On-site treatment of turbid river water using chitosan, a natural organic polymer coagulant

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Abstract Chitosan, acetylate of chitin, is a biodegradable cationic polymer. The objective of this study is to assess the applicability of chitosan as an on-site treatment agent of turbid water caused by river construction works and other diffused pollutions. The results of jar-tests indicate that floc of chitosan is much larger than that of aluminium sulfate, and turbidity treated by chitosan under moving water conditions is much lower than that of aluminium sulfate. Chitosan is applied to Imou River in Yamaguchi prefecture, where river construction work is going on. St.1 is located just below the construction work, St.2 is located about 250 m downstream from St.1, and St.3 is located about 350 m downstream from St.2. Initial turbidity of each station is 1,100, 937 and 313 NTU, respectively. By applying chitosan at St.1, turbidity of each station is drastically reduced to 1,100, 12 and 0 NTU. Chitosan could be helpful to reduce problems caused by turbidity in rivers.

Keywords Chitosan; coagulation; fish toxicity; sedimentation; turbidity removal

Introduction

Although there are a lot of demands for on-site turbidity treatment methods in relation with river construction works, there is no effective method applicable to small rivers especially under a cost sensitive situation. In our former study, we proposed a chemical precipitation using aluminium sulfate combined with temporary dams (Takeshita *et al.*, 2002). In the field experiment, we could reduce turbidity of 250 NTU down to 50 NTU in a river in which construction work was going on. But the appearance of the water was still not clear enough, and our proposal was not adopted after comparing the effectiveness of the treatment and the risk of aluminium to living organisms in the river. In this study, we focus on chitosan, acetylate of chitin, as a coagulant (Huang *et al.*, 1996; Pan *et al.*, 1999; Huang *et al.*, 2000). Chitosan is a cationic polymer obtained from natural resources like shells of shrimps. Thinking the fact that chitosan is not only widely used for a coagulant in food industry but also sold as a health food, chitosan can be a safer coagulant than aluminium sulfate for applying directly in rivers. The objective of this study is to assess the applicability and safety of chitosan as an on-site treatment agent of turbid water caused by river construction works and other diffused pollutions.

Jar-tests of chitosan and aluminium sulfate

Determining optimum coagulant concentrations

A test solution of 210 NTU, pH 7.6 and 20 °C is prepared by using river water and mud. After two minutes pre-stirring at 181 s^{-1} (G value (Camp, 1943)), coagulants are injected in various concentrations, then kept stirring for three minutes at 181 s^{-1} and ten minutes

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at $49\,s^{-1}$. After five minutes of still standing conditions, the turbidity of the supernatant water is measured. For aluminium sulfate, we need to add sodium hydroxide to make it work as coagulant, whereas for making a solution of chitosan, we need to add the same amount of acetic acid. Although these additional agents are needed, pH of the test solution changes little after coagulant injection. Figures 1 and 2 show the results of the jar-tests. Based on these results, the optimum coagulant concentrations are determined as 1.0 mg-chitosan/L for chitosan and 4.1 mg-Al_2O_3/L for aluminium sulfate.

Stirring condition and treatment performance

A test solution of 213 NTU, pH 8.03 and 20 °C is prepared by using river water and mud. After two minutes pre-stirring at $181\,s^{-1}$, coagulants are injected in optimum concentrations, and then kept stirring for three minutes at $181\,s^{-1}$ and ten minutes with different G values. After five minutes of still standing conditions, the turbidity of supernatant water is measured. Figure 3 shows the result. Aluminium sulfate receives small influence from the stirring conditions, whereas chitosan shows higher performance in higher stirring conditions. In addition, much larger particles are observed in chitosan solution which seem almost to settle down even under stirring conditions.

Based on this observation, we test coagulant performance under stirring conditions in the next experiments. After two minutes pre-stirring at $181\,s^{-1}$, coagulants are injected in optimum concentrations, and then kept stirring for three minutes at $181\,s^{-1}$ and 160 minutes with various stirring conditions. During the 160 minutes stirring, the turbidity is measured several times at a depth of 2 cm (out of 12.7 cm total depth). Figure 4 shows the turbidity at the end of 160 minutes stirring. The figure also contains G values at pools and rapids in a river. Chitosan shows high performance under high G value compared to aluminium sulfate. Figure 5 shows the particle size created by chitosan and aluminium sulfate under stirring conditions. The particle size created by chitosan is ten times larger than that of aluminium sulfate. This characteristic might be another strong point of chitosan as an on-site river turbidity treatment coagulant. Easily we hit on an on-site turbidity treatment process of injecting chitosan before the rapids of a river then let particles precipitate in a pool of it.

Field experiment in Imou River

We conducted a field experiment on 18 November 2003 in Imou River in Yamaguchi prefecture. Figure 6 shows the location of observing stations. St.1 is a rapid right downstream from a construction site. Coagulant is injected at St.1 (Figure 7). The stirring condition of St.1 is: B = 0.95 m, v = 0.35 m, H = 11 cm, $354\,s^{-1}$ of G value and two minutes retention time. St.2 is a pool with B = 2.46 m, v = 0.07 m, H = 18.1 cm, $42\,s^{-1}$ of G value and seven minutes retention time. St.3 is a rapid with B = 1 m,

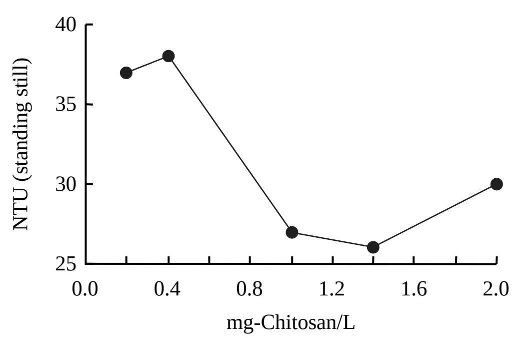

Figure 1 Chitosan concentration and turbidity under standing still conditions

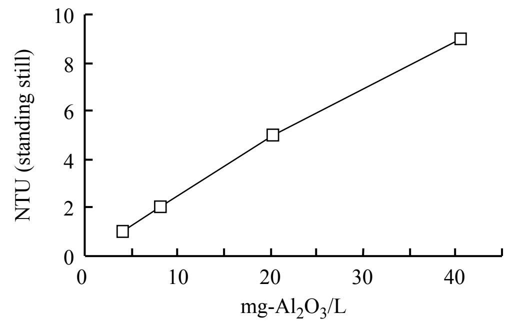

Figure 2 Aluminium sulfate concentration and turbidity under standing still conditions

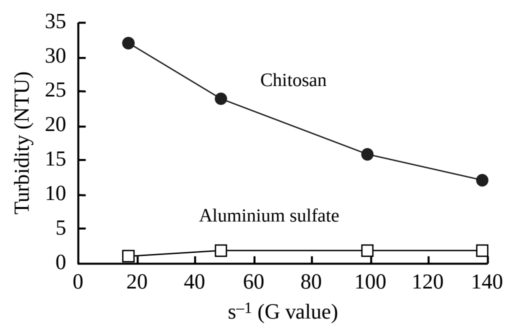

Figure 3 Turbidity under standing still conditions with different G values

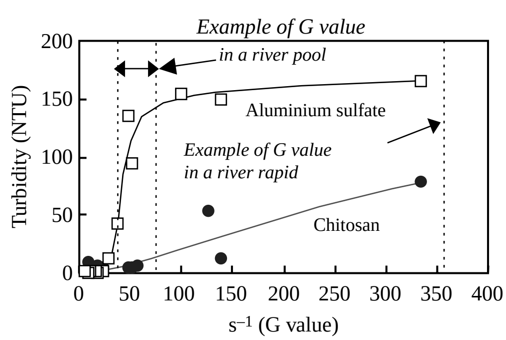

Figure 4 Turbidity under stirring conditions with different G values (after 160 min stirring)

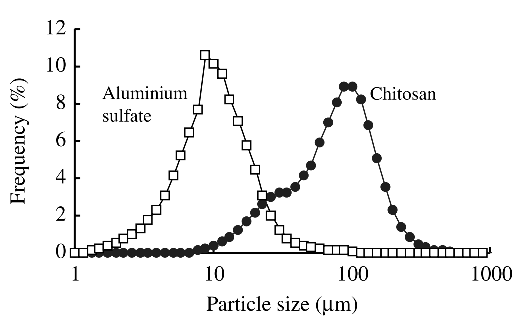

Figure 5 Particle size distribution created by chitosan and aluminium sulfate under stirring conditions

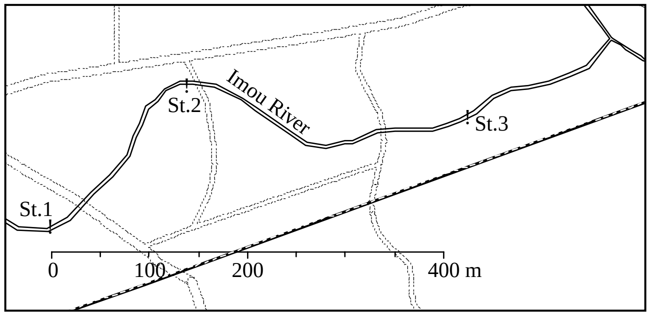

Figure 6 Location of observing stations in Imou River

Figure 7 St.1

v = 0.38 m, H = 7.7 cm (Figures 8 and 9). In this experiment, pure chitosan is not used but FLONAC #250 is used, which is a trade name of 1:1 mixture flake of chitosan and acetic acid to increase solubility of chitosan. The optimum coagulant concentration is determined as 1.5 mg-FLONAC/L from a jar-test. The retention times are about 45 minutes from St.1 to St.2 and 60 minutes from St.2 to St.3. FLONAC solution is continuously injected at St.1 for two hours and turbidity and SS are measured at all stations. Figure 10 shows the time series of turbidity and Figure 11 shows SS concentrations taking retention time into account. As you can see from these figures and photos, chitosan shows quite high performance in removing turbidity compared to our experience with aluminium sulfate in former research. Precipitation effectively occurs in natural pools and we don't even need a temporary dam.

Safety tests of coagulants

Although we reported the excellent on-site treatment performance of chitosan in the previous chapter, we also observed the strange behavior of fish in the high turbidity section

Figure 8 St.3 before coagulant injection (You cannot see bottom materials)

Figure 9 St.3 after coagulant injection (You can see bottom materials clearly)

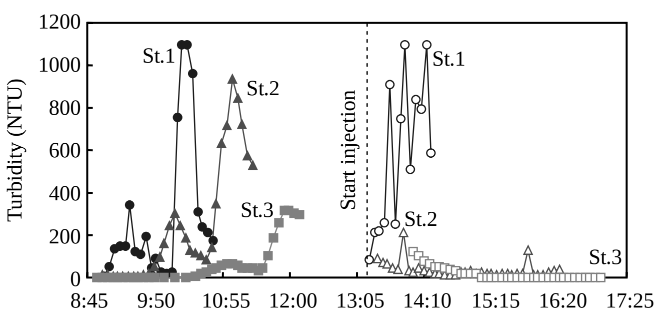

Figure 10 Time series of turbidity in Imou River

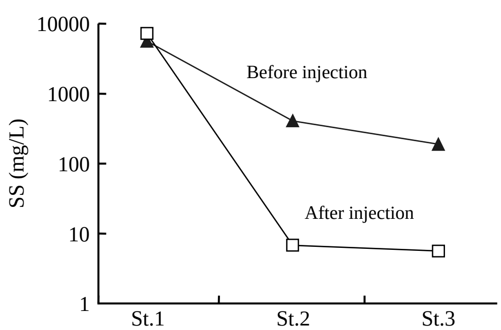

Figure 11 SS change caused by chitosan injection

which was about 50 m downstream from St.1. In the section, a bunch of fish exhibited "surfacing", but the behavior was somewhat different from the common behavior known as surfacing. They didn't take breath at the surface but just stayed calm and quiet right below the surface with heads slightly up (Figure 12). We didn't observe any dead fish or quickly moving fish in the section, nor any strange behavior of fish in the other downstream sections. Although we started this research based on the expectation that chitosan is safer than aluminium sulfate, now a toxicity test is required.

An acute toxicity test using larva of *Oryzias latipes* is employed. Ten larvae with 25 mL test water are put into a Petri dish (φ90 mm × 40 mm) and cultivated 48 hours under 25 °C. The number of dead larvae and abnormal larvae is counted at 1, 2, 3, 6, 12, 24, 48 hours. A control test is also conducted using water treated with activated carbon at the same time. In case the mortality rate of the control test exceeds ten per cent, the result is omitted. Figures 13 and 14 show the results of the toxicity tests.

Chitosan shows a low rate but constant abnormal behavior. From the close observation of the abnormal behavior, fins of the larva seem to cling to its body. In the other experiment, we observe that 96% of chitosan goes to the bottom sediment by precipitation very shortly. Supernatant water causes no abnormal larva behavior.

A fishery science researcher privately mentioned to us that the observed "surfacing" might be the common behavior for fish when they are in turbid water. He added that it was no wonder that no one had observed the behavior before because we couldn't see fish through turbid water. We haven't found any method to test his opinion, but it could be one reason for the "surfacing" behavior.

Although we couldn't clearly prove the safety of chitosan from these tests, the abnormal behavior of fish seems not to be caused by toxicity but to be caused by the physical viscosity of chitosan. High turbidity also causes the avoiding behavior of fish or deadly effects on bottom living organisms. One should compare the risk of turbidity over a long distance and the "toxicity" of chitosan over a short distance.

Cost analysis

The cost of FLONAC is ¥2,000/kg and aluminium sulfate is ¥326/kg. The optimum coagulant concentrations for 1,000 NTU water are 1.2 mg-FLONAC/L and 6.1 mg-Al_2O_3/L. Based on these conditions, the cost of chitosan is 1.2 times higher than aluminium sulfate. But you should remember that there is a big difference in on-site treatment performance. By using chitosan, you don't need any special settling pool.

Figure 12 "Surfacing" fish 50 m downstream from St.1. They just stayed calm and quiet near the surface

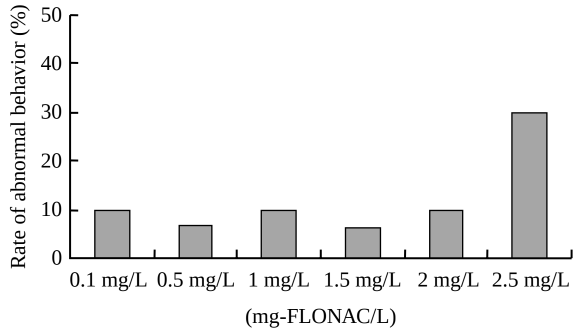

Figure 13 Rate of abnormal behavior of larvae for FLONAC

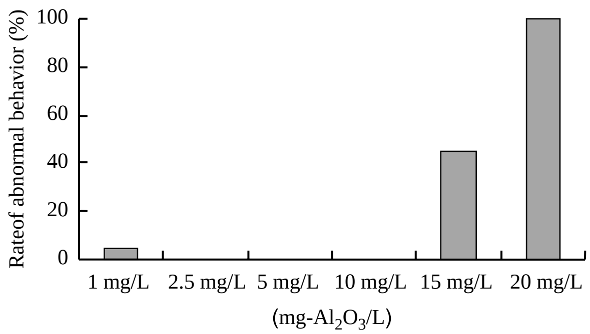

Figure 14 Rate of abnormal behavior of larvae for aluminium sulfate

Conclusion

In this research, chitosan shows excellent performance and usability as an on-site turbidity treatment agent. It is comparable in cost and much better in performance compared with aluminium sulfate. Although we still need to be careful about the effect of chitosan on living organisms, chitosan can greatly reduce the distance where turbidity reaches. The supernatant water treated by chitosan is quite safe. We hope this technique can reduce the impact of turbid water on living organisms.

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