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Evaluating the potentials of complexing agents in multi-metal extractions using 4,4´-(1e,1e´)-1,1´-(Ethane-1,2-Diylbis(Azan-1-Yl-1ylidene))Bis(5-Methyl-2-Phenyl-2,3-Dihydro-1*h*-Pyrazol-3-Ol) (H₂BuEtP)

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Heavy metals toxicity has led to the continuous study of new and efficient methods for their removal from the environment. Solvent extraction method was used to study the potentials of the auxiliary complexing agents Ethylenediaminetetraacetic acid (EDTA), Oxalate ($C_2O_4^{2-}$), Thiocyanate (SCN^-) and Tartrate ($C_4H_4O_6^{2-}$) ions in the simultaneous extraction of Cadmium, Iron, Nickel and Lead from aqueous solutions buffered to either pH 4.75 or 7.5 using the organic extractant 4,4´-(1*E*,1*E*´)-1,1´-(ethane-1,2-diylbis(azan-1-yl-1ylidene))bis(5-methyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-ol) (H₂BuEtP) alone or in the presence 4-butanoyl-2-4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (HBuP). 0.001 to 0.1 M of the auxiliary complexing agents and equilibration time of 60 min was used. Distribution ratios and percentage extraction was calculated using raffinates and metal standard absorbances. EDTA, Oxalate and Thiocyanate ions and pH 4.75 was found not suitable for the multi-metal extraction of the four metals attributed to the formation of very stable complexes with these auxiliary complexing agents' ions masking the extraction of the metals, although statistically, there were no significant differences in most cases between the extractions of the metals in the two buffers. Using the ligand H₂BuEtP alone with a buffer of pH 7.5 and 0.001 M Tartrate, 7 batches of extraction are theoretically required to achieve 99.9% simultaneous extraction of the four metals as the best result while with the mixed ligands H₂BuEtP/HBuP organic extractant system, 7 batches are required for 0.001 to 0.005 M Tartrate, 5 batches for 0.05 M Tartrate and 4 batches for 0.01 M Tartrate as the best results. Statistically, there was no significant difference between the two organic phases with the exception being Thiocyanate for Nickel with buffer of pH 7.5 that showed slight synergic effect of HBuP.

Key words: Auxiliary complexing agents, ligands, multi-metal, buffers, extraction.

INTRODUCTION

Metals have played major roles in the industrial revolution with their applications in almost all types of industrial processes. However, there are growing concerns due to the many reported health effects from these metals

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(Jaishankar et al., 2014: Mahurpawar, 2015; Okereafor, et al., 2020). Heavy metals based on their high densities are a class of metals that have shown serious bio-toxic effects due to their ability to bind to enzymes and proteins, altering their activities and resulting in cellular damage (Martin and Griswold, 2009; Engwa et al., 2019). Numerous studies have been done on methods to remove these heavy metals from the environment and reported (Luptakova et al., 2012; Alfarra et al., 2014; Jha and Kumar, 2017; Awa and Hadiba, 2020). The use of ligands especially chelating agents such as Schiff bases in the extraction of heavy metals have shown very good promises with reported cases of a single batch extractions of above 90% achieved for most heavy metals (Hassan et al., 2013; Radi et al., 2016; Salga et al., 2018). Their successes in the extraction of metals have been attributed to the formation of very stable ring structured chelates (Mohamed et al., 2006; Abu-Dief and Mohamed, 2015). Many metal chelates have been synthesized and studied for their biochemical activities and have found uses in medicine as antitumor agents (Tripathi et al., 2006; Reedijk, 2009), antipyretics (Shanmugam and Thangaraj, 2019), antibacterials, antifungi agents and also used in agriculture to protect plants from invasive organisms (Abo-Aly et al., 2015; Srivastva et al., 2016). These studies have also shown promises in the area of separating metals based on the fact that different metals show varying dependence on pH and oxidation states in their extractions with different ligands and thus, utilized in recovery and purification of metals (Silva et al., 2005; Li et al., 2019).

The Schiff base 4,4´-(1E,1E´)-1,1´-(ethane-1,2-diylbis(azan-1-yl-1ylidene))bis(5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-3-ol) (H_2BuEtP) since its synthesis by Uzoukwu et al. (1998) have been studied for its potentials in the extraction of Lead (Godwin and Uzoukwu, 2012a), Uranium (Godwin and Uzoukwu, 2012b), Nickel (Godwin et al., 2012), Iron (Godwin et al., 2013; Godwin et al., 2014) and Cadmium (Godwin et al., 2019) using the ligand alone and in the presence of another ligand 4-butanoyl-2-4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (HBuP) to ascertain any synergic effects. These studies show that though the different metals show varying pH at which optimal extractions occur, all the five studied metals had greater than 90% extractions between pH 4.75 to 7.5 in the presence of common acids, anions and auxiliary complexing agents. The effects of acids, anions and auxiliary complexing show that at some concentrations, they act as releasing agents by forming unstable compounds with the heavy metal ions, thereby making it easy for the metal ions to bind with the Schiff base and aiding their extractions from the aqueous media to the organic phases while at some other concentrations, they act as masking agents as they form very stable compounds with the metal ions and preventing formation of the metal chelates and thus bulk of the metals are retained in the aqueous media (Uzoukwu, 2009). The results from bimetal extractions studies using this Schiff base H_2BuEtP gave separation factors β_{XY} in most cases < 5 (Godwin et al., 2019), indicating that the Schiff base (H_2BuEtP) has potentials in multi-metal extractions. Since the aim in these metals extraction studies is to obtain optimal conditions in which 99.9% extraction of the metals can be achieved, getting optimal conditions in which the simultaneous extraction of more than one metal can be obtained, will go a long way in designing methods for extracting metals from effluents that can save time.

In the first of such studies, the effects of the anions CH_3COO^-, PO_4^{3-}, and SO_4^{2-} in the multi-metal extraction of Cadmium (II), Iron (II), Lead (II), and Nickel (II) from aqueous solutions buffered to pH 4.75 and 7.5 was studied using ligand H_2BuEtP alone, and in the presence of the ligand 4-butanoyl-2-4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (HBuP) in chloroform organic phases using solvent-solvent extraction methods using 2 batches of extractions based on theoretical number of batches needed to achieve 99.9% extractions of the four metals from single metal extractions studies with same organic phases. The results showed that even though all the three anions can be used to simultaneously extract 99.9% of the four metals after 5 – 8 batches of extractions in either aqueous media buffered to pH 4.75 or 7.5 and using either H_2BuEtP alone or in the presence of HBuP, aqueous solution containing 0.05 M PO_4^{3-} and buffered to pH 7.5 using H_2BuEtP/HBuP organic phase can achieve 99.9% extraction of the four metal theoretically after 5 batches of extractions. CH_3COO^- and SO_4^{2-} effects were significantly different for Cadmium and Iron extractions at both pH 4.75 and 7.5 for H_2BuEtP alone but not significantly different in H_2BuEtP/HBuP organic phases. PO_4^{3-} and SO_4^{2-} effects were significantly different for Iron extractions alone at both pHs for H_2BuEtP alone and significantly different for Cadmium and Iron at pH 4.75 for H_2BuEtP/HBuP organic phases (Godwin and Young, 2020). In a similar study with halide ions, aqueous solutions buffered to pH 7.5 and containing either 0.05 M Cl^- or F^- using chloroform solutions of the ligand H_2BuEtP alone gave the best results with 99.9% extraction of Cadmium, Lead, Nickel and Iron theoretically possible after 2 batches of extractions as mixed ligands H_2BuEtP/HBuP extractant, requiring at least 4 batches theoretically to extract 99.9% of the four metals from aqueous solutions buffered to pH 7.5 and containing either 0.05 M Br^-, 0.001 M Cl^-, or 0.01 M F^-. In this study, the extractants H_2BuEtP and H_2BuEtP/HBuP were not significantly different in the extractions of the four metals in both buffers and efficiencies of the halide ions in the multi-metal extractions of Cadmium. Lead, Nickel and Iron was shown to be in the order $Cl^- = F^- > I^- > Br^-$. The extraction of the metals from the aqueous to the organic phases was attributed to favourable energetics in the transfer of the metal complexes in the ligand H_2BuEtP alone or adducts in mixed ligands H_2BuEtP/HBuP organic

phases as a result of changes in permittivities/dielectric constants of the two phases (Godwin et al., 2021).

In continuation of our study to fully evaluate the effects of acids, anions and auxiliary complexing agents in simultaneous multi-metal extraction of Cadmium, Iron, Lead and Nickel, we have studied the potentials of the auxiliary complexing agents Ethylenediaminetetraacetic acid (EDTA), Oxalate ($C_2O_4^{2-}$), Thiocyanate (SCN^-) and Tartrate ($C_4H_4O_6^{2-}$) ions in aqueous solutions buffered to pH 4.75 and 7.5 containing the four metals using chloroform solutions of the Schiff base H_2BuEtP alone and in the presence of HBuP as extractant. The study is aimed at obtaining the optimal conditions in which the four metals can be simultaneously extracted from the aqueous solutions using the auxiliary complexing agents. The objectives are; to evaluate the effects of the concentrations of the complexing agents in these extractions, as well as statistically compare results for the complexing agents, the two pHs and the organic extractants in these extractions.

EXPERIMENTALS

Synthesis, purification and characterization of the ligands HBuP and H_2BuEtP were done as outlined by Uzoukwu et al. (1998). Ammonium and sodium salts of the auxiliary complexing agents were used and all chemicals used were of analytical grade.

10 mL extraction bottles with lids were used for the study. Eighty of these bottles were divided into 4 sets of 5 for the five concentrations of the auxiliary complexing agent ions EDTA, Oxalate, Thiocyanate and Tartrate ions labelled; ligand H_2BuEtP alone at pH 4.75, ligand H_2BuEtP alone at pH 7.5, mixed ligands $H_2BuEtP/HBuP$ at pH 4.75 and mixed ligands $H_2BuEtP/HBuP$ at pH 7.5. 1000 mgL^{-1} stock solutions of Pb^{2+}, Ni^{2+}, Fe^{2+} and Cd^{2+} ions were prepared using equivalent weight of their salts in distilled water with addition of 2 mL of 2 M HNO_3 to prevent hydrolysis. Each bottle contained 2 mL aqueous solutions containing 50 mgL^{-1} each of four metals ions by taking 0.1 mL from 1000 mgL^{-1} stock solutions of the metals along with 0.001 – 0.1 M of each auxiliary complexing agent ions from appropriate volume of stock solutions of the different ions, made up to the 2-mL mark with buffers of 4.75 or 7.5. 2 mL of either 0.05 M H_2BuEtP in chloroform or 9:1 volume ratio chloroform solutions of 0.05 M H_2BuEtP and 0.05 M HBuP were added to get 2 sets of ligand H_2BuEtP alone and mixed ligands $H_2BuEtP/HBuP$ organic phases. The bottles with both phases were agitated mechanically for an hour. One hour has been reported to be suitable for equilibration to occur (Godwin and Uzoukwu, 2012a, b; Godwin et al., 2012, 2013). The phases were allowed to separate out; 0.1 mL for Cadmium, Lead and Nickel and 0.4 mL for Iron was taken from each aqueous raffinate; analysed by comparing absorbances with standards of each metal; Equations 1 and 2 were used to calculate Distribution Ratios (D) and Percentage Extraction (%E), tabulated in tables and plotted in Figures. Cadmium, Lead and Nickel was analysed with an Atomic Absorption Spectrophotometer while Iron was analysed colorimetrically with a UV Spectrophotometer at 520 nm with 0.1 mL of 0.01% 1,10-phenanthroline after addition of 0.1 mL each of 10% CH_3COONa and 10% NH_2OH solutions (Saywell and Cunningham, 1937).

$$\text{Distribution Ratio D} = \frac{\text{Standard Absorbance} - \text{Raffinates Absorbance}}{\text{Raffinate Absorbance}} \qquad (1)$$

$$\text{Percentage Extraction } \%E = \frac{\text{Standard Absorbance} - \text{Raffinates Absorbance}}{\text{Standard Absorbance}} \times 100 \qquad (2)$$

Distribution ratios data for pH 4.75 and 7.5 and ligand H_2BuEtP alone and in the presence of HBuP for each auxiliary complexing agent ion was compared with others statistically using the p test. That is, if the two groups were significantly different in these extractions or not. The null hypothesis (H_0), that the two groups of interest are not significantly different is rejected if the value of the test statistics is less than the significant level $\alpha = 0.05$, and the alternative hypothesis (H_a), the two groups of interest are significantly different is accepted. If the p value is greater than the significant level $\alpha = 0.05$, the null hypothesis is accepted and we conclude that there is no significant difference between the groups of interest [Sprinthall, 2011].

Equation 3 was used to calculate n batches of extractions needed theoretically to achieve 99.9% extraction of metal ions shown in Tables 1 to 8, where C_{aq} is the amount of metal ions originally present in the aqueous phases and C is the amount of metal ions that remains in an aqueous phase after extractions.

$$C/C_{aq} = [\frac{1}{D+1}]^n \qquad (3)$$

RESULTS AND DISCUSSION

The results obtained and the extraction parameters are stated in Tables 1 to 8 while the percentage extractions of the various metals are expressed in Figures 1 to 8.

The EDTA results for organic phases of H_2BuEtP alone for pH 4.75 and 7.5 shown in Table 1 and Figure 1 indicated that Iron formed very stable complexes at both buffer pHs as the extraction of Iron was masked at all concentrations of EDTA used for the study with percentage extraction of 0.26%. In a related study with Iron (II) alone and same organic phases, >85% extraction of Iron was obtained at 0.001 M EDTA and thereafter a steady decrease in extraction as the concentration of EDTA increases (Godwin et al., 2014). The results above confirm as reported in many studies (Hovey and Tremaine, 1985; Blesa et al., 1984) that Iron (III) forms more stable complexes than Iron (II) with EDTA. Thus, extraction with this ligand system in the presence of EDTA ions is better suited with Iron (II) as they form unstable complexes and make the formation of $Fe(BuEtP)_2$ possible, leading to quantitative extraction of Iron at 0.001 M EDTA. Although masking was also very pronounced for the other three metals except for 0.001 M EDTA at pH 7.5 that was slightly better with percentage extraction for Cadmium 56.90%, Nickel 21.46% and Lead 29.53% as the best results, there was no significant difference between pH 4.75 and 7.5 results with using EDTA as all p values were > 0.05 (Cd 0.1494, Ni 0.1334, Pb 0.2175 and Fe 1.000). Results with $H_2BuEtP/HBuP$ shown in Table 2 and Figure 2 were almost similar to results with H_2BuEtP alone with Iron masked in all EDTA concentrations at both buffer pHs and the other three metals had < 30% extraction apart from Cadmium and Lead that had 64.87 and 79.81% respectively in 0.001 M EDTA at pH 7.5 in $H_2BuEtP/HBuP$ organic phase.

Table 1. Extraction parameters for the four metals in EDTA ion at (a) pH 4.75 and (b) pH 7.5 for ligand H_2BuEtP alone.

5.00 mgL^{-1} Cd, Ni, Pb and Fe Standards Absorbance				Cd = 0.0464		Ni = 0.4288		Pb = 0.8118		Fe = 0.380	
EDTA (M)	Raffinates absorbance			Distribution ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D_{Cd}	D_{Ni}	D_{Pb}	D_{Fe}	n_{Cd}	n_{Ni}	n_{Pb}	n_{Fe}
pH 4.75												
0.001	0.0463	0.4287	0.8117	0.379	0.0022	0.0002	0.0001	0.0026	3144	4543	9081	2661
0.005	0.0463	0.4287	0.8117	0.379	0.0022	0.0002	0.0001	0.0026	3144	4543	9081	2661
0.01	0.0436	0.4243	0.8117	0.379	0.0642	0.0106	0.0001	0.0026	111	656	9081	2661
0.05	0.0379	0.3995	0.7696	0.379	0.2243	0.0733	0.0548	0.0026	34	98	130	2661
0.1	0.0463	0.4287	0.8117	0.379	0.0022	0.0022	0.0001	0.0026	3144	3144	9081	2661
pH 7.5												
0.001	0.0200	0.3368	0.5721	0.379	1.3200	0.2732	0.4190	0.0026	9	29	20	2661
0.005	0.0410	0.3535	0.6911	0.379	0.1317	0.2130	0.1747	0.0026	56	36	43	2661
0.01	0.0414	0.3992	0.8024	0.379	0.1208	0.0741	0.0117	0.0026	61	97	594	2661
0.05	0.0337	0.4269	0.8117	0.379	0.3769	0.0045	0.0001	0.0026	22	1539	9081	2661
0.1	0.0389	0.4287	0.8117	0.379	0.1928	0.0002	0.0001	0.0026	40	4543	9081	2661

Table 2. Extraction parameters for the four metals in EDTA ion at (a) pH 4.75 and (b) pH 7.5 for mixed ligands $H_2BuEtP/HBuP$.

5.00 mgL^{-1} Cd, Ni, Pb and Fe standards absorbance				Cd = 0.0464		Ni = 0.4288		Pb = 0.8118		Fe = 0.380	
EDTA (M)	Raffinates absorbance			Distribution ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D_{Cd}	D_{Ni}	D_{Pb}	D_{Fe}	n_{Cd}	n_{Ni}	n_{Pb}	n_{Fe}
pH 4.75												
0.001	0.0364	0.4234	0.7145	0.379	0.2747	0.0128	0.1362	0.0026	29	543	54	2661
0.005	0.0334	0.4287	0.8011	0.379	0.3892	0.0002	0.0134	0.0026	21	4543	519	2661
0.01	0.0463	0.4287	0.8117	0.379	0.0022	0.0002	0.0001	0.0026	3144	4543	9081	2661
0.05	0.0328	0.4096	0.8016	0.379	0.4146	0.0469	0.0127	0.0026	20	151	548	2661
0.1	0.0460	0.4287	0.8028	0.379	0.0087	0.0002	0.0112	0.0026	798	4543	621	2661
pH 7.5												
0.001	0.0163	0.4287	0.1639	0.379	1.8466	0.0002	3.9530	0.0026	7	4543	4	2661
0.005	0.0463	0.4287	0.5987	0.379	0.0022	0.0002	0.3559	0.0026	3144	4543	23	2661
0.01	0.0421	0.3238	0.8117	0.379	0.1021	0.3243	0.0001	0.0026	71	25	9081	2661
0.05	0.0426	0.4287	0.7997	0.379	0.0892	0.0002	0.0151	0.0026	81	4543	461	2661
0.1	0.0463	0.4287	0.7370	0.379	0.0022	0.0002	0.1015	0.0026	3144	4543	72	2661

Statistically, as with H_2BuEtP alone, pH 4.75 results are not significantly different from those of pH 7.5 with all p > 0.05 (Results for both organic phases were also not significantly different with all p > 0.05 (pH 4.75; $Cd_{0.1495}$, $Ni_{0.7628}$, $Pb_{0.418}$ and $Fe_{1.000}$ and pH 7.5: $Cd_{0.9637}$, $Ni_{0.5894}$, $Pb_{0.3525}$ and $Fe_{1.000}$). In the single metal extractions study, the general trend was increase in masking as the concentration of EDTA increased (Godwin et al., 2012, 2014, 2019), however, the results in this study had no particular trend.

The results showed EDTA is not suited for the multi-metals extraction of the four metals with H_2BuEtP alone and in the presence of HBuP at both pHs, and this may be attributed to no differences in permittivities of the aqueous media in the presence of the four metals and those of the single metals system resulting from the formation of very stable complexes of EDTA with the four metals and resulting in the masking of the metals as reported in previous studies (Sapeika, 1954; Jawaid, 1980; Blesa et al., 1984; Hovey and Tremaine, 1985; Zhao et al., 2014).

Results for Oxalate with H_2BuEtP alone in Table 3a also showed complete masking of Iron and Nickel at pH 4.75 while Cadmium and Lead extractions were relatively better, and with a percentage extraction of > 67% as shown in Figure 3a, 99.9% extraction of both metals is

Table 3. Extraction parameters for the four metal in Oxalate ion at (a) pH 4.75 and (b) pH 7.5 for ligand H_2BuEtP alone.

$C_2O_4^{2-}$ (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction				
	Cd	Ni	Pb	Fe	D_{Cd}	D_{Ni}	D_{Pb}	D_{Fe}	$\%E_{Fe}$	n_{Cd}	n_{Ni}	n_{Pb}	n_{Fe}
pH 4.75													
0.001	0.0380	0.4287	0.6441	0.379	0.2211	0.0002	0.2604	0.0026	0.26	35	4543	30	2661
0.005	0.0209	0.4287	0.2124	0.379	1.2201	0.0002	2.8220	0.0026	0.26	9	4543	6	2661
0.01	0.0150	0.4287	0.2175	0.379	2.0933	0.0092	2.7324	0.0026	0.26	7	4543	6	2661
0.05	0.0380	0.4287	0.6957	0.379	0.2211	0.0002	0.1669	0.0026	0.26	35	4543	45	2661
0.1	0.0261	0.4287	0.5463	0.379	0.7778	0.0002	0.4860	0.0026	0.26	12	4543	18	2661
pH 7.5													
0.001	0.0024	0.4247	0.0049	0.121	18.3333	0.0097	164.6735	2.1405		3	716	2	6
0.005	0.0427	0.4182	0.7710	0.379	0.0867	0.0254	0.0529	0.0026		83	276	134	2661
0.01	0.0332	0.4287	0.6781	0.379	0.3976	0.0002	0.1972	0.0026		21	4543	38	2661
0.05	0.0223	0.3638	0.5667	0.379	1.0807	0.1787	0.4325	0.0026		10	42	20	2661
0.1	0.0444	0.4287	0.8108	0.379	0.0451	0.0002	0.0012	0.0026		157	4543	5760	2661

Table 4. Extraction parameters for the four metals in Oxalate ion at (a) pH 4.75 and (b) pH 7.5 for mixed ligands $H_2BuEtP/HBuP$.

5.00 mgL^{-1} Cd, Ni, Pb and Fe Standards Absorbance					Cd = 0.0464	Ni = 0.4288		Pb = 0.8118	Fe = 0.380			
$C_2O_4^{2-}$ (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D_{Cd}	D_{Ni}	D_{Pb}	D_{Fe}	n_{Cd}	n_{Ni}	n_{Pb}	n_{Fe}
pH 4.75												
0.001	0.0424	0.3947	0.1208	0.108	0.0943	0.0864	5.7202	2.5185	77	84	4	6
0.005	0.0387	0.1586	0.4315	0.154	0.1990	1.7037	0.8813	1.4675	38	7	11	8
0.01	0.0292	0.4287	0.5093	0.342	0.5890	0.0002	0.5940	0.1111	15	4543	15	66
0.05	0.0137	0.2932	0.4042	0.379	2.3869	0.4625	1.0084	0.0022	6	19	10	2661
0.1	0.0353	0.4287	0.5705	0.379	0.3145	0.0002	0.4230	0.0022	26	4543	20	2661
pH 7.5												
0.001	0.0359	0.0910	0.4122	0.379	0.2925	3.7121	0.9694	0.0022	27	5	11	2661
0.005	0.0152	0.4287	0.0708	0.379	2.0526	0.0002	10.4661	0.0022	7	4543	3	2661
0.01	0.0026	0.2501	0.0499	0.171	16.8462	0.7145	15.2685	1.2222	3	13	3	9
0.05	0.0012	0.3304	0.0017	0.085	37.6667	0.2978	476.5294	3.4706	2	27	2	5
0.1	0.0411	0.3670	0.5117	0.379	0.1290	0.1684	0.5865	0.0022	57	45	15	2661

theoretically achievable after seven batches of extractions. At pH 7.5 shown in Table 3b, masking was still pronounced for Iron and Nickel at all concentrations of Oxalate ions with the exception being Iron with 68.16% extraction for 0.001 M Oxalate ion from Figure 3b. Figure 4b showed that with $H_2BuEtP/HBuP$ organic phases, while Iron is completely masked at Oxalate ion concentrations of 0.05 M and 0.1 M and Nickel at 0.01 M and 0.1 M with the buffer of pH 4.75, complete masking of Iron occurred at 0.001 M, 0.005 M and 0.1 M and Nickel at only 0.005 M with buffer of pH 7.5. At pH 4.75, Iron best extraction of 71.57% was in 0.001 M Oxalate and 77.63% in 0.05 M Oxalate at pH 7.5. Cadmium and Lead extractions as observed with H_2BuEtP alone were also better with $H_2BuEtP/HBuP$ in pH 4.75 giving 70.47% extraction of Cadmium and 85.12% Lead with 0.05 M and 0.001 M Oxalate respectively and pH 7.5 giving 97.41% extraction of Cadmium and 99.79% Lead with 0.05 M Oxalate. Figure 4b indicates that pH 7.5 gave improved extractions for the four metals. Table 4b showed that 0.01 M Oxalate with a pH 7.5 using $H_2BuEtP/HBuP$ organic extractant phase will theoretically require 13 batches of extractions to achieve 99.9% extraction of the four metals The results confirm that at an alkaline environment, Oxalate salting out ability is enhanced and formation of the adducts Pb(HBuEtP)(BuP), Ni(HBuEtP)(BuP), Fe (HBuEtP)(BuP) and Cd(HBuEtP).BuP leads to transfer of the metals to the mixed ligands $H_2BuEtP/HBuP$ organic

Table 5. Extraction parameters for the four metals in Tartrate ion at (a) pH 4.75 and (b) pH 7.5 for ligand H_2BuEtP alone.

5.00 mgL⁻¹ Cd, Ni, Pb and Fe Standards Absorbance				Cd = 0.0464		Ni = 0.4288		Pb = 0.8118		Fe = 0.380	
Tartrate (M)	Raffinates Absorbance			Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D_{Cd}	D_{Ni}	D_{Pb}	D_{Fe}	n_{Cd}	n_{Ni}	n_{Pb}	n_{Fe}
pH 4.75												
0.001	0.0460	0.4287	0.194	0.379	0.0087	0.0002	3.1845	0.0026	798	4543	5	2661
0.005	0.0360	0.3892	0.305	0.379	0.2889	0.1018	1.6616	0.0026	28	72	7	2661
0.01	0.0440	0.4287	0.267	0.340	0.0546	0.0002	2.0405	0.1177	130	4543	7	62
0.05	0.0390	0.3388	0.427	0.379	0.1897	0.2656	0.9012	0.0026	40	30	11	2661
0.1	0.0390	0.4287	0.561	0.348	0.1897	0.0002	0.4471	0.0920	40	4543	19	79
pH 7.5												
0.001	0.0004	0.148	0.0043	0.041	115	1.8973	187.7907	8.2683	2	7	2	3
0.005	0.0055	0.326	0.0467	0.018	7.4364	0.3153	16.3833	20.1111	4	26	3	3
0.01	0.0161	0.368	0.0781	0.100	1.8820	0.1652	9.3944	2.8000	7	46	3	6
0.05	0.0463	0.428	0.6697	0.015	0.0022	0.0019	0.2122	24.3333	3144	3639	36	3
0.1	0.0024	0.365	0.0075	0.017	18.3333	0.1748	107.2400	21.3529	3	43	2	3

Table 6. Extraction parameters for the four metals in Tartrate ion at (a) pH 4.75 and (b) pH 7.5 for mixed ligands $H_2BuEtP/HBuP$.

5.00 mgL⁻¹ Cd, Ni, Pb and Fe Standards Absorbance				Cd = 0.0464		Ni = 0.4288		Pb = 0.8118		Fe = 0.380	
Tartrate (M)	Raffinates Absorbance			Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D_{Cd}	D_{Ni}	D_{Pb}	D_{Fe}	n_{Cd}	n_{Ni}	n_{Pb}	n_{Fe}
pH 4.75												
0.001	0.0397	0.4287	0.4331	0.379	0.1688	0.0002	0.8744	0.0022	44	34542	11	2661
0.005	0.0463	0.4287	0.5830	0.379	0.0022	0.0002	0.3925	0.0022	3143	34542	21	2661
0.01	0.0441	0.4287	0.5179	0.379	0.0522	0.0002	0.5675	0.0022	136	34542	15	2661
0.05	0.0350	0.4287	0.5869	0.379	0.3257	0.0002	0.3832	0.0022	25	34542	21	2661
0.1	0.0331	0.4287	0.4528	0.379	0.4018	0.0002	0.7929	0.0022	21	34542	12	2661
pH 7.5												
0.001	0.0014	0.0195	0.0016	0.139	32.1429	20.9897	506.375	1.7338	2	2	1	7
0.005	0.0036	0.0699	0.0141	0.139	11.8889	5.1345	56.5745	1.7338	3	4	2	7
0.01	0.0051	0.0755	0.1124	0.001	8.0980	4.6795	6.2224	379	3	4	4	1
0.05	0.0097	0.0766	0.0065	0.048	3.7835	4.5979	123.8923	6.9167	5	4	2	3
0.1	0.0192	0.4287	0.0081	0.079	1.4167	0.0002	99.2222	3.8101	8	34542	2	5

phase due to the favourable energetics in their transfer (Housecroft and Sharpe, 2001). There was also no trend in the extractions in relation to the concentration of the Oxalate ion as also observed with results for EDTA even though in the single metals extraction studies it was generally observed that masking is more pronounced at higher Oxalate ion concentration (Godwin et al., 2014, 2019). Statistically, there was no significant differences between the two buffers with H_2BuEtP ($Cd_{0.4178}$, $Ni_{0.2682}$, $Pb_{0.3625}$ and $Fe_{0.3466}$) and $H_2BuEtP/HBuP$ ($Cd_{0.1807}$, $Ni_{0.51}$, $Pb_{0.3228}$ and $Fe_{0.8909}$) and between the two organic extractants in pH 4.75 ($Cd_{0.7395}$, $Ni_{0.2045}$, $Pb_{0.7225}$ and

$Fe_{0.1456}$) and pH 7.5 ($Cd_{0.3876}$, $Ni_{0.2147}$, $Pb_{0.5158}$ and $Fe_{0.5158}$) in the extractions of the four metals. Oxalate results were not statistically different from those of EDTA with $p > 0.05$ except for H_2BuEtP alone in pH 4.75 for Cadmium with $p = 0.0433$.

Nickel and Iron was masked in most Tartrate concentrations, slight masking of Cadmium at 0.001 M Tartrate and moderate extraction for Lead with decreasing extraction as the concentration of Tartrate increased with 0.001 M Tartrate having the highest percentage extraction of 78.10% as shown in Figure 5a. The results indicate that at pH 4.75, Tartrate formed more stable

Table 7. Extraction parameters for the four metals in Thiocyanate ion at (a) pH 4.75 and (b) pH 7.5 for Ligand H_2BuEtP alone.

5.00 mgL^{-1} Cd, Ni, Pb and Fe Standards Absorbance				Cd = 0.0464		Ni = 0.4288		Pb = 0.8118		Fe = 0.380	
SCN$^-$ (M)	Raffinates Absorbance			Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D_{Cd}	D_{Ni}	D_{Pb}	D_{Fe}	n_{Cd}	n_{Ni}	n_{Pb}	n_{Fe}
pH 4.75												
0.001	0.0353	0.4227	0.7595	0.379	0.3145	0.0144	0.0689	0.0026	26	484	104	2661
0.005	0.0444	0.4227	0.7698	0.379	0.0451	0.0144	0.0546	0.0026	157	484	130	2661
0.01	0.0463	0.4227	0.8117	0.379	0.0022	0.0144	0.0001	0.0026	3144	484	9081	2661
0.05	0.0463	0.4227	0.8117	0.379	0.0022	0.0144	0.0001	0.0026	3144	484	9081	2661
0.1	0.0437	0.4005	0.8117	0.379	0.0618	0.0707	0.0001	0.0026	116	102	9081	2661
pH 7.5												
0.001	0.0353	0.3512	0.7056	0.379	0.3145	0.2210	0.1505	0.0026	26	35	50	2661
0.005	0.0396	0.3562	0.6745	0.379	0.1717	0.2038	0.2036	0.0026	44	38	38	2661
0.01	0.0436	0.3237	0.7113	0.379	0.0642	0.3247	0.1413	0.0026	111	25	53	2661
0.05	0.0421	0.3923	0.5881	0.379	0.1021	0.0930	0.3804	0.0026	71	78	22	2661
0.1	0.0393	0.4278	0.6574	0.375	0.1807	0.0023	0.2349	0.0133	42	3007	33	2661

Table 8. Extraction parameters for the four metals in Thiocyanate ion at (a) pH 4.75 and (b) pH 7.5 for mixed Ligands $H_2BuEtP/HBuP$.

SCN$^-$ (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D_{Cd}	D_{Ni}	D_{Pb}	D_{Fe}	n_{Cd}	n_{Ni}	n_{Pb}	n_{Fe}
pH 4.75												
0.001	0.0374	0.2245	0.6675	0.379	0.2406	0.9100	0.2162	0.0022	32	11	36	2661
0.005	0.0442	0.4194	0.7611	0.379	0.0498	0.0224	0.0666	0.0022	143	312	108	2661
0.01	0.0382	0.4287	0.7313	0.379	0.2147	0.0002	0.1101	0.0022	36	4543	67	2661
0.05	0.0445	0.3510	0.7522	0.379	0.0427	0.2217	0.0792	0.0022	166	35	91	2661
0.1	0.0463	0.4287	0.6089	0.379	0.0022	0.0002	0.3332	0.0022	3144	4543	24	2661
pH 7.5												
0.001	0.0430	0.1066	0.5177	0.371	0.0791	3.0225	0.5681	0.0243	91	5	16	288
0.005	0.0451	0.0809	0.7137	0.379	0.0288	4.3004	0.1375	0.0022	244	4	54	2661
0.01	0.0392	0.0950	0.6660	0.379	0.1837	3.5137	0.2189	0.0022	41	5	35	2661
0.05	0.0365	0.0994	0.7823	0.379	0.2712	3.3139	0.0377	0.0022	29	5	187	2661
0.1	0.0418	0.0873	0.7955	0.379	0.1101	3.9118	0.0205	0.0022	67	5	341	2661

complexes with Iron and Nickel than with Cadmium and Lead and thus, masked the extraction of Iron and Nickel. The results for buffer pH 7.5 shown in Table 5b indicated improved extraction of the four metals at Tartrate concentration of 0.001 M and as shown in Figure 5b, percentage extractions were in the order; Cadmium 99.14%, Lead 99.47%, Iron 89.21% and Nickel 65.49%. The results were similar to those of the metals alone as Tartrate was acting as a salting out agent for the four metals at lower concentrations leading to the formation of extractable and hydrophobic complexes Cd(HBuEtP)X (Godwin et al., 2019), Ni(HBuEtP)$_2$ (Godwin et al., 2012), Pb(BuEtP)(BuEtP)$_2$$^{4-}$·4H$^+$ (Godwin and Uzoukwu, 2012b) and Fe(BuEtP) (Godwin et al., 2014) with favourable energetics in their transfer from the aqueous phase to the organic phase (Housecroft and Sharpe, 2001).

Table 5b also show that at 0.001 M Tartrate with a buffer of pH 7.5, 99.9% of the four metals can be theoretically extracted after 7 batches, Cadmium, Lead and Iron after 3 batches and Cadmium and Lead after 2 batches. Despite the seemingly better extractions at pH 7.5, there was no significant difference (p > 0.05) between the two buffers for Cadmium$_{0.2301}$, Nickel$_{0.2517}$ and Lead$_{0.1241}$ with only Iron extractions showing significant difference with p = 0.0062. The extractions with H$_2$BuEtP/HBuP for pH 4.75 shown in Table 6a and Figure 6a as also observed with H$_2$BuEtP, showed that at all concentrations of Tartrate, Nickel, Iron and Cadmium
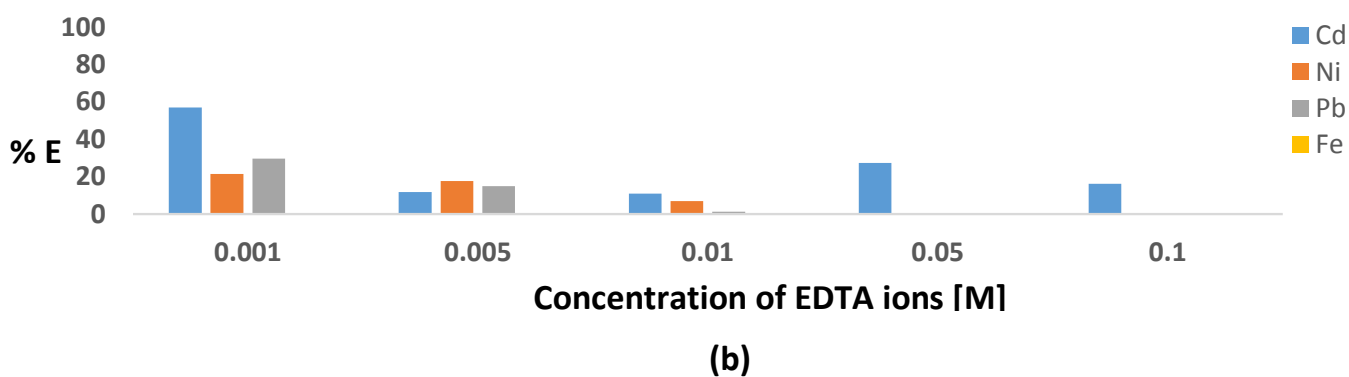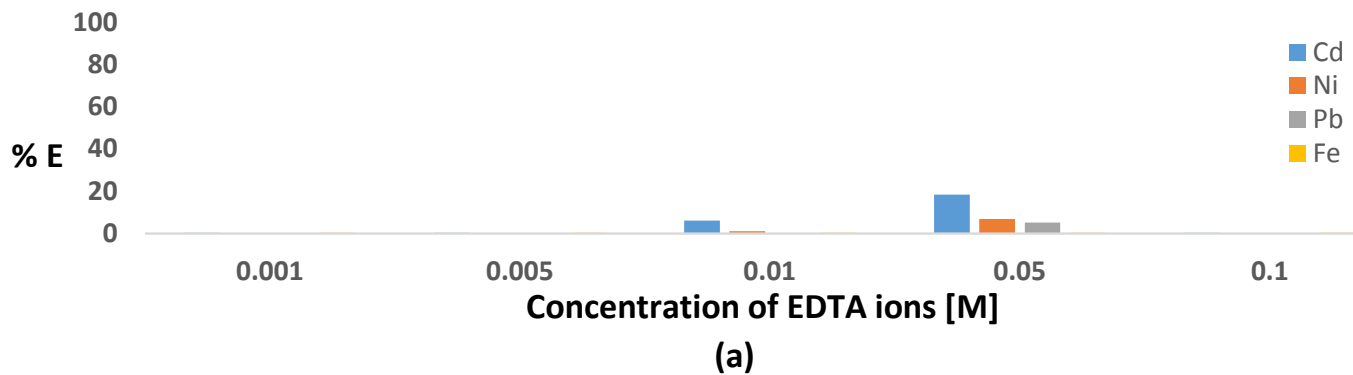
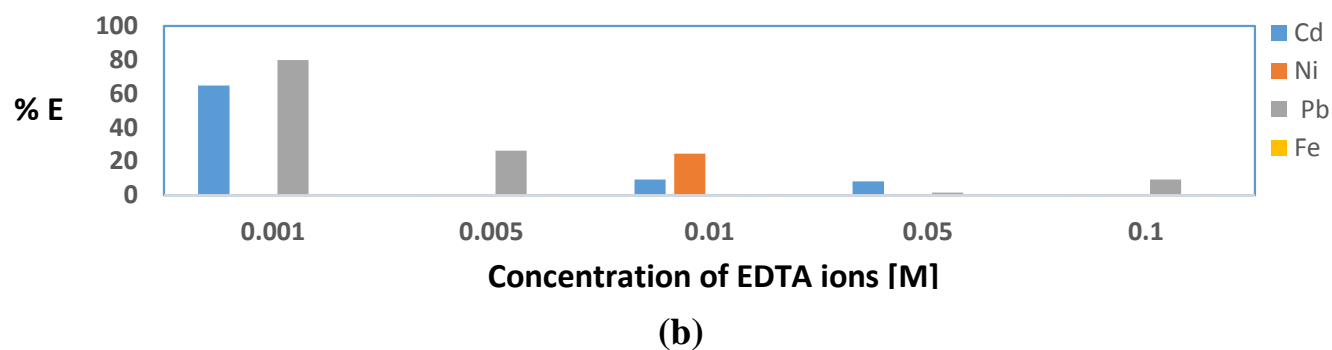**Figure 1.** Plots of percentage extraction of metals in EDTA ions using H₂BuEtP alone at (a) pH 4.75 and (b) 7.5.
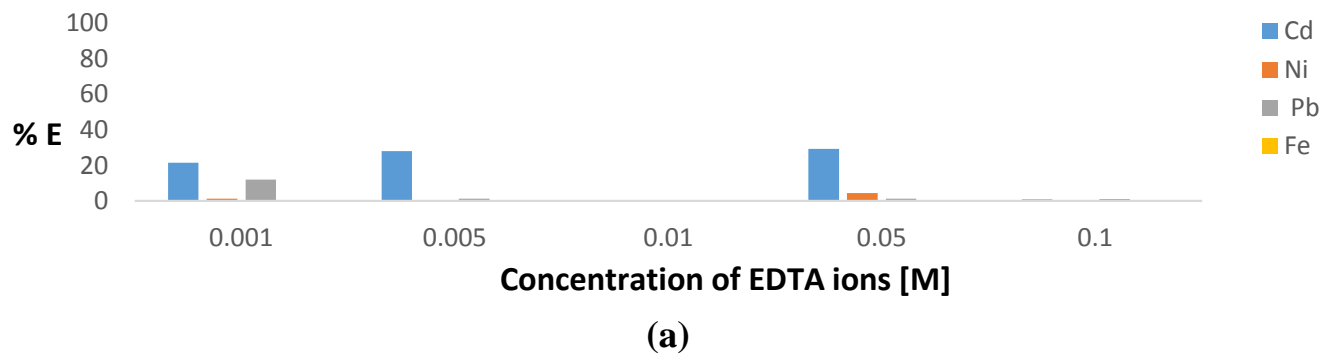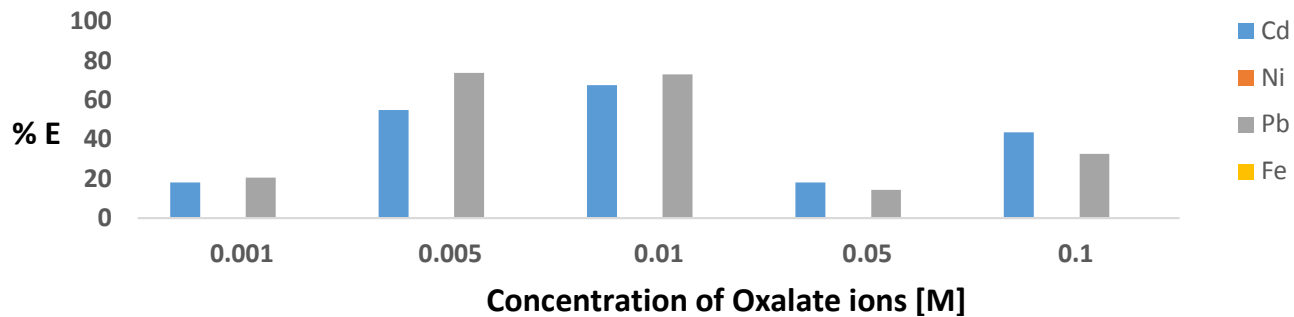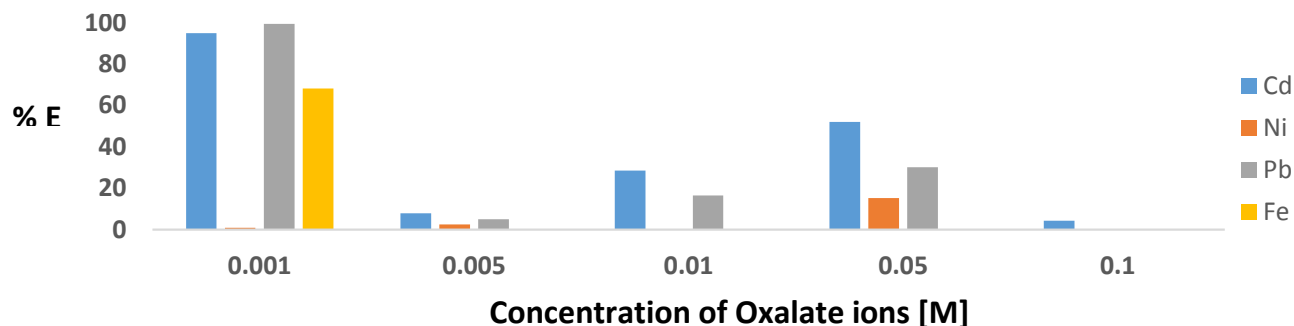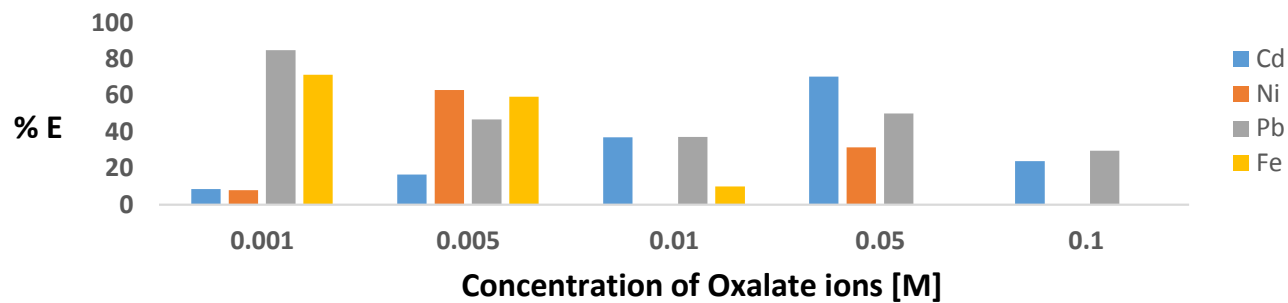

Figure 2. Plots of percentage extraction of metals in EDTA ions using H₂BuEtP/HBuP at (a) pH 4.75 and (b) 7.5.
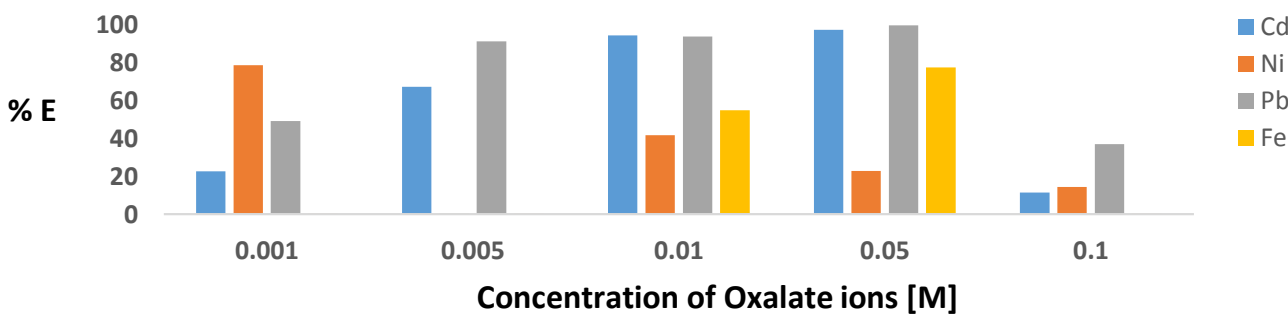
Figure 3. Plots of percentage extraction of metals in oxalate ions using H_2BuEtP alone at (a) pH 4.75 and (b) 7.5.
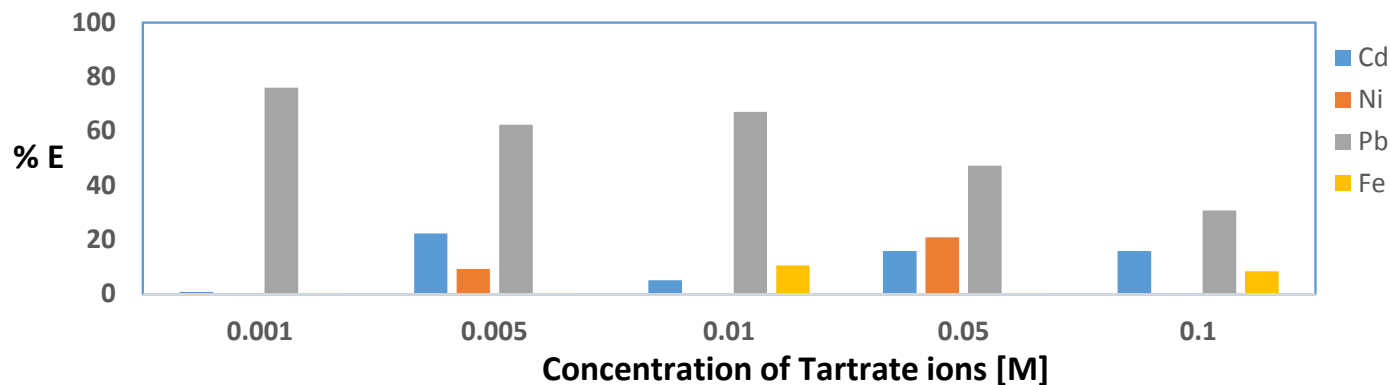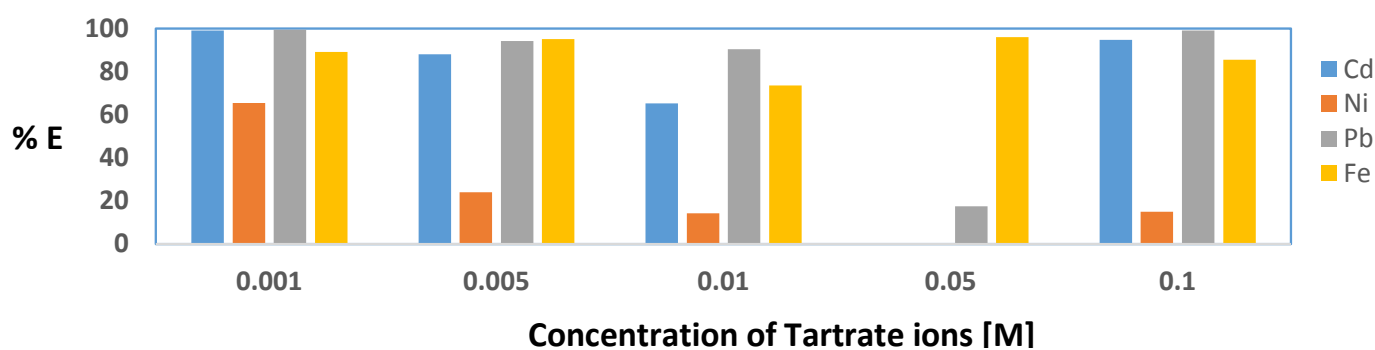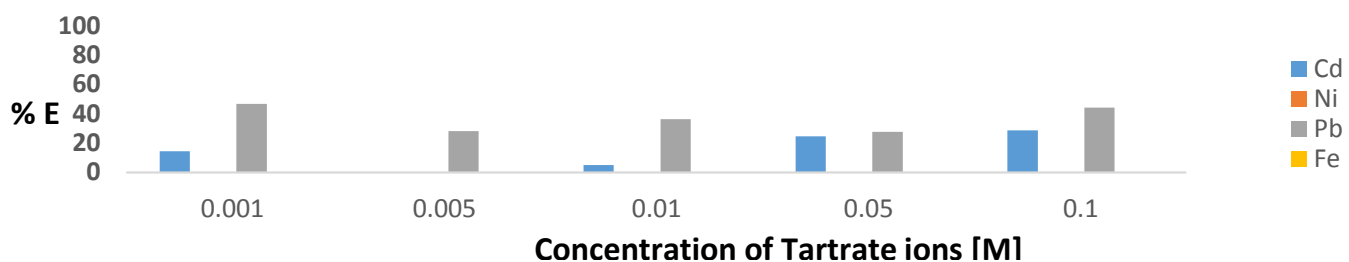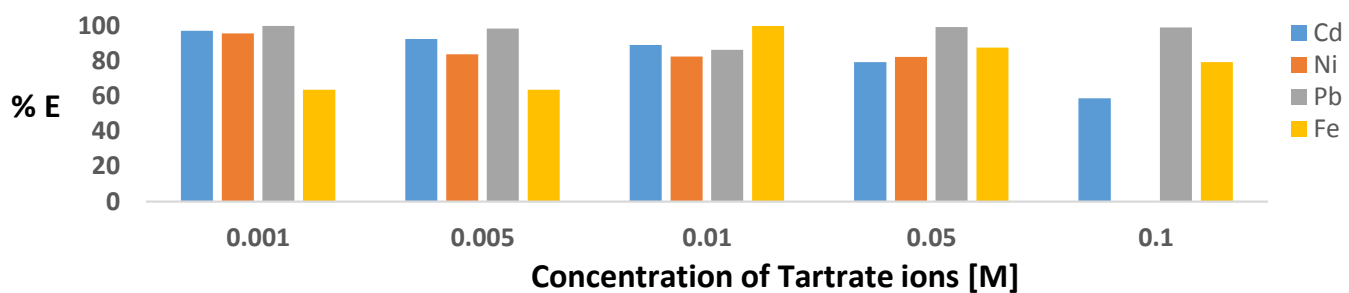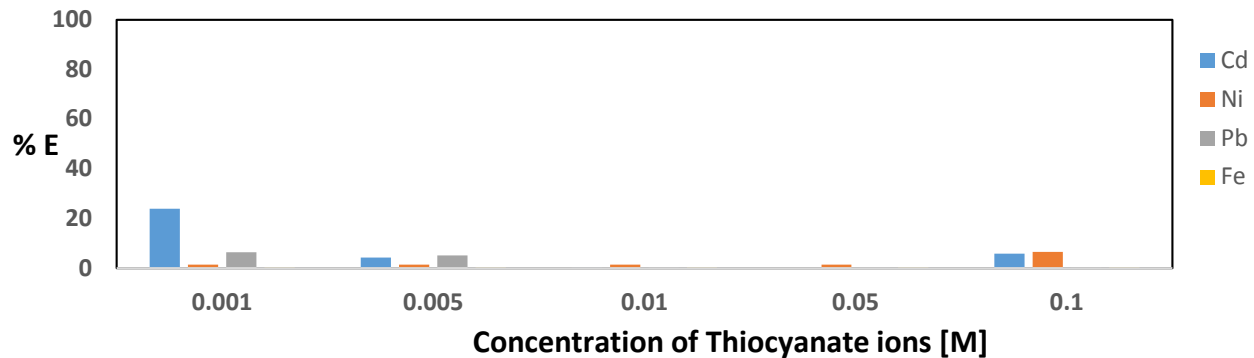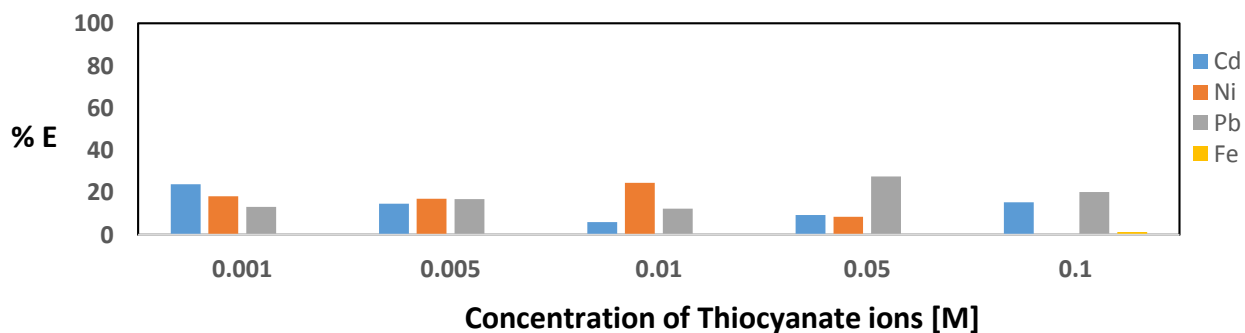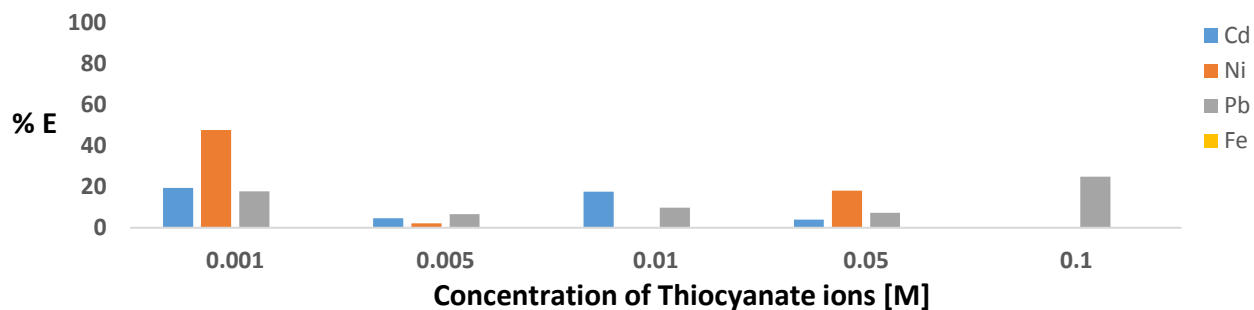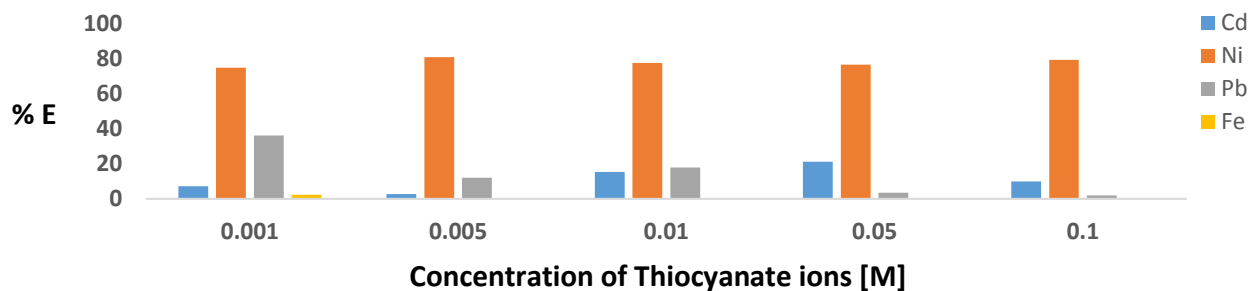

Figure 4. Plots of percentage extraction of metals in Oxalate ions using $H_2BuEtP/HBuP$ at (a) pH 4.75 and (b) 7.5.

(a)

(b)

Figure 5. Plots of Percentage extraction of metals in Tartrate ions with H_2BuEtP alone at (a) pH 4.75 and (b) 7.5.

(a)

(b)

Figure 6. Plots of percentage extraction of metals in Tartrate ions using $H_2BuEtP/HBuP$ at (a) pH 4.75 and (b) 7.5.

Figure 7. Plots of percentage extraction of metals in Thiocyanate ions with H_2BuEtP alone at (a) pH 4.75 and (b) 7.5.

Figure 8. Plots of percentage extraction of metals in Thiocyanate ions using $H_2BuEtP/HBuP$ at (a) pH 4.75 and (b) 7.5.

with 0.005 M Tartrate, was completely masked and indicating formation of very stable Tartrate complexes of the metals at this pH. Figure 6a also showed that Lead extractions were slightly better than the other 3 metals with percentage extraction between 27.70 - 46.65%. However, buffer of pH 7.5 results in Table 6b and Figure 6b showed quantitative extractions (58.62 - 99.80%) of the four metals at all concentrations of Tartrate except Nickel that was completely masked at 0.1 M Tartrate. The results also showed salting out behaviour of Tartrate leading to the formation of hydrophobic adduct complexes Cd(HBuEtP.BuP) (Godwin et al., 2019), Ni(HBuEtP)(BuP) (Godwin et al., 2012), *Pb(HBuEtP).BuP* (Godwin and Uzoukwu, 2012b) and Fe(HBuEtP)(BuP) (Godwin et al., 2014) that may also have very favorable energetics in their transfer from the aqueous media to the mixed ligands organic phase (Housecroft and Sharpe, 2001). Calculated number of batches needed to achieve 99.9% extractions of the four metals in Table 6b showed that with 0.001 M – 0.005 M Tartrate, 7 batches of extractions are theoretically required and 2 batches of extractions are needed for Cadmium, Nickel and Lead with 0.001 M Tartrate. 0.01 M and 0.05 M Tartrate gave the best results with 4 and 5 batches required to have 99.9% extraction of the four metals. Statistically however, there was no difference between the two buffers in the extractions of the four metals as all p values were all > 0.05. Tartrate effects on the extractions of the four metals with buffer pH 4.75 and pH 7.5 using H_2BuEtP alone were not significantly different from those of Oxalate and EDTA except for $Lead_{0.0088}$ with EDTA for pH 4.75 and $Iron_{0.0073}$ with Oxalate in pH 7.5. However, for mixed ligands $H_2BuEtP/HBuP$, there was no significant difference between Tartrate and EDTA/Oxalate for both pHs except with EDTA for $Lead_{0.0006}$ extractions in pH 4.75.

Table 7a showing the effects of Thiocyanate ions for pH 4.75 using H_2BuEtP alone indicates complete masking of the metals in almost all concentrations of Thiocyanate as observed for the other three auxiliary complexing agents at this pH. Confirming that with the ligand H_2BuEtP alone, pH 4.75 was not suitable for the multi-metal extraction of the four metals due to the formation of stable complexes of the complexing agents with the metals. With buffer of pH 7.5, complete masking of Iron was observed at all concentrations of Thiocyanate and Nickel at only 0.1 M Thiocyanate. Cadmium, Lead and Nickel had slightly better extractions than those shown for pH 4.75 by comparing percentage extraction values in Figure 7. Figure 6b also show that all the percentage extraction were < 28% and implies that the conditions were not also suitable for the multi-metal extraction of the metals with the H_2BuEtP alone organic phase system. Statistically, while $Cadmium_{0.2939}$ and $Iron_{0.3466}$ extractions were not significantly different, those for $Nickel_{0.03534}$ and $Lead_{0.0026}$ were significantly different for the two buffers. With the $H_2BuEtP/HBuP$ organic

phase, Table 8a showing the extraction parameter with buffer of pH 4.75 indicates complete masking of Iron at all concentrations of Tartrate, Nickel at 0.01 M and 0.1 M Tartrate and Cadmium at 0.1 M Tartrate. Figure 8a also shows that the best extractions for the other three metals was in 0.001 M Tartrate with percentage extractions of Cadmium 19.40%, Nickel 47.65% and Lead 17.78%. Results with pH 7.5 buffer in Table 8b and Figure 8b also showed complete masking of Iron at all concentrations of Thiocyanate except 0.001 M Tartrate that had extraction of 2.37%. The results also did not show any trend in relating extractions to the concentration of Thiocyanate, but percentage extraction values in Figure 8b indicated that while masking due to formation of stable Thiocyanate complexes with Cadmium, Lead and Iron resulted in poor extractions of the three metals with the highest percentage extractions being Cadmium 21.34% in 0.05M Tartrate, Lead 36.23% and Iron 2.37% both at 0.001 M Tartrate, Nickel had moderately better percentage extractions of 75.14% - 81.13% at all concentrations of Thiocyanate requiring 4 – 5 batches of extractions to theoretically achieve 99.9% of Nickel from Table 8b. Thus, Thiocyanate is salting out the Nickel which results in the formation of the hydrophobic adduct complex Ni(HBuEtP)(BuP) with favourable energetics in its transfer from the aqueous media to the organic phases. As expected, there was significant difference in the extraction of Nickel only between the two buffers. Thiocyanate was also not suitable for the multi-metal extraction of the four metals using the ligand alone or the presence of HBuP also attributed to high stabilities of Thiocyante ions with the studied metals (Hon-Gee and Kwang-Hsien, 1957, 1961; Altun and Suozer, 2017; Kratochvil and Long, 1970). Statistically, Thiocyanate ion effects for pH 4.75 in H_2BuEtP alone were not significantly different from those of EDTA for the four metals but slightly significantly different for those of Oxalate for $Cadmium_{0.04980}$ and Tartrate for $Lead_{0.0092}$. With the mixed ligands $H_2BuEtP/HBuP$ in pH 4.75, Thiocyanate extractions were only significantly different from Tartrate extractions for only $Lead_{0.0045}$ while in pH 7.5 there was significant difference with EDTA and Oxalate for $Nickel_{0.0000/0.0069}$ extractions only.

Conclusion

The ions of EDTA, Oxalate and Thiocyanate were generally not suited for the multi-metal extraction of Cadmium, Iron, Nickel and Lead with the ligand H_2BuEtP alone or in the presence of HBuP as a result of their tendency to form very stable complexes with the metals and masking their extractions at both acidic and alkaline conditions.

Tartrate ion can be used for the multi-metal extraction of Cadmium, Iron, Nickel and Lead at alkaline pH of 7.5 and 99.9% extraction of the four metals theoretically

achievable after 7 batches of extraction with 0.001 M Tartrate using H_2BuEtP alone and 4 batches with 0.01 M Tartrate using $H_2BuEtP/HBuP$.

pH 7.5 was slightly better as extraction medium than pH 4.75 even though in most cases there was no significant differences in the multi-metal extractions of the four metals with the auxiliary complexing agents which can be attributed to the formation of less stable complexes of the ions with the metals and thus the ions functions as salting out agents at pH 7.5.

Generally, there was no significant difference between the ligand H_2BuEtP alone and mixed ligands $H_2BuEtP/HBuP$ organic phase in the extraction of the metals in both buffers with the only exception being Thiocyanate for Nickel with buffer of pH 7.5 that showed slight synergic effect of HBuP.

There is no reasonable solubility difference between the metal complexes formed with H_2BuEtP and adducts formed with the mixed ligands $H_2BuEtP/HBuP$ in the two phases.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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