Front. Chem. Sci. Eng.

https://doi.org/10.1007/s11705-019-1806-3

RESEARCH ARTICLE

Investigation of solution chemistry to enable efficient lithium recovery from low-concentration lithium-containing wastewater

Chunlong Zhao[1,2], Mingming He[2], Hongbin Cao[2], Xiaohong Zheng[2], Wenfang Gao[2], Yong Sun[3], He Zhao[2], Dalong Liu[4], Yanling Zhang[1], Zhi Sun(✉)[2]

1 State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, Beijing 100083, China

2 Beijing Engineering Research Center of Process Pollution Control, Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

3 University of Nottingham Ningbo China, Ningbo 315100, China

4 Henan Bingsheng Biotechnology Company Limited, Kaifeng 475103, China

Received July 26, 2018; accepted December 9, 2018

E-mail: zhisun@126.com

Electronic Supplementary Material

Table S1 Equilibrium reactions

Eq	Equilibrium reaction	Eq	Equilibrium reaction
1	$H_2SO_4+Na_2CO_3=Na_2SO_4+CO_2\uparrow+H_2O$	9	$Ca^{2+}+CO_3^{2-}=CaCO_3$
2	$H_2O=OH^-+H^+$	10	$Mg^{2+}+CO_3^{2-}=MgCO_3$
3	$Fe^{3+}+3OH^-=Fe(OH)_3$	11	$Ca^{2+}+2OH^-=Ca(OH)_2$
4	$Al^{3+}+3OH^-=Al(OH)_3$	12	$Mg^{2+}+2OH^-=Mg(OH)_2$
5	$Ca^{2+}+SO_4^{2-}=CaSO_4$	13	$Li^++F^-=LiF$
6	$Mg^{2+}+SO_4^{2-}=MgSO_4$	14	$2Al(OH)_3+2OH^-=2AlO_2^-+4H_2O$
7	$Ca^{2+}+2F^-=CaF_2$	15	$3Li^++PO_4^{3-}=Li_3PO_4$
8	$Mg^{2+}+2F^-=MgF_2$	16	$2Li^++CO_3^{2-}=Li_2CO_3$

Table S2 The initial molar concentration of different ions in the LCW

Element	Li	Na	Fe	Al	F	Ca	SO_4^{2-}	Mg
Molar Concentration / mol/L	0.288	0.087	0.00143	0.0148	0.0105	0.0075	0.278	0.0125

Table S3 The initial concentration of Fe^{3+}, Al^{3+}, Ca^{2+} and Mg^{2+}, the solubility product constant *Ksp* and the lowest precipitation pH for $Fe(OH)_3$, $Al(OH)_3$, $CaCO_3$ and $Mg(OH)_2$

Element	Concentration / mol/L	Element	*Ksp*	Initial precipitation pH	Ref
Fe^{3+}	1.432×10^{-3}	$Fe(OH)_3$	3×10^{-39}	2.10	1
Al^{3+}	1.48×10^{-2}	$Al(OH)_3$	1.3×10^{-33}	3.65	1
Ca^{2+}	7.5×10^{-3}	$CaCO_3$	2.8×10^{-9}	6.10	1
Mg^{2+}	1.25×10^{-2}	$Mg(OH)_2$	5.6×10^{-12}	9.32	1

1 Removal of impurities from low concentrated Li-containing wastewater

Based on the previous thermodynamic analysis and the E-pH diagram, the impurities removal process can be divided into two procedures, of which the lower pH range where impurities of Fe^{3+} and Al^{3+} are removed and higher pH range where Ca^{2+} and Mg^{2+} impurities are removed. According to the E-pH diagram, the main factors of impurity removal are solution pH and additive dosage. In order to determine the control step and the equilibrium time of chemical reaction, reaction temperature, agitation speed and reaction time were also investigated during the impurity removal process. The effects of agitation speed and reaction time on the impurities removal rate and lithium loss rate were described in supporting information.

1.1 Impurities removal at lower pH range

To avoid introducing other impurities, sodium hydroxide NaOH(aq) (5 mol/L), solid calcium carbonate ($CaCO_3$(s)), solid sodium carbonate (Na_2CO_3(s)) and sodium carbonate solution (Na_2CO_3(aq)) with a concentration of 1.88 mol/L were chosen as the removal reagent at lower pH range, but the $CaCO_3$(s), Na_2CO_3(s) and Na_2CO_3(aq) presented completely different performances at lower range pH during impurity removal. The contrast among three kinds of removal reagent was given in Figs. S1 and S2. As shown in Fig. S1, the ion removal rate of Fe^{3+} and Al^{3+} presented no significant change when NaOH(aq), $CaCO_3$(s), Na_2CO_3(s) and Na_2CO_3 (aq) were added. The ion removal rate of Fe^{3+} and Al^{3+} increased sharply in only one minute in Fig. S2 when NaOH(aq), $CaCO_3$(s) and Na_2CO_3(s) were employed as the removal reagent. The reaction rate was so fast that the apparent kinetics of impurities removal couldn’t be nicely revealed. The Ca^{2+} should also be removed by adding excessive Na_2CO_3 in the second step when $CaCO_3$(s) was used as the removal reagent at the first step. According to Fig. S2 (d), the ion removal rate of Fe^{3+} and Al^{3+} increased slowly and the reaction rate was also slow when Na_2CO_3(aq) was employed as the removal reagent. Therefore, the Na_2CO_3(aq) was chosen as the removal reagent in this experimental procedure.

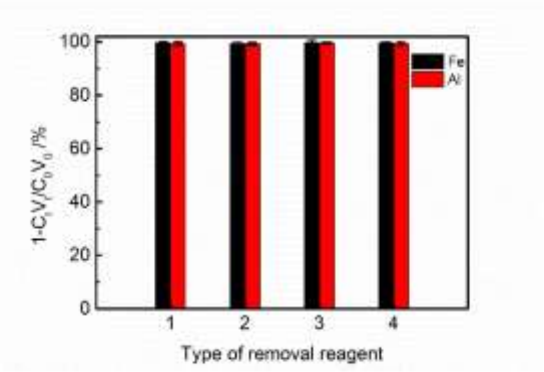


Fig. S1 The ion removal rate of Fe^{3+} and Al^{3+} by adding 1: Na_2CO_3(s), 2: $CaCO_3$(s), 3: Na_2CO_3(aq) and 4: NaOH(aq) as the removal reagent

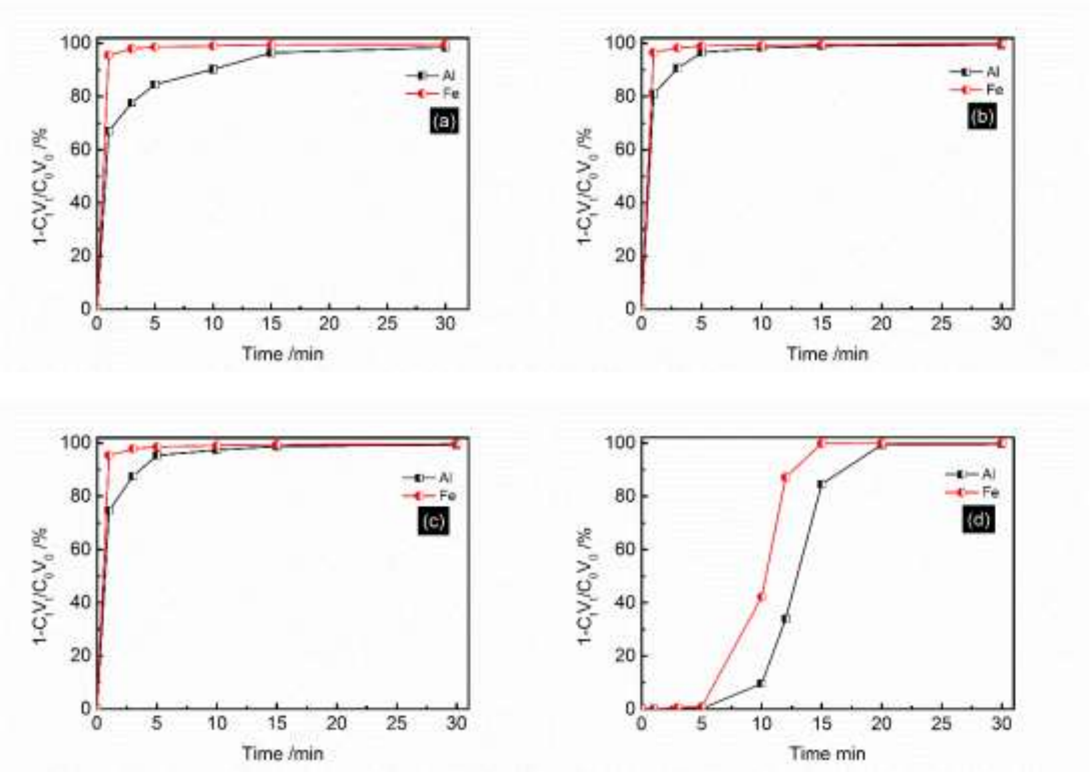


Fig. S2 Effect of reaction time on the ion removal rate of Fe^{3+} and Al^{3+} with adding Na_2CO_3(s) (a), $CaCO_3$(s) (b), NaOH(aq) (c) and Na_2CO_3(aq) as the removal reagent

1.1.1 Effect of additive dosage

To study the effect of Na_2CO_3 dosage on the removing of Fe^{3+} and Al^{3+}, experiments were carried out to optimize the conditions for the removal of Fe^{3+} and Al^{3+} as follows: the Na_2CO_3 dosage ranging from 4.8−12.0 (g/L), agitation speed, removing temperature and reaction time were set at 400 rpm, 298 K, and 30 min, respectively. The removal rate of Fe^{3+} and Al^{3+} under the different Na_2CO_3 dosage is presented in Fig. S3. With an increase of Na_2CO_3 dosage, the removal rate of Fe^{3+} increased significantly while the Li loss rate remained at a low level. The ion removal rate of Fe^{3+} increased from 1.7% to 98.69% when Na_2CO_3 dosage increased from 4.8 g/L to 8.4 g/L. No appreciable rate variations were observed with a further increase of Na_2CO_3 dosage over 8.4 g/L. The corresponding removal rate of Al^{3+} was also observed when Na_2CO_3 dosage increased from 4.8 g/L to 9.6 g/L. Ion removal rate of Al^{3+} reached a plateau when Na_2CO_3 dosage exceeded 9.6 g/L. According to the Eqs. 1 and 2 (Table S1), the concentration of OH^- was raised by increasing the dosage of Na_2CO_3. The Fe^{3+} and Al^{3+} tended to be combined with OH^- to form $Fe(OH)_3$ and $Al(OH)_3$ (Eqs. 3 and 4 in Table S1), respectively. This is because the values of *Qc* ($Fe(OH)_3$ and $Al(OH)_3$) were higher than those of *Ksp* ($Fe(OH)_3$ and $Al(OH)_3$). When the Na_2CO_3 dosage increased from 4.8 g/L to 12 g/L, the ion loss rate of Li was less than 5%. For the sake of optimized removing conditions, 9.6 g/L for the Na_2CO_3 dosage was chosen in the following experiments.

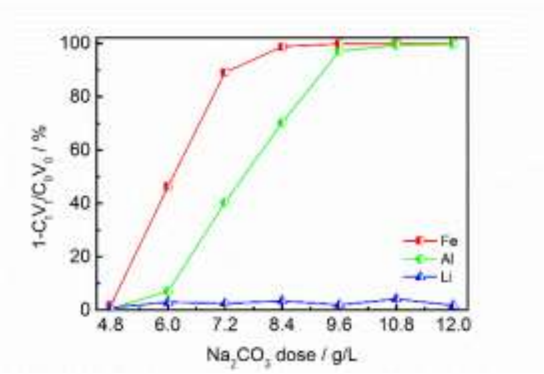


Fig. S3 Effect of Na_2CO_3 dosage on the ion loss rate of Li^+ and ion removal rate of Fe^{3+} and Al^{3+} (reaction temperature 298 K, agitation speed of 400 rpm and reaction time of 30 min)

1.1.2 Effect of reaction time

The effect of reaction time (0-45 min) on the ion removal rate of Fe^{3+} and Al^{3+} were studied under the following experimental conditions: Na_2CO_3 dosage of 9.6 g/L, agitation speed of 400 rpm and reaction temperature of 298 K. From Fig. S4, a positive but non-significant (after 15 min) effect upon removal of Fe^{3+} and Al^{3+} was observed as reaction progressed. Nearly no ion removal of Fe^{3+} and Al^{3+} were observed during the first 5 min because of there were not enough hydroxide ion. The ion removal rate could finally approach 99.9% for Fe^{3+} and 99.3% for Al^{3+} when reaction duration reached 45 min. The ion removal rate of Fe^{3+} sharply increased when the reaction time approached 8 min while the pH was 2.12, which agreed well with Fig. 2(a) because no adequate OH^- generated before the chemical reaction lasted for 8 min. The ion removal rate of Al^{3+} increased rapidly when the reaction time approached 10 min with the pH of the solution at 3.74, which is also consistent with Fig. 2(a). A plateau appeared when the reaction time elapsed further from 25 min. As shown in Fig. S4, the selective removal can be divided into three stages. Firstly, the Fe^{3+} and Al^{3+} were adequate, but OH^- was scarce, which made the chemical reaction rates of removing Fe^{3+} and Al^{3+} at low level. Secondly, the chemical reaction rates increased sharply as a result of a significant increase of OH^- in solution, which accelerated the formation of the $Fe(OH)_3$ and $Al(OH)_3$ (Eqs. 3 and 4 shown in Table S1) and the Fe^{3+} and Al^{3+} were quickly consumed. Thirdly, the concentration Fe^{3+} and Al^{3+} was depleted and the chemical reaction rate reached the plateau. During the entire period of experiment, the ion loss rate of Li^+ remained below 5%. Therefore, the reaction time of 25 min was taken as an optimum value for the subsequent experiments.

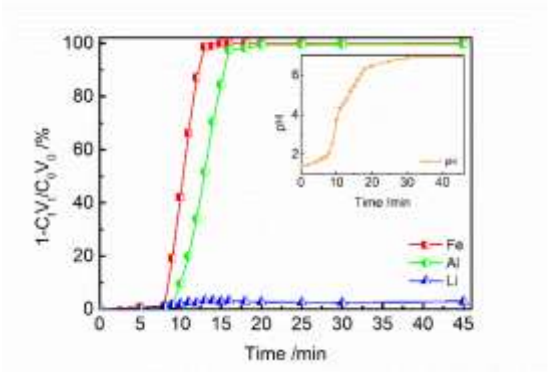


Fig. S4 Effect of reaction time on the ion loss rate of Li^+ and ion removal rate of Fe^{3+} and Al^{3+} (Na_2CO_3 dosage of 9.6 g/L, reaction temperature of 298 K, and agitation speed of 400 rpm)

1.1.3 Effect of agitation speed

The effect of agitation speed was investigated while other operational parameters were kept as follows: Na_2CO_3 dosage of 9.6 g/L, reaction temperature of 298 K, and reaction time of 25 min. The removing kinetics and mass transfer tend to be enhanced with an increase of agitation speed. The effects of agitation speed on ions removal were shown in Figs. S5(a)-(c). Clearly, the effects of agitation speed on ions removal rate were not observed when agitation speed varied from 300 to 500 rpm. Thus, the agitation speed of 400 rpm was chosen in the subsequent experiments.

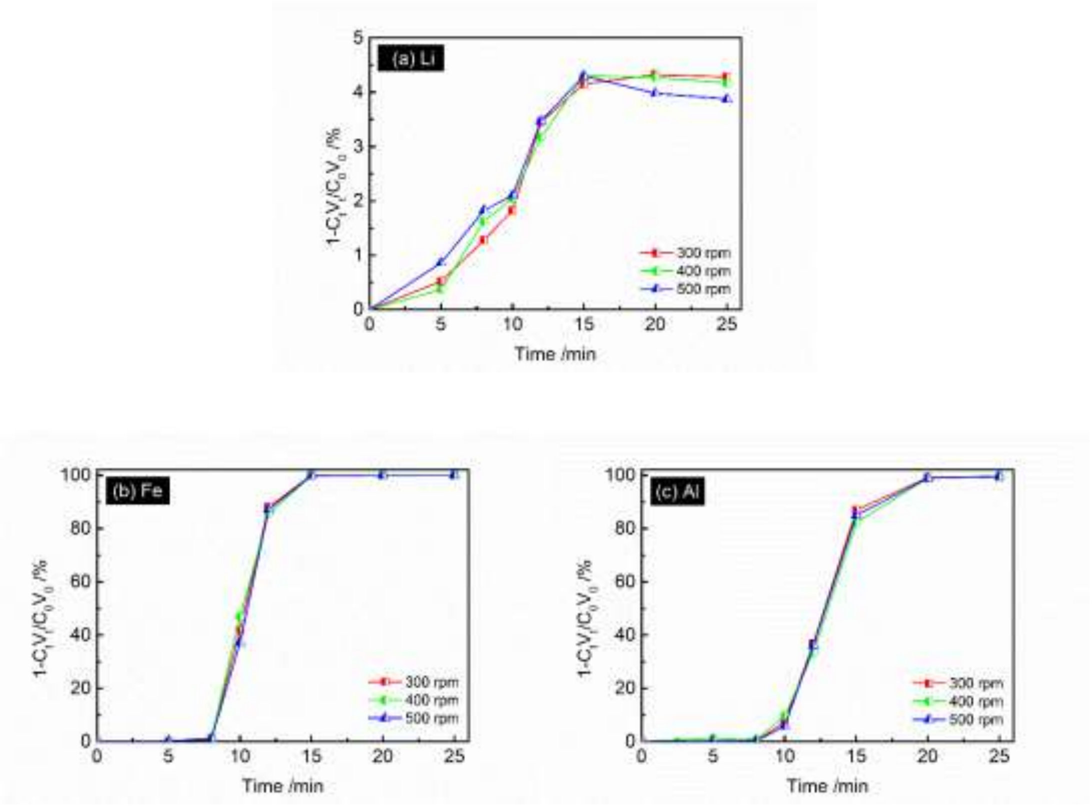


Fig. S5 Effect of agitation speed on the ion loss rate of Li^+ (a), ion removal rate of Fe^{3+} (b) and Al^{3+} (c) (Na_2CO_3 dosage of 9.6 g/L, reaction temperature of 298 K, and reaction time of 25 min)

1.1.4 Effect of reaction temperature

Temperature is an important factor that affects the rate of chemical reactions by increasing the collision frequency among the corresponding ions. In the process of removing impurity ions, the reaction temperatures varied from 298 K to 323 K while other operational parameters were kept as follows: Na_2CO_3 dosage of 9.6 g/L, agitation speed of 400 rpm, reaction time of 25 min. In Figs. S6(b) and (c), the ion removal rate of Fe^{3+} and Al^{3+} were clearly improved when the reaction temperature increased from 298 K to 323 K. This is due to the decreased CO_2 solubility as an increasing of reaction temperature (shown in Fig. S7). In addition, as much more H^+ was consumed, the chemical reaction rate of Eq. 1 (Table S1) was accelerated and the level of OH^- increased because of hydrolysis (Eq. 2 in Table S1) was promoted. The ion removal rate of Fe^{3+} and Al^{3+} was significantly improved as a result of formation of the $Fe(OH)_3$ and $Al(OH)_3$. Although the time that takes reaction to reach equilibrium can be shortened by increasing temperature, the final ion removal rate of Fe^{3+} and Al^{3+} remains approximately the same. According to Fig. S6(a), by increasing the temperature, the improved ion removal rate of Fe^{3+} and Al^{3+} and no appreciable variation of the ion loss of Li were observed. Therefore, the optimal condition of removing Fe^{3+} and Al^{3+} was determined: Na_2CO_3 dosage of 9.6 g/L, agitation speed of 400 rpm, reaction time of 25 min, and the reaction temperature at 298 K. At the optimal conditions, the Li loss rate was below 5% and the ion removal rate of Fe^{3+} and Al^{3+} can reach 99.8% and 99.5%, respectively.

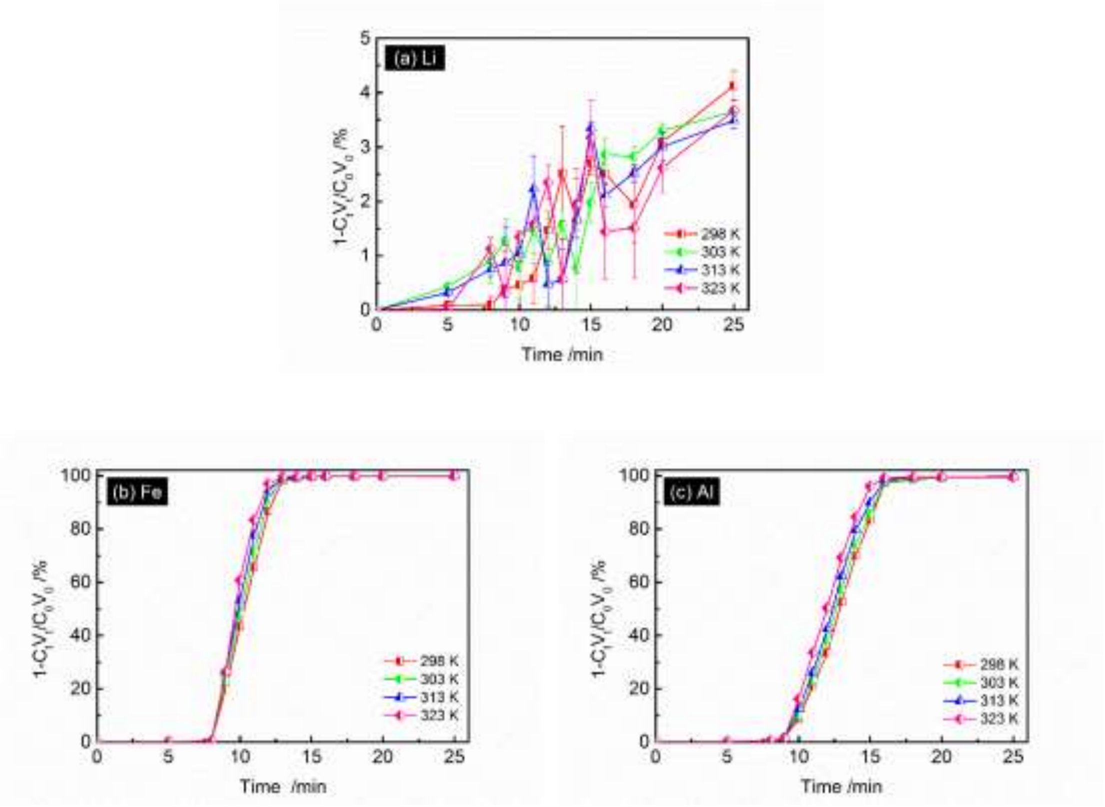


Fig. S6 Effect of reaction temperature on the ion loss rate of Li^+ (a), ion removal rate of Fe^{3+} (b) and Al^{3+} (c) (Na_2CO_3 dosage of 9.6 g/L, agitation speed of 400 rpm, and reaction time of 25 min)

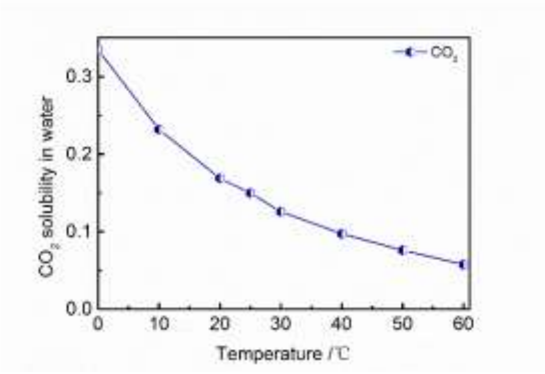


Fig. S7 The CO_2 solubility in water (g/100g H_2O) [1]

1.2 Impurities removal at higher pH range

1.2.1 Effect of sodium carbonate to calcium ion molar ratio

Na_2CO_3 has been extensively applied as an effective reagent to eliminate Ca^{2+}. By adjusting pH to a proper range, the formation of $CaCO_3$ occurs (Fig. 2(b)). The molar ratio of sodium carbonate to calcium ion (Na_2CO_3 to Ca^{2+}) was determined by the chemical reaction of Eq. 9 (Table S1). To investigate the effect of Na_2CO_3 dosage on the removal of Ca^{2+} and Mg^{2+}, experiments were performed under the conditions as follows: the molar ratio of Na_2CO_3 to Ca^{2+} ranging from 1 to 4, reaction temperature 298 K, endpoint pH of 10.5, agitation speed of 400 rpm and reaction time of 30 min. The results were shown in Fig. S8, the removal behave of Li^+, Ca^{2+} and Mg^{2+} was found to be very different. A significant improvement of ion removal rate of Ca^{2+} was observed when the molar ratio of Na_2CO_3 to Ca^{2+} increased from 1 to 2. With a further increase of molar ratio of Na_2CO_3 to Ca^{2+}, no obviously change of the ion loss rate of Ca^{2+} was observed. $CaCO_3$ may not be precipitated completely while the pH was kept at 10.5. The ion removal rate of Mg^{2+} was low when molar ratio of Na_2CO_3 to Ca^{2+} increased from 1 to 2. With an increase of molar ratio of Na_2CO_3 to Ca^{2+} from 2 to 4, the ion removal rate of Mg^{2+} raised to 20% as a result of formation of the $MgCO_3$, which is a compound with low solubility in water. The possible reason that could explain the different removal behavior between Ca^{2+} and Mg^{2+} during the addition of Na_2CO_3 is that the formation of $CaCO_3$ is favorable at lower molar ratio of Na_2CO_3 to Ca^{2+} because of the K_{sp} of $CaCO_3$ is smaller than $MgCO_3$. The excessive Na_2CO_3 will react with Mg^{2+} to form $MgCO_3$ while the molar ratio of Na_2CO_3 to Ca^{2+} increased from 2 to 4, which leads to about 20% removal rate of Mg^{2+}. This is because the combination of Ca^{2+} and CO_3^{2-} reaches an equilibrium. Therefore, it was also demonstrated that ion interaction between Ca^{2+} and CO_3^{2-} was stronger than Mg^{2+} at a low Na_2CO_3 to Ca^{2+} molar ratio. During the entire molar ratio range, only about 5% Li loss was observed. Thus, the molar ratio of Na_2CO_3 to Ca^{2+} of 2 was chosen in the subsequent experiments.

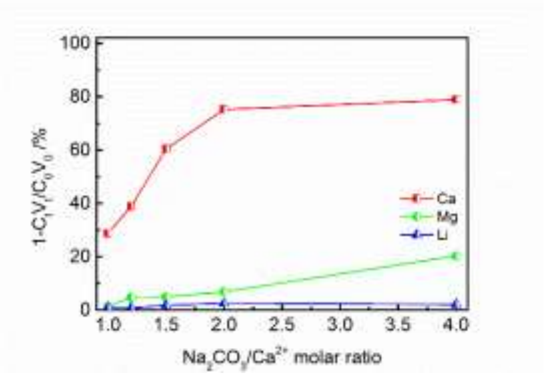


Fig. S8 Effect of Na_2CO_3 to Ca^{2+} molar ratio on the ion loss rate of Li^+ and ion removal rate of Ca^{2+} and Mg^{2+} (reaction temperature 298 K, endpoint pH of 10.5, agitation speed of 400 rpm and reaction time of 30 min)

1.2.2 Effect of endpoint pH

The effect of endpoint pH on the ion removal rate was examined under the following experimental conditions: Na_2CO_3 to Ca^{2+} molar ratio of 2, reaction temperature 298 K, agitation speed of 400 rpm and reaction time of 30 min. The ion removal rate of Li^+ was not obviously changed with an increase of endpoint pH in Fig. S9. The ion removal rate of Ca^{2+} was improved with an increase of the endpoint pH and the ion removal rate of Ca^{2+} reached to 97.3% at pH of 12. By comparing the ion removal rate of Ca^{2+} (75.2%) obtained at pH 10.5, it was found that the higher endpoint pH was beneficial to remove Ca^{2+}. The ion removal rate of Mg^{2+} was different. When the endpoint pH is lower than 10.5, the ion removal rate of Mg^{2+} was hardly observed. The ion removal rate of Mg^{2+} was sharply enhanced while the endpoint pH increased from 10.5 to 12. This is because the Mg^{2+} was combined with a sufficient amount of OH^- which was depicted from Eq. 12 (Table S1). It can conclude that the Mg^{2+} was easier to form with OH^- rather than CO_3^{2-} when the OH^- was enough because of the *Ksp* of $Mg(OH)_2$ is smaller than $MgCO_3$. Therefore, endpoint pH of 12 was employed in the subsequent experiment.

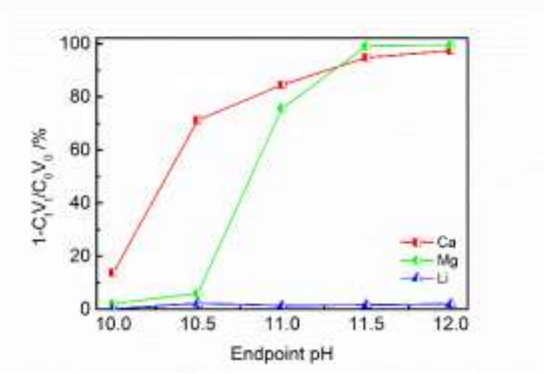


Fig. S9 Effect of endpoint pH on the ion loss rate of Li^+ and ion removal rate of Ca^{2+} and Mg^{2+} (reaction temperature 298 K, Na_2CO_3 to Ca^{2+} molar ratio of 2, agitation speed of 400 rpm and reaction time of 30 min)

1.2.3 Effect of reaction time

The effect of reaction time upon removing Ca^{2+} and Mg^{2+} was investigated while other operational parameters were kept the same: Na_2CO_3 to Ca^{2+} molar ratio of 2, reaction temperature of 298 K, endpoint pH of 12 and agitation speed of 400 rpm. According to Fig. S10, the ion removal rate of Ca^{2+} change rapidly from zero to nearly 95% within the first 7 min, while ion removal rate of Mg^{2+} also approached its maximum within the first 5 min. As reaction duration further increased from 5 to 10 min, no appreciable changes of ion removal rate of Ca^{2+} and Mg^{2+} were observed. Over the entire experimental reaction, the ion loss rate of Li^+ was found to be below 5%. To ensure the completion of reaction, 15 min was chosen for the subsequent experiments.

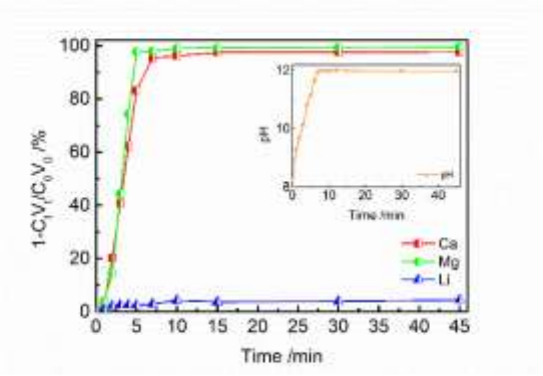
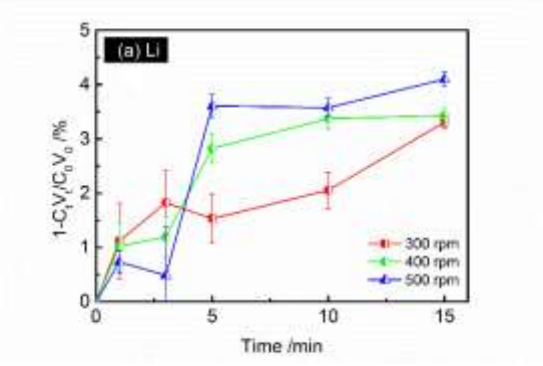


Fig. S10 Effect of reaction time on the ion loss rate of Li^+ and ion removal rate of Ca^{2+} and Mg^{2+} (reaction temperature 298 K, Na_2CO_3 to Ca^{2+} molar ratio of 2, agitation speed of 400 rpm and endpoint pH of 12)

1.2.4 Effect of agitation speed

In this experiment, the effect of agitation speed was investigated while other operational parameters were kept as follows: Na_2CO_3 to Ca^{2+} molar ratio of 2, endpoint pH of 12, and 298 K for 15 min. From Figs. S11 (a)-(c), it was found that the agitation speed had no significant effect on the ion removal rate of Ca^{2+} and Mg^{2+}. The solution was immediately mixed when the Na_2CO_3 and NaOH solution were added to the FIA, the Ca^{2+} and Mg^{2+} reacted with CO_3^{2-} and OH^- rapidly with an increase of the concentration of CO_3^{2-} and OH^-. With an increase of agitation speed, no appreciable ion removal rate of Li^+ was observed. Therefore, the agitation speed of 400 rpm was chosen in the subsequent experiments.



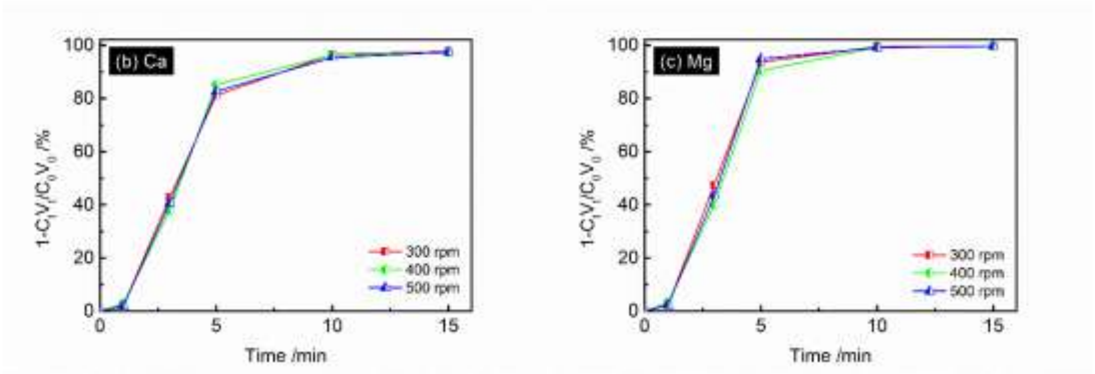
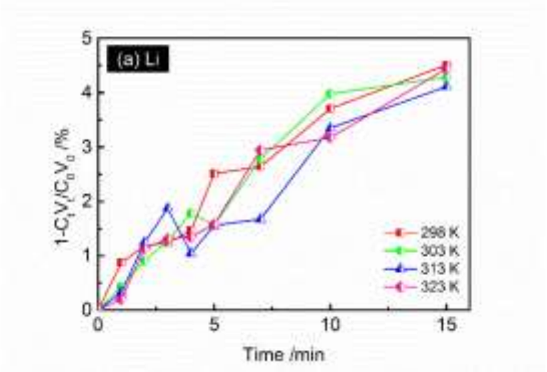


Fig. S11 Effect of agitation speed on the ion loss rate of (a) Li^+, ion removal rate of (b) Ca^{2+} and (c) Mg^{2+} (reaction temperature 298 K, Na_2CO_3 to Ca^{2+} molar ratio of 2, reaction time of 15 min and endpoint pH of 12)

1.2.5 Effect of reaction temperature

The effect of reaction temperature was investigated under the following experimental conditions: Na_2CO_3 to Ca^{2+} molar ratio of 2, endpoint pH of 12, agitation speed of 400 rpm, reaction time of 15 min and the temperature range of 298-323 K. It can be seen from Figs. S12(a)-(c), the ion removal rate of Ca^{2+} and Mg^{2+} were obviously enhanced when the reaction temperature increased from 298 K to 323 K. The chemical reaction rate was increased by two to three times by increasing the temperature for every ten degrees. This increased temperature will enhance the chances of collision of different ions, and increases the number of activated molecules, which in turn accelerates the chemical reaction rate. This also agrees with our experimental results of significant improvement of removal rate of Ca^{2+} and Mg^{2+} with an increase of temperature. However, the reaction temperature of 298 K was chosen as the optimum reaction temperature because of the final removal rate of Ca^{2+} and Mg^{2+} was unchanged. The final optimal condition for impurities removal at higher pH range was obtained as follows: Na_2CO_3 to Ca^{2+} molar ratio of 2, endpoint pH of 12, agitation speed of 400 rpm, reaction time of 15 min and the reaction temperature of 298 K. Under the optimal conditions, the ion removal rate of Li^+ was below 5% and the ion removal rate of Ca^{2+} and Mg^{2+} can reach 97.2% and 99.5%, respectively.



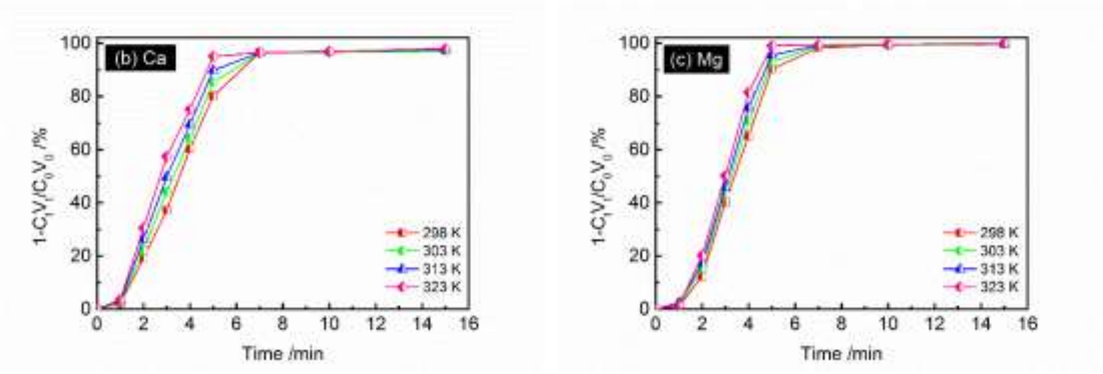


Fig. S12 Effect of reaction temperature on the ion loss rate of (a) Li^+, ion removal rate of (b) Ca^{2+} and (c) Mg^{2+} (Na_2CO_3 to Ca^{2+} molar ratio of 2, agitation speed of 400, reaction time of 15 min and endpoint pH of 12)

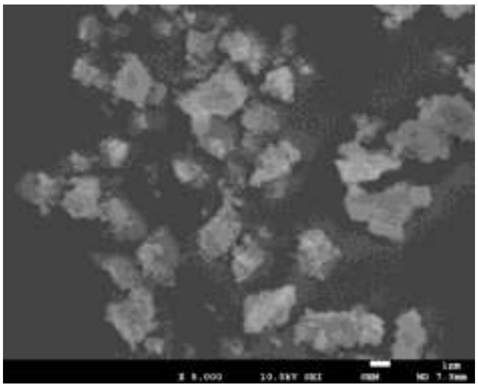


Fig. S13 The SEM image of residue after removing Fe^{3+} and Al^{3+}

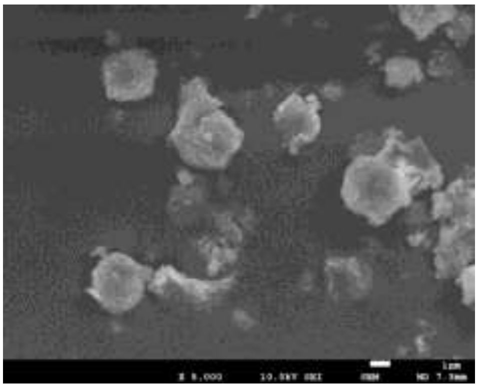


Fig. S14 The SEM image of residue after removing Ca^{2+} and Mg^{2+}

References

1. Liang Y J. Practical Inorganic Thermodynamic Data Sheet. China: Northeastern University Press, 1993, 614-620

2. https://wenku.baidu.com/view/74e236dba58da0116c1749cb.html