

Original Article: Cloud Point Extraction of Trivalent Chromium from Aqueous Solutions Using Different Nonionic Surfactants

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ABSTRACT

Cloud point extraction (CPE) of trace metals from aqueous solutions is based on clouding phenomena of non-ionic surfactant used. This work aimed to separate Cr (III) ions from water samples using a cost-effective and environment-friendly method as CPE at high efficiency. Four different types of non-ionic surfactants have been selected and investigated for CPE to achieve high performance. Polyethylene glycol, glycerine, PO/EO block polymer, and ethoxylated polyamine surfactants are used in CPE experiments. The influence of important factors has been studied and optimized on the percent of extraction yield, pH, surfactant amount, Cr (III) ions concentration, temperature, and centrifugation time as well as ammonium pyrrolidine dithiocarbamate (APDC) as chelating agent to enhance the separation process. As a result, polyethylene glycol, PO/EO block polymer, and ethoxylated polyamine were excellent surfactants since a complete separation of Cr (III) at pH 8 and a lower equilibrium time of about 2 minutes has been achieved.

Introduction

Environmental pollution resulting from technological and industrial development is one of the most important risks facing the world today. Heavy metals like chromium, cadmium, copper, etc. in water bodies at specific concentrations that pose a threat to the ecosystem. These metals cannot biodegrade or detoxify easily and have a high tendency to accumulate, especially in living matter [1].

Besides, discharge of heavy metals into water recurses affecting water quality and causing harm to aquatic organisms due to its high toxicity, which makes it unsuitable even for human consumption.

The widely used of chromium in many industrial activities has contributed to a significant increase in chromium concentration in the environment. Chromium chemical forms play an essential role in determining chromium's toxic and biological properties. Chromium exists in aqueous solutions mainly in

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two stable oxidation states, trivalent chromate Cr (III) and hexavalent chromate Cr (VI). The widely used of Cr (III) in the industries such as leather industry which is used as a tanning agent is considered as one of the major sources of pollution due to the large amounts of sewage discharges and solid sludge generated. As a consequence, the presence of its compounds in high concentrations is micro- and chronically toxic and can cause serious problems and diseases such as genotoxic effects, skin ulcers, nausea, and lung cancer [2-4]. Therefore, many regulatory agencies around the world have reported the maximum allowable chromium concentration in water samples. Brazilian National Council for the Environment (CONAMA) established the maximum allowed concentration of Cr (III) and Cr (VI) for effluent discharges in water bodies are 1.0 and 0.1 mg/L, respectively, while in Japan, the maximum allowed concentration are 0.5 and 0.05 mg/L for total chromium and Cr (VI), respectively [5]. The World Health Organization (WHO) and the US Environmental Protection Agency (EPA) have set the maximum allowable total concentration of chromium in drinking water that is considered safe for consumption to be 0.05 mg/L and 0.1 mg/L, respectively [6]. Several sources contribute to environmental chromium pollution, the most important of which are dyes, mining, cement industry, leather tanning, electroplating, production of refractory steel, catalytic manufacture, photographic material, corrosive paints, and rubber manufacturing industries [7-10]. Therefore, the determination of chromium in aqueous and biological matrices is an extremely important tool for environmental and toxicological monitoring. Accordingly, it is difficult due to the complex matrix and the presence of these pollutants at trace levels in such samples, which requires sensitive automated techniques such as flame atomic absorption spectrometry (FAAS) and frequently a pre-concentration step such as liquid-liquid extraction (LLE), solid phase extraction (SPE), co-precipitation, electro-deposition, and cloud point extraction (CPE).

Traditional separation methods, such as liquid-liquid extraction and other mentioned

methods, consume a long time to achieve the separation. In addition, they are labor intensive and use relatively large amounts of high purity solvents, which are frequently toxic [11,12]. Today, most industries are looking for alternative technologies that are competitive and can overcome some of the defects in the mentioned methods. Therefore, CPE is a new environmental-friendly method that has gained significant interest in separation science.

In recent years, CPE, as an alternative suitable separation technique, was successfully used in the separation of trace heavy metals from aqueous solutions [13,14]. The mechanism of the CPE process is achieved in three main steps: solubilization of chromium ions in the micellar aggregates, forming hydrophobic complex, and phase separation after clouding for analysis.

Cloud point phenomena are mainly dependence on the phase behavior of ionic and/or non-ionic surfactants in aqueous media. Most non-ionic surfactants in aqueous media form micelles and become more turbid when heated to the cloud point temperature (CPT) or in the presence of a salting-out agent. Above the CPT, the micellar solution easily separates into two immiscible phases, a small volume of surfactant-rich phase containing the required solute and a diluted aqueous phase which represents the rest of solution in which the concentration of the non-ionic surfactant is at equal, or below to, its critical micelle concentration (CMC) system [15-19]. Thus, in the present study, the extraction of chromium ions from the initial aqueous solution was achieved by concentrating these ions into the surfactant-rich phase after the formation of a hydrophobic complex with an appropriate chelating agent.

According to some previous studies, the removal of Cr (III) from aqueous solutions using CPE is an increasing interest in the scientific community. However, most recent investigations have focused on the use of low-cost surfactants with/without appropriate reagent such as Triton X-114 with 1-(2-pyridylazo)-2-naphthol (PAN) [20], Triton X-114 with 8-hydroxyquinoline [21], PMBP [22], and Triton X-100 with Br-PF [23]. Recently, in

our research group, Asweisi *et al.* (2020) used PO/EO Block Polymer as a surfactant with APDC for extraction of some metal ions, with satisfactory results [24]. In 2022, this study was applied to separate cadmium from aqueous solutions using a group of surfactants with APDC, where the results were very satisfactory [25].

Therefore, in this study, the CPE method developed for the pre-concentration of Cr (III) ion in various aqueous samples using four different non-ionic surfactants, prior to the FAAS determination. Polyethylene glycol, glycerine, PO/EO block polymer, and ethoxylated polyamine were selected as surfactants because of their low CPT (20-80°C) and high density of the surfactant-rich phase as well as their low cost, commercial availability, and lower toxicity [25]. The reagent APDC used as a chelating ligand. Some parameters that influence on the percent of extraction yield like sample pH, ligand amount, amount of surfactant, temperature, concentration of metal ions, and extraction time have been investigated and optimized.

Experimental method

Reagents

All solutions were prepared with water of high purity. Mineral acids, methyl alcohol, and other reagents used in this study were of analytical grade and obtained from Merck, Darmstadt, Germany. The standard calibration curve method used to determine metal ion

concentrations. A 1.0% (w/v) of surfactants from Clariant. The ligand APDC was prepared according to the literature [24].

Instruments

A Novaa 350 FAAS instrument with deuterium background correction and hollow-cathode lamp as the source of radiation used for absorbance measurements. All parameters of instruments were set as recommended by manufacturer's operation manual. A Hettich centrifuge was used to accelerate the phase separation process. A JENWAY model 3150 pH meter used for pH measurements.

Test Procedure

A CPE experiments were prepared for CPE, as displayed in Figure 1. Aliquots of 12 mL of the sample containing Cr (III) (10 mL), surfactant (1 mL), and APDC (1 mL), were kept in temperature controlled water bath at (20-100°C) for 15 min. Separation of surfactant-rich phase and the diluted aqueous phase was achieved after centrifugation at 3000 rpm for 2 min. After cooling in an ice for 5 minutes, the diluted aqueous phase and surfactant-rich phase became immiscible. The supernatant aqueous phase then easily separated completely. The resulting solution was then introduced into the FAAS by conventional aspiration for analysis.

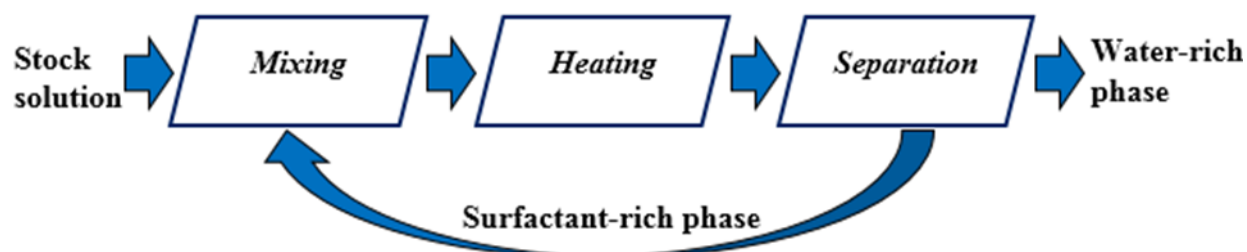


Figure 1: CPE producer.

Analytical response

The experimental study of chromium separation using CPE method was evaluated by the extraction yield percent (Equation 1) which

was estimated from mass balance based on initial and final ions concentrations in the original and final solution:

$$\%E = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

Where, %E is the percent of extraction yield of chromium from aqueous solution, C_0 and C_t are the initial concentration of Cr (III) ions in feed phase and final Cr (III) ions concentration in bulk aqueous phase, after extraction, respectively.

Results and Discussion

Experimental optimization of Cr(III) CPE

Effect of pH

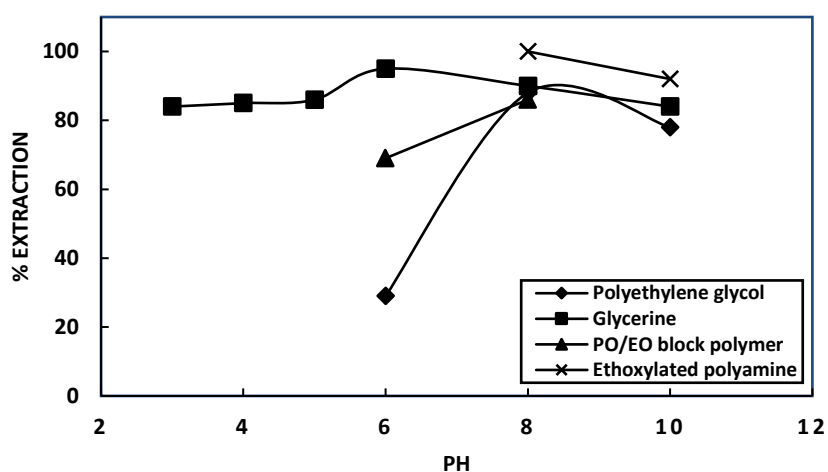


Figure 2: Effect of pH on CPE of Cr (III) ions.

Generally, it is observed that the ions uptake increased at higher pH range, while at lower pH values the percent of extraction yield become less. This behavior can be clearly observed over a different pH ranges for all surfactants used in this experiment. The extraction of Cr (III) ions from aqueous solution was started at pH 3 for glycerine, pH 6 for PO/EO block polymer and polyethylene glycol, and pH 8 for ethoxylated polyamine when using as surfactants. For glycerine, the extraction rate increased about 10% when the pH value was doubled, to reach its highest value of 95%, while PO/EO block polymer, polyethylene glycol, and ethoxylated polyamine, the highest value of extraction rate

The medium pH is one of an essential parameter that influences extraction process especially for ionic species such as metal ions. Amines and phenols may also affect the stability of the metal ion complexes and hence critically affects the separation of metal ions by CPE [11]. In general, the optimum pH range is required for each CPE procedure. Within this range, uncharged form of the species exists and could be incorporated into the micelles [26]. Consequently, the effect of pH on extraction percent of Cr (III) was studied in the range of 3-10 for each surfactant. Figure 2 depicts the effect of pH on the extraction percent and sensitivity of the method.

has been reached at pH 8 since the percentage of extraction yield increased about 17%, 50%, and 100%, respectively. The possible explanation for higher extraction in the alkaline region refers to the competition between Cr (III) ions and hydrogen ions for the binding to the ligand. When increasing in pH value, the potential of active sites of ligand for metal ion binding increases, and thus the Cr (III) ion uptake will increase. In other words, at higher pH, the ligand is de-protonated, and it behaves as a hydrophilic molecule and easily solubilized in the micelles and vice versa at low pH, leading to decrease its solubilization in the hydrophobic micelles, this is consistent with

some reported literature [14,25,27-30]. On the other hand, an excessive increase in pH value has no effect on the extraction rate, which led to a gradual decrease in the percentage of extraction yield to its initial value.

Effect of APDC concentration

Chelating agent is one of the key factors influencing the extraction efficiency. The APDC

ligand was employed as a complexing agent for Cr (III) ions in cloud point experiments, since the solubility and stability of the ligand is relatively high in the selective solution samples. As depicted in Figure 3, the effect of APDC concentration on the percent of extraction yield of Cr (III) was investigated over the range of (1-13 mL).

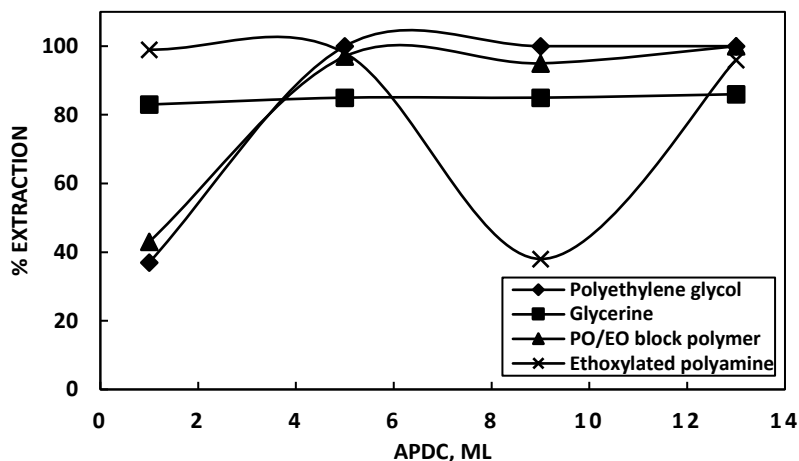


Figure 3: Effect of APDC on CPE of Cr (III) ions.

From Figure 3, it observed that the APDC addition has no effect on the percent of extraction yield when using glycerine and ethoxylated polyamine as surfactant, a very good separation may be achieve without adding APDC as a chelating agent. If an excessive amount of reagent added, a decrease in extraction yield percentage was clearly observed at 13 mL of APDC when using ethoxylated polyamine as surfactant, because using a higher concentration of ligand causes an increase in the volume of organic as a solvent to enter the solution, which can prevent the micelle formation and reduce the extraction yield or possibly lead to the formation of charged species. Nevertheless, in case of two other surfactants, it is clearly noticed that the APDC addition is required to improve separation process. The extraction yield percentage of Cr (III) ion increased from 37 to 100% at 5 mL of APDC, and from 43 to 100% at 13 mL of APDC, when using polyethylene glycol, and PO/EO block polymer as surfactants,

respectively. APDC reacts with metal ion to form a nonpolar complex [14]. The formed nonpolar complex is extracted into the nonpolar environment of micelle.

Effect of surfactant volume

The polyethylene glycol, glycerine, PO/EO block polymer, and ethoxylated polyamine surfactants have been selected because of their commercial availability in a highly purified homogeneous form, low toxicological properties, and cost. The high density of surfactant-rich phase facilitates phase separation by centrifugation. In addition, the lower CPT (20-80°C) of non-ionic surfactants permits their use in the extraction and /or pre-concentration of many molecules and chelate at that temperature. The pre-concentration efficiency was evaluated using non-ionic surfactants concentration ranging from 1 to 4 mL. Figure 4 demonstrates the effect of surfactant volume on the percent of extraction yield.

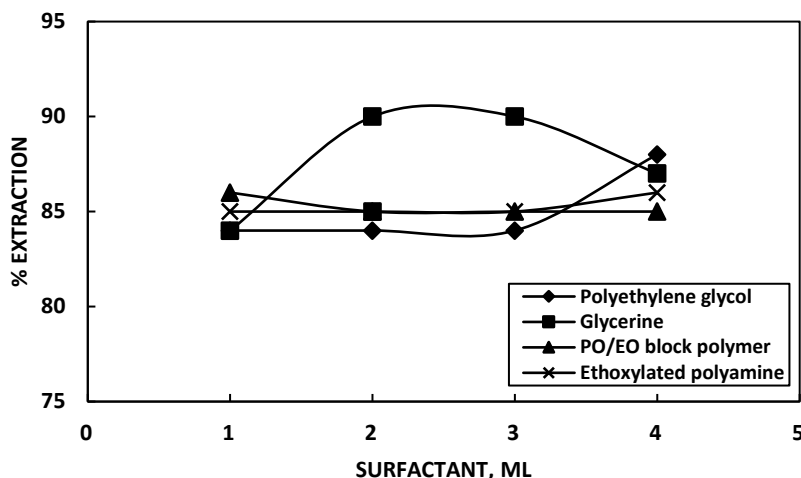


Figure 4: Effect of surfactant volume on CPE of Cr (III) ions.

In general, it was observed that as very small increase in ions uptake as the amount of the surfactant increases. The highest extraction yield percentage of Cr (III) ion was obtained when using 2 and 4 mL of glycerine and polyethylene glycol as surfactants, respectively. A very little change in the percent of extraction yield was observed when excessive amounts of PO/EO block polymer and ethoxylated polyamine were used as surfactants. Therefore, 1 mL selected for CPE experiment to minimize the cost due to consumptions of more chemicals.

The influence of Cr (III) ion concentration on the CPE process and percentage of extraction yield was tested with the other experimental variables remaining constant. As can be seen in Figure 5, 10 to 40 ppm with a good extraction rate was obtained for all types of surfactants used in CPE experiment, except glycerine, above 10 ppm of Cr (III) ion added to the samples, the percentage of extraction yield decreased with the increase of metal ion concentration in the aqueous samples. This may attributed to the saturation of the surfactant active sites [30].

Effect of metal ions concentration

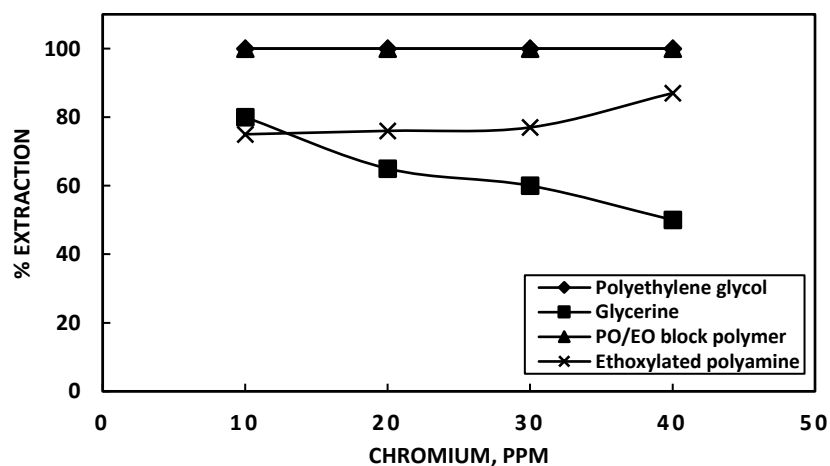


Figure 5: Effect of metal concentration on CPE of Cr (III) ions.

Effects of equilibration temperature and time

A successful CPE depends on choosing the appropriate equilibrium temperature and time. The low CPT of selected surfactants contributes to speeding up the separation process by forming micelles in a short time, which makes it more practical in terms of use. Separation of Cr (III) examined over a wide range of temperature (2-100°C) for each surfactant. It could be observed that the phase separation started at 20°C with different extraction rates

at different temperatures. Figure 6 illustrates the effect of temperature on the percent of extraction yield. Therefore, a higher extraction yield percentage of Cr (III) was obtained at 60°C, 80°C, and 100°C. Likewise, the effect of centrifugation time on the extraction rates has been studied in the range of (2-14 min) upon the analytical signal. It showed that there is no enhancement in extraction rates at longer times. Therefore, a 2 min of centrifugation time at 3000 rpm selected for the entire procedure.

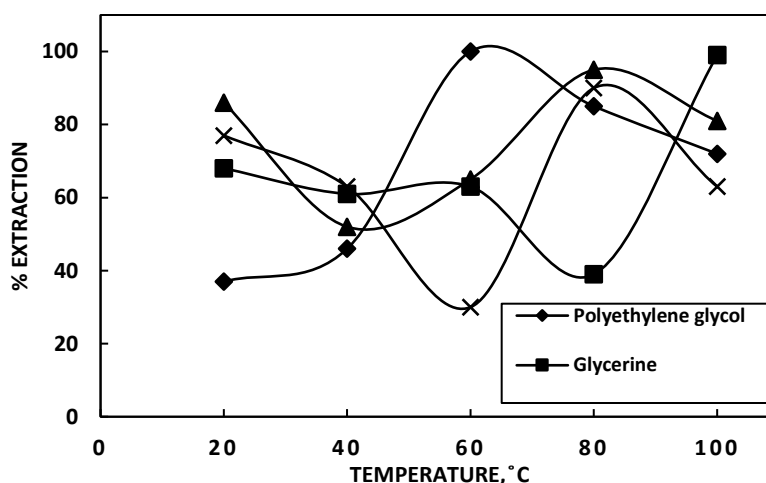


Figure 6: Effect of temperature on CPE of Cr (III) ions.

Conclusion

The presented method was successfully employed for extraction of some trace elements, such as Cr (III) ions, from its aqueous samples. It has many features compared with other extraction methods such as low cost, rapidity, use of nontoxic solvents, simplicity of operation, high sensitivity, and selectivity, and environment-friendly, benign methodology, which is alternative to other separation/pre-concentration techniques, which use different organic solvents. Polyethylene glycol, glycerine, PO/EO block polymer, and ethoxylated polyamine were selected for the formation of the hydrophobic complex due to their excellent physicochemical characteristic, which make phase separation easily by centrifugation. As a result, a high separation rate has been obtained. Polyethylene glycol, PO/EO block polymer and ethoxylated polyamine were considered as excellent surfactants, since a complete

separation of Cr (III) ions has been achieved. Furthermore, ethoxylated polyamine surfactant has the ability to reach at the high extraction rate without adding APDC at 80°C and pH 8. On the other hand, polyethylene glycol, PO/EO block polymer surfactant reached at the same high rate at same pH value and temperature of 60°C and 80°C, when 5 mL and 13 mL of APDC is added, respectively. Extraction methods at lower pH values (3-9) enhance the stability of metal ions in aqueous solution by avoiding precipitation of metal hydroxides and oxides at pH values above 10. The present method can be successfully applies for the separation of Cr (III) ions from aqueous samples at equilibrium centrifugation time 2 min and 3000 rpm.

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Disclosure statement

The authors declare that they have no conflict of interest.

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