

Imprinted Polymers in Wastewater Treatment

Chris Eastman¹ and Dr. Anja Mueller²
Department of Chemistry

Wastewater treatment is an especially important process in modern day society. Carried out on multiple levels, ranging from industrial wastewater to local sewage treatment facilities, it has been a process that has lacked a certain degree of efficiency throughout its existence. For example, when examining the processes that are undergone in a sewage treatment facility, it is necessary to mention the reliance on the anaerobic and aerobic bacteria that aid in the overall treatment process. These bacteria are used to naturally remove pollutants and impurities contained in the incoming wastewater.

The removal of pollutants and impurities by means of these bacteria is a process that has failed to reach its optimal potential. As with various other techniques used to treat wastewater, there comes with it a level of difficulty, especially when dealing with complex mixtures. Studies have shown that compounds such as toluene, heavy metal ions, ammonia, and sodium chloride, greatly inhibit the effectiveness of the bacteria involved in treating wastewater (Nahar et al., 2000; Sin et al., 2000; Lee et al., 2000; Pollice et al., 2000). This is due to the fact that these compounds are toxic to the bacteria, often debilitating them or destroying them altogether. Along with phenol-based compounds and other organic compounds as inhibitors, there is an obvious need for more efficient extraction methods when examining the complex aqueous mixtures entering wastewater treatment facilities.

In the form of flocculents or resins, polymers are actively used in wastewater treatment facilities (Liu et al., 2000; Annesini et al., 2000). Used in the purification of a variety of compounds, the method of imprinting polymerization offers great promise to solving the issue of efficiently treating wastewater. Monomers such as (meth)acrylates and acrylamides are introduced into a wastewater stream where self-assembly around specified compounds occurs. The impurities present act as the template for the imprinting polymer. The radical polymerization is initiated by AAPD (2,2'-Azobis(2-aminopropane)dihydrochloride), which is a water soluble, UV activated (256 nm) radical initiator. A nitrogen atmosphere must also be provided because radical polymerizations are inhibited by oxygen. When polymerization runs to completion, there will be a polymer left with an imprint of the specified impurities. Polymer stability will be insured with the addition of a cross linker. The wastewater will be purified by means of filtration, and upon removal of the impurities, the polymer will ultimately be reused.

An ideally important part of the procedure is to optimize polymer length with respect to the concentration of monomer and weight percentage of initiator used. In studies conducted using methyl

¹ Class of 2003, Department of Chemistry, Clarkson University

² Project Advisor, Department of Chemistry, Clarkson University

acrylate, low concentrations ranging from .1M to .2M have been used. It is important to use as little monomer as possible. This keeps the introduction of additional toxins to a minimum, which is crucial when dealing with large-scale systems such as sewage treatment facilities. A wide range of weight percentages of initiator (.1%-1%) used has also been studied. The amount of initiator used is important primarily because it aids in the chain formation of the polymer itself. Using larger amounts of initiator creates shorter polymers, whereas using lower amounts creates longer chains. It is more efficient to create longer polymer chains because it creates more binding sites for impurities, thus allowing for more impurities to be removed from the wastewater.

Multiple polymerization trials have been run using a 150 milliliter round bottom reaction flask with the above mentioned conditions. Five milliliter samples were taken over a six hour time period at one hour intervals. Separation was then used to dissolve the product in an organic solvent. Testing for compatible organic solvents was also conducted. Vials with predetermined masses were used for the dissolved product. An overall percent yield was calculated once the solvent was evaporated off of the product. For example, trial number ten, which consisted of a .1M reaction solution of methyl acrylate in fifty milliliters of water with a .3 weight percent of the initiator AAPD, had a calculated overall percent yield of 54.85%.

The study of the kinetics of the polymer has also been a focal point of the research conducted. UV spectroscopy has been used for the study of the kinetics. It made possible the examination of the ratio between unreacted monomer and polymer formed. It has been made clear from reviewing the spectra that indeed polymerization is occurring, but the degree of polymerization is still unknown. Spectra have been showing that there is still unreacted monomer in the reaction mixtures. The polymer peak, which has been forming around 274 nm, is often weak or partially formed. There also haven't been any noticeable patterns, such as an increased polymer peak and decreasing monomer peak, when comparing the spectra from the different time intervals. Trial number ten at a reaction time of two hours produced the most desirable results. The monomer peak had an absorbance reading of .09264 at 246 nm and the polymer peak had an absorbance of .09056 at 272 nm. Further examination of the spectrum illustrated that the polymer peak appeared to be increasing as the monomer peak was decreasing. This data supports a successful polymerization.

Infrared spectroscopy has been used to help determine the structure of the polymer polymethyl acrylate. However, the results obtained by using the IR have been poor quality. The IR has not been receiving a clear signal from the samples being used. This could either mean that the samples are too concentrated or simply too dilute. In defense of either outcome, there have been efforts to make the samples both more concentrated as well as more dilute. These changes have not had any effect on the quality of the spectra. Another possible explanation for the data collected can be attributed to the

solubility of the polymer in the solvent used. Inaccurate results will be obtained if the polymer is not completely dissolved in the solvent.

In summary, there is still much work to be done to optimize the polymer length before the experiment can progress to completion. It is quite apparent that successful polymerization is occurring. However, results from calculating percent yield of product formation as well as using IR and UV spectroscopy techniques suggest shortcomings in the procedure. Changes in the procedures should produce a higher yield as well as longer polymer chains. For example, more attention must be paid to the separation process due to the fact that the polymer may be soluble in the organic solvent as well as the water phase.

References:

1. Nahar N., Alauddin M., Quilty B. *World J. Microbiol. Biotechnol.* **2000**, 16, 307-311.
2. Sin S.N., Chua H., Lo W., Yu P.H.F. *Appl. Biochem. Biotechnol.* **2000**, 84-6, 487-500.
3. Lee. S.M., Jung J.Y., Chung Y.C. *Biotechnol. Lett.* **2000**, 22, 991-994.
4. Pollice A., Rozzi A., Tomei M.C., Di Pinto A.C., Limoni M. *Environ. Technol.* **2000**, 21, 535-544.
5. Liu Y., Wang S., Hua J.J. *Appl. Polym. Sci.* **2000**, 76, 2093-2097.
6. Annesini M., Gironi F., Monticelli B. *Wat. Res.* **2000**, 34, 2989-2996.