Supporting Information

Boosting Cu Ions Capture in High-Salinity Environments with Amino-Functionalized Millispheres

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DLVO theory

Developed by Derjaguin and Landau, Verwey and Overbeek in 1940s, DLVO theory was employed to predict well adsorption performance caused by salinity [1-3]. This states that the colloid stability is related to the total interaction potential, which is the sum of attractive London-van der Waals energy (E_{vdW}) and the electrostatic repulsion energy (E_{EDL}) for charged colloidal particles:

$$E_{DLVO} = E_{vdW} + E_{EDL} \tag{1}$$

However, DLVO theory can be used to describe the adsorption of colloids on a surface. If the colloidal particles are approximately spherical and the surface of the adsorbent is assumed to be flat, the interaction between the particles and collectors can be described using sphere-plate DLVO energy profile. For a spherical particle interacting with a flat plate, the van der Waals energy is related to the separation distance as[1, 2, 4, 5]:

$$E_{vdW} =- \frac{A}{6}[\frac{2R^2}{H_0(4R+H_0)} + \frac{2R^2}{(2R+H_0)^2} + ln\frac{H_0(4R+H_0)}{(2R+H_0)^2}] \tag{2}$$

Where A is the Hamaker constant, R is the radius of the sphere, and H_0 is the distance of closet point on the sphere surface from the flat plate.

The double layer force is evaluated from the swelling pressure acting between two charged plates, for which the linearized Poisson-Boltzmann equation is solved numerically. In a monovalent electrolyte, the electric potential φ(x) satisfies the equation:

$$\frac{d^2\varphi}{dx^2} = \frac{k^2}{\beta e} sinH_0(\beta e\varphi) \tag{3}$$

Where e is the elementary charge, $\beta^{-1}=kT$ is the thermal energy. Thereby, k is the Boltzmann constant and T is the absolute temperature. The Debye parameter k is given by:

$$k^2 = \frac{2\beta e^2 c}{\varepsilon_0 \varepsilon} \qquad (4)$$

Where c is the concentration of the monovalent aqueous electrolyte, ε_0 is the permittivity of vacuum, and ε is the dielectric constant of water. A temperature of 25 °C and $\varepsilon = 80$ are being used. The Poisson-Boltzmann equation is solved between two plates situated at $x = \pm H_0/2$ where h is the distance between the two plates numerically subject to the constant regulation boundary condition.

$$\pm \varepsilon_0 \varepsilon \frac{d\varphi}{dx}|_{x = \pm H_0/2} = \sigma - C_I[\varphi\left(\pm \frac{H_0}{2}\right) - \varphi_D] \qquad (5)$$

Where σ, φ_D, and C_I are the surface charge density, diffuse layer potential, and inner capacitance of the isolated surface. The surface charge density and the diffuse layer potential of the isolated surfaces are related by the Grahame relation:

$$\sigma = \frac{2\varepsilon_0 \varepsilon k}{\beta e} sinH_0(\frac{\beta e \varphi_D}{2}) \qquad (6)$$

The interface is characterized by the regulation parameter:

$$p = \frac{C_D}{C_I + C_D} \qquad (7)$$

Where C_D is the diffuse layer capacitance given by

$$C_D = \varepsilon_0 \varepsilon k cosH_0(\frac{\beta e \varphi_D}{2}) \qquad (8)$$

Thereby, the constant regulation boundary condition is being used, which introduces a regulation parameter p. This parameter assumes simple values for the constant charge (p = 1) and constant potential (p = 0) boundary conditions. The independent parameters entering this model are thus the diffuse layer potential φ_D, regulation parameter p, and the electrolyte concentration c.

The double layer force is obtained by calculating the disjoining pressure originating from the double layer from the relation:

$$\Pi_{dl} = 2kTc[\cosh(\beta e\varphi) - 1] - \frac{1}{\varepsilon_0\varepsilon}(\frac{d\varphi}{dx})^2$$

And subsequently one invokes a subsequent integration and the Derjaguin approximation

$$E_{EDL} = 2\pi R \int_h^\infty \Pi_{dl}(H_0^{'})dH_0^{'} \quad (9)$$

Table S1. BJH specific surface areas, average pore diameters, pore volumes, and pore size distributions of EDA@CMPS and CMPS.

Adsorbents	Functional group	BJH Specific Surface Area (m^2/g)	Average Pore Diameter (nm)	BJH dV/dw pore distribution (%)		
				Micropore < 2 nm	Mesopore 2~50 nm	Macropore > 50 nm
CMPS	$-CH_2Cl$	30.15	26.45	4.34	82.62	13.04
EDA@CMPS	$-NH_2$	39.40	25.65	4.5	81.81	13.69

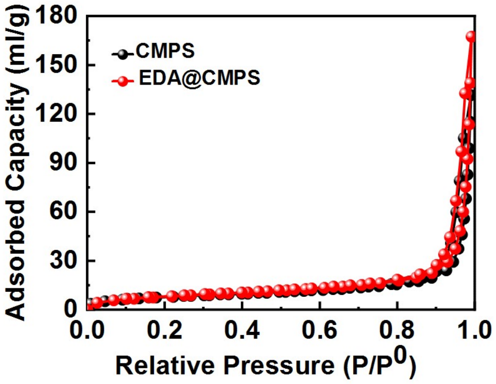

Figure S1. N_2 adsorption-desorption isotherm curves of CMPS and EDA@CMPS.

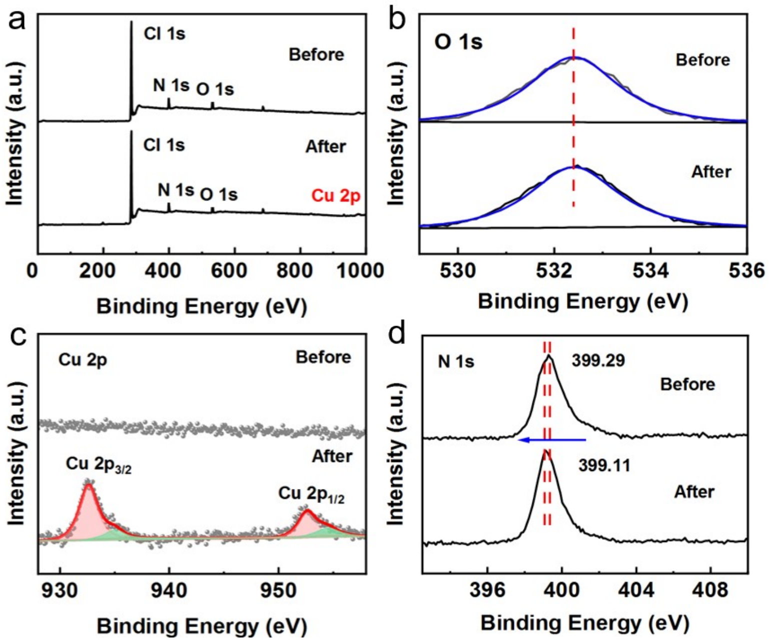

Figure S2. The XPS spectra (a) in O 1s (b), Cu 2p (c), and N 1s (d) before and after adsorption.

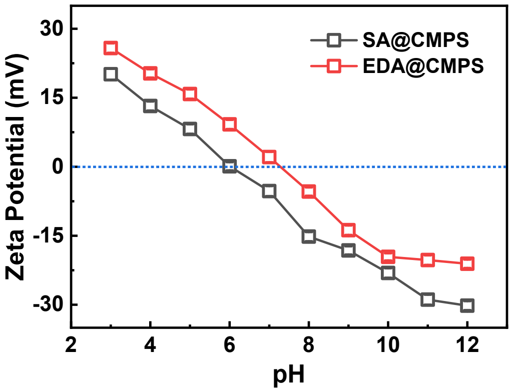

Figure S3. Zeta potential as a function of pH for SA@CMPS and EDA@CMPS.

Table S2. Kinetic parameters and intra-particle diffusion simulation for the adsorption of Cu^{2+} on EDA@CMPS in saline solution and non-saline solution.

[Cu:NaCl]	Pseudo-second-order model			Intraparticle diffusion					
				First stage		Second stage		Third stage	
	k_2, ×10^{-2} min^{-1}	Q_e mmol/g	R^2	k_1, ×10^{-3} $min^{-0.5}$	C_1 mmol/g	k_2, ×10^{-3} $min^{-0.5}$	C_2 mmol/g	k_3, ×10^{-3} $min^{-0.5}$	C_3 mmol/g
1:0	1.3	0.65	0.992	0.8	-0.04	0.4	0.19	0.056	0.50
1:10	1.7	1.15	0.997	1.4	-0.06	0.6	0.39	0.076	0.90

Table S3. Thermodynamic parameters of Cu(II) removal by EDA@CMPS.

[Cu : NaCl]	**Temperature, K**	**ΔG (kJ/mol)**	**ΔH (kJ/mol)**	**ΔS (J/mol·K)**	**TΔS (J/mol)**
1:0	283	-15.92	14.20	106.56	30.16
	298	-17.61			31.75
	313	-19.11			**33.35**
1:10	283	-19.21	17.60	130.86	37.03
	298	-21.87			38.99
	313	-23.09			40.96

Table S4. Zeta potentials of EDA+Cu(II) in different salinity.

Samples	Zeta potential, mV
EDA+Cu(II)	-44.48
EDA+Cu(II)+5 mM NaCl	-35.1
EDA+Cu(II)+25 mM NaCl	-15.2
EDA+Cu(II)+50 mM NaCl	-10.1
EDA+Cu(II)+100 mM NaCl	-2.18
EDA+Cu(II)+500 mM NaCl	0.08

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