

Silk/polyamidoamine membranes for absorbing chromium (VI) from water

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Introduction

Hexavalent chromium, Cr(VI), is one of the highly toxic and carcinogenic pollutants that can be found in groundwater. The most common remediation strategies for Cr(VI) contaminated water include reactive barriers, ion exchange, electrochemical precipitation, reverse osmosis, chemical precipitation, adsorption and combined reduction-coagulation-filtration. However, to satisfy EU drinking water regulations particularly efficient techniques are required to reduce Cr(VI) concentration below 50 ppb. Polyamidoamines (PAAs) are a family of synthetic polymers obtained by the aza-Michael polyaddition of prim- or sec-amines to bisacrylamides. α,ω -Acrylamide-terminated PAA oligomers can be radically polymerized affording hydrogels, i.e., crosslinked polymers that absorb large amounts of water. The bidentate guanidinium ion strongly and reversibly binds bidentate oxo-anions, including carboxylates, phosphates, sulfate, chromate, or nitrate, due to its optimal charge distribution and ability to form hydrogen bonds. PAA hydrogels bearing guanidine pendants, obtained by the polymerization of 4-aminobutyl guanidine with N,N'-methylenebisacrylamide, proved efficient absorbers of Cr(VI). However, they exhibited poor mechanical properties. In this work, they were reinforced with raw silk mats obtaining tough composite membranes capable to withstand compressive stresses in ultrafiltration processes. By properly tuning composition and morphology, high Cr(VI) absorption efficiency was achieved.

Experimental

Silk mats with thickness 130 μm were prepared by griding raw silk and then filtering. Circular membranes of different diameters were obtained by impregnating silk mats with a 40 wt-% aqueous solution of an α,ω -acrylamide-terminated guanidine-bearing PAA oligomer and then crosslinking it by UV-activated radical polymerization. The hydrogel content varied in between 50 – 60 wt-%. Cr(VI) absorption tests were first performed in static conditions by incubating silk/PAA membranes in Cr(VI) solutions of concentration between 2.5 and 20 ppm for 24 h. Absorption tests in dynamic conditions were performed by using the silk/PAA hydrogels as filtrating membranes in an AMICON® ultrafiltration equipment subjected to a 2.5 bar pressure and filled with Cr(VI) solutions with concentration between 10 and 1 ppm. The amount of absorbed Cr(VI) was determined by monitoring the change of the Cr(VI) concentration in the aqueous phase either by UV measurements at 349 nm (Cr(VI) > 1 ppm) or by atomic absorption (Cr(VI) < 1 ppm).



Results and Discussion

The structure of the PAA used as Cr(VI) absorbent and its ionic species distribution at pH 7.0 is shown in Fig. 1.a. The experimental set up used in ultrafiltration experiments is shown in Fig. 1b.

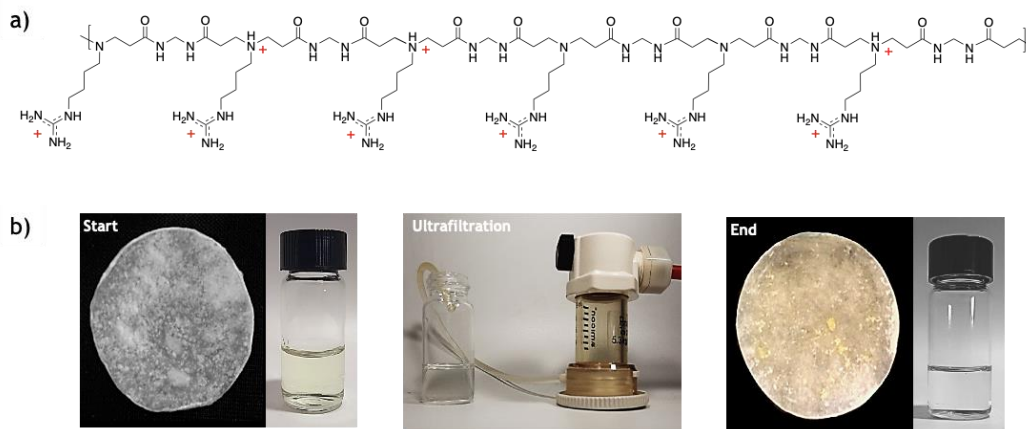


Figure 1: a) Structure of the guanidine-containing PAA used as Cr(VI) absorber and ionic species distribution at pH 7.0. b) Ultrafiltration set up: silk-reinforced hydrogel membrane and 10 ppm Cr(VI) solution (left); ultrafiltration equipment (middle); silk-reinforced hydrogel membrane after Cr(VI) absorption and Cr(VI) solution after ultrafiltration through the membrane.

In both static and dynamic tests, the membranes showed an uptake capacity from 0.8 to 1.6 μg Cr(VI) per mg PAA hydrogel. Ultrafiltration tests performed by stacking from 1 to 10 membranes in the cell demonstrated that overall absorption was additive. Tests carried out with 1 ppm solutions brought the residual Cr(VI) down to 4 ppb. By incubating in a single static step the saturated membranes in a 1 M NaOH solution for 24 hours, about 80% of the absorbed Cr(VI) was released. The regenerated membranes showed a Cr(VI) uptake ability similar to that of the native membrane.

Conclusions

The reported synthetic procedure provides a broadly applicable and easily scalable method for reinforcing active PAA hydrogels using silk wastes otherwise destined for disposal. Since, in the frame of water purification, the mechanism of action of the PAA matrix is based on the presence in its structure of guanidinium pendants and on its ability to interact with oxo-anions stably and reversibly, it can be reasonably expected that such membranes could effectively remove different types of oxo-anions, thus broadening their application range.

Biography

Elisabetta Ranucci serves as full professor of Industrial Chemistry at the University of Milan, Italy, where she teaches polymer chemistry classes for the bachelor's and master's degree programs in Industrial Chemistry. She started her career as assistant professor at the University of Brescia, Italy. Afterwards, she spent a three-year stage at the Royal Institute of Technology, Stockholm, Sweden. Her research interests focus on the synthesis of biodegradable and biocompatible polymers and modification of natural polymers for applications in different technical fields, including nanomedicine, tissue engineering, polymeric flame retardants, water purification.