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Study on Cation-Exchange of Removal Metallic Ions at PPy/PVS Film

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***Abstract* — Due to the presence of heavy metals in wastewater treatment and manufacturing water purification processes in industries, investigations into potential methods have been widely conducted. In this paper, we report the incorporation of cation-exchange for removing heavy metals from aqueous solutions. We further investigated the properties cation-exchange using potential step method on PPy/PVS film at titanium electrode. Satisfactory results have been obtained with the small scale of experimental. It was found that the PPy/PVS film is able to remove heavy metal ions such as copper, nickel, and cobalt at very low concentrations, less than or equal to 10 mg/L, reducing them to approximately 1 mg/L. The Leica Q500MC Image Processing and Analysis system displayed the uneven deposition of heavy metal ions on the surface of PPy/PVS. Furthermore, Electron Spectroscopy for Chemical Analysis (ESCA) demonstrated the deposition of heavy metals on the PPy/PVS film.**

Keywords— PPy/PSS, ESCA, Cation-exchange, Potential step method, Heavy metals.

I. INTRODUCTION

Water pollution, particularly contamination by heavy metals, poses a serious threat to all living beings day by day. If humans consume contaminated water, the heavy metals accumulated in the human body can cause serious health effects such as damage to vital organs, nervous system failure, hormonal imbalance, etc [1]. The toxic heavy metals mainly present in wastewater include cadmium, cobalt, copper, iron, mercury, nickel, silver, tin, and zinc. However, these toxic metals in wastewater are directly or indirectly discharged into streams, lakes, rivers, or oceans, especially in some developing countries. According to the guidelines of the World Health Organization, the acceptable limits of some heavy metal ions in drinking water are as follows: Pb (50 µg/L), Cd (5 µg/L), Cr (50 µg/L), Zn (5000 µg/L), Cu (1500 µg/L), Co (10 µg/L), and Ni (100 µg/L) [2]. Therefore, many researchers [3-5] have reported their studies on removing heavy metal ions from wastewater pollution.

Polypyrrole (PPy) film is considered one of the extensively used conducting polymers due to its good electrical conductivity, environmental stability under ambient conditions [6-8], and fewer toxicological problems [7]. Many of researchers reported the potential of polypyrrole in its applications, such as the fields of energy storage [9], electrochemical biosensor [10], solid state batteries [11], ion-selective sensors [12], ion-exchangers for water purification [13], ion-exchangers for wastewater treatment [14, 15].

Various resource recovery techniques can be utilized to reclaim these metallic ions for their economic value or to minimize the quantity of waste sludge generated by a downstream conventional treatment plant. Different methods have been reported for removing metallic ions from wastewater, such as ion-exchange methods [1, 3], removal by precipitation [4], solvent extraction with freeze/thaw [5], and electrochemical treatment [15]. Maity *et al.* [1] employed polypyrrole-coated composites to remove heavy metals from wastewater through water treatment. Wang *et al.* [16] reported that a hydrous CeO_2-polypyrrole nanocomposite can remove fluoride from simulated and industrial wastewater.

In this work, we employed a polypyrrole-poly (vinylsulfonic acid, sodium salt) (PPy/PVS) film and applied a potential step to investigate its cation-exchange properties on metallic ions. The study demonstrated the applicability of the potential step method using the PPy/PVS film for removing metallic ions from aqueous solutions.

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II. EXPERIMENTAL

A. *Chemicals and Reagents*

A titanium foil with a thickness of 0.127 mm and 99.7% purity from Aldrich Chemical Co. Inc. was used as the anode material. The counter electrode material used was platinised titanium gauze from Morgett Electrochemicals Ltd., UK, and pyrrole from Fluka Chemicals was distilled. Analytical-grade poly(vinylsulfonic acid, sodium salt) from Aldrich Chemical Co. Inc. was used without further purification. Doubly-distilled water was used for solution preparations. $CuSO_4$ test solutions were prepared by dilution of 1000 ppm stock solution. Cobalt (II) chloride and copper sulphate were recrystallized before use. They were dried in the oven and then kept in a vacuum desiccator. Nickel (II) Sulphate Hexahydrate from Fluka was used.

B. *Instruments*

The electropolymerization cell consisted of a flag-shaped Ti anode plate and two rectangular pieces of platinised Ti gauze cathodes placed on either side of the anode plate. The electropolymerization cell put in the forming solution at a 150 cm^3 beaker. An Ag/AgCl/KCl ceramic junction electrode used as a reference electrode and put a magnetic stirring in the solution. An EG&G PAR Model 363 Potentiostat-Galvanostat was used with a Keithley Model 197 Digital Multimeter. Optical images of the surfaces of samples were obtained using a Leica Microscope System. The image analyser consisted of a Leica Image Processor and microscope system interfaced to a 486-microcomputer system via a Sony video camera. ESCA data were generated using a VG Microtech Spectrometer with a dual anode (Mg/Al) X-ray source and Clam 2/4 V triple channeltron analyser (Fissons Instruments). VG Microtech's VGX 900I data system was used for data acquisition and analysis. The atomic absorption spectrophotometer measurements were carried out with a Thermo Jarrell Ash Corporation, model Smith Hieftie 1000, Atomic Absorption Spectrophotometer. Copper, nickel, and cobalt hollow cathode lamps manufactured by Photron Pty. Ltd. were used.

C. *Ion Exchange*

A PPy/PVS film coated on Ti was used as the working electrode and immersed in a 125 ml solution containing copper, nickel, or cobalt ions. A platinised titanium gauze was used as the counter electrode. A cathodic potential of -1000 mV (versus Ag/AgCl reference electrode) was applied at the working electrode to reduce the copper ions solutions. After 30 minutes, the copper ions were deposited on the PPy/PVS film and the film taken out from the solution. 10 ml of solution was pipetted out and put in a storage plastic bottle. To analyze the concentrations of copper ions, 10 ml solutions from storage plastic bottle were analysed using Atomic Absorption Spectrophotometry (AAS). Then PPy/PVS film deposited with copper ions was soaked in 60 ml diluted sulphuric acid (0.1 M H_2SO_4). The anodic potential +1000 mV (versus Ag/AgCl reference electrode) was applied to the working electrode for 15 minutes to allow copper to re-dissolve. The copper ions dissolved easily in dilute sulphuric acid. The whole procedure was repeated until the copper concentration was reduced to 1 ppm.

The same procedure was applied for the testing of cobalt and nickel ions solutions.

The whole process could be described as in Fig. 1.

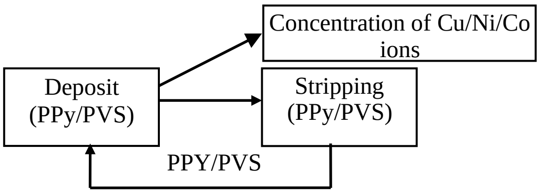


Fig. 1. A Diagram showing the steps in copper/nickel/cobalt ions removal processes.

III. RESULTS AND DISCUSSION

A. Results of Image Processing from Leica and AAS

A fixed -1000 mV cathodic potential was applied on PPy/PVS film to reduce the copper ions from aqueous solution. The copper ions were attracted to the PPy/PVS film and deposited on the surface of the film. It was observed that the copper deposited on the PPy/PVS film. The film changed the colour from black to blue, then to reddish colour. However, the deposition of copper ions was not distributed evenly on the surface of the film as shown in the Fig. 2. The deposition of copper ions was more rapid on the edges of the film due to poor throwing power and uneven distribution of copper ions on the surface of the PPy/PVS film. of Secondary Electron Image image of electrolyte side of PPy/PVS film [17] shown in previously paper.

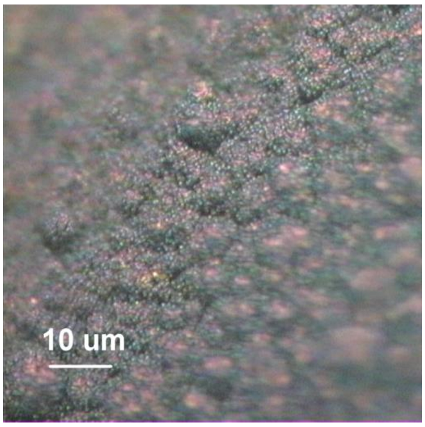


Fig. 2. Leica Q500MC image Processing and Analysis system shows deposition of copper ions on surface PPy/PVS film.

The differences of deposition in colours were due to the copper ions and metallic copper (reddish colour) [18] shown in Fig. 2. The blue colour was caused by concentrating copper sulphate [18] at the surface. Due to oxidation in air, some of the metallic copper turned to greenish (hydroxo carbonate) [18]. It was found that few of yellowish colour at surface of the film. There is cuprous oxide [18] formed when the film was exposed to air.

Table I. The time after cathodic potential applied versus concentration of copper ions.

Time/minutes	Concentration of copper ions /ppm
0	10.0067
30	9.77
60	7.247
90	3.725
120	1.83
150	0
180	0
210	0

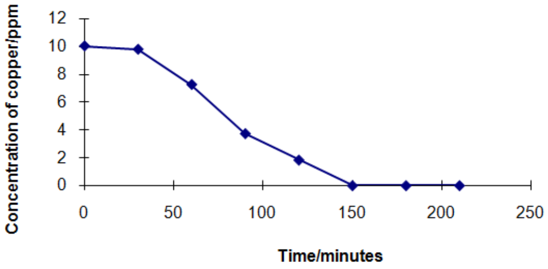


Fig. 3. The graph showing the concentration of copper ions versus time.

Table I shown that the results of concentration copper ions versus the time after cathodic potential applied. The results of Table I plotted in the graph as illustrated in Fig. 3. Figure 3 shows the graph of the concentration of copper ions versus time. It was found that concentration of copper ions decreased with every 30 minutes. The concentration of copper ions decreased from 10 ppm to 0 ppm after applied 150 minutes as illustrated in Table I and Fig. 3.

The same procedure of potential method applied in reducing nickel and cobalt ions at the PSS/PVS film. The nickel ions were attracted and deposited on the surface of the film. The colour of the film changed from black to blue before turning to brown. It was observed that nickel ions were not distributed evenly on the surface of the film, occurred more rapidly on the edges of the film and uneven distribution of deposition nickel ions on the surface of the film.

Figure 4 shown the uneven deposition of nickel ions at the surface of PPy/PVS film. The blue colour probably caused by concentrating of nickel ions [19] at the film. In Fig. 4, the deposition of the metallic nickel in silver white colour [18] are shown. Some of the metallic nickel changed from bright-yellow to dark green colour (hydrous nickel oxide) [18, 20]. The colour turned darker (black) [19, 21, 22] as the oxygen content increased.

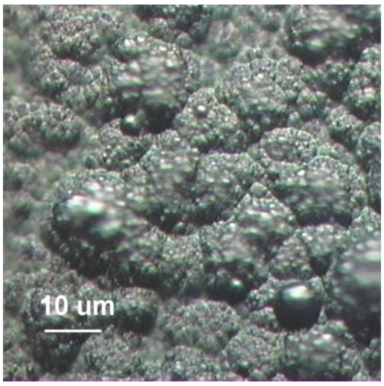


Fig. 4. Leica Q500MC image Processing and Analysis system shows surface of PPy/PVS film after nickel ions deposition.

Table II. The time after cathodic potential applied versus concentration of nickel ions

Time/minutes	Concentration of nickel ions/ppm
0	7.996
30	7.303
60	5.944
90	4.327
120	2.378
150	1.806
180	1.108

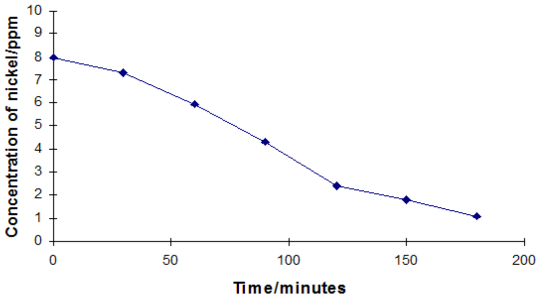


Fig. 5. The graph showing the concentration of nickel ions versus time.

Table II shown the results of nickel ions from AAS versus the time. The graph plotted from the results of Table II as shown in Fig. 5. Figure 5 shows the graph of the concentration of copper ions versus time. It was found that concentration of copper ions decreased with every 30 minutes. The concentration of copper ions decreased from 8ppm to approximately 1 ppm after applied 180 minutes as illustrated in Table II and Fig. 5.

In removing cobalt ions, the deposition of cobalt was not evenly distributed on the surface of the film. Again, this was due to the deposition of cobalt ions occurred more rapidly on the edges of the film. The blue [21] appearance was probably caused by the concentrating of cobalt ions on the surface of the film. However, the brown colour was probably due to the oxide layer (cobalt (II) oxide[19] or cobalt (III) oxide [22]) formed on the surface.

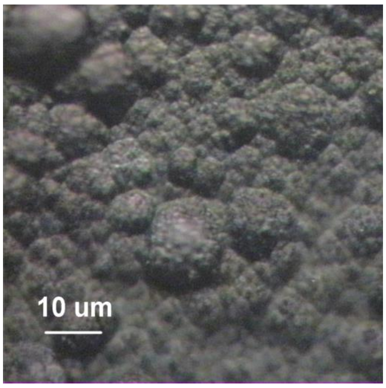


Fig. 6. Leica Q500MC image Processing and Analysis system shows surface of PPy/PVS film after nickel ions deposition.

In Fig. 6, the uneven deposition of cobalt ions on the surface PPy/PVS film was indicated. On the surface PPy/PVS film, the deposition of cobalt ions and metallic cobalt was shown in bluish white colour [18]. Some metallic cobalt changed to olive-green (cobalt oxide) [18] due to oxidation in air. The colour of the cobalt (II) oxide became darker (brown to black colour) [23] as the oxygen content increased. The brown colour material was probably due to the cobalt (III) oxide[22] formed on the surface.

Table III. The time after cathodic potential applied versus concentration of cobalt ions

Time/minutes	Concentration of cobalt ions/ppm
0	7.98712
30	7.352
60	5.51
90	3.767
120	2.651
150	1.955
180	1.193
210	0.7745

Table III shown the results of cobalt ions from AAS versus the time after applied the anodic potential. The graph plotted from the results of Table III as shown in Fig. 7. Figure 7 shown the graph of the concentration of cobalt ions versus time. It was found that concentration of cobalt ions decreased at every 30 minutes. Figure 7 shows the concentration of cobalt ions decreased from 8 ppm to 0.77 ppm after 210 minutes applied.

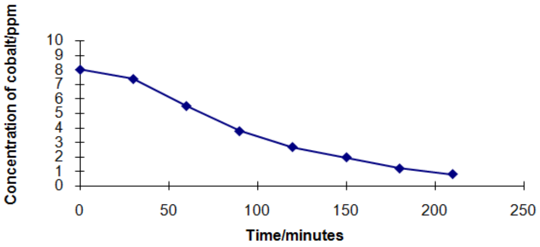
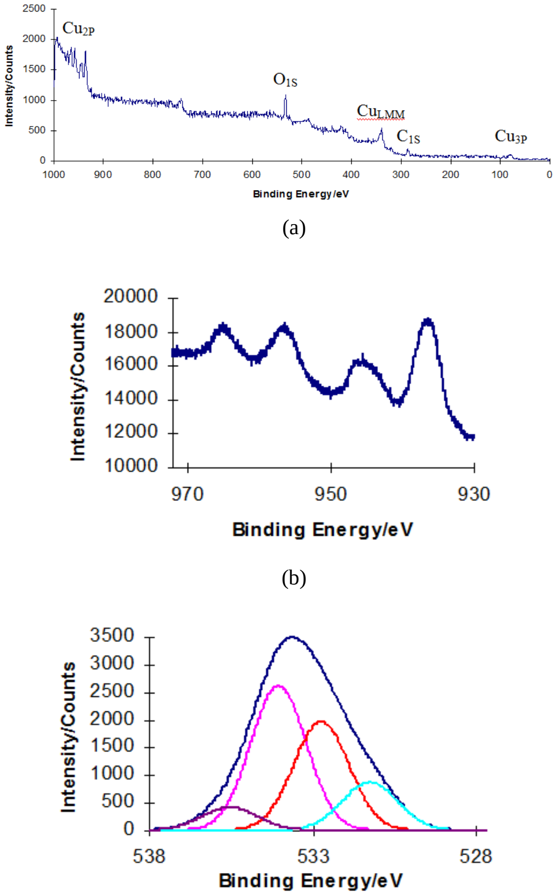


Fig. 7. The graph showing the concentration of cobalt ions versus time.

B. Results of Electron Spectroscopy for Chemical Analysis (ESCA)



(a)

(b)

(c)

Fig. 8. The ESCA spectra for copper ions deposited on PPy/PVS film (a) on wide scan, (b) region of Cu 2p core-level spectra and (c) O 1s core-level spectra on the surface of PPy/PVS film.

The study on the reduction of metallic ions (copper, cobalt and nickel) deposited at PPy/PVS film, was investigated using ESCA. Figure 8(a) shown ESCA wide scan spectra for the copper ions deposited on surface of PPy/PVS film. The ESCA spectra showed C_{1S} attributed to neutral carbons (~284.5 eV), O_{1S} core-level signal (~531 eV), Cu_{LMM} signal level (~335 eV), Cu_{3p} (~75-77 eV), (Cu) $2p_{1/2}$ (~953 eV), and $2p_{3/2}$ (~934 eV) photolines [24].

It was observed that the ESCA spectra shown C_{1S} that attributed to the neutral carbons (~284.5 eV), O_{1S} core-level signal (~531 eV), Cu_{LMM} signal level (~335 eV), Cu_{3p} (~75-77 eV), (Cu) $2p_{1/2}$ (~953 eV) and $2p_{3/2}$ (~934 eV) photolines [24].

It was found that the shifting of signal (Cu) $2p_{1/2}$ (~960 to 970 eV) and $2p_{3/2}$ (~936 eV) photolines are illustrated in Fig. 8(b). The complex satellite structures may associate with (Cu) $2p_{1/2}$ and $2p_{3/2}$ photolines. It was probably due to oxidisation of copper ions at the surface of PPy/ PVS film when the film exposed to air. Figure 8(c), the oxygen O_{1s} spectra is resolved into 529.4, 531.0 and 532.8 eV, corresponding to the oxide oxygen, oxygen from PVS$^-$ sulfonate groups, and water and/or adsorbed oxygen species [25].

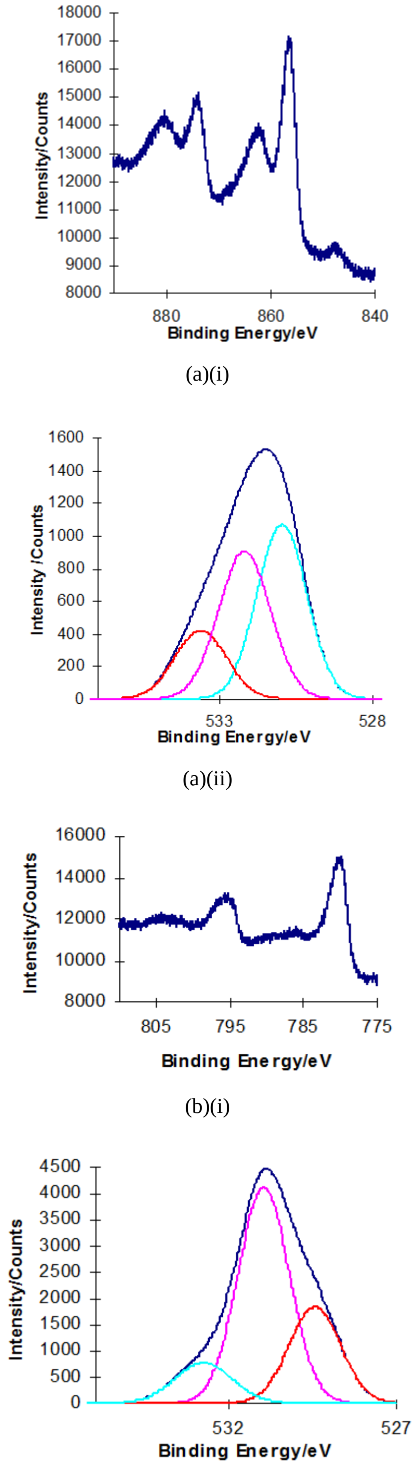
The ESCA spectra for the reduction of nickel and cobalt ions at PPy/PVS appeared similar with copper ions. The complex satellite structures associated with (Ni) $2p_{1/2}$ and $2p_{3/2}$ photolines are illustrated in Fig. 9(a)(i). Here, it was observed that the signal shifted to the left of the main 2p lines, a satellite structure was found. The (Ni) $2p_{1/2}$ and (Ni) $2p_{3/2}$ binding energy were shifted from 870eV and 853 eV to be approximately 876 eV and 857 eV respectively, which was related to the nickel in NiO [25]. The oxygen O_{1s} spectra for PPy/PSS film shown in Fig. 9(a)(ii), could be resolved into three peaks at 531.0, 532.2 and 533.6 eV which were due to nickel (III) oxide oxygen [26], oxygen from PVS sulfonate groups [25] and water absorbed species [27]. This indicated that there could be a layer of deposition of nickel oxide on the surface of PPy/PVS film.

Similar results appeared at Co 2p core-level spectra. The complex satellite structures associated with (Co) $2p_{1/2}$ and $2p_{3/2}$ photolines are shown in Fig. 9(b)(i). Here, it was observed that the signal shifted to the left of the main 2p lines, (Co) $2p_{1/2}$ and (Co) $2p_{3/2}$ binding energy were shifted from 793 eV and 778 eV to be approximately 800 eV and 780 eV respectively. The signal of 780 eV was due to forming Cobalt oxide (CoO) on the surface of PPy/PVS film. In Fig. 9(b)(ii), the oxygen O_{1s} spectra is resolved into 529.4, 531.0 and 532.8 eV, corresponding to the oxide oxygen [25], oxygen from PVS sulfonate groups [25] and water and/or adsorbed oxygen species [25].

Obviously, Cu photolines shown that the copper ions deposited on the surface of PPy/PVS film. Oxygen O_{1s} core-level spectra shown the oxidisation of copper ions when the PPy/ PVS film exposed to air, PVS$^-$ sulfonate groups, and water and/or adsorbed oxygen species at the surface of the film. Similar results are observed with Ni and Co ions. ESCA demonstrates the photolines of Ni and Co ions on the surface of the PPy/PVS film. The appearance of oxygen O_{1s} spectra is also due to the same results as those with copper ions.

In summary, metal ion deposition had occurred on surface of PPy/PVS film under controlled potentials. Oxidisations on metal ions (Cu/Ni/Co) were observed for signals of 2p spectra and O_{1s} core-level spectra at the surface of PPy/PVS film.

The purification of water can be observed with the results of removing heavy metallic ions. Our studies on the PPy/PVS film is able to remove heavy metal ions (Cu/Ni/Co) at very low concentrations, less than or equal to 10 mg/L, reducing them to approximately 1 mg/L.



(a)(i)

(a)(ii)

(b)(i)

(b)(ii)

Fig. 9. The ESCA spectra (a) for nickel ions deposited on PPy/PVS film (i) at region of Cu 2p core-level spectra and (ii) O 1s core-level spectra on the surface of PPy/PVS film; (b) for cobalt ions deposited on PPy/PVS film (i) at region of Cu 2p core-level spectra and (ii) O 1s core-level spectra on the surface of PPy/PVS film.

IV. CONCLUSION

The clean water supply and the effects of wastewater on humans are crucial to consider for public health and environmental sustainability. Due to water pollution, particularly contamination by heavy metals, poses a serious threat to all living beings day by day, it is important to remove the heavy metals in wastewater before they are discharged into streams. Our studies on removing heavy metal ions (Cu/Ni/Co) on a small scale were presented.

The results showed that potential step method successful to reduce metals ions on the surface of PPy/PVS film. Leica Q500MC image Processing and Analysis system shows the deposition of metallic ions (Cu/Ni/Co) at the surface of PPy/PVS film. It was found that the PPy/PVS film was useful for removal of metal ions at very low concentrations (≤ 10 mg/L) from the results of AAS. The removal of copper ions resulted in a reduction from 10 to 0 ppm, nickel ions were reduced from 8 to approximately 1 ppm, and cobalt ions were reduced from 8 to 0.77 ppm. Careful use of these films was found to be able to reduce the metal ions concentrations down to approximately 1 mg/L. The ESCA spectra results show the oxidisation of metals ions (copper, cobalt and nickel ions) for signals of 2p core-level and O_{1s} core-level spectra on surface of PPy/PVS film. The work has been performed with the small scale of experimental without the large scale.

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