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Removal of Cd^{2+} from Zinc Smelter Wastewater Using Graphene Oxide Foam Cross-Linked with Epichlorohydrin: Comprehensive Optimization, Isotherm, Kinetic and Real Water Column Studies

Lakshmi Prasanna Lingamdinne[a], Ganesh Kumar Reddy Angaru[a], Yeeun Jeon[a], Suhyun Lee[a], Janardhan Reddy Koduru[a]*, Jae-Kyu Yang[a], Yoon-Young Chang[a]*

[a] Department of Environmental Engineering, Kwangwoon University, Seoul 01897, Republic of Korea

*Corresponding author: reddyjchem@gmail.com (JR Koduru), yychang@kw.ac.kr (YY Chang),

2.1. Materials and Characterization techniques

2.1.1 Materials

All reagents used in the present study, including Cadmium Nitrate ($Cd(NO_3)_2$), acetic acid, sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium chloride (NaCl), calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$),sodium carbonate (Na_2CO_3), sodium nitrate ($NaNO_3$), sodium sulfate (Na_2SO_4), and sodium phosphate (Na_3PO_4), were of analytical grade and were purchased from Samchun Chemicals in South Korea. GO was supplied by the Stranded Graphene Company (South Korea). Chitosan was purchased from Sigma–Aldrich (United).

2.1.2 Analytical studies

X-ray Diffraction analysis was analyzed in the 2θ range of 0 –80° with Cu Kα radiation to identify the crystalline/amorphous nature of the GO, CSGO foam, and EPCSGO foam. The presence of different functional groups was detected using Fourier transform infrared (FT-IR) spectrometry (IR Spirit, Shimadzu Corporation, Japan) in the range 4000–400 cm−1 and X-ray photoelectron spectroscopy (XPS) (PHI Quantera-II, Ulvac-PHI, Kanagawa, Japan). Scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS) (S-4300 with QUANTAX EDS, Bruker, Germany) was used to investigate the surface morphologies of the CSGO and EPCSGO foams. The N_2 adsorption & desorption isotherms of the fabricated composite were obtained using an Autosorb-1 (Quantachrome Instruments, Boynton Beach, FL, USA) instrument, which was also used to measure the pore size, surface area, and pore width. Inductively coupled plasma-optical emission spectroscopy (ICP-OES; Perkin-Elmer, USA) was used to measure metal concentration. A 340i pH meter was employed to measure all pH readings (WTW, Germany).

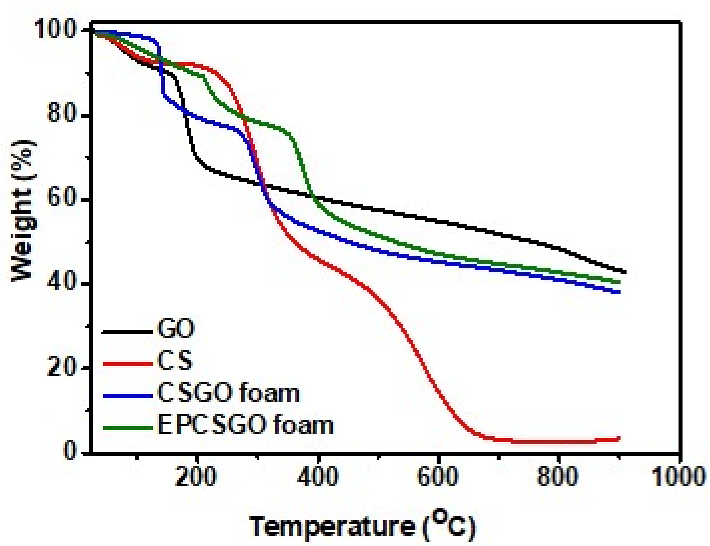

Fig. S1.TGA of GO, CS, CSGO foam and EPCSGO foam. Analyzed at a heating rate of 10 °C min^{-1}.

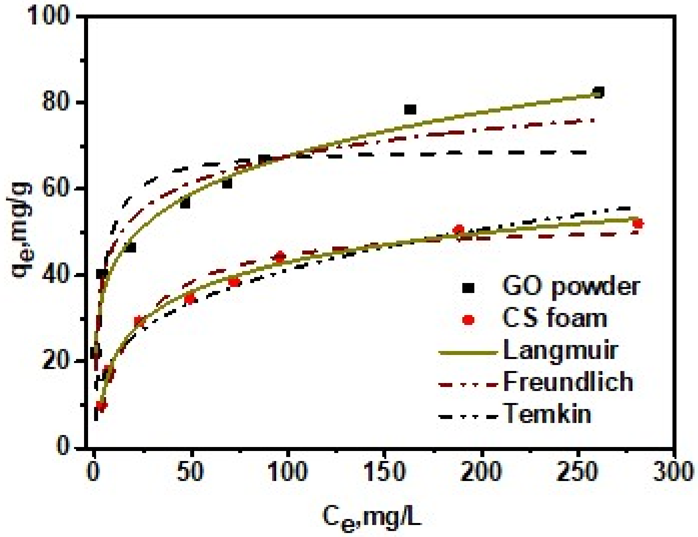

Fig. S2. Cd^{2+} adsorption isotherm on GO powder and CS foam (0.5 g/L), at 298 K, pH 6.0 for 300 min equilibrium time.

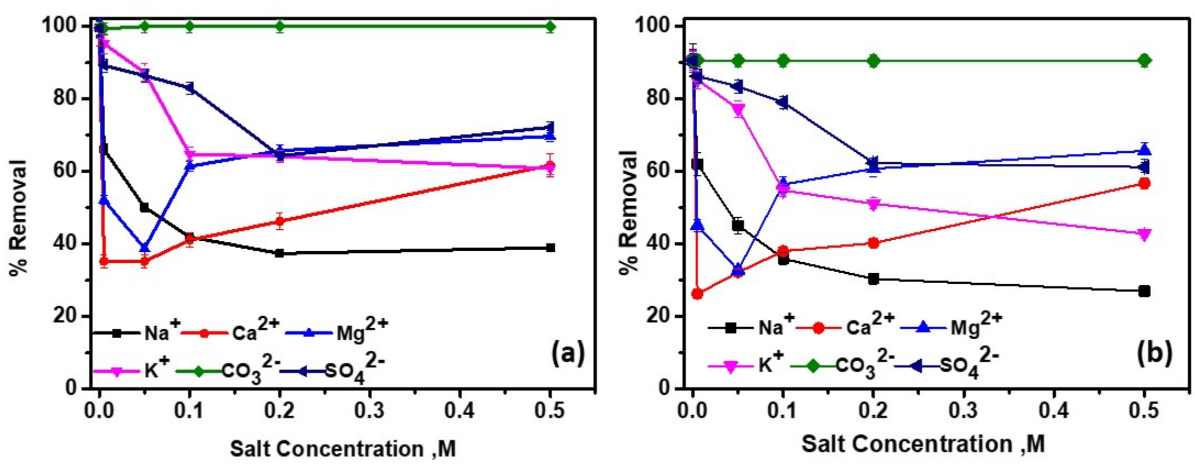

Fig. S3. Salt effect on Cd^{2+} (20 mg/L) adsorption on CSGO foam and EPCSGP foam (0.5 g/L), at pH 6.0 and 298K.

Table S1. Heavy metal concentrations in a groundwater sample from the smelter, compared to Korean industrial wastewater effluent standards and Korean drinking water quality standards (Korea Ministry of Environment).

Factor	Concentration in groundwater (mg/L)
Cd	81.81
Zn	988.7
Fe	39.6
Mn	113.0
Cu	3.7
Al	119.8
K	38.9
Na	125.8
Ca	227.3
Mg	133.9
SO_4^{2-}	5120
Cl^-	96
NO_3^-	23.3
NH_4^+	21.30
TOC	1.9

Table S2. Thermodynamic studies of Cd^{2+} on EPCSGO foam (pH = 6.0 and dose = 0.5 g /L)

Temperature, K	$\Delta G° = -RT\ lnK_c$, **(kJ/mol)**	(ΔH°), **kJ/mol**	(ΔS°), **J/mol. K**	**lnKc**
298	-38.885	33.831	122.66	13.120
308	-40.637			13.526
323	-43.668			13.931

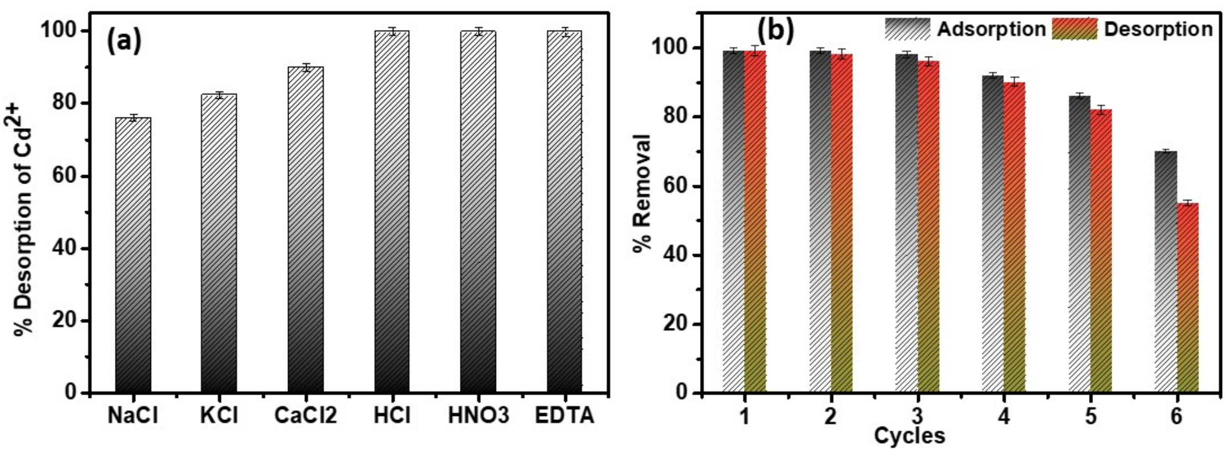

Fig. S4. Cd^{2+} desorption on EPCSGO foam with different desorption reagents (a), Cd^{2+} adsorption and desorption on EPCSGP foam with 0.1 M EDTA.

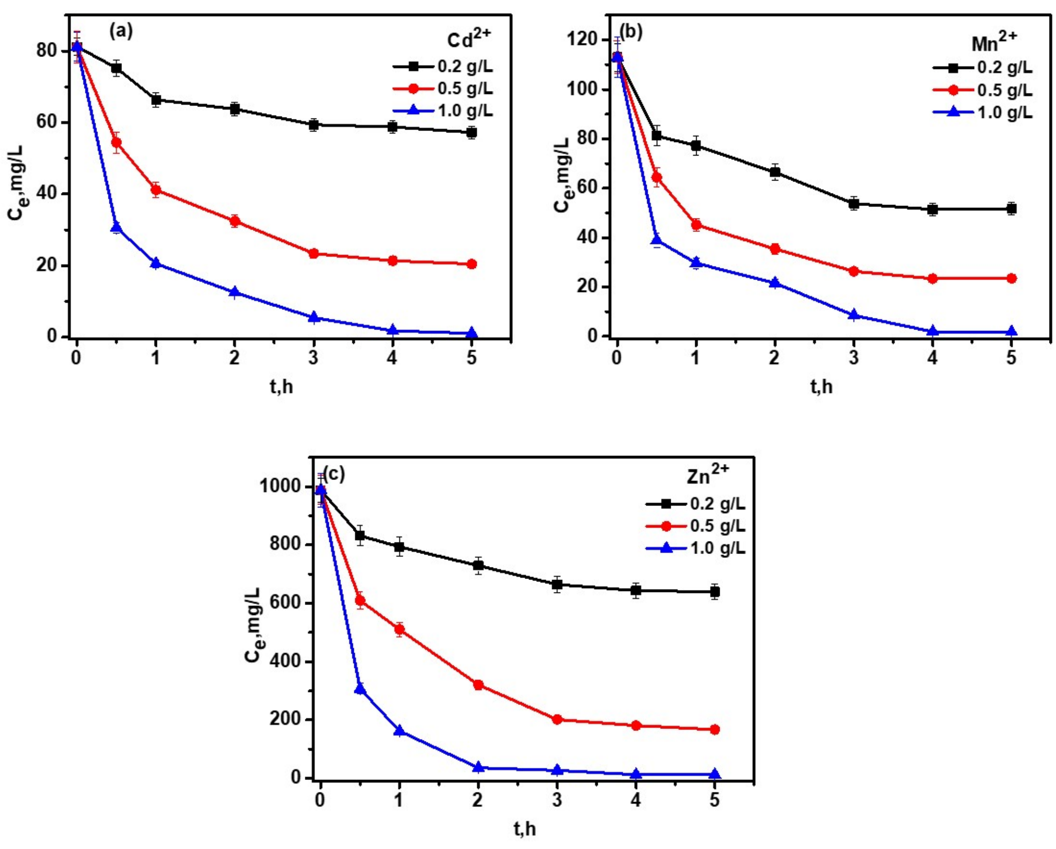

Fig. S5. (a)Cd^{2+}, (b)Mn^{2+} and (c)Zn^{2+} removal after injection of various concentration of $NaHCO_3$ into the industrial smelt wastewater.

Table S3. Modeling of Cd^{2+} removal in a fixed bed column utilizing EPCSGO foam.

	Thomas		R^2	**Bohart–Adams**		R^2	**Yoon–Nelson**		R^2
	k_{Th} (L/ mg·h)	Q_{Th} **(mg/g)**		**k_{ab} (L/mg·h)**	Q_{ab} **(mg/cm³)**		**k_{YN} (h^{-1})**	**τ (h)**	
Synthetic water	0.003	122.08	0.992	0.002	25.41	0.914	0.073	692	0.955
Industrial waste water	0.25	35.95	0.989	0.114	0.54	0.916	0.008	299	0.955