CATALYTIC DETOXIFICATION OF AQUEOUS CYANIDE USING COPPER CROWN ELECTROSPUN CHITOSAN NANOFIBER

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Received 06 March 2021; accepted 28 March 2021, published online 10 April 2021

Abstract

Owing to the common phenomenon of cyanide toxicity, this study focused on oxidative catalytic detoxification of aqueous cyanide in the presence of copper-crown chitosan nanofiber. To overcome the difficulty in electrospinning chitosan, chitosan-salicylaldehyde was initially synthesized via Schiff base condensation, electrospun, and post neutralised into chitosan nanofiber. The copper-crown nanofiber was prepared using the impregnation method. The nanofiber material was characterized using FT-IR, SEM, TGA and DSC. The observed pseudo first-order rate constant for the catalytic H₂O₂ oxidation of aqueous cyanide with copper-crown nanofiber as catalyst was found to be 16 times greater than the oxidation with only copper catalyst. In addition, the reaction was found to be dependent on the size of the copper-crown nanofiber, pH, temperature, and H₂O₂/CN⁻. The reusability of the copper-crown nanofiber catalyst makes the process economically and potentially viable for commercial application.

Key words: chitosan; nanofiber; copper; oxidation; cyanide; detoxification

1.0 INTRODUCTION

Cyanide contamination is one of the environmental problems which can be linked to both natural and antropogenic sources. There is a proliferation of compounds either in solid, liquid and gaseous forms containing cyanide moiety which are used industrially in which cyanide acts as the primary toxic agents. [1].

The level of exposure to cyanide determines the extent of the severity of the health effects. Some of the symptoms of acute exposure to cyanide includes tachypnoea, headache, vertigo, lack of motor coordination, weak pulse, cardiac arrhythmias, vomiting, stupor, convulsions and coma [2]. Numerous methods exist for cyanide detoxification, but with some set-backs; biological treatment, oxidative method, sulphur(IV) oxide assisted

oxidation, natural degradation, acidification, volatilization, and reneutralization[3].

Cyanide oxidation by hydrogen peroxide has been confirmed to be the most viable option as it avoids the formation of toxic intermediates and does not add to the total dissolved solids [4]. However, it suffers from the long reaction time. The inclusion of heterogenous catalyst has been shown to promote the reaction between cyanide and hydrogen peroxide [5]. The oxidation of dilute aqueous cyanide solution using hydrogen peroxide at room temperature was enhanced by the presence of Ru/MgO catalyst [6]. Kitis *et al.*, [5] carried out the oxidative destruction of free cyanide with hydrogen peroxide and copper-impregnated pumice as a heterogeneous catalyst. The peroxide oxidizes free and weakly complexed metal cyanides (i.e. nickel, copper, cadmium,

and zinc cyanides), forming one or less toxic compounds according to the reaction pathways (Equations 1 and 2) [7].

Previously, our group considered the complexing ability of chitosan-ligated metal and ease of coordination of cyanide to form stable complexes [8]. This approach served as a cheap alternative for cyanide removal from waste water. Building on this inherent property of chitosan, the development of a system which can combine both the catalytic oxidative approach and utilizing complexing solid support of a large surface area is highly imperative. Characteristically of nanofibers, they possess a large surface area which makes them an excellent matrix for catalyst support, enabling metal dispersion as small particles and inhibiting the formation of flocs. Chitosan, an optically active biopolymeric ligand with a strong affinity for transition metals and has been used as support for the preparation of heterogeneous catalysts in many forms among which the fibrous form has been reported to be of most importance [9]. Using electrospinning technique to form chitosan nanofiber, the copper-crown fibers were subsequently applied as a new oxidative catalyst for total cyanide detoxification in an aqueous solution. The results of the detoxification efficiency of this composite approach are herein presented.

2.0 EXPERIMENTAL PROCEDURE

2.1. Materials

Chemicals of pure analytical grade were used for the preparation of all reagents. Chitosan with 90% degree of deacetylation and high molecular weight 600 kDa.

2.2 Preparation of iminochitosan nanofiber

Chitosan (100 g) was first reacted with 130 mL of salicylaldehyde to form a chitosan Schiff base by adopting the method of El-Tahlawy *et al.*[10]. A mixture of the iminochitosan and TFA in acetone/dry ice bath was then frozen and later thawed in a water bath at ambient temperature. The solution was left overnight for electrospinning which was carried out using

the following conditions; 24 KV, 0.9 mlh⁻¹, 15 cm, 1.2 mm needle, 44.9%, 17.3 °C [11]. High Powered Electron Microscope (Olympus BX51) was used for the preliminary characterization of the electrospun chitosan. Electrospun nanofibrous structures were sputter-coated with gold (Denton Desk-1 Sputter Coater) the morphology of the electrospun nanofibers was determined with Scanning Electron Microscope (SEM; Vega Tescan, USA). A thermogravimetric analyser model TA-2960 was employed to determine thermogravimetric curves using Ca. 10 mg samples of the iminochitosan materials in a dynamic atmosphere, under a dry nitrogen flux, with heating from room temperature to 800 °C at a heating rate of 10°Cmin⁻¹. The thermal transitions of the iminochitosan were detected using DSC (TAQ10). The temperature and heat flow were calibrated using standard materials (indium and zinc) at cooling and heating rates of 10 °C/min. Samples with a typical mass of 3–10 mg were encapsulated in sealed aluminum pans.

2.3. Preparation of copper-crown nanofiber

Neutralization of the iminochitosan nanofiber mats was carried out in a 1 molL⁻¹ K₂CO₃ aqueous solution for 3 h at 25 °C. After neutralization, it was washed repeatedly with deionized water until a pH 7 was achieved. The fiber was first dried at ambient temperature for 24 h in the hood and then at 60 °C under vacuum for 24 h [12]. Impregnation method was used to prepare the copper-crown nanofiber catalyst according to Ye *et al.*[13]. A dried sample (0.05 g) of the post-neutralised and pretreated nanofiber was placed in a glass beaker and a stock solution of CuSO₄ (1 g/L) was added until all the nanofiber was completely immersed for 30 minutes. The mixture was filtered and the nanofiber was rinsed several times with the copper stock solution and once with water. Finally, samples were dried at room temperature until all moisture was removed and

constant weight achieved. IR spectra of KBr disc pellets of the nanofiber was recorded on

a Bulk Scientific, spectro 500 FT-IR spectrometer (East Norway, USA).

2.4. Catalytic oxidation of cyanide

The oxidation reaction was set up in a 250 mL Erlenmeyer flask mounted on a shaker and covered with aluminum foil to prevent photodegradation of cyanide or peroxide during mixing. The shaker was equipped with a temperature controller and was run at 150 rpm. The flask was initially loaded with the copper-crown nanofiber catalyst (500 mg g⁻¹) and then spiked with 50 mL cyanide (100 ppm) from the stock solution. Solution pH values were adjusted using reagent grade NaOH (3 M) and/or HCl (2 M) solutions. The oxidation reaction was initiated by the addition of the hydrogen peroxide (160 mg/L) oxidant. At the selected time intervals range of 0 to 40 mins, aliquot samples were collected and the reaction was quenched using Na₂SO₃[14]. The samples were thereafter analyzed for residual cyanide using ninhydrin method [15]. Atomic Absorption spectrophotometer (Tokyo, Japan) was used to determine the concentration of copper in the kinetic experiments. Cyanide was analyzed at 590 nm wavelength with Shimadzu, UV-1650PC UV-vis Spectrophotometer. A control experiment was set up in parallel in the absence of the nanofiber and all other reaction conditions remained unchanged. All readings were done in triplicates (n = 3).

3.0 RESULTS AND DISCUSSION

3.1. Synthesis and characterization of nanofiber products

The chemical modifications of chitosan involving the primary amino functionality along the polymer chain resulted in the formation of imine based chitosan. This is confirmed by the appearance of new $\nu_{N=C}$ around 1625 cm⁻¹ in the IR band of the iminochitosan nanofiber (Fig. 1). Also, Figure 2 shows the IR bands of copper crown nanofiber. The bonding of Cu(II) ion brings about a noticeable change in the shape of the broad absorption around 150–100 cm⁻¹ suggesting an interaction between the metal ion and the nanofiber.

Fig. 1: Infrared spectra of Post-neutralised iminochitosan nanofiber (KITOCOM) and iminochitosan nanofiber (IMINOKITO).

Fig. 2: Far IR region of Cu crown nanofiber.

The surface morphology of the nanofiber mat was studied (using a scanning electron microscope (SEM)) to have a clear insight into the formation of the fiber (Figure 3). Since fiber formation and morphologies are dependent on the properties of the polymer solution[16], the Schiff base chitosan was dissolved in TFA to form electrospinnable solution aided by sudden freezing and thawing. The optimal spinning parameters which gave bead-free nanofibers in the range 70–200 nm, from 6 wt% solution are 24 kV voltage, 15 cm working distance and 0.9 mLh⁻¹.

Fig. 3: SEM image of electrospun iminochitosan.

According to the thermogram, the nanofiber mat shows a high degree of stability to change in temperature (Figure 4). The nanofiber show little change in weight loss over a wide range of temperature. There was an observed weight loss around 100 °C, which can be attributed to the removal of adsorbed water molecules. The second weight loss occurred at 320 °C ascribed to the decomposition of the polysaccharide chain [17].

Fig. 4: TGA curve of copper crown nanofiber under nitrogen atmosphere

In addition, a differential scanning calorimetry (DSC) curve of the nanofiber shows distinct deviations from the usual step like changes in heat flow. A broad endothermic peak in the range of 100–150 °C was observed and this is related to the evaporation of water molecules in the nanofiber. The area and position of the

endothermic peaks was outsized at higher temperature suggesting that the nanofiber has a high water holding capacity and strong interaction with water molecules. The exothermic peak expected clearly at 274 °C due to the decomposition of amino (GlcN) has been significantly reduced meaning that it has been masked [18]. However, the exothermic peak around 390 °C can be attributed to the decomposition of the N-acetyl (GlcNAc) residues [19]. The last two exothermic peaks were observed clearly at 490 °C and 520 °C due to the thermal decomposition of imine (C=N) and benzene ring (C₆H₆) residues, respectively [9].

Fig. 5: DSC of the copper crown nanofiber

3.2 Cyanide oxidation in the presence of copper-crown nanofiber

Figure 6 compares cyanide oxidation efficiency of copper-crown nanofiber with only copper catalyst. Copper-crown nanofiber obviously displayed improved oxidation of cyanide (100% after 20 mins) than only Cu catalyst (~39% after 40 min) in the presence of H₂O₂ oxidant and initial cyanide concentration (C₀) of 100 mg/L. The cyanide oxidation kinetics for copper-crown nanofiber displayed a two-phase profile, a rapid initial stage (≤ 10 min) followed by a gradual reduction for 20 mins. By employing pseudo-first order reaction kinetics, the initial cyanide oxidation could be described by the model (Equation 3) [7, 18].

$$d \frac{[CN^-]}{dt} = -K_{SA} a_s p_m [CN^-] = -K_{obs} [CN^-] \quad (3)$$

Where $[CN^-]$ is the aqueous cyanide concentration (mg/L) at time t (min). K_{SA} is the specific reaction rate constant based on the surface area of the nanofiber ($L/(min \cdot m^2)$), a_s is the specific surface area of the nanofiber (m^2/g), p_m is the mass concentration of the nanofiber (g/L) and K_{obs} is the observed pseudo-first-order rate constant (min^{-1}). Therefore, using equation 3, the rate constants can then be determined by fitting the rate expression to the experimental data. The value of k_{obs} was $0.236 min^{-1}$ for the 56.3 mg copper-crown nanofiber and $0.015 min^{-1}$ for non-supported copper catalyst suggesting the copper-crown nanofiber to be 16 times greater than the the oxidation with copper catalyst only. This marked difference can be attributed to increased specific surface area of the resultant nanofiber which greatly enhanced the surface reactivity of the catalyst.

Fig. 6: Catalytic oxidation of aqueous cyanide solution in the presence of copper-crown nanofiber of different sizes (Values were represented as the mean of 3 readings i.e $n=3$).

3.3 Effect of H_2O_2/CN mole ratio

In order to accomplish optimal cyanide oxidation, the ratio of the oxidant to cyanide was investigated (Fig. 7). At the H_2O_2/CN ratio of 2.0 in the presence of the copper-crown nanofiber, the oxidation profile displayed the highest efficiency. This observation is in accord with the study of Kim *et al.*[20] which reported that cyanide removal efficiency and rate of reaction

increased considerably with an increase in H_2O_2 concentration.

Fig. 7: Effects of H_2O_2/CN ratio on the catalytic oxidation of aqueous cyanide solution by hydrogen peroxide in the presence of copper-crown nanofiber (Values were represented as mean of 3 readings i.e $n=3$).

3.4 Effect of pH on cyanide oxidation

Figure 8 shows the plot of the residual concentration of cyanide at various time intervals and pH. At pH 7, almost 100% cyanide catalytic oxidation has been attained within the first 10 min of the reaction. However, at lower pH, the percentage conversion was reduced. This observation could be attributed to the fact that at acidic pH, cyanide is mainly present in the form of HCN gas which is difficult to oxidize [7]. Also, the percentage conversion was further reduced at higher pH, which is largely due to the decomposition of hydrogen peroxide in an alkaline solution [21].

Fig. 8: Effect of pH on the catalytic oxidation of aqueous cyanide solution by hydrogen peroxide in the presence of copper-crown

nanofiber (Values were represented as mean of 3 readings i.e n = 3).

3.5 Effect of temperature on cyanide oxidation

Figure 9 shows the effects of temperature on the oxidation of cyanide by the copper-crown nanofiber. The temperature effect was studied by the oxidation of 100 mg/L cyanide solution using 160 mg/L H_2O_2 in the presence of 37.5 mg/L catalyst mix and was conducted over temperature range from 18 to 50 °C. It was observed that increase in temperature generally affected the catalytic oxidation of cyanide. At the optimum temperature of 50 °C, over 80% cyanide conversion was achieved within the first 2 min. This observation is in accord with Pak and Chang [6] where high temperature higher than 50 °C was required for complete oxidation of cyanide.

Fig. 9: Effect of temperature on the catalytic oxidation of aqueous cyanide.

3.6 Copper-crown nanofiber reusability studies

Figure 10 shows the results obtained for the reusability of the copper-crown nanofiber catalyst for 5 runs under the same conditions. After the fifth cycle of catalytic oxidation of cyanide, the percentage efficiency yield is more than 65%. This is an indication that the catalyst mix could be reused for at least 5 cycles without much loss in its activity. Obviously, this confers a better advantage above other heterogeneous

systems previously used for cyanide conversion.

Fig. 10: The reusability tests of the different weights of copper-crown nanofiber for the catalytic oxidation of aqueous cyanide by hydrogen peroxide (Values were represented as mean of 3 readings i.e n = 3).

4.0 CONCLUSION

The oxidation of aqueous cyanide solution using hydrogen peroxide was greatly enhanced when copper-crown chitosan nanofiber was used as a catalyst. The observed pseudo-first-order rate constant (k_{obs}) for the oxidation process with copper-crown nanofiber was found to be 16 times greater when compared with oxidation using only copper catalyst. The catalytic oxidation in the presence of copper-crown nanofiber was observed to be dependent on the reaction conditions of pH, temperature and H_2O_2/CN^- ratio. The reusability of the copper-crown nanofiber catalyst confers a special advantage on this heterogeneous system making it potentially viable for commercial applications.

Acknowledgement

This work was supported by the Department of Chemistry, University of Agriculture, Abeokuta, Nigeria and Chemistry Department, Rhodes University, Grahamstown, South Africa.

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