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Synthesis, Characterization and Heavy Metal Removal Efficiency of β-Cyclodextrinethylamine Inclusion Complex

[1*]Iorungwa, M. S., [1]Gav, B. L., [2]Ama, S. O. [1]Iorapuu, D. T., Iorungwa, P. D., [3]Adegbe, C. S., [1]Danat, B. T. and [1]Kutshak, P. I.
[1]Inorganic/Physical Chemistry Research Group, Joseph Sarwuan Tarka University, Makurdi 970001 – Nigeria
[3]Department of Chemistry, Federal University, Wukari - Ngeria
[2]Department of Chemistry, Federal College of Education Odugbo, Benue State – Nigeria
***Correspondence Email:** iorungwa.moses@uam.edu.ng

ABSTRACT

Environmental contamination with heavy metals is one of the main concerns on a global scale and the risk related to heavy metal exposure in water as a serious threat to human health. Removal of heavy metal contaminants from water can be done in many ways using conventional and membrane techniques. This study synthesized, characterized and investigated the removal efficiency of inclusion complex of β – cyclodextrinethylamine in the removal of some heavy metals in contaminated water samples obtained from Makurdi, Benue State, Nigeria. β– cyclodextrinethylamine metal complex was prepared and characterized by Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Fourier Transformed Infrared Spectroscopy (FTIR) while the heavy metal concentrations for the removal efficiency was determined using Atomic Absorption Spectroscopy (AAS). The results indicated that the removal of heavy metals was efficient in the study areas with the highest average percentage removal efficiency and a trend of Cu = Co (99.85 %) > Zn (99.80 %) > Ni (99.75 %) > Cd (99.1 %) obtained in Tse – Chivir sample area while the efficiency of heavy metal removal obtained from **Joseph Sarwuan Tarka University, Makurdi** (**JOSTUM**) showed the order of Ni = Co(99.8 %) > Zn = Cu > Cd (99.5 %). Indicating that the inclusion compound can be used for effective removal of heavy metals in contaminated solutions and purification processes in water treatment.

Keywords: β– cyclodextrinethylamine, Heavy metals, Wastewater, Percentage efficiency

INTRODUCTION

Human activities including industrialization and agricultural practices, contributed enormously to the degradation and pollution of the environment, which has an adverse effect on the bodies of water that is a necessity for life (Owa, 2014). Pollution occurs through the addition of contaminants into natural sources. Toxic substance present as contaminants affects more than two hundred million people on earth, according to Pure Earth (non-profit environmental organization). Water pollution occurs when dangerous foreign substances are introduced into water bodies and such substances include; pesticides and fertilizers from agricultural, or metals such as lead or mercury (Bradford, 2018). The world health organization (WHO) reports that 80 % of diseases are transmitted by water. Industrialization, the discharge of domestic waste, radioactive waste, and population growth, excessive use of pesticides, fertilizers and leaking water tanks are the main sources of water pollution. These wastes have negative effects on human health (Haseena *et al.*, 2017). Industrial wastewater containing lead, copper, cobalt and chromium can contaminate groundwater resources and thus lead to a serious groundwater pollution problem (Sambasevam *et al.*, 2013).

Water of high quality is essential to human life and water of acceptable quality is essential for other activities such as agriculture, industrial, domestic and commercial uses. All these activities pollute the water system when thrown to freshwater every day. As known, fresh water quality decreases remarkably day by day (Amha *et al.*, 2001). Therefore, there is an increased demand for innovative and low cost technologies to enhance the quality of water. The adsorption technique is favoured over other methods since it is environmentally safe, economical and technically easy to separate as the requirement of the control system is minimum (Quadri *et al.*, 2007). Instead of using synthetic adsorbents or commercial activated carbon, researchers have worked on inexpensive materials such as eggshell (Arunlertaree *et al.*, 2007), orange peels (Gunatilake *et al.*, 2015), oil palm shell (Saenger *et al.*, 2008), shrimp shell (Messner *et al.*, 2010) and other adsorbents (Zhou *et al.*, 2014), which have high adsorption capacity and are locally available.

Cyclodextrins (CDs) are a class of cyclic oligosaccharides with six, seven, or eight-glucose units linked by α-1,4 glycosidic bond. These three types of CD are named α, β, and γ-CD, respectively (Monti and Sortino, 2002). These oligomers are capable of enclosing a large number of organic and inorganic species in their cavity. The neutral lipophilic cyclodextrins were recognized by three types of non covalent interactions, conventional hydrophobic bonding, –N–H–N and N–C–H–N hydrogen bonding, and Van der Waals forces, cooperatively determine the inclusion complex behavior of the cyclodextrin host (Sun *et al*., 2022). Native water-soluble cyclodextrins have been rendered lipophilic and used for molecular and ionic recognitions (Aghamohammadi and Alizadeh, 2007). This property has led to the wide application of cyclodextrins in various fields, such as analytical chemistry, enzymology, they have been widely used in pharmaceutical, in food industry. They can be utilized in foods mainly as carriers for molecular encapsulation of flavours, in separate chromatography technique (Schneiderman and Stalcup, 2007), and in environmental protection (Muoele *et al.*, 2015). The CDs are well known to form inclusion complexes with a variety of organic compounds, among them, with drug substances (Jianbin *et al.*, 2014; Louiz *et al.*, 2015; Alonso *et al.*, 2016).

Cyclodextrins are molecular chelating agents. They possess a cage-like supra-molecular structure thus they attract attention as strong adsorbents of natural origin. Cyclodextrins (CDs) are cyclic oligosaccharide composed of 6 to 8 glucopyranose units (namely α-, β- and γ-CDs) linked by glycosidic bonds. All are water soluble, non-toxic and hydrophilic at the surface and hydrophobic in the central cavity. The large number of the hydroxyl groups in cyclodextrins are considered binding sites and able to form various types of linkages. A cross-linking with other compounds or polymers, or their derivatization are considers the main reactions of these cyclodextrins. β-cyclodextrin (β-CD) is a starch derivative, non-toxic to humans and easily available. The cyclic structure with a visible cavity allows for the formation of inclusion complexes of hydrophobic compounds. Despite the average solubility, it is very popular as a base for systems that absorb hydrophilic compounds. Cross-linked β-cyclodextrin polymers (β-CD) are a group of polymers based on β-cyclodextrins linked with a cross-linking compound (Rafati *et al.*, 2019; Cecone *et al.*, 2019). Particular attention is paid to cross-linked polymers, which have an abundant porous structure, as they are promising absorbent systems. The modification of cyclodextrin hydroxyl groups with substituents significantly affects the interaction between the polymer and the absorbed compounds. Cyclodextrin polymers are successfully used as pollution-absorbing systems (Wang *et al.*, 2020; Sun *et al.*, 2022).

Following report of high level of contamination of soils and water sources around Makurdi by Iorungwa *et al.* (2009), the present study focuses on the application of β - cyclodextrinethylamine host inclusion complex for the removal of heavy metals in contaminated water samples obtained around Makurdi metropolis.

MATERIALS AND METHODS

The following instruments were used: pH meter, Fourier transform infrared (FTIR) 400−4000 cm^{-1} (GRIFFINS LTD), Thermogravimetric Analyzer (TGA), Differential scanning calorimetry (DSC) (PERKINS 119), Atomic Absorption Spectrophotometer (UNICAM 929). The following reagents were used: β-cyclodextrin, Ethylamine, Deionized water, HCl, NaOH.

Synthesis of β-cyclodextrinethylamine inclusion complex

Exactly 10^{-4} mol (1.13 g) of β-CD was dissolved in 20 mL distilled water. Then 10^{-4} mol (0.31 g) of ethylamine in ethanol solution was dropped into β-CD aqueous solution with continuous stirring. The stirring operation was left for 72 h at room temperature. The inclusion complex of ethylamine and β –CD was obtained by filtration, which yielded a yellow solid product. The product was washed with ether three times to clean the residual guest and host monomers. Next, it was dried in a vacuum oven at 50 ºC for 48 h (yield = 70 %).The product was confirmed by TGA and DSC.

Extraction of Toxic Metals

A batch extraction process was used, whereas exactly 2 g of the inclusion compound was added to 2 mL 0.04 $moldm^{-3}$ of the metal ions solution in a bottle, then the bottle was closed and shaken in the shaker apparatus at constant temperature and at a specific speed for 30 min. A sample of each mixture was withdrawn with a syringe, filtered through a 0.45 μm filter and subjected to analysis for residual metal ions concentrations by atomic absorption spectroscopy. The proportion of metal absorption (% Absorption) is recognized as the ratio of disparity of the metal ions concentration before and after absorption to the initial concentration of the metal ions in the aqueous solution and was calculated using equation 1 (Iorungwa *et al.*, 2009):

$$\text{Removal efficiency (\%)} = \left[\frac{C_o - C_e}{C_o}\right] x100 \qquad (1)$$

Where, C_o is the Initial metal ions concentration (mg/L) in the sample and Ce is the final metal ions concentration in the sample solution after treatment.

RESULTS AND DISCUSSION

FTIR Spectroscopy

The results of FTIR spectroscopy for β-Cyclodextrin and the β-Cyclodextrin ethylamine inclusion compound is presented in Figures 1 and 2 respectively:

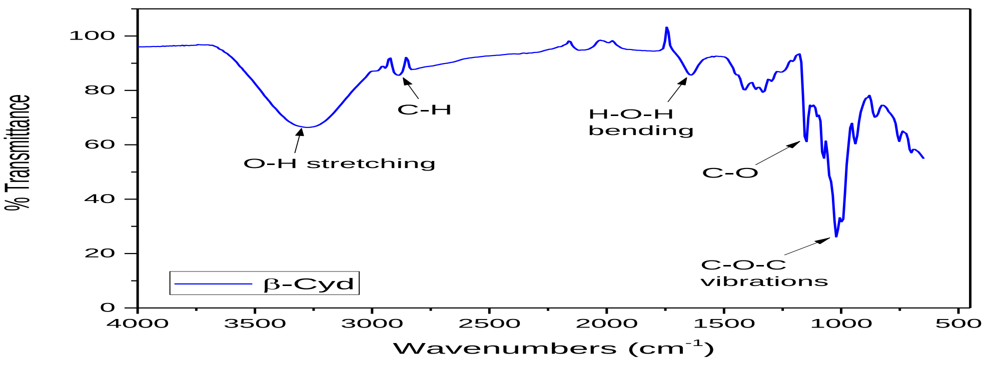

Figure 1: FTIR Spectrum of β-cyclodextrin (β-CD)

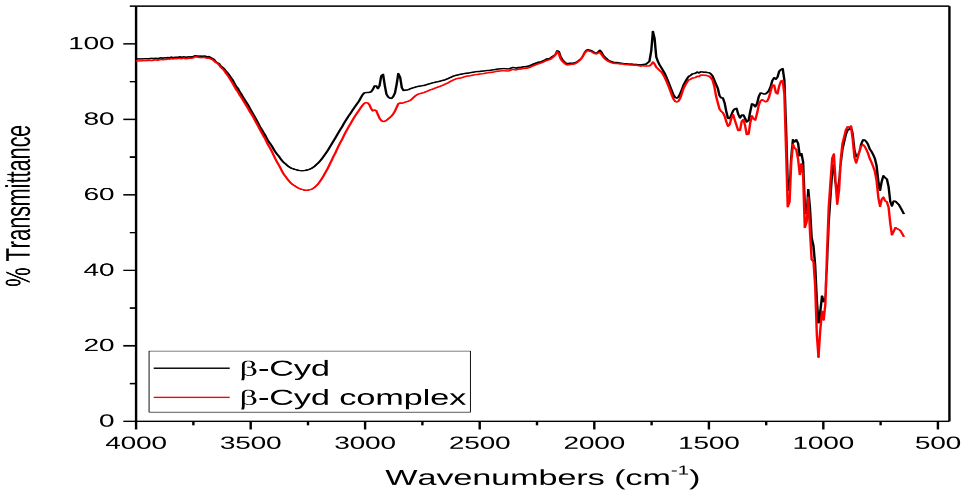

Figure 2: FTIR Spectrum of β – cyclodextrin ethylamine inclusion compound

FT-IR is a useful technique used to characterize inclusion complex. The spectra of β-cyclodextrin and inclusion complex are presented in Figures 1 – 2. The FT-IR spectrum of β-cyclodextrin (Figure 1) showed prominent absorption bands at 3288 cm^{-1} for O–H stretching vibrations, 2903 cm^{-1} for C-H stretching vibrations, 1638 cm^{-1} for H–O–H bending, 1150 cm^{-1} for C–O stretching vibration, and 1012 cm^{-1} for the C–O–C stretching vibration. The FT-IR spectrum of β-cyclodextrin complex (Figure 2) however, consisted of these prominent absorption bands ca: 3275, 2930, 1640, 1158, and 1012 cm^{-1} for O−H, C−H, H−O−H bending, C−O stretching, and C−O−C stretching vibrations respectively.

Both spectra showed some increase and decrease in peak intensities. The increment is due to the insertion of the ethylamine into the electron-rich cavity of β-cyclodextrin and will increase the density of the electron cloud, which will lead to an increase in frequency (Tang *et al.*, 2006). The decrease in the frequency between the inclusion complex and its constituent molecule is due to the changes in the micro-environment which lead to the formation of hydrogen bonding and the presence of van der Waal's forces during their interaction to form the inclusion complex (Hamdi *et al.*, 2010). On the other hand, the FTIR spectrum of physical mixtures imitated the characteristic peaks of β-CD and ethylamine, which can be regarded as a simple superimposition of those host and guest molecules. Thus, the FTIR spectra significantly prove the formation of the ethylamine-β-CD inclusion complex as validated by previous reports for analogous complexes (Sambasevam *et al.*, 2013).

Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

Thermogravimetry analysis is a powerful technique for the measurements of thermal stability of materials including polymers. In this method changes in weight of (beta cyclodextrins, and the inclusion compound) are measured. While its temperature is increased this can be seen in Fig. 3, and 4 for beta cyclodextrin, and the cyclodextrin ethylamine inclusion compound.

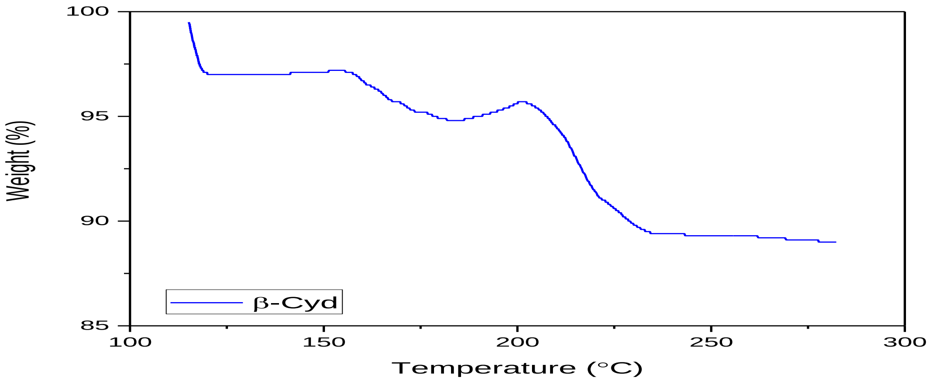

Figure 3: TGA plot of β-cyclodextrin (β-CD)

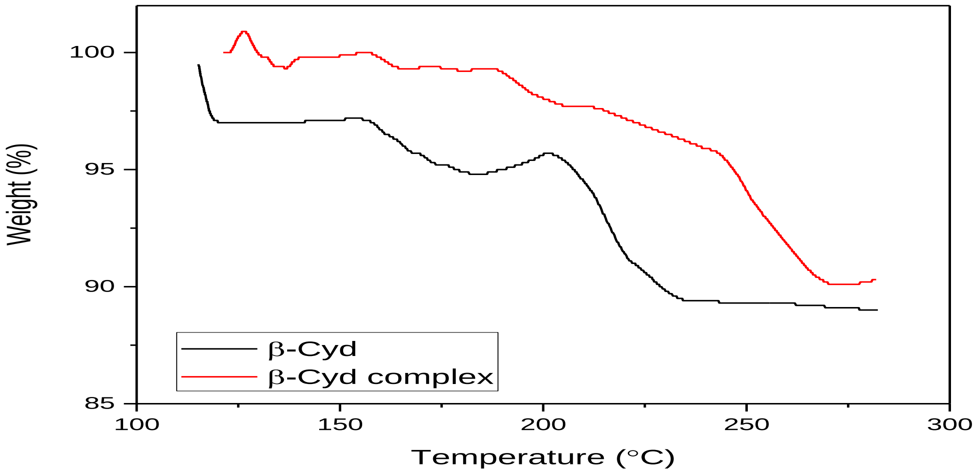

Figure 4: Stacked TGA Plots of β-cyclodextrin ethylamine Inclusion Compound

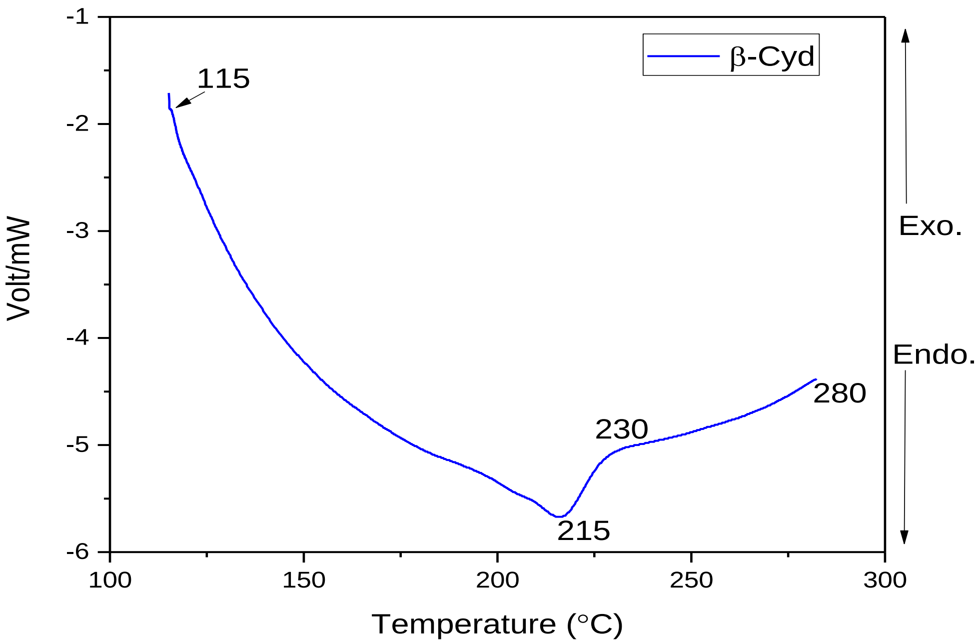

Figure 5: DTA Plot of β-cyclodextrin (β-CD)

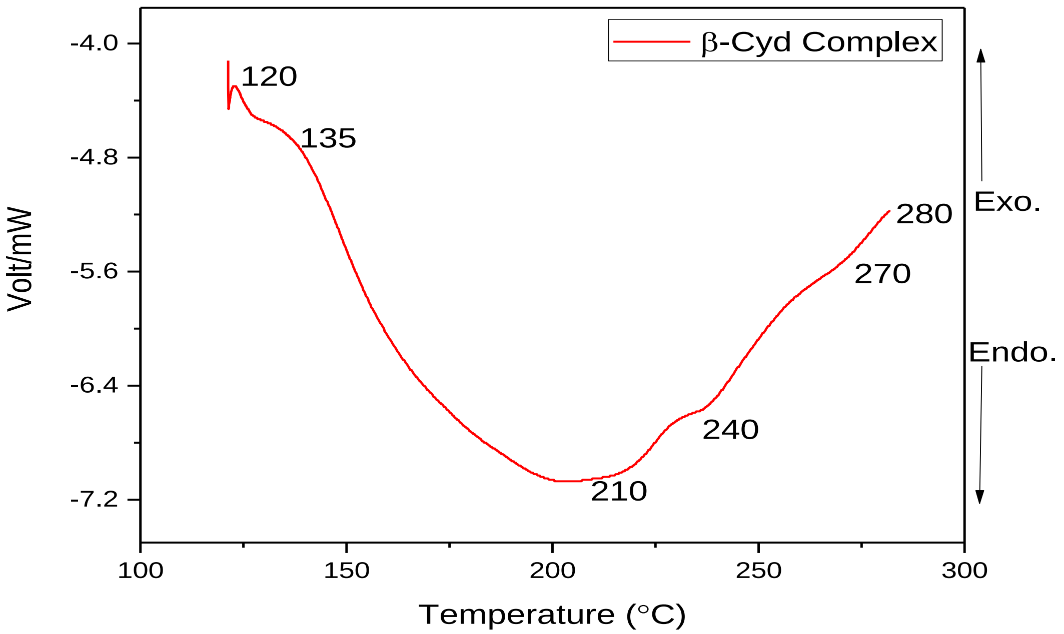

Figure 6: DTA Plot of β-cyclodextrin Inclusion Complex

The interpretation of the variation in the mass of a sample with a change in temperature is done by thermogravimetric analysis (Han *et al*., 2004). It is usually done on samples to identify the changes in weight percent with respect to temperature change. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out from 50 to 300 °C in the atmosphere to determine the changes that occurred during the heat treatment of the pure β-cyclodextrin and its inclusion complex. The TG curve of β-cyclodextrin is shown in Figure 3 and the inclusion compound is presented in Figure 4 where ethylamine was added. It can be observed that β-cyclodextrin exhibits two separate weight losses due to the loss of water molecules at an onset degradation temperature that occurred at ca. 120°C implying that moisture and other impurity loss were observed until 160°C with a mass loss of 3 %. In the TG curve of the inclusion complex, the onset degradation temperature occurred at of 125°C while the loss of impurities and other decomposition temperatures appear at three different positions viz, 160, 190, and 210°C. The disparity in peak positions for similar decomposition processes can be ascribed to the formation of the inclusion complex. Similarly, the steep curve of β-cyclodextrin shows a sudden decrease in the mass seen at 200°C followed by the formation of residues at ca. 235°C, an observation which deviated in the TG curve of the inclusion complex where the sudden decrease in mass occurred at 10°C higher (245°C) and 270°C for the formation of residues. Consequently, 235°C and 270 °C have been assigned as the calcination temperature for the free β-cyclodextrin and its inclusion complex respectively, with a major part of the weight loss occurring above 200 °C. This phenomenon suggests that the formation of the inclusion complex increases the thermal stability of β-cyclodextrin (Hassan *et al*., 2022).

From the DTA plots (Figures 5 – 6), exothermic and endothermic events taking place within the samples have been analyzed over a programmed range of temperatures. During the endothermic process in the DTA thermogram, the temperature of a sample fell behind the reference temperature, and a down peak was observed whereas in the exothermic process, the sample temperature exceeded the reference temperature, and a minimum is observed on the graphical plot. The analysis was done between 50 °C and 300 °C with air as the atmosphere for all samples (Han *et al*., 2004; Chen *et al*., 2021).

The DTA plot of β-cyclodextrin appeared to have an endothermic peak assignable to absorbed water evaporation at about 115°C and another endothermic peak at of 215°C which can be ascribed to the decomposition of impurities. Two exothermic peaks appear at about 230 and 280 °C which can be assigned to further degradation of impurities and completion of the reaction respectively. The peak at 280 °C thus forms the calcination temperature of the β-cyclodextrin sample. In the DTA curve of the ethylamine inclusion complex, however, three endothermic peaks were observed at of 120, 135, and 210 °C. The first is assignable to the evaporation of absorbed water while the second and third are ascribed to the decomposition of impurities. Similarly, three exothermic peaks were observed at 240, 270, and 280 °C corresponding to the degradation of impurities, decomposition of the ethylamine moiety, and completion of the reaction respectively. This observation is a confirmation that the ethylamine- β-cyclodextrin inclusion complex was formed as validated by literature reports (Sambasevam *et al*., 2013).

Differential Scanning Calorimetry (DSC)

DSC is a thermal analysis apparatus measuring how physical properties of a sample changes along with temperature. This technique was used, and a plot in Figure 7 and 8 clearly spelt out the changes in the physical properties of the sample

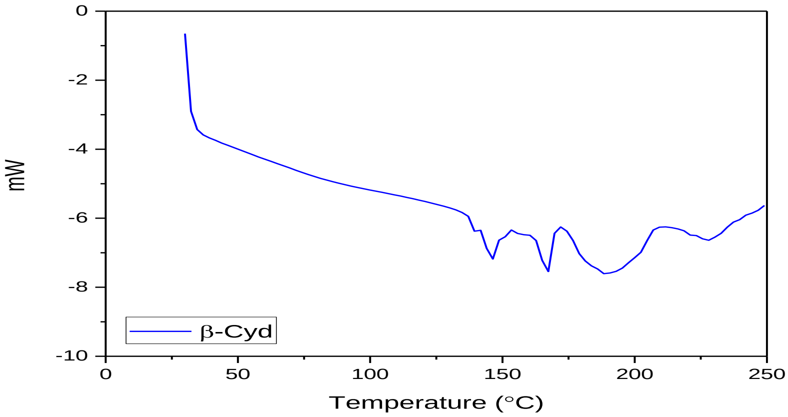

Figure 7: DSC Thermogram of β-cyclodextrin

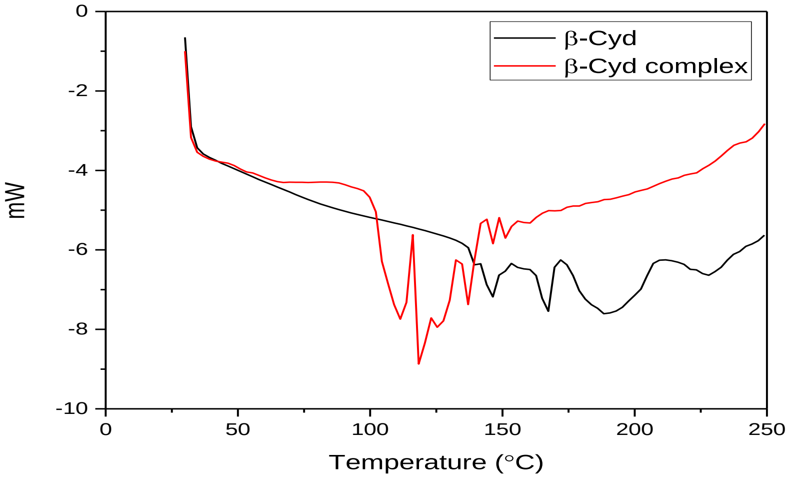

Figure 8: Stacked DSC Thermograms of β-cyclodextrin and its Inclusion Complex

The thermal curves of β-cyclodextrin and β-cyclodextrin inclusion complex are shown in Figures 7 and 8. The thermogram of β-cyclodextrin showed wide endothermic peaks at about 145 and 190 ^{0}C (Figure 10). These sharp endothermic peaks are related to the dehydration of water molecules that bind to cyclodextrin molecules (Kohata *et al*., 1993; Wang *et al*., 2011). These endothermic peaks appear to have shifted to lower temperatures in the thermogram of the β-cyclodextrin inclusion complex (Figure 7) occurring at of 110 and 137 ^{0}C respectively. This is strong evidence indicating the formation of the complex. In addition, two exothermic peaks observed at of 172 and 210 ^{0}C for β-cyclodextrin are related to its oxidation. This is likely due to the elimination of included water molecules with different strengths of interaction with the β-cyclodextrin ring (Kohata *et al*., 1993). The DSC curve of β-cyclodextrin and β-cyclodextrin inclusion complex were superimposed, and a clear shift in important peak position is observed (Figure 8). The shifts in peak positions in the inclusion complex system can be explained based on a major interaction between β-cyclodextrin and ethylamine. The two exothermic peaks associated with oxidation of β-cyclodextrin were not present in the DSC scan of the inclusion complex, indicating that ethylamine is protected from oxidation, being inside the β-cyclodextrin cavity, and offering an indirect proof of ethylamine inclusion (Wang *et al*., 2011). The results herein agree with those of previous studies for similar kinds of materials.

Heavy metal Removal Efficiency of Inclusion complex

The removal efficiency of the synthesized inclusion complex was calculated for the four sample areas considered and presented in Tables 1, 2, 3 and 4 by adopting the formula presented by Iorungwa *et al.*, (2009). The global view of the four tables show a removal efficiency of over 98 %. This simply implies that the β – cyclodextrinethylamine inclusion compound is an excellent candidate for heavy metal removal in contaminated sites.

Table 1: Site A. Tse-Chivir welfare quarters extension Makurdi labeled (SF)

Analyte	Initial conc. (Co) mg/L	Conc. trapped (Ct) mg/L	Percentage efficiency (%E)	Difference (D)
Cd	5.294	5.316	99.5	0.022
Co	17.0887	17.103	99.8	0.0143
Cu	17.135	17.103	99.9	0.032
Ni	25.51	25.57	99.7	0.06
Zn	3.5626	3.56744	99.8	0.00484

Table 2: Site B. Tse-Chivir welfare quarters extension Makurdi labeled (AS1)

Analyte	Initial conc. (Co) mg/L	Conc. trapped (Ct) mg/L	Percentage efficiency (%E)	Difference (D)
Cd	5.1662	5.2298	98.7	0.0662
Co	16.249	16.27	99.9	0.024
Cu	16.19	16.21	99.8	0.02
Ni	24.911	24.949	99.8	0.038
Zn	3.6405	3.6455	99.8	0.005

Table 3: Site A. Joseph Sarwuan Tarka University, Makurdi labeled (US1)

Analyte	Initial conc. (Co) mg/L	Conc. trapped (Ct) mg/L	Percentage efficiency (%E)	Difference (D)
Cd	5.3022	5.3338	99.4	0.0316
Co	16.124	16.156	99.8	0.032
Cu	16.23	16.25	99.8	0.02
Ni	24.938	24.963	99.8	0.025
Zn	3.643	3.653	99.7	0.01

Table 4: Point B. Joseph Sarwuan Tarka University, Makurdi labeled (UW1)

Analyte	Initial conc. (Co) mg/L	Conc. trapped (Ct) mg/L	Percentage efficiency (%E)	Difference (D)
Cd	5.3041	5.3219	99.6	0.0178
Co	16.161	16.179	99.8	0.018
Cu	16.247	16.333	99.4	0086
Ni	24.956	25.004	99.8	0.048
Zn	3.6361	3.6519	99.5	0.0158

The percentage removal efficiency values from Tables 1 to 4 show minimal variation and considering the fact that the inclusion compounds are benign in nature and are biodegradable makes them greener for utilization as candidates for effective heavy metal removal. Table 1 has a range of 99.5 – 99.9 % removal of the metals which occurred between Cd and Cu, while Table 2 has a range of 99.7 – 99.9 % removal efficiency as recorded for Cd and Co. The trend still continued in Tables 3 and 4 with a range of 99.4 – 99.8 % removal efficiency occurring for Cd while Co, Cu and Ni had 99.8 % respectively. Table 4 had a percentage removal efficiency of 99.8 for Co and Ni while the lowest percentage removal efficiency was observed in the case of Cu where a value of 99.4 % was recorded.

CONCLUSION

It can be confidently concluded that the beta CD offers a promising future in the field or area of water treatment and purification. Although the researches are still in the preliminary stage, beta CD has showed a huge potential for being replaced by the conventional water purification techniques such as those with activated carbon, sand which contain silica. A variety of researches are being carried across the globe by prominent scientists and it is only a matter of time that beta-CD based adsorbent will be available for commercial use and become a widely preferred choice for the purpose of heavy metal ions removal from water.

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