



**Application of Noncyclic 2,2'-[ethane-1,2-diylbis(iminomethanediyl)]
diphenol for heavy metal extraction (Mn^{2+} , Fe^{3+} and Co^{2+})**

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ABSTRACT

Noncyclic 2,2'-[ethane-1,2-diylbis(iminomethanediyl)]diphenol (EDIMD) bearing amine linkages and hydroxyl groups have been designed and synthesized for use as an extracting agent for the heavy metals and its concentration estimation on spectrophotometric method. The composition of the complex between EDIMD and metals (Mn^{2+} , Fe^{3+} and Co^{2+}) was elucidated by continuous Job's variation method. The solvent variation study shows that the butan-1-ol was suitable diluent and other diluents were not effective for EDIMD. The metals present in waste water were extracted in butan-1-ol and transferred to organic liquid. The effects of solvent, time, pH, ligand and salt variation on metal extraction been studied. The parameters are optimized for highest extraction ability of EDIMD for metal (Mn^{2+} , Fe^{3+} and Co^{2+}). The more important ligand reused study has been established and extraction efficiency was observed well for first, second and third extraction cycles. The above developed method is directly applied to real sample such as industrial sample and industrial waste water effluent.

Keywords: Spectrophotometric method, heavy metals, Job's continuous variation method.

INTRODUCTION

Trace elements can be classified into several essential and nonessential elements in regards to living things. The essential elements are those that, even in minute concentrations, play a vital role in the metabolism of organisms and in a large number of physiological processes. Some trace elements, such as Mn, Fe, Co and Cu are essential to life. However, other trace elements (non-essential), such as Ni, Pb and Cd have no known biological function and are generally toxic to a variety of organisms. In addition, these elements at high concentrations exhibit high toxicity in biological function of organisms in plants and animals[1,2]. Under precise circumstances, they may cause negative impacts to terrestrial and aquatic ecosystems becoming pollutants or contaminants in soil and water. For elements that exhibit the characteristic of damage (i.e., intrinsic factor that represents any danger), reducing the exposure is the only effective way to reduce the risk to the environment and human health. Thus, monitoring of trace elements in the environment is extremely important because it helps to control exposure of humans and animals to these substances[3-5].

In biology, Mn (II) ions function as cofactors for a large variety of enzymes with many functions. Manganese enzymes are particularly essential in detoxification of superoxide free radicals in organisms that must deal with elemental oxygen. Manganese also functions in the oxygen-evolving complex of photosynthetic plants. The element is a required trace mineral for all known living organisms. In larger amounts, and apparently with far greater activity by inhalation, manganese can cause a poisoning syndrome in mammals; with neurological damage which is sometimes irreversible[6]. The human body contains four grams of iron. Most of the iron present in biological systems is tightly associated with enzymes and specialized transport and storage proteins and found in hemoglobin, the red pigment in the erythrocytes and rest of stored in ferretin. It plays a vital role in oxygen transfer processes in DNA and RNA synthesis. The deficiency of Fe^{3+} causes anaemia, hemochromatosis, liver damage, diabetes, Parkinson's disease and cancer[7,8]. Co^{2+} plays an important role in the metabolism of iron synthesis of ligands and synthesis of haemoglobin and Vitamin B₁₂ coenzymes. Co^{2+} is required in human body in ultra micro trace quantity. Some heavy metals are toxic in nature[9,10]

Several methods involving preconcentration techniques, such as cloud point extraction (CPE), solid phase extraction (SPE) and liquid-liquid extraction (LLE), have been developed for the quantification of trace elements. LLE is a well-established technique and is noted for its efficiency, simplicity and possibility of using a large number of solvents that are pure and commercially available while providing a wide range of solubility and selectivity[11,12].

In the present work, we have developed a method for the extraction of heavy metals (Mn^{2+} , Fe^{3+} and Co^{2+}) using EDIMD in butan-1-ol : aqueous solution using solvent extraction method, So, if an EDIMD acts as an extractant, a successful solvent extraction process for metal ions will be established. In this study, extraction equilibrium experiments were performed by changing several operating parameters such as solvent, time, pH, ligand and salt variation have been studied and developed the better method for Mn^{2+} , Fe^{3+} and Co^{2+} extraction.

MATERIALS AND METHODS

Reagents and Apparatus: The reagents used in this work were all of spectroscopic grade with high purity and used without further purification. The salts and reagent used of analytical grade. The extractant 2,2'-[ethane-1,2-diylbis(iminomethanediyl)]diphenol (EDIMD) is synthesized in laboratory and characterized by various spectroscopic technique. IR spectra were recorded using KBr with FTIR Shimadzu IRPrestige-21 model Spectrum One Spectrophotometer, ¹H NMR, ¹³C NMR spectra were recorded using CDCl₃ with Varian-300 spectrometer NMR instrument using TMS as internal standard. Mass spectra were recorded on Agilent 6520 Accurate-Mass Q-TOF LC/MS. The AA spectrometer analysis and UV-Visible spectra were recorded on Thermo scientific S-series AA spectrometer and Shimadzu UV-24500 with 5 nm slit of fluorescence and 1 cm path length of cuvette. Ultrapure water with a Millipore Purification System (Milli-Q water) was used throughout the analytical experiments. The metal salt (chloride and nitrate) were used throughout the experiment.

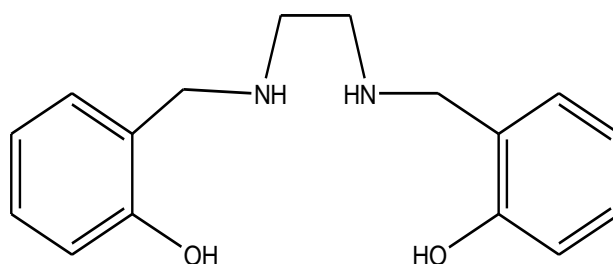


Figure 1. Extractant 2,2'-[ethane-1,2-diylbis(iminomethanediyl)]diphenol (EDIMD)

Solution Preparation: Stock 1000 $\mu\text{g mL}^{-1}$ of Mn^{2+} , Fe^{3+} and Co^{2+} AA standard solutions were purchased from Merck. Working standards were prepared from these solutions by dilution. The salt solution is prepared from metal salt of 100 ppm and it is diluted up to the concentration 5 ppm.

Extraction procedure: The experiments were carried out in solvent extraction separating funnel of volume 100 mL. Initially 40 mL of mixed salts solution and 40 mL EDIMD solution was mixed in separating funnel. After the method development the EDIMD is directly applied to environmental sample. All the extraction and stripping experiments were carried out batchwise at the temperature of 25 ± 0.1 $^{\circ}\text{C}$. All aqueous solutions were prepared using deionised water. After 5 min, the organic and the aqueous phases were separated and the metal ion concentrations were determined from the aqueous phase. The concentrations of the metal ions in the organic phase were calculated from the difference of the metal ion concentrations in the aqueous phase before and after extraction. The results were expressed as percentage of extracted metals.

Real sample preparation: Ore samples and pre-treated ore effluent were collected from industry and the mixed industrial effluent is collected from ETP plant India. The effluent sample is collected and filtered for removing the solid waste and directly used for the application purpose. A fixed amount of ore sample is digested with con HCL + HNO_3 and heated on hot plate till the acid is evaporate and after that the distilled water is added for maintaining the proper concentration and filtered for removing solid waste. The filter water is applicable for the extraction procedure.

RESULTS AND DISCUSSION

Stoichiometry of metals with EDIMD: To determine the binding stoichiometry between EDIMD and cations, the Job's continuous variation method[13-15] was used. **Figure S1, S2 and S3** in supporting data shows the Job's plot of the fluorescence intensity of free EDIMD and the intensity of the system with the molar fraction of the host $[\text{H}]/([\text{H}]+[\text{G}])$ for a series of solutions, in which the total concentration of host and guest was kept constant, with the molar fraction of host continuously varying. The results indicate the formation of a 1:1 (Host: Guest) complex. Using the equation: $[\text{G}]_{\text{tot}} = a/2K(1-a)^2[\text{H}]_{\text{tot}} + a[\text{H}]_{\text{tot}}/2$, where $[\text{G}]_{\text{tot}}$ is total concentration of guest, $[\text{H}]_{\text{tot}}$ is the total concentration of host, $a = (I - I_0)/(I_i - I_0)$ with I being the fluorescent intensity at a particular Mn^{2+} , Fe^{3+} and Co^{2+} concentration while I_0 and I_i are the intensities at zero and infinite Mn^{2+} , Fe^{3+} and Co^{2+} concentrations, respectively.

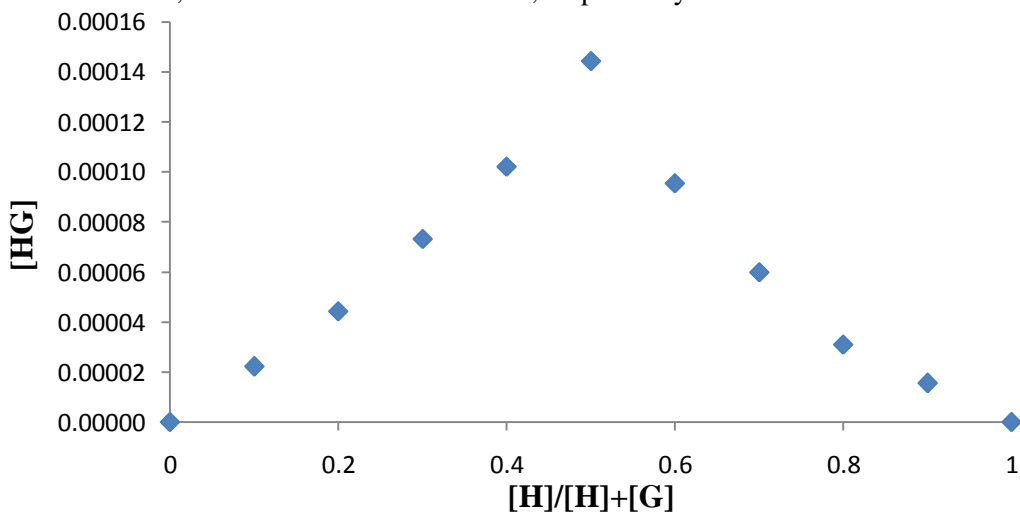


Figure S1 1:1 Stoichiometry of the host guest relationship realised from the Job plot between receptor EDIMD and Mn^{2+} .

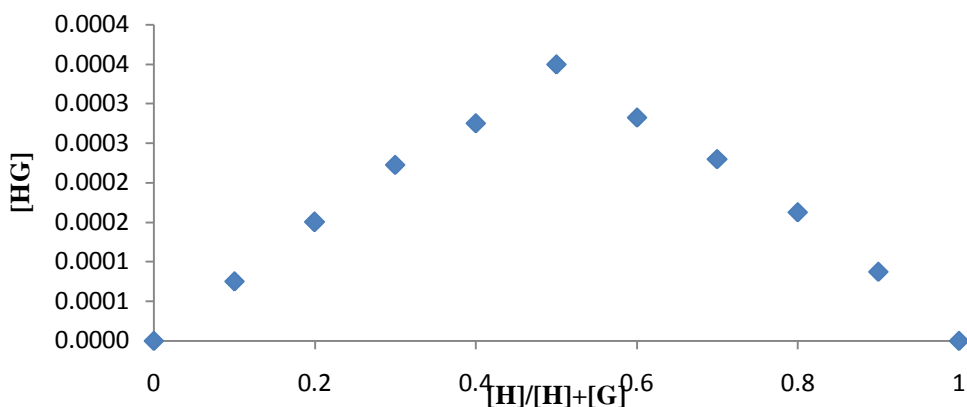


Figure S2 1:1 Stoichiometry of the host guest relationship realised from the Job plot between receptor EDIMD and Fe^{3+} .

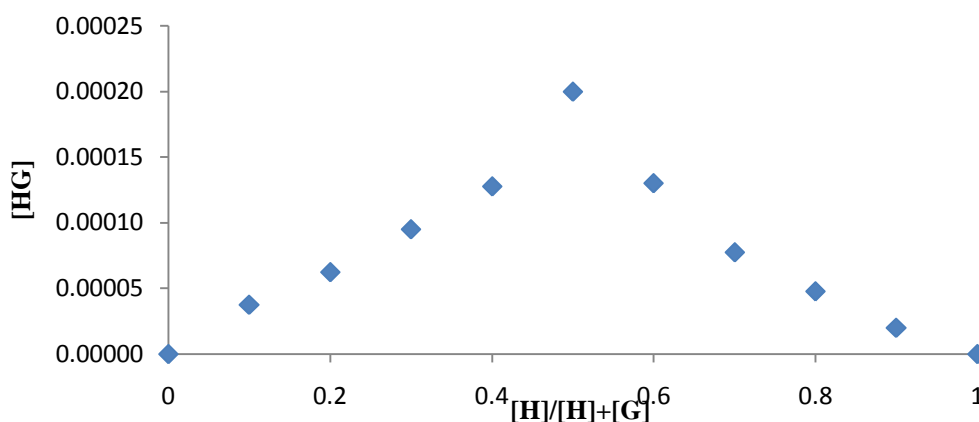


Figure S3 1:1 Stoichiometry of the host guest relationship realised from the Job plot between receptor EDIMD and Co^{2+} .

Effect of the diluents: The EDIMD mixed in different diluents, which were chloroform, cyclohexane, butan-1-ol, ethyl acetate, dichloromethane and toluene and were studied for the extraction of Mn^{2+} , Fe^{3+} and Co^{2+} . The experiment was planned for investigating the EDIMD efficiency for the best extraction of metal in solvent. The results presented in **figure 2** show that butan-1-ol was suitable diluent and other diluents were not found so effective for EDIMD. Eventually, in the present work, butan-1-ol was selected as diluent for EDIMD due to its superior extractability, high polarity, solvation and dissolution properties towards the EDIMD and Mn^{2+} , Fe^{3+} and Co^{2+} complexes.

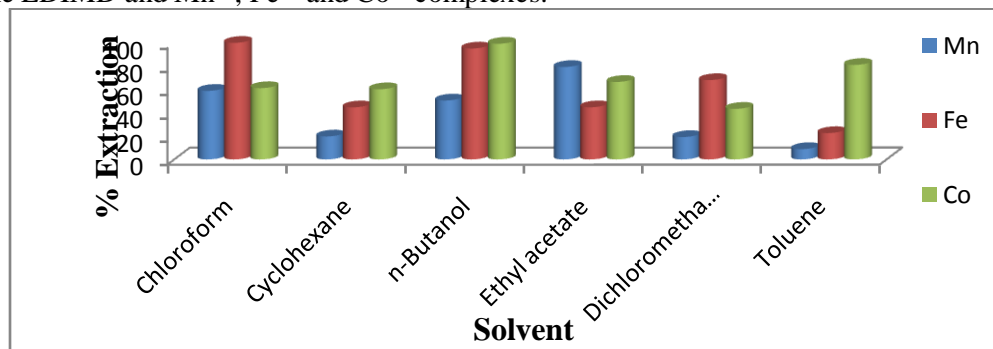


Figure 2 Effect of diluent; 5ppm; metals concentration of extraction time 10 min, phase ratio: 1.0 and equilibration time 5 min.

Effect of mixing time : In solvent extraction the extraction efficiency is best affected by time. So the mixing time experiments were carried out in which the solvent extraction funnel was mechanically shaken by hand for 2, 4, 6, 8, 10, 12, 14, 16, 18, 20 min and after equilibration time of 5 min the extracted metal is determined on AA spectrometer. The effect of mixing time on the extraction was shown in **figure 3**. The first observation is that the extraction of metals is increased with increasing the time of shaking. At the time of 2, 4 and 6 min the percent extraction of metals is increases but after 10 min and more it was approximately stable. The optimum mixing time for Mn^{2+} , Fe^{3+} and Co^{2+} were 4, 4 and 12 min respectively. As the present study is combined extraction of all the metals, 10 min extraction time is common for all the experiment.

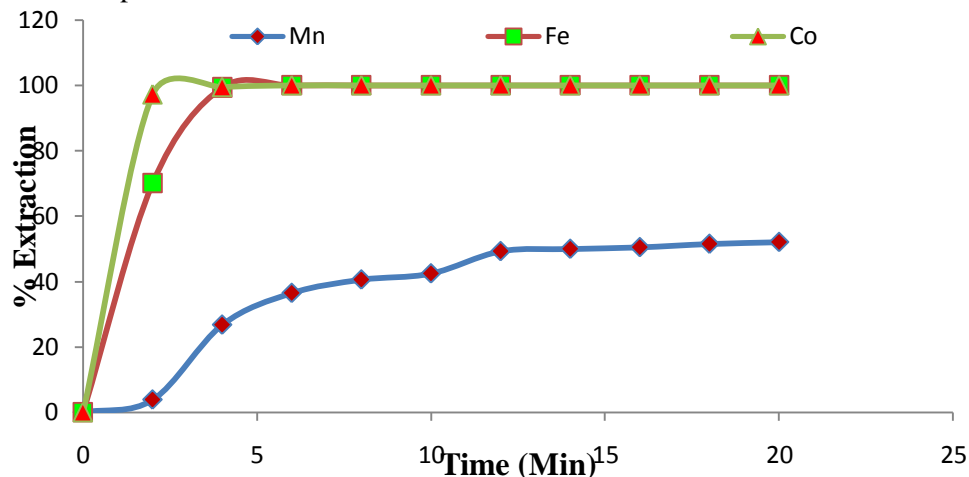


Figure 3 Effect of mixing time; butan-1-ol; 5 ppm; metals concentration; phase ratio: 1.0; equilibration time 5 min.

Effect of the acidic leach solution pH: The pH of the solution has a deep effect on the extraction behavior. In work, the pH of the solution was varied from 0.5 to 9.0 and the results obtained were shown in **figure 4**. It was observed that by increasing pH of the solution from 0.5 to 4.0 the percentage of metals extraction increased. With further increase in solution pH from 6.0 to 9.0, the rate of (Mn^{2+} , Fe^{3+} and Co^{2+}) extraction started to slightly decrease. The increase of extraction ability at pH 0.5 to 5.0 is because in low pH the formation of complex is confronted by the acid condition. Similarly on the above pH 5.0 the metal salts is converted in to its hydroxide form in such condition the extraction ability of the EDIMD is decreased. Therefore, pH 5.5, 4.0 and 4.5 were selected as the best for Mn^{2+} , Fe^{3+} and Co^{2+} extraction respectively.

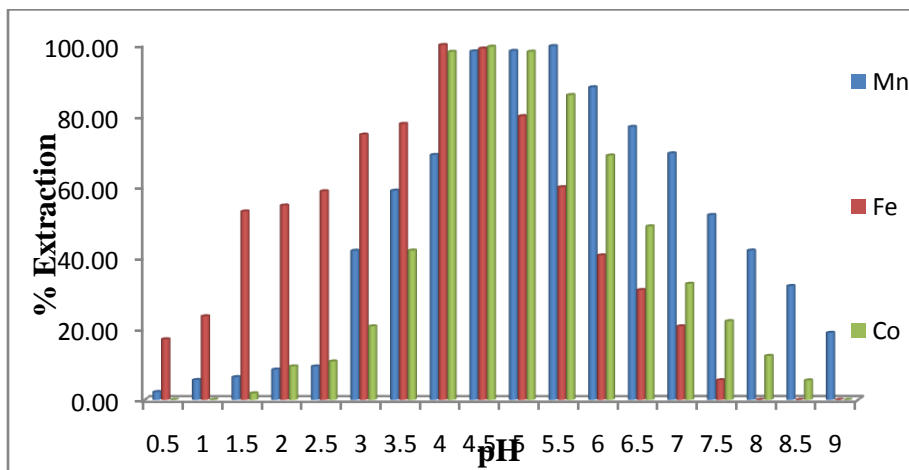


Figure 4 Effect of pH; butan-1-ol; 5 ppm; metals concentration; pH of the solution varies from 0.5 to 9.0; extraction time 10 min; phase ratio: 1.0; equilibration time 5 min.

Effect of extractant concentration : To investigate the effect of the extractant concentration on the extraction of metal ions, the (EDIMD) concentration was varied in the range from 50 to 800 mg L⁻¹ in butan-1-ol as diluent (**Figure 5**). The maximum extraction (99.9 %) was achieved at 500 mg L⁻¹ EDIMD in butan-1-ol. The extractant concentration in the organic phase played an important role in the overall extraction of the metal ions. A further increase in the EDIMD concentration from 500 to 800 mg L⁻¹ did not give any further positive effect on the extraction of metal ions. Although the diluent (butan-1-ol) was not directly involved in the extraction of metal species, it modified the viscosity and the surface tension properties of the organic phase, important to longer phase detachment time and insignificant entrainment. Therefore, the percentage of extracted metal can be considered a response to the percentage of active extractant in the diluent.

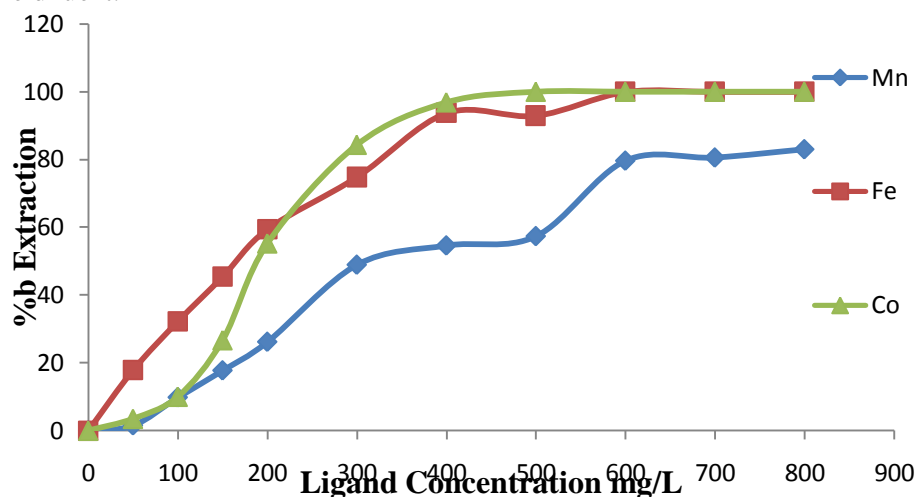


Figure 5 Effect of EDIMD concentration; 5 ppm metal concentration of solution; the concentration of EDIMD solution varies from 50 to 800 mg/L; pH 5.0; extraction time 10 min; phase ratio: 1.0; equilibration time 5 min.

Effect of stripping reagent concentration: 5 ppm metals concentration was used for the extraction study and once the extraction was completed the stripping experiment was planned for getting the proper concentration of HCl as a stripping reagent. HCl concentration was varied in range from 0.01 M to 5.0 M. The results are shown in **figure 6**. In case of HCl as a stripping reagent, the stripping of Mn²⁺, Fe³⁺ and Co²⁺ were increased up to 1M HCl and above it is constant for 2 to 5 M. So the 1M HCl concentration is used for the stripping of Mn²⁺, Fe³⁺ and Co²⁺ complexes.

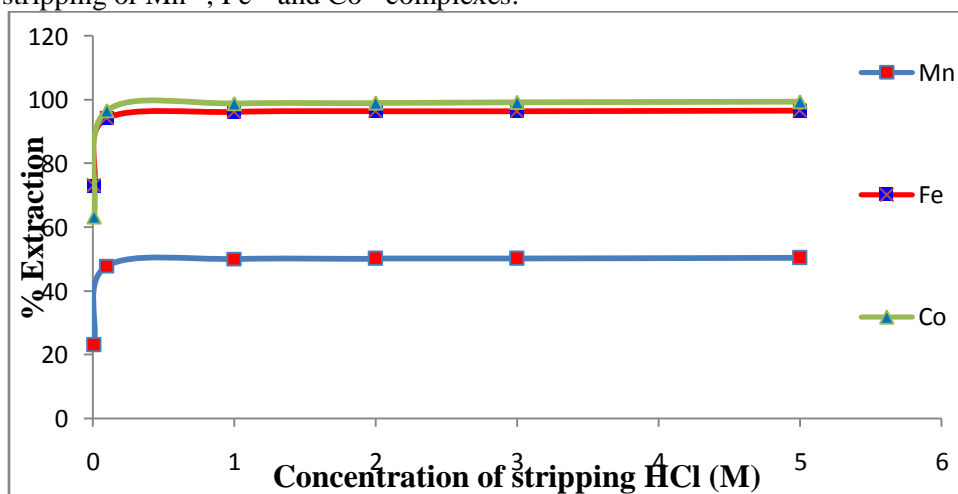


Figure 6 Effect of stripping agent concentration (HCl); 5 ppm metals concentration of solution; the concentration of HCl solution varies from 0.01 to 5.0 M; extraction time 10 min; stripping time 5 min; phase ratio: 1.0; equilibration time 5 min.

Reuse of the solvent: To estimate the reusability of the organic phase, the complex form of metals with EDIMD during the extraction process stripped with HCl and the free EDIMD in organic phase is used again and again three times and the experiment shows the extraordinary results. After three extraction/stripping cycles, the organic phase had lost little of its volume but retained good extraction efficiency as results shows in **figure 7**.

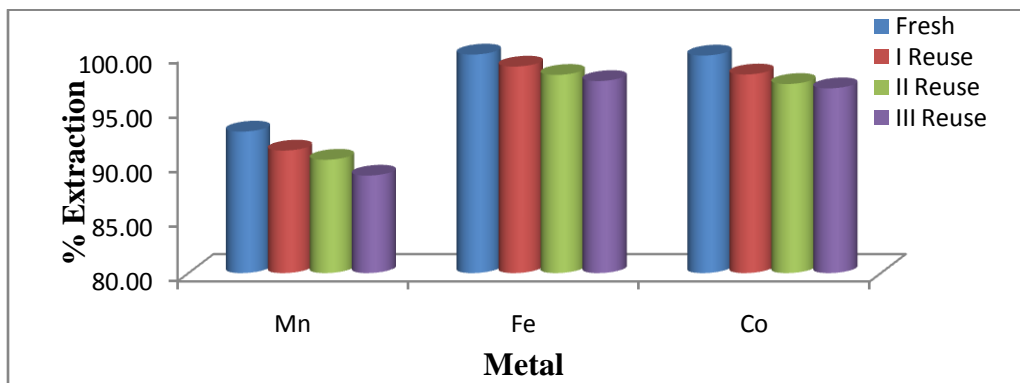


Figure 7 Effect of reused (EDIMD); 5 ppm metal concentration of solution; the concentration of HCl solution varies from 1.0 M; pH 5.0; extraction time 10 min; stripping time 5 min; phase ratio: 1.0; equilibration times 5 min.

Effect of salting: The salting experiments have been designed to evaluate the effect of salting on the extraction efficiency of EDIMD in butan-1-ol solvent. The experiment was carried out in the presence of KNO_3 , CaCl_2 , KH_2PO_4 , NaCl , NaH_2PO_4 , Na_2CO_3 and NaNO_3 and the results are shown in **figure 8**. It shows that the extraction efficiency of metals was approximately stable except for KH_2PO_4 and NaH_2PO_4 the appreciable decrease was observed due to the salting out effect. And in the case of Mn the use of Na_2CO_3 the extraction efficiency was up to 92% due to the salting in effect.

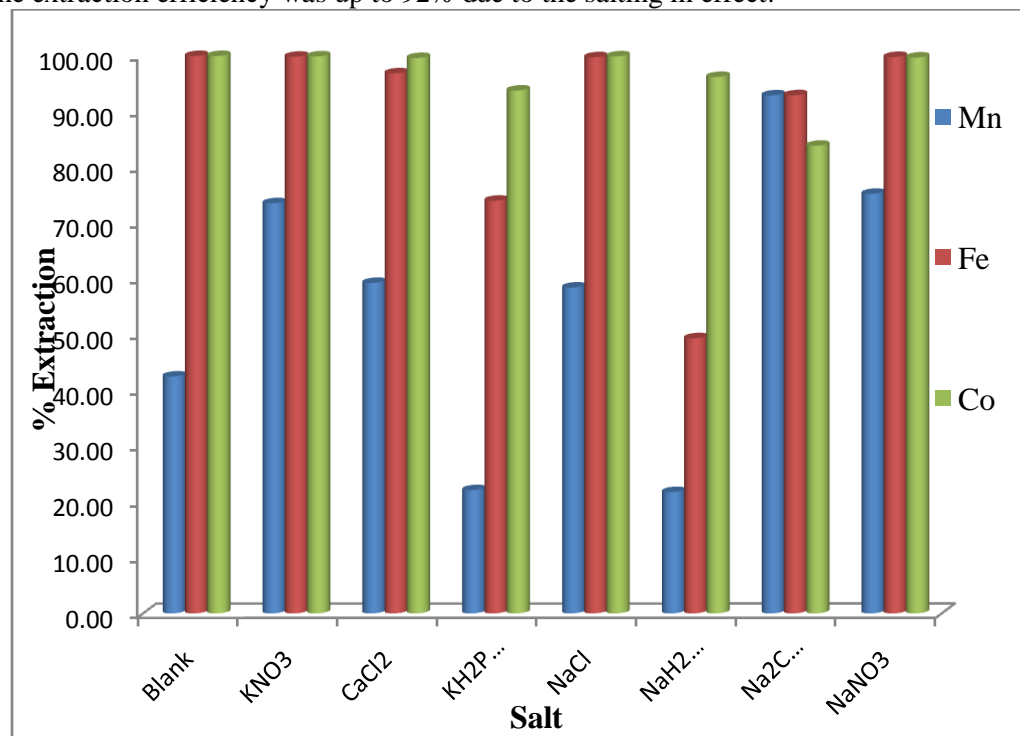


Figure 8 Effect of salt used in extraction; 5 ppm metal concentration of solution; the concentration salt 0.01M; pH 5.0; extraction time 10 min; phase ratio: 1.0; equilibration time 5 min.

Colorimetric colour change: The importance of ligand increases when it can detect the metal and its presence can be seen by naked eye. It means that the ligand and metal gives colorimetric colour change on complexation. The EDIMD is colourless but on addition of metals the colours were appeared. The addition of metals Mn^{2+} , Fe^{3+} and Co^{2+} gives dark black green, black brown and dark orange coloured solutions respectively shown in **figure 9**.



Figure 9 The colorimetric colour change on mixing of EDIMD with metals (From right to left: only EDIMD, EDIMD+Mn(II), EDIMD+Fe(III) and EDIMD+Co(II)).

Effect of the optimum conditions on extraction of metals: The optimum conditions experimentally determined are shown in **table 1**.

Table 1 Optimum condition for the extraction of metals

S. No	Parameter	Mn status	Fe status	Co status
1	Solvent	Butan-1-ol		
2	Stoichiometry	1:1		
3	Extraction Time	12 min	4 min	4 min
4	pH	5.5	4.0	4.5
5	EDIMD concentration	600 mg/L	600 mg/L	400 mg/L
6	Striping agent	1M HCl		
7	No of reuse of ligand	3 times		
8	Salt effect	Na_2CO_3 , KH_2PO_4 and NaH_2PO_4	KH_2PO_4 and NaH_2PO_4	KH_2PO_4 and NaH_2PO_4
9	LOD	3 $\mu g/L$	0.1 $\mu g/L$	0.3 $\mu g/L$

APPLICATIONS

To evaluate the accuracy of this method, the developed method was applied to the determination of Mn(II), Fe(III) and Co(II) ions in real ore sample, ore effluent and mixed industrial effluent. The samples were filtered and analyzed immediately after collection. The % extraction calculations were made by determining the metal concentration before and after extraction for aliquots of each sample. The results are shown in Table 2 and confirm the applicability of the method on metal processing industry effluent and mixed industrial effluent also.

Table 2

Sample	Metal	Metal Concentration (ppm)	Metal Concentration after extraction (ppm)	% Extraction
Ore Sample	Mn	0.0837	0.0059	92.94
	Fe	0.3152	0.0004	99.87
	Co	0.0562	0.0009	98.23
Ore effluent	Mn	0.0667	0.0051	92.24
	Fe	0.0125	0.0002	98.39
	Co	0.0090	0.0001	98.86
Mixed Industrial Effluent	Mn	2.0903	0.1749	91.63
	Fe	15.2788	0.1802	98.82
	Co	0.0514	0.0006	98.69

CONCLUSIONS

A solvent extraction process using EDIMD to separate out metals has been investigated. From this study the following conclusions can be drawn:

1. The optimum conditions have been determined experimentally as stated above in **table 1**.
2. The highest extraction efficiency was obtained at pH 5.5, 4.0 and 4.5 for metals Mn^{2+} , Fe^{3+} and Co^{2+} respectively.
3. Extraction efficiency increased by increasing the extractant (EDIMD) concentration which stabilised at an excess of the EDIMD in the organic phase.
4. A higher concentration of HCl in the stripping solution increased the concentration driving force, hence, stripping efficiency also increased up to 1M but after it remain steady.
5. From the application point of view, butan-1-ol could be a good choice for practical purpose for dilution of EDIMD.
6. Based on the analysis of Job's continuous variation plot method we explain 1:1 stoichiometry of the complexes of Mn^{2+} , Fe^{3+} and Co^{2+} .
7. The compound EDIMD is useful with the point of reuse for extraction of metals.

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