

Role of Acids in Multimetal Distributions Using 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)

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Abstract: The role of some common acids CH₃COOH, HCl, HNO₃, H₃PO₄ and H₂SO₄ in the multi-metal distribution/extraction of Cadmium, Nickel, Lead and Iron from aqueous media buffered to either pH 4.75 or 7.5 using the ligand 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 and in the presence of 1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl) butan-1-one (HBuP) was studied using solvent-solvent extraction method. An equilibration time of 60 minutes was used. The extraction raffinate were analysed for Cadmium, Nickel and Lead with an Atomic Absorption Spectrophotometer (AAS) while Iron was colorimetrically determined with 1,10-phenanthroline and absorbances compared with standards and extraction parameters; distribution ratios, percentage % E and number of batches *n* needed to achieve 99.9% extraction of the four metals calculated. The distribution ratios of the metals were statistically analysed for differences between the two buffers, organic extractants and the acids. All the acids showed good potentials in the selective separation of Iron from Cadmium, Nickel and Lead. The conditions for the use of the different acids for the selective separations of Cadmium/Iron from Nickel/Lead, Nickel/Iron from Cadmium/Lead and Lead/Iron from Cadmium/Nickel were established with calculated number of batches needed to obtain 99.9% extractions of the metals. Only 0.01 M – 0.05 M H₃PO₄ showed good potentials in the multi-metal extraction of the four metals from an aqueous medium containing the four metals and buffered to pH 7.5 using the mixed ligands H₂BuEtP/HBuP organic phase and 99.9% extraction of the four metals calculated to be achievable after 9 batches of extractions with fresh organic phase. The synergic effect of the second ligand HBuP was observed in only a few cases.

Keywords: Distribution Ratio, Multimetal, Acids, Buffers and Ligands

1. Introduction

The quest to tackle heavy metals pollution due to their reported numerous toxic effects on plants and animals [5, 7] has led to many studies and development of various methods in the removal of heavy metals from the environment [8, 31, 37]. Solvent-solvent extraction is one of such methods that studies have shown to have recorded successes in the extraction of almost all the heavy metals [6, 33]. The methods are based on the distribution of an analyte between two immiscible liquids as stated in the Nernst distribution

law [19]. Various ligands/complexing agents have been studied for their effectiveness in the extraction of heavy metals and the first step in such studies is to ascertain the pH range in which the extractions are optimal for that metal in the presence of a particular complexing agent as these distributions are pH and equilibration time dependent [24, 27]. This is followed by the studies of the effects of reagents such as anions, auxiliary complexing agents and common acids in the distribution of a particular heavy metal between the two solvents at the optimal pH ranges and appropriate equilibration time. These reagents have been reported from

all the studies to have either releasing/salting out effects or inhibiting/masking effects at different concentrations [9, 30]. In most cases in these studies, a second ligand is added to the organic phase containing the main ligand/complexing agent and studied alongside to ascertain if synergic effects occurred or not [29, 35]. These solvent-solvent extraction methods have been exploited as synthetic routes for the synthesis of a range of metal complexes that have been found useful in medicine and other important applications [1, 2]. The method has also been found to be useful as a method for separating metals exploiting either the difference in the pH at which they are extracted with a particular ligand/complexing agent or using a particular concentration of a reagent (anions, auxiliary complexing agents or acids) that functions as a releasing/salting out agent for one metal and also completely masked the other metal, resulting in a Separation Factor $\beta_{XY} = D_X/D_Y$ that is $\geq 10^4$ [23, 25]. In some other instances, the specificity of most ligands in their reactions with a particular oxidation of a metal is also exploited [3, 4]. Most of the initial studies concentrated on the optimal conditions for the achievement of 99.9% extraction of a single metal [22, 26]. However, recent studies are geared towards multi-metal extractions as this will save time and cost. The ligand 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), a Schiff base has been reported to be an excellent extractant for Uranium, Lead, Nickel, Iron and Cadmium. The effect of anions such as nitrate (NO₃⁻), sulphate (SO₄²⁻), phosphate (PO₄³⁻), acetate (CH₃COO⁻), halide ions (Cl⁻, Br⁻, F⁻ and I⁻), auxiliary complexing agent ions (EDTA, Oxalate, Tartrate and Thiocyanate) and some common acids (HCl, HNO₃, H₂SO₄, H₃PO₄ and CH₃COOH) were also studied and their varying effects well reported. These studies gave 4.75 - 7.5 as optimal range for the extraction of the five metals with an equilibration time of 60 minutes [10, 12, 13, 15, 16]. In the bimetal extraction distribution studies with this ligand H₂BuEtP, it was reported that the presence of a second metal affected the distribution pattern of the first metal due to changes in the dielectric constant/permittivity of the aqueous phase which can result in a masked metal being extracted quantitatively with the second metal and vice versa [18]. Thus the need to study the multi-metal distributions pattern with the ligand (H₂BuEtP) and the effect of anions such as nitrate (NO₃⁻), sulphate (SO₄²⁻), phosphate (PO₄³⁻), acetate (CH₃COO⁻), halide ions (Cl⁻, Br⁻, F⁻ and I⁻), auxiliary complexing agent ions (EDTA, Oxalate, Tartrate and Thiocyanate) and some common acids (HCl, HNO₃, H₂SO₄, H₃PO₄ and CH₃COOH).

In the first of such studies, it was reported that it was theoretically possible to simultaneously extract 99.9% Cadmium, Iron, Nickel and Lead after five (5) batches of extraction from aqueous media containing either 0.1 M CH₃COO⁻ at pH 4.75 with ligand H₂BuEtP alone or 0.05 M PO₄³⁻ at pH 7.5 with mixed ligands H₂BuEtP/HBuP organic phase as the best multi-metal extraction conditions [17]. In the multi-metal extraction study with halide ions, 99.9% extraction of the four metals were extractable after two (2)

batches of extraction from an aqueous media buffered to pH 7.5 and containing either 0.05 M Cl⁻ or F⁻ using chloroform solutions of the ligand H₂BuEtP alone. With mixed ligands H₂BuEtP/HBuP as extractant, four (4) batches was calculated as least required to achieve 99.9% extraction of the four metal from aqueous media also buffered to 7.5 and containing either 0.05 M Br⁻ or 0.001 M Cl⁻, or 0.01 M F⁻ [14]. In related studies with auxiliary complexing agent; EDTA, Oxalate and Thiocyanate ions at pH 4.75 was reported not suitable for multi-metal extraction of the metals. 0.001 M – 0.05 M Tartrate ion was suitable for multi-metal extraction of the four metals from aqueous media of pH 7.5 and using either ligand H₂BuEtP alone or mixed ligands H₂BuEtP/HBuP as organic extractant. The best result was for 0.01 M Tartrate ion in which four (4) batches of extraction is required to simultaneously extract 99.9% of the four metals from an aqueous solution buffered to pH 7.5 and using ligands H₂BuEtP/HBuP as organic extractant. However, the results also showed that, Cadmium and Lead can be selectively extracted from an aqueous phase containing the four metals either with 0.001 M EDTA ion at pH 7.5 with mixed ligands H₂BuEtP/HBuP organic phase or with 0.01 M Oxalate ion at pH 4.75 with ligand H₂BuEtP alone after seven (7) batches of extractions. In these studies, statistically, there was no difference in the multi-metal extractions of the four metals either between pH 4.75 and 7.5 or ligand H₂BuEtP alone and mixed ligands H₂BuEtP/HBuP as organic extractants even though pH 7.5 had slightly better extraction and HBuP showed little synergic effects [11]. In the last of these series, we have studied the role of some common acids in the multi-metal distribution of Cadmium, Iron, Nickel and Lead from aqueous media containing the four metals and buffered to either pH 4.75 or 7.5 using either a chloroform solution of the H₂BuEtP alone or mixed ligands H₂BuEtP/HBuP as organic extractant. The aim is to evaluate the effects of the acids in the distribution pattern of the four metals at the different conditions of studies with the objectives; to ascertain the optimal conditions for the simultaneous extractions of the four metals, to evaluate any other role that the acids can play as regards selective extraction or separation of the metals and statistically compare the performance of the buffers pH 4.75 and 7.5, alongside the organic extractants H₂BuEtP alone and mixed ligands H₂BuEtP/HBuP and the acids.

2. Experimental

All reagents were of analytical grade, ligands 1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-4-yl) butan-1-one (HBuP) and 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) were synthesized and characterized with methods reported by Uzoukwu *et al.*, (1998) [36]. 100 extraction bottles (10 mL) with lids were used for the study. These were arranged in four sets (H₂BuEtP alone at pH 4.75; H₂BuEtP alone at pH 7.5; H₂BuEtP/HBuP at pH 4.75 and H₂BuEtP/HBuP at pH 7.5) of

the five acids (HCl, CH₃COOH, HNO₃, H₃PO₄ and H₂SO₄) that were investigated. Acids concentrations were in the range 0.001 M – 0.1 M and working concentration of the metals was 50 mgL⁻¹. 0.1 mL each from 1000 mgL⁻¹ stock solutions of the four metals prepared from their salts with addition of 2 mL of 2 M HNO₃ to prevent hydrolysis using either the pH 4.75 or 7.5 buffers, were put into labelled extraction bottles. Appropriate volumes from stock solutions of the acids were added to the different bottles according to the different concentrations (0.001 M - 0.1 M) and volumes of the aqueous phases made up to the 2 mL marks with either buffer 4.75 or 7.5 based on the labels. 2 mL of a 0.05 M chloroform solution of the ligand H₂BuEtP were added to the bottles labelled ligand H₂BuEtP while 2 mL from a solution containing 9:1 by volume ratio of a 0.05 M of H₂BuEtP and 0.05 M of HBuP chloroform solution were added to the bottles labelled mixed ligand (H₂BuEtP/HBuP). The bottles were mechanically agitated for sixty (60) minutes and phase

allowed to separate out. 0.4 mL from the aqueous raffinate was taken with a micropipette and analysed for Cadmium, Nickel and Lead with an Atomic Absorbance Spectrophotometer, while 0.6 mL from the raffinate was taken and analysed for Iron using 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% CH₃COONa and 10% NH₂OH solutions [32].

Standard absorbances were used to calculate Distribution ratios (D) and Percentage extractions (% E) of the metals using equations 1 and 2. Equation 3 was used to calculate the number of n batches of extractions required to achieve 99.9% extraction of the metals. The extraction parameters are tabulated in Tables 1 – 5 while Figures 1-10 are bar charts of the percentage extractions against different concentrations of the acids. The results were statistically analysed using p-test for significant differences [34].

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

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

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

Where C_{aq} is the amount of metal ions originally present in the aqueous phase and C is the amount of metal ions that remains in an aqueous phase after extractions.

3. Results and Discussion

3.1. CH₃COOH

The extraction parameters for the four metals in CH₃COOH shown in Table 1 indicated that Iron distribution was excellent with distribution ratios greater than 470 for most conditions except H₂BuEtP alone with pH 4.75 that was poor with the highest distribution ratio 1.06 (Table 1a). The results from the plots in Figures 1b and 2 and from last columns in Table 1b - d also show that, it is possible to get 99.76% extraction of Iron after the first batch of extractions. The results also indicated that CH₃COOH masked the extraction of the other three metals in almost all concentration except Nickel with the mixed ligands H₂BuEtP/HBuP that had very good distribution ratios and percentage extractions for Nickel with pH 4.75 having 44.85 distribution ratio (Table 1c) and 97.82% extraction (figure 2a) with 0.05 M CH₃COOH and with pH 7.5 having 3.05 distribution ratio (Table 1d) and 75.25% extraction (figure 2b) with 0.005 M CH₃COOH. Thus, 0.05 M CH₃COOH at pH 4.75 and 0.005 M CH₃COOH at pH 7.5 can be utilized for selective extraction/separation of Iron and Nickel from Cadmium and Lead with three batches of extractions required with 0.05M CH₃COOH at pH 4.75 (Table 1c) and five batches of extraction with 0.005 M CH₃COOH at pH 7.5

(Table 1d)) to achieve greater than 99% extraction of Iron and Nickel using mixed ligands BuEtP/HBuP as organic extractant (figure 2). The results from Table 1b-c and figure 1b and 2 also indicated that CH₃COOH at concentrations of 0.1 M in pH 4.75 with H₂BuEtP alone or with the mixed ligands H₂BuEtP/HBuP and 0.05 M at pH 7.5 with the mixed ligands H₂BuEtP/HBuP can be utilized for the selective extraction of Iron from Cadmium, Nickel and Lead with above 99% Iron extracted after the first batch of extraction. The results even though were similar for Iron distribution with those for CH₃COO⁻ [10], the distribution for the other three metals were quite different and confirmed that salts of CH₃COO⁻ functions as good salting out agents for the four metals than CH₃COOH which only salts out Iron but masks the other three metals in most of the conditions. The results are consistent with other studies on stability constants of acetate salts of the four metals and thus, the lower stability of the Iron acetate compared with the acetates of the other metals [21, 28] is responsible for CH₃COOH being able to salt out Iron in almost all conditions while the distributions and extraction of the other metals were very poor in almost all conditions. The results for CH₃COOH were generally not as good for those reported for CH₃COO⁻ in which simultaneous extraction of 99.9% of four metals is achievable with 0.1 M CH₃COO⁻ after 4 batches of extractions from an aqueous medium buffered to pH 4.75 using chloroform solution of H₂BuEtP [17]. Statistically for CH₃COOH, there was no significant difference (p > 0.05) between the two buffers and also between the two organic extractants except for Iron with p = 0.0029 for buffer pH 4.75 in the distributions of the four metals.

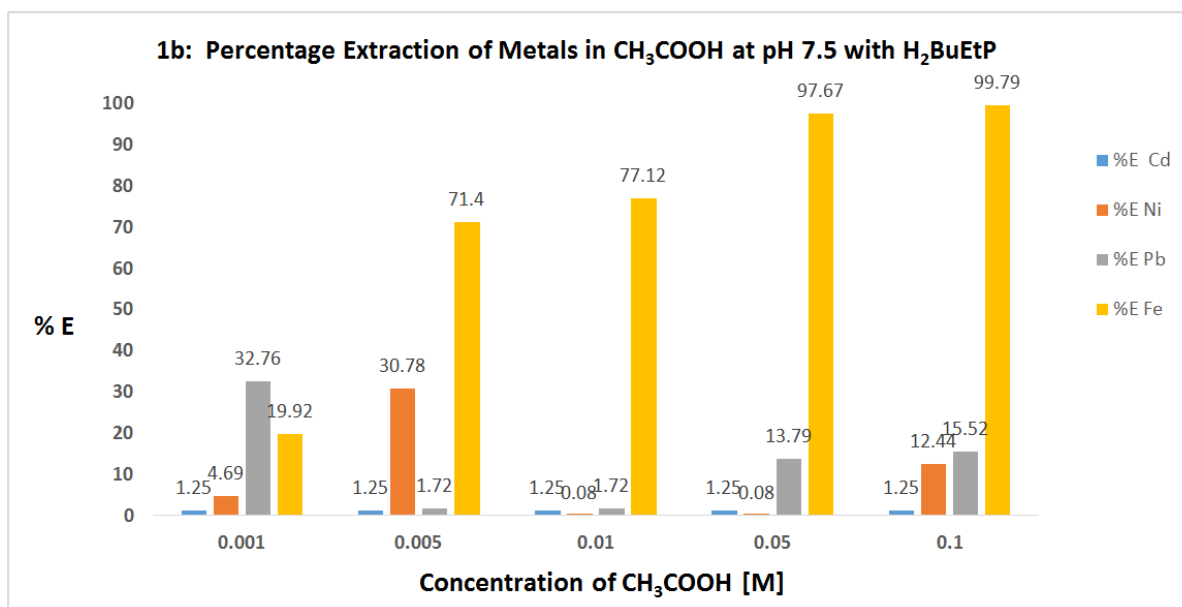
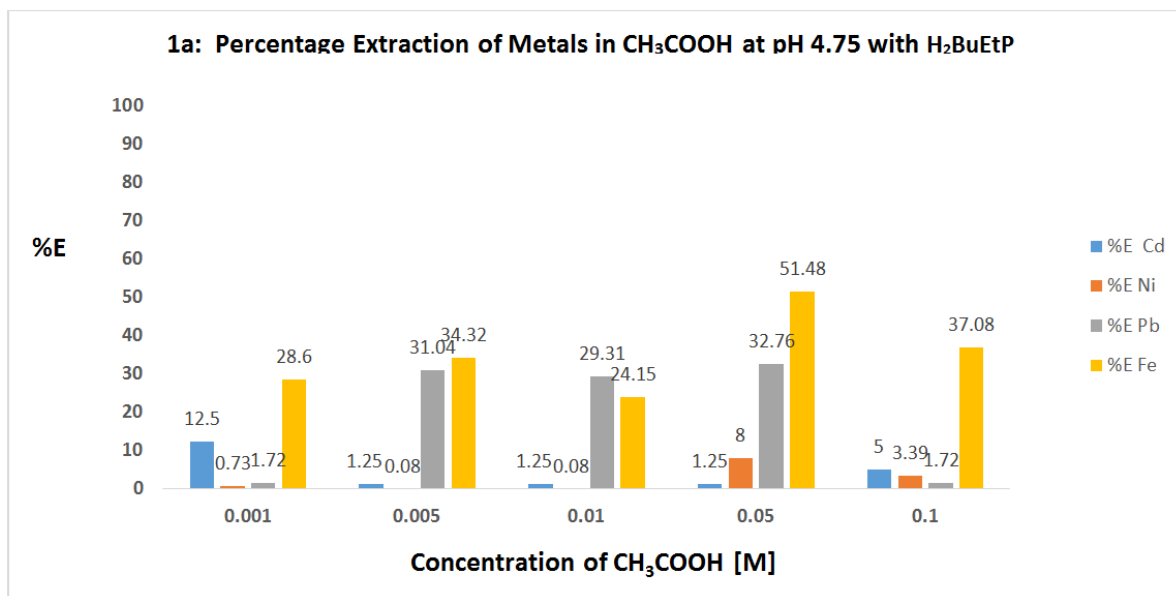
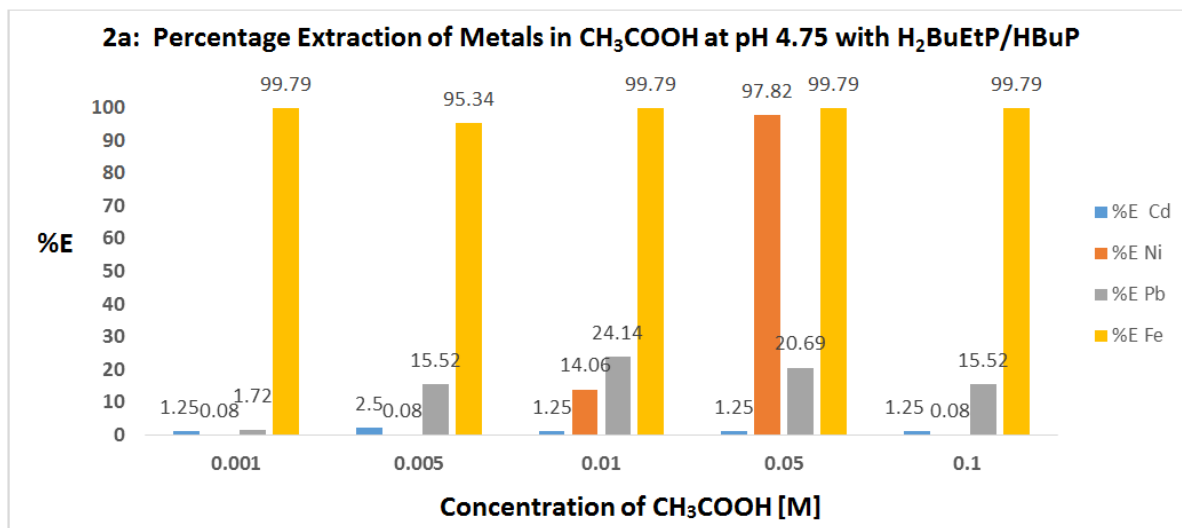


Figure 1. Charts of Percentage Extraction of Metals in CH₃COOH with Ligand H₂BuEtP alone (a) at pH 4.75 and (b) at pH 7.5.



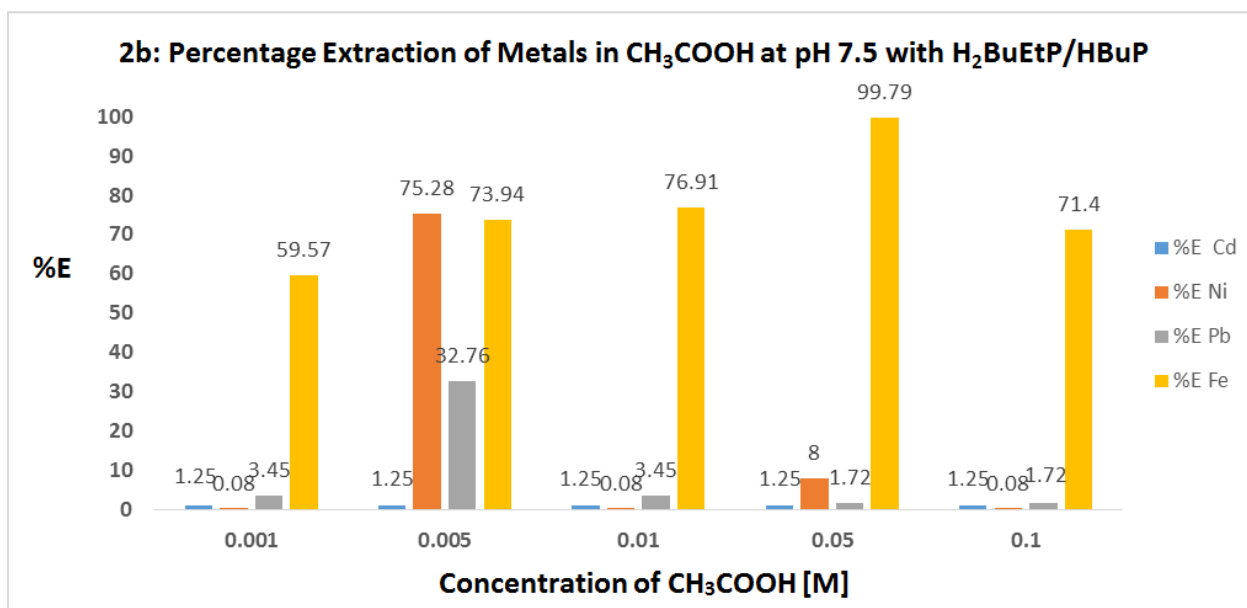


Figure 2. Charts of Percentage Extraction of Metals in CH₃COOH with Mixed Ligands H₂BuEtP/HBuP (a) at pH 4.75 and (b) at pH 7.5.

Table 1. Distribution Ratios and number of batches needed to achieve 99.9% extraction of metals in CH₃COOH.

1a: For the four metals at pH 4.75 for Ligand H₂BuEtP alone

5.00 mgL ⁻¹ Cd, Ni, and Pb Standards Absorbance				Cd = 0.008	Ni = 0.1238	Pb = 0.0058			7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472			
CH ₃ COOH (M)	Raffinates Absorbance			Distribution Ratios D					n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb		D _{Cd}	D _{Ni}	D _{Pb}	D _{Fe}	n _{Cd}	n _{Ni}	n _{Pb}	n _{Fe}
0.001	0.0070	0.1229	0.0057	0.337	0.1429	0.0073	0.0175	0.4006	52	950	398	21
0.005	0.0079	0.1237	0.004	0.310	0.0127	0.0008	0.45	0.5226	546	8638	19	17
0.01	0.0079	0.1237	0.0041	0.358	0.0127	0.0008	0.4146	0.3184	546	8638	20	25
0.05	0.0079	0.1139	0.0039	0.229	0.0127	0.0869	0.4872	1.0611	546	83	18	10
0.1	0.0076	0.1196	0.0057	0.297	0.0526	0.0351	0.0175	0.5892	135	200	398	15

1b: For the four metals at pH 7.5 for Ligand H₂BuEtP alone

5.00 mgL ⁻¹ Cd, Ni, and Pb Standards Absorbance				Cd = 0.0464		Ni = 0.4288		Pb = 0.8118		7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472			
(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}	
0.001	0.0079	0.118	0.0039	0.378	0.0127	0.0492	0.4872	0.2487	546	144	18	31	
0.005	0.0079	0.0857	0.0057	0.135	0.0127	0.0381	0.0175	2.4963	546	185	398	6	
0.01	0.0079	0.1237	0.0057	0.108	0.0127	0.0008	0.0175	3.3704	546	8638	398	5	
0.05	0.0079	0.1237	0.0050	0.011	0.0127	0.0008	0.16	41.9091	546	8638	47	2	
0.1	0.0079	0.1084	0.0049	0.001	0.0127	0.1421	0.1837	471	546	52	41	1	

1c: For the four metals at pH 4.75 for Mixed Ligands H₂BuEtP/HBuP

5.00 mgL ⁻¹ Cd, Ni, and Pb Standards Absorbance				Cd = 0.008		Ni = 0.1238		Pb = 0.0058		7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472			
CH ₃ COOH (M)	Raffinates Absorbance			Distribution Ratios D					n Batches needed to get 99.9% extraction				
	Cd	Ni	Pb		D _{Cd}	D _{Ni}	D _{Pb}	D _{Fe}	n _{Cd}	n _{Ni}	n _{Pb}	n _{Fe}	
0.001	0.0079	0.1237	0.0057	0.001	0.0127	0.0008	0.0175	471	546	8638	398	1	
0.005	0.0078	0.1237	0.0049	0.022	0.0256	0.0008	0.1837	20.4546	273	8638	41	3	
0.01	0.0079	0.1064	0.0044	0.001	0.0127	0.1635	0.3182	471	546	46	25	1	
0.05	0.0079	0.0027	0.0046	0.001	0.0127	44.8519	0.2609	471	546	3	30	1	
0.1	0.0079	0.1237	0.0049	0.001	0.0127	0.0008	0.1837	471	546	8638	41	1	

Id: For the four metals at pH 7.5 for Mixed Ligands H₂BuEtP/HBuP

5.00 mgL ⁻¹ Cd, Ni, and Pb Standards Absorbance				Cd = 0.008		Ni = 0.1238		Pb = 0.0058		7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472		
CH ₃ COOH (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}
0.001	0.0079	0.1237	0.0056	0.191	0.0127	0.0008	0.0357	1.4712	546	8638	197	8
0.005	0.0079	0.0306	0.0039	0.123	0.0127	3.0458	0.4872	2.8374	546	5	18	5
0.01	0.0079	0.1237	0.0056	0.109	0.0127	0.0008	0.0357	3.3303	546	8638	197	5
0.05	0.0079	0.1139	0.0057	0.001	0.0127	0.0869	0.0175	471	546	83	398	1
0.1	0.0079	0.1237	0.0057	0.135	0.0127	0.0008	0.0175	2.4963	546	8638	398	6

3.2. In HCl

Cadmium and Nickel distributions in HCl as shown in Table 2 were very poor with distribution ratios < 0.16 at all conditions except for Cadmium with D equal to 1.35 corresponding to 57.5% extraction (Figure 3b) in 0.005 M HCl at pH 7.5 with H₂BuEtP alone. Iron distributions were very good with distribution ratios ≥ 5.05 at all conditions which correspond to ≥ 83.48% extraction of Iron. Lead distributions were relatively better than those of Cadmium and Nickel even though the distributions did not follow a regular trend as regards concentrations of HCl. The best distribution ratio of 13.5 for Lead was gotten at 0.1 M HCl at pH 7.5 with mixed ligands H₂BuEtP/HBuP, which also had distribution ratio of 471 for Iron but with very poor distributions or masking of Cadmium and Nickel. Thus, 0.1M HCl at pH 7.5 with mixed ligands H₂BuEtP/HBuP can be used for the separation of Iron and Lead from Cadmium and Nickel with 99.9% extraction of two metals after three (3) batches of extractions (Table 2d and figure 4b) as the best conditions for the separation even though the separations can

also be achieved with other conditions as shown in Table 2 and figures 3 and 4. 0.001 M – 0.01 M HCl at pH 4.75 with ligand H₂BuEtP alone show potentials as good conditions for the extraction of Iron from the other three (3) metals with a single batch extraction required for 99.76% extraction of Iron (Table 2a and figure 3a). 0.01 M HCl with mixed ligands H₂BuEtP/HBuP also show potentials in selective Iron extraction but will require two (2) batches to get above 99% extraction of Iron (Table 2c and figure 4a). While results at pH 4.75 where close to those reported for Cl⁻ and not suitable for the multi-metal extraction of the four metals, there is a contrast in results for Cl⁻ and those for HCl at pH 7.5 as Cl⁻ showed good potentials as reagent for multi-metals of the four metals [14]. There was no significant difference statistically in the results between the buffers and even between organic extractants in HCl as p > 0.05 even though pH 7.5 and mixed ligands H₂BuEtP/HBuP results appears slightly better. Most results of HCl were also not significantly different from those for CH₃COOH except for mixed ligands H₂BuEtP/HBuP at pH 4.75 for Nickel with p = 0.006 and in pH 7.5 for Iron with p = 0.014.

Table 2. Distribution Ratios (D) and number of batches (n) needed to achieve 99.9% extraction of metals in HCl.

2a: For the four metals at pH 4.75 for Ligand H₂BuEtP alone

5 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.008	Ni = 0.1238	Pb = 0.0058	7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472					
HCl (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}
0.001	0.0079	0.1237	0.0057	0.001	0.0127	0.0008	0.0175	471	546	8638	398	1
0.005	0.0079	0.1237	0.0057	0.001	0.0127	0.0008	0.0175	471	546	8638	398	1
0.01	0.0069	0.1237	0.0057	0.001	0.1594	0.0008	0.0175	471	47	8638	398	1
0.05	0.0079	0.1237	0.0021	0.001	0.0127	0.0008	1.7619	471	546	8638	7	1
0.1	0.0079	0.1237	0.0018	0.001	0.0127	0.0008	2.2222	471	546	8638	6	1

2b: For the four metals at pH 7.5 for Ligand H₂BuEtP alone

5 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.008		Ni = 0.1238		Pb = 0.0058		7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472			
HCl (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}	
0.001	0.0079	0.1237	0.0011	0.063	0.0127	0.0008	4.2727	6.4921	546	8638	4	4	
0.005	0.0034	0.1237	0.0047	0.078	1.3529	0.0008	0.2340	5.0513	8	8638	33	4	
0.01	0.0074	0.1237	0.0030	0.001	0.0811	0.0008	0.9333	471	89	8638	11	1	
0.05	0.0079	0.1237	0.0034	0.001	0.0127	0.0008	0.7059	471	546	8638	13	1	
0.1	0.0079	0.1237	0.0054	0.001	0.0127	0.0008	0.0741	471	546	8638	97	1	

2c: For the four metals at pH 4.75 for Mixed Ligands $H_2BuEtP/HBuP$

5 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0008	Ni = 0.1238	Pb = 0.0058			7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472			
HCl (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}
0.001	0.0079	0.1237	0.0036	0.001	0.0127	0.0008	0.6111	471	546	8638	15	1
0.005	0.0079	0.1237	0.0026	0.001	0.0127	0.0008	1.2308	471	546	8638	9	1
0.01	0.0079	0.1237	0.0057	0.006	0.0127	0.0008	0.0175	77.6667	546	8638	398	2
0.05	0.0079	0.1237	0.0034	0.004	0.0127	0.0008	0.7059	117	546	8638	13	2
0.1	0.0074	0.1237	0.0044	0.001	0.0811	0.0008	0.3182	471	89	8638	25	1

2d: For the four metals at pH 7.5 for Mixed Ligands $H_2BuEtP/HBuP$

5 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0008	Ni = 0.1238	Pb = 0.0058	7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472					
HCl (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}
0.001	0.0079	0.1237	0.0038	0.002	0.0127	0.0008	0.5263	235	546	8638	17	2
0.005	0.0069	0.1237	0.0028	0.001	0.1594	0.0008	1.0714	471	47	8638	10	1
0.01	0.0079	0.1237	0.0019	0.001	0.0127	0.0008	2.0526	471	546	8638	6	1
0.05	0.0079	0.1237	0.0050	0.001	0.0127	0.0008	0.16	471	546	8638	47	1
0.1	0.0071	0.1234	0.0004	0.001	0.1268	0.0032	13.5	471	58	2162	3	1

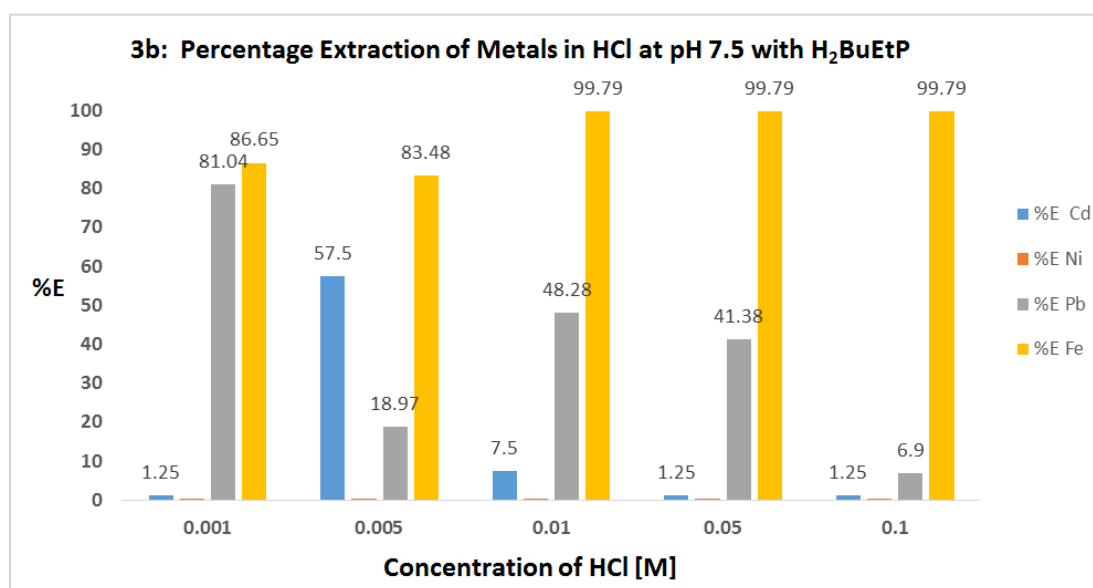
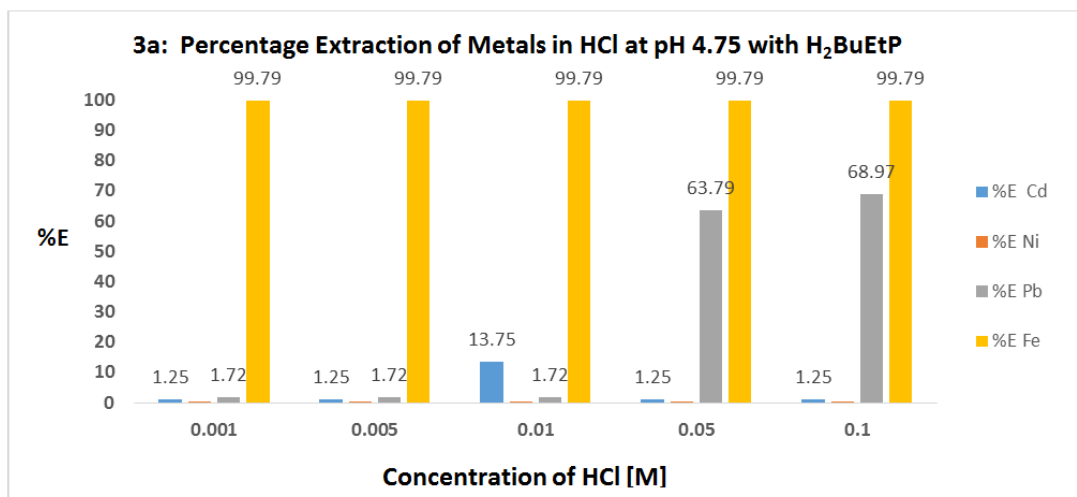


Figure 3. Charts of Percentage Extraction of Metals in HCl with Ligands alone (a) at pH 4.75 and (b) at pH 7.5.

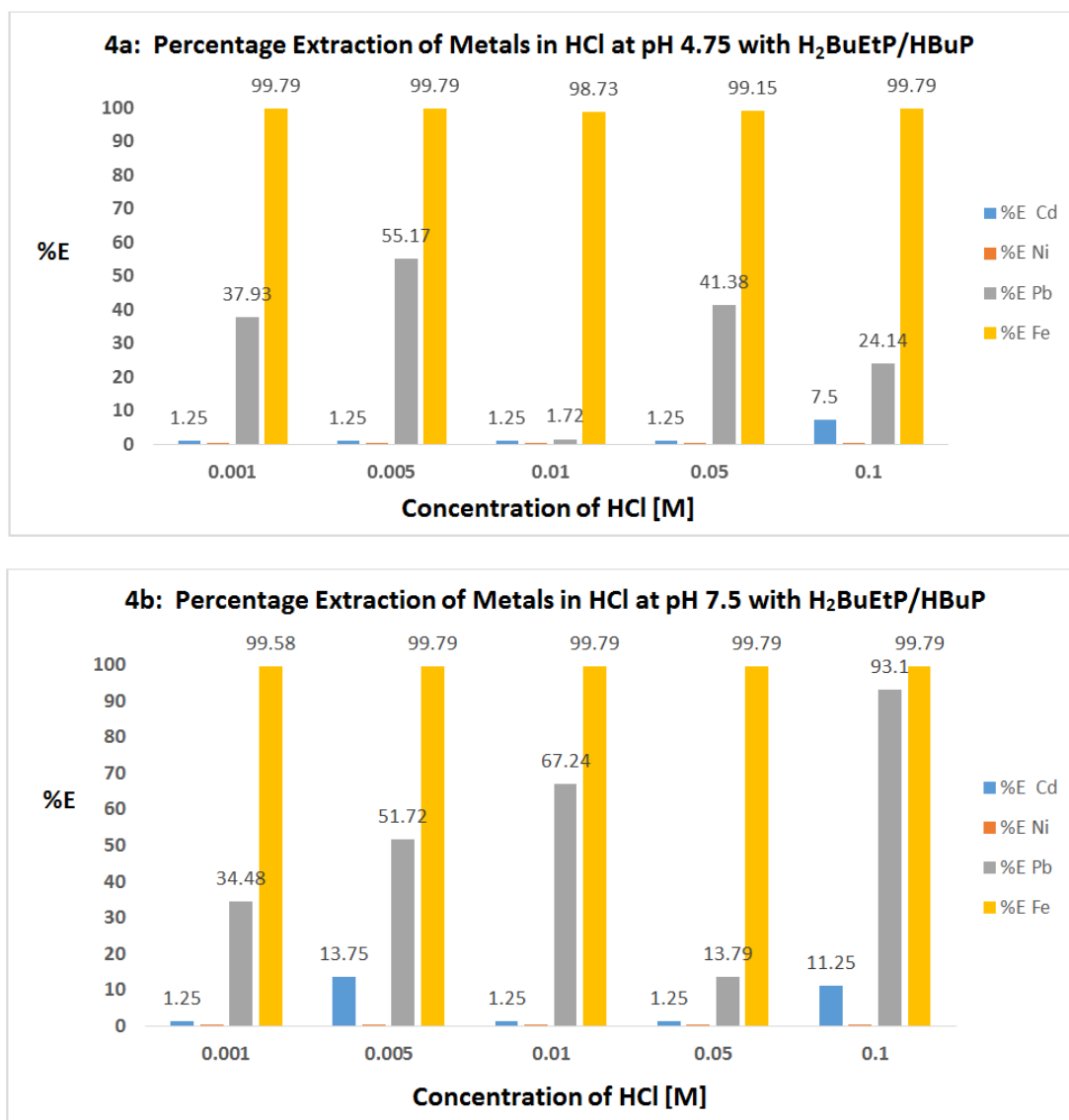


Figure 4. Charts of Percentage Extraction of Metals in HCl with Mixed Ligands H₂BuEtP/HBuP (a) at pH 4.75 and (b) at pH 7.5.

3.3. In HNO₃

The results for HNO₃ shown in Table 3 all indicated that the distribution of Iron to the organic phases was very high and required < 5 batches to achieve 99.9% extraction of Iron at all conditions. Thus, HNO₃ can be utilized in selective extraction of Iron from an aqueous media containing the other three metals with 99.9% extraction of Iron achievable after a single batch of extraction. In this regard, pH 7.5 with mixed ligands H₂BuEtP/HBuP organic extractant show excellent potentials as all concentrations of HNO₃ gave > 87% extraction of Iron after the first batch of extraction as shown in figure 6b. The other three metals were masked in most cases with the exceptions noticed for Lead with 0.01M HNO₃ in buffer pH 4.75 that had Distribution ratio of 4.8 and this can be exploited in the extraction of Iron and Lead from Cadmium and Nickel from an aqueous solution containing 0.01M HNO₃ and buffered to pH 4.75 using H₂BuEtP alone. This was

slightly better than pH 7.5 buffer for this process with 4 batches of extraction needed theoretically to extract 99.9% of Lead and Iron as against a minimum of 7 batches of extractions needed with 7.5 buffer containing 0.05 M - 0.1 M HNO₃. 0.1 M HNO₃, in pH 4.75 buffer using H₂BuEtP/HBuP organic extractant had distribution ratio of 6.37 for Nickel and can also be used as a condition for selectively extracting Nickel and Iron from Cadmium and Lead and 99.9% extraction of Nickel and Iron achievable after 4 batches of extractions (Table 3c). The results were not very different for those reported for the effect of HNO₃ in the extraction of the metals alone as masking was observed in these studies except for Iron that releasing effect was reported at lower concentrations of the acids [10, 12, 15, 16].

Statistically, apart from Iron extractions in which slight difference ($p = 0.048$ for H₂BuEtP alone and $p = 0.012$ for H₂BuEtP/HBuP) was observed, there was no significant difference in distribution ratios between the buffers 4.75 and

7.5 in both organic extractants. There was also no significant difference between the two organic extractants in the metals distributions except for Cadmium with $p = 0.017$ in H_2BuEtP alone and Nickel with $p = 5 \times 10^{-5}$ for pH 7.5 buffer and in both cases there was no synergic effect from $HBuP$. With both buffers using H_2BuEtP alone, there was no significant difference between CH_3COOH and HNO_3 in the distributions of the metals as all $p > 0.05$. However, with $H_2BuEtP/HBuP$ with both buffers there was significant difference between CH_3COOH and HNO_3 in only Iron distribution with $p =$

0.0042 with HNO_3 showing better releasing effect for Iron. In both buffers and with H_2BuEtP alone, there was only significant difference between HNO_3 and HCl in the distribution of Nickel with $p = 0.0059$ and 0.00 for pH 4.75 and pH 7.5 respectively with HNO_3 also showing higher releasing effects in both cases. With $H_2BuEtP/HBuP$, there was no significant difference between HCl and HNO_3 in the distribution ratios of the metals with both buffers except for Lead with $p = 0.031$ at pH 4.75 and $p = 0.000$ for Nickel at pH 7.5.

Table 3. Distribution Ratios and number of batches needed to achieve 99.9% extraction of metals in HNO_3 .

3a: For the four metals at pH 4.75 for Ligand H_2BuEtP alone

5 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance					Cd = 0.008		Ni = 0.1238		Pb = 0.0058		7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472	
HNO ₃ (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}
0.001	0.0068	0.1110	0.0054	0.001	0.1765	0.1153	0.0741	471	43	63	97	1
0.005	0.0064	0.1124	0.0043	0.001	0.2500	0.1014	0.3488	471	31	72	23	1
0.01	0.0069	0.1137	0.0010	0.001	0.1594	0.0888	4.8000	471	47	81	4	1
0.05	0.0079	0.1237	0.0045	0.001	0.0127	0.0008	0.2889	471	546	8638	27	1
0.1	0.0074	0.1084	0.0053	0.002	0.0811	0.1421	0.0943	235	89	52	77	2

3b: For the four metals at pH 7.5 for Ligand H_2BuEtP alone

5 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0008		Ni = 0.1238		Pb = 0.0058		7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472		
HNO ₃ (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}
0.001	0.0060	0.1126	0.0057	0.002	0.3333	0.0995	0.0175	235	24	73	398	2
0.005	0.0079	0.1120	0.0057	0.001	0.0127	0.1054	0.0175	471	546	69	398	1
0.01	0.0079	0.1139	0.0057	0.037	0.0127	0.0869	0.0175	11.7568	546	83	398	3
0.05	0.0079	0.1109	0.0021	0.002	0.0127	0.1163	1.7619	235	546	63	7	2
0.1	0.0079	0.1136	0.0025	0.004	0.0127	0.0898	1.3200	117	546	80	8	2

3c: For the four metals at pH 4.75 for Mixed Ligands $H_2BuEtP/HBuP$

5 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0008		Ni = 0.1238		Pb = 0.0058		7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472		
HNO ₃ (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}
0.001	0.0079	0.1138	0.0057	0.001	0.0127	0.0879	0.0175	471	546	82	398	1
0.005	0.0079	0.1103	0.0055	0.001	0.0127	0.1224	0.0546	471	546	60	130	1
0.01	0.0079	0.1136	0.0052	0.003	0.0127	0.0898	0.1154	156.3	546	80	63	2
0.05	0.0079	0.1136	0.0057	0.001	0.0127	0.0898	0.0175	471	546	80	398	1
0.1	0.0079	0.0168	0.0057	0.002	0.0127	6.3691	0.0175	235	546	4	398	2

3d: For the four metals at pH 7.5 for Mixed Ligands $H_2BuEtP/HBuP$

5 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0008		Ni = 0.1238		Pb = 0.0058		7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472			
HNO ₃ (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}	
0.001	0.0079	0.1202	0.0057	0.061	0.0127	0.0230	0.0175	6.7377	546	31	398	4	
0.005	0.0079	0.1187	0.0057	0.011	0.0127	0.0430	0.0175	41.9091	546	164	398	2	
0.01	0.0079	0.1193	0.0057	0.004	0.0127	0.0377	0.0175	117	546	187	398	2	
0.05	0.0079	0.1179	0.0057	0.002	0.0127	0.0500	0.0175	235	546	142	398	2	
0.1	0.0079	0.1175	0.0057	0.004	0.0127	0.0536	0.0175	117	546	132	398	2	

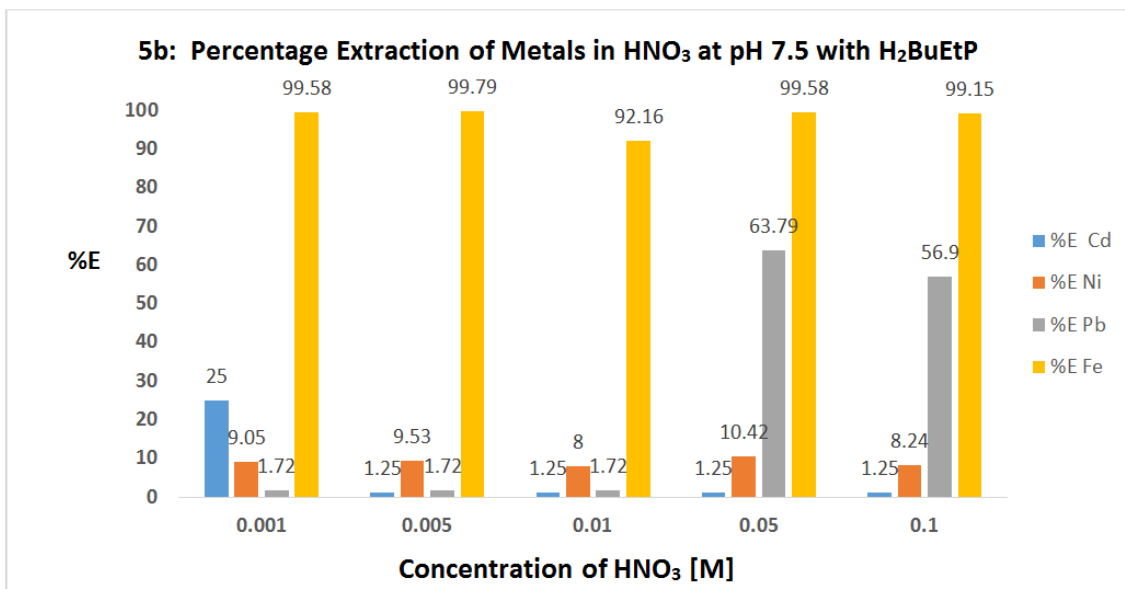
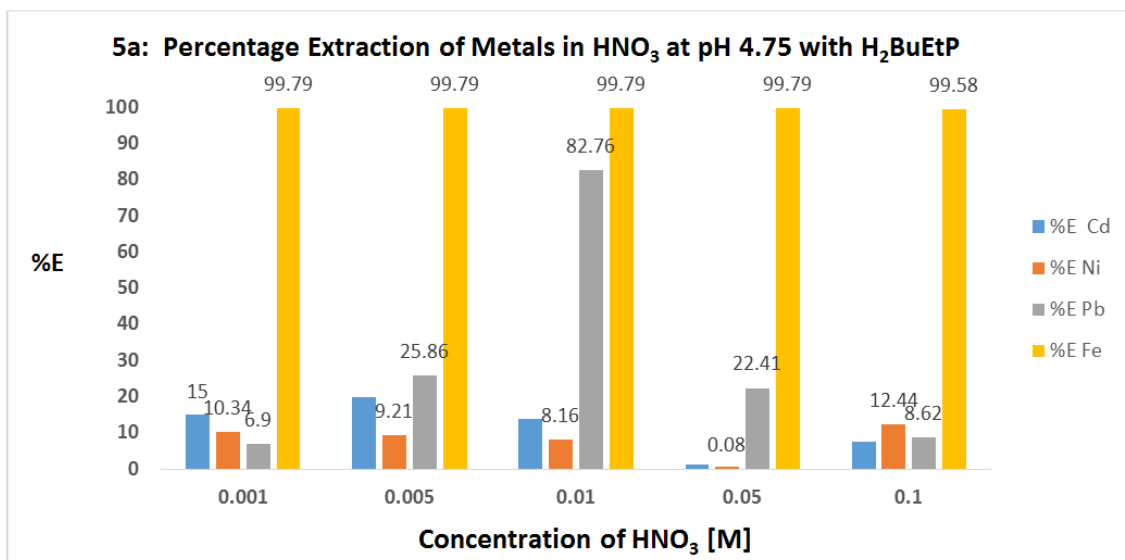
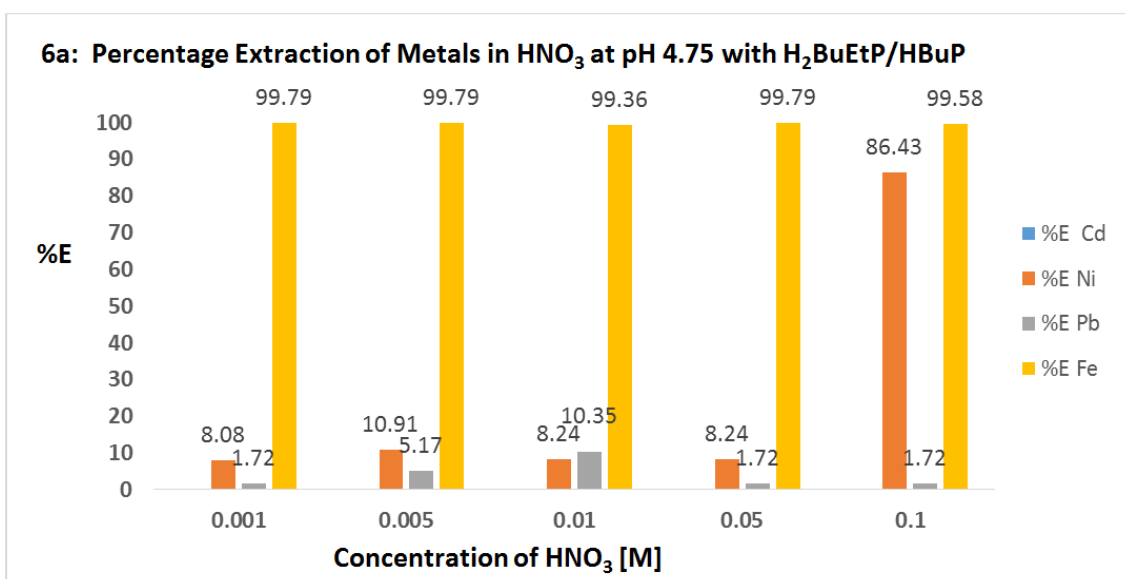


Figure 5. Charts of Percentage Extraction of Metals in HNO₃ with Ligands alone (a) at pH 4.75 and (b) at pH 7.5.



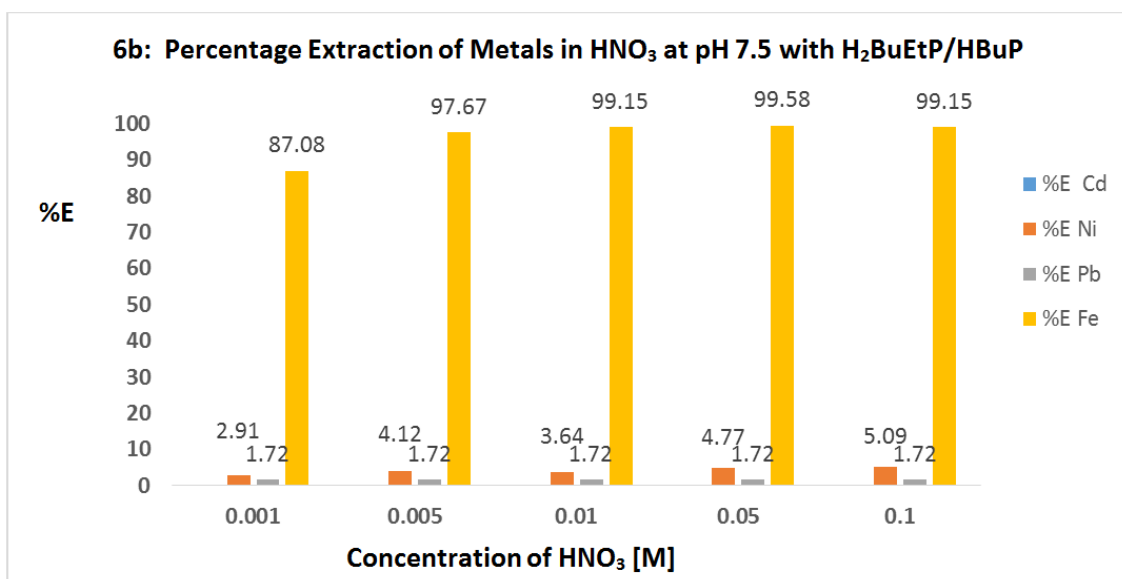


Figure 6. Charts of Percentage Extraction of Metals in HNO₃ with Mixed Ligands H₂BuEtP/HBuP (a) at pH 4.75 and (b) at pH 7.5.

3.4. In H₃PO₄

Table 4 results indicated good distribution of Iron from the aqueous media to the H₂BuEtP organic phases at all concentrations of H₃PO₄ with > 99.9% extraction of Iron except for pH 7.5 with H₂BuEtP alone that had < 90% extractions of Iron from 0.001M – 0.01 M H₃PO₄ as shown in figures 7 and 8. Cadmium, Nickel and Lead was masked in most conditions with few exceptions; Cadmium with distribution ratios of 2.2 – 12.3 from 0.05 M – 0.1 M H₃PO₄ at pH 4.75, 2.2 with 0.001 M H₃PO₄ at pH 7.5 with H₂BuEtP alone and distribution ratio of 12.33 for 0.01 M – 0.1M H₃PO₄ at pH 7.5 with H₂BuEtP/HBuP, Nickel with distribution ratio of 153.75 for 0.005 M – 0.05 M H₃PO₄ at pH 7.5 with H₂BuEtP/HBuP and Lead with distribution ratios of 1.23 in 0.05 M H₃PO₄ at pH 475 with H₂BuEtP alone, 1.23 – 1.90 in 0.001 M – 0.005 M H₃PO₄ at pH 475 and > 1.23 for all concentrations of H₃PO₄ at pH 7.5 with H₂BuEtP/HBuP organic phase. The data indicates that 0.05 M H₃PO₄ at pH 7.5 with H₂BuEtP alone can be used for the selective extraction of Iron from a mixture of the four metals with > 99% extraction of Iron attainable after a single batch of extraction (Table 4b) as the best condition for this extraction. For the extraction of Lead and Iron from Cadmium and Nickel, table 4c indicates that 0.001M H₃PO₄ at pH 7.5 using H₂BuEtP/HBuP as organic extractant can be utilized with 99.9% of Lead and Iron extractable after 4 batches (Table 4d) of extractions as the best condition for this task. 0.005 M H₃PO₄ at pH 7.5 using H₂BuEtP/HBuP can also be used for the extraction of Nickel, Lead and Iron from Cadmium as it's the only metal completely masked in this condition with 99.9% extraction of the three metals possible after 7 batches of extractions while 0.1 M H₃PO₄ at pH 7.5 using H₂BuEtP/HBuP can be used for the extraction of cadmium, Lead and Iron from Nickel as Nickel is completely masked under this condition while there was releasing effect from H₃PO₄ for the other three metals and

99.9% extraction of the three metals possible after 4 batches of extractions (Table 4d). For the simultaneous extraction of the four metals, 0.01 M – 0.05 M H₃PO₄ aqueous solutions buffered to pH 7.5 gave the best results with all four metals having distribution ratios > 1.23 with 7 batches of extractions required for 99.9% extractions of the metals (Table 4d) and a single batch extraction giving > 53.45% extraction of the four metals (figure 8b). The results were only completely different from those reported for H₃PO₄ for Lead alone studies in which complete masking was reported for all concentrations of H₃PO₄ [12] as those for Cadmium, Nickel and Iron had > 90% extractions [10, 15, 16]. Results for PO₄³⁻ in multimetal studies [17] were far better than those for H₃PO₄. Statistically in H₂BuEtP alone organic phase, there was no significant difference between buffers pH 4.75 and pH 7.5 extractions with all $p > 0.05$. However in H₂BuEtP/HBuP organic phase, there was significant differences between the buffers pH 4.75 and pH 7.5 in the distribution of the metals between the two phases (Cd and Ni with $p = 0.04$ and Fe with $p = 0.0076$) with the only exception being the distribution of Lead that showed no significant difference between the two buffers in its' distribution with $p = 0.069$). Also with buffer pH 4.75, there was no significant difference between the two organic extractants H₂BuEtP alone and mixed ligands H₂BuEtP/HBuP with all $p > 0.05$ while there was significant difference between the two organic extractants with buffer 7.5 in the distribution of Nickel_{0.04} and Lead_{0.025} indicating slight synergic effect of HBuP as H₂BuEtP/HBuP distribution ratios were higher (Table 4). The results were also not very different for those reported for the single extraction studies of the four metals in H₃PO₄ as Cadmium, Nickel and Lead were completely masked by H₃PO₄ with Iron results slightly better at lower concentrations of H₃PO₄ [10, 12, 15, 16].

The cases were cadmium, Nickel and Lead are showing good distribution ratio can be attributed to changes in permittivities/dielectric constants leading to favourable energetics in the transfer of the metals from the aqueous

phases to the organic phases [20]. Comparing distribution ratios in H₃PO₄ with those of CH₃COOH, HCl and HNO₃ statistically showed, with H₂BuEtP alone there was no significant difference with both buffers except with HNO₃ for Nickel at pH 7.5 with $p = 0.00$. With H₂BuEtP/HBuP as organic extractant at pH 4.75, distribution ratios of the metals in H₃PO₄ only showed significant difference with

those of CH₃COOH for Nickel_{0.0074} and Iron_{0.0000} respectively while at pH 7.5, the distribution ratios in H₃PO₄ were significantly different from those of CH₃COOH, HCl and HNO₃ for most of the metals with the few exceptions of no significant difference being with CH₃COOH and HNO₃ for Iron with $p = 0.67$ and 0.63 respectively and HCl for Lead with $p = 0.80$.

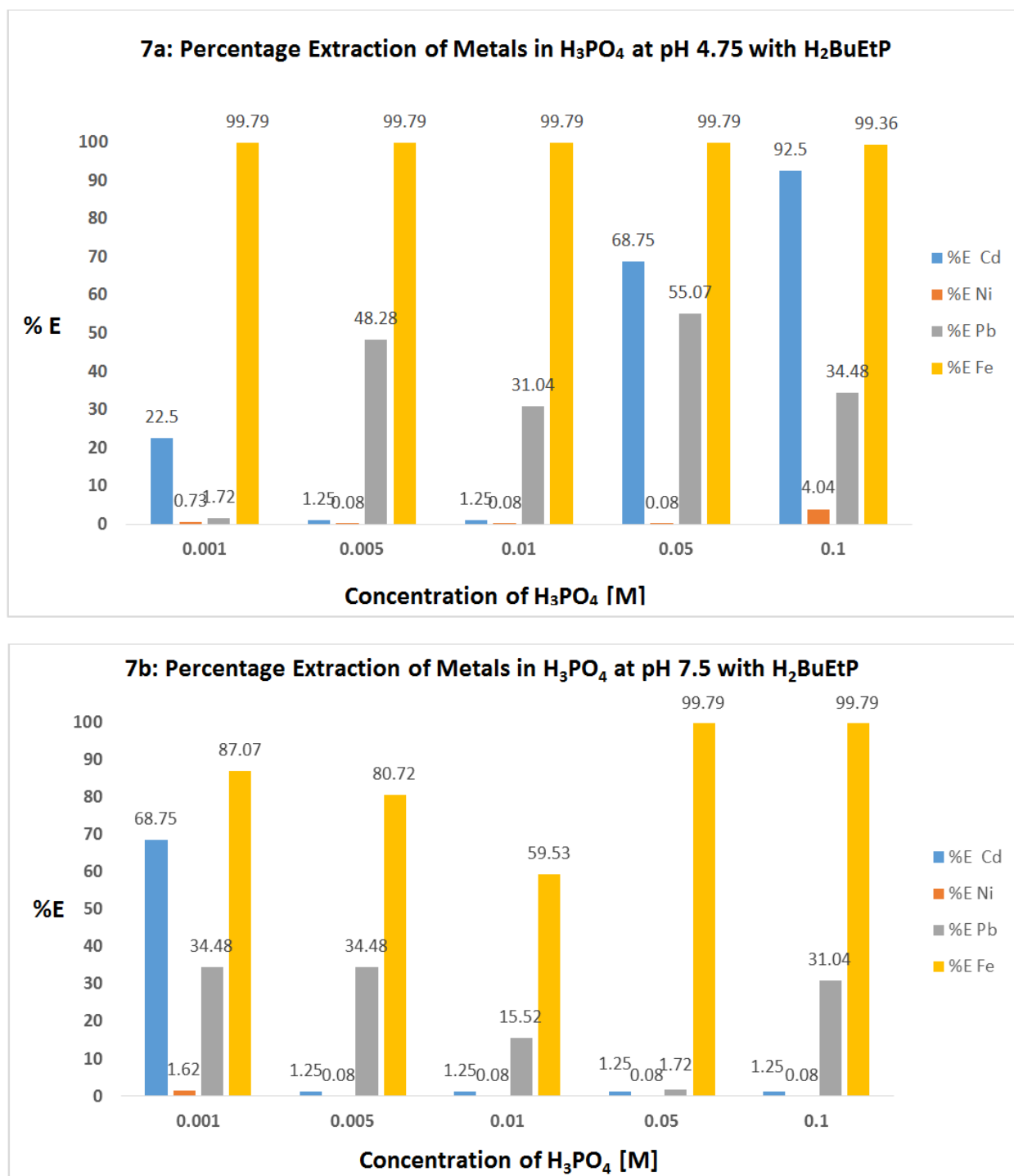


Figure 7. Charts of Percentage Extraction of Metals in H₃PO₄ with Ligands alone (a) at pH 4.75 and (b) at pH 7.5.

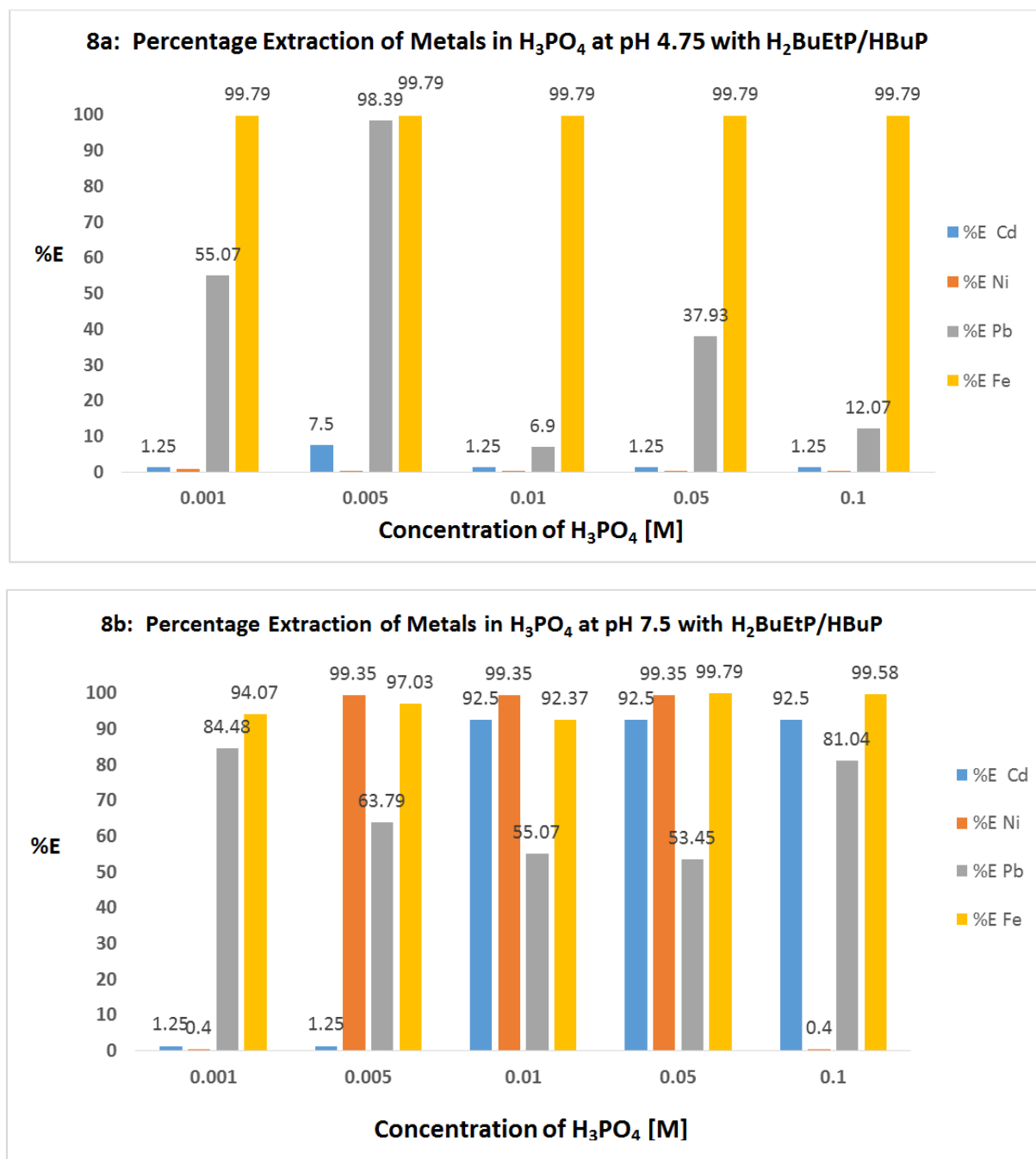


Figure 8. Charts of Percentage Extraction of Metals in H_3PO_4 with Mixed Ligands $H_2BuEtP/HBuP$ (a) at pH 4.75 and (b) at pH 7.5.

Table 4. Distribution Ratios (D) and number of batches (n) needed to achieve 99.9% extraction of metals in H_3PO_4 .

4a: For the four metals at pH 4.75 for Ligand H_2BuEtP alone

5 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0008		Ni = 0.1238		Pb = 0.0058		7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472		
H ₃ PO ₄ (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}
0.001	0.0062	0.1229	0.0057	0.001	0.2903	0.0073	0.0075	471	27	950	925	1
0.005	0.0079	0.1237	0.0030	0.001	0.0127	0.0008	0.9300	471	546	8638	11	1
0.01	0.0079	0.1237	0.0040	0.001	0.0127	0.0008	0.4500	471	546	8638	19	1
0.05	0.0025	0.1237	0.0026	0.001	2.2000	0.0008	1.2308	471	6	8638	9	1
0.1	0.0006	0.1188	0.0038	0.003	12.3000	0.0421	0.5263	156.3	3	172	16	2

4b: For the four metals at pH 7.5 for Ligand H₂BuEtP alone

5 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance	Cd = 0.0008				Ni = 0.1238				Pb = 0.0058				7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472
H ₃ PO ₄ (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}	
0.001	0.0025	0.1218	0.0038	0.061	2.2000	0.0164	0.5263	6.73	6	423	16	3	
0.005	0.0079	0.1237	0.0038	0.091	0.0127	0.0008	0.5263	4.19	548	8638	16	4	
0.01	0.0079	0.1237	0.0049	0.191	0.0127	0.0008	0.1837	147	548	8638	41	8	
0.05	0.0079	0.1237	0.0057	0.001	0.0127	0.0008	0.0075	471	548	8638	925	1	
0.1	0.0079	0.1237	0.0040	0.001	0.0127	0.0008	0.4500	471	548	8638	19	1	

4c: For the four metals at pH 4.75 for Mixed Ligands H₂BuEtP/HBuP

5 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance	Cd = 0.0008				Ni = 0.1238				Pb = 0.0058				7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472
H ₃ PO ₄ (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}	
0.001	0.0079	0.1228	0.0026	0.001	0.0127	0.0081	1.2308	471	546	856	9	1	
0.005	0.0074	0.1236	0.0020	0.001	0.0811	0.0016	1.9000	471	89	4321	7	1	
0.01	0.0079	0.1237	0.0054	0.001	0.0127	0.0008	0.0741	471	546	8638	97	1	
0.05	0.0079	0.1237	0.0036	0.001	0.0127	0.0008	0.6111	471	546	8638	15	1	
0.1	0.0079	0.1237	0.0051	0.001	0.0127	0.0008	0.1373	471	546	8638	54	1	

4d: For the four metals at pH 7.5 for Mixed Ligands H₂BuEtP/HBuP

5 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance	Cd = 0.0008				Ni = 0.1238				Pb = 0.0058				7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472
H ₃ PO ₄ (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}	
0.001	0.0079	0.1233	0.0009	0.028	0.0127	0.0041	5.4444	15.8571	546	1688	4	3	
0.005	0.0079	0.0008	0.0021	0.014	0.0127	153.75	1.7619	32.7143	546	2	7	2	
0.01	0.0006	0.0008	0.0026	0.036	12.3333	153.75	1.2308	12.1111	3	2	9	3	
0.05	0.0006	0.0008	0.0027	0.001	12.3333	153.75	1.1482	471	3	2	9	1	
0.1	0.0006	0.1233	0.0011	0.002	12.3333	0.0041	4.2727	235	3	1688	4	2	

3.5. In H₂SO₄

The results for H₂SO₄ shown in Table 5 like those for the other four acids, had excellent distribution of Iron at all conditions with percentage extraction %E of Iron > 88% from figures 9 and 10. However, while Cadmium and Nickel distribution to the organic phases were masked in almost all condition, Lead showed appreciable good distribution ratios D in a few case; H₂BuEtP alone for pH 4.75 in 0.005 M and 0.01M H₂SO₄ with D = 57.00 and 4.25 respectively, for pH 7.5 in 0.1 M H₂SO₄ with D = 2.05, H₂BuEtP/HBuP for pH 4.75 in 0.001 M H₂SO₄ with D = 2.87, for pH 7.5 in 0.001 M – 0.005M H₂SO₄ with D = 117.00 and 77.67 respectively. These conditions can be exploited also in the separation of Iron and Lead from Cadmium and Nickel from an aqueous media containing the four metals with the best conditions for this separation being an aqueous medium containing the four metals with 0.005 M H₂SO₄ buffered to pH 4.75 using chloroform solution of H₂BuEtP alone as organic extractant with 99.9% extraction of Lead and Iron achievable after 2 batches of extraction (Table 1a). As with the other four acids, H₂SO₄ also show good potentials in separation of Iron from Cadmium, Nickel and Lead with 99.9% extraction of Iron after 1-2 batches of extraction as shown in Table 5 and figures 9-10. The results when compared with those for each

metal alone in H₂SO₄ showed close similarities with Lead giving > 80% extractions [12], Nickel completely masked [15] and Iron giving > 90% extraction in 0.001 M – 0.01 M H₂SO₄ although masking was evident above 0.01 M H₂SO₄ [10] but Cadmium with > 50% extraction [16] was in contrast to the complete masking in the presence of the other three metals. For the simultaneous extraction of the four metals, SO₄²⁻ results as reported by Godwin and Young, 2020 [17], were far better than those for H₂SO₄. Statistically in H₂SO₄ with both organic extractants, there was no significant difference between the two buffers in the distribution of Cadmium, Nickel and Lead with only Iron distribution ratios showing significant between them with p = 0.0096 in both buffers with pH 4.75 having better distribution ratios. There was also no significant difference between the two organic phases except for Nickel at pH 4.75 with p = 0.0013 and showing synergic effect of HBuP. Comparing H₂SO₄ results with those of the four other acids statistically with H₂BuEtP alone with pH 4.75 buffer, showed significant differences only in distribution ratios for Iron and Nickel between CH₃COOH and H₂SO₄ with p = 0.0021 and Nickel for H₃PO₄ with p = 0.022, HCl and HNO₃ with p = 0.0162 and in all cases H₂SO₄ distribution ratios were better. However, H₂BuEtP alone with pH 7.5 in H₂SO₄ showed no significant difference in distribution ratios of the four metals with those

of CH_3COOH and HNO_3 with all $p > 0.05$ but significantly different for Nickel distributions only when compared with HCl with $p = 0.0065$ and H_3PO_4 with $p = 0.0087$ and also like pH 4.75 had H_2SO_4 having better distribution ratios. $\text{H}_2\text{BuEtP/HBuP}$ as organic extractant in buffer of pH 4.75 showed no significant difference in distribution ratios of the four metals between HNO_3 and H_2SO_4 but showed significant difference in distribution ratios of Iron with $p = 0.0042$ compared with those of CH_3COOH and Nickel with $p = 0.000$ compared with those of HCl and H_3PO_4 with H_2SO_4 also having better distribution ratios. Buffer 7.5 in

$\text{H}_2\text{BuEtP/HBuP}$ statistically showed no significant difference between H_2SO_4 and CH_3COOH in distribution ratios for the metals but showed significant differences only in Nickel distribution ratios between H_2SO_4 and those for HCl with $p = 0.0001$ and HNO_3 with $p = 0.012$ with H_2SO_4 distribution ratios for Nickel better than those of HCl and HNO_3 . Also, distribution ratios of Cadmium and Nickel between H_2SO_4 and H_3PO_4 in buffer 7.5 with $\text{H}_2\text{BuEtP/HBuP}$ were significantly different for Cadmium and Nickel with $p = 0.04$ and in both cases H_3PO_4 having better distribution ratios for the two metals.

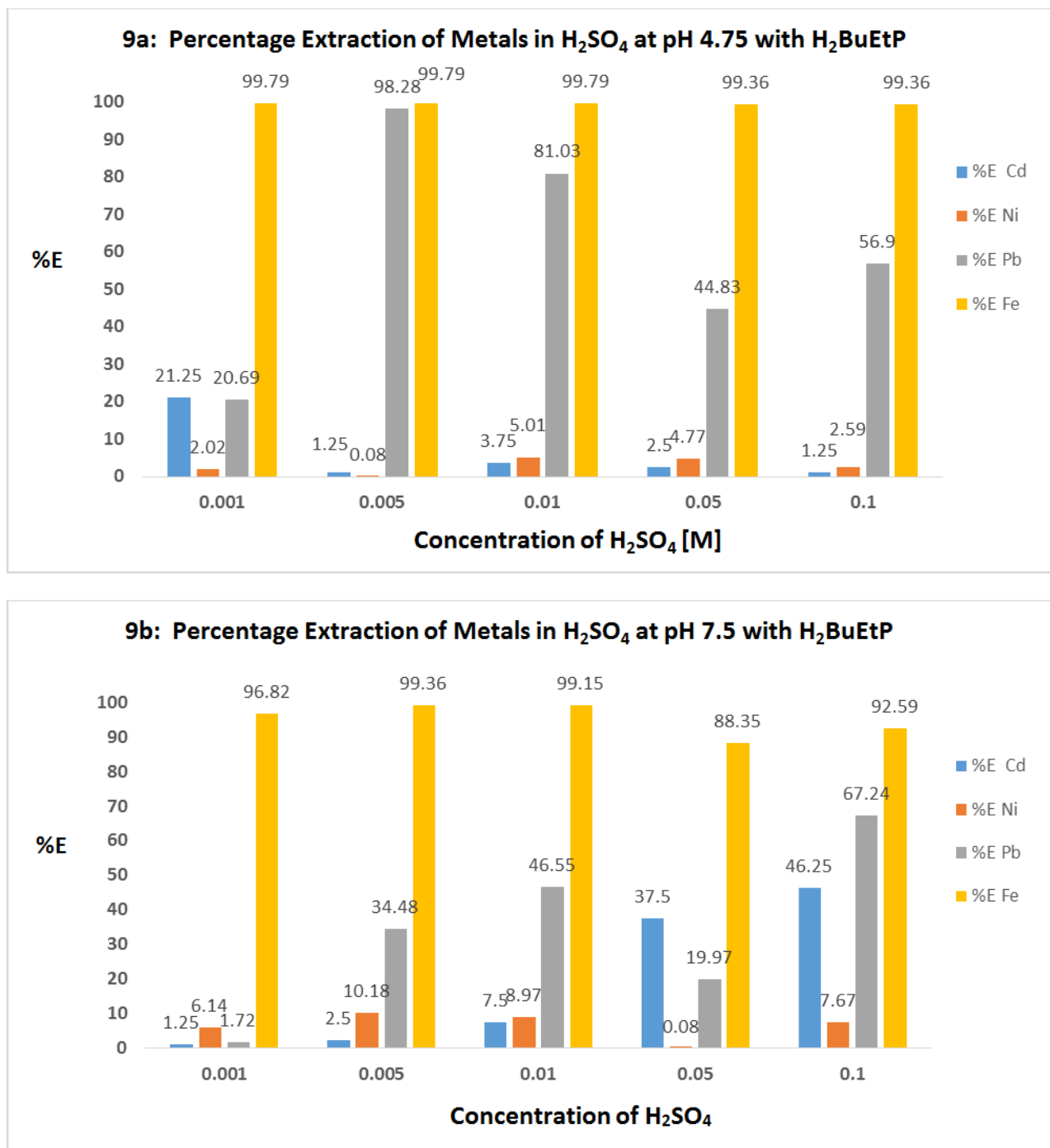


Figure 9. Charts of Percentage Extraction of Metals in H_2SO_4 with Ligands alone (a) at pH 4.75 and (b) at pH 7.5.

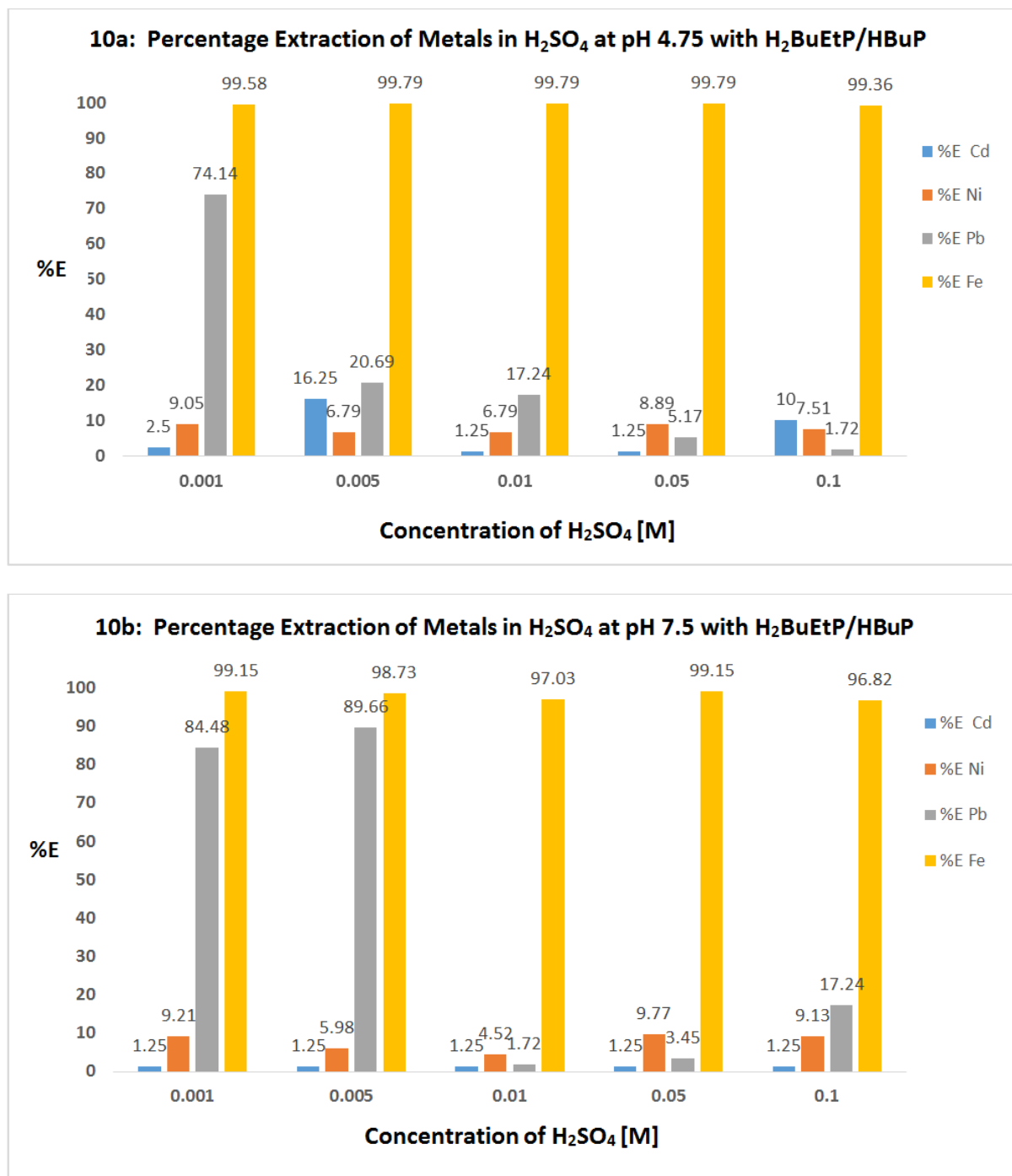


Figure 10. Charts of Percentage Extraction of Metals in H₂SO₄ with Mixed Ligands H₂BuEtP/HBuP (a) at pH 4.75 and (b) at pH 7.5.

Table 5. Distribution Ratios and number of batches needed to achieve 99.9% extraction of metals in H₂SO₄.

5a: For the four metals at pH 4.75 for Ligand H₂BuEtP alone

5 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance					Cd = 0.008		Ni = 0.1238		Pb = 0.0058		7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472	
H ₂ SO ₄ (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}
0.001	0.0063	0.1213	0.0046	0.001	0.2698	0.0206	0.2609	471	29	339	30	1
0.005	0.0079	0.1237	0.0001	0.001	0.0127	0.0008	57	471	546	8638	2	1
0.01	0.0077	0.1176	0.0011	0.001	0.0390	0.0527	4.2727	471	181	135	4	1
0.05	0.0078	0.1179	0.0032	0.003	0.0256	0.0500	0.8125	156.3	273	142	12	1
0.1	0.0079	0.1206	0.0025	0.003	0.0127	0.0265	1.3200	156.3	546	264	8	1

5b: For the four metals at pH 7.5 for Ligand H_2BuEtP alone

5 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance	Cd = 0.008				Ni = 0.1238				Pb = 0.0058				7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472
H ₂ SO ₄ (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}	
0.001	0.0079	0.1162	0.0057	0.015	0.0127	0.0654	0.0175	30.4667	546	109	398	2	
0.005	0.0078	0.1112	0.0038	0.003	0.0256	0.1133	0.5263	156.3	273	64	16	1	
0.01	0.0074	0.1127	0.0031	0.004	0.0811	0.0985	0.8710	117	89	74	11	2	
0.05	0.0050	0.1237	0.0047	0.055	0.6000	0.0008	0.2340	7.5818	15	8638	33	3	
0.1	0.0043	0.1143	0.0019	0.035	0.8605	0.0831	2.0526	12.4857	11	87	6	3	

5c: For the four metals at pH 4.75 for Mixed Ligands $H_2BuEtP/HBuP$

5 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance	Cd = 0.0008				Ni = 0.1238				Pb = 0.0058				7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472
H ₃ PO ₄ (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}	
0.001	0.0078	0.1126	0.0015	0.002	0.0256	0.0995	2.8667	235	273	73	5	2	
0.005	0.0067	0.1154	0.0046	0.001	0.1940	0.0728	0.2609	471	39	98	30	1	
0.01	0.0079	0.1154	0.0048	0.001	0.0127	0.0728	0.2083	471	546	98	37	1	
0.05	0.0079	0.1128	0.0055	0.001	0.0127	0.0975	0.0546	471	546	74	130	1	
0.1	0.0072	0.1145	0.0057	0.003	0.1111	0.0812	0.0175	156.3	66	89	398	2	

5d: For the four metals at pH 7.5 for Mixed Ligands $H_2BuEtP/HBuP$

5 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance	Cd = 0.0008				Ni = 0.1238				Pb = 0.0058				7.5 mgL ⁻¹ Fe Standard Absorbance = 0.472
H ₃ PO ₄ (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}	
0.001	0.0079	0.1124	0.0009	0.004	0.0127	0.1014	5.4444	117	546	72	4	2	
0.005	0.0079	0.1164	0.0006	0.006	0.0127	0.0636	8.6667	77.6667	546	112	4	2	
0.01	0.0079	0.1182	0.0057	0.014	0.0127	0.0474	0.0175	32.7143	546	149	398	2	
0.05	0.0079	0.1117	0.0056	0.004	0.0127	0.1083	0.0357	117	546	67	197	2	
0.1	0.0079	0.1125	0.0048	0.015	0.0127	0.1004	0.2083	30.4667	546	72	37	2	

The results generally showed the acids were not suited for multimetal extraction of the four metals as in almost all cases at least one of the metals is completely masked except for 0.01 M – 0.05 M H_3PO_4 with solutions buffered to pH 7.5 and using mixed ligands $H_2BuEtP/HBuP$ as organic extractant that had > 53% extraction of the four metals and theoretically 99.9% extraction of the metals extractable after 9 batches of extractions. The distribution ratios were different for at least one of the metals when compared to those reported for the metals alone in the same acid and this can be attributed to changes in permittivity/dielectric constants of the aqueous media with the four metals. High distribution ratios results from favourable energetics in the transfer of either the formed metal complexes $Cd(HBuEtP)X$ [16], $Ni(HBuEtP)_2$ [15], $Pb(BuEtP)(BuEtP)_2 \cdot 4H^+$ [12], and $Fe(BuEtP)[10]$ with ligand H_2BuEtP alone or metal adducts $Cd(HBuEtP \cdot BuP)$ [16], $Ni(HBuEtP)(BuP)$ [15], $Pb(HBuEtP) BuP$ [12], and $Fe(HBuEtP)(BuP)$ [10] in the case of mixed ligands $H_2BuEtP/HBuP$ [20] and in such cases, the acid is functioning as a releasing/salting out agent. Masking of the metals by the acids in contrast results from formation of strong salts of the acids with the metals leading to unavailability of the metals for complex or adduct formation.

4. Conclusion

CH_3COOH , HCl , HNO_3 and H_2SO_4 were not suited for multi-metal extraction of Cadmium, Nickel, Lead and Iron.

Aqueous medium containing 0.01 M – 0.05 M H_3PO_4 and buffered to pH 7.5 and using Chloroform solutions of mixed ligands $H_2BuEtP/HBuP$ as organic extractant can be utilized in multi-metal extraction of Cadmium, Nickel, Lead and Iron with 99.9% extraction of the four metals theoretically achievable after 9 batches of extractions with fresh organic extractant.

Acids are well suited for the separation of Iron from Cadmium, Nickel and Lead.

Nickel and Iron can be selectively separated from Cadmium and Lead from an aqueous solution containing 0.05M CH_3COOH and buffered to pH 4.75 using Chloroform solution of mixed ligands $H_2BuEtP/HBuP$ as organic extractant with 99.9% extraction of Nickel and Iron achievable after 3 batches of extractions with fresh organic phases.

Lead and Iron can be selectively separated from Cadmium and Nickel from an aqueous solution containing 0.005 M H_3PO_4 and buffered to pH 4.75 using Chloroform solution of H_2BuEtP with 99.9% extraction of Lead and

Iron achievable after 2 batches of extractions with fresh organic phases.

Cadmium and Iron can be selectively separated from Nickel and Lead from an aqueous medium containing 0.005 M HCl or 0.001 M H₃PO₄ and buffered to pH 7.5 using Chloroform solution of H₂BuEtP with 99.9% extraction of Cadmium and Iron achievable after 8 batches of extractions for solution containing 0.005 M HCl and 6 batches of extractions for solution containing 0.001 M H₃PO₄ with fresh organic phases.

For the multi-metal distribution of the four metals in the five acids, the performance of the acids were in the order H₃PO₄ > HNO₃ > H₂SO₄ > CH₃COOH > HCl.

There was no significant difference between the two buffers pH 4.75 and 7.5 and between the H₂BuEtP alone and mixed ligands H₂BuEtP/HBuP in distribution ratios for the four metals in the acids with only a slight synergic effect of HBuP.

Since all the separations and multimetal extractions conditions outlined with numbers of batches of extractions required to achieve 99.9% of the metals are theoretically calculated, experimental studies should be undertaken to compare with these values as developing these methods for industrial applications will contribute greatly in heavy metals remediation, metal recovery and spectral studies where interference of separated metals occur.

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