THE TREATMENT OF WASTEWATERS FROM SUGAR CANE ALCOHOL PRODUCTION WITH MODIFIED BENTONITES

P. M. Büchler

Department of Chemical Engineering, São Paulo University, P.O. Box 61.548, São Paulo – SP–CEP 05508, Brazil

ABSTRACT

The recent use of hydrated ethanol as an alternative automotive fuel in Brazil has created a major environmental problem to the country. The final product of sugar cane juice fermentation is a ten percent ethanol solution. In order to reach the concentration of the hydrated ethanol (96%) the weak solution has to be distilled. Therefore for each liter of alcohol produced ten liters of liquid residue will be generated. This residue, known as vinasse, is a 5 to 10% solution of mostly organic molecules. Therefore the BOD of vinasse can be as high as 50,000 mg/l.

The present work is a study of the adsorption of some organic components of vinasse in a tetra methyl ammonium derivative of Wyoming bentonite. A sodium Brazilian bentonite was also studied. The hydrophobic nature of this ammonium quaternary cation makes the silicate surface of the clay more receptive to organic molecules and, above all to polar organic molecules. Several organic compounds, beyond vinasse, at temperatures close to ambient were tested. Isotherms were plotted and their shapes were compared with Freundlich isotherm. The adsorption is higher at lower temperatures. This means that the treatment is less effective at hot climates.

The adsorption of phenol at 1,000 ppm and 20°C has shown a removal effectiveness of 85%. For lower concentrations and higher temperatures the adsorption was less effective. Other organics tested were glucose, glycine, dextran, ethanol, glycerol and fructose. All showed a lower adsorption pattern.

KEYWORDS
Vinasse; bentonite; ethanol; adsorption.

INTRODUCTION

Vinasse, the liquid residue from alcohol distillation, is the most abundant pollutant from industrial origin in Brazil. The juice from sugar cane, after fermentation, produces a beer which has a concentration of 5 to 10% in ethanol. Therefore, the final purification by distillation will generate 10 or more volumes of vinasse per volume of hydrated ethanol. In order to reduce the amount of vinasse it is, sometimes, concentrated and burned. In both cases the amount of hazardous materials generated is very high: heavy metals as ash or BOD generating organics. Beyond that the phosphorus present will cause lake eutrophication with the consequent growth of water hyacinth.

In most developing countries, the residue is stored in stabilization ponds without any lining. The final result is leakage to rivers and infiltration to underground water. The leakage to rivers and lakes will cause death of
fishes. But worse than that is the infiltration to the underground water which will be used for human consumption. This is causing a high toll of infant deaths. This fact puts Brazil among the developing countries with the highest index of children dead before one year of age. In the case of Brazil, this problem is specially serious because the hydrated ethanol is used as an alternative automotive fuel. Therefore, the number of stabilization ponds is extremely high and the degree of contamination of underground water keeps increasing. The use of bentonites proved to be a very effective treatment method because of its high capacity to adsorb organic molecules. The objective of this paper is to study the adsorption of the organic components of vinasse in bentonites reacted with tetra methyl ammonium chloride (TMA) cations. Two bentonites were studied: the Wyoming bentonite and a Brazilian bentonite from the State of Paraiba known as Boa Vista bentonite.

LITERATURE REVIEW

There is no information in the literature about the adsorption of vinasse on bentonites. But a substantial amount of data is available on the adsorption of the organic components of vinasse on bentonites reacted with several different cations (Theng, 1974). The TMA derivatives of sodium bentonites are specially active in the adsorption of polar organic molecules (McBride, 1985). Therefore, the adsorption is high on the surface of this clay mineral. TMA is a hydrophobic cation therefore it is more likely to attract organic molecules which are not too miscible with water. This is specially true in the adsorption of aliphatic alcohols (German and Harding, 1969) and amino acids on bentonites (Sieskind, 1985 and Talibudeen, 1954). The adsorption of glucose is not so intense (Greenland, 1956) because it is a highly hydrated molecule as compared with the methyleated glucose which is more intensively adsorbed by calcium bentonite. Dextran, which is the gum more frequently found in sugar cane, follows the "chain length rule" which means that the high molecular weight found in vinasse is well adsorbed (Olness, 1975). Studies with glycerol (Brindley, 1966) show that the problem of its adsorption comes from the presence of 3 OH groups which make the molecule too bulky to fit into the interbasal space.

MATERIALS AND METHODS

The materials used in the laboratory experiments were: analytical grade glycerol, ethanol, glucose, fructose and phenol; clinical grade dextran (molecular weight = 2 million) and glycine. Two bentonites were tested: the Wyoming bentonite supplied by Laporte Industries from the U.K. and Boa Vista bentonite supplied by Bentonita União from Brazil. The tetra methyl ammonium chloride (TMA) is an analytical grade chemical.

The following procedures were adopted:

1. Method to react the bentonite with TMA
   - The bentonites were ground in a ball mill until a size smaller than 147 micrometers was achieved.
   - 3 grams of the clay were mixed with 60 ml of a molar aqueous solution of TMA.
   - The suspension was stirred for 24 hours in a 100 ml plastic flask.

DISCUSSION

The idea of using TMA derivatives of bentonites is not new (Barrer, 1955). Replacement of inorganic cations in smectites by TMA opens up the interbasal space and cause profound changes in the sorption and intercalation of organic molecules. Also, because of the hydrophobic nature of the TMA cation, the interbasal space becomes less sensitive to the presence of water. The temperature used in the present experiments is 30°C, which is the average temperature in a tropical country, where most cane sugar plantations are located. Lower temperatures do occur but they are the exception rather than the general rule. Besides, since the adsorption capacities are lower for higher temperatures the present results are conservative.
The phenolic bodies present in vinasse (as simulated by phenol) are strongly adsorbed by the TMA derivatives of both bentonites used. Other components are adsorbed to a lesser extent. The results for vinasse are surprisingly high, since we would expect an average value for the adsorption capacity as compared with the same capacity of the components. The suspended organic solids in the vinasse seem to be responsible for the higher value of the adsorption.

CONCLUSIONS

The capacity of modified bentonites to adsorb organic molecules make them useful in the treatment of vinasse. Activated carbon has been traditionally used in the adsorption of organic molecules from wastewaters. Modified bentonites are less effective than activated carbon but they are also less expensive; therefore its use can be economical if the bentonite is locally available as in Brazil.

ACKNOWLEDGEMENTS

The author wants to thank several persons and institutions, both in Brazil and abroad, for making this work possible: Professor Roger Perry from the Imperial College of Science and Technology, Dr. Joseph A. Polack from Louisiana State University, Dr. Persio de Souza Santos from São Paulo University, Dr. Walter J. Weber, Jr. from The Michigan University, The British Council, United States Department of Agriculture, Brazilian Research Council, São Paulo Research Foundation, São Paulo University, Brazilian Ministry of Education and The Fulbright Commission.

REFERENCES


