Effect of pH, Anions and Acids on the Extraction of Zinc (II) from Aqueous media using Acetylacetone Solutions of Sulphamethoxazole

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Abstract

The challenge of heavy metal contaminations have been remediated to a certain level by the application of several methods of their extractions from aqueous media. Solvent extraction of zinc (II) ions from buffered aqueous solutions into acetylacetone solution of sulphamethoxazole as a function of pH and concentration of anionic substances and certain mineral acids were investigated in this work. The aqueous medium was prepared by dissolving 1.0995g of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in 250 ml volumetric flask to form 1000mg/L solution. 50mg/L working concentration was prepared from the 1000mg/L by dilution method. The organic phase is 0.5 M Sulfamethoxazole solution prepared by dissolving 12.664g of the salt in 100 ml acetylacetone. 2 ml each of aqueous and organic phases were taken with micro pipette and transferred into a set of 20 ml extraction bottle and the mixture was agitated mechanically for about 30 minutes. The mixture was allowed to settle and separate into two layers. 1 ml of the aqueous phase was taken, diluted and analysed for Zn (II) ions using atomic absorption spectrophotometer at a wavelength of 213.9. The results obtained on studying the effect of pH showed that Zn (II) ion was quantitatively extracted between pH of 7.0 to pH 8.0. The highest percentage extraction 85.37% was observed at pH 8.0 in acetylacetone solution of sulphamethoxazole. Increase in pH above 8.0 resulted in a steady decrease in the extraction of Zn (II). Studies on the effect of anions showed significant extractions which changes as the anions concentrations increased. All studies on mineral acids also showed significant extractions and increase in the concentrations of the acids affected the percentage extraction. Generally Zinc (II) ions can be extracted quantitatively in mild acids and anions concentrations when buffered from slightly acidic pH ranges of 6.0 to slightly alkaline pH values of 8.5.

Keywords: Zinc (II) ion Extraction, pH, Anions, acids, sulphamethoxazole in acetylacetone

INTRODUCTION

The separation and extraction of heavy metals and ions from contaminated aqueous media have been of interest for long [1]. The term "heavy metal" refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. "Heavy metals" is a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm^3 , or five times or more, greater than water [2-3]. These metals have

been extensively studied and their effects on human health when taken in large amounts are very harmful to the human body because of their toxicity [4-5]. Heavy metals can be emitted into the environment by both natural and anthropogenic causes. Common sources of heavy metals include mining, industrial wastes, vehicle emissions, lead-acid batteries, paints, fertilizers, treated woods, aging water supply infrastructure etc. [6-8]. Solvent extraction is a way of separating solutes through two solvents (usually liquid) that can dissolve the substances of solutes, but both these solvents are

immiscible. The sample is dissolved in water to make an aqueous solution which comes in contact with extractant so that the displacement of solute molecules due to differences in solubility in both solvents occur [9]. In a simple liquid-liquid extraction, the solute partitions between two immiscible phases. One phase usually is aqueous and the other phase is an organic solvent. Because the phases are immiscible they form two layers, with the denser phase on the bottom. The solute is initially present in one of the two phases; after the extraction it is present in both phases. Solutes have different strength of interactions with different solvents or different solubilities in different solvents [10]. So, in the system of two immiscible or partly miscible solvents, different solutes become differently distributed between these two phases. This is the basis of solvent extraction technique. Solvent extraction is commonly used to separate the desired substance from other substance which may be interfering in an analysis. Sometimes, these interfering clusters can be selectively extracted [11].

Solvent extraction is now a very well-established process in hydrometallurgy. It is used for hydrometallurgical processing of transition metals, rare earth metals (lanthanides and actinides), reprocessing nuclear fuels, purification of wet process phosphoric acid, nitric acid recovery, etc. [12]. Pure zinc can be recovered through solvent extraction, electrolysis refining or vacuum distillation [13]. Among the available processing alternatives, solvent extraction is a technique that not only meets the strict environmental regulations but also high purity value added products could be produced. Acidic extractants, including carboxylic acids, dialkyl phosphoric and dialkylphosphinic acids, can be used to extract cadmium (II) ions. The extraction of zinc (II) ions is selective in the presence of the divalent ions of Zn, Ni, Co, Mn, Fe, Ca and Mg. However, copper (II) and lead (II) ions can be co-extracted [14].

Sulfamethoxazole (SMZ or SMX) is an antibiotic. It is used for bacterial infections such as urinary

tract infections, bronchitis, and prostatitis and is effective against both gram negative and positive bacteria such as Listeria monocytogenes and E. coli. Common side effects include nausea, vomiting, loss of appetite, and skin rashes [15]. It is a sulfonamide and bacteriostatic. It resembles a component of folic acid. It prevents folic acid synthesis in the bacteria that must synthesize their own folic acid. Mammalian cells, and some bacteria, do not synthesize but require preformed folic acid (vitamin B9), they are therefore insensitive to sulfamethoxazole [14].

Figure1. Structure of sulfamethoxazole

MATERIALS and METHODS

The following apparatus were used during the course of this research;

- 0-1000 μ l micropipette(MICROPET ISO 9001) with polymer tips,
- Labtech digital pH meter,
- Digital weighing balance (model; Adventurer Pro AV313),
- Thermostatic water bath shaker SHZ-82 Searchtech instruments,
- Buck Scientific. atomic absorption spectrophotometer

Reagents

All chemicals used were of analytical grade and was used without further purification. Non primary standards (deliquescent and hygroscopic reagents) were all standardized using the appropriate reagents. $(\text{CH}_3\text{CO})_2\text{CH}_2$ was obtained from Guangdong GuanghouSci-Tech Co., Ltd, China. NaOH, KCl, NaF, KSCN, KH_2PO_4 , Na_2SO_4 , $\text{Na}_2\text{B}_4\text{O}_7$, HCl, HNO_3 , H_2SO_4 ,

CH₃COOH, CH₃COONa, NaNO₃ and ZnSO₄·7H₂O were obtained from Analar. BDH chemical limited Poole, England.

Extraction of metal ion from aqueous phase at different pH values

The working concentration for the Zn²⁺ was 50 mg/L (ppm) in 2 ml of aqueous phases.

0.1 ml from 1000 mg/L (ppm) stock solution of the metal was quantitatively transferred into a set of 10 ml extraction bottles (volumetric flask). Subsequently, 1.9 ml of the buffer solutions of known pH values was added accordingly to make 2ml of aqueous phase. Two milliliters (2 ml) organic phase of 0.5 M sulphamethoxazole dissolved in acetylacetone was added to each extraction bottle in the set containing the metal ion of study (Zn²⁺). The mixture was shaken using a thermostatic water bath shaker for 30 minutes. Thereafter, the immiscible phases were allowed to settle and separate out. 1 ml of aqueous raffinate was then taken diluted and analyzed using atomic absorption spectrophotometer at a wavelength of 213.9. The process was repeated in the presence of the mineral acids and anions and anions solutions were buffered at pH 8.0

Determination of Distribution ratio, D

The distribution ratios were calculated from the absorbance values of the various solutions using the formula;

$$D = \frac{\text{absorbance of standard solution} - \text{absorbance of raffinate}}{\text{absorbance of raffinate}}$$

Determination of percentage extraction, % E

The percentage extractions were calculated from the absorbance values of the various solutions using the formula;

$$\% E = \frac{\text{absorbance of standard solution} - \text{absorbance of raffinate}}{\text{absorbance of standard solution}} \times \frac{100}{1}$$

RESULTS AND DISCUSSION

Results on Effect of pH

Figure 2 and 3 below shows the effect of pH on the extraction of the Zn (II) ions using sulphamethoxazole and acetylacetone. Figure 2 is a plot of Log D against pH while Figure 3 is a plot of percentage Extraction (% E) against pH.

Fig. 2: A plot of Log D against pH on extraction of Zn (II) ions

Fig. 3: A plot of Percentage extraction (% E) against pH on the extraction of Zn (II) ions.

The results show that percentage extraction increases as pH increased, with all extractions in acidic pH giving below 50%. Optimum extraction of 85.37% was observed at pH 8.0 which corresponds to Log D value of 0.766 while the least extraction of 0.98% was observed at a very strong acidic pH of 1.0 and this value corresponds to Log D of -2.006. The % E of Zn(II) ions was observed to decrease rapidly on increase in pH above 8.0 indicating that acetylacetone solution of sulphamethoxazole is not an excellent extractant for Zn (II) at extreme alkaline or acidic pH. A regression coefficient of 0.709 was obtained which indicates that quantitative extraction of the metal occurred progressively as pH increased up to its maximum at 8.0. A similar observation was made by Lee and Fujinaga [16] in their study of determination of effect of pH of aqueous phase

on extractibility of U (VI) where uranyl ion was extracted quantitatively in the pH range between 7.8 and 8.2. Also Asrafi *et al* [17] in their work 'solvent extraction of zinc from sulfate medium by bis(2-ethylhexyl) phosphoric acid in toluene' show that, the extraction of Zn (II) in the pH range of 5.0 to 6.0 is quantitative. Their findings is at variance with our results which gave quantitative extraction of Zn (II) in a pH range of 7.0 to 8.0 and this variation can be attributed to the structural and chemical properties differences of the ligands used in both cases

Results on Effect of Anions

The effects of some anions on the solvent extraction of Zn (II) were determined at various concentrations. Figure 4 shows a plot of the percentage extractions (% E) against anion concentrations.

Fig. 4: A plot of percentage extraction against concentration of anions in the extraction of ZnSO_4 .

From the results obtained, it was observed that over 50% extraction occurred at very low concentrations of the anions and as their concentrations increased, the percentage extraction decreased. For SO_4^{2-} the highest % E of 81.70% with Log D value of 0.6493 was obtained at 0.005 M concentration and the least % E of 45.4% with Log D value of -0.0809 was obtained at 0.05 M. For F^- the highest percentage extraction of 85.27% with Log D value of 0.756 was obtained at 0.01 M and the least % E of 38.50% with Log D value of -0.203 was obtained at 0.001 M, for SCN^- the highest percentage extraction of 85.37% with Log D value of 0.766 was obtained at 0.001 M and for NO_3^- the highest percentage extraction of 74.6% with Log D value of 0.469 was obtained at 0.01 M. The anions seem to extract well at concentrations lower than 0.01 M and

increasing their concentrations beyond 0.01 M resulted to a decrease in percentage extraction of the metal. A similar observation was made by Naglaa and Jacqueline [18] when they measured the distribution ratios of Pd (II) by varying the chloride ion concentration in the range of 1 to 5 M. When the chloride ion concentrations increases, the distribution ratio decreases, the increase in chloride concentration favoured the formation of PdCl_4^{2-} complex which leads to the decrease in the concentration of free Pd (II) ions.

Results on Effect of Mineral Acids

The effect of some mineral acids was determined at various concentrations of the acids. A plot of the percentage extractions against acid concentrations is presented in figure4.below

Fig. 5 A plot of percentage extraction against concentration of Mineral Acids used in the extraction of Zn (II) ions.

The results show that extraction of Zn (II) ions occurred only at lower concentration of the acids. % E of Zn (II) ions in sulphuric acid was quantitative at concentration of 0.001 M where 81.80 %E of Zn (II) was observed and 0.005 M which gave 83.90% E for Zn (II) ions and further increase in sulphuric acid concentration results to a decrease in percentage extraction. The highest percentage extraction of Zn (II) ions in the presence of hydrochloric acid; 77.60% with Log D value of 0.539 occurred at 0.001 M and % E decreased steadily as the concentration of HCl increased beyond 0.001 M. A similar result obtained by Naglaa and Jacqueline [18] shows that the extraction efficiency decreases as HCl acid concentration increases and the extraction percentage decreases to a minimum value of 2 M HCl and remains constant with further increase in HCl concentration. The decrease may be attributed to the probable extraction at high acidity together with the formation of extractable species such as PdCl_4^{2-} and CdCl_4^{2-} .

The extraction of Zn (II) ions increased as the nitric acid concentration was increased from 0.001 M to 0.05 M and gave the highest % E of

50.20% with Log D value of 0.004 at 0.05 M. Daoud *et al.*, [19] also observed a slight increase in the extraction of Zr (IV) by CYANEX 301 (Bis(2,4,4-trimethylpentyl)dithiophosphonic acid) with the increase in nitric acid concentration from 0.1 to 2 M and then decreases with further increase in the acidity of the medium resulting from the possible decomposition of CYANEX 301 into nitric acid of more than 2 M.

From the results obtained, it was observed that among the three mineral acids used H_2SO_4 gave the best extraction of Zn (II) ions with highest % E of 83.90% with Log D value of 0.717 at 0.005 M.

CONCLUSION AND RECOMMENDATION

CONCLUSION

Zinc (II) removal by acetylacetone solution of sulphamethoxazole from aqueous media was investigated. The extraction efficiency is dependent on pH and is also affected by the presence of mineral acids and anions. A recovery of 84 – 86 % of Zn (II) ions occurred

within the pH range of 7.0–8.0. at a constant concentration of sulphamethoxazole in acetylacetone, the extraction efficiency increases with increasing pH and reached a maximum at pH 8.0. In all cases of extraction done in the presence of anions, increasing the concentration of the anions beyond 0.01 M resulted to the decrease in percentage extraction of the metal. Mineral acids such as H_2SO_4 and HCl decreased the percentage extraction of the metal as their concentrations increased while the increase in the concentration of HNO_3 results to increase in percentage extraction of the metal.

From all observation, the extraction of Zn (II) into acetylacetone solution of sulphamethoxazole is obtainable in medium of low F^- , SO_4^{2-} , SCN^- and NO_3^- concentrations, high HNO_3 concentration and is more efficient in a moderately acidic to slightly alkaline medium.

RECOMMENDATION

Acetylacetone solution of sulphamethoxazole can be employed in the industries as an effective extractant of Zinc ions from aqueous media. The extraction can be done in the pH range of 6 – 8, in media of low concentrations of fluoride, thiocynate, sulphate and nitrate ions and as well as high nitric acid concentration.

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