CARITAS UNIVERSITY AMORJI-NIKE, EMENE, ENUGU STATE

Caritas Journal of Physical and Life Sciences

CJPLS, Volume 2, Issue 1 (2023)

Article History: ***Received: 6th July, 2023; Revised: 4th September, 2023; Accepted: 30th September, 2023.***

Evaluating the Efficiency of Modified Silica Gel with N, N'-Ethylenebis (acetylacetone)diamine for Copper (II) Ions Removal in Aqueous Solutions

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ABSTRACT

This study evaluated the adsorption capacity of physically modified silica gel (SG), for copper (II) ion using aqueous solutions of N, N'-Ethylenebis(acetylacetone)diamine-$C_{18}H_{28}N_2O_4$ *(EAD). Copper (II) adsorptive efficiency was studied under different experimental conditions and optimized before spectrophotometric analysis using EAD reagent. Results indicated that sorption of Cu(II) was favourable at pH 4, and sample volume of 50 mL, themin*$^{-1}$*. The quantitative recovery of Cu(II) ion was achieved by elution with 5.0 mL of 1.0 molL*$^{-1}$ HNO_3*. Equilibrium data were tested and found to follow the Langmuir isotherm model. Kinetic data fitted well in pseudo-second-order kinetics. These results suggest that modified SG is an excellent metal extractor for the preconcentration of Cu(II) from the spiked aqueous phase. In conclusion, the physically modified silica gel showed a high potential for the removal of copper (II) ions from aqueous solutions. The adsorption capacity was influenced by the concentration of EAD in the solution, with the highest adsorption capacity observed at an EAD concentration of 2 mM. The study provides valuable insights for the development of effective and efficient adsorbents for heavy metal ion removal from wastewater.*

Keywords: ***copper (II) ion, spectrophotometry, pre-concentration, unconventional protocol***

1.0 Introduction

Heavy metal pollution has become a global issue as it poses a threat to the environment and human health. Copper (II) ion is one of the common heavy metals that can contaminate soil and water due to several anthropogenic activities. Therefore, the removal of copper (II) ion from the aqueous environment is of utmost importance[1]. Adsorption has emerged as a promising technique for the removal of copper (II) ions from aqueous solutions. Silica gel, a mesoporous material, has been reported for its excellent adsorption capacity for various heavy metal ions. However, the application of silica gel in the removal of copper (II) ions is limited due to its poor surface properties. Various physically modified silica gels have been developed to enhance their adsorption properties for heavy metal ions[2]. One such modification is the use of N, N'-Ethylenebis(acetylacetone)diamine as a chelating agent. The complexation of copper (II) ion with this chelating agent leads to its deposition onto the silica gel surface, thereby increasing its adsorption capacity.

There are two possible causes of copper pollution in the environment, most notably both anthropogenic and natural sources. Wind-borne dust, decomposing plants, forest fires, and sea spray are examples of natural sources. Human activities include mining, burning fossil fuels, industrial effluent discharges containing copper, and other things. In our time, food, water, and air are all contaminated with copper[3]. Although copper is a necessary micronutrient for people, animals, and plants, it is toxic in high doses[4]. Although copper absorption is necessary, excessive or prolonged exposure to copper may cause some health problems, including irritation of the sensory organs. According to, symptoms of hepatic cirrhosis included brain damage, renal disease, brain damage, diarrhoea, liver and kidney damage, copper fume fever, and renal illness.

Because of these harmful effects of copper ions on human health, copper contamination in the environment and food presents a serious threat to public health. Because of the low concentrations of these heavy metal ions in the samples, which frequently fall below the detection limits of many analytical techniques and the matrix effects, direct determination of these heavy metal ions, including copper ions, in environmental samples is always a major concern[5]. Preconcentration procedures must be used to identify the trace amounts of these heavy metals in the environmental samples due to the aforementioned difficulties. Metal ions in solution can be preconcentrated and separated using a variety of enrichment processes[6,7] These enrichment methods include solid phase extraction, liquid-liquid extraction (LLE), precipitation/co-precipitation, flotation, membrane filtering, ion exchange, and precipitation/co-precipitation. Solid phase extraction (SPE) is the most used enrichment process for preconcentrating and separating different organic and inorganic components.

Because of its unique benefits of being inexpensive, reusable, mechanically stable, not swelling in solvents, and simple to modify with chelating agents, silica gel is widely preferred among the many adsorbents used for the preconcentration of metal ions in SPE. These include activated carbon or charcoal, polymeric fibres, ion exchangers, cellulose, and ambulate XAD resins. This study aims to assess the adsorption capacity of physically modified silica gel for copper (II) ion using aqueous solutions of 4,4'-(1,2-Ethanediyldinitrilo) bis-(2-Pentanone). This modification has the potential for practical applications in the treatment of copper (II) ion-contaminated wastewater. The findings of this study will contribute to the development of an efficient and cost-effective method for the removal of copper (II) ions from aqueous solutions

2.0 Materials and Method

2.1 Material

The current study outlines a novel approach for solid phase extraction of copper ions from silica gel modified with EAD using a column method. The pH of the solution, sample volume, sorption flow rate, elution flow rate, etc. were only a few of the preconcentration parameters that were afterwards examined to establish the ideal circumstances for the quantitative recovery of copper (II) ion.

The materials used in this study include: Physically modified silica gel, Copper (II) ion solution, N, N'-Ethylenebis(acetylacetone)diamine solution, Distilled water, Beakers, Graduated cylinder, Magnetic stirrer, pH meter, Spectrophotometer, Stopwatch

2.2 Method

2.2.1 Preparation of copper (II) ion solution

Prepare a copper (II) ion solution by dissolving 0.25 g of copper (II) sulfate in 100 ml of distilled water.

2.2.2. Preparation of N,N'-Ethylenebis(acetylacetone)diamine solution. Prepare an N, N'-Ethylenebis(acetylacetone)diamine solution by dissolving 2.5 g of the compound in 100 ml of distilled water.

2.2.3 Activation of silica gel (SG)

After incubation in 6 M HCl for 48 hours to activate the SG, it was continuously filtered and washed until the pH of the SG solution was neutral. To completely remove all traces of water from the SG surface, the residue was subsequently dried at 110° C.

2.2.4 Determination of Solubility of EAD

The solubility of EAD was determined by using a solubility test. In this test, a small amount of the substance is added to a specific solvent and stirred until the substance is dissolved. The maximum amount of the substance that can be dissolved in a specific volume of solvent is its solubility in that solvent. To determine the solubility of EAD, a range of solvents can be chosen to perform the test. The solvents used in this study were water, ethanol, methanol, and chloroform. The procedure for determining the solubility of EAD in a specific solvent was as follows: Weigh a small amount of EAD (~100 mg) accurately using a balance and record the mass. Add the EAD to a small glass vial containing a specific volume of the solvent, 5 ml. Stir the mixture using a magnetic stir bar or vortex mixer until the EAD is dissolved. Alternatively, the mixture can be heated to aid dissolution if required. If the EAD does not dissolve, add more solvent and repeat steps 3 and 4 until the maximum solubility of EAD is determined. Record the highest concentration of EAD that can be dissolved in the solvent, which represents the solubility of EAD in that solvent. Repeat the above procedure with different solvents and record their respective solubilities of EAD. By comparing the solubility of EAD in different solvents, we determined which solvent is best suited for dissolving the compound to perform further experiments or synthesis. [2,3]

2.2.5 Determination of the absorption spectra of EAD in solvents

To determine the absorption spectra of EAD in solvents, the following steps were followed: Prepare a stock solution of EAD in a suitable solvent, such as ethanol or methanol, and dilute the stock solution to obtain a solution with a suitable concentration for UV-vis spectroscopy analysis. The concentration will depend on the expected absorbance values of EAD in the solvent, but a good starting point is usually in the range of 1-10 µM. Prepare a blank solution using the same solvent used for the EAD solution. Measure the UV-vis spectrum of the blank solution using a suitable spectrophotometer[8,9]. Measure the UV-vis spectrum of the EAD solution using the same spectrophotometer and subtract the blank spectrum to obtain the corrected spectrum. Analyze the spectra to determine the absorption maxima and the extinction coefficient of EAD in the solvent. The extinction coefficient can be obtained by measuring the absorbance of the EAD solution at the absorption maximum and dividing it by the path length and concentration of the solution. Repeat the measurement for different solvents chosen: chloroform, methanol, ethanol and water to determine the effect of the solvents on the absorption spectra of EAD.

2.2.6 Determination of pH

50 ml of copper (II) ion solution was added to 0.1 g of physically modified silica gel. The pH of the solution was measured using a pH meter before stirring and after stirring for 30 minutes.

2.3 Preparation of Sorbent (Si-EAD)

The preparation of Sorbent (Si-EAD) involves various factors that can affect the quality and properties of the final product. Some of these factors include the following: The silica source used for the preparation of the sorbent can affect the surface area, pore size distribution, and purity of the final product. Common sources of silica include fumed silica, colloidal silica, and mesoporous silica. Pore-forming agent: Pore-forming agents are used to create pores in the sorbent, which can improve its adsorption properties. Examples of pore-forming agents include surfactants, organic solvents, and polymers[10]. The type and amount of pore-forming agent used can affect the pore size, shape, and distribution of the sorbent. Precursor concentration: The concentration of the precursor used in the preparation of the sorbent can affect its surface area, pore size, and crystallinity. Higher precursor concentrations tend to result in larger surface areas and greater porosity. The pH of the reaction mixture can affect the morphology, surface area, and pore size of the sorbent. Generally, lower pH values tend to result in smaller particle sizes, while higher pH values can promote the formation of larger particles. The temperature at which the preparation is carried out can affect the crystallinity, surface area, and pore size distribution of the sorbent. Higher temperatures tend to result in greater crystallinity and larger pore sizes[11]. A catalyst can be added to the reaction mixture to improve the yield and quality of the sorbent. Common catalysts include acids, bases, and template molecules. Overall, the preparation of Sorbent (Si-EAD) is a complex process that involves careful control of various factors to achieve a product with optimal adsorption properties.

The different extraction bottles each included 0.1 g of activated SG, 2 mL of a 2% EAD solution, and 5 mL of various buffers ranging in pH from 1 to 12. The mixtures were stirred for five minutes, filtered, and the residues were then cleaned with one millilitre of distilled water. With diluted HCl or NaOH, the filtrate was brought to the appropriate pH before being produced up to 10 mL at that pH. After extrapolating from the calibration curve, the concentration of EAD in the filtrate was measured at 320 nm and estimated by mass balance[12].

2.4 Column method for preconcentration of Cu (II) ions

The column method for pre-concentrating copper II ions in EAD solution involves the use of a solid phase extraction (SPE) column, which contains a resin designed to selectively bind and retain the copper II ions in the sample. The following steps are typically followed in the column method: Preparation of the SPE column: The resin in the SPE column is first conditioned by passing through it a suitable solvent (e.g., methanol, water), followed by the addition of the binding agent. In this case, the binding agent is usually iminodiacetic acid, which selectively binds to copper II ions. Loading of sample onto the column: The EAD solution containing the copper II ions is then passed through the SPE column, allowing the copper II ions to specifically bind to the iminodiacetic acid in the resin. During this step, other interfering compounds in the sample are washed away. Elution of the copper II ions: Once the copper II ions have been captured by the resin in the SPE column, they can be selectively eluted from the column using a suitable eluant. In this case, a solution of glycine-HCl is typically used, which causes the copper II ions to dissociate from the resin and be collected in a smaller volume of eluate. The concentration of the eluate: The eluate containing the concentrated copper II ions can then be further concentrated by evaporating the solvent (e.g. using a rotary evaporator), allowing the copper II ions to be obtained in a smaller volume of solution[7]. Overall, the column method for pre-concentration of copper II ions in EAD solution using a solid phase extraction column allows for selective extraction and concentration of the target metal ion from a complex sample matrix, providing increased sensitivity and accuracy in subsequent analysis.

The different extraction bottles each included 0.1 g of activated SG, 2 mL of a 2% EAD solution, and 5 mL of various buffers ranging in pH from 1 to 12. The mixtures were stirred for five minutes, filtered, and the residues were then cleaned with one millilitre of distilled water. With diluted HCl or NaOH, the filtrate was brought to the appropriate pH before being made up to 10 mL at that pH. After extrapolating from the calibration curve, the concentration of EAD in the filtrate was measured at 320 nm and estimated by mass balance.

$$\text{Adsorption yields (\%)} = \frac{Co-Ce}{Co} \times 100 \qquad (1)$$

Where Co is the initial copper concentration (mg/L) and Ce is the concentration of the copper solution (mg/L) at equilibrium.

$$\text{Désorption (\%)} = \frac{released\ metal\ concration}{initially\ sorbed\ metal\ concentration} \times 100 \qquad (2)$$

2.4.1 Determination of the effects of pH on the adsorption of EAD on the activated SG

The different extraction bottles each included 0.1 g of activated SG, 2 mL of a 2% EAD solution, and 5 mL of various buffers ranging in pH from 1 to 12. The mixtures were stirred for five minutes, filtered, and the residues were then cleaned with one millilitre of distilled water. With diluted HCl or NaOH, the filtrate was brought to the appropriate pH before being produced up to 10 mL at that pH. After extrapolating from the calibration curve, the concentration of EAD in the filtrate was measured at 320 nm and estimated by mass balance.

2.4.2 Determination of the effects of contact time on the adsorption of EAD on the activated SG

The different extraction bottles each included 0.1 g of activated SG, 2 mL of a 2% EAD solution, and 5 mL of various buffers ranging in pH from 1 to 12. The mixtures were stirred for five minutes, filtered, and the residues were then cleaned with one millilitre of distilled water. With diluted HCl or NaOH, the filtrate was brought to the appropriate pH before being produced up to 10 mL at that pH. After extrapolating from the calibration curve, the concentration of EAD in the filtrate was measured at 320 nm and estimated by mass balance.

2.4.3 Determination of the effects of the initial amounts of EAD on its adsorption onto activated SG

Activated SG (0.1 g) was placed into different extraction bottles. A 2 % EAD solution in phosphate buffer at pH 1 was prepared (2 % w/v). From the solution, 0.1, 0.3, 0.5, 1.0, 2.0 and 5.0 mL were withdrawn into the bottles accordingly. All solutions were made to 5 mL using distilled water except that which is 5 mL already. The solutions were agitated for 5 min, filtered and the residues washed with 1 ml of distilled water. The filtrate was adjusted with dilute and then made up to 10 mL with pH 1. The absorbance of the ligand was obtained at 320 nm spectrophotometrically against a reagent blank.

2.5 The quantification of adsorbed copper (II) ion in physically modified silica gel

This was determined by using an aqueous solution of N, N’-Ethylenebis(acetylacetone)diamine and a spectrophotometer. First, the physically modified silica gel was prepared and physically characterized. Then, a known amount of copper (II) ion solution was added to the silica gel and left to equilibrate for a specified time. After equilibration, the silica gel was filtered and the concentration of the unbound copper (II) ion in the solution was determined using a UV-Vis spectrophotometer[13]. Subsequently, an aliquot of N, N’-Ethylenebis(acetylacetone)diamine was added to the solution with unbound copper (II) ion, causing the copper (II) ion to form a complex with the ligand. The absorbance of this complex was read at a particular wavelength, which allows for the determination of the concentration of copper (II) ion in solution. The amount of copper (II) ion adsorbed onto the physically modified silica gel was determined by subtracting the concentration of unbound copper (II) ion in solution from the initial concentration of copper (II) ion added. The adsorption capacity was then calculated by dividing the amount of copper (II) ion adsorbed by the mass of silica gel used. In summary, the quantification of adsorbed copper (II) ion in physically modified silica gel for copper (II) ion using aqueous solutions of N, N’-Ethylenebis(acetylacetone)diamine involves the use of a spectrophotometer to determine the concentration of copper (II) ion in solution before and after the addition of a ligand. This method allows for the determination of the adsorption capacity of the silica gel for copper (II) ions.

2.6 **Kinetic study**

Take 50 ml of copper (II) ion solution and add 0.1 g of physically modified silica gel. Stir the mixture using a magnetic stirrer and measure the concentration of copper (II) ions in the solution at different time intervals (1 minute, 2 minutes, 3 minutes, 4 minutes, 5 minutes, 10 minutes, 15 minutes, 20 minutes, 30 minutes, 40 minutes, 50 minutes, and 60 minutes. Plot the graph of the adsorption capacity of physically modified silica gel against time[14].

3.0 Results and Discussion

3.1 Physical Characterization of EAD

Table 1. Physical data of the ligand (EAD)

Ligand	Color	Texture	Melting Point	Observed Yield (g)	Percent yield (%)
EAD	White	Crystalline	106 °C	15.2	97

Table 1 summarizes the physical characteristics of EAD. As seen in Table 1, EAD is a white crystal with a melting temperature of 106 °C. From the same Table, the observed and per cent yields of the ligand ($C_{18}H_{28}N_2O_4$) are found to be 15.2 g and 97 % respectively. These reports obtained are similar to the results [15,16].

3.1.1 Solubility test

The results of the solubility test of EAD in some common solvents are displayed in Table 2. Table 2 also outlines the extent of the solubility of the ligand in different solvents. It indicates that EAD is readily soluble in ethanol, and methanol is moderately soluble in chloroform and slightly soluble in doubly distilled water (DDW).

The obtained data are similar to that reported by [10,17]

Table 2. Solubility of the ligand in some common solvents

Schiff base	Water	Ethanol	Methanol	Chloroform
EAD	SS	S	S	MS
Legend: SS = slightly soluble, S = Soluble, and MS = moderately soluble				

3.2 Absorption spectra data of EAD

Ultraviolet absorption spectra of the ligand ($C_{18}H_{28}N_2O_4$) in solvents are presented in Table 3

Table 3. Electronic spectra data of EAD in various solvents

Solution of EAD in solvents	ʌmax^1 (nm)	ʌmax^2 (nm)	molar absorptivity^1 ($Lmol^{-1}cm^{-1}$)	molar absorptivity^2 ($Lmol^{-1}cm^{-1}$)
EAD in Ethanol	303	253	5.0×10^3	1.9×10^3
EAD in methanol	322	251	3.0×10^3	2.0×10^3
EAD in DDW	322	250	2.6×10^3	4.6×10^2
EAD in chloroform	285	-	9.3×10^3	-

3.3 Electronic spectra studies of the ligand (EAD)

The absorption spectra data of the ligand in some common solvents are presented in Table 3. The spectra data of EAD in all the given solvents prove that the ligand absorbs maximally in the ultraviolet region of the electromagnetic spectrum (200 – 400 nm) [18]. The results in Table 3 indicate that the methanolic solution of EAD shows an absorption maximum at 322 nm with a shoulder at 251 nm and molar absorptivity of 3.0 x 103 $Lmol^{-1}cm^{-1}$ and 2.0 x 103 $Lmol^{-1}cm^{-1}$ respectively. These results conform with the results reported by [19].

Table 3 indicated that EAD in ethanol solution shows absorbance maxima at 303 nm and 253 nm and with their molar coefficients of 5.0 x 103 Lmol^{-1}cm^{-1} and 1.9 x 103 Lmol^{-1}cm^{-1} respectively. The ligand in DDW absorbs maximally at 322 nm with a shoulder at 250 nm and their molar absorptivity is 2.6 x 103 and 4.6 x 102 Lmol-1cm-1 respectively. In chloroform, the ligand shows a prominent peak at 285 nm with a molar absorptivity of 9.3 x 103 Lmol-1cm-1. Except for chloroform. EAD in other solvents is capable of n→π and π→π electronic transitions. These results obtained suggest that EAD under test contains atoms with lone pairs that provide the non-bonding electrons as well unsaturated group that affords the π electrons [20,21]

The level of significant differences in the electronic spectra of EAD in DDW and each organic solvent was tested at a 95 % confidence level ($\alpha = 0.05$) using F – the test (Microsoft Excel). The F – test was to determine whether the variances for the spectra of the ligand in DDW and a particular organic solvent are equal or unequal. The null hypothesis was that the variances of the two variables are equal: there are no significant differences in the spectra of the ligand as against the alternative hypothesis which signifies that their variances are unequal: there are significant differences in the spectra of the ligand. The null hypothesis is accepted if F critical is one–tail value > F value and it is rejected if F critical value < F value. The F – test results aligned with the latter in that their variances are unequal since F critical < F value. This means that there are significant differences in the spectra of EAD in DDW and organic solvents used. This remarkable difference in the spectra of EAD was thought to be a result of the contributory effect of solvents on EAD absorption.

3.4 Spectroscopic Characterization of EAD in some buffer media

Table 4 outlines the spectroscopic properties of EAD in some different buffer additives. The ligand in ammoniacal buffer at pH 10 shows an absorption maximum at 303 nm with a molar absorptivity coefficient of 2,475 Lmol^{-1}cm^{-1} while in acetate buffer at pH 1.0, it absorbs maximally at 305 nm and its molar absorptivity is 19,910 Lmol^{-1}cm^{-1}. As can also be seen in Table 4, in citrate buffer at pH 9.0, the ligand shows a prominent peak at 320 nm with a molar absorptivity of 731 Lmol^{-1}cm^{-1}. In the phosphate buffer of pH 1.0, the ligand absorbs favourably at 320 nm with an absorptivity coefficient of 898 Lmol^{-1}cm^{-1}. The results in Table 4 indicate that the ligand in oxalate buffer at pH 7 shows an absorption maximum at 322 nm and has 1,729 Lmol^{-1}cm^{-1} as the molar absorptivity.

Table 4. Absorption spectra data of the ligand (EAD)

Buffer media	Wavelength (nm)	Absorbance	Molar absorptivity (Lmol^{-1}cm$^{-1)}$	Optimal pH
Ammoniacal buffer	303	2.203	2,475	10
Acetate buffer	305	1.772	19,910	1
Citrate buffer	320	0.651	731	9.0
Phosphate buffer	320	0.799	898	1
Oxalate buffer	322	1.539	1,729	7

3.5 Optimization strategy

The optimization procedure was employed to determine the most efficient experimental conditions for the EAD- SG modification process. Some parameters dealt with in the optimization process are stated as given below.

3.5.1 Effects of pH

The effect of pH on the deposition of 40 mg initial amount of EAD onto the SG surface is represented in Fig.1. The curves are plots of the amount of EAD adsorbed as a function of pH. Too many complexing agents have a strong preference for protons since they are conjugate bases of weak acid groups and so exhibit pH-dependent behaviour in aqueous media [22,23]. The adsorption behaviour of EAD onto SG was investigated while varying the solution pH from 1.0 – 12.0 in the five different buffer media. As observed in Figure 1, the adsorption of EAD in the phosphate buffer was significant at low pH of 1 – 2 but declined suddenly afterwards. The results in Figure 1 show that there was no adsorption at high pH. A similar adsorption pattern at low pH was recorded for the acetate buffer. In oxalate buffer, though the amount of EAD adsorbed was moderately high, there was no remarkable change in the value as the pH was increased from 1 – 12. For the ammoniacal buffer, adsorption was greater at pH 4 – 6 and pH 8-11. While in the citrate buffer, there was little or no adsorption seen from pH 1 – 12.

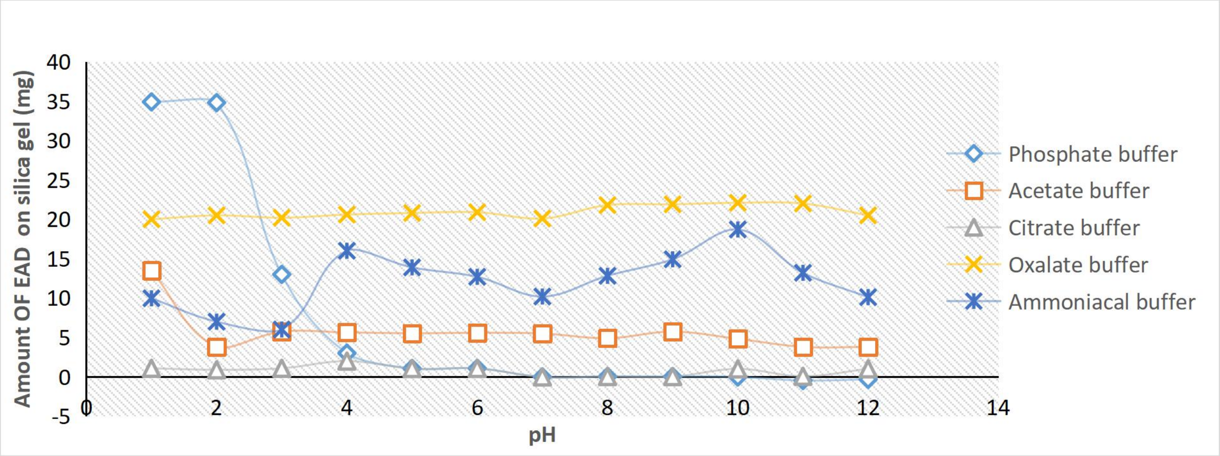


Fig.1. The effects of various buffer media on the adsorption of EAD onto the SG

The pH-dependent behaviour of adsorption of EAD onto SG using the different buffer media can be explained by considering the presence of silanol groups on the SG surface which permits it to behave like a weak Lewis acid, hence it can combine with polar compounds via strong hydrogen bonding and dipole-dipole interactions [1]. The silanol groups on the SG surface can act as electron acceptors through Si central atoms. The presence of oxygen-containing groups, phosphate (PO_4^{3-}), oxalate($C_2O_4^{2-}$), citrate($C_6H_5O_7^{3-}$) or lone pair in ammoniacal buffer (NH3 – N) group from the buffers could behave as weak Lewis bases and electron donors. These indicate that electron donor-acceptor, dipole-dipole interactions or Lewis's acid/ base interactions between active groups on the SG surface and the oxygen or nitrogen-containing groups of the buffer created ideal sites for the ligand to build up through hydrogen bonding and dipole-dipole interaction and improve its adsorption onto the SG. But as seen earlier, a complex molecule that is directly entrapped at the surface of SG produces steric hindrances at the silanol site and as a result, limits the number of incoming molecules [2]. Also, the bulkiness of the buffer additives could affect the degree of adsorption of EAD on the SG surface. This offered a possible explanation for the reduced amount of EAD adsorbed on the SG in the citrate buffer. Besides oxalate buffer which showed virtually a constant amount of EAD adsorbed on the SG, the extent of adsorption could have been influenced by steric concepts.

The level of significant differences in the effects of various buffer media on the adsorption of EAD on the SG was tested at a 95 % confidence level ($\alpha = 0.05$) using analysis of variance (ANOVA). The study provides a test of the hypothesis that the differences in the effects among the five-buffer media are due to chance (i.e., there is a significant difference in their effects). There is a significant difference in the effect if $\rho < 0.05$ and there is no significant difference if $\rho > 0.05$. The analysis results aligned with the first statement that there are significant differences in the effects of the five-buffer media used ($\rho < 0.05$; F4,55, $\rho = 0.00$). This signifies that the sort of buffer media used influences the amount of EAD entrapped.

3.5.2 Effects of contact time on the adsorption of EAD onto the activated SG

Figure 2 shows the effect of contact time on the adsorption of EAD onto the activated SG. The curve is a plot of the amount of EAD adsorbed on the SG versus contact time. The curve showed that the adsorption appreciated with increasing contact time and attained equilibrium in 5 min. With the further rise in contact time, the adsorption of EAD onto the SG remains fairly constant which implies that adsorption has reached equilibrium. This reveals that there are uniform adsorption sites on the SG surface which are steadily filled with time by the ligand through hydrogen bonding and dipole-dipole interactions. Once a site is filled, no further adsorption can take place at that site. At equilibrium, 5 min in this instance, the SG surface becomes saturated with adsorbed EAD.

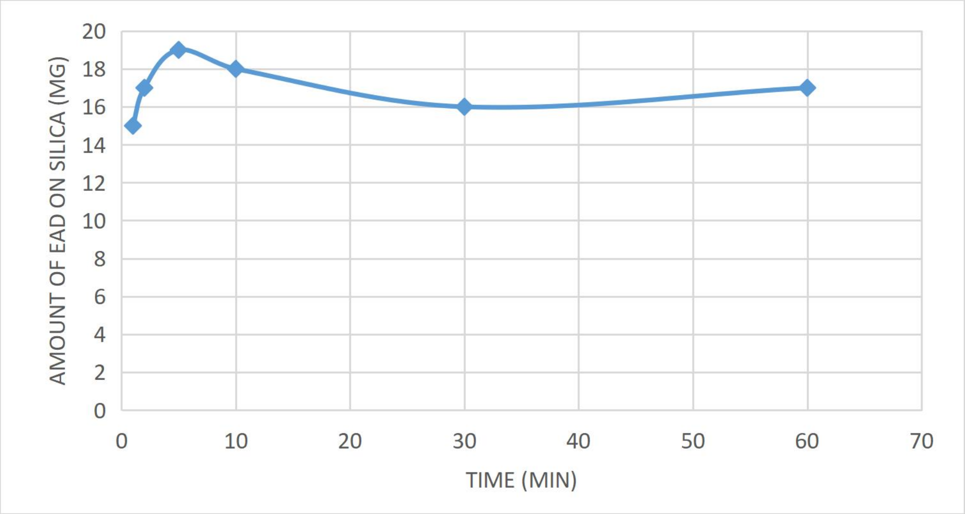


Fig. 2. Effect of contact time on the adsorption of EAD onto SG

3.5.3 Effect of the initial amount of EAD on the adsorption of EAD onto the activated SG

The effect of the initial amount of EAD on its adsorption onto the activated SG surface is displayed in Fig.3. The curve is a plot of the amount of EAD adsorbed against the initial amount of EAD. Figure 3 indicated that the amount of EAD deposited on the SG increased progressively to about 2.4 mg at pH 1 in the phosphate buffer in the 40 – 50 mg range of the initial amount of EAD but declined rapidly thereafter. This suggested that empty adsorption sites on the SG surface were steadily filled as the amount of EAD was increased from 2 mg to

50 mg and with further increase in the amount of EAD, strong hydrogen bonding among molecules of EAD in the solution alters the equilibrium and favoured desorption of some EAD molecule from the SG surface into the solution due to concentration effect.

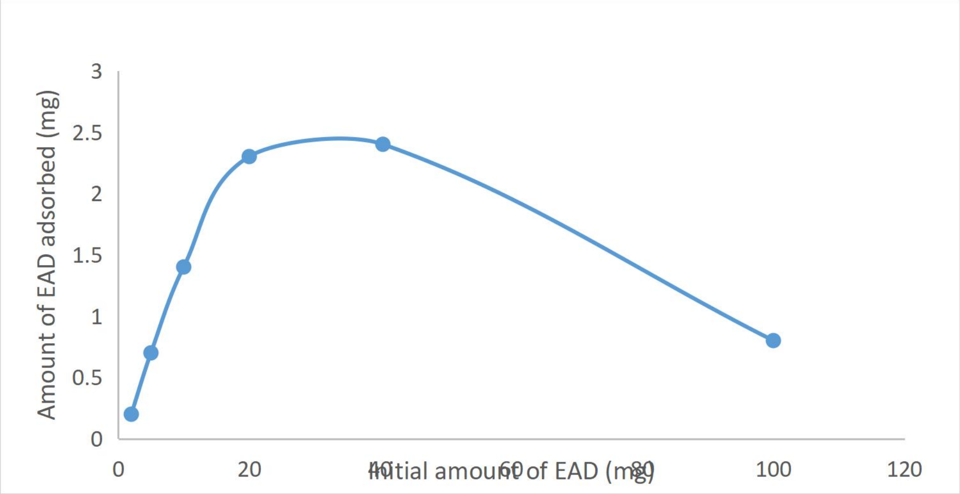


Fig.3. Effect of initial EAD amount on its adsorption onto SG at pH 1.0

3.6 Adsorption isotherm

Adsorption is a process by which ions, molecules, or particles adhere to the surface of a solid or liquid material. In the context of Cu2+ adsorption, it refers to the ability of a material to attract and retain Cu2+ ions on its surface. Silica is a common material used for Cu2+ adsorption due to its high surface area and chemical stability. The adsorption capacity of silica can be improved by modifying its surface properties[24]. Modification techniques involve functionalizing the surface of the silica with organic or inorganic compounds that can enhance its adsorption properties. Common modification techniques include chemical vapour deposition, sol-gel, and co-precipitation. Studies have shown that modified silica has a higher Cu2+ adsorption capacity than non-modified silica. For example, one study reported that modified silica had a Cu2+ adsorption capacity of 123.5 mg/g, compared to 38.1 mg/g for non-modified silica. This difference can be attributed to the surface functionalization of the modified silica, which provides additional sites for Cu2+ adsorption. The specific adsorption capacity of both modified and non-modified silica can vary depending on factors such as the type of modification, the concentration of Cu2+ in the solution, and the pH of the solution. It is essential to consider these factors when selecting a material for Cu2+ adsorption in a particular application[25]. In summary, modified silica has a higher Cu2+ adsorption capacity than non-modified silica due to its surface functionalization. However, the specific adsorption capacity can vary depending on various factors, making it essential to consider the appropriate material for a specific application carefully.

To gain some level of insight into the behaviour and mechanism of the adsorption of EAD on the activated SG surface, both Langmuir and Freundlich isotherms were employed in the study. They were also used to describe the correlation between the amount of EAD adsorbed and its equilibrium concentration in solution at constant pH and room temperature.

3.6.1 The Langmuir and Freundlich Isotherms

The curves of Langmuir and Freundlich isotherms are shown in Figs. 4 – 5. Table 5 clearly stated the obtained parameters and regression coefficients of these isotherms at 301 ± 1K

Table 5. Modified-SG isotherm parameters for both isotherm models at pH 1

Isotherm	Parameters	
Langmuir R^2	q_{max}(mg/g)	K_L(mL/mg)
0.9797	250	2.22
Freundlich n		K_F
0.9694	4.13	2.27

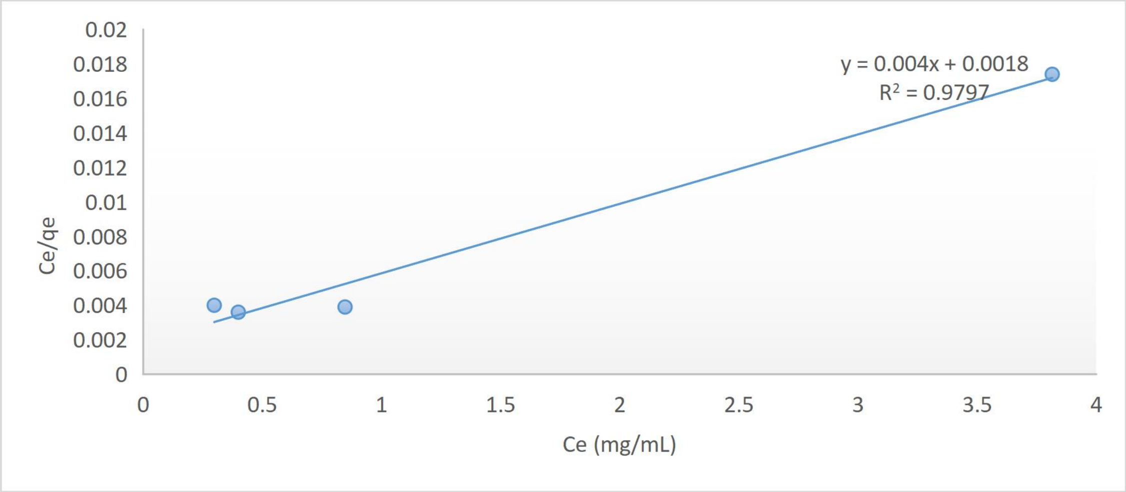
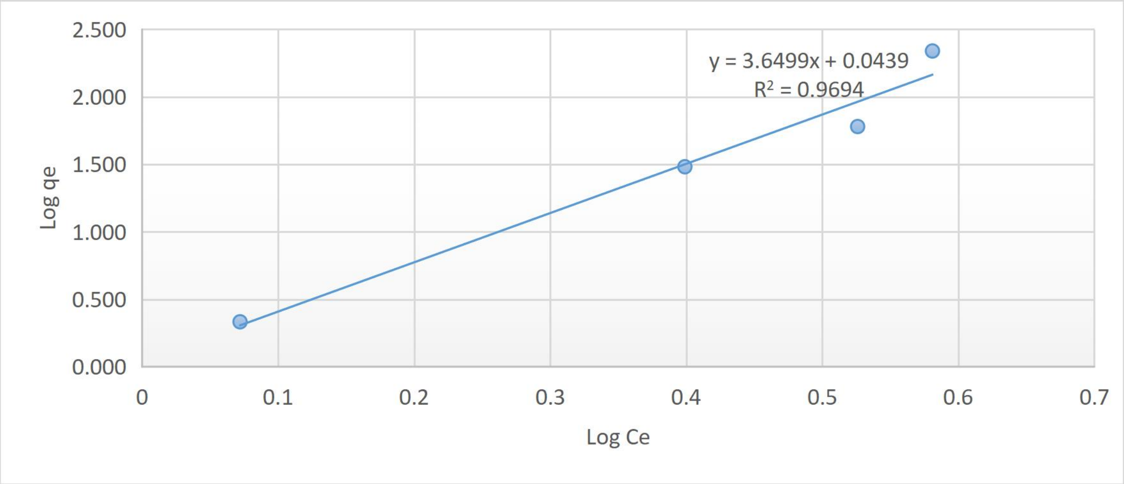


Fig.4. Langmuir adsorption isotherm for EAD onto the activated SG at pH 1.0 and 301±1K



Fig, 5. The Freundlich adsorption isotherm for EAD onto activated SG at pH 1.0 and 301±1K

The Langmuir conceptually projected monolayer maximum adsorption capacity (q_{max}) of EAD onto SG at pH to be 250 mg/g which is in close range with the experimental adsorption capacity of 218.50 mg/g. The Langmuir affinity (K_L) of the SG binding site for EAD was found to be 2.22 mL/mg. The value of Freundlich adsorption strength (n) obtained from the adsorption process elucidates the extent of nonlinearity between the concentration of the solution and the adsorption process. Expectedly, if n = 1, it shows that the adsorption process was linear, if n < 1, it means the chemisorption process; if n > 1, then the adsorption process was physisorption. The Freundlich adsorption strength (n) was determined as 2.63 which portrayed a possible physisorption process corresponding to increased heterogeneity of the SG surface. The regression correlation coefficient (R^2) values of 0.9797 and 0.9694 were obtained for the Langmuir and Freundlich isotherm models respectively. However, the value of 0.9797 suggested that the Langmuir model provided a better fit with the equilibrium data than the Freundlich isotherm model[26].

The fitness of the experimental data into Langmuir isotherm expression predicted not only the monolayer coverage of EAD on the SG surface at pH 1 and 301 ± 1K but also suggested that the entire adsorption sites on the SG are equal and uniform.

The essential feature of the Langmuir isotherm expressed as separation factor, RL, can be defined by the equation (3);

$$R_L = \frac{1}{1+KLCo} \qquad (3)$$

Where Co equals the initial concentration and *KL* is related to the Langmuir equilibrium constant. The shape of the Langmuir isotherm depends on the value of the separation factor, R_L. The isotherm is irreversible if $R_L = 0$; Linear if $R_L = 1$; unfavorable if $R_L > 1$ or favorable if $0 < R_L < 1$. The separation factor, R_L, values were found to range from 0.070 to 0.333 which suggested that the adsorption of EAD on the SG was favourable.

3.7 Adsorption Kinetics

The kinetic studies were carried out by withdrawing and analyzing the samples at different time intervals. The kinetic data for the adsorption of EAD onto silica gel were tested with the popular kinetic models, notably, pseudo first–order and pseudo-second–order kinetics. The kinetic empirical data showed that the values of log (qe – q) were all negative and indeterminate, therefore the pseudo-first-order kinetic plot could not be achieved. Figure 6 captured the linear plot of t/q against time (t) for the pseudo-second-order kinetic model. The equilibrium rate constant of the pseudo-second-order adsorption(k2) (g/mg min). and the calculated adsorption capacity(qe) were obtained from the intercept and the slope of the plot respectively.

The physisorption phenomenon is characterized by weak intermolecular forces between the adsorbent and the adsorbate, which leads to adsorption kinetics that follow the pseudo-second-order. The pseudo-second-order model assumes that the rate-limiting step for adsorption is the chemisorption of the adsorbate onto the surface of the adsorbent, which is a more gradual and irreversible process than physisorption. This model can accurately describe the adsorption kinetics for many systems that exhibit physisorption behaviour. Therefore, the physisorption fits well with the pseudo-second-order model, which provides a mathematical representation of the adsorption process and is useful for predicting the adsorption capacity and rate of equilibrium attainment[27].

Table 6. The pseudo-first-order and pseudo-second-order kinetic parameters for the adsorption of EAD on SG

Kinetic model	Parameters			
Pseudo first- order	$q_{e\ exp}$ (mg/g)	q_{e1cal}(mg/g)	K^1(min^{-1})	R^2
	280	-	-	-
Pseudo second-order			q_{e2cal} (mg/g)	K^2(g/mg.min)
	280	278	0.14	1.0

The Langmuir isotherm is a model used to describe the adsorption of gas or solute molecules onto a solid surface at a given temperature. It assumes monolayer adsorption where the adsorbent is homogeneous and that the adsorption rate decreases as the surface becomes saturated.

On the other hand, physisorption is the adsorption of gas molecules onto solid surfaces due to physical forces, such as Van der Waals interactions, without creating any chemical bonds. This process is commonly observed in porous materials like zeolites, activated carbon, and metal-organic frameworks. In summary, the Langmuir isotherm can describe the adsorption process of gas or solute molecules onto a solid surface, but it may not specifically correspond to physisorption. Physi-sorption involves physical interactions between gas or solute molecules and solid surfaces without creating any chemical bonds[28].

The kinetic model of Cu2+ adsorbed on the modified silica surface refers to the description of the processes involved in the adsorption of copper ions onto the surface of silica particles that have been chemically modified. The following are some of the properties of this kinetic model: It describes the adsorption of Cu2+ onto the modified silica surface as a reversible process. This means that copper ions can be adsorbed onto the surface and subsequently desorbed, depending on the conditions, such as pH and temperature. The model is based on the assumption that adsorption occurs at the interface between the modified silica surface and the aqueous phase, where the concentration of Cu2+ ions is high. The kinetic model assumes that the adsorption of copper ions is a first-order process, with the rate of adsorption being proportional to the concentration of Cu2+ ions in the solution. The kinetic model also takes into account the effect of temperature on the adsorption process, with higher temperatures resulting in greater adsorption rates[29]. It is also assumed that the chemical modification of the silica surface creates additional adsorption sites for Cu2+ ions, resulting in enhanced adsorption capacity compared to unmodified silica surfaces. The model predicts that as the initial concentration of Cu2+ ions in the solution increases, the rate of adsorption will initially increase but eventually reach a maximum value beyond which no further adsorption will occur. Overall, the kinetic model of Cu2+ adsorbed on the modified silica surface provides a useful framework for understanding the fundamental factors that govern the adsorption process and provides a basis for predicting the behaviour of this system under different conditions.

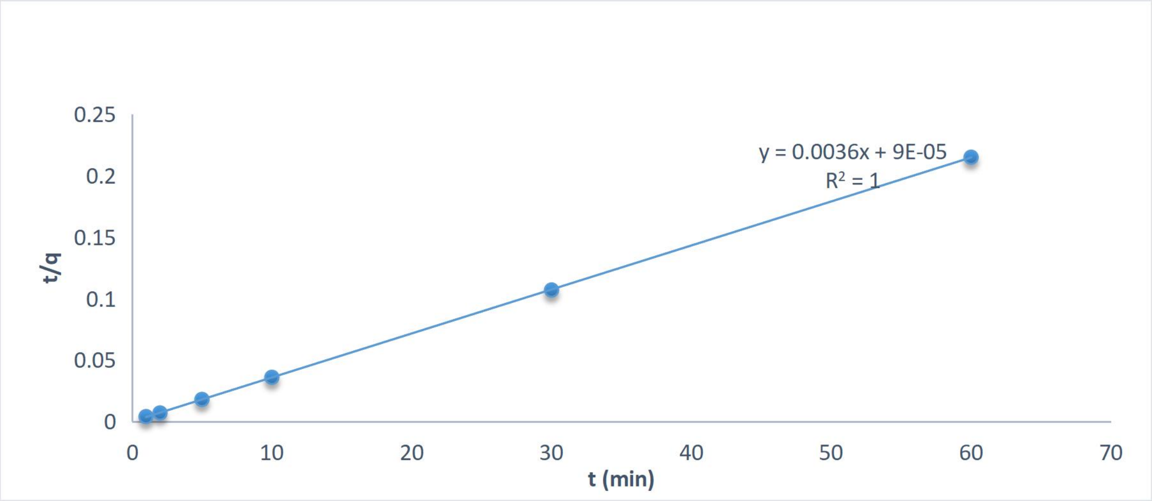


Fig.6: Pseudo–second–order kinetic plot for the adsorption of EAD onto activated SG

Table 6 summarizes the experimentally determined data on kinetic parameters, adsorption capacity and correlation coefficients of adsorption for the kinetic models at room temperature. The high correlation (R^2) value of 1.0 as indicated in Fig.9 confirms that the kinetic data are well represented by pseudo-second-order kinetics for the entire sorption period. The calculated adsorption capacity value q_{e2cal} of 278 nearly agrees with the experimentally obtained value $q_{e\ exp}$ of 280. The rate constant (k^2) was determined to be 0.14 g/mg.min.

Adsorption isotherm and kinetic results are two different aspects of the adsorption process that provide different information about the behaviour of adsorbate molecules on a surface. The isotherm describes the relationship between adsorbate concentration and the number of molecules adsorbed on the surface, whereas the kinetic result describes the rate at which adsorption occurs. The isotherm can be used to determine the type of adsorption mechanism that is operating between the adsorbate molecules and the surface. Generally, adsorption isotherms can be divided into several categories, including Langmuir, Freundlich, BET, and Dubinin-Radushkevich isotherms. Each isotherm reflects a type of interaction between the surface and adsorbate molecules[30].

On the other hand, kinetic results provide information about the rate at which an adsorption process is occurring. Kinetic studies provide insight into the mechanism of adsorption and can be used to predict the time required for adsorption to occur. Generally, the kinetic study is conducted by measuring the number of adsorbate molecules on the surface at specific intervals. In some cases, the adsorption isotherm and kinetic study results may not align. The reason for these contrasting results could be due to various factors such as pore size, surface area, adsorbate concentration, and temperature. Sometimes, the isotherm may depict a certain type of adsorption mechanism but the kinetic study may indicate that the adsorption process is not following the typical mechanism. This could be due to other factors affecting the adsorption process. In conclusion, while the adsorption isotherm and kinetic results offer valuable information, they should not be used independently to conclude the adsorption behaviour. It is important to analyze both the isotherm and kinetic data together to develop a comprehensive understanding of the adsorption mechanism.

3.8 Surface coverage values of the modified SG extractor

The surface coverage values of the EAD-modified SG extractor were obtained spectrophotometrically. In the phosphate buffer, the surface coverage value was found to be 0.97 mmolg^{-1}, in the oxalate buffer, it was 0.098 mmolg^{-1} while in the ammoniacal buffer, it was determined as 0.73 mmolg^{-1}. Compared with the findings of those who reported surface coverage values of 0.17 mmolg^{-1}(by metal probe testing method) and 0.160 mmolg^{-1}(by elemental analysis method) for the chemisorbed SG – extractor and 0.251 mmolg^{-1} by elemental analysis method) for the physisorbed SG – extractor in the present study showed superiority over those obtained by conventional physical or chemical modification processes.

3.9 Effect of pH on the sorption of Cu(II)

Since the pH of the aqueous solution is a very important factor for the quantitative recoveries of the metal ions in the solid phase extraction studies, the effects of the pH of the analyte solutions on the recoveries of Cu(II) as EAD complex on silica gel were studied in the pH range of 1 – 12. As can be seen in Fig. 7, the sorption efficiencies decreased due to the protonation of the active sites of sorbent in more acidic media. The quantitative sorption efficiency was obtained at pH 4.0 due to the formation of an unprotonated sorbent surface.

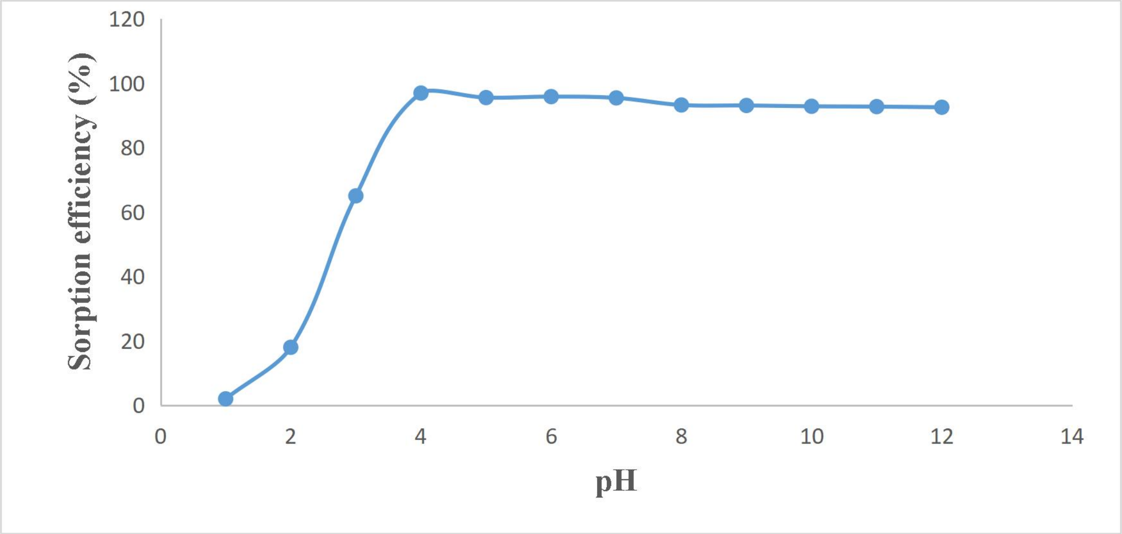


Fig.7. Effect of pH on the sorption of Cu(II) ion onto Si – EAD

3.10 Effects of sample volume on sorption of Cu(II)

Sample volume is the most important parameter for obtaining a high preconcentration factor. The preconcentration factor for the simultaneous separation and preconcentration is calculated by the ratio of the highest sample volume (mL) for the metal ions to the lowest eluent volume (mL).

The effect of sample volume on the retention of Cu(II) ions was investigated by passing sample volumes of 50 – 1000 mL containing 10 µg mL^{-1} Cu(II) through the column. The results are shown in Fig. 8. The results demonstrated that the recovery of Cu(II) was quantitative(> 99.6 %) for all the volumes. Considering 5.0 mL of elution volume, the preconcentration factor was found to be as high as 200 for Cu(II).

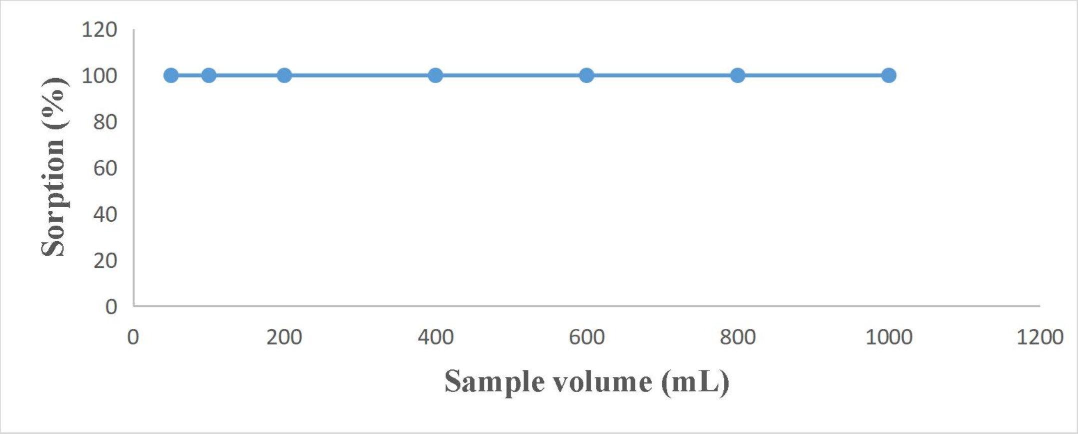


Fig 8. Effect of sample volume on the preconcentration of Cu(II) at pH 4

3.11 Effect of sorption flow rate on sorption of Cu(II)

A 50 mL working solution containing 10 μg mL^{-1} Cu(II) was passed through the Si – EAD column at 5 – 11 mL min^{-1} flow rates. As shown in Fig.9, sorption efficiencies decreased with increasing flow rate. Therefore, to increase the contact time of solutions with the sorbent, a 5.0 $mLmin^{-1}$ flow rate was chosen for the sorption of Cu(II). The sorption efficiency was 97.8(±0.2) % for Cu(II) at the selected sorption flow rate.

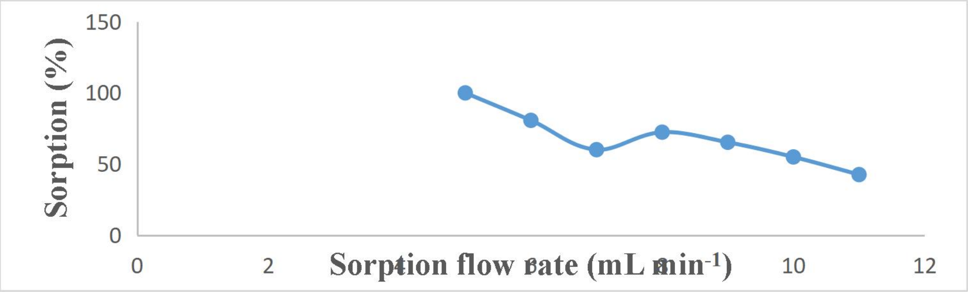


Fig.9. Effect of sorption flow rate on sorption of Cu(II) ions

3.12 Effect of elution flow rate on desorption of Cu(II)

The flow rate of 5.0 mL desorption reagent was examined in the range of 2 – 8 mLmin^{-1}. The results in Fig. 10 showed that after a 7.0 mLmin^{-1} flow rate, desorption efficiencies were not quantitative (< 60 %). Thus, a 2.0 mLmin^{-1} flow rate was selected for further studies.

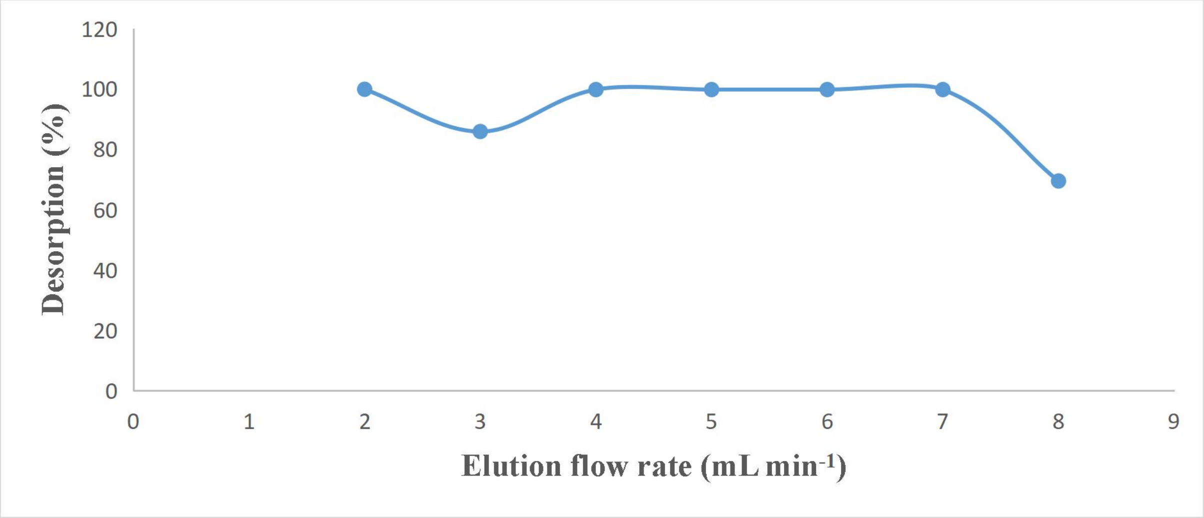


Fig.10. Effect of flow rate on desorption of Cu(II) ions from Si – EAD

3.13 Effect of eluent concentration on desorption of Cu^{2+}

The effect of nitric acid concentration on the desorption of Cu^{2+} was investigated in the concentration range of 1.0 – 4.0 molL^{-1} to obtain an applicable nitric acid concentration. As seen in Fig. 11, the desorption efficiencies were not quantitative when the concentration of nitric acid less than 1.0 mol L^{-1} was used as a concentration of desorption reagent. Thus, 1.0 mol L^{-1} HNO_3 was used for the quantitative recovery of copper from the column sorbent. The detachment of ligands from modified silica gel when Cu^{2+} is eluted using HNO_3 depends on the type of ligand used for modification. If the ligand is strongly attached to the silica surface, it may not detach easily during the elution process. However, if the ligand is weakly attached, it may detach and elute along with the Cu^{2+} ions. The final result also depends on the concentration and pH of the nitric acid used for elution. [18,19].

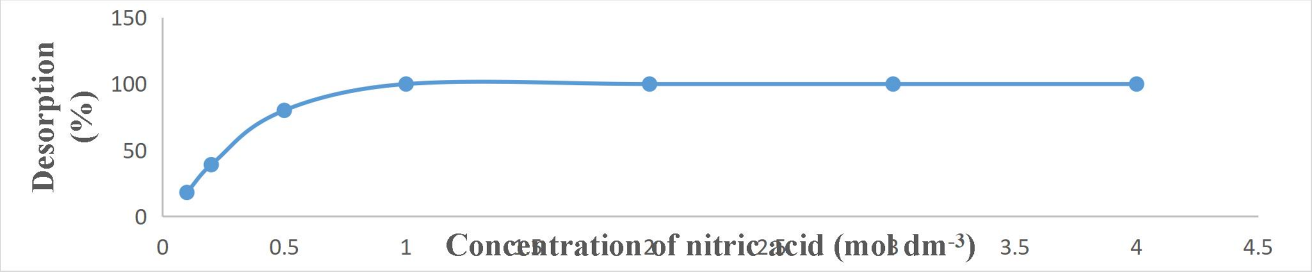


Fig.11. Effect of eluent concentration on the desorption of Cu(II) ions from Si – EAD

4.0 CONCLUSION

In the present study, a highly sensitive EAD reagent was used for copper determination. The usage of activated silica gel physically modified with EAD as a sorbent for simultaneous separation and preconcentration of Cu(II) ion from the synthetic samples by column technique and determination by UV- Vis spectrophotometer has been reported. The preparation of the modified-SG metal extractor is simple, rapid and cheap. Adsorption experiments were carried out at room temperature (301 ± 1K) by optimizing pH, contact time and initial ligand amount using batch mode. Equilibrium data were tested with both Freundlich and Langmuir adsorption isotherm models. The Langmuir model provided a better fit with the equilibrium data since it has a higher regression correlation coefficient. The observed parameters of the two adsorption isotherm models showed that the adsorption of EAD onto SG was favourable (separation factor, R_L) and followed a physisorption process (Freundlich adsorption strength). The adsorption kinetic data were also analyzed. The data obtained from the pseudo-second-order kinetic model also confirmed the adsorption process was physisorption. In conclusion, physically modified silica gel has shown promising results in effectively adsorbing copper (II) ions from aqueous solutions containing N, N'-Ethylenebis(acetylacetone)diamine. The adsorption capacity was found to increase as the concentration of copper ions increased, indicating that physically modified silica gel has a high affinity towards copper (II) ions. This study suggests that physically modified silica gel could be a potential solution for the removal of copper (II) ions from industrial wastewater, thus providing a cost-effective and environmentally friendly approach towards water treatment. Further studies are required to optimize the adsorption process and assess the viability of large-scale implementation of this method.

Declarations

Ethics approval and consent to participate

Not applicable

Consent for publication

Not applicable

Availability of data and material

Not applicable

Competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

Authors contributions

E M E and C S A: Conceptualization, Methodology, Original draft preparation, Performed experimental work, and Writing

Funding

The author received no funding for this study.

Acknowledgements

This work received administrative support from the Department of Science Laboratory Technology, Institute of Management and Technology, Enugu, Nigeria and the Department of Chemical Engineering, Federal University Otuoke, Nigeria.

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