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Effective Removal of Copper Ion from Aqueous Solution using Beads of Chitosan-Choline Chloride/ Glycerol Deep Eutectic Solvent

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ABSTRACT

Herein, an adsorption process based on a new adsorbent was utilized to remove copper ion (Cu(II)), an environmental pollutant, from water. Reprocessed porous beads based on powder chitosan highly aid the industrial treatment of water. Chitosan–deep eutectic solvent (DES) beads were prepared from chitosan and DES. The DES used were choline chloride–urea (DES A) and choline chloride–glycerol (DES B). Both chitosan–DES beads were used to remove Cu(II) from an aqueous solution. Based on the characterisation results, chitosan-DES A showed a higher chemical and thermal stability when compared to chitosan-DES B. For the type of adsorbents, chitosan-DES B showed a higher removal percentage of Cu(II) (90.92 %) than chitosan-DES A (7.5 %). Therefore, chitosan-DES B was chosen as the preferred adsorbent for Cu(II). The optimum conditions for the removal of Cu(II) from an aqueous solution were using 0.09 g of chitosan-DES B with 40 min of shaking time and 1 mg L^{-1} of initial concentration.

Keywords: Choline chloride; urea; glycerol; adsorption; heavy metal.

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INTRODUCTION

Rapid developing industries involving mining, agricultural, textile, and sewage had contributed to a significant amount of heavy metal-containing wastewater released into the nearest water resources leading to water pollution [1]. Copper is the common contaminant in wastewater due to its wide application in many industries such as etching, electroplating, and plastics [2]. Copper is a highly water-soluble metal and can be easily adsorbed by aquatic organisms, therefore, causing undesirable threats to aquatic life [3]. Copper is important to humans as a micro nutrient, however, a high level in the human body leads to eyes irritation, vomiting, diarrhoea, liver damage, and insomnia [1,3,4]. Therefore, it is necessary to remove copper from the water.

There are considerable efforts to the removal of copper ion (Cu(II)) from water through photocatalysis, electrodialysis, membrane filtration method, and cementation [1]. Besides, biological treatment is also a commonly used method, but it is not preferable due to low biodegradability [2,3]. Chemical and physical methods are effective, but these methods are complicated and required high cost. Therefore, the adsorption process is introduced as one of the most relevant and efficient methods for the removal of Cu(II) from aqueous solution due to its economic feasibility, simple operation, and high effectiveness.

Recently, various adsorbents were used for the adsorption of Cu(II) from an aqueous solution such as activated carbon [5], zeolite materials [6], clay [7], and ash [8]. Activated carbon requires a high production cost and is difficult to regenerate [9]. Zeolite materials have a high affinity for water which may affect its adsorption capacity for Cu(II) [10]. Clay and ash have a low adsorption capacity for Cu(II) [8,11]. Therefore, in this paper, chitosan based adsorbent is introduced for the adsorption of heavy metal ions from water with low concentration [12]. Chitosan is known as a linear amino polysaccharide from the chitin deacetylation process [13]. Hydroxyl and amino functional groups of chitosan act as the adsorption site [12,13]. However, acid dissolution and non-porous powdered of raw chitosan had limit the application of chitosan [12]. This can be overcome by modifying the powdered chitosan into a bead with high porosity using Deep Eutectic Solvent (DES), as an alternative dissolution solvent.

DES is a combination of Bronsted, or Lewis acid and base through hydrogen bonding in the formation of a homogenous liquid [14]. DES can be produced even using the non-ionic starting materials [12]. Recently, DES has gained the researchers' attention for their environmentally friendly, simple preparation at lower temperature, and lower preparation cost [12,15]. Due to its advantages, it had been utilised for various applications such as separation and dissolution, catalysis reaction, organic synthesis, electrodeposition, and plasticizing agent [12,16–18]. Previously, we were pioneers in preparing and using chitosan-DES beads as adsorbent for malachite green dye [12]. And to date, there is no research on the use of these chitosan-DES beads for heavy metal removal.

Therefore, in this work, we present the synthesis of chitosan-DES beads using choline chloride-urea (DES A) and choline chloride-glycerol (DES B) and their potential as adsorbent for Cu(II) ion. The beads are used to remove Cu(II) from aqueous solutions. The effect of different type of chitosan-DES beads and other parameters is investigated as preliminary study to obtain the optimum removal of Cu(II).

METHODOLOGY

Materials and chemicals

Chitosan ($C_{56}H_{103}N_9O_{39}$), urea (CH_4N_2O), choline chloride ($C_5H_{14}ClNO$), sodium hydroxide (NaOH) and ethanoic acid (CH_3COOH) were obtained from Sigma-Aldrich, United States. Glycerol ($C_3H_8O_3$) and copper standard for AAS were obtained from Merck & Co., United States.

Preparation of DESs and chitosan-DES beads

The DESs and chitosan-DES beads were prepared as previous procedure [12]. DES A was prepared by mixing choline chloride and urea at molar ratio of 1:2. The mixture was heated at 70 °C with constant stirring until a homogeneous and clear solution was formed. Similar procedure was used to prepare DES B using choline chloride and glycerol.

Chitosan-DES A bead was prepared by mixing 5.0 g of chitosan powder into a 100-mL of DES A. The mixture was heated at 70 °C in a water bath for 5 hours. The mixture was left for overnight stirring until the chitosan was completely dissolved. A 100-mL of 0.5 M NaOH solution was added and mixed with the mixture until the beads were formed. The bead was filtered and washed with distilled water before dried in an oven at 50 °C for 24 hours. The dried bead was sieved into constant size prior to further use. A similar procedure was applied for the synthesis of chitosan-DES B using chitosan powder and DES B.

Preparation of stock and calibration standard of Cu(II)

A stock solution (100 mg $L^{-1)}$ was prepared form 1000 mg L^{-1} of Cu(II) standard into 250 mL of volumetric flask. Calibration curve of Cu(II) was prepared from a series of standard solutions (1 − 5 mg L^{-1}). Distilled water was used as blank solution.

INSTRUMENTATIONS

The chemical structure of raw materials and synthesised chitosan-DES beads were investigated using FT-IR spectrometer (DRAWELL, China). The FT-IR spectra of the raw materials and chitosan-DES beads were obtained using the wavelength ranged from 600 cm^{-1} to 4000 cm^{-1} for the identification of the functional groups in the samples.

The thermal stability of DESs and chitosan beads were analysed using a thermogravimetric analyser (Perkin Elmer, United Kingdom). The samples were scanned from 30 °C to 700 °C at a rate of 20 °C min^{-1} under nitrogen gas atmosphere.

The solubility property of the raw chitosan and the beads were tested using 0.1 M ethanoic acid, 0.1 M NaOH solution and distilled water. For the solubility test, 0.02 g of chitosan-DES A was weighed and added into 50 mL of each solution. The solutions were stirred for 24 hours before tested for solubility. Same procedure was applied to determine the solubility of chitosan-DES B.

Atomic absorption spectrometer (Mettler Toledo, United States) was used to measure the change of Cu(II) concentration in aqueous solution.

Adsorption studies

The adsorption of Cu(II) using chitosan-DES beads was performed by shaking 0.09 g of chitosan-DES beads into conical flasks containing 20 mL of Cu(II) solution with concentration of 3 mg L^{-1}. The solution was shaken at a constant rate at room temperature for 60 min, followed by filtration. The residual of Cu(II) concentration in the aqueous solution was determined using atomic absorption spectrometer by calculating the percentage removal of Cu(II) as equation below:

$$\frac{C_i - C_f}{C_i} \times 100\ \%$$

Where C_i and C_f are initial and final concentrations of Cu(II) solution (mg L^{-1}), respectively.

The effect of shaking time (20 − 60 min), adsorbent dosage (0.03 − 0.15 g) and initial concentration (1 − 5 mg L^{-1}) were investigated to obtain the optimum condition for Cu(II) removal.

RESULTS AND DISCUSSION

Characterisation

Fourier Transform Infrared (FT-IR) analysis

The chemical structures of DESs and chitosan-DES beads were compared with raw materials of choline chloride, urea, glycerol, and chitosan using FT-IR spectrometer as shown in Figure 1(a)-(f). For choline chloride (Figure 1 (a)), the bending -OH group at 1644 cm^{-1} and bending of $-CH_3$ and $-CH_2$ groups at 1480 cm^{-1} and 1082 cm^{-1}, respectively. For urea (Figure 1 (b)), the prominent peaks at 3430 cm^{-1} and 3334 cm^{-1} were attributed to asymmetric and symmetric stretching of $-NH_2$ groups, respectively. Besides, the absorption band at 1676 cm^{-1} and 1586 cm^{-1} indicates the bending of the $-NH_2$ group and stretching of C=O, respectively. Moreover, the absorption band at 1458 cm^{-1} and 1144 cm^{-1} were attributed to the in-plane bending of the $-NH_2$ group and C-N stretching, respectively. Additionally, as for glycerol (Figure (c)), the C-H stretching is observed at 2934 cm^{-1} and 2880 cm^{-1}. Also, the C-O-H bending and C-O stretching are presented at 1416 cm^{-1} and

1030 cm^{-1}, respectively. Strong and broad peaks at 3330 cm^{-1}, 3288 cm^{-1}, 3356 cm^{-1} and 3360 cm^{-1} exhibited the -OH stretching for choline chloride, glycerol, chitosan, chitosan-DES A, and chitosan-DES B, respectively.

The chitosan – DES formation is confirmed by the presence of a broad -OH stretching vibration at 3356 cm^{-1} in chitosan-DES A (Figure 1 (e)) compared to raw chitosan (Figure 1 (d), which is caused by the formation of intermolecular hydrogen bonding. All the compounds obtained similar wavenumber around 3294-3356 cm^{-1} attributed to stretching vibration of -NH and -OH, while the peak at 2976 cm^{-1} indicated the presence of $-CH_2$ stretching in CH_2OH group. The peak at 1376 cm^{-1} was ascribed by $-CH_3$ bending of secondary amide group. Chemical shifts are presented at 1630 cm^{-1}, 1560 cm^{-1}, and 1316 cm^{-1} for C=O stretching of secondary amide group, N-H bending in the primary amine group, and C-H bending, respectively. These chemical shifts are evident in the successful formation between chitosan and DES A (choline chloride-urea).

For the chitosan-DES B bead (Figure 1(f)), the broad peak around 3026-3360 cm^{-1} indicated the -NH and -OH stretching vibration, while the peak at 2934 cm^{-1} was attributed to the $-CH_2$ stretching in glycerol. The peak of -OH at 3356 cm^{-1} was shifted to 3360 cm^{-1} in chitosan-DES B due to the intense group of -OH in glycerol, leading to increase of atoms electronegativity [12] and resulting strong hydrogen bond. This formation is shortened the bond length and resulted in a higher stretching frequency [19]. The significant shifting in the wavenumber of $-CH_3$ bending at 1376 to 1478 cm^{-1} and -CH bending at 1314 to 1416 cm^{-1} in chitosan suggested the DES B (choline chloride-glycerol) has been successfully attached to chitosan [12].

Thermogravimetric analysis (TGA)

The thermal stability of DESs and chitosan beads were studied using thermogravimetric analysis (TGA). From Figure 2, the TGA curve of DES A showed two different slopes. The first weight loss at region between 150 – 200 °C due to the decomposition of urea into cyanic acid, ammelide, and biuret, generating a 15 % weight loss. The second weight loss which start at 253.63 °C is due to the decomposition of cyanuric acid which derived

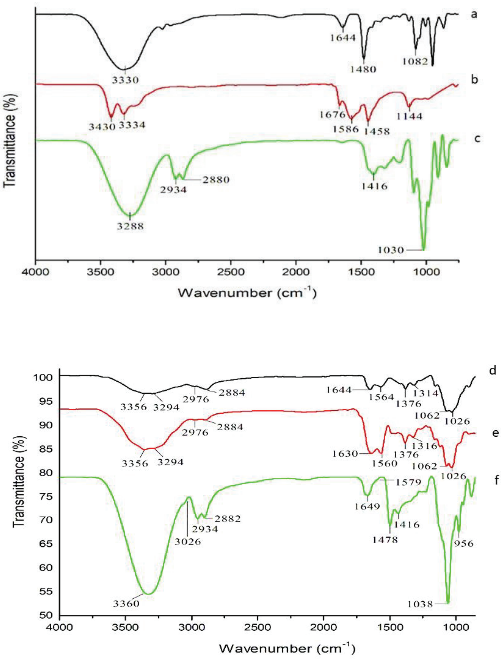

Figure 1: FT-IR spectra of (a) choline chloride, (b) urea, (c) glycerol, (d) raw chitosan, (e) chitosan-DES A, and (f) chitosan-DES B.

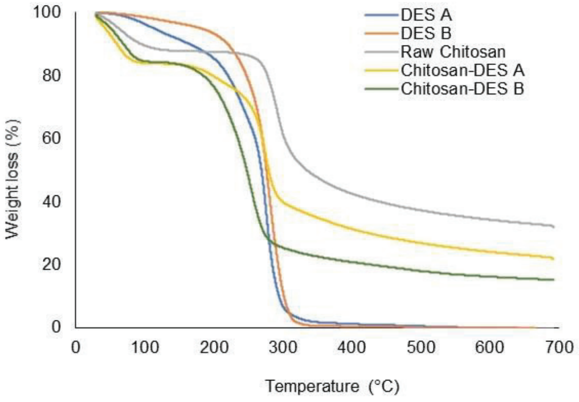

Figure 2: TGA curves of DES A, DES B, raw chitosan, chitosan-DES A, and chitosan-DES B.

from biuret [14]. This second decomposition step coincides with the thermal decomposition of ChCl. The TGA curve for DES B showed one weight loss step (in the range of 150 to 300 ^{o}C) caused by the vaporization of glycerol simultaneously with decomposition of ChCl.

The process is occurring in a single step because of glycerol boiling point (289 ^{o}C) is closed to the ChCl decomposition temperature (304 ^{o}C) [14]. Multiple -OH numbers in glycerol formed strong hydrogen bonding with choline chloride, thus required high temperature for decomposition. Therefore, DES B is thermally stable than DES A [14]. It can be concluded that component such as glycerol which is thermal stabile with high boiling point that can affect the strength of hydrogen bond formed, thus increasing the thermal stability of DES [17].

As can be seen in Figure 2, there are two stages of thermal degradation for raw chitosan and the beads (chitosan-DES A, and chitosan-DES B). The initial weight loss in the range of 50 to 150 ^{o}C is due to the evaporation of water from the surface of the samples. At the range of 150 to 300 °C, the chitosan pyranose ring is decomposed causing the significant weight loss. Chitosan-DES A and chitosan-DES B exhibited lower onset decomposition temperature (180.67 ^{o}C and 216.52^{o}C) than that of pure chitosan (283.73 ^{o}C). The low onset decomposition temperature in the chitosan beads contributed from the fast decomposition of urea and glycerol from DESs [18]. Moreover, from the result, it shows that the chitosan beads obtained lower thermal stability compared to chitosan powder.

Solubility test

The solubility of chitosan-DES beads is important criteria to allow the adsorption process to occur. As our previous study, chitosan-DES beads were found to be insoluble in all media even after 24 hours of stirring, as shown in Table 1. But the raw chitosan and chitosan-DES A were found to be soluble and partially soluble, respectively in acidic solution. The weak intermolecular bonding between chitosan and DES A (choline chloride: urea) resulting from protonation a part of amine groups in chitosan forming cationic -NH_3^+ [20] causing of partially soluble in ethanoic acid. Meanwhile, strong ionic interaction between chitosan and DES B (choline chloride: glycerol) had improved the chemical stability [21], thus causing insolubility of chitosan-DES B in acidic solution.

Table 1: Solubility test of raw chitosan, chitosan-DES A, and chitosan-DES B.

Adsorbents	*Solubility*		
	0.1 M ethanoic acid	*0.1 M NaOH*	*ultrapure water*
Chitosan	*Soluble*	*Insoluble*	*Insoluble*
Chitosan-DES A	*Partially soluble*	*Insoluble*	*Insoluble*
Chitosan-DES B	*Insoluble*	*Insoluble*	*Insoluble*

Adsorption studies

Effect of chitosan beads on removal of Cu(II)

The efficiency of the chitosan-DES A and chitosan-DES B were compared for removal of Cu(II) from an aqueous solution. Figure 3 shows chitosan-DES B obtained more efficient removal than chitosan-DES A. Higher mass transfer rates can be achieved since Cu(II) easily dispersed into chitosan bead with glycerol, which is low viscosity [22]. Chitosan-DES A contain urea, a strong hydrogen bond donor with high viscosity and high surface tension. This is why small free volume is available in chitosan-DES A and consequently lower the mass transfer rates of Cu(II) [22]. Therefore, chitosan-DES B was chosen as the preferred adsorbent for Cu(II) adsorption.

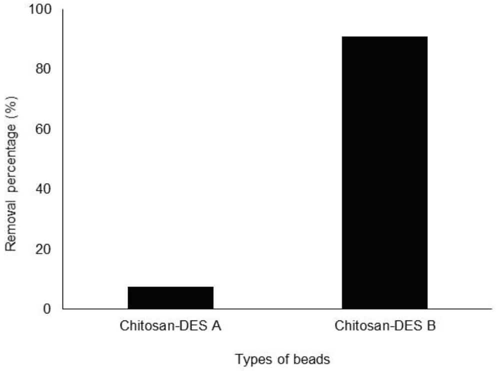

Figure 3: The efficiency of chitosan-DES beads for Cu(II) removal. Condition: [Cu(II)] = 3 mg L^{-1}, volume of Cu(II) = 20 mL, dosage of adsorbents = 0.09 g.

Effect of shaking time for the Cu(II) adsorption

The time required for Cu(II) to reach the equilibrium state after contact with chitosan–DES B was determined. It was found that the optimum time required to reach equilibrium state is 40 min (Figure 4). The removal percentage of Cu(II) is rapidly increased for the first 40 min due to the availability of adsorption sites [22]. However, the adsorption sites of chitosan-DES B became saturated after 40 min, resulting to the constant removal [23]. The colour of chitosan-DES B also changed from cream yellow to green after adsorption process.

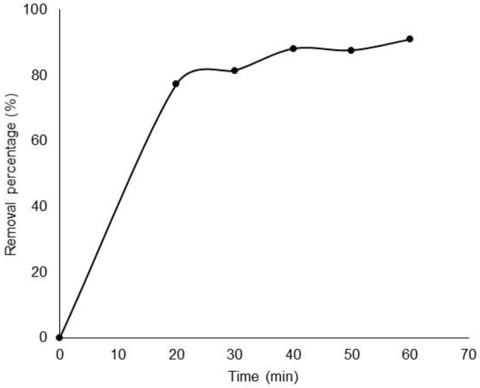

Figure 4: The equilibrium effect of Chitosan-DES B. Condition: [Cu(II)] = 3 mg L^{-1}, volume of Cu(II) = 20 mL, dosage of adsorbents = 0.09 g.

Effect of adsorbent dosage

The quantity of adsorbent (as a function of the number of available sites) indicates the surface area available for adsorption. The surface area of an adsorbent is increased by the increment of adsorbent's dosage. As presented in Figure 5, the removal percentage of Cu(II) is increased with the increase of dosage of chitosan-DES B due to the increased of surface area. Therefore, availability of active binding sites on the surface of adsorbent also increase [12,22]. However, the percentage of removal is constant when the dosage used is higher than 0.09 g. This can be explained by the overcrowding of chitosan-DES B that caused of overlapping of adsorption sites, thus limited the availability for the adsorption of Cu(II) [22]. Therefore, the optimum dosage used is 0.09 g.

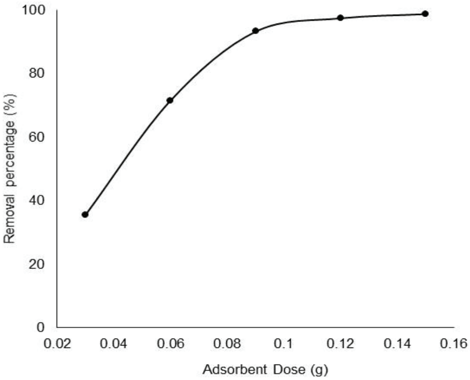

Figure 5: The effect of adsorbent dosage for Chitosan-DES B. Condition: [Cu(II)] = 3 mg L^{-1}, volume of Cu(II) = 20 mL, shaking time = 40 min.

Effect of initial concentration of Cu(II)

Figure 6 shows the removal of Cu(II) at different initial concentration. The removal is decreased as the initial concentration of Cu(II) is increased. This is due to the ratio of Cu(II) to the accessible adsorption sites on chitosan-DES B is consider high with low concentration of Cu(II), resulting in maximum of removal percentage. When the initial concentration is increased, the number of available sites on chitosan-DES B for the adsorption of Cu(II) is started to decrease, limiting the ratio of Cu(II) for available adsorption sites, resulting to decrease the removal percentage.

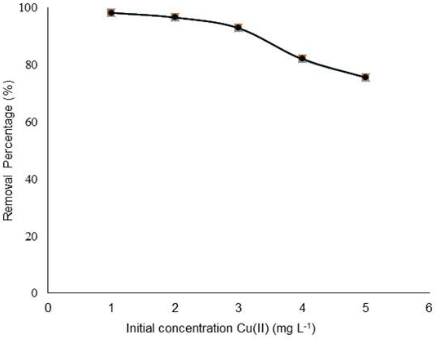

Figure 6: The effect of initial concentration Cu(II) of Chitosan-DES B. Condition: Volume of Cu(II) = 20 mL, dosage of adsorbent = 0.09 g, shaking time = 40 min.

CONCLUSION

This paper examined the effect of newly synthesised chitosan-DES beads with chitosan and DES A (choline chloride- urea) and DES B (choline chloride – glycerol) in removal of Cu (II) ions from aqueous solution. The synthesised chitosan-DES beads were characterised using FTIR and TG analyses. A solubility test was also conducted to discover the optimal condition for the adsorption process. Important parameters affecting the adsorption of Cu (II) from an aqueous solution were successfully optimised. From the FTIR and TGA characterisation, raw chitosan was more thermally stable than chitosan beads. Due to strong ionic interaction between chitosan and DES B (choline chloride: glycerol) had improved the chemical stability, thus causing insolubility of chitosan-DES B in acidic solution. With that, chitosan–DES B beads are highly stable in acidic solution and suitable for the adsorption process. This was proved by that chitosan-DES B of chitosan with choline chloride and glycerol, which demonstrated an effective Cu(II) removal from an aqueous solution under optimum condition.

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