

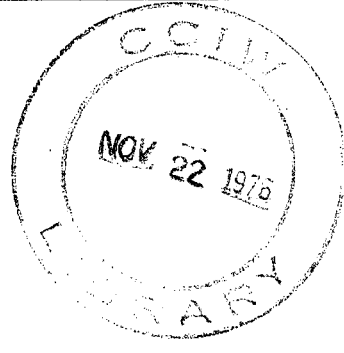
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SLUDGES IN SOUTHERN ONTARIO
BY
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ALUM RECOVERY FROM SOME WATER TREATMENT PLANT
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CANADA CENTRE FOR INLAND WATERS
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ABSTRACT

A general method is described for the recovery of aluminum sulfate from water filtration plant sludges. Acidification to $\text{pH } 1.5 \pm 0.5$ with 20% sulfuric acid followed by sedimentation or centrifugation, carbon adsorption and either evaporative or freeze concentration results in 70-100% aluminum sulfate recovery. The reclaimed alum solution is colourless, odourless and low in total organic carbon and heavy metal ions. The much reduced volume and higher solids content of the residual sludge renders it suitable for trucking to local land-disposal sites.

INTRODUCTION

1
2
3 The alum sludge from a water filtration plant is formed by
4 the hydrolysis of the trivalent aluminum ion in aqueous solution. It
5 is a bulky, gelatinous mixture of aluminum oxides, hydroxides, inorganic
6 particles (sand, clay, etc.), organic matter (including plankton and
7 microorganisms) and other colloidal material. The total solids content
8 varies from plant to plant but is usually in the range of 1-7%.

9 The discharge of water treatment plant sludge into natural
10 water courses is now considered an unacceptable method of sludge
11 disposal even though it is still practised in the majority of water
12 treatment plants. It is particularly unacceptable where the flow of
13 the receiving water is relatively low - a situation which often
14 materializes after a long dry spell. The two methods most often
15 considered for sludge disposal are sludge dewatering with subsequent
16 trucking of the dried sludge to nearby land-fill sites (Albrecht, 1972;
17 Krasauskas, 1969; Taflin et al, 1975; Novak and Calkins, 1975; Hubbs and
18 Pavoni, 1974) or alum reclamation (Chen, King and Randall, 1976; King,
19 Chen and Weeks, 1975; Fulton, 1974.) Although the latter method does not
20 dispose of the entire sludge it does reduce the volume and water content
21 by up to 75%.

22 The concept of alum recovery dates back to the first quarter
23 of this century when several patents were granted for alum recovery
24 processes based on acidification with sulphuric acid (Jewell, 1903;
25 Mathis, 1923). From 1950 increasing interest has been shown in Europe
(Webster, 1966), Japan (Fujita, 1967) and the U.S. (Roberts and Roddy,

1960) first from a purely economic standpoint but more recently combined
1 economic/environmental aspects are being considered. It has been shown
2 that alum recovery can be made an economic proposition (Fulton, 1974) and
3 when this is combined with the current environmental awareness the
4 advantages are obvious. Some of the problems and reservations which have
5 been expressed about alum recovery in the past have centred on the continuous
6 recycling of trace substances (eg. organic colour and odour producing compounds
7 and heavy metal ions), the very dilute nature of the reclaimed aluminum
8 sulfate solution and the varying characteristics of alum sludge both
9 from plant to plant and seasonal variations within any one plant. It is
10 the purpose of this paper to show that a general alum recovery system could
11 be used at the majority of water treatment plants, that many of the trace
12 substances can be removed by suitable treatment and that the dilute
13 reclaimed alum solution can be further concentrated by either evaporation
14 or freezing.

15
16 Experimental

17 Sludge samples were collected in clean polyethylene containers
18 from Hamilton, Burlington, Brantford, Toronto and Oakville filtration
19 plants in Southern Ontario. With the exception of Brantford, all these
20 plants treated Lake Ontario water by conventional processes, i.e., pre-
21 chlorination, alum flocculation, sedimentation, post chlorination and
22 fluoridation. Brantford draws its raw water from the Grand River and
23 treats it by superchlorination, flocculation (with the addition of alum,
24 lime, activated silica and carbon), sedimentation, chlorine adjustment and
25 fluoridation.

The alum sludges were batch acidified with 20% sulfuric acid. 1 Acid was added slowly to constantly stirred sludge to minimize frothing 2 and to prevent overshooting of desired pH. The pH was continuously 3 monitored with an expanded scale pH meter and electrode assembly 4 (Corning Scientific Instruments, Digital model 110). Sedimentation of 5 the sludges, both before and after acidification was carried out in 250 ml 6 graduated cylinders. Occasionally air would become entrapped within the 7 sludge causing part of it to break off and float to the surface during the 8 sedimentation tests. When this occurred the results were discarded and 9 the experiments repeated. Where centrifuging was employed the sludges were 10 placed in 50 ml tubes and centrifuged at 2000 g for 10 minutes (International 11 Equipment Company -Model HN-S, equipped with IEC.801 angle head).

12 The settled or centrifuged alum solutions were treated for TOC 13 removal with activated carbon in a down flow column. A 30 cm bed of 14 Filtrasorb 200 carbon was supported in a 4 cm id column: the flow rate 15 through the column was maintained at approximately 1 l hr^{-1} . The maximum 16 loading of such a column was not determined but the breakthrough point 17 was in excess of 10 l alum solution. Economics at the specific filtration 18 plants should dictate whether the spent carbon should be thermally regenerated 19 or discarded.

20 Samples were analyzed for aluminum by atomic absorption according 21 to a standard method (Environment Canada, 1974).

22 Solutions of reclaimed alum were freeze concentrated in open trays 23 surrounded by an ice-salt mixture adjusted to -4°C . Periodic agitation was 24 employed to ensure uniform freezing. When the required amount of freezing 25 had occurred the mixture was passed through a 0.85 mm screen to separate the ice from the concentrated alum solution. The same trays were employed for the evaporative concentration process. The filled trays were placed out-of-doors

in an area where they were in direct sunlight and frequently subjected to
1 a gentle breeze.

2
3 Results and Discussion

4 The amphoteric nature of aluminum hydroxide allows aluminum
5 to be recovered from alum sludge by either acidic or basic extraction
6 according to the following equations:



10 Basic extraction using sodium hydroxide or lime has only been used to
11 extract alum from tertiary wastewater treatment plants containing high
12 concentrations of phosphate (Culp and Culp, 1971). This method will not
13 be considered further in this report. For water filtration plant sludges,
14 acid regeneration has received considerable attention but the reported
15 optimum pH has varied from study to study. King et al. (1975) evaluated
16 the use of hydrochloric and sulfuric acids and concluded that both were
17 equally effective. However, the higher cost of hydrochloric acid and the
18 fact that 3 moles acid/mole Al are required compared with 1.5 moles acid/
19 mole Al for sulphuric acid (equations 2 and 3) led the present author to
20 limit his study to sulphuric acid only.

21 The characteristics of the sludges used in the present study are
22 given in Table 1. The higher solids content and aluminum concentration
23 of the Hamilton sludge are a reflection of the more efficient sedimentation
24 chambers at this plant. Settling of these sludges in the laboratory for
25 24 hrs. resulted in sludge volume reductions of 40% for Oakville, 10% for
26 Burlington but no further settling was observed for either Hamilton or Brantford
27 sludges. Acidification of the sludges with sulfuric acid to various final

pH's greatly improved the sedimentation characteristics -both velocity
1 and final volume. The sludge volume (expressed as a percentage of the
2 initial volume after acidification) is shown as a function of time in
3 Figure 1 for nine values of pH between pH 1 and 7. These results are
4 for Hamilton sludge but sludges from the other cities exhibited similar
5 behaviour. Two points are evident from Figure 1: firstly, decreasing the
6 pH decreases the final volume of sludge and secondly, most of the settling
7 occurs in the first 5 to 7 hours after acidification. After the first
8 24 hours further volume reduction was less than 5% per day with no change
9 being observed after 72 hours.

10 Figure 2 shows volume of sludge remaining after 24 hours of
11 settling as a function of pH. This figure includes data from Hamilton,
12 Burlington, Toronto and Brantford. Although each sludge exhibits its
13 own characteristics due to varying physical and chemical properties, it
14 is evident that minimum sludge volume always occurs in the pH range from
15 1.0 to 2.5 with 1.5 - 2.0 being preferred. It was interesting that
16 Brantford sludge behaved so similarly since it was the only sludge containing
17 significant amounts of activated carbon, silica and lime. Centrifuging of
18 these settled sludges further reduced their volume by approximately 50-60%.

19 The reduction in sludge volume at low pH's was accompanied by a
20 corresponding increase in solids content of both settled and centrifuged
21 sludges. Figure 3 shows that the solids content of 24 hr. settled sludge
22 can be increased from 7% to 14% by acidification while centrifuged sludge
23 is increased from 18% to 30%. This figure shows the averaged results
24 from Hamilton, Burlington, Oakville and Toronto. The maximum solids content
25 of the centrifuged sludges appears to occur at pH 2.5-3.0 rather than at
26 pH 1-2 for the settled sludge but it is doubtful whether much significance

should be attached to that peak.

1 The amount of Aluminum recovered from the supernatant of the
2 acidified sludges expressed as % Al in original sludge is shown in Figure 4a.
3 as a function of pH. This figure shows data for Hamilton sludge but the
4 other sludges behaved similarly. The yield is surprisingly good -100% for
5 centrifuged sludge at pH 1 and 78% for settled sludge at that pH. However,
6 at pH > 3.5 virtually none of the Al was in the solution phase. Figure 4b
7 shows the concentration of aluminum as $Al_2(SO_4)_3$ in the supernatant of the
8 acidified sludge. The absolute concentration of $Al_2(SO_4)_3$ in the supernatant
9 obviously depends upon the initial concentration in the sludge, which in turn
10 depends on the concentration of alum used at the particular treatment plant,
11 but the trend of maximum alum concentration at pH < 2 was independent of sludge
12 source.

13 The concentration of approximately 2% (4% as $Al_2(SO_4)_3 \cdot 18H_2O$)
14 at pH < 2.5 is still much less than the initial stock concentration of 48%
15 $Al_2(SO_4)_3 \cdot 18H_2O$ employed by the majority of water treatment plants but is
16 nevertheless within a usable range. Since filter backwash water is much
17 more dilute than settled sludge, it would be advantageous to concentrate
18 backwash water in settling lagoons prior to reclaiming the alum. Otherwise,
19 a general reduction in reclaimed alum concentration would result.

20 If concentrations of alum > 2% $Al_2(SO_4)_3$ are required to facilitate
21 handling and re-use, either evaporation or fractional freezing can be used
22 effectively to concentrate the solution. The latter method is obviously
23 limited to certain climatic regions but offers a low cost, fast concentration
24 process where it can be utilized. For example a laboratory scale, simulated
25 freezing lagoon maintained at $-4^{\circ}C$ in an ice-salt bath froze sufficient water

out of the alum solution to double the concentration in three hours.

1 One can easily envisage lagoons which could concentrate the alum by

2 freezing in the winter months and by evaporation during the summer.

3 Since the volume of solution is relatively small it could always be

4 stored during the intermediate seasons.

5 The reclaimed alum solution both before and after concentration
6 tended to have a yellow straw colour (TOC prior to concentration -250-
7 400 mg ℓ^{-1}). Treatment of this solution with activated carbon (Filtrisorb
8 200) completely eliminated the yellow colouration and reduced the TOC to
9 <50 mg/ ℓ . The resulting solution was clear and odourless. Analysis for
10 selected heavy metals gave typical concentrations shown in table 2 for
11 the few treatment plants sampled. The build-up of heavy metal concentrations
12 during repeated recycling of alum is a definite possibility but with the
13 laboratory facilities at our disposal we were not able to study this aspect.
14 Continuous pilot scale studies would be required before any definite
15 conclusions could be reached. If heavy metal build-up is a problem there
16 are several possible solutions: a) occasionally discard the alum when
17 heavy metal concentrations exceed acceptable limits b) periodically treat
18 the alum solution for heavy metals removal by carbon adsorption or
19 selective ion-exchange. If continuous carbon adsorption is employed for
20 TOC and colour removal this should simultaneously control the heavy metals
21 concentration.

22 In conclusion, it has been demonstrated that alum can be
23 successfully regenerated using a general acidification process applicable
24 to the majority of sludges generated by water treatment plants. Even though
25 there is some variation in sludge characteristics, acidification to pH
26 1.5±.5 with 20% sulphuric acid followed by 24 hours of settling results in

1 55-75% alum recovery or 80-100% if centrifuging is employed after
2 acidification. Under these conditions the solids contents of the
3 remaining sludge is of the order of 12% for settled and 28% for
4 centrifuged. With a typical 50 mgd plant using 800-1000 gals 48%
5 alum solution per day a recovery of only 50% should result in significant
6 savings and a significant reduction in the volume of sludge. A detailed
7 cost analysis would only be meaningful after pilot scale tests have
8 been conducted for an extended period of time. The reduced volume
9 of sludge remaining after alum recovery contains a much higher solids
10 content than raw sludge making it more suitable for trucking to nearby
11 land-fill sites. The recovered alum can be used to augment the supply
12 of fresh alum or used alone depending on availability. If further
13 concentration is required this can be simply and cheaply accomplished
14 by evaporation or freezing in suitable lagoons.

15 ACKNOWLEDGEMENTS

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17 analytical service section, Water Quality Branch of Environment
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19 and Mr. Walter Zimmermann for assistance with many of the experiments.

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REFERENCES

- 1
- 2 Albrecht, A.E. (1972) "Disposal of Alum Sludges, J. Am. Wat. Wks.
- 3 Ass. 64 (1) 46-52.
- 4 Chen, B.H.H., King, P.H. and Randall, C.W. (1976) "Alum Recovery from
- 5 Representative Water-Treatment-Plant Sludges. J. Am. Wat.
- 6 Wks. Ass. 68 (4) 204-207.
- 7 Culp, R.L. and Culp, G.L. (1971). Advanced Wastewater Treatment,
- 8 Van Nostrand Reinold Co. New York. pages 202-205.
- 9 Environment Canada (1974). Analytical Methods Manual, Inland Waters
- 10 Directorate Publication, Ottawa.
- 11 Fulton, G.P. (1974) Recover Alum to Reduce Waste-Disposal Costs:
- 12 J. Am. Wat. Wks. Ass. 66 (5) 312-318
- 13 Fujita, H. (1967). "Tokyo's Asaka Purification Plant". Wat. and
- 14 Sewage Wks. 114 (3), 73-82.
- 15 Hubbs, S.A. and Pavoni, J.L. (1974) "Optimization of Sludge Dewaterability
- 16 in Sludge-Disposal Lagoons". J. Am. Wat. Wks. Ass. 66 (11) 658-663.
- 17 Jewell, W.M. (1903). U.S. Patent No. 718, 465.
- 18 King, P.H., Chen B.H.H. and Weeks R.K. Jr. (1975) Recovery and Reuse
- 19 of Coagulants from Treatment Water and Wastewater". Virginia Water
- 20 Resources Research Centre, Blacksburg, Virginia, Bulletin 77.
- 21 Krasauskas, J.W., (1969) Review of Sludge Disposal Practices. J. Am.
- 22 Wat. Wks. Ass. 61 (5) 225-230.
- 23 Mathis, W.R. (1923) U.S. Patent No. 1, 441, 731
- 24 Novak, J.T. and Calkins, D.C. (1975) Sludge Dewatering and its Physical
- 25 Properties J. Am. Wat. Wks. Ass. 67 (1) 42-45.
- Roberts, J.M. and Roddy, C.P. (1960) Recovery and Reuse of Alum Sludge
- at Tampa. J. Am. Wat. Wks. Ass. 52. 857-866.

Taflin, C.O., Weber, N.F., Kramer, A.J., and Whitaker, J. (1975).

1

"Minneapolis Keeps on Truckin." Wat. and Waste Engrg.

2

Webster, J.A. (1966). Operational and Experimental Experience at Daer

3

Water Treatment Works with Special Reference to the use of

4

Activated Silica and the Recovery of Alum from Sludge. J. Inst.

5

Wat. Engrs 20 (3) 167-198. 12 (5), 24-29.

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TABLE 1

CHARACTERISTICS OF ALUM SLUDGES

	Hamilton	Burlington	Brantford	Toronto	Oakville
Total Solids (mg ℓ^{-1})	75,600	25,000	34,000	43,200	17,000
Aluminum (mg ℓ^{-1} as metal)	6,400	3,400	3,100	4,300	950
pH	6.9	6.8	6.9	7.0	6.9

TABLE 2

METAL CONCENTRATIONS OF SOME RECLAIMED ALUM SOLUTIONS

	Al mg ℓ^{-1}	Cu mg ℓ^{-1}	Cr mg ℓ^{-1}	Pb mg ℓ^{-1}	Zn mg ℓ^{-1}
Burlington	2,400	<.01	0.05	<0.05	0.60
Oakville	>50	0.66	0.9	0.5	2.5
Hamilton	4,700	0.01	0.05	0.05	2.7
Brantford	2,800	0.5	0.9	0.25	2.2

CAPTIONS TO FIGURES

Figure 1

Sludge volume as a function of settling time for nine values of pH between pH 1 and pH 7. The volumes are expressed as a percentage of the corresponding volumes at T=0. Data are for Hamilton sludge.

Figure 2

Sludge volume after 24 hours settling as a function of the pH. Volumes are expressed as percentage of the corresponding volumes at T=0. Graph includes data from Hamilton, Burlington, Brantford and Toronto.

Figure 3

Per cent solids in 24-hour settled and centrifuged sludges as a function of sludge pH. These are averaged data from Hamilton, Burlington, Oakville and Toronto.

Figure 4A

Per cent aluminum (as Al) recovered from Hamilton sludge as a function of sludge pH.

Figure 4B

Concentration of alum (as $Al_2(SO_4)_3$) in the supernatant as a function of pH of acidified Hamilton sludge.

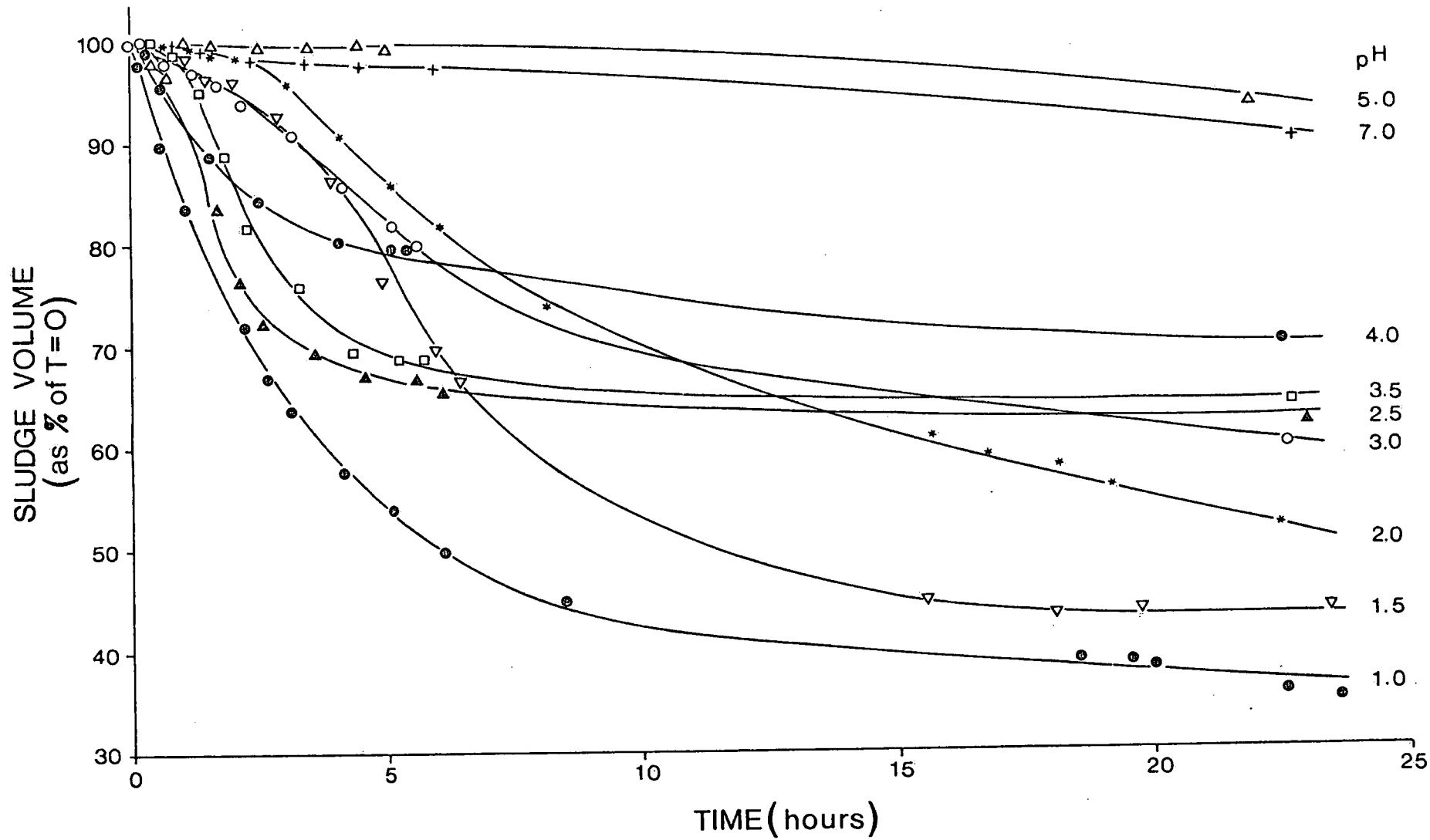


Fig. 1

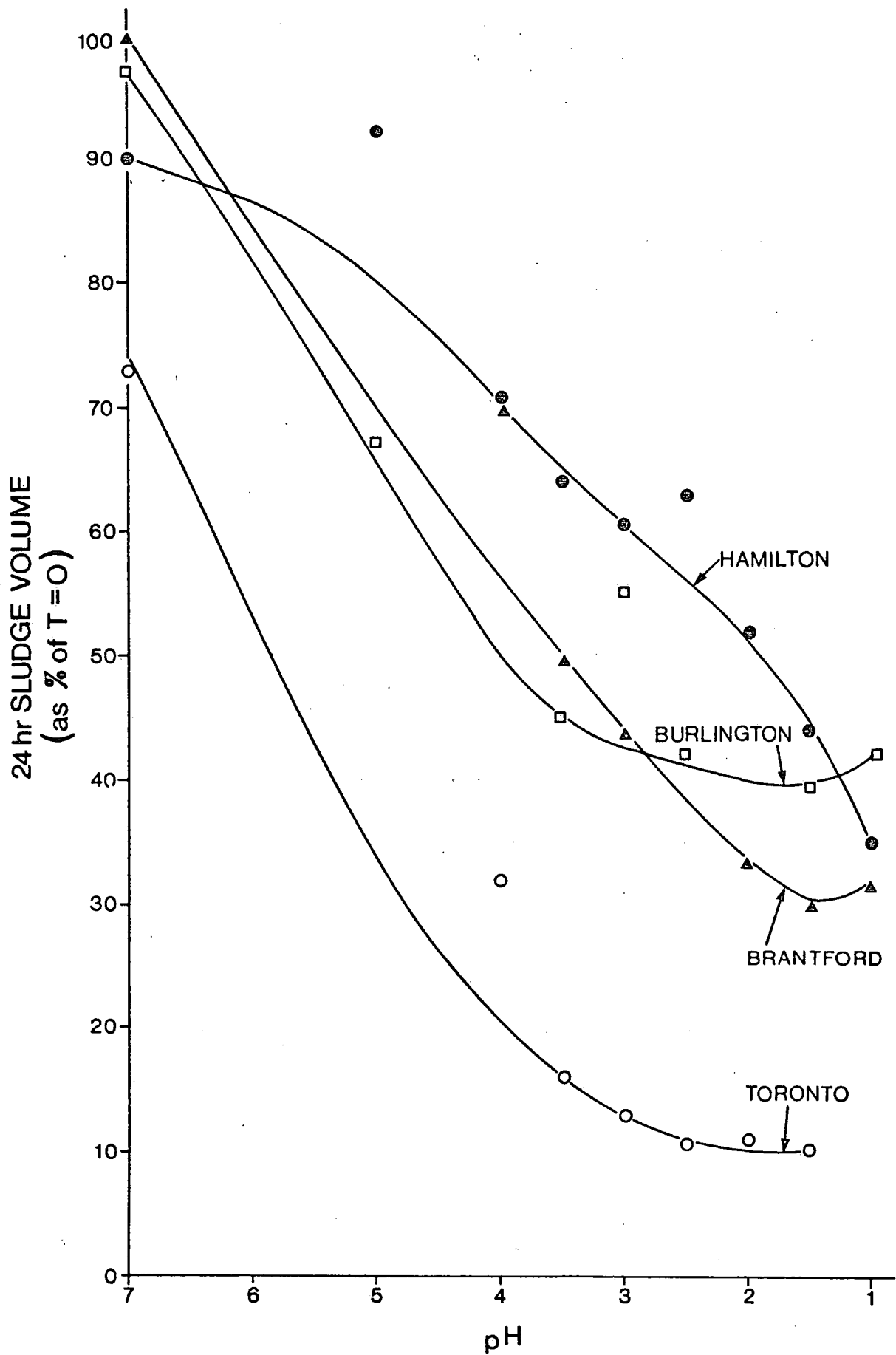


Fig. 2

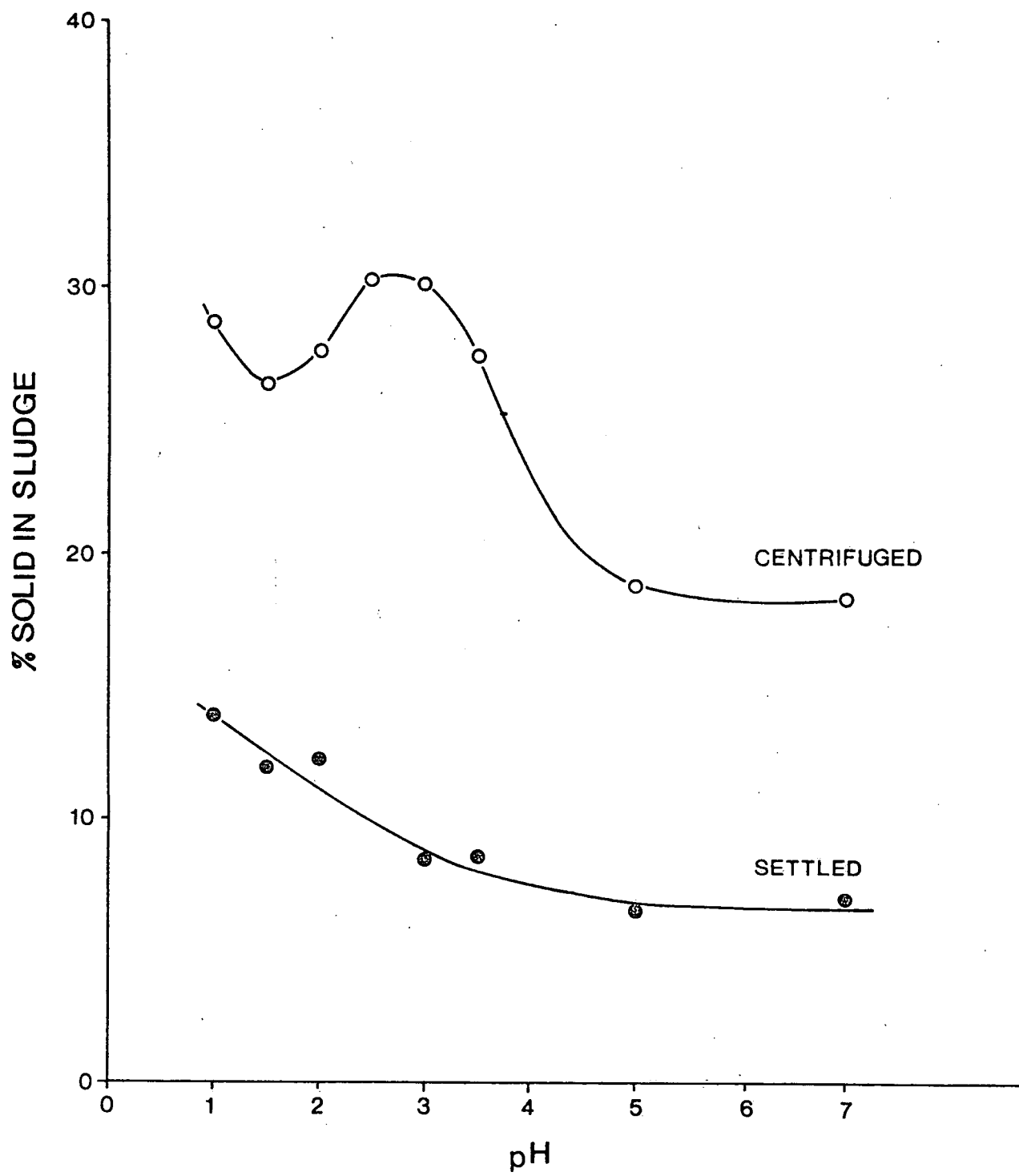


Fig. 3

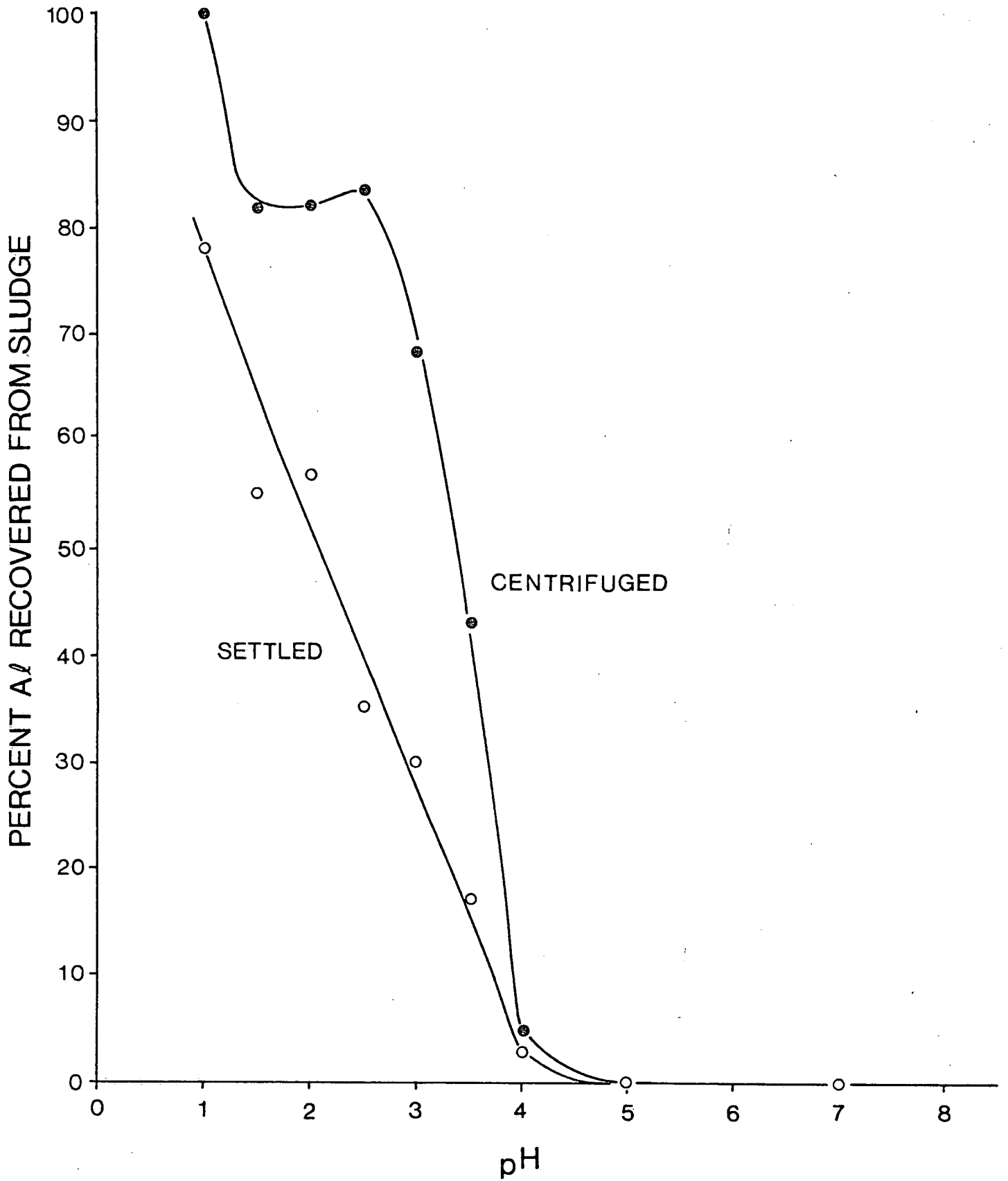


Fig. 4A

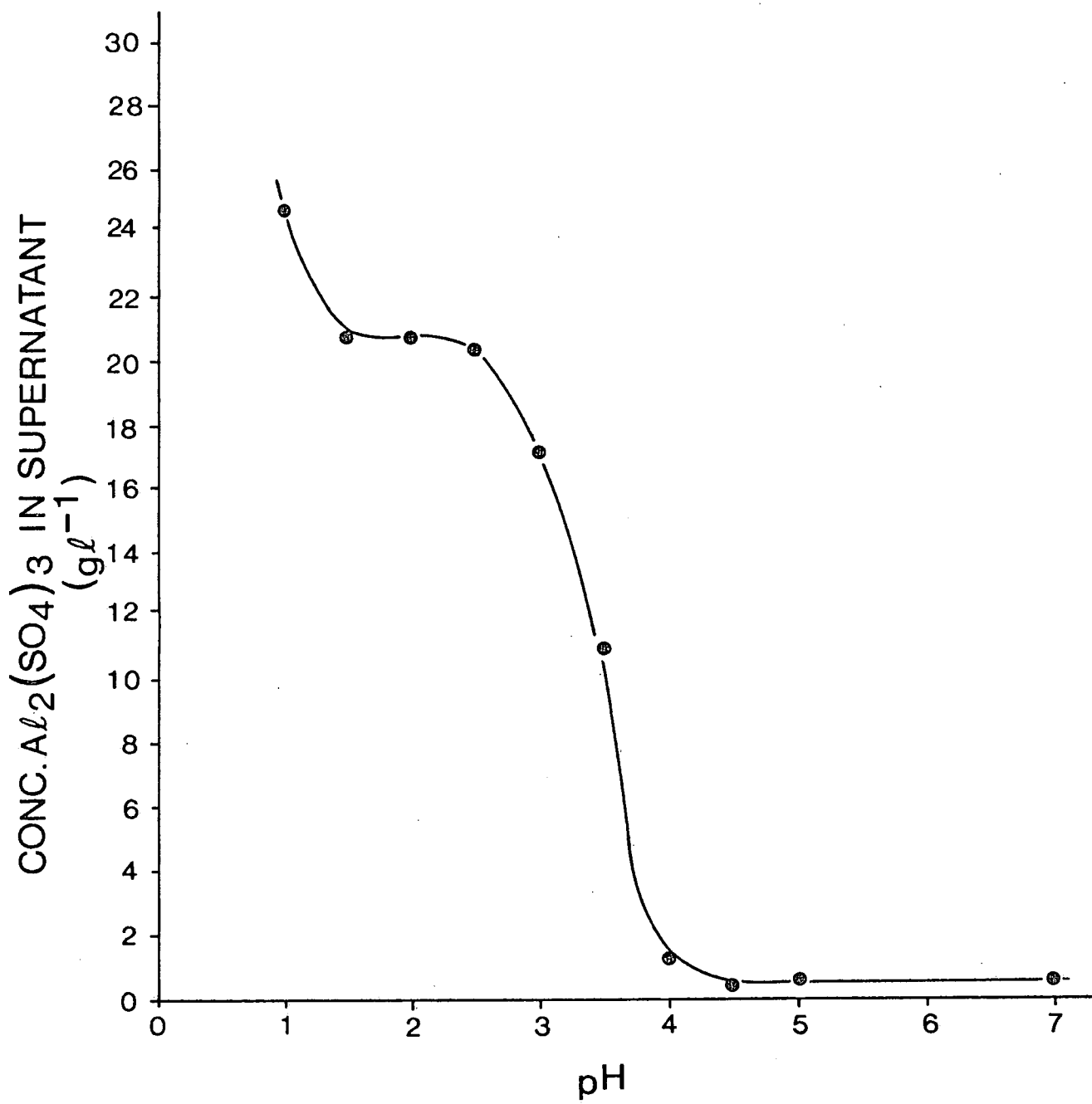


Fig. 4B

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