

## CONVERSION OF CELLULOSIC WASTE TO POLYMERIC ADSORBENT RESIN FOR WATER CONTAMINANTS REMOVAL

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### ABSTRACT

This study describes a method of converting cellulose-containing wastes into a polymeric resin (cellulose graft polyacrylonitrile), and for using the resulting material to remove hazardous contaminants from water. The technique appears to offer significant economic, energy, and environmental advantages over alternative methods of removing contaminants from water, and to provide a way to improve various waste disposal and recovery systems.

Solid and liquid wastes are generated continuously by all communities. These waste materials burden the environment insofar as they are not disposed of in a harmless fashion. It is sometimes surprising to see that the intensive "know-how" in industrialized countries has not resulted in a hygienic and inexpensive scheme of disposal. Many methods of disposal have been proposed and incineration appears to top the list. Incineration of solid waste with recovery of energy has been advocated and practiced by several communities serving large populations. However, this has not been economical, because the waste yields a low heating value comparable to low-grade coal. Furthermore, it provides a very small percentage of the total energy requirements for the community. Other methods used to dispose of solid waste are also being questioned by scientists because of their high cost.

The ever increasing generation of waste, the increasing contamination of water, the increasing cost of treatment of liquid waste, and the disposal of solid waste, have put pressure on the scientific community to propose new methods of treating the waste at a reasonable cost. A wide spectrum of organic and inorganic contaminants have been identified in liquid waste, and many of these are toxic to animals including man. It is therefore necessary to devise methods to convert waste from residential and commercial sectors into useful material, and at a reasonable cost. U.S. cities dispose of about 450,000 tons of municipal solid waste daily. It is estimated that approximately 25 billion gallons of liquid waste (domestic and industrial) are treated daily in this country.

Solid municipal waste material contains 28 to 60 percent (by weight) cellulosic material. This study describes the utilization of the cellulosic waste as a raw material for producing a polymeric adsorbent resin for removal of hazardous components from water.

## WASTE TREATMENT

A serious problem facing the engineer is the disposal of solid waste. A vast majority of cities and towns in this country dispose municipal solid waste (MSW) in garbage dumps and landfills. These methods contaminate the water resources, as well as increase the cost of disposal because of limited available space. It is estimated that municipalities will run out of landfill space in the next seven to ten years. To minimize the volume of waste, authorities recommend separation and recycling, i.e., segregation of organic material and inorganic contents (iron, aluminum, glass, etc.). The organic waste contents are converted into energy or fuels. The composition of MSW varies from town to town, with variable amounts of paper waste in particular. In addition, it has measurable quantities of yard wastes and wood. Some cities are constructing facilities to produce energy from waste. The estimated cost of the production of energy from MSW will fluctuate, depending upon many floating factors. Already there has been a shift in emphasis on waste to energy disposal as the top priority alternative. Meanwhile, the cost of landfilling has risen by about 500 percent in the last fifteen years, from nearly \$11.0/ton in 1970 to \$50/ton in 1985. Thermal chemical gasification, thermochemical liquification, and anaerobic digestion are also under investigation.

Currently, emphasis is being placed on obtaining energy from municipal waste by converting it into fuel that provides calorific value. However, in European countries scientists do not advocate biomass conversion into fuel because of economic feasibility. In the United States some cities advocate incineration as the method for managing rapidly increasing large quantities of solid waste.

Several years ago solid waste incineration gained popularity due to the general concept that it reduces the volume of the waste and breaks complex chemical molecules down to simpler ones that do not cause contamination. However, in

the last few years it has been realized that incineration plants emit a wide variety of pollutants such as dioxins and heavy metals ( $\text{Cd}^+$ ,  $\text{Hg}^+$ ,  $\text{Pb}^+$ , etc.). The emersion of some of the pollutants may be controlled via expensive devices, but total elimination is not practically possible. For example, dioxins are released in conjunction with the cooling of gases in the stacks; also, incineration cannot destroy heavy metals.

### **SIGNIFICANCE OF THIS STUDY**

1. Predictions by knowledgeable experts clearly state that the current available petroleum supplies will be essentially depleted by the year 2050. Following the two oil crises in the 1970s, the economy of the world is undergoing a structural shift from overwhelming dependence on nonrenewable natural resources to supplementary renewable resources. Cellulose, which forms the structural components of all biomass, is the most abundant renewable resource. Considering that cellulose will be supplied as a renewable source, one can see the potential for energy conservation as well as the economical and ecological benefits of this research.
2. Grafted cellulose copolymer is less expensive than other comparable adsorbents prepared from synthetic based fossil fuels, because cellulose could be supplied from agricultural waste or from other non-industrial waste sources.
3. The cellulosic portion of solid waste may be converted to cellulose grafted polyacrylonitrile. This would reduce the quantity of solid waste.
4. The cellulose graft copolymer has distinct and improved ion exchange properties. The high sorbency of grafted material offers many potential industrial applications. For example it can be used as adsorptive material for detoxifying various industrial wastes including liquid nuclear waste.
5. Small quantities of this material along with the toxic ingredients can be disposed of safely without further contaminating the environment.

### **SYNTHESIS AND CHARACTERIZATION OF CELLULOSE GRAFT POLYACRYLONITRILE**

There are a number of different methods available to synthesize cellulose graft copolymer, each with its own particular advantages and disadvantages. Hone and Chan [1] and Ang, et al. [2] reported the use of UV light for surface grafting to cellulose. Arthur described use of plasma for the graft copolymerization [3]. Most of the earlier approaches have employed heterogeneous reactions. Shiraishi, et al. reported grafting to cellulose in the solution phase with newer cellulose solvent [4]. By careful control of reaction variables one could synthesize a copolymer that would exhibit physical and

and chemical properties that are superior to those of cellulose. The copolymerization could significantly increase the sorbency rate of cellulose and make it extremely useful in waste filtration and other processes that require high fluid absorbency. Numerous methods have been reviewed in a number of papers for the grafting of vinyl-monomers to cellulose [5-9]. Among the most promising and practical is the ceric ion technique. This method of initiation for cellulosic substrate was first used by Schwab, et al. [10]. Angaji, et al. carried out a graft copolymerization reaction of acrylonitrile onto cellulose using ceric ammonium nitrate as an initiator [11]. The temperature and concentration of ceric ammonium nitrate was varied to optimize the reaction of acrylonitrile onto cellulose. The procedure initiated by these authors was followed.

## EXPERIMENTAL PROCEDURES

The cellulosic portion of waste was recovered according to the method described by Okieimen, et al. [12]. Cellulose was then allowed to react with acrylonitrile monomers in the presence of the initiator. The reaction mixture was kept constant at different temperatures using a temperature bath (varying from 10 to 70°C) for a constant period of time. The time of reaction was varied from one hour to two days. The grafting reaction was discontinued by cooling the mixture in ice water. The reaction mixture was filtered and graft copolymer was extracted with an appropriate solvent. A selective solvent extraction method using different solvents such as methanol, toluene, cyclohexane and N-N-dimethyl formamide was employed.

The grafting percentage was computed as the percent increase in the weight of grafted sample over the original weight of cellulose as follows:

$$\text{Grafting Percentage} = \frac{W_g - W_o}{W_o} \times 100$$

where  $W_g$  is the weight of grafted cellulose and  $W_o$  is the original weight of cellulose. In practice, it is difficult to minimize homopolymer formation. We limited the homopolymer formation to about 5 percent by the addition of small amounts of a bifunctional monomer such as ethylene glycol dimethacrylate. Presumably this tied any homopolymers to grafted chains, thus maximizing grafting efficiency. Another problem was the production of many short side chain grafts. This was resolved by minimizing the amount of initiator into the reaction mixture. As mentioned earlier, performing a number of different experiments at different conditions of time, temperature, amount of initiator, monomer and pH (4-8) provided enough data to optimize the reaction variables to the highest possible graft efficiency. Finally, the gravimetric results were checked by IR spectroscopy.

## APPLICATION

The adsorption process has been used for many years for the removal of contaminants from water. Currently powdered activated carbon and granulated carbon are being used as water and wastewater adsorbents. The dissolved contaminants in water may be cationic, anionic, and sometimes these may be in a nonionic form. Currently, metallic contaminants are removed by co-precipitation, ion exchange, activated alumina or reverse osmosis. Co-precipitation appears to be a popular technology.

Removal of toxic organic pollutants from aquatic environmental systems has been given much attention, and polymeric adsorbent resins can remove contaminants from aqueous systems.

The preliminary laboratory studies conducted by the authors showed that cellulose grafted polyacrylonitrile removed 99.5 percent of nonylphenol from aqueous solutions. High performance liquid chromatography (HPLC) was used for measuring nonylphenol. It was also found that 78 percent of cadmium was removed. Cadmium was measured using atomic absorption techniques. The limited results show that cellulose grafted copolymer has promising industrial application for removing water contaminants from aqueous solution.

## ECONOMICS

Economics is the most important factor that limits the conversion of solid municipal waste to energy. The high cost of recovering low value materials and the consequent relative unprofitability seem to prevent many industries from adoption of recycling or recovery techniques from waste by-products. Many projects which began as attempts to economically recover energy from waste have ended up as mere efforts to minimize the volume of the waste by combustion. Furthermore, little is known about the nature and the environmental and health impacts of air pollution associated with mass burning.

Conversion of the cellulosic portion of solid municipal waste to an adsorbent material is a new technique for recovering energy from cellulosic waste. Following many European countries and Japan, numerous U.S. cities are requiring citizens to separate paper products and cellulosic materials in domestic garbage. For example, Montgomery County in Maryland and some areas in the District of Columbia already require the separation of cellulosic waste from municipal solid waste at the household level. This should reduce separation costs. Another important economic factor is that the cellulose comes from renewable sources. The overall capital cost of producing the adsorbent material appears to be less than that of producing a comparable synthetic material from fossil fuel or that of producing activated carbon.

Considering the fact that small energy inputs are required for the desorption process, the operating cost of separating water contaminants with this material

appears to be less than the cost of activated carbon. In fact, this is an important regenerating aspect of the value of using CGPA resins for adsorption, since it is possible to recover the valuable compound from aqueous streams.

## REFERENCES

1. O. N. S. Hone and H. C. Chan, Graft Copolymerization of Ligno Cellulosic Fibers, *ASC Symposium*, 187, p. 101, 1982.
2. C. H. Ang, J. L. Garnett, S. V. Jankiewicz, and D. Sangster, Graft Copolymerization of Ligno Cellulosic Fibers, *ASC Symposium*, 187, p. 101, 1982.
3. J. C. Arthur, *Advanced Macromolecular Science*, 2, p. 1, 1970.
4. N. Shiraishi, J. L. Williams, and V. Stannett, *Radiation Physics and Chemistry*, 1981.
5. S. R. Rao and S. L. Kapur, *Journal of Applied Polymer Science*, 13, p. 1619, 1969.
6. H. Kubota and Y. Ogiwara, *Journal of Applied Polymer Science*, 13, p. 1569, 1969.
7. Y. Ogiwara, H. Kubota, and K. Arai, *Journal of Applied Polymer Science*, 14, p. 1049, 1970.
8. A. Kantouch, A. Hebeish, and M. H. El-Rafie, *Journal of Applied Science*, 15, p. 11, 1971.
9. O. Y. Mansour and A. Nagaty, *Journal of Polymer Science, Polymer Chemistry Edition*, 12, p. 1887, 1974.
10. E. Schwab, V. Stannett, D. H. Rakowitz, and J. K. Magrane, *TAPPI*, 45, pp. 390-400, 1962.
11. T. M. Angaji and P. D. Johnson, Graft Copolymerization of Acrylonitrile onto Cellulose Using Ceric Ammonium Nitrate as an Initiator, *Proceedings of the 14th Annual Conference of the National Organization for the Professional Advancement of Black Chemists and Chemical Engineers (NOBCCHE)*, April, 1987.
12. E. F. Okieimen and E. Rasmusen, *Journal of Applied Polymer Science*, 31, p. 1257, 1986.

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