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Full Length Research Paper

Applicability of an ionic liquid in the removal of chromium from tannery effluents: A green chemical approach

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The task specific ionic liquid tricaprylmethyl ammonium thiosalicylate proved to be an excellent extraction agent for chromium from aqueous solution. Chromium was removed from tannery effluents to a greater extent than the conventional methods; using the water insoluble, thiol containing task specific ionic liquid.

Key words: Task- specific ionic liquid (TSIL), heavy metals, chromium, sequesterization, tricaprylmethyl ammonium thiosalicylate, tannery wastes.

INTRODUCTION

Water supply is a daily necessity and key factor in human health and well being. The international standard for drinking water (WHO, 1971) states that water intended for human consumption must be free from organisms and from concentrations of chemical substances that may be a hazard to health (Larson and Schierup, 1981). In addition, drinking water should be as pleasant to drink as circumstances permit. Ground water is a replenishable source and is also an economical resource; however pollution of these resources is widespread (Dean, 1972). In particular, insufficient removal of toxic metals like chromium leads to contamination of water sources (Logsdon and Cullote, 1972). For example, in areas such as Trichy and Karur in Tamil Nadu, India tannery effluents discharged to nearby water systems, leads to unacceptable levels of chromium contamination (Cheo-Junli and Barry, 2008).

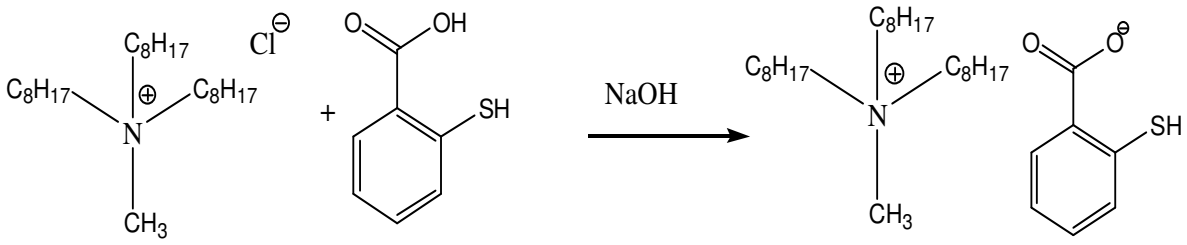
The heavy metal chromium is a carcinogenic, tasteless and odourless chemical that is associated with industrial waste from metal plating operations and other manufacturing concerns. In higher doses it may result in the manifestation of certain abnormalities. Chromium has been linked to concern and other serious health problems through inhalation, ingestion and contact. Chromium is found in many effluents and is found to be highly toxic to living organisms. Aerosol from chromium refining planets affects a number of people causing cancer and chromates act as irritants to eyes. Chromium exposure causes damage to liver and kidney. It also causes chromosome abnormalities (Kilivelu and Yatimah, 2008).

Over exposure of workers to dust and mists of chromium species reported to lead to lung carcinoma. Its ingestion leads to nausea and hemorrhage. Chromium is also reported to cause skin dermatitis, nasal membrane, inflammation, ulceration and liver damage. When adsorbed into the body, they severely irritate gastro-intestinal tract, leading to circulatory shock and renal damage.

Numerous techniques have been employed for the removal of heavy metal ions such as chromium. These include chemical precipitation, co-precipitation, coagulation, evaporator recovery process, reverse osmosis, electrolytic recovery, and adsorption (Visser et al., 2001).

Ionic liquids are liquid at or near the room temperature. They are the salts that typically consist of bulky organic cations and inorganic anions, and strongly resemble ionic melts that may be produced by heating metallic salts, but are liquid at much lower temperatures. The constituents of ionic liquids are constrained by columbic forces, exhibiting practically no vapor pressure. This unique property gives them the capability to expand traditional laws of chemistry.

For example, these ionic liquids are highly polar, yet none coordinating, they can be miscible with water and/or a number of organic solvents (providing flexibility for a number of reaction and separation schemes) and they



Scheme 1. Tricaprylmethyl ammonium thiosalicylate.

Table 1. Physico-chemical properties of the TSIL.

S/no.	Physical state	Decomposition temperature (°C)	Cl^- content (Wt %)	Density (ρ) g cm^{-3} at 20°C
1.	Liquid	201	< 0.1	0.96

Table 2. Solubility of the TSIL in various solvents.

Solvent	Miscibility
Ethyl acetate	Soluble
Acetone	Soluble
Methanol	Soluble
Ethanol	Soluble
Aceto nitrile	Soluble
Water	Insoluble

are non-volatile even at elevated temperature. The physical and chemical properties (e.g. density, conductivity, viscosity, Lewis acidity, hydrophobicity and hydrogen bonding capability) of ionic liquids can be tuned by varying the structure of the component ions to obtain desired solvent properties. These unique traits of ionic liquids allow the possibility for more efficient reactions and separations to occur.

Though many conventional extraction or removal methods (like adsorption, chromatographic separation, etc.) have been carried out, only a very few methods have been so far adopted to remove such toxic metals using ionic liquids (chemical separation) from effluents. This present work is one such effort. The main advantages of this extraction procedure are (i) Simple (ii) Cost-effective (iii) Rapid (iv) Ionic liquids can be recovered and re-used, and (v) higher % removal of toxic metals. A widespread research field is the use of Ionic Liquids (ILs) as well as Task Specific Ionic Liquids (TSILs) incurporating disulfidethioether-, urea - or hydroxybenzylamine groups as extracting agents for metals (Visser et al., 2001; Visser et al., 2002; Holbery et al., 2003; Ouadi et al., 2006; Papaicomomou et al., 2007; Mikkola et al., 2006). Usually the ionic liquids such as imidazolium, piperinium pyrrolidium- and pyridinium cations and fluoride groups are generally appended to the anions (Visser et al., 2001; Visser et al., 2002; Holbery et al., 2003; Ouadi et al., 2006; Papaicomomou et al., 2007; Mikkola et al., 2006).

In this work, the task specific ionic liquid containing hydrophobic, long chain tricapryl methylammonium thiosalicylate containing a thiol containing anion has been employed for extraction of chromium.

EXPERIMENTALS

Synthesis of ionic liquids

Tricaprylmethyl ammonium thiosalicylate was prepared as described in the literature (Daniel et al., 2008). It was prepared by stirring equimolar amount of aliquot Tricaprylmethyl ammonium chloride as a precursor and selected bronsted acids (Thiosalicylic acid) in a sodium hydroxide solution. Deprotonation of the acid followed by anion metathesis led to the desired ionic liquids (Scheme 1).

Aliquot itself is an ionic liquid and is regarded as a 2:1 mixture of mixture of methyltrioctyl ammonium and methyl trideccylammonium chloride with a proposed mean molar weight of 432 g/mol (Mikkole et al., 2006).

The formation of ionic liquid was confirmed by spectral analysis such as ^{1}H-NMR, FT-IR techniques. The physico-chemical properties such as physical state, decomposition temperature, chloride content, density, solubility and the spectral data are presented in the Tables 1, 2 and 3.

FT-IR spectra of the precursors thiosalicylic acid methyltricaprylammonium chloride and the product ionic liquid methyltricaprylammonium thiosalicylate anion in KBr were taken separately. Typical absorption bands of the carboxylic acid diminished after the reaction, indicating that the deprotonation was successful. New absorption bands at 743, 1468 and 1565 cm^{-1} are assigned to stretching and bending vibrations of aromatic C-H groups. An absorption band at 2500 cm^{-1} was obtained for S-H proton of thiocarborboxylic acid. ESI-MS experiments confirmed that the thiol group was not deprotonated.

Considering the physico-chemical properties of the ionic liquid methyltricaprylammonium thiosalicylate anion, it is a liquid at room temperature which on heating decomposed at 200°C. The Cl^- content was determined to be 0.96 g cm^{-3} at 20°C. The Cl^- content was determined by Volhard's method and it was found to be less

Table 3. Spectral data of the TSIL.

^{1}H-NMR data of thiosalicylate anion	
Chemical Shift, δ, ppm	**References**
6.68, triplet	Aromatic hydrogen flanked by one hydrogen on either side
6.69, triplet	Aromatic hydrogen flanked by one hydrogen on either side
7.25, doublet	Aromatic hydrogen flanked by one hydrogen on either side
7.87, singlet	SH proton
^{1}NMR data of methyl tricapryl ammonium cation	
0.8, Singlet	-CH_3 protons
1.2, triplet	-CH_3 protons connected to -CH_2 proton
3.0, triplet	-CH_3 proton connected to -CH_2 group on one side and 'N' atom on the other side
2.5, multiplet	-CH_2 envelope

than one. Solubility of ionic liquid was tested in various organic solvents and water. It was noted that the ionic liquid was completely miscible with organic solvents such as ethyl acetate, acetonitrile, acetone, ethanol and methanol, etc., and immiscible with water.

Sample collection and extraction methods

Effluents containing chromium were collected from several sampling stations from Karur and Trichy area, Tamil Nadu where several textile and tannin industries are functioning. Samples were collected in polythene bottles and labeled with information like temperature, time, date, pH and name of the sampling station. They were tested for the presence of chromium with biphenyl carbazide in order to ratify that they contain appreciable amount of chromium. 0.5 ml of ionic liquid methyltricaprylammonium thiocarboxylate and 10 ml of chromium containing effluent were shaken for 10 min, followed by centrifugation at 3500 rpm. The aqueous phase was separated from the IL phase and acidified for measurements.

The samples were subjected to quantitative analysis by colorimetric method; flame atomic absorption spectroscopy was also used for quantization of chromium in the effluents.

RESULTS AND DISCUSSION

As the prepared ionic liquid contains a carboxylic functionality and additionally a thiol group, it was evaluated as potential extracting agent for removal of chromium from industrial effluents. To evaluate the extracting potential of this ionic liquid under neutral conditions and the influence of a natural buffered fluvial system, the pH value of the water samples was kept at the pH as measured after spiking with chromium standard. 0.5 ml of ionic liquid methyltricaprylammonium thiocarboxylate and 10 ml of chromium containing effluent were shaken for 10 min, followed by centrifugation at 3500 rpm. The aqueous phase was separated from the IL phase and acidified for measurements.

Then the samples were subjected to quantitative analysis by colorimetric method. Flame atomic absorption spectroscopy was also used for quantization of chromium in the effluents. It is believed that metal is snatched away by the ionic liquid by the well documented process called sequestration. Compared to other extracting agents, working well under neutral conditions, on which research was recently published, the ionic liquid which is proposed in this method displays some interesting advantages: the extracting efficiency (> 90%) lies even above other extracting agents, (Mikkole et al., 2006) and its use may be regarded to use as more sustainable, as no volatile and flammable organic solvents are needed. Other environmental friendly, low - cost biomaterials, for example, bio film covered granular activated carbon, or Crab shells, demonstrating adsorption of organic residues or slow adsorption kinetics, respectively are out numbered by the proposed ionic liquid in this method by displaying an undisturbed fast metal uptake and a high affinity for chromium under neutral conditions, even in a complex neutral matrix. The ionic liquid used in this investigation removed chromium from the tannery effluents with > 90% efficiency which is found to be remarkably greater than other conventional methods such as chemical precipitation, co-precipitation, coagulation, evaporator recovery process, reverse osmosis, electrolytic recovery and adsorption.

After the extraction procedure in this method is over, the ionic liquid present in the organic layer was separated using separating funnel under controlled pressure. The recovered ionic liquid was reused successively to the same kind of extraction method and it was ascertained that the extracting efficiency remains same at least for half-a-dozen times. Not only the extraction efficiency is greater but also the other advantages like the following are entertained;

1. No requirement of volatile and flammable organic solvents.
2. More sustainability.
3. Eco and environmentally friendly procedure.
4. Fastness and reliability.
5. Recoverability and reusability of ionic liquid hence more economical.

Conclusion

The metathesis reactions are potential candidates for those preparing task specific ionic liquids as they are very simple. When these water-insoluble (hydrophobic) ionic liquids come in contact with effluents containing heavy metal ions, they snatch away the metal ions from the effluents and sequester them in the hydrophobic task specific ionic liquid. The ionic liquid was synthesized by simple metathesis route and characterized by analyzing spectral and physico - chemical properties. This task specific ionic liquid was proved to be an excellent extractor of heavy metals especially chromium from the tannery effluents. This removal procedure using ionic liquid outnumbered the conventional removal processes like adsorption, chemical precipitation, reverse osmosis, evaporator recovery process and electrolytic recovery in terms of removal efficiency, fastness, ejection of no hazardous and inflammable chemicals and ability to recover and reuse. This piece of work will also create a kind of enthusiasm among the scientists especially the chemists and environmentalists to investigate more on the synthesis of similar hydrophobic ionic liquids and their utilization for the removal of heavy metals from the contaminated water resources and industrial effluents.

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