Supplementary Information (SI)

Recovery of Lithium from Industrial Li-Containing Wastewater Using Fluidized-Bed Homogeneous Granulation Technology

Van Giang Le [1], The Anh Luu [1], Huu Tuan Tran [2,3], Ngoc T. Bui [4], M. Mofijur [5,6], Minh Ky Nguyen [7], Xuan Thanh Bui [8], M. B. Bahari [9], Hoang Nhat Phong Vo [10], Chi Thanh Vu [11], Guo-Ping Chang Chien [12] and Yao-Hui Huang [13,*]

[1] Central Institute for Natural Resources and Environmental Studies, Vietnam National University, Hanoi, 100000, Viet Nam; levangiangcres@vnu.edu.vn (V.G.L.); ltanh@cres.edu.vn (T.A.L.)
[2] Laboratory of Ecology and Environmental Management, Science and Technology Advanced Institute, Van Lang University, Ho Chi Minh City 700000, Viet Nam; huutuan.tnx@gmail.com
[3] Faculty of Applied Technology, School of Engineering and Technology, Van Lang University, Ho Chi Minh City 700000, Viet Nam
[4] School of Chemical, Biological, and Materials Engineering and School of Civil Engineering and Environmental Science, University of Oklahoma, Norman, OK 73019, USA; ngoctbui21@ou.edu
[5] Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology Sydney, Ultimo, NSW 2007, Australia; mdmofijur.rahman@uts.edu.au
[6] Mechanical Engineering Department, Prince Mohammad Bin Fahd University, Al Khobar 31952, Saudi Arabia
[7] Faculty of Environment and Natural Resources, Nong Lam University, Hamlet 6, Linh Trung Ward, Ho Chi Minh City 700000, Viet Nam; nmky@hcmuaf.edu.vn
[8] Faculty of Environment and Natural Resources, Ho Chi Minh City University of Technology, Ho Chi Minh City 700000, Viet Nam; bxthanh@hcmut.edu.vn
[9] Faculty of Science, Universiti Teknologi Malaysia, Johor Bahru 81310, Malaysia; mahadibahari@utm.my
[10] Climate Change Cluster, Faculty of Science, University of Technology Sydney, 15 Broadway, Ultimo, NSW 2007, Australia; phong.vo@uts.edu.au
[11] Civil and Environmental Engineering Department, The University of Alabama in Huntsville, Huntsville, AL 35899, USA; thaanhchivu@gmail.com
[12] Center for Environmental Toxin and Emerging Contaminants Research, Cheng Shiu University, Taiwan; guoping@gcloud.csu.edu.tw
[13] Department of Chemical Engineering, National Cheng Kung University, Tainan 71710, Taiwan
* Correspondence: yhhuang@mail.ncku.edu.tw

Text S1. Analysis of purity of the pellet products and pellet size distribution

Purity analysis

Pellets (5.0 g) were used for the analysis their soluble components and Li_3PO_4 purity. Pellets were dissolved in 100 mL of 0.5 M HCl and then measured by ICP-OES. Li_3PO_4 purity (P_{Li}) was calculated as follows.

$$P_{Li} = \frac{n_{Li} \times M_{Li3PO4}}{m_{Li3PO4}} \times 100\% \quad \text{(S1)}$$

where n_N is the molar concentration of Li^+ (mol), $\mathrm{M_{Li3PO4}}$ the molar mass (g/mol) of Li_3PO_4, and $\mathrm{m_{Li3PO4}}$ the pellet mass (g).

Size distribution

The dried pellets were sieved at different meshes (0.15, 0.25, 0.50, 0.75, and 1.0 mm) using the Auto Mechanical Sieve Series. Then, pellets with same dimensions were weighed for the estimation of size distribution as follows.

$$[Li - pellet]_W = \frac{W_{sieve}}{W_{total}} \times 100\% \quad \text{(S2)}$$

where $\mathrm{w_{sieve}}$ is the weight of pellets greater than that specific mesh size (g), and $\mathrm{w_{total}}$the total weight of the pellets (g).

Text S2. Thermodynamic calculations of reaction products in the FBHo-G reactor

In a water matrix containing Li^+, PO_4^{3-} and H_2O, there could be species like H^+, OH^-, Li^+, LiOH, $LiHPO_4^-$, PO_4^{3-}, HPO_4^{2-}, H_3PO_4, and the precipitated $Li_3PO_{4\,(s)}$. Thermodynamic data of equilibrium reactions in such a water matrix follow Eq. (S3)–(S9).

$$LiOH \leftrightarrow Li^+ + OH^- \qquad K_1 = 10^{-0.36} \qquad (S3)$$

$$LiHPO_4^- \leftrightarrow Li^+ + HPO_4^{2-} \qquad K_2 = 10^{-0.72} \qquad (S4)$$

$$H_2O \leftrightarrow OH^- + H^+ \qquad K_2 = 10^{-14} \qquad (S5)$$

$$H_3PO_4 \leftrightarrow H_2PO_4^- + H^+ \qquad K_{p1} = 10^{-2.5} \qquad (S6)$$

$$H_2PO_4^- \leftrightarrow HPO_4^{2-} + H^+ \qquad K_{p2} = 10^{-7.2} \qquad (S7)$$

$$HPO_4^{2-} \leftrightarrow PO_4^{3-} + H^+ \qquad K_{p3} = 10^{-12.35} \qquad (S8)$$

$$3LiNO_{3(aq)} + PO_4^{3-}{}_{(aq)} \rightarrow 3Li_3PO_{4(solid)} + 3NO_3^-{}_{(aq)} \qquad K_{sp} = 10^{-10.63} \qquad (S9)$$

The total concentrations of lithium and phosphorus should be related to the amount of free lithium ions, lithium hydroxides, phosphate ions, and lithium complexations as shown in Eq. (S10)–(S11).

$$[Li]_{total} = [Li^+] + [LiOH] + [LiHPO_4^-] \qquad (S10)$$

$$[P]_{total} = [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4] + [LiHPO_4^-] \qquad (S11)$$

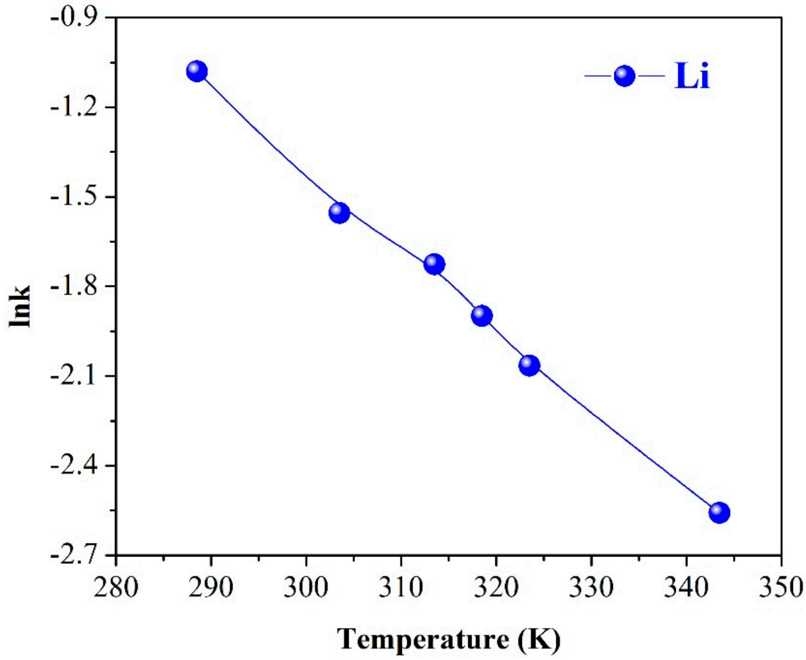

Figure S1. Arrhenius plot calculated for precipitating lithium phosphate at different temperatures [data were fitted with the Arrhenius equation: $lnk = -\frac{E_a}{RT} + lnA$, where R is the energy gas constant (J/(mol·K)), A the pre-exponential factor, E_a the activation energy (kJ/mol), and T (K) the temperature.

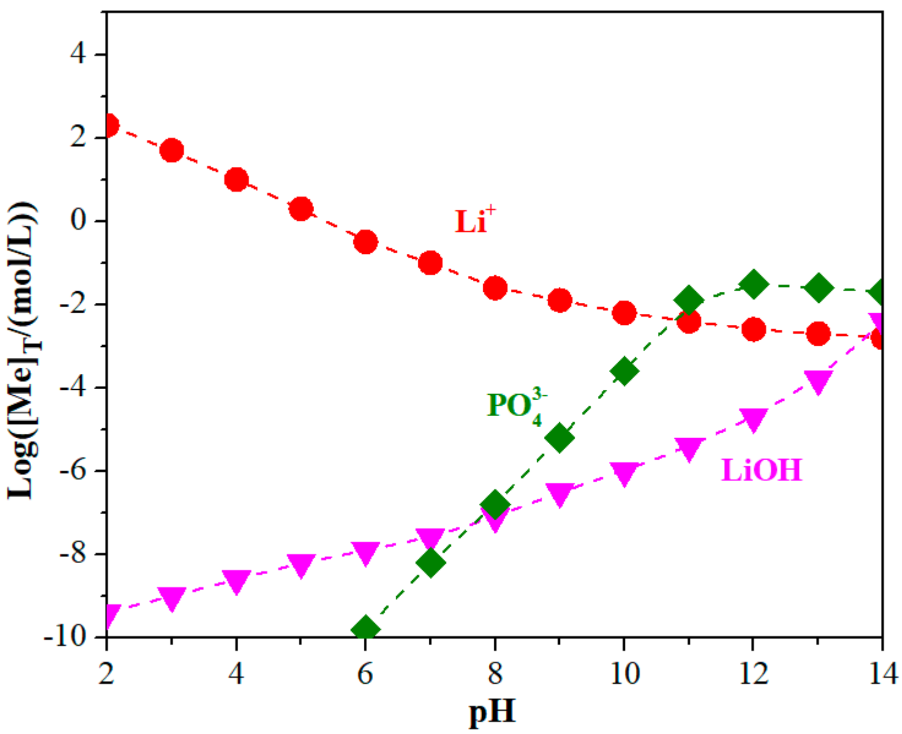

Figure S2. The Log$[Me]_T$-pH diagram of species existing in the FBHo-G reactor.

Figure S3. Photo of lithium phosphate crystal products and their different particle sizes.

Table S1. Experimental parameters of the FBHo-G process.

Symbols	Definitions	Units	Remarks
Q_{Li}, Q_P	Influx rates of lithium and phosphorus ions	mL/min	
Q_t	Total influx rate	mL/min	$= Q_{Li} + Q_P$
Q_r	Reflux rate	mL/min	
C_{Li}, C_P	Conc. of lithium and phosphorus ions in tanks	mM	
$[Li]_t$, $[Li]_s$	Total and soluble effluent lithium ions	mM	
$[P]_t$, $[P]_s$	Total and soluble effluent phosphorus ions	mM	
$[Li]_{in}/[P]_{in}$	Inlet lithium to phosphorus molar ratio		$= C_{Li}Q_{Li}/C_PQ_P$
A_{low}	Internal cross-sectional area of the reaction region	cm^2	
A_{up}	Internal cross-sectional area of the effluent region	cm^2	
U_{out}	Effluent velocity	m/h	$= Q_t/A_{up}$
U	Upflow velocity (hydraulic loading)	m/h	$= (Q_t + Q_r)/A_{low}$
L	Cross-sectional loading	kg m^2/h^{-1}	$= C_PQ_P/A_{low}$
V_T	Total volume of solution in the reactor	mL	
HRT	Hydraulic retention time	Min	$= V_T/Q_t$

Table S2. ICP elemental analysis of FBHo-G pellets.

Elements.	Mean ± SD* (wt%)
Na	3.02 ± 0.05
Li	7.66 ± 0.08
P	24.8 ± 0.05
K	< 0.005

*SD: standard deviation of duplicate measurements.