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- Supporting Information -

Quantification and isotherm modelling of competitive phosphate and silica adsorption onto micro-sized granular ferric hydroxide

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Figure S1: Redlich-Peterson isotherms for phosphate (left) and silica (right) in Di+NaCl for pH 6.0, 7.0 and 8.0.

Langmuir con	nstants					
Adsorbate	Matrix	pН	$K_L (L/mg)$	$q_m (mg/g)$		R ²
Phosphate	DI+NaCl	6	69.00	20.70		0.96
	DI+NaCl	7	40.00	16.70		0.90
	DI+NaCl	8	15.00	11.80		0.92
	DW	7	12.00	22.70		0.98
Silica	DI+NaCl	6	0.84	17.50		0.91
	DI+NaCl	7	0.60	28.00		0.95
	DI+NaCl	8	1.83	18.00		0.90
	Di+NaCl+Ca	7	0.64	29.90		0.92
	DW	7	0.29	23.8		0.98
Freundlich co	onstants					
Adsorbate	Matrix	pН	$K_f((mg/g)^*(L/mg)^n)$	n		R ²
Phosphate	DI+NaCl	6	20.40	0.16		0.96
	DI+NaCl	7	15.50	0.14		0.99
	DI+NaCl	8	10.70	0.16		0.96
	DW	7	20.00	0.25		0.95
Silica	DI+NaCl	6	7.41	0.42		0.98
	DI+NaCl	7	10.50	0.42		0.99
	DI+NaCl	8	10.2	0.39		0.99
	Di+NaCl+Ca	7	11.4	0.40		0.97
	DW	7	7.19	0.40		0.99
Redlich-Peter	rson constants					
Adsorbate	Matrix	pН	A (L/g)	b (L/mg)	β	R ²
Phosphate	DI+NaCl	6	1500.00	70.10	0.96	0.99
	DI+NaCl	7	500.00	30.30	0.95	0.99
	DI+NaCl	8	300.00	26.30	0.92	0.99
	DW	7	400.00	18.20	0.88	0.99
Silica	DI+NaCl	6	220.00	28.50	0.59	0.99
	DI+NaCl	7	200.00	24.50	0.45	0.98
	DI+NaCl	8	250.00	23.30	0.64	0.99
	Di+NaCl+Ca	7	200.00	15.30	0.65	0.99
	DW	7	200.00	27.10	0.61	0.00



Figure S2: Application of different multi-component isotherms on binary adsorption data for phosphate (left) and silica (right) with c0(P) = 5 mg/L and c0(Si) = 15 mg/L (DI+NaCl, pH 7.0).

NLMI

ELMI



NRPMI



MLMI



SRS



MRPMI



Figure 3: Multi-component isotherms for phosphate



ELMI



NRPMI



MLMI



SRS



MRPMI



Figure 4: Multi-component isotherms for silica

Influence of order of addition

The competition between phosphate and silica is dependent on pH value and order of adsorbate addition. As the equilibrium concentration of both adsorbates differ significantly from the single component isotherm independent of pH value, competition for same adsorption sites takes place, when sites are limited. For high adsorbent doses loadings identical to mono-component adsorption were observed. As phosphate loadings decrease and silica loadings increase with increasing pH in the range 6.0 to 8.0, the influence of competition increases for phosphate with increasing pH. Phosphate loadings are reduced by 33%, 41% and 50% compared to single component adsorption for pH 6.0, 7.0 and 8.0 respectively. Also through the addition of silica, previously adsorbed phosphate is replaced. Is silica adsorbed first, it shifts the pH_{PZC} of iron hydroxides to lower values (Luxton et al. 2006) and thus complicates phosphate adsorption. P loadings were reduced by 26% ($c_{eq} = 2 \text{ mg/L}$, pH = 6.0) in comparison to loadings with phosphate addition first. Silica adsorbs exclusively as Si(OH)₄ up to pH 8.0.

Another possible explanation for the decrease in adsorbed phosphate is the polymerization of silica on the iron surface which blocks adsorption sites from the contact with phosphate. For silica adsorption no influence of addition order was observed for pH 6.0. At pH 7.0 and 8.0 an increase in loadings of 15 to 28% was measured if silica was adsorbed first. Due to the induced rise in surface charge phosphate adsorption and consequently silica replacement was reduced.



Figure S5: Adsobent loadings of phosphate and silica dependent on pH and order of addition.



Figure S6: Species distribution of adsorbed phosphate (left) and silica (right) on ferric hydroxide dependent on pH; modelled using double layer model of Mineql5.0.