INVESTIGATING THE POSSIBILITIES OF UTILIZING PRAWN-SHELLS IN WATER AND WASTEWATER TREATMENT

S.I. PADMASIRI

Department of Chemical Engineering, Faculty of Engineering, University of Peradeniya.

ABSTRACT

Prawn-shell derivatives extracted in the laboratory in two different methods were tested for their turbidity removal efficiency and pH dependency and the results were compared with those of alum and commercially available chitosan. One method gave a product, which behaved similar to commercial chitosan in turbidity removal efficiency. It was discovered that the diluted supernatant also showed very high turbidity removal capabilities.

INTRODUCTION

Chitin, the second most abundant natural polymer after cellulose, is found in prawn shells and in other exoskeleton of crustacea (Ashford 1977). An acid soluble derivative of chitin, known as chitosan has shown good turbidity removal capability (Murcott and Harleman 1993). This is due to its cationic nature (Murcott and Harleman 1993) promoting coagulation and flocculation, which are important processes in water and wastewater treatment.

Prawn farming is carried out in large scale, in the western coastal area of Sri Lanka. At present, the shellfish industries have a problem in the disposal of their waste. The waste, mainly consisting of outer shells and heads of prawns, lobsters, etc. are buried or disposed in wastelands. These reasons have made prawn shells an attractive raw material to be tried out in water and wastewater treatment in Sri Lanka.

Our interest was in producing chitosan or some other derivative of chitin for turbidity removal, from the locally available prawn shells, waste from prawn farm industry. Prawn shells were processed using an acid-alkali method (Ashford 1977) and the derivatives so obtained were tested for their turbidity removal efficiency in a series of jar tests with different dosages of the solutions. Water samples used were taken from the Mahaweli River with bentonite added when the initial turbidity was found to be too low. Initial and final turbidity and the pH were measured in each jar.

TURBIDITY REMOVAL PERFORMANCE OF CHITOSAN

The turbidity removal efficiency was tested in a series of jar tests. These were conducted in six jars of 1 liter each with Mahaweli River water with benotanite added to increase the initial turbidity. The initial turbidity and pH values were measured. The jar test runs were done with 1 min fast stirring (100 rpm), 20 min slow stirring (20 rpm) and 30 min settling. The jar 1 was kept as the control, while different dosages of the chitosan dissolved in

acetic acid (with a concentration of 0.1 mg/ml) were added to the other five jars. The commercially available chitosan is in the form of a white powder and dissolves in 1% acetic acid solution to form a gelatinous precipitate. The final turbidity and pH were measured and the results are plotted in Figs.1 and 2.

Turbidity removal efficiency was calculated using the formula below.

Turbidity removal efficiency = $\frac{(\text{Initial Turbidity-Final Turbidity})}{\text{Initial Turbidity}} * 100$

The tests were repeated with alum, the commonly used coagulant in water treatment, which had a concentration of 5mg/ml, and these results are also plotted in Figs. 1 and 2.



Fig. 1. Turbidity Removal Efficiency of Alum Vs Commercial Chitosan

The chitosan is showing high turbidity removal as alum (Fig. 1). It is also noteworthy that a higher turbidity removal efficiency can be achieved with a lower dosage of chitosan than alum. This would also reduce the amount of sludge produced. Due to the limited supply of commercial chitosan available for the study, sufficient jar tests could not be carried out to obtain an optimal dosage in the case of chitosan.



Fig. 2. Final pH of Alum Vs Commercial Chitosan

The pH has remained constant with increase in dosage of chitosan (Fig. 2) whereas in the case of alum, the pH has reduced with increase in dosage. Therefore, by using chitosan in water treatment, less subsequent chemical treatment will be necessary to adjust pH thereby reducing chemical costs.

PERFORMANCE OF PRAWN-SHELL DERIVATIVES

Acid-alkali method consisting of the three distinct steps, deprotienation, demineralization, and deacetylation was carried at laboratory scale for the production of chitosan or another chitin derivative. Since the exact procedure was not available in the literature to the best of my knowledge, several methods were tried out by varying parameters. Outcome of two methods (A & B) and the results are given in this section.

Method A

The prawn shells were cleaned thoroughly by removing the meat and were dried and powdered. Fifty grammes of the powder were mixed with 500 ml of 1N NaOH solution for 2 hrs between 50-60 °C to deproteinise. The mixture was decanted and the powder was washed with water. For demineralization, the powder was mixed with 500 ml of 2N HCl solution for 2 hours between 40-50°C. This mixture was cooled, decanted, and the resulting powder was washed with water. The final deacetylation was carried out by adding 250 ml of 50% NaOH solution and by heating the mixture to 100°C for 2 hrs. The product was separated and washed.

The extract obtained from this method did not show any turbidity removal capability. However, interestingly, the supernatant of the extraction process showed very high turbidity removal efficiency even with a dilution of 1:10 as shown in Fig. 3. The pH also increased with the increase in dosage, but this is expected since the supernatant is made up of 50% NaOH solution.



Fig. 3. Performance of diluted supernatant (Method A)

Method B

In this method, the 50% NaOH solution in the final deacetylation step was neutralized with an equimolar HCl solution before separation of the extract. This was done in order to neutralize the extract, which has to be dissolved in 1% acetic acid solution in order to be used as a coagulant. The extract obtained from this method showed high turbidity removal capability as shown in Fig. 4.



Fig. 4. Performance of prawn-shell derivative (Method B)

Compared with commercial chitosan, a higher concentration of the laboratory extract had to be used (20 mg/ml) to obtain the same turbidity removal efficiency. This was because the laboratory-produced extract had low solubility in acetic acid. Since the solubility is low, the solution was acidic and due to this, the pH has also decreased with increase in dosage.

The supernatant of method B was showing high turbidity removal efficiency as shown in Fig. 5 as the supernatant in method A.



Fig. 5. Performance of diluted supernatant (Method B)

The pH has also increased with increase in dosage, showing that the supernatant is still alkaline.

DISCUSSION

From the study it is evident that the prawn shell extract of method B has turbidity removal capabilities. Not only this, the supernatants of the extraction process of methods A & B are also showing very good turbidity removal capability.

The supernatant cannot remove turbidity unless some derivative of prawn-shells is present. Therefore, the compounds responsible for promoting turbidity removal in the supernatant must be identified. Whether it is chitosan, or some other derivative of chitin, has to be verified by testing before any further methods of extraction are tried out.

The test for chitosan is that it should be dissolvable in 1% acetic acid solution forming a gelatinous precipitate. The derivative of the prawn-shell extracted in the laboratory of both methods did not answer this test. But the extract in method B, mixed in 1% acetic acid and the solution so obtained (the extract was still visible at the bottom of the vessel after mixing), has shown good turbidity removal efficiency. Acetic acid solution alone cannot remove turbidity. Therefore it is conclusive that some other compound in the extract has got dissolved in the acetic acid solution. This could be chitosan in a very crude form and only slightly soluble in 1% acetic acid such that no gelatinous precipitate is formed. This indicates that it is necessary to devise a laboratory test to identify this crude form of chitosan.

It is also worthy to mention the limited resources available to carry out this extraction process in our laboratory. Keeping the temperature constant while mixing, in the deproteination and demineralization steps in the extraction process was difficult to adhere to. This may also have affected the results.

CONCLUDING REMARKS

The prawn-shell derivative extracted locally in laboratory scale, is showing the potential of being a substitute for alum, in water treatment applications. However, it will be necessary to identify compounds in the extract and the supernatant in order to improve the existing extraction method.

ACKNOWLEDGEMENTS

I am very grateful to my project supervisor, Mr. E.J.H. Corea of Department of Civil Engineering, University of Peradeniya, for the guidance and support given during the project. I also thank Prof. T. D. M. A. Samuel and Dr. R. Shanthini, of Faculty of Engineering, University of Peradeniya, for the constructive criticism, encouragement and guidance given during preparation of the paper. The support extended by the academic and the laboratory staff of the Environmental Engineering Laboratory of the Department of Civil Engineering, University of Peradeniya, is gratefully acknowledged.

REFERENCES

- 1. Ashford, N.A. 1977. Industrial Prospects for Chitin and Protein from Shellfish Waste. Massachusetts Institute of Technology. Report No. MITSG 77-3, Index No. 77-703-Zle.
- 2. Murcott, S. and D.R.F. Harleman 1993. Jar tests of the natural polymer chitosan. Proc. AWWA WQTC, Miami Fl. Nov.7-11
- 3. Pennisi, E. and C. Craze, 1993. Science News, Vol. 144, No. 5, pp. 72-74.