

Phosphorus removal with chitosan in a facultative aerated lagoon system

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Abstract Physical-chemical techniques for wastewater treatment use large quantities of metallic coagulants and synthetic polymers. These chemicals generate by-products in the biosolids that can be harmful and unacceptable to the environment. This research aims at optimizing the use of chitosan (CH), for phosphorus removal in municipal wastewaters treated in facultative aerated lagoons. Chitosan is a polymer derived from naturally occurring chitin, which is abundant in seashells. It has strong coagulating and flocculating capability, but is also non-toxic, biodegradable and biocompatible with living organisms. These highly desirable properties render it most suitable for the treatment of waters. Series of jar tests were conducted in 5-litre reactors on wastewaters sampled from the facultative aerated lagoons of the Deauville district in the City of Sherbrooke (Quebec, Canada) for three seasonal conditions (summer, fall and the following spring), where various acetic acid/chitosan (AA:CH) ratios were tested. Results show that chitosan was effective in removing mainly the particulate phosphorus, but soluble phosphorus was little removed, basically below 10%.

Keywords Chitosan; coagulant; facultative aerated lagoon; phosphorus; removal

INTRODUCTION

Phosphorus concentrations above 10 µg/l can induce algal growth in water bodies and trigger eutrophication (Vollenweider, 1975). Also blue-green algae produce toxins that can be lethal for fish and animals that drink in water bodies and toxic to humans via drinking water. Physical-chemical techniques for phosphorus removal in lagoons from wastewater use large quantities of synthetic coagulants and polymers that generate by-products in the biosolids that can be harmful and unacceptable to the environment. Human health and ecotoxicology concerns exist with commonly used synthetic coagulants and flocculants (aluminum salts and polymers; Al-Mutairi, 2006; Petala et al, 2006).

This research aims at optimizing the use of chitosan (CH), a coagulant of natural origin, for phosphorus removal in municipal wastewaters treated in facultative aerated lagoons. A polymer derived from naturally occurring chitin, chitosan offers many valuable properties for wastewater treatment such as strong coagulating and flocculating capability, non-toxicity, biodegradability and compatibility with living organisms.

Many studies show that chitosan removes metals by complexation of the metallic ions (Muzzarelli and Weckx 1969; Jha et al, 1988 among others), but very few concern the removal of phosphorus from the wastewaters especially at full scale systems.

METHODOLOGY

Wastewaters were sampled at the Deauville facultative aerated lagoon system (Municipality of Sherbrooke, Quebec, Canada). A schematic plan is in Figure 1. Length and width approximate 115 and 45 m respectively, and depth about 3 m. The average flow and hydraulic retention time (HRT) were in the order of 1600 m³/d and 25 d, respectively, at the time of the study.

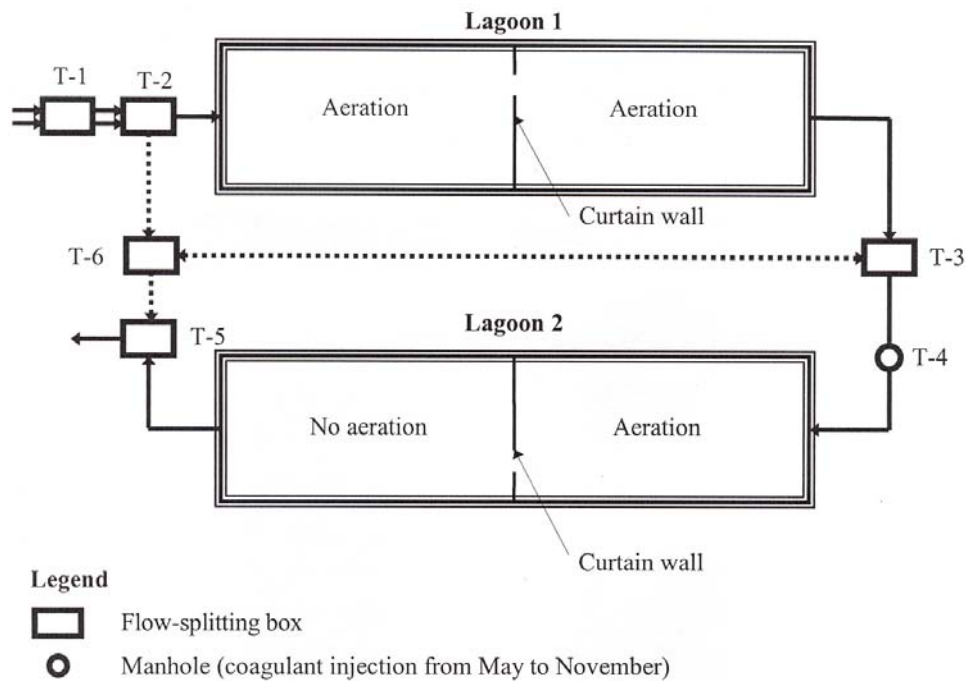


Figure 1. Schematic plan of the Deauville lagoon system

The two lagoons operate in series. Each is separated in two parts of equal surface area by a curtain wall which allows the water to flow from one cell to the next through an opening near the surface. The effluent standard is 1 mg P/l during the seasonal phosphorus removal period (May 15th – November 15th). This is achieved by injecting alum as a coagulant in manhole T-4 (Fig. 1). Settling of the flocs and precipitated material occurs in the last cell of Lagoon 2.

A series of jar tests were realized in 5-litre jars on the wastewaters sampled from the facultative aerated lagoons (box T-3, Fig. 1) for summer, autumn and spring (following year) conditions. Preliminary tests to the study and to each of the seasonal tests were run in 1-liter jar testing apparatus (Phipps and Bird, model 7790-400).

Figure 2 shows schematics and dimensions of the 1-liter and 5-liter jars and of the paddles. Dimensions of the 5-liter reactor and paddle, and rotation velocity of the paddles were obtained by ensuring that the velocity gradient (G) was the same in the 1-liter and 5-liter jars. Rotational speeds appear in Table 1. The mixing protocol used was: rapid mixing (15 s), slow mixing (10 min) and

settling (30 min). Various acetic acid/chitosan (AA:CH) ratios were tested, where acetic acid is used to solubilize chitosan. Table 2 shows the wastewater characterizations and jar testings performed.

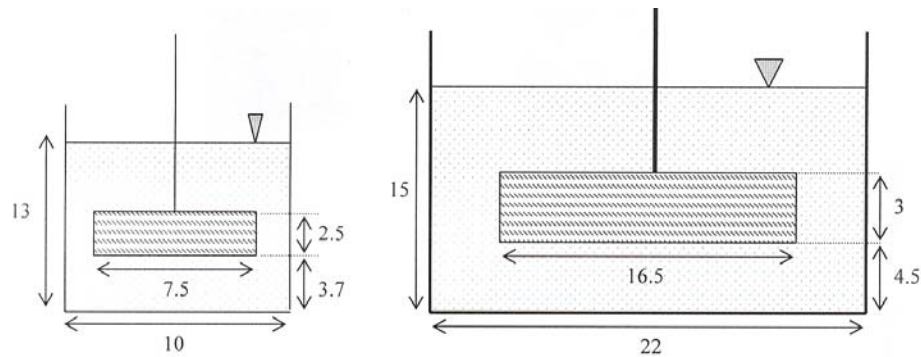


Figure 2. Schematics and dimensions (cm) of 1-liter and 5-liter reactors and paddles for the coagulation-flocculation tests

Table 1. Rotational speed (rpm) and velocity gradient G (s^{-1}) for the jar tests

Mixing intensity	1-liter jars	5-liter jars	G
Rapid (coagulation)	220	151	466
Moderate (flocculation)	33	23	41

Table 2. Wastewater characterization, sampling and jar testing

Characterization and jar testing	Objectives and description
Characterization	Wastewater characterization, performed before each series of test.
Preliminary tests	Validate results obtained in a former study. Jar testing in 1-liter beakers.
Main seasonal tests	Testing during the spring, summer and fall seasons (wastewater sampling in dry periods on August 19-20 th , October 29-30 th and May 12-13 th , respectively). 24-hour composite samples with automatic sampler, 700 liters sampled in summer, 500 litres in autumn and spring tests. Testing in 5-liter jars.

Chitosan from shrimps was supplied by AlphaBiotech (Quebec, Canada), with 156 kDa molecular weight determined by the viscosity method (Roberts et Domszy, 1982), and 78.2 % deacetylation obtained by the infrared spectrometry method (Moore et Roberts, 1980). CH and AA concentrations varied according to Table 3. Analyses were performed according to *Standard Methods* (APHA, AWWA and WEF, 1998).

Table 3. Ranges of CH and AA concentrations in solutions

Test	CH (g/100 ml)	AA (g/100 ml)	AA:CH ratio
Preliminary	0.1	1.0	10
Seasonal : summer	0.1 to 1.0 (0.1 g intervals)	0.1 to 1.0 (0.1 g intervals)	0.33-10
Seasonal : autumn	0.01 to 0.4 (variable intervals)	0.4 to 1.6 (0.2 g intervals)	1-160
Seasonal : spring	0.007 to 0.4 (variable intervals)	0.2 to 1.6 (0.2 g intervals)	1-160

RESULTS AND DISCUSSION

Phosphorus fractions

Characteristics of phosphorus in the wastewaters used during the summer, autumn and spring (5-liter) tests are shown in Table 4. One notes the lower values for the spring tests.

Table 4. Characteristics of the wastewaters used with the 5-litre jar tests

Phosphorus fraction	Values (mg/L)		
	Summer	Autumn	Spring
Total phosphorus (TP)	2,28	2,83	1,77
Total dissolved phosphorus	1,38	1,67	1,05
Reactive phosphorus	1,83	2,13	1,22
Dissolved reactive phosphorus (DRP)	1,30	1,58	0,84

Preliminary tests

A first preliminary test was conducted a few weeks before the first seasonal (summer) test, and three more a few days before each of the seasonal tests. The results are shown in Table 5.

Table 5. Results of the preliminary tests

Description	Residual TP (mg/L)		TP removal (%)	Optimal CH concentration (mg/l)	AA:CH ratio
	Initial	Optimum			
Preliminary	2.50	0.75 ^a	70.0	3.0	10 ^b
Pre-seasonal - summer	2.11	1.40	33.6	5.5	10 ^b
Pre-seasonal - autumn	2.73	1.78	34.8	6.0	10 ^b
Pre-seasonal - spring	1.78	1.17	34.3	6.5	10 ^b

^a Below effluent standard (1 mg/l) ^b 0.1 g CH/100 ml and 1.0 g AA / 100 ml

Summer seasonal tests

The results of the summer tests for residual total phosphorus are in Figure 4. Similar plots were obtained for reactive phosphorus, dissolved orthophosphate and dissolved phosphorus.

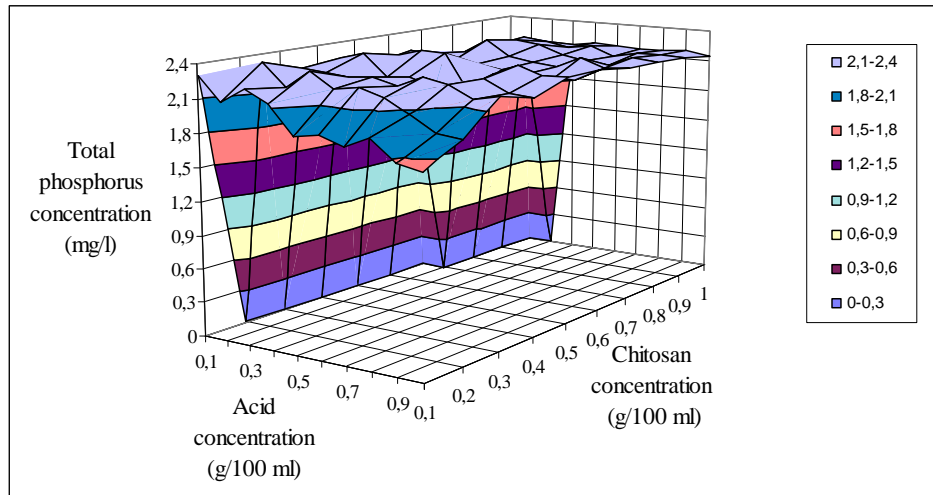


Figure 4. Residual total phosphorus for the summer seasonal tests

Concentrations of the four phosphorus fractions decrease slightly in the lower ranges of CH and the higher ranges of AA. These results reveal that the ranges used for chitosan and AA are not optimal, pointing for a change in the ranges to be used for the autumn tests (see Table 3). Moreover the results show that dissolved phosphorus is not removed practically by the process, which is in agreement with Buelna et al, (1990). AA:CH ratios ranging from 4 to 100 (0.4:1.6 to 0.01:1.0 g/100 ml) yielded an average total reactive phosphorus residual of 1.57, compared to 1.61 mg/l for the blank.

Autumn seasonal tests

The results of the autumn tests appear in Figure 5 for residual total phosphorus. The presence of a valley and a minimum indicate that the optimal acid and chitosan concentrations are obtained. Phosphorus removal is significant, but the effluent standard of 1 mg/L is not reached. The lowest value is 1.67 mg TP/l, representing 41 % removal, which is the same as initial soluble phosphorus.

Spring seasonal tests

The results of the spring tests are in Figure 6. Like the autumn tests, a valley occurs but with an overall saddlehorse shape. Two local minima of 1.02 mg TP/l are obtained (0.007 g CH/100 ml : 0.6 g AA/100 ml, and 0.01 g CH/100 ml : 0.4 g AA/100 ml), which practically meet the effluent standard of 1 mg/l. These correspond to 42.4% TP removal.

Here again the value of 1.02 is very close to the initial value of 1.05 mg/l for dissolved phosphorus. Clearly again, see Figure 7, dissolved phosphorus is limiting.

Both the autumn and spring tests show that a limited range of AA:CH ratios contribute significantly to TP removal, these ratios being in the 4-30 interval for the solutions tested. Removal efficiency is greatly reduced beyond these limits.

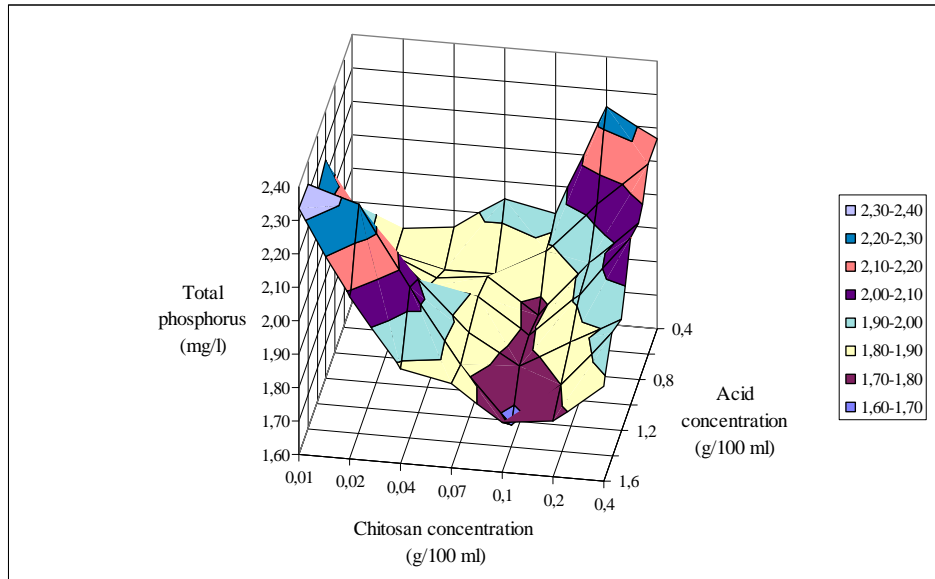


Figure 5. Residual total phosphorus for the autumn seasonal tests

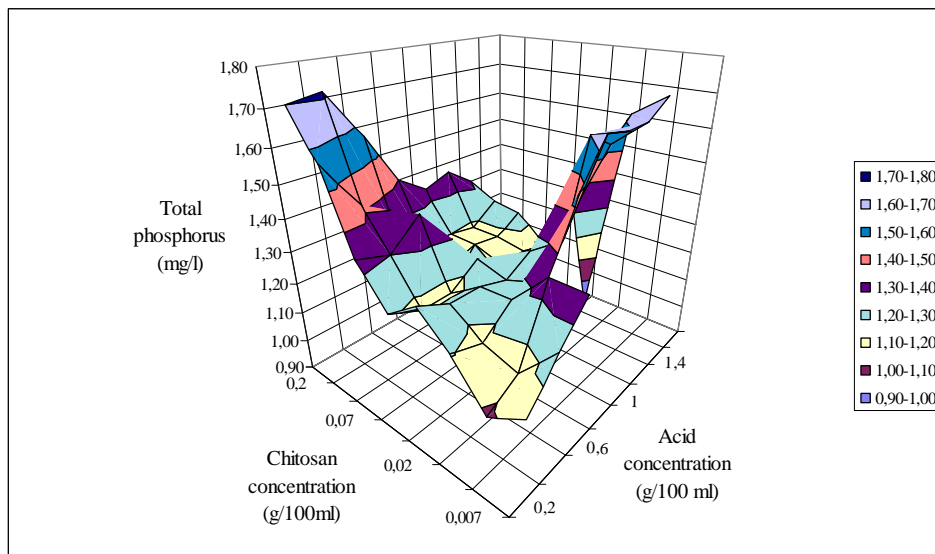


Figure 6. Residual total phosphorus for the spring seasonal tests

Variations of the TP exist in the valley for the spring tests (Figure 6). These are apparently due to numerous flocs in suspension that were observed in the supernatant. Floc sizes were observed to increase in size with the chitosan concentration. For the larger concentrations the flocs tended to be both taller and thinner in shape, but were shorter and settled well in the case of lower concentration because they were more compact.

Dissolved reactive phosphorus (DRP), results showing mainly orthophosphate, is the greatest limitation to the removal. In the best conditions DRP removal reaches about 10 %. These results fall in between those from Marucca et al, (1982) (20% removal) and Gao et al, (1993) (no significant removal). One possible explanation is that the amine groups on chitosan, which are cationic and responsible for the reaction mechanism, are associated with acetate groups of AA. These acetate groups, because of their size, would prevent orthophosphate ions from approaching the active

groups on chitosan. A possibility exists that a fraction of the phosphorus was transformed into orthophosphates under the effect of acidity resulting from acetic acid.

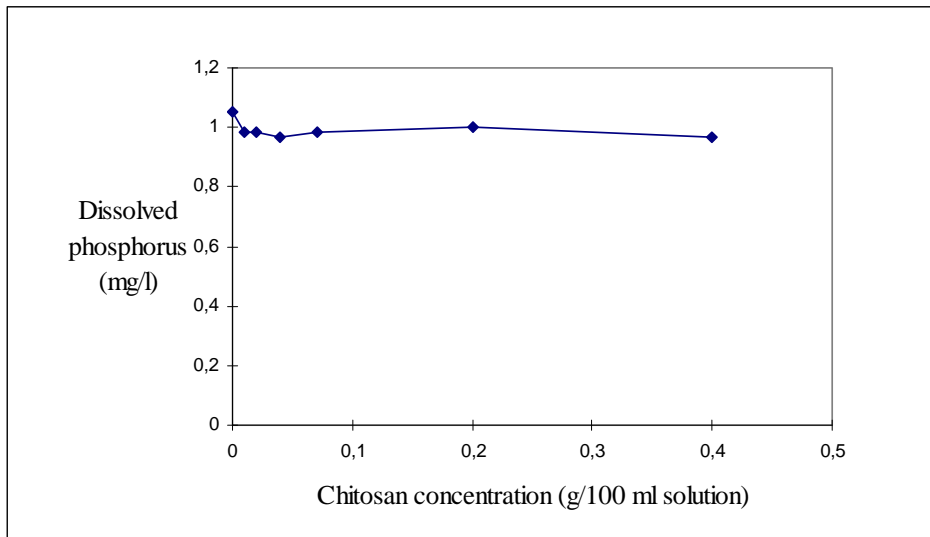


Figure 7. Dissolved phosphorus for the spring seasonal tests

AA in the chitosan solutions has the potential of raising residual COD as a result of the treatment. In the autumn tests results (not shown) indicate, logically, that residual COD increases with the AA:CH ratio, with significant increases in residual COD being obtained for AA:CH ratios greater than 4. On the other hand no residual COD increase was obtained in the spring tests (Figure 8) with a selected concentration of 1.0 g AA / 100 ml with CH varying up to 0.4 mg/100 ml solution.

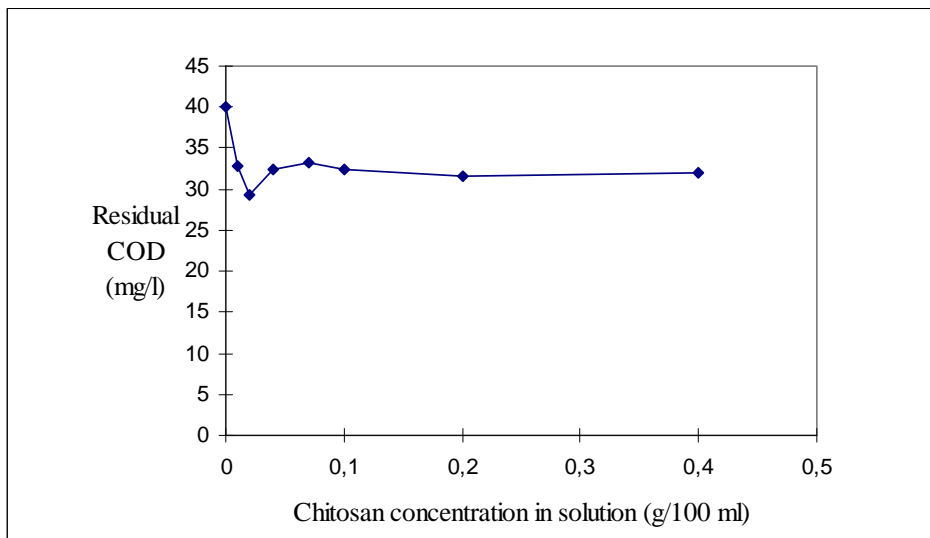


Figure 8. Residual COD as a function of CH concentration in the spring tests

CONCLUSIONS

The autumn and spring tests, show an optimal response to carefully selected ratios of chitosan (CH) and acetic acid (AA) in solution. Optimum removal of phosphorus occurred mainly with AA:CH ratios varying between 2.5 and 10.

Most of the phosphorus removed is particulate, soluble reactive phosphorus was little or not removed.

The 1 mg/l effluent standard was met with the two best combinations for the spring test, however the spring condition corresponding to the lowest strength among the wastewaters tested.

Careful selection of the AA:CH ratios should ensure that no significant increase in residual COD is obtained.

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