Effectiveness of commercial reagents for heavy metal removal from water with new insights for future chelate designs

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Abstract

Toxic heavy metals in air, soil, and water are global problems that are a growing threat to the environment. To meet the federal and state guidelines for heavy metal discharge, companies often use chemical precipitation or chelating agents. In order to be competitive economically, many of these chelating ligands are simple, easy to obtain, and, generally offer weak bonding for heavy metals. Laboratory testing of three commercial reagents, trimercaptotriazine (TMT), Thio-Red® potassium/sodium thiocarbonate (STC), and HMP-2000 sodium dimethyldithiocarbamate (SDTC) has shown that the compounds were unable to reduce independent solutions containing 50.00 ppm of divalent cadmium, copper, iron, lead, or mercury to meet EPA standards. Additionally, the compounds displayed high leaching rates and in some cases decomposed to produce toxic substances. In contrast, the studies demonstrate that a recently reported sulfur-containing multidentate ligand is both safe and effective for the removal of these metals. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Water treatment; Remediation; Heavy metals; Chemical precipitation

1. Introduction

Toxic heavy metals in air, soil, and water are global problems that are a growing threat to the environment. There are hundreds of sources of heavy metal pollution, including the coal, natural gas, paper, mining, and chlor-alkali industries [1,2]. In response to the growing problems, federal and state governments have instituted environmental regulations to protect

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the quality of surface and ground water from pollutants, such as Cd, Cu, Pb, Hg, and Fe [3]. To meet the federal and state guidelines for heavy metal discharge, companies often use chemical precipitation or chelating agents. For example, acid mine drainage (AMD) and wastewater treatment plants typically utilize pH neutralization and precipitation with lime, peroxide addition, reverse osmosis, or ion exchange in an effort to reduce metal concentrations [4,5].

As an alternative to the liming process many companies use chelating ligands to precipitate heavy metals from aqueous systems, presumably as metal chelates. In order to be competitive economically, many of these ligands are simple and easy to obtain but not specifically designed to bind the targeted heavy metals. This poor and indiscriminant metal binding often results in unstable metal–ligand precipitates which can decompose and release the metals back into the environment over varying, but usually short, periods of time [6–8]. Remarkably, some have even been shown to release toxic organic byproducts during the decomposition process [6]. Additionally, many of the current remediation ligands on the market require high ligand to metal dosages to meet US Environmental Protection Agency (EPA) and state limits.

The purpose of this article is to examine the effectiveness of three widely used commercial reagents for heavy metal binding and to introduce new research which promises to not only produce low-cost, highly selective ligands for heavy metal treatment, but also, products that can be used at low dosages. The heavy metal binding agents used in remediation and wastewater treatment that will be examined in this article are trimercaptotriazine (TMT), potassium/sodium thiocarbonate (STC), and sodium dimethyldithiocarbamate (SDTC), Fig. 1a–c.

TMT, or 2,4,6-trimercaptotiazine, trisodium salt nonahydrate, $Na_3C_3N_3S_3 \cdot 9H_2O$ (Fig. 1a), is a chemical reagent commonly used for precipitating divalent and univalent heavy metals from water [9]. Despite the widespread use of TMT, until recently only limited information was available on how the product reacts with heavy metals in aqueous solutions and the chemistry and stability of the resulting heavy metal–TMT precipitates [7,8,10,11].

A second chemical reagent for precipitating divalent heavy metals from wastewaters is STC. STC is a sodium (with or without potassium) thiocarbonate ($[Na, K]_2CS_3 \cdot nH_2O$, where $n \geq 0$), which has the trade name of Thio-Red® (Fig. 1b); [6,12]. Previous laboratory studies have demonstrated that Thio-Red® ultimately removes copper, mercury, lead, and cadmium from aqueous solutions through the formation of metal sulfides (that is, CuS, HgS, PbS, and ZnS) rather than metal thiocarbonates (that is, $CuCS_3$, $HgCS_3$, $PbCS_3$, and

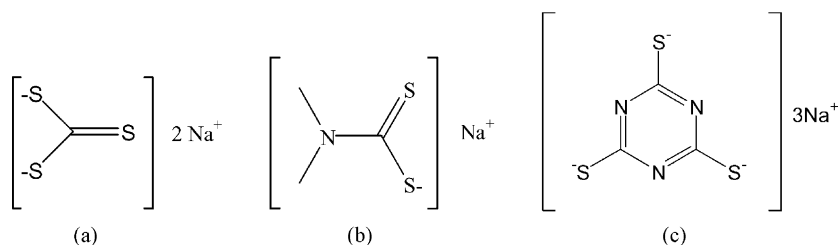
Fig. 1. (a) potassium/sodium thiocarbonate (STC); (b) sodium dimethyldithiocarbamate (SDTC); (c) 2,4,6-Trimercaptotiazine, trisodium salt nonahydrate (TMT).

ZnCS$_3$) as originally expected [6,12]. A byproduct of the metal sulfide precipitation with STC is carbon disulfide, a volatile and toxic liquid [6].

Another type of commercial remediation agent is sodium thiocarbamate (SDTC), which has the trade name HMP-2000 (Fig. 1c); [13]. A serious problem with this compound is its tendency to decompose into toxic secondary products. One major accident associated with the use of SDTC occurred in December of 1999, where the Guide Corporation (an auto parts manufacturer in Anderson, IN) accidentally released over 1.5 million gallons of contaminated wastewater laced with SDTC into the city's wastewater system. The SDTC-laced wastewater was eventually discharged into local state waters [13] where the SDTC apparently decomposed into toxic secondary compounds, including

Table 1
ICP-OES and CVAF results of SDTC at stoichiometric doses and at 10% molar dosage increases

Chelating agent	Metal	Dose	Time (hours)	Solution pH	Initial metal concentration (ppm)	Final metal concentration (ppm)	EPA discharge limit (ppm) [3]
SDTC	Pb	Stoichiometric	1	3.5	50.00	21.90	5.0
SDTC	Pb	Stoichiometric	6	3.5	50.00	21.89	5.0
SDTC	Pb	Stoichiometric	20	3.5	50.00	23.77	5.0
SDTC	Pb	10% dose increase	1	4.0	50.00	15.46	5.0
SDTC	Pb	10% dose increase	6	4.0	50.00	16.21	5.0
SDTC	Pb	10% dose increase	20	4.0	50.00	16.31	5.0
SDTC	Cu	Stoichiometric	1	3.5	50.00	12.55	
SDTC	Cu	Stoichiometric	6	3.5	50.00	12.58	
SDTC	Cu	Stoichiometric	20	3.5	50.00	12.46	
SDTC	Cu	10% dose increase	1	4.0	50.00	7.08	
SDTC	Cu	10% dose increase	6	4.0	50.00	7.10	
SDTC	Cu	10% dose increase	20	4.0	50.00	7.19	
SDTC	Cd	Stoichiometric	1	3.0	50.00	11.52	1.0
SDTC	Cd	Stoichiometric	6	3.0	50.00	11.51	1.0
SDTC	Cd	Stoichiometric	20	3.0	50.00	12.08	1.0
SDTC	Cd	10% dose increase	1	4.0	50.00	10.47	1.0
SDTC	Cd	10% dose increase	6	4.0	50.00	10.54	1.0
SDTC	Cd	10% dose increase	20	4.0	50.00	10.96	1.0
SDTC	Fe (II)	Stoichiometric	1	4.0	50.00	25.18	2.0
SDTC	Fe (II)	Stoichiometric	6	4.0	50.00	23.07	2.0
SDTC	Fe (II)	Stoichiometric	20	4.0	50.00	23.92	2.0
SDTC	Fe(II)	10% dose increase	1	4.5	50.00	24.28	2.0
SDTC	Fe(II)	10% dose increase	6	4.5	50.00	23.21	2.0
SDTC	Fe(II)	10% dose increase	20	4.5	50.00	23.94	2.0
SDTC	Hg	Stoichiometric	1	4.0	50.00	1.01	0.2
SDTC	Hg	Stoichiometric	6	4.0	50.00	1.50	0.2
SDTC	Hg	Stoichiometric	20	4.0	50.00	2.78	0.2
SDTC	Hg	10% dose increase	1	4.0	50.00	0.69	0.2
SDTC	Hg	10% dose increase	6	4.0	50.00	1.24	0.2
SDTC	Hg	10% dose increase	20	4.0	50.00	1.63	0.2

tetramethylthiuram and thiram. The SDTC relese ultimately killed 117 tons of fish over a 50 mile stretch from Anderson to Indianapolis, Indiana, as reported by the Indiana Department of Environmental Management [13].

2. Materials and methods

2.1. Methodology

The laboratory studies between the metal salts and TMT, STC, and SDTC utilized reagent-grade materials purchased either from the manufacturer or a chemical distributor.

Table 2
ICP-OES and CVAF results of STC at stoichiometric doses and at 10% molar dosage increases

Chelating agent	Metal	Dose	Time (hours)	Solution pH	Initial metal concentration (ppm)	Final metal concentration (ppm)	EPA discharge limit (ppm) [3]
STC	Pb	Stoichiometric	1	6.0	50.00	38.24	5.0
STC	Pb	Stoichiometric	6	6.0	50.00	44.83	5.0
STC	Pb	Stoichiometric	20	6.0	50.00	48.17	5.0
STC	Pb	10% dose increase	1	5.5	50.00	33.67	5.0
STC	Pb	10% dose increase	6	5.5	50.00	41.55	5.0
STC	Pb	10% dose increase	20	5.5	50.00	47.99	5.0
STC	Cu	Stoichiometric	1	5.0	50.00	27.77	
STC	Cu	Stoichiometric	6	5.0	50.00	28.99	
STC	Cu	Stoichiometric	20	5.0	50.00	28.86	
STC	Cu	10% dose increase	1	4.5	50.00	27.08	
STC	Cu	10% dose increase	6	4.5	50.00	25.77	
STC	Cu	10% dose increase	20	4.5	50.00	26.79	
STC	Cd	Stoichiometric	1	5.5	50.00	34.38	1.0
STC	Cd	Stoichiometric	6	5.5	50.00	39.53	1.0
STC	Cd	Stoichiometric	20	5.5	50.00	47.07	1.0
STC	Cd	10% dose increase	1	5.0	50.00	27.09	1.0
STC	Cd	10% dose increase	6	5.0	50.00	34.87	1.0
STC	Cd	10% dose increase	20	5.0	50.00	41.50	1.0
STC	Fe (II)	Stoichiometric	1	6.0	50.00	35.15	2.0
STC	Fe (II)	Stoichiometric	6	6.0	50.00	34.38	2.0
STC	Fe (II)	Stoichiometric	20	6.0	50.00	32.98	2.0
STC	Fe (II)	10% dose increase	1	5.0	50.00	34.79	2.0
STC	Fe (II)	10% dose increase	6	5.0	50.00	34.56	2.0
STC	Fe (II)	10% dose increase	20	5.0	50.00	33.56	2.0
STC	Hg	Stoichiometric	1	6.0	50.00	8.59	0.2
STC	Hg	Stoichiometric	6	6.0	50.00	8.07	0.2
STC	Hg	Stoichiometric	20	6.0	50.00	6.85	0.2
STC	Hg	10% dose increase	1	6.0	50.00	6.72	0.2
STC	Hg	10% dose increase	6	6.0	50.00	5.20	0.2
STC	Hg	10% dose increase	20	6.0	50.00	3.97	0.2

STC was obtained from ETUS Inc., as a pH 12.6 solution. TMT was supplied by Degussa Corporation USA. SDTC was obtained from Aldrich chemicals (SDTC hydrate, lot #02825CS). Reagent-grade materials were used as sources for the metals: lead acetate ($PbC_4H_6O_4$, Mallinckrodt, lot #5688N52585), cadmium chloride ($CdCl_2$, J.T. Baker Inc., lot #45062), ferrous sulfate ($FeSO_4$), mercuric chloride ($HgCl_2$, ACROS, lot #B0100782), and copper (II) chloride ($CuCl_2$, Aldrich, lot #17923CS). For reactions in a sodium acetate buffer solution, the buffer was prepared at pH 6.0 using sodium acetate ($NaC_2H_3O_2 \cdot 3H_2O$, J.T. Baker Inc., lot #744103), and glacial acetic acid ($C_2H_4O_2$, Mallinckrodt, lot #V193N08-H38). All metal–ligand reactions were carried out at room temperature and under normal atmospheric conditions.

Table 3
ICP-OES and CVAF results of TMT at stoichiometric doses and at 10% molar dosage increases

Chelating agent	Metal	Dose	Time (hours)	Solution pH	Initial metal concentration (ppm)	Final metal concentration (ppm)	EPA discharge limit (ppm) [3]
TMT	Pb	Stoichiometric	1	5.0	50.00	18.21	5.0
TMT	Pb	Stoichiometric	6	5.0	50.00	18.50	5.0
TMT	Pb	Stoichiometric	20	5.0	50.00	21.05	5.0
TMT	Pb	10% dose increase	1	5.5	50.00	16.06	5.0
TMT	Pb	10% dose increase	6	5.5	50.00	16.58	5.0
TMT	Pb	10% dose increase	20	5.5	50.00	17.31	5.0
TMT	Cu	Stoichiometric	1	5.0	50.00	16.18	
TMT	Cu	Stoichiometric	6	5.0	50.00	13.30	
TMT	Cu	Stoichiometric	20	5.0	50.00	10.13	
TMT	Cu	10% dose increase	1	5.5	50.00	16.19	
TMT	Cu	10% dose increase	6	5.5	50.00	14.21	
TMT	Cu	10% dose increase	20	5.5	50.00	12.59	
TMT	Cd	Stoichiometric	1	5.0	50.00	37.14	1.0
TMT	Cd	Stoichiometric	6	5.0	50.00	36.12	1.0
TMT	Cd	Stoichiometric	20	5.0	50.00	38.22	1.0
TMT	Cd	10% dose increase	1	5.5	50.00	21.04	1.0
TMT	Cd	10% dose increase	6	5.5	50.00	21.04	1.0
TMT	Cd	10% dose increase	20	5.5	50.00	21.62	1.0
TMT	Fe (II)	Stoichiometric	1	5.0	50.00	25.04	2.0
TMT	Fe (II)	Stoichiometric	6	5.0	50.00	25.46	2.0
TMT	Fe (II)	Stoichiometric	20	5.0	50.00	25.27	2.0
TMT	Fe(II)	10% dose increase	1	5.5	50.00	23.64	2.0
TMT	Fe(II)	10% dose increase	6	5.5	50.00	22.38	2.0
TMT	Fe(II)	10% dose increase	20	5.5	50.00	21.77	2.0
TMT	Hg	Stoichiometric	1	5.5	50.00	18.07	0.2
TMT	Hg	Stoichiometric	6	5.5	50.00	13.39	0.2
TMT	Hg	Stoichiometric	20	5.5	50.00	9.82	0.2
TMT	Hg	10% dose increase	1	5.5	50.00	15.15	0.2
TMT	Hg	10% dose increase	6	5.5	50.00	16.90	0.2
TMT	Hg	10% dose increase	20	5.5	50.00	10.50	0.2

2.2. Analytical methods

Lead, cadmium, iron, and copper analyses were performed with a 1999 Thermo Jarrell Ash Duo HR Iris Advanced Inductively Coupled Plasma Optical Emission Spectrometer
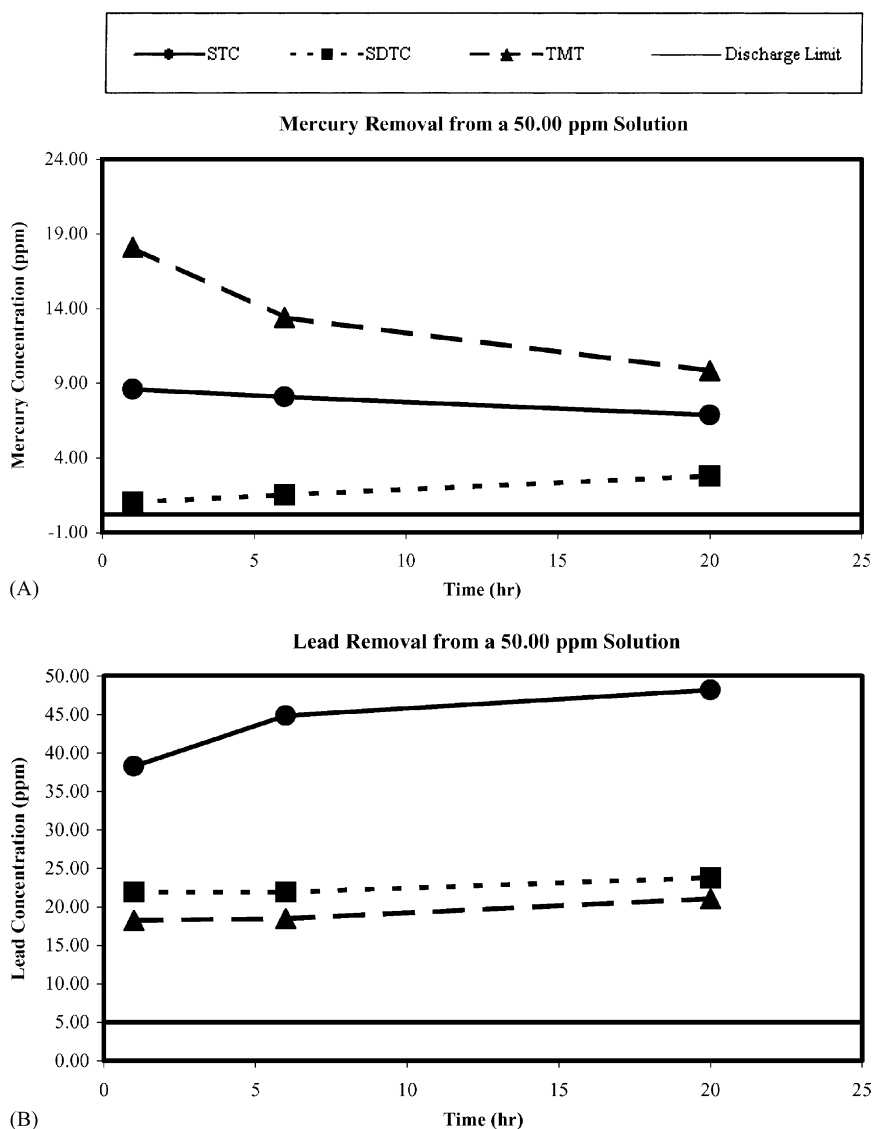

Fig. 2. Graphical depiction of metal removal over a 20 h time period. Each metal begins at a starting standard concentration of 50.00 ppm, and each reaction was carried out utilizing a stoichiometric ligand dosage: (A) mercury removal at a stoichiometric dose; (B) lead removal at a stoichiometric dose; (C) cadmium removal at a stoichiometric dose; (D) copper removal at a stoichiometric dose; (E) ferrous removal at a stoichiometric dose.

Cadmium Removal from a 50.00 ppm Solution

(C)

Copper Removal from a 50.00 ppm Solution

(D)
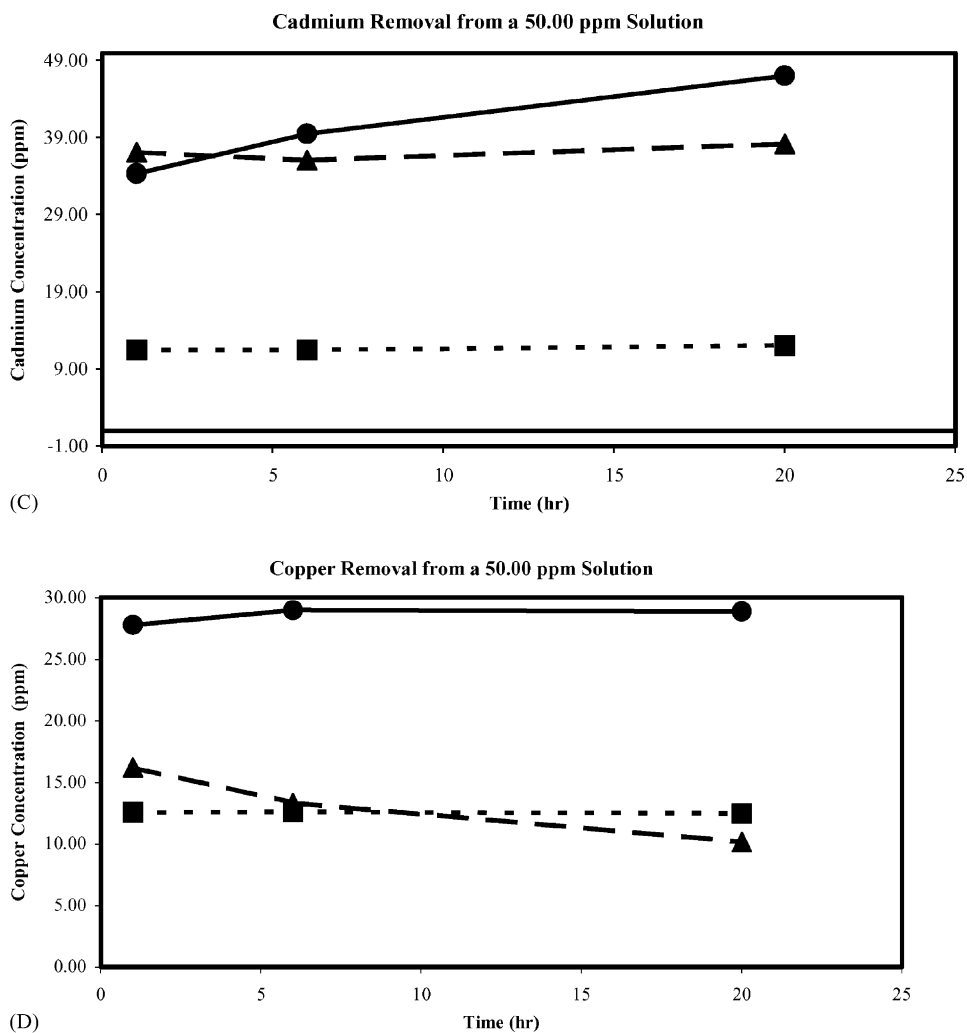
Fig. 2. (*Continued*).

(ICP-OES). Mercury results were obtained using cold vapor atomic fluorescence spectroscopy (CVAF) on a Varsal Atomic Fluorescence Spectrometer, model number VI2000, using EPA techniques for mercury analyses [14]. For powder XRD analyses, the samples were mounted on glass slides with ethanol and analyzed with a Rigaku unit at 40 kV and 20 mA using Cu Kα_1 ($\lambda = 1.540598$ Å) radiation. Infrared spectroscopy (IR) data on TMT and SDTC were obtained from the Aldrich IR library [15]. For the metal–ligand complexes, the IR spectra were collected as pellets using spectroscopy grade KBr (Mallinckrodt, lot #0505 KXRX) using a Nicolet-Avatar 320 FT-IR series spectrometer. Elemental analyses were determined on a Vario Elementar III.

Ferrous Removal from a 50.00 ppm Solution

(E)
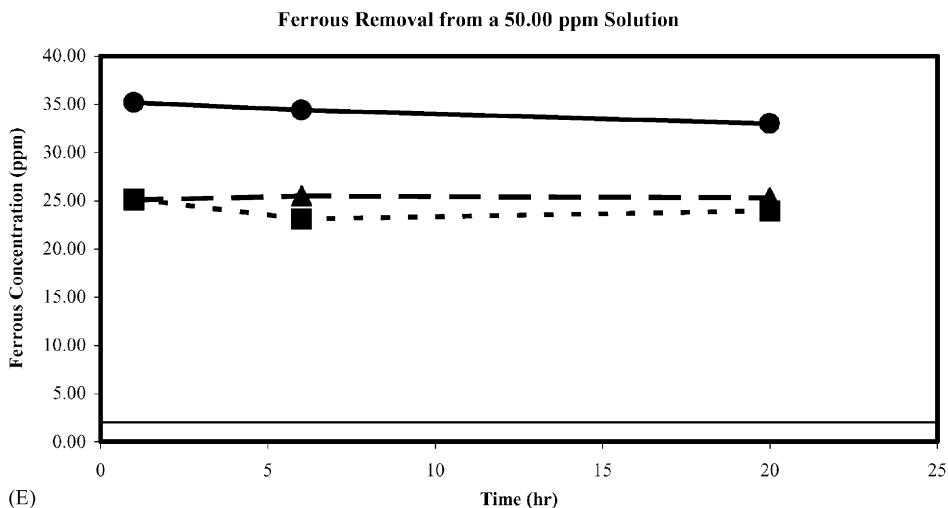
Fig. 2. (*Continued*).

2.3. Analytical procedures for ICP-OES and CVAF analyses

2.3.1. Cadmium, copper, lead, iron, and mercury analyses

Manufacturers supply dosage formulas to allow industrial users to quickly calculate the amount of compound needed to treat varying volumes of contaminated water. Often these dosage rates are incorrect and generally lead to under-dosing and, consequently, a failure to meet permitted discharge limits. In an effort to make a valid comparison of the effectiveness of TMT, STC and SDTC, the reactions were carried out using a stoichiometric molar amount of the reagent (and also a 10% increase in the stoichiometric molar dosage) with solutions of mercury, lead, cadmium, copper, and iron (II).

Each of the reagents were added separately to a series of 100 ml 50.00 ppm (part-per-million) Hg^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, and Fe^{2+} solutions. Aliquots (10 ml) were collected and filtered at 0.2 μm (Nalgene® syringe filters lot #322238) at intervals of 1, 6, and 20 h following the addition of the reagent (Tables 1–3, and Fig. 2A–D). In addition to the stoichiometric dosages, the use of a 10% increase in ligand concentration was tested for each metal under the same experimental conditions as the stoichiometric reactions. Again, for the 10% dose increase in ligand addition, aliquots were collected and filtered at 0.2 μm at 1, 6, and 20 h following reagent addition (Tables 1–3, and Fig. 3A–D).

3. Results and discussion

3.1. Characterization of precipitates

The reactions generating metal–reagent (TMT, STC or SDTC) complexes have been explored previously [6–8]. For the STC reactions, it was shown that the resulting products

are metal sulfides and carbon disulfide [6]. The SDTC–metal complexes are molecular with two ligands forming a bidentate chelate on the metal [16,17]. Here, the identity of each of the TMT, STC, and SDTC–metal complexes was confirmed using elemental analyses, IR, NMR, and XRD spectroscopy.
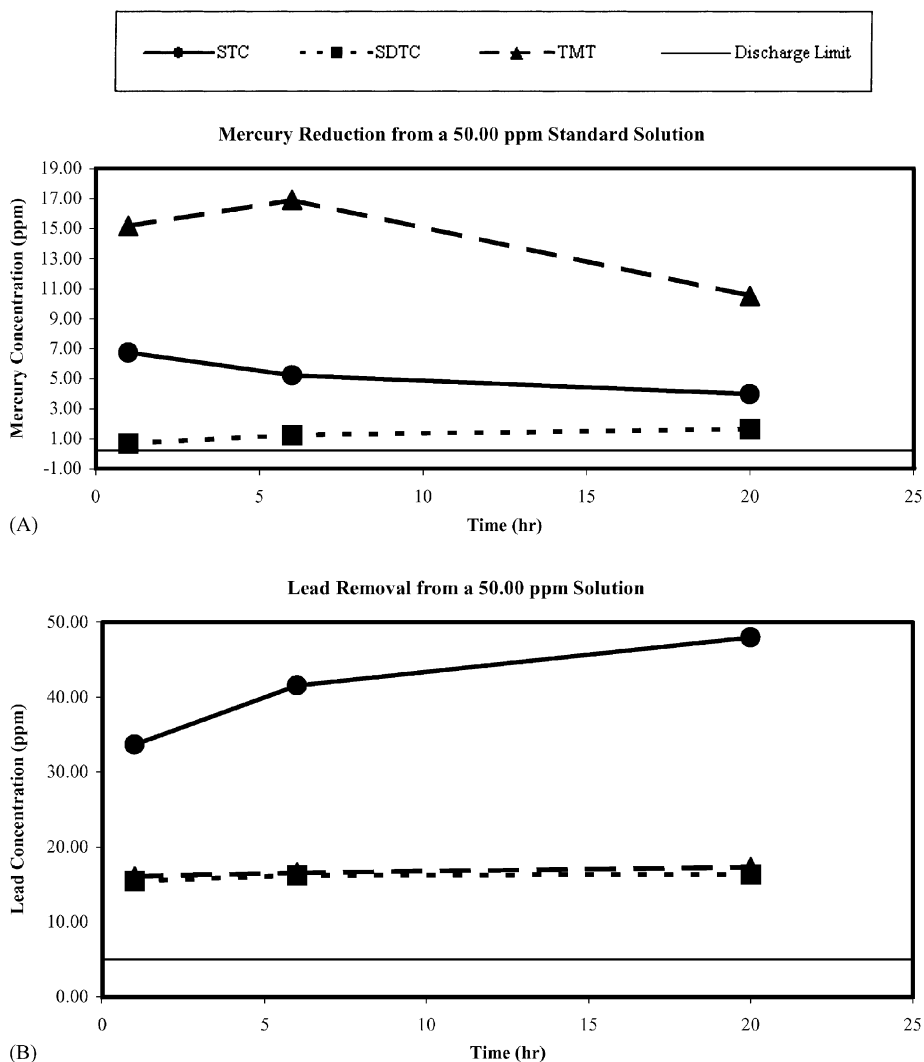

Fig. 3. Graphical depiction of metal removal over a 20 h time period. Each metal removal begins at a starting standard concentration of 50.00 ppm, and each reaction was carried out utilizing a 10% molar dose increase: (A) mercury removal at a 10% molar dose increase; (B) lead removal at a 10% molar dose increase; (C) cadmium removal at a 10% molar dose increase; (D) copper removal at a 10% molar dose increase; (E) ferrous removal at a 10% molar dose increase.
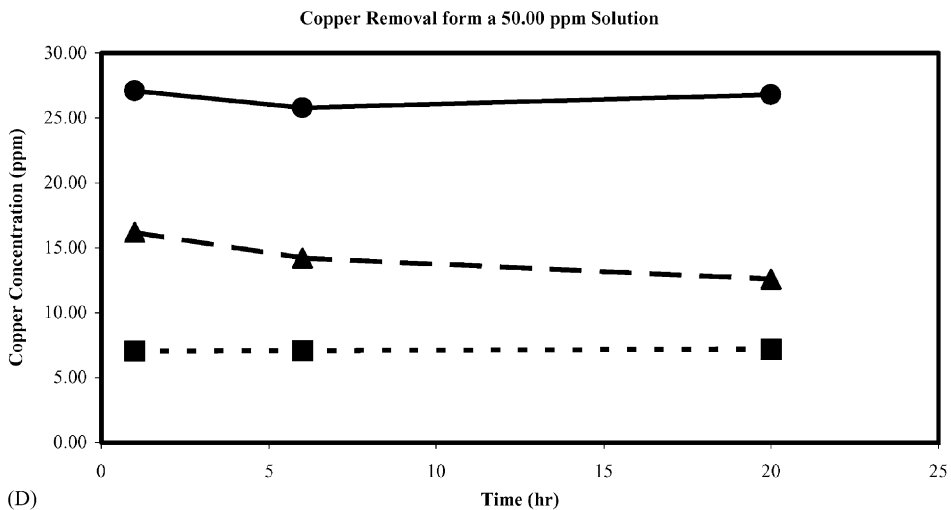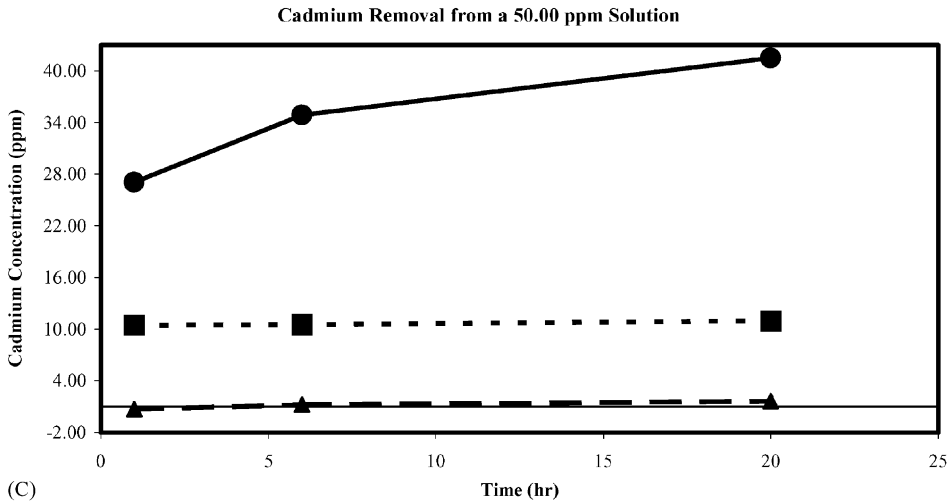
Cadmium Removal from a 50.00 ppm Solution

(C)

Copper Removal form a 50.00 ppm Solution

(D)

Fig. 3. (*Continued*).

3.2. Metal stoichiometry and removal ICP-OES analysis

It was found that at stoichiometric doses STC, SDTC, or TMT were unable to reduce cadmium, lead, copper, or iron concentrations from 50.00 ppm to levels sufficient to meet EPA discharge limits (Tables 1–3 and Fig. 2B–E); [3]. Even with a 10% molar excess dose, no additional significant removal was observed (Tables 1–3 and Fig. 2B–E). The SDTC displayed a higher affinity for cadmium, lead, copper, and iron than the STC. TMT provided similar results as the SDTC with the highest removal seen for lead and copper.
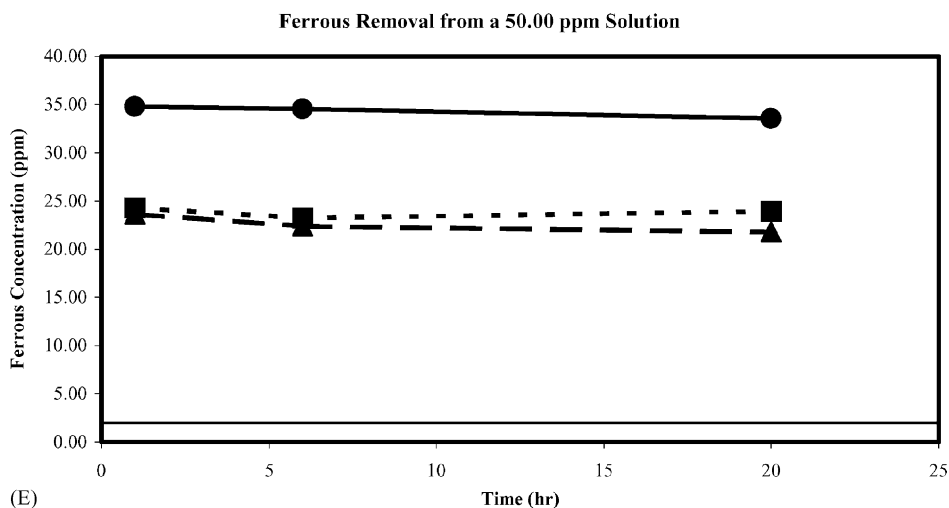
Ferrous Removal from a 50.00 ppm Solution

(E)

Fig. 3. (*Continued*).

Once again, it was found that even at a 10% molar increase in dosage TMT was unable to reduce lead or cadmium concentrations to meet EPA standards [3].

In some of the reactions the metal concentrations increased over time. This may be attributed to the formation of soluble metal–ligand complexes or decomposition of the metal–ligand complexes. Additionally, it is possible that the metal–ligand precipitates are not sufficiently stable to prevent metal leaching (or more simply, the reverse of the precipitation reaction is occurring).

3.3. Mercury stoichiometry and removal-CVAF analysis

For the mercury analyses, it was found that at stoichiometric and 10% molar dose increases the STC, SDTC, and TMT were all unable to reduce the concentration of mercury in a 50.00 ppm solution to meet the EPA limit (Tables 1–3 and Figs. 2A and 3A) [3]. Maximum results for mercury removal with STC occurred after 20 h at a 10% molar dose increase with an average value of 3.97 ppm. After 1 h the results of the SDTC at a 10% molar dose increase indicate a reasonably high removal of mercury with a final concentration of 0.69 ppm. Within 20 h at stoichiometric doses, TMT was able to reduce the 50.00 ppm mercury concentrations to an average final concentration of 9.82 ppm (Tables 1–3 and Figs. 2A and 3A).

3.4. The new multidentate ligand, PyDET

Based upon these studies of some widely used heavy metal precipitants there is a definite need for new and more effective reagents meet Federal and State requirements. Reagents on the market today either lack the necessary binding criteria to be effective or pose too many environmental risks to be safely utilized. For this reason, ligands utilizing both multiple binding sites and the same binding criteria for heavy metals as seen in biological
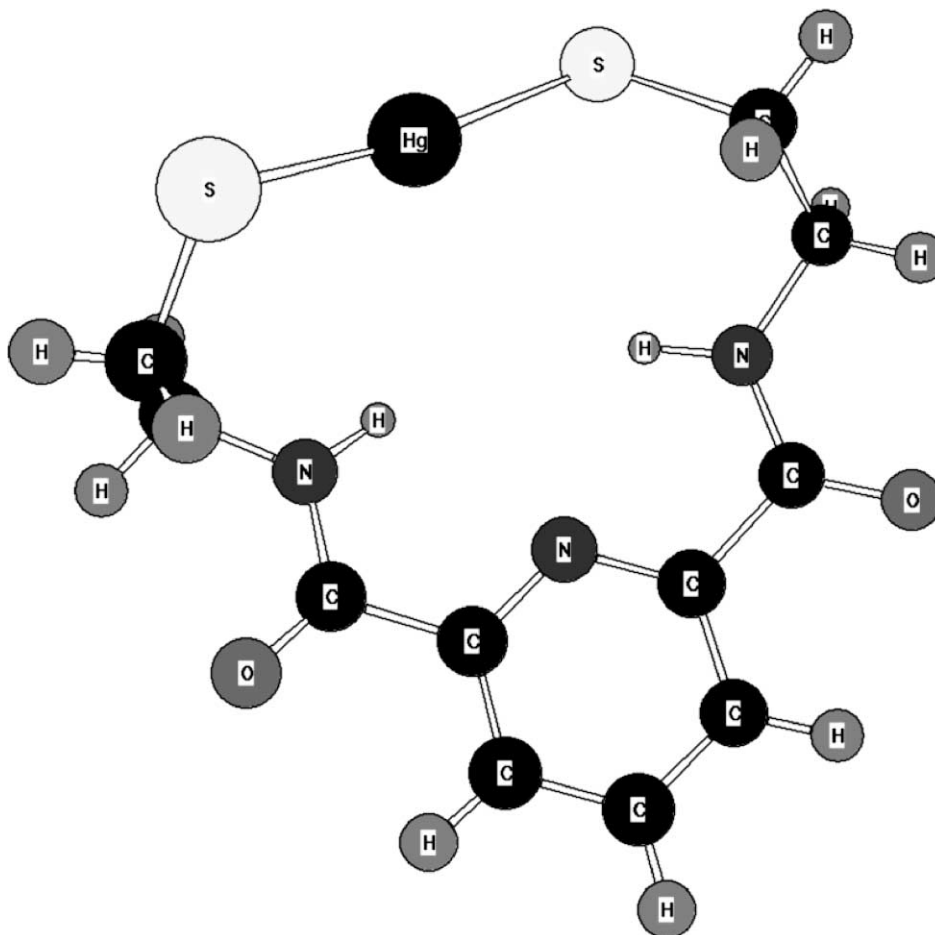
Fig. 4. Computer calculated structure of the PyDET-Hg compound.

systems are a possible answer to heavy metal wastewater treatment. In order to create more effective, economical, and robust ligands we have developed and synthesized a series of ligands which are designed to irreversibly bind heavy metals. One such ligand is 2,6-pyridinediamidoethanethiol (PyDET). This ligand mimics the active site of bacterial binding proteins [18,19]. Fig. 4 illustrates the type of binding predicted by computer modeling between the ligand and mercury. Early results with these ligands show that heavy metal concentrations from aqueous solutions can be reduced well below EPA discharge limits and produce precipitates that are insoluble in organic solvents and stable over a pH range of 0.0–14.0 [18–21]. For example, PyDET (at stoichiometric doses) reduces mercury concentrations from 50.00 to 0.094 ppm and lead concentrations from 50.00 to 0.050 ppm [18–21].

4. Conclusion

Heavy metal pollution is a growing environmental problem which requires immediate attention. With current commercial remediation reagents failing to provide the needed requirements for safe and effective metal precipitation agents, the need for new compounds is critical. One such chelation agent, 1,6-pyridinediamidoethanethiol appears to be effective in irreversibly binding metals as insoluble precipitates. This indicates that specifically designed ligands may be the best method for providing a final solution to heavy metal pollution.

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