Erc. Ünv. Fen Bil. Derg., 10, 1-2 (1993) 83-97

REMOVAL OF BORON FROM WASTEWATER BY COAGULATION

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SUMMARY

Sources of pollution by boron are considered and a brief account of the chemical properties of borax and boric acid is given. The literature dealing with boron toxicity in relation to water pollution is summarized. The removal of boron in the liquid wastes discharged from boric acid and borax plants under different conditions using the chemical coagulants have been investigated. Subsequently, the boron removal in the liquid wastes from boric acid and borax plants have been determined by means of the laboratory experiments. Results of removal of boron in wastewaters are given.

Key words: Boron, removal, coagulation, wastewater, boric acid.

KOAGÜLASYONLA ATIKSULARDAN BOR GİDERİLMESİ

ÖZET

Bor ile olan kirlenme değerlendirilmiş ve borik asit ve boraksın kimyasal özellikleri kısaca verilmiştir. Borun zararlı etkilerine ait literatürdeki bilgiler özetlenmiştir. Borik asit ve boraks tesislerinden çıkan sıvı atıklardan borun giderilmesi değişik şartlarda kimyasal koagülantlar kullanılarak incelenmiştir. Bunun için borik asit ve boraks tesislerinden çıkan sıvı atıklardan alınan nümunelerde bor giderilmesi laboratuvar deneyleri ile tayin edilmiştir. Atıksulardan bor giderilmesine ait sonuçlar verilmiştir.

INTRODUCTION

Two compounds, boric acid and borax are produced in the city of Bandırma by the Etibank Company. The production of boric acid in Turkey utilizes colemanite as raw material. Since sulphuric acid is used in the process, significant amounts of calcium sulphate is produced which is seperated by filtration and then discharged in the environment as a waste product causing environmental problem. The present production of borax in Turkey utilizes tincal as raw material. After the condensation of the aqueous solution of tincal a residue is produced as a waste product

The wastewaters from borax and boric acid plants in Bandırma are generaly discharged into Bandırma Bay and sometimes into inland waters causing detrimental effects to the marine environment. It has been observed, that boron concentrations, have reached a level of, 30 mg/l in the marine environment at a distance of 50 meters away from the discharge point. The maximum boron concentration specified by the Turkish Aquatic Products Law is 3 mg/l.

The concentration of boron in water used for irrigation of crops has long been recognized as an important factor when considering possible toxicity effects. Although boron is an essential trace element for the nutrition of higher plants, concentrations exceeding 0.5 mg/l boron is irrigation waters may be harmful to certain crops. At the same time it is doubtful whether a continuous application of more than 0.5 mg/l will not eventually produce toxic effect on plants. It is thought that the maximum safe concentration for even the least sensitive plants is approximately 4 mg/l boron. Many varieties of fruit, e.g. apples, plums and pears are listed among the most sensitive crops which can tolerate, no more than 0.5-1.0 mg/l boron. However, sugar beet, onions, cabbages, carrots, can tolerate boron concentrations of 2-4 mg/l while po.tatoes, peas, wheat and oats are among the crops listed as being able to withstand 1-2 mg/l of boron (1,2).

Boron in aqueous solution is normally present as boric acid and borate ions. The dominant form of inorganic boron in natural aqueous systems is the undissociated boric acid. Boric acid is a waxy solid, slightly soluble in water (5.5 gr/100 gr of solution at 25°C) with a large negative heat of solution. Its solubility, therefore, increases markedly with temperature (28.7 gr/100 gr of solution at 100°C). It is a very weak and exclusively monobasic acid which acts not as a proton donor but as a Lewis acid, accepting OH^-

$$B(OH)_3 \rightleftharpoons B(OH)_4^- + H^+$$

Since boric acid is a very weak acid, borate ions have a strong affinity for protons. Although borate salt solutions contain several ionic species, tetrahedral $B(OH)_4^-$ ions usually predominate (3,4). Such solutions are alkaline and contain free boric acid :

$$B(OH)_4^- \rightleftharpoons H_3BO_3 + OH^-$$

Since industrial plants using boron are located only in few places in the world, suitable treatment processes have not been developed in a sufficient level. The adsorption of boron by clays, soils and other minerals has been extensively studied by many investigators (5). Other widely reported techniques for removing boron from a solution, namely evaporation-crystallization and solvent extraction processes , are effective in high concentrated streams and are geared more to the production of boric acid rather than to its removal from waters containing boron (6). Ion-exchange processes with strong base anion-exchange resins are effective for removing boron (7,8,9).

The problem of removal of boron by an economic method has remained the premier objective of these studies.

MATERIALS AND METHODS

Chemicals and Apparatus

The chemicals used were reagend grade quality. IKA-Werk jar test, Beckman-DU-2 Spectrophotometer and WTW-Type 390 pH meter were used for the measurements.

Early studies showed that boron most frequently occurs as boric acid in magmatic rock and usually as the sodium, potassium or ammonium borates in water. The anions containing boron are the orthoborate, the metaborate and the tetraborate. These various anions of boron exist in equilibrium with one another in water solution.

Most borates occur as metaborates. Adsorption is pH dependent with a maximum adsorption occurring at pH 7-8.5. Griffin and Burau (10) report that boron retention may be due to adsorption on clay mineral platelet edges and possibly interlayer regions by anion exchange or hydroxyl substitution. The choise of a suitable method for the determination of boron in waters largely depends upon the range of concentration of boron, the accuracy required and the concentration of mineral salts and their possible interference effects. The most popular colorimetric reagent employed for boron determination is carmine. It has the advantage that the large concentrations of mineral salts which may be present in natural waters do not usually interfere with colour development.

Procedure

In general three types of wastewaters are obtained in boric acid and borax production plants.

These are :

1- Thickener waste: It is farmed during the solution of tincal mineral through the thickener.

2- Filter cake: It is a by product which results during the filtration of the sulphuric acid solution of the roasted colemanite mineral in the boric acid production.

3- Wastewaters as remnants of calcination: Composite samples prepared from the calcination of these wastewaters has been used in the laboratory works. These wastes collected in the tank composite sample prepared in this tank has been used in the laboratory works. This liquid sample having a concentration of 1600 mg/l.

The method for determination of these elements were chosen on the basis of accuracy and precision. Chemical coagulation is commonly accomplished by the addition of one of the following floc forming subtances: ferric chloride, $FeCl_3$ and aluminium sulfate, $Al_2(SO_4)_3.18H_2O$. The removal of certain cations as well as anions in hydrous metal precipitates has been demonstrated many times; essentially the adsorption process is one of collecting the soluble subtances that are in solution on a suitable inter-face, in this case a hydroxide. Ferric chloride and aluminium sulfate (all with pH adjustment by limes) were chosen as precipitants and coagülants.

In coagulation experiments 1000 ml of boron contaminated wastewater was taken into 1500 ml erlanmayer and subsequently 5,10,15,20,25,30,35,40,45, 50,55,60,65,70,75,80,85,90,95 and 100 mg/l of aluminum sulfate and ferric chloride were added. The experiments were carried out at 22 ∓ 2^oC. In order to determine parameters appropriate with waste treatment plant design, rapid mixture of one minute duration, fourty minutes flocculation time and a thirty minutes sedimentation time were considered diring the laboratory work. To find the optimum pH for these coagulants, sulphuric acid and lime were used for pH ranging from 1 to 13. The analytical procedures followed standart Methods for the Examination of Water and Wastewater (11).

RESULTS

Coagulation method is considered to be the most practical way for purifying water, especially in industrial wastewater treatment. Chemical coagulation removes the suspended solids through the destabilization of colloids and the increase of settling velocity of the settleable matter. Further, precipitation and coagulation were chosen as the form of treatment. for the wastewater on the basis of economic considerations, familiarity of present treatment plant personel with the operation and the relative ease of operation. Initial studies determined that the minimum effective dose of ferric chloride was in the range of 40 to 50 mg/l. According to the relevant literature it is worthy to notice that far the process to be effective the pH values should range between 8.0-9.5. Because of the variability of the boron content of the raw waste, a series of experiments was performed using known quantities of boron (in the term of boric acid) in water and treated with varying dosages of coagulant. The results of the experiments are shown in Tables 1-2.

Table 1. Removal of Boron From Wastewater with Varying Dosages of Coagulant (Boron Content of raw Sample= 1600 mg/l)

Dosage of Ferric Chloride (D, mg/l)	pH	D/Do	Ln D/Do	Concentration of Boron (B, mg/l)	B/Bo	Ln B/Bo
5	8	0.12	-2.07	1551	0.96	-0.03
10	8	0.25	-1.38	1550	0.96	-0.03
15	8	0.37	-0.98	1547	0.96	-0.03
20	8	0.50	-0.69	1545	0.96	-0.03
25	8	0.62	-0.47	1541	0.96	-0.03
30	8	0.75	-0.28	1540	0.96	-0.03
35	8	0.87	-0.13	1535	0.95	-0.04
40	8	1.00	0.00	1530	0.95	-0.04
45	8	1.12	0.11	1530	0.95	-0.04
50	8	1.25	0.22	1532	0.95	-0.04
55	8	1.37	0.31	1531	0.95	-0.04
60	8	1.50	0.40	1532	0.95	-0.04
65	8	1.62	0.48	1536	0.96	-0.04
70	8	1.75	0.55	1536	0.96	-0.04
75	8	1.87	0.62	1538	0.96	-0.04
80	8	2.00	0.69	1540	0.96	-0.04
85	8	2.12	0.75	1538	0.96	-0.04
90	8	2.25	0.81	1538	0.96	-0.04
95	8	2.37	0.36	1537	0.96	-0.04
100	8	2.50	0.91	1538	0.96	-0.04

Table 2 Removal of Boron From Wastewater with Varying Dosages of Coagulant (Boron content of raw sample= 1600 mg/l)

Dosage of Aluminum Sulfate (D, mg/l)	pH	D/Do	Ln/ D/Do	Concentration of Boron (B, mg/l)	B/Bo	Ln B/Bo
5	8	0.10	-2.30	1554	0.97	-0.02
10	8	0.20	-1.60	1554	0.97	-0.02
15	8	0.30	-1.20	1550	0.96	-0.03
20	8	0.40	-0.91	1547	0.96	-0.03
25	8	0.50	-0.69	1540	0.96	-0.03
30	8	0.60	-0.51	1530	0.95	-0.04
35	8	0.70	-0.35	1535	0.95	-0.04
40	8	0.80	-0.22	1535	0.95	-0.04
45	8	0.90	-0.10	1531	0.95	-0.04
50	8	1.00	0.00	1530	0.95	-0.04
55	8	1.10	0.09	1533	0.95	-0.04
60	8	1.20	0.18	1531	0.95	-0.04
65	8	1.30	0.26	1535	0.95	-0.04
70	8	1.40	0.33	1540	0.96	-0.03
75	8	1.50	0.40	1542	0.96	-0.03
80	8	1.60	0.47	1542	0.96	-0.03
85	8	1.70	0.53	1542	0.96	-0.03
90	8	1.80	0.58	1544	0.96	-0.03
95	8	1.90	0.64	1540	0.96	-0.03
100	8	2.00	0.69	1542	0.96	-0.03

Hydrous flocs of aluminum have long been used as a spot·quantitative test for the detection of anions in water. It was only natural that the anions would be adsorbed into the floc and demonstrate the excellent removals as indicated above. The results of this test, when interpreted in the light of the results obtained on wastewater samples, clearly indicated that the range of dosage of coagulant demonstrated in the early tests was confirmed. However, they clearly indicated that, if the quantitiy of boron in the waste exceeded 5 mg/l, only semitolerant and tolerant crops could be irrigated with such water and although such irrigation is permissible, it is not recommended. While not classified as doubtful or completely unsuitable for crops, when one realizes that soil concentrations of boron may rise to eight times the level of that in the water applied (12,13), the situation is not satisfactory:

Obviously, on the face of it, only if the boron level in the raw wastewater could be hold to below 1 mg/l it will be suitable for irrigation of sensitive crops.

The results obtained to evaluate experimental facts with various coagulants were plotted on graphs with different scales. The coagulant volume was expressed as dimensionless parameters showing the ratio of the total dosage of coagulant (D), to the optimum dosage (Do), as (D/Do). On the other hand, the concentration of the solution applied to the coagulation was expressed as a dimensionless ratio (B/Bo), where B is the effluent boron concentration and Bo is the initial boron concentration.

It is attempted to obtain a better equation for this problem making use of the experimental results. By this various combinations of (B/Bo) and (V), (D/Do) are established and the values obtained by means of these combinations are plotted a logarithmic scales and semilogarithmic scales. It was seen that, the results could be generalized on the logarithmic plots. The data obtained for each of the coagulant were grouped around a straight line (Fig.1). The equations representing these straight lines were expressed by the general equation, $\ln Y = \ln a + b. \ln X$ (1). If the linear equation

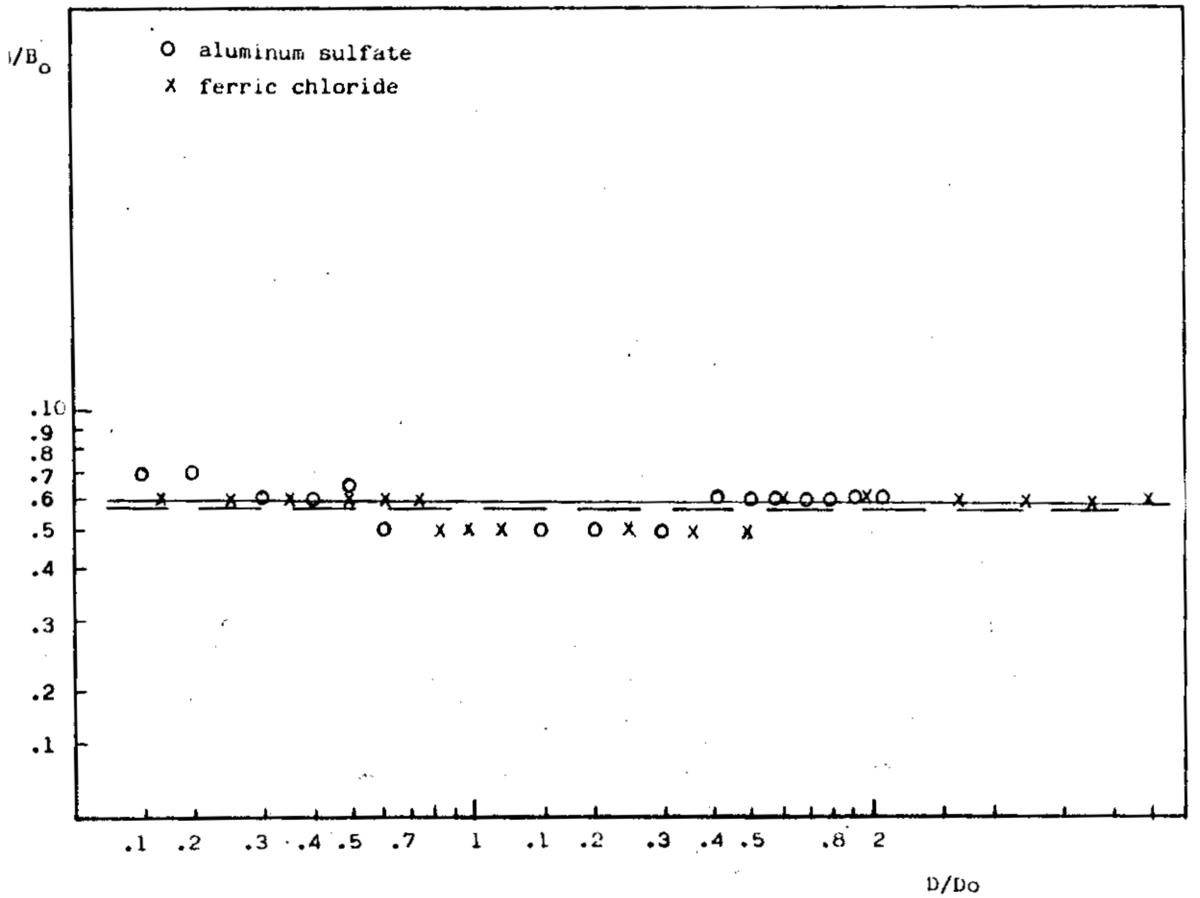

Fig.1 Variations of B/B_o **vs** D/D_o

is shown, the coefficients a and b can be determined, by the below set of simultane linear equations. These equations can be found in any statistics textbook.

a and b coefficients can be obtained from the mathematical analysis as a = -0.04 and b = 0.009. As the consequence the measured results of experimental study accumulates around equation 2.

$$Y = -0.04 + 0.009\,X \qquad (2)$$

Since X ⟶ Ln(D/Do), Y ⟶ Ln(B/Bo), equation (2) can be written as

$$Ln(B/Bo) = -0.04 + 0.009\,Ln(D/Do) \qquad (3)$$

or it can be shown in exponential form as below,

$$B = 0.96\,Bo.(D/Do)^{0.009} \qquad (4)$$

Comparison of the calculated boron concentrations from Equation (4) with some of the measured values are presented in Tables 3-4.

CONCLUSIONS

Coagulation method is considered the most practical way for purifying water, especially in treating industrial wastewater. Described here is a carmine method suitable for the determination of boron in most wastewaters.

When heavy metals are removed by coagulation and precipitation of added iron salts (ferric chloride), in an alkaline media the boron removals and the boron content of the wastewater can be reduced to levels which boron tolerant plants can endure.

However, there are serious limitations to the process, particularly in the ability of the process to reduce boron to levels acceptable for irrigation. Within these limitations the treated wastewater is acceptable for irrigation of golf courses and city parks. The work established that aluminum sulfate and ferric chloride were not satisfactory for the removal of objectionable metallic ions from wastewaters, these coagulants were more

Table 3 Comparison of boron concentrations from Equation (4) with experimental results (Ferric Chloride)

Sample No	Boron Concentration (mg/l)			Relative error in percent
	Measured	Calculated	Difference	
1	1551	1506.96	44.02	2.83
2	1550	1516.95	33.05	2.13
3	1547	1522.50	24.50	1.58
4	1545	1526.44	18.56	1.20
5	1541	1529.51	11.49	0.74
6	1540	1532.02	7.98	0.52
7	1535	1536.00	-1.00	0.06
8	1530	1537.62	-7.62	0.49
9	1530	1539.08	-9.08	0.59
10	1532	1540.40	-8.40	0.54
11	1531	1541.61	-10.61	0.69
12	1532	1542.72	-10.72	0.69
13	1536	1543.75	-7.75	0.50
14	1536	1544.71	-8.71	0.56
15	1538	1545.61	-7.61	0.49
16	1540	1546.45	-6.45	0.41
17	1538	1547.25	-9.25	0.60
18	1538	1548.00	-10.00	0.65

Table 4. Comparison of boron concentration from Equation (4) with experimental results (Aluminum Sulfate)

Sample No	Boron Concentration(mg/l) Measured	Calculated	Difference	Relative error in percent
1	1554	1504.49	49.51	3.18
2	1554	1513.91	40.09	2.57
3	1550	1519.44	30.56	1.97
4	1547	1523.38	23.62	1.52
5	1540	1526.44	13.56	0.88
6	1530	1528.95	1.05	0.06
7	1535	1531.07	3.93	0.25
8	1535	1532.91	2.09	0.13
9	1530	1534.54	-4.54	0.29
10	1530	1536.00	-6.00	0.39
11	1533	1536.00	-3.00	0.19
12	1530	1536.00	-6.00	0.39
13	1535	1539.63	-4.63	0.30
14	1540	1540.65	-0.65	0.04
15	1542	1541.61	0.39	0.02
16	1542	1542.51	-0.51	0.03
17	1542	1543.35	-1.35	0.08
18	1544	1544.14	0.14	0.009
19	1540	1544.89	-4.89	0.31
20	1542	1545.61	-3.61	0.23

succesful in the removal of boron from the wastewaters.

Additional treatment methods for treatment of a diverted portion by reverse osmosis and specific boron adsorptive ion exchange resins are under study. The cost of wastewater treated as compered to the next most economic treatment with ferric chloride and aluminum sulfate. Advanced wastewater treatment to best quality tolerances effectively doubles the cost of treatment. In this study, the optimum dosage of ferric chloride was established at 40 mg/l and boron removal efficiency was from a boron level of 1600 to 1538 mg/l. The optimum dosage of aluminum sulfate was established at 50 mg/l and boron removal efficiency was from a boron level of 1600 to 1543 mg/l.

REFERENCES

[1] J.E.Mc Kee and H.W.Wolf, "Water Quality Criteria", The State of California Water Pollution Control Board, (1963).

[2] L.V.Wilcox, "Water Quality from the Standpoint of Irrigation", Journal AWWA, 50, 651, (1958).

[3] F.Cotton and G.Wilkinson, "Advanced Inorganic Chemistry", Interscience Publishers, London, (1962).

[4] S.Şahin, "Borik Asit ve Boratlar Üzerine Bir Çalışma", Marmara Üniversitesi Fen Bilimleri Dergisi, 4, (1987).

[5] W.W.Choi and K.Y.Chen, "Evaluation of Boron Removal by Adsorption of Solids", Envir.sci.Technol., 13, 189, (1979).

[6] S.Basol and S.Eren, "Extraction of Boron by Polyoles", TBTAK-MAG, 351, (1975).

[7] R.Kumin and A.F.Preuss, "Characterisation of a boron Specific Ion Exchange Resin, I and Ec Product Research and Development, 3,4, 304, (1964).

[8] S.Şahin, "Adsorption of Boron from Waste Solution", Chim.Act.Turc., 18, (1990).

[9] S.Şahin, "The Logistic Curve As a Model for Ion Exchange Column", Chim.Act.Hung. 129, 95-105, (1992).

[10] R.A.Griffin and R.Burau,"Kinetic and Equilibrium Studies of Boron Desorption from Soil", Soil Science Society of America, 38, 891, (1978).

[11] Standart Methods for the Examination of Water and Wastewater, APHA, AWWA, WPCF, (1989).

[12] J.M.Mc Kee and R.W.Wolf, "California Water Quality Criteria", Publication 3A, Agricultural Water Supply, 106-114, (1963).

[13] C.Scofield, "The Salinity of Irrigation Water", Smithsonian Institute Annual Report, 275, (1936).