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**Review on the Removal of Metal Ions from Effluents
Using Seaweeds, Alginate Derivatives and Other Sorbents**

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Résumé de l'article

Les biosorbants, particulièrement ceux préparés à partir des algues macroscopiques et des dérivés d'alginate, démontrent une très bonne capacité d'adsorption des ions métalliques toxiques. Ces biosorbants étant facilement disponibles (biodégradable) et moins coûteux que les adsorbants (industriels) synthétiques, ils présentent un grand potentiel d'utilisation pour l'enlèvement des métaux toxiques des effluents industriels. Les récents développements dans ce domaine ont été revus et font l'objet de la présente synthèse. Des applications spécifiques sont décrites et discutées.

Diverses technologies sont disponibles pour enlever les métaux des effluents industriels tels que la précipitation (sous forme d'hydroxydes ou de sulfures), la coprecipitation, l'adsorption, l'extraction par solvant, la cémentation, l'électrodéposition, l'électrocoagulation, l'échange d'ions et les technologies de séparation membranaire. Néanmoins, la plupart de ces techniques présentent des coûts d'exploitation élevés et, dans certains cas, sont limitées en terme de rendement d'élimination des métaux. Dans ce contexte, l'utilisation d'adsorbants naturels (dérivés de matière organique ou inorganique) constitue une alternative intéressante aux produits synthétiques. De nombreux articles ont d'ailleurs été publiés au cours des dernières années faisant état de la performance d'une grande variété d'adsorbants naturels pour enlever les métaux des effluents.

Plusieurs espèces d'algues marines ont aussi démontré des propriétés pour adsorber les métaux, mais les algues marines brunes, telles que *Sargassum* et *Ascophyllum* semblent avoir la plus grande capacité de rétention des métaux, à cause de leur grande concentration en polysaccharides. L'intégrité physique des algues est également importante, ceci afin de prévenir leur désintégration pendant les processus d'adsorption. Afin d'améliorer la stabilité et les propriétés mécaniques des algues fraîches, diverses méthodes ont été suggérées : i) greffage dans des polymères synthétiques; ii) incorporation dans des matériaux inorganiques; iii) liaison sur un support adéquat; et iv) séquestration par un agent de liaison.

L'acide alginique est un polymère naturel se trouvant dans les algues brunes. Ce polymère est extrait en traitant les algues avec une solution de carbonate de sodium, puis l'acide alginique est précipité, ou converti en sel d'alginate de calcium. Lorsque l'acide alginique réagit avec des ions polyvalents, tel que le calcium, une séquestration se produit procurant un gel d'alginate ayant des forces structurales significatives. L'alginate de calcium peut être préparé sous plusieurs formes, telles que des billes, de la poudre, des membranes, des fibres ou des supports d'immobilisation cellulaire. Les billes sont particulièrement intéressantes du point de vue de leur application et de leur réutilisation.

L'utilisation des algues marines en tant que procédé d'enlèvement des métaux doit tenir compte de plusieurs considérations techniques. Les systèmes de biosorption utilisent les biomasses sous forme solide en un procédé conventionnel de contact solide-liquide et, dans certains cas, les systèmes comprennent plusieurs étapes de biosorption et de désorption. L'effluent à traiter peut entrer en contact avec la biomasse selon un procédé en mode discontinu, semi-continu ou continu. Une fois saturés en métaux lourds, les adsorbants peuvent être disposés de façon sécuritaire, ou être réutilisés après élution des métaux. Dans ce cas, la plupart des métaux lourds (Cd, Co, Cu, Mn, Pb, Zn) peuvent être élués à l'aide d'acides dilués (chlorhydrique, sulfurique, nitrique) ou de solutions salines concentrées. Certains métaux qui sont moins dépendants du pH d'adsorption (Al, Ni, Hg) ne peuvent être élués en utilisant un acide dilué. Des solutions de thiourée ou de mercaptol peuvent être utilisées pour l'or et l'acétate de sodium pour la récupération de l'argent. La combustion des algues est également possible, néanmoins, elle n'est envisageable que si l'adsorbant est peu dispendieux et grandement disponible.

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REVIEW ON THE REMOVAL OF METAL IONS FROM EFFLUENTS USING SEAWEEDS, ALGINATE DERIVATIVES AND OTHER SORBENTS

*Revue sur l'enlèvement des ions métalliques des effluents par l'utilisation des macro-algues, des dérivés d'alginate
et autres sorbants*

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ABSTRACT

Biosorbents, especially those derived from seaweed (macroscopic algae) and alginate derivatives, exhibit high affinity for many metal ions. Because biosorbents are widely abundant (usually biodegradable) and less expensive than industrial synthetic adsorbents, they hold great potential for the removal of toxic metals from industrial effluents. Various studies have demonstrated the efficiency of living and non-living micro-organisms, such as bacteria, yeasts, moulds, micro-algae, cyanobacteria and biomass from water treatment sewage to remove metals from solution. Several types of organic and inorganic biomass have also been used as sorbent materials. In addition, by-products from the forestry industry, as well as agriculture waste and natural sorbents, have also been studied. This paper reviews and summarizes some key recent

developments in these areas and it describes and discusses some specific applications of selected natural sorbents.

Key Words: *Metal, removal, adsorption, alginate, seaweed, natural sorbent, wastewater, effluent, treatment.*

RÉSUMÉ

Les biosorbants, particulièrement ceux préparés à partir des algues macroscopiques et des dérivés d'alginate, démontrent une très bonne capacité d'adsorption des ions métalliques toxiques. Ces biosorbants étant facilement disponibles (biodégradable) et moins coûteux que les adsorbants (industriels) synthétiques,

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ils présentent un grand potentiel d'utilisation pour l'enlèvement des métaux toxiques des effluents industriels. Les récents développements dans ce domaine ont été revus et font l'objet de la présente synthèse. Des applications spécifiques sont décrites et discutées.

Diverses technologies sont disponibles pour enlever les métaux des effluents industriels tels que la précipitation (sous forme d'hydroxydes ou de sulfures), la coprecipitation, l'adsorption, l'extraction par solvant, la cémentation, l'électrodéposition, l'électrocoagulation, l'échange d'ions et les technologies de séparation membranaire. Néanmoins, la plupart de ces techniques présentent des coûts d'exploitation élevés et, dans certains cas, sont limitées en terme de rendement d'élimination des métaux. Dans ce contexte, l'utilisation d'adsorbants naturels (dérivés de matière organique ou inorganique) constitue une alternative intéressante aux produits synthétiques. De nombreux articles ont d'ailleurs été publiés au cours des dernières années faisant état de la performance d'une grande variété d'adsorbants naturels pour enlever les métaux des effluents.

Plusieurs espèces d'algues marines ont aussi démontré des propriétés pour adsorber les métaux, mais les algues marines brunes, telles que *Sargassum* et *Ascophyllum* semblent avoir la plus grande capacité de rétention des métaux, à cause de leur grande concentration en polysaccharides. L'intégrité physique des algues est également importante, ceci afin de prévenir leur désintégration pendant les processus d'adsorption. Afin d'améliorer la stabilité et les propriétés mécaniques des algues fraîches, diverses méthodes ont été suggérées : i) greffage dans des polymères synthétiques; ii) incorporation dans des matériaux inorganiques; iii) liaison sur un support adéquat; et iv) séquestration par un agent de liaison.

L'acide alginique est un polymère naturel se trouvant dans les algues brunes. Ce polymère est extrait en traitant les algues avec une solution de carbonate de sodium, puis l'acide alginique est précipité, ou converti en sel d'alginate de calcium. Lorsque l'acide alginique réagit avec des ions polyvalents, tel que le calcium, une séquestration se produit procurant un gel d'alginate ayant des forces structurales significatives. L'alginate de calcium peut être préparé sous plusieurs formes, telles que des billes, de la poudre, des membranes, des fibres ou des supports d'immobilisation cellulaire. Les billes sont particulièrement intéressantes du point de vue de leur application et de leur réutilisation.

L'utilisation des algues marines en tant que procédé d'enlèvement des métaux doit tenir compte de plusieurs considérations techniques. Les systèmes de biosorption utilisent les biomasses sous forme solide en un procédé conventionnel de contact solide-liquide et, dans certains cas, les systèmes comprennent plusieurs étapes de biosorption et de

désorption. L'effluent à traiter peut entrer en contact avec la biomasse selon un procédé en mode discontinu, semi-continu ou continu. Une fois saturés en métaux lourds, les adsorbants peuvent être disposés de façon sécuritaire, ou être réutilisés après élution des métaux. Dans ce cas, la plupart des métaux lourds (Cd, Co, Cu, Mn, Pb, Zn) peuvent être élués à l'aide d'acides dilués (chlorhydrique, sulfurique, nitrique) ou de solutions salines concentrées. Certains métaux qui sont moins dépendants du pH d'adsorption (Au, Ag, Hg) ne peuvent être élués en utilisant un acide dilué. Des solutions de thiourée ou de mercaptol peuvent être utilisées pour l'or et l'acétate de sodium pour la récupération de l'argent. La combustion des algues est également possible, néanmoins, elle n'est envisageable que si l'adsorbant est peu dispendieux et grandement disponible.

Plusieurs types de biomasses organiques ou inorganiques peuvent être utilisés comme matériaux adsorbants. Des études ont démontré l'efficacité des microorganismes vivants ou morts incluant les bactéries, les levures, les moisissures, les microalgues, les cyanobactéries et les biomasses issues du traitement des eaux usées (boues d'épuration). Les rejets de l'industrie forestière, incluant les sciures et les écorces de bois riches en lignine et en tannins, ont été également étudiés de façon intensive. Certaines plantes aquatiques (*Ceratophyllum demersum*, *Lemna minor*, *Myriophyllum spicatum*) ont également été évaluées pour leur capacité en phytofiltration et phytoassainissement. D'autres études ont été effectuées sur la performance de fixation des métaux de la chitine, cette dernière étant un biopolymère naturel très abondant, lequel est classé second après la cellulose en terme d'abondance. Ce biopolymère se retrouve largement dans l'exosquelette des crustacés et des coquillages. Le chitosan est produit en effectuant la dé-acétylation de la chitine en milieu alcalin. La mousse de tourbe, les déchets d'agriculture (résidus de thé et de café, pelures de certains légumes, écailles de noix, d'arachides, de cacao) et divers autres adsorbants de nature inorganique (sable, argile, oxyde, zéolites) ont également été étudiés pour la récupération des métaux en solution.

D'un point de vue économique, plusieurs méthodes existent pour traiter les eaux usées. La sélection d'une méthode dépend de plusieurs critères, tels que la compatibilité avec les opérations existantes, les coûts d'exploitation, la flexibilité des procédés afin de pouvoir traiter des variations de charges hydrauliques et de concentrations de contaminants. La méthode doit être aussi fiable, robuste et simple d'utilisation. Dans certains cas, des économies substantielles peuvent être réalisées en faisant appel à l'adsorption des métaux sur des biomasses, comparativement aux procédés conventionnels, tel que la précipitation des métaux.

Mots clés : métal, enlèvement, adsorption, alginate, algue, eau usée, sorbant naturel, effluent, traitement.

INTRODUCTION

The preservation of the environment has become increasingly important in view of the ecological problems brought about by industrialization and urbanization. Lakes and rivers are particularly vulnerable to contamination as a result of the discharge of large quantities of effluents from industries and municipalities. The presence of heavy metals, such as cadmium, chromium, cobalt, copper, lead, mercury, nickel, silver, tin and zinc in rivers and watercourses may cause serious health problems to living organisms (ALLOWAY and AYERS, 1993; WASE and FORSTER, 1997).

Consequently, the norms and regulations imposed on industrial effluents are becoming increasingly stringent. These restrictions stem largely from recent advances in the understanding of the behaviour of heavy metals in the environment. Being non-biodegradable, toxic metals tend to accumulate in lower plants and animals, thereby entering the food chain (CHANG *et al.*, 2003; LIPPMANN, 2000; WATTS, 1998).

Various technologies are available to remove metal ions from industrial effluents, including precipitation (usually as metal hydroxide or sulphide) and coprecipitation, sorption, solvent extraction, cementation, electrodeposition, electrocoagulation, ion exchange, and membrane technology (BLAIS *et al.*, 1999; BROOKS, 1991; CHMIELEWSKI *et al.*, 1997; PATTERSON, 1989). However, most of these techniques require expensive, usually toxic, reagents, and this fact significantly increases the capital and operating costs. In this context, biosorbents (*i.e.*, ion exchangers and adsorbents derived from organic matter) present an attractive alternative to synthetic and chemical products because they are widely available, generally biodegradable and relatively inexpensive.

The main characteristics and past applications of biosorbents have been summarized and discussed by several researchers (ATKINSON *et al.*, 1998; BABEL and KURNIAWAN, 2003; BAILEY *et al.*, 1999; Fiset *et al.*, 2000; KUYUCAK and VOLESKY, 1988; VEGLIO and BEOLCHINI, 1997; VOLESKY, 1990; VOLESKY and HOLAN, 1995; WASE and FORSTER, 1997). This present review summarizes the recent research carried out on the use of biosorbents, especially those derived from seaweeds, as substrates to remove heavy metal from solutions and effluents. The various systems, mechanisms and results presented in the scientific literature are analyzed and compared.

1. SEAWEED SORBENTS

1.1 Seaweed-derived sorbents

The ability of biosorbents derived from marine *algae* to adsorb metal ions has been demonstrated by several researchers (LEE and VOLESKY, 1997; LEUSCH *et al.*, 1995; VEGLIO and BEOLCHINI, 1997; VOLESKY and HOLAN, 1995; VOLESKY and PRASETYO, 1994; WILSON and EDYVEAN, 1994).

According to FAO (2002), the world aquaculture production of brown, red and green seaweeds in 2002 was approximately 5, 2.5 and 0.018 Megatons (wet basis), respectively. Whereas all these seaweed species exhibit good metal adsorption properties, the brown marine *algae* (*Sargassum* and *Ascophyllum*) have the highest capacity for heavy metal ions because of their high polysaccharide content (VOLESKY and HOLAN, 1995). Tables 1 and 2 summarize the research carried out on the adsorption of metal ions using various seaweed species.

KLIMMEK *et al.* (2001) compared the efficiency of thirty strains of *algae* for their abilities to extract cadmium, lead, nickel and zinc from aqueous solution. These researchers found that the *cyanophyceae* *Lyngbya taylorii* exhibited high uptake capacities for the four metals. Similarly, VOLESKY and HOLAN (1995) provide some 23 examples of algal biomass metal adsorption.

The physical integrity of *algae* is important to prevent them from disintegrating during the sorption process. HOLAN *et al.* (1993) summarized various techniques used to improve the stability and the mechanical properties of fresh biopolymers:

- Grafting into synthetic polymers;
- Entrapment into inorganic material;
- Binding to a suitable carrier; and
- Cross-linking.

1.2 Algins and alginates derivatives

Algins are salts of alginic acid, a natural polymer found in brown *algae* (*Phaeophyceae*). This polymer is extracted by treating the seaweed with a sodium carbonate solution and recovered by precipitation as alginic acid and afterward as the sodium salt. The alginic acid molecules have a complicated structure. Figure 1 shows two of the main segments found in alginic acid. The abundance of carboxylic, hydroxyl and oxo

Table 1. Studies on the metal sorption using seaweeds
Tableau 1. Études portant sur l'adsorption des métaux par utilisation d'algues macroscopiques

References	Seaweeds	Metals	Studied parameters
ARAVINDHAN <i>et al.</i> (2004)	<i>Turbinaria</i> sp.	Cr(III)	Pre-treated with H ₂ SO ₄ , CaCl ₂ and MgCl ₂
AXTELL <i>et al.</i> (2003)	<i>Microspora</i> sp.	Ni(II), Pb(II)	Batch and semi batch process, kinetic study
BORBA <i>et al.</i> (2006)	<i>Sargassum filipendula</i>	Ni(II)	Pre-treatment, fixed bed column, mathematical modeling
CEPRIÁ <i>et al.</i> (2006)	<i>Ulva rigida</i>	Au(III), Hg(II), Ag(I),	Biomass modified electrode, factors affecting biosorption
CHAIKUSANT (2003)	<i>Gracilaria fisheri</i> (red marine algae)	Cd(II), Cu(II)	Langmuir model, effect of pH, pre-treated with CaCl ₂ .
COSSICH <i>et al.</i> (2004)	<i>Sargassum</i> sp.	Cr(III)	Fixed-bed column, mass balance
DA COSTA and DE FRANÇA (1996)	<i>Codium</i> sp., <i>Colpomenia</i> sp., <i>Gelidium</i> sp., <i>Padina</i> sp., <i>Sargassum</i> sp., <i>Ulva</i> sp.	Cd(II)	Langmuir and Freundlich models, ion-exchange mechanism, effect of pH
DA COSTA <i>et al.</i> (1996)	<i>Sargassum</i> sp.	Al(III), Ca(II), Cd(II), Mg(II), Na(I), Zn(II)	Synthetic and natural effluents, kinetic
GONG <i>et al.</i> (2005)	<i>Spirulina maxima</i>	Pb(II)	pH, contact time, biomass concentration, Freundlich model, desorption, pre-treated with CaCl ₂ .
GUPTA <i>et al.</i> (2001)	<i>Spirogyra</i> sp.	Cr(VI)	Batch sorption, kinetic studies, effect of pH, Langmuir model
HOLAN <i>et al.</i> (1993)	<i>Ascophyllum nosodum</i> , <i>Fucus vesiculosus</i>	Cd(II)	Cross-linking, desorption
HOLAN and VOLESKY (1994)	<i>Ascophyllum nosodum</i> , <i>Fucus vesiculosus</i>	Ni(II), Pb(II)	Langmuir model, effect of pH, crosslinked with formaldehyde, bis(ethenyl)sulfone and 1-chloro-2,3-epoxypropane
KAEWSARN and YU (2001)	<i>Padina</i> sp.	Cd(II)	Batch and column experiments, kinetic studies, effect of pH
KAEWSARN <i>et al.</i> (2001)	<i>Durvillaea potatorum</i>	Cu(II)	Co-ions effect (light and heavy metals, EDTA)
KAEWSARN (2002)	<i>Padina</i> sp.	Cu(II)	Langmuir isotherm, kinetic studies, effect of pH, batch and fixed-bed experiments
KHANI <i>et al.</i> (2006)	<i>Cystoseira indica</i>	U(VI)	Batch sorption, kinetic modelling, effect of pH, protonated algae, Ca-pretreated algae
KRATOCHVILL <i>et al.</i> (1998)	<i>Sargassum</i> sp.	Cr(III), Cr(VI)	Protonated seaweed, pH optimization
KUYUCAK and VOLESKY (1988)	<i>Ascophyllum nodosum</i> , <i>Chondrus crispus</i> , <i>Halimeda opuntia</i> , <i>Palmaria palmata</i> , <i>Porphyra tenera</i> , <i>Sargassum natans</i>	Ag(I), Au(III), Cd(II), Co(II), Cu(II), Pb(II), U(VI), Zn(II)	Algal biomass, dead and living yeast, comparison with activated carbon, anion exchange resin (IRA-400) and cations exchange resin (Duolite-C20)
KUMAR <i>et al.</i> (2006)	<i>Ulva fasciata</i> sp.	Cu(II)	Effect of pH and algae concentration, effect of particle size, adsorption kinetics, pseudo-first and pseudo-second models, adsorption equilibrium
LAU <i>et al.</i> (2003)	<i>Ulva lactuca</i>	Cu(II), Ni(II), Zn(II)	Langmuir isotherm, effect of cations and anions, kinetic study, effect of pH, seaweed biomass concentration, effect of reaction time, desorption

References	Seaweeds	Metals	Studied parameters
LEE and VOLESKY (1997)	<i>Sargassum fluitans</i>	Al(III), Ca(II), K(I), Mg(II), Na(I)	Light metals affinity, proton uptake
LEUSCH <i>et al.</i> (1995)	<i>Ascophyllum nodosum</i> <i>Sargassum fluitans</i>	Cd(II), Cu(II), Ni(II), Pb(II), Zn(II)	Crosslinked with formaldehyde, glutaraldehyde and embedded in polyethylene imine, Langmuir, Freundlich and Dubinin-Radushkevich models, effect of particle size
LODEIRO <i>et al.</i> (2006)	<i>Cystoseira baccata</i>	Cd(II), Pb(II)	Kinetic experiments, temperature effect, Langmuir-Freundlich model, effect of salinity on metal uptake, FTIR analysis
LUO <i>et al.</i> (2006)	<i>Laminaria japonica</i>	Pb(II)	Chemical modification, Langmuir isotherm, effect of pH, effect of solid/liquid ratio.
MATHEICKAL <i>et al.</i> (1997)	<i>Ecklonia radiata</i>	Cu(II)	pH effect, effect of EDTA, acetate, nitrate and chloride on metal uptake, packed bed system
MATHEICKAL and YU (1997)	<i>Phellinus badius</i>	Pb(II)	Langmuir isotherm, kinetic studies, effect of pH, batch and fixed-bed experiments
NAJA and VOLESKY (2006)	<i>Sargassum fluitans</i>	Cu(II), Zn(II), Cd(II)	Equilibrium and sorption models
OFER <i>et al.</i> (2003)	<i>Padina pavonia</i> , <i>Sargassum vulgare</i>	Cd(II), Ni(II)	Kinetic studies, desorption studies, Langmuir isotherm
PARK <i>et al.</i> (2004)	<i>Ecklonia</i> sp.	Cr(III), Cr(VI)	Redox reaction with the biomass, thermal treated biomass, SEM, BET, FTIR characterization
PRASHER <i>et al.</i> (2004)	<i>Palmaria palmate</i> (red algae)	Cd(II), Cu(II), Ni(II), Pb(II), Zn(II)	Freundlich, Langmuir and Brunauer Emmer and Teller (BET) models, effect of contact time, pH, initial concentration and temperature
SENTHILKUMAR <i>et al.</i> (2006)	<i>Gracilaria crassa</i> , <i>Gracilaria edulis</i> , <i>Hypnea valentiae</i> , <i>Ulva lactuca</i> , <i>Ulva reticula</i> , <i>Codium tomentosum</i> , <i>Chaetomorpha antennina</i> , <i>Turbinaria conoides</i> , <i>turbinaria ornata</i> , <i>Sargassum polycystium</i>	Zn(II)	Batch experiments, Langmuir, Freundlich, Redlich-Peterson and Sips models, columns experiments, biosorption kinetics, sorption thermodynamics, influence of co-ions, desorption studies
TSUI <i>et al.</i> (2006)	<i>Sargassum hemiphyllum</i>	Ag(I), As(V), Cd(II), Co(II), Cr(III), Cr(VI), Mn(II), Ni(II), Pb(II), Zn(II)	Ca-treated biomass, different ionic strengths, binding mechanism
VOLESKY (1994)	<i>Sargassum natans</i> , <i>Sargassum fluitans</i> , <i>Sargassum vulgare</i> , <i>Ascophyllum nodosum</i> , <i>Palmaria palmata</i> , <i>Chondrus crispus</i> , <i>Halimeda opuntia</i> , <i>Fucus vesiculosus</i> , <i>Padina gymnospora</i> , <i>Codium taylori</i>	Cd(II), Pb(II)	
YU <i>et al.</i> (1999)	<i>Ascophyllum nodosum</i> , <i>Lessonia flavicans</i> , <i>Lessonia nigrescens</i> , <i>Laminaria japonica</i> , <i>Laminaria hyperborea</i> , <i>Ecklonia maxima</i> , <i>Ecklonia radiata</i> , <i>Durvillaea potatorum</i>	Cd(II), Cu(II), Pb(II), U(VI)	Langmuir isotherm, radionuclides, effect of grown media

Table 2. Recent studies on the adsorption capacities (mg/g) of marine algae for selected heavy metals.
Tableau 2. Études récentes sur la capacité d'adsorption (mg/g) des l'algues marines pour des métaux lourds sélectionnés.

References	Sorbents	Cd(II)	Cu(II)	Cr(III)	Ni(II)	Zn(II)
ARAVINDHAN <i>et al.</i> (2004)	<i>T. ornata</i>			31		
CHAISUKANT (2003)	<i>G. fisheri</i>	71	46			
COSSICH <i>et al.</i> (2004)	<i>Sargassum</i> sp.			68		
KUMAR <i>et al.</i> (2006)	<i>Ulva fasciata</i> sp.		26.9			
LAU <i>et al.</i> (2003)	<i>Ulva</i> sp. 1		47		10	34
	<i>Ulva lactuca</i>		55		19	44
	<i>Ulva</i> sp. 3		51		16	31
LODEIRO <i>et al.</i> (2004)	<i>S. muticum</i>	154				
LODEIRO <i>et al.</i> (2006)	<i>C. baccata</i>	101				
OFER <i>et al.</i> (2003)	<i>S. vulgaris</i>	135			62	
	<i>P. pavonia</i>	88			34	
PAVASANT <i>et al.</i> (2006)	<i>Caulerpa lentillifera</i>	1.59	5.56			2.66

groups gives alginic acid and alginate salts strong chelating properties for metal ions.

When alginic acid reacts with polyvalent ions, such as calcium, a cross-linking effect takes place, which gives the resulting alginate gel a significant structural strength (NESTLE and KIMMICH, 1996). The cross-linking is caused by a polyvalent ion binding two or more carboxylic groups on adjacent polymer chains, and this can be accompanied by chelation of the ion by the hydroxyl and carboxyl groups of the polymer chains (SHIMIZU and TAKADA, 1997).

The alginate products are not only used for metal removal, but also for other commercial applications, including some in the food industry (HOLAN *et al.*, 1993; RENN, 1997). The main advantage of using algae or biomass derivatives is that they do not require nutrients and they are resistant to the physical-chemical properties of heavy metal solutions (ARAÚJO and TEIXEIRA, 1997). Alginate products have been used as supporting substrate for a variety of active agents, including microorganisms, algae (AL-RUB *et al.*, 2004; SINGHAL *et al.*, 2004), chitosan (GOTOH *et al.*, 2004; HUANG *et al.*, 1996), activated sludge (WANG *et al.*, 2004), cellulose and humic acid (MISRA and PANDEY, 2001). Tables 3 and 4 present alginate derivatives studied for their capacity to adsorb different metals.

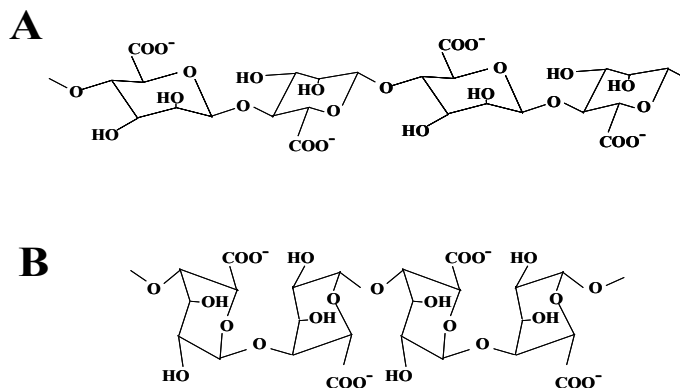


Figure 1. Main segments of alginic acid: A) a poly(D-mannuronosyl) segment and B) a poly(L-guluronosyl) segment.
Principales parties de l'acide alginique : A) une portion poly(D-mannuronosyl, et B) une portion poly(L-guluronosyl).

Calcium alginate may be prepared in various forms, such as beads, powder (CRIST *et al.*, 1994), membranes (HIRAI and ODANI, 1994; TOTI and AMINABHAVI, 2002) or fibers (SHIMIZU and TAKADA, 1997; WILLIAMS and EDYVEAN, 1997) and can be used as cell-immobilization support (IBÁÑEZ and UMETSU, 2002). Bead particles have practical advantages in terms of applicability to a wide variety of process configuration and reusability (GOTOH *et al.*, 2004). Also, the alginate beads may be protonated (IBÁÑEZ and UMETSU, 2002, 2004) or doped with another metallic ion to obtain various bead properties (MIN and HERING, 1998). GOTOH *et al.* (2004) improved the mechanical strength and resistance to chemical and microbial degradation without affecting adsorption capacity by cross-linking the alginate beads with 1,6-Diaminohexane. Producing alginate gels “in-situ” is also feasible when a high concentration of metal ions is

Table 3. Studies on the metal sorption using alginate products.
Tableau 3. Études portant sur l'adsorption des métaux sur les produits d'alginate.

References	Sorbents	Metals	Studied parameters
AL-RUB <i>et al.</i> (2004)	Alginate beads	Ni(II)	Effect of immobilized algae cells (living and death), effect of pH and initial concentration, alginate beads, Langmuir model, sorption desorption cycle
AKSU <i>et al.</i> (1998)	Ca-alginate beads agarose, <i>Chlorella vulgaris</i>	Cu(II)	Packed-bed column, flow rates
CHEN <i>et al.</i> (1993)	Alginate beads	Cu(II)	Linear absorption model, diffusion coefficient, density of alginate
CRIST <i>et al.</i> (1994)	<i>Vaucheria</i> , <i>Rhizoclonium</i> , Ca-alginate powder	Ag(II), Al(III), Ba(II), Cd(II), Cu(II), La(III), Mg(II), Pb(II), Sr(II), Zn(II)	Ion exchange constant, rate of removal of sorbed metal, ion exchange model
FOUREST and VOLESKY (1997)	Alginate extraction from <i>Sargassum fluitans</i> , <i>Ascophyllum nodosum</i> , <i>Fucus vesiculosus</i> , <i>Laminaria japonica</i>	Ca(II), Cd(II), Cu(II), Pb(II), Zn(II)	Characterization of physical properties of alginate by potentiometric titration and ¹³ C NMR, metal binding
GOTOH <i>et al.</i> (2004)	Alginate gel beads	Cu(II), Mn(II)	Doped alginate beads with cyanogens bromide and 1,6-diaminohexane, FTIR and SEM characterization
HIRAI and ODANI (1994)	Alginic acid film, sodium alginate film, alginate-Co complex	Co(II)	Absorption, desorption, diffusion coefficient, film characterization
HUANG <i>et al.</i> (1996)	Alginate and chitosan beads	Cu(II), Ni(II)	Metal selectivity, particle size, kinetic, isotherm, effect of pH
IBÁÑEZ and UMETSU (2002)	Protonated alginate beads	Co(II), Cr(III), Cu(II), Ni(II), Zn(II)	Metal uptake, beads morphology, effect of protonation, effect of: ionic strength, pH and protonation
IBÁÑEZ and UMETSU (2004)	Protonated dry alginate beads	Cr(III)	Batch tests, effect of pH, mechanism, EPMA-EDX analysis
JANG <i>et al.</i> (1995)	Alginate beads	Co(II), Cu(II)	In-situ crosslinking, metal selectivity, fluidized bed reactor, Langmuir model
JANG <i>et al.</i> (1999)	Alginate beads	Cu(II), Zn(II)	In-situ crosslinking, extended Langmuir model, binding group density, binding stability constant
JEON <i>et al.</i> (2002)	Carboxylated alginic acid	Pb(II)	Carboxylated alginic acid using KMnO ₄ , FTIR and ¹³ C NMR characterization, elemental analysis, desorption
JEON <i>et al.</i> (2005)	Carboxylated alginic acid	Cu(II), Pb(II)	Effect of ionic strength and organic material effect, desorption
KARAGUNDUZ <i>et al.</i> (2006)	Dried alginate beads	Cu(II)	Kinetic sorption, equilibrium experiment, surfactant entrapped dried alginate beads.
LU and WILKINS (1996)	<i>Sacharomyces cerevisiae</i> immobilized in alginate gels	Cd(II), Cu(II), Zn(II)	Caustic treatment, metal desorption, biosorbent reactivation
NESTLE and KIMMICH (1996)	Alginate beads	Cu(II)	NMR analyses, spatial distribution, diffusion coefficient
PAPAGEORGIOU <i>et al.</i> (2006)	Alginate beads, alginate extracted from <i>Laminaria digitata</i>	Cu(II), Cd(II), Pb(II)	Alginate beads characterization, batch metal uptake, Langmuir, Freundlich and Sips models, kinetic model, batch kinetic model
PARK and CHAE (2004)	Alginate beads, alginate capsules, alginate gel coated	Pb(II)	Regeneration of alginate adsorbent, SEM characterization

SEKI and SUZUKI (1996)	Alginic acid and humic acid membranes	Pb(II)	Equilibrium parameters, complexation model
SHIMIZU and TAKADA (1997)	Alginate fibers	Bi(III), Cu(II), Pb(II), Sr(II)	Effect of nitric acid, fibers characterization
SINGHAL <i>et al.</i> (2004)	<i>Chlorella pyrenoidosa</i> impregnated beads Ca-alginate	U(IV), U(VI)	Column, desorption, kinetic, FTIR characterization
VEGLIO <i>et al.</i> (2002)	Ca-alginate beads	Cu(II)	Effect of pH, Langmuir isotherm

Table 4. Recent studies on the adsorption capacities (mg/g) of alginate for selected heavy metals.

Tableau 4. Études récentes sur la capacité d'adsorption (mg/g) de l'alginate pour des métaux lourds sélectionnés.

References	Sorbents	Cu(II)	Cr(III)	Cr(VI)	Ni(II)	Pb(II)
AL-RUB <i>et al.</i> (2004)	Alginate beads				26	
	Free dead algal cell				14	
	Immobilized dead algal cells				31	
BAJPAI <i>et al.</i> (2004)	Bio-polymeric (Ca and gelatin)			0.83		
IBÁÑEZ and UMETSU (2004)	Protonated dry alginate beads		112			
NGOMSİK <i>et al.</i> (2006)	Magnetic alginate microcapsule				26	
OZDEMİR <i>et al.</i> (2005)	Alginate beads	96			59	
	Alginate-Extracellular polysaccharide	126			71	
PARK and CHAE (2004)	Alginate beads					450
	Alginate capsule					1540

present in solution (ARAÚJO and TEIXEIRA, 1997; JANG *et al.*, 1999).

Various chemical treatments may be applied on alginic acid in order to increase metal uptake capacity such as carboxylation, phosphorylation, and sulfonation (JEON *et al.*, 2002), although these treatments tend to increase the cost of the resulting product.

ARAÚJO and TEIXEIRA (1997) studied the transport properties of Cr(III) on alginate beads using the Linear Adsorption model and the Shrinking Core model. For low Cr(III) concentration, ion exchange was the rate-controlling mechanism and the experimental results fit well with the Shrinking Core model. At higher concentrations, however, the Linear Adsorption model was a better fit for the experimental results and ionic exchange was no longer the main mechanism of sorption. The study of CHEN *et al.* (1993) indicated that Linear Adsorption model was preferable for the Cu calcium alginate gel.

1.3 Algal biosorption systems

Engineering considerations are very important during the development of an algal-based sorption system. All biosorption systems used biomass in solid form in a basic solid-liquid contact process, with, in certain cases, cycling of the process through biosorption and desorption stages (GARNHAM, 1997). The effluent to treat would make contact with the biosorbent in a batch, semi-continuous or continuous flow system. The following reactor types have been described by BANKS (1997) as potential biosorption systems:

- Conventional stirred tank reactors;
- Packed bed reactors (upflow and downflow);
- Expanded bed reactors;
- Fluidised bed reactors;
- Airlift reactors.

In the cases of algal-based processes using actively growing biomass these can also be based on ponds, lagoons, streams and artificial stream meander units (VOLESKY, 1990).

1.4 Adsorption mechanisms

The chemical structure and metal sorption mechanisms of biomass have been extensively studied. VEGLIO and BOELCHINI (1997) classified the biosorption mechanisms into two main categories, according to their cell functionality, *i.e.*, metabolism-dependant and non-metabolism-dependant. The metabolism-dependant mechanism involves transport across the cell membrane and a precipitation step (BRIERLEY, 1990; COSTA and LEITE, 1990), whereas the non-metabolism-dependant mechanism consists of precipitation (HOLAN *et al.*, 1993; SCOTT and PALMER, 1990), physical adsorption (AKSU *et al.*, 1992; ZHOU and KIFF, 1991), ion exchange (FRISS and MYERS-KEITH, 1986; MURALEEDHARAN and VENKOBACHAR, 1990) and complexation (CABRAL, 1992; TSEZOS and VOLESKY, 1981). Another way to classify the mechanism is based on the location where the extracted metal accumulates; for example, there is intracellular accumulation (transport across membrane), cell surface adsorption/precipitation (ion exchange, complexation, physical adsorption, precipitation) and extra-cellular accumulation/precipitation (VEGLIO and BOELCHINI, 1997).

1.5 Adsorption models

Various models have been used to evaluate the experimental data in order to identify the sorption mechanisms, *i.e.*, chemisorption, physical adsorption or ion exchange. Some studies have compared the ion exchange model with the Langmuir adsorption model (DA COSTA and DE FRANÇA, 1996; FIGUEIRA *et al.*, 2000). The Langmuir adsorption model assumes that only one type of adsorption site exists (*i.e.*, all surface sites have equal activity) and that adsorption equilibrium is reached with the formation of a monolayer (STUMM and MORGAN, 1996). This model does not take into account the speciation of the metal in solution and, therefore, it applies only if the ionic strength, the pH and the ligand concentration are constants.

The ion exchange model has been found to give the best fit for metal sorption on algae biomass because the sorption is accompanied by the release of ions (*e.g.*, Ca^{2+} , Mg^{2+} , Na^+ and K^+) (CRIST *et al.*, 1994; KRATOCHVIL *et al.*, 1998; KUYUCAK and VOLESKY, 1988; SCHIEWER and VOLESKY, 1995). Experiments have been carried out to study several system variables, such as the initial concentration (CRIST *et al.*, 1994), the sorbent particle size (FISHER, 1985), and the solution pH (JANG *et al.*, 1995; LEE and VOLESKY, 1997). Similarly, experimental data have been analyzed to determine the reaction kinetic order of a pore/solid phase diffusion mechanism (HO and MCKAY, 2000).

Other models used to describe various biosorption isotherms include the Freundlich model, a combination of the Langmuir and Freundlich models, the Radke and Prausnitz model, the Reddlich-Peterson model, the Brunauer (BET) model, and the Dubinin-Radushkevich model (VOLESKY, 2003). The «Ideal Absorbed Solution Theory» (IAST) and the «Surface Complexation» (SCM) models have also been used for solutions containing a mixture of metal ions (VOLESKY, 2003). Some other structured types of models taking into consideration the metal speciation in solution, the pH and the electrostatic attraction in solution have been proposed by SCHIEWER and WONG (1999) and YANG and VOLESKY (2000).

1.6 Metal recovery

The metal-laden biosorbent can be either eluted and reused or disposed of in a safe manner. In the former case, the biosorbent operates much like an ion exchange resin. Metals can be eluted using a specific solution (the eluant) to generate a small volume of a concentrated solution (the eluate). The choice of eluant depends on the metal ion to be eluted. Common and heavy metals (*e.g.*, Cd, Co, Cu, Mn, Pb, Zn) are usually eluted with dilute mineral acids (*e.g.*, HCl, H_2SO_4 , and HNO_3) or concentrated saline solutions (*e.g.* 0.5 M NaCl) (GARNHAM *et al.*, 1992b). EDTA has been used in certain cases, but it is generally more expensive than mineral acids or saline solutions (HORIKOSHI *et al.*, 1979). The adsorption of some noble metals, such as gold, silver and mercury, shows little or no dependence on pH and, consequently, these metals cannot be removed with dilute acid solutions (EDYVEAN *et al.*, 1997). Thiourea or mercaptoethanol solutions have been used for recovering gold from biosorbents (DARNALL *et al.*, 1986; GREENE and DARNALL, 1990). Similarly, sodium acetate solutions are effective for eluting copper and silver (HARRIS and RAMELO, 1990). Sodium carbonate has been used to desorb uranium from the algae *Chlorella regularis* (NAKAJIMA *et al.*, 1982).

In general, biosorbents decompose and char at relatively low temperatures. Therefore, metal-laden biosorbents can be readily burned to produce an ash residue having a high metal concentration. This alternative may be economically viable for systems dealing with valuable metals and/or inexpensive biosorbents (GARNHAM, 1997). Alginate powder and calcium alginate beads have high affinity and capacity sorption for Fe(III), and the extraction of Fe(III) from acid synthetic solution is technically feasible (RIVEROS *et al.*, 2001). Applied to acid mine drainage, the Fe(III) extraction would result in a significant reduction of the lime consumption and the volume of the neutralization sludge (RIVEROS, 2004). Once adsorbed, the Fe may be eluted and precipitated as hematite in

order to obtain marketable and useful product (DUTRIZAC and RIVEROS, 1999).

1.7 Cost analyses

Preliminary costing evaluation for biosorption treatment options were conducted by ADERHOLD *et al.* (1996) and VOLESKY (1999). The results indicate that biosorption is a cost-effective technology. The cost-benefit analysis of any treatment option presents various difficulties, such as the lack of publicly available information on operating cost and the long-term impact of the treatment operation. This is particularly true for biotechnological processes. However, a comparative cost study was conducted for biosorptive processes with ion exchange and chemical precipitation (ECCLES, 1995). The selection of an effluent treatment system needs to comply with various criteria, such as compatibility with existing operations, cost effectiveness, flexibility to handle fluctuation in quality and quantity of effluent feed. The system should also be reliable, robust, selective and simple (ECCLES, 1995). Eccles compared the AMT-Bioclaim-process-based hard granular biomass, *Bacillus subtilis* (BRIERLEY *et al.*, 1986) with the chemical precipitation method. The predicted results showed that the AMT-Bioclaim method could reduce the cost per gallon by over 50% when compared with a chemical treatment method. A second study was completed by the author to compare the Biofix process with chemical precipitation to treat acid mine drainage. The Biofix process consists of a mixture

of biomass including bacteria, algae and fungi immobilized in polyethylene beads. Using the data from JEFFERS (1994), the acid mine drainage (AMD) treatment cost was 1.4 US\$ per 1000 US gallons for the Biofix process and for conventional lime treatment, it was calculated the cost would correspond to 1.5 US\$ (ECCLES, 1995). Table 5 summarizes the treatment options, along with their advantages and disadvantages.

2. OTHER NATURAL SORBENTS

Several research papers have been published about the use of a variety of natural sorbents to remove metals from synthetic or industrial effluents. Table 6 shows different studies conducted on the utilization of natural sorbents for the removal of several metals (Ag, Al, As, Au, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, Ir, Mg, Mn, Mo, Na, Ni, Os, Pb, Pd, Pt, Ra, Sb, St, Ti, Tl, V, Zn, Zr), lanthanides (Ce, Eu, La, Yb) and actinides (Th, U).

2.1 Microorganisms

Many studies have been carried out on the utilization of dead or living microorganisms, including bacteria, yeasts, fungi, microalgae, cyanobacteria and activated sludge biomass for metal removal from solutions. Some examples of different microorganisms used for their metal adsorption capacity are

Table 5. Treatment options for the removal of heavy metals (adapted from ADERHOLD *et al.*, 1996).
Tableau 5. Options de traitement pour l'enlèvement des métaux (adapté d'ADERHOLD *et al.*, 1996).

Treatment options	Advantages	Disadvantages
Lime precipitation	Relatively inexpensive Bulk removal	Non selective
Ion exchange	Multiple ion-exchange resins High specificity for heavy metal Several sorption and desorption cycles No sludge production Electrolysis allows metal recycling	High capital and operating costs Economic of these process depends on energy price and the amount of electricity used per treated volume of solution
Membrane processes Osmosis Reverse osmosis		Very specialized application Limited flow rate Membrane instability in salt and acid conditions Prohibitive cost
Adsorption processes	Versatile, simple Selectively sorbed the sorbate Low cost technology	

Table 6. Studies on the adsorption of different metals using natural adsorbents.**Tableau 6. Études portant sur l'adsorption de différents métaux sur des adsorbants naturels.**

Metals	References
Aluminium (Al) (III)	CRIST <i>et al.</i> (1994), ORHAN and BÜYÜKGÜNGÖR (1993), CUI <i>et al.</i> (2006)
Antimony (Sb) (III)	COUPAL and LALANCETTE (1976), MASRI and FRIEDMAN (1974)
Arsenic (As) (II, V)	LOUKIDOU <i>et al.</i> (2003), MASRI and FRIEDMAN (1974)
Barium (Ba) (II)	CRIST <i>et al.</i> (1994), SMITH <i>et al.</i> (1977)
Bismuth (Bi) (III)	MASRI and FRIEDMAN (1974), SHIMIZU and TAKADA (1997)
Cadmium (Cd) (II)	VOLESKY and PRASETYO (1994), YU <i>et al.</i> (1999)
Calcium (Ca) (II)	FISSET <i>et al.</i> (2002), FOUREST and VOLESKY (1997)
Cerium (Ce) (III)	MASRI and FRIEDMAN (1974)
Chromium (Cr)(III, VI)	BAILEY <i>et al.</i> (1992), FISHER <i>et al.</i> (1984)
Cobalt (Co) (II)	FLYNN <i>et al.</i> (1980), KUYUCAK and VOLESKY (1988)
Copper (Cu) (I, II)	MCKAY <i>et al.</i> (1999), YU <i>et al.</i> (1999), CUI <i>et al.</i> (2006)
Europium (Eu) (III)	ANDRES <i>et al.</i> (1993)
Gold (Au) (III)	KUYUCAK and VOLESKY (1988), NAKAJIMA (2003)
Iridium (Ir) (IV)	RUIZ <i>et al.</i> (2003)
Iron (Fe) (II, III)	FISSET <i>et al.</i> (2002), NASSAR <i>et al.</i> (2004), CUI <i>et al.</i> (2006)
Lanthanum (La) (III)	BLOOM and MCBRIDE (1979), CRIST <i>et al.</i> (1994)
Lead (Pb) (II)	HOLAN and VOLESKY (1994), YU <i>et al.</i> (1999), MURATHAN and BÜTÜN (2006)
Magnesium (Mg) (II)	CRIST <i>et al.</i> (1994), FISSET <i>et al.</i> (2002), CUI <i>et al.</i> (2006)
Manganese (Mn) (II)	FISSET <i>et al.</i> (2002), NASSAR <i>et al.</i> (2004), CUI <i>et al.</i> (2006)
Mercury (Hg) (I, II)	FISHER <i>et al.</i> (1984), VIRARAGHAVAN and KAPOOR (1994)
Molybdenum (Mo) (VI)	GUIBAL <i>et al.</i> (1999), SAKAGUSHI <i>et al.</i> (1981)
Nickel (Ni) (II)	FLYNN <i>et al.</i> (1980), LEUSCH <i>et al.</i> (1995)
Osmium (Os) (IV)	RUIZ <i>et al.</i> (2003)
Palladium (Pd) (II)	BABA and HIRAKAWA (1992), GUIBAL <i>et al.</i> (2001)
Platinum (Pt) (IV)	BABA and HIRAKAWA (1992), GUIBAL <i>et al.</i> (2001)
Radium (Ra) (II)	TSEZOS (1997), TSEZOS and KELLER (1983)
Silver (Ag) (I)	FISHER <i>et al.</i> (1984), FLYNN <i>et al.</i> (1980)
Sodium (Na) (I)	FISSET <i>et al.</i> (2002), SPINTI <i>et al.</i> (1995)
Strontium (Sr) (II)	SHIMIZU and TAKADA (1997); SMALL <i>et al.</i> (1999)
Technetium (Tc) (VII)	GARNHAM <i>et al.</i> (1992a, 1993b)
Thallium (Tl) (I)	MASRI and FRIEDMAN (1974)
Thorium (Th) (IV)	MASRI and FRIEDMAN (1974), TSEZOS and VOLESKY (1981)
Titanium (Ti) (IV)	PARKASH and BROWN (1976)
Uranium (U) (IV, VI)	GUIBAL <i>et al.</i> (1994), TSEZOS and VOLESKY (1982)
Vanadium (V) (V)	GUIBAL <i>et al.</i> (1994)
Ytterbium (Yb) (III)	ANDRES <i>et al.</i> (1993)
Zinc (Zn) (II)	ARTOLA and RIGOLA (1992); KUYUCAK and VOLESKY (1988)
Zirconium (Zr) (IV)	GARNHAM <i>et al.</i> (1993a), PARKASH and BROWN (1976)

Table 7. Some examples of the microorganisms studied for the metal recovery from solutions.
Tableau 7. Exemples de microorganismes étudiés pour la récupération de métaux en solution.

Microorganisms	References
Bacteria	
<i>Bacillus subtilis</i> and spp.	BEVERIDGE <i>et al.</i> (1982), COTORAS <i>et al.</i> (1992), GREEN-RUIZ (2006)
<i>Micrococcus</i> spp.	COTORAS <i>et al.</i> (1992), LO <i>et al.</i> (2003)
<i>Mycobacterium</i> spp.	ANDRES <i>et al.</i> (1993)
<i>Pseudomonas</i> spp.	CABRAL (1992), LOPEZ <i>et al.</i> (2002), D'SOUZA <i>et al.</i> (2006)
<i>Streptomyces</i> spp.	FRISS and MYERS-KEITH (1986), MATTUSCHKA and STRAUBE (1993)
<i>Zooglea ramigera</i>	AKSU <i>et al.</i> (1992), NORBERG and PERSSON (1984)
Yeasts	
<i>Candida</i> spp.	AKSU and DONMEZ (2001)
<i>Candida utilis</i>	KUJAN <i>et al.</i> (2006)
<i>Saccharomyces cerevisiae</i>	KUYUCAK and VOLESKY (1988), VOLESKY <i>et al.</i> (1993)
Fungi	
<i>Aspergillus niger</i>	VENKOBACHAR (1990)
<i>Aureobasidium pullulans</i>	GADD and DE ROME (1988)
<i>Cladosporium resinae</i>	GADD and DE ROME (1988)
<i>Funalia trogii</i>	ARICA <i>et al.</i> (2004)
<i>Ganoderma lucidum</i>	VENKOBACHAR (1990)
<i>Penicillium</i> spp.	LOUKIDOU <i>et al.</i> (2003), SAY <i>et al.</i> (2003)
<i>Rhizopus arrhizus</i>	FOUREST and ROUX (1992), TSEZOS and VOLESKY (1982)
<i>Trametes versicolor</i>	BAYRAMOGLU <i>et al.</i> (2003)
Micro-algae	
<i>Chlorella vulgaris</i> and spp.	AKSU and ACIKEL (1999), MEHTA <i>et al.</i> (2002)
<i>Chlamydomonas</i> spp.	GARNHAM <i>et al.</i> (1992a), SAKAGUCHI <i>et al.</i> (1981)
<i>Eudorina</i> spp.	TIEN (2002)
<i>Engelena</i> spp.	MANN <i>et al.</i> (1988)
<i>Scenedesmus</i> spp.	GARNHAM <i>et al.</i> (1993a), SAKAGUCHI <i>et al.</i> (1981)
<i>Synechocystis aquatilis</i>	ERGENE <i>et al.</i> (2006)
Cyanobacteria	
<i>Anabaena</i> spp.	GARNHAM <i>et al.</i> (1993b), TIEN (2002)
<i>Nostoc</i> spp.	FERNANDEZ-PINAS <i>et al.</i> (1991), HASSETT <i>et al.</i> (1981)
<i>Oscillatoria</i> spp.	FISHER <i>et al.</i> (1984), TIEN (2002)
<i>Synechococcus</i> spp.	GARNHAM <i>et al.</i> (1993a, b), SAKAGUCHI <i>et al.</i> (1978)
Other	
Activated sludge	ARTOLA and RIGOLA (1992), HAMMAINI <i>et al.</i> (2003)

presented in Table 7. The metal adsorption on the cell surface of non-living microorganisms usually involves different functional groups such as carboxyl, amino, hydroxyl, sulfhydryl, phosphate and sulfate groups (KAPOOR and VIRARAGHAVAN, 1997; URRUTIA, 1997).

2.2 Forestry industry wastes

Forestry industry wastes including sawdust and tree barks, which are lignin/tannin-rich materials, have been

also intensively studied for metal recovery from solutions (FISET *et al.*, 2000; SEKI *et al.*, 1997; VAISHYA and PRASAD, 1991). The polyhydroxy polyphenol groups of tannin are thought to be the active species in the metal adsorption (ion-exchange) process (VASQUEZ *et al.*, 1994). Lignin extracted from black liquor, a waste product of the paper industry, has been considered for metal adsorption, specifically Hg, Pb and Zn (MASRI *et al.*, 1974; SRIVASTAVA *et al.*, 1994). Lignin (Figure 2) contains polar functional groups, such as alcohols, acids, aldehydes, ketones, phenol hydroxides and ethers, which have varying metal binding capabilities (BAILEY *et al.*, 1999).

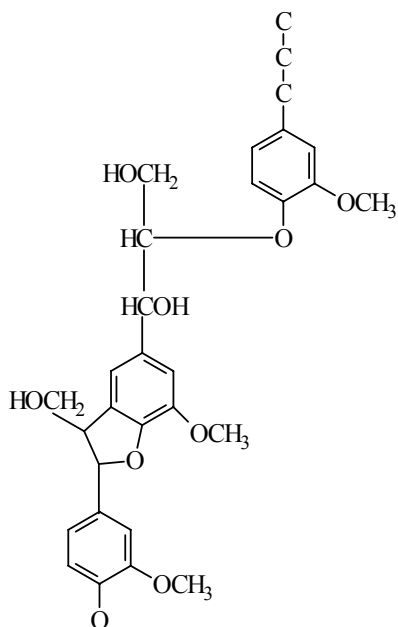


Figure 2. The chemical structure of lignin.
Structure chimique de la lignine.

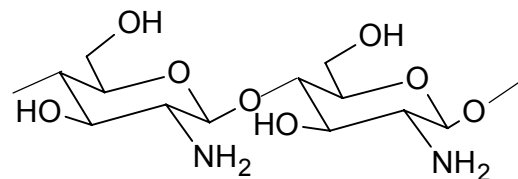


Figure 4. The chemical structure of chitosan.
Structure chimique du chitosan.

most abundant natural biopolymers after cellulose (BABEL et al., 2003). This natural biopolymer is widely found in the exoskeleton of shellfish and crustaceans (KIM and PARK, 2001). Chitosan (Figure 4) is produced by alkaline N-deacetylation of chitin. Crab shells or seafood processing waste sludge can also be used directly for metal adsorption without chitin extraction (KIM and PARK, 2001; LEE and DAVIS, 2001). The metal ions adsorption on chitosan mostly involved free amine groups. However, the binding ability of these sorbents for various metal ions is not directly proportional to the degree of free amine content (EDYVEAN et al., 1997).

2.3 Aquatic plants

Some aquatic plants (e.g. *Ceratophyllum demersum*, *Lemna minor*, *Myriophyllum spicatum*) have also been tested for phytoremediation or phytofiltration of metal-contaminated effluents (AXTELL et al., 2003; KESKINKAN et al., 2004; SCHNEIDER et al., 2001). Chemical modification and spectroscopic studies have shown that the cellular components include carboxyl, hydroxyl, sulfate, sulfhydryl, phosphate, amino, amide, imine, and imidazol moieties, which have metal binding properties and are, therefore, the functional groups in these plants (GARDEA-TORRESDEY et al., 2004).

2.4 Chitin and chitosan

Various researchers have utilized chitin and chitosan for removing metal ions from effluents (MCKAY et al., 1989; HSIEN and RORRER, 1995). Chitin (Figure 3) is the second

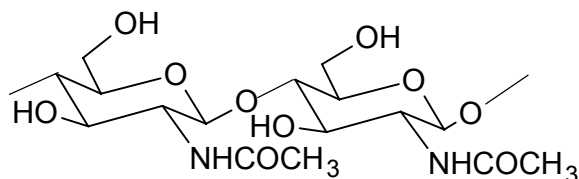


Figure 3. The chemical structure of chitin.
Structure chimique de la chitine.

2.5 Peat moss

Peat moss, which is also very abundant in nature, has been intensively studied for water decontamination and particularly for the metal removal from waste streams (KERTMAN et al., 1993; SHARMA and FORSTER, 1993; VIRARAGHAVAN and RAO, 1993). Peat moss is a complex material, having lignin and cellulose as its major components. Both these components contain polar functional groups, such as carboxylic acids, phenol hydroxides, alcohols, aldehydes, ketones and ethers, which bind metal ions (BROWN et al., 2000; COUILLARD, 1994; WASE et al., 1997).

2.6 Agricultural wastes

Other types of natural sorbents proposed in the literature for metal retention include different agricultural wastes (e.g., tea/coffee and rice residues, fruit and vegetable peels, nut skins/husks). Some examples of these inexpensive and readily available materials are presented in Table 8. The polyhydroxy polyphenol groups, as well as, carboxylic and amino groups, found in these materials are involved in the metal adsorption (ion-exchange) process (MEUNIER et al., 2003b; RANDALL et al., 1974).

2.7 Miscellaneous sorbents

Finally, other natural sorbents studied include notably animal bones (BANAT et al., 2002), clays (e.g. bentonite, kaolinite,

Table 8. Agricultural wastes studied for the metal recovery from solutions.
Tableau 8. Déchets agricoles étudiés pour la récupération de métaux en solution.

Wastes	References
Banana pith and peels	ANNADURAI <i>et al.</i> (2003), LOW <i>et al.</i> (1995)
Canola meal	AL-ASHEH and DUVNJAK (1996)
Carrot residues	NASERNEJAD <i>et al.</i> (2005)
Cassava fibre	ABIA <i>et al.</i> (2006)
Chicken feathers	AL-ASHEH <i>et al.</i> (2002)
Cocoa shells	FISET <i>et al.</i> (2002), MEUNIER <i>et al.</i> (2003a, b, 2004)
Coconut byproducts	RANDALL <i>et al.</i> (1974), OFOMAJA and HO (2007), MOHAN <i>et al.</i> (2006)
Coffee residues	MINAMISAWA <i>et al.</i> (2002)
Corn cobs and roots	BOSINCO <i>et al.</i> (1996), GOLDBERG and GRIEVE (2003)
Grape stalks	FIOL <i>et al.</i> (2006), ESCUDERO <i>et al.</i> (2006)
Indian mustard	CRIST <i>et al.</i> (2004)
Modified wool	MARSHALL and CHAMPAGNE (1995)
Nut and walnut shells	ORHAN and BÜYÜKGÜNGÖR (1993)
Olive mill residues	GHARAIBEH <i>et al.</i> (1998), VEGLIO <i>et al.</i> (2003)
Onion peels	KUMAR and DARA (1982)
Orange peels	AJMAL <i>et al.</i> (2000), MASRI <i>et al.</i> (1974)
Palm kernel fibre	HO and OFOMAJA (2006)
Peanut skins	CHAMARTHY <i>et al.</i> (2001), RANDALL <i>et al.</i> (1974)
Petiolar felt-sheath of palm	IQBAL and SAEED (2002)
Rice byproducts	AJMAL <i>et al.</i> (2003), MONTANHER <i>et al.</i> (2005)
Sheep manure wastes	AL-RUB <i>et al.</i> (2003)
Sunflower seed peel	OZDEMIR <i>et al.</i> (2004)
Tea leaves	ORHAN and BÜYÜKGÜNGÖR (1993), TEE and KHAN (1988)

montmorillonite, wollastonite) (CELIS *et al.*, 2000; PRADAS *et al.*, 1994), human hair and teeth (HELAL *et al.*, 2002; TAN *et al.*, 1985), leaf mould (SHARMA and FORSTNER, 1994), sand (AWAN *et al.*, 2003), metal oxides (Al, Fe, Mn – oxides) (BAILEY *et al.*, 1992; TRIVEDI and AXE, 2001), vermicompost (PEREIRA and ARRUDA, 2003), xanthate (FLYNN *et al.*, 1980; JAWED and TARE, 1991), and zeolites (*e.g.*, clinoptilolite and chabazite) (GENÇ-FUHRMAN, 2007; LEPPERT, 1990; KALLO, 2001; OLIVEIRA *et al.*, 2004).

2.8 Industrial applications

The majority of studies on metal adsorption on biosorbents have been carried out using synthetic solutions containing one or several metal ions (BLAIS *et al.*, 2003; CRIST *et al.*, 1994; MASRI and FRIEDMAN, 1974). However, many research papers have shown the efficiency of biosorbents for the removal of metal ions from industrial wastewaters and acid mine drainage solutions (MCGREGOR *et al.*, 1998; UTGIKAR *et al.*, 2000; ZOOMIS *et al.*, 2000), landfill leachates (ABOLLINO *et al.*, 2003; CECEN and GURSOY, 2001), tannery wastewaters (ALVES *et al.*, 1993), electroplating effluents (AJMAL *et*

al., 1996, 2000; ALVAREZ-AYUSO *et al.*, 2003; LO *et al.*, 2003), acid leachates from sewage sludge decontamination (FISET *et al.*, 2002), acid leachates from soil decontamination (MEUNIER *et al.*, 2004), and alkaline leachates from air pollution control residues from municipal solid waste incinerators (BLAIS *et al.*, 2002a, BLAIS *et al.*, 2002b).

Biosorption has proved to be effective for removing metal ions from contaminated solutions and effluents. The main advantages of biosorption over conventional treatment techniques include lower capital and operating costs, arising from the use of abundant and inexpensive natural products, and lower disposal cost of the spent adsorbents because of their biodegradable nature. However, industrial applications of biosorption are rare, and this situation has been attributed to the non-technical gaps involved in the commercialization of technological innovations (VOLESKY and NAJA, 2005). Furthermore, most biosorption studies have been conducted in batch systems, rather than in the continuous systems that are typical of industrial applications, such as fluidized bed and packed bed columns and continuous stirred tank reactors (MEHTA and GAUR, 2005). Despite these facts, VOLESKY

and NAJA (2005) have identified some industrial operations which represent a big potential market for biosorption applications; these include electroplating and metal finishing, mining and ore processing, smelting, leather processing and printed circuit board manufacturing. However, as some of these sectors may be reluctant to novel biotechnology applications, biotechnology industries may have to share the risk with the industry. Therefore, biotechnology industry may have to develop partnership with industries in order to finance, build and operate the treatment plant or to provide a turnkey operating plant.

CONCLUSIONS

Biosorbents, especially those derived from seaweed and alginic acid, have attracted much interested in recent years as a source of inexpensive adsorbents for toxic metallic ions. Biosorbents are widely available in nature, can be readily produced under various forms, and are both non-toxic and biodegradable. These characteristics give them a definitive advantage over synthetic products for the removal of toxic metals from industrial effluents. The physical stability of biosorbents, especially in alkaline conditions continues to be a drawback and more research is needed in this area.

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