Supporting Information

Enhanced Recovery of Zn from carbonate-type mixed oxidized ore (CMO) by combining organic acid leaching with mechanical activation

Hao Deng[1], Xuelin Pan[1], Fanyun Chen[1], Qingshan Gao[1], Chen Tian[1,2,*], Zhang Lin[1,2]

1. School of Metallurgy and Environment, Central South University, Changsha, Hunan 410083, China

2. Chinese National Engineering Research Center for Control & Treatment of Heavy Metal Pollution, Changsha, Hunan 410083, China

** Corresponding author*

Table S1. Parameter levels and coded values used in the experimental design.

Factors	**Code**	**+ 2**	**+ 1**	**0**	**− 1**	**− 2**
Time (h)	A	30	45	60	75	90
Conc (M)	B	0.5	0.75	1	1.25	1.5
Temp (^{o}C)	C	30	45	60	75	90
L/S ratio (mL/g)	D	5	10	15	20	25

Table S2. Brief Summary of Zn recover from low-graded Zn ores.

No	Sources	Leaching efficiency (%)	Optimum condition	Ref
1	Pb-Zn carbonate tailing (Zn5%, Pb7%, Fe21%)	90%	(1M Malic acid, 80°C, 60 min, 1/10 S/L)	[1]
3	Pb-Zn carbonate tailing (Zn5%, Pb7%, Fe21%)	89.3% 74.7%	(1M Sulfuric acid, 40°C, 60 min, 1/5 S/L) (0.5M Citric acid, 60°C, 120 min, 1/10 S/L)	[2]
4	Mixed sulfide–oxide lead and zinc ore (ZnS23.6%, $ZnCO_3$ 10.1%, PbS12.3%, $FeS_2$12%, $CaCO_3$35.3%, $SiO_2$12.3%)	94.9%	(0.25 M $(NH_4)_2SO_4$+ 0.5 M $(NH_4)_2S_2O_8$, 50°C, 240 min, 1/10 S/L)	[3]
5	Low-grade zinc carbonate source (Ca12.2% Si12% Zn7.65% Fe6.08% Al4.13% Pb1.04% Mg1.10% Na1.04%)	90%	(1M Glycine, pH = 9.5, 70°C, 240 min, 1/10 S/L)	[4]
6	Pb-Zn carbonate tailing (Zn5%, Pb7%, Fe21%)	91% 90.6% 90% 90% 88.7% 82.6%	(1 M Sulfuric acid, 40 °C, 30 min, 2/10 S/L) (1 M Citric acid, 80 °C, 180 min, 2/10 S/L) (0.5 M Hydrochloric, 80 °C, 30 min, 1/10 S/L) (1 M Malic acid, 80 °C, 60 min, 1/10 S/L) (1 M Sulfosalicylic acid; 80 °C, 30 min, 1/10 S/L) (1 M Formic acid, 60 °C, 180 min, 1/10 S/L)	[5]
7	Mixed sulfide–oxide lead and zinc ore (ZnS21.94%, $ZnCO_3$ 14.07%, $PbCO_3$8.09%, $FeS_2$5.61%, $CaCO_3$3.21%, $SiO_2$7.35%)	90.07%	(1 M Lactic acid, 75 °C, 75 min, 1/20 S/L)	This work

Table S3. Experiment design.

Run	Time (min)	Conc (M)	Temperature (°C)	Liquid/solid ratio (mL/g)	Leaching efficiency of Zn (%)
1	75	1.25	45	20	38.70
2	60	1	30	15	23.03
3	60	1	60	15	38.48
4	45	1.25	75	20	46.10
5	90	1	60	15	39.03
6	75	0.75	45	10	25.47
7	45	0.75	45	20	28.81
8	60	1	60	15	37.32
9	60	1.5	60	15	36.84
10	60	0.5	60	15	25.90
11	75	1.25	75	20	46.15
12	75	0.75	45	20	34.88
13	75	1.25	75	10	40.10
14	60	1	60	5	26.10
15	30	1	60	15	34.65
16	75	1.25	45	10	27.74
17	45	0.75	75	10	30.39
18	60	1	60	15	34.92
19	60	1	60	15	35.02
20	60	1	90	15	43.93
21	45	0.75	75	20	43.02
22	60	1	60	15	37.96
23	75	0.75	75	20	42.29
24	45	1.25	45	20	29.59
25	45	0.75	45	10	16.32
26	60	1	60	25	47.10
27	45	1.25	75	10	36.35
28	45	1.25	45	10	24.86
29	60	1	60	15	32.75
30	75	0.75	75	10	31.39

Table S4. Fit Summary.

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	
Linear	< 0.0001	0.3806	0.8889	0.8618	
2FI	0.2770	0.4178	0.8979	0.8424	
Quadratic	**0.0166**	**0.7867**	**0.9396**	**0.8828**	**Suggested**
Cubic	0.8619	0.4106	0.9140	0.0842	Aliased

Table S5. ANOVA for Quadratic model.

Source	**Sum of squares**	**df**	**Mean Square**	***F*-value**	**p-value**	
Model	1626.41	13	125.11	38.16	< 0.0001	significant
A-Time	66.70	1	66.70	20.34	0.0004	
B-Conce	144.51	1	144.51	44.07	< 0.0001	
C-Temp	717.55	1	717.55	218.85	< 0.0001	
D-S/L	589.24	1	589.24	179.72	< 0.0001	
AB	0.0059	1	0.0059	0.0018	0.9668	
AC	33.52	1	33.52	10.22	0.0056	
AD	0.3246	1	0.3246	0.0990	0.7571	
BC	2.40	1	2.40	0.7314	0.4050	
BD	12.12	1	12.12	3.70	0.0725	
CD	0.1892	1	0.1892	0.0577	0.8132	
A^2	0.1570	1	0.1570	0.0479	0.8295	
B^2	46.79	1	46.79	14.27	0.0016	
C^2	16.44	1	16.44	5.01	0.0397	
Residual	52.46	16	3.28			
Lack of Fit	28.06	11	2.55	0.5228	0.8281	not significant
Pure Error	24.40	5	4.88			
Cor Total	1678.87	29				

R^2 = 0.9669; R^2_{adj} = 0.9543; R^2_{pre} = 0.9397; Adeq Precision = 32.6569

Table S6. ANOVA for Revised Quadratic model.

Source	Sum of squares	df	Mean Square	F-value	p-value	
Model	1623.34	8	202.92	76.73	< 0.0001	significant
A-Time	66.70	1	66.70	25.22	< 0.0001	
B-Conc	144.51	1	144.51	54.64	< 0.0001	
C-Temp	717.55	1	717.55	271.34	< 0.0001	
D-L/S	589.24	1	589.24	222.82	< 0.0001	
AC	33.52	1	33.52	12.67	0.0018	
BD	12.12	1	12.12	4.58	0.0442	
B^2	48.23	1	48.23	18.24	0.0003	
C^2	17.11	1	17.11	6.47	0.0189	
Residual	55.54	21	2.64			
Lack of Fit	31.14	16	1.95	0.3988	0.9263	not significant
Pure Error	24.40	5	4.88			
Cor Total	1678.87	29				

$R^2 = 0.9688$; $R^2_{adj} = 0.9434$; Adeq Precision = 23.5153

Table S7. pH before and after leaching process.

	Lactic acid	Malonic acid	Citric acid	Amber Acid	Acetic acid	Tartaric acid	HCl	HNO_3	H_2SO_4
pH-Before	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
pH-After	4.05	4.25	4.77	4.76	3.92	4.55	6.21	6.05	5.89

Table S8. Chemical descriptors of organic acids.

	Lactic acid	Malonic acid	Citric acid	Amber Acid	Acetic acid	Tartaric acid
E	0.29	0.36	0.66	0.39	0.18	0.57
S	0.80	0.66	1.79	1.23	0.46	1.43
A	0.94	1.67	2.79	1.52	0.66	1.29
B	0.70	0.78	1.30	1.04	0.50	1.05
V	0.67	0.71	1.27	0.84	0.47	0.96

⋆ The LFER descriptors used were as follows:

E [cm^3 mol^{-1}/10]: the excess molar refraction, meaning dispersive force induced by *p*/*n*-electron pair interaction;

S [dimensionless]: dipolarity and polarizability;

A and *B* [dimensionless]: hydrogen bonding acidity and basicity, respectively;

V [cm^3 mol^{-1}/100]: the McGowan characteristic molecular volume, representing cavity formation and hydrophobicity.

**All data was referenced from Jong-WonChoi's work[6,7]

Note: The linear free energy relationship (LFER) model is developed to correlate leaching activity and structural properties of a chemical reactant[6-8]. 4 molecular descriptors are adopted to predict leaching performance, namely, *A (*hydrogen bonding acidity*)* and *B* (hydrogen bonding acidity basicity), *E* (dispersive force induced by *p*/*n*-electron pair interaction), *S* (dipolarity and polarizability), respectively, and *V* (McGowan characteristic molecular volume), representing cavity formation and hydrophobicity. As displayed in Table S8, Tartaric acid has the lowest leaching efficiency, but the *A* value is not the smallest. This might be the fact that the solubility of zinc tartrate is low in water (Ksp = 2.2×10^{-2} at 20°C). Citric acid has the highest *A* among selected organic acids, but leaching efficiency is the third in comparison (35.7%). The reason is complex. Firstly, metal selection should be considered. Apart from Zn, Pb and Fe are also largely extracted by citric acid[9]. As revealed in Fig. S1, the leaching concentration of Pb and Fe are both the highest among the 6 organic acids. The competition among Zn, Fe, and Fe indicated that stronger acid strength is not preferred in single metal leaching. The selectivity could also be predicted according to complex stability constant values. The stability constant of lg K_1(Zn) is 4.71 (HL^{2-}), but lgK_1(Pb) is 6.5, indicating poor selectivity on Zn leaching. Secondly, the steric factor influenced the solubility of the complex[10,11]. The *V* value of citric acid (1.27) is the largest among selected acids, resulting in slight solubility of zinc citrate. Lactic acid has moderated acidity, a small steric hindrance on zinc lactate, and the selectivity of zinc complex is high (lgK_1(Zn)=2.20). Based on comprehensive analysis, lactic acid has the best performance on Zn leaching.

Table S9. Optimum conditions by RSM results.

Solution Order.	Time (min)	Lactic acid concentration (mol/L)	Temperature (°C)	Liquid/Solid ratio	Leaching efficiency (%)	Desirability
1	**74.95**	**1.15**	**75.00**	**20.00**	**46.52**	**0.36**
2	74.84	1.16	75.00	20.00	46.51	0.36
3	75.00	1.15	74.98	20.00	46.51	0.36
4	74.96	1.16	74.98	20.00	46.51	0.36
5	75.00	1.14	75.00	20.00	46.51	0.36
6	74.67	1.14	75.00	20.00	46.51	0.36
7	74.65	1.17	75.00	20.00	46.51	0.36
8	75.00	1.18	75.00	20.00	46.50	0.36
9	74.16	1.14	75.00	20.00	46.50	0.36
10	75.00	1.18	75.00	20.00	46.50	0.36
11	73.52	1.15	75.00	20.00	46.49	0.36
12	74.66	1.15	75.00	19.97	46.49	0.36
13	75.00	1.18	74.87	20.00	46.48	0.36
14	72.52	1.15	75.00	20.00	46.48	0.36
15	72.31	1.17	75.00	20.00	46.47	0.36
16	73.49	1.14	74.89	20.00	46.47	0.36
17	73.01	1.12	75.00	20.00	46.46	0.36
18	71.54	1.14	75.00	20.00	46.46	0.36
19	75.00	1.20	74.99	19.99	46.46	0.36
20	74.90	1.14	74.68	20.00	46.46	0.36

Table S10. BET surface area of CMO at different rotation speed.

Rotation speed (rpm)	**BET surface area (m^2/g)**
0	3.28
200	3.46
300	3.98
400	4.72
500	5.82

Table S11. BET surface area of CMO at different ball/mass ratio.

Ball/mass ratio	**BET surface area (m^2/g)**
0	3.28
1:1	5.82
5:1	5.35
10:1	6.63
20:1	2.12
40:1	3.46

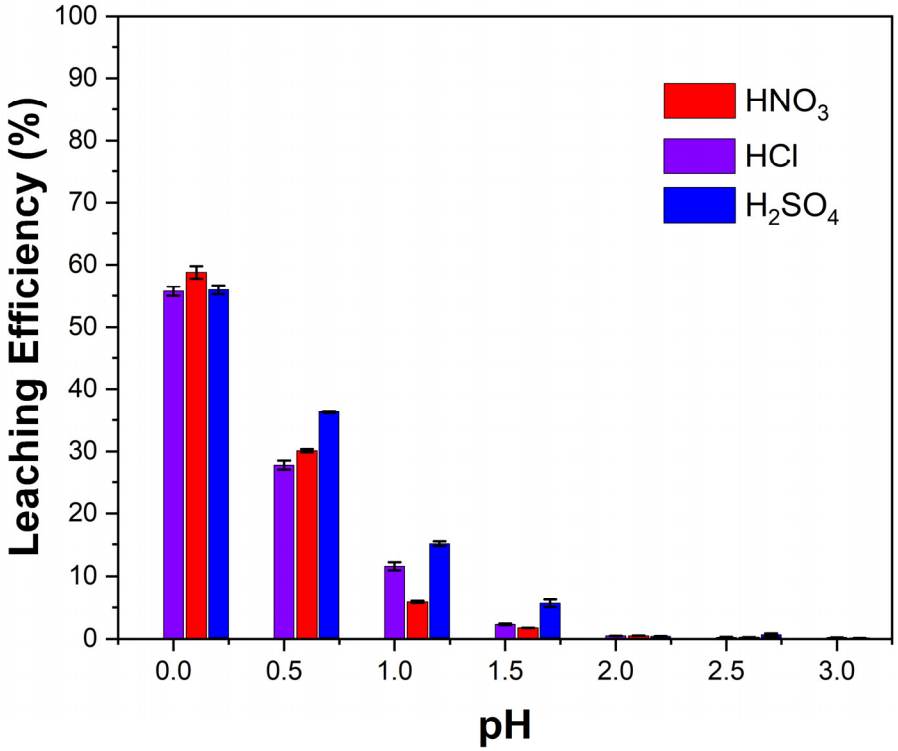

Figure S1. Inorganic acid leaching at different pH.

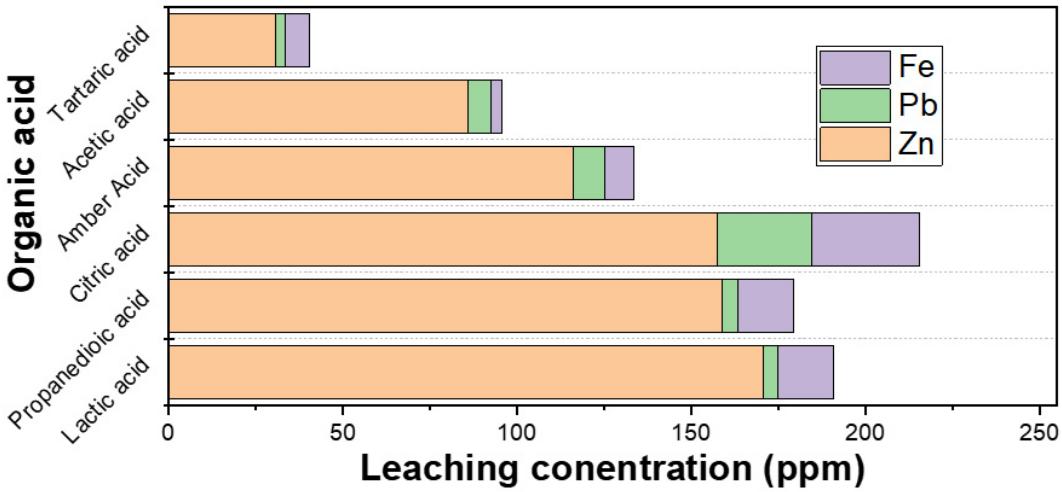

Figure S2. Organic Acid Leaching efficiency of various metal.

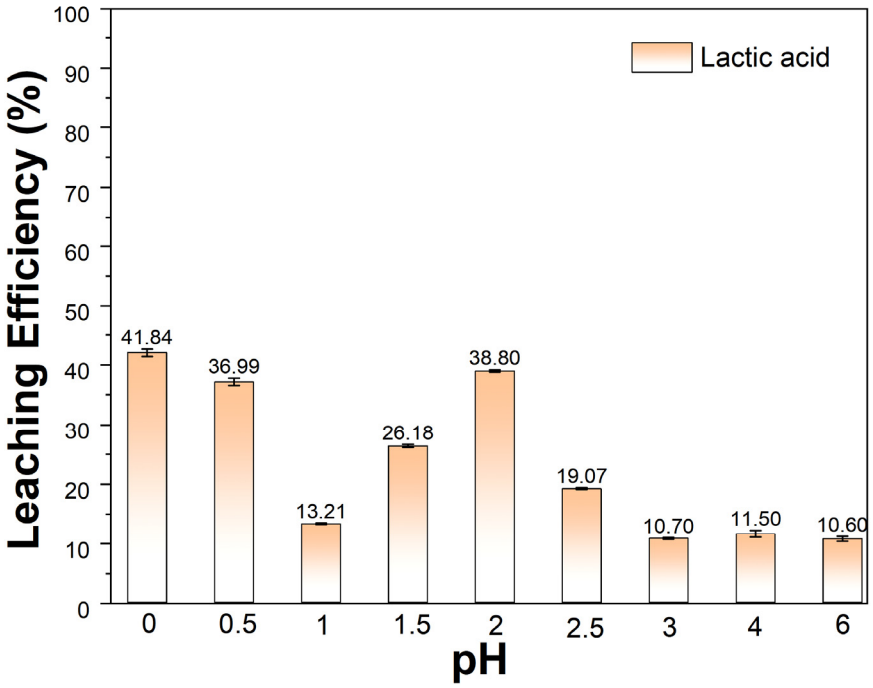

Figure S3. Lactic acid leaching at different pH [Lactic acid (1 M), Liquid/Solid ratio: 10 mL/1 g; Time: 1 h; Temperature: 60 °C].

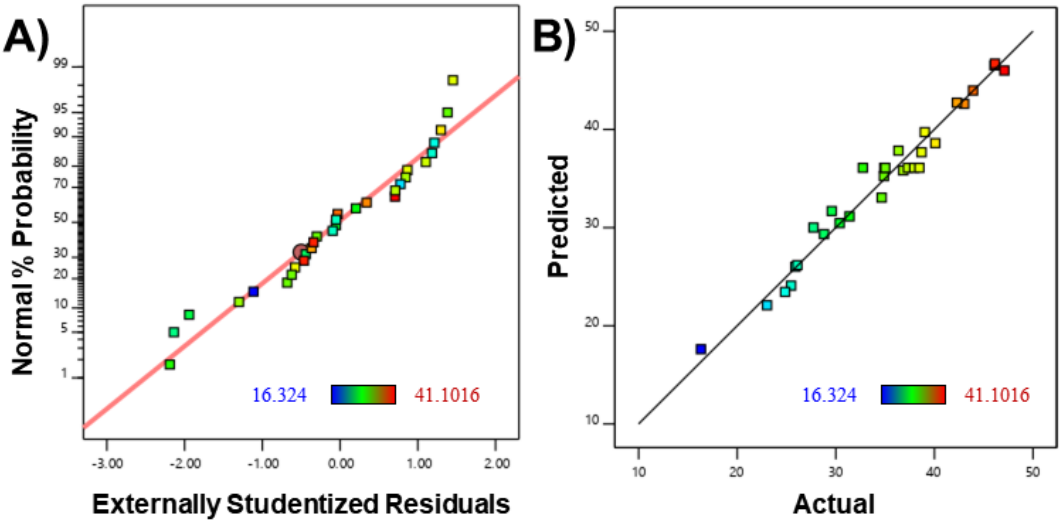

Figure S4. (a) The normal probability plot of externally studentized residuals of the predictable Zn leaching efficiency; (b) the predicted and actual response slope of Zn leaching efficiency.

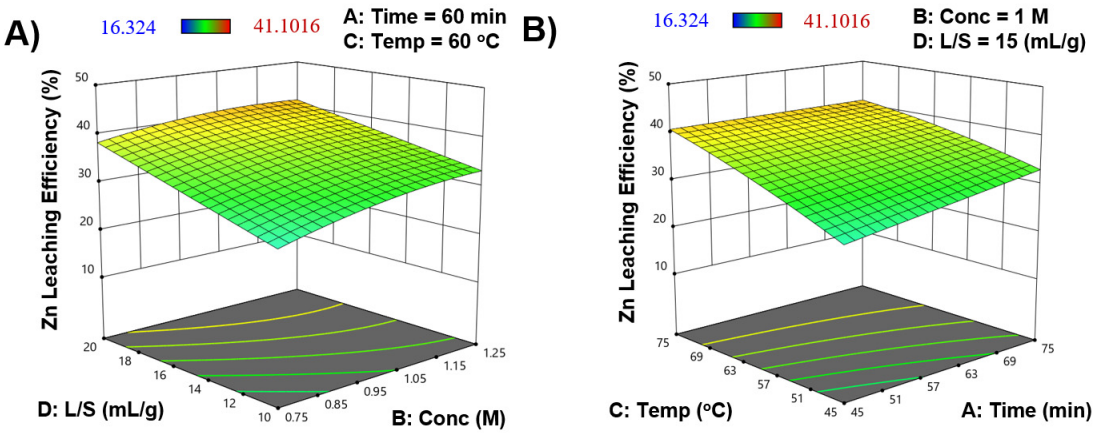

Figure S5. The 3D plot of response surface analysis: (a) L/S ratio and lactic concentration; (b) temperature and time.

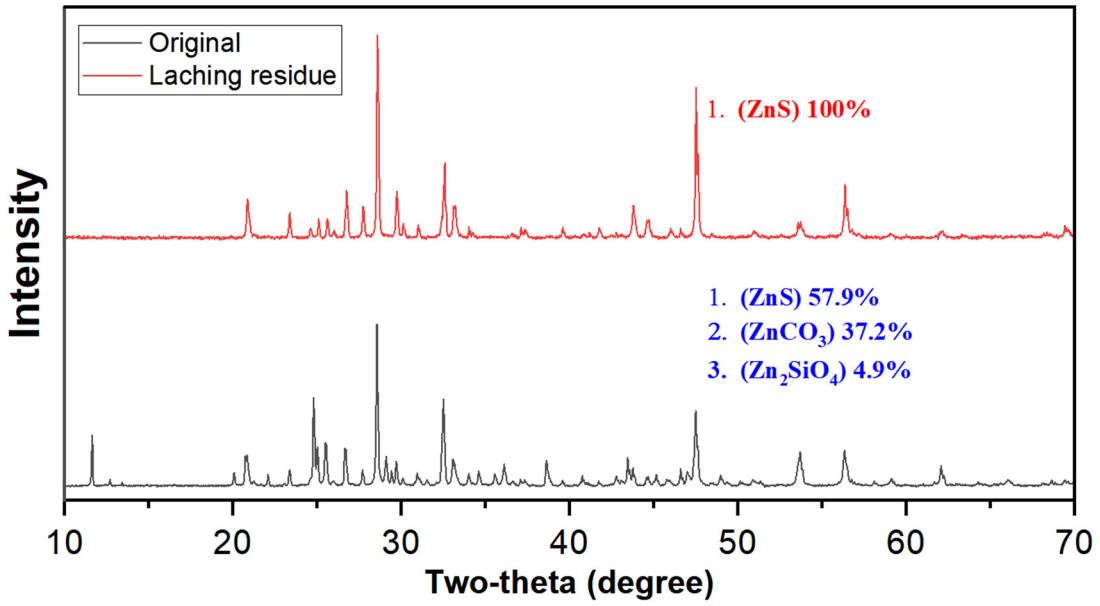

Figure S6. XRD pattern of leaching residue.

Note:

According to element composition analysis of original CMO (Table 1 and Fig 1), 63.5% of Zn speciation is in the form of sulfide, 4.7% of Zn speciation is in the form of silicate, and 31.8% of Zn is in the form of carbonate. While the XRD result of leaching residue showing that only sphalerite was found as Zn-bearing phases. By comparing phase composition between original CMO and leaching residue, it's purposed that carbonate were totally leached out (31.8% of Zn-bearing species). However, sulfide was partially leached out (36.5% of Zn-bearing species). Zn-bearing silicate was not found in XRD. Although acidic soluble, the solubility of sphalerite is extremely low at pH=2 (Ksp = 1.6*10^(-24)[12,13]). Faced with this issue, additional pretreatment is necessary to increase the Zn leaching efficiency from sphalerite in CMO.

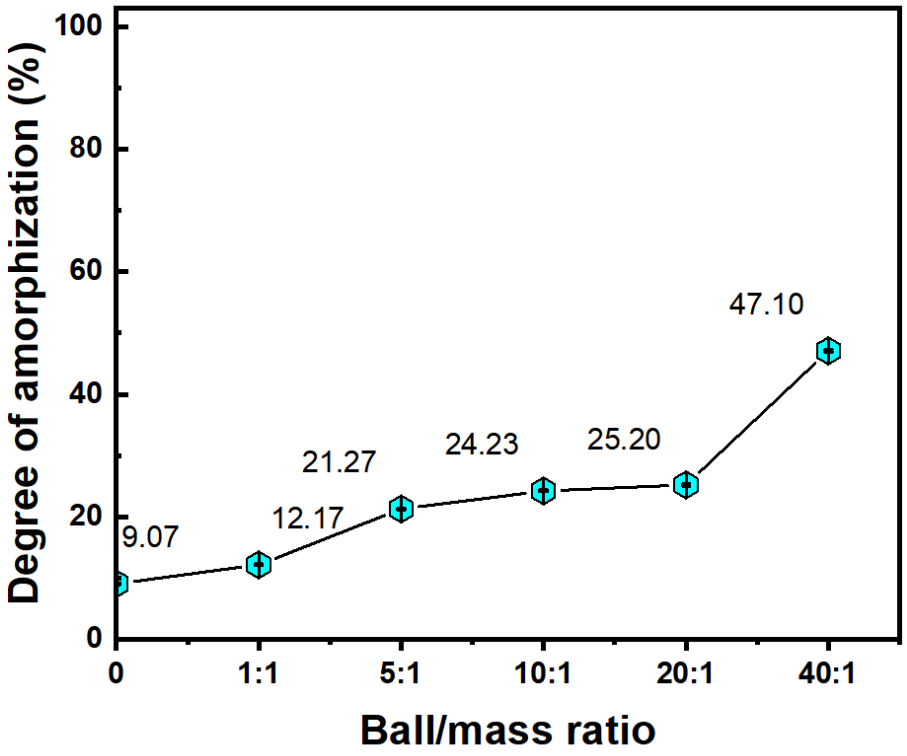

Figure S7. Degree of amorphization at different ball/mass ratio.

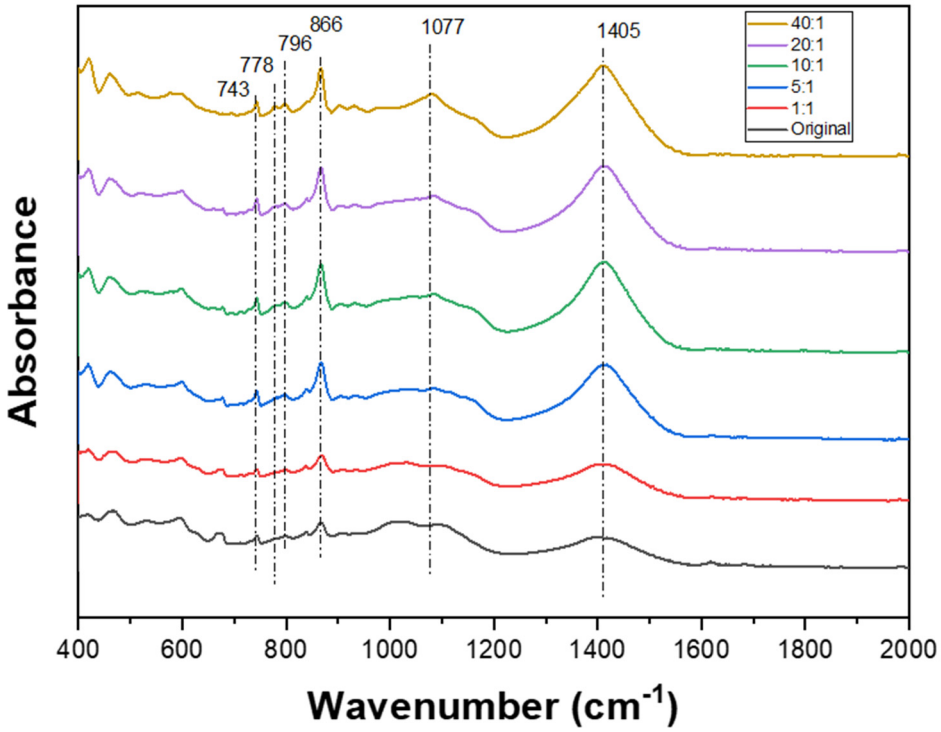

Figure S8. ATR-FTIR spectra of CMO at different ball/mass ratio.

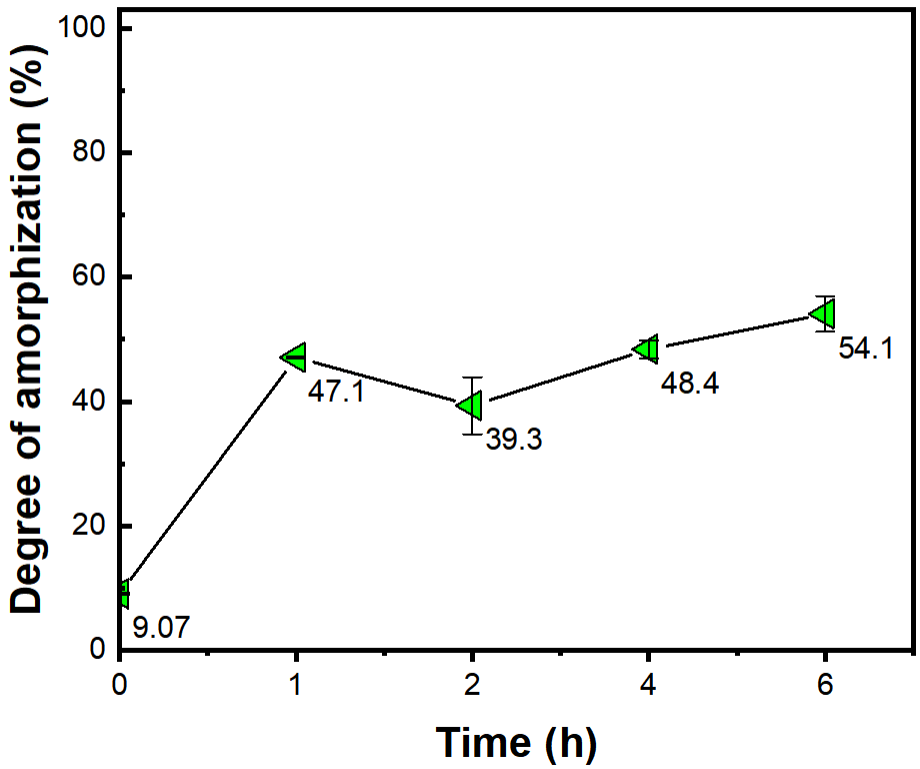

Figure S9. Degree of amorphization at different rotation time.

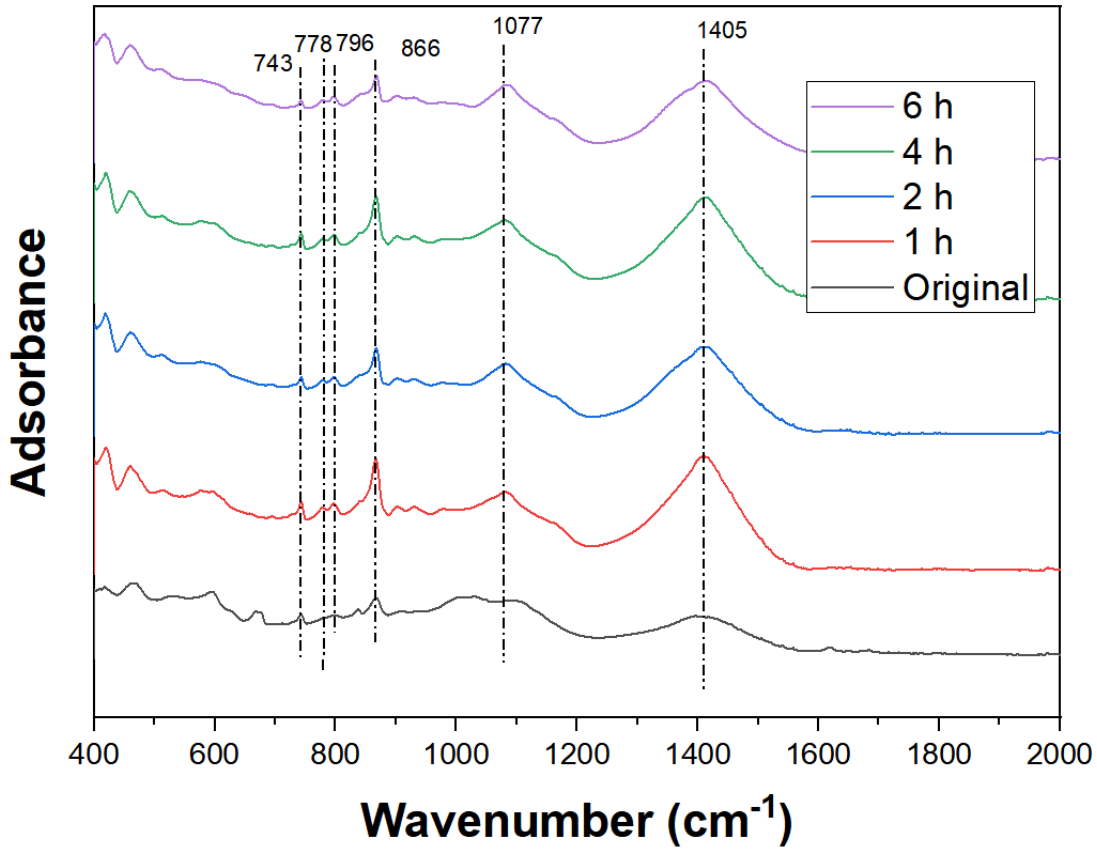

Figure S10. ATR-FTIR spectra of CMO at different time.

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