Ligand-Grafted Biomaterials for Adsorptive Separations of Uranium in Solution

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Many organic molecules, particularly biologicals, contain functional groups (ligands) that actively interact with metal ions in solution by adsorption, ion exchange, or chelation/coordination/complexation. Water-soluble organics have limitations as reagents for metal-ion separations from aqueous solutions. However, if the ligand molecule(s) are grafted on to an insoluble matrix, the resulting ligand(s)-containing product becomes useful for separations applications related to metal recovery or remediation. It was discovered that biomolecules containing a primary amino group, secondary amino group, or hydroxyl group could be grafted into a polyurethane polymeric network via in situ polymerization reactions. With carboxyl groups, grafted material showed good selectivity among a group of divalent metal cations, and a uranium-binding capacity of more than 10 mg/g of polymer. The material can be regenerated by sodium bicarbonate or sodium carbonate solution and reused. Data from a stirred-tank reactor showed fast uranium-binding kinetics, and breakthrough-elution studies with a packed-column reactor indicated promising process behavior.

Introduction

Various types of biosorbents have been identified and applied to the extraction and/or separation of metals/radionuclides from aqueous environmental solutions, either for recovery of valuable metals or for environmental remediation. Most of the studied biosorbents are of biological origin (''nonartificial'' materials); examples include biomass from bacteria, fungi, and algae. The basis of metal biosorption (that is, nonmetabolically related metal binding to the biosorbent material) has been attributed to the existence of active components, or sites, in the biomass. These active sites may interact with metal ions through different mechanisms such as adsorption, ion exchange, chelation, complexation, and coordination (Volesky, 1990). Many functional groups inside the cell or on the cell-wall biopolymers have been reported to be responsible for the metal binding. These functional groups include carboxyl, phosphoryl, sulfhydryl, amino, sulfate, imidazole, thioether, phenol, carbonyl, amide, and hydroxyl moieties (Bedell and Darnell, 1990). For engineering process applications, the biomass needs either to be immobilized in a supporting material (usually polymeric) or to be treated by cross-linking reagents for higher mechanical strength.

Based on the metal-binding chemistry in natural biomass or biopolymer biosorbents, we envisioned a biomimetic approach to developing adsorptive materials that contain ligands corresponding to those metal-binding functional groups found in natural biosorbents. The capability for artificially grafting a biomolecule containing specific metal-binding ligand(s) onto an insoluble support allows us to create a material with enhanced selectivity over that of a natural biosorbent. Selectivity is a property that is especially critical to the removal of a certain metal from a metal-mixture stream. If needed, multiple metal-binding sites could be added by grafting selected biomolecular ligand molecules simultaneously into a support material. Such ligand(s)-grafted material would provide a wide range of flexibility in the molecular design of active metal-binding sites relative to biomass, although chemical modification of biomass is also possible. In this article, we report efforts to synthesize a new type of biomimetic adsorbent material selective for metal ions such as uranium. Urethane polymer was chosen as the support material onto which ligand(s) were grafted. Molecules that

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are of biological origin and contain metal-binding functional groups or configurations were selected for covalent linkage with the polymeric network, or backbone, in pendant ligand(s) form. The use of natural-origin biochemical molecules to create pendant ligand(s) in the polymeric material offers several advantages over synthetic organic chemicals. First, the biochemicals that are capable of specific interactions with different metal ions are numerous. Second, the ligand(s) of biochemical origin could biomimetically simulate the function of a real biosorbent in its interaction with metal ions. Third, chemicals of biological origin are often more environmentally benign than synthetic chemicals. Biomimetic polymer preparation requires only mild conditions, while the preparation of conventional metal-binding ion-exchange resins, such as sulfonated polystyrene divinylbenzene beads, involves harsh conditions such as high temperature, pressure, and the use of strong acid.

The concept of introducing metal-binding ligand(s) onto an insoluble support material, either by *in situ* grafting during material synthesis or by chemical treatment/or modification after the material formation, has been used to generate many types of metal-binding adsorbents, including organic or inorganic ion-exchange and chelation resins (Yang et al., 1995; Gao et al., 1995). However, the use of biochemical molecules as the source of metal-binding ligand(s) for separation applications has been given relatively little attention, although Holbein et al. (1987) reported that the material produced by immobilization of cysteine onto a silica gel has potential for removing mercury from a liquid medium.

The ubiquitous interactions between biomolecules and metal ions, particularly in biological systems, including the animals, plants, and microorganisms, are well known (Sigel, 1973, 1974). Several types of biological molecules, ranging from low-molecular-weight primary or secondary metabolites such as amino acids and siderophores to macromolecules such as peptides, proteins, and biopolymers, have the capacity for metal binding with rather high-stability constants. In the case of amino acids in solution, chelating activity can occur with the primary amine and carboxyl groups. All amino acids contain at least three donor groups: N:, $O-$, and $=O$. Generally, the $=O$ of a carboxyl group does not complex with the same metal as the amino or hydroxyl group of an amino acid. Formation of a hemichelate structure between a metal and the two carboxyl oxygens with water as a bridging molecule is possible (William, 1971).

In addition to the terminal amino and carboxyl groups, some amino acids contain other potential metal-binding groups such as serine and threonine (with aliphatic hydroxyl side chains, $-OH$), cysteine and methionine (with sulfur-containing side chains, $-SH$ and $-S-$), glutamine and asparagine (with amide group, $-CONH_2$), histidine (with basic side chain, that is, imidazole reactive side group), aspartate and glutamate (with additional acidic side chains, $-COO^-$), γ-carboxyglutamate (with two additional carboxyl, $-COO^-$, groups on side chain), and *o*-phosphoserine (with a side chain of $-PO_3^{2-}$). Peptides and proteins are also reported to bind heavy metals (Jackson et al., 1990; Blundell and Jenkins, 1977). In addition to the active sites on each individual amino-acid component, the binding of a metal could be coordinated by several groups such as histidine imidazoles. However, proteins and peptides combine less strongly with metal ions than do their constituent amino acids, primarily because of the loss of the amino group to peptide bonding. This leaves only the terminal groups or a limited number of side-chain ligands to bind. In proteins, the side-chain ligands are even more important than the terminal groups and consist of carboxyl, imidazole, sulfhydryl, primary nitrogen, and hydroxyl groups (Huber et al., 1990). For example, metallothioneins have a large percentage of cysteine-containing ($-SH$) groups, but some binding is from other amino-acid components. The metal-transport protein transferrin has been reported to bind various metals (Spires and Vincent, 1995). Polypeptides, such as poly (γ-glutamylcysteinyl) glycines, have the potential for removing metals from aqueous solution (Jackson et al., 1990). Secondary and tertiary structures of certain specialized proteins may also limit, or promote, metal binding.

Nonproteinaceous molecules (sugars or polysaccharides) have also been reported to form complexes with metals (Rendelman, 1978). Some other biosynthetic metabolite molecules, such as protoporphyrin IX, vitamins, pigments, and siderophores, are also potential metal-binding ligand molecules. Among many biological chelating reagents, siderophores (hydroxamate or catecholate compounds with molecular weight of 500 to 1000) have received some attention (Messenger and Ratledge, 1985; Neilands, 1982, 1984). The soluble siderophore molecules were immobilized on a solid carrier for metal extraction applications (Holbein, 1990; DeVoe and Holbein, 1985, 1986). These examples of metal interaction with diversified molecules of biological origin, should convince us of their potential application in metal extraction/separation applications. In the current work, we used a very fundamental biological molecule, glutamic acid (an amino acid), as a model system to further justify the significance of biomolecular molecules in metal binding.

Knowledge and understanding of the chemical basis of the interaction between metal ions and biosorbents (whole biomass, biopolymers, and low-molecular-weight biochemical molecules) will aid us in our efforts to synthesize and/or graft effective functionalities (or metal-binding ligand groups) onto a solid support material. Thus, the grafted material could bind metal ions with similar or higher affinities, specificities, and capacities. In our study, attempts were made to understand the underlying principles of metal binding and to identify active sites (or ligand functional groups) based on up-to-date information in the literature.

Current knowledge of interactions between metal ions and biosorbents is quite limited. Generally, metal binding is thought to occur as a result of adsorption, ion exchange, complexation, chelation, coordination, and microprecipitation (or deposition) of metal ions by the functionalities in the biosorbents. There are two types of metal-binding molecules in biological systems: induced and constitutive. In extensive studies of metal biosorption by bacterial, fungal, or algal biomass, most of the authors attributed the metal-removal properties of the biosorbent either to cell-wall components or to intracellular components. Particularly, the cell wall interacts with metallic ions in the liquid medium due to the anionic characteristics of the cell wall (Remacle, 1990; Beveridge, 1986). The anionic cell walls of bacteria are remarkable in their ability to fix metals and to provide sites for nucleation and growth of minerals (Beveridge and Fyfe, 1985). The metal-binding capacity depends on the presence of the

functional groups and the spatial structure of the cell wall. For cell walls of gram-positive bacteria, metal-binding sites include peptidoglycan, teichoic acid, teichuronic acid, and proteinaceous materials. Peptidoglycan is the primary agent for metal deposition via carboxyl-group ion exchange using glutamic acid COOH groups (Macaskie and Dean, 1990). Cation bridges between polymer strands via the phosphate groups were suggested as possible mechanisms for metals binding to teichoic acid components. Different from bacterial cell walls, fungal cell-wall chitin (poly-*N*-acetylglucosamine) and its derivative chitosan accumulate metals effectively. Uranium biosorption by *Rhizopus arrhizus* biomass has been attributed to the complex formation of uranium with chitin nitrogen by coordination bonding, hydrolysis of the uranium-chitin complex, and then the precipitation of the hydrolysis product (uranyl hydroxide) in the cell wall to leave the chitin nitrogen free for subsequent uranium complexation (Tsezos and Volesky, 1982; Tsezos, 1983). These examples of metal-binding molecules all likely fall into the constitutive category.

Biopolymers are a significant type of biosorbent in metal-binding applications because of their diversity (Hunt, 1986). Biomass-constituting biopolymers, such as polysaccharides, proteins, and nucleic acids, and hybrid polymers, such as glycoproteins, proteoglycans, and lipopolysaccharides, are potential biosorbent materials. Lipopolysaccharide (LPS), an integral component of the outer membrane of gram-negative bacteria, is often regarded as a site of metal binding, although its metal-binding capacity is low. LPS phosphoryl groups were identified as the metal-binding sites present in the lipid constituents of the outer membrane. One of the three carboxyl groups in the molecule is available for metal interaction (Macaskie and Dean, 1990). Glycoprotein may also be a possible site of metal binding. Heavy-metal-binding biopolymers extracted from isolated cell walls of yeast *Saccharomyces cerevisiae* were reported to provide a greater metal binding than intact cell-wall material (Brady et al., 1994). Protein was claimed to be a major heavy-metal-accumulating component. Many proteins bind metal ions very specifically by coordination (Brill, 1977). Nonproteinaceous biopolymers, such as alginic acid, chitin, chitosan, and poly (*p*-aminostyrene), can be chelating polymers (Muzzarelli, 1973, 1977; Chiessi et al., 1992). Modified polysaccharide-derivative chelators, such as glycine glucan, can also have high capacities for metal ions due to the existing amino and hydroxyl ligands (Muzzarelli, 1985; Muzzarelli et al., 1985).

In addition to the cellular constituent components (that is, cell wall and related biopolymers) described earlier, extracellular biopolymers (that is, capsular and slime exopolymers) were also reported to have potential applications to metal binding (Geesey and Jang, 1990; Sterritt and Lester, 1986; Scott et al., 1986; Lester et al., 1984). Although most capsule and slime exopolymers are composed of polysaccharide, considerable amounts of protein, DNA, and RNA are also recovered in crude exopolymer preparations. There are different mechanisms of metal binding to microbial exopolysaccharides, such as acid–base reaction or bond formation with functional groups containing electron-donating atoms. Many microbial exopolymers act as polyanions. The anionic character of polysaccharides that contain uronic acids, ketal-linked pyruvate groups, or sialic acids (derivatives of neuramic acid) is conferred by the lone-pair electron on oxygen atoms of the carboxylic acid moiety present (Geesey and Jang, 1990). At neutral to alkaline pHs, the partially ionized carboxyl groups are available to interact with positively charged metal ions. Polysaccharides also contain an abundance of hydroxyl groups. Oxygen atoms in the ether bonds and hydroxyl groups of sugar subunits act as weak electron donors in both acidic and neutral polysaccharides. In addition, nitrogen-containing functional groups (such as amino sugars or sugars with amide-linked functional groups) are likely to react with some metals. The most important two types of interactions between metal ions and exopolymers are those involving salt bridges with carboxyl groups (COO^-) on acidic polymers and those involving weak electrostatic bonds with hydroxyl groups on neutral polymers. Alginic acid gelatins are good examples of exopolymers, which can act as polyhydroxy- or polycarboxylic acid chelating agents, or a mixture of both (Huber et al., 1990). In summary, various ionizable groups in biological polymers, including carboxyl, sulfate, sulfonic acid, phosphate, hydroxyl, sulfhydryl, amino, lactam $-$NH, imidazole $-$NH, imidazole, guanidino $-NH_2$, and imino groups, have been suggested as being responsible for metal binding (Hunt, 1986). These metal-binding functional groups can be located on a polysaccharide, a protein, a peptide, a nucleic acid, an amino acid, an enzyme, or a coenzyme molecule of the biopolymer.

Low-molecular-weight biochemical molecules could be quite useful in metal-binding applications if they can be grafted onto a solid carrier. Two major mechanisms may be generally involved in the binding of metal ions to biomolecules: ion exchange and formation of complexes (coordination compounds) (Macaskie and Dean, 1990). Carboxyl, organic phosphate, and organic sulfate groups in biopolymers belong to cation-binding ionizable groups. Carboxylic acid groups, in particular, are widely distributed in biopolymers. Organic nitrogen-based groupings may be responsible for the anion exchange on biopolymers. The amino, imino, and heterocyclic nitrogens of proteins and nuclic acids; the carbonyl and hydroxyl oxygens variously distributed in proteins, nucleic acids, polysaccharides, polyphenolics, and polyheterocyclics; and cysteine thiol and methionine thioether groups in proteins contain atom(s) having a single pair of electrons to donate, and thus can form complexes with metals at ligand centers. An additional third mechanism involves subsequent deposition of the metal in a chemically altered state (Macaskie and Dean, 1990).

In addition to the information gained from biosorbent studies, knowledge of traditional chelation chemistry can help the development of new biomolecular ligand(s)-grafted materials that function like chelation biosorbents. Chelating agents are those compounds containing donor atoms that can combine by coordinate bonding with a single metal ion to form a cyclic structure called a chelating complex, or simply a chelate (Huber et al., 1990). The metal acts as a Lewis acid (that is, it tends to acquire enough electrons to reach an inert state), and the ligand acts as a Lewis base (that is, it has electron pairs that can be shared with the metal). Coordination, then, is a Lewis acid—Lewis base neutralization process. The propensity of a given metal to bind with a given ligand is based on the theory of hard and soft acids and bases (HSAB). Huber et al. (1990) has reviewed the HSAB classification of acids and bases. A general rule of thumb is that hard acids

tend to form strong bonds with hard bases and soft acids tend to form strong bonds with soft bases. The Irving and Williams relationship between chelate stability and atomic number of metals applies when a given multidendate ligand interacts with a series of metal ions in the same oxidation state. Substances known for chelating properties include polyphosphates, aminocarboxylic acids, 1,3-diketones, hydroxycarboxylic acids, polyamines, amino alcohols, aromatic heterocyclic bases, phenols, amino phenols, oximes, Schiff bases, tetrapyrroles, thiols, xanthates, and sulfur compounds, and polymers (such as polyethyleneimine, polymethylacryloylacetone, and polyacrylic acid) (Huber et al., 1990). The principal donor atoms are nitrogen, oxygen, and sulfur, but phosphorus, arsenic, and selenium also form chelates.

Chelating molecules with oxygen as the sole donor include polyhydroxy compounds (such as simple sugars and polysaccharides in a biological system), polycarboxylic acid ethers, and phenolic compounds (such as biological siderophores). Amino acids are the only groups of chelating molecules with nitrogen as the sole donor in biological systems. However, a large group of biological ligand molecules use both nitrogen and oxygen as donors; these include amino acids, peptides, proteins, other natural chelating polymers such as chitin and chitosan, and some specialized chelating molecules such as hydroxaminic acids and phytosiderophores. The thiol ($-SH$) moiety, being a soft-base ligand with sulfur as the sole electron donor, will readily form covalent bonds with soft-acid metals such as mercury, cadmium and lead. Substitution of a thiol group for a carboxyl group can increase selectivity. The metal-binding sulfide groups usually originate from cysteine side chains in the enzymes or other proteins. Cysteine, with its soft sulfur as a side group, binds more strongly than any other amino acid to the soft-acid metal, as reported by DeVoe and Holbein (1985). However, the sulfur atom of methionine can also play a role in metal binding. Many simple thiol-containing molecules, which include mercaptoethanol ($HSCH_2CH_2OH$), thiomalic acid ($HOOCCHSHCH_2COOH$), ethionine [CH3CH2S(CH2)$_2$CH(NH2)COOH], and dithiothreitol [$HSCH_2(CHOH)_2CH_2SH$], are biologically significant. Sulfur-containing chelating agents can be used to alleviate soft-metal poisoning. In some cases, such as binding to the amino acid alone, both nitrogen and sulfur may serve as donors.

In biological systems, ''hard'' ions (those forming strong bonds with F^-, such as Na^+, Mg^{2+}, and Ca^{2+}) form stable bonds (of more covalent character) with oxygen-containing radicals such as OH^-, HPO_4^{2-}, CO_3^{2-}, $R-COO^-$, and $=C=O$. ''Soft'' ions, such as heavy metal ions, form very strong bonds (of mainly ionic nature) with CN^-, $R-S^-$, $-SH^-$, NH_2^-, and imidazole (that is, groups containing nitrogen and sulfur atoms) (Remacle, 1990). Based on another metal classification, metals are discriminated into three classes: oxygen seeking, nitrogen- and sulfur-seeking, and a borderline, or intermediate, class. The following three types of ligands encountered in biological systems have been proposed by Remacle (1990) to be important in metal binding: (I) F^-, O^{2-}, OH^-, CO_3^{2-}, SO_4^{2-}, $R-OSO_3^-$, NO_3^-, HPO^{2-}, HPO_4^-, $R-OH$, $R-COO^-$, $-CO-$, and $R-O-R$; (II) Cl^-, Br^-, N_3^-, NO_2^-, SO_3^{2-}, NH_3, N_2, $R-NH_2$, R_2NH, R_3N, $=N-$, $-CO-N-R$, O_2^-, and O_2^{2-}; (III) H^-, I^-, R^-, CN^-, CO, S^{2-}, RS^-, R_2S, and R_3As. Here, R represents an alkyl radical or, in a few cases, an aromatic moiety. It is also important to note that knowledge of synthetic (nonbiological) chelating ion-exchange and/or chelation resins could also aid in the elucidation of the functional groups responsible for metal binding and stimulate the novel design of biomolecular ligand-grafted material. Imino-nitrogen (polyethyleneimine), poly(*N*-vinylimidazole), diphenylcarbazone, 2,3,2-tetramine, iminodiacetic acid, 2,6-pyridine-dicarboxylic acid, carboxylic acid hydrazides, imidazole rings of four histidine residues, oxime ($C=NOH$) and hydroxamic acid, aliphatic thiol group, aryl-aliphatic thiol groups, and carboxyl groups such as $-N(CH_2COO^-)_2$ are the active metal-binding groups in a few commercial chelating ion-exchange resins (Gao et al., 1995; Blasius and Brozio, 1967). With the chelation chemistry information, as described earlier, for any target metal ion, we could easily identify the biochemical molecules that contain potential metal-binding ligand(s). The next step would involve grafting of the biomolecules onto an insoluble carrier for process applications.

Because of the advantages of high distribution coefficient, low cost, simplicity of apparatus required, and excellent hydrodynamic properties due to its quasi-spherical membrane structure, PMF has received particular attention in the areas of separation science for metal extraction, trace-metal recovery (or enrichment, preconcentration), and analytical determination. The two general types of PMF available are polyether-based and polyester-based materials. Both plain (or unloaded) polyurethane foams and extractant-impregnated polyurethane foams have shown their potential applications in metal-ion extraction from aqueous stream or preconcentration into polyurethane foam. Both polyether- and polyester-based polyurethane unloaded foam has been used as a sorbent for removing compounds from aqueous solution. In particular, some of the unloaded polyurethane foams could bind metals such as uranium under certain conditions, and their extraction behavior of uranium(VI) have been investigated extensively (Huang et al., 1992, 1993; Gesser and Gupta, 1989; Pearson and Bowen, 1985, Korkish et al., 1981). Polyether-based polyurethane was used in studies for extraction of uranium(VI) from aqueous nitrate solutions (Huang et al., 1992, 1993). It was found that the uranium can be extracted only in the presence of a nitrate salting-out agent, and the extraction efficiency increased significantly with increasing nitrate concentration and hydration of the cation of the nitrate salt. The salting-out effects of different nitrate salts increase in the sequence $KNO_3 < NH_4NO_3 < NaNO_3 < Ca(NO_3)_2 < Mg(NO_3)_2 < Al(NO_3)_3$, which is the same as the order of the hydration of their cations (Huang et al., 1992). The extraction behavior of uranium(VI) with the polyurethane foam was described as an etherlike solvent extraction mechanism. Similarly, by using open-cell polyurethane foam sponge (OCPUFS) for the extraction of uranyl nitrate from aqueous solution in the presence of salting agents, Gesser and Gupta (1989) interpreted their results in terms of OCPUFS acting as a viscous organic ether of moderate dielectric constant. In general, the polyester-based material acts through a solvent extraction type of mechanism, while the polyether-based material indicates a more complicated process that is sometimes based on a solvent extraction mechanism and, at other times, involves a cation chelation mechanism (Stewart and Chow, 1993).

It is possible that our ligand-grafted material could be applied for analytical purposes. Excellent overviews have been given by Palágyi and Braun (1992, 1994) and Braun (1983, 1989) in the extensive analytical use of the unloaded polyether type polyurethane foams as solid extractants (or sorbents) in enrichment (or preconcentration) and separation for determination of trace elements. More than 50 elements have been successfully separated and/or preconcentrated with unloaded polyurethane foam sorbents from various types of aqueous solutions.

Studies using organic extractant-impregnated (or -loaded) polyurethane foams because of their applications in metal extraction and enrichment/preconcentration of trace elements have been reported. For uranium extraction or recovery, polyurethane foams have been impregnated (or loaded) with various types of metal extractants such as dibenzoylmethane (Shakir et al., 1992a); solutions of di-(2-ethylhexyl)-phosphoric acid and tributylphosphate in *o*-dichlorobenzene (Shakir et al., 1992b; Aziz et al., 1992); solutions of di-(2-ethylhexyl)-phosphoric acid in nitrobenzene (Aziz et al., 1991); adogen (Gesser and Ahmed, 1990); 5,8-diethyl-7-hydroxy-6-dodecanone oxime (Akiba and Hashimoto, 1989); tri-*n*-octylphosphine-oxide in diethyl ether (Pearson and Bowen, 1985); and methylisobutyl ketone (Korkisch et al., 1981). Foams loaded with di-(2-ethylhexyl)-phosphoric acid (HDEHP) in nitrobenzene have also been studied for the extraction of cerium(III) from acidic chloride solutions (Shakir et al., 1991a) and from acid perchlorate solutions of constant ionic strength (Shakir et al., 1991b). One disadvantage of using impregnated foams is that the metal-binding organic reagent in the foam may be gradually washed out; however, there is no such concern for our ligand-grafted material because the active reagents (ligand molecules) are covalently linked with solid carrier.

Biomolecular ligand-grafted materials could be an important new type of material for selectively removing and recovering metal ions and/or radionuclides from aqueous solutions in a number of industrial applications, including mining, nuclear power, nuclear weapons production, site remediation, and laboratory research. We have initiated studies that will develop novel ligand-grafted polymers that are biomimics of known biological sorbents and can selectively extract metal ions. The results indicate that even relatively simple biochemicals such as amino acids, after being grafted into an insoluble support, could become useful and selective adsorbent reagents for metal separations. We focused on the study of one model system—uranium adsorption by polyurethane membrane foam grafted with glutamic acid (MSG-PMF)—in which carboxyl groups in pendant form were thought to be the metal-binding sites. Equilibrium and kinetic data were collected for the characterization of MSG-PMF through batch stirred-tank reactor and packed-bed column breakthrough-elution studies.

Experimental Studies

Materials

A prepolymer technique was used to synthesize ligand-grafted urethane polymers because of its simplicity, decreased toxic organic monomer involvement, and mild requirements for polymerization and ligand-linkage reactions. This technique is one of the most convenient methods for preparing polyurethane polymeric matrix, particularly in large-scale operations. Polyurethane prepolymers are isocyanate-terminated (or -capped) adducts, which can be produced by the reaction of an excess of diisocyanates, triisocyanates, and other polyisocyanates with compounds containing an active hydrogen (such as glycols, polyglycols, polyester polyols, polyether polyols, other polyols, and mixtures of two or more such polyols). The prepolymers formed by reactions of hydroxyl-terminated polyethers or polyesters with toluene diisocyanate (TDI) are particularly popular in applications.

The advantages of using prepolymer as a starting material in polyurethane polymer preparation needs to be addressed. To mention a few favorable factors, for example, no catalyst (either tin or tertiary amines) was needed in the production of flexible polyurethane foam. The prepolymer is much less toxic than the monomer component like TDI. Most of the time, the feed materials simply included the isocyanate-capped liquid polyurethane prepolymer and an aqueous stream that contained effective ingredients (that is, a metal-binding ligand). The polymerization could be carried at mild conditions, including room temperature. Commercially available urethane prepolymers such as the HYPOL series of products (TDI-polyether-based, isocyanate-capped liquid polyurethane prepolymers), including FHP 2002, 2000, 3000, 5000, and PreMA-G60, were purchased from the Hampshire Chemical Corporation (Lexington, MA). Biochemical ligand molecules used in the grafting procedure, such as glutamic acid (monosodium form, MSG) and cysteine, were ordered from Sigma and Aldrich catalogs. A uranium stock solution (10,000 mg/L) was prepared by dissolving uranyl nitrate salt $(UO_2)(NO_3)_2 \cdot 6H_2O$ (from the J. T. Baker Chemical Co., Phillipsburg, NJ) in deionized water. Experimental solutions were made from a stock solution of uranyl nitrate by dilution with deionized water and, if necessary, the pH was adjusted to the desired value by addition of nitric acid or sodium hydroxide solutions. Other chemicals were of reagent grade and were used as received.

Unless otherwise indicated, the typical MSG-PMF adsorbent was prepared as follows: One part of MSG was dissolved in ten parts of deionized water. The resulting solution was then mixed vigorously with five parts of HYPOL FHP 2002 urethane prepolymer for approximately 1 min at room temperature (~ 22°C) while the mixture was foaming, increasing in temperature, and becoming more viscous. The polymeric foam was cured for approximately 30 min before it was crushed into small foam particles (1 to 3 mm) by a blender. The foam particles were washed by soaking in extensive volume ($> 5{,}000$ parts) of deionized water overnight, dried with a freeze-dryer, and stored in a refrigerator at 4°C.

Ligand-grafting and polyurethane synthesis chemistry

Polyurethanes are characterized by the linkage of $-NH-COO-$, although other groups, such as ether, ester, biuret, allophanate, and amide, may be present in the polymer molecules (Frisch, 1969). The preparation of polyurethanes, in most cases, is the reaction of di- or polyfunctional hydroxyl compounds, such as hydroxyl-terminated polyethers or polyesters with di- or polyfunctional isocyanates. The two most important reactions in the formation of urethane poly-

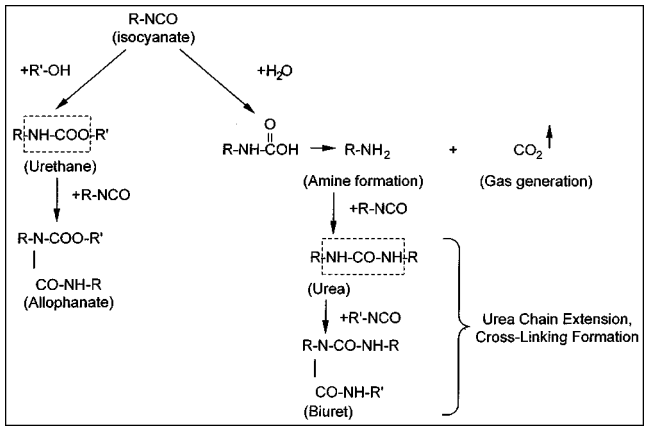

Figure 1. Polyurethane synthesis chemistry and mechanisms for ligand grafting.

mers are those between isocyanate and the hydroxyl-containing compounds and between isocyanate and water (Figure 1). The former is the basic reaction for the formation of urethane groups and may be considered the chain-propagating reaction. The second reaction is responsible for the foaming of urethane polymers, in the manufacture of flexible foams, by the liberation of carbon dioxide with simultaneous formation of substituted urea groups. The first step in the prepolymer–water reaction is the formation of the unstable carbamic acid, which decomposes to form an amine and carbon dioxide (the gas for foam formation). The amine then immediately reacts with additional isocyanate to form a substituted urea. These amine groups may react with free isocyanate groups on neighboring polyurethane molecules, and this urea linkage reaction will cause further growth of the polyurethane molecule and may also introduce cross-links between the polyurethane molecules. Such growth and cross-linking are essential to the formation of a good-quality polyurethane foam. Apparently, the formation of polyurethanes ($R-NH-COO-R'$) may be accompanied by a number of side reactions that produce allophanate and biuret, which usually are the sources of additional cross-linkage (Figure 1).

An understanding of polyurethane synthesis chemistry allows us to recognize the potential mechanism of grafting a ligand molecule onto the polyurethane polymer matrix. The ligand-grafting mechanism is closely related to the uniqueness of polyurethane synthesis chemistry. Either a single ligand or multiple ligands can be grafted onto the same polymeric backbone. Generally, potential ligand molecules can be of natural or synthetic origin, inorganic or organic, soluble or insoluble, as long as they contain a primary amine group ($-NH_2$), a hydroxyl group ($-OH$), an isocyanate group ($-NCO$), or sometimes a secondary amine group ($-NH-$). Through these functional groups, ligand molecule(s) could be covalently linked to the polymer backbone by involving the *in situ* urethane polymerization reactions. Most of the molecules of biological origin, such as amino acids, peptides, and proteins, are amine-containing molecules; a few of them are hydroxyl-containing molecules. Use of biomolecules creates a ligand(s)-grafted polymer to a real biosorbent, which is unique in metal binding. The basic criteria for preparing a useful metal-binding product are that the ligand molecule should contain one grafting site (such as $-NH_2$) and at least one metal-binding site. Also, the urethane polymerization process should not inhibit or react with the metal-binding site of the ligand molecule. The availability of a large number of biomolecules that meet such criteria will allow us flexibility in designing and creating ligand(s)-polyurethane polymer products with various metal-binding properties. It has been suggested that the order of the reactivity of isocyanate group with other compounds is as follows (Kumakura and Kaetsu, 1983): $R-NH_2 > R-NH-R > RCH_2-OH > H_2O >$ RCOOH, where R represents an aliphatic or aromatic moiety. To obtain a good-quality ligand(s)-grafted polyurethane material, it is important to ensure that the isocyanate groups of the prepolymer are not consumed by reaction with the linkage functional groups (that is, $-NH_2$, $-OH$, $-NH-$, etc.) of the ligand molecule, thereby leaving unreacted isocyanate groups available to react with the curing agent such as water (for the foaming method of curing) and amine (for the nonfoaming method of curing).

Amino-acid assays

The ninhydrin procedure (Rosen, 1966) was adapted for quantitative determination of the amount of glutamic acid (in the form of the monosodium salt, MSG) in aqueous solutions. In principle, the amino acids react with ninhydrin to yield CO_2, ammonia, and, usually, an aldehyde containing one fewer carbon atom than the original amino acid. The assay procedure can be briefly described as follows: (1) prepare 1-mL samples of standards (0.02 to 0.4 μmol of MSG) and test solutions; (2) to each 1-mL sample, add 0.5 mL of cyanide-acetate buffer and 0.5 mL of 3% ninhydrin solution; (3) immediately after removal from the bath, add 5 mL of the isopropyl alcohol–water diluent; (4) shake the mixture vigorously and then permit it to cool to room temperature; (5) repeat steps (2), (3), and (4) for standards; (6) the color density of purple samples is read at 570 nm with a UV/VIS recording spectrophotometer (in our case, a Shimadzu UV-160, Shimadzu Corp., Kyoto, Japan). The amount of glutamic acid linked to the urethane polymer was determined by the material balance (that is, the initial amount of MSG used in the grafting process minus the amount recovered in washing solutions). The ligand-grafting yield was defined as the amount of MSG linked in the polymer divided by the initial amount of MSG introduced in the polymerization process.

Procedure

In our preliminary screening studies of ligand-grafted polyurethane, various types of amino-containing biochemical molecules, including L-glutamine, L-monosodium glutamate (MSG), L-cysteine, thiamine HCl, β-glycerophosphate disodium, dopamine (3-hydroxyamine HCl), D(+)-glucosamine, and adenosine triphosphate (ATP) disodium, were tested for uranium-binding capability. In each case, 1.0 mL of aqueous solution containing the ligand molecule was mixed with 0.5 g of HYPOL FHP 2002 urethane prepolymer. The mixture polymer was then cured and cut into small particles ($\sim$ 5 mm), which were rinsed extensively with deionized water to eliminate any free biochemical molecules inside the polymer. The ligand-grafted polymer particles were contacted with a 30-mL volume of uranyl nitrate solution (50 mg

of uranium per liter, pH 4.0) contained in a 50-mL capped centrifuge tube that was shaken on an orbital shaker at 250 rpm at room temperature. After overnight contact, the solution was withdrawn for pH measurement and analyzed for uranium by an inductively coupled plasma (ICP) spectrometer (Perkin-Elmer Plasma 400, The Perkin-Elmer Corp., Norwalk, CT). Other equilibrium studies with MSG-PMF, such as those to determine its selectivity, isotherm, pH profile, regeneration reagent screening, and multiple-cycle adsorption/regeneration experiments, were carried out in similar conditions, except as otherwise indicated.

A 1-L batch stirred-tank reactor was used for uranium sorption/desorption kinetic studies. The tank has an inside diameter (ID) of 11.3 cm and a baffle width of 1.0 cm (four baffles). The Rushton turbine agitator has a center disk diameter of 4 cm, a blade width of 2 cm, and a blade height of 1.5 cm; the blade is welded halfway into the disk. The agitator is positioned at one-third of the liquid depth in the tank. Twenty grams of MSG-PMF particles was contacted with 1.0 L of uranyl nitrate solution (50-mg/L uranium, pH 4.5) at room temperature. The agitation speed was set at 500 rpm, a level high enough to avoid the external mass-transfer resistance. Aliquots (~ 5-mL volumes) were taken at predetermined times for uranium analyses and pH measurements. A similar procedure was used for experiments designed to measure selectivitiy among various metal cations (Fe, Cu, Zn, Mn, U). Each metal was tested in a separate batch containing a single metal cation as a solution of a soluble salt containing that particular metal cation.

To study the breakthrough behavior in the metal-loading cycle, a packed-bed column was operated under the following conditions: column ID = 1.3 cm; bed height = 24 cm; bed volume = 30 mL; residence time ≈ 2 min; flow rate = 2 mL/min; upflow mode. The feed solution was a uranyl nitrate solution with a uranium concentration of 102.4 ppm and a pH of 4.1. For the purpose of column regeneration, the column bed was eluted (upward-flow mode) with 0.1 M $NaHCO_3$ solution at 2 mL/min. Samples were collected by using a Super Fraction Collector (Pharmacia LKB). Multiple cycles of column loading/regeneration were carried out. To obtain the ideal shape of breakthrough curve, it was necessary to rinse the column completely with deionized water after each regeneration process with sodium bicarbonate solution.

Results and Discussion

In this work, ligand-grafted materials were prepared in the form of polyurethane membrane foam (PMF) because of the following advantages: (1) PMF has a unique quasi-spherical membrane-shaped geometric structure; (2) in comparison with resin bead and cylindrical or planar membrane, quasi-spherical membrane geometry is most advantageous with regard to volume/surface ratio; (3) PMF offers less intramatrix mass-transfer resistance relative to the solid resin bead, thus ensuring high process efficiency; (4) the PMF powders can be used as a substitute for traditional granular or spherical resin particles in packed-bed column operations; and (5) the resilient character of PMF offers a flexible operation mode such as batch sequeezing–pulsated column and flow-pulsated column. Although the current work, to our knowledge, is the first and so far the only report on the use of metal-binding ligand(s) that are covalently grafted onto a polyurethane solid foam material, extensive research studies of ready-made polyurethane solid foams (either plain foams or reagent-impregnated foams) in extraction of metals or organics from aqueous stream have been undertaken for decades. The major difference between our work and the work reported in the literature is that our ligand-grafting preparation requires *in situ* polymerization involvement, while the latter does not. We took an entirely different approach to utilizing polyurethane foam in metal separation.

Table 1. Uranium Extraction by Ligand(s)-Grafted Polyurethane Membrane Foams

Molecules Used for Grafting Polyurethane Polymers*	Uranium Conc. Left in Aqueous Phase (ppm)**	Final pH of Aqueous Solution
Control (no polymer added in uranyl nitrate solution)	50.0	4.0
Distilled and deionized water (ddH_2O)—polymer blank	49.3	4.1
Sodium phosphate buffer solution (0.2 M, pH 7.95)	5.4	4.2
0.05 g/mL L-glutamine in ddH_2O (solubility limitation)	27.9	3.9
0.05 g/mL L-glutamic acid monosodium in ddH_2O	1.0	5.5
0.015 g/mL L-cysteine in ddH_2O	8.5	3.4
0.05 g/mL thiamine HCl in ddH_2O	49.8	4.1
0.05 g/mL β-glycerophosphate disodium in ddH_2O	39.7	4.3
0.05 g/mL dopamine (3-hydroxyamine HCl) in ddH_2O	49.1	4.1
0.05 g/mL D(+)-glucosamine in ddH_2O	49.6	4.1
0.05 g/mL ATP disodium in ddH_2O	36.7	4.0

*Grafted polyurethane foams (GPF) were prepared by mixing 0.5 g of HYPOL2002 prepolymer with 1.0 mL of aqueous solution containing grafting molecules. After being cured, the polymeric foam was cut into small particles (5 mm), rinsed with extensive ddH_2O, and then dried with a paper towel.

**The uranyl nitrate solution contained approximately 50 ppm uranium, and its pH was adjusted to 4.0 by titration with NaOH solution. Each GPF preparation (~ 0.5 g) was contacted with 30 mL of uranium-containing solution in a 50-mL plastic, capped centrifuge tube, which was shaken on an orbital shaker at 250 rpm and 22°C. After 24-h contact, a sample was withdrawn for ICP analysis and pH measurement.

Extensive screening studies were performed to find suitable uranium-binding ligand molecules. Table 1 shows the results of a parallel comparison test. For ligand grafting, urethane prepolymer (HYPOL FHP 2002, 1 g) was mixed with 2.0 mL of aqueous solution of dissolved ligand molecules at room temperature. The polyurethane polymer (that is, blank PMF, no ligand molecule grafted) per se did not contain any activity with respect to uranium binding. However, the PMF grafted with various ligands such as $-COO^-$, $-SH$, or $-PO_3^{2-}$ showed good uranium-binding capability under the test conditions. Polyurethane membrane foam grafted with glutamic acid (MSG-PMF) gave the highest removal (> 98%) of uranium from an initial aqueous solution that contained 50 mg of uranium per liter. A similar grafted product containing cysteine as the pendant ligand also performed reasonably well under the conditions employed, removing ~ 83% of the uranium in a 50-mg-per-liter solution. The other potential ligands tested in this experiment demonstrated poor or no capability for binding uranium under these assay condi-

tions. In this work, the concept of using biochemical ligand-grafted material for uranium binding was demonstrated by using the product synthesized with the urethane prepolymer (HYPOL FHP 2002, polyether-based polyisocyanates) and the amino acid (MSG, containing one $-NH_2$ and two $-COO^-$ functional groups). The ninhydrin amino-acid assay procedure confirmed $>10\%$ grafting yields of the glutamic acid onto the polyurethane backbone. Glutamic acid molecules were thought to be linked to the backbone through primary amino groups, and the pendant carboxyl groups in the MSG-PMF are postulated to be responsible for the uranium binding. Strong complex formation between carboxyl groups and uranyl ions has been thoroughly discussed in a recent review article (Leciejewicz et al., 1995), and the importance of carboxyl group in metal binding by biosorbents has been addressed (Geesey and Jang, 1990; Macaskie and Dean, 1990).

To optimize the formulation of a ligand-grafting procedure, various concentrations of MSG solution (0–0.5 g/mL) were evaluated in the preparation of MSG-PMF. Obviously, the MSG concentration used in the grafting process affected the uranium-binding activity of the final product dramatically (Figure 2). When the MSG concentration was below 0.2 g/mL, the uranium-binding activity of final MSG-PMF material increased as the MSG concentration used for grafting increased. However, an MSG concentration of more than 0.2 g/mL interfered with urethane polymerization, and the integrity of final polymeric material was affected. At MSG concentrations > 0.2 g/mL, the carboxyl functional that was originally designed as the pendant metal-binding ligand might also be involved with the polymerization reaction, and thus would not be available for uranium binding. High concentrations of $-NH_2$ groups might have consumed too many isocyanate groups, and thus could inhibit the polymerization reactions and affect the integrity of the polymer.

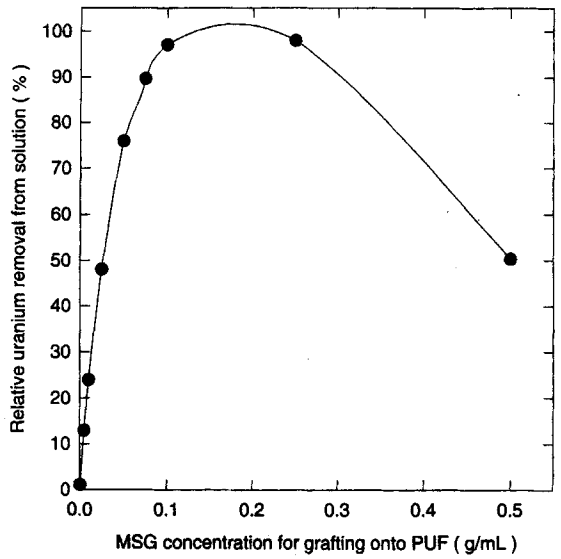

Figure 2. Effect of ligand molecule concentration in grafting procedure on the metal-binding capacity of final MSG-PMF material.

For each data point, 0.5 g of MSG-PMF was contacted with 30 mL of 100 ppm U uranyl nitrate solution (with initial pH of 3.9) overnight at 22°C.

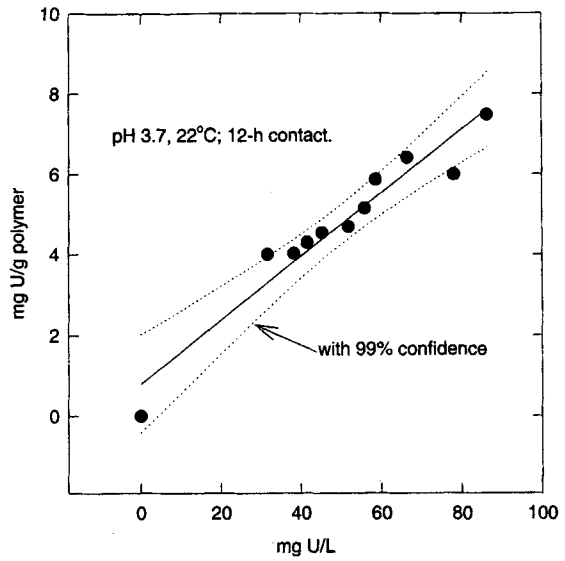

Figure 3. Uranium sorption isotherm by polyurethane foam grafted with glutamic acid (MSG- PMF).

The MSG-PMF material showed a rather linear uranium sorption isotherm when the uranium concentration was below 100 mg/L (Figure 3). From the data presented in Figure 3, we can estimate an optimum binding capacity of ~10 mg U per mg MSG-PMF. The pH of the uranium-containing solution significantly affected the uranium removal by the MSG-PMF, as shown in Figure 4. At pH levels below 6.0, the uranium-binding activity of MSG-PMF increased nearly 100 times with increasing pH from 1.5 to 5.0. This effect can be explained by the strong proton competition with uranium for the same binding site at low pH values.

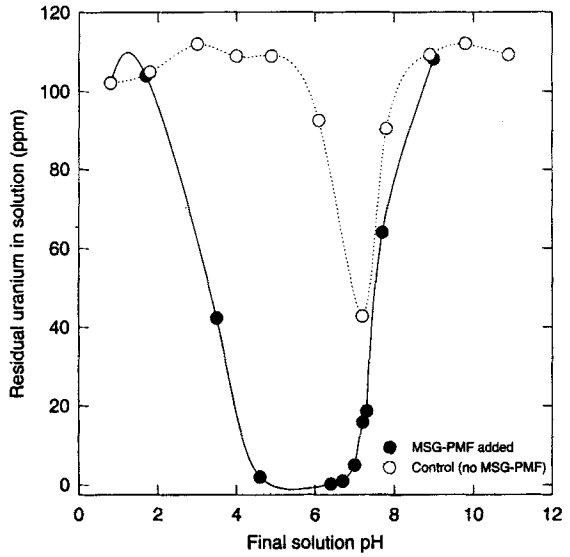

Figure 4. Effect of pH on uranium extraction by MSG-PMF.

At each pH, 0.5 g of MSG-PMF was contacted with 30 mL of 100-ppm-U uranyl nitrate solution overnight at 22°C.

Table 2. Selectivity of MSG-PUF for Uranium Relative to Other Heavy Metals*

Metal Sorbent	Iron (Fe^{2+})		Copper (Cu^{2+})		Zinc (Zn^{2+})		Manganese (Mn^{2+})		Uranium [$(UO_2)^{2+}$]	
	Equil. Conc. (ppm)	Metal Removal (%)	Equil. Conc. (ppm)	Metal Removal (%)	Equil. Conc. (ppm)	Metal Removal (%)	Equil. Conc. (ppm)	Metal Removal (%)	Equil. Conc. (ppm)	Metal Removal (%)
Control	113.7	0	109.4	0	166.2	0	104.4	0	100	0
MSG-PUF	110.4	< 3	106.7	< 3	158.0	< 5	102.5	< 2	< 0.5	> 99.5
P. aeruginosa CSU**	56.1	60	65.35	40	120.5	27.5	78.0	25	< 0.5	> 99.5
BIOFIX†	45.5	51	83.21	24	144.7	13	91.9	12	ND‡	ND

*A 50-mg quantity of sorbent was used to contact a 30-mL volume of metal solution (pH 5.0) overnight on a rotary shaker (200 rpm) at room temperature (22°C).
**In the form of lyophilized biomass powder.
†A composite material from entrapment of peat moss in polysulfone; pellet diaameter ~ 3 mm.
‡Not determined.

Table 2 presents the selectivity data for MSG-PMF material among metal ions Fe^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, and $(UO_2)^{2+}$. These experiments were conducted using separate solutions of these cations as salts in aqueous solution, rather than a single mixture containing all the cations. As seen, the selectivity of MSG-PMF material is higher than that of biosorbents such as *Pseudomonas aeruginosa* CSU, which was previously reported to have a greater affinity and specificity for uranyl ion than traditional ion-exchange/chelation resins (Hu et al., 1995). Therefore, the high specificity/selectivity of our novel ligand-grafted material obtained from highly flexible molecular designs is one of the unique properties competing with conventional metal-binding adsorbents.

The data in Table 2 indicate that the MSG-PMF material had a binding affinity for uranium 10 to 100 times higher than its affinity for any of the other metal cations. The affinities of biomass from *P. aeruginosa* CSU and the prepared product BIOFIX for uranium compared to the other four cations were only ~1.5 to 4 (*P. aeruginosa* CSU) and ~2 to 10 (BIOFIX).

Table 3 indicates that various aqueous solutions of mineral acids, organic acids, salts, and chelation reagents are capable of eluting the uranium from the MSG-PMF material; up to 95% uranium recovery was achieved in the cases where sodium bicarbonate and sodium carbonate solutions (0.01 *M*) were used. Mineral acids (hydrochloric, sulfuric, and nitric; 0.5 *M*) and acetic acid (0.5 *M*) were also good at stripping uranium from the MSG-PMF material. However, from a process standpoint, acids would be a less desirable medium for regeneration of the sorbent material than carbonate or biocarbonate salts because of the increased difficulty of handling and disposal. No significant differences were observed in the uranium elution efficiency between sodium bicarbonate solution and sodium carbonate solution. One of the important criteria for any metal adsorbent is its capability for reuse since this factor improves both the materials cost and the economics of related metal separation technology. Multiple-cycle adsorption/desorption equilibrium data (Table 4) have confirmed the feasibility of reusing MSG-PMF material. No decay of uranium-binding capacity was observed after 10 cycles of repeated use.

Kinetic studies for repeated adsorption and desorption are shown in Figures 5 and 6, respectively. The bicarbonate regeneration process did not inactivate the uranium-binding ki-

Table 3. Screening of Reagents for Regeneration of MSG-PMF

Sample No.	Adsorption Cycle*		Regeneration (or Desorption) Cycle**		
	Final U Conc. in Solution (ppm)	Uranium Removal (%)†	Regeneration Reagent	Uranium Conc. Eluted (ppm)	Uranium Recovery (%)‡
1	1.3	98.7	Deionized water	0.0	0.0
2	1.7	98.3	0.5 M HCl	87.9	90.5
3	1.3	98.7	0.5 M H_2SO_4	89.1	91.4
4	1.3	98.7	0.5 M HNO_3	86.4	88.6
5	1.3	98.7	0.5 M NaOH	9.4	9.6
6	1.3	98.7	0.5 M acetic acid	118.3	> 100
7	1.3	98.7	0.5 M sodium citrate	56.4	57.8
8	1.3	98.7	0.01 M $NaHCO_3$	90.2	92.5
9	1.4	98.6	0.01 M $(NH_4)_2SO_4$	19.5	20.1
10	1.4	98.6	0.01 M $NH_4H_2PO_4$	0.3	0.30
11	1.4	98.5	0.01 M Na_2CO_3	93.2	95.8
12	1.6	98.4	0.01 M Na_2HPO_4	0.8	0.86
13	1.4	98.6	0.01 M NaH_2PO_4	0.1	0.12
14	1.4	98.6	0.1 M EDTA in 0.1 M NaOH	79.4	81.5

*In the adsorption cycle, foam particles (0.5 g) were contacted with uranyl nitration solution (30-mL, 100 ppm U, pH 4.0) in a centrifuge tube on a rotary shaker (200 rpm, 22°C) for 4 d.
**After adsorption, foam particles were collected via vacuum filtration and dried with a filter paper. Each foam sample was contacted with regeneration reagent (30 mL) in a centrifuge tube, which was shaken on a rotary shaker overnight at 22°C.
†Uranium was bound to foam particles relative to the initial total uranium.
‡Uranium was eluted from sorbent by the regeneration reagent relative to the uranium bound to the sorbent.

Table 4. Multiple Cycles of Uranium Adsorption/Desorption Using MSG-PMF Material*

	0.01 M $NaHCO_3$				0.01 M Na_2CO_3			
	Adsorption		Desorption		Adsorption		Desorption	
Cycle No.	Final Uranium Conc. (ppm)	Final pH	Final Uranium Conc. (ppm)	Final pH	Final Uranium Conc. (ppm)	Final pH	Final Uranium Conc. (ppm)	Final pH
1	1.3	6.8	90.2	9.0	1.4	6.8	93.2	10.5
2	0.4	6.7	83.9	9.1	1.0	6.9	80.7	9.7
3	0.0**	6.9	88.2	9.0	0.0	7.2	88.2	10.3
4	0.0	5.4	82.0	9.1	0.0	6.5	86.4	10.4
5	0.0	ND†	95.2	8.9	0.0	ND	85.9	11.0

*MSG-PMF particles (0.5 g) were repeatedly contacted with 30 mL of uranyl nitrate solution (initial uranium conc., 100 ppm; pH 4.0) or 0.01 *M* bicarbonate and carbonate solutions. The foam particles and solution were contacted in a capped centrifuge tube and shaken overnight at 22°C and 200 rpm.
**This value means that the uranium concentration is too low (< 0.005 ppm) to be detected by the ICP.
†Not determined.

netics of MSG-PMF material in adsorption cycles. The adsorption processes could reach equilibrium (99.9%) in 5 min (Figure 5), indicating a true binding interaction between uranyl ions and the pendant carboxyl ligand(s) in MSG-PMF material. In addition, the concentration of sodium bicarbonate used for the material regeneration affected the desorption process kinetics (Figure 6). The higher the bicarbonate concentration, the faster the uranium could be eluted from the MSG-PMF material. The regeneration process could be completed within 5 to 10 min by using 0.01 to 0.1 M bicarbonate aqueous solution.

The applicability of our ligand-grafted material to removal of U from aqueous solutions was investigated through packed-bed column studies using MSG-PMF granules (1 to 3 mm). These porous granules consist of quasi-spherical membrane structures. The granules were packed in the column, as is the case for conventional adsorbents. A typical breakthrough curve, obtained from the adsorption/loading cycle, is given in Figure 7. For a feedstream containing 100 mg of uranium per liter at pH 4.0, 20 column bed volumes of the stream were treated before breakthrough (uranium in effluent, < 0.001% of original concentration). A typical elution curve for the column elution/regeneration cycle is shown in Figure 8. Two bed volumes of bicarbonate solution (0.1 M) were sufficient to completely elute the uranium and thus regenerate the column. Based on the material balance, the uranium recovered in the elution/regeneration cycle constituted more than 99% of the uranium accumulated in the column during the adsorption/loading cycle. After one adsorption-elution cycle, uranium in fraction sample was concentrated up to 900 times relative to the initial uranium concentration in the feed uranyl nitrate solution. In addition, similar to the results from multiple-cycle tests for the batch stirred-tank reactor, our ligand-grafted polyurethane material showed

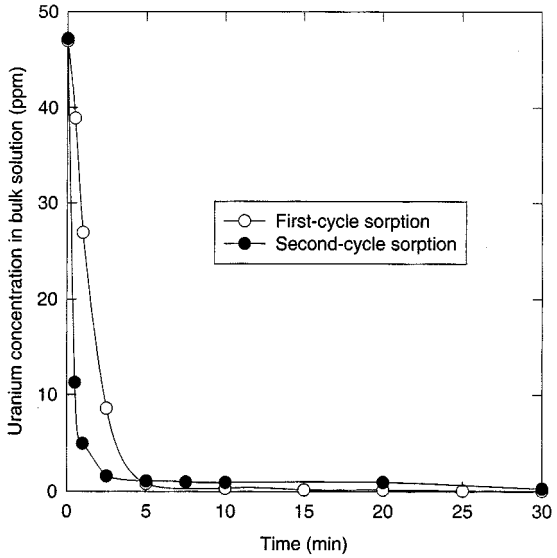

Figure 5. Uranium sorption kinetics in a stirred-tank reactor.

In the first cycle, foams were added in clumps (5 to 8 mm) of small foam powders (1 to 3 mm). In the second cycle, foams were dispersed into small powders and then added to the stirred-tank reactor, which contains 1.0 L of uranyl nitrate solution at pH 4.5.

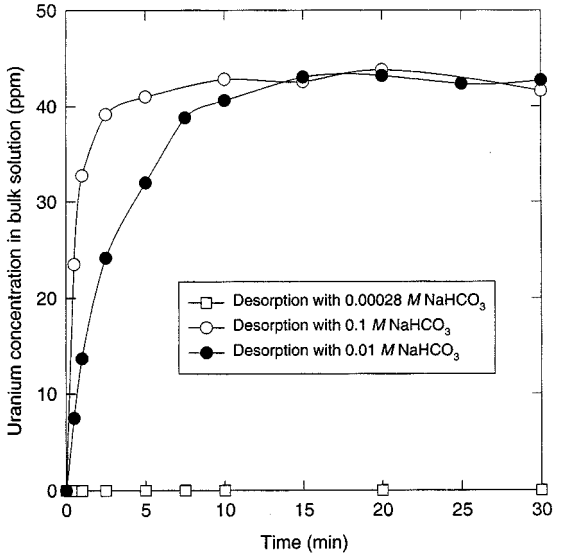

Figure 6. Uranium desorption kinetics in stirred-tank reactor using MSG-PMF powders (1 to 3 mm) at various bicarbonate concentrations.

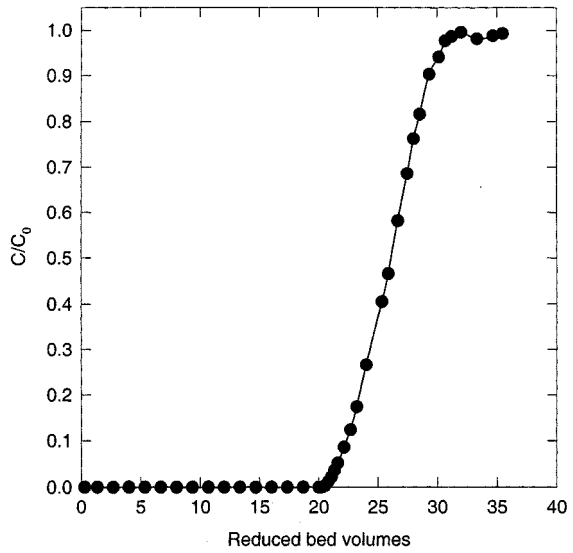

Figure 7. Packed-bed column breakthrough curve for uranium sorption/loading cycle.

promise in multiple-cycle adsorption-elution applications in the packed-bed column.

The advantages of using biochemicals, including their availability, flexibility in molecular design, mild reaction-conditions requirements, and environmentally benign nature, were discussed in the Introduction section. The key objective in our work was to utilize the diversified metal-interactive properties of biomolecules by linking them to an insoluble matrix, which, in this case, was polyurethane membrane foam.

Conclusions

A ligand-grafting approach was proposed in our work to utilize the unique metal-binding properties of biological molecules (either low-molecular-weight biochemicals or macromolecules) and to generate a new series of biomimetic sorbents for metal extraction/separation applications. The extraction of uranium from aqueous solution by our biomimetic material (that is, polyurethane foam grafted with glutamic acid, MSG-PMF) was studied as a model system; however, the significance of this original work goes beyond this system. In our MSG-PMF material, we only utilized the metal-binding activity of pendant carboxyl groups of a simple biochemical molecule, glutamic acid, which were thought to be predominantly linked to the solid polyurethane network through a primary amino group of the glutamic acid. Characterization data from both equilibrium, batch-stirred tank kinetics, and packed-bed column breakthrough-elution studies showed promise of MSG-PMF sorbent in process applications. It was demonstrated that the resulting material was stable, and to have excellent binding capacity for uranium in the form of uranyl ion in aqueous solutions. In addition, this material was shown to be quite selective for uranium by virtue of its high binding affinity for uranium compared to its binding affinity for iron, copper, zinc, and manganese. From a process standpoint, deployment of this and similar materials should be convenient, owing to our demonstration that the material can be regenerated an indefinite number of cycles by the use of simple, dilute solutions of carbonate or bicarbonate salts.

By considering the flexibility of molecular functionality (or ligand) introduction with the grafting technique, it is thought that our biomimetic sorbent could be easily tailored to different metal separation processes. It should be possible, for example, to employ ligands containing sulfhydryl and other groups to induce a desired type of functionality with regard to interaction with particular chemical moieties. Polyurethane foam was selected as the ligand support material because of its advantageous attributes such as quasi-spherical membrane geometric structure and synthesis chemistry with amino group involvement, while most of the biological molecules contain amino group(s). Generally speaking, other materials and techniques that were developed for enzyme/protein immobilization should be, at least, helpful in developing new grafting methods for metal-binding biomolecules. Ligand-grafting yields need to be improved. In future extension of this work, studies should be conducted with different biomolecular ligand molecules and support materials for selectively binding target metal ions.

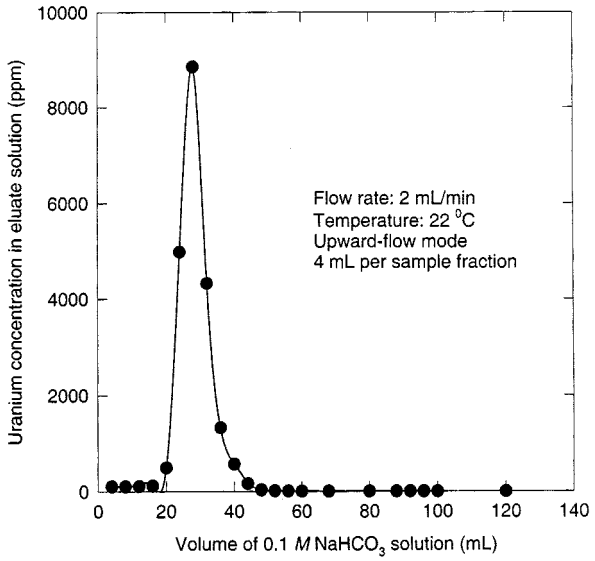

Figure 8. Bicarbonate elution curve for column regeneration cycle.

Acknowledgments

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