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The Clarification and Retention of Zinc and Manganese from Raw Water by Alginate and Carrageenan

Alginat ve Karrageenan ile Ham Suyun Tasviyesi ve Çinko ve Manganın Tutulması

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Abstract

In this work was investigated the clarification and uptake of zinc and manganese with a mixture of alginate and aluminum sulfate / carrageenan in raw water. The best results were obtained with aluminum sulfate 12 ppm and alginate sodium 10 ppm where NTU value was decreased to 2.4. The uptake of metals by algal polysaccharides were 22.9 ppb Zn and 30.48 ppb Mn for aluminum sulfate 12 ppm + sodium alginate 10 ppm and 27.53 ppb Zn, 7.49 Mn for 5 ppm carrageenan. Thus it was concluded that sodium alginate effectively binds Mn while Zn by carrageenan.

Introduction

The marine algae accumulate metals which are bound to their proteins and especially to their polysaccharides. The polysaccharide types are divided mainly into two groups. The first group contains carboxyl and the second group sulfate. Alginate is a carboxylated group polysaccharide extracted from the brown algae especially *Laminaria* spp, *Fucus* spp, *Ascophyllum* spp and the giant algae *Macrocystis pyrifera*. It was obtained first by Stanford (1888). Alginates were used for many purposes in industries and for purifications of raw water since it is able to bind metals. Carrageenan is a sulfated group polysaccharide

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extracted from red algea. Marine algae retained metals in sea water. It bound metals from sea water by ion-exchange mechanism between their polysaccharides and the metal cations in the surrounding (Veroy *et al.,* 1980). This retention capacity and mechanism is due to their polysaccharide content. The binding is possible by algal polysaccharides such as alginate and carrageenanes.

Many papers were published on metal uptake by algae from sea water (Lunde 1970; Munda 1978; Whyte and Englar 1980; Güven and Topçuğlu, 1991; Bildacı, 1992; Güven *et al.*, 1992; 1993; Haritonidis and Kevrekidis 1998; Fytianos *et al.*1999; Kut *et al.*, 2000; Topçuoğlu *et al.,* 2001; Topçuoğlu *et al.*, 2003). Selectivity of heavy metal binding and ion exchange properties of algal polysaccharides have been studied by various authors (Haug, 1959; Schweigen, 1962; Haug and Smidsrod, 1965, 1967; Smidsrod and Haug, 1965; Veroy *et al.*, 1980; Güven *et al.,* 1992;1995). For this purpose the marine algae were used for monitoring of metal pollutions in sea water.

Algal polysaccharides contains polyuronate or polysulfate ester groups. Alginate is a polymannuronic and polyguluronic acid derivative. Its composition varies in different species of brown algae. Polyuronate interacts with some divalent cations through their carboxyl group. The molecular chain of polymannuronic acid is a flat ribbon-like molecule whose conformation appears to be stabilized by the formation of an intramolecular hydrogen bond between the- O-3H of one unit and the ring oxygen atom O (5) of the next sugar unit in the chain in a zig-zag shaped macromolecule of polyuronic acid. There exists also several possibilities for formation of intraresidue hydrogen bonds between the equatorial hydroxyl group of the C (2) atom and either oxygen atom in the carboxyl group of the adjacent sugar unit in the chain (Kohn, 1975).

It was proposed that the binding mechanism was primarily by chelation, in which both vicinal hydroxyl groups of the uronic acid unit were used. The approach of carboxyl groups to the distance necessary for the formation of such a chelate bond of calcium requires free rotation of the D-galacturonic acid units around the glycosidic bond. One of the most important and useful properties of alginates is the ability to form gels by reaction with calcium salts due to the effect of divalent metals on alginate (Smidsrod and Haug 1965; Haug and Smidsrod, 1965;1967).

Algal polysaccharide alginates and carragenans were used for coagulation and floculation of suspended matter in raw water (Brathy, 1980; Güven *et al.*, 1992b; Anon).

On the other hand many inorganic salts such as aluminium sulfate, aluminium chloride, polyaluminium, sodyum aluminate, ferric / ferrous sulfate, copper chloride and natural polyelectrolytes; guar gums, starch, tannin and also sodium alginate were used as coagulants for water purifications. The concentration of sodium alginates used for coagulation of raw water varied through 0.1-0.6 ppm (Bratby, 1980). This finding was confirmed in our earlier work (Güven *et al.*, 1992b).

Meanwhile alginates were used in human medicine as prophylactic substance against intoxication by radioactive strontium and heavy metals.

In this work alginate and carrageenan were investigated for its clarification and retention of metal as zinc and manganese in raw water.

Materials and Methods

Aluminium sulfate $Al_2(SO_4)_3$, $12H_2O$, in a concentration of 12 ppm.

Sodium alginate (Extra Synthese, Genay), in a concentration of 1-10 ppm.

Carrageenan Type (L.C.) Pectin Factory (Copenhagen), in a concentration of 5ppm.

Standard metal solutions for plotting of calibration curve were prepared in a conc. of 5-20 ng of $Zn(NO_3)_2 . 4H_2O$ and $Mn(NO_3)_2 .4 H_2O$.

Raw water was taken from Alibeyköy reservoir of ISKI, Istanbul.

All chemical used were Merck product.

Jar –Test apparatus, Turbidimeter (Trubung Photometer, Dr. Lange LTP5), Germany.

Procedure

1 liter of raw water was taken from Alibeyköy reservoir of ISKI / Istanbul and put into a glass beaker, added on it separately

1. 12 ppm $Al_2(SO_4)_3$, $12H_2O$
2. 12 ppm $Al_2(SO_4)_3$, $12H_2O$ + 1-10 ppm sodium alginate
3. 1-10 ppm Sodium alginate
4. 5 ppm Carrageenan

NTU test

Each test was run with 1.- 4.,2.,3., individually , stirred at 160 rpm for 1.5 min, then settled 15 min.

The supernatant part was pipetted without agitation and the turbidity was measured by Trubung Photometer Dr. Lange. Nephalometric Turbidity Unit (NTU) was calculated through Standard Methods. After determination of NTU value it was centrifuged, the residue was dried at 105 ^{0}C for 8 hours. It was added to dried residue 5 ml 0.1 N HNO_3, the supernatant part was filtered through Millex-HV 0.45 μm then applied 20 μl on HPLC. The metals retained were determined by (HPLC) liquid chromatography (Waters Corporation, Milford, MA), consisted of Waters 600E multisolvent delivery system pumps, a Waters 486 tunable absorbance UV detector, and Rheodyne, Model 7725 sample injection valve with a 20 μl loop. Column: Delta Pak C_{18}, 5 μm, 3.9x150 mm Spherical (Waters Corporation, Milford, MA).

The mobile phase: 2 mM sodium octansulfonat, 35 mM sodium tartrate, and 5 % acetonitrile (adjusted to pH 3.65 with NaOH).

Flow rate: 0.8 ml/min. The eluents were monitored by UV detection at 500 nm. Post column reagent 0.2 mM PAR [4-(2-pyridylazo) resorcinol, monosodium salt 1 M acetic acid, 3 M ammonium hydroxid, 0.5 ml / min. The eluent was filtered through a Millipore HA (0.45) membran filter and degassed by immersion in a ultrasonic bath. Detection limit of metals are (ppb): Zn 5, Mn 10.

Calibration curve of zinc and manganese were plotted from 1000 ppm stock metal solution which were prepared in 100 ml for 62.33 mg zinc acetate and 108.8 mg manganese nitrate. Standard curve was plotted from HPLC chromatogram using specific areas of each metal. Its equation was calculated according to Waters Data Module Manual.

Results

The standard curve of Zinc and Manganese are shown in Fig. 1 and 2.

Fig 1. Standard curve of Zinc

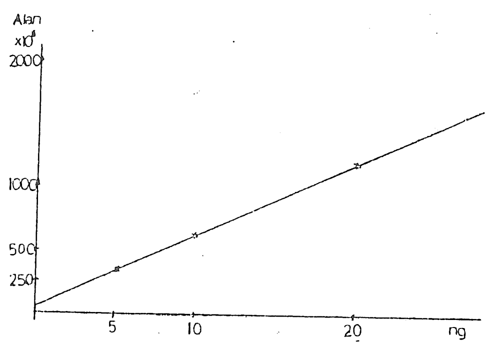
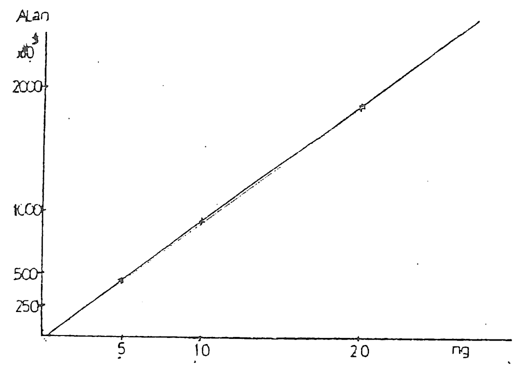


Fig 2. Standard curve of Manganese



The standard equation metals are:

for; Zinc Nitrate

$y = 1153791x\text{-}49301.5 \quad r^2 = 0.999$

for; Manganese nitrate

$y = 1954255x\text{-}50584 \quad r^2 = 0.999$

The clarification value (NTU) of examined compounds / mixture are shown in Table1

Table 1. NTU value of examined compounds.

Compounds		NTU value
Aluminum sulfate		
	6 ppm	17.6
	8 ppm	13
	10 ppm	8.3
	12 ppm	7.5
	14 ppm	5.6
	16 ppm	4.6
Na alginate		
	1 ppm	17.9
	2 ppm	14.9
	5 ppm	11.6
	6 ppm	11.6
	8 ppm	10.4
	10 ppm	8.3
Aluminum sulfate 12 ppm + Na alginate		
	1 ppm	4.1
	2 ppm	3.4
	5 ppm	2.6
	8 ppm	2.6
	10 ppm	2.4
Carrageenan	5 ppm	16.5

As seen in the Table 1, neither Na alginate nor Aluminum sulfate was effective on clarification of raw water, when the mixture of both were used, the results were satisfactory. The best results were obtained with aluminum sulfate 12 ppm and alginate sodium 10 ppm where NTU value was decreased to 2.4. The dose of sodium alginate effected on NTU value and when of sodium alginate amounth was increased, NTU value decreased.

The bound metals in examined compounds are shown in Table 2.

Table 2. The bound metals in examined compounds

Compounds	Metals(ppb)	
	Zn	Mn
Aluminum sulfate	9.5	15.06
Aluminum sulfate 12 ppm + Na alginate 10 ppm	22.9	30.48
Carrageenan 5 ppm	27.53	7.49

The uptake of metals by algal polysaccharides were 22.9 ppb Zn and 30.48 ppb Mn for aluminum sulfate 12 ppm + sodium alginate 10 ppm and 27.53 ppb Zn, 7.49 Mn for 5 ppm carrageenan. Thus it was concluded that sodium alginate effectively binds Mn while Zn by carrageenan.

HPLC chromatogram of tested compounds are shown in Fig 3.,4.

Fig 3. HPLC chromatogram of aluminum sulfate 12 ppm + Na alginate 10 ppm

a) Zn, b) Mn

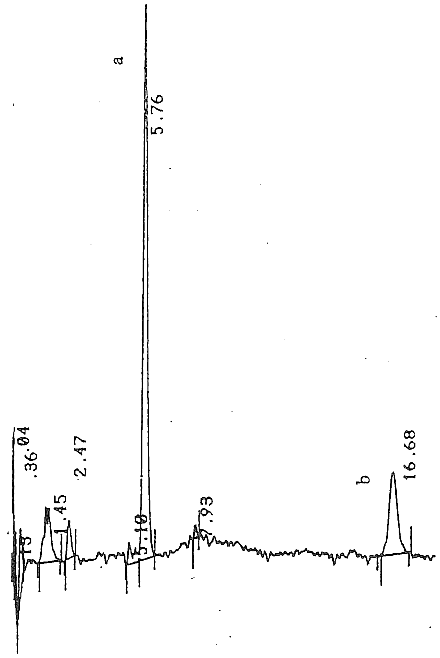
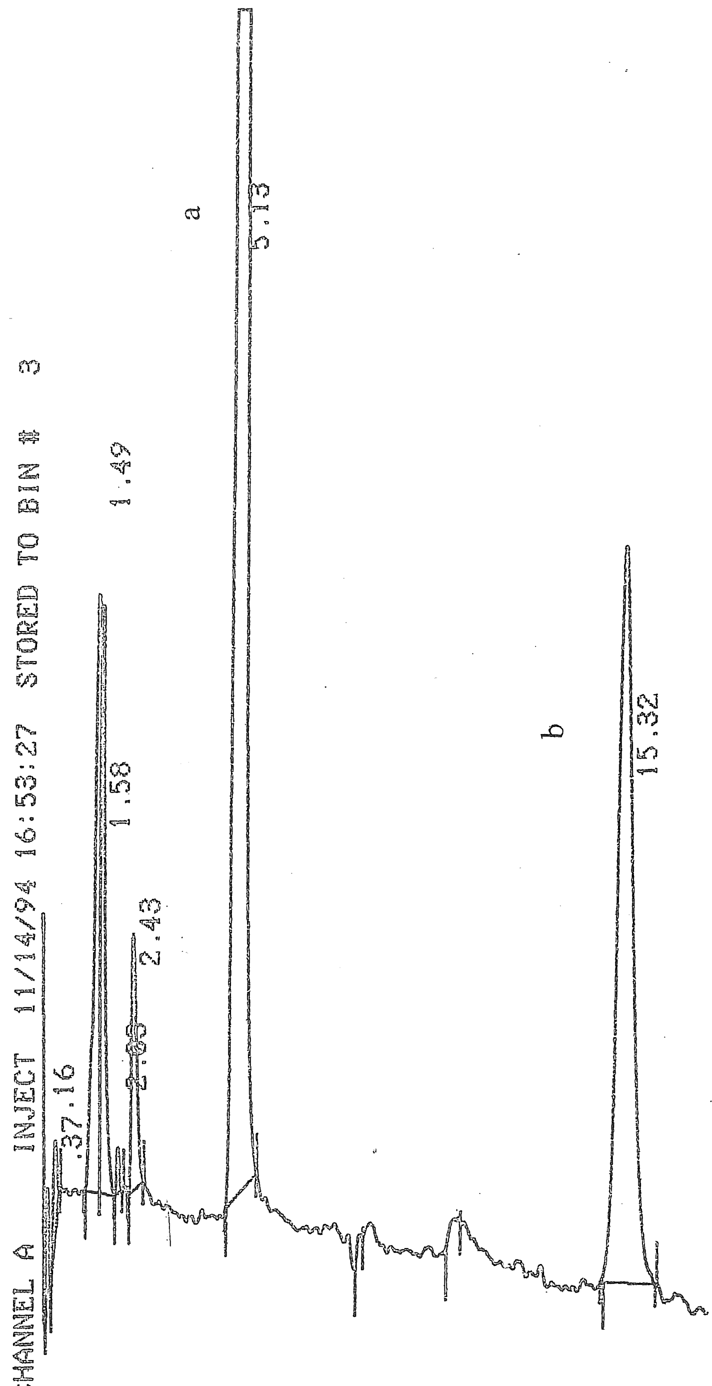


Fig 4. HPLC chromatogram of carrageenan 5 ppm



Discussion

Alginates were used for purifications of raw water (Anon) and aluminum sulfate and sodium alginate used for clarification of raw water (Güven *et al.*, 1992b).

According to the present work alginate can be used in a combination of aluminium sulfate as adjuvant for clarification of raw water and also to retain of zinc and manganese

As indicated in our earlier studies alginate was found to be more effective than carregeenans (Güven *et al.*, 1992).

In addition binding property was high Mn for alginate while Zn for carrageenan

Özet

Bu çalışmada aluminyum sülfat, aluminyum sülfat + sodyum alginatın bir arada ve ayrıca karrageenin kullanılması halinde ham suyun tasfiyesindeki rolü ve ham su içindeki çinko ve manganın tutulması incelenmiştir. 16 ppm aluminyum sülfat ve 10 ppm sodium alginat ham suyun NTU değerini 2.4'e karrageende ise 16.5 'a düşürdüğü saptanmıştır. Bu durumda aluminyum sülfat + sodyum alginatın bir arada kullanılması halinde suyun berraklaşmasında iyi sonuç verdiği tespit edilmiştir. Bu karışımın metal tutulması üzerindeki çalışmada ise ham suda 22.9 ppb çinko ve 30.48 ppb manganı tuttuğu, karragenanın ise 27.53 ppb çinko ve 7.49 ppb manganı tuttuğu tespit edilmiştir. Alginat ve karrageenin metal tutması seçimliliği mukayesesinde ise alginatın manganı, karrageenin çinkoyu tuttuğu saptanmıştır.

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