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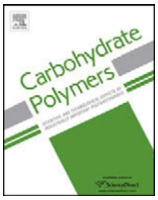

Review

Potential of chitin/chitosan-bearing materials for uranium recovery: An interdisciplinary review

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ABSTRACT

Isolated mollusk shells and crustacean exoskeletons adsorb from waters almost twice their weight of Pb in a few minutes. Likewise, the chitin-based sorbents of animal and fungal origin adsorb U and transuranium elements: some are manufactured commercially in a form suitable for high flow-rates. Supported viable *Trichoderma harzianum* is quite effective in collecting microcrystals of U oxides. Chitosan as well can induce deposition of mixed U oxides, to the point that the final material contains a prevailing inorganic component. Metal-reducing bacteria also offer good performances. These data are exploitable for preventing pollution in civilian operations: the pollution case of Colonie, NY, is discussed in the light of the high toxicity of uranium. The disappointing results of the programs aimed at the collection of uranium from seawater with the aid of synthetic poly(amidoamine) induce to envisage that chitin/chitosan-bearing materials might be involved in the future exploitation of the marine uranium resources.

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1. Introduction

Certain metal ions for which no biological function has been found, such as cadmium and lead, are known carcinogens; mercury targets the central nervous system causing mental and motor dysfunctions, as demonstrated by the Minamata Bay disease generated by the presence of mercury in the food chain. Still others, essential to human nutrition at low doses, have adverse effects at higher doses: these include Cr, Cu, Ni and Zn (Ciardelli, Tsuchida, & Woehrle, 1996; Guy, Hostynek, Hinz, & Lorence, 1999; Lynam, Piantanida, & Cole, 1981). On the other hand, uranium is in demand for nuclear power production (Kaikan & Kaikan, 1983). The subject of metal complexation by chitosan has been reviewed by Muzzarelli (1973, 1977) and Varma, Deshpande, and Kennedy (2004), biosorption has been addressed by Li, Hein, and Wang (2008); the development of chelating resins has been examined by Elwakeel (2010); sorption of heavy metals by inorganic and organic low-cost materials has been reviewed by Bailey (1999) and Zhou and Haynes (2010), and the applications to wastewaters have been reviewed by Bhatnagar and Sillanpaa (2009) and

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No, Prinyawiwatkul, and Meyers (2005). General review articles are available (Guibal, 2004; Wu, Tseng, & Juang, 2010).

Countless living systems utilize chitin together with non-collagen-like proteins; chitin is usually formed as an amorphous extracellular secretion that becomes conspicuously crystalline at different hierarchical levels (nanofibrils → microfibers → fibers): the latter are the sites for eventually heavy deposits of either amorphous or crystalline inorganic compounds, thus chitin is considered an universal template in biomineralization (Ehrlich, 2010; Poulicek, Voss-Foucart, & Jeuniaux, 1986).

The present review is devoted to uranium that unfortunately contaminates certain locations as a consequence of misuse and careless handling, while pollution could have been prevented by adopting reasonable provisions according to natural models. The scope of this review is to direct attention to emerging novel views that might involve polysaccharides in future projects related to pollution prevention or marine uranium collection, and to find out models in the natural environment that might be mimicked when planning on field recovery of metals.

2. Uranium pollution prevention in civilian operations: the missed opportunity

Uranium eventually reaches the top of the food chain causing severe damage to liver and kidneys, and even death (Kurttio et al., 2006). The World Health Organization has determined that hexavalent uranium is a carcinogen, and its concentration in water should not exceed 50 mg/l. The USA Environmental Protection Agency has recommended a drinking water standard of 20 mg/l for ^{238}U. In fact, uranium intake generates biochemical and genetic damages to the mammalian organisms. Experiments on animal models using moderate to high doses revealed chemical toxicity, with the lungs as an entry point, and kidney and bones as contaminated organs. Uranium assimilated via inhalation or ingestion, rapidly enters the bloodstream and forms uranyl hydrogen carbonate complexes. The fraction absorbed into the blood is quickly cleared, with two thirds leaving the body in the urine within 24 h, but in kidneys and bones uranium remains for years being slowly released at the rate of bone turnover; the renal function impairment has been attributed to complexes with phosphate ligands and proteins. Among the genes altered by uranium, Prat et al. (2010) identified a gene coding for osteopontin, a secreted protein linked to ectopic mineralization. In fact, the uranyl ions alter macroscopically the urinary excretion of osteopontin in a time and dose-dependent manner, so that osteopontin, described as associated with bone resorption and kidney mineral stones, is a potential indicator of altered mineralization under the effects of uranyl ions. In genotoxicity studies, mouse embryo fibroblasts were contaminated with either depleted or enriched U at μM concentration, and received low doses (0.3–760.5 μGy). The frequency of binucleated cells with one micronucleus increased linearly with U concentration in the same way, but enriched U induced more centromere-negative micronuclei and nucleoplasmic bridges. Aneugenic effects linked to depleted uranium internal exposure might have a role in carcinogenesis (Darolles et al., 2010).

In its natural form, uranium is a mixture of the 3 isotopes ^{238}U, ^{235}U and ^{234}U with relative abundance of 99.2745%, 0.72% and 0.0055%, and half-life of 4470, 704, and 0.245 million years, respectively. It is present in the earth's crust and in seawater, and occurs in trace amounts in foods and drinking water in some parts of the world.

The by-product of uranium enrichment, where the fissile isotope ^{235}U is artificially concentrated for use as nuclear fuel or weapons, is depleted uranium with altered isotopic ratios, typically ^{235}U/^{238}U = 0.003, and only traces of ^{234}U. It is used in military munitions (kinetic energy penetrators) because its high density and pyrophoric characteristics permit to damage heavily the artillery targets (Wilkinson, 1962). In the Desert Storm and Balkans conflicts, and the recent Iraq invasion the use of depleted uranium has been highly controversial, because a radioactive and toxic material was dispersed into the environment (Bleise, Danesi, & Burkart, 2003) and troops were contaminated.

It has been calculated that civilian industries, as a consequence of their nuclear programs based on enriched uranium, have amassed worldwide ca. 1.2 million tons of useless depleted uranium, most of which is stored in fluoride form (NEA-IAEA, 2001). A civilian factory in Colonie (NY, USA) in the period 1958–1984 reduced the fluoride to metal, and machined depleted uranium articles. Because the storage of scrap uranium metal is hazardous, that waste was converted to uranium oxides in a furnace, which resulted in emissions of uranium oxide aerosols to the atmosphere. This was not contemporary best practice: the use of filters would have prevented pollution. In fact Lloyd, Chenery, and Parrish (2009), measured ^{235}U/^{238}U and quantified the extent and spatial distribution of contamination within the superficial 5.1 cm soils: they found a total of 4.8 tons of depleted uranium spread in the radius of 5.6 km from the Colonie site.

3. Interactions of chitosans with metal ions

A prevailing portion of the research data on the interactions between chitin/chitosan and metal ions refer to laboratory conditions involving purified chitin/chitosan, pure salts, demineralized water or filtered seawater. Under these conditions early research has demonstrated the indifference of alkali and alkali-earth metal ions to chitosan, and concomitant chelation of a number of transition metal ions according to the complex stability series of Irving and Williams (1953), with retention of a certain degree of crystallinity of the polysaccharide as evidenced by X-ray diffraction measurements (Muzzarelli & Sipos, 1971; Muzzarelli & Tubertini, 1969; Muzzarelli, Raith, & Tubertini, 1970).

When complicated conditions are faced or enhanced performances are desired, the chitosan can be derivatized chemically or enzymatically to impart enhanced chelating capacity, or can be prepared as composites (for example with cellulose or with calcium carbonate); raw chitinous materials can be used such as spent fungal mycelia and clean crustacean shells; the aqueous solutions can be made to simulate various fluids of industrial or biochemical interest, and field conditions may vary from sea floor to polluted lakes. Chitosan can be further manipulated: it is often crosslinked to confer better microbiological and mechanical resistance; it is electrospun to make nanofilaments; it is manufactured in the form of nanoparticles and nanocrystals that have enormous specific surface area; it can be associated to other compounds to improve its porosity; it can be grafted to artificial polymers to obtain superabsorbents; its molecular weight and its degree of acetylation can be altered as desired. Experiments were carried out with the aid of microwaves, ultrasounds, gamma rays. This is just to say that the collection of metal species can be performed in a large variety of ways that prevent direct comparisons of metal ion behavior, but are tuned to perform exceptionally sharp separations/isolations.

In practice, the alkali metal ions (from lithium to cesium) and the alkali-earth metal ions (from magnesium to strontium) are not collected by chitosans to the point that retained traces are below detection limits. The first transition metal ions are collected by chitosan with the notable exception of manganese, because they form oxyanions (titanate, vanadate and chromate): vanadate is collected on chitosan at the impressive ratio of 2.3:1 by weight in the product obtained. This demonstrates that this is not anionexchange, but the sum of interactions of various kinds (Muzzarelli & Rocchetti, 1974). Opposite to that, the metal ions from iron to zinc undergo genuine chelation (see below). On the other hand, when we deal with elements of the second transition row, we must consider that their chemical behavior toward chitosan does not match the behavior of their mentioned homologues, and we should be aware that it will deviate from the rules of ion-exchange and chelation: for example, Zr, Mo and Ru behave in peculiar ways as demonstrated by specific research data enabling their isolation from marine water and nuclear plant effluents (Muzzarelli, Rocchetti, & Marangio, 1972): insoluble chitosan polymolybdate forms immediately even in the presence of the most effective complexing agents like thiocyanate enabling one to perform spectacular separations of chitosan molybdate from practically all metal ions (Muzzarelli & Rocchetti, 1973). Ru is collected even in the form of nitrosyl ruthenium complex, that is the species generated in certain nuclear operations (Muzzarelli & Tubertini, 1970). W, Au and Hg (third transition) are also atypical, insofar as chitosan tungstate, a light blue compound exhibiting reversible photochromic effect, can contain a prevailing portion of polytungstate; chlorocomplexes of gold (as well as of other precious metals) are promptly collected on chitosan to be supported on silica as a catalyst for hydrogenation reactions; the exposure of a thin film of chitosan tetrachloroaurate to UV light (253.7 nm) generates a clear photoinduced mirror made of aggregated colloidal gold particles stabilized by chitosan. Less than 15 g of chitosan were used to lower the Hg concentration from 1 to 0.02 ppm with volume reduction factors of 2000–10,000 (Muzzarelli and Rocchetti, 1974a,b); even the extremely toxic dimethyl mercury does not escape collection on chitosan. The three natural actinides Th, Pa and U are also peculiar, considering their affinity for oxygen among other aspects, as demonstrated by the fact that the uranyl ion collection on chitosan leads to deposits of mixed uranium oxides. Seawater spiked with μg amounts of ^{233}U and percolated through a 6 cm×0.5 cm chitosan column was completely depurated from U (Muzzarelli, 1971). The thorium(IV) removal from sea water was studied at different adsorbent doses between 0.25 and 10.0 g/l using chitosan and poly(methacrylic acid)-grafted chitosan + bentonite. For the quantitative removal of 100 mg/l Th(IV) from 1.0 l sea water, a minimum of 8.2 g chitosan or 2.0 g poly(methacrylic acid)-grafted chitosan + bentonite was required. In fact, the latter was about 4.1 times more effective than chitosan. The desorption produced by 0.1 M HNO_3 was 97.2% (Anirudhan, Rijith, & Tharun, 2010).

Incidentally, two adjacent elements (atomic number 81 and 82), namely Tl and Pb behave in opposite ways toward chitosan, the former being insensitive to chitosan (Muzzarelli and Tubertini, 1970a,b), while the latter is strongly bound. Certain topics, such as the collection of chromate, lead and silver are still attracting much attention and each of them is currently the subject of a large scientific production, mainly involving modified chitosans, rather than plain chitosan or chitin-bearing biomaterials.

Prior to examining the problem of the collection of uranium from sea water, we must consider the natural conditions rather than the analytical approaches. To become feasible, the collection of U from waters should be planned in such a way as to take into consideration the following aspects: (i) chemical species, generally carbonate or hydroxide complexes of the uranyl cation, depending on the pH value; (ii) seasonal variations of salinity and temperature; (iii) occurrence of reducing compounds and microbes, besides hydrolytic microbial enzymes, and suspended matter undergoing slow sedimentation; (iv) immersion and anchoring of a device holding the supported chitosan exposed to currents and tides; (v) physical form of chitosan, in principle offering large porosity and specific surface area, but capable to sustain mechanical stress; (vi) chemical form of chitosan, preventing degradation and colonization, but still capable to collect enough uranyl complexes to initiate the U oxide deposition and spontaneous growth; (vii) microbiological resistance of the manufactured components; (viii) engineering and financial aspects.

These being the essential terms of the problem, it is possible to find in the interdisciplinary literature enough data to provide inspiration and to support novel approaches for a better exploitation of the inherent characteristics of uranium and chitosan. Of course the recovery of uranium from contaminated waters in urban areas and battlefields appears simpler as far as chitosan is concerned, but more problematic due to the presence of inhabitants.

3.1. The chitin–glucan complex

Filamentous fungi, such as *Aspergillus niger* used for manufacturing citric acid, are not associated with proteins; mycelia do not contain many carbohydrates. Therefore, the preparation of the polysaccharide complex from the chitosan–glucan is not so expensive as the preparation of the chitin and chitosan from crustacean shells. Moreover, the fungal chitosan–glucan complex is less crystalline and more expanded, which means that it is more accessible to chemicals. In contrast to crustacean chitin/chitosan, information related to the metal removal using the fungal chitin–glucan complex or its derivatives is scarce; however, recent applications coherently show the advantages of fungal polysaccharides in the removal of metal ions (Skorik, Pestov, & Yatluk, 2010). Muzzarelli, Tanfani, and Scarpini (1980) and Muzzarelli, Tanfani, and Emanuelli (1981) studied the chitosan–glucan complexes isolated from different fungi (*A. niger*, *Streptomyces*, *Mucor rouxii*, *Phycomyces blakesleeanus*, *Choanephora cucurbitarum*) and found that they were more powerful than crustacean chitosan in selectively collecting transition metal ions from aqueous solutions. Among others, Yakubu and Dudeney (1986) studied the biosorption of U with *A. niger*, and concluded that the mycelia would not compete with synthetic resins in conventional U production, based on considerations about mechanical resistance to high flow-rates, and poor selectivity (except in the presence of prevailing concentrations of alkali metal ions). The recovery of uranium was mentioned as one of the biotechnological applications of chitosan (Hirano, 1996).

The Cu^{2+} adsorption onto fungal chitosan derived from *Absidia glauca* were studied by Hu, Hu, Ho, and Yeung (2004) with particular attention to the kinetics and thermodynamics; Nud'ga, Petrova, Ganicheva, Baklagina, and Petropavlovskii (2000) reported the adsorption capacity of chitin–glucan derivatives of different origin (*A. niger* and *Fomes fomentarius*) with respect to Cr^{3+} ions and found the carboxymethylated chitin–glucan complex to be the most effective adsorbent for Cr^{3+} in acidic media. *A. niger* structural cell-wall polysaccharides were also used for the sorption of radioactive isotopes $^{54}Mn^{2+}$, $^{60}Co^{2+}$, $^{137}Cs^{+}$, $^{233}UO_2{}^{2+}$, and stable lead and uranium (Feofilova, Mar'in, Tereshina, Nemsev, & Kozlov, 2000; Tereshina, Marin, Kosyakov, Kozlov, & Feofilova, 1999). High collection capacity for U on *Mucor miehei* (>230 mg/g) was explained in terms of hydroxide deposition at pH 5 or higher (Guibal, Roulph, & Le Cloirec, 1992).

3.2. Deposition on clean crab shells

Adsorption on clean crab shells generated from seafood processing byproducts is an important and cheap process. In fact, chitin is known to chelate heavy metal ions for wastewater treatment purposes: for instance, chelation of cadmium and lead from contaminated effluents by chitin has been reported by Barriada, Herrero, Prada-Rodriguez, and Sastre de Vicente (2007), as well as of chromium, cadmium, copper, lead, and zinc by Yang and Zall (1984). Cadmium, chromium, mercury, zinc, copper, lead, iron, silver, molybdenum, vanadium and nickel are major pollutants in

Table 1
Binding constants and thermodynamic parameters for the chelation of transition metals by Sigma–Aldrich chitin. Metal ions in 5 mM solutions added to chitin 0.05 mM suspension in nanopure degassed water at 25 °C. Data obtained by isothermal microcalorimetry by Camci-Unal and Pohl (2010).

Cation	Binding constant ($K\,10^{-3}\,M^{-1}$)	Enthalpy ΔH (kJ/mol)	Free energy of binding ΔG (kJ/mol)
Hg^{2+}	116 ± 12	−174 ± 2.1	−29.3
Cu^{2+}	29.1 ± 1.6	−142 ± 2.9	−25.6
Ni^{2+}	22.5 ± 3.0	−37.7 ± 3.8	−24.9
Fe^{2+}	22.4 ± 3.5	−439 ± 15.9	−23.9
Cr^{3+}	14.5 ± 1.4	−249 ± 12.1	−23.6
Fe^{3+}	14.1 ± 0.9	−498 ± 15.5	−22.6
Pb^{2+}	10.6 ± 0.8	−136 ± 5.9	−23.1
Zn^{2+}	6.90 ± 0.5	−87.0 ± 3.8	−22.0
Cd^{2+}	6.81 ± 0.7	−41.6 ± 2.5	−21.9
Ag^{+}	5.77 ± 0.4	−233 ± 5.9	−21.0
Co^{2+}	3.96 ± 0.5	−82.8 ± 5.9	−20.7

industrial wastewater and are of particular interest (Niu & Volesky, 2006).

In a series of isothermal microcalorimetry titrations, Co^{2+} gave the weakest interaction with chitin, with a binding constant of 3960 M^{-1}, while Hg^{2+} gave 116,000 M^{-1} (ca. 30-fold difference). No detectable binding of Mg^{2+} and Ca^{2+} with chitin was found, nor with Mn^{2+} and Tl^{+}, as a brilliant confirmation of data obtained 40 years before by radiochemistry and atomic absorption spectrometry. The overall order of binding constants toward chitin was determined to be the one in Table 1.

The binding of all these cations to chitin takes place with negative enthalpy and negative free energy values and it is enthalpically driven with negative change in entropy values at 25 °C (Camci-Unal & Pohl, 2010). Said binding trend is similar to that of chitin–cellulose composite fiber, i.e., $Hg^{2+} > Cu^{2+} > Pb^{2+} > Ni^{2+} > Cd^{2+}$ (Izumi, Shimizu, & Higashimura, 2002) because in both instances the accessible surface is much larger than in chitosan beads. In addition, the Irving and Williams (1953) series of metal complex stability was found to hold for the chelation efficacy of chitosan in pure aqueous solutions. This trend is consistent with previously reported studies on chitosan in which the binding followed the pattern: $Cu^{2+} > Fe^{2+} > Zn^{2+} > Cd^{2+}$ (Kim, 2004).

An additional important point is that certain metals capable to form oxyanions such as Mo, W and V, or exhibiting a plurality of oxycations as it is the case for U, recognize certain surfaces where they are initially collected by ionic mechanisms, as surfaces favoring the growth of inorganic deposits. The initial collection is followed by nucleation so that nodules grow on the polysaccharide surface. This phenomenon parallels the spontaneous formation of manganese nodules at certain depths in the marine environment, as promoted by certain debris like shark teeth. In aqueous samples uranium forms oligomeric species with increasing pH values. It exists predominantly as uranyl ion ${UO_2}^{2+}$ and partially as $UO_2(OH)^+$ at pH values ≤5, and it forms colloidal or oligomeric species, such as $(UO_2)_2(OH)_2{}^{2+}$, $(UO_2)_3(OH)_5{}^{+}$, $(UO_2)_4(OH)_7{}^{+}$, and $(UO_2)_3(OH)_7{}^{-}$ at approximately neutral pH values.

3.3. Some insight on geochemical data

Water and sediment measurements of iron, manganese, vanadium, uranium, rhenium, and molybdenum along a transect off Washington State (USA), carried out by Morford, Emerson, Breckel, and Kim (2005), Morford et al. (2007) proved that trace metals respond to the extent of reducing conditions in a predictable way. Concentrations of redox-sensitive trace metals (U, Re, V and Mo), which are soluble under oxic conditions but precipitate (or adsorb) under anoxic conditions, have been used to identify the redox state of sediments. There has been extensive research of these elements under oxic and anoxic conditions (Anderson, LeHuray, Fleisher, & Murray, 1989; Barnes & Cochran, 1993; Calvert & Piper, 1984; Cochran, Carey, Sholkovitz, & Surprenant, 1986; Wanty, Goldhaber, & Northrop, 1990), but more recent research has focused on continental margin settings where intermediate reducing conditions prevail (Crusius & Thomson, 2000; Klinkhammer & Palmer, 1991; Zheng, Anderson, van Geen, & Fleisher, 2002).

A compilation of literature shows large Re accumulation rates (>100 ng cm^{-2} kyr^{-1}) when oxygen penetrates less than 1 cm below the sediment–water interface. Re accumulation in sediments appears to be solely due to the extent of reducing conditions, and therefore rhenium is a model tracer for intermediate reducing conditions. Both V and Mo clearly associate with Mn cycling, whereas U may be associating with either Mn oxides and/or Fe oxyhydroxides. From peaks of uranium in deep sea sediments, we learn that this redox-sensitive trace element diffuses from seawater into reducing sediments and accumulates there: it should be no surprise then if a material surface endowed with reducing power can induce the deposition of considerable amounts of uranium species.

The observation in the marine environment that uranium accumulates at higher rates in reducing than in oxidized sediments raised considerable scientific interest for its use as a proxy of past environmental changes of the ocean (Mangini, Jung, & Laukenmann, 2001). The most commonly identified pathway to explain the accumulation of authigenic U in reduced sediments is the microbially mediated reduction of U(VI), which exists as a soluble carbonate complex in oxygenated seawater, to less soluble U(IV) at redox conditions close to those allowing Fe(III) or sulfate reduction (Klinkhammer & Palmer, 1991; Lovley, Phillips, Gorby, & Landa, 1991). As a result of this redox transformation, a U concentration gradient develops across the sediment–water interface, driving a flux of dissolved U into the sediments whose magnitude is believed to depend on the depositional rate of organic matter at the seafloor and/or the O_2 level in bottom water. However, the quantitative use of U as a paleoceanographic tracer is still limited by incomplete knowledge of the exact U fixation mechanism. Laboratory batch experiments, together with spectroscopic measurements, have also shown that U(VI) can be partially reduced by sulfide minerals such as galena, pyrite, mackinawite and amorphous FeS and precipitated as UO_2 or mixed U(VI) and U(IV) solids. Of particular interest is the fact that U(VI) removal by amorphous FeS occurs in two steps: a rapid exchange of Fe(II) for U(VI), followed by a slow and partial reduction of U(VI) by structural Fe(II), leading to the formation of UO_2 and other solids involving U(IV) (Chappaz, Gobeil, & Tessier, 2010).

Preliminary works with uranyl nitrate solutions have shown that chitosans in a reducing milieu can induce deposition of U mixed oxides to the point that the final material is more inorganic than organic in nature, i.e., the inorganic content calculated as UO_3 is over one half by weight. A chitosan modified with ascorbic acid, a reducing compound, collected 800 mg U/g from uranyl nitrate solutions at pH 4.6; and exhibited a bright orange color. In the concentration interval 0.5–5.0 mM, the collection percent-

Table 2
Isotherms for the collection of uranium (mg/g) at pH 4.5 on the ascorbate derivative of chitosan (NDTC), emulsan, the bioemulsifier of *Acinetobacter calcoaceticus* composed of *N*-acetylgalactosamine and *N*-acetylaminouronans, and the *Rhizopus arrhizus* mycelia.

U equilibrium concentration, mg/l	Polysaccharidic materials		
	U, mg/g of NDTC chitosan	U, mg/g of emulsan	U, mg/g of *R. arrhizus* mycelia
1	50	11	33
10	190	60	42
100	>1000	215	160
1000	$\gg$1000	360	190

Muzzarelli et al. (1986), original results.

age was higher than 90 in the batch mode within minutes after contact (Muzzarelli, 1985a,b,c; Muzzarelli, Bregani, & Sigon, 1986; Muzzarelli, Tanfani, & Emanuelli, 1984a,b) evidently because of reduction and nucleation phenomena promoted by the ascorbate moiety and the chitosan, respectively. The chitosan derivative was tested simultaneously as the *Rhizopus arrhizus* mycelia, and emulsan, the bioemulsifier of *Acinetobacter calcoaceticus*, under the same conditions: the data in Table 2 underline the superiority of said modified chitosan.

The *R. arrhizus* mycelia biomass was examined in detail by Tobin, Cooper, and Neufeld (1984) who reported that all of the 11 cations tested were adsorbed, but not the alkali metal ions, the highest uptake being observed for the uranyl ion (0.82 mmol/g at pH 3.5, that appears to be the maximum capacity, in agreement with the data in Table 1). These results were confirmed one decade later by another group (Sauceso, Guibal, Roulph, & Le Cloirec, 1992).

4. Ecologically acceptable removal of U, Pb and other heavy metals

Effective treatments of industrial waste streams and toxic spills containing heavy metals depend on the rapid removal of metal ions. Tudor, Gryte, and Harris (2006) described a method using minimally processed mollusk shells and crustacean exoskeletons. Compared to calcium carbonate of geologic origin, biomineralized shell materials exhibit extremely rapid sequestration of metal ions: the 1 g/l Pb concentration was reduced to less than 0.5 mg/l in 5 min by using comminuted shell of clam *Mercenaria mercenaria*, while at higher initial concentrations, the shells of both oyster *Crassostrea virginica* and clam can extract almost twice their weight of Pb.

The uptake mechanism involves the exchange of Ca for Pb in the inorganic fraction of the shell structure. Results highlight the importance of both surface area and the presence of the organic matrix of biominerals in determining the rate and quantity of metal ions collected. For example, the specific surface area of the materials used was: lobster carapaces 19.1; oyster shells 8.7; chitosan 2.0; limestone 1.5; calcite 0.8 m^2/cm^3: this point is confirmed by measurements with electrospun chitosan nanofibers (ca. 235 nm diameter) for which the equilibrium adsorption capacity (from Langmuir isotherm data) for Pb^{2+} was as high as 263.15 mg/g (Haider & Park, 2009). The $CaCO_3$ content was ca. 93 and 57% for the oyster and lobster materials, respectively. Remarkably, the lobster carapace had porosity 26.3%, i.e., ca. 6-fold higher than the oyster shells. The consequent results indicated that over a 24-h period the clam, oyster and crustacean materials collected nearly the total amount of Pb from dilute solutions under the adopted conditions, while chitosan collected just 35.8%. At high metal concentrations however, ion exchange favored Ca-bearing materials. The equilibrium isotherm showed that crab shell particles collected lead to the extent of 1.3 g Pb/g. The removal of lead occurred mainly through dissolution of $CaCO_3$ followed by precipitation of $Pb_3(CO_3)_2(OH)_2$ and $PbCO_3$ near the surface of crab shell. Micro precipitates were adsorbed to the chitin on the surface of the crab shell particles (Lee, Park, & Yang, 1997; Tudor et al., 2006).

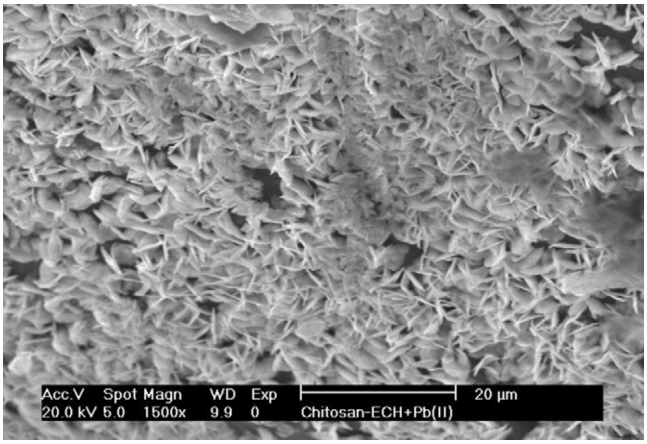

Fig. 1. An example of spontaneous deposition and growth: SEM image of epichlorohydrin-crosslinked chitosan (having specific surface area $2.9 \pm 0.6\,m^2/g$) after sorption of Pb^{2+}. A striking feature is the appearance of needle-edge crystal-like deposits on the surface. Unpublished image.
Courtesy of Dr. A. Kamari, School of Chemistry, University of Glasgow, Glasgow, Scotland, UK. (Experimental details in Kamari, Pulford, & Hargreaves, 2011).

The removal of Pb by crab shell particles was investigated by Lee, Lee, Shin, Kajiuchi, and Yang (1998): approximately 99% of the lead was removed within 2 h after contact with the particles. The removal efficiency was slightly affected by the initial pH over 3.0. In addition, when the crab shell amount increased from 0.5 to 1.5 g/l, the 84% removal efficiency went up to 99.8% at initial pH 2.0. Maximum uptake of lead was 870 mg Pb/g crab shell at initial pH 3.0 (Lee et al., 1998) (Fig. 1).

Crab shells from *Portunus sanguinolentus* (0.5–1 mm, etched with 0.1 M HCl and washed with water) were used as a potent biosorbent for the removal of Ce^{3+} and Eu^{3+} as well. The study revealed that calcium carbonate was responsible for adsorption through microprecipitation of the rare earth ions onto the surface of crab shell. At the optimum pH 6, crab shell exhibited maximum Ce^{3+} and Eu^{3+} collection of 144.9 and 49.5 mg/g, respectively, according to the Langmuir model (instead of 45 and 18 mg/g for fully demineralized shells). The pseudo-first order kinetic equation predicted the experimental data accurately with high correlation coefficients and low percent errors. About 96% of Ce^{3+} and 85% of Eu^{3+} were removed within 60 min (Vijayaraghavan & Balasubramanian, 2010). Under the same conditions the micro-precipitation of lanthanum carbonate $La_2(CO_3)_3$ on the surface of crab shell was found to be the main mechanism of La adsorption (see Fig. 2 in Vijayaraghavan, Mahadevan, Joshi, & Balasubramanian, 2009). That crab shell can also bind Mn^{2+} and Zn^{2+} with a maximum of 69.9 and 123.7 mg/g, respectively, at pH 6, according to the Langmuir model (Vijayaraghavan, Winnie, & Balasubramanian, in press). One may note that the collection data of manganese and europium are the lowest among the ions tested, and very far from the above reported data for lead.

What is important in these works is the illustration of the concept that the porosity of the materials, and even more their specific surface area, must be taken into account when optimizing a process. This concept was also supported in studies dealing with biosorption. The main feature of Mycoton® is the exceptionally large specific surface area ($\gg$100 m^2/g), accompanied by low ash content (<1%); Mycoton® in fact is produced from higher Basidiomycetes that include edible cultivated fungi; it has a fine fibrous structure of hollow cylindrical fibers (3–5 μm diameter, several mm length). The chitin-based fiber wall (0.2–1.0 μm thick) contains 70% chitin, 20% glucans and 10% melanins; it is strong and elastic and it is not affected by α and γ irradiation. Additional characteristics defined in decontamination operations at the Chernobyl NPP center, are efficient sorption of practically all long-lived fission products, besides uranium and transuranium elements; good chelation of many transition metal ions, low production costs and ample availability. The properties of Mycoton® were defined for U, Pu, Am, Cm (all of them with distribution coefficients as high as 10,000–40,000 in the pH interval 3.4–7.9), for the long-lived fission isotopes of Sr, Ca, Ce, Eu, and for some heavy metals: Pb, Hg, Cr, Cd, Bi (Gorovoj, Kosyakov, & Veleshko, 2002; Kosyakov, Yakovlev, & Gorovoj, 1997).

Likewise, in a study with porous and hydrophilic cellulose + chitin beads, it was observed that lead hydroxides are generated by hydrolysis, and lead carbonate results from the dissolution in water of CO_2 from the atmosphere. The stability constants, pK_{sp}, of lead precipitates are as follows: $Pb(OH)_2$, 14.93; $PbCO_3$, 13.13; $Pb_3(CO_3)_2(OH)_2$, 18.80; thus the lead carbonates might enhance the removal of lead, because it was speculated that the contribution of lead–oxygen interaction to lead adsorption may be mainly through non-specific electrostatic attraction (physical interaction). The Pb^{2+} was adsorbed by the cellulose + chitin beads at initial pH 5 as a result of three concurrent processes: complexation, adsorption and precipitation of hydrolysis products (Zhou, Zhang, & Guo, 2005).

5. Bioaccumulation, biosorption, reduction and nucleation

The immobilization of bacterial or fungal biomass in biopolymer beads has clearly improved uranium yield as well as stability of biosorbent. Biosorption is the property of spent biomasses to bind and concentrate heavy metals and radionuclides from very dilute aqueous solutions. Among microbial and non-microbial biomaterials reported to possess metal binding properties, a few have been commercialized: Algasorb® manufactured from algae, AMT-Bioclaim® developed by Advanced Mineral Technologies, Inc., and Bio-Fix® in the form of beads containing sphagnum moss, developed by the Bureau of Mines; they are manufactured in the form of a packed bed suitable for contacting a stream (Das, Vimala, & Karthika, 2008; Volesky, 2001) but do not appear to have been the subject of much research so far.

The most widely used technique for cell immobilization is cell entrapment: the living cells are enclosed in a polymeric matrix porous enough to allow the diffusion of substances to the cells, and of products away from the cells. Agar, agarose, alginate, k-carrageenan, collagen, chitin, chitosan, polyacrylamide, polyurethane, and polysulfone have been used for this purpose. For example, according to Akhtar, Khalid, Akhtar, and Ghauri (2009), *Trichoderma harzianum* (a chitin-containing fungus) once immobilized in Ca alginate performed much better than free biomass in the removal of uranium: Ca alginate itself contributed to the removal efficiency significantly (42–43% removal was achieved in controls). The collection achieved at 100, 200 and 400 mg/l initial U concentrations after 8 h of incubation at 28 °C and 200 rpm was 75.3%, 56.0% and 40.3% by free biomass and it increased to 97.3%, 89.8% and 87.5% with *T. harzianum* supported by Ca alginate. Ca alginate is *per se* a good sorbent material for recovery of uranium from aqueous solutions (Gok & Aytas, 2009).

A column (35 cm × 1.5 cm; flow-rate 5 ml/min) containing 1.5 g dry weight of immobilized *T. harzianum* purified 8.5 l of solution having 58 mg/l U concentration before breakthrough occurred, and the biosorbent became saturated after percolating 25 l. Sorbed uranium was eluted in 200 ml of 0.1 N HCl with 99% yield, with good volume reduction ratio. Akhtar et al. (2009) underlined that the SEM micrographs taken on the Ca alginate with *T. harzianum* beads showed crystals all throughout, indicative of the capacity of deposition of aggregated U compounds (see their Fig. 5): in fact when said used biomass was analyzed by EDX, signals typical of uranium were observed.

Metal-reducing microorganisms have been investigated for their capability to remove uranium selectively from aqueous solutions: *Pantoea* sp., *Pseudomonas* sp. and *Enterobacter* sp., isolated from mine soils, reduced U from hexa- to tetravalent state, $U(OH)_4(aq)$, at pH 5–6. The initial reduction rate was highest in *Pseudomonas* sp. at 30 mg/l, followed by *Pantoea* sp. Rapid and complete U reduction was observed at concentrations as high as 200 mg/l, and up to 88% removal after 24 h was reported in batches with the initial U(VI) concentration of 400 mg/l (Chabalala & Chirwa, 2010). The cultures of *Enterobacter cloacae* generally showed high resistance against U(VI) toxicity, and good performance under stress conditions. The suggested mechanisms by which bacteria may immobilize the uranyl ion, are therefore: (a) biosorption on spent biomass, (b) bioaccumulation by viable biomass, (c) precipitation by reaction with inorganic ligands such as phosphate, and (d) microbial reduction of soluble metal species to insoluble species (Chojnacka, 2010; N'Guessan, Vrionis, Resch, Long, & Lovley, 2008).

6. Cross-linked chitosans of practical interest

Cross-linked chitosans carrying catechol, iminodiacetic acid, iminodimetylphosphonic acid, phenylarsonic acid or serine functions were prepared for the collection of uranium(VI). The adsorption behavior of uranyl and other ionic species, such as metal ions and oxo-acid ions, on the cross-linked chitosan and chitosans modified with said chelating moieties was examined by column chromatography (sample, 10 ml; element concentration, 10 ng/ml; column volume, 1 ml; eluent, 1 M nitric acid). The collected uranium at pH 2–7 formed a stable chelate with the hydroxyl groups of the catechol moiety linked to the chitosan. The serine chitosan and catechol chitosan could adsorb uranyl at wider pH intervals (pH 2–7) than the other chitosans. On the serine-chitosan, U could be adsorbed quantitatively at all investigated pH values, while the other secondary amine derivatives did not adsorb it: possibly, the formation of the chelate required amino groups in the primary form, besides the carboxyl group. Also, the uranium collected was readily eluted with 1 M nitric acid. The adsorption behavior of over 50 elements was systematically examined under the same conditions (Oshita & Motomizu, 2008; Oshita, Sabarudin, Takayanagi, Oshima, & Motomizu, 2009; Oshita, Takayanagi, Oshima, & Motomizu, 2007). The uranyl ion UO_2^{2+} can be chelated by the modified chitosan with adsorption capacity of 330 mg U/g. Through the column treatment, the complete removal of large amounts of alkali and alkaline earth matrices without any loss of adsorption efficiency over prolonged usage were achieved with this modified chitosan (Sabarudin et al., 2007).

Adsorption of uranium(VI) from aqueous solution was investigated in a batch system, onto a chitosan crosslinked with epichlorohydrin (a rigid transparent gel). The uranium removal from 50 mg/l was total at pH 3.0, and then declined slightly up to pH 6. In strongly acidic solutions (pH < 2.5), the removal efficiency of uranium was negligible. Equilibrium data agreed very well with the Langmuir model; the calculated value of adsorption capacity (52.63 mg U/g) was close to the experimental value (49.05 mg U/g) (Wang, Liu, Wang, Xie, & Deng, 2009). Nevertheless, besides the kinetics data, said capacity values are not high enough for planning large scale applications. Instead it is possible to take advantage of the hydrolytic phenomena occurring when the solutions are neutral or slightly alkaline. Dutta et al. (2008)

soaked chitosan in tetrachloromethane and irradiated it with ^{60}Co γ-rays to produce two types of stably crosslinked chitosans (with >CCl_2 or >CO crosslinks), and used them as solid phase extractors for several radionuclides: the uptake followed this trend for both: $^{233}UO_2{}^{2+} > {}^{234}Th^{4+} > {}^{137}Cs^{+} > {}^{152-154}Eu^{3+} > {}^{241}Am^{3+} > {}^{85}Sr^{2+}$. In particular, they remarked that the capacity for U and Th, 35 and 39 mg U/g at pH 2, became 384 and 203 mg U/g at pH 6, respectively. The desorption with 1 M Na_2CO_3 yielded 97% ^{233}U recovery.

Oshita et al. (2008) extended their work to seawater samples for analytical purposes, and reported that U(VI) could be adsorbed almost quantitatively from pH 4 to 8. It was then easily eluted with 1 M nitric acid, and the 25-fold preconcentration of U was achieved for the determination of trace U in seawater by ICP-AES, with detection limit 0.1 ng/ml. This is the only extension of the most recent studies on chitosan to the problem of U recovery from seawater.

Chitosan was also coated on perlite, an inert support prepared as spherical beads, for adsorption of uranium from aqueous solutions. The uptake capacity of chitosan-coated perlite beads varied from 0.099 to 149 mg/g when the equilibrium concentration of uranium in the solution ranged from 11 ppb to 1000 ppm and the pH was 5. The adsorption capacity of said beads for uranium decreased by 75% in the presence of 0.45 M NaCl, whereas the adsorption capacity decreased by 55% when TiO_2 was added to the beads during their preparation. The adsorption capacity of titania-chitosan beads was 2.5–40 μg of uranium per gram of beads when the concentration of uranium was 39–734 μg/l in the presence of 0.45 M NaCl. It was 18–302 μg/g when the concentration was 0.99–47 mg/l in the presence of 0.45 M Na_2CO_3. Chitosan-coated beads were found to preferentially adsorb uranium, instead of Sr and Cs of which only a negligible amount was collected. Overall, the data suggest that the chitosans can be used for extraction of uranium from waste streams and reprocessing streams (Hasan, Ghosh, Prelas, Viswanath, & Boddu, 2007; Pang et al., 2010).

Chitosan entrapped in polyacrylamide by direct polymerization of acrylamide in a chitosan solution had higher adsorption capacity than plain chitosan for all said ions so that the sequence was $Th^{4+} > Pb^{2+} > UO_2{}^{2+}$. The affinity of the composite was higher for Pb^{2+} and $UO_2{}^{2+}$. The reusability of the composite for Pb^{2+} for five runs showed that complete recovery of the ion was possible (Akkaya & Ulusoy, 2008).

Magnetic chitosan nanocomposites were synthesized on the basis of magnetite nanoparticles functionalized with amino groups. The nanocomposites can be removed conveniently from water with the help of an external magnet. The nanocomposites were applied to remove heavy metal ions from water: those ions can be removed from chitosan in weak acidic deionized water with the aid of sonication. These nanocomposites have been used as a fast recyclable tool for Pb^{2+}, Cu^{2+} and Cd^{2+} removal from water. The relationship among the pH value, adsorption capacity, regeneration of magnetic nanocomposites, and mechanism for absorption and desorption was studied using Pb^{2+} ions. It is noteworthy that these nanocomposites have a high removal efficiency of Pb^{2+} not only in the first cycle but also in subsequent cycles (Liu, Hu, Fang, Zhang, & Zhang, 2009).

7. The collection of U from seawater: a future opportunity?

The huge amount of uranium dissolved in the seawater is 4.5 billion tons, and therefore there is interest in uranium extraction (Davies, Kennedy, McIlroy, Spence, & Hill, 1964; Kaikan and Kaikan, 1983; Ogata, 1980). The first experimental plant for collection of uranium from seawater was operated by the Agency for Natural Resources and Energy, the Ministry of International Trade and Industry, and the Metal Mining Agency of Japan from 1981 to 1988. Hydrous titanium oxide was used as an adsorbent, notwithstanding its low capacity (0.1 g U/kg). In that plant, electricity for pumping of seawater pushed up the collection cost: pumping was necessary to retard the sedimentation of adsorbents in moving bed system for effective contact between adsorbent and seawater. Additionally, the mechanical strength of adsorbent was not enough due to wearing in a moving bed system. After screening many other uranium adsorbents, the acrylonitrile fiber converted to the amidoxime form by reaction with hydroxylamine was preferred (Astheimer, Schenk, Witte, & Schwochau, 1983; Egawa & Harada, 1979).

While an adsorbent in bead form needs a package for handling and for effective contact with seawater, the fibrous adsorbent takes advantage of the ocean current and the wave motion when it is moored in the sea. In this case, however, the mechanical strength of the amidoxime fiber was not satisfactory for mooring in the seawater. To overcome this problem, the following preparation was made: (1) fibrous polyethylene (as a supporting polymer) was irradiated with electron beam of 200 kGy in nitrogen gas. (2) Irradiated nonwoven fabric was immersed into a solution composed of 35% acrylonitrile, and 15% methacrylic acid in 50% dimethyl sulfoxide, and blanketed with nitrogen. (3) It was maintained at 40 °C for 4 h for graft polymerization (Kawai et al., 2000; Nobukawa et al., 1992).

Though this adsorbent had low affinity against the alkaline metals such as Na^+ and K^+, some ionic forms of Pb, Fe, Co, Ni, and V were preferentially adsorbed from the seawater along with uranyl ions. While the U concentration in seawater is 3.2 μg/l (100-fold higher than for Pb), the distribution coefficients for said adsorbent were 2.0×10^4 for U and 3.6×10^6 for Pb, indicative of preferential uptake of Pb. Despite said major drawbacks (presence of a large percentage of inert poly(ethylene), and unfavorable distribution coefficients), the adsorbent fabric (6000 m^2, 700 kg) was produced and used for marine experiments, in the form of stacks of sheets encased in a floating frame anchored to the sea floor. The uranium collection experiment was performed from 1999 to 2001 in the Pacific Ocean 7 km offshore (Mustu-Sekine, Aomori prefecture, Japan). The total amount of uranium collected reached roughly 1 kg in terms of yellow cake (U_3O_8). The average capacity of the adsorbent was 0.5 g U/kg for 30 days soaking (Seko et al., 2003).

As an alternative, the uranium adsorption of a braid adsorbent, 60 m long, was evaluated in the sea of Okinawa, Japan. After the braid adsorbent was anchored to the sea floor, it took immediately the vertical position: its yield was 1.5 g U/kg for 30 days soaking (Seko, Tamada, Kasai, Yoshii, & Shimizu, 2002). The higher temperature of the seawater in Okinawa (30 °C) favored the U uptake, and the simpler operations lowered the costs (Shimizu & Tamada, 2004) that however were so high as to discourage scaling-up (Tamada, Seko, Kasai, & Shimizu, 2006). The cost of the uranium collection calculated for the braid system was 25,000 yen/kg U, which was roughly twice the current price, \$48/lbU_3O_8 (August, 2009). Nothing is known so far about the performance of the adsorbent after repeated regenerations, nor about the measures to be adopted if the adsorbent capacity has to be drastically improved.

On the other hand, there are indications that spent or viable chitinous biomasses might offer good performances such as those of Mycoton®: for example, the removal of uranium from seawater by *Talaromyces emersonii* biomass was not depressed by the ionic species present in the seawater (Bengtsson, Johansson, Hackett, McHale, & McHale, 1995). The production of chitosan from *M. rouxii* is being refined (Trutnau, Suckale, Groeger, Bley, & Ondruschka, 2009) and the technology for entrapping microbial cells is known (Yang & Wang, 1990). A wide range of crosslinked chitosans is available (Muzzarelli, Weckx, Filippini, & Sigon, 1989; Wang et al., 2009). Uranyl-imprinted chitosans are being developed (Liu et al., 2010), as well as specific chitosan + inorganics and chitosan+synthetics composites (Akkaya & Ulusoy, 2008; Hasan et al., 2007; Wan, Kan, Rogel, & Dalida, 2010).

8. Conclusion

The above cited Colonie pollution case has been pointed out as a reasonable analogue of battlefield contamination by depleted uranium (Lloyd et al., 2009). Uranium isotope ratios have revealed the extent and spatial distribution of contamination by depleted uranium (Vukanac, Novkovic, Kandic, Djurasevic, & Milosevic, in press). Of course it is very hard to plan the decontamination of such a heavily inhabited area, but the story tells that the prevention of the contamination by the use of filters, although feasible, was neglected. This is significant within the context of emissions from battlefield deployment of depleted U ammunitions. In the Balkans, soils, agricultural goods, and drinking water supplies were not compromised with depleted U from ammunition used in the war. Although there are concerns related to the environmental fate of ammunition left in the battlefield, analyses of foods and uranium bioassay in human urine indicated that uranium concentrations are similar to general background levels in the Balkans: areas contaminated with depleted U deserve monitoring and surveillance to avoid occasional contamination of persons (Macfarlane et al., 2003). Lethal poisoning of troops has been reported, however.

The impression is that chitins and chitosans still have chances to play some significant role in the scenario of U collection from seawater, because the recently reported chitin + nylon textiles (He, Christopher, Zhou, Nie, & Zhu, 2010; Tseng, Hsu, Wu, Hsueh, & Tu, 2009; Zhang et al., 2009, 2010) might be suitable for marine operations in terms of resistance to mechanical stress and to biodegradation, and certain marine materials could be used in economically acceptable ways to collect spontaneously growing aggregates of uranium compounds.

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References

Akhtar, K., Khalid, A. M., Akhtar, M. W., & Ghauri, M. A. (2009). Removal and recovery of uranium from aqueous solutions by Ca alginate immobilized *Trichoderma harzianum*. *Bioresource Technology*, *100*, 4551–4558.

Akkaya, R., & Ulusoy, U. (2008). Adsorptive features of chitosan entrapped in polyacrylamide hydrogel for Pb^{2+}, ${UO_2}^{2+}$ and Th^{4+}. *Journal of Hazardous Materials*, *151*, 380–388.

Anderson, R. F., LeHuray, A. P., Fleisher, M. Q., & Murray, J. W. (1989). Uranium deposition in Saanich Inlet sediments, Vancouver Island. *Geochimica et Cosmochimica Acta*, *53*, 2205–2213.

Anirudhan, T. S., Rijith, S., & Tharun, A. R. (2010). Adsorptive removal of thorium(IV) from aqueous solutions using poly(methacrylic acid)-grafted chitosan/bentonite composite matrix: Process design and equilibrium studies. *Colloids and Surfaces*, *A-368*, 13–22.

Astheimer, L., Schenk, H. J., Witte, E. G., & Schwochau, K. (1983). Development of sorbers for the recovery of uranium from seawater. Part 2. *Separation Science and Technology*, *18*, 307–339.

Bailey, S. E. (1999). A review of potentially low-cost sorbents for heavy metals. *Water Research*, *11*, 2469–2479.

Barnes, C. E., & Cochran, J. K. (1993). Uranium geochemistry in estuarine sediments: Controls on removal and release processes. *Geochimica et Cosmochimica Acta*, *57*, 555–569.

Barriada, J. L., Herrero, R., Prada-Rodriguez, D., & Sastre de Vicente, M. E. S. (2007). Waste spider crab shell and derived chitin as low-cost materials for cadmium and lead removal. *Journal of Chemical Technology and Biotechnology*, *82*, 39–46.

Bengtsson, L., Johansson, B., Hackett, T. J., McHale, L., & McHale, A. P. (1995). Studies on the biosorption of uranium by *Talaromyces emersonii* CBS 814.70 biomass. *Applied Microbiology and Biotechnology*, *42*, 807–811.

Bhatnagar, A., & Sillanpaa, M. (2009). Applications of chitin and chitosan derivatives for the detoxification of water and wastewater: A short review. *Advances in Colloid and Interface Science*, *152*, 26–38.

Bleise, A., Danesi, P. R., & Burkart, W. (2003). Properties, use and health effects of depleted uranium: A general overview. *Journal of Environmental Radioactivity*, *64*, 93–112.

Calvert, S, & Piper, D. Z. (1984). Geochemistry of ferromanganese nodules from Domes Site A, Northern Equatorial Pacific: Multiple diagenetic metal sources in the deep sea. *Geochimica et Cosmochimica Acta*, *48*, 1913–1928.

Camci-Unal, G., & Pohl, N. L. B. (2010). Quantitative determination of heavy metal contaminant complexation by the carbohydrate polymer chitin. *Journal of Chemical and Engineering Data*, *55*, 1117–1121.

Chabalala, S., & Chirwa, E. M. N. (2010). Uraniun(VI) reduction and removal by high performing purified anaerobic cultures from mine soil. *Chemosphere*, *78*, 52–55.

Chappaz, A., Gobeil, C., & Tessier, A. (2010). Controls on uranium distribution in lake sediments. *Geochimica et Cosmochimica Acta*, *74*, 203–214.

Chojnacka, K. (2010). Biosorption and bioaccumulation, the prospects for practical applications. *Environmental International*, *36*, 299–307.

Ciardelli, F., Tsuchida, E., & Woehrle, D. (Eds.). (1996). *Macromolecule-Metal Complexes*. Berlin: Springer.

Cochran, J. K., Carey, A. E., Sholkovitz, E. R., & Surprenant, L. D. (1986). The geochemistry of uranium and thorium in coastal marine sediments and sediment pore waters. *Geochimica et Cosmochimica Acta*, *50*, 663–680.

Crusius, J., & Thomson, J. (2000). Comparative behavior of authigenic Re, U, and Mo during reoxidation and subsequent long-term burial in marine sediments. *Geochimica et Cosmochimica Acta*, *64*, 2233–2242.

Darolles, C., Broggio, D., Feugier, A., Frelon, S., Dublineau, I., De Meo, M., & Petitot, F. (2010). Different genotoxic profiles between depleted and enriched uranium. *Toxicology Letters*, *192*, 337–348.

Das, N., Vimala, R., & Karthika, P. (2008). Biosorption of heavy metals: An overview. *Indian Journal of Biotechnology*, *7*, 159–169.

Davies, R. V., Kennedy, J., McIlroy, R. W., Spence, R., & Hill, K. M. (1964). Extraction of uranium from seawater. *Nature*, *203*, 1110–1115.

Dutta, S., Mohapatra, P. K., Ramnani, S. P., Sabharwal, S., Das, A. K., & Manchanda, V. K. (2008). Use of chitosan derivatives as solid phase extractors for metal ions. *Desalination*, *232*, 234–242.

Egawa, H., & Harada, H. (1979). Recovery of uranium from sea water by using chelating resins containing amidoxime groups. *Nippon Kagaku Kaishi*, *1979*, 958–959.

Ehrlich, H. (2010). Chitin and collagen as universal and alternative templates in biomineralization. *International Geology Review*, *52*, 661–699.

Elwakeel, K. Z. (2010). Environmental application of chitosan resins for the treatment of water and wastewater: A review. *Journal of Dispersion Science and Technology*, *31*, 273–288.

Feofilova, E. P., Mar'in, A. P., Tereshina, V. M., Nemsev, D. M., & Kozlov, V. R. (2000). Role of components of cell walls in metal uptake by *Aspergillus niger*. *Resources and Environmental Biotechnology*, *3*, 61–69.

Gok, C., & Aytas, S. (2009). Biosorption of uranium(VI) from aqueous solution using calcium alginate beads. *Journal of Hazardous Materials*, *168*, 369–375.

Gorovoj, L., Kosyakov, V., & Veleshko, I. (2002). Chitin biosorbents for radioactive waste decontamination. In R. A. A. Muzzarelli, & C. Muzzarelli (Eds.), *Chitosan in Pharmacy and Chemistry* (pp. 353–358). Grottammare, Italy: Atec.

Guibal, E. (2004). Interactions of metal ions with chitosan-based sorbents: A review. *Separation and Purification Technology*, *38*, 43–74.

Guibal, E., Roulph, A., & Le Cloirec, P. (1992). Uranium biosorption by a filamentous fungus *Mucor miehei* pH effect on mechanisms and performances of uptake. *Water Research*, *26*, 1139–1145.

Guy, R. H., Hostynek, J. J., Hinz, R. S., & Lorence, C. R. (1999). *Metals and the Skin*. New York: Dekker.

Haider, S., & Park, S. Y. (2009). Preparation of the electrospun chitosan nanofibers and their applications to the adsorption of Cu(II) and Pb(II) ions from an aqueous solution. *Journal of Membrane Science*, *328*, 90–96.

Hasan, S., Ghosh, T. K., Prelas, M. A., Viswanath, D. S., & Boddu, V. M. (2007). Adsorption of uranium on a novel bioadsorbent-chitosan-coated perlite. *Nuclear Technology*, *159*, 59–71.

He, Z. Y., Christopher, B. W., Zhou, Y. T., Nie, H. L., & Zhu, L. M. (2010). Papain adsorption on chitosan-coated nylon-based immobilized metal ion (Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}) affinity membranes. *Separation Science and Technology*, *45*, 525–534.

Hirano, S. (1996). Chitin biotechnology applications. *Biotechnology Annual Review*, *2*, 237–258.

Hu, K. J., Hu, J. L., Ho, K. P., & Yeung, K. W. (2004). Screening of fungi for chitosan producers, and copper adsorption capacity of fungal chitosan and chitosanaceous materials. *Carbohydrate Polymers*, *58*, 45–52.

Irving, H., & Williams, R. J. P. (1953). The stability of transition-metal complexes. *Journal of the Chemical Society*, *1953*, 3192–3210.

Izumi, S., Shimizu, Y., & Higashimura, T. (2002). Absorption behavior of metal ions on chitin/cellulose composite fibers with chemical modification by EDTA. *Textile Research Journal*, *72*, 515–519.

Kaikan, K., & Kaikan, T. (Eds.). (1983). *Recovery of Uranium From Seawater*. Tokyo: Atomic Energy Society of Japan.

Kamari, A., Pulford, I. D., & Hargreaves, J. S. J. (2011). Chitosan as a potential amendment to remediate metal contaminated soil: A characterisation study. *Colloids and Surfaces*, *B-82*, 71–80.

Kawai, T., Saito, K., Sugita, K., Kawakami, T., Kanno, A., Katakai, A., Seko, N., & Sugo, T. (2000). Preparation of hydrophilic amidoxime fibers by cografting acrylonitrile and methacrylic acid from optimized composition. *Radiation Physics and Chemistry*, *59*, 405–411.

Kim, H. S. (2004). Thermodynamic studies of interaction between chitosan and metal ions by isothermal titration calorimetry. *Journal of Industrial Engineering and Chemistry*, *10*, 273–277.

Klinkhammer, G. P., & Palmer, M. R. (1991). Uranium in the oceans: Where it goes and why. *Geochimica et Cosmochimica Acta*, *55*, 1799–1806.

Kosyakov, V. N., Yakovlev, N. G., & Gorovoj, L. F. (1997). Utilisation of chitin–chitosan biosorbents for environmental deactivation and radioactive waste management. *Biotechnology for Waste Management and Site Restoration*, *34*, 119–131.

Kurttio, P., Harmoinen, A., Saha, H., Salonen, L., Karpas, Z., Komulainen, H., & Auvinen, A. (2006). Kidney toxicity of ingested uranium from drinking water. *American Journal of Kidney Diseases*, *47*, 972–982.

Lee, M. Y., Lee, S. H., Shin, H. J., Kajiuchi, T., & Yang, J. W. (1998). Characteristics of lead removal by crab shell particles. *Process Biochemistry*, *33*, 749–753.

Lee, M. Y., Park, J. M., & Yang, J. W. (1997). Micro precipitation of lead on the surface of crab shell particles. *Process Biochemistry*, *32*, 671–677.

Li, C. B., Hein, S., & Wang, K. (2008). Biosorption of chitin and chitosan. *Materials Science and Technology*, *24*, 1088–1099.

Liu, X. W., Hu, Q. Y., Fang, Z., Zhang, X. J., & Zhang, B. B. (2009). Magnetic chitosan nanocomposites: A useful recyclable tool for heavy metal ion removal. *Langmuir*, *25*, 3–8.

Liu, Y. H., Cao, X. H., Le, Z. G., Luo, M. B., Xu, W. Y., & Huang, G. L. (2010). Preconcentration and determination of trace uranium(VI) in environments using ion-imprinted chitosan resin via solid phase extraction. *Journal of the Brazilian Chemical Society*, *21*, 533–540.

Lloyd, N. S., Chenery, S. R. N., & Parrish, R. R. (2009). The distribution of depleted uranium contamination in Colonie, NY, USA. *Science of the Total Environment*, *408*, 397–407.

Lovley, D. R., Phillips, E. J. P., Gorby, Y. A., & Landa, E. R. (1991). Microbial reduction of uranium. *Nature*, *350*, 413–416.

Lynam, D. R., Piantanida, L. G., & Cole, J. F. (1981). *Environmental Lead*. New York: Academic Press.

Macfarlane, G. J., Biggs, A. M., Maconochie, N., Hotopf, M., Doyle, P., & Lunt, M. (2003). Incidence of cancer among UK Gulf war veterans: Cohort study. *British Medical Journal*, *327*, 1373–1379.

Mangini, A., Jung, M., & Laukenmann, S. (2001). What do we learn from peaks of uranium and of manganese in deep sea sediments? *Marine Geology*, *177*, 63–78.

Morford, J. L., Emerson, S. R., Breckel, E. J., & Kim, S. H. (2005). Diagenesis of oxyanions (V, U, Re, and Mo) in pore waters and sediments from a continental margin. *Geochimica et Cosmochimica Acta*, *69*, 5021–5032.

Morford, J. L., Martin, W. R., Kalnejais, L. H., Francois, R., Bothner, M., & Karle, I. M. (2007). Insight on geochemical cycling of U, Re and Mo from seasonal sampling in Boston Harbor, Massachusetts, USA. *Geochimica et Cosmochimica Acta*, *71*, 895–917.

Muzzarelli, R. A. A. (1971). *Applications of Natural Polymers in Marine Ecology* Principauté de Monaco: Musée Océanographique: Revue Internationale d'Océanographie Médicale., pp. 93–103.

Muzzarelli, R. A. A. (1973). *Natural Chelating Polymers*. Oxford, UK: Pergamon Press.

Muzzarelli, R. A. A. (1977). *Chitin*. Oxford, UK: Pergamon Press.

Muzzarelli, R. A. A. (1985a). Chitin. In G. O. Aspinall (Ed.), *The Polysaccharides* (pp. 417–450). New York: Academic Press.

Muzzarelli, R. A. A. (1985b). Chitin. In J. I. Kroschwitz (Ed.), *Encyclopedia of Polymer Science and Engineering* (pp. 430–441). New York: John Wiley.

Muzzarelli, R. A. A. (1985c). Removal of uranium from solutions and brines by a derivative of ascorbic acid and chitosan. *Carbohydrate Polymers*, *5*, 85–89.

Muzzarelli, R. A. A., Bregani, F., & Sigon, F. (1986). Chelation capacity of aminoacid glucans and sugar acid glucans derived from chitosan. In H. Eccles, & S. Hunt (Eds.), *Immobilization of ions by bio-sorption* (pp. 173–182). Chichester, England: Ellis Horwood.

Muzzarelli, R. A. A., Raith, G., & Tubertini, O. (1970). Separations of trace elements from sea water, brine and sodium and magnesium salt solutions by chromatography on chitosan. *Journal of Chromatography*, *47*, 414–420.

Muzzarelli, R. A. A., & Rocchetti, R. (1973). The determination of molybdenum in sea water by hot graphite atomic absorption spectrometry after concentration on *p*-aminobenzyl cellulose or chitosan. *Analytica Chimica Acta*, *64*, 371–379.

Muzzarelli, R. A. A., & Rocchetti, R. (1974a). The determination of vanadium in sea water by hot graphic atomic absorption spectrometry on chitosan, after separation from salt. *Analytica Chimica Acta*, *70*, 283–289.

Muzzarelli, R. A. A., & Rocchetti, R. (1974b). The use of chitosan columns for the removal of mercury from waters. *Journal of Chromatography*, *96*, 115–121.

Muzzarelli, R. A. A, Rocchetti, R., & Marangio, G. (1972). Separation of zirconium, nobium, cerium and ruthenium for the determination of cesium in nuclear fuel solutions. *Journal of Radioanalytical Chemistry*, *10*, 17–26.

Muzzarelli, R. A. A., & Sipos, L. (1971). Chitosan for the collection from seawater of naturally occurring zinc, cadmium, lead and copper. *Talanta*, *28*, 853–858.

Muzzarelli, R. A. A., Tanfani, F., & Emanuelli, M. (1981). The chelating ability of chitinous materials from Streptomyces, *Mucor rouxii*, *Phycomyces blakesleeanus*, and *Choanephora cucurbitarum*. *Journal of Applied Biochemistry*, *3*, 322–327.

Muzzarelli, R. A. A., Tanfani, F., & Emanuelli, M. (1984a). Chelating derivatives of chitosan obtained by reaction with ascorbic acid. *Carbohydrate Polymers*, *4*, 137–151.

Muzzarelli, R. A. A., Tanfani, F., & Emanuelli, M. (1984b). Enhanced uptake of uranium on a new derivative of chitosan and ascorbic acid. In K. Kaikan, & T. Kaikan (Eds.), *Recovery of Uranium From Sea Water* (pp. 284–291). Tokyo, Japan: Atomic Energy Society.

Muzzarelli, R. A. A., Tanfani, F., & Scarpini, G. (1980). Chelating, film forming and coagulating ability of the chitosan–glucan complex from *Aspegillus niger* industrial wastes. *Biotechnology and Bioengineering*, *22*, 885–896.

Muzzarelli, R. A. A., & Tubertini, O. (1969). Chitin and chitosan as chromatographic adsorbents and supports for collection of trace metals from aqueous and organic solutions and sea water. *Talanta*, *16*, 1571–1579.

Muzzarelli, R. A. A., & Tubertini, O. (1970a). Purification of thallium (I) nitrate by chromatography on chitosan. *Mikrochimica Acta*, *1970*, 892–899.

Muzzarelli, R. A. A., & Tubertini, O. (1970b). Uptake of nitrosyl 106-ruthenium on chitin and chitosan from waste solutions and polluted sea water. *Water Research*, *4*, 451–455.

Muzzarelli, R. A. A., Weckx, M., Filippini, O., & Sigon, F. (1989). The removal of trace metal ions from industrial waters, nuclear effluents and drinking water with the aid of cross-linked carboxymethyl chitosan. *Carbohydrate Polymers*, *11*, 293–306.

N'Guessan, A. L., Vrionis, H. A., Resch, C. T., Long, P. E., & Lovley, D. R. (2008). Sustained removal of uranium from contaminated groundwater following stimulation of dissimilatory metal reduction. *Environmental Science and Technology*, *42*, 2999–3004.

NEA-IAEA. (2001). *Management of Depleted Uranium*. Paris: OECD Publications.

Niu, H. C., & Volesky, B. (2006). Biosorption of chromate and vanadate species with waste crab shells. *Hydrometallurgy*, *84*, 28–33.

No, H. K., Prinyawiwatkul, W., & Meyers, S. P. (2005). *Treatment of Wastewaters with the Biopolymer Chitosan. Handbook of Carbohydrate Engineering*. Boca Raton, USA: CRC Press-Taylor & Francis., pp. 535–562.

Nobukawa, H., Kitamura, M., Kobayashi, M., Nakagawa, H., Takagi, N., & Tamehiro, M. (1992). Development of floating type-extraction system of uranium from sea water using seawater current and wave power. *Journal of the Shipbuilding Society of Japan*, *172*, 519–528.

Nud'ga, L. A., Petrova, V. A., Ganicheva, S. I., Baklagina, Y. G., & Petropavlovskii, G. A. (2000). Carboxymethylation of fungal chitin–glucan complexes and sorption characteristics of products. *Russian Journal of Applied Chemistry*, *73*, 312–316.

Ogata, N. (1980). Review on recovery of uranium from seawater. *Bulletin of the Society for Sea Water Science of Japan*, *34*, 3–12.

Oshita, K., & Motomizu, S. (2008). Development of chelating resins and their ability of collection and separation for metal ions (Review, Japanese). *Bunseki Kagaku*, *57*, 291–311.

Oshita, K., Sabarudin, A., Takayanagi, T., Oshima, M., & Motomizu, S. (2009). Adsorption behavior of uranium(VI) and other ionic species on cross-linked chitosan resins modified with chelating moieties. *Talanta*, *79*, 1031–1035.

Oshita, K., Seo, K., Sabarudin, A., Oshima, M., Takayanagi, T., & Motomizu, S. (2008). Synthesis of chitosan resin possessing a phenylarsonic acid moiety for collection/concentration of uranium and its determination. *Analytical and Bioanalytical Chemistry*, *390*, 1927–1932.

Oshita, K., Takayanagi, T., Oshima, M., & Motomizu, S. (2007). Adsorption behavior of cationic and anionic species on chitosan resins possessing amino acid moieties. *Analytical Sciences*, *23*, 1431–1434.

Pang, C., Liu, Y. H., Cao, X. H., Hua, R., Wang, C. X., & Li, C. Q. (2010). Adsorptive removal of uranium from aqueous solution using chitosan-coated attapulgite. *Journal of Radioanalytical and Nuclear Chemistry*, *286*, 185–193.

Poulicek, M., Voss-Foucart, M. F., & Jeuniaux, C. (1986). Chitinoproteic complexes and mineralization in mollusk skeletal structures. In R. A. A. Muzzarelli, C. Jeuniaux, & G. W. Gooday (Eds.), *Chitin in Nature and Technology* (pp. 7–12). New York: Plenum Press.

Prat, O., Berenguer, F., Steinmetz, G., Ruat, S., Sage, N., & Quemeneur, E. (2010). Alterations of gene expression in cultured human cells after acute exposure to uranium salt. *Toxicology In Vitro*, *24*, 160–168.

Sabarudin, A., Oshima, M., Takayanagi, T., Hakim, L., Oshita, K., Gao, Y. H., & Motomizu, S. (2007). Functionalization of chitosan with 3,4-dihydroxybenzoic acid for the adsorption /collection of uranium in water samples and its determination by inductively coupled plasma-mass spectrometry. *Analytica Chimica Acta*, *581*, 214–220.

Sauceso, I., Guibal, E., Roulph, C., & Le Cloirec, P. (1992). Sorption of uranyl ions by a modified chitosan: kinetics and equilibrium studies. *Environmental Technology*, *13*, 1101–1115.

Seko, N., Katakai, A., Hasegawa, S., Tamada, M., Kasai, N., Takada, H., Sugo, T., & Saito, K. (2003). Aquaculture of uranium in seawater by fabric-adsorbent submerged system. *Nuclear Technology*, *144*, 274–278.

Seko, N., Tamada, M., Kasai, N., Yoshii, F., & Shimizu, T. (2002). Synthesis and evaluation of long braid adsorbent for recovery of uranium from seawater. In *Proceedings of Civil Engineering in the Ocean, vol. 18* (pp. 737–742).

Shimizu, T., & Tamada, M. (2004). Practical scale system for uranium recovery from seawater using braid type adsorbent. In *Proceedings of Civil Engineering in the Ocean, vol. 20* (pp. 617–622).

Skorik, Y. A., Pestov, A. V., & Yatluk, Y. G. (2010). Evaluation of various chitin–glucan derivatives from *Aspergillus niger* as transition metal adsorbents. *Bioresource Technology*, *101*, 1769–1775.

Tamada, M., Seko, N., Kasai, N., & Shimizu, T. (2006). Cost estimation of uranium recovery from seawater with system of braid type adsorbent. *Transactions of the Atomic Energy Society of Japan*, *5*, 358–363.

Tereshina, V. M., Marin, A. P., Kosyakov, V. N., Kozlov, V. P., & Feofilova, E. P. (1999). Different metal sorption capacities of cell wall polysaccharides of *Aspergillus niger*. *Applied Biochemistry and Microbiology*, *35*, 389–392.

Tobin, J. M., Cooper, D. G., & Neufeld, R. J. (1984). Uptake of metal ions by *Rhizopus arrhizus* biomass. *Applied and Environmental Microbiology*, *47*, 821–824.

Trutnau, M., Suckale, N., Groeger, G., Bley, T., & Ondruschka, J. (2009). Enhanced chitosan production and modeling hyphal growth of *Mucor rouxii* interpreting the dependence of chitosan yields on processing and cultivation time. *Engineering in Life Sciences*, *9*, 437–443.

Tseng, H. J., Hsu, S. H., Wu, M. W., Hsueh, T. H., & Tu, P. C. (2009). Nylon textiles grafted with chitosan by open air plasma and their antimicrobial effect. *Fibers and Polymers*, *10*, 53–59.

Tudor, H. E. A., Gryte, C. C., & Harris, C. C. (2006). Seashells: Detoxifying agents for metal-contaminated waters. *Water, Air and Soil Pollution*, *173*, 209–242.

Varma, A. J., Deshpande, S. V., & Kennedy, J. F. (2004). Metal complexation by chitosan and its derivatives: A review. *Carbohydrate Polymers*, *55*, 77–93.

Vijayaraghavan, K., & Balasubramanian, R. (2010). Single and binary biosorption of cerium and europium onto crab shell particles. *Chemical Engineering Journal*, *163*, 337–343.

Vijayaraghavan, K., Mahadevan, A., Joshi, U. M., & Balasubramanian, R. (2009). An examination of the uptake of lanthanum from aqueous solution by crab shell particles. *Chemical Engineering Journal*, *152*, 116–121.

Vijayaraghavan K., Winnie, H.Y.N., & Balasubramanian, R. Biosorption characteristics of crab shell particles for the removal of manganese(II)and zinc(II) from aqueous solutions, doi:10.1016/j.desal.2010.08.026, in press.

Volesky, B. (2001). Detoxification of metal-bearing effluents: biosorption for the next century. *Hydrometallurgy*, *59*, 203–216.

Vukanac I., Novkovic D., Kandic A., Djurasevic M., & Milosevic Z. A simple method for determination of natural and depleted uraniumin surface soil samples. *Applied Radiation and Isotopes*, doi:10.1016/j.apradiso.2009.11.056, in press.

Wan, M. W., Kan, C. C., Rogel, B. D., & Dalida, M. L. P. (2010). Adsorption of copper(II) and lead(II) ions from aqueous solution on chitosan-coated sand. *Carbohydrate Polymers*, *80*, 891–899.

Wang, G. H., Liu, J. S., Wang, X. G., Xie, Z. Y., & Deng, N. S. (2009). Adsorption of uranium (VI) from aqueous solution onto cross-linked chitosan. *Journal of Hazardous Materials*, *168*, 1053–1058.

Wanty, R. B., Goldhaber, M. B., & Northrop, H. R. (1990). Geochemistry of vanadium in an epigenetic sandstone-hosted vanadium uranium deposit, Henry basin, Utah. *Economical Geology*, *85*, 270–284.

Wilkinson, W. D. (1962). *Uranium metallurgy*. *Uranium process metallurgy* New York: Interscience Publishers.

Wu, F. C., Tseng, R. L., & Juang, R. S. (2010). A review and experimental verification of using chitosan and its derivatives as adsorbents for selected heavy metals. *Journal of Environmental Management*, *91*, 798–806.

Yakubu, N. A., & Dudeney, A. W. L. (1986). Biosorption of uranium with *Aspergillus niger*. In H. Eccles, & S. Hunt (Eds.), *Immobilization of ions by bio-sorption* (pp. 201–218). Chichester, England: Ellis Horwood.

Yang, P. Y., & Wang, M. L. (1990). Entrapment of microbial cells for wastewater treatment. In R. D. Tyagi, & K. Vembu (Eds.), *Wastewater treatment by immobilized cells* (pp. 45–77). Boca Raton, Florida: CRC Press, Inc.

Yang, T. C., & Zall, R. R. (1984). Adsorption of metals by natural polymers generated from seafood processing wastes. *Industrial Engineering Chemical Product Research Development*, *23*, 168–172.

Zhang, H. T., Li, S. B., White, C. J. B., Ning, X., Nie, H. L., & Zhu, L. M. (2009). Studies on electrospun nylon-6/chitosan complex nanofiber interactions. *Electrochimica Acta*, *54*, 5739–5745.

Zhang, H. T., Wu, C. Y., Zhang, Y. L., White, C. J. B., Xue, Y., Nie, H. L., & Zhu, L. M. (2010). Elaboration, characterization and study of a novel affinity membrane made from electrospun hybrid chitosan/nylon-6 nanofibers for papain purification. *Journal of Materials Science*, *45*, 2296–2304.

Zheng, Y, Anderson, R. F., van Geen, A., & Fleisher, M. Q. (2002). Remobilization of authigenic uranium in marine sediments by bioturbation. *Geochimica et Cosmochimica Acta*, *66*, 1759–1772.

Zhou, Y. F., & Haynes, R. J. (2010). Sorption of heavy metals by inorganic and organic components of solid wastes: Significance to use of wastes as low-cost adsorbents and immobilizing agents. *Critical Reviews in Environmental Science and Technology*, *40*, 909–977.

Zhou, D., Zhang, L., & Guo, S. L. (2005). Mechanisms of lead biosorption on cellulose/chitin beads. *Water Research*, *39*, 3755–3762.