

Algae-Silica Hybrid Materials for Biosorption of Heavy Metals

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Abstract

Algae-silica hybrid materials for biosorption purposes were prepared using sol-gel technology. The resulting biological ceramics (biocers) ought to combine the mechanical stability and porosity of the silicate matrix with the algae's capability for the biosorption for heavy metals. The structure, mechanical properties, and sorption capability of such algae-silicate materials were investigated. Comparative equilibrium sorption experiments were performed batchwise with 13 different microalgae and macroalgae powders, and the corresponding algae biocers using waters loaded with either concentrations of nickel below 3mg/L or a mixture of different heavy metals (Cr, Ni, Cu, Pb). The algae biocers showed good mechanical stability up to an algae content of 30-50% and a total porosity of 40-60%. The silica matrix itself was involved in the sorption of metals. The metal binding capability of embedded macroalgae biomass was unaffected by immobilisation in the silica matrix. In contrast, for waters with nickel or different heavy metals, reduced sorption capability was shown by embedded microalgae.

Keywords: Biosorption, Algae, Sol-Gel Process, Immobilisation, Heavy Metals, Biological Ceramics

1. Introduction

The removal of low concentrations of heavy metals from industrial wastewater and naturally occurring waters remains a problem, both technically and economically. For example, depending on local geology, many aquifers contain heavy metals such as nickel, uranium or arsenic in the lower $\mu\text{g/L}$ range, but sometimes in concentrations which cannot be tolerated for drinking water. Using the high biosorption capability exhibited by many algae [1-5], bacteria [6,7], and yeasts [8] might be a cost-effective way of treating such waters.

The biosorption behaviour (selectivity and capacity) of a biocomponent depends on the composition of binding sites on its surface. Consequently, different biocomponents are suitable biosorptive materials for different water compositions. In this regard, algae appear very promising. Several micro- and macroalgae are commercially available on a large scale and at low cost. Since viability is not necessary for biosorption, dried algae or even algal extraction residues (by-products from the high-pressure extraction of valuable algal components) [1,2] can be

used as biosorptive material.

Biomass used for the sorption of heavy metals from waters in commercial applications must be immobilised in order to meet technical demands. Generally, packed-bed columns are used, calling for a stable, porous material with a specific grain size. Moreover, immobilisation must prevent the release of biomass or of biomass compounds (e.g. dyestuffs).

The sol-gel technology offers a cost effective way to fulfill these requirements. In last years the use of sol-gel matrices for immobilizing biocomponents has attained increasing importance [9-13]. The sol-gel process is characterised by the aggregation and condensation of nanoparticles of silica or metal oxide sols, resulting in a lyogel and after drying in a xerogel. This solidification process can be used to embed biocomponents within the three-dimensional gel network. Combining a ceramic-like oxide matrix with biological systems ("biocers") offers important advantages. The mechanical, chemical, thermal and photochemical stability of the inorganic host matrix and the broad range of applicative forms of sol-gel derived materials (e.g., coatings, granules, shaped

bulk products, extremely porous aerogels) make such biocomposites very promising for technical applications. The porosity and the degree of immobilisation of the embedded biocomponents can be controlled over a wide range. Depending on the preparation conditions, embedded biocomponents may be easily accessible to external reagents, and chemical reactions can proceed within the inorganic layer at high speed. So far, sol-gel matrices have been used to immobilise different types of living cells such as bacteria, yeasts, and plant or animal cells, and it has been demonstrated that they retain their bioactivity [10,13–16]. For biosorption purposes, the structure and metal-binding capacity of different types of sol-gel immobilised bacteria [17] and yeast [18,19] have been investigated with regard to their practical use for the selective and reversible accumulation of heavy metals and radionuclides.

This paper focuses on the use of silica sols for the embedding of algae biomass within stable and porous silica matrices, and on characterising the biosorption capabilities of such composites.

2. Materials and Methods

2.1. Algae

Algae were obtained as dried powders from the Institute for Cereal Processing (Nuthetal, Germany). The algae used are shown in Table 3.

2.2. Silica Sols

Nanosol A: 10mL TEOS (tetraethoxysilane, Fluka), 40mL ethanol and 20mL 0.01N HCl were stirred for 20 h at ambient temperature, resulting in an acidic nanosol with approximately 4.2% solid content.

Nanosol B: Nyacol 1440 (Akzo Nobel Chemicals Wurzen). This is an aqueous silica sol with 40% solid content and a mean particle diameter of 14nm.

Nanosol C: The sol was prepared by mixing 78wt% Nyacol 1440 (Nanosol B) with an organically modified sol D (22wt%).

Nanosol D: 52g TEOS, 69.5g GLYEO ((3-glycidioxypropyl)triethoxysilane, Fluka), 150mL 0.01M HCl and 150mL ethanol were stirred for 20 h at ambient temperature, resulting in an acidic nanosol with a solid content of approximately 8.4%.

2.3. Preparation of Algae Biocers

Algae biocers were produced by mixing the nanosols A-C with algae mass which had been pre-washed in deionised water. Before mixing, the sol was adjusted to about

pH 7. After neutralisation the gelling occurred rapidly, embedding the algae within the silica matrix. The algae contents were 20% (wt/wt SiO₂). In some cases, algae content up to 50% was used. The gels were aged for 3 days at 4°C, then cut into small pieces, dried, and sieved to give particles with a size of approximately 0.5-1.2mm. Those algae biocers made from nanosols B or C were heated for 1 h at 120°C after gelling and drying.

2.4. Sorption Experiments

Comparative equilibrium sorption experiments were performed batchwise with different algae and algae biocers that had been double washed in H₂O beforehand. The non-immobilised algae and the biocers (30-1000mg) were shaken for 24 h at 30°C in a volume of 30 or 300 mL. Nickel sorption experiments were carried out in drinking waters (pH 7) with initial concentrations of 1.7 or 2.2mg/L. For experiments with a mixture of copper, nickel, chromium and lead, the initial concentration of each metal was 0.2mM. pH was adjusted to 4.5 to avoid precipitation.

The residual metal concentrations were determined by inductively coupled plasma mass spectroscopy (ICP-MS).

2.5. Characterisation of the Biocers

Pore size distribution was measured by mercury intrusion (Pascal 140 and 440, Porotec) which evaluates pore diameters in the range of 4nm to 100µm.

To characterise particle stability, aliquots of 5mL biocer material with a grain size between 400-600µm were exposed to different compressive forces (3, 5, 7, and 9kN) in a stainless steel cylinder, inner diameter 25mm and height 90mm. The compressed material was retained by a loosely fitted steel cap on the bottom of the cylinder. Compression assays were carried out with a compression testing machine LP1 (Heckert Werke, Germany). After compression the biocers were subjected to sieve analysis.

The structures of the biocers were monitored by light microscopy (Keyence VHX-100 digital microscope) and by scanning electron microscopy. For the latter, the samples were embedded in liquid colloidal silver on conductive carbon sheets. After shadow casting with carbon (Baltec MED 010, BAL-TEC, Liechtenstein), the biocers were examined using a Gemini 982 scanning electron microscope (LEO, Oberkochen) with an energy dispersive X-ray analyser (NORAN X-ray detector) at 1–5kV.

Polished specimens were produced by embedding the biocer particles within epoxy resin, which then underwent fractionated grinding with abrasive paper of different grain sizes and polishing with a diamond suspension of 6µm particles.

3. Results and Discussions

3.1. Preparation and Properties of the Algae Biocers

The immobilisation matrix has to fulfil partly contradictory requirements. It must have good mechanical stability, high porosity, safe immobilisation, good accessibility of the binding groups of the biocomponents, and allow cost-effective production on a large scale.

Two silica-sol variants were tested for algae immobilisation: a sol prepared by the acid-catalysed hydrolysis of tetraethyl orthosilicate (TEOS, sol A), and the commercially available Nyacol® (sol B). Nanosols produced from aqueous sodium silicate using ion exchange techniques are very cost effective. Diverse aqueous dispersions of colloidal polysilic acid are commercially available, e.g. Nyacol®/Akzo Nobel, Ludox®/Grace, Levasil®/Bayer, and Köstrosol®/Chemiewerke Bad Köstritz. To prepare the biocers, the silica sol was neutralised. Then the algae were admixed into it by vigorous shaking. Neutralisation promotes the sol-gel transition that results in the embedding of the algae biomass within the inorganic network. Dried and, in the case of macroalgae, ground biomass was used in preparing the biocer. Once solid, the gels were cut into small pieces and dried. Air-drying resulted in noticeable shrinkage of the silica network, with the formation of a hard, non-compressible material. Before performing the experiments, the biocers were sieved to a particle size of 0.5-1.2mm (Figure 1).

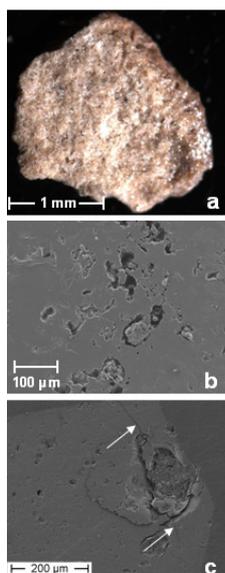


Figure 1. (a) Microscope picture of a *Fucus* biocer particle. (b) Cross-section (SEM micrograph, polished specimen) of a *Spirulina* biocer. (c) Cross-section of a *Spirulina* biocer (polished specimen). The arrows mark cracks starting from aggregated *Spirulina platensis* algae.

Table 1. Percentage of different particle size classes for different algae-biocers after compression at distinct forces.

Sample	particle size class µm	compressive force (kN)			
		3	5	7	9
<i>Fucus</i> biocer (sol B)	>0 up to ≤ 200	15	17	24	24
	>200 up to ≤ 400	19	26	23	24
	>400	66	57	53	52
<i>Spirulina</i> biocer (sol B)	>0 up to ≤ 200	9	16	19	14
	>200 up to ≤ 400	16	20	21	26
	>400	75	64	60	60
<i>Fucus</i> biocer (sol A)	>0 up to ≤ 200	7	11	14	17
	>200 up to ≤ 400	10	14	15	18
	>400	83	75	71	65
<i>Spirulina</i> biocer (sol A)	>0 up to ≤ 200	5	7	11	14
	>200 up to ≤ 400	10	12	16	17
	>400	85	81	73	69

Homogeneous distribution of the embedded algae within the silica matrix was crucial for the mechanical stability of the resulting biocers. Aggregated algae promoted crack formation (Figure 1(c)). Adding the coating additive Addid® 200 (Wacker-Chemie GmbH, Munich, Germany), a polyether-modified polysiloxane, to the silica sol improves the uniformity of the algae distribution.

To evaluate the mechanical stability of the prepared algae biocers, changes in the particle size distribution were noted after agitation in water for 24 hours. It was shown that biocers made with Nyacol broke up into smaller particles, as a result of swelling of the embedded algae after wetting. In particular, biocers with macroalgae powder showed reduced stability due to their swelling behaviour and larger particle size of about 100-400 µm. Matrix stability could be sufficiently enhanced by heating the biocers for one hour at 120°C, and by the admixture of a GLYEO ((3-glycidioxypropyl)triethoxysilane) modified sol (sol C). Using the Nyacol-based sol C, mechanically stable biocers could be made with a microalgae content up to 50% (wt/wt SiO₂), or 30% in the case of macroalgae.

Further demonstrating mechanical stability, Table 1 shows the particle size distribution of algae biocers after compression experiments with different forces. The starting material had a grain size of 400-600µm.

The compression experiments revealed the stability of the dry bulk material. More than 50% of the particles remained unchanged in size (detected by the fraction greater than 400 µm) for each of the samples under investigation, even after exposure to 9kN pressure force. Generally, the two samples prepared by using sol A were more stable than those with Nyacol, as indicated by the greater fractions of unbroken particles.

Shrinkage of the gel matrix during drying resulted in a compaction of the embedded biocomponents and decreasing porosity of the biocer material. The shrinkage,

pore structure and rigidity of the matrix could be controlled by the SiO₂ solid content, the drying regime (e.g. air- or freeze-drying), the residual water content, the addition of fillers (e.g. ceramic fibres) [20], or by the leaching of admixed pore-forming additives [21,22]. Also, the structure and size of the embedded biocomponents were crucial to the exhibited porosity. Mercury intrusion was used to evaluate the pore diameters of dry algae biocers in the range of 4nm to 100µm. Figure 2 shows the pore size distribution of Fucus biocers made by using sol variants A and B. Biocers based on sol B showed higher total porosity with a high quantity of mesopores in the range of 10nm. The embedded Fucus vesiculosus biomass presumably caused the exhibited macroporosity. A similar pore distribution was also shown by Chlorella vulgaris biocers (Table 2); although the total porosity was marginally lower. However, total porosity between 38% and 60% allowed a good mass transfer.

3.2. Biosorption of Nickel by Different Algae and Algae Biocers

To examine how embedding algae within a silica matrix affects their metal-binding capability, non-immobilised

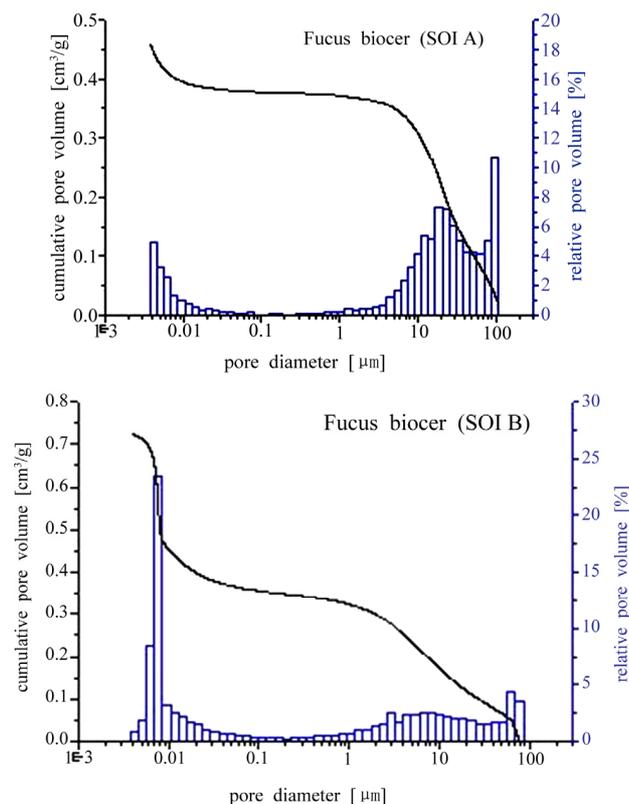


Figure 2. Pore size distribution in two Fucus biocer variants prepared using sol A or sol B. Columns=relative pore volume, curve=cumulative pore volume.

Table 2. Porosity of Fucus and Chlorella biocers prepared using sol A or sol B.

	Fucus biocers		Chlorella biocers	
	Sol A biocer	Sol B biocer	Sol A biocer	Sol B biocer
Total cumulative volume (cc/g)	0,4595	0,7240	0,3697	0,6645
Total porosity (%)	43,9	60,2	37,8	57,7
Bulk density (g/cm ³)	0,9558	0,8314	1,0233	0,8687
Apparent density (g/cm ³)	1,7042	2,0883	1,6459	2,0550

Table 3. Biosorption of nickel by different algae.

Algae	Bound Ni	
	%	mg/g
<i>Scenedesmus obliquus</i>	60	0.80
Kelp	48	0.64
<i>Laminaria saccharina</i>	46	0.61
<i>Chlorella vulgaris</i>	43	0.58
<i>Laminaria digitata</i>	41	0.55
<i>Ascophyllum nodosum</i>	39	0.52
<i>Nannochloropsis oculata</i>	38	0.51
<i>Haematococcus pluvialis</i>	36	0.48
<i>Fucus vesiculosus</i>	31	0.41
<i>Spirulina platensis</i>	29	0.38
<i>Scytonema hofmanni</i>	27	0.36
<i>Porphyridium cruentum</i>	20	0.27
<i>Dunaliella salina</i>	12	0.16

algae and algae biocers were tested. Nickel contaminated waters and a solution of different heavy metals were used for comparative sorption experiments.

The nickel sorption capabilities of the selected algae were tested under equilibrium conditions (contact time 24 h) using drinking water loaded with 2.2mg Ni²⁺/L. To reveal sorption capability differences between the algae, the algae/nickel ratio was selected so that only part of the offered nickel would be removed. A total of 1.34mg was offered per gram of algae. Table 3 shows the results of the equilibrium sorption experiments. Best results were shown by the microalgae *Scenedesmus* and *Chlorella* and the phaeophyceae *Kelp* and *Laminaria*.

To examine to what extent nickel binding was influenced by immobilising the algae in a silica matrix, the nickel sorption capability of algae, algae biocers, and the silica matrix were tested with respect to the quantity of the adsorbent. For these tests 20, 40, or 100mg algae or algae biocers were exposed to 250mL of a 1.7mg/L

nickel solution for 24 h (Table 4).

C. vulgaris and *S. platensis* algae and biocers have shown a linear correlation, with nearly the same gradient between the amount of algae or biocer used and the resulting nickel concentration. Due to the algae content of the biocers, 100mg biocer granules contained approximately 17mg algae biomass. The silica matrix itself possessed a good nickel sorption. On the basis of the results for 20mg non-immobilised algae and 100mg silica a theoretical nickel binding of 197 μ g/100mg for *Chlorella* biocers and 183 μ g/100mg for *Spirulina* biocers can be calculated. This means that by *Chlorella* biocers 62% and *Spirulina* biocers 75% of the theoretical values were reached. The reason is probably a mutual blockage of adsorption places by these algae and the silica matrix.

A reduced biosorption capability of microalgae after immobilisation was also observed by others. For example Rangsayatorn *et al.* [23] studied the biosorption of cadmium by *Spirulina platensis* immobilised by using alginate or sodium silicate. They showed that after immobilisation the maximum biosorption capacities were reduced to 38% in case of silica immobilised algae and 72% by using alginate. Similar results were reported by Mahan & Holcombe [24] for algae immobilised on silica gel. By comparison of the extrapolated saturation values for free and immobilised algae they observed a 40% loss of adsorption efficiency as a result of the immobilisation. Wong

& Pak [25] used alginate for immobilisation of four *Chlorella* strains. They also reported reduced removal efficiencies for copper and nickel after immobilisation.

The ground macroalgae biomass of *Fucus vesiculosus* and Kelp showed no or only a slight decrease of the residual nickel concentration for an increasing amount of algae biomass used. The tendency of the used *F. vesiculosus* and Kelp powder to agglomerate at higher biomass contents could be responsible for these results. However, after homogeneously embedding the macroalgae in the silica matrix, enhanced nickel sorption was observed. This could be explained by a better disposability of the algae surface while preventing the agglomeration tendency. Approximately 114% of the calculated theoretical binding capacity was reached by the *Fucus* and Kelp biocers.

3.3. Biosorption of Cr, Ni, Cu and Pb from a Mixed Solution

To evaluate the biosorption behaviour of different algae in the presence of several heavy metals, sorption experiments were carried out in a system containing copper, nickel, and chromium and lead ions. An aqueous solution with 0.2mM of each of the metal ions was used, and pH was adjusted to 4.5 to avoid precipitation. Table 5 shows the results of the biosorption experiments.

Table 4. Removal of nickel from solution by algae and algae biocers with respect to quantity.

	20 mg			40 mg			100 mg		
	mg/L ^a	μ g ^b	% ^c	mg/L	μ g	%	mg/L	μ g	%
<i>Chlorella vulgaris</i>	1.43	56	14	1.32	85	21	1.12	136	33
<i>Spirulina platensis</i>	1.47	39	10	1.36	65	16	1.15	118	29
<i>Fucus vesiculosus</i>	1.03	139	35	1.06	132	33	1.03	138	35
Kelp	0.96	153	39	0.83	186	47	0.77	202	51
<i>Chlorella</i> biocer	1.58	45	10	1.51	62	14	1.27	123	28
<i>Spirulina</i> biocer	1.59	49	11	1.48	76	17	1.24	137	31
<i>Fucus</i> biocer	1.28	109	26	1.04	168	39	0.50	305	71
Kelp biocer	1.31	106	24	1.05	173	40	0.47	317	73
Silica matrix	1.65	29	7	1.59	44	10	1.04	181	41

^aRemaining nickel concentration. ^bBound nickel in μ g. ^cRemoval of nickel from solution in %.

Table 5. Biosorption of Cr, Ni, Cu, and Pb by different algae.

	[μ mol / 200 mg algae dw]				
	Cr	Ni	Cu	Pb	Σ
<i>L. saccharina</i>	5.32	5.26	7.50	6.92	25.00
<i>F. vesiculosus</i>	5.00	4.96	7.46	6.96	24.38
<i>S. obliquus</i>	5.74	3.32	7.88	7.08	24.02
<i>P. cruentum</i>	5.52	2.80	7.62	6.92	22.86
<i>C. vulgaris</i>	5.72	3.52	6.48	7.00	22.72
<i>S. platensis</i>	5.38	0.56	6.40	6.20	18.54
<i>S. hofmanni</i>	5.02	0.56	5.18	6.12	16.88
<i>H. pluvialis</i>	3.84	0.40	4.48	6.12	14.84
Total offered	5.82	5.68	7.98	7.08	26.56

Best results were attained by the brown marine algae *L. saccharina* and *F. vesiculosus* which removed nearly all of the offered metals under the test conditions. Even recalcitrant metals such as Ni were removed to a high degree. In contrast, the microalgae showed a lower Ni sorption capability.

To estimate the effect of immobilisation on the bio-sorption behaviour of the embedded algae biomass, non-immobilised algae were compared with algae embedded in a silicate matrix (Table 6).

In the case of the marine macroalgae *F. vesiculosus* and *L. saccharina*, no adverse effect to their metal binding capability was visible as a result of immobilisation in the silica matrix. By contrast, the sorption capability of the embedded microalgae *P. cruentum*, *C. vulgaris* and *S. obliquus* was clearly reduced after immobilisation.

Differences in the sorption capability of different biocers were confirmed after higher loading of the algae biocers. For this purpose the algae biocers were exposed four times to the solution containing heavy metals. About 30 µmol/g of each metal were offered. Table 7 shows the results.

The best metal-binding properties were shown by the *Laminaria* and *Fucus* biocers. These removed about 78% and 71% respectively of the total offered metals. The

microalgae biocers take up Cr preferentially, with relatively low removal rates for Ni, Cu, and Pb. The silica matrix itself is only involved in the sorption of Cr under the given conditions.

4. Conclusions

By use of silica nanosols different microalgae and macroalgae powders were successfully immobilised within granular silica gel matrices. The dry gels were mechanical stable and could be grounded to smaller particle sizes. The stability of the granules in water depends strongly on the biomass content, and the size and distribution of the biocomponents. TEOS based biocers showed the highest stability. Nevertheless, even in Nyacol based biocers microalgae contents up to 50% (wt/wt SiO₂), or 30% in the case of macroalgae, could be realized using the GLYEO modified sol variant C or heat treatment. Using commercially available nanosols like Nyacol a very cost effective production of algae biocers is possible. The biocers had shown a total porosity up to 60% allowing a good accessibility of the embedded biocomponents. By the sorption experiments no adverse effect on the sorption capability was visible in case of

Table 6. The effectiveness of different algae and algae biocers in removing heavy metals from a solution containing Cr, Ni, Cu, and Pb^a.

	Removing heavy metals from solution by sorption onto algae or algae biocers [%]							
	non-immobilised algae				algae biocers			
	Cr	Ni	Cu	Pb	Cr	Ni	Cu	Pb
<i>L. saccharina</i>	92	93	94	98	99	99	> 99.5	> 99.5
<i>F. vesiculosus</i>	86	88	94	98	99	97	99	99
<i>P. cruentum</i>	95	49	95	98	91	25	62	63
<i>C. vulgaris</i>	98	62	81	99	96	19	57	57
<i>S. obliquus</i>	99	59	99	100	50	3	24	16
Silica-matrix					62	4	2	1

^aThe water at pH 4.5 contained 0.2mmol/L of each metal. 200mg algae (dw) or 1g granulate biocer material (equivalent to 200mg immobilised algae) were exposed to approx. 7 µmol of each metal.

Table 7. Removal of heavy metals by different algae-biocers^a.

	bound metal in mg/g biocer				total bound metal µmol/g biocer
	Cr	Ni	Cu	Pb	
<i>Laminaria</i> biocer	1.444	0.677	1.445	5.776	89.91
<i>Fucus</i> biocer	1.418	0.550	1.139	5.589	81.54
<i>Porphyridium</i> biocer	0.976	0.119	0.348	1.026	31.21
<i>Chlorella</i> biocer	1.040	0.099	0.323	0.900	31.12
<i>Scenedesmus</i> biocer	0.518	0.063	0.207	0.429	16.36
SiO ₂ granules	0.517	0.066	0.036	0.177	12.49
Total offered	1.464	1.536	2.028	6.000	115.50

^a1g biocer material was exposed to approximately 30 µmol of each metal.

embedded macroalgae biomass. In contrast, immobilised microalgae showed a reduced binding of nickel, copper and lead, as expected on basis of the results for non-immobilised algae and the silica matrix. The silica matrix itself was involved into the metal binding.

Overall, the use of silica nanosols for the production of granular algae-silica hybrid materials is a promising way to integrate biosorption capabilities of algae-biomass into the conventional technical equipment of water treatment plants. To overcome still existing uncertainties by embedding of microalgae in shape of reduced binding of heavy metals, further investigations in the composition of the immobilisation matrix are necessary. On the base of appropriate chemical modifications, the preservation of the binding capability of the embedded bio-component as well as the exploration of synergistic effects by providing additional binding sites on the immobilisation matrix itself is aspired.

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