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Efficient Purification of Water from Arsenic by Amyloid-Carbon Hybrid Membranes

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Methods

BioPURE β-lactoglobulin was purchased from the Technische Universität Munich, department of food process engineering and dairy technology, Munich, Germany. Purification of the β-lactoglobulin and fibrils preparation is carried out using the protocol according to Jung et al[1]. The Arsenic salts were purchased from Sigma-Aldrich. The arsenic real contaminated water was kindly provided by Dr. Michael Berg, Eawag, Dubendorf, Switzerland, and it was originally collected in Romania in 2008.

Hybrid composite membrane having 10% amyloid membranes were prepared, by initial mixing of 1 ml of the 2% β-lactoglobulin fibril solution with 2 ml of 10 wt% activated carbon solution. The homogeneous membranes are prepared by vacuum filtering the 1 ml of above solution using 0.22 μm cellulose filters. These adsorption membranes were then used by vacuum filtration to adsorb arsenic ion pollutant water. The final surface of the membrane is having the diameter of 25 mm.

Graphite furnace Atomic absorption spectroscopy

Arsenic metal content before and after filtration was measured by atomic absorption spectroscopy using AA240Z Zeeman graphite-furnace (GTA 120) equipped with PSD 120 programmable sample dispenser. The sample was measured by atomic absorption spectroscopy in triplicates. A separate calibration was established by measuring standard solutions with various concentration regimes.

Binding Isotherms

Binding isotherms studies were performed by titration of fixed concentrations of β-lactoglobulin (pH 2) protein fibrils solution (350 μL of 2 wt.%) with various concentrations ranges of arsenate and arsenite metal ions having a final volume of 2 ml. The unbound free

metal ions were removed by filtration, the concentration of bounded heavy metal ions on the fibrils were estimated by measuring the permeate concentrations by atomic absorption spectroscopy. The binding isotherms were fitted using the approach by Swillens and Motulsky[2, 3]. The model assumes a single binding metal-ligand pair, with a single associated binding constant:

$$K_a = \frac{[M \cdot L]}{[M_0 - M][L_0 - L]} = \frac{[M \cdot L]}{[M_0 - M \cdot L][L_0 - M \cdot L]} \quad \text{(eq. 1)}$$

where K_a is the binding constant, $[M \cdot L]$ is the concentration of the metal:ligand bound pair, $[M_0 - M]$ is the unbound metal concentration and $[L_0 - L]$ is the unbound ligand concentration. $[M]$ and $[L]$ are the bound metal and ligand concentration (identical to $[M \cdot L]$), respectively and $[M_0]$ and $[L_0]$ are the initial total metal and ligand concentration, respectively.

This equation can be solved for $[M \cdot L]$ yielding the following solution:

$$[M \cdot L] = \frac{1}{2}\left([M_0] + [L_0] + \frac{1}{K_a}\right) - \frac{1}{2}\sqrt{\left([M_0] + [L_0] + \frac{1}{K_a}\right)^2 - 4[M_0][L_0]} \quad \text{(eq. 2)}$$

which allows fitting $[M \cdot L]$ as a function of the titration increasing concentration $[M_0]$, with of K_a and $[L_0]$ as fitting parameters.

Relative Adsorption Capacity of Amyloid Membranes

In order to estimate the relative adsorption capacity of amyloids, the filter membranes were prepared first with only activated carbon solution without adding any amyloid fibrils. Arsenate and arsenite solutions were filtered individually by the activated carbon membranes.

The adsorption of the heavy metal ions inside the membrane is estimated by measuring the solution concentration of heavy metal ions before (feeding solution) and after filtration (permeate) using atomic absorption spectroscopy techniques. This allows resolving the adsorption efficiency per mg and per cycle for the activated carbon.

In a second step, we produce hybrid membranes made of amyloid fibrils and activated carbon, by maintaining identical the total weight of the activated carbon in the membrane (i.e. as in the pure carbon membranes). We then process the same volumes of feeding solutions with the same concentrations of arsenic metal ions. By difference between the adsorption in the two experiments series, we can resolve the specific adsorption efficiency per mg and per cycle of the amyloid fibrils as well.

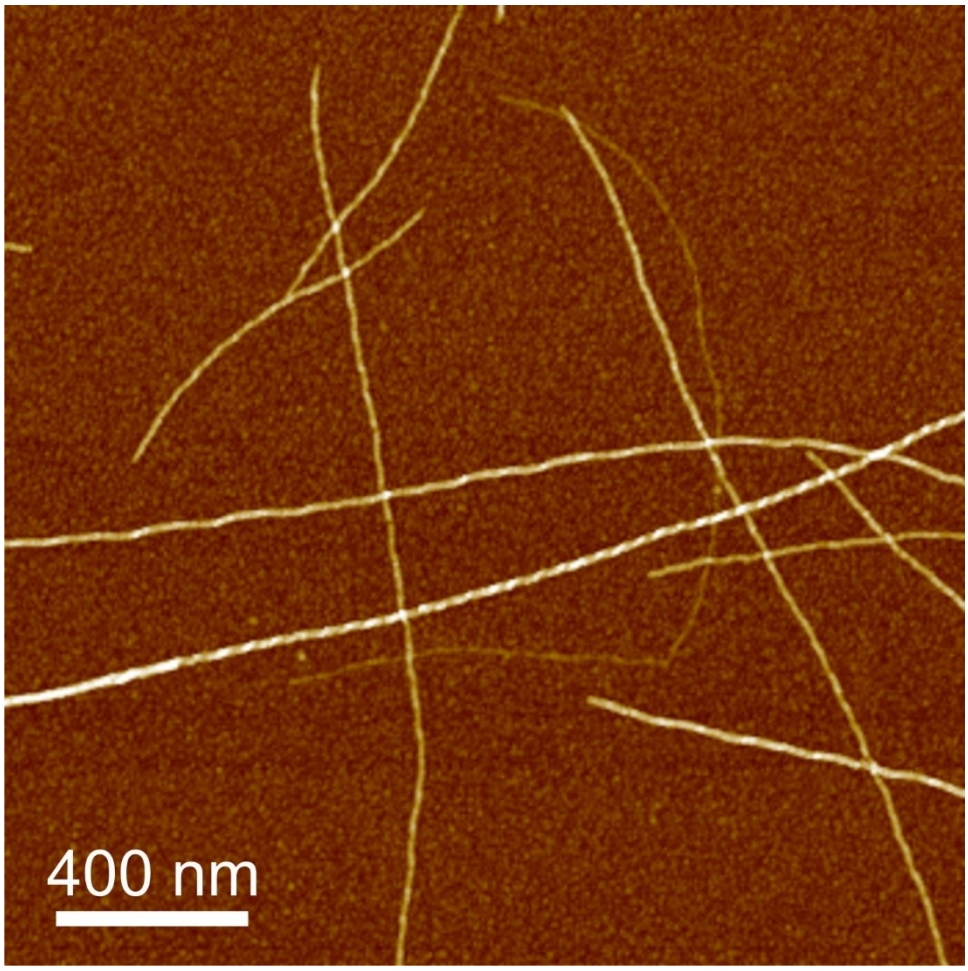

Fig. S1. Atomic force microscopic (AFM) image of the β-lactoglobulin amyloid fibrils prepared at 90° C and pH 2 for 5 h.

Water flux	3397 L/m^2.h
Intrinsic permeability	0.884*10^{-14} m^2
Thickness of membrane	1 mm
Protein content	10 wt.%
Activated carbon total surface area (B.E.T.)	1050 m^2/g
Methylene blue	240 mg/g
Iodine number	1500

Table 1. Characteristics of the membrane

ESI References

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3 H. Motulsky, *GraphPad Software, Inc., San Diego, CA*. 1996