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Utilizing Carbowax-Sulphate Salt in Aqueous Biphasic System for Cd(II) ions Extraction from Produce Water

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Abstract

Because of their non-toxicity, durability, and low cost, the application of aqueous Carbowax (PEG) – inorganic salt two-phase systems for the extraction of hazardous metal ions holds a lot of promise. Combining aqueous solutions of certain organic salts with watery arrangements of certain water-soluble polymers (most commonly Carbowax) in specified quantities yields Aqueous biphasic systems. Centrifugation can easily separate the aqueous phases, and the procedure can be performed within the range of experimental variance. The extraction competence of metal ions in such Aqueous biphasic systems is primarily determined by the pH of the salt solution, the concentration of metal ions, the quantity of iodide extractant added, the M.wt of Carbowax and The Aqueous biphasic system's volume ratio, according to the experimental results. All of these factors will be discussed in this study in order to determine the best experimental conditions for efficient extraction of the potentially toxic heavy metal ion Cadmium (II) in aqueous Carbowax-based two-phase systems. The best condition was 10%

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(w/w)Carbowax8000 and 10% (w/w) $(NH_4)_2SO_4$ at pH=2.1 with NaI =0.7 as extraction agents and Vr=0.1 as the optimum condition with extraction efficiency of 90%.

Keyword : Aqueous biphasic System; Cd(II) Extraction; Carbowax; $(NH_4)_2SO_4$; Produced Water.

I. INTRODUCTION

The billions of gallons of produced water created each potentially be connected to in excess of 65,000 onshore and offshore oil and gas fields throughout the world [1][2]. The amount of water produced varies between 0.4 and 1.6 times the amount of oil removed [3]. Through oil and gas explorations, produced water (locked in underground formations) is carried to the surface, containing heavy metals such as Cu, Cd, Pb, Cr, Hg, Ag, Ni, and Zn as dissolved inorganic matter[4]. The bulk of these produced water ingredients are hazardous to the ecosystem [5] , Heavy metals should be effectively regulated when produced water is leaked on the ground surface or released into water bodies since they impair the ecology [6]

Heavy metals can be removed from produced water by a variety of methods sush as reverse osmosis, ion exchange, chemical precipitation, electro dialysis, membrane filtering, solvent extraction, and adsorption [7], among others. These technologies, however, have a number of drawbacks, including tall costs, only partial metal expulsion from waste water, poor selectivity, and substantial energy consumption, especially when used to recover precious metal ions[8]. The most effective method in this case is liquid-liquid extraction, in which the valuable metal particles are expelled using organic solvents .It is possible to successfully apply the method of particular partition and concentration of metal particles follows from an watery arrangement using liquid-liquid extraction with organic solvents. This method is also cost-effective because it allows for the use of a variety of solvents, extracting agents, and fluid stages. Extraction in a short length of time, flexibility to a wide range of solutes and experimental settings (concentration of solute, pH, ionic strength, temperature), and the capacity to recycle the solvent are all advantages of organic solvent extraction. However, because of the vast amounts of solvent required, as well as the high pricing, toxicity, flammability, and volatility of organic solvents, alternate extraction procedures that were less detrimental to the environment were developed[9].

When a water soluble polymer (typically Carbowax,) is collective with another (dextran) or an inorganic salt e.g.(Na_2SO_4, $(NH_4)_2SO_4$, K_2HPO_4, Na_2CO_3) at a given concentration, two immiscible aqueous phases are produced. [10][11][12][13]. The top phase, which is high in Carbowax, functions similarly to the organic solvent used in classic extraction procedures, whereas the bottom phase is high in inorganic salt[14][15]. There are several advantages of using aqueous Carbowax-based two-phase systems for metal ion extraction., including the fact that they are practically non-flammable and non-toxic, which all of the components are readily accessible. Furthermore, because Carbowax is biodegradable, the hazard of environmental contamination is minimal[16][12].

The degree of hydration and stability of the metallic species shaped in the extraction system, as well as the characteristics of the formed Aqueous biphasic system (decided by the molecular mass and concentra-

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tion of Carbowax and nature and concentration of the inorganic salt) determine metal ion extraction in such Aqueous biphasic systems[10]. The second condition necessitates the use of an extracting agent to ensure the extraction process' selectivity if the best characteristics of an Aqueous biphasic system (system stability, phase separation time, and pure interface) can be achieved through careful choice of phase forming components.

According to literature, in aqueous Carbowax-based two-phase systems, some metal ions e.g. (Hg(II), Cd(II), Bi(III), Zn(II), Co(II), Ni(II), Fe(III), etc.) can be quantitatively extracted into the Carbowax-rich phase by adding halide or pseudo-halide ions , and extraction efficiency is determined by the hydrophobicity of Carbowax-rich phases as well as the constancy of metal halide species produced in extraction systems[17][11][18][19][20] [21][22][23].

The goal of this study was to use an Aqueous biphasic system to extract heavy metals from produced water brought in from an Iraqi oilfield: this study proposes the selective extraction of Cd(II) ions from aqueous media using Aqueous biphasic systems made up of Carbowax (PEG) and inorganic sulphate $(NH_4)_2SO_4$ in the presence of iodide ions as extracting agents. The pH of the salt solution, the concentration of metal ions, the quantity of iodide extractant added, the M.wt of Carbowax and The Aqueous biphasic system's volume ratio are some of the experimental parameters.

II. MATERIALS AND METHODS

The experimental work was use batch system by(ATPS). The effect of the pH, the concentration of metal ion , the quantity of added iodide extractant, M.wt of Carbowax and the volume ratio studied in the batch process.

2.1 Materials

The experiments used Carbowx aqueous solutions containing 10% (w/w) Carbowx, which were produced by dissolving a sufficient amount of solid Carbowax with average M.wts of (1500(INDIA), 4000(CDH), 6000 (Russian fed), and 8000(99.9% purity, France) g/mol in distilled water. The inorganic salt aqueous solution $(NH_4)_2SO_4$ 10 percent (w/w) (98.5 % purity, England) was ready by dissolving the hard salt weighted at technical balance in distilled water. By dissolving and diluting to the necessary concentration salt solution volume, NaI (99.5% purity, India) was employed to generate 1 mol/L solutions of inorganic extraction agent. This approach reduces the amount of phase forming salt by a significant amount in tests. A stock solution of 1000 mg/L $CdSO_4.8H_2O$ (98 %, India) was used for the experimental extraction assays. Cadmium sulphate was dissolved in distilled water to make this and then standardizing the solution[24]. NaOH (98 % Purity ,India)and H_2SO_4 (96 % purity, Belgium) were utilized.

Classification of produced water from Al-Rumaila oilfield and south Iraq show in Table 1.

Table 1. The characteristics of the produced water.

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Parameters.	Values
pH	6.8
TDS	250000mg/L
Conductivity	58600µs/cm
TSS	300mg/L
Oxygen dissolved in water	2mg/L
Cadmium	0.2mg/L
Copper	1.5mg/L
Mercury	0.3mg/L
Calcium	25800mg/L

2.2 Methods

The Carbowax (PEG) used in the tests had a molecular mass of 1500,4000, 6000,8000 g/mol on average. All of the chemicals were analytical reagent grade, which meant they didn't need to be purified before use.

By dissolving an appropriate quantity of solid reagent in distilled water, solutions of 10 % (w/w) Carbowx(1500,4000,6000,8000) were created. The different pH values (2,2.1; 3. 2; 4.5 and 7) were gotten by including little volumes of mineral acids (H_2SO_4) or bases (NaOH concentrated solutions) to the solutions of inorganic salts (10 % (w/w) $(NH_4)_2SO_4$, as well as the various pH levels (2,2.1; 3. 2; 4.5 and 7) were achieved by addition smaller quantity of concentrated mineral acids (H_2SO_4) or bases (NaOH), which were included in the overall solution mass.

Metal sulphate salt was dissolved in distillate water to produce a 1000 mg/l solution of metal ions Cd(II). After preparation, the solutions were standardized. NaI generated 1 mol/L inorganic extracting agent solutions by dissolving and diluting to a given amount of salt stock solution. All of the aqueous solutions were made with distilled water.

An (ATPS) was created for the extraction experiment by Different quantities of Carbowx(1500,4000,6000,8000)g/mol solution and inorganic salt solutions were mixed together., each with a dissimilar pH (measured with a pH meter/pH 3110/WTW (Germany) (Plate3-7) at room temperature (24+2 °C). Cd(II) 1000 ppm metal ion solutions (1.5–5.5 mL) and 1mol/L NaI solutions (0.1–0.9 mL) were added. With double distilled water, the extraction system's ultimate volume was adjusted to 10 mL. The systems were centrifuged at 2000 rpm for 10 minutes before being turned off for at least 30 minutes. The phases were carefully isolated and put into separate glass tubes before analysis.

Analytic method

The metal ions content in both phases was evaluated using an atomic absorption spectrophotometer after the two phases had been properly diluted (AAS). (NOVAA 350ANALYTIKJENA). The metal ion content of each phase was estimated in identical using a arranged calibration chart

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Using the distribution coefficients (D) and extraction percentages, the extraction efficiency was quantified (E %). According to their specifications, These parameters were calculated with a standard deviation of less than 0.5 percent based on experimental results.

$$D = \frac{concentration\ of\ metal\ ion\ in\ uper\ phase}{concentration\ of\ metal\ ion\ in\ lower\ phase}$$

$$E\ \% = \frac{D}{D+Vr}\ .100$$

Where: Vr is the salt volume ratio –rich phase and Carbowax-rich phase.

III. RESULTS AND DISCUSSION

Polymer/salt systems emerged as promising alternatives with very good performance at a significantly reduced cost[25]. sulfate are the most commonly used salts .sulphate[26][27][28].

The extraction efficiency of heavy metals depends mainly on: (ii) acidity of salt phase forming solution; (iii) the concentration of metal ion , the amount of added iodide extractant, M.wt of Carbowx and the volume ratio of the Aqueous biphasic system. In order to found the optimal experimental conditions for the efficient extraction of toxic heavy metal ion Cadmium (II), in aqueous CARBOWAX-based two-phase systems, in presence of halide extracting agents, all these factors will be discussed in this study.

3.1 The effect of pH

The effect of the PH value of the produced water was checked for different experiments in this study within the different value (2,2.1, 3.2,4.5,7) .other parameter are constant throughout the experiments (Cd =25ppm, PEG4000, NaI=0.5mL, Vr=1 at room temperature) .

From the figure(1) ,it was look at when the pH=2.1, the highest extraction efficiency of up to (97.28%)is achieved , while when the pH above increases above 2.1 , extraction efficiency begin decrees grouted until reaches 94 % at pH = 7. It has been proven that the optimum pH many researches [20][29][30][31][32].

In the Aqueous biphasic extraction method, the acidity of the salt solution is a significant experimental parameter., as it influences not only the hydrophobicity of the Carbowax-rich phases of the extraction system (which is directly related to the amount of water in these phases), but also the speciation and solubility of metal ions [15].

The acidity of the salt solution was changed in the pH range of 2.0 to 7.0 throughout the experiments. Because the components that create phases (NH_4^+, SO_4^{-2}, Carbowx, etc.) are virtually not involved in secondary processes, the pH variety in this domain has an insignificant impact on The two aqueous phases' production and separation, according to Li and his co-authors [12]. This means that the characteristics of Aqueous biphasic systems are not significantly changed.

Nonetheless, raising a salt solution's acidity increases the hydrophobicity of the Carbowx-rich phase of extraction systems, as well as heavy metal ion extraction efficiency [20].

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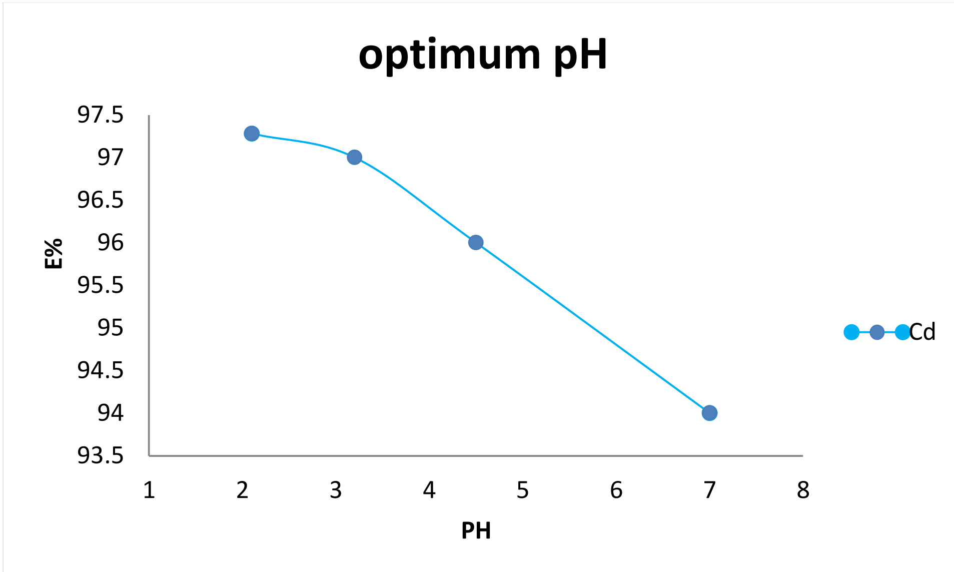

Figure 1. The effect of PH on Extraction efficiency of Cd(II) ions in Carbowax4000 + $(NH_4)_2SO_4$.

3.2 The effect of concentration of metal ion

Five different Cd(II) starting concentrations ranging from 15 to 55 ppm were tested with 0.5 ml NaI, vr= 1, Carbowax4000, and pH 2.1 to see how the initial concentration of Cd(II) ions affected efficiency. The final result is presented in Fig. 2, where the greatest extraction efficiency is found at 45ppm. The extraction efficiency increases with metal concentration up to 45ppm at low concentrations, but subsequently drops as the concentration of metal increases. The reduction in proficiency as a result of the overload of the Carbowax phase with metal ions. Bulgariu and Bulgariu arrived to similar conclusions[15]. Similar results were obtained using Carbowax1550/ $(NH4)_2SO_4$ ATPS to extract Zn (II) ions in the initial concentration range of 30 to 65 g/mL. Furthermore, The extraction proficiency of Zn(II) ions increased up to 55 ppm in the presence of 0.05 M chloride ions with an increase in starting concentration and thereafter reduced. [32]. Similar results were observed for the extraction of Copper(II) ions employing the Carbowax 2000-ssulfate of soda system, where the extraction proficiency climbed to 7 ppm before declining[33].

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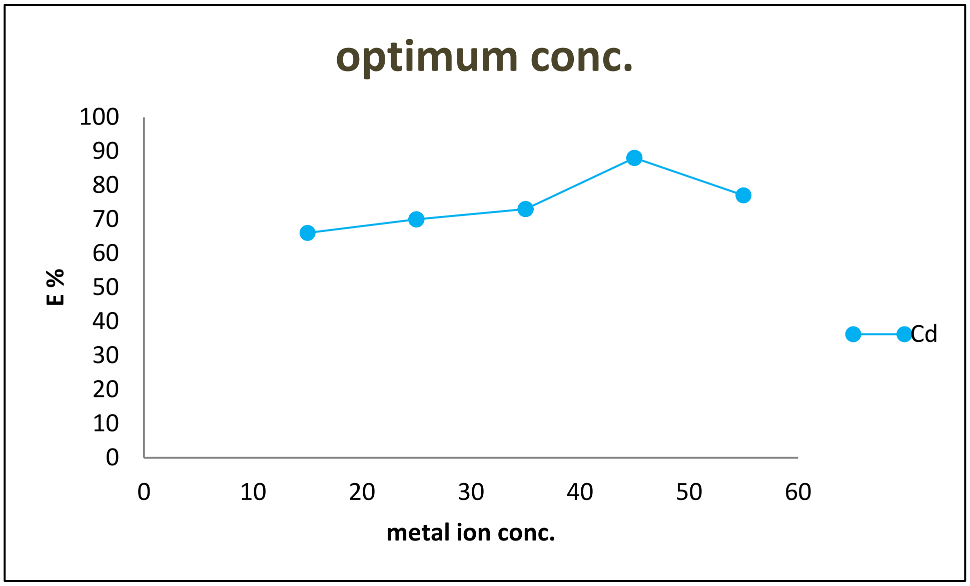

Figure 2. The concentration of metal ion effect on Efficiency of extraction Cd(II) ions in Carbowax4000 + $(NH_4)_2SO_4$.

3.3 Effect of concentration of extracting agents

1- Extraction of Cd in absence extracting agents:

Heavy metal ions are removed insignificantly with the Carbowax-rich phase of (ATPS)in the nonappearance of a suitable extracting agent, according to experiments (Table 2), and increasing the pH of the salt solution had little effect on extraction efficiency. in Aqueous biphasic systems metal ion extraction does not contain direct chemical metal ions and PEG molecules from the Carbowax-rich phase interactions, as evidenced by the low extraction percentages recorded in all cases.

Table 2. The extraction percentages obtained for Cd, in absence of extracting agent, in the Aqueous biphasic systems.

Metal Ions	E %				References
	pH = 2.05	pH=3.12	pH=4.48	pH=7.09	
Cd	15.67	15.39	21.93	20.89	[29]

The aqueous Carbowax(1550) + $(NH_4)_2SO_4$ two-phase system

The results that were made in the laboratory are shown in Table 3.

Table 3. The extraction percentages obtained for Cd, in absence of extracting agent, in the ATPS in laboratory.

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Metal Ions			
	C salt	C Carbowax	E%
Cd	9.01	2.71	23

The aqueous Carbowax(4000) + $(NH_4)_2SO_4$ two-phase system, pH 2.1.

The Cd(II) species persisted largely in the extraction system's salt-rich phase in the absence of supplemental iodide extractants, as shown in Table 1. As a result, it's possible that the extraction of Cd(II) species does not include Carbowax molecules interact chemically with metal species, and their extraction is minor because the Cd(II) species are excessively hydrated[34]. To increase metal ions extraction efficiency, [34] must change the nature of metal species utilizing an appropriate extracting agent, It should be at a lower hydration degree and generate more stable species than those seen in the salt-rich phase.

2- **Extraction of Cd(II) in existence of supplementary iodide Extractants**:

Because of their high solubility in water and significant partitioning in the Carbowax-rich phase in the absence ions of metal, the halide ions (Cl^-, Br^-, and I^-) can be utilized as inorganic extracting agents. [18]. The influence of the extracting agent on Cadmium extraction has been studied using a number of different factors. For a constant pH of 2.1, Cd= 45 ppm,Carbowax4000 and Vr=1, the NaI concentration employed in the tests ranged from 0.1 mL to 0.9 mL. At 0.7 mL, the maximum efficiency of 93.18% is achieved. The effectiveness of the extraction achieved a greatest at 0.7mL iodide ions and suggested to drop off for all other evaluated iodide ion levels, shown in figure 3. From figure 3 , The extraction of metal ions in the Carbowax -rich phase increased as the halide ion concentration increased .similar to[35].

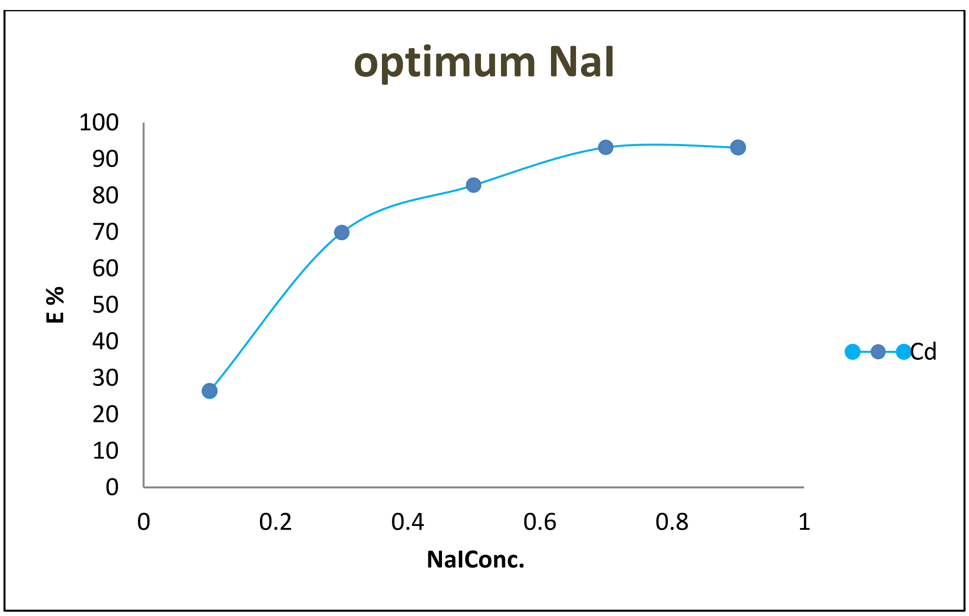

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Figure 3. The influence of metal ion concentration on the effectiveness of Cd(II) ion extraction in Carbowax4000 + $(NH_4)_2SO_4$.

3.4 Effect of M.wt of Carbowax on the Extraction of Cadmium Ions

In order to choose a phase-forming polymer with an appropriate M.wt for Cd(II) ions extraction. ATPE was performed with different M.wts of Carbowax (MW 1500, 4000, 6000 and 8,000)

Figure (4) shows the effect of the M.wt of Carbowax on the percent extraction of Cd(II) , the other variables such as pH 2.1, NaI solution of (0.7 mL) initial concentration of Cd(II) =(45ppm) and Vr=1were kept constant.

The results below, the extraction of Cd(II) rise as the M.wt of the polymer increases, owing to the larger size of Carbowax molecules, which causes the system's hydration to decrease. [36]

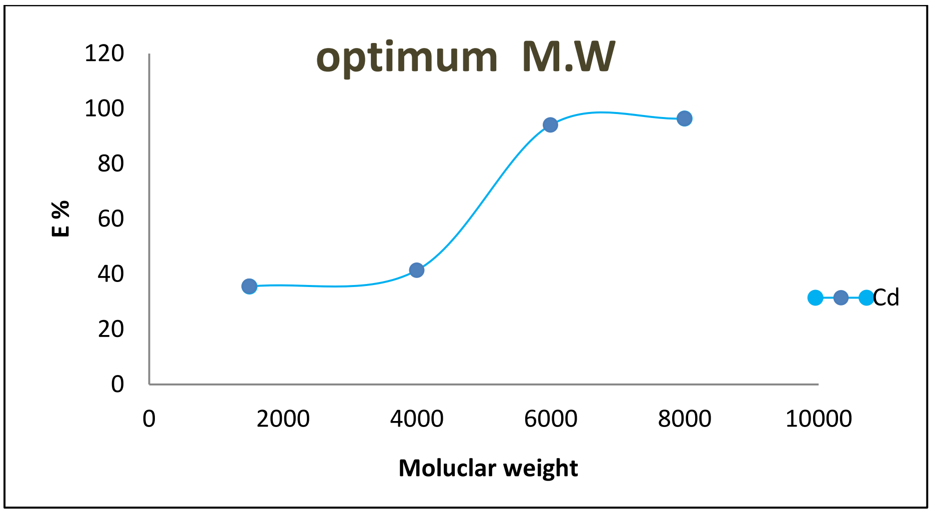

Figure 4. The effect of polymer molecular Wight on Extraction efficiency of Cd(II) ions in bowax(1500,4000,6000,8000) +$(NH_4)_2SO_4$.

3.5 **Effect of Volume ratio(salt/Carbowax)**

The phase volume ratio was changed between 0.1 and 1 so as to investigate the influence of volume ratio on the extraction yield of Cd(II) ions. the other variables such as pH 2.1 NaI solution of (0.7 mL) initial concentration of Cd(II) =45ppm and Carbowax8000 were kept constant.

The findings of the experiment show that Increasing the volume ratio between phases resulted in a reduction in Cd(II) extraction percentages from 90% to 75% in the defined circumstances of the experimentshown in figure 5. This difference in efficiency of Cd(II) extraction can be explained by the fact that when volume ratios are higher between phases, the extraction system's polymer-rich phase becomes greater hydrophobicity (because of the large volume of inorganic salt exerting a salting-out effect), and thus Cd(II)–iodide species extraction decreases. As a result, a significant amount of polymer-

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rich phase was required to extract Cadmium (II) ions in the extractants containing iodide, which was achieved when the phases' volume ratios was equal to 0.1[9][32] .

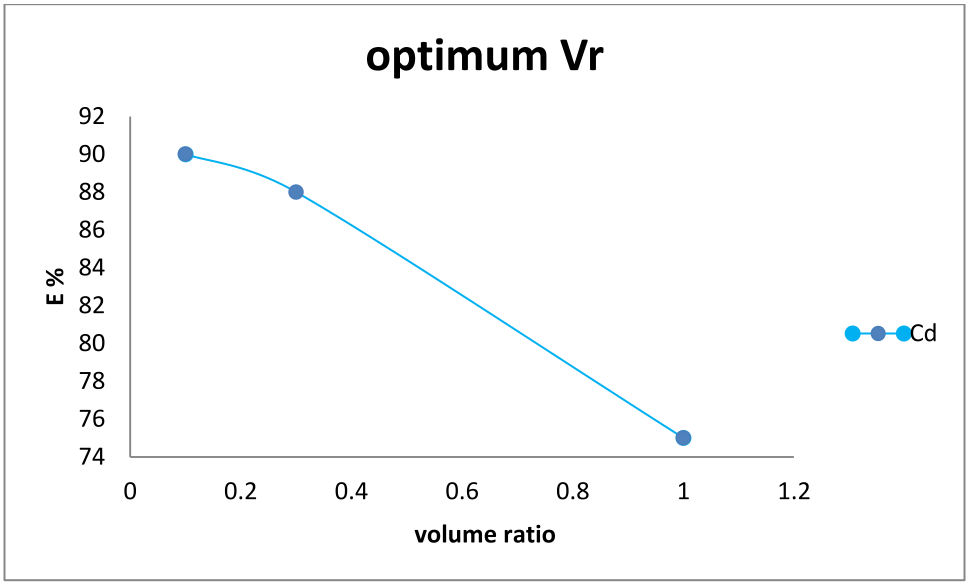

Figure 5. The effect of volume ratio on Extraction efficiency of Cd(II) ions in Carbowax(8000) + $(NH_4)_2SO_4$.

Conclusions

An alternate procedure for selective extraction of Cd(II) ions from aqueous solutions has been described, which can be used instead of the traditional solvent extraction technique. This approach involves combining a Carbowax aqueous solution (8000) with an inorganic salt aqueous solution, as well as iodide as an extracting agent, to create Aqueous biphasic systems. The utilization of aqueous biphasic systems is ecologically friendly and follows green chemistry principles., as well as efficient and cost-effective. The pH of the salt solution, the concentration of the metal ion, the amount of additional iodide extractant, the M.wt of Carbowax, and the volume ratio of the Aqueous biphasic system are all factors that influence the extraction effectiveness of the metal ions under discussion. All of these factors were considered in this study in order to determine the best experimental conditions for the efficient extraction of heavy metal ions in Carbowax aqueous -based systems with two phases. The best condition was 10 % (w/w)Carbowax8000 and 10 % (w/w) $(NH_4)_2SO_4$ at pH=2.1 with NaI as extraction agents and Vr=0.1 as the optimum condition with extraction efficiency of 90%.

IV. ACKNOWLEDGMENT

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