Technical Report

BENCH-SCALE TESTS OF CHITOSAN/BENTONITE AT CHICAGO'S SOUTH WATER PURIFICATION PLANT JUNE 1994

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MIT Sea Grant College Program

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INTRODUCTION

This report describes the findings from bench-scale tests performed at the City of Chicago South Water Purification Plant (SWPP) from May 31 to June 4, 1994. The purpose of the tests was to evaluate chitosan and bentonite as a viable chemical coagulant combination for the treatment of Lake Michigan water. The approach was first to duplicate, as best as possible given the different season and water temperature, the bench-scale work performed by Gil Crozes for Montgomery Watson in January 1994 using the same or similar coagulants he tested and reproducing at the bench-scale the current chemical coagulant treatment at the plant, then second, to determine the efficacy of chitosan and bentonite in comparison to that benchmark.

BACKGROUND

The SWPP is a conventional water treatment plant using horizontal shaft flocculators, conventional sedimentation and granular filtration. The filter waste washwater is settled and the decant is periodically pumped back to the raw water header. Sludge is discharged to the sewerage system.

The City of Chicago pumps raw water from Lake Michigan using two intakes. The crib intake is located about two miles off shore and connected to the plant header by a pipeline. The second intake is located directly on the lake shore and consists of a basin with gates allowing raw water intake. The use of shore water is dependent on demand. Demand greater than the capacity of the crib pipeline (approximately 500 mgd) necessitates the use of shore water.

Average flow at the SWPP can regularly exceed the filter design capacity. Given the expanding population and water demand at this municipality, bench-scale and pilot studies are underway to determine the possibility of increasing the existing plant capacity. It is in this context that Gil Crozes of Montgomery Watson performed bench-scale tests in January, 1994 at SWPP; pilot tests are planned for late summer 1994 and winter 1994-1995.

STUDY APPROACH

The study approach of the MIT bench-scale tests is described in the following section:

Parameters Investigated

The parameters investigated included: temperature, pH, turbidity, and particle count. Turbidity was measured using a Hach 2100P portable turbidimeter. Particle count was measured using a Met One Model 250.

Raw Water

Taps in the SWPP laboratory provide samples from many different points in the treatment system. After preliminary analysis of the crib and shore water samples, it was determined that the raw water to be used during this study would be from the shore tap. This was a departure from the Crozes study, in which crib water was used to conduct all jar tests. Whereas during the Crozes study, only crib water was being treated, during this study, high demand meant that between 20% to 35% shore water was being treated. However, the decision to use shore water was not based primarily on the proportion of crib to shore water, but rather on the low turbidity readings of crib water (0.6 - 1.2 NTU) -- often as low as the minimum turbidity values for 1993. With such low crib water turbidities, the effect of different coagulant combinations would be hard to determine. Shore water contained sufficient turbidity (1.1 - 4.3 NTU) to be able to show effects of bench-scale coagulation and filtration. Moreover, shore water turbidity during this study period closely matched crib water turbidity during the Crozes study (Table 1):

Table 1
Comparison of Raw Water Turbidities in Crozes and MIT Studies

	Range Turbidity NTU (Crozes)	Average Turbidity NTU (Crozes)	Range Turbidity NTU (MIT)	Average Turbidity NTU (MIT)
Crib	2.4 - 3.6	2.7	0.6 - 1.2	0.9
Shore			1.1 - 4.3	2.5
Header	8 - 12	10	9.7 - 9.9	9.8

From Table 1 we see that the crib water turbidity during Crozes' January study are close in value to the shore water turbidity during the MIT study.

Turbidity throughout the system, according to several different measures, is given in Table 2:

Table 2
Turbidity (NTU) at SWPP

	May 31 - June 4, '94 (SWPP)	May 31 - June 4, '94 (MIT)	1993 Annual Average (SWPP)	Jan. 1994 Study (Crozes)
Crib	0.5	0.8	3.8	2.7
Shore	1.1	2.5	7.1	
Header	1.3	9.8	4.6	10
Settling Basin #3	0.8	1.0		
Clearwell #3	0.11	0.15		
79th St. Outlet	0.11		0.14	

Table 2 gives an overview of turbidity in the entire system and shows the variability in some of the measures. (It should be noted that SWPP measures turbidity at many other points in the system. The points presented in Table 2 were selected to give a representative snapshot of the system).

Header water shows the greatest fluctuation in turbidities, due to periods throughout the day when settled filter waste washwater is recycled to the raw water header. Clear-well and Outlet water is typically about 0.10 to 0.15 NTU.

Jar Tests

A standard Phipps & Bird jar test apparatus with six rectangular 2-liter jars was used throughout the MIT study. We followed the standard procedure described in the Crozes report:

1. Two liters of raw water are added to each jar.
2. The prescribed dose of coagulant is added to each jar while mixing at a speed of 110 rpm for 1 minute.
3. If a coagulant aid is considered, it is added during the last 15 seconds of the rapid mix stage.
4. The water is flocculated as follows:
   - 80 rpm for 7.5 minutes;
   - 50 rpm for 7.5 minutes;
   - 35 rpm for 5 minutes.
5. The water is allowed to settle for 20 minutes (0 rpm).
6. For settled water, 250 ml is decanted for turbidity analysis; 500 ml is decanted for particle count analysis.
7. For filtered water, 70 ml of the 250 ml sample of settled water is used for the turbidity filterability test. For particle count analysis, an additional 500 ml is decanted for the filterability test.

The reader is referred to Crozes (1994) and Kawamura (1991) for a more detailed description of this procedure, including a discussion of mixing energy (i.e. velocity gradient) and time.

Filtration Tests

For turbidity analysis, 250 ml of settled water was decanted. 20 ml of this sample was used to wash the filter, then 50 ml was vacuum filtered (with a Fisher pump and Millipore glassware) though 1.0 micron glass filters (Gelman Science Product #61631).[1] Whatman #1 filters were also tested for comparative purposes. In common with the Crozes study, the 1 micron filters used in the MIT study gave conservative data in comparison with actual full-scale filter performance.

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[1] Whatman #1 was used in the Crozes study. Kamamura recommends use of 1 - 2 micron filter paper, and suggests Whatman #1. The author's communication with a technical assistant at the Whatman Corp. prior to this test indicated that Whatman #1 is an 11 micron filter, not in the 1 - 2 micron range.

Particle Count

Many contaminants of concern to the water industry are either particles or associated with particles. While particle measurement has traditionally been taken by the indirect means of turbidity or suspended solids concentration, particle count provides a direct measure of the number of particles.

There are several different types of particle counters. The Met One (Grants Pass, Ore) at the SWPP uses the light obscuration method. The reader is directed to Operational Control of Coagulation and Filtration Processes (AWWA, 1992) for a detailed description of this technique.

Use of a Met One Model 250 particle counter began at SWPP in October 1993 to improve process control. A 250 ml is placed in a beaker inside the instrument, and 25 ml samples are consecutively withdrawn. Data is reported in terms of numbers of particles. Each count is an average of three 25 ml runs. Particles are counted into six preset size ranges: 2-5, 5-10, 10-15, 15-20, 20-50 and >50 micron size ranges.[2] The instrument is run by the SWPP engineer, Al Opitz.

The instrument is calibrated every three months, and, by lucky coincidence, it was calibrated on the day we tested the ten MIT samples.

Chemicals Used at the SWPP

The City of Chicago uses prechlorination for zebra mussel control. Alum is the primary coagulant in a dose range from 3 to 6 mg/l and the widely used cationic polymer, Dadmac, is employed both as a coagulant aid and as a filtration aid.

A complete list of the chemicals used at the SWPP in the year 1993 are presented in Table 3, based on annual averages:

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[2] Particles of about 70 micron can be seen with the human eye. Bacteria are generally in the 0.1 - 1.2 micron range; *Giardia* cysts are about 5 - 15 micron and *Cryptosporidium* are about 4 - 7 micron.

Table 3
Chemicals Used at the SWPP in 1993

	Amount lb/Mgal	Conc. mg/l	Purpose	Point of Addition	Cost $/Mgal
Chlorine (pre)	13.5	1.6	zebra mussels, disinfection	col.11 (pre), filtered water collectors (post)	2.61
Activated carbon	8	1.0	odor	bypass shaft	3.45
Fluoride	6.9	0.8	cavies	col. 11	2.62
Alum	26	3.0	primary coagulant	col. 11	1.62
Dadmac	2.7	0.3	coagulant aid, filter ripener	center uptake shaft, 43 line	0.48*
Lime	22	2.6	pH adjustment	col. 14	0.92
Potassium permanganate	0.28	0.03	oxidant for taste & odor	center uptake shaft	0.18
Phosphate	3	0.4	lead & copper	filtered water collectors	6.00
Chloride (post)	1.2	0.1	post chlorination	filtered water collectors	(see above)

* $/Mgal cost on a wet basis (all other chemical costs are on a dry basis). Average flow for 1993 was 418 mgd.

Chemicals Tested

The chemicals tested in the MIT study are listed in Table 4:

Table 4
Chemicals Tested in the MIT Study
May 31 - June 4, 1994

PRODUCT	CHARACTERISTICS	FUNCTION
Alum	Aluminum sulfate	primary coagulant
Dadmac[3]	synthetic cationic polymer	coagulant aid
Chitosan	natural cationic polymer	primary coagulant and coagulant aid
Bentonite	montmorillonite clay with negative surface charge	coagulant aid
Starch	natural cationic polymer	primary coagulant
Moringa	natural cationic polymer	primary coagulant
Alginate	natural anionic polymer	flocculant aid
Carrageenan	natural anionic polymer	flocculant aid

RESULTS

Results will be discussed under four subject headings:

* primary coagulant evaluation;
* other natural polymer evaluation;
* coagulant aid evaluation;
* comparison of two different filters types.

Primary Coagulant Evaluation

The principal task of the primary coagulant evaluation was to compare the Alum/Dadmac chemical regime with the Chitosan/Bentonite chemical regime. However, other chemical coagulant regimes were also tested. Turbidity and particle count were the measures used to determine the best results.

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[3] This Cytech (American Cyanimid) product is the type of cationic polymer of the trade name "Magnifloc" referred to in the Crozes study.

Turbidity

After initial work allowed the determination of the lowest optimal primary coagulant concentrations, multiple tests were run at that optimum. Three to five tests each were run for the following chemical regimes:

* 3 mg/l alum
* 3 mg/l alum + 0.35 mg/l Dadmac
* 0.5 mg/l chitosan + 5 mg/l bentonite

Results of these tests are given in Table 5:

Table 5
Average Results for Different Chemical Regimes

	Average Settled Turbidity Conc. (NTU)	Average Settled Turbidity % Removal	Average Filtered Turbidity Conc. (NTU)	Average Filtered Turbidity % Removal
3 mg/l alum	0.8	64	0.65	70
3 mg/l alum + 0.35 mg/l Dadmac	1.4	46	0.66	78
0.5 mg/l chitosan + 5 mg/l bentonite	1.9	20	0.66	74

Although the alum regimes gave considerably better settled water results, all three regimes gave essentially comparable average filtered turbidity concentrations.

When evaluating chitosan and other cationic polymers as primary coagulants, Crozes looked at the same range of concentrations as for the metal salts. Yet the cationic polymers are effective as primary coagulants in much lower doses. Crozes also noted the poor settleability of chitosan. This approach led to his conclusion that "because of low settleability and for economic reasons, natural and synthetic polymers should not be used as primary coagulants." The MIT experiments typically tested chitosan in dosages between 0.25 to 1.0 mg/l. The use of bentonite as a coagulant aid improved settleability.

One surprising result of the turbidity analyses was that high settled water turbidities, not just of chitosan/bentonite chemical regimes but of other chemical regimes and even of raw water samples, could give low filtered water turbidities (and low settled water turbidities would sometimes show little improvement after filtration). Figure 1 is an example of this tendency. In this figure, on a series run on June 1, 1994, we see that although there is considerable variability in settled water turbidity results, there is essentially no difference in filtered water results. Some investigators suspect that bench-scale filtration does always successfully reflect full-plant results for turbidity and particle count, whereas it can better reflect full-plant results for color, UV absorbance, TOC and metals (Pinksy, 1994). This subject needs further work and clarification.

Particle Count

At SWPP, particle count analysis is performed three times per week at eight points in the system. These are grab samples, drawn from the appropriate laboratory tap. The first drawn sample is typically taken from the crib water tap at 8:00 am, and subsequent samples are drawn based on the detention time at each point in the system. The day that MIT samples were analyzed for particle count, June 3, 1994, was also a day SWPP did its usual plant analysis. The SWPP particle count results for that day are given in Table 6:

Table 6
Particle Count of SWPP Treatment System Samples
June 3, 1994

	2-5	5-10	10-15	15-25	25-50	>50	TOTAL
Crib	2,332	325	25	5	2	0	2,689
Shore	5,464	1,474	172	57	36	2	7,205
Header	4,740	1,220	235	69	30	1	6,295
Settling Basin	2,781	583	75	15	1	0	3,455
Clearwell #2	16	5	1	1	0	0	23
N. Reservoir	21	4	1	1	0	0	27
S. Reservoir	62	11	2	1	0	0	76
73rd St. Outlet	18	5	1	1	0	0	25
79th St. Outlet	11	2	0	0	0	0	13
Distribution	195	31	4	1	0	0	231

Looking at the total particle count results in the last column of Table 6, we see that the number of particles in crib water is less than half that of shore or header water. Settling basin water has a higher particle count than the crib water. This is probably on account of the various chemicals added. Particle count drops significantly after filtration, as evidenced in Clearwell #2, the North and South Reservoirs, and the two outlets. Particle count increases in the distribution system; particles are perhaps contributed by the distribution pipes themselves.

The ten individual MIT bench-scale study samples analyzed by particle count are presented in Table 7. The best bench-scale test results are about equivalent to the number of particle in the distribution system at the full-scale:

Table 7
Particle Count of MIT Bench-Scale Study Samples
June 3, 1994

	#	Settled Water Total Particle Count	#	Filtered Water Total Particle Count
Shore	1	6,562	2	221
0.75 mg/l chitosan + 0.35 mg/l Dadmac	3	7,191	4	257
3 mg/l alum + 0.35 mg/l Dadmac	5	1,304	6	823
0.5 mg/l chitosan + 5 mg/l bentonite	7	7,195	8	163
5 mg/l starch + 5 mg/l bentonite	9	7,006	10	251

In commom with samples #3, #5, #7, and #9, the #1 shore water sample is a "settled water" sample, meaning it was allowed to settle for 20 minutes prior to analysis. The total particle count of 6,562 for this shore sample indicates fewer particles than the full-plant shore sample count (7,205) shown in Table 6. The filtered water shore sample has a particle count of 221. This is a surprisingly low count, however, low turbidity readings were also evidenced on filtered shore water samples. Of the four chemical coagulant regimes analyzed as filtered samples, chitosan/bentonite ranked #1 for the lowest filtered water particle count, starch/bentonite and chitosan/Dadmac ranked closely as #2 and #3, and alum/Dadmac trailed the other chemical regimes in fourth place.

Particle Count/Turbidity Correlations

Figure 2, 3, and 4 are attempts to determine correlations between number of particles and turbidity at the SWPP. Figure 2 uses the particle count data of Table 6 from June 3, 1994 and the 1993 annual average turbidity data for the identical sample points in the system. Figure 3 compares settled water particle count and turbidity data for the same June 3, 1994 samples. Figure 4 compares filtered water particle count and turbidity data for the same June 3, 1994 samples. These figures do not indicate a close correlation between turbidity and particle count. Particle count is probably considered the more accurate measure.

Other Natural Polymer Tests

Three cationic potato starches (designated A, P and N) were tested as primary coagulants with bentonite as a coagulant aid. Although all the starches increased settled water turbidity above the raw shore water turbidity of 2.0 NTU, Starch N gave the best filtered water results, as shown in Table 8.

This is the same starch on which the particle analysis was run (Table 7, samples #9 and #10):

Table 8
Potato Starch and Bentonite Tests
(Raw Shore Water Turbidity = 2.0 NTU)

	Settled Turbidity NTU	Filtered Turbidity NTU
5 mg/l starch A + 5 mg/l bentonite	2.7	0.76
5 mg/l starch P + 5 mg/l bentonite	2.7	0.81
5 mg/l starch N + 5 mg/l bentonite	2.2	0.63

Seeds from two species of the tropical tree Moringa: Moringa Stenopetala and Moringa Oleifera were also tested as primary coagulants, alone and with bentonite, without giving favorable results. Two other natural polymers, alginate and carrageenan, were tested as flocculation or filtration aids. The results of those tests were inconclusive and more work is needed.

pH

The use of alum in a dose range of 3 - 6 mg/l at SWPP depresses pH and requires the use of a roughly comparable dose of lime for pH adjustment. Figure 5 shows that effective doses of three natural cationic polymers: chitosan, Moringa and starch have only a very slight effect on pH.

Chitosan as a Coagulant Aid

Chitosan as a coagulant aid with 4 mg/l alum was compared to chitosan as a primary coagulant with bentonite. Results are given in Table 9:

Table 9
Chitosan as a Coagulant Aid

Chemical Regime	Raw Water Turbidity NTU	Settled Turbidity NTU	Filtered Turbidity NTU
4 mg/l alum + 0.5 mg/l chitosan (Crozes)	3.0	1.8	0.16
4 mg/l alum + 0.5 mg/l chitosan (MIT)	1.1	0.65	0.61
0.5 mg/l chitosan + 5 mg/l bentonite (MIT)	1.1	1.58	0.63

While Crozes' filtered turbidity values tended to be lower than MIT's, this is probably simply a difference between turbidimeters. The key point is that Crozes concludes that chitosan, along with the synthetic cationic polymer "should be reserved for use at lower doses as a coagulant aid in combination with an inorganic coagulant. However, the filtered water results in Table 9 suggest that chitosan can be just as effective at the low dose of 0.5 mg/l as a primary coagulant, provided it is used in conjunction with the coagulant aid bentonite.

Comparison of Whatman #1 and Gelman Filters

Table 10 shows the different results when the same samples were filtered through Gelman #61631 versus Whatman #1:

Table 10
Comparison of Filtered Water Turbidity with Two Different Filters

	Gelman #61631 Filtered Water Turbidity NTU	Whatman #1 Filtered Water Turbidity NTU
0.5 mg/l chitosan	0.42	1.44
0.5 mg/l chitosan + 5 mg/l bentonite	0.53	1.44
3 mg/l alum	0.45	0.88
3 mg/l alum + 0.35 mg/l Dadmac	0.54	1.08

This issue needs clarification.

CONCLUSIONS

1. A chitosan/bentonite chemical coagulant regime gave the best filtered water particle count results, followed by a starch/bentonite and a chitosan/Dadmac chemical regime. Alum/Dadmac gave the least successful filtered water particle count results.

2. Alum alone, alum/Dadmac and chitosan/bentonite gave essentially the same filtered water turbidity, based on averages from multiple trials.

3. At an effective dose of 0.5 mg/l, chitosan should be used as a primary coagulant, with bentonite as a coagulant aid, instead of using alum with chitosan as a coagulant aid.

4. A cationic potato starch used as a primary coagulant with bentonite gave good filtered water results, both for turbidity and particle count.

5. For a given sample, low settled water turbidity was not necessarily an indication of low filtered water turbidity. In fact, sometimes high settled water turbidity results gave equivalent or better filtered turbidity water results.

6. Particle count did not correlate well with turbidity, based on the limited data available.

7. pH was reduced from 8.34 to 7.48 in the concentration range from 1 mg/l to 4 mg/l for alum; pH was reduced by 0.04 to 0.07 when chitosan, potato starch, or Moringa was used as the primary coagulant at effective concentrations. Use of these natural polymer primary coagulants would allow reduced use of pH adjustment chemicals.

8. Whatman #1 filter paper gave less favorable filtered water results compared to the Gelman # 61631 glass filters.

FUTURE CONSIDERATIONS

Chitosan as a primary coagulant with bentonite as a coagulant aid showed favorable results at the SWPP in bench-scale tests. The bentonite used in these tests is supplied by a Chicago-based firm, American Colloid Company, and is of a nominal cost. The cost of chitosan is a major factor in its gaining wider acceptance. The SWPP bench-scale tests did not look at chitosan's documented ability to remove metals from natural waters. But given the high cost of phosphate at the SWPP ($6.00/Mgal), which is used for the removal of lead and copper, it is possible that chitosan could serve a second function in copper and lead removal, making it considerably more cost-effective. Moreover, were a large municipality such as the Chicago SWPP to initiate the use of chitosan, its cost would drop substantially. It is with the conclusions given above and these future considerations in mind that a proposal for participation in pilot studies at the SWPP accompanies this report.

REFERENCES

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Crozes, Gil. 1994. "Bench-Scale Studies at the Chicago South Water Purification Plant." February 26, 1994 Memorandum from Gil Crozes to Susumu Kawamura. Pasadena, Ca.

Kawamura, Susumu. 1991. Integrated Design of Water Treatment Facilities. New York: John Wiley & Sons, Inc.

Pinsky, David. 1994. Tighe & Bond, Inc. Personal communication. April, 1994.

Figure 1: Comparison of Settled and Filtered Turbidity

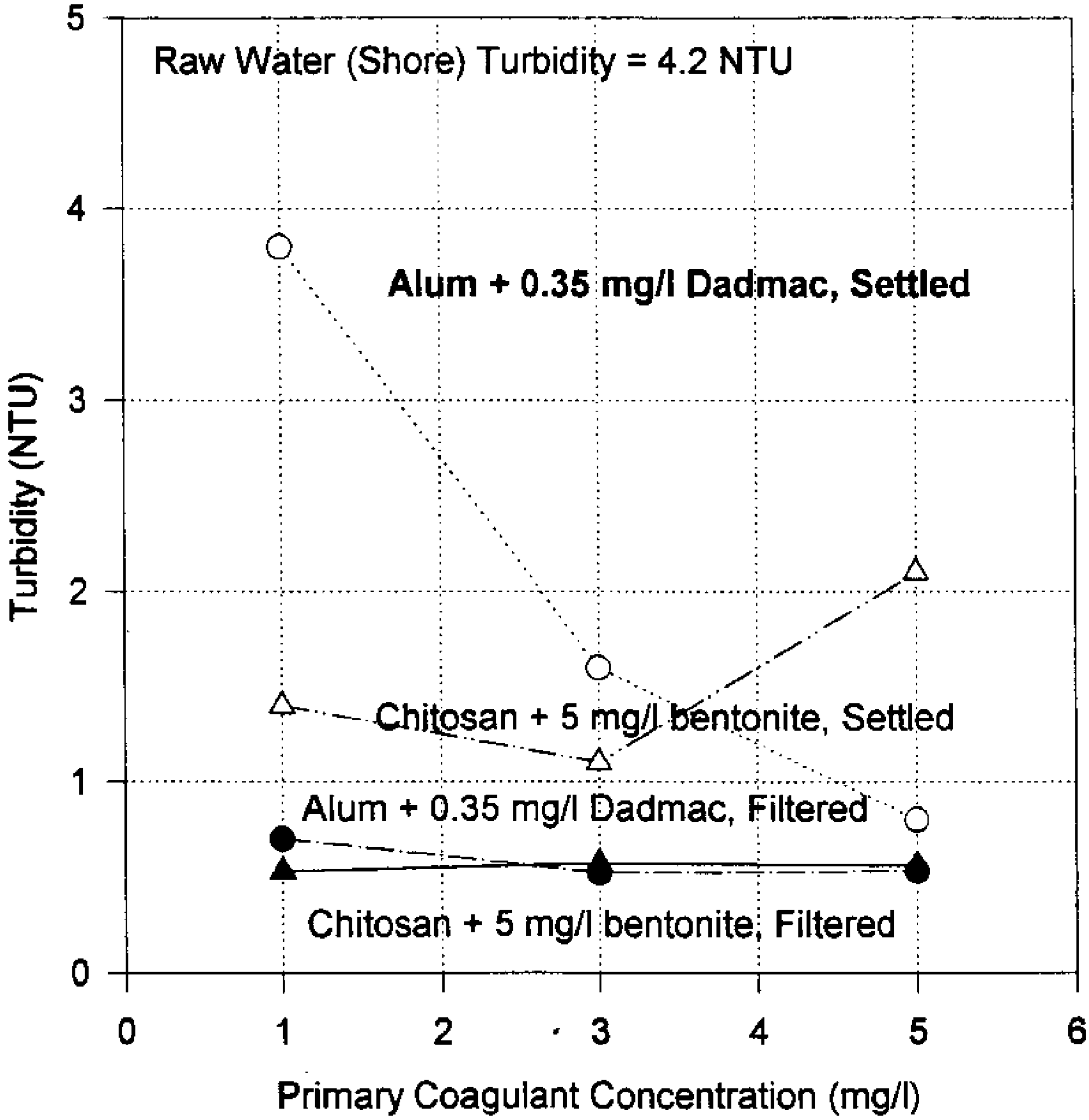

Fig.2: Correlation between # of Particles and Turbidity

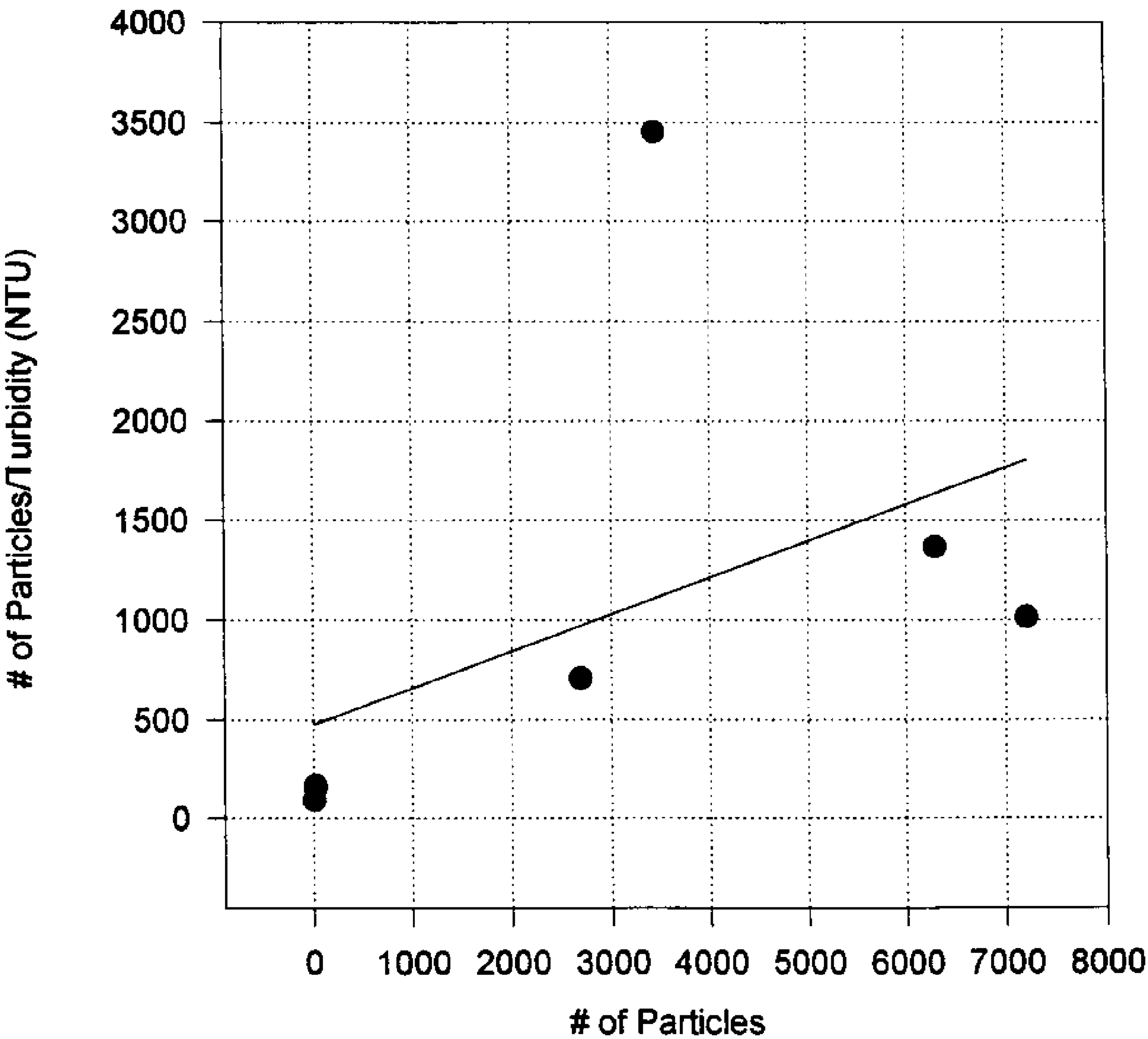

Fig.3: Correlation of # of Particles and Turbidity for Settled Water

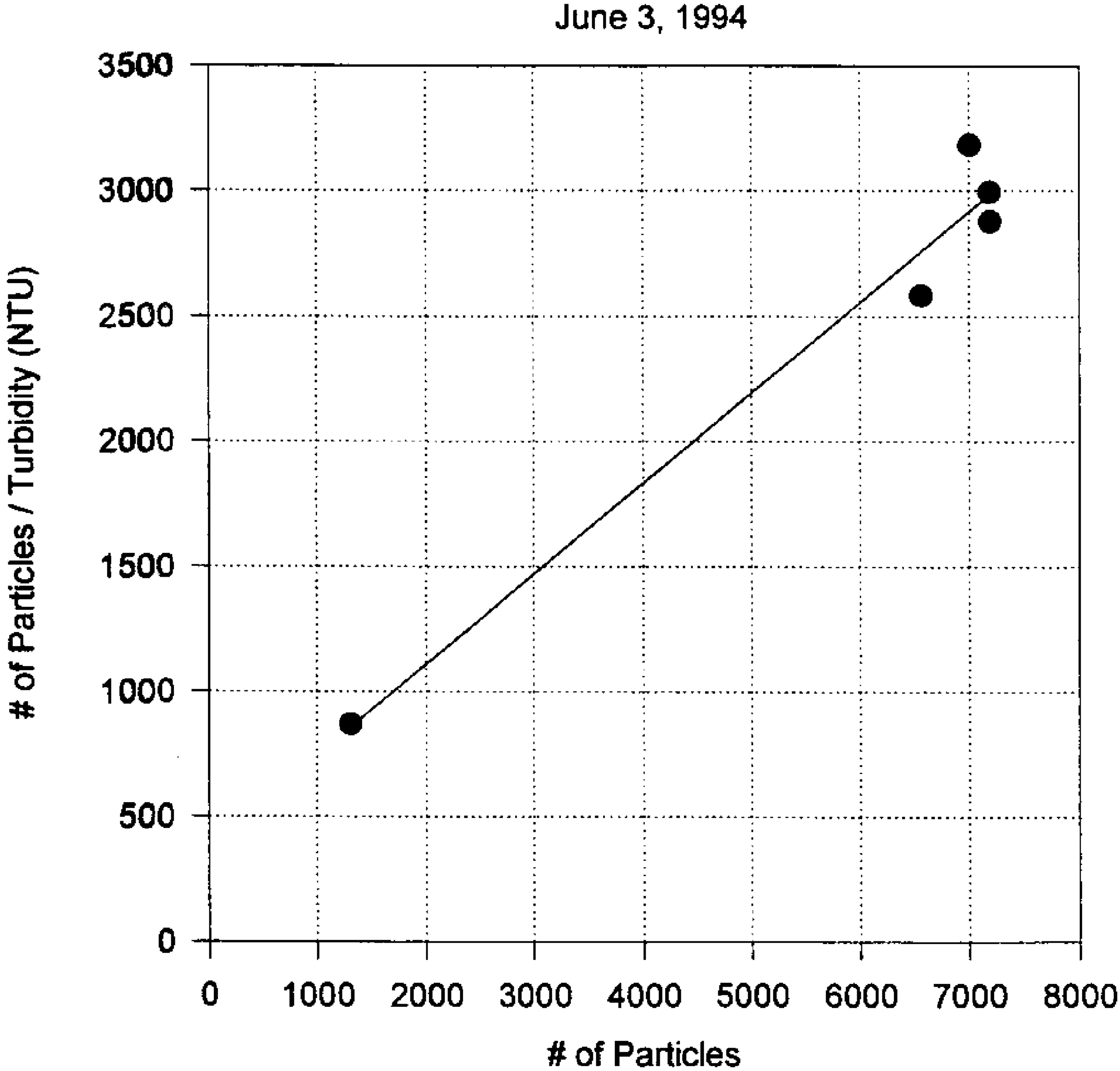

Fig.4: Correlation of # of Particles and Turbidity for F iltered Wate

June 3, 1994

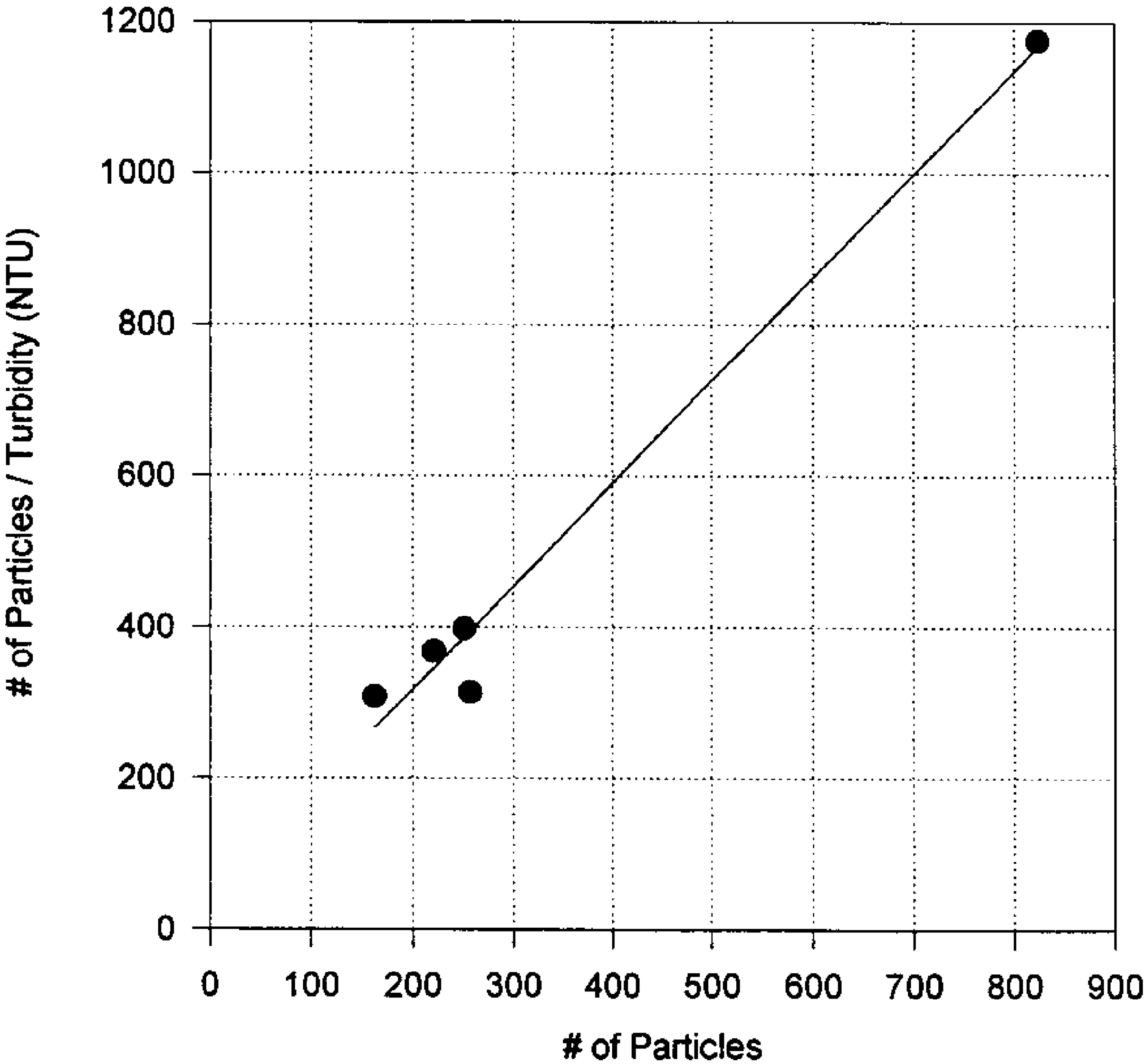

Figure 5: Effect of Alum vs. Polymers on pH