Micelle-based Extraction of Cr (III) from Water and Sediment

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A B S T R A C T

Miceller Extraction of metalion from aqueous to Trition X-100 is carried out as a sample preconcentration and prior to determination in different matrices coupled with atomic absosopion spectroscopy (AAS). The metalion-Schiff base complex formation and it was subsequently transferred from the aqueous phase to the surfactant phase. The pH, concentration of the surfactant as well as the ligand, incubation time and temperature etc. play a vital role in this extraction. The cloud point temperature (CPT) was established in presence of different salts with varying their concentrations and its role like salting-in and salting-out effect were tested and optimized. The efficiency of extraction was more than 86%. The change of -ΔG indicates that the process was spontaneous and favorable. Application of this process was applied for extraction and recovery of Cr (III) from water and sediment sample.

Key words: Cloud point extraction (CPE), Cr (III)-Schiff base complex, Surfactant, Water and sediment, AAS

The chromium containing liquid effluent from leather industry is treated with ferrous sulphate (or) sodium sulphide to convert all Cr (VI) to Cr (III) form. Recently, inadequate use of this compound in the industry led to discharged large quantities into the environment. Cr (III) is an essential nutrient for living animal and shortages may cause heart conditions, disruptions of metabolisms and diabetes. But the too much uptake of Cr (III) symptom and causes sleep disturbance, irregular heartbeat, allergic reaction, for instance skin rashes and mood change etc. [1]. As an analytical chemist separation and preconcentration and reduction of load of hazardous substances in the environment some technique like [2], liquid extraction [3], coprecipitation [4], cloud point extraction [5,6], solid phase extraction [7], is necessary prior to determination step for overcome this problem. The most popular and traditional methodology used for extraction and/or separation of solute is the liquid-liquid extraction (LLE). However, the technique has serious drawbacks, like excess amounts of toxic and flammable organic solvents used, slow extraction speed and high dilution factor that lead to low extraction efficiency for solute. A considerable attention has recently been paid towards the development of simple and rapid extraction methods together with the use of minimum of solvents, reducing the analysis step, increasing the sample throughput and improving the quality and the sensitivity of the analytical methods.

Currently, CPE has been put forward as a clean and alternative to conventional technique for extraction of both metal ions and organic compounds. The first use of the CPE

methodology for metal ion was pioneered by Watanabe and co-workers [8-10]. The concept of CPE that arises from the use of organized molecular assemblies [11] have received wide acceptance in different fields of analytical chemistry. The different reported methods sows that critical temperatures of nonionic surfactants depend on the nature of the surfactants and experimental conditions [12]. Substrate solubilization in micelles has traditionally been treated in terms of a two-phase process [13-16]. Solute distribution between two extreme sites is considered in this model. In CPE, for separation of metal ion several complexing reagent were used with maintained solution buffered. Watanabe and coworkers [17-18] were the first to study the extraction of copper, cadmium, nickel, iron, and zinc for preconcentration via complexation with some ligand. The micellar solubilization equilibrium of some analytical reagents in aqueous solution of non-ionic surfactants [19]. The process involves several equilibrium and chemical species. The equations presented below represent in a simplified way the acid dissociation step of chelating reagent (HL) and the formation of a hydrophobic chelate following by its transference into a micellar phase [20]. During separation of the surfactant-rich phase containing the micelles from the aqueous bulk, there is a decrease of the solubility of the amphiphile in water or to a sharp increase in the micelle aggregation number [21-24]. The phases consist of a surfactant-depleted (or dilute) phase and a surfactant rich aggregate (or concentrated) phase, sometimes also referred to as the coacervate phase that appears only in the vicinity of the CPT [25]. The actual physical separation of the phases is facilitated by the difference in density between the two (dilute aqueous and surfactant-rich) phases. The phase separation process is reversible and, upon cooling the mixture to a temperature below the cloud point, the two phases again combine to form an isotropic, homogeneous solution [26]. Thus, separation of Cr(VI) and Cr(III) could be

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realized [27]. Zhu et al. separate vanadium with the help of Triton X-100 as a surfactant and methylene blue as complex agent [28] in CPE. The distribution of arsenic species occurs depending on solution pH. At low pH arsenic (III) is present as H_3AsO_3, but at high pH it is present as AsO_3^{3-}. Kiran *et al.* [29] used pH as an important factor for the cloud point extract ion of Cr (VI) and Cr(III) through complexation by using different chileting ligand [30-33] .The use of nonionic surfactants was increased dramatically over the ionic surfactants [34-36].The cloud point extraction is an environmentally benign process, which is based on simple sensitive and effective method for extraction of metal ion form water and sediment samples.

MATERIALS AND METHODS

Instrument

The spectrophotometrical measurements of metal ion were performed in a UV-Vis spectrophotometer (Model Shimadzu, UV-2401PC). The flame atomic absorption spectrophotometer in Varian AA1407model fitted with an air-acetylene flame and HCL (hollow cathode lamp) as the radiation source at a wave length of 357.9 nm. A Systronics digital pH meter with model 335 were used for measurements the pH of solution.

Reagents

The Analytical grade reagents and obtained from E. Merck, India. Stock standard solution of Cr(III) were prepared by dissolving appropriate amounts of $CrCl_3.6H_2O$ respectively in deionised water. Working solutions were prepared by proper dilution of the stock. Buffer solutions of NaOAc-HOAc maintained the pH of the solutions. The non-ionic surfactant, TritonX-100 was used without further purification. The glassware was kept in extran solution for 12 hours in an ultrasonic bath for 30 minutes then rinsed with distilled water. Next, it was kept in HNO_3: HCl (1:3) solution for overnight. Finally, it was rinsed with double distilled water, dried and packed in plastic bags until use.

Analytical methods

The influence of the variables, viz. pH, temperature, incubation time, ionic strength, viscosity and concentration of surfactant, ligand and metal, on the metal extraction was investigated and determined by AAS in an air-acetylene flame with respective hollow cathode lamp.

Preparation of sample solution for CPE

The soil and sediment samples for metal extraction were first digested with hydrochloric acid and perchloric acid (1:1) mixture. The solutions were filtered and neutralized for preparation of the stock solutions.

Determination of metal by atomic absorption spectrometry

The metal solutions in the present miceller extraction were analyzed using flame AAS. The operational condition for Cr (III) determined by AAS, when weve length 357.9 nm, slit 0.7nm, and lamp current 15mA in calibration ranges from 0.0 to 3.0 μgdm^{-3} at detection limit 0.015μgdm^{-3}in the present study.

Synthesis of ligand

The Schiff base ligand, Salen-H_2, was synthesized via condensation of ethylene diamine with salicylaldehyde in 1:3 molar ratios under reflux condition in methanol for 3 hours. The solids appeared on cooling were subsequently filtered, washed and dried in a desiccator over fused $CaCl_2$. The ligand thus prepared was recrystallized and characterized by elemental analysis, melting point determination, infra-red and visible absorption spectral data.

Procedure for metal extraction

An aliquot of 15 cm^3 solution containing a definite proportion of metal and the ligand, buffered with desired pH was mixed with $(NH_4)_2SO_4$ and TritonX-100 of suitable concentrations. The solution was taken in a typical glass tube, shaken for 5 minutes and left to stand in a thermostatic bath at 348±2 K for 30 minutes. As the cloud formation occurs the solution was cooled immediately in an ice-bath. The surfactant-rich phase became viscous and settled down at the bottom of the test tube. The metal content in the miceller phase was determined by atomic absorption spectrophotometer. Calibration curves with known concentrations of each metal solution were constructed separately for the spectral measurements via atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Generally, CPE of metals proceeds in two steps, formation of hydrophobic metal complex by use of suitable chelating ligand and transfer of the complex to the miceller from aqueous phase.

After careful choice of the chelating ligand and its concentration with respect to metal concentration the operational parameters need to be optimized are: pH, concentration of surfactant, temperature, incubation time, ionic strength and viscosity for efficient CPE. In order to find the range of variables each of the parameter is varied one at a time keeping all other parameters fixed to a certain level.

Choice of ligand and surfactant

The choice of the Schiff base ligand, in the present CPE of Cr(III) is primarily due to the ease of preparation, quantitative yield, stoichiometric composition, hydrophobic nature and stability of metal-Schiff base complex. The transfer of the complex from water phase to the core of the micellar aggregates.

From experiment of phase diagram data, the highest cloud point temperature (Tcp) value for TritonX-100 is 74.5°C at 0.6% (concentration by weight), whereas the lowest cloud point temperature is 61.8°C at 3% (concentration by weight). Moreover, the cloud point temperature, found to be 67.5°C, at the surfactant concentration of 1% (by weight) was in good agreement with that reported by Mata [37], for the surfactant solution of Triton X-100 without any additives. It is found that the CPT remains almost constant up to TX-100 concentration of 10% in absence of $(NH_4)_2SO_4$ while the CPT lowers down with addition of $(NH_4)_2SO_4$ $(1.0.10^{-3}$ $mol.dm^{-3})$ and remains constant up to a concentration of 15%.

Effect of pH

It is believed that pH plays a unique role in metal-chelate formation and hence subsequent extraction yield as well as the CPE preconcentration is expected to be influenced by the solution pH [38-39]. In separation-preconcentration, involves a small volume of surfactant. In the present situation pH of the solution is varied using NaOH or HCl $(1.10^{-1}$ to 1.10^{-2} moldm^{-3}) and the extraction percent for metal was evaluated for each complex.

It is observed that the extraction behavior of the complexes differ with respect to variation in pH (Fig 1). The effect of pH range 2-10 were studied. The extraction increases with an increase in the pH of the solution until an optimum pH was reached at about pH 6.0 for Cr(III) (Fig 1). The pH of the

solution was maintained using NaOAc-HOAc (1.10^{-2} moldm^{-3}) buffer solution for Cr(III).
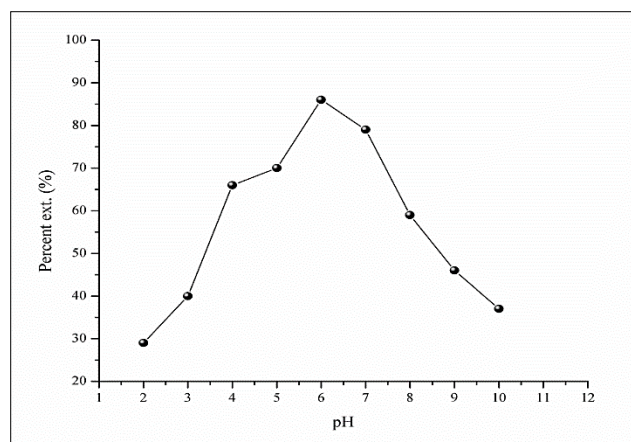

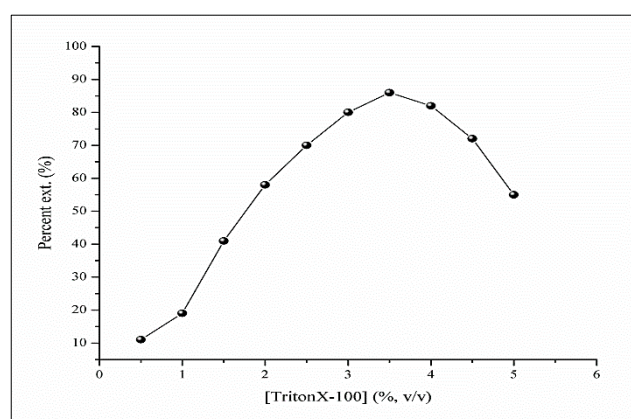Fig 1 Effect of pH for Cr(III) extraction

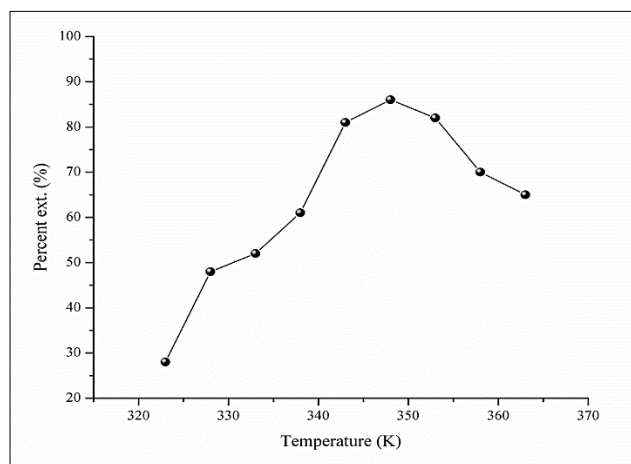Fig 2 Influence of TritonX-100 concentration form Cr (III) extraction

Fig 3 Influence of temperature for Cr(III) extraction

The (Fig 3) for Cr(III) and (Fig 4) represent the effect of incubation temperature and time respectively on the extraction efficiency of metal complexes. The range of temperature and time were varied from 323K-363K and 5.0 - 45.0 minutes respectively. In this experiment at the optimized concentration of metal, ligand and surfactant (TX-100) a heating period of 30 minutes at 348±2°K and cooling for 20 minutes in an ice-bath leads to high recovery of metal in this case.

Effect of ionic strength

Some common electrolytes viz. NaCl, KCl, KNO$_3$ and (NH$_4$)$_2$SO$_4$ were used for investigate the extraction efficiency

Effect of Triton X-100 concentration

The commercially available, pure, homogeneous, low toxic and low cost of Triton X-100 surfactant were used. The present CPE is aimed to improve the efficiency of extraction through minimizing the phase volume ratio, thus maximizing the enrichment factor. This can be achieved by transfer of high amount of metal in low volume of surfactant rich phase. The extraction efficiency of metals was examined for varying Triton X-100 concentration ranged from 0.5-5% (V/V). Extraction was watch at Triton X-100 concentration of 3.5% for Cr(III)-Salen complex (Fig 2).

At lower Triton X-100 (TX-100) concentration the separation of the micelle formation was very low, probably due to micellar assemblies formation of inadequate to quantitatively entrap the hydrophobic complex [40]. At high concentration of Triton X-100 the extraction efficiency also decreases. As higher surfactant concentration needs more volume of surfactant. The ultimate volume of surfactant phase increases and thus resulting the dilution effect extraction yield decreases.

Effect of the relative concentration of ligand

As CPE of metal proceeds via complexation, an effective CPE operation must be associated with chelation of the total metal content in solution. Metal-chelate stoichiometry it is essential to keep the ligand concentration higher than the metal stoichiometric concentration in solution. In the present study the molar concentration ratio of ligand:metal is varied from 0.5 to 3.0. The ratio increases the extraction percent increases and reaches a maxima at value of 1.2 for Cr(III). The percent extraction of metal remains unaltered even with further increase in ligand concentration.

Effect of incubation temperature and time

In an effort to achieve adequate phase separation for improved extraction efficiency, the optimization of incubation temperature and time is required.
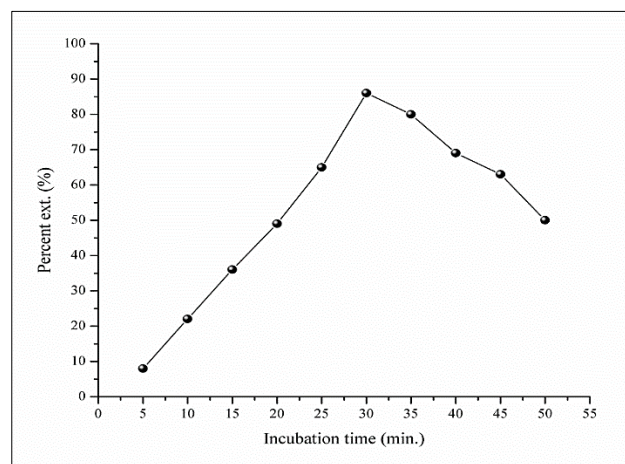

Fig 4 Effect of incubation time (min) for Cr(III) extraction

which shown in (Table 1) for Cr(III) and in (Fig 5). All the cases same concentration of electrolyte ($1.0.10^{-3}$ moldm^{-3}) were taken to each experiment. It is found that CPT and the extraction extent vary with addition of the electrolyte but in different extents. The salting-in or salting-out character depend on the nature of the electrolyte [41]. As addition of (NH$_4$)$_2$SO$_4$ provides lower CPT yielding highest extraction of metal ion.

The role of (NH$_4$)$_2$SO$_4$ concentration on the extraction percent is presented in (Fig 5) for Cr(III). Smaller amount of (NH$_4$)$_2$SO$_4$ results insufficient extraction probably due to limited clouding. Larger amount of (NH$_4$)$_2$SO$_4$ beyond the

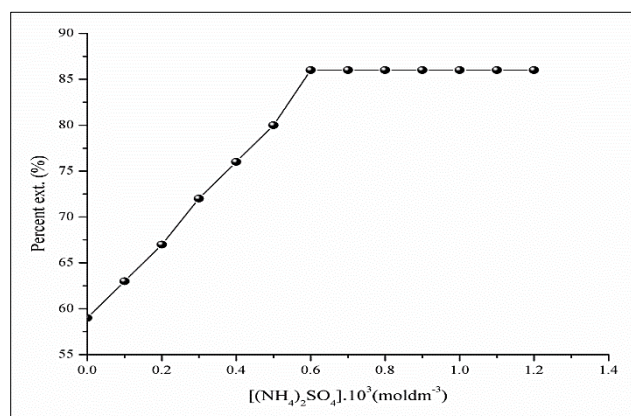optimum concentration, however, shows no change in percent extraction.

Fig 5 Effect of salt concentration for Cr(III) extraction

Table 1 Influence of electrolyte on CPT and extraction of Cr (III) complex

Salt added	Percent extraction (%) [CPT (K)]
-	75 [361±2]
$(NH_4)_2SO_4$	86 [348±2]
KCl	67 [354±2]
NaCl	64 [353±2]
KNO_3	71[366±2]

Effect of viscosity

The surfactant rich phase does not influence spectrophotometric determination of metal ion it is very viscous in nature. A portion of 2 cm^3 methanol mixed the solution after CPE to transfer the solution the spectrophotometric identification. Similarly for atomic absoption spectros copy (AAS) operation CH_3OH containing HNO_3(0.1 moldm^{-3}) were added to the TX-100 rich phase after CPE. in order to facilitate introduction and aspiration of the solution into the nebulizer. 50 cm^3 volume of methanol was necessary to yield a good analytical signal. Small volume of acidified CH_3OH were added, the signal was low due to the inappropriate state of the solution for nebulization and aspiration, whereas for greater volume decreases signal results due to dilution.

Effect of foreign ions

The interferences in CPE yield may arise from one or both of the complexation step and the determination step. Determination of Cr(III) in presence of different cations and anions was made and the limit of tolerance was evaluated. For visible spectrometry both the complexation and determination steps were interfere the extraction yield. The limit of tolerance in respect to initial metal concentration (50 g dm^{-3}) in the present case for different ions is evaluated as: Na$^+$, K$^+$:1000µgdm^{-3}, Ca^{2+}, Mg^{2+}: 500µgdm^{-3}, Fe^{3+}, Al^{3+}: 50µgdm^{-3},

Cu^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Cr^{3+}: 20µgdm^{-3}, PO$_4^{3-}$, CH$_3$COO$^-$, C$_2$O$_4^{2-}$:100µgdm^{-3}, EDTA: 20µgdm^{-3}.

Quality assurance of the method
Analytical figure or merit

Precision of this method was evaluated from the standard deviation value of six replicate analyses of spiked samples. Nine equal portions the stock metal solution (50.0 µgdm^{-3}) was taken. The metal concentration in the first five portions was determined individually following the proposed method and the mean was calculated. Metal solution of definite concentrations was spiked with each of the remaining five portions of the stock and the concentration was evaluated for each case. The recovery of each metal was also evaluated.

Recovery of the Cr(III) in the samples was found to be greater than 85% with a standard deviation less than 0.05 at the 95% confidence level for five degree of freedom (Table 2).

Table 2 Recovery of Cr (III) in spiked samples

Concentration of metal solution (µgdm^{-3})			Recovery
Mean	Spiked	Found	(%)
50.0	0.0	43.00±0.022	86.0
50.0	1.0	42.70±0.241	85.4
50.0	3.0	42.90±0.310	85.8
50.0	5.0	42.65±0.284	85.3
50.0	10.0	42.75±0.275	85.5

Effectiveness of the proposed method

Effectiveness of the process is defined by the LOD (limit of detection) and LOQ (limit of quantification). LOD and LOQ of the developed procedure were calculated taking eight consecutive measurements of the blank signal, the background equivalent concentration and relative standard deviation (RSD). The P.F. (preconcentration factors), i.e., the ratio of the slopes of the analytical curves before and after preconcentration. The characteristic features of the proposed method are presented in (Table 3).

Table 3 Characteristic features of the proposed method

Feature	Cr(III)
Regression equation	0.007 C$_0$ ± 0.004
Linear range (µgdm^{-3})	2.3-80.0
Limit of detection (µgdm^{-3})	0.12
Relative standard deviation (%)	0.05
Preconcentration factor	60
C$_0$= 50µgdm^{-3}	

Feasibility of the operation

Distribution ratio (D) values for the extraction of Cr(III)-Salen complex is found 8.0. The feasibility of the process was judged by -Ve, ΔG (Gibb's free energy) values is 6.02 kJmol^{-1} for Cr(III)-Salen complex respectively indicating the process as spontaneous and favorable one.

Table 4 Recovery and preconcentration of chromium (III) from wetland areas

Wetland sample*	Composition	Recovery (%)	Std.dev (n=6)	P.F.
Water	Dissolved oxygen: 0.2; C^{l-}:550; NO^{3-}: 34, TDS: 780; Alkalinity: 15; Total hardness: 222; Ca^{2+}: 198; Cr^{6+}: 5.1; Mn^{2+}: 8.5; Fe^{3+}: 2.9; Ni^{2+}: 0.81; Cu^{2+}: 0.55; Zn^{2+}: 3.4; Pb^{2+}: 1.0; pH: 7.1 (in mgdm^{-3}except pH)	84	0.053	54
Sediment	Ca^{2+}: 7439; Cr^{3+}: 394; Mn^{2+}: 218; Fe^{3+}: 9881; Ni^{2+}: 890; Cu^{2+}: 133; Zn^{q}: 187; Pb^{2+}: 75, TOC: 1527 (in mgdm^{-3})	82	0.054	54

*Location of tannery agglomerates from Dhapa-Tangra-Topsia to the Calcutta Leather Complex at Bantala (lat. 22°27'–22° 40' N; long. 88° 27'–88° 35' E) area

Applicability of this CPE method

    The applicability of this extraction method is judged form analysis of environmental samples Cr(III) (Table 4). Somples (waste water, sediment) collected form tannery agglomerates from Dhapa-Tangra-Topsia to the Calcutta, West Bengal, India was analyzed for the recovery and preconcentration of the studied metal ions. The sample composition and the location point, whenever necessary are indicated in the (Table 4).

CONCLUSION

    This CPE method provides a unique extraction technique for separation of Cr (III) from aqueous solution which includes environmentally safe, low cost, high recoveries and very good extraction efficiency in comparison with solvent extraction method. In comparison to other reported CPE techniques the present method is claimed to be green and simpler. The process was optimized for its individual principle variables viz. pH, surfactant concentration and concentration of ligand over the metal concentration as well as secondary variables viz. temperature, incubation time, ionic strength and viscosity. The characteristic features including detection limit, tolerance level and efficiency of extraction in presence of other foreign ions was evaluated. The method is suitable for extraction of trace level (Mg) of metals. The method is thermodynamically feasible and spontaneous. The applicability of the method is judged using real samples like industrial waste water, soil and sediment sample for Cr(III) preconcentration. It can be concluded that for both the cases the extraction is feasible. They are efficient, simple, require less time of operation and environmentally benign.

Conflict of interest

    There is no conflict of interest.

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