Sustainable and Green Ultrasound-Assisted Zinc Cementation for Efficient Removal of Cu^{2+} and Cd^{2+} from Zinc Sulfate Electrolytes: Mechanism, Kinetics, and Environmental Benefits

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Supplementary Note 1: $ZnSO_4$ (98%), $CdSO_4$ (98%) and $CuSO_4$ (98%) were purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd. (Tianjin, China). H_2SO_4 (98%) were purchased from Chongqing Chuandong Chemical (Group) Co., Ltd. (Chongqing, China). Zn powder (20–200 mesh) was bought from Beijing Zhongke Yannuo New Materials and Technology Co., Ltd, China. 5,5-Dimethyl-1-pyrroline N-oxide was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd (Shanghai, China).

Supplementary Note 2: In this study, an ultrasound-enhanced zinc powder replacement method was employed to remove Cu^{2+} and Cd^{2+} impurities from $ZnSO_4$ electrolyte. All experiments were carried out in a controlled 500 mL reactor containing 100 g/L $ZnSO_4$ as the base solution, with initial concentrations of Cd^{2+} and Cu^{2+} were 0.1 and 0.5 g/L, respectively. High-purity zinc powder (99.9%) was added at dosages of 1–3 g/L, and a 20 kHz ultrasonic field (0–100 W) was applied to promote the displacement reaction. Magnetic stirring at 400 rpm ensured uniform mixing throughout the process. After reaction, solid–liquid separation was performed, and the filtrate was analyzed using inductively coupled plasma optical emission spectroscopy to determine residual metal concentrations. The removal efficiencies (Re) of Cu^{2+} and Cd^{2+} ions were calculated using Equation (1).

$$R_e = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

where C_0 and C represent the Cu^{2+} and Cd^{2+} concentrations before and after removal, respectively. The Cu^{2+} and Cd^{2+} concentration was measured thrice to avoid errors.

Supplementary Note 3: The purified slag were determined using field-emission scanning electron microscopy (SEM; S-4800, Hitachi, Japan) and transmission electron microscopy (TEM; JEM-2100F, Electron Optics Laboratory Co., Ltd., Japan). The crystal structures and chemical surface states of the purified slag were analyzed

using X-ray diffraction (XRD; PANalytical, Nicolet Inc., Netherlands) and X-ray photoelectron spectroscopy (XPS; PHI-5000 Versaprobe II, Japan). Electron paramagnetic resonance (EPR) spectroscopy (JES-X320, JEOL Ltd., Japan) was used to detect the free radical in the ultrasonic system. The pore size, specific surface area, and adsorption isotherms of the purified slag were measured using an automatic specific surface and porosity analyzer (BET, Micromeritics 3Flex, USA). The element distribution of the purified slag was analyzed using an electron probe microanalyzer (EPMA, JXA-8530F PLUS, Japan). The particle size distribution of purified slag was measured using a laser particle size meter (Mastersizer 2000, Britain). The contact angle measuring instrument (JY-82B Kruss DSA, Germany) was used to analyze the wettability purified slag.

All electrochemical measurements were performed on RST-5200 electrochemical workstation (RST-5200; Zhengzhou Shiruisi Instrument Technology Co. Ltd., Zhengzhou, China) in a simulated purification solution ($ZnSO_4$) at 60℃. This study used a three electrode system, with zinc sheet as the working electrode, carbon rod as the counter electrode, and saturated mercuric sulfate electrode (MSE) as the reference electrode. Electrochemical impedance spectroscopy (EIS) was performed across a frequency range of 100 kHz to 0.01 Hz, with an AC amplitude of 5 mV. The Tafel curve is recorded in the potential of -3 to 3 V. Perform electrochemical testing three times to maintain repeatability.

Supplementary Note 4:

Economic analysis:

The cost breakdown includes: 1 $ = 7.0996 RMB, 1 kWh = 0.05 $, 1 ton of industrial water = 0.41 $.

Purification of Cu^{2+} and Cd^{2+} ions by ultrasonic enhanced zinc powder replacement

ultrasonic power 70 W, temperature 60°C, time 30 min, pH =4 zinc powder content 2 g/L.

① Material cost:

2 g/L zinc powder: 0.36608 $; 500 mL H_2O: 0.000205 $.

The total material cost = 0.36608 $ + 0.000205 $ = 0.366285 $.

② Energy consumption:

Stirring + heating: 60 W * 1.5 h+ 70 W * 1.5 h = 0.171 kWh =0.00975 $

③ Total costs:

Material cost + Energy consumption: 0.366285 $ + 0.00975 $= 0.376035 $

Purification of Cu^{2+} and Cd^{2+} ions by conventional zinc powder replacement

① Material cost:

4 g/L zinc powder : 0.73216 $; 500 mL H_2O : 0.000205 $.

The total material cost = 0.73216 $ + 0.000205 $ = 0.732365 $

② Energy consumption:

Heating: 80 W * 2 h= 0.16 kWh = 0.008 $

Material cost + Energy consumption: 0.732365 $+ 0.008 $= 0.740365 $

Thus, ultrasound-enhanced zinc powder purification of Cu^{2+} and Cd^{2+} is more economical and lower energy consumption, which contributes to the green and sustainable development of purification zinc sulfate solution.

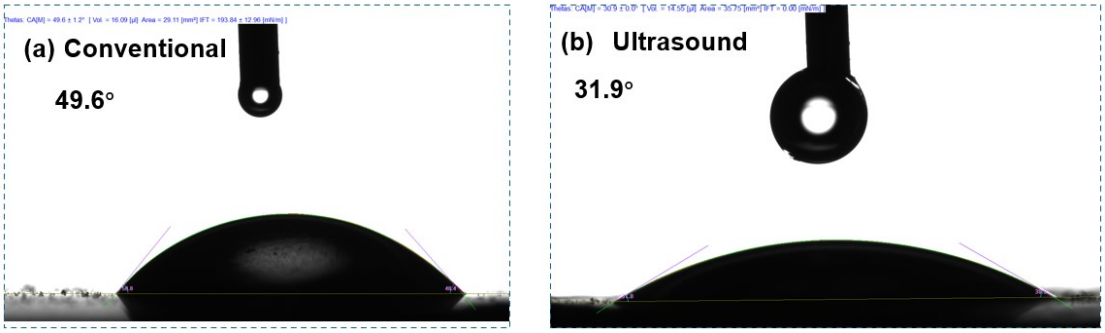

Fig. S1. Contact angle of purified slag. Conventional (a) and Ultrasound (b).

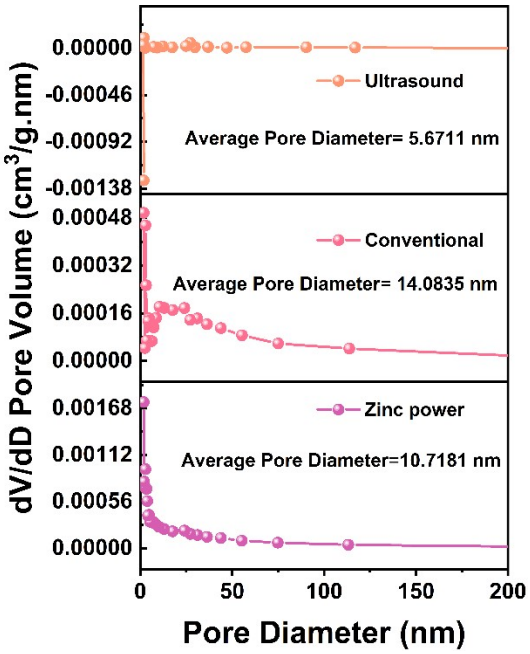

Fig. S2. Pore Diameter distribution of purification slag

Table S1 The E-pH equilibrium equations of Cu-H_2O and Cd-H_2O systems at 25°C and standard pressure

Number	electrode reaction equation
1	$Cd^{2+}+2e=Cd$
2	$2H^{+}+2e-=H_2$
3	$Cd(OH)_2+2e-=Cd+2OH^{-}$
4	$O_2+4H^{+}+4e-=2H_2O$
5	$Cu^{2+}+2e=Cu$
6	$Cu_2O+2H^{+}+2e-=Cu+H_2O$
7	$Cu(OH)_2+2e-=Cu+2OH^{-}$