



Fabrication of a magnetic cellulose sorbent functionalized with amine moieties and studying its selective sorption behaviour towards copper (II) ions from their aqueous solutions



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Abstract

The present work aimed to treat cellulose chemically to obtain a magnetic cellulose sorbent that possesses improved textural and adsorption properties towards Cu(II) ions from their aqueous solutions. For these purposes, magnetic cellulose was modified via chlorination followed by functionalization with amine moieties to obtain amine functionalized cellulose (Cell-N). The amine group concentration on the resins was determined. The structure of the prepared resin was investigated using Fourier transform infrared, Energy Dispersive X-ray microanalysis (EDX), N₂ adsorption-desorption, and scanning electron microscopy. Batch experiments were performed to examine the uptake behavior of Cu(II) ions from their aqueous solutions using the investigated resin. The maximum uptake capacity was recorded at the optimum pH value of 5.8 and was found to be 2.4 mmol/g with fast kinetics (after 20 minutes of the batch experiment). Magnetic properties of Cell-N made resin easy to be collected from the media of batch experiments simply by using an external magnet. The studied resin showed high selectivity towards Cu(II) ions over other interfering ions in their solution and good durability towards mineral acids. Besides, the studied resin was regenerated efficiently where a nearly complete regeneration of Cu(II) ions was achieved using 0.5M HNO₃ solution for several cycles.

Keywords: Cell-N, Cu (II) ions, magnetic cellulose.

1. Introduction

Cellulose is the most abundant, naturally occurring, renewable polymer. It is available from various sources, including cheap wastes, such as agricultural residues [1]. On the other hand, Heavy metal ions (like Cu(II) ions) in different wastewater streams are a major threat to human beings and the environment due to their toxicity [2,3]. Extraction of metal ions from their solutions was the main goal for many researchers in the last decades [4-6]. Different techniques have been conducted for such purpose such as precipitation, solvent extraction, co-precipitation, ion exchange and sorption [7]. Chelating resins have been widely applied as sorbents for various metal ions in different water streams [8-10]. Many attempts have also been made toward the use of cheap and effective adsorbents, in particular natural and biosorbent materials. Cellulose may be a good candidate for this purpose as it is the most abundant, naturally occurring, and renewable polymer and has been used as an

adsorbent for many decades [11-13]. Chemical treatments of cellulose were conducted to improve certain properties of cellulose such as its elasticity, hydrophilic character, water absorbency, ion exchange or adsorptive capability, and resistance. [13-15]. The present work aimed to treat cellulose chemically to obtain a magnetic cellulose sorbent that possesses improved textural and adsorption properties towards Cu(II) ions from their aqueous solutions. Batch experiments were conducted to examine its selective adsorption behavior towards Cu(II) ions from their aqueous solution.

2. Materials and Methods

2.1. Chemicals and instruments

Cellulose, ethylenediamine (EDA), magnetite were Sigma-Aldrich products. All other chemicals were Prolabo products. Copper acetate was used as a source for Cu(II). All chemicals were used as received. FTIR spectra of the synthesized materials were recorded on a Pye-Unicam Sp-883 Perkins-Elmer,

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Germany, spectrophotometer between 4000 and 400 cm^{-1} using KBr pellets technique.

EDX analysis were determined using an FESEM–EDX system (Quanta FEG 200, equipped with an OXFORD Inca 350 Energy Dispersive X-ray microanalysis (EDX) system) at an accelerating voltage of 30 keV and a working distance of 10 μm .

BET surface area, average pore diameter, and BJH pore volume were measured at $77 \pm 1 \text{ K}$ by a Quanta chrome NOVA automated gas sorption system using N_2 as the adsorbate, while SEM images were obtained using a high-resolution Scanning Electron Microscope, Model Quanta 250 FEG, Netherlands.

Dilute metal ion concentrations were analyzed using an inductively coupled plasma-atomic emission spectroscopy (ICP-AES) instrument (Thermo Scientific, EU).

2.2. Preparation of functionalized cellulose-magnetite sorbents

2.2.1. Synthesis of cellulose-magnetite hybrid

In a pre-cooled ($-12 \text{ }^\circ\text{C}$) mixture of $\text{H}_2\text{O}/\text{NaOH}/\text{urea}$ (162 mL of distilled water, 15 g of NaOH, and 23 g of urea) was dissolved four grams of cellulose powder to get a transparent solution of cellulose within 2 minutes. According to J. Cai et.al. [16], NaOH hydrates could be more easily attracted to cellulose chains through the formation of new hydrogen-bonded networks at low temperature, while urea hydrates could not be associated directly with cellulose. However, the urea hydrates could be self-assembled at the surface of NaOH hydrogen-bonded cellulose to form an inclusion complex leading to cellulose dissolution.

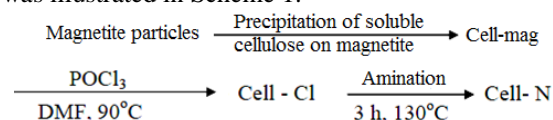
To the formed solution was added 1 g of magnetite powder at room temperature with continuous stirring to mix well followed by drop-wise addition of 2 M HCl solution till pH = 7 is reached. As the solution is highly sensitive to rising temperature and acid addition, a precipitate of cellulose-magnetite hybrid was obtained which was subjected to successive washings with distilled water then drying at room temperature. The obtained hybrid was referred to as Cell-mag. The magnetic properties of Cell-mag was examined simply by its efficient attraction to an external magnet.

2.2.2. Preparation of chlorodeoxy cellulose (Cell-Cl)

In 200 mL dimethylformamide (DMF) was suspended a sample of 10 g of Cell-mag for one hour then reacted with 6 mL phosphorous oxychloride (POCl_3) under mechanical stirring for 15 minutes. Obtained cellulose chloride (Cell-Cl) was filtered off then washed with distilled water, DMF, and 5% NaOH followed by distilled water. The product was then dried in air at room temperature [17].

2.2.3. Preparation of amine cellulose (Cell-N)

Without using any solvent, a sample of 1.0 g Cell-Cl was directly reacted with 6 mL of EDA. At $90 \text{ }^\circ\text{C}$, the reaction mixture was stirred for 3 hours. The obtained product was filtered off, washed several times with distilled water followed by methanol then dried in air at room temperature [18]. The obtained product was referred to as Cell-N. The synthesis route of Cell-N was illustrated in Scheme 1.



Scheme 1. Synthesis route of Cell-N

2.3. Estimation of the amine groups loaded on Cell-N

The concentration of the amine groups was estimated using the previously used volumetric method [19]. To 0.1 g resin was added twenty milliliters of 0.05 N HCl and conditioned for 12 hours with efficient shaking. The remaining concentration of HCl was measured through the titration against 0.05 N NaOH. The number of moles of HCl reacted with the amine groups (which is equivalent to the amine group concentration) was measured.

2.4. Uptake studies using batch method

A stock solution of $1 \times 10^{-2} \text{ M}$ Cu(II) was prepared in distilled water. A stock solution of $5 \times 10^{-3} \text{ M}$ EDTA was prepared and standardized against $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ solution of using Eriochrome Black-T (EBT) as an indicator. Buffers (pH range of 3.8–5.8) of acetic acid/acetate, sodium phosphate (pH range of 6–8), and ammonium hydroxide/ammonium chloride (pH range of 9–10) were used for the experiments performed at different pH values [20].

Uptake experiments carried out at different pH values were conducted using batch experiments by conditioning 0.1 g resin with 100 mL Cu(II) solution at an initial concentration of $5 \times 10^{-3} \text{ M}$ for 1 hour using efficient shaking at $22 \text{ }^\circ\text{C}$. Buffer solutions were used to adjust the pH to the desired value required for the experiment. At the end of the batch process, five milliliters of the solution was taken where the residual concentration of metal ion was determined via the titration against EDTA using murexide as a suitable indicator. The loaded resin was collected simply by using an external magnet. Kinetic studies were performed using batch experiments similarly as listed above but at the optimum pH value of 5.8. Five mL portions of the solution were taken at different time intervals where the concentration of metal ions for each portion was determined as a function of time [21]. Dilute metal ion concentrations in the synthetic sample were analyzed using the inductively coupled plasma-atomic emission spectroscopy (ICP-AES) instrument as mentioned in the experimental section.

2.5. Durability and regeneration experiments

Regeneration experiments were conducted by shaking 0.1 g Cell-N with 100 mL 5×10^{-3} M Cu(II) solution at the optimum pH of 5.8 for 1 hour. The maximum uptake was estimated and then the solution was decanted then washed thoroughly with distilled water. The obtained loaded resin was treated with 100 mL HNO_3 using concentrations of 0.5 M. After shaking for 1 hour, the concentration of the released metal ion was detected. Afterward, distilled water was used for washing Cell-N several times and the previous steps were repeated for 5 cycles. Regeneration Efficiency (RE) was gained from the following equation:

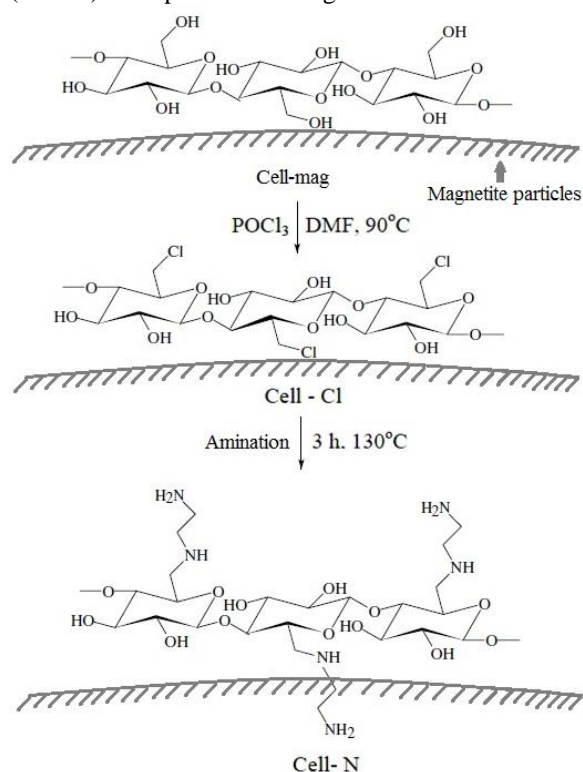
$$RE = q_n / q_1 \times 100\% \quad (1)$$

where RE is the regeneration efficiency, and q_1 and q_n are the uptake of the first and n^{th} cycle, respectively

3. Results and discussion

3.1. Characterization of the adsorbent

Cell-mag was chlorinated with POCl_3 at C6, preferentially, [18] through substitution of the hydroxyl group with chlorine atom as shown in Scheme 2. Cell-Cl was chemically modified with ethylenediamine at the substituted moieties giving Cell-N. The success of the treatment of cellulose with amine moieties was confirmed by FTIR spectra. FTIR spectra of cellulose and amine-modified cellulose (Cell-N) were presented in Fig. 1.



Scheme 2. Detailed schematic illustration of Cell-N synthesis from Cell-mag.

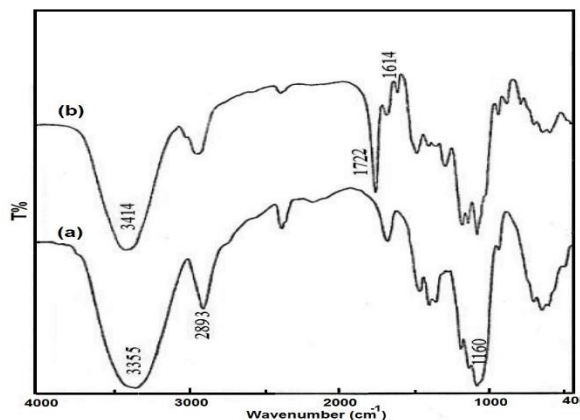


Fig. 1 Infrared spectra of cellulose (a), Cell-N (b)

The spectrum of cellulose showed absorption bands at 3355, 2893, and 1160 cm^{-1} , these bands were assigned to hydrogen-bonded νOH , $\nu\text{C-H}$, and anti-symmetric stretching vibration of C-O-C bridge, respectively [22,23]. Cell-N spectrum showed an additional new band at 1722 cm^{-1} assigned to carbonyl group which may be attributed to the rupture of some cellulose rings during the reaction, and the broad/strong band appeared at 3414 cm^{-1} in Cell-N spectra may be assigned to νOH or overlapped $\nu\text{OH} + \nu\text{NH}$. Besides, Cell-N spectrum showed a new band at 1614 cm^{-1} which may be assigned to primary and/or secondary NH bending vibration in ethylenediamine anchored moiety, which was considered as strong evidence for the success of the amination process [24].

Another evidence for the success of modification was the estimated value of amine group content (4.6 mmol/g) which was found to be consistent with the obtained uptake capacities be discussed in the upcoming section.

The surface area, total pore volume, and average pore diameter were calculated from the BET- N_2 adsorption isotherm and the data were listed in Table 1. For Cell-N, The observed surface area increase while recording a decrease in total pore volume (if compared with these values for cellulose) may be due the fusion or opening of pores through the drastic conditions of preparation (specially during the chlorination step), and the formation of relatively thin smooth stretched layer of cellulose on the magnetite fine particles during the preparation of cellulose-magnetite hybrid (Cell-mag).

The morphology of cellulose and Cell-N was examined using scanning electron microscopy (SEM) (Fig. 2 a and b). The SEM micrograph of used cellulose before modification showed a coarse surface with many small pores (Fig. 1a). On the other hand, an obvious difference in the surface morphology was observed in Cell-N SEM micrograph (Fig. 1b).

The surface roughness was decreased and some of the formerly existing pores have vanished. These findings were found to be consistent with the decreased value

of total pore volume for Cell-N illustrated in Table 2. These findings may be also considered as another evidence for the formation of a stretched thin film of cellulose on magnetite particles during the synthesis process.

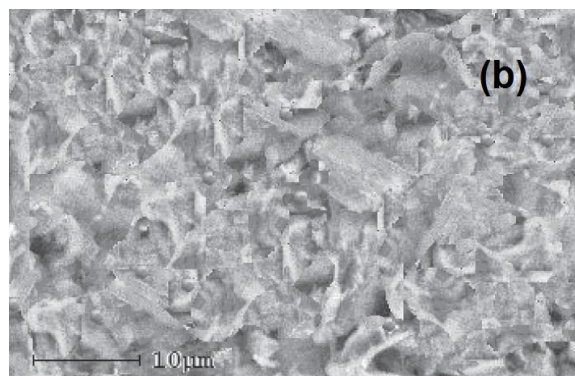
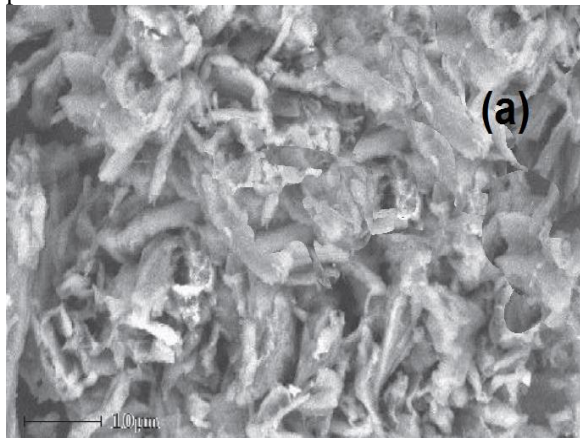


Fig.2 Scanning electron micrographs of Cellulose (a) and Cell-N (b)

To map elemental copper qualitatively in Cell-N loaded with copper ions (Cell-N-Cu) after batch experiments, a comparative EDX measurements were performed for cellulose-base polymer and Cell-N-Cu which showed additional distinct signals at 0.9 and 8.1 keV corresponding to copper (Fig. 3).

Table 1. Textual properties of cellulose and Cell-N

Resin	Surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
Cellulose	89.1	0.93	114.3
Cell-N	765.6	0.49	116.2

Table 2. Batch experiment data for the removal of Cu(II) ions from the simulating synthetic solution at pH 5.8, Cell-N weight of 0.1 g, solution volume of 100 mL, 30 minute conditioning time, and 22°C

Conc. (ppm)	Cu(II) ions	Interfering metal ions in the simulating synthetic solution.
Initial (C _i)	3.00	Fe(III), 3.25; Mn(II), 2.89; Zn(II), 3.50; Al(III), 4.09; Pb(II), 3.03; Cd(II), 4.05; Hg(II), 3.01; Ni(II), 5.30; Co(II), 4.50; Cr(III), 6.41; Sb(III), 4.50; Ca(II), 33.34; Mg(II), 21.12; Na(I), 140.08; K(I), 4.75.
Final (C _f)	0.07	Fe(III), 2.81; Mn(II), 2.38; Zn(II), 3.38; Al(III), 3.80; Pb(II), 2.67; Cd(II), 3.88; Hg(II), 2.79; Ni(II), 5.11; Co(II), 4.39; Cr(III), 6.12; Sb(III), 4.48; Ca(II), 32.88; Mg(II), 18.34; Na(I), 120.76; K(I), 4.64.

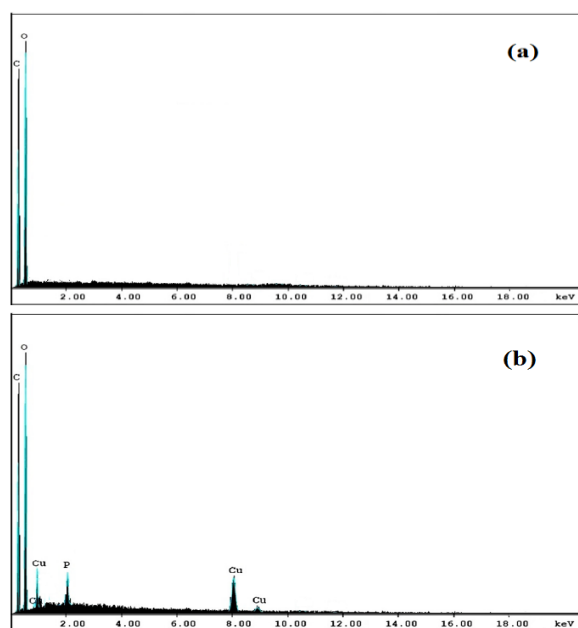


Fig.3 EDX spectra of Cellulose (a) and Cell-N-Cu (b).

3.2. Metal ions uptake studies

Fig. 4 shows the uptake of Cu(II) as a function of pH and indicates a maximum uptake capacity of 2.4 mmol/g at pH = 5.8 (natural pH). The observed high uptake may be due to the fact that each nitrogen atom possesses lone pair of electrons suitable for coordination with Cu(II) ions to give the corresponding Cell-N→Cu(II) complex with high binding affinity. The uptake capacities show lower values in both basic and acidic media.

The observed lower values of uptake in basic medium (these values were determined through the regeneration of Cu(II) ions from loaded resin portions) may be explained by the probable precipitation of copper hydroxide species and/or formation of amine complexes in the solution. Such complexes may decrease the affinity of Cu(II) to attack nitrogen atoms resulting in a lowering of recorded uptake capacities. In the acidic medium, partial protonation of amine groups takes place and therefore the coordination capability with Cu(II) is lowered giving lower uptake values [25].

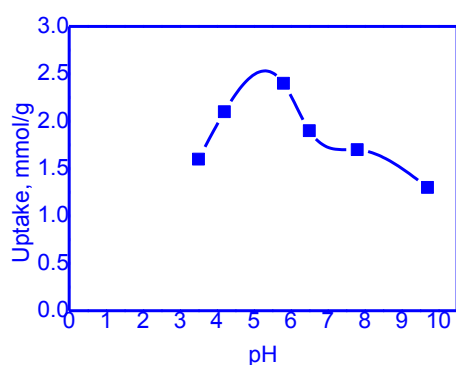


Fig. 4. Effect of pH on the uptake of Cu(II) by resins Cell-N

Fig. 5 showed the increase of the uptake capacity of Cu(II) as a function of conditioning time by Cell-N resin at the optimum pH condition of 5.8 and at 22 °C. The uptake equilibrium was recorded after noticeable fast kinetics of 20 min. afterward, there is no observed uptake increase recorded because of the occupation of all amine groups capable of interaction with Cu(II) ions.

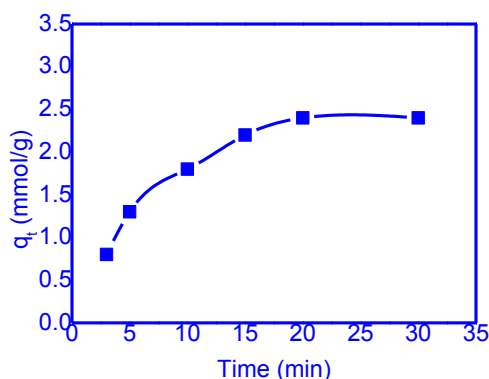


Fig. 5. Uptake of Cu(II) by Cell-N resin as a function of conditioning time at pH 5.8

First-order rate plots for the uptake of Cu(II) ions on resin Cell-N are shown in Fig. 6. In the first 10 minutes, the rate follows the first-order kinetics clearly where a straight line was obtained and passed through the origin. Afterward, the line has deviated at advanced stages of interaction. These findings may be explained by the fact that the uptake was controlled by two steps: (i) surface interaction in the first period (according to first-order kinetics) where the rate of adsorption is mainly controlled by Cu(II) ions concentration in the bulk of the solution, (ii) diffusion mechanism of Cu(II) ions through the pores of Cell-N (advanced period) in order to interact with the internal surface where the rate of interaction is mainly controlled by the textural properties of the Cell-N.

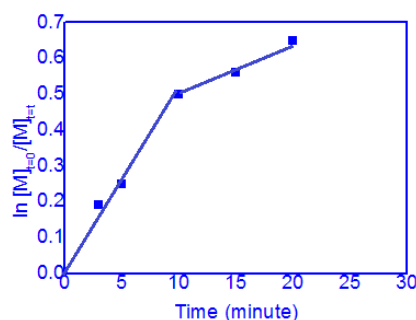


Fig. 6. Plots of the relative concentration of Cu(II) ions on resin Cell-N against conditioning time

A high binding affinity of Cell-N towards Cu(II) ions adsorption even from their very dilute solutions consisting of other interfering ions was observed. A 100 mL simulating synthetic solution containing 3 ppm Cu(II) ions and other common interfering ions, like Mn(II), Ni(II), Fe(III), Hg(II), Cr(III), Sb(III), Zn(II), Pb(II), Mg(II), Ca(II), Cd(II), K(I), Al(III), Co(II), and Na(I) with different concentrations (listed in Table 2) at pH 5.8 was examined towards adsorption on 0.1 Cell-N through a batch experiment. Comparing C_i and C_f values listed in Table 2 indicate that Cell-N can be used as a selective sorbent for Cu(II) from different waste streams.

Cell-N showed good durability against different concentrations of HNO_3 . Nearly complete regeneration of copper was achieved by using 0.5 HNO_3 as a stripping agent. The resin showed high regeneration efficiency over 4 cycles after that it showed a sudden decrease (Fig. 7) if compared with the fresh sorbent.

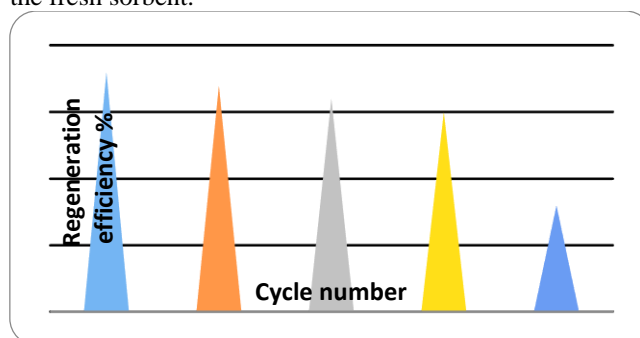


Fig. 7. Recyclability of Cell-N resin using HNO_3 .

4. Conclusions

Magnetic properties of Cell-N made it easy to be collected from the media of batch experiments simply by using an external magnet.

The observed increase in surface area ($765.6 \text{ m}^2/\text{g}$) may be due to the formation of a stretched thin film of cellulose on magnetite particles during the synthesis

process of Cell-N. The studied resin showed a remarkable high uptake capacity with fast kinetics towards Cu(II) ions from their aqueous solution. Adsorption rate followed the first-order kinetics where a straight line was obtained and passed through the origin during the first period. The studied resin showed high selectivity towards Cu(II) ions over other interfering ions in their solution and good durability towards mineral acids. Loaded Cell-N resin was regenerated efficiently up to 5 cycles using HNO₃ where nearly a complete copper ions regeneration was achieved using 0.5M HNO₃ solution over 5 cycles.

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