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COPPER NANOPARTICLES IMMOBILIZED ON CATION EXCHANGE RESIN AS AN EFFECTIVE DISINFECTANT FOR REMOVAL OF PATHOGENIC BACTERIA IN WATER TREATMENT

HẠT NANO ĐỒNG GẮN TRÊN NHỰA TRAO ĐỔI CATION HOẠT ĐỘNG NHƯ CHẤT TẨY UẾ CHO VIỆC LOẠI BỎ VI KHUẨN PATHOGNIC TRONG XỬ LÝ NƯỚC

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ABSTRACT

In this study, copper nanoparticle immobilized on cation exchange resin (R-CuNPs) has been prepared using $NaBH_4$ as a reducing agent at room temperature for removal of pathogenic bacteria from water. Characteristics of R-CuNPs were determined by XRD, SEM, EDS and FTIR. The results showed that copper nanoparticles with average particle size of 76.92 nm were obtained with crystalline structure in nature and were well distributed on the cation exchange resin surface. Antibacterial activity of R-CuNPs was tested using batch methods. The obtained results shown that Escherichia coli strain was completely removed after 30 min and the antibacterial effectiveness of R-CuNPs was dependant on the mass of copper on the resin. The average concentration of copper in the effluent from the column packed with 5 g R-CuNPs and at the flow rate of 2 ml/min was found to be 0.92 mg/l which is lower than the guideline value of WHO (2 mg/L). From the research results, it could be concluded that R-CuNPs can be used in disinfection in water treatment.

***Keywords**: Copper nanoparticles; Nanotechnology; Cation exchange resin; Water treatment.*

TÓM TẮT

Trong nghiên cứu này, các hạt nano đồng cố định trên nhựa trao đổi ion (R-CuNPs) đã được điều chế bằng cách sử dụng $NaBH_4$ là tác nhân khử ở nhiệt độ phòng để khử vi khuẩn gây bệnh trong nước. Đặc trưng của R-CuNPs được xác định bằng XRD, SEM, EDS và FTIR. Kết quả cho thấy các hạt nano đồng với kích thước trung bình 76.92 nm đã thu được với cấu trúc tinh thể và phân bố đều trên bề mặt nhựa trao đổi cation. Hoạt tính kháng khuẩn của R-CuNPs được kiểm tra bằng phương pháp gián đoạn. Các kết quả nhận được cho thấy dòng vi khuẩn Escherichia coli bị loại bỏ hoàn toàn trong thời gian 30 phút và hiệu suất kháng khuẩn phụ thuộc vào khối lượng của đồng trên nhựa. Nồng độ trung bình của đồng trong nước rửa từ cột nhồi với 5g R-CuNPs và với tốc độ lọc 2 ml/ phút đã xác định được là 0,92 mg/l thấp hơn giá trị chỉ đạo của WHO (2 mg/l). Từ kết quả thu được đi đến kết luận R-CuNPs có thể được sử dụng để khử trùng trong xử lý nước.

***Từ khóa:** Đồng nano; Công nghệ nano; Nhựa trao đổi cation; Antibacterial activity; Xử lý nước.*

1. INTRODUCTION

Effective and economically water purification process is a constant challenge for government, industry and academia, even in this 21st century. Water shortage is another major issue; however, in place that water is available, having clean and drinkable water sources is a major concern. According to WHO [1], about a billion people do not have access to clean water, and approximately 6 to 8 million people die annually from multiple waterborne diseases. The current ability of providing clean water is outpaced by the increasing consumption rate due rapid boom in population in the last century.

The need to have an effective integrated water management to fully utilise all the available resources have been emphasized throughout [2]. Especially, an effective method to removal pathogenic bacteria is sufficient to make majority of accessible water sources become drinkable. New technologies in water purification has been developed and implemented to remedies the issues. However, most of the new technologies require expensive investment for centralized treatment facilities and comprehensive distribution networks. This is often out of reach for most of the low income regions, especially in developing countries where scattering water bodies are the main water supply sources. To address this concern, many studies have been conducted on the technology which can be employed as point-of-use purification process, which is more suitable for implementation in aforementioned low income areas [3-6]. One of the promising focuses in this research area is the use of nanotechnology. This is one of solutions is affordable and convenient to augment water supply through safe use of unconventional water sources Silver nanoparticles (AgNPs) which is known for their excellent antimicrobial agents in water [7-12]. Due to its promising properties, further studies have been conducted to identify if it could be refined for use in water purification. The current focus is on it potential bio-toxicity and cost [13]. The toxicity can be controlled by reducing metal leaching into the final water product; and the cost can be alleviated by replacing silver with less expensive metals such as copper nanoparticles [14-19].

In this study, our objective is to continue develop the line of copper nanoparticles by immobilizing on the ion exchange resin (R-CuNPs). This is to provide an easy to use resin for removal bacteria from water, especially effective for small uses in low income area. This method involves in exchanging Cu^{2+} onto the cation exchange resin following by reduction process to form Cu nanoparticles on the surface. The antibacterial activity of the final resin R-CuNPs was evaluated by conducting bacterial removal experiments on standard samples containing *Escherichia coli*. Copper ions leaching and recycle ability of R-CuNP also were also examined.

2. MATERIALS AND RESERCH METHOD

2.1. Materials

All chemical used in this study is analyzed grade. Copper (II) sulfate pentahydrate 98.0%, cation exchange resin 50WX2-200 with mesh size of 100-200, and sodium borohydride ($NaBH_4$ - 98%) were purchased from Sigma Aldrich, USA. The microbial strain *Escherichia coli* (ATTCC 43895) were used to determine the bacterial growth rate in the presence of the copper nanoparticles immobilized on exchange resin.

2.2. Preparation of copper nanoparticles immobilized on cation exchange resin

A known amount (20g) of cation exchange resin in H^+ form with the exchange capacity for Cu ion of 3.72 meq/g was added into a beaker containing 200ml solution 0.002 M of copper (II). The mixture was shaken for 200 min at room temperature. The resin containing copper (II) was collected by filtration through a filter paper. This resin was washed thoroughly with distillated water to completely remove unbounded copper ions. Then it was transferred to a 500ml beaker containing 50ml distilled water. Solution of 0.1 M $NaBH_4$ was slowly added under constant stirring, during this, the resin changed color from green to a maroon color. This color change indicates that coper nanoparticles are formed. After $NaBH_4$ addition, the mixture was stirred for another 30 min then the resin was washed with 100ml distilled water to remove the residue of $NaBH_4$. The resin was then dried was dried at 60°C for 1h to collect the copper unsaturated cation exchange resin (R-CuNP). It was stored in a closed container for further use.

2.3. Characterization

The surface morphology of resin R-CuNPs surface was examined using a JSM-7610F (USA) Scanning Electron Microscope (SEM). Semi-quantitative analysis of nanoparticles was performed by coupled with an energy dispersive spectroscope (EDS, JOEL JSM 7401F, USA). The crystallinity of R-CuNP was determined using X-ray diffractometer (XRD, Philips PW3040/60 X'per PRO, The Netherlands).

2.4. Bacterial activity testing

The bactericidal activity experiments were conducted in batch mode. The batch experiments were conducted at 30°C in sterilized 250 mL flasks containing 0.2, 0.5 and 1.0 g R-CuNPs and 50ml distilled water with concentration of $2.5.10^6$ CFU of *Escherichia coli* per ml. The mixtures were stirred on a magnetic stirrer. Liquid samples were collected at regular time interval to analyze the residual of *Escherichia coli*. Cu(II) ions in the samples were analyzed using UV-vis spectrophotometry [20].

3. RESULTS AND DISCUSSION

3.1. Characterization of R-CuNPs

The XRD patterns of unsaturated Cu nanoparticles immobilized on the cation exchange resin is shown in Figure.1. As shown, this diffraction pattern was matched with the face centered cubic (FCC) structures of copper via characteristic peaks indexed to (111), (200) and (220) at corresponding 2-theta value of 43.8°, 51.0° and 75.6° respectively. This is the evidence that Cu nanoparticles were on the surface of the R-CuNPs resin [21]. A weak peak below 40° (200) was also observed, indicating a trace amount of Cu_2O was formed on the surface of R-CuNPs [22].

The SEM image R-CuNPs are presented in Figs. 2a. The EDX pattern of R-CuNPs is showed in Figure. 2b. A high intensity EDS peaks for copper at 0.93 keV confirmed the formation of copper nanoparticles on the cation exchange resin, which is consistent with the obtained results from XRD spectra. On the other hand, the EDX data confirmed mostly Cu and other elements in cation exchange resin including O, C and S, indicating that this resin is free from other metal contamination. The R-CuNPs prepared has a fairly wide particle size distribution in range 10 to 130 nm, majority of particles are within range of 72.5 – 92.5 nm (Figure. 2c). The average particle size is approximately 76.92 nm.

The FTIR spectra of precursor resin and the final resin R-CuNPs are presented in Figure. 3, confirming the characteristics of function groups on both materials. On the spectrum of the cation exchange resin (red solid line), the characteristic peaks includes a large intensity peak at 3446 cm^{-1} is assigned to the stretching vibration of sulfonic group; a low intensity peak at 2925 cm^{-1} is from CH group; and a peak at 1601 cm^{-1} from C-C bonds. A lower bands from 1412 cm^{-1} to 835 cm^{-1} may be attributed to the stretching vibrations of sulfonic group ($-SO_3$) [23]. On the spectrum of the final resin R-CuNPs (green solid line), the intensity of peaks characterised sulfonic function groups greatly increased due to bonding with copper, confirming the changes on the surface of the resin, *i.e.*, covered with the copper nanoparticles.

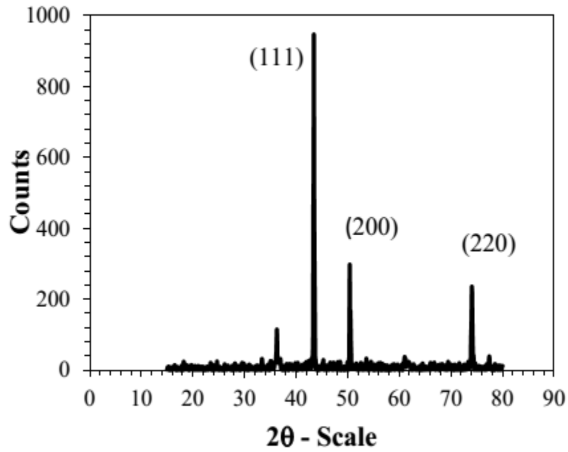

Figure 1. *XRD pattern of copper nanoparticles immobilized on cation exchange resin*

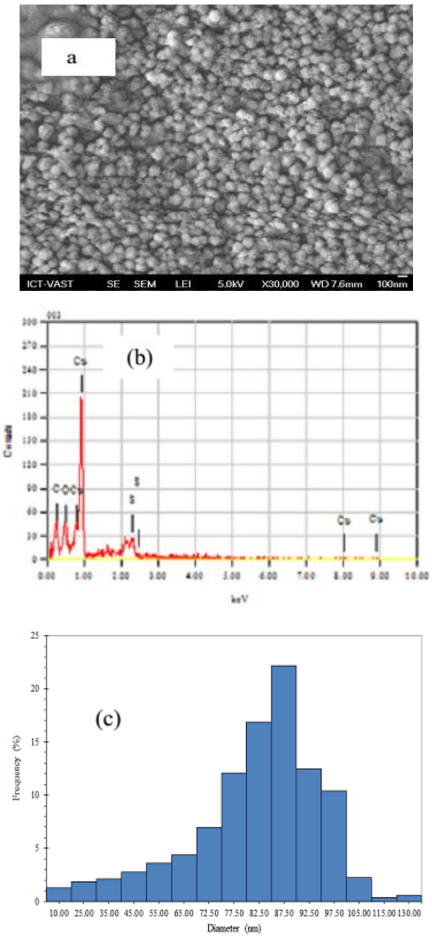

Figure 2. *SEM images (a), distribution of size (b), and EDS analysis (c) of copper nanoparticles immobilized on cation exchange resin*

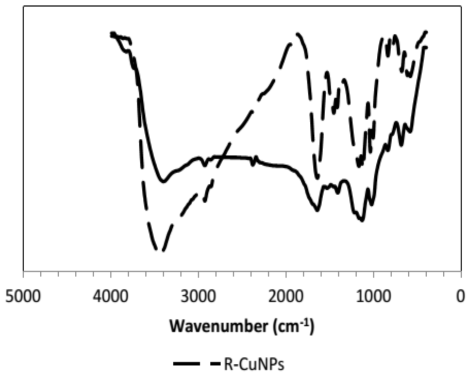

Figure 3. *FTIR of cation exchange resin before and after immobilization of copper nanoparticles*

3.2. Antibacterial activity test

Figure. 4 shows the results of the batch antibacterial activity experiments using R-CuNPs. These results indicate that while the uncoated resin (R) did not show any antibacterial activity against the bacteria *E.coli*, the final resin R-CuNPs inhibited a strong characteristic of a bactericidal agent. This bactericidal ability is proportional to the mass of R-CuNPs, as measured via bacteria reduction percentage. It was evident that a complete removal of *E. coli* was achieved within 30 min with 1.0 g of R-CuNPs while up to 60 and 80 min were required with 0.2 and 0.5 g of R-CuNPs used, respectively. The time for complete removal of *E. coli* from water samples reduced with increasing the mass of R-CuNPs can be explained that there are more active copper sites to inactivate the bacteria at high mass of R-CuNPs. These sites are used to attach, accumulate and penetrate the inside of the bacterial membrane to inactive and cause cell malfunction [24-27]. Additionally, the effect of the CuNPs - cation exchange resin matrix may be further enhanced the antibacterial activity due to increasing the lifetime of CuNPs.

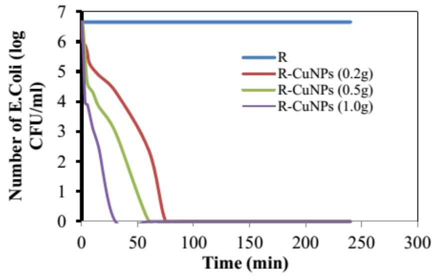

Figure 4. *Antibacterial activity testing using batch method*

The antibacterial effectiveness of copper nanoparticles mobilized on the cation exchange resin is more higher comparing with those of the copper nanoparticles incorporated into paper [24], including the operation time and the treated volume of water. Additionally, this material can be regenerated for multi-time use.

3.4. Copper in effluent analysis

This analysis was conducted to monitor the amount of copper leached into the affluent. It is an important parameter since this will degrade the effectiveness of the R-CuNPs resin overtime and created undesirable contamination in the final water product. Figure. 5 shows the copper concentration in the final water effluent. The average concentration of copper in the effluent of column packed with 5 g R-CuNPs and at the flow rate of 2 ml/min was found to be 0.92 mg/l which is lower than the guideline value of WHO (2 mg/L) [28].

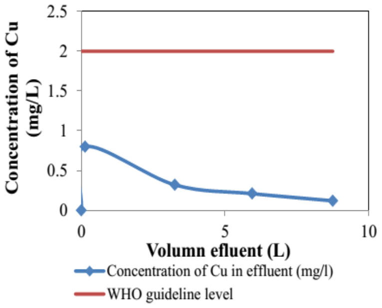

Figure 5. *Result analysis of released Cu concentration in the effluent*

3.5. Regeneration of R-CuNPs

To evaluate the potential of R-CuNPs recycling, experiments were conducted with used R-CuNPs. The used resin was washed with 100 mL of distilled water then retreated with solution of 0.05 M $NaBH_4$ under conditions as described above. After that, the resin R-CuNps was loaded on the column and the experiments were repeated with the same conditions (the initial concentration of E.coli was $2.5.10^6$ CFU. mL^{-1}, water flow rate at 2 $mL.min^{-1}$). Within this study, three cycles of regeneration were conducted without any significant degrading of the resin R-CuNPs effectiveness in bacteria removal, indicating the stability of the copper nanoparticles from this immobilization process. The results of these experiments are summarized in Table 1. Results from more exhausted tests will be available in future studies, nevertheless these initial results indicate this resin is indeed a potential cost effective alternative for the disinfection step in water purification.

Table 1. *Results of E. coli effective removal by using the regeneration of R-CuNPs (initial concentration of E.coli: 2.5×10^6 CFU/ml)*

Regeneration cycle	Log reduction	Effluent volume (l)
1	6.4	10
2	6.4	10
3	6.3	10

4. CONCLUSION

The high effectiveness of copper nanoparticles immobilized on cation exchange resin prepared in this research was demonstrated with *E.coli* strain. The experimental results up to this point, have demonstrated that this material is a potential cost effective for water disinfection in remote, under-developing areas where potable water distribution systems are not available.

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