United States
Environmental Protection
Agency

Research and Development

Water Engineering Research
Laboratory
Cincinnati OH 45268

EPA/600/S2-85/003 Mar 1985

EPA

Project Summary

Removal of Heavy Metals Using Aluminum Salts for Phosphorus Removal

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A study was conducted to determine whether the removal of heavy metals from wastewater would be enhanced if an aluminum salt was added in a concentration sufficient to remove phosphorus. The practice of removing phosphorus with aluminum salts such as alum and sodium aluminate is common to wastewater treatment plants.

The project examined three publicly owned treatment works (POTWs) in Massachusetts where sodium aluminate or alum was used for phosphorus removal during the summer months. Samples were taken during the last 30 days of aluminum salt addition in the fall and during the first 30 days without it. A statistical analysis was then made of the impact of aluminum salts on heavy metal removals. Some 15,000 metal analyses were conducted, and phosphorus and total organic carbon (TOC) removals were also measured.

Statistically, the only metal whose removal was enhanced by the addition of both aluminum salts was copper. Sodium aluminate appeared to improve chromium removal, but alum did not. Some removal of lead was apparent, but because of the variation in the concentrations, this result could not be confirmed statistically. Phosphorus was effectively removed by the added aluminum. The other metals detected (silver, arsenic, cadmium, mercury, antimony, selenium, and zinc) were all reduced below detectable limits by the conventional treatment process without the addition of any aluminum salt. Beryllium, nickel, and thallium were not present above detection limits in the treatment plant influent.

This Project Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Domestic wastewaters, especially those containing industrial wastes, may contain heavy metals in varying degrees. The removal of these metals (specifically, the 13 on the priority pollutant list), is of concern because of the toxic nature of these metals. Another concern in wastewater treatment is the removal of phosphorus because it is a stimulant to biological growth in the receiving waters. Phosphorus removal is required year-round in publicly owned treatment works (POTWs) in the Great Lakes basin. In other locations, phosphorus removal may be required only during the warmer months when the element would have a greater tendency to stimulate algae and aquatic weed growth.

Aluminum salts such as alum and sodium aluminate have been commonly used to remove phosphorus from waste water. Studies have also shown that these aluminum salts can remove heavy metals, but at dosages higher than those normally used for phosphorus removal. This study investigates the possibility that aluminum salt addition in a concentration sufficient to remove phosphorus could also enhance the removal of heavy metals.

Three POTWs in Massachusetts were studied. Two use sodium aluminate, and the third uses alum for phosphorus removal. All three plants are required to remove phosphorus during the summer only. Thus the heavy metal removals with and without the aluminum salt additions could be compared by sampling for the last 30 days of aluminum salt addition in the fall and for the first 30 days after it was discontinued. All three POTWs were activated sludge plants treating primarily domestic waste with a small industrial input. Some variations occurred in the design of each plant. One used a trickling filter before the activated sludge process. Another plant did not use primary sedimentation but had a final sand filter following secondary clarification after the activated sludge treatment. The third plant had two entirely separate aeration systems; the system with the longer aeration time was in operation at the time of the study.

Procedures

At all three POTWs, daily composite samples were taken from the influent, the primary sedimentation effluent where applicable, and the secondary clarifier following the activated sludge treatment. In addition, composite samples were taken from the sand filter effluent for the POTW that used no primary sedimentation. Weekly sludge and supernatant samples were also secured. Most of the composite samples were refrigerated, but because sampling was done in October and November, refrigeration requirements were minimal. All samples were transported under ice to the laboratories at Rensselaer Polytechnic Institute (RPI) where the samples were filtered to separate the soluble from the particulate fractions. In addition to aluminum and the 13 metals on the priority pollutant list, measurements were made for phosphorus, TOC, biochemical oxygen demand (BOD), and suspended solids. These latter measurements were made to determine whether the aluminum salt addition enhanced their removal. Obviously phosphorus removal was anticipated.

Except for mercury, the metal analyses were performed using either a Perkin-Elmer 303 Atomic Spectrophotometer* in the graphite furnace mode or a Beckman Atomic Absorption Spectrophotometer in the flame mode. Mercury was analyzed by the cold vapor technique. Other analyses were conducted according to Standard Methods (*Standard Methods for the Examination of Water and Wastewater*, 15th Edition, APHA, AWWA, WPCF, 1980).

Because some 15,000 analyses were conducted, a statistical analysis of the results was performed. Mean values of the metal concentrations in the influent, the intermediate effluent, and the final effluent were made for both the soluble and the total fraction and were compared both with and without the addition of the aluminum salt. Standard deviations were also determined. An attempt was made to corrolate the various parameters both with the addition of the aluminum salt and with each other. An attempt was also made to make a mass balance of the heavy metals in the various portions of the treatment plant. Because of the unknown flow rates of the sludge and the supernatant return, it was not possible to perform precise mass balances.

In numerous instances, the metal analyses indicated concentrations at or below the minimum detectable limit. Since it was not possible to determine how much they were below the detectable limit, the values were arbitrarily listed as being present at the minimum detectable limit, though many were probably present at much lower levels. Thus some of the mean values are probably somewhat high because of this procedure.

Results

Three metals—thallium, beryllium, and nickel—were not found at concentrations above the minimum detectable limit of the methods used. Therefore no evaluation was made of the impact of the aluminum salt addition on the removal of these heavy metals. Copper, chromium, and to some extent lead were removed significantly. Sodium aluminate addition appeared to improve chromium removal, but alum had no similar effect. Lead removal was somewhat obscured by the large variation in the daily values obtained. Aluminum salt addition appeared to have no significant impact on antimony and cadmium removal. The impact of alum or sodium aluminate addition on the remaining metals (arsenic, mercury, selenium, silver, and zinc) could not be determined. They were removed in the treatment system without the addition of the aluminum salt. Though it is good to know that normal activated sludge treatment is quite effective in removing heavy metals, information is still lacking on the enhancement of their removal by the aluminum.

Phosphorus removal was definitely enhanced by adding the aluminum salt, but TOC removal appeared to be unaffected.

Tables 1, 2, and 3 show the reduction in the various metals in the total sample at each of the three treatment plants. The overall reductions are shown comparing the concentrations of the metals in the influent with those in the final effluent.

Discussion

Even though thallium, beryllium, and nickel were not found in detectable levels in the POTW influents, beryllium and thallium were measured in sludges. Since the sludges represent a concentration of materials, it may be assumed that small amounts of these metals are present in the influent, though below the detectable limits. Also, the concentrations of these metals in the sludges were generally higher during the period when the aluminum salts were added, indicating an enhancement of removal by the addition of the aluminum salt.

Silver was found mostly in the particulate phase. Little removal occurred in the primary sedimentation, but the activated sludge treatment provided significant silver removal even without the aluminum salt.

Arsenic was found in only the Pittsfield influent, and the removal was nearly complete in the treatment system without the addition of the aluminum salt. Thus no conclusions can be made about the effect of alum on arsenic removal.

About 25 to 30 percent of the cadmium was in the soluble phase in the influent to the three treatment plants. Primary sedimentation achieved little removal, but the overall activated sludge system provided significant removal, again negating any measureable impact from the addition of the aluminum salt.

Chromium was present primarily in the insoluble phase in the influent to all three treatment plants. Little removal occurred during primary treatment, but there was significant removal in the activated sludge system. Sodium aluminate addition at Pittsfield significantly improved the chromium removal.

Total copper concentrations were about five times the soluble concentrations in all three POTW influents Little copper was removed by primary treatment. Though some measureable removal of copper occurred in the treatment system

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use

Table 1. *Mean Removal of Wastewater Constituents in Fitchburg POTW*

Constituent	With Alum			Without Alum		
	Influent	Final Effluent	% Reduction	Influent	Final Effluent	% Reduction
	µg/L			µg/L		
Aluminum	1,823.7	652.8	54.2	2,006.4	533 8	73.4
Antimony	12.66	11.58	8.5	15.9	12.36	18 6
Arsenic	7 05	5 73	18.7	7.58	7.51	0.9
Beryllium	0.5*	--	--	0 5	--	--
Cadmium	5.86	0.57	90 3	7.56	0 92	87.8
Chromium	158.8	17 3	89.1	182.4	18.6	89.8
Copper	528.9	42.3	92.0	391.8	65.5	83.3
Lead	767.3	78.2	89 8	872.1	150.0	82.8
Mercury	0.29	0 20*	31 0+	0.34	0 22	35.3
Nickel	1,000.*	--	--	1,000 *	--	--
Selenium	12.19	10.83	11.2	10.75	10.16	5.5
Silver	28.79	2.00*	93 1+	23.42	2.46	89.5
Thallium	5.0*	--	--	5.0*	--	--
Zinc	550.	300.	45.5+	580	300.	48.3+
	mg/L			mg/L		
Phosphorus	4.33	0.68	84.3	4.74	2.03	57 2
TOC	44.09	8.88	79.9	51.01	9.36	81 7

*Minimum detectable limit.

Table 2. *Mean Removal of Wastewater Constituents in Medfield POTW*

Constituent	With Sodium Aluminate			Without Sodium Aluminate		
	Influent	Final Effluent	% Reduction	Influent	Final Effluent	% Reduction
	µg/L			µg/L		
Aluminum	1,889.8	97.4	94.8	2,546.0	73.3	97.1
Antimony	14.06	12.39	11.9	13.45	12.73	5.4
Arsenic	7 70	5.99	22 2	6.15	6.21	0
Beryllium	0.5*	--	--	0.5*	--	--
Cadmium	7.70	0.80	89.6	4.23	0.50	88.2
Chromium	25.5	3 3	87.1	18.8	5.2	72.3
Copper	418.3	19 1	95.4	157.5	17.1	89 1
Lead	85.1	9 0	89.4	62.9	9.3	85.2
Mercury	1.03	0 20*	80.6+	1.55	0.20*	87.1
Nickel	1,000.*	--	--	1,000.*	--	--
Selenium	13.53	12 11	10.5	10.46	10.00*	4.4+
Silver	11.04	2 00*	81.9+	7.67	2.00*	73 9+
Thallium	5 0*	--	--	5.0*	--	--
Zinc	970.	300.*	69.1+	490.	300.*	38.8
	mg/L			mg/L		
Phosphorus	5.58	0.59	89.4	4.18	2.59	38.0
TOC	80.71	6.44	92.0	46.97	6.95	85.2

*Minimum detectable limit.

without the aluminum salts, the addition of the aluminum salts definitely enhanced the copper removal.

None of the POTWs had other than very low levels of mercury, all of which were removed by the primary treatment. Thus no evaluation could be made of the impact of the aluminum salt addition on the mercury removal.

Lead was found in significant concentrations in all of the treatment plants, especially at Fitchburg. The soluble portion was less than 10 percent of the total lead concentration. Lead removal varied in the primary treatment systems studied. High overall lead removals were observed when the aluminum salts were used, but because of the large variation in the data, this result could not be confirmed statistically.

A small amount of antimony was detected in all of the POTW influents. Analyses showed a higher concentration of antimony following primary treatment than in the influent. This increase was attributed either to removal of some interferring substance in primary treatment or to the laboratory techniques. The overall removal of antimony was poor, both with and without the aluminum salt addition.

Selenium was present in small concentrations at Pittsfield, but most of this was removed by the normal treatment without the addition of the sodium aluminate.

No soluble zinc was found above the detection limits in any of the treatment plants, but it must be pointed out that the 1-mg/L detection limit for zinc is rather high. In the few instances where zinc was detected, it was all removed by the normal treatment process without the aluminum salt addition.

Aluminum measurements were made to assure that the addition of the aluminum salts did not produce an undesirable aluminum content in the final effluent. Significant aluminum removal was achieved both with and without the aluminum salt addition, thus indicating that the normal treatment procedures at these POTWs are adequate for controlling aluminum in the final effluent.

The activated sludge treatment removed about 80 percent of the TOC in all cases. No significant difference occurred in TOC removal when the aluminum salts were added.

The addition of the aluminum salts did significantly reduce the phosphorus content of each treatment plant effluent. As a general rule, the phosphorus concentration in the effluent with the aluminum salt addition was less than 1 mg/L. Thus the aluminum salt addition was very effective in phosphorus removal.

Conclusions

Statistically, copper was the only metal whose removal was enhanced by the addition of both alum and sodium aluminate. Lead appeared to be removed to some extent, but this result could not be confirmed statistically because of the wide variations in influent lead concentrations. Sodium aluminate appeared to improve chromium removal, but alum did not. Phosphorus was effectively reduced

Table 3. *Mean Removal of Wastewater Constituents in Pittsfield POTW*

Constituent	With Sodium Aluminate: Influent	With Sodium Aluminate: Final Effluent	With Sodium Aluminate: % Reduction	Without Sodium Aluminate: Influent	Without Sodium Aluminate: Final Effluent	Without Sodium Aluminate: % Reduction
	μg/L			μg/L		
Aluminum	23,367.	1,032.1	95.6	13,352.	1,024.9	92.3
Antimony	20.3	11.45	42.8	18.58	13.05	29.8
Arsenic	21.49	7.39	65.6	15 28	7.91	48.2
Beryllium	0.5*	--	--	0 5*	--	--
Cadmium	17.29	4.10	76.3	23.59	4.23	82.2
Chromium	48.1	3 8	92 1	58.4	7.0	88.0
Copper	536.1	57.9	89.2	603.8	102.4	83.0
Lead	72.3	5.9	91.8	108.5	28.3	73.9
Mercury	0.64	0.23	64.1	0.52	0 23	55.8
Nickel	1,000.*	--	--	1,000.*	--	--
Selenium	25.06	16.81	32.9	16.04	10.65	33.6
Silver	20.86	2.00*	90.4	31.97	2.57	92.0
Thallium	5.0*	--	--	5.0*	--	--
Zinc	990	300 *	69.7+	790.	300.*	62.0+
	mg/L			mg/L		
Phosphorus	6.95	1.09	84.3	5.55	2.41	56 6
TOC	78.30	13.64	82.6	126.19	18.14	85.6

*Minimum detectable limit.

by the added aluminum salts. Thallium, beryllium, and nickel were never found in detectable quantities in the treatment plant influent. Cadmium and antimony removals were not significantly affected by the addition of aluminum salts. The other heavy metals (arsenic, mercury, selenium, silver, and zinc), were all reduced below the detectable limits by the conventional treatment process without the addition of any aluminum salt. Thus adding aluminum in concentrations designed for effective phosphorus removal in a POTW can also be effective to a limited degree in removing certain heavy metals. For the most part, conventional activated sludge treatment appears to be effective in reducing the heavy metal contents of wastewaters.

The full report was submitted in fulfillment of Cooperative Agreement 809226 by Rensselaer Polytechnic Institute under the sponsorship of the U.S. Environmental Protection Agency.

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The complete report, entitled "Removal of Heavy Metals Using Aluminum Salts for Phosphorus Removal," (Order No. PB 85-147 445/AS; Cost: $23.50, subject to change) will be available only from:
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