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## Physical modification of silica gel with bis(2,2'-methylenephenol) diaminoethane for separation and spectrophotometric determination of Cu(II) from Ni(II) ions

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## ABSTRACT

Physical modification of silica gel with bis(2,2'-methylenephenol)diaminoethane (BMPDE) for extraction of Cu(II)and Ni(II) ions was investigated in four different acids;  $H_2SO_4$ , HCl, HNO<sub>3</sub> and HClO<sub>4</sub> in the concentration range of  $10^{-1} \cdot 10^{-4}$  M and pH 1-11. The stability of the BMPDE-physically-modified silica gel was investigated in the same acid concentrations and pH range. Maximum adsorption of BMPDE onto silica was observed at pH 10 with percentage removal of 92.50 % while the presence of HCl,  $H_2SO_4$ , HNO<sub>3</sub>, HClO<sub>4</sub> in the concentration range  $10^{-1} \cdot 10^{-4}$ M depressed adsorption of BMPDE onto activated silica gel. Optimum separation of Cu(II) occurred at pH 9 while that of Ni(II) was at pH 7. Extraction of the two metal ions in the four acids HCl,  $H_2SO_4$ , HNO<sub>3</sub>, and HClO<sub>4</sub> in the concentration range of  $10^{-1} \cdot 10^{-4}$  M was between 8-77%.

Keywords: Adsorption, bis(2,2'-methylenephenol)diaminoethane, recovery, salen-type Schiff base, silica gel.

#### INTRODUCTION

The chemistry of metal complexes with Schiff base ligands have attracted continuous attention for the synthetic chemists due to their ease of synthesis, stability under a variety of oxidative and reductive conditions especially in aqueous medium [1]. Bis(2,2'-methylenephenol)diaminoethane is a salen-type Schiff base which results when two equivalents of salicylaldehyde react with an ethylenediamine in a condensation process [2]. Over the years, there has been a growing interest in the use of salen-type Schiff base in metal ion separation. This is because of the exceptional ability of salen-type Schiff base to complex heavy metals especially the transition metals through its four coordination sites [3]. The potential of BMPDE to form coloured complexes with transition metals Cu and Ni has eased its application as a spectrophotometric reagent.

The search for new methods of metal ions separation from environmental samples has continued with attention being paid to analytical methods, which are cost effective, time saving, specific, sensitive and accurate. This drive towards scavenging metal ions is because of the detrimental effects these metals have on our environment and the complexity of some common methods such as atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry, graphite carbon mass spectrometry, inductively coupled plasma mass spectrometry, flame atomic absorption spectrometry. These methods usually involve combination of two techniques; the sample preparation section and the detection tools [4]. The high operational cost of these instruments limits their applications. These methods are also limited by matrix interferences and results obtained may be erroneous if the limitations of these instruments are not considered because the metal ions may be present with other elements [5].

Adsorption of heavy metals at trace levels on readily available and low cost activated carbon materials has been reported [6]. The use of activated carbon materials has major drawbacks such as non selectivity in metal ion separation, non reusability and irreversible adsorption of the metal ions [7]. Solid phase separation of metal ions using BMPDE-physically-modified silica gel is therefore exigent because of the many advantages it has over conventional methods of metal ion separation and these include thermal and chemical stability, discriminatory removal of metal ions, enhanced sensitivity and cost effectiveness [8]. Solid phase extraction is also a green analytical method since it does not involve the use of toxic solvents and it saves time [9, 10]. The present work studied the modification of silica gel in acids and in different pH ranges using a chelating ligand, BMPDE, which has the potential to enhance the separation of metal ions.

#### MATERIALS AND METHODS

#### 2.1 Activation of silica gel and preparations of stock solutions.

#### 2.1.1 Synthesis of the ligand

The chelating ligand bis(2,2)-methylenephenol)diaminoethane was synthesized as reported in previous work[4]. The silica gel was activated by heating in a 1:3 mixture of HCl/H<sub>2</sub>O. Stock solutions of BMPDE were prepared by dissolving appropriate weights of the compound in absolute ethanol to obtain a 5% stock solution.

#### 2.1.2 Preparations of stock solutions

Stock solutions of Cu(II) and Ni(II) were prepared by dissolving appropriate weights of CuSO<sub>4</sub>.5H<sub>2</sub>O and NiSO<sub>4</sub>.7H<sub>2</sub>O respectively in distilled water to obtain 1.0 mg/mL solution.

The acid solutions;  $H_2SO_4$ ,  $HNO_3$ , HCl and  $HClO_4$  were prepared in the concentration range of  $10^{-1}-10^{-4}$  M and standardized with  $Na_2CO_3$  for use in the adsorption studies. Buffer solutions (pH 1-11) were prepared following the method reported by Dhanlad De Iloyd [4]. The pH of the solutions was confirmed using pH meter (product of Hanna instruments). The reagents used in the preparation of the buffer solutions were of Analar grade. The samples were agitated using RF-12 rotary shaker 500 rpm, Remi equipment while the absorbances of the solutions were measured using spectrum Lab 22pc spectrophotometer.

#### 2.1.3 Activation of Silica Gel

In the activation of silica gel, 10 g of silica gel of average particle diameter (APD) of 75  $\mu$ m was weighed into a 500 cm<sup>3</sup> beaker. Then, 200 cm<sup>3</sup> of HCl/H<sub>2</sub>O solution (1:3V/V) was added and heated for 10 h in an oven at 103°C to remove metals if present and to maximize the number of silanol groups on the porous silica gel surface [11]. The silica gel was then removed from the oven and allowed to cool to room temperature and then filtered with whatman filter paper 110 mm. The activated silica was washed several times with copious amount of distilled water until the pH was 7. Subsequently, the activated silica gel was dried in an oven at 120°C for 13 h and then kept in desiccators for use.

## 2.1.4 Determination of wavelength of maximum Absorption ( $\lambda_{max}$ ) of BMPDE in Acid and in buffer solutions.

In the determination of the maximum wavelength of absorption, 1.0 cm<sup>3</sup> of BMPDE solution was pipetted into two different extraction bottles and each of the extraction bottles made up to 5 cm<sup>3</sup> separately with  $10^{-4}$  M HCl and a buffer solution of pH 8. The mixture was equilibrated for 5 min and then extracted with 5 cm<sup>3</sup> of chloroform. The absorbance of the extract was measured at various wavelengths to determine the wavelength of maximum adsorption ( $\lambda_{max}$ ) of BMPDE in both HCl and buffer solutions.

#### **2.2 Experimental Procedure**

# 2.2.1 Influence of contact time, acid concentration and varying pH on the adsorption of the BMPDE onto silica.

The effect of equilibration time on adsorption of BMPDE on the activated silica gel was investigated by weighing 1.0 g of the activated silica gel into six extraction bottles.  $2.0 \text{ cm}^3$  of BMPDE was added to each bottle and finally made up to 5 cm<sup>3</sup> with buffer solution of pH 10. The mixtures were agitated in a rotary shaker at 200 rpm at different contact times of 5 min, 10 min, 15 min, 30 min, 1h and 2 h. The content of each bottle was filtered at the end of each time interval. The residue was rinsed with 1 cm<sup>3</sup> of ethanol. 5 cm<sup>3</sup> of distilled water was added to the filtrate from each bottle and then unabsorbed BMPDE was extracted with 5 cm<sup>3</sup> of chloroform. The absorbance of extract from each bottle was measured at 370 nm.

The effect of buffer pH on adsorption of BMPDE on the activated silica gel was carried out by weighing 1.0 g of the activated silica gel into eleven extraction bottles and then adding 5 cm<sup>3</sup> of the different buffer solutions of pH 1-11 as appropriate. The mixtures were agitated on a rotary shaker for 30 min to allow for optimum adsorption of the BMPDE on the silica gel. At the end of 30 min, the content of each bottle was filtered and the residue rinsed with

 $1 \text{cm}^3$  of ethanol. Then, the BMPDE in the filtrate was extracted with 5 cm<sup>3</sup> of chloroform and the absorbance of each extract measured at 370 nm.

The effect of various acid concentrations on adsorption of BMPDE onto the activated silica gel was also investigated by weighing 0.1 g of activated silica gel into four extraction bottles. 2.0 cm<sup>3</sup> of BMPDE solution was added and then made up to 5 cm<sup>3</sup> with 0.1 M, 0.01 M, 0.001 M and 0.0001 M HCl. The bottles were agitated for 30 min at 200 rpm after which the silica gel was filtered off and washed with 1 cm<sup>3</sup> of distilled water. The unadsorbed BMPDE in the filtrate was extracted with 5 cm<sup>3</sup> of chloroform and the absorbance of the extracts measured at 370 nm. The same exercises were also carried out on 0.1 M, 0.01 M, 0.001 M and 0.0001 M solutions of H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HClO<sub>4</sub> acids.

The stability of BMPDE-Physically-Modified Silica gel in buffer solutions of different pHs and in various concentrations of different acids was also investigated by weighing 0.1 g of modified silica gel into eleven extraction bottles. Then, 5 cm<sup>3</sup> of buffer solutions of pHs 1-11 was pipetted into the different bottles and agitated on a rotary shaker at 200 rpm for 30 min. The same procedure was repeated in various acid concentrations;  $10^{-4}$  M,  $10^{-3}$  M,  $10^{-2}$  M,  $10^{-1}$  M, 0.5 M, 1.0 M and 2.0 M for the different acids HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HClO4. Then, the content of each bottle was filtered and the filtrate neutralized with aqueous ammonia and then the desorbed BMPDE extracted with 5 cm<sup>3</sup> of chloroform. The absorbance of the extracts from the different bottles was measured at 370 nm.

#### 2.2.2 Determination of wavelength of maximum absorption $(\lambda_{max})$ of metal–BMPDE complexes

The determination of wavelength of maximum absorption ( $\lambda_{max}$ ) of metal–BMPDE complexes in acids and buffer of different pHs was also investigated by introducing 1.0 cm<sup>3</sup> of 0.102 mg/cm<sup>3</sup> of copper(II) solution into four extraction bottles and the solutions made up to 5 cm<sup>3</sup> with 10<sup>-1</sup> M, 10<sup>-2</sup> M, 10<sup>-3</sup> M and 10<sup>-4</sup> M solutions of HCl. Then 0.10 cm<sup>3</sup> of 0.5% BMPDE was added and equilibrated for 5 min for colour development. The Cu<sup>2+</sup>-BMPDE was then extracted with 5 cm<sup>3</sup> of chloroform. The absorbance of the extracts was then measured at various wavelengths to determine the wavelength at which the Cu<sup>2+</sup>-BMPDE complex absorbed maximally. The same procedure was applied for Cu<sup>2+</sup> in 10<sup>-1</sup> M, 10<sup>-2</sup> M, 10<sup>-3</sup> M and 10<sup>-4</sup> M solutions of HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub>. The same exercise was carried out on Ni<sup>2+</sup> in the different concentrations of the four acids. The same procedures were applied to determine the wavelength of maximum absorption of the metal-BMPDE complexes in buffer solutions of pH 1-11.

#### 2.2.3 Effect of Equilibration Time on solid phase Extraction of Cu<sup>2+</sup> and Ni<sup>2+</sup>

0.1 g of the modified silica gel was weighed into five extraction bottles. Then 1 cm<sup>3</sup> of Ni<sup>2+</sup> solution containing 0.102 mg/cm<sup>3</sup> of Ni<sup>2+</sup> was added. The volume was made up to 5 cm<sup>3</sup> with buffer solution of pH 8. The bottles were equilibrated at various times of 1 min, 5 min, 10 min, 15 min and 30 min respectively. At the end of various time intervals, each bottle was removed and the mixture filtered and then 0.1 cm<sup>3</sup> of BMPDE solution was added to the filtrate for colour development of any Ni<sup>2+</sup> unextracted in the aqueous phase and the complex formed was extracted with 5 cm<sup>3</sup> of chloroform and the absorbance of the extract was measured. The Ni<sup>2+</sup> adsorbed on the solid support was desorbed with 5 cm<sup>3</sup> of 2 M HNO<sub>3</sub>. The desorbed metal ion was neutralized with aqueous ammonia, and then 0.1 cm<sup>3</sup> of BMPDE solution was added for colour development and then extracted with 5 cm<sup>3</sup> of chloroform and the assorbed was applied to determine the effect of contact time on solid phase extraction of Cu<sup>2+</sup>.

#### 2.2.4 Effect of pH on Solid phase Extraction of Cu<sup>2+</sup> and Ni<sup>2+</sup>.

The influence of pH on the extraction of the metal ions was carried out by weighing 0.1 g of modified silica gel into eleven extraction bottles. Then 1 cm<sup>3</sup> Ni<sup>2+</sup> solution containing 0.102 mg/cm<sup>3</sup> of Ni<sup>2+</sup> was added into each of the bottles and made up to 5 cm<sup>3</sup> with buffer solutions of pHs 1-11. The bottles were then equilibrated for 5 min on a rotary shaker at 200 rpm and then filtered and washed with 1 cm<sup>3</sup> of distilled water. 0.1 cm<sup>3</sup> of BMPDE solution was added to the filtrate for colour development and then Ni<sup>2+</sup>-BMPDE was extracted with 5 cm<sup>3</sup> of chloroform. The absorbance of the extracts was determined at 370 nm and at 36<sup>o</sup>C. Ni<sup>2+</sup> adsorbed on the solid support was then desorbed with 5 cm<sup>3</sup> of 2 M HNO<sub>3</sub> and neutralized with few drops of aqueous ammonia. Then 0.1 cm<sup>3</sup> of 0.5% BMPDE solution was added to the desorbed metal ion and then extracted with 5 cm<sup>3</sup> of chloroform. The absorbance of each extract was measured at 420 nm. The same procedure was applied to determine the effect of pH on solid phase extraction (SPE) of Cu<sup>2+</sup>.

#### 2.2.5 Effect of Acid Concentration on Solid Phase Extraction of Cu<sup>2+</sup> and Ni<sup>2+</sup>

0.10 g of modified silica gel was weighed into four extraction bottles. This was followed by addition of  $1.0 \text{ cm}^3$  of  $\text{Cu}^{2+}$  solution containing 0.102 mg/cm<sup>3</sup> of  $\text{Cu}^{2+}$  to each of the bottles and made up to 5.0 cm<sup>3</sup> with different concentrations ( $10^{-1}$  M,  $10^{-2}$  M,  $10^{-3}$  M and  $10^{-4}$  M) of HCl solutions separately into the different bottles and then equilibrated for 5 min. The mixtures were filtered, and then 0.1 cm<sup>3</sup> of BMPDE was added to the filtrate for colour development and equilibrated for 5 min and then extracted with 5 cm<sup>3</sup> of CHCl<sub>3</sub>. The absorbances of the extracts

were measured at 400 nm. Cu(II) ions adsorbed on the modified silica gel were then eluted with 5 cm<sup>3</sup> of 2 M HNO<sub>3</sub>. The eluent was adjusted to a pH 8 and then the colour was developed with 0.1 cm<sup>3</sup> of BMPDE. The eluent was then extracted with 5 cm<sup>3</sup> of chloroform and the absorbances of the extracts measured. The same procedure was applied to Cu<sup>2+</sup> in H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HClO<sub>4</sub> at 10<sup>-1</sup> M, 10<sup>-2</sup> M, 10<sup>-3</sup> M and 10<sup>-4</sup> M concentration. This was also carried on Ni<sup>2+</sup> in the different acids HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HClO<sub>4</sub> of concentrations10<sup>-1</sup> M, 10<sup>-2</sup> M, 10<sup>-3</sup> M and 10<sup>-4</sup> M.

#### 2.2.6 Separation of nickel from copper

0.1 g of the physically modified silica gel was weighed into an extraction bottle. Then 1 cm<sup>3</sup> solution of Ni<sup>2+</sup> and Cu<sup>2+</sup> containing 0.102 mg/cm<sup>3</sup> each of Ni<sup>2+</sup> and Cu<sup>2+</sup> was added to buffer solution of pH 7 and the volume made up to 5 cm<sup>3</sup> using distilled water. The mixture was equilibrated for 5 min and then filtered and then Ni<sup>2+</sup> adsorbed on the solid sorbent was desorbed with 5 cm<sup>3</sup> of 2 M HNO<sub>3</sub> and the absorbance was determined. The pH of the filtrate was again adjusted to 9 using NH<sub>4</sub>OH, then 0.1 g modified silica gel added and the mixture equilibrated for 5 min and then filtered. Cu<sup>2+</sup> adsorbed on the solid sorbent was desorbed with 5 cm<sup>3</sup> of HNO<sub>3</sub> and then the absorbance was determined.

#### **RESULTS AND DISCUSSION**

#### 3.1 $\lambda_{max}$ of bis(2,2'-methylenephenol)diaminoethane in Acids and Buffer pH

The ligand, BMPDE in  $10^{4}$ M HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HClO<sub>4</sub> has wavelength of maximum absorbance at 370 nm. Also at pH 10, BMPDE also exhibited a  $\lambda_{max}$  of 370 nm. The non variation in the wavelength of maximum absorbance of the ligand in both acidic medium and in the buffer of pH 10 showed non-interference in the buffer and acid absorption spectra of BMPDE.

#### 3.2 Influence of equilibration time on BMPDE adsorption onto Activated Silica Gel.

The exposure time required for the deposition of the ligand on activated silica gel and adsorption of metal ions on modified silica gel and attainment of equilibrium is of utmost importance. Optimum deposition of the BMPDE on activated silica gel at pH 10 occurred within 15 min with a percentage removal of 92.00 % as shown in Table 1.

#### Table 1: Effect of Time on Adsorption of the Salen onto Activated Silica

t(min)	m <sub>s</sub> (g)	C <sub>os(mg)</sub>	C <sub>t(mg)</sub>	C <sub>o</sub> -C <sub>t</sub>	% R
5	0.10	10	3.65	6.35	63.50
10	0.10	10	1.60	8.40	84.00
15	0.10	10	0.80	9.20	92.00
30	0.10	10	1.00	9.00	90.00
60	0.10	10	1.60	8.40	84.00

 $C_{os}$  = initial amount (mg) of Salen in 5 cm<sup>3</sup> of aqueous phase  $C_t$  = amount (mg) of Salen in 5 cm<sup>3</sup> aqueous phase after time (t)

t = time of equilibration in min.

 $m_s = mass of silica gel in g$ 

% R = percentage of salen adsorbed

#### 3.3 Effect of pH on Adsorption of BMPDE on Activated Silica Gel

Figure 1 shows the influence of pH on adsorption of BMPDE on activated silica gel. The figure shows that about 92.5% of the ligand was adsorbed at pH 10 which is the pH of optimum adsorption. Quantitative adsorption of BMPDE at this pH could be due to the formation of hydrogen bond between the silanol groups of the silica gel and the phenyl groups in the Schiff base. The structure of BMPDE which has four donor atoms (ONNO) also makes it easy for it to bind with the silica gel. At pH beyond 10, precipitation of the ligand sets in diminishing its adsorption on the solid support, while at pH 1-4 incomplete dissociation of the ligand as a result of high  $H^+$  concentration lowered the adsorption of BMPDE on activated silica gel.

#### 3.4 Effect of Various Acid Concentrations on Adsorption of Salen on Activated Silica gel

The effect of four common acids, HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> in the concentration range of  $10^{-1}$ - $10^{-4}$  M on adsorption of BMPDE onto activated silica gel was investigated. Variation of acid concentrations with the amount of BMPDE adsorbed on activated silica is shown on Table 2. These acids are common in the natural environment, so to obtain the optimum adsorption conditions, their interference on the adsorption process was examined. From Table 2, it could be seen that the four acids at higher concentrations of  $10^{-1}$ - $10^{-2}$  M significantly decreased the adsorption process. This could be due to the higher concentration of H<sup>+</sup> ions and subsequent protonation of the adsorption sites of the BMPDE. The adsorption of the BMPDE on the activated gel; however increased with decreasing concentration of the acids. This is in line with the behaviour of the ligand in pH media. At lower concentration range

of  $10^{-3}$ – $10^{-4}$  M, more of the ligand is adsorbed on the silica. Overall, there were no marginal differences on the effect of the four acids on the adsorption process.



Figure 1: Plot of percentage of BMPDE Adsorbed on Activated Silica gel as a function of pH

Table 2: Effect of Various Acid Concentrations on Adsorption of Salen onto Activated Silica gel (mg/g)

[Acid] M	I M <sub>s</sub> (g)	C <sub>os</sub> (mg)	HC1	HNO <sub>3</sub>	$H_2SO_4$	HClO <sub>4</sub>			
0.1	0.10	10	2.0	0.9	1.3	3.8			
0.01	0.10	10	4.0	1.7	1.5	4.2			
0.001	0.10	10	5.9	3.5	2.2	4.4			
0.0001	0.10	10	6.7	4.8	4.3	4.6			

[Acid]= concentration of acid in mol/dm

 $M_s = mass \ of \ silica \ gel \ in \ g$ 

 $C_{os} = initial amount (mg) of Salen solution in 5 cm<sup>3</sup>$ 

#### 3.5 Stability of BMPDE-Physically-Modified Silica Gel in Acid and pH Media

The stability of the BMPDE-physically-modified silica gel in the various acid solutions viz; HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> in the concentration range  $10^{-4} - 2.0$  M and buffer solutions of different pH 1-11was examined. The results obtained in these studies are shown in Figures 2 and 3. From the results, it could be seen that the stability of the BMPDE-physically-modified silica gel decreased as the concentration of the acids increased. More of the ligand was desorbed from the silica gel at higher concentrations ( $10^{-1}$ -2.0 M) of the acids while minimum desorption was observed in the concentration range  $10^{-2}$  and  $10^{-4}$  M of the four acids.



Figure 2: Plot of Amount of BMPDE (mg/g) Desorbed at different pH

In the different buffer solutions of pH 1-11 used, the trend was also the same. Highest percentage desorption of the ligand from the silica gel occurred at the pH range 1-3 which is strongly acidic pH range. From pH 4 – 11, the desorption percentage decreased. Hence, the percentage desorption of the ligand from silica gel decreased as the pH increased. At pH above 10 however, the ligand slightly formed precipitates [12]. This indicates that the stability of modified solid phase increased as the acid concentration decreased and also increased as the pH increased. This shows that the ligand was physically adsorbed on the silica gel. This observation further confirms the limitation of the ligand in its application in either strongly acidic or basic media [3]. However, outside the strongly acidic or basic

medium, the BMPDE modified silica gel is very stable. The modified silica gel was kept in a desicator for over six months without degeneration in colour or capacity. The modified silica gel was also not affected by ordinary atmospheric pressure and temperature.



Figure 3: Plot of Stability of BMPDE Modified Silica gel in Various Acid Media

#### 3.6 Equilibration Time for metal Extraction

Optimum recovery of the metal ions under study occurred within 5 min. For the metal ions,  $Ni^{2+}$  and  $Cu^{2+}$ , the agitation (stirring) period of 5 min was sufficient for their equilibrium retention as shown in Tables 3 and 4. This confirms the fact that modification of a silica gel surface with organic complexing agent results in metal ion extractions which need only a few minutes for complete extraction process [12]. This is one of the advantages of using silica gel support for immobilization of chelating compounds. Figure 4 shows that equilibrium adsorption was attained in 5 min.





Figure 4: Plot of Amount of Metal ions (mg/cm<sup>3</sup>) Adsorbed at Various Contact Times

#### 3.7 Effect of Acidity on Metal ion Extraction

Adsorption of  $Ni^{2+}$  and  $Cu^{2+}$  as a function of various acid concentrations is presented in Tables 5 and 6. The influence of various acid concentrations on metal ion recovery was examined in four acids at four different concentrations,  $10^{-1}$ - $10^{-4}$  M in HCl, HNO<sub>3</sub>, HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>. The four acids examined significantly influenced the

metal ions recovery. At higher concentrations  $10^{-1}$  and  $10^{-2}$  M, the recovery of the metal ions was poor, this could be due to the protonation of the adsorption sites of the ligand and the competition between the positively charged metal ions and hydrogen ions. At lower concentrations ( $10^{-3}$  and  $10^{-4}$  M solution) of the acid, the recovery of the metal ions increased. This could be due to decrease in concentration of the hydrogen ions and lesser competition between H<sup>+</sup> and metal ions for the adsorption sites of the ligand. This decrease in H<sup>+</sup> concentration also implies a reduction in the repulsion between positively charged metal ions and the hydrogen ions.

Time <sub>(min)</sub>	C <sub>o(mg)</sub>	C <sub>t(mg)</sub>	Co-Ct(mg)	$\mathbf{q}_{\mathrm{t}}$
1	0.102	0.0630	0.0390	0.39
5	0.102	0.0082	0.0938	0.938
10	0.102	0.0082	0.0938	0.938
15	0.102	0.0082	0.0938	0.938
30	0.102	0.0122	0.0898	0.898
60	0.102	0.0143	0.0877	0.877
$C_o = i$	nitial am	ount (mg)	of Ni <sup>2+</sup> in 5 a	$cm^3$

 $C_i = amount (mg) of Ni^{2+} in 5 cm^3 of aqueous phase at time (t)$  $<math>C_o$ - $C_t = amount (mg) of Ni^{2+} adsorbed by 0.1 g solid phase at time (t).$  $<math>q_t = adsorption capacity of the solid phase at time (t) in mg/g.$ 

The recovery of the metal ions increased as the acid concentrations decreased and there was no significant difference in the effects of the four acids studied. At lower acid concentrations, the metal ions were present in free cationic form and the charge density of the functional groups of solid silica gel material played a crucial role in the metal ion sorption. The dissociation of the acidic functional groups on the ligand, which provided binding sites for the metal ions were governed by the acidity of the solution. At higher acidity, the dissociations were suppressed greatly due to excess  $H^+$  in the sample solution and therefore very low sorption took place. The decrease in acidity facilitated the dissociation of functional groups and thus more binding sites were released for sorption of metal ions. As a result, increased retention efficiency was achieved.

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[Acid] M	M <sub>s</sub> (g)	C <sub>o</sub> (mg/cm <sup>3</sup> )	$H_2SO_4$	HClO <sub>4</sub>	HNO <sub>3</sub>	HCl
10-1	0.10	0.102	0.00836	0.0204	0.00816	0.00408
10-2	0.10	0.102	0.03060	0.04896	0.04488	0.05916
10-3	0.10	0.102	0.04488	0.05202	0.04590	0.07152
10-4	0.10	0.102	0.05712	0.06018	0.04692	0.08160

[Acid] = acid concentration in mol/dm

 $M_s = mass \ of \ silica \ gel \ in \ g$ 

 $C_o = initial amount (mg) of Ni^{2+} in 5 cm^3 of aqueous solution$ 

Table 6: Amount of Cu	<sup>2+</sup> (mg/g) Extracted in Acids Mo	edia by Modified Solid phase
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[Acid] M	M <sub>s</sub> (g)	C <sub>o</sub> (mg/cm <sup>3</sup> )	$H_2SO_4$	HNO <sub>3</sub>	HCl	HClO <sub>4</sub>
10-1	0.10	0.102	0.0102	0.00816	0.03264	0.0306
10-2	0.10	0.102	0.0510	0.04794	0.05712	0.04896
10-3	0.10	0.102	0.05712	0.06732	0.06834	0.06936
10-4	0.10	0.102	0.06528	0.07242	0.07752	0.07344

[Acid] = acid concentration in moldm<sup>3</sup>

 $M_s = mass \ of \ silica \ gel \ in \ g$ 

 $C_o = initial amount of Cu^{2+} in 5 cm^3 of aqueous solution$ 

## 3.8 Effect of pH on Ni<sup>2+</sup> and Cu<sup>2+</sup> Extraction

Adsorption of  $Ni^{2+}$  and  $Cu^{2+}$  by the modified silica gel as a function of pH of the solution is shown in Table 7. The pH of the aqueous metal ion solution is an important controlling factor in the sorption process. The pH of the solution affects the adsorbent capacity. The adsorption of metal typically increases with increase in pH; and the mechanism of metal ion binding, by changing it from ion exchange and/or adsorption at acidic region to adsorption and/or complexation and possible precipitation at the basic region [13]. BMPDE used in this study as chelating agent has two hydroxyl groups and two donating electron pairs, so it can form stable chelates with metal ions. The two hydroxyl groups can be ionized in a basic solution. In this work, the pH values of the metal solutions were adjusted within the range of 1-11 using HNO<sub>3</sub> or NH<sub>4</sub>OH.

The two types of functional groups; Lewis base (OH) at acidic pHs and Lewis acid (-NH<sub>2</sub>) at basic pHs, seem to be involved in the binding of the metals studied. With very strong acidic (pH < 2) or basic (pH > 10) solution, the metal is not retained by the sorbent [14]. The increase in metal ion removal as pH increased can be explained on the basis of a decrease in competition between  $H^+$  and positively charged metal ions (Ni<sup>2+</sup> and Cu<sup>2+</sup>) at the surface sites, which results in a lower electrostatic repulsion of the adsorbing metal ions and consecutively increased metal ion removal [15]. The low recovery of metal ions at lower pH can be associated with the protonation of functional groups of the sorbent and a low degree of swelling. At such a pH value, metal ions occur in a hydrated (M(OH<sub>2</sub>)n)<sup>2+</sup> form. The swelling capacity grows as the solution pH increases (pH 4-9), which favours the interaction between the metal ions and active groups of the sorbent [16]. The formation of aqua and hydroxo-complex species of a given metal ion depends on the pH value of the solution and the metal ion concentration. Depending on the pH of the metal ion aqueous solution, the total concentration of the metal ion in the solution is the sum of the concentration of the metal ion and presence of metal-hydroxy species [13]. The speciation of a metal has a significant impact on the adsorbent extraction efficiency and can influence the mechanism of metal ion binding. The metal ion-adsorbent selectivity is also influenced by the character of the metal complex that predominates at a particular solution pH. The pH range (4-9) was chosen for the ligand to ensure the complete adsorption of metal ions. The differences in the behaviour of the metal ions may be attributed to the difference in their ionic sizes and their stability with the Schiff base [13]. Copper and nickel were optimally recovered at pH 9 and 7 respectively. At higher pH values, the adsorption decreases due to precipitation of metal hydroxide, in this case, the solid phase works as a normal sieve.

Table 7: Variation in Amount of Metal ions (mg/g) Extracted in Buffer pH by Modified Solid Phase

pН	M <sub>s</sub> (g)	C <sub>o</sub> (mg/cm <sup>3</sup> )	Ni <sup>2+</sup> (mg/g)	$Cu^{2+}(mg/g)$	
1	0.10	0.102	0.02448	0.01734	
2	0.10	0.102	0.02856	0.01938	
3	0.10	0.102	0.04284	0.03264	
4	0.10	0.102	0.04488	0.04488	
5	0.10	0.102	0.04692	0.06120	
6	0.10	0.102	0.05304	0.07344	
7	0.10	0.102	0.09925	0.07752	
8	0.10	0.102	0.09180	0.08568	
9	0.10	0.102	0.05508	0.09792	
10	0.10	0.102	0.04896	0.06936	
11	0.10	0.102	0.04692	0.06528	

 $M_s = mass of silica gel in g$ 

 $C_o = initial amount (mg) of metal ions in 5 cm<sup>3</sup> of aqueous solution.$ 

#### 3.9 Metal ion Separation

Table 8 shows the separation of metal ions from aqueous solutions by varying the pH using the modified solid phase.  $Ni^{2+}$  was quantitatively separated from  $Cu^{2+}$  at pHs of 7.0 and 9.0 respectively. On this basis, it is possible to separate the metal ions quantitatively using the BMPDE modified solid sorbent.

Ni <sup>2+</sup> 0.102 99.3	Metal ions	Initial Amount in Aqueous phase (mg/m <sup>3</sup> )	Recovery (%)	
	Ni <sup>2+</sup>	0.102	99.3	
Cu <sup>2+</sup> 0.102 97.9	$Cu^{2+}$	0.102	97.9	

#### CONCLUSION

This study is based on the separation of two environmentally related and important heavy metal ions,  $Cu^{2+}$  and  $Ni^{2+}$  using solid phase (silica) physically modified with Schiff base bis(2,2-methylidenephenol)diaminoethane (BMPDE). Different experimental factors such as time, pH and effects of various acid concentrations were examined to optimize the conditions for the physical modification of the silica gel with the ligand. The wavelengths of maximum absorbance ( $\lambda_{max}$ ) of the ligand and ligand-metal complexes were determined in various acids and pH media to be 370 nm for the ligand, 420 nm and 400 nm for Ni<sup>2+</sup> and Cu<sup>2+</sup> ligand complex. The study revealed that a maximum equilibration time of 15 min was required for the optimum adsorption of the ligand onto activated silica gel at a temperature of  $45\pm1^{\circ}$ C. Adsorption of the ligand onto the silica gel was observed to be poor at lower pH <4, and at pH >10 precipitation of the ligand sets in. Various acids, HCl, HNO<sub>3</sub>, HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> with concentrations  $10^{-1}$  M,  $10^{-2}$  M,  $10^{-3}$  M,  $10^{-4}$  M impaired the adsorption of the ligand onto the activated silica gel. Optimum adsorption of the ligand onto the activated silica gel occurred at pH 10. The stability studies of the physically modified solid sorbent were carried out in the various acids concentrations and pH media. Results showed that the silica gel physically modified with the ligand BMPDE, was not stable in strongly acidic medium and the ligand precipitated in strongly basic medium. Optimum time of 5 min was observed to be effective for the separation of the metal ions from

aqueous solutions. The pH of optimum recovery of  $Cu^{2+}$  is 9 and  $Ni^{2+}$  is 7. The metal ions in the eluent were spectrophotometrically determined. The newly developed procedure, SPE-spectrophotometry using BMPDE ligand has been found to be successful in separation of the metal ions from complex matrices.

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