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Removal of Trace Metal Ions from Industrial Waters, Nuclear Effluents and Drinking Water, with the Aid of Cross-Linked *N*-Carboxymethyl Chitosan

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ABSTRACT

Chitoplex (cross-linked N-carboxymethyl chitosan) is particularly effective in removing trace metal ions (0·01 mg/liter) from brines (50 g/liter), carrier-free radioisotopes such as cobalt-60 from nuclear effluents, and toxic contaminants such as lead and cadmium (0·01 mg/liter) from drinking waters. Chitoplex is indifferent to large concentrations of magnesium.

INTRODUCTION

The legislations of a number of countries establish mandatory, health-related standards for water quality, including those for human consumption and for the fabrication of foods and beverages. For instance, in the United States, the 1986 amendments to the Safe Drinking Water Act require that 83 contaminants must be regulated by June 1989. Contaminants designated by the US Environment Protection Agency as highest priority for increased research and development, and enforcement includes lead. Table 1 presents the maximum permissible concentrations of metals in waters used in the food industry in Italy and the United States (Craxi, 1985; Rozelle, 1987; Yoo, 1987).

Industrial waters are also submitted to regulations and their treatment for metal abatement is compulsory in many countries. Radioisotope

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TABLE 1
Maximum Permitted Concentrations (μg/liter) in Waters to be Used for Food Production and in Drinking Waters

Metal	*Italy*			*United States*	
	Definition	*Analysis*	*Concentration*	*NAS &EPA concentration*	*California concentration*
Lead	Toxic	Periodic	50	50	
Chromium	Toxic	Periodic	50	50	
Cadmium	Toxic	Periodic	5	10	
Nickel	Toxic	Occasional	50		
Mercury	Toxic	Occasional	1	2	
Iron	Undesirable	Periodic	200		300
Manganese	Undesirable	Occasional	50		50
Copper	Undesirable	Occasional	1 000		1 000
Zinc	Undesirable	Occasional	3 000		5 000
Silver	Undesirable	Occasional	10		

collection from extremely dilute waste waters originating from nuclear power plant decommissioning activities is another field where effective and selective treatments are required. Currently available resins and activated charcoals are or become ineffective when the metal concentration is below certain levels or when the trace metals are accompanied by major quantities of common salts, and when the removal of carrier-free radioelements is attempted (Muzzarelli *et al.*, 1985*b*).

The introduction of aminoacid moieties in glucosamine polymers and the instrumental characterization of the resulting aminoacid glucans has been the subject of a previous publication (Muzzarelli *et al.*, 1985*a*). In particular, the glycine derivative *N*-carboxymethyl chitosan lends itself to a number of applications in the field of the removal of toxic metals from industrial and contaminated drinking waters because of its enhanced ability (Muzzarelli *et al.*, 1986).

N-Carboxymethyl chitosan, here indicated with the trade name Chitochel, once dried is an insoluble product that can be used to adsorb metal ions from aqueous solutions. Some disadvantages related to its use, however, are its tendency to swell and surface alteration at strongly acidic pH values due to gel formation.

Chitoplex is the cross-linked form of Chitochel. Cross-linking imparts rigidity, chemical and microbiological resistance, and enhances chelation capacity, while depressing swelling and chain association. Chitoplex is therefore a chitin-based polysaccharide in the form of a rigid granular gel, most suitable for the chelation of metal ions and metal complexes. The cross-linked backbone is insoluble but hydrophilic and quite accessible to solutes. It is an amorphous substance, as indicated by the absence of X-ray diffraction peaks.

The purpose of the present paper is to provide evidence of the performances of the *N*-carboxymethyl chitosans Chitochel and Chitoplex, under conditions close to those encountered in practice, and to give examples of practical applications with three types of waters where contaminants may be present at extremely low concentrations, namely, industrial waters, radioisotope bearing waters and drinking water.

EXPERIMENTAL

Materials

Chitoplex was manufactured by Chito-Bios Srl, Casella Postale 67, I-60020 Torrette, Italy. The trademarks Chitochel and Chitoplex are the property of Chito-Bios Srl. The radioactive waste waters from industrial and decommissioning activities were supplied by ENEL, Milano, Italy.

Atomic absorption spectrometry

Analyses were performed with a Perkin-Elmer 2380 spectrometer, according to standard methods. The mineralization of chitosan and Chitoplex before analysis was performed with a microwave drying system manufactured by CEM Corp., USA, in special teflon containers, with the aid of nitric acid (Spectrapur, 65%; Merck, Darmstadt); for chitosan the programme was 1 min at 360 W, 3 min at 480 W, 3 min at 180 W, and for Chitoplex it was 1 min at 360 W, 3 min at 600 W, 1 min at 180 W. The metal impurities found in chitosan and Chitoplex are listed in Table 2.

Capacity, q (mg/g), is defined as $q = V(C_{\text{in}} - C_{\text{eq}})/M$, where V is the sample volume (liters), C_{in} is the initial concentration (mg/liter), C_{eq} is the equilibrium concentration (mg/liter) and M is the powder weight (g) at 60°C.

Electron microscopy

Samples were preliminarily frozen in liquid nitrogen and then examined in the cryogenic mode in a Philips electron microscope.

TABLE 2
Trace Metals in Chitosans and in Various Preparations of Chitoplex (μg/g)

	Fe	*Co*	*Ni*	*Cu*
Bentech chitosan	44·0	0·19	3·46	1·36
Crangon chitosan	13·6	0·02	1·33	1·18
Euphausia chitosan	347·4	0·05	1·88	21·93
Chitoplex (X)	33·36	0·348	4·68	8·08
Chitoplex (XI)	29·28	0·180	2·92	2·68
Chitoplex (XII)	32·40	0·220	4·32	3·52
Metal present (μg)	7·32	0·045	0·73	0·67
Metal collected (μg)	50·00	50·00	50·00	50·00
Ratio (%)	12·8	0·09	1·44	1·32

Comparison of the amount present in Chitoplex (250 mg) with the amounts collected from solutions (5 liters, 0·01 mg/liter).

Radiochemical measurements

Cobalt-60 was determined by gamma-ray spectrometry with a Ge(Li) detector coupled to a Selenia spectrometer.

RESULTS AND DISCUSSION

Both Chitochel and Chitoplex are pale yellow powders of defined particle size. Specifications for Chitoplex are given in Table 3. The irregularly shaped particles exhibit a quite porous and accessible structure which favors the chelation of metal ions.

Upon chelation, the polymers assume typical colors: yellow for Fe(II), dark violet for Cr(III), pink for Co(II), green for Ni(II) and blue for Cu(II). A number of ions, including Zn, Cd, Pb and Ag, while being effectively chelated, do not develop any color. Typical data under reference conditions, given in Table 4, show that transition and post-transition metal ions are effectively chelated. Of the alkali-earth group, Mg is not collected at all, while Ca, Sr and Ba are collected to a limited extent. Thermodynamic data relevant to water-soluble *N*-carboxymethyl chitosan indicate that Ca is not chelated (Delben & Muzzarelli, 1989; Delben *et al.*, 1989), and therefore it is reasonable to suppose that Ca is collected by Chitoplex by a different mechanism, possibly a weak physical absorption favored by cross-linking.

TABLE 3
Bulk Characteristics of Chitoplex

Bulk density	0·64 g/ml
Particle size	17·6% larger than 40 mesh 53·0% larger than 60 mesh
Moisture	9·8%
Lead capacity	125 mg Pb/g (equilibrium capacity at 500 mg Pb/liter) Greater than 20 mg Pb/g (dynamic capacity at Pb concn *c.* 0·3 mg/liter with filtration velocity *c.* 2 100 cm/h)
Volume expansion	225% (standard USP absorbing power/swelling volume test)
Pressure drop	3·6 psig at 1 060 cm/h 7·6 psig at 2 100 cm/h

TABLE 4
Collection (%; batch mode) of Metal Ions from 1 mM Solutions (100 ml) on Chitoplex (*c.* 150 mg), after 30 min Stirring at 25°C

Metal ion	*At pH 1·0*	*At pH 5·0*
Lead	0	80
Cadmium	0	83
Silver	23	77
Gold	54	77
Chromium(III)	0	90
Nickel	0	80
Iron	0	85
Copper	0	91
Magnesium	0	0
Calcium	0	59
Strontium	0	48
Barium	0	41

Dependence of the chelating capacity on pH

The chelating capacity of Chitochel and Chitoplex (mg metal/g polymer) depends on the pH of the metal ion solution to be treated. Figure 1 shows that the most convenient pH interval is between 4 and 7 where high capacities (up to 150 mg/g) can be easily obtained. The data shown are for a starting metal concentration of 300 mg/liter.

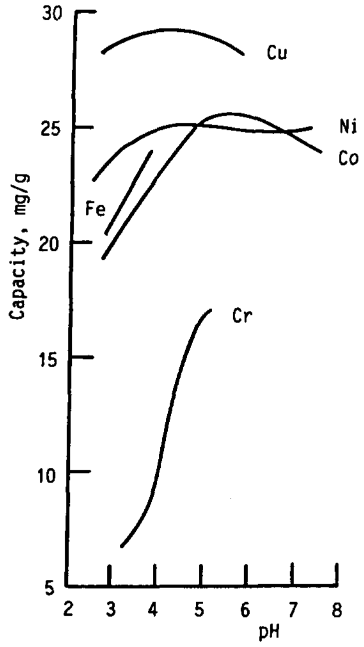

Fig. 1. Dependence on pH of the chelating capacity (mg/g) of thermally dried Chitochel powder at 25°C, for a number of metal ions in the mg/liter concentration range.

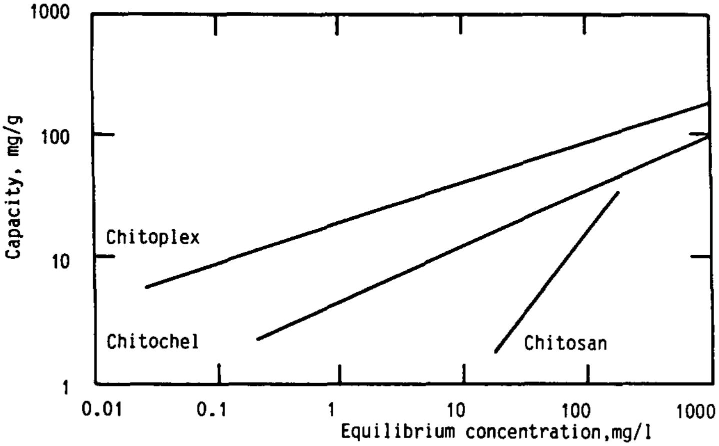

Fig. 2. Chelation isotherms of Chitoplex, Chitochel and chitosan, for cobalt at 25°C.

Concentration dependence of the chelating capacity

The isotherms in Fig. 2 are for the collection of Co on chitosan, Chitochel and Chitoplex at 25°C and at the optimum pH value. The positions and the slopes of these curves are different. The low position, concentration range covered and remarkable slope for the chitosan isotherm indicate that capacity rapidly declines with decreasing Co concentration. The Chitochel curve has a much more favorable slope which indicates that Chitochel is suitable for cobalt collection from more dilute solutions. The Chitoplex isotherm covers higher capacity values and shows an even more favorable slope, thus indicating that cross-linking improves capacity, for instance from 4 to 18 mg Co/g at C_{eq} 1 mg/liter. Chitoplex is effective at low Co concentration; for instance, its capacity is 6 mg/g at C_{eq} 0·02 mg/liter. Chitoplex has higher capacity than Chitochel for Cu and Fe as well, as shown in Figs 3 and 4. This trend has been observed for a number of other ions.

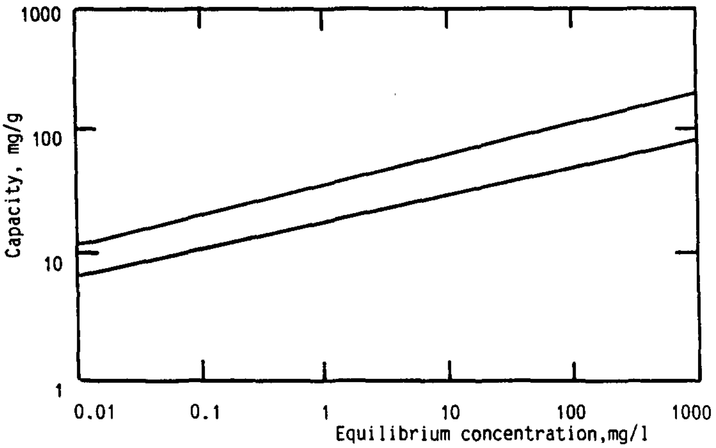

Fig. 3. Chelation isotherms of Chitoplex (upper curve) and Chitochel (lower curve) for copper at 25°C.

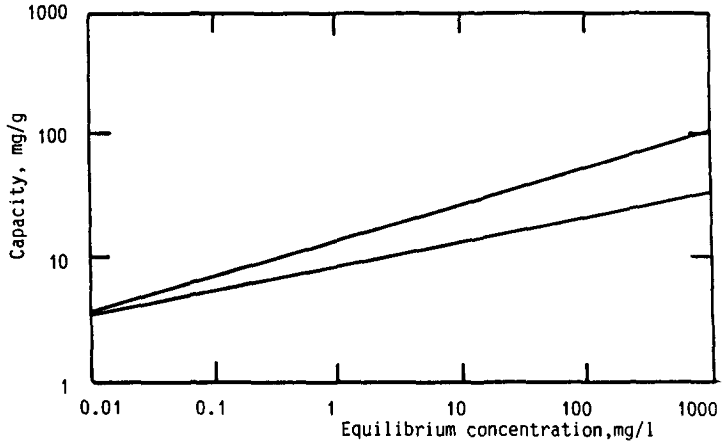

Fig. 4. Chelation isotherms of Chitoplex (upper curve) and Chitochel (lower curve) for iron(II) at 25°C.

Temperature dependence of the chelating capacity

Figure 5 shows the temperature dependence of capacity for iron and copper in the range 25–110°C. A significant decrease in chelation capacity occurs at temperatures above 55°C of the aqueous solutions to be treated. The capacity drop is described for both cations at three reference concentrations: 0·1, 1·0 and 10·0 mg/liter. The trend illustrated by these data could give the impression that a thermal treatment applied to suspensions of Chitoplex in waters could lead to inactivation of the polymer, but it was verified that autoclaved Chitoplex (gel beads at 110°C) is still effective as a chelating polymer. Heating Chitoplex at close to 100°C for prolonged periods could release trace amounts of sugar monomers into the water, as revealed by the presence of an absorption band at 189·4 nm in the ultraviolet spectrum recorded on contact water, and attributed to glucosamine or its derivatives.

Consequences of drying on capacity

While Chitoplex is synthesized and supplied in the form of rigid beads with high water content and can be used as such in column and in batch

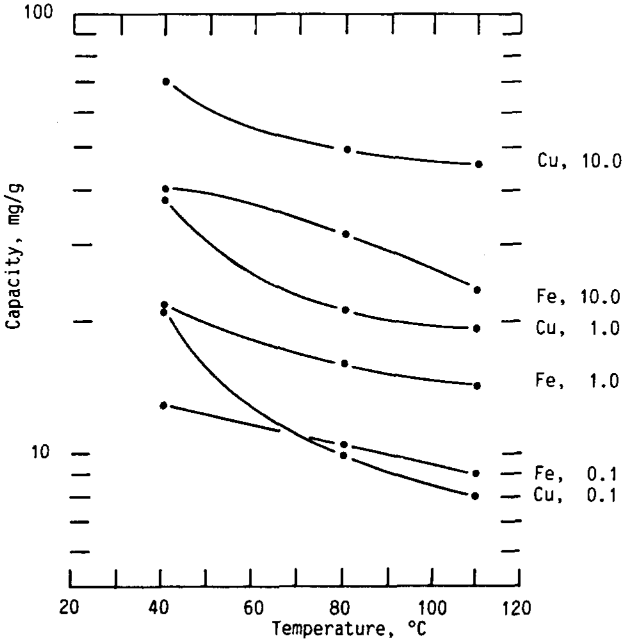

Fig. 5. Temperature dependence of the chelation capacity of Chitoplex for iron and copper at three concentrations.

operations, the dry powder obtained by heating Chitoplex at 60°C overnight has lower capacity than the original gel beads. Observations in the SEM in the cryogenic mode reveal that the bead is made up of an outer crust which is rather compact and an inner part where polysaccharide fibrils are amply spaced (Fig. 6). Because the outer surface of the beads has been affected by serious thermal dewatering and mechanical abrasion during milling and sieving, it can be speculated that the lower chelating capacity for the dried Chitoplex depends on the external crust of the particle which it is more difficult to penetrate with metal ions than the original gel.

Figure 7 illustrates this trend for lead, cadmium and chromium(III). The isotherms for Chitoplex in the original wet form are higher and have a better slope than the corresponding isotherms for Chitoplex preliminarily dried at 60°C. Lead isotherms are steeper than the others, indicating that, for lead concentrations in the order of 10^{-5}–10^{-4} g/liter (10–100 ppm), capacity is as high as for other elements, for instance 14 mg Pb/g at C_{eq} 7×10^{-5} g Pb/liter (18 mg/g for Cd and ~ 5 for Cr(III)); it

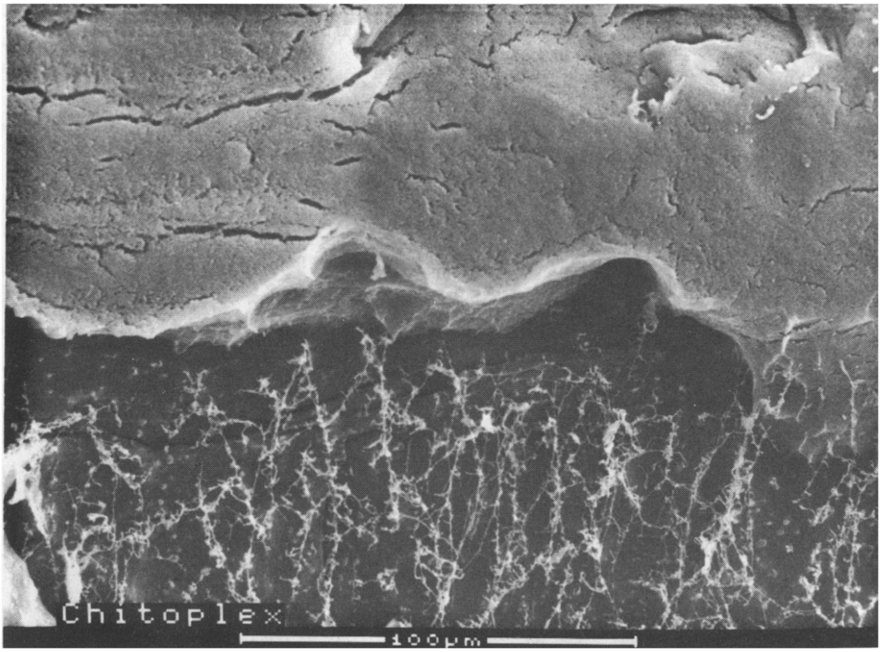

Fig. 6. Electron micrograph obtained in the cryogenic mode for Chitoplex. The external crust (upper part of the illustration) of the gel granule covers a loose network of highly hydrated fibrils (lower part) easily accessible to metal ions.

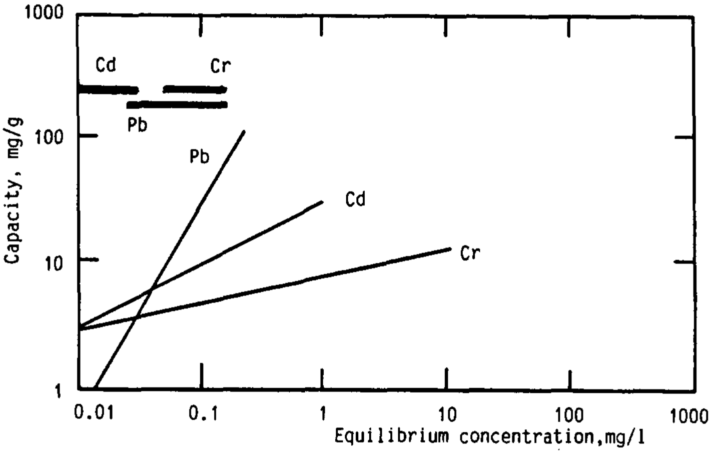

Fig. 7. Chelation isotherms of Chitoplex for lead, cadmium and chromium(III) at 25°C; bars indicate the concentration intervals recommended for testing.

reaches higher values for more concentrated solutions and decreases for more dilute solutions.

The capacity reduction consequent to thermal drying of Chitoplex is reflected in other drying treatments. For instance, freeze-dried Chitoplex has slightly higher capacity for Co than Chitoplex dried in a microwave oven.

Removal of iron, cobalt, nickel and copper from brines.

Sodium chloride (50 g/liter) and a mixture of sodium fluoride and sodium nitrate (50 + 5 g/liter) were made up with water from a Millipore Milli-Q unit and with analytical grade salts. They were preliminarily purified with the aid of a service Chitoplex column at 25°C. Then they were spiked with iron, cobalt, nickel and copper solutions made up by dissolving the respective chlorides, to obtain 0·1 and 0·01 mg/liter final concentrations. Aliquots (5 liters) were passed through Chitoplex (wet gel) columns made with plastic Baker SPE supports of 3 and 6 ml capacities, having diameters of 8 and 12 mm respectively, and a 20 μm porous plastic bottom. Columns were operated with the Baker 10-SPE system which was kept in a thermostatted room at 25°C together with reservoirs and stock solutions. The flow-rates were 1 and 6 ml/min.

At the end of the filtration, colored bands were visible at the top of each column. The polymer was carefully transferred from the column into a teflon cup, mixed with nitric acid and mineralized in the microwave oven, to yield solutions suitable for atomic absorption spectrometry (see Experimental). The results for a total of 116 columns are in Table 5. The volume reduction was over 2900 times (from 5000 to 1·7 ml) for the smaller columns. The latter appeared most suited for the treatment of 5-liter aliquots of both 0·1 and 0·01 mg/liter solutions. Iron at 0·01 mg/liter concentration was collected with yields lower than 100% from chloride brines, while the copper data were slightly higher than

TABLE 5
Collection (%; column mode) of Metal Ions from Chloride or Fluoride + Nitrate Brines

Column			*Fe*	*Co*	*Ni*	*Cu*
Height (mm)	*Diameter (mm)*	*Flow rate (ml/min)*				
0·01 mg/liter in chloride brine						
35	8	1	95	105	96	104
			87	102	98	106
			74	90	86	126
70	8	6	103	100	94	99
70	12	6	104	98	103	102
35	12	1	81	98	102	120
		6	82	100	94	133
35	8	6	105	97	100	103
			83	97	98	109
0·01 mg/liter in fluoride + nitrate brine						
35	8	1	95	101	99	100
70	8	6	98	100	97	99
70	12	6	103	107	94	97
35	12	6	99	101	96	96
35	8	6	89	102	100	102
0·10 mg/liter in chloride brine						
35	8	1	100	109	100	102
70	8	6	96	106	100	100
			103	94	93	105
70	12	6	100	102	100	102
35	12	1	101	102	100	100
35	8	6	100	102	100	102
			98	103	96	104
0·10 mg/liter in fluoride + nitrate brine						
35	8	1	96	104	100	100
70	8	6	100	101	100	100
			98	100	104	96
70	12	6	102	101	100	103
			104	100	97	101
35	12	1	98	100	100	101
35	8	6	100	100	105	102
			103	96	100	99

100%, possibly due to inhomogeneities and errors in the blank subtraction (see Table 2 for impurities in Chitoplex). Cobalt and nickel gave recoveries very close to 100%. The standard deviations, calculated on the percentage yields in Table 5, for the determinations made on 0·1 mg/liter solutions were Fe ± 2·3, Co ± 3·8, Ni ± 2·8 and Cu ± 2·8, while on 0·01 mg/liter solutions they were Fe ± 12·5, Co ± 3·6, Ni ± 5·3 and Cu ± 13·4.

Removal of lead, chromium(III) and cadmium from drinking waters

The experimental conditions suggested by the National Sanitation Foundation to test filters claimed to cause metal ion abatement are listed in Table 6. As can be seen by comparing the recommended effluent concentrations with the equilibrium concentrations in Fig. 7, Chitoplex would meet the recommended standards even by simple batch operations, and therefore its suitability in filter unit operations can be easily predicted.

Under the experimental conditions of Table 6, filter units having the following parameters were tested: dimensions, 1·1 × 10 cm; volume, 9·5 cm^3; Chitoplex dry weight, 1·3 g; flow rate, 2 liters/h; velocity, 21 m/h; volume of treated water, 50 liters. The concentrations of the three metals in the effluent were found to be much lower than the recommended standards.

Sulphate, which is normally present in drinking waters at typical concentrations of 50–60 mg/liter, and which is permitted up to 250 mg/liter, favors the chelation process, as already indicated in an early study on chitosan. While filters were far from saturation, it is possible to state that 1 kg of Chitoplex can treat at least 38 tons of water.

TABLE 6

Experimental Conditions Suggested by the National Sanitation Foundation (1982) for the Definition of the Decontamination Efficacy of New Materials

Metal	*Concentration (μg/liter)*		
	Influent	*Effluent, recommended*	*Effluent, with Chitoplex*
Lead	150	25	11
Chromium(III)	150	50	7
Cadmium	30	10	1
Magnesium	400 000		
Calcium	400 000		
Sulfate	250 000		

Removal of cobalt-60 from nuclear waste waters

Backer disposable filtration columns were filled with wet Chitoplex: bed volume, 51 ml; diameter, *d*, 30 mm; height, *h*, 73 mm; ratio d/h, 0·40; flow rate, 5 ml/min; velocity, *V*, 0·71 cm/min. The following solutions were treated:

Chloride solution (500 ml; HCl, 40 g/liter; pH 5), exhibiting a radioactivity of 218·7 cpm/50 ml under the geometry conditions adopted for counting. At the end of the filtration process, the upper 35 mm of the column were brown, the central part was gray and the lower part unaltered. The effluent was free from radioactivity. The reduction of the weight associated with the radioactivity was 360.

Fluoride solution (900 ml; HF, 30 g/liter, together with HNO_3, 50 g/liter; pH 5·5), exhibiting a radioactivity of 21·2 cpm/50 ml under the geometry conditions adopted for counting. The upper part of the column (8 mm) was green, the lower part was unaltered. The effluent was free from radioactivity. The reduction of weight associated with radioactivity was 200.

Cobalt-60 was completely removed in both cases, together with accompanying metals (mainly iron and copper). Columns were far from saturation, and therefore the weight reduction factors could be even higher than those given above if the columns were saturated; they could be further increased if Chitoplex was incinerated.

CONCLUSIONS

The chelating ability of Chitoplex appears to be enhanced not only by the *N*-carboxymethyl function but also by the cross-linkage which prevents chain association as well as swelling. The performances of Chitoplex are at their best in the temperature interval 15–60°C, and the granular rigid gel not exposed to drying processes has higher capacity than a gel dried by thermal or microwave treatment. In all cases Chitoplex exhibits the peculiar characteristic of maintaining a remarkable capacity for metal ions present in waters at very low concentrations (lower than 0·1 mg/liter). Therefore Chitoplex is suitable to fill columns or filter units for the purification of waters and brines from trace transition and post-transition elements.

In view of the fact that chitosan has already been approved as a food and feed additive and its presence in drinking waters is admitted up to 10 mg/liter, Chitoplex can safely contact waters in food production and processing. It not only removes toxic metals such as cadmium and lead, whose presence in the environment today is a source of worry, but also prevents accidental contamination by radioactive isotopes such as cobalt-60, and eliminates undesirable though harmless metals like Fe, which is known to impart unpleasant organoleptic properties. The versatility of Chitoplex can be further appreciated when point-of-use filters are envisaged.

Chitoplex is also suitable for the treatment of certain solutions used to decontaminate equipment and facilities in nuclear plants. Chitoplex is powerful enough to remove transition metal ions from those waters which contain large quantities of water soluble complexing agents.

The positive features of Chitoplex may well be even further enhanced by a direct comparison of the above results with those obtained by other workers in this field, such as Nishi *et al.* (1987).

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