtrate was analyzed using UV-Vis while the nHAp residue was analyzed using FTIR. The same procedure was followed for 0.5 g and 0.7 g of nHAp photocatalyst to atrazine solution to investigate the effect of the catalyst dosage on the degradation rate. The photocatalytic efficiency was calculated using equation (1).

\[
\text{\% eff} = \left(1 - \frac{C}{C_o}\right) \times 100
\]

Where Co is the initial concentration of atrazine solution prior to photodegradation, and C is the concentration upon withdrawal.
3. RESULTS AND DISCUSSION

3.1. Characterization of Hydroxyapatite

3.1.1. Fourier Transform Infrared Spectrum (FTIR)

Shown in figure 1 is the FTIR spectra of the nHAp produced in SBF solution for the various soaking time. All samples having similar peaks confirmed the presence of functional groups associated with the presence of hydroxyapatite. The large strong peak around 3350 cm$^{-1}$ can be attributed to the stretch in mode of the $\text{-OH}$ vibration (Tahriri, 2008). Also the presence of $\text{-OH}$ functional group at this wavelength is associated with the hydroxyl end member of the complex apatite group (Liao et al., 2016). The intense peaks at 1016 cm$^{-1}$ and 599 cm$^{-1}$ can be attributed to the presence of $\text{PO}_4^{3-}$ which is a major functional group for hydroxyapatite (Ma, 2012). Interestingly, some carbonate content can be seen at peak equal to 1635 cm$^{-1}$. This may be due to the adsorption of carbon dioxide from the atmosphere resulting in the formation of carbonates (Tahriri, 2008).

![Figure 1. FTIR Result of Nano-hydroxyapatite synthesized in SBF solution at the varying soaking time](image-url)
3.1.2. X-ray Diffraction (XRD)

Figure 2 illustrates the crystalline nature of the synthesized nano-Hydroxyapatite as confirmed by the XRD analysis. All samples demonstrated a sharp peak at $2\theta = 26.73^\circ$, $32.37^\circ$, and $46.26^\circ$ which agree with the XRD standard for hydroxyapatite, ICDD (09-0432) (Ma, 2012) as shown in figure 3. The additional peaks in the patterns indicate the presence of other phases in the hydroxyapatite lattice that consists mostly of tricalcium phosphate (TCP). TCP has a calcium to phosphorus ratio of 1.5 in comparison to 1.67 for HAp (Azadeh Rezakhani, 2012). This is due to the depleting amount of calcium and phosphorus ions in the SBF solution the longer the soaking time increases. Finally, the crystallinity of the hydroxyapatite can be ascribed to the activation energy of nHAp that has to conquer at high temperature during the drying process which then results to the configuration of multi-crystalline nanocrystals (Leena, 2012).

Figure 2. XRD Results of Hydroxyapatite synthesized in SBF solution at varying soaking time

Figure 3. XRD Standard for hydroxyapatite
3.1.3 Scanning Electron Microscope (SEM)

Figure 4 shows the SEM results of the synthesized nHAp using SBF method. The produced nHAp appear to be powdery white and spherical in shape. The average particle size of nHAp as observed under high magnification of x35000 was found to be ranging from 22 nm to 114 nm, regardless of soaking time. Therefore, soaking time has no significant effect on the particle size of the hydroxyapatite since there are observed differences among the three samples. However, longer soaking time only affects the amount of precipitate formed within the SBF solution. In fact, a highly agglomerated form of nHAp was observed in the sample. This could be due to the presence of water molecules in the form of moisture attached to the samples (Leena, 2012). This showed that the SBF method is effective in synthesizing hydroxyapatite and was able to produce nanoparticles which are more desirable for photocatalytic reaction since smaller particles have a large surface area which can absorb more pollutants in a wastewater sample.

![SEM results of Hydroxyapatite synthesized in SBF in (a) 1 day, (b) 2 days and (c) 3 days soaking time respectively](image)

**Figure 4.** SEM results of Hydroxyapatite synthesized in SBF in (a) 1 day, (b) 2 days and (c) 3 days soaking time respectively

### 3.2. Photocatalytic Degradation of Atrazine

In this section, the hydroxyapatite synthesized at 3 days soaking time in SBF solution were used as the photocatalyst to degrade atrazine in the aqueous solution. The initial concentration of atrazine in all samples was 70 mg/L. The concentration of atrazine after the degradation process at different time intervals was determined based on the adsorption rate using UV-VIS.

Table 1 shows the result of photocatalytic degradation of atrazine with varying photocatalyst loading and different time exposure to UV light. Different dosage of 0.3g, 0.5g, and 0.7g was used to degrade atrazine in an aqueous solution with an initial concentration of 70 ppm. The samples were exposed to UV light at different time limits: 30 minutes, 60 minutes, 90 minutes, 120 minutes, and 150 minutes. It is shown that the largest decrease in the concentration of atrazine occurred at 150-minute exposure to UV light was using 0.7 g of photocatalyst with 51.94% of degradation efficiency.

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On the other hand, the trend demonstrated by the photocatalyst loading from 0.3 g to 0.7 g shows a direct proportion with increasing the amount of catalyst, increases the degradation efficiency. This implies that catalyst is capable of adsorbing pollutant by increasing its initial concentration (Hassena, 2016).
Table 1. Concentration of Atrazine after photocatalytic degradation at varying time of exposure to UV light.

| Time of UV light exposure (min) | Amount of photocatalyst (nHAP) used | Amount of Atrazine remaining (ppm) |
|--------------------------------|------------------------------------|-----------------------------------|
|                                | 0.3 g                              | 0.5 g                             | 0.7 g                             |
|                                |                                    |                                   |                                   |
| 30                              | 66.21                              | 61.16                             | 61.47                             |
| 60                              | 60.14                              | 60.35                             | 57.70                             |
| 90                              | 54.38                              | 54.79                             | 47.91                             |
| 120                             | 47.76                              | 46.23                             | 41.79                             |
| 150                             | 44.44                              | 40.32                             | 33.64                             |

Figure 5 relates photodegradation efficiency to catalyst dosage. It can be seen that for different exposure time to UV light, a catalyst amount of 0.3g leads to a low degradation efficiency with only 5.42% for first 30 minutes and 36.51% for the next 2 hours while a catalyst amount of 0.7g leads to a high degradation rate of 51.94% for 150 minute time exposure. A direct relationship can be seen in the figure in which the degradation efficiency increases as the catalyst dosage increases, regardless of UV exposure time, with an allowance for instrumental errors causing the minimal descent of the graph.

Generally, the figure shows that increasing the catalyst dosage increases degradation efficiency. This can be explained by the concepts of heterogeneous kinetics, wherein a larger amount of catalysts provides more active sites for the target reactants to settle and react. With more catalyst particles evenly scattered throughout the solution, external diffusion of a reactant to a catalyst will not be a problem despite the fluid being stagnant, thus increasing the overall conversion within a certain amount of time (Swaminathan et al., 2013).

Figure 5. Degradation efficiency of Atrazine vs catalyst dosage under different UV light exposure time.
Figure 6 shows that degradation efficiency increases when the time of exposure to UV light increases. Regardless of the amount of catalyst, more exposure time leads to a more efficient process. It can be seen that for atrazine solution sample with different amount of catalyst, the degradation efficiency is highest at the given maximum time exposure of 150-minutes.

Longer exposure time allows the reactant to adhere to the catalyst and react. Additionally, the catalyst particles can accommodate more reactants if the degradation period is longer, thus increasing the percentage conversion and the overall efficiency of the process (Vijayabalan et al., 2013).

Figure 6. Degradation efficiency of atrazine vs UV light exposure time for varying catalyst dosage

In addition, the photocatalytic degradation of HAP is dependent on its lattice structure, due to the capability of HAP to produce surface phosphate ions, excited electrons, and holes when exposed to UV radiation. Also, generated oxygen free radicals (O$_2^-$) and hydroxyl radicals (OH$^-$) in the presence of water and oxygen under UV radiation facilitates rapid oxidation reaction (Nishikawa, 2004). Here, the oxygen provides the oxidant source for indirect oxidation, which aids in the separation of photo-generated charges and decreases the recombination of generated electron-hole pairs. (Shariffuddin et al., 2013)

3.3 Statistical Treatment

The data obtained from the photocatalytic degradation of atrazine were statistically treated using a general factorial model in Design Expert 11. The ANOVA was used to determine if the exposure time and catalyst dosage have a significant effect on the residual concentration of atrazine during photocatalytic degradation.

The ANOVA results showed the F-values and p-values of the variables. It showed that the model has an F-value of 79.83, which implies that the model is significant. Furthermore, at a p-value of < 0.0001, it was shown that exposure time varied at 30, 60, 90, 120, and 150 minutes significantly affects the residual concentration of atrazine. Additionally, at a p-value of <
0.0001, it was shown that catalyst dosage varied at 0.3, 0.5 and 0.7 grams significantly affects the residual concentration of atrazine. The interaction of the two variables has a p-value of 0.0052, deeming the significance of the interaction of exposure time and catalyst dosage on the residual concentration of atrazine. Therefore, the two variables are important parameters in the photocatalytic degradation of atrazine.

Table 2 ANOVA results

| Source    | Sum of Squares | df | Mean Square | F-value | p-value |
|-----------|----------------|----|-------------|---------|---------|
| Block     | 15.86          | 2  | 7.93        |         |         |
| Model     | 3780.41        | 14 | 270.03      | 79.83   | < 0.0001 Significant |
| A-Time    | 3393.92        | 4  | 848.48      | 250.83  | < 0.0001 |
| B-Time    | 288.36         | 2  | 144.18      | 42.62   | < 0.0001 |
| Dosage    | 98.13          | 8  | 12.27       | 3.63    | 0.0052  |
| AB        | 94.72          | 28 | 3.38        |         |         |
| Residual  | 3890.99        | 44 |             |         |         |
| Cor Total | 15.86          | 2  |             |         |         |

Also, it was observed that at time of 150 minutes, and catalyst dosage of 0.7 grams, the best result for the residual concentration of atrazine was obtained. It was also found out that at 0.5g-30 min and 0.7g-30 min, there is only a slight difference between the residual concentrations of atrazine. A slight difference between the residual concentrations were seen at 0.3g-30 min and 0.5g-30 min, as well as 0.3-90 min and 0.5-90 min. Also, a lower residual concentration of atrazine is seen at 0.7g, which shows that 0.7g gave the best result in combination with 150 minutes.
4. CONCLUSION

The hydroxyapatite was successfully synthesized using cow bone as a calcium source via biomimetic deposition. The peak of the FTIR result showed the functional groups that are present in the produced sample confirming that this is hydroxyapatite. The special bands detected in the hydroxyapatite are falling in between the range 3350 cm\(^{-1}\) to 559 cm\(^{-1}\). Based on SEM findings, the hydroxyapatite produced are nanoparticles ranging from 22 nm to 114 nm. Also, the soaking time of hydroxyapatite in SBF solution has no considerable effect on the particle size since there are no large differences observed among the three samples. The crystalline nature of the synthesized nano-hydroxyapatite was determined by X-ray diffractometer. Based on XRD findings, the samples demonstrated sharp peaks at \(2\theta = 26.73^\circ, 32.37^\circ,\) and \(46.26^\circ\) which are in agreement with the XRD standard for hydroxyapatite, ICDD (09-0432).

The nano-hydroxyapatite produced in this study was proven to degrade atrazine in aqueous solution. Using hydroxyapatite produced in SBF solution at 3 days soaking time, the highest degradation efficiency that was achieved for atrazine was 51.95\% which was acquired at 70 ppm sample solution with catalyst dosage of 0.7 g time of exposure to UV light of 150 minutes.

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