Supplementary Information

Nanostructured Layered double hydroxide (NLDH) - Zn/Al-based materials: Strategy to Improve Performance for Zirconium Sorption from Acidic Sulfate Solution

Ahmed M. Masoud [1], ***Amal E. Mubark*** [1*], ***Mohamed H. Taha*** [1], ***Saber Ibrahim*** [2, 3]

[1] *Nuclear Materials Authority, P.O. Box 530, El Maddi, Cairo, Egypt*
[2] *Packaging Materials Department, National Research Centre, 12622, Dokki, Cairo, Egypt*
[3] *Nanomaterials Investigation Laboratory, central Laboratories Network, National Research Centre, Dokki, Cairo, 12622, Egypt*

*Corresponding author: *amal_mubark2014@yahoo.com, Tel.:+201018600164*

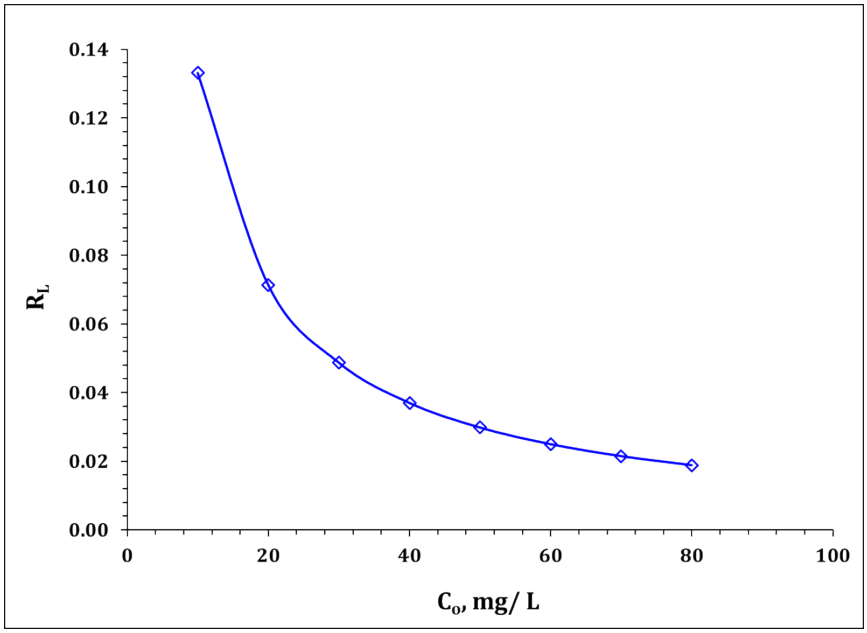

Figure S1: *Separation factor R_L of Zr(IV) adsorption process.*

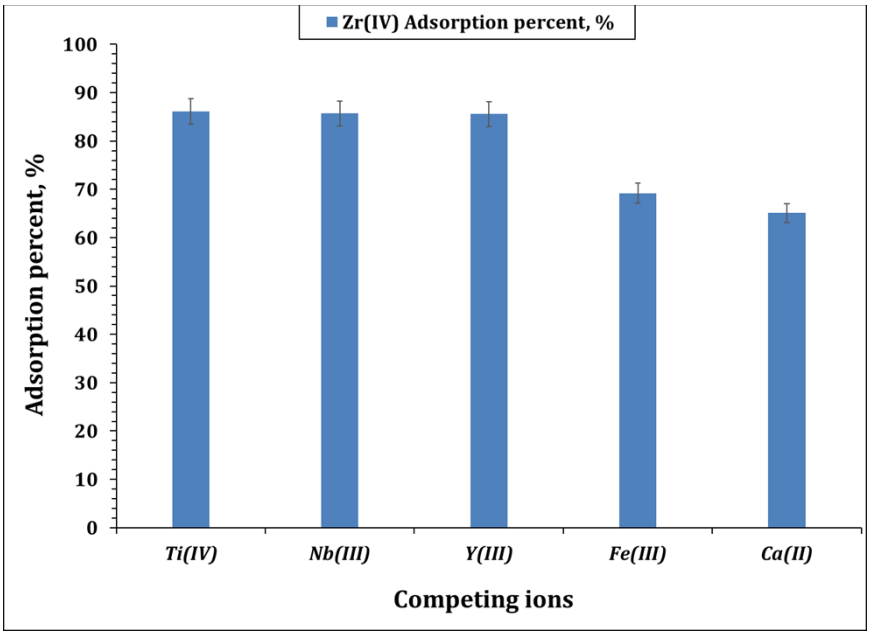

Figure S2: *Effect of co-existing elements on Zr(IV) ions adsorption process.*

Table S1: *Kinetic, isotherm, and thermodynamics equations for Zr(IV) adsorption process* ***[1-11]***.

Kinetics	Equations
Pseudo-first-order	$q_t = q_1\left(1 - e^{-k1t}\right)$
Pseudo-second-order	$q_t = \frac{1}{\left(1 \middle\vert k_2 q_2^2\right) + \left(t \middle\vert q_2\right)}$
Intra-particle diffusion model (IPD)	$q_t = K_{id}\, t^{0.5} + C_i$
Isotherms	**Equations**
Langmuir model	$q_e = \frac{q_m k_L C_e}{1 + k_L C_e}$
Freundlich model	$q_e = K_F C_e^{1/n_F}$
Temkin model	$q_e = \frac{RT}{b_T} \ln K_T C_e$
Sips model	$q_e = \frac{q_S \left(k_S C_e\right)^{mS}}{1 + \left(k_S C_e\right)^{mS}}$
Thermodynamics	**Equations**
	$\log K_C = -\frac{\Delta H^o}{2.303\, R} X \frac{1}{T} + C$
	$-\Delta G^o = 2.303\, RT \log K_C$
	$\Delta G^o = \Delta H^o - T\, \Delta S^o$
Fitting	**Equations**
Coordination coefficient (R^2)	$R^2 = 1 - \frac{\sum_1^n \left(q_{exp} - q_{pred}\right)^2}{\sum_1^n \left(q_{exp} - \bar{q_{exp}}\right)^2}$
Chi-square coefficient (x^2)	$x^2 = \sum \left[\frac{\left(q_{exp} - q_{pred}\right)^2}{q_{pred}}\right]$

qe (mg g^{-1}) is the equilibrium concentration of Zr(IV) species, and qt (mg g^{-1}) is the adsorbed amount of Zr(IV) species ions after time t (min), Ce (mg L^{-1}) is equilibrium concentration of Zr(IV) species. k_1 (min^{-1}) and k_2 (min^{-1}) are the rate constants for the pseudo first and second order, respectively. K_{id} (mg/g. $min^{0.5}$) is a rate constant, and C is the thickness of the boundary layer. q_m and q_S are the maximum sorption capacity (mg. g^{-1}) of Langmuir and Sips models. k_L (L. mg^{-1}), K_F (L/ mg), K_T (L min^{-1}), and K_S (L/ mg) are represent the constants of Langmuir, Freundlich, Temkin, and Sips models. n refer to the sorption intensity, b_T is Temkin constant that refers to the adsorption heat, mS is Sips constant. $\boldsymbol{q_s}$ is the theoretical isotherm saturation capacity (mg/g). K_C is a non-dimensional equilibrium constant and it equals K_d X 1000 X ρ **[8-10]**; T is the temperature (K), $\boldsymbol{R}$ is the universal gas constant (8.314 J mol^{-1}. K^{-1}), ρ is solution denisty g/ L, and C is a constant. R^2 and x^2 are the coordination and Chi-square coefficients respectively, the number of test points is n, the experimental equilibrium capacity is q_{exp} (mg g^{-1}), while the predicted capacity is q_{pred} (mg g^{-1}).

References:

1) Hu, Q., Pang, S. and Wang, D., 2022. In-depth insights into mathematical characteristics, selection criteria and common mistakes of adsorption kinetic models: a critical review. Separation & Purification Reviews, 51(3), pp.281-299.
2) Yao, C. and Chen, T., 2017. A film-diffusion-based adsorption kinetic equation and its application. Chemical Engineering Research and Design, 119, pp.87-92.
3) Elzoghby, A., Fahmy, H., Taha, M. and Ibrahim, S., 2023. Active carbon-based waste packaging materials for uranium sorption from aqueous solution. Environmental Science and Pollution Research, pp.1-16.
4) Abou-Hadid, A.F., El-Behairy, U.A., Elmalih, M.M., Amdeha, E., El Naggar, A.M., Taha, M.H. and Hussein, A.E., 2022. Production of efficient carbon fiber from different solid waste residuals for adsorption of hazardous metals from wastewater samples. Biomass Conversion and Biorefinery, pp.1-16.
5) Wang, J. and Guo, X., 2020. Adsorption isotherm models: Classification, physical meaning, application and solving method. Chemosphere, 258, p.127279.
6) Al-Ghouti, M.A. and Da'ana, D.A., 2020. Guidelines for the use and interpretation of adsorption isotherm models: A review. Journal of hazardous materials, 393, p.122383.
7) M. H. Taha, "Sorption of U(VI), Mn (II), Cu(II), Zn(II), and Cd(II) from multi-component phosphoric acid solutions using MARATHON C resin," *Environ. Sci. Pollut. Res. Int.*, vol. 28, no. 10, pp. 12475–12489, Mar. 2021, doi: 10.1007/S11356-020-11256-3.
8) Saleh, T.A., 2022. Kinetic models and thermodynamics of adsorption processes: classification. In Interface Science and Technology (Vol. 34, pp. 65-97). Elsevier.
9) Kausar, A., Naeem, K., Iqbal, M., Nazli, Z.I.H., Bhatti, H.N., Ashraf, A., Nazir, A., Kusuma, H.S. and Khan, M.I., 2021. Kinetics, equilibrium and thermodynamics of dyes adsorption onto modified chitosan: a review. Zeitschrift für Physikalische Chemie, (0), p.000010151520191586.
10) Morsy, A., Taha, M.H., Saeed, M., Waseem, A., Riaz, M.A. and Elmaadawy, M.M., 2019. Isothermal, kinetic, and thermodynamic studies for solid-phase extraction of uranium (VI) via hydrazine-impregnated carbon-based material as efficient adsorbent. Nuclear science and techniques, 30, pp.1-11.

11) Mubark, A.E.,2024. Sequestration of zirconium and hafnium content using magnetic cellulose/chitosan nanocomposites from waste effluents, J. Water Process Eng. 58, 104759. https://doi.org/10.1016/J.JWPE.2023.104759.

Table S2: *The values of* Morris-Weber model terms *for Zr(IV) sorption using Zn/Al-LDH sorbent.*

Weber and Morris model	**Stage I**	
	k_i (mg/g $min^{1/2}$)	10.12
	C	18.1
	R^2	0.97
	Stage II	
	k_i (mg/g $min^{1/2}$)	0.88
	C	78.3
	R^2	0.96

Table S3: Zr(IV) desorption from loaded Zn/Al-LDH material using different solutions (0.5 g/L, room temperature; 120 min).

Eluent type	Sorption efficiency, %
1.0 M Hydrochloric acid	98.1
1.0 M Sulfuric acid	76.7
1.0 M Nitric	64.3

Table S4: Sorption/ desorption cycles for Zr(IV) recovery using *Zn/Al-LDH* material.

No. of cycle	Zr(IV)	
	Sorption	**Desorption**
1	90.6	98.0
2	90.2	98.0
3	89.9	97.8
4	89.4	97.2
5	88.9	96.7
6	88.7	95.8

Table S5. Chemical composition of the real waste solution before, and after the adsorption process, as well as the adsorption efficiency.

Constituents	**C_o mg/ L**	**C_e mg/ L**	**E%**
Zr (IV)	120	15	87.5
V (IV)	100	97	3.0
Ti (IV)	66	56	15.2
Fe(III)	230	190	17.4
Na (I)	640	622	2.8
K (I)	252	239	5.2
SO_4(-II)	980	973	1