Precipitation of cations by alginate, polyguluronate and polymannuronate

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Abstract

The relative affinity of seaweed alginate, polyguluronate and polymannuronate for cations was investigated. The cations used in this study were Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Pb^{2+}, Rb^{1+}, Sr^{2+} and Zn^{2+}. The ability of cations to precipitated polymers was determined as the relative affinity of seaweed alginate, polyguluronate and polymannuronate for cations. The relative affinity of polymers for cations in order are as follow:

Seaweed alginate: Fe^{3+},Cu^{2+},Cd^{2+}>Pb^{2+}>Co^{2+},Zn^{2+}>Ca^{2+}>Sr^{2+},Rb^{1+}>Mn^{2+}>Mg^{2+},Hg^{2+}.

Polyguluronate: Fe^{3+},Cu^{2+},Cd^{2+}>Ca^{2+},Co^{2+},Pb^{2+}>Sr^{2+},Rb^{1+},Zn^{2+}>Hg^{2+},Mn^{2+}>Mg^{2+}

Polymannuronate: Fe^{3+},Cd^{2+},Cu^{2+}>Ca^{2+},Pb^{2+}>Zn^{2+},Rb^{1+},Sr^{2+},Hg^{2+}>Co^{2+}>Mn^{2+}>Mg^{2+}

Introduction

Seaweed alginates are (1-4) linked block copolymers of β-D-mannuronic acid and α-L-guluronic acid[1]. The affinity of seaweed alginate for divalent ions has been studied since the discovery that the addition of calcium ions to a solution of seaweed alginate caused gel formation and precipitation[2,3]. The affinities of alginate for metal ions vary. Alginate prepared from *Laminaria digitata* (rich in mannuronate residues) have a different affinity for divalent metal ions than alginates prepared from *Laminara hyperborea* stipes (rich in guluronate residues)[2]. Adsorption affinities of various alginates from different algae strains have been studies[4]. The primary mechanism for metal adsorption is ion exchange[5]. covalent bonding also plays a role[6]. Carboxylic groups are involved

in this binding[7].

The objective of this study was to find out the relative affinity of alginate and its partially hydrolyzed products, polyguluronate, and polymannuronate, for cations.

Materials and Methods

The purified seaweed alginate, polymannuronate and polyguluronate were dissolved in distilled water and their concentration were adjusted to 400 μg/ml. Metal salts were dissolved in distilled water to prepare for the solutions with concentrations of 0 to 50 or 100 mM. Cations used in this study were Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Pb^{2+}, Rb^{1+}, Sr^{2+} and Zn^{2+}. Four volumes of seaweed alginate, polymannuronate and polyguluronate solution were mixed with one volume of each cation solution, respectively. The mixture was incubated 2 hr at room temperature and centrifuged (1,8000 x g for 20 min). The concentration of polymer in each supernatant was measured by phenol-sulfuric acid method[8]. The concentration of precipitated polymer was calculated and its value was used for determination of relative affinity of polymers for cations.

Results and discussions

Precipitation of seaweed alginate, polygluronate, and polymannuronate by lead and cadmium ions was shown in Fig. 1 and 2. At low concentration of lead ions, about 80% of polymers was precipitated. More than 90% of polymers was also precipitated at low concentration of cadmium ions. It means that seaweed alginate, polygluronate, and polymannuronate have relatively high afinity for lead and cadmium ions. Precipitation of seaweed alginate, polygluronate, and polymannuronate by cobalt and mercury ions was shown in Fig. 3 and 4. More than 30 mM of cobalt ions was needed to precipitate about 70 to 90% of polymers with concentration of 320 μg/ml. Polymannuronate has different affinity for mecuric ions. At 40 mM of mecury ions, less than 20% of alginate and polygluronate was precipitated whereas about 50% of polymannuronate was precipitated. It showed that polymannuronate has higher affinity for mecuric ions than seaweed alginate and polygluronate.

Relative affinity of seaweed alginate, polygluronate, and polymannuronate for 12 cations was compared in term of $P_{1/2}$ value which is defined as the

concentration of cations to precipitate 50% of polymers with concentration of 320 μg/ml in Table 1. On basis of the $P_{1/2}$ value, the relative affinity of polymers for cations in order are as follow:

Seaweed alginate: Fe^{3+},Cu^{2+},Cd^{2+}>Pb^{2+}>Co^{2+},Zn^{2+}>Ca^{2+}>Sr^{2+},Rb^{1+}>Mn^{2+}>Mg^{2+},Hg^{2+}

Polyguluronate: Fe^{3+},Cu^{2+},Cd^{2+}>Ca^{2+},Co^{2+},Pb^{2+}>Sr^{2+},Rb^{1+},Zn^{2+}>Hg^{2+},Mn^{2+}>Mg^{2+}

Polymannuronate: Fe^{3+},Cd^{2+},Cu^{2+}>Ca^{2+},Pb^{2+}>Zn^{2+},Rb^{1+},Sr^{2+},Hg^{2+}>Co^{2+}>Mn^{2+}>Mg^{2+}

Results from this study can be used for selection of good materials for biosorption to precipitate and concentrate some of heavy metals.

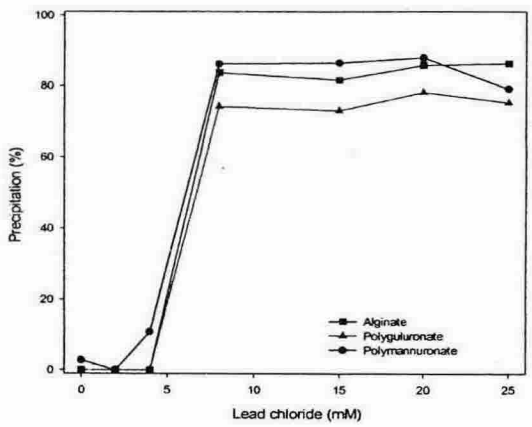


Fig.1. Precipitation of polymers by lead ions

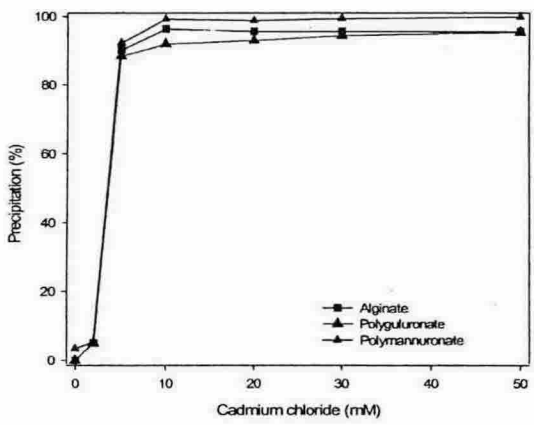
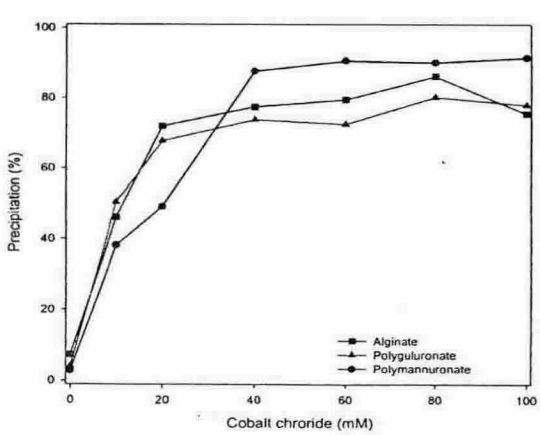


Fig.2. Precipitation of polymers by cadmium ions



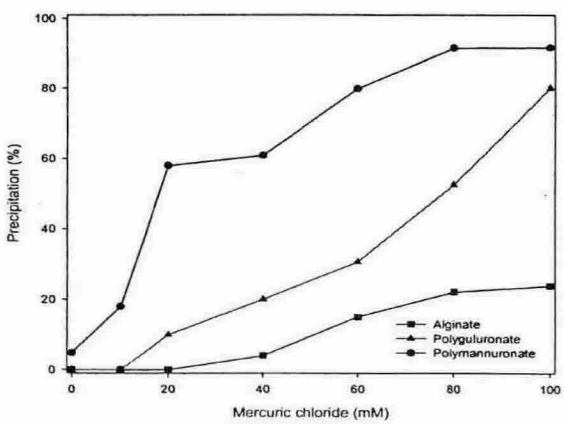


Fig.3. Precipitation of polymers by cobalt ions

Fig.4. Precipitation of polymers by mercury ions

Table1. Precipitation of alginate, polyguluronate and polymannuronate by cations

Ions	$P_{1/2}$[1]		
	Alginate	Polyguluronate	Polymannuronate
Ca^{2+}	17.6	8.5	8.0
Cd^{2+}	3.6	3.6	3.5
Co^{2+}	11.5	9.9	20.2
Cu^{2+}	3.2	4.6	3.5
Fe^{3+}	2.7	3.4	2.7
Hg^{2+}	100<	77.7	18.0
Mg^{2+}	100<	100<	100<
Mn^{2+}	63.5	90.2	37.2
Rb^{1+}	24.1	16.9	15.5
Sr^{2+}	23.1	16.6	15.6
Zn^{2+}	14.5	18.3	15.2

1) $P_{1/2}$ is the concentration of metal ions(mM) required to precipitate 50%(w/v) of the alginate from 400μg/ml(w/v) alginate solution.

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