Fabrication of Chitosan-complexed Electrode and Evaluation of Its Efficiency in Removal of Copper Ion from Aqueous Solution

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Abstract. In this study, we fabricated chitosan/PVA/activated carbon complexed electrode to remove copper ion from aqueous solution. The prepared composite electrode was analyzed by BET and SEM to investigate its physicochemical properties. Electrochemical properties of prepared composite electrodes were analyzed via cyclic voltammetry. Adsorption performance of copper ion on chitosan composite complexed electrodes was evaluated. Almost similar pore size distribution results were observed in the series of ACP not included electrodes while observed differences in pore size distribution for the ACP included one. Cyclic voltammetry results exhibited that oxidation-reduction reaction does not occur in a potential range of -1.0 ~ 1.0 V. The amount of copper ion during adsorption reaction is increase according to increase of adsorption potential to 1.0 V.

Keywords: Chitosan; PVA; Activated carbon; Electrode; Electrosorption

1 Introduction

Removal of copper ion from aqueous solution is an important issue because expose to high concentration of copper ion for a long period is harmful for human and other living being. Several technologies such as precipitation, ion exchange, electrode filtration, coagulation, flocculation, flotation and electrochemical treatment have been used to remove the copper ions in waste water [1-4].

Electrosorption is one of the promising considerable copper removal techniques because it has many advantages compare to previous technologies; for examples, low energy consumption, environmental friendliness, and simplified step. In detail, ions are extracted from aqueous solution by applying an electric potential between a pair of electrodes, in

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which the ions are temporarily stored via the formation of an electrical double-layer between
the electrode and electrolyte interface [5]. Electrosorption can also improve the energy
efficiency because the process operates at a low voltage region. Moreover, it is well known
as eco-friendly process that does not produce the secondary by-product because it can
proceed with desorption by applying a reverse potential in an aqueous solution [6].

Electrosorption efficiency is related to the specific surface area of electrode and it also
affected by the type of surface functional group. Chitosan has a large amount of the amino
group. It can form a chelate with copper ions in the solution using a lone pair of electrons and
which can absorb the copper ions. Therefore, many studies have been conducted relating to
the removal of copper ions using chitosan [7-9].

In this study, we prepared chitosan complexed electrode. It composed with chitosan and
activated carbon, and polyvinyl alcohol used as a binder to removal of copper ions from the
aqueous solution. Physical and chemical properties of the complexed electrode were
analyzed by the BET and SEM, and its electrochemical properties were analyzed by cyclic
voltammetry. Also, applied potential varied to evaluate its copper ion removal efficiency.

2 Experimental

2.1 Fabrication of Chitosan-complexed Electrode

1 wt% acetic acid solution using deionized water and acetic acid (99.0%, Deajung) and
chitosan (medium molecular weight, Sigma-Aldrich) was mixed and stirred for 24 h at 50 ºC
to prepare chitosan solution. PVA solution was prepared by adding polyvinyl alcohol (PVA,
Mw 31,000-50,000, 98-99% hydrolyzed, Sigma-Aldrich) a weight ratio of 15 to deionized
water. Afterwards, PVA solution stirred for 12 h at 70 ºC in a water bath. Prepared chitosan
solution and 15 wt% PVA solution was homogeneously mixed using a mechanical stirrer for
2 h. The CTS/PVA mixture was coated on graphite sheet (150 /μ541m of thickness, Dongbang
Carbon Co.) using a doctor blade to a thickness of 450 /μ541m. Afterwards, chitosan-complexed
electrode was dried for 12 h at room temperature and baked at 100 ºC for 30 min in an oven.
Finally, it was soaked for 1 h in 1 M NaOH solution, and washed with deionized water until
the pH of the washed liquid reached to that of deionized water.

Fabrication of chitosan-complexed electrode containing activated carbon powder (ACP,
P-60, Deadong AC Corp., Specific surface area of 1,260 m²/g) was similar to the procedure
as stated above. For this, ACP was added into the PVA solution before mixing chitosan/PVA.
The fabricated complexed electrode was named according to the ratio of chitosan, PVA and
ACP. (Ex. CTS/PVA/ACP = 1 / 2 / 3 for M123).

2.2 Characterization of the Chitosan-complexed Electrode and Adsorption
Experiment

Physical and chemical properties of the prepared chitosan-complexed electrode were
analyzed by SEM and BET. Electrochemical properties of the chitosan-complexed electrode
were analyzed by cyclic voltammetry measurement. M311, M212 and M113 containing
activated carbon were selected as cyclic voltammetry measurement samples. Fig. 1 shows the
schematic diagram of the equipment for electrochemical experiment. The water analyzer
(HS-3100, HUMAS) was used to measure the concentration of copper ions in aqueous
solution.
3 Results and Discussion

3.1 Physical and Chemical Characterization

Fig. 2 shows the morphologies of CTS/PVA and CTS/PVA/ACP complexed electrodes. Two complexed electrode was observed smooth surface, and the cross sectional view was similar to each other. The roughness of surface with differ from CTS/PVA complexed electrode by adding of activated carbon. The 3d network pores observed for the ACP added electrode in the cross section of the electrode.

Fig. 2. SEM images of prepared CTS/PVA and CTS/PVA/ACP electrodes. Surface view (a) M710 , (c) M410(e) M113 and cross sectional view (b) M710, (d) M410 and (f) M113.
Fig. 3 shows the pore size distribution results for the CTS/PVA complexed electrode and CTS/PVA/ACP complexed electrode calculated by the BJH method using the nitrogen adsorption-desorption isotherm result. Almost similar pore size distribution results were observed in the series of ACP not included electrodes while observed differences in pore size distribution for the ACP included one. This result indicates that the pore structure was affected by the addition of ACP.

3.2 Electrochemical Characterization of Chitosan-complexed Electrode

Fig. 4 shows the cyclic voltammetry of chitosan-complexed electrode was measured to analyze the electrochemical properties with the potential range is from -1.0 V to 1.0 V and 0.01 mV/s scan rate under the presence of 20 ppm CuSO₄ solution. The cyclic voltammogram did not have a prominent peak in a range of -1.0 ~ 1.0 V, which means that oxidation-reduction reaction does not occur in this experimental range.

![Fig. 3. Pore size distribution of fabricated (a) CTS/PVA and (b) CTS/ACP/PVA electrode.](image)

![Fig. 4. Cyclic voltammograms of M311, M212 and M113 electrodes in copper ion 20 ppm solution; -0.1 ~ 0.1 V of voltage range, 0.01 mV/s of scan rate.](image)
Fig. 5 shows the changes of copper ion concentration in the reservoir solution during adsorption reaction. In this case, CTS/PVA/ACP complexed electrode of M311 was used, and the adsorption potential varied from 0.2 to 1.2 V. It confirmed that the copper ion adsorption equilibrium time using chitosan-complexed electrode in the electrochemical adsorption is around 300 min. The adsorption amount of the copper ions kept constant irrespective of the change of potential. From the results, the amount of adsorption is increase according to increasing of applied adsorption potential, and amount of adsorption is similar at 1.0 V and 1.2 V.

![Graph showing effects of adsorption voltage and adsorption time on copper ion electrosorption using M311 electrode.](image)

**Fig. 5.** Effects of adsorption voltage and adsorption time on copper ion electrosorption using M311 electrode.

### 4 Conclusions

We successfully fabricated chitosan-complexed electrode with a different composition of chitosan, PVA and activated carbon for removal of copper ions in the aqueous solution. Physical, chemical and electrochemical properties of fabricated electrodes were analyzed. The specific surface area of chitosan-complexed electrode was increased by adding of activated carbon, which confirmed by SEM and BET. Electrosorption result indicates that the equilibrium was reached in 300 min irrespective of the change of the adsorption potential. The amount of copper ion during adsorption reaction is increase according to increase of adsorption potential to 1.0 V. Cyclic voltammetry results exhibited that oxidation-reduction reaction does not occur in a potential range of -1.0 ~ 1.0 V.

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