Electronic supporting information for

Magnetic EDTA: Coupling heavy metal chelators to metal nanomagnets for rapid removal of cadmium, lead and copper from contaminated water

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Functionalization of the magnetic nanoparticles

The magnetic carbon coated iron nanoparticles (Fe/C, Turbobeads LLC, Switzerland, 25 m^2/g) were washed 5 times for 24 h in concentrated HCl (Fluka, puriss) / deionized water (Millipore, resistivity 18.2 MΩ) mixture (2/1). Afterwards the acid was removed by washing with millipore water (3x) and the particles were dried at 50°C in a vacuum oven.

The physisorption of the polymer was done by dispersing 500 mg of acid treated particles in 10 ml of dry (Molecular Sieve: Z4-0.1, 2.0-3.0 mm; Zeochem) N, N-Dimethylformamide (DMF) (puriss ≥ 99.8 %, Fluka) and then adding 50 ml of the Polyethyleneimine (PEI) solution. This solution was prepared by dissolving 4 g of PEI (99 %, Mw: 10'000, Polysciences Inc.) in 60 ml of dry DMF. The particles were stirred with the polymer at room temperature for 20 h, then collected with a magnet and washed 3x with DMF. For the functionalization of the physisorbed polymer with the diethylenetriaminepentaacetic acid (DTPA) moieties, 50 ml of dry DMF was added to the Fe/C-PEI particles and a clear solution of 30 ml dry DMF, 1.8 ml triethylamine (TEA, Fluka, puriss 99.5 %) and 1 g diethylenetriaminepentaacetic acid dianhydride (DTPAda, Aldrich, 98%) was added to the particles. The mixture was heated to 80°C for 15 minutes and left stirring overnight at room temperature. The particles were separated by a permanent magnet and washed 3x with 1% TEA in DMF, 3x with water, 3x with acetone and dried in an exsiccator. The Fe/C-Pei-DTPA particles were stored at -18°C.

A quantitative measure was carried out by elemental analysis as shown in table S1, where the increase in nitrogen content is a clear indicator for the adsorbtion of PEI and the later on attachment of the DTPA. From the difference in the nitrogen content the heavy metal ion chelator loading of the nanoparticles was calculated. The increase of 0.51 mmol of nitrogen in the last reaction means that about 170 µmol of DTPA (containing three nitrogens) is bound to the particle surface.

Table S1. Elemental analysis data of each functionalization step and amount of nitrogen added, compared to the prior step.

	C (wt %)	N (wt %)	ΔN (mmol)
Fe/C	11.25	0.03	
Fe/C-PEI	14.21	1.91	1.34
Fe/C-PEI-DTPA	15.86	2.62	0.51

PEI desorption experiments

The PEI desorption experiments were carried out by weighing 100 mg of Fe/C-PEI and diluting the

particles with 100 ml of an acetate buffer (pH 3.5). After sonicating the mixture for 1h the particles

were removed from the solution and washed 3x with water, 3x with acetone and dried in an exsiccator.

As the error of the microanalysis data is about 3% the carbon and nitrogen content of the particles

before and after washing stays constant, PEI seems to be irreversibly adsorbed on the particle surface.

Table S2. Elemental analysis data of PEI desorption experiments.

	C (wt %)	N (wt %)
Fe/C-PEI before	14.21	1.91
Fe/C-PEI after	14.18	1.89

Batch adsorption experiments

5 mg of the functionalized Particles were weight in purified plastic tubes (24 h in 1 % HNO_3 (Fluka,

TraceSelect), 75 °C) and contaminated using a 10 ml heavy metal containing standard. These solutions

were prepared by diluting 10 mg/L heavy metal stock solution with a buffered solution at pH 6.5 with 1

g/l BisTris (Bis(2-hydroxyethyl) iminotris(hydroxymethyl) methane, Fluka, BioChemika, 99%) and

acidified with concentrated HNO_3. The 10 mg/L stock solutions were prepared with heavy metal

standards (for Pb: Lead ion chromatography standard solution, 1000 mg/l, Fluka. For Cd: Cadmium

standard for AAS, 1000mg/l, Fluka. For Cu: Copper standard for AAS, 1004 mg/l, Fluka) and diluted

with a buffer at pH 6.5 with 1 g/l BisTris (Bis(2-hydroxyethyl) iminotris(hydroxymethyl) methane,

Fluka, BioChemika, 99%) and acidified with concentrated HNO_3. The mixture was sonicated for 10

seconds to disperse the particles and shaken for 4 min 50 sec. The particles were removed with a

permanent magnet for 20 sec. The decanted solutions were spiked with Ir at a concentration of 20 μg/L,

which was used as an internal standard for ICP-MS analysis.

In the experiments where the influence of the pH on the adsorption was tested, the different pH solution

were prepared for pH 2.2 and 3.2 with a acetate puffer (1 g/l, Sodium acetate, Fluka, purum) acidified

with HNO_3. The other puffers were created using 1 g/l BisTris and sodium hydroxide (Fluka, purum).
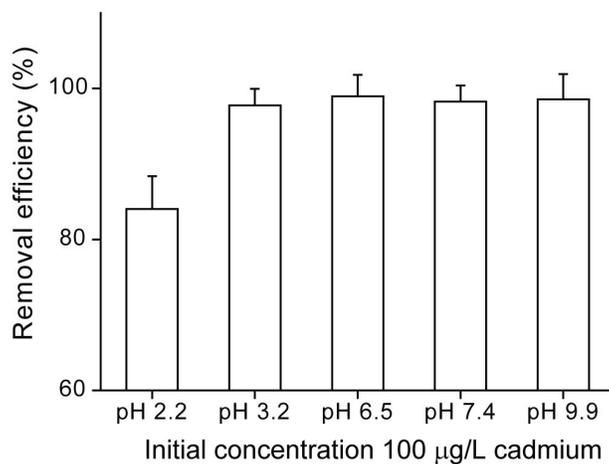
The results are shown in figure S2.

Figure S2. Removal efficiency depending on the pH is shown.

Recycling experiments

Following the copper adsorption the particles were washed two times in 5 ml solution of 8 g DTPA and 14 g Bis(2-hydroxyethyl) iminotris(hydroxymethyl)methane (Bis-Tris, Axon Lab AG, molecular biology grade) in 1 l water (pH ~5.5). Then three times in 5 ml of 5 g Bis-Tris in 1 l water at pH 5.5 and afterwards two times with water. The complete washing solution was collected and copper ion concentration was measured with AAS (Varian Spectra AA 220FS).

In the recycling experiments 60 mg EDTA functionalized particles were used in 20 ml of 20 ppm contaminated water. In the first adsorption run about 93 % of copper was extracted (Figure S3). The following first washing procedure removed 29 % copper ions from the particles. Meaning that about 71 % of the adsorbed copper ions remained on the particles, this behavior suggests a heterogeneous surface with surface sites where it is difficult to remove adsorbed species. In the second extraction the copper removal efficiency was only 69 %. The second and third washing step removed nearly all ions from the adsorption step. According to the second and third adsorption the amount of adsorbed cooper ions does not dramatically decrease anymore. The ability to remove adsorbed metal ions by washing can be used for recycling or concentrating metal ions from contaminated waste streams, indicating that the beads can be used numerous times.
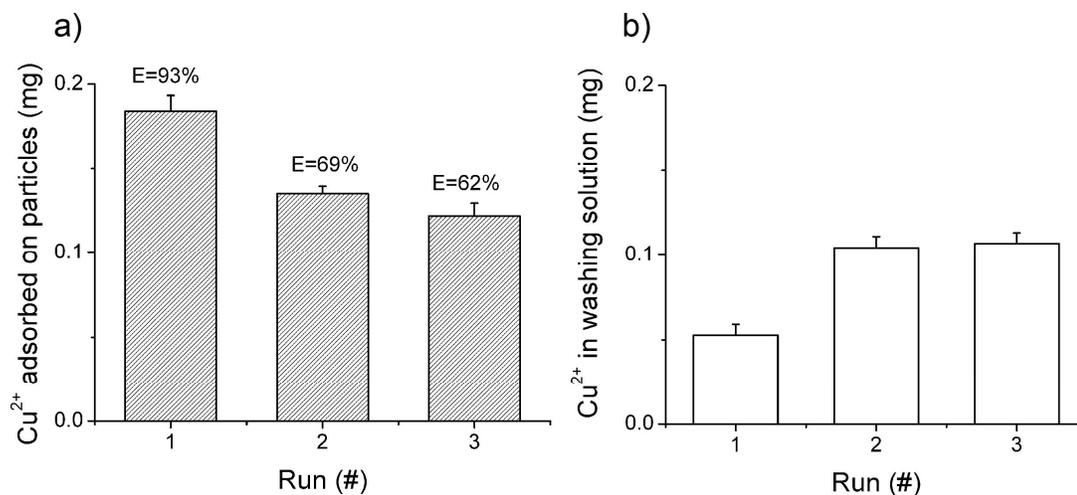
Figure S3. a) Amount of adsorbed copper ions on particles (0.11 vol %) for copper extraction out of 10 ml with 20 ppm copper ions after each run, with corresponding removal efficiency (E). b) Amount of copper ions released in solution during washing procedure following the adsorption step.

Determination of residual particles

With a Nanosight LM20 (Nanosight Ltd., UK) the particle concentration could be estimated. The Nanosight LM20 visualizes each individual nanoparticle by a light scattering technique. In the analysis of the magnetically purified solutions less than 10^6 particles/ml were detected.

ICP-MS Measurements

The ICP-MS measurements were performed on an Agilent 7500cs (Agilent Technologies, Waldbronn, Germany).

Table S3. Settings of the ICP-MS

Rf power	1500 W
Sampling depth	5.2 mm
Nebulizer gas	0.97 L/min Ar
Makeup gas flow	0.24 L/min Ar
Measured isotopes	^{63}Cu, ^{65}Cu, ^{111}Cd, ^{114}Cd, ^{191}Ir, ^{193}Ir, ^{206}Pb, ^{208}Pb
Internal standard	^{193}Ir