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Honors Thesis

Extraction Studies of Toxic Multiply Charged Oxoanions From Aqueous Media Using Nanojars

Christian K. Hartman and Gellert Mezei

Abstract

In this paper, the potential of nanojars as extracting agents of chromate and arsenate from aqueous media into a non-polar organic medium is investigated. Nanojars are a class of compounds that consist of multiple [cis-Cu^{II}(μ-OH)(μ-pz)]$_n$ cyclic polymerization isomers (n = 6, 8, 9, 10, 12, 14; pz = pyrazolato anion) that form from self-assembly reactions around a multiply-charged oxoanion core with capping counterions to render an overall neutral complex. This incarcerates the anion, preventing it from escaping the complex without the use of any covalent bonding, making it a potentially highly effective and unique extracting agent. We have concluded that our system is capable of extracting both arsenate and chromate from water to below their respective EPA limits of 10 ppb and 100 ppb, and they do so better than another extracting agent, trioctylammonium nitrate. It has also been demonstrated in past publications by our group that nanojars are indeed capable of incarcerating the multiply-charged oxoanions via mass spectrophotometric and X-ray crystallographic analysis.

Introduction and Context

Multiply charged water soluble oxoanion salts are common water contaminants in water supplies around the world. Some of these contaminants come from natural sources whilst others are often byproducts of industrial processes. As one example, mixtures of trivalent chromium salts are used extensively in modern leather tanning operations because they provide increased resistance. The wastewater from the tanning operations is often still high in chromium content, although recycling efforts such as precipitation reactions are often performed, chromium is eventually released into the natural environment (1). In its trivalent state chromium is an essential nutrient for the body, required in trace amounts. Yet, hexavalent chromium is a potent mutagen, carcinogen and toxin. Furthermore it has been found that chromium (III) can naturally be oxidized to chromium (VI) as chromate in the environment (2, 3).

Natural sources of contaminants, such as arsenic from minerals, have caused considerable problems for populations in nations like Bangladesh who depend on contaminated wells for drinking water (4). Despite its toxicity, the arsenic has many industrial applications. Arsenic is used in agricultural herbicides, wood preservatives, semiconductors, glass manufacture, and it has uses in alloys with copper and lead, for example in lead alloys for lead-acid batteries (5, 6).

Phosphates are often used in fertilizers, but excess concentrations in runoff from fields can contribute to algal blooms and eutrophication of water supplies because they are an essential nutrient for the naturally-occurring populations of phytoplankton. Many of these phytoplankton species then consume the dissolved oxygen present in the water necessary for the support of aquatic life at rapid rates due to their fertilizer-induced explosive growth, or some even produce chemicals that are toxic to animal and plant life in large quantities during algal blooms. These algal blooms often lead to eutrophication of the waters in which they occur (7). Thus, some multiply charged oxoanions may not be a toxin, but may indirectly contaminate important water supplies.

Despite all of the dangers to the environment the above mentioned oxoanions present, they are all widely used—or the metallic components in the case of arsenate and some applications of the chromium present in chromates—in industry where they serve important roles. For this reason, the potential of nanojars to serve as an extractant of these oxoanions from an aqueous phase as part of a continuous process that would allow the recycling of both the extracted anions and the extractants, nanojars, was investigated as a possible improvement or supplement to currently available water treatment methods.

The Proposed System

It has been demonstrated that nanojars are capable of incarcerating multiply charged oxoanions such as arsenates, phosphates, carbonates and sulfates (8, 9, 10). They are also capable of protecting them from further reaction with other chemicals in solution. For example, once a sulfate anion was incarcerated by nanojars not even Ba^{2+} ions were capable of precipitating the anion out of the nanojar complex (10). Extraction of carbonate anions was also demonstrated to be accomplished in a biphasic system using 4-octylpyrazole as a pyrazolate ligand in the nanojar, the first of this kind to the best of our knowledge. By expanding on the design of the prior system, the hope is that a similar feat may be accomplished with a variety of other anions as well (9).

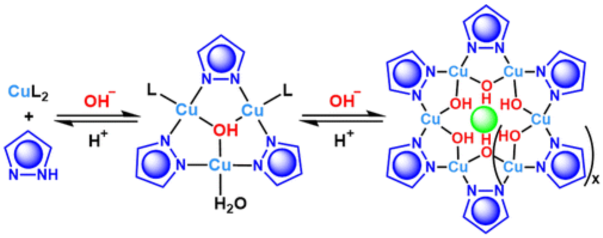

Figure 1: Depicting pH dependent equilibrium of trimeric structure and nanojars containing simple pyrazole, represented by only one of three rings for clarity and simplicity. The green sphere represents the incarcerated oxoanion (11).

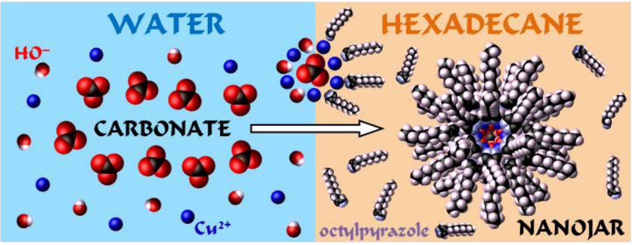

Figure 2: Depicting extraction of carbonate from aqueous media into aliphatic solvent with 4-octylpyrazolate-based nanojars (9).

Additionally, it has been discovered that nanojars undergo a reversible pH-dependent breakdown to a trimeric structure at even a mildly acidic pH, while reforming and remaining stable at even a strongly basic pH (>14), see Fig. 1 (11). Thus, the ideal system would be one that would form both an aliphatic solvent soluble nanojar and trimeric unit that would be simultaneously insoluble in the aqueous phase, whilst also using an aliphatic base to generate the hydroxide ion required for the formation of the nanojar that would also remove the proton from the aqueous phase in order to avoid acidifying it while the extraction is taking place. We hypothesize that by stirring the biphasic system vigorously and carefully choosing the aliphatic solvent so separation will be total and rapid, one could accomplish the oxoanion extraction and be left with a neutral, contaminant-free aqueous layer. The clean aqueous layer could then be drained from the extraction tank and a weakly acidic aqueous layer could be pumped in, resulting in the breakdown and back-extraction of the oxoanions into this new layer with vigorous stirring. All breakdown products other than water from the protonation of the OH groups in the nanojar would remain in the organic phase, and then this aqueous layer could be drained from the tank for harvesting of the oxoanions and recycling them. Finally, by adding more aliphatic base the nanojars could be regenerated upon exposure to the next aqueous extraction layer.

If such a system were implemented in which multiple biphasic tanks were in use at once, then a continuous extraction process could be established, as one tank could be undergoing extraction while another is being stripped of its oxoanions by acid. With proper timing, the tanks could finish their tasks simultaneously and reverse roles with a simple switch of a couple valves so that the contaminated water and acidic stripping water would be pumped to the opposite tanks. The goal of this thesis was to study the chemical conditions necessary to create this system as well as its possible limits, as the quantitative extraction potential of the nanojars has yet to be determined in the prior research done by this group.

Results and Discussion

The biphasic reaction system used distilled water for the aqueous layer with a dissolved salt of the material targeted for extraction. The aliphatic layer in an industrial process would likely be something like Isopar, but for these experiments a layer of n-heptane was used for the nonpolar layer. Separations were done using a separatory funnel to allow for testing of the aqueous layer's content of the extractant after extraction.

The first challenge was encountered during the extractions was that not all incarcerated anions are equally preferred by the nanojars. Carbonate seems to be the anion with the highest preference and so experiments had to be done with the reaction vessels sealed with parafilm immediately after reagents began mixing, otherwise the carbon dioxide from the atmosphere could dissolve into the system and become carbonate and interfere greatly with our extraction system. However, even with simply sealing the reaction vessel with parafilm, the 4-octylpyrazolate nanojar system appeared to accomplish suitable levels of extraction. For maximum efficiency, extractions would most likely have to be done in carbon dioxide-free environment. Arsenate is particularly vulnerable to exchange with carbonate, and so limiting the potential for exchange to occur was essential. After it was discovered that this had to be done to carry out an effective extraction, the next task was to determine the optimum time for mixing of the phases for extraction before separating the organic and aqueous phases and testing for arsenic in the aqueous phase.

As shown in Table 1, arsenic could be extracted from high concentrations to below the EPA drinking water limit of 10 ppb within an hour of extraction time and with a 50% excess of nanojar-forming reagents (12). For these experiments our aqueous layer was distilled water that contained only the reagents necessary to form nanojars and Na_2HAsO_4.

Table 1

Reaction Code	Ini. Conc. (ppm As)	Final Conc. (ppb As)	Time Extracted
CKH46	83.2	<10	1.00 hour
CKH45	83.2	<10	5.75 hours
CKH44A	83.2	<10	21.5 hours

This table shows three separate extractions of arsenic with the initial and final concentrations of the aqueous phase. Initial concentrations were calculated while final concentrations were measured using HACH colormetric arsenic testing kits.

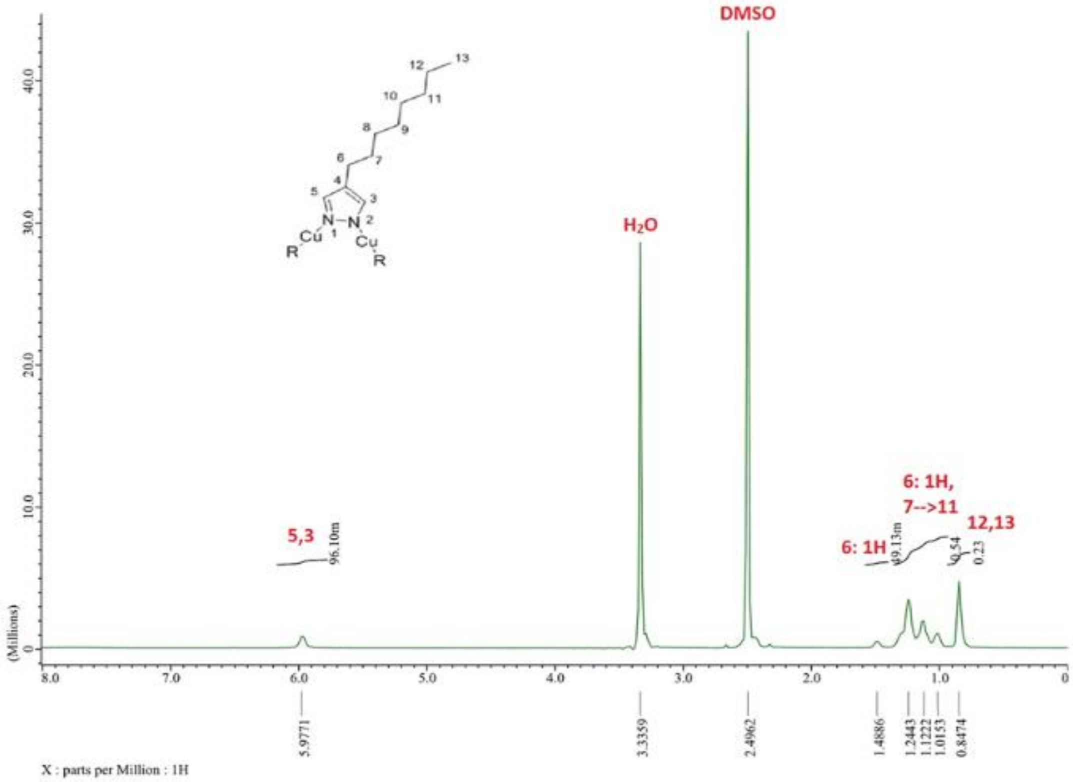

Figure 3: ^1H NMR in deuterated DMSO of the 4-octylpyrazolate trimer sodium salt. 5,3 peak integrates to 2H, peak at 1.4886 integrates to 1H, 7→11 peak cluster integrates to 11H, and 12,13 peak integrates to 5H. Water is an impurity. DMSO is due to proton exchange with NMR solvent. Integration values will be triple their reported number of hydrogens if the trimer was indeed made, but for now this cannot be concretely proven with current data because we cannot determine the mass of the species by mass spectrometric analysis.

These samples also showed that some of the copper and nitrate from the nanojar forming reagents was also leaching back into the aqueous phase with levels at about 100 ppm copper and 100-250 ppm nitrate according to colormetric testing strips, which are well above the EPA limits for drinking water. These experiments were done using $Cu(NO_3)_2 \cdot 2.5H_2O$ as the copper source to form the nanojars, and this salt is water soluble. It was suspected that this leaching was due in part to the excess of reagents and the solubility of the copper source in the aqueous phase.

In an effort to combat this problem, we attempted to make the trimeric unit of the nanojars containing 4-octylpyrazole, which would have a similar appearance to that of the trimeric unit shown in Fig. 1 except there would be an octyl chain extending from the four position carbon. This trimer has not been previously synthesized or isolated. The trimer proved extremely difficult to analyze. Containing paramagnetic coppers, we suspect that the peaks for the hydroxo groups are simply too broad due to copper's paramagnetism to be readily distinguished and thus only the octyl chains at the four position and the protons on the pyrazole could be clearly identified through ^{1}H NMR analysis. Additionally, owing to the long alkyl chains, the product formed from this reaction proved to be rather insoluble in polar solvents while being extremely soluble in nonpolar solvents like diethyl ether. As a result, the product was not suitable for ESI mass-spectrometric analysis to confirm its identity. The blue-green color it forms in solution and the dark green color it exhibits as a solid imply the presence of copper and the NMR confirm the presence of 4-octylpyrazole in the product. The 4-octylpyrazolate nanojar and the trimers of the simple pyrazolate nanojar have been studied and confirmed to exist. Thus, we felt confident that the product formed from the reaction was indeed as expected. Crystallization and analysis by X-ray crystallography might be used to positively identify the complete structure of the product, but this has not yet been accomplished.

Using the trimer to form the nanojar rather than simple reagents did succeed in reducing the amount of nitrate present in the aqueous layer to the point that the amount was not detectable by our colormetric testing strips. However, the copper content of the aqueous layers was less affected despite the fact that the trimer itself was not very soluble in neutral or even acidic aqueous solutions. Due to these results, we had to determine whether or not nanojars were actually forming and doing the extracting in these reactions. The color of the organic layer was not the typical color of the nanojars, rather it was still similar to that of the trimer in solution.

Another complicating factor was that our aqueous layers from the extractions consistently had pH readings in the range of 4.0-5.0, which was thought to be incompatible with nanojar formation. We attributed the low pH to the excess copper ions from the nitrate salt hydrolyzing the water in the original extractions, but the trimer should not give free copper ions to enter the aqueous phase and acidify it so it became clear something else was happening.

Reaction 1

$$(CH_3(CH_2)_7)_3N + H_2O \rightarrow [(CH_3(CH_2)_7)_3NH]^+ + [OH]^-$$

Reaction 1 shows the reaction that occurs between the aqueous layer and the base during the nanojar formation. Trioctylamine (TOA) reacts with water to form hydroxide and a trioctylammonium (TOA$^+$) cation. Our initial thought was that the TOA$^+$ would pair up with a nitrate anion and then go into the organic phase since TOA is not significantly soluble in water, removing the acidic proton from the water from contact with the aqueous layer after hydrolysis. The hydroxide is incorporated in the nanojar as one of the ligands that binds to the copper centers, so the basic component of the hydrolysis reaction is also removed from the aqueous solution. In a perfectly stoichiometric reaction, the pH of the resulting aqueous layer should be neutral, and since our extractions used excess reagents perhaps a basic pH could be expected in the aqueous layer due to the presence of excess base, yet the resulting layer was acidic.

Reaction 2

$$[(CH_3(CH_2)_7)_3NH]^+ + [NO_3]^- + H_2O \rightarrow (CH_3(CH_2)_7)_3N + HNO_3 + H_2O \rightarrow (CH_3(CH_2)_7)_3N + [H_3O]^+ + [NO_3]^-$$

Upon reflection, the Reaction 2 was devised as a possible source of the acidity. TOA^+ nitrate could transfer its proton to the nitrate to form nitric acid and TOA, with the TOA being dissolved in the n-heptane layer and the nitric acid acidifying the aqueous layer. Due to the acid being strong, nitrate levels could remain below detection while still reaching a significant level of acidity with minimal acid formation. We hypothesize that this is the major contributor to the acidity of the aqueous layer.

Whilst attempting to solve that mystery, extraction studies were begun on chromate, using dried sodium chromate as the chromate source for extraction. Initial chromium testing was done using colormetric test strips, similarly to the copper and nitrate testing that was done, but the strips were not precise or sensitive enough to test if the chromium was being extracted to below EPA limits of 100 ppb.

We consulted Dr. Koretsky on how she tested specifically for chromate and was directed to a UV-Vis spectroscopic method that could more precisely detect lower levels of chromate. Literature was also consulted in order to learn more about the method and attempt to determine its limits (13, 14).

The method is well-established and based on the formation of a chromium-diphenylcarbazide complex that has an absorbance band at about 540 nm that can be measured to quantitatively determine the concentration of chromate in the solution through the Beer-Lambert Law. Extraction to the EPA limits or below was accomplished; this will be discussed in greater detail shortly.

During investigation of the chromium content analysis method, a further problem with the system was discovered. Repeatedly, quaternary ammonium compounds (nitrogenous compounds with four alkyl chains bonded to the nitrogen to generate a cation with an anion to balance the charge), or more specifically the quaternary ammonium cation, were used as extracting agents for chromium as chromate or dichromate in acidic conditions (15, 16). While our base would form a tertiary ammonium cation and not a quaternary ammonium compound, it was indeed possible that it could also serve as an extracting agent. The TOA^+ that would be formed during this reaction is present in much larger amounts (i.e. 62 times more) than the nanojars being formed, and so if this cation could also extract the targeted oxoanions into the organic layer, then we could not claim that the nanojars were indeed doing the extracting in this case—or at least not by themselves.

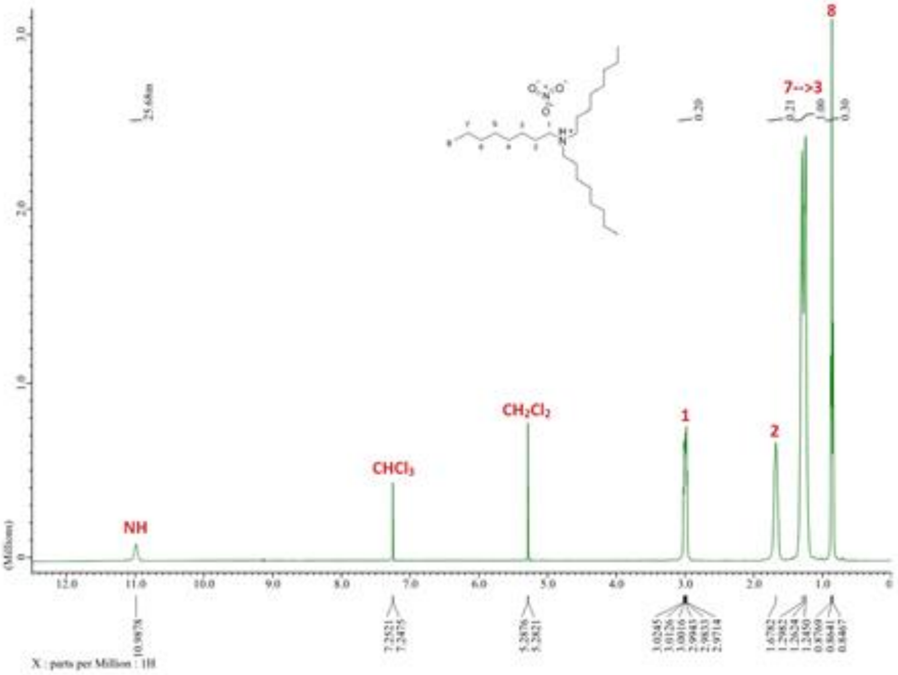

Figure 4: ^{1}H NMR of $TOANO_3$. Red numbers correspond to those on the structure. CH_2Cl_2 remains from the synthesis, and $CHCl_3$ is due to proton exchange between product and the deuterated chloroform used as a solvent. Peaks match those reported in reference

$TOANO_3$ had to be synthesized in order to test whether or not the TOA^+ cation has extraction potential. The compound was synthesized using a modified version of a published procedure (17). The synthesized product's NMR peaks matched those reported in the publication, see Fig. 4. Both TOA and $TOANO_3$ were not very water soluble, but $TOANO_3$ in its pure form was also not noticeably soluble in n-heptane unlike TOA. Despite the $TOANO_3$ not being extremely soluble in water, it could still easily

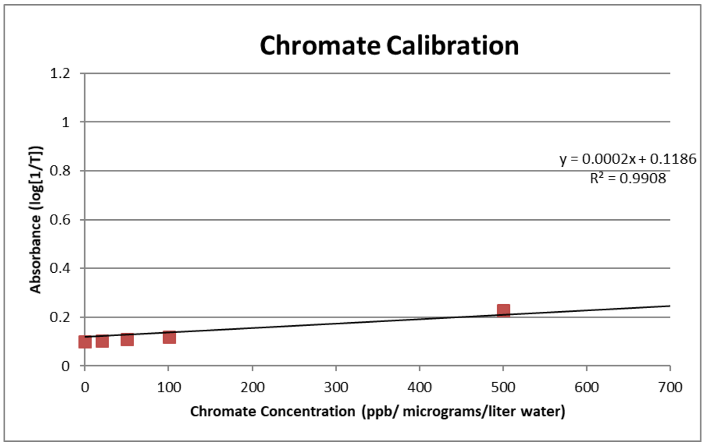
Chromate Calibration

Figure 5: Chromate colormetric method calibration curve. Linear range for the Beer-Lambert law was determined to be from 20.01 ppb to 5003 ppb, or about 5 ppm. Standards at different concentrations were prepared using potassium chromate and serial dilutions with four significant figures of accuracy.

Table 2

Concentration (ppb)	Absorbance
5003	1.008
1001	0.365
500.3	0.227
100.1	0.120
50.03	0.111
20.01	0.105
0.000 (Blank)	0.100

This table displays the data from the calibration curve in greater detail. Variance in the instrument was +/- 0.001 for the absorbance.

acidify water to the pH observed in the aqueous layer of the extractions. TOA and $TOANO_3$ are both colorless liquids in their pure form, and so it is possible that some $TOANO_3$ could convert to TOA and nitric acid without any visually discernable changes occurring. This would account for the appearance of insolubility in water while still changing the pH of the aqueous solution.

Table 3

Sample	Absorbance	Concentration of Original (ppb)
Blank	0.112	0
Trimer Rxn	0.126	67.7 (+/- 4.84)
$Cu(NO_3)_2$ Rxn	0.132	96.7 (+/- 4.84)
$TOANO_3$	0.163	247 (+/- 4.84)

Post-extraction chromium content of aqueous layers from a reaction starting with trimers to form nanojars, copper(II) nitrate salt as the copper source for nanojars, and $TOANO_3$ as the extracting compound.

Additionally, experiments were done using stoichiometrically equivalent amounts of $TOANO_3$ suspended in an n-heptane layer and sodium hydrogen arsenate (Na_2HASO_4) in aqueous solution to the nanojar extractions. The same was done for sodium chromate (Na_2CrO_4). The purpose here was to establish the extraction potential of this system and determine whether the nanojars or trimers were doing any of the extracting at all. The arsenate extractions with $TOANO_3$ alone appeared to be largely unsuccessful. Our testing kits indicated that the remaining concentration of the arsenate in aqueous solution was well over 500 ppb. This seems to indicate that TOA^+ cannot effectively extract hydrogen arsenate/arsenate from an aqueous layer by itself. However, the trimers/nanojars can somehow extract the arsenate/hydrogen arsenate—possibly in conjunction with TOA^+—to levels that are below 10 ppb.

The chromate extraction experiments with TOA^+ were very different, however. They extracted chromate to a great degree, and their extraction capability appeared to be identical to that of the nanojar/trimer system when measured with our test strips. So, I made a calibration curve for the colormetric chromate determination to attempt to determine whether or not that more precise and accurate method could discern any difference between the two systems (see Fig. 4 and Table 2).

Curiously, the reaction that uses the trimer as the copper source for the nanojars to form was the only reaction to extract chromium until it was well below the EPA limit of 100 ppb. The reaction that used copper(II) nitrate hemipentahydrate as the copper source for the nanojars extracted to about the EPA limit in chromium. $TOANO_3$ alone, in contrast, was only able to accomplish the extraction to a level about 2.5 times the current EPA limit for total chromium in drinking water, 247 ppb.

Thus, for both oxoanions studied in our system, $TOANO_3$ is not an extracting agent that can accomplish extractions to levels below those set by the EPA. Although we cannot be sure of what exactly is accomplishing the extraction in our reactions that should form the nanojar, it is certain that our current system can simply and easily extract both arsenic and chromium as chromate and arsenate to levels below the EPA standards. Unfortunately, our system in its current form is not as recyclable as initially imagined due to the leaching of copper and nitrate into the aqueous layer. We believe that our system could be realized if another type of non-polar base of sufficient strength were used.

Experimental Details

Materials and Instrumentation

All solvents were pure and reagents were reagent grade and used as purchased from Sigma-Aldrich, unless otherwise noted. Chemical reactions were done at room temperature and atmospheric pressure unless otherwise noted. All NMR spectra were collected on a Jeol JNM-ECP400 instrument. UV-Vis measurements were carried out on a Shimadzu UV-1650PC spectrophotometer. Mass spectrophotometric analysis was attempted and proved unsuccessful on a Waters Synapt G1 HDMS instrument using electrospray ionization (ESI).

Arsenic Extraction Reactions Listed in Table 2

CKH44A:

$31\ Cu(NO_3)_2\cdot 2.5H_2O + 31\ (4\text{-octylpyrazole}) + 60\ NaOH + 2\ (CH_3(CH_2)_3)_4NOH + Na_2HAsO_4\cdot 7H_2O \rightarrow (\{CH_3(CH_2)_3\}_4N)_2[\{Cu(4\text{-Octpz})OH\}_nHAsO_4] + 62\ NaNO_3$

The chemicals in purple were those that went into the n-heptane layer, whilst the red reagent contains the material attempting to be extracted. This reaction is essentially the classic nanojar synthesis method with 4-octylpyrazole (4-OctpzH) swapped out for pyrazole. All reagents were present in 1.5× stoichiometric amounts relative to the arsenate salt to drive equilibrium towards maximal extraction. 0.5595 g of 4-OctpzH were added to 50 mL of n-heptane in a 200 mL round bottom flask and then set aside. 0.2005 g of aqueous 1.0 molar $(CH_3(CH_2)_3)_4NOH$ (TBAOH) solution were added to 60 mL of distilled water from a Milli-Q filtration system in a beaker, along with 0.2405 g NaOH and 0.0208 g of sodium hydrogen arsenate. The aqueous solution was mixed in the beaker until all added reagents were dissolved and then this was added to the round bottom flask contained the n-heptane solution. Lastly, 0.7220 g of $Cu(NO_3)_2{\cdot}2.5H_2O$ were added into the round bottom flask. The flask was immediately stoppered and sealed with parafilm tightly, and then stirred at a rate sufficient to cause the non-polar and polar layers to mix with minimal splashing. The organic layer turned blue-green almost immediately. The stirring continued for about 21.5 hours. Afterwards, the contents of the round bottom flask were transferred to a 150 mL separatory funnel and allowed to separate. The mixture separated into two discrete phases after several minutes, and then it was immediately separated—with 50 mL of aqueous layer being used for total arsenic testing. If the mixture is allowed to rest in the separatory funnel for longer than necessary, extraction will be less complete because of carbonate replacing the incarcerated arsenate, as it seems to bind more strongly to the nanojar.

CKH45 and CKH46 were prepared in the same way as the previous reaction. However, their stirring times for extraction were those listed in Table 1 rather the 21.5 hours listed in the previous case. Additionally, in place of the 60 equivalents of NaOH, 60 equivalents of TOA were used and present in 1.5× stoichiometric amounts relative to the arsenate salt. So, 2.1265 g of TOA were added into the organic layer with the 4-OctpzH in place of the NaOH in the aqueous layer.

Synthesis of 4-octylpyrazolate trimer

$3\ Cu(NO_3)_2{\cdot}2.5H_2O + 3\ (\text{4-octpyrazole}) + 4\ NaOH \rightarrow Na[Cu_3(OH)(\text{4-Octpz})_3(NO_3)_3] + 3\ NaNO_3$

The following reaction was carried out in 25mL of THF (tetrahydrofuran) in a 100 mL round bottom flask. All reagents were solids and added directly to the flask before adding the THF: 0.2500 g copper nitrate, 0.1938 g 4-OctpzH, and 0.0573 g NaOH. Reactions were stirred for 3 days. Blue-green color developed in solution as well as a brown precipitate, which contains sodium nitrate. The solution was filtered by gravity into a 250 mL round bottom flask using filter paper and the paper was rinsed with THF until no blue-green color remained in the paper; the washings also drained into the 250 mL round bottom flask.

The solution was then evaporated with a Rotavapor until a thick blue-green oil was left. The oil was then put on a Schlenk line for 3 days until a dark green, glassy, brittle solid had formed on the walls of the flask. Final yield 100% based on the copper nitrate salt was 0.3425 g product.

Synthesis of $TOANO_3$

The published procedure was followed except the dichloromethane solution and aqueous solutions were stirred vigorously in a round bottom flask rather than shaking. Also, the product was dried under vacuum using a Schlenk line rather than P_2O_5 for several days. Initially the organic layer had a carmine color, which faded with time. Our final product was a viscous clear, colorless liquid rather than a pale-yellow solid as described in the paper. ^1H NMR matched that of the product as described in the paper. δ = 10.9878 (s, 1H, NH), 2.9714—3.0245 (m, 6H, CH_2), 1.6782 (m, 6H, CH_2), 1.2450—1.2982 (m, 30H, CH_2), 0.8757—0.8769 (t, 9H, CH_3).

Chromium and Chromate Content Determination

The chromate content was determined using a UV-Vis spectroscopy method and the Beer-Lambert Law to calculate the chromate content based on the absorbance. The chromium content was then calculated by conversion from the chromate content. To a quartz cuvette 1850 µL of sample were added (deionized water was used in the case of the blank), followed by 150 µL of concentrated HNO_3, and 40 µL of 1,5-diphenylcarbazide 0.5% in acetone solution using micropipettes with disposable tips. The cuvette was then stoppered and shaken vigorously to mix. The solutions were allowed to stand 10 minutes before testing. The absorbance at 540 nm was measured to determine the chromate concentration of the sample.

Arsenic Testing

A ground water arsenic testing kit was used to determine the arsenic content of our post-extraction aqueous layers. A HACH Test Kit (Cat. No. 2800000) was used as purchased from the HACH company and all instructions were followed exactly as listed in the procedure of the kit. This kit tests for total arsenic content of aqueous solutions.

Semi-Quantitative Test Strips

Some testing was conducted using chemical test strips to gain an approximate range of concentration of the different components of the system. Quantofix brand tests strips for copper, nitrate, nitrite, and chromate were purchased from Sigma-Aldrich and used according to the provided instructions.

Conclusion

My research has demonstrated that we have designed a system that is capable of extracting both arsenic and chromium from water as arsenate and chromate into a highly nonpolar, organic medium from an aqueous solution to below the current EPA limits of each contaminant. The system is simple and quick, but our efforts have shown that the lack of selectivity of this system is both a merit and demerit as in the case of arsenate, carbonate interfered with our system and so careful isolation from carbon dioxide as well as an excess of reagents are required to accomplish the most effective and efficient extractions. However, it is this general selectivity towards multiply charged oxoanions that makes this system particularly interesting as one system could potentially be used to eliminate sulfates, arsenates, chromates, phosphates, and carbonates from a water supply without any variation of materials or conditions.

The system has also been demonstrated to have greater extraction results for these oxoanions than the ionic liquid trioctylammonium nitrate, which is significant because tertiary and quaternary ammonium compounds are commonly used as extracting agents in both industrial and research settings. Despite some current limitations, this system shows great promise due to its general yet efficient and effective extraction capability and simple preparation from relatively common and inexpensive chemicals. Our system in its current state leaks a significant amount of copper back into the aqueous layer and acidifies it, making the water nonpotable.

Future research into this topic will seek to elucidate what is actually extracting the oxoanions as the extracting agent is ionizable via ESI-MS methods, which is our main method outside of X-ray crystallography for investigation of the nanojar complexes. Additionally, we hope to find another suitable base that will not form a conjugate acid capable of acidifying the post-extraction aqueous layer, as this acidity could be in part responsible for the leaching of copper back into the aqueous layer.

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