Simultaneously remove multiple heavy metals from soil by washing with citric acid and ferric chloride

Jiyan Shi[a], Jingli Pang[a], Qinglin Liu[a], Yating Luo[a], Jien Ye[a], Qiao Xu[a], Bibo Long[c], Binhui Ye[d] and Xiaofeng Yuan*[b]

[a]Department of Environmental Engineering, College of Environmental and Resource Sciences, Zhejiang University, Hangzhou, 310058, China.

[b]College of Life Science, Zhejiang Chinese Medical University, Hangzhou, 310053, China.

[c]Guangzhou Sugarcane Industry Research Institute, Guangdong Bioengineering Institute, Guangzhou, 510316, China.

[d]Chengbang Eco-Environment Co., Ltd., Hangzhou, 310002, China.

***Corresponding Author**

Xiaofeng Yuan, College of Life Science, Zhejiang Chinese Medical University, 310053 Hangzhou, China.

Tel.: +86-0571-88613051;

E-mail: yuanxiaofeng@zcmu.edu.cn.

Electronic Supplementary Information:

Number of pages: 7

Number of tables: 1

Number of figures: 5

Materials and methods

2.3. Determination of optimal washing conditions

Batch washing experiments were set to explore the optimal washing conditions by CA and $FeCl_3$ (v/v, 5:5). Experiments were performed as following parameters:

(1) Washing solution concentrations: 0.25, 0.5, 0.75 and 1.00 mol L^{-1} (washing time of 10 h, liquid: soil ratio of 10:1). The optimal washing concentrations will be used in the further experiments.

(2) Washing time: 0, 5, 10 and 15 min, 0.5, 1, 1.5, 2, 4, 6, 8, 10, 12, 18 and 24 h (liquid: soil ratio of 10:1). The optimal washing time will be used for further studies.

(3) Liquid: soil ratios: 1: 1, 3: 1, 5: 1, 7: 1, 10: 1, 12: 1, 15: 1, 20: 1 and 30: 1 (washing time of 10 h).

40

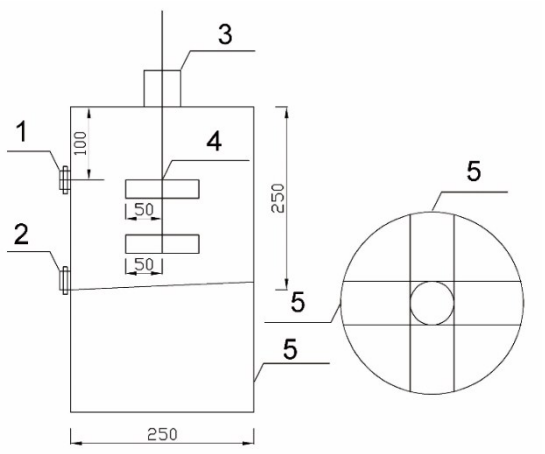

Fig. S1. Schematic illustration of experiment apparatus. 1, liquid sampling valve; 2, sludge sampling valve; 3, stirring paddle controller; 4, stirring paddle; 5, retractable frame.

42

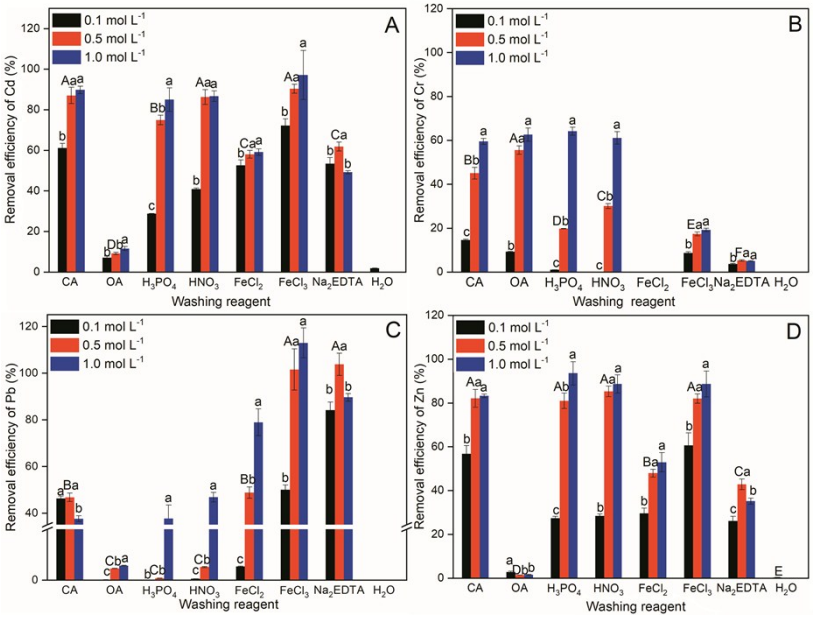

Fig. S2. Removal efficiencies of Cd (A), Cr (B), Pb (C) and Zn (D) by washing with different agents. Error bar indicate the standard deviation of the mean (n=3); Different letters (a-c) on the top of the error bars indicate significant difference among different agent concentration groups; Different letters (A-F) on the top of the error bars indicate significant difference among different agents at the concentration of 0.5 mol L^{-1} (one-way ANOVA, $P<0.05$).

Table S1. Removal efficiencies of heavy metals in different treatments. Different letters indicate significant difference among different treatments (one-way ANOVA, $P<0.05$).

Composite washing combination	Ratio (v/v)	Cd (%)	Cr (%)	Pb (%)	Zn (%)
HNO_3	/	93.6±1.6 (a)	46.8±1.7(de)	10.6±0.8 (g)	87.0±1.0 (a)
CA	/	78.4±2.0 (ef)	44.4±1.4 (ef)	51.5±3.5 (d)	81.2±0.6 (b)
OA	/	10.4±0.6 (m)	63.8±0.4 (a)	5.4±0.3 (ij)	9.0±0.2 (mn)
$FeCl_3$	/	67.7±1.0 (hi)	15.6±0.4 (l)	98.2±1.3 (c)	69.4±0.5 (f)
HNO_3: CA	8:2	89.4±2.7 (b)	42.0±1.4(fg)	8.2±0.4 (ghi)	81.0±1.4 (b)
HNO_3: CA	5:5	82.0±2.8 (cde)	38.8±1.3 (h)	9.5±0.6 (gh)	77.7±0.9 (c)
HNO_3: CA	2:8	79.9±2.3 (def)	42.8±0.0(fg)	27.5±0.8 (e)	80.4±0.8 (b)
HNO_3: OA	8:2	83.8±1.6 (c)	48.7±3.5 (d)	24.8±3.4 (e)	80.8±1.3 (b)
HNO_3: OA	5:5	29.5±2.3 (l)	58.8±3.3 (b)	5.6±1.5 (ij)	30.3±0.4 (k)
HNO_3: OA	2:8	12.2±0.6 (m)	59.2±1.2 (b)	4.6±0.3 (j)	10.2±0.8 (m)
HNO_3: $FeCl_3$	8:2	83.0±1.8 (cd)	32.8±1.2 (i)	51.3±1.9 (d)	79.9±0.6 (b)
HNO_3: $FeCl_3$	5:5	77.7±3.6 (f)	18.5±0.2 (k)	100.5±3.1(abc)	72.9±1.8 (d)
HNO_3: $FeCl_3$	2:8	72.9±1.5 (g)	16.1±0.5 (kl)	102.9±1.8 (a)	70.1±1.4 (ef)
CA: OA	8:2	33.4±3.8 (k)	46.0±1.1 (e)	7.1±2.3 (hij)	44.1±1.2 (j)
CA: OA	5:5	12.6±1.5 (m)	53.6±1.1 (c)	6.0±0.6 (ij)	12.9±0.2 (l)
CA: OA	2:8	7.8±0.4 (n)	60.6±1.2 (b)	3.9±0.2 (j)	8.0±0.2 (n)
CA: $FeCl_3$	8:2	80.4±1.6(cdef)	43.2±0.8(fg)	19.8±0.4 (f)	78.0±1.0 (c)
CA: $FeCl_3$	**5:5**	**73.7±3.0 (g)**	**41.3±0.8 (g)**	**98.0±1.3 (c)**	**71.4±1.3(de)**
CA: $FeCl_3$	2:8	73.1±1.4 (g)	27.2±0.8 (j)	99.5±4.1 (bc)	70.9±0.6 (ef)
OA: $FeCl_3$	8:2	61.9±3.3 (j)	59.5±3.0 (b)	24.9±0.6 (e)	56.3±1.2 (i)
OA: $FeCl_3$	5:5	70.3±1.8 (gh)	38.2±1.5 (h)	98.2±1.1 (c)	67.5±0.4 (g)
OA: $FeCl_3$	2:8	65.9±0.7 (i)	16.7±0.2 (kl)	102.0±0.5 (ab)	65.5±0.6 (h)

47

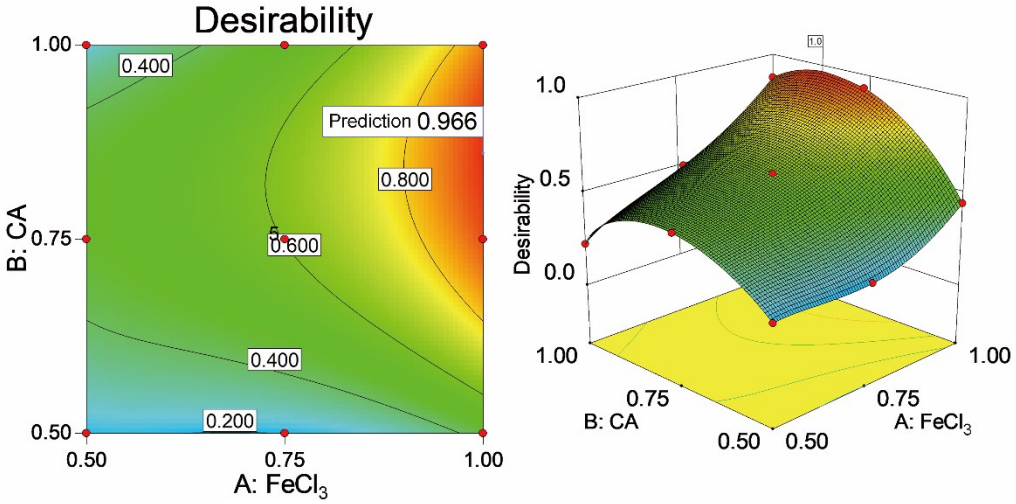

Fig. S3. The desirable washing agents concentration maps for the removal of heavy metals from soil obtained by response surface maps of model.

48

49

50

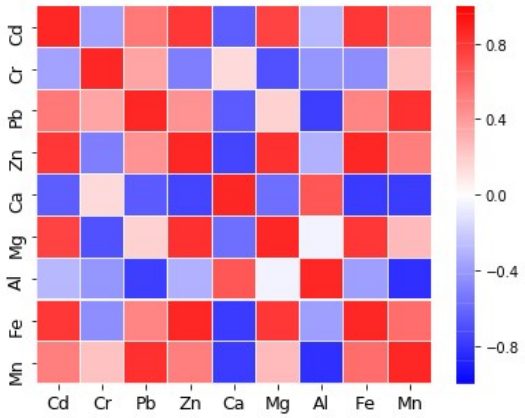

Fig. S4. Correlation analysis of the content of heavy metals and soil elements (Ca, Mg, Al, Fe, Mn) in different treatments.

51

53

54

55

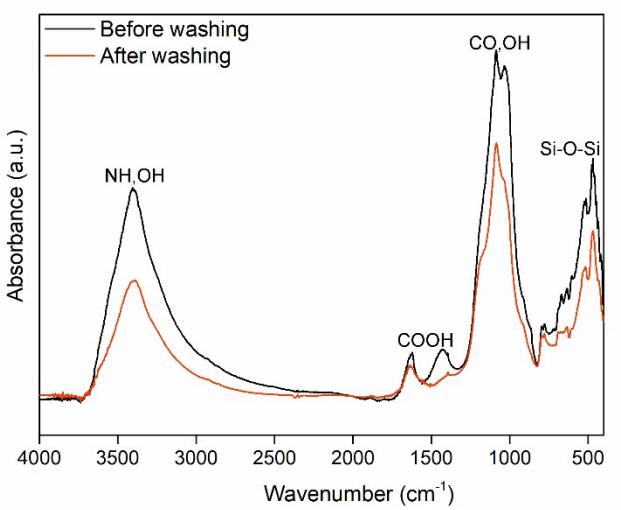

Fig. S5. FTIR image of the original soil before and after washing with CA and $FeCl_3$.

56