Electronic Supplementary Material (ESI) for Analyst.

An interdisciplinary review of selenium sorbents and reduction

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Table S1: Employment of gold nanoparticles on for determination of selenium

Nanomaterial	Method	Determined species	Electrolyte	Linear range; detection limit	Ref #
AuNP Electrodeposited on GCE	ASSWV, peak at ca 0.85 V[a]	Se(IV)	0.1M H_2SO_4	0.001-50 ppm; 0.34 ppb	[1]
Au nanostars on carbon screen-printed electrode	ASSWV, peak at ca 0.65 V[a]	Se(IV)	Britten-Robinson buffer	0 – 100 ppm; 1.6 ppm	[2]
Electrochemically obtained AuNP on GCE	ASSWV, peak at ca 0.7 V[a]	Se(IV)	1 M $HClO_4$	10 – 50 ppm; 0.12 ppm	[3]
AuNP electrodeposited on Au-embedded carbon film electrode	ASSWV, peak at ca 0.9 V[a]	Se(IV)	0.1M H_2SO_4	N/A; <10 ppb	[4]
AuND@perforated rGO	ASSWV, peak at ca 0.9 V[a]	Se(IV)	1 M $HClO_4$	0.24 – 23.7 ppm; 0.07 ppm	[5]

[a] potential versus Ag|AgCl reference electrode

AuNP – gold nanoparticles; GCE – glassy carbon electrode; ASSWV – anodic stripping square wave voltammetry; AuND – gold nanodendrites; rGO - reduced graphene oxide

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Table S2: Selected studies on different aspects of selenium adsorption on zero-valent iron (ZVI)

Se form	Features assessed	Findings	Reference
Se(VI)	Se removal in presence of other ions	PO_4^{3-} and SO_4^{2-} most influencing; Se(VI) reduced to Se(IV) upon adsorption to ZVI	[6]
Se(VI), Se(IV)	Preconcentration of total inorganic Se for analysis	Se(IV) and Se(VI) adsorbed to ZVI between pH 1-7, 95% recovery by $NaOH+Na_2SO_3$ solution	[7]
Se(VI)	pH and aeration rate	Intense aeration responsible for oxidation of Fe^{2+} to Fe^{3+} which is unfavourable for Se(VI) reduction and adsorption; highest adsorption rate → low aeration, acidic conditions	[8]
Se(IV)	Effect of ageing and WMF application	WMF increased the absorption rate 10 to 100 fold, longer ageing slowed the Se sorption rate	[9]
Se(IV)	Effect of WMF	At lower Se(VI) concentrations, pH 6, oxic conditions, WMF effect was the highest; detailed Se sequestration kinetics	[10]
Se(VI)	Influence of H_2O_2, ZVI-packed column	H_2O_2 promoted ZVI corrosion which correlated with increased Se adsorption	[11]
Se(VI), Se(IV)	Influence of brining with different salts	ZVI corrosion induced in the order: $NH_4Cl>NaH_2PO_4>Na_2SO_4>NaCl>NaHCO_3>$ $>Na_2SiO_3$,	[12]
Se(VI)	Influence of nitrate, sulphate under neutral pH, oxic condition	SO_4^{2-} slowed the absorption rate approximately 30-fold, NO_3^- cca 20-fold. Identification of product of ZVI oxidation	[13]
Se(VI)	Influence of aeration and presence of Fe^{2+} ions	Synergic effect of O2 and Fe^{2+} presence improved ES → positive effect on ZVI surface oxidation and Se(IV) reduction; approx. 2.5-fold higher absorption capacity	[14]
Se(VI)	Influence of pH, interfering ions on ES	The highest ES at pH 5. Sulphate, phosphate increased ES at low concentration and decreased it at higher concentrations	[15]
Se(VI), Se(IV)	Effect of buffer solution, decoupled from influence of pH	Buffer solution effect (decoupled from effect of pH) much higher on Se(VI) sequestration which was suppressed by buffer at pH 4-10.	[16]
Se(VI)	Effect of sulfidation and Fe^{2+} ions	Synergic effect of both factors by sulfidation-induced ZVI corrosion and Fe^{2+}-improved electron efficiency	[17]

ES – electron selectivity; WMF – weak magnetic field

Table S3: Selected studies on selenium adsorption on **nano**ZVI

NanoZVI form	Se form	Performance	Notes	Reference
NanoZVI in porous polymeric ion exchanger	Se(VI)	200 ppm sequestered by 99% after 12 h; pseudo-first order kinetics rate = 0.161 h^{-1}	Synergy of nanoZVI and polymer; efficient at pH 3-10	[18]
NanoZVI alone and entrapped at Ca alginate	Se^{a}	From 34 ppm to <1ppm after 3 hours	Encapsulation in Ca alginate decreased adsorption rate	[19]
Bare nanoZVI	Se(VI)	Initial (0-30) reaction rate 4 fold higher compared to ZVI; q = 138.18 mg g^{-1}	Analyses shown Se(IV) was reduced to Se(-II) (FeSe)	[20]
Bare nanoZVI	Se(IV)	20.5 mg g^{-1} of Se(IV) removed from water in 3 min	Detailed microscopic and spectroscopic study of Se sorption mechanism	[21]
Bare nanoZVI	Se(VI), Se(IV)	Se(IV) – 92.2% sequestration in 5 min; Se(VI) - 69%. Both pH 4, initial concentration 2 mg l^{-1}	Se(VI) adsorbed well only under low pH, Se(IV) adsorbed better also at higher pH. Sulfate, bicarbonate decreased Se(VI) adsorption, humic acid hindered Se(IV) ads.	[22]
Z-nanoZVI	Se(VI)	Comparison with pristine nanomaterials; batch, 15 mg l^{-1} initial Se concentration	Adsorption rates: 0.0003, 0.0318 and 0.076 min^{-1} for zeolite, nanoZVI and Z-nanoZVI	[23]
AC-nanoZVI	Se(IV)	Batch, 20-160 mg L^{-1} initial Se concentration; EK-PRB system also tested	q = 46.5 and 33.7 mg g^{-1} for AC-nanoZVI and AC-Fe(II), respectively	[24]
BC-nanoZVI	Se(VI), Se(IV)	Compared with AC-nanoZVI, influence of pH, ions.	q = 62.5 and 35.4 mg g^{-1} for Se(IV) and Se(VI), respectively. q for AC-nanoZVI was lower. In all cases anions competed with Se sorptions	[25]

q – maximum sorption capacity

[a] – unspecified selenium form

Z-nanoZVI – zeolite-supported nanoZVI; AC-nanoZVI – activated charcoal-supported nanoZVI; EK-PRB – electrokinetics combined with permeable reactive barrier

Table S4: Selected studies on selenium adsorption on iron (hydr)oxides

Fe species studied	Se form	Notes	Results	Reference
α-, β-, γ-, δ-FeOOH, amFe	Se(IV)		α-FeOOH – *q* is about 6.3 mg g^{-1}; amorphous ferrihydrite – *q* is about 32 mg g^{-1}; capacity increased in the order, β-<α-<γ-<δ-FeOOH	[26]
α-FeOOH, amFe	Se(VI), Se(IV)		Optimum pH found 5; *q* for α-FeOOH “much less than for am-Fe”	[27]
α-FeOOH	Se(VI)		Positive effect of low concentrations of carbonate, acetate and formate on Se(VI) sorption	[28]
Amorphous Fe oxide	Se(IV)	Compared with clays, soils and Al oxide	Triple layer model developed for Se(IV) adsorption, function of pH	[29]
ferrihydrite	Se(VI), Se(IV)		Citric acid suppressed sorption of selenium, salicylic acid did not	[30]
FeOOHs prepared at diverse pH	Se(VI), Se(IV)	Lower synthesis pH increased surface positive charge	Maximum *q* = 4.3 mg g^{-1} (Se(IV)) and 0.01 mg g^{-1} (Se(VI)) for synthesis pH=2.5	[31]
Commercial FeOOH	Se(IV)		29.4 mg g-1 at pH 5, temperature 35°C; only minor decrease of Se(IV) removal efficiency by phosphate (50 mg L^{-1}).	[32]
Fe oxide (91.5% Fe), majority as α-FeOOH	Se[a]	Field test	Fe oxide-ammended soil removed 76.1% Se from the treated leachate	[33]
Fe_3O_4 (magnetite)	Se(VI), Se(IV)		At pH=4 similar *q* for Se(IV) and Se(VI) (3.5 and 3.1 μmol m^{-2}, respectively)	[34]

q – maximum theoretical sorption capacity

[a] – unspecified selenium form

amFe – amorphous ferrihydrite

Table S5: Selected studies on selenium adsorption on layered double hydroxides(LDH)-based (nano) materials

LDH type	Se form	Performance	Notes	Reference
Mg-Al, Zn-Al LDHs	Se(VI), Se(IV)	Se(IV): q =120 and 98.7 mg g^{-1} for Mg-Al and Zn-Al LDH	Se(VI) – "similar adsorption trend as Se(IV)"; adsorption at pH 4.5-10; interference by phosphate, sulfate	[35]
Mg-Al LDH	Se(VI), Se(IV)	Se(VI): q = 24.8 mg g^{-1} Se(IV): q = 22.3 mg g^{-1}	interference by phosphate, sulfate	[36]
calcinated Mg-Al LDH	Se(IV)	q = 179.6 mg g^{-1}, at pH 6	the calcination increased q approximately 3-fold; only 20% decrease of q in presence of phosphate	[37]
Mg-Al-CO_3 LDH	Se(VI), Se(IV)	Se(VI): q = 103 mg g^{-1} Se(IV): q = 168 mg g^{-1}	Se(IV): low sulfate interference at lower pH (4.5), higher pH=higher SO_4^{2-} competition; Se(VI) sorption more affected by sulfate	[38]
granulated Mg-Al LDH	Se(VI)	q = 66 mg g^{-1}, at deionized water, < 0.001 mg g^{-1} at wastewater	much higher adsorption of sulfate observed; but field study shown Se was removed from wastewater	[39]

q – maximum theoretical sorption capacity

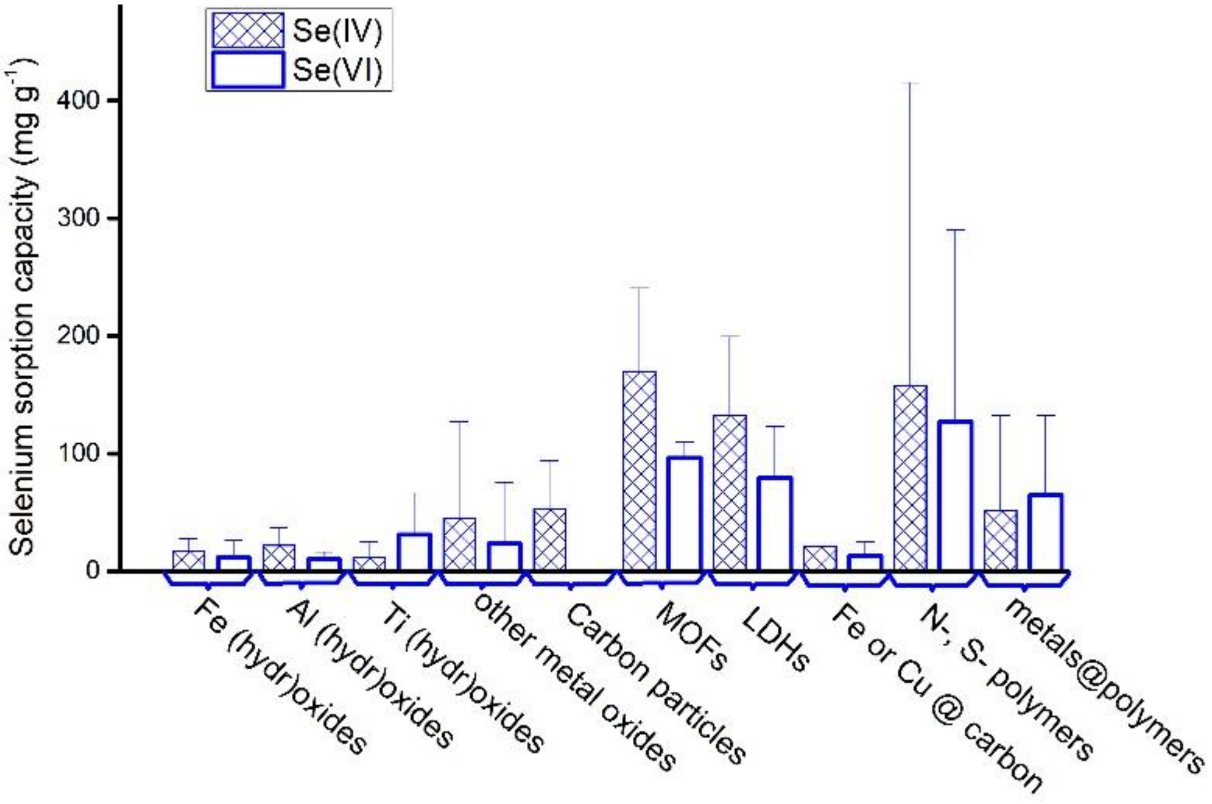

Figure S1: Average (bars) and maximum (standard deviations) theoretical sorption capacities towards selenite and selenate ions (indicated in the graph) for the following groups of materials (from left to right): iron oxides and/or hydroxides; materials/particles based on aluminium oxides; materials/particles based on titanium oxides; other materials based on metal oxides including binary oxides, Ca, Cu, Mn oxides and so on; materials/particles derived from waste biomass; metal organic frameworks (MOFs); layered double hydroxides (LDHs); activated carbon or charcoal decorated with Fe or Cu ions; engineered polymers, polycations and (nano)materials. Where possible, optimum conditions, that is, the highest sorption capacities achieved, were considered for the average calculation to point out the potential of the material.

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