

Electrochemical Removal of Copper Ions Using Coconut Shell Activated Carbon

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Abstract: In this work, coconut shell activated carbon (CSAC) electrode was evaluated to remove copper ions via electrochemical processes. CSAC electrode and graphite were applied as the cathode and the anode, respectively. The reusability of the electrode, the effects of initial pH, applied voltage and initial concentration were studied. The electrochemical process was carried out for 3 h of treatment time, and the electrodes (anode and cathode) were separated by 1 cm. The results revealed that CSAC is proven as a reusable electrode to remove copper ions, up to 99% of removal efficiency from an initial concentration of 50 ppm after it had been used three times. From the observation, the removal efficiency was optimum at an initial pH of 4.33 (without any initial pH adjustment). The applied voltage at 8 V showed a higher removal efficiency of copper ion compared to at 5 V.

Keywords: activated carbon; copper; electrosorption; coconut shell; wastewater

■ INTRODUCTION

In recent years, the heavy metal content in waste and wastewater has become one of the major concerns in the environment. Its concentration must be limited to a minimum amount as regulated by the local authority. Metal processing, electroplating, battery production, fertilizer production, and mining industries are the main sources discharging effluents of industrial wastewater containing heavy metals [1]. Heavy metal exposure via drinking water is a serious problem faced by humans. Copper removal recently has been eagerly studied since it is widely used in industries, such as electroplating, circuit-board manufacturing and as catalysts. A large quantity of copper with high concentration is commonly found in industrial effluents, and most of them are incompletely removed from the wastewater [2]. United States Environmental Protection Agency (EPA) regulates that the maximum limit of copper concentration in drinking water is 0.05 ppm. Copper is a non-biodegradable element and might be persistent in the aquatic environment. It tends to contaminate agricultural fields, disturb natural balance and accumulate in the ecosystem. Thus, the

accumulation of copper in the food chain will affect aquatic life [3].

Several conventional treatments for heavy metal removal from wastewater and water such as adsorption, chemical precipitation, coagulation-flocculation and ion exchange process have been implemented. Adsorption is widely recommended and used in industries due to its low cost, high removal efficiency depending on the types of adsorbent and simple process of chemical reaction [4]. Chemical precipitation is removing the heavy metals by using a large amount of chemicals to precipitate the metal ions so that they are easily removed from the wastewater [5]. However, some researchers observed that conventional chemical-physical treatments have encountered several disadvantages such as complex process plant to build, the high cost for a large quantity of chemical used, and the use of high energy. Moreover, the environment will be affected due to the large amounts of sludge produced from the processes that would require high cost and a large area for disposal [6].

Electrochemical processes nowadays has become a popular method for treating industrial wastewater

containing heavy metals due to its cost-efficiency and the high ability for metal removal from water. Electrocoagulation, electro-flotation, electrodeposition, electro-sorption, and electro-dialysis are examples of electrochemical processes. The electrochemical process offers several advantages such as being cost-effective by not consuming chemicals in the system, offers high efficiency on heavy metal removal and also the fact that the process occurs at ambient temperature and pressure [7]. In electrochemical processes, there are various types of electrodes either porous or non-porous materials.

A porous material basically refers to carbon-based materials (e.g., agricultural activated carbon, granular activated carbon) that allows the removal of heavy metal on the surface of the electrode. The non-porous material is referring to metal-based electrodes (e.g., platinum, silver, zinc). The carbon-based electrode can also be a non-porous material for example graphite [8]. Carbon-based electrodes are low-cost materials compared to metal-based electrodes which are expensive in the industry. The evaluation of coconut shell activated carbon (CSAC) characteristics and properties show the advantages and its capability of removing heavy metals from water [9]. Hence, this work aims to evaluate the performance of coconut shell activated carbon as a porous electrode for the removal of copper from aqueous solution.

■ EXPERIMENTAL SECTION

Preparation of Electrode

The CSAC was provided by a local supplier. The preparation of the electrode was adapted from Maarof et al. [1]. CSAC was ground to fine particles and sieved to obtain the desired particle size ($< 100 \mu\text{m}$). Carbon black (CB) (Super P, Alfa Aesar), and polytetrafluoroethylene (PTFE) suspension (Sigma Aldrich, 60 wt.%) were mixed with CSAC powder at a mass ratio of 1:1:4 for electrode preparation. CSAC with 20% of CB was labeled as CSAC20CB. The mixture was thoroughly hand-mixed with the addition of 1,3-propanediol as a solvent to produce an electrode paste. The paste was kneaded and pressed in a stainless-steel mold then dried at $80 \text{ }^\circ\text{C}$ for 2 h, $150 \text{ }^\circ\text{C}$ for 1 h and $250 \text{ }^\circ\text{C}$ for 1 h. The dried electrodes

were packed into a 25 mm diameter stainless steel mold and pressed at 20 N/m^2 by using mechanical load to produce approximately 0.5 mm thick CSAC electrodes.

Batch Electrochemical Removal of Copper

The electrochemical cell was filled with 100 mL of copper solution and 5 mL of NaCl as supporting electrolyte. Two electrodes were placed in the cell at 1 cm apart. CSAC and graphite were the cathode and the anode, respectively. A magnetic stirrer was placed inside the cell, and hot plate stirrer was used to allow the mixing of the solution at 250 rpm. The voltage of 8 V was introduced into the system to provide electricity for the process of the removal of copper. The initial current of 150 mA was recorded. There was no pH adjustment of the copper solution except for the study of the effect of initial pH. This electrochemical process was carried out for 3 h. The samples were collected at regular time intervals to analyze the residual metal content.

Effect of initial pH

The electrochemical cell was set up with a voltage of 8 V, and the same conditions were applied as described in the previous paragraph except for initial pH value. The copper solution was adjusted to acidic and alkaline pH to study the effect of initial pH on the electrochemical removal of copper. The pH was adjusted at the start of each run by using either 1 M NaOH or 1 M HCl. The initial concentration was fixed at 50 ppm. The subsequent experiments were conducted at the optimum initial pH.

Effect of applied voltage

For the effect of applied voltage on the electrochemical process, voltages at 5 and 8 V were supplied for each treatment. The initial concentration and treatment time were fixed at 50 ppm and 3 h, respectively.

Effect of initial concentration

The initial concentrations of the copper solution were 50 and 100 ppm. The voltage was fixed at 8 V and no pH adjustment was made to the copper solution. For the initial copper concentration of 50 ppm, the electrochemical process was conducted for 3 h, while, for

100 ppm, the treatment time was 5 h.

Reusability of CSAC electrode

The reusability of the electrode was determined by repeating the experiment three times using the same CSAC electrode. The electrochemical process conditions were fixed at the concentration of the copper solution of 50 ppm, voltage of 8 V, no pH adjustment and 3 h of treatment time. The electrodes were rinsed with distilled water after every treatment to prevent the carry-over effect of the copper solution.

Analysis using ICP-OES

The concentration of copper ion was analyzed by using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Perkin Elmer, Optima 7000 DV). The dilution factor of 10 was applied for each sample whereby 1 mL sample of the copper solution was diluted with 9 mL of 1% nitric acid. All samples were collected at regular time intervals within 3 h. The concentration of copper was determined by using an external standard calibration method. The concentrations of copper used to prepare the calibration curve were 1, 2, 3, 4 and 5 ppm. The removal efficiency of CSAC electrode is calculated by using Eq. (1).

$$\text{Removal Efficiency (\%)} = \frac{C_{\text{Initial}} - C_{\text{Final}}}{C_{\text{Initial}}} \times 100 \% \quad (1)$$

RESULTS AND DISCUSSION

Effect of Initial pH

The initial pH of the solution is an important operating parameter that influences the performance of electrochemical removal of copper ions. The aqueous solution (100 mL) had the initial concentration of 50 ppm copper ion and 5 mL 0.1 M NaCl as the supporting electrolyte. The pH of this solution was 4.33. The removal efficiency of copper ions was studied at acidic and alkaline conditions for which the pH was adjusted accordingly. The pH of the aqueous solution was adjusted by adding a few drops of 1 M NaOH to obtain alkaline pH in the range of 8–10. While adjusting the pH to alkaline condition, the solution became an emulsion for which the copper ion was observed to be insoluble in the aqueous solution. Hussin et al. [10] observed a similar outcome and

reported that at higher pH values (nearest to alkaline), solid copper was formed and precipitated out of the solution. The insoluble copper had affected the performance of the CSAC electrode to remove the copper ions; copper ions were not deposited on the surface of the electrode. While sampling the solution, copper in solid form was clearly observed in the syringe filter. Therefore, it is noted that the electrochemical removal of copper ion is not suitable under alkaline as well as neutral conditions. The copper solution was adjusted to an acidic condition by adding drops of 1 M HCl, and the obtained pH was 2.62. Fig. 1 illustrates the removal efficiency of copper ions by CSAC electrode at the acidic initial condition and without pH adjustment. The removal efficiency of copper ions at pH 4.33 (99.3%) was better than at pH 2.62 (96.4%). During the first 60 min, the removal efficiency at the initial pH 2.62 was below 70%, and only 90.1% removal was achieved after 2 h of treatment time.

In contrast, initial pH 4.33 shows higher removal efficiency of 81.4% after 1 h of treatment time. The result shows that some of the copper ions were not recovered because of the hydrogen ions were attached to the surface of the CSAC electrode [11]. Alebrahim et al. [12] described that at lower initial pH of electrolyte (lower than pH 2), the discharged hydrogen ions in the solution are competing with the discharged copper ions at the cathode surface. They also reported that increasing the initial pH of the solution resulted in precipitation. Chen et al. [13]

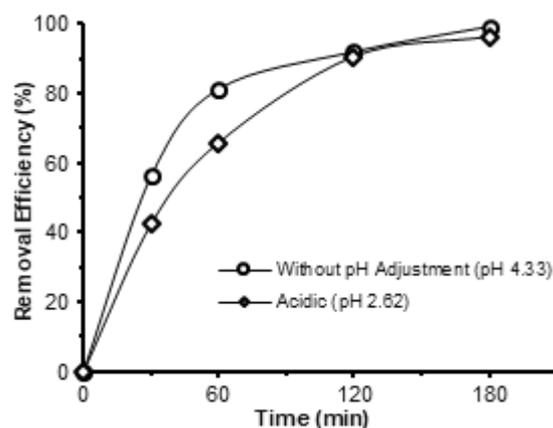


Fig 1. Removal efficiency of copper ions by CSAC electrode at acidic condition (pH 2.62) and without pH adjustment (pH 4.33)

reported that a lower pH resulted in a faster reaction rate due to the higher mass transfer rate. However, it tends to form concentration and electrochemical polarization which results in hydrogen evolution and reduce the current efficiency [13]. Thus, the competitive environment of hydrogen ions and copper ions occurred during the electrodeposition process. The optimum pH was reported at a value of 3.5. Therefore, the copper solution without initial pH adjustment (pH 4.33) is preferred compared to pH 2.62 for copper removal. Consequently, the initial pH of the copper solution at pH 4.33 (without any pH adjustment) was chosen as the optimum value and subsequently applied in the experiments for the other parameters studied.

Effect of Applied Voltage

The effect of the applied voltage was investigated at 5 and 8 V. The solution mixing rate was fixed at 250 rpm, the initial pH of the electrolyte was 4.33, and the initial copper ions concentration was 50 ppm. Fig. 2 shows the removal efficiency of copper ions by CSAC electrode at 5 V and 8 V applied voltage. As shown in Fig. 2, the removal of copper ions was at a higher rate for the first 60 min of treatment time using higher applied voltage (8 V). It achieved 81.4% of removal efficiency. At this point, the increase of percentage removal at 8 V, from 0 to 60 min was faster than at 5 V. At 60 min of treatment time, the difference in the percentage removal was 30.5%. As the treatment time was extended to 3 h, the removal efficiency at an applied voltage of 8 and 5 V was 99.3 and 94.9%,

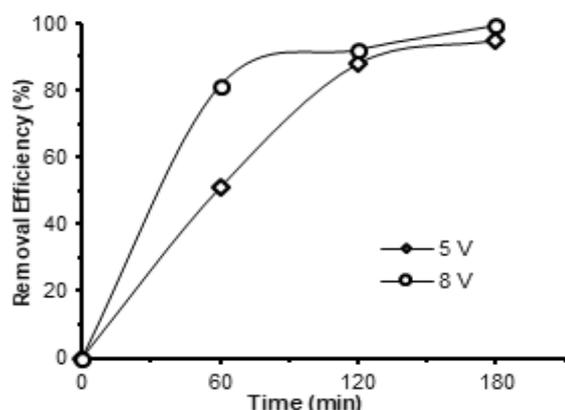


Fig 2. Removal efficiency of copper ions by CSAC electrode at applied voltage of 5 and 8 V

respectively. This indicates that the transfer of electrons and charged ions attached to the cathode is more effective at higher voltages. Marmaris et al. [14] studied the effect of the voltage supplied at 0.4, 0.8 and 1.2 V and reported that the highest removal efficiency of cadmium was at 1.2 V. It is also claimed that the electrochemical processes for cadmium using nano-carbon electrode required high supplied voltage to remove cadmium ion from solution. Elsherief [15] reported that low voltage supply resulted in the formation of hydrogen ions on the surface of the electrode (spiral wound steel electrode); thus, the removal efficiency was low. The electrostatic attraction of ions by the reticulated vitreous carbon electrode was effective at a higher voltage as it increased the flow velocity of electrons to be attached to the porous electrode [11]. Duan et al. [16] also described that electrodeposition rates of copper ion increased gradually when a higher cell voltage was supplied.

Effect of Initial Concentration

The effect of the initial concentration of copper by CSAC electrodes was carried out at the initial concentration of 50 and 100 ppm. Fig. 3 shows that the removal efficiency of the copper ion at 50 and 100 ppm were 99.3 and 94.2%, respectively. The results demonstrate that a lower initial concentration (50 ppm) gave higher removal efficiency than higher initial copper ion concentration (100 ppm). The higher removal efficiency was achieved at an initial concentration of 50 ppm copper solution after 3 h of treatment time. However,

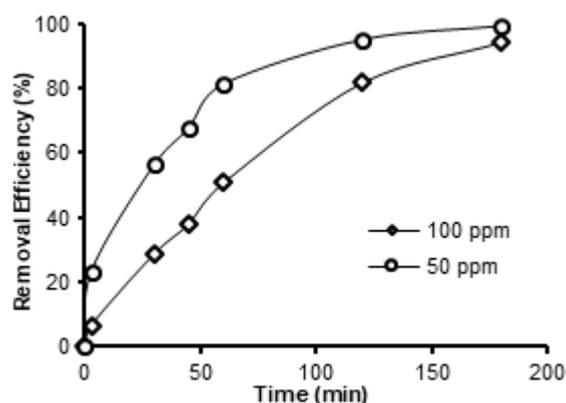


Fig 3. Effect of initial copper concentration on removal efficiency of CSAC electrode

at an initial concentration of 100 ppm, approximately similar efficiency (99.4%) was only achieved after the treatment time was prolonged to another 2 h. Khattab et al. revealed that the initial concentration has an influence on the removal efficiency of copper whereby high initial concentration tends to transport the ions through the pores easily. Therefore, it will be resulting in effective electrochemical removal of copper by carbon electrode [17].

Reusability of CSAC Electrode

The reusability of the CSAC electrode was studied by repeating the experiment three times using the same electrode for removal of copper ion from aqueous solution. Similar operating conditions of the electrochemical process were applied for the three experiments whereby, the initial concentration was fixed at 50 ppm, applied voltage at 8 V (approximately 150 mA), the solution was stirred at 250 rpm, initial pH of 4.33, and with the addition of 5 mL supporting electrolyte 0.1 M NaCl. The initial pH for copper solution was acidic for each experiment. Fig. 4 illustrates the removal efficiency of copper ions by CSAC electrode versus time, the removal efficiency of copper ion at the first run was 99.3%, higher than the subsequent second and third runs. The second and third run of the experiment gave the removal efficiency of 98.2 and 96.4%, respectively. This shows that at the first run, the removal of copper ion was the most effective. This is because of the charged particles of the surface electrode that was efficient in attracting the electrons of copper ions. The high porosity of electrode

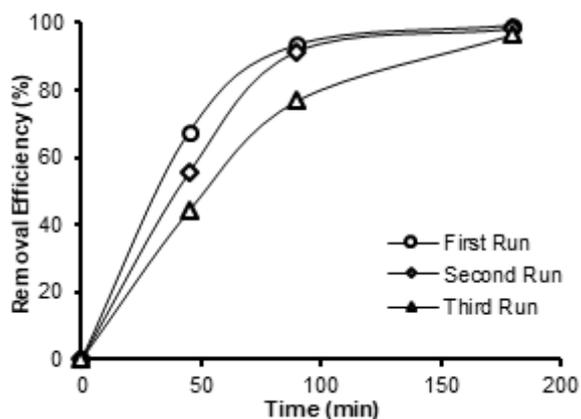


Fig 4. Successive copper ion removal efficiency of CSAC

gives the advantage in removing copper ion whereby it is allowing a greater mass transfer to occur during the electrochemical process [8].

In contrast, the performance of the CSAC electrode decreased slightly in its effectiveness for the second and third runs. The decrease in removal efficiency of copper ions after the first run is probably due to the less active surface area of the CSAC electrode. Reusability study of the electrode was carried out three times/runs, whereby CSAC electrode was rinsed with distilled water after each run was completed. Copper was observed to be deposited on the surface of the CSAC electrode. Thus, the availability of the active site of the surface of the electrode is lower due to the solid copper attached on the CSAC electrode.

CONCLUSION

Copper ions were recovered from synthetic wastewater by using the coconut shell activated carbon (CSAC) electrode via the electrochemical process. The reduction of copper ions was facilitated by the chemical reaction with the aid of applied voltage. CSAC, a carbon-based electrode was used as the cathode to attract the copper ions and deposit on the porous surface electrode. The CSAC electrode is an effective electrode with high removal efficiency and is a reusable electrode which can be used several times to remove copper ions, more than 99% removal efficiency was achieved after it had been used three times. The electrochemical removal of copper ions by the CSAC electrode was found more effective in acidic solution. In this work, the higher removal efficiency was achieved without any pH adjustment of the solution, which was at pH 4.33. The applied voltage of 8 V gave higher removal efficiency compared to 5 V. High initial concentration (100 ppm) required longer treatment time than 50 ppm whereby 5 h was needed to obtain 99.4% of copper removal. In contrast, 99% removal efficiency was achieved with only 3 h of treatment by 50 ppm copper ion. In conclusion, the CSAC electrode has high potential to remove copper ions through an electrochemical process. The CSAC electrode has the potential to replace metal-based electrode material as it has high removal efficiency due

to its porous properties and more importantly, it is cost effective. Coconut shell is an agricultural waste, available in large quantities in tropical countries globally that can be utilized to create value-added products.

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