

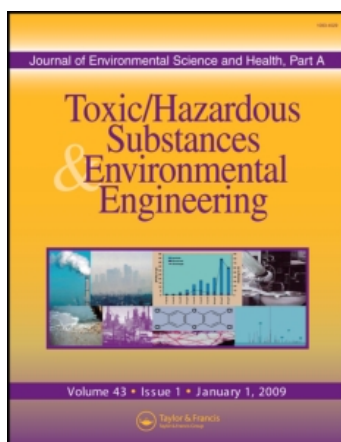
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# Comparison of effectiveness of removal of nuisance anions by metalloligs, metal derivatives of Octolig<sup>®</sup>

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The present study describes the effectiveness of removal of selected aqueous anions by several metalloligs, i.e., metal derivatives of a commercially available immobilized ligand, IMLIG, Octolig<sup>®</sup>. This material consists of polyethylenediamine moieties covalently bound to a high-surface area silica gel (CAS Registry number = 404899-06-5). The metals involved are copper, cobalt, iron, nickel, manganese, and thorium. The nuisance anions, studied as aqueous solutions, were arsenate, orthophosphate, selenite, sulfate, nitrate, and nitrite. All six metalloligs tested were able to remove arsenate (280 ppb, > 99% removal) effectively. The effectiveness for other anions varied, but all anions were removed by one metallolig or another. For example, for Colbaltilig, in deionized water samples, removal was 96% for 20.9 ppm NO<sub>3</sub>-N, 98% for 29.6 ppm sulfate (as sodium sulfate). For Cuprilig, removal was 98% for 9.82 ppm boron as boric acid, >99% for Cr as 212 ppm dichromate, 97% for P as 10 ppm HPO<sub>4</sub>-P, and 90% for sulfate as 29 ppm sulfate. Removal of nitrate by Cobaltilig appeared to be adversely affected by the presence of sulfate. Manganilig and Nickelig were able to remove >97% of 10 ppm P as Na<sub>2</sub>HPO<sub>4</sub>. Mechanisms of interaction are proposed that suggest six types of behavior and several classes of materials are represented by these metalloligs.

**Keywords:** Arsenic, arsenic removal, Bangladesh, drinking water, Ferrilig, immobilized ligands, Octolig<sup>®</sup>, toxicity.

## Introduction

A variety of nuisance anions can be recognized. These include, but are not limited to, arsenic (III) and arsenic (V) species, nitrate and nitrite, phosphate, and sulfate.

The problems of arsenic have been described previously and extensively.<sup>[1–16]</sup> Briefly, the presence of arsenic species in water can lead to skin lesions, hyperkeratosis, melanosis, skin cancer, “black-foot” disease, and cancer of internal organs.<sup>[16]</sup> Problems with arsenic contamination occur worldwide in such countries as Argentina, Bangladesh, India, Japan, Mexico, Mongolia, Peoples Republic of China, Philippines, Taiwan, and the United States. A problem in the United States involves a recent reduction of the drinking water standard from 50 ppb to 10 ppb and the impact that this decision by EPA has on water producers in the West with comparatively few customers. Previous research<sup>[13,17]</sup> demonstrated that arsenate and arsenite can be removed by

chromatography using Ferrilig, the iron(III) derivative of Octolig<sup>®</sup>, a polyethylimine covalently attached to silica gel.

Other anions, however, are nuisance species that deserve attention, including nitrate, which is thought to be the world's most common contaminant of groundwater aquifers,<sup>[18]</sup> and about 42% of the U.S. population has groundwater as the source of their drinking-water supply.<sup>[19]</sup> Nitrogen contamination is use-based: total nitrogen in streams and nitrate in groundwater are highest in agricultural areas, according to Ward and co-workers,<sup>[20]</sup> followed by urban areas and areas of mixed land use.

The maximum concentration level (MCL) mandated by the US Environmental Protection Agency (EPA) for nitrate in drinking-water is 10 ppm (mg/L) nitrate-nitrogen (NO<sub>3</sub>-N) or 44 mg/L of nitrate.<sup>[20]</sup> The World Health Organization has a slightly higher standard, 50 ppm as nitrate or 11 ppm NO<sub>3</sub>-N.<sup>[21]</sup> The standards are provided out of concern to protect infants from “blue baby syndrome” or methemoglobinemia, among other reasons.<sup>[20]</sup>

Phosphate ion is a nuisance species because in excess concentrations in surface water, it can assist the over abundance of various algae, given other macro and micro nutrients.

Sulfate can be a nuisance anion for two reasons. First, it is an ion that can form a scale on pipes, with all the attendant problems that require some method of control and related

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expense.<sup>[22]</sup> Second, it tends to be corrosive. Third, sulfate ion is a problem in nuclear waste disposal.<sup>[23]</sup> While radioactive waste might be incorporated into transportable glass, the low solubility of sulfate (~1%) in borosilicate glass is a problem, as is removal of sulfate from nitrate-rich mixtures presently stored in underground tanks.<sup>[24]</sup> A promising sulfate anion extractant could be the solution to the problem, according to Eller and co-workers.<sup>[24]</sup> We believe that we may have a cheaper method.

Finally, one may mention other nuisance anions: chromate, molybdate, and selenite. These appear to be removable using Ferrilig. This paper examines the efficacy of anion extraction through use of metalloligs, i.e., metal derivatives of supported ligands (IMLIGs), most notably those derived from Octolig®.<sup>[13,17]</sup>

## Materials and methods

### Synthesis of Cobaltilig

*Method A.* Octolig® (200 mL, ~120 g) as received, was suspended in 150 mL of purified water in a 1-L Erlenmeyer flask. Then a solution of 45.5 g (0.19 mole) of cobaltous chloride hexahydrate (Mallinkrodt) in 150 mL of purified water was added. The flask was stoppered, placed on a gyrorotary shaker bath (Model G67, New Brunswick Scientific) at a setting of 5 for 2.5 hours, then the mixture was poured into a plastic funnel with the bottom covered with mesh (1000 $\mu$  Nylon macro filtration material, Spectrum Medical Material Industries, Los Angeles, CA 90054), and the solid was collected. The dark pink solid was dried overnight at 60°C, whereupon it appeared as a blue color (82.1 g, density 0.42 g/mL).

*Method B.* The same procedure was followed, except for the matter of time. After shaking for 2–2.5 hours, the sample was allowed to stand overnight open to the air before the solid was collected. The product was a purple solid, and when dried overnight at 60°C, the sample remained purple. An analysis was performed by Evergreen Analytical Co.; Reported: 5900 mg Co/kg. When the sample was allowed to stand overnight, but with the top covered by a piece of filter paper, material identical to Method A was obtained, i.e., a dark pink solid that turned blue when heated overnight at 60°C. Obviously an excess of cobalt was used: the filtrate(s) were evaporated to dryness, and the weights for three samples were averaged  $22.7 \pm 3.4$  g.

*Synthesis of Ferrilig.* A previous procedure<sup>[13,17]</sup> was followed with modifications, e.g., consisting of dissolving 300 g (1.0 mole) of ferrous sulfate heptahydrate in 400 mL of deionized (DI) water at 80°C contained in a 4-L Buchner flask with a nitrogen atmosphere, followed by 300 g of Octolig® all at once. The mixture was shaken on a New Brunswick Gyrorotary shaker bath (Model G76) at a setting of 4 for overnight or for 30 minutes. The sample was

then collected by passing the mixture through a 1000- $\mu$  Nylon macro filtration material (Spectrum Medical Material Industries, Los Angeles, CA 90054) attached to the bottom of a plastic funnel. The green filtrate was collected, placed in a glass bottle, and stored under nitrogen until needed for the assay. For both syntheses, a 10-mL sample of green unreacted sample was titrated with 0.1781 *N* KMnO<sub>4</sub>, which had been standardized against sodium oxalate.<sup>[25]</sup> For two preparations, the amount of unreacted ferrous ion was 0.213 (24 hr.) and 0.219 (4 hr) mole, respectively.<sup>[17]</sup>

*Synthesis of Thorilig.* The procedure used was similar to that for Ferrilig. Thorium nitrate tetrahydrate (28 g, 0.05 mole) in 200 mL of DI water was treated with 30 g of Octolog, placed on a shaker bath, and over a 15-min period, 250 mL of 0.2 *M* NaOH was added over a 10-min period. Shaking was continued for 90 min, then the white solid was collected by sieving (as with the Ferrilig preparation), dried overnight in a 60°C oven.

*Synthesis of Cuprilig.* Octolig® (120 mL, 81.5 g) suspended in 150 mL of DI water and a solution of cupric acetate monohydrate (38 g, 0.2 mole) in 450 mL of DI water were mixed in a 1-L Erlenmeyer flask, placed on a shaker bath. Shaking was continued overnight, then the sample was collected (same procedure as with the other metalloligs) and washed with several 100-mL aliquots of DI water. After drying at 60°C the weight was 47 g. The sample was placed in the chromatography column and treated with 0.2 *M* NaOH, testing with neutral litmus until positive for hydroxide, then the column was washed with a liter of DI water. The filtrate was evaporated to dryness and weighted:  $34.5 \pm 2.1$  g. This would indicate that about 10% of the cupric ion was taken up.

*Synthesis of Nickelig and Manganilig.* A suspension of Octolig® (120 mL, 80.4 g as received, 43.8 g after drying overnight at 60°C) 150 mL of DI water in a 1-L Erlenmeyer flask was treated with a solution of either 0.1 mole of nickel sulfate hexahydrate (Sigma) or 0.1 mole of manganous sulfate monohydrate (MCB), respectively, in 200 mL of DI water, placed on a shaker bath overnight. Then the product was collected as with the other metalloligs. Nickelig was a bright blue solid, and Manganilig was a rust brown solid.

### Chromatography experiments

Aqueous samples of deionized (DI) water or well water were prepared and subjected to column chromatography. As before,<sup>[13,17]</sup> a Spectra/chron peristaltic pump was used to deliver aqueous samples to a chromatography column, 2 cm (id) by 20 cm and equipped with a glass frit and a Teflon stopcock. The column was packed with 24 cm of appropriate metallolig. Before packing, the solid was suspended in water, swirled, and the fines were decanted, a process that was repeated until no fines were observed. After packing

and before use, dilute (0.1 or 0.2 M) aqueous NaOH was passed through the sample until the effluent turned neutral litmus paper blue, then the column was washed with about 1L of DI water. Then the water samples were chromatographed. A rate of 10 mL/min was used. The fourth 50-mL aliquot of effluent was used for analysis, Total dissolved solids were measured and used as a guide to assess a state of equilibrium.

A sample of tap water was analyzed by Evergreen Analytical (EPA Method 300). Anal.:96.6 ppm sulfate.

### Analyses

Arsenic analyses were done on 250-mL aqueous samples using Quick Low Range-test strips from Industrial Test Systems, Inc. Rock Hill, SC. Nitrate and nitrite analyses were done by a colorimetric procedure using a HACH kit (Model NI-14). Orthophosphate was analyzed colorimetrically using a HACH kit (Model PO-24).

Analytical services were provided by two firms: (1) Constellation Technology Corp., 7887 Bryan Dairy Road, Suite 100, Largo, Florida 33777-1452 for chromium analyses (using ICP-MS by diluting the sample with an internal standard) and (2) by Evergreen Analytical, Inc, Wheat Ridge, CO for boron (EPA Method 200.8), and for sulfate (EPA Method 300).

### Results and discussion

Metalloligs are defined as metal derivatives of immobilized ligands (IMLIGs), in the present study all are derivatives of Octolig<sup>®</sup>, and we believe that they can function in at least five ways.

First, solubility changes can be a factor in one or more ways. In the instance of Ferrilig, the iron(III) derivative of Octolig<sup>®</sup>, one may suspect, if not yet prove, the possibility of hydrated iron(III) oxide in pores of a high-surface area silica-gel substrate. In that event, solubility of ferric arsenate, for example, could be a key factor in reducing the amount of arsenate in test waters.

Second, metalloligs can also function as ion-exchange composites, as for example, when the hydroxide form is available in Ferrilig. At a pH of 7, arsenous acid, H<sub>3</sub>AsO<sub>3</sub> exists as essentially the free acid. But hydroxide ions associated with Ferrilig would be able to form various species of arsenic, e.g., H<sub>2</sub>AsO<sub>3</sub><sup>-</sup>, HAsO<sub>3</sub><sup>2-</sup>, and AsO<sub>3</sub><sup>3-</sup> that would remain associated with the Ferrilig.

Third, simple chelation by non-coordinated monoethylimine moieties, -NHCH<sub>2</sub>CH<sub>2</sub>NH- is feasible. This is likely the situation in removal of uranyl ion UO<sub>2</sub><sup>++</sup> by Ferrilig in comparison with Octolig<sup>®</sup>.<sup>[26]</sup> Here the results are similar, and one may presume that the coordinated iron is not playing a significant role.

Fourth, entry of an undesirable anion into the coordination sphere of the metallolig metal, most plausibly cobalt(II) or cobalt(III), may be expected. This is a likely

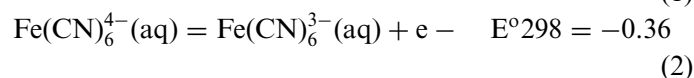
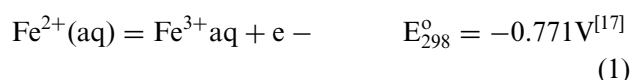
mode of action for Cobaltilig (*vide infra*), and is a plausible mechanism for sulfate, phosphate, nitrate or nitrite ions.

The fifth mode is as a bactericidal action, which could be exemplified by Thorilig, a combination of thorium(IV) and Octolig<sup>®</sup>. A common isotope of thorium is Th- 229, (t<sub>1/2</sub>= 7 × 10<sup>3</sup>y) which is an alpha emitter.<sup>[27]</sup> And the potential for bacterial control is evident, though it is unlikely that permission could be easily obtained for this application.

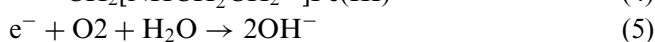
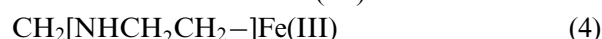
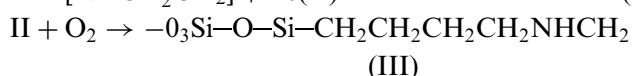
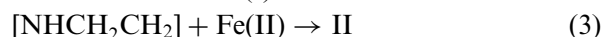
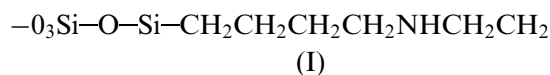
A sixth mode of action may involve formation of a cyclic complex, based on our observations with sulfate ion removal (*vide infra*).

### Synthesis of Ferrilig and Cobaltilig

Both materials represent a process of oxidation assisted by the act of coordination, and this can be illustrated by considering the oxidation potentials E<sub>298</sub><sup>o</sup>. For example, the oxidation of iron(II) to iron(III) is not favorable (Equation 1), But in the presence of cyanide, (Equation 2), the process becomes much more favorable as indicated by the increase in the value of the oxidation potential. <sup>[28,29]</sup>

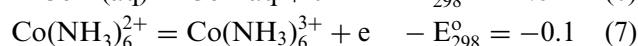
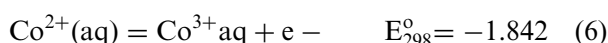


We presume that the availability of chelating moieties in Octolig<sup>®</sup>, i.e, NHCH<sub>2</sub>CH<sub>2</sub>NH would enhance the oxidation potential even more, because of a chelate effect not involving p<sub>π</sub>-d<sub>π</sub> bonding as in *ortho*-phenanthroline. And one may note the progression of the oxidation process in the synthesis of Ferrilig starting with a suspension of Octolig<sup>®</sup> (I,white) in aqueous ferrous sulfate (green) that leads to a green solid (II, Equation 3) that slowly changes to Ferrilig (rust brown, III, Equation 4) upon standing while in moist air.



Presumably, hydroxide is produced as part of the redox process (Equation 5).

Similar considerations apply to Cobaltilig. The oxidation process for cobalt(II) to cobalt (III) is not favorable for the aquated ions (Equation. 6), but it is enhanced in the presence of a better coordinating agent, such as ammonia (Equation 7). With an even better coordinating agent (CN-), the value of E<sub>298</sub><sup>o</sup> is +0.83.<sup>[28,29]</sup>



**Table 1.** Effect of passage of samples over a 2-cm (id) column packed with about 22 cm of Cobaltilig (Method 1) at a rate of 10 mL/min (50-mL aliquots were collected).

Sample conc.	Medium water	Fraction	TDS ppm	Eluant ppm	% removal
Na <sub>2</sub> HAsO <sub>4</sub> 280 ppb					
AsO <sub>4</sub> -As	DI	4-9	83 ± 28	< 2 × 10 <sup>-3</sup>	99
AsO <sub>4</sub> -As	DI	10-14	84 + 47	< 2 × 10 <sup>-3</sup>	99
AsO <sub>4</sub> -As	Well	4-7	—	15 × 10 <sup>-3</sup>	95%
KNO <sub>3</sub> 23 ppm NO <sub>3</sub> -N DI		4-6	147 ± 5	0.43 ± 0.15*	98
NaNO <sub>2</sub> 20.4ppm NO <sub>2</sub> -N DI		4-7	80 ± 5	0.005 ± 0.005	~100
Na <sub>2</sub> HPO <sub>4</sub> 50 ppm PO <sub>4</sub> -P DI water		4-5	—	9 ± 3	8

\*Nitrite was not detected in these samples.

And oxidation is achieved by allowing the mixture to stand overnight in the presence of air. Again, presumably, coordination by chelating groups, —NHCH<sub>2</sub>CH<sub>2</sub>NH—, would be associated with an even more favorable oxidation potential. One may presume that given the structure of Octolig<sup>®</sup> (I), cobalt(II) ion could have a trans structure —[Co(II) A,B —{NHCH<sub>2</sub>CH<sub>2</sub>NH}₂], where the moiety in { } represents a portion of Octolig<sup>®</sup>, and A and B are unidentate ligands, chloride or water. This seems to be the initial product that is obtained upon mixing (Method I), and is characterized by a pink color when moist and a blue color when dried in the oven. That material is transformed upon standing overnight in the presence of air (Method II) to the cobalt(III) versions —[Co(III) A,B —{NHCH<sub>2</sub>CH<sub>2</sub>NH}₂], which is pink when moist and blue after drying.

More attention was paid to the cobalt(III) product because it seemed that this would be the product that would be ultimately standing in a moist environment. Either method seemed to produce a product capable of removing certain nuisance anions from deionized water. Arsenate in DI water, for example, is removed by Ferrilig (99%) as well as by Thorilig (99%), Cobaltilig (99% by both versions), and Cuprilig (Table 3). Also, both forms of Cobaltilig were successful in removing nitrate-nitrogen from DI water (>96%, Tables 1 and 2). And there was no nitrite ion detected in the eluants. In addition, nitrite-nitrogen was quantitatively removed from DI water by the Co(II) version of Octolig<sup>®</sup>. And both forms were capable of removing phosphorus as Na<sub>2</sub>HPO<sub>4</sub> from DI water, though less impressively than the other anions [82% removal with the Co(II) version of Cobaltilig]. And while 82% may not be as impressive as 97% or 100% removal [Cuprilig, Manganilig, or Nickelilig], it was far superior to that observed for phosphorus removal by Ferrilig, which was zilch [Martin and Aguinaldo, unpublished results].

Phosphorus can be a nuisance nutrient, but it can also be a point-source problem because of liquid and power coating systems. Zinc coating can be achieved by spraying objects with either liquid or powder formulations. One procedure

produced zinc ion as a component of waste water, which is controlled by use of Octolig<sup>®</sup>.<sup>[30]</sup>

There were complications when samples were tested in well water or tap water, presumably because of interfering anions. Sulfate, for example in DI water, was quantitatively removed (98%) by elution over Cobaltilig (Table 2). But when nitrate was eluted using tap water or well water, reduced removal success was noted (Table 2), presumably because of competition with sulfate ion, which could have been significant, given the analysis of sulfate in the tap water (96.6 ppm). On the other hand, it is possible that what is exhibited here is a reflection of differences in preparations, and the data in Table 2 indicate that up to 84 percent of the 10 ppm NO<sub>3</sub>-N was removed in the presence of 3 ppm sulfate.

The results with another matrix suggest a mechanism of action, i.e., reaction with the coordination sphere of cobalt atoms, something that would depend on relative nucleophilicity, and in turn might be related to base strength. In this regard, one might expect sulfate ion to be superior to nitrate ion. The problem of sulfate interference may not be as serious in practical terms as first glance would indicate when one considers what is involved in reaching the 10 ppm nitrate-nitrogen requirement for drinking water, as for example in Des Moines, Iowa.

“Nitrate removal during drinking water is expensive” as noted by Jones and co-workers<sup>[31]</sup> who are operators at the Des Moines Water Works. The Fleur Drive Treatment Plant, built in 1991 (\$4 million) is said to be the world’s largest ion-exchange nitrate removal facility.

Their description of the process notes some significant aspects of the process involved. River water is pretreated (ferric chloride and powdered activated carbon). Subsequently the pretreated water is mixed with chemicals and goes through underground “conventional” lime softeners, which includes precipitation and settling processes. The ion-exchange facility costs nearly “\$3,000/day on many days”, and generates up to 60,000 gallons/day of nitrate-laden brine waste from media generation.<sup>[31]</sup>

**Table 2.** Effect of passage of samples over a 2-cm (id) column packed with about 22 cm of metallolig (ca. 30 g) at a rate of 10 mL/min (50-mL aliquots were collected).

Sample conc.	Water	Fraction	TDS ppm	Eluant ppm	% removal
Cobaltilig (Method 2)					
Na <sub>2</sub> HAsO <sub>4</sub> 280 × 10 <sup>-3</sup> ppmAs	DI	2-7	2.7 ± 0.4	<2 × 10 <sup>-3</sup>	99
KNO <sub>3</sub> 20.9 ppm NO <sub>3</sub> -N	DI	4-7	146 ± 4	0.91 ± 0.1	96
10 ppm NO <sub>3</sub> -N	DI	4-7	225 ± 33	6.5 ± 1.5	~ 35
3 ppm SO <sub>4</sub> <sup>=</sup> 10 ppm NO <sub>3</sub> -N	DI	4-9	86 ± 42	1.6 ± 0.7	84
3 ppm SO <sub>4</sub> <sup>=</sup> 10.7 ppm NO <sub>3</sub> -N	Tap Well	4-6 4-6	185 ± 1 181 ± 2.5	9.91 ± 0.05 10.3 ± 2.2	< 2 ~ 49
Na <sub>2</sub> HPO <sub>4</sub> 36 ppm P	Well	7	161.6	22	39
Na <sub>2</sub> SO <sub>4</sub> 29.6 ppm SO <sub>4</sub>	DI	4-8	35.5 ± 1.9	0.58	98
Cuprilig H <sub>3</sub> BO <sub>3</sub> 9.82 ppm B	DI	5	99.3	0.192	98
"	DI	6	103	BDL	> 99
Na <sub>2</sub> HPO <sub>4</sub> 10.1 ppm P	DI	4-8	?	BDL	> 97
NaNO <sub>3</sub> 2.0 ppm NO <sub>3</sub> -N	DI	5-10	7.± 0	0.92 ± 0.07	54
Na <sub>2</sub> SO <sub>4</sub> 29.8 ppm SO <sub>4</sub>	DI DI	6-7 6-7	23.5 35±0.5	2.9 BDL	90 > 99*
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> 103 ppm Cr	DI	7	104	< 0.04	> 99
Manganalig Na <sub>2</sub> HPO <sub>4</sub> 10.0 ppm P	DI	4-7	11.5 ± 0.5	BDL	> 97
10.3 ppm P	DI	5-7	15.3 ± 0.8	BDL	> 97
Na NO <sub>3</sub> 8.9 NO <sub>3</sub> -N	DI	5-7	28.7 ± 1.6	3.2 ± 0.4	64
8.8 NO <sub>3</sub> -N	DI	5-7	43.8 ± 2.7	4.2 ± 0.5	52
Nickelig Na <sub>2</sub> HPO <sub>4</sub> 10.1 ppm P	DI	5-6, 8	?	BDL	> 97
Ferrilig**					

\*Control run using Octolig<sup>®</sup> only.\*\*Significant removal (>95%) of arsenate, chromate, molybdate, and selenite was achieved.<sup>[7]</sup>

The problem of such brine was described by Martin and co-workers<sup>[32]</sup> who referred to the Eliminate Project whose goal is zero effluent nitrate.<sup>[33]</sup> Some 40 selected sites in the UK have used specially developed nitrate-selective ion-exchange resins. Though the drinking water is very good, the resulting effluent (brine with high nitrate concentrations) constitutes a significant disposal challenge. An electrochemical means of converting the nitrate-containing brine effluent to nitrogen gas and reuse the ion-exchange resin regeneration material is necessary.

One good example of this type of approach is the removal and destruction of nitrate using water-compliant selective materials such as Purolite's A520E or Rohm & Haas' Amberlite PWA 555. These materials are regenerated with a concentration brine to regenerate the ion-exchange materials. Then the brine solution is sent to an electrochemical cell (EDA's SERIX-systems) to produce molecular nitrogen and water.<sup>[34]</sup>

To return to the situation at Des Moines, calcium sulfate is a sparingly soluble salt ( $K_{sp} = 2.5 \times 10^{-5}$ ).<sup>[35]</sup> So the

**Table 3.** Effect of passage of  $\text{Na}_2\text{HAsO}_4$  (in DI water),  $280 \times 10^{-3}$  ppm As samples over a 2-cm (id) column packed with about 22 cm of Metallolig at a rate of 10 mL/min (280 mL aliquots was collected for analysis).

Metallolig	Eluant ppm	% removed	Source
Cobaltilig	$<2 \times 10^{-3}$	99	This Study
Ferrilig	$<2 \times 10^{-3}$	99	Ref [7]
Ferrilig	$<2 \times 10^{-3*}$	99	Ref [7]
Thorilig	$<2 \times 10^{-3}$	99	This Study
Cuprilig	$<2 \times 10^{-3}$	99	This Study
Nickelig	$<2 \times 10^{-3}$	99	This Study
Manganilig	$<2 \times 10^{-3}$	99	This Study

\*Well water.

concentration of sulfate in the treated water might well be at a non-interfering level, owing to the presence of lime. And the appropriate use of Cobaltilig would not produce the problems of nitrate-laden brine.

Phosphate results (in different water) indicate that Cobaltilig could plausibly be used to remove phosphate from point sources. One example that comes to mind is the application to powder-coating systems for coating metal parts. When galvanized steel is involved, waste water can contain dissolved zinc, and Metre-General, Inc. devised a system for removing this by-product with Octolig®.<sup>[30]</sup> But phosphate can also be a component of the wastewater, and it is likely that Cobaltilig or Cuprilig could be used to maintain acceptable levels of phosphate in the waste water, and, perhaps, the zinc as well.

The results presented here indicate the significant potential for the use of metalloligs. Six metalloligs—Cuprilig, Cobaltilig, Ferrilig, Manganilig, Nickel, and Thorilig—are capable of removing arsenic(V) from 300 ppb to 2 ppb. Ferrilig is capable of removing other nuisance species chromate, selenite, and molybdate.<sup>[17]</sup> Cobaltilig is capable of removing sulfate, nitrate, nitrite, and phosphate, and this can speak to potential application in water purification. The evident inhibition of nitrate removal by Cobaltilig in the presence of sulfate may indicate preferential removal of sulfate ion, which could be an asset in the treatment of radioactive waste by incorporation into glass “logs” (vitrification), which is a problem with sulfate ion because of low (<1%) solubility.<sup>[24]</sup> One suggested solution, is a cyclic molecule that is a promising sulfate extractant.<sup>[24]</sup> Another solution may well be Cobaltilig or another metallolig, or even Octolig®, based on the removal of sulfate ion by this material (Table 2). It is easy to envision cyclic entities involving polyethylenediamine moieties of Octolig® with or without metal ions, but with protons on appropriate nitrogens.

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## References

- [1] Nickson, R.; Sengupta, C.; Mitra, P.; Dave, S.N.; Banerjee, A.K.; Bhattacharya, A.; Basu, S.; Kakoti, N.; Moorthy, N.S.; Wasuja, M.; Kumar, M.; Mishra, D.S.; Ghosh, A.; Vaish, D.P.; Srivastava, A.K.; Tripathi, R.M.; Singh, S.N.; Prasad, R.; Bhattacharya, S.; Deverill, P. Current knowledge on the distribution of arsenic in groundwater in five states of India. *J. Environ. Sci. Health, Pt. A* **2007**, *42*(12), 1707–1718.
- [2] Mandal, B.K.; Suzuki, K.T.; Anzai, K. Impact of arsenic in food-stuffs on the people living in the arsenic-affected areas of West Bengal-India. *J. Environ. Sci. Health, Pt. A* **2007**, *42*(12), 1741–1752.
- [3] Guillot, S.; Charlet, L. Bengal arsenic, an archive of Himalaya orogeny and paleohydrology. *J. Environ. Sci. Health Pt. A* **2007**, *42*(12), 1785–1794.
- [4] Acharyya, S.K.; Shah, B.A. Groundwater arsenic contamination affecting different geologic domains in India—A review: influence of geological setting, fluvial geomorphology and quaternary stratigraphy. *J. Environ. Sci. Health Pt. A* **2007**, *42*(12), 1795–1805.
- [5] Islam, L.N.; Nabi, A.H.M.N.; Rahman, M.M.; Zahid, M.S.H. Association of respiratory complications and elevated serum immunoglobulins with drinking water arsenic toxicity in human. *J. Environ. Sci. Health Pt. A* **2007**, *42*(12), 1807–1814.
- [6] Guo, J.X.; Hu, L.; Yand, P.Z.; Tanabe, K.; Miyatalre, M.; Yao Chen, Y. Chronic arsenic poisoning in drinking water in inner Mongolia and its associated health effects. *J. Environ. Sci. Health Pt. A*, **2007**, *42*(12), 1853–1858.
- [7] Hussam, A.; Munir, A.K.M. A simple and effective arsenic filter based on composite iron matrix: development and deployment studies for groundwater of Bangladesh. *J. Environ. Sci. Health Pt. A* **2007**, *42*(12), 1869–1878.
- [8] Johnston, R.B.; Sarker, M.H. Arsenic mitigation in Bangladesh: National screening data and case studies in three Upazilas. *J. Environ. Sci. Health Pt. A* **2007**, *42*(12), 1889–1896.
- [9] Adamson, G.C.D.; Polya, D.A. Critical pathway analysis to determine key uncertainties in net impacts on disease burden in Bangladesh of arsenic mitigation involving the substitution of surface water for groundwater drinking water supplies. *J. Environ. Sci. Health Pt. A* **2007**, *42*(12), 1909–1917.
- [10] Shibasaki, N.; Lei, P.; Kamata, A. Evaluation of deep groundwater development for arsenic mitigation in Western Bangladesh. *J. Environ. Sci. Health Pt. A* **2007**, *42*(12), 1919–1932.
- [11] Ahmad, S.A.; Sayed, M.H.S.; Khan, M.H.; Karim, M.N.; Haque, M.A.; Bhuiyan, M.S.A.; Rahman, M.S.; Faruquee, M.H. Socio-cultural aspects of arsenicosis in Bangladesh: community perspective. *J. Environ. Sci. Health Pt. A* **2007**, *42*(12), 1945–1958.
- [12] Chakraborti, D.; Hussam, A.; Alauddin, M. Guest Eds. Arsenic: Environmental and health aspects with special reference to groundwater in South Asia. *J. Environ. Sci. Health Pt. A* **2003**, *38*(1), 1–305.
- [13] Martin, D.F.; O'Donnell, L.; Martin, B.B.; Alldredge, R. Removal of aqueous arsenic using iron attached to immobilized ligands (IM-LIGS). *J. Environ. Sci. Health Pt. A* **2007**, *42*, 97–102.
- [14] Cumbal, L.; Sengupta, A.K. Arsenic removal using polymer-supported hydrated iron(III) oxide nanoparticles: Role of Donan membrane effect. *Environ. Sci. Technol.* **2005**, *39*, 6508–6515.
- [15] Zade, P.D.; Dharmadhikari, D.M. Removal of arsenic as arsenite from groundwater/wastewater as stable ferrite. *J. Environ. Sci. Health Pt. A* **2007**, *42*, 1073–1079.
- [16] Smith, A.H.; Lingas, E.O.; Rahman, T. Contamination of drinking water by arsenic in Bangladesh: a public health emergency. *Bull. World Health Org.* **2000** *78*(9), 1093–1103.

- [17] Martin, D.F.; O'Donnell, L.; Martin, B.B.; Alldredge, R. Removal of nuisance aqueous anions with Ferrilig. *J. Environ. Sci. Health Pt. A* **2008**, *43*(7), 700–704.
- [18] Spalding, R.F.; Exner, M.E. Occurrence of nitrate in groundwater—A review. *J. Environ. Qual.* **1993**, *22*, 392–402.
- [19] Hutson, S.S.; Barber, N.L.; Kenny, J.F.; Linsey, K.S.; Lumia, D.S.; Maupiiin, M.A. Estimated use of water in the United States in 2000, USGS Circular 1268, Denver CO., U.S. Geological Survey, 2004.
- [20] Ward, M.H.; deKok, T.M.; Levallois, P.; Brender, J.; Gulls, G.; Nolan, B.T.; VanDerslice, J. Workgroup report: Drinking-water nitrate and health—Recent findings and research needs. *Environ. Health Perspect.* **2005**, *113*, 1607–1614.
- [21] WHO, *Guidelines for Drinking Water Quality, Recommendations*, World Health Organization, Geneva, Switzerland, 3rd ed., Vol. 1, 2004.
- [22] Benson, R.F.; Carpenter, R.K.; Martin, B.B.; Martin, D.F. Using magnetic fields to prevent scale. *Chemtech* **1997**, *24*(2), 34–38.
- [23] National Research Council. *Nuclear Wastes: Technologies for Separations and Transmutations*. National Academy Press, Washington, DC, 1996.
- [24] Eller, L.R.; Stepień, M.; Fowler, C.J.; Lee, J.T.; Sessler, J.L.; Moyer, B.A. Octamethyl-octaundecylcyclo[8]pyrrole: A promising sulfate anion extractant. *J. Am. Chem. Soc.* **2007**, *129*, 11020–11021.
- [25] Kolthoff, I.M.; Sandell, E.B. *Textbook of Quantitative Inorganic Analysis*, 3rd Ed.; Macmillan, New York, 1952.
- [26] Martin, D.F.; Alldredge, R. Removal of uranium(VI) from water samples using Octolig<sup>®</sup> and Ferrilig, an iron derivative of Octolig<sup>®</sup>, a supported chelating agent. *Florida Scient.* **2008**, *71*, 208–214.
- [27] Friedlander, G.; Kennedy, J.W. *Introduction to Radiochemistry*, John Wiley & Sons, New York, 1949; 385.
- [28] Moeller, T. *Inorganic Chemistry*, John Wiley & Sons, Inc., New York, 1952.
- [29] Lattimer, W.M. *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2nd Ed., Prentice Hall, Englewood Cliffs, NJ, 1952; 223–227.
- [30] Anon. Water treatment system, drains manufacturer's compliance concerns. *Powder Coating* **2007**, April 28–31.
- [31] Jones, C.S.; Hill, D.; Brand, G. Use a multifaceted approach to manage high source–water nitrate. *Opflow* **2007**, June 20–22.
- [32] Martin, D.F.; Martin, B.B.; Alldredge, R. Arsenic, nitrate, and perchlorate in water—dangers, distribution, and removal. *Bull. Hist. Chem.* **2008**, *33*, 17–24.
- [33] Waite, M.J.; Tucker, P.M.; Foster, D. The eliminate project: Zero effluent nitrate removal and destruction from drinking water sources. Ion Exchange at the Millennium, Proc. IEX 2000, 8th Cambridge, UK, July 16–21, 2000.
- [34] Removal and destruction of nitrate with SERIX-N (Selective Electrochemically Reagent Extraction). [www.e-d-a.com/html/water/nitrate/nitrate.html](http://www.e-d-a.com/html/water/nitrate/nitrate.html) [Accessed: March, 2007].
- [35] Moeller, T.; Martin, D. F. *Laboratory Chemistry*, DC Heath, Boston, 1964; 270.