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Chromatographic Separations with Selected Supported Chelating Agents

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Additional information is available at the end of the chapter

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1. Introduction

In this chapter, *ligands* have a more focused definition than they typically do. Ligands are molecules having donor atoms with a pair of electrons that form coordinate covalent bonds with metal ions. Unidentate ligands have a single donor atom, while chelating agents have two or more donor atoms, and in attaching to the metal ions form rings that are associated with enhanced stability. Further, two kinds of chelating agents are involved: *molecular* and *supported*.

Molecular chelating agents, such as ethylenediaminetetraacetic acid, $(\text{HOOCCH}_2)_2\text{NCH}_2 - \text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2$ EDTA react with metal ions, such as magnesium, calcium, or transition metal ions to form soluble molecular entities in aqueous solutions. These chelating agents are said to “sequester” the metal ions, much as a prisoner in jail is sequestered or removed from society. The metal ion is sequestered in the sense that the act of forming the compound changes the properties of the metal ion. For example, EDTA may be added in small quantities to beer to prevent a haze in the solution due to formation of insoluble, dispersed calcium carbonate. Two molecules of iminodiacetic acid, $\text{HN}(\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2)_2$, H_2L may react to form soluble complexes of the type $\text{Mg}(\text{L})_2^-$. Other ligand-complex entities may be insoluble, but the coordination compounds formed, soluble or insoluble, are molecular entities.

1.1. Examples of supported chelating agents

Supported chelating agents are attached physically or chemically to a solid, and the coordination entities that result from reaction of metal ions are insoluble polymeric materials. Iminodiacetic acid can be attached to a solid and is one of six chelating agents attached to a solid and sold as “QuadriPure™ Scavengers” sold by Sigma/Aldrich. One of these may be depicted as $\text{Solid} - \text{CH}_2\text{N}(\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2)$.

“Chelex 100” is another example of a commercially available supported chelating agent. The material was available from Bio-Rad and was used to purify compounds, most notably transition metal ions. [1] The preference for transition metal ions, e.g., copper (II) or iron(II) ions, over such univalent metal ions as sodium or potassium is said to be about 5000 to 1 [1]. The material consists of a styrene-divinylbenzene copolymer to which is attached iminodiacetic acid moieties.

In addition, Chelex 100 can be used for purification of DNA [2]. Though the mechanism of action seems uncertain, a plausible suggestion is that Chelex protects DNA from the effect of heating that is used to release DNA from cells. In addition, Chelex can sequester magnesium and heavy metal ions that would adversely affect the DNA. After treatment, DNA and RNA remain in the aqueous supernatant above the Chelex sample.

Supported chelating agents serve three major functions, i.e., concentration, elimination, and recycling metal ions.

Concentration of metal ions is a significant function that enhances analytical capabilities. Measuring the concentration of trace metals in dilute sea water is a significant analytical challenge. Using supported chelators allows an analyst to concentrate transition metals present in trace amounts from a large volume of sea water onto a solid in, say, a chromatography column, then eluting with dilute nitric acid to obtain a suitably concentrated solution. The technique can also be used to eliminate matrix effects. Unfortunately, Chelex seems to be less effective in sea water than in fresh water [3].

Also, users of Chelex may encounter problems with certain natural waters that are colored with samples of naturally occurring chelating agents such as soil organic acids (e.g., fulvic or humic acids) that provide competition for metal ions and reduce the effectiveness of Chelex [4,5]. Ryan and Weber [6] studied this problem and made pre-concentration comparisons of trace levels of copper ion in standard solutions comparing Chelex-100 with three different chelating agents supported on silica. The reagents tested were N-propylethylenediamine, the bis-dithiocarbonate of that compound, and 8-hydroxyquinoline. The results indicated that in the presence of organic compounds typical organic-rich natural waters reduced the effectiveness of Chelex-100 in comparison with the three silica-supported agents. In general, immobilized 8-quinolinol was the most effective, as prepared by a modified Hill procedure [7]. It is not the purpose of this review to criticize use of a successful commercial supported chelator; rather one may note that no such product can be expected to be highly effective under all conditions and circumstances, so it seems appropriate to consider examples of custom-made agents.

Elimination of metal ions is a second major function of supported chelators. And a variety of conditions may be envisioned. Electroplating firms can be faced with the need to remove metal ions from solutions as part of an EPA-approved disposal protocol. A radiator shop may be faced with a need to remove waste zinc ion before allowing water to go into a sewer, in an effort to minimize the danger of killing bacteria used in sewage treatment procedures. The Berkeley Pit (*vide infra*) represents an outstanding example of the need to remove waste copper.

Elimination of metals by chelators benefits from a recognition that the ability of the chelator depends on several factors, the size of the metal-chelate ring, the donor atoms involved, and

the metal ions involved. For example, the chelating tendency, expressed as log K, where K is the equilibrium constant for the formation of the metal complex, follows a certain order for many chelating agents. That order for divalent metal ions of the first transition metal series is known as the Irving-Williams Order [8] and may be represented as



This may be compared with the results reported for a supported material called Octolig® (Table 1)

Divalent metal	Hg	Fe	Co	Ni	Cu	Zn
Log K	29	11.1	15.6	19.1	22.4	16.2

Table 1. Calculated formation constants for Octolig® [9, 10]

Recycling metal ions is part of the concentration process noted above. It can typically be achieved by treatment of the sorbed metals with dilute nitric acid. This is a strong acid, and the nitrate ion is not a strongly coordinating anion. In addition, recycling can be a useful means of paying for the removal process. An example of this was a laboratory bench-scale experiment to treat water from the Berkley Pit, recycle the copper and sell the copper to help pay the processing costs. The Berkley Pit [11] was once an open pit copper mine that was opened in 1955 and closed in 1982.

When the mine was closed, water pumps in a 3,800 ft shaft were turned off and the pit was slowly filled [11]. It is now a mile long, a half mile wide, and about 900 feet deep. It is said to be one of the largest Superfund sites. The chemistry of the Pit is complicated, one may say unfavorable, and certainly challenging. The bench-scale project considered the possibility of using Octolig® to remove copper and help pay for the process, but additional study would be needed [12].

2. Preparation of supported chelating agents

These materials can be made in several ways depending upon the method of linkage that is chosen. The procedures can be placed in three categories. They are covalent linkage, ionic linkage, and London-forces linkages. As an example of the covalent linkage, it is interesting to compare (*vide infra*) two sources: the detail in the patent (Examples 1-4) [14] with a journal article by Gao and co-workers [13], as in the experiments section 2.3 (entitled "Preparing and characterizing of composite absorption particles of PEI/SiO₂ ").

2.1. Covalent linkages

Lindoy and Eaglen [14] noted that metal ions were removed by the material produced and noted in Figure 1. A special feature was that due to the spacing established by the three-carbon

bridge or linkage “ the material maintains a high ion-complexation capacity.” These workers also demonstrated metal-ion removal capacity for representative metals (transition metal ions, alkali metal ions, etc). The material under dynamic conditions removed 50 mg Cu(II) /g composite. The metal absorbing ability followed the order $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$.

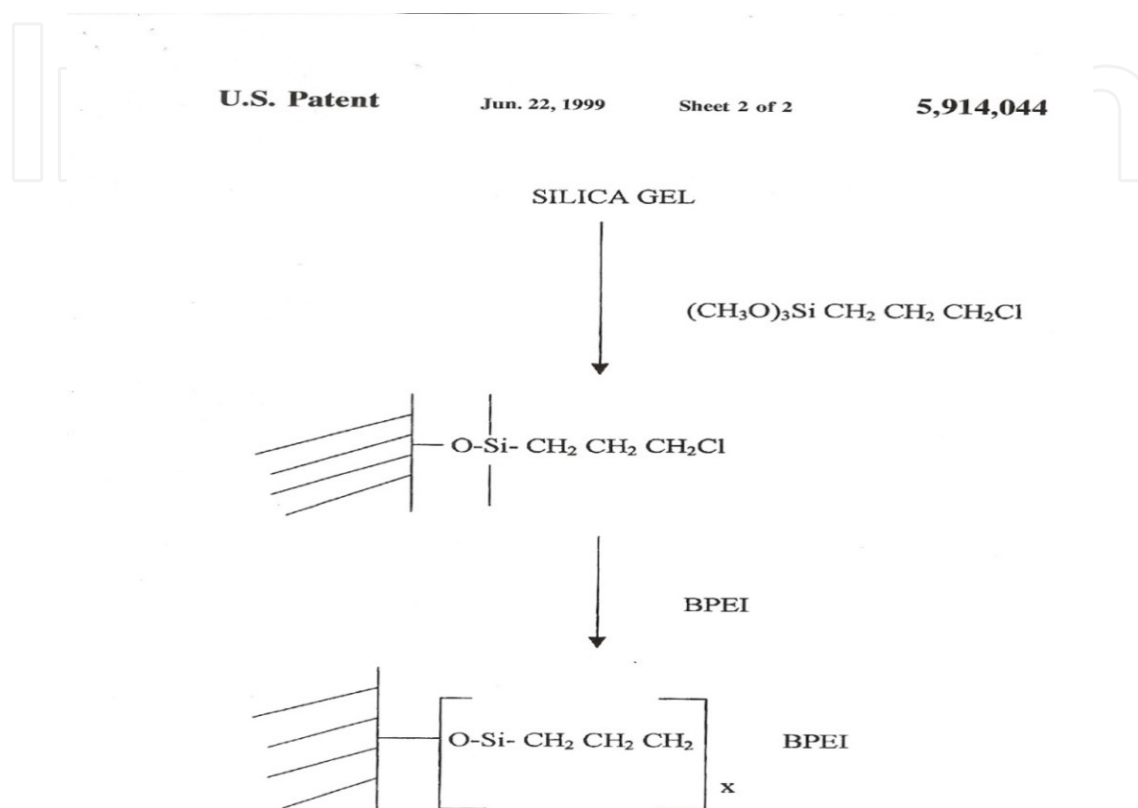
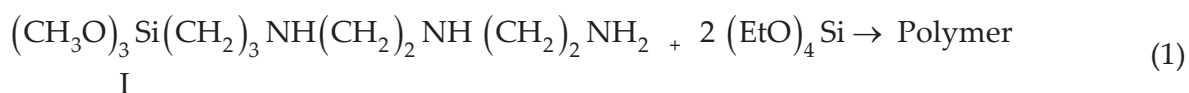


Figure 1. Flow chart for the synthesis of a supported chelating agent. BPEI consists of branched ethylenediimino moieties [14]

A similar technique was used by Soliman, who also used a silica gel matrix and a covalent linker to tie to a series of amines, mono-, di-, tri-, and tetra-amine [15]. Using a batch equilibrium technique, he measured the removal capacities (mmole/g) for divalent forms of cobalt, nickel, copper, zinc, cadmium, and lead. In general maximum removal values (at optimum pH values) were obtained for the tetra-amine species.

El Ashgar used a variation on the technique [16]. Specifically, 3-chloropropyltrimethoxysilane was used to alkylate diethylenetriamine, i.e, reaction with the halide end to produce a precursor of a polymer (I, Eqn. 1). The reaction of I with tetraethylorthosilicate resulted in a “diethylenetriamine polysiloxane immobilized ligand system.”



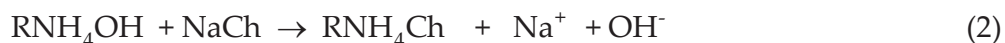
The system was effective as a solid-phase preconcentration agent for cobalt(II), nickel(II), and copper(II) at pH 5.5 using column chromatography. A especially desirable feature was that the three metals could be cleanly separated by adjusting the pH of the eluent [16].

Another covalent approach is condensation of a potential ligand of the type HO-Y-Z where Y is a hydrocarbon moiety and Z is a coordinating group NH or NH₂ or SH. The mixture of solid substrate (clay, silica) was suspended in toluene with the potential ligands and a drop of sulfuric acid in a flask attached to a Dean-Stark tube, which is attached to a condenser. The reaction occurs between OH on the potential ligand and OH group on silica with the elimination of water using azeotropic distillation. Water produced in the reaction flask (2, Figure 2) distills as a constant-boiling mixture (3), that is cooled in a condenser (5), and separates into two components, which drop into a calibrated Dean-Stark tube (8). The water drops to the bottom of the tube; toluene returns to the reaction flask (2). The progress of the reaction can be measured, e.g., condensation of 0.1 mole of HO-Y-Z should give 1.8 milliliters of water. The reaction is allowed to proceed until completion [17, 20]. Clays were also used as supports [18, 19].

2.2. Ionic linkages

Examples are available from a number of studies. The authors demonstrated that the use of ion-exchange resins as supports for chelators that can be derivatized or converted to ions is a versatile technique [22]. Examples involving two different ion-exchange resins help indicate the range of the technique.

An *anion-exchange resin* in the hydroxide form RNHOH (e.g., IR-120), can be treated with other chelating agents HCh converted to the anionic forms, NaCh (Eqn. 2).



A *cation-exchange resin* exists as a polyalkylsulfonic acid, RSO₃H and can react with a chelating agent in a protonated form HCh⁺ (Eqn. 3).



Lee and coworkers [23] used the technique shown (Eqn 2) to load a number of chelating agents, among them chromotropic acid, onto the anion exchange resin Dowex® 1-X8 (chloride form). These composites are easy to prepare, and loading of metal ions on the chromatography columns showed the metal ion loading as a color change.

An anion exchange resin (e.g. Amberlite® R-120) was treated with protonated dithiooxamine, H₂NC(S)C(S)NH₂. Using the supported ligand, quantitative removal of copper, cadmium, and lead ion solutions at neutral or slightly alkaline solutions of deionized or tap water, but poor results were obtained with sea water [22].

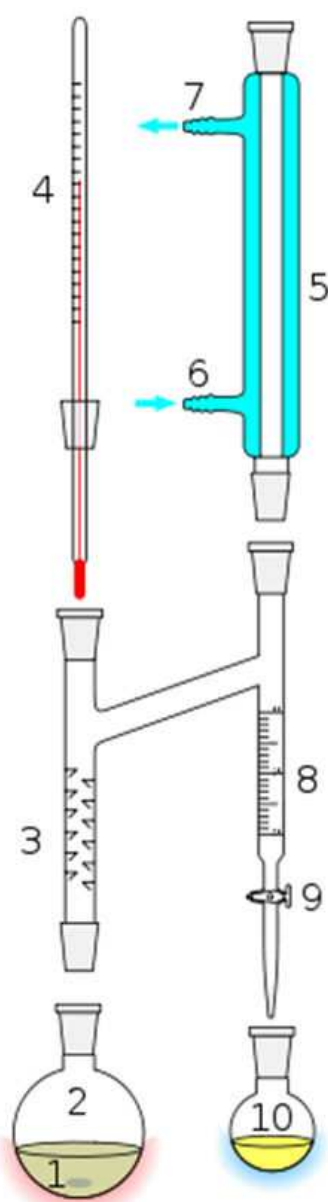


Figure 2. Schematic representation of a Dean-Stark Apparatus [21]

2.3. London-forces (corkscrew) approach

On occasion useful ligands are available, but need to be converted to supported ligands.

Examples of such ligands include LIX54 [$\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{COCH}_2\text{COCH}_3$], LIX860 (*n*-dodecylsaldoximine), oleoylacetone, and *N, N'*-didodecylthiooxamide (all were once commercially available). A two-step procedure was used [24-27]: First, silica gel (5 g) was mixed with 25 mL of hexane, and the excess solvent allowed to evaporate to produce silica gel with pores loaded with hexane. Next the treated silica gel was mixed with a solution of a chelating agent in hot hexane. After stirring, the hexane was allowed to evaporate. It was hypothesized that a change in environment resulted with the evaporation of the hexane, i.e., that the long-chain hydro-

carbon in the pores experienced changed environment, e.g., from hydrophobic to a hydrophilic condition. It was presumed that in the new environment, the form of the long-chain hydrocarbon altered, going from a stretched-out to a coiled version (idealized form, Figure 3) as a result of association of London forces. The coiled version would lead to a wedged ligand.

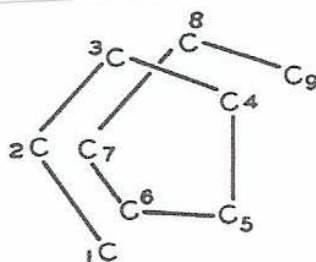


Figure 3. Idealized depiction of a long chain hydrocarbon coiled by virtue of London forces in a hydrophobic environment. Redrawn from [24]

The efficacy of the approach is considered later (*cf.* Table 8).

3. Removal of heavy metal ions with Octolig®

Remaining sections of this chapter are concerned with research involving the commercially available supported chelating agent called Octolig® because large quantities were available for a very reasonable cost (a wholesale price prior to 2008 was \$40 per kilogram), and a collaboration was established with Robert Alldredge on the basis of mutual interest in the supported chelators, as noted elsewhere [10].

Examples of the removal of heavy metal ions by Octolig® may be found in three areas: patents, company literature, and refereed journals.

3.1. Patent literature

Lindoy and Eaglin [14] provided useful information about their experiments demonstrating the efficacy of removal of representative transition metal ions.

3.2. Company literature

Several examples are available in literature provided by Metre-General, Inc. [28].

A *first example* involved a Colorado plating shop with numerous plating lines, removal of Cr, Cu, Ni, and Zn was a matter of concern. The existing precipitation process did not consistently reduce heavy metal concentrations to less than required limits. By use of an Octolig® column

chromatography system (cf. Figure 4), the plating shop was able to recycle the treated water and reduce the fresh water usage from 18,000 GPD (gallons per day) to 8,000 GPD [28].



Figure 4. Application example –The Octolig® ENVIRO-4000 of Metre-General, Inc.

Specifications included two 56-gallon HDPE tanks, a 120 V pump, on/off float switch, rotameter with flow-rate adjustment, two pre-filters, and four filters with refillable Octolig® cartridges. Size is 52" x 52" with a 68 gallon spill containment. From [28] and reproduced with permission.

The results of the study are summarized in part in Table 2 and demonstrate two useful consequences. The first result was an effective removal of nuisance transition metal ions: 98% removal of zinc ion, 93% removal of nickel(II), 73% removal of copper(II) species. The second result, as a consequence, was the ability to reduce the fresh water intake by recycling reducing water usage by 67%.

Element	Cr	Cu	Ni	Zn
Untreated water	0.30	0.80	0.60	4.20
Treated water	N/D	0.21	0.04	0.0

Table 2. Effect of Octolig® treatment on concentrations, ppm, of selected metals [28]

A *second example* involved a similar unit installed at a gold mine located in mountains west of Denver, Colorado [27]. The chief contaminant in the mine drainage water was zinc, and about 4 million gallons of mine drainage water was discharged yearly at the gold mine. A two-fold treatment was tested. First, water flowing into a settling pond (33 ft. by 40 ft., 3 ft. deep) was crudely treated with lime. Second, the overflow was pumped through pre-filters then into an Octolig® MRP (metal removal plant) unit. In a pilot study, treated water contained only 0.02 ppm zinc. It was calculated that costs of the installation were less than \$0.70 per 100 gallons of drainage water [28]. And probably one should remember the value of water in certain arid parts of the western United States.

A *third example* [28] involved a Superfund site. Octolig® was used in a bench test of material from the Liberty Industrial Finishing Superfund site, a 30-acre parcel in the village of Farmingdale, Nassau County, New York state. At this location, Republic Aviation produced military aircraft for the US government from the late 1930s until the 1960s. Operations involved

electroplating aircraft parts. The area became contaminated with solvents that were used for cleaning parts as well as solutions of cadmium and chromium. Waste material was dumped into sand pits on the company property during the 1930s and 1940s. As a consequence, ground water became contaminated with low levels of solvents and low levels of cadmium and chromium, ca.0.300 mg/L (ppm). US Environmental Protection Agency designated the area as a Superfund site in the 1990s [28],

Metre-General, Inc. tested undiluted groundwater samples as received and at two dilutions to test the efficiency for removal at different influent concentrations. Dilute organics were removed by charcoal column chromatography. Heavy metals were removed by Octolig® column chromatography. The removal system was one like that shown in Figure 4. Some 10 columns made of HDPE plastic about 35 in (89 cm) in diameter held 300 kg of Octolig®21. The columns were arranged in two banks of five each operated in parallel and designed to treat 300 GPM (gallons per minute). The results in Table 3 indicate that concentrations of metals of concern were reduced to below required limits.

The data also indicate that Octolig® can have a long “recycling life” because the heavy metal ions were removed, not comparatively innocuous ones like calcium that affect TDS (Total Dissolved Salts). The contrast between removal of cadmium or chromium versus non-removal of calcium ion shows the advantage of being able to design supported chelators for specific purposes. Supported iminodiacetic acid, for example would have removed cadmium, but also calcium ions as well, reducing in this instance the useful capacity of this material..

Dilution Element Influent Concentration, ppm		Effluent Concentration, ppm	
None	Cd	0.280	0.029
1:5	Cd	0.061	0.007
1:10	Cd	0.032	<0.005
None	Cr	0.090	<0.005
1:5	Cr	0.023	<0.005
1:10	Cr	0.010	<0.005
None	Ca	25.0	25.0
1:5	Ca	5.1	4.8
1:10	Ca	2.7	2.5

From [28] and used with permission

Table 3. Summary of results of bench-scale treatment of Liberty Industrial Finishing Superfund Site.

3.3. Refereed literature

Quantitative removal of uranyl ion, UO_2^{++} , from aqueous solutions (well water) was demonstrated using the standard chromatography technique. Solutions of uranyl acetate (50 ppm)

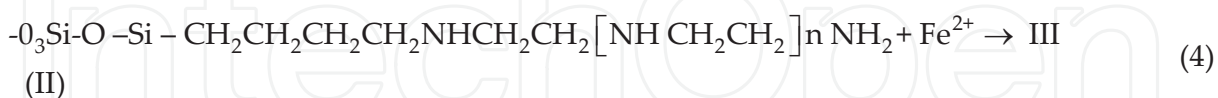
were quantitatively removed by Ferrilig, Thorilig, or Octolig® [29]. Uranium is a contaminant of the mineral apatite in Florida that is a basis of the phosphate industry. Uranium can also contaminate sources of drinking water in certain areas of Colorado, and is a matter of concern for water supplies for small towns [29].

Gao and co-workers measured the absorption properties of an Octolig®- like material [13] by a batch and a flow methods. Quantitative reaction was reported, and the absorbing ability of the PEI-silica material followed the order of $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$ at a pH of 6-7 [13]. They also measured the saturated absorption uptake and reported values for copper(II) of 25.95 mg/g and 50.01 mg/g, respectively, for static and dynamic conditions [13].

4. Removal of anions with Octolig® and metal derivatives of Octolig®

Some initial studies in our laboratory were concerned with removal of nuisance species by means of chromatography with Ferrilig, the iron(III) derivative of Octolig®. These species, existing as anions, were arsenate and arsenite, chromium as chromate, molybdenum as molybdenum(VI), and selenium as selenite and selenate species. All four are nuisance species in the western United States as well as elsewhere. Molybdenum is an essential element, whose compounds are useful, but it is a nuisance in areas of molybdenum mining when mining runoff water or processing water in ponds becomes a disposal problem. The initial focus was on removing arsenic species by chromatography, and a specific focus was on the iron(III) derivative of Octolig® (named "Ferrilig") because of the known insolubility of ferric arsenate [30-32].

The synthesis of Ferrilig (IV, Eqn 5), originally described [30] has been studied with view toward improving the amount of iron taken up. The synthesis is summarized (Eqn. 4-6) [31]. Octolig® (II) was treated with aqueous ferrous sulfate under a nitrogen atmosphere. The product (material III Eqn. 4, 5) after spontaneous oxidation and production of hydroxide ion (Eqn. 6) is termed Ferrilig (material IV). The structure of Octolig® was that given in the company literature [28].



Oxidation of the ferrous form (material III, green) to the ferric form (material IV, rust brown) occurs spontaneously in the presence of air, e.g., as the wet sample is standing exposed to the air.

The role of coordination in reducing the oxidation potential of iron(II) is well known, and was noted by Moeller [33], a process that is enhanced when the coordinating agent is a chelating agent. Thus the oxidation potential for hydrated ferrous-ferric species is - 0.771V; whereas the value in the presence of oxalate ion is -0.02 V [34]. Octolig® has a plethora of chelating species, i. e., ethylenediimino moieties or extended ethylenediamines, that should be capable of lowering the oxidation potential of coordinated iron(II). Accordingly, the ease of oxidation should hardly be surprising. Nevertheless, it was surely interesting to note and watch. Species II was white, species III was green, and species IV was rust-brown.

Considering the effectiveness of Ferrilig, the study of other metal derivatives (“metalloligs”) was effected using what may be described as facile syntheses. The metals used were copper(II), cobalt(II), nickel(II), manganese (II), and thorium(IV) [32]. An exhaustive study can not be claimed, e.g., for all metalloligs and all anions. But all six metalloligs exhibited 99% removal of arsenic by means of column chromatography using 280×10^{-3} ppm As as Na_2HAsO_4 [32]. Other anions were tested using various metalloligs, and quantitative removal (98-99%) was achieved for nitrate, nitrite, phosphate, sulfate, and fluoride ions in deionized water [31, 32, 35].

A *standard test* for removal ions by chromatography involved the following: A Spectra/chrom peristaltic pump was used to deliver aqueous samples to a chromatography column, 2 cm (id) by 31cm and equipped with a glass frit and a Teflon stopcock. The column was packed with about 22 cm of Octolig® or other solid. Before packing, the solid was suspended in water, swirled, and the fines were decanted, a process that was repeated until no fines were observed. Water samples were chromatographed using a rate of 10 mL/min. Usually, the first three or four 50-mL aliquots of effluent were discarded, and later ones were used for analysis (Table 4). Total dissolved solids were measured, and used as a guide to assess a state of equilibrium [29-31, 35-38].

Element	Form	Sample	Initial Concentration, ppm	% Removal
As	Na_2HAsO_4	Well water	280×10^{-3}	99.3
Cr	Na_2CrO_4	DI water	50.6	95.5
Mo	$(\text{NH}_4)_6 \text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	DI water	50.7	94.7
Se	Na_2SeO_3	Well water	258	99.9

Table 4. Effect of column chromatography of nuisance species using Ferrilig [31]

In a subsequent study, some attention was focused on the use of Cuprilig, obtained by a truly facile synthesis by shaking a suspension of Octolig® in deionized water and a standard solution of copper sulfate in deionized water. Cuprilig was tested for removal of perchlorate ion, which is a serious problem in certain areas, most notably in Rialto, California where one source of well water contained 10,000 ppb perchlorate. This remarkable concentration was probably a consequence of a plume of contaminated water, owing to proximity to a facility that produced ammonium perchlorate, the propellant for the sidewinder missile [37]. Obvi-

ously it was of interest to determine whether a metallolig, e.g., Cuprilig, could remove perchlorate ion from aqueous solutions using column chromatography, and it was a success [37]. Using perchlorate solution, the effluent was below detection limit, i.e., <1 ppb. But success also raised the question of a “control” experiment, one kind being to eliminate the role of the metal ion, and use only Octolig®. Doing so, the results were equally good, i.e., >99% removal with Octolig® alone using deionized water or well water [37].

Clearly a different model for understanding the removal process was in order. And the current hypothesis is that nitrogens are protonated at low pH values probably as well, even somewhat above the pH at which Octolig® should not be used. A working hypothesis consistent with Figure 5 is that at least two important considerations are involved: (1) The nitrogens must be protonated, and (2) species to be removed must be anions or if weak acids convertible to anions [39].

Further studies [35, 37, 38] have found that simple anions can be quantitatively removed by Octolig® at reasonable values of pH, and the order of removal is consistent with an ionic model of anions being attracted to protonated moieties of the Octolig® as represented (Figure 5).

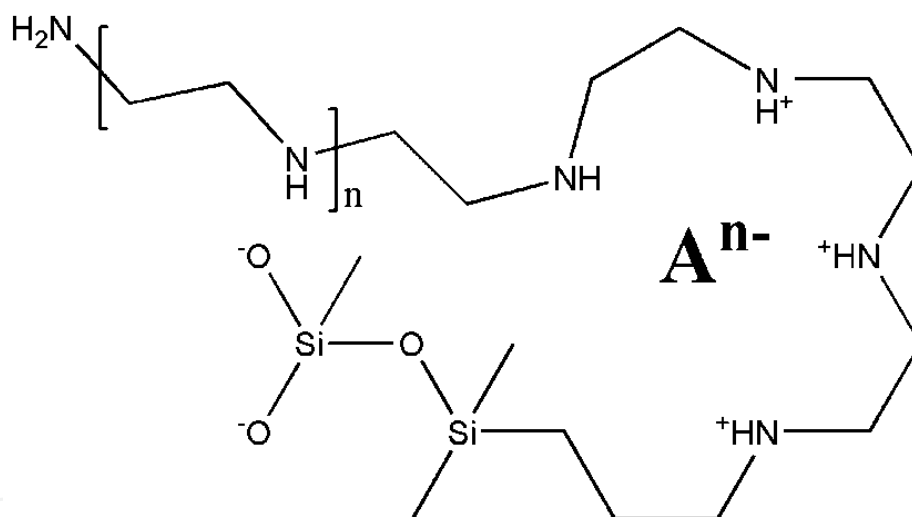


Figure 5. Proposed structure of Octolig® -anion (A-) interaction [38]. Reproduced with permission of the publisher

A range of compounds can be quantitatively removed provided the pKa of the material is less than about 8 [40]. Above that value, the per cent removal was less than 20% [40]. This is demonstrated in Figure 6. It may be presumed that for those compounds having pKa values greater than 7+, the anion concentration vs. the degree of protonation of Octolig® reaches an unfavorable balance. One substance of special interest is BPA (*vide infra*).

Compounds in order of increasing pKa values (in parentheses): Amoxicillin (2.4), Eosin Y (2.7), Lissamine Green (~3), Erythrosine (3.6), Rose Bengal (3.9), 4-nitrophenol (7.15), 2-nitrophenol (7.22), 3-nitrophenol (8.36), 4-tert-butylphenol (10.16) 4-isopropylphenol (10.19). From [47] used with permission

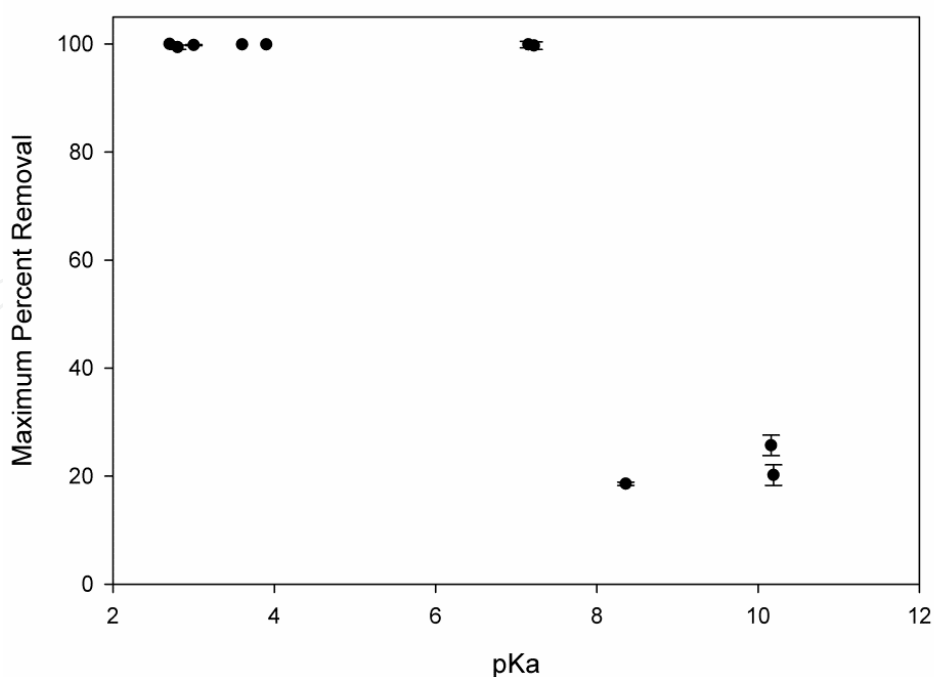


Figure 6. Maximum per cent removed as a function of the pKa for the compound under study [47]

5. Control of pharmaceuticals and other large anions

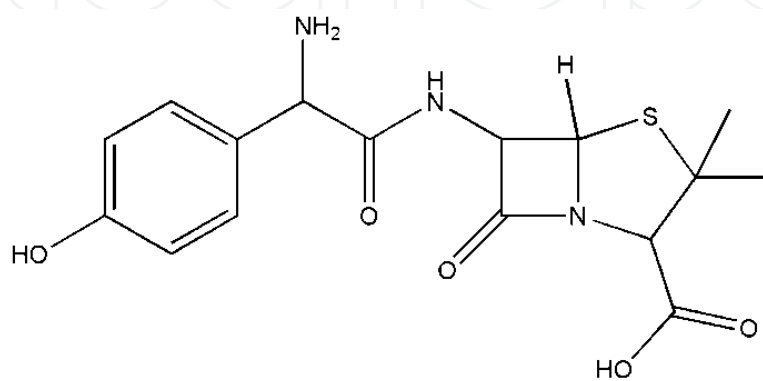
Three diverse groups of compounds can be usefully considered for their impact, but the need to be able to separate them from aqueous solution: Pharmaceuticals, BPA, and food dyes. These will be considered in succession.

5.1. Pharmaceuticals

The range of anions that can be quantitatively removed by Octolig® and column chromatography include some significant pharmaceuticals. These substances are chemical compounds (inorganic or organic) that can be used in the diagnosis, mitigation, treatment, or prevention of a disease [41,42]. Unfortunately, because of their usefulness and the magnitude of production they can represent a disposal problem [41-43]. Pharmaceuticals have an impressively wide range of applications – human medicine, veterinary medicine, aquaculture, livestock production, and agriculture. [43]. A recent review [42] quoted a statistic that of the 16,200 tons of antibiotics produced in the United States in 2000, about 70-% was used for livestock [40]. Unfortunately, about 75% of the antibiotics involved was not absorbed and was delivered to the environment in the form of urine and feces [41].

On the positive side, a study using Octolig® as a separating agent showed that Amoxicillin (Figure 7), a very popular antibiotic in the United States was among those quantitatively removed [44], as noted in Table 5. This a result that is consistent with the information provided in Figure 6. It is also noteworthy that results for DI (deionized) water and well water from the Floridan Aquifer were similar. The lack of a matrix effect, at least for these two solvents may be promis-

ing if one considers that hospitals can represent a significant source of un-metabolized drugs as well as metabolic products of these drugs /in waste products. The concern raised more recently is the fate of such waste materials. One may consider an analogy, i.e., radiator shops in certain localities must be careful not to release zinc ion water leaving the establishment lest the concentration affect bacterial used in sewage treatment. Will a similar concern arise with respect to hospitals? The possible causes for concern were raised in a review on the topic [43].



Amoxicillin

Figure 7. Structure of Amoxicillin, $pK = 2.4$

Matrix	TDS, ppm	pH	Stock Conc. (10 ⁶ M)	% removed
DI water	4	6.17	639	99.4±0.4
	3	6.19	1230	99.8±0.3
	2	5.97	741	98.8±0.6
Well water	119	6.56	750	99.2±0.4
	153	7.12	912	96.9±1.2

Table 5. Passage of aqueous Amoxicillin samples over a 3.0 (id) chromatography column packed with ~130 mL of Octolig[®] at a flow rate of 10 mL/min (50-mL aliquots were collected and concentrations of fractions 4-10 were measured spectrophotometrically) [44]

5.2. PBA

Another large molecule of potential interest would be anions derived from Bisphenolacetone (Figure 8) synthesis (Eqn 7), notable reactions to produce polycarbonate (Eqn. 8) or epoxy resins (Eqn. 9). As reviewed recently elsewhere [45]. Bisphenol A (BPA), the synthesis of which is shown (Eqn. 7), is a component in the synthesis of polycarbonate plastics and epoxy resins (Eqn. 8, 9) that have a variety of significant uses.

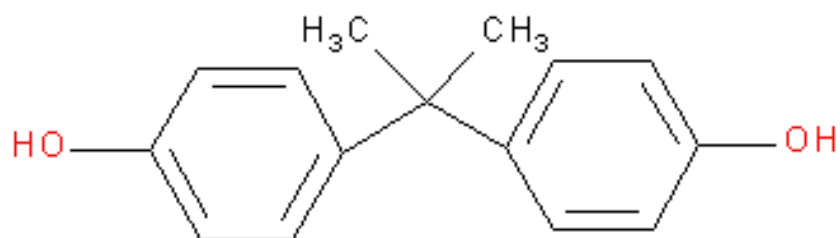
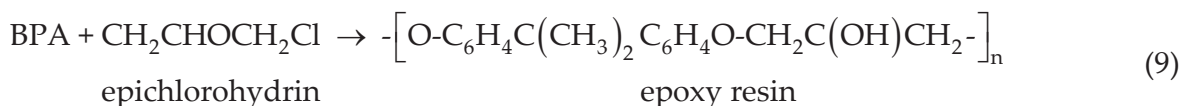
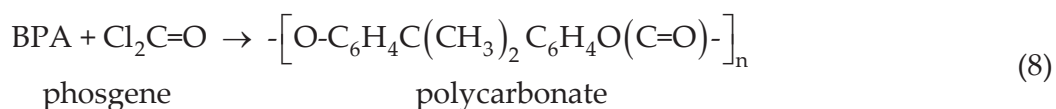
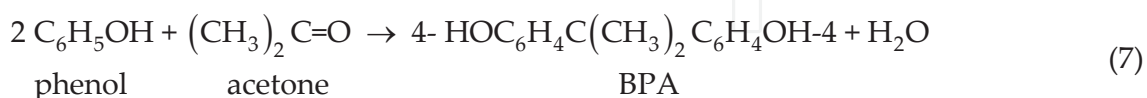


Figure 8. Bisphenol A, BPA. pK values = 9.59, 11.3



As noted in the review [45], these plastics can fail with age, and BPA or other substances possessing estrogenic activity (EA) can be released. The review noted other points of significance (with documentation provided in the review) including:

- BPA is also present in our bodies in detectable amounts in our blood stream.
- It is present in the rivers and estuaries in detectable amounts, despite its low solubility in water.
- Though BPA may have a short half-life in soil, the ubiquity of the substance provides a continuous supply in the environment.
- A significant concern arises as to the toxicity of this material, which because of the ubiquity of the material and the uncertainty of the toxicity has become a matter of concern and significant debate, which seemingly leads to three choices: ban, restrict, or ignore [45, 46].
- Two better approaches are avoidance of exposure to EA-containing polycarbonates or treatment of EA-containing polycarbonates.

The potential control of EA materials in plastics needs to be considered because the volume of plastics used annually means that there will be no sudden cessation of use. But there is reason for optimism, based on a recent study. Results of a survey of 455 commercially available plastic products for release of estrogenic active (EA) material gives pause for the thoroughness as well as for the implications [46]. These workers discovered that EA materials could be removed by

extraction with two solvents, e.g. ethanol and saline, and the potential for control of EA materials in plastics may be considered.

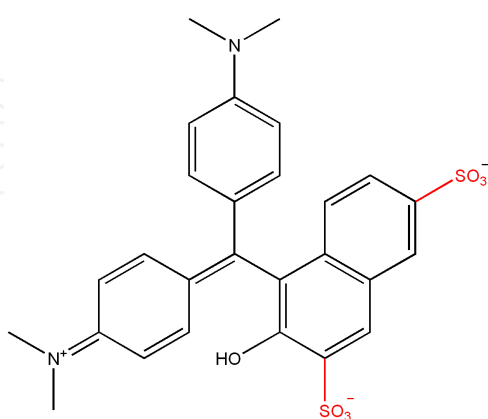
The hypothesis that anions of BPA might be removed by column chromatography with Octolig® was considered but not pursued because of the warnings in a MSDS (Material Safety Data Sheet) about hazards of BPA and because the pKa values of BPA were listed as 9.59 and 11.3.

The expectation of success was limited, based on the hypothesis and the prediction based on available data (Figure 6).

5.3. Dyes

As Rosales and co-workers noted [48], vast amounts of chemical dyes (around 10^6 tons) are made annually worldwide [49]. Dye-containing effluents can make their way into runoff and wastewater, eventually settling in the soil. As these workers noted [48], with textile industries, as much as 50% of the dyes can be lost and disposed in effluents [50]. These dyes can have adverse effects on the environment and ecosystems they pollute. Previous extraction methods have had limited success in removal from soil, and a recent approach involved the use of Fenton's reagent with electrochemistry [48] testing removal of Lissamine Green (Figure 9) from a pseudo-soil matrix (kaolin).

Martin and Nabar [51] noted that previous studies [39] had demonstrated the ability to remove Lissamine Green from aqueous solutions, using column chromatography with Octolig® so it might be cheaper to extract Lissamine Green from soil using hot water, then remove the Lissamine by column chromatography with Octolig®. They were successful with kaolin and montmorillonite, but discovered that mixtures of clay and peat were less successful depending on the amount of peat present, then success of extraction decreasing linearly with the concentration of peat present. accordingly, the two step procedure would save same on electricity, depending on the availability of hot water and the type of soil present.



Lissamine Green B

Figure 9. Structure of Lissamine Green

5.4. Food dyes

Other dyes such as food dyes may be commonly present, but the amount actually used is uncertain, and some workers have been concerned with the impact of these commonplace substances.

Food dyes are among the commonplace aspects of our daily life that may need more scrutiny [52]. These artificial colors are added to food for several reasons, chiefly to make the food more appealing, or perhaps to fool the consumer into thinking the food has fruit or other helpful ingredients [52]. As noted elsewhere [52], synthetic food dyes have no nutritional value, they have no health benefits, they are not preservatives, but they do make us feel good about eating the food.

One significant concern is the suspicion that for over three decades the dyes have not been safe for all consumers [52, 53]. Specifically, some dyes are suspected of being responsible for behavioral problems in children, including "short attention span, aggressiveness, impulsivity, distractibility [54]." Feingold is credited with proposing that food dyes induce or aggravate symptoms of hyperactivity in children [55], and suggesting a "Feingold diet" is one that eliminates artificial food colorings.

Conflicting results, however, made it difficult to determine whether a Feingold diet is beneficial, despite a number of studies that have been conducted that have led to the view that food dyes did impair performance of hyperactive children [54], or did not in a controlled study [56], or that it did and that a one-week experimental diet could be used to detect a "sub-group of children hyperactive from specific food dyes [57]."

One common food dye is FD&C No 1 (Figure 10), a dye which should be removable by column chromatography by Octolig® were this to be desired. The structure (Figure 10) showing sulfonate groups indicates on the basis of Figure 6 that a low pKa would be expected, as would be ease of separation.

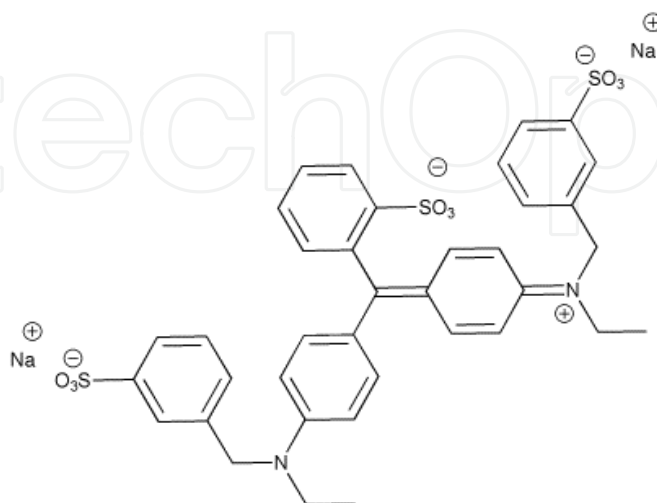


Figure 10. Structure of blue dye FD&C No 1 [Brilliant Blue FCF]

Using the *standard method*, noted earlier, quantitative removal (100.1±0.04 %) of FD&C No 1 was achieved [58] This is one of seven food dyes approved for use in the United States under the Pure Food and Drug act of 1906 (abbreviated as FD&C), the other six dyes also appear to be easily removable by Octolig® based column chromatography based on an consideration of their structure.

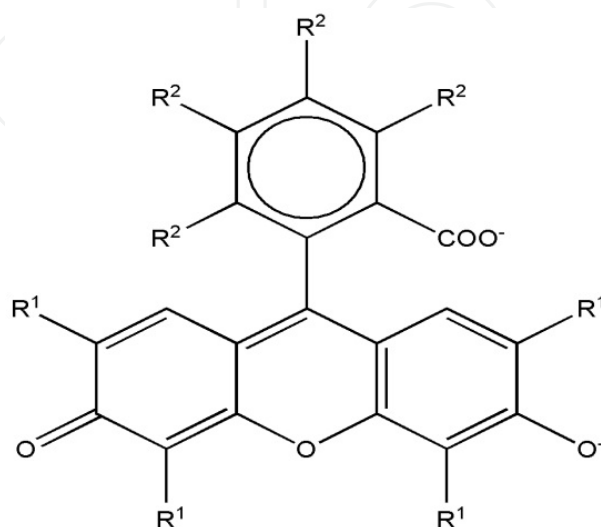


Figure 11. FiFD&C No 3., Erythrosine B, R¹ = I ; R² = H

Matrix	pH	Concentration., μM	% Removed
DI water	8.66	78.8	99.9 ±0.0
Tap water	7.76	94.9	99.9 ± 0.0
Well water	8.33	105.5	98.6 ± 0.1

Table 6. Column chromatography of aqueous Erythrosine B samples over a 3.0 cm (id) column packed with ~130 mL of Octolig® at a flow rate of 10 mL/min (50-mL aliquots were collected and concentrations of fractions 4-10 were measured spectrophotometrically) [44]

Similarly, using our standard method for column chromatography, quantitative separation was obtained. for Erythrosine, but also for the other food dyes in contemporary use It is also notable that there was no significant matrix effect observed for DI, tap or well water.

6. Batch separations versus column chromatography using Octolig®

Removal of metals by immobilized ligands frequently involves a choice of two techniques, a batch method or column chromatography. The batch method can be faster when samples are taken from the supernatant for replicate analyses. This method also can establish when equilibrium (or stasis) has been established. One flaw is that the sample of solid may not be

adequate to remove all the sample in the supernatant (which is an asset for measuring capacity of the solid). But there are at least three applications of the batch method that can be considered.

One application was determining the time course for of the batch methods. The example (Figure 13) shows the time course of removal can be fairly rapid, and an estimate of the capacity is indicated by the “plateau phase.”

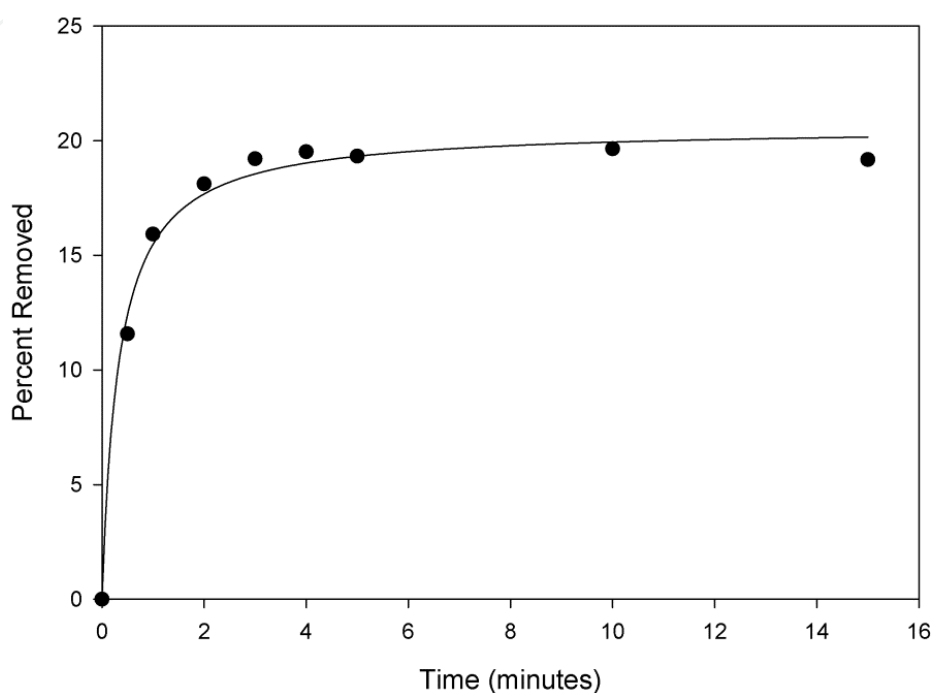


Figure 12. method with Octolig®: Percent removed by Octolig® as a function of time for aqueous 3-nitrophenol. Octolig® was suspended in 100 mL of aqueous 3-nitrophenol) and shaken (.at a rate of 240 rpm. Aliquot portions taken periodically as noted and analyzed. (Figure from [47], used with permission of the author).

A second application of the batch method was being able to evaluate a mechanism of sorption, as noted by Gao and co-workers [13].

A third application was that of comparison. Many in academe seem to have favored batch methods. In contrast, a valued colleague [9, 10] noted that information obtained from column chromatography was more applicable to the needs of industry. Column chromatography was used with Octolig® in practical applications as noted previously.

Accordingly, a series of experiments was designed and performed to evaluate comparisons of batch versus column chromatography (cf. Table 7). A standard batch method is presented here for the sake of comparison [59]. A sample of Octolig® (5 g as received) was placed in a 250-mL Erlenmeyer flask covered with 100 mL of about 1600 ppm phosphate as NaH_2PO_4 . The samples were placed in a gyrotory water bath and subjected to shaking (>170 rpm) overnight. At the end of the shaking period, an aliquot was removed, and diluted ca. 1:8 for phosphate. Mean and SD values were calculated. The result was subtracted from the initial phosphate concentration to determine the capacity, expressed as moles per kg of Octolig®.

Results of the study with Octolig[®], summarized in Table 7 indicate that there was no statistically significant difference [59] between the two methods. Similar results were obtained for a capacity for arsenate [59]. The results (Table 7) were also used to see if there was a major difference between different preparations of Octolig[®] by comparing capacity for phosphate (Sample 1 vs. Sample 2),

Substrate	Anion	Chromatography*	Batch method*
Cuprilig	Phosphate	0.178±0.003	0.185±0.003
Octolig [®] (Sample 1)	Phosphate	0.304±0.02	0.299±0.004
Octolig [®] (Sample 2)	Phosphate	0.341±0.06	0.327±0.001

*Standard method (see text) was used

Table 7. Selected removal capacities (moles/kg) calculated for phosphate comparing the chromatography method versus a batch method (= 3) [59]

A *fourth application* is a convenient assessment of the removal of a transition metal by a supported chelator vs sorption on the substrate. It appears that the supported chelators were able to remove copper ion in a quantitative manner, but a goodly proportion (83%) was removed by sorption on silica gel. In contrast, a Linde molecular sieve (alone) with fairly defined pores removed about half of the copper ion through sorption.

Chelator	Support	% Removed
LIX [®] 54	silica gel	97.7±3.3
Oleoylacetone	silica gel	100±1.1
-----	silica gel	83.2±2.2
LIX [®] 54	Linde 3A	89.4±2.2
-----	Linde 3A	42.4±5.5

Table 8. Extraction of 5 ppm copper from ammoniacal solution using supported chelating agents and supported chelators prepared by the corkscrew method as noted above. Modified from [26] Summary

Supported chelating agents can effectively satisfy three needs: concentration for analysis, removal from solution, and removal coupled with regeneration. Their use on a commercial scale has been demonstrated for many years with Chelex as well as Octolig[®] for removal of transition metals ions and other uses. It seems likely that Octolig[®] could be competitive with a highly selective ion-exchange resin and, perhaps, commercially competitive, but this remains to be demonstrated. The examples demonstrated indicate a number of chelating agents can be attached using one of three different methods, though covalent attachment seems the easiest

and most assured. The range of separations --- metals ions, simple anions, pharmaceuticals, industrial dyes, and food dyes – seem impressive, and indicates the utility of separation by column chromatography using appropriately supported chelating agents.

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References

- [1] Chelex 100 and Chelex 220 Chelating Ion exchange Resin Instruction Manual, http://www.biorad.com/webmaster/pdfs/9184_Chelex.PDF (accessed 26 May 2012).
- [2] Ceo RN, Kazerouni MR, Rengan K. 1993. Chelex 100 as a Medium for Simple Extraction of DNA for PCR-based Typing from Forensic Material. *Biotechnology* 1993; 10 506-513.
- [3] Pai SC, Whung PY, Lai RL. Preconcentration Efficiency for Chelex-100 Resin for Heavy Metals in Sea Water, parts 1 and 2 *Analytica Chimica Acta* 1998; 211 257-280.
- [4] Florence TM, Batley GE. Trace Metal Species in Sea Water-I. Removal of Trace Metals from Seawater by a Chelating resin. *Talanta* 1976; 23 179.
- [5] Figura P, McDuffie B. Characterization of the Calcium Form of Chelex-100 for Trace Metal Studies. *Analytical Chemistry* 1977; 49 1950-1953.
- [6] Ryan DH, Weber JH. Comparison of Chelating Agents Immobilized on Glass with Chelex-100 for Removal and Preconcentration of Trace Copper. *Talanta* 1985; 32 859-863.

- [7] Hill JM. Silica Gel as an Insoluble Carrier for the Preparation of Selective Chromatographic Absorbents. The Preparation of 8-Hydroxyquinoline Substituted Silica Gel for the Chelation Chromatography of Some Trace Metals. *Journal of Chromatography* 1973; 76 455-458.
- [8] Irving HMNH, Williams RJP. The Stability of Transition-metal Complexes. *Journal of the Chemical Society* 1953;3192–3210. DOI:10.1039/JR9530003192.
- [9] Alldredge RL 2004 Personal communication; cf [10].
- [10] Martin DF, Martin BB. Robert L Alldredge, Chemical Engineer, Inventor, Entrepreneur. *Technology and Innovation* 2011; 13 203-21.
- [11] Anon. Berkeley Pit http://en.wikipedia.org/wiki/Berkeley_Pit (accessed 18 June 2012).
- [12] Anon. Berkley Pit Innovative Technologies Project, Phase II Metre General, Inc. demonstration. Mine Waste Technology Program Activity IV, Project7; MSE Technology Applications, Inc. and Montana Tech of the University of Montana, Butte, MT. prepared for USEPA IAD ID No. DW89938513-01-0. No date given..
- [13] Gao B, An F, Liu K. Studies on Chelating Adsorption Properties of Novel Composite Material Polyethyleneimine/silica Gel for Heavy-metal Ions. *Applied Surface Science* 2006; 253 1946-1952.
- [14] Lindoy L F, Eaglen P. Ion Complexation by Silica-immobilized Polyethyleneimins, U.S. Patent 5,190,660, Awarded March 2, 1993.
- [15] Soliman EM. Synthesis and Metal Collecting Properties of Amines, Mono, Di, Tri, and Tetraamine Based on a Silica Gel Matrix. *Analytical Letters* 1997; 30 1739-1751.
- [16] El-Ashgar, N M Column Extraction and Some Metal Ions by Diethylenetriamine Polysiloxane Immobilized Ligand System. *E-Journal of Chemistry* 2008; 5 107-113.
- [17] Martin DF, Bowe CA. Extraction of Metals by Mercaptans Attached to Silica Gel by Azeotropic Distillation. U.S. Patent 7,193,114. Awarded March 20, 2007.
- [18] Bowe CA, Krikorian N, Martin DF. Extraction of Heavy Metals Using Modified Montmorillonite KSF. *Florida Scientist* 2004; 67 74-79.
- [19] Krikorian N, Martin, DF. Extraction of Selected Heavy Metals Using Modified Clays. *Journal of Environmental Science and Health, Part A* 2005; A40 601-607.
- [20] Bowe, CA.; Martin, DF. Extraction of Heavy Metals by 2-Mercaptoethoxy Groups Attached to Silica Gel. *Journal of Environmental Science and Health, Part A* 2004; A39 1479-1485.
- [21] http://en.Wikipedia.org/wiki/Dean-Stark_apparatus (accessed 8 August 2012).
- [22] Norris CW, Benson RF, Martin DF. Extraction of Heavy Metals by Resin-supported Chelators. *Florida Scientist* 1996; 59 174-18.

- [23] Lee KS, Lee W, Lee DW. Selective Separation of Metal Ions by a Chelating-loaded Anion Exchanger. *Analytical Chemistry* 1978; 50 255-258.
- [24] Benson RF, Martin DF. Supported Chelating Agents. The Corkscrew Model. *Journal of Environmental Science and Health, Part A* 1992; 27 2191-2197.
- [25] Pooré DD, Benson RF, Martin DF. Removal of Heavy Metal Ions From Aqueous Solutions Using Dithiooximides Supported on Silica Gel. *Journal of Environmental Science and Health, Part A* 1996; A31 2167-2172.
- [26] Norris CD, Benson RF, Martin DF. Extraction of Heavy Metals by Chelators Attached to Silica Gel by a Corkscrew Mechanism. *Journal of Environmental Science and Health, Part A* 1997; A32: 123-132 (1997).
- [27] Bowe CA, Benson RF, Martin DF. Extraction of Heavy Metals by Mercaptans Attached to Silica Gel by a Corkscrew Mechanism. *Journal of Environmental Science and Health, Part A* 2002; A37 1391-1398.
- [28] Anon. Tomorrow's Solution Today. Metre-General, Inc. Frederick Colorado 2005 <http://www.octolig.com> (Accessed 19 July 2012).
- [29] Martin, DF Alldredge R. Removal of Uranium(VI) from Water Samples Using Octolig® and Ferrilig, an Iron Derivative of Octolig®, a Supported Chelating Agent. *Florida Scientist* 2008 ; 71: 208-214.
- [30] Martin DF, O'Donnell L, Martin BB, Alldredge R.. Removal of Aqueous Arsenite Using Iron-attached to Immobilized Ligands (IMLIGs). *Journal of Environmental Science and Health* 2007 42A, 97-102.
- [31] Martin DF, O'Donnell L, Martin BB, Alldredge R L. Removal of Aqueous Nuisance Anions with Ferrilig. *Journal of Environmental Science and Health* 2008; 43A: 700-704.
- [32] Martin DF, Aguinaldo JS, Kondis NP, Stull FW, O'Donnell LF, Martin BB, Alldredge R L. Comparison of Effectiveness of Removal of Nuisance Anions by Metalloligs, Metal Derivatives of Octolig®, *Journal of Environmental Science and Health* 2008; 43A 1296-1302.
- [33] Moeller, T. *Inorganic Chemistry*. New York: John Wiley & Sons, Inc.; 1952.
- [34] Lattimer, WM. *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2nd ed., Englewood Cliffs, NJ, : Prentice Hall; 1952 223-227.
- [35] Stull FW, Martin DF. Comparative Ease of Separation of Mixtures of Selected Nuisance Anions (Nitrate, Nitrite, Sulfate, Phosphate) using Octolig®. *Journal of Environmental Science and Health* 2009; 44 1551-1556.
- [36] Martin DF, Martin BB, Alldredge, RL.. Arsenic, Nitrate, and Perchlorate in Water --- Dangers, Distribution, and Removal. *Bulletin for the History of Chemistry* 2008; 33 17-24.

- [37] Martin DF, Kondis NP, Alldredge RL. Effectiveness of Removal of Aqueous Perchlorate by Cuprilig, a Copper(II) Derivative of Octolig. *Journal of Environmental Science and Health Part A* 2009; 44 188-191.
- [38] Martin DF, Lizardi C L, Schulman E, Vo B, D. Wynn D., Removal of Selected Nuisance Anions by Octolig®, *Journal of Environmental Science and Health, Part A* 2010; 45 1145-1149.
- [39] Chang, W-S, Martin DF, Small M, Use of model compounds to study removal of pharmaceuticals using Octolig® Technology and Innovation. 2010; 12 71-77.
- [40] Alessio RJ, Li X, Martin DF. Removal of BPA model compounds and related substances by means of column chromatography using Octolig®. *Journal of Environmental Science and Health* 2012; 47 000-000.
- [41] Kümmerer K. Significance of Antibiotics in the Environment. *Journal of Antimicrobial Chemotherapy* 2003;52 5-7.
- [42] Kümmerer, K., editor, *Pharmaceuticals in the Environment. Sources, Fate, Effects and Risk*. 3rd ed. Berlin/Heidelberg: Springer; 2008.
- [43] Martin DF, Ward DR, Martin BB., *Agricultural Pharmaceuticals In The Environment. A Need For Inventiveness, Technology and Innovation*. 2010; 12 (3), 129-141.
- [44] Chang, W-S, Martin DF, Small M. Removal of Selected Pharmaceuticals Using Octolig®, *Technology and Innovation* 2010; 12 143-152.
- [45] Martin DF, Martin BB. Polycarbonates from Bisphenol A: A Good Invention Gone Awry? *Technology and Innovation* 2012; 14 7-15.
- [46] Yang CZ, Yaniger SI, Jordan VC, Klein D J, Bittner GD. Most Plastic Products Release Estrogenic Chemicals: A Potential Health Problem That Can Be Solved. *Environmental Health Perspectives* 2011; 119 989-996.
- [47] Alessio, RJ. Removal of Bisphenol A model compounds using Octolig®MS Thesis. University of South Florida; 2012.
- [48] Rosales E, Pazos M, Longo MA.; Sanromán, MA. Influence of Operational Parameters on Electro-Fenton Degradation of Organic Pollutants from Soil. *Journal of Environmental Science and Health. Part A* 2009; 44 1104-1111.
- [49] Sanroman M, Pazos M, Ricart M, Cameselle C Decolourisation of Textile Indigo Dye by DC Electric Current. *Engineering Geology* 2005;; 77 (3-4),253-61
- [50] Zollinger H. Color of Organic Compounds. *Color Chemistry: Synthesis, Properties, an Applications of Organic Dyes and Pigments*, 3rd Ed.; Wiley-VCH: Zurich, 2003; 1, 3-146.

- [51] Martin DF, Nabar N. Studies on the Removal of Lissamine Green from Soil and Comparison with Contemporary Approaches *Journal of Environmental Science and Health. Part A* 2012; 47 260-266
- [52] Erickson B. Food dye debate resurfaces. *Chemical and Engineering News* 2011, April 18, pp 27-31.
- [53] McCann D, Barrett A, Cooper A, Cumpul D, Dalen L, Grimshaw K, Kitchin E., Lok K, Porteous L, Prince E, Sonuga-Barke E, Warner JO, Stevenson J. Food Additives and Hyperactive Behavior in 3-year-old and 8/9-year-old Children in the Community: a Randomized, Double-blinded, Placebo-controlled Trial. *Lancet*. Published online September 6, 2007 DOI: 10.1016/S0140-6736(07)61306-3.
- [54] Swanson JM, Kinsbourne, M. Food Dyes Impair Performance of Hyperactive Children on a Laboratory learning test. *Science* 1980; 207 1485-1487.
- [55] Feingold BF. *Why Your Child is Hyperactive*, New York: Random House; 1975.
- [56] Mattes JA, Gittleman R. Effects of Artificial Food Colorings in Children with Hyperactive Symptoms. *Archives of General Psychiatry* 1981; 39 714-718.
- [57] Rapp DJ. Does Diet Affect Hyperactivity? *Journal of Learning Disabilities* 1978; 11 56-62
- [58] Martin DF Alessio RJ, McCane CH. Removal of Synthetic Food Dyes in Aqueous Solutions by Octolig®, *Journal of Environmental Science and Health. Part A*. accepted
- [59] Martin DF, Franz D. Comparison of Anion Percent Removal Capacities of Octolig® and Cuprilig, *Journal of Environmental. Science and Health, Part A* 2011; 46 1619-1624.

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