

Toward Bioderived Intelligent Nanocarriers for Controlled Pollutant Recovery and pH-Sensitive Binding

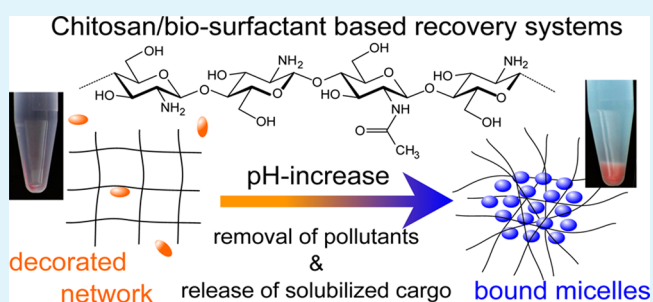
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S Supporting Information

ABSTRACT: The pH-triggered formation of supramolecular complexes between the cationic biopolysaccharide chitosan and an environmentally friendly anionic surfactant is exploited for the formulation of selective and controlled-recovery systems. A strong advantage of this system is the very small pH range in which the binding/release process takes place. Because of this high pH responsiveness, chitosan–surfactant complexes are employed for the sequestration of various compounds by binding or releasing them from the complexes. In particular, the selective recovery of a model hydrophobic pollutant in the presence of a hydrophilic one is presented. The process is highly selective and effective, with more than 90% of the hydrophobic dye and ca. 10% of the hydrophilic dye recovered. Furthermore, the method can be extended to the selective recovery of metal ions, and in both cases, the original surfactant and chitosan mixture can be recovered, thereby rendering this an efficient and sustainable process. These showcase experiments depict quite different scenarios in which pH-responsive fully biodegradable polysaccharide–surfactant complexes can be employed and may substitute synthetic products in various fields, e.g., wastewater treatment, cosmetics, and agriculture, thereby yielding environmentally improved approaches.

KEYWORDS: chitosan, alkyl oligoethylene oxide carboxylic acid, pH-responsive, pollutant recovery, polyelectrolyte–surfactant complexes, wastewater treatment



INTRODUCTION

The recovery of contaminants from complex aqueous environments is still a major scientific challenge not only from the perspective of a sustainable economy, in which a clean waste cycle is an essential part, but also given the increasing value of rare elements that have to be recovered during production cycles. Accordingly, the use of tunable and biofriendly systems that can selectively bind and/or release specific targets is needed.¹

In particular, self-assembled colloids and their solubilization capacity can be exploited for the removal of waste products, e.g., by ultrafiltration,^{2,3} flocculation,^{4,5} or cloud-point extraction.^{6,7} Colloid-assisted purification has the advantage of being selective with respect to the physicochemical properties of the pollutant, e.g., its hydrophobicity, charge, or specific functional groups.^{8,9} Moreover, high efficiency can be obtained when polymers or surfactant with functional groups that selectively bind to a specific target are employed.^{10–12} Yet, high binding efficiency often comes with low biocompatibility and high costs. Moreover, given the high stability constant of the formed complexes, elution with strong acids is usually needed for the recovery of the original absorber.¹³

A different approach in pollutant removal consists of using mixtures of oppositely charged polyelectrolytes and surfactants.^{5,14–16} They can be employed as flocculants given their

low solubility near charge neutralization, therefore sequestering the desired compound solubilized within the micellar aggregate.^{5,14,15} Differently, a polyelectrolyte can be added for reducing the critical micelle concentration, therefore increasing the surfactant solubilization power and reducing its leakage in colloid-assisted ultrafiltration.¹⁴

For large-scale recovery purposes, the use of biofriendly and readily available components is a fundamental requirement in order to reduce the environmental impact and the costs of such processes. Accordingly, the interest in responsive systems based on natural polymers, e.g., polysaccharides, has enormously increased in the past decades. In particular, mixtures of ionic polysaccharides and oppositely charged surfactants show a large diversity in structure, functionality, and stimuli responsiveness,^{17–19} which can be employed for pollutant-recovery or drug-delivery purposes. For details, we refer to some recent reviews.^{20–22}

Well-suited candidates for the pH-triggered recovery of target molecules are mixtures of chitosan and oppositely charged alkyl oligoethylene ether carboxylic acids. Both components are available in large quantities and are fully

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biodegradable,²³ and their self-assembly can be finely controlled via pH changes.^{24,25} For instance, the structural behavior observed in mixtures of chitosan and nonaonyethylene oleyl ether carboxylic acid (C_{18:1}E₉Ac) is summarized in the structural phase diagram reported in Figure 1. In contrast to

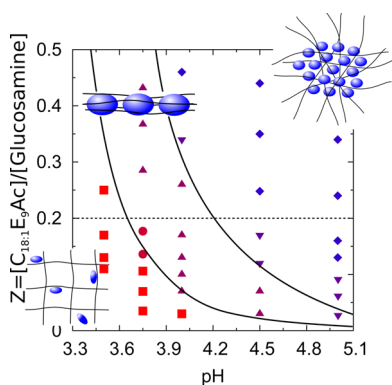


Figure 1. Structural phase diagram of mixtures of chitosan–C_{18:1}E₉Ac micelles as a function of the pH and mixing ratio at a constant chitosan concentration of 0.3 wt % (in a 0.2 mol kg⁻¹ acetate buffer). Full lines represent the ranges of different structural arrangements; along the broken line are the samples studied in this work. See the text and ref 24 for more details. Adapted with permission from ref 24. Copyright 2014 American Chemical Society.

most chitosan–surfactant mixtures, these systems are colloidal stable over a wide range of pH and mixing ratio values. In particular, three main structures can be identified, as a function of the degree of ionization of the surfactant: at low pH, where the surfactant is mostly in its nonionic form, the micelles loosely decorate the polymer network; at intermediate pH, the chitosan chains collapse to form supramolecular complexes with one-dimensional symmetry; at high pH, core–corona structures are found, with the core formed by densely packed micelles surrounded by a stabilizing chitosan shell.^{24,25} Moreover, both components are attractive by themselves in the field of pollutant recovery. Chitosan is one of the most promising low-cost biosorbents used in wastewater treatment.^{26–29} Alkyl oligoethylene ether carboxylic acids are a rather mild and low-toxicity class of surfactants,²³ and their pH-responsive behavior was exploited for metal cation removal via micellar-enhanced ultrafiltration.^{30–32} The presence of the oligoethylene block strongly increases their solubility with respect to classic fatty acids and imparts a temperature responsiveness at low pH, without affecting the typical pH-dependent behavior of carboxylic acids.

While a large number of examples are available in which pH-responsive self-assembly and disassembly processes are exploited for drug-delivery purposes,^{33,34} few studies deal with responsive colloids for pollutant recovery and are mostly based on temperature-responsive polymers.^{35,36} The aim of this work was to study the pH-switchable recovery properties of chitosan–C_{18:1}E₉Ac mixtures, for both organic compounds and inorganic ions. In particular, the pH-tunable binding of target molecules with successive separation by centrifugation was investigated. With respect to the polyelectrolyte–surfactant systems studied so far, we here introduce strongly responsive components, with structural changes taking place within 1 unit of pH. In addition to offering large control over the system, this responsiveness allows also for easy recycling of the starting material.³⁰ In addition, both chitosan and alkyl oligoethylene

oxide carboxylic acids constitute an environmentally friendly alternative to established systems based on synthetic polymers.^{16,37}

EXPERIMENTAL SECTION

Materials. Chitosan (TCI Europe) is characterized by a viscosity-average molecular weight of 100 kDa and a degree of acetylation of 0.15 determined by ¹H NMR.²⁴ Nonaonyethylene oleyl ether carboxylic acid (C_{18:1}E₉Ac) is a technical surfactant produced by Kao Chemicals under the trade name AKYPO RO90 VG (711 g mol⁻¹, ca. 92% purity). The surfactant was used as received. Nile red (Fluka, ≥98% purity), methylene blue (Merck, microscopy grade), Sudan red (Fluka, ≥96% purity), copper(II) chloride dihydrate (Fluka, ≥98% purity), iron(II) chloride tetrahydrate (Sigma-Aldrich, ≥99% purity), iron(III) chloride (Merck, ≥98% purity), and ammonium pyrrolidine dithiocarbamate (Sigma-Aldrich, ≥99% purity) were used as received. Solutions were prepared in an acetic acid–acetate buffer, with a total concentration of acetate–acetic acid (Roth, ≥99% purity) of 0.2 mol kg⁻¹. The pH was adjusted using a concentrated sodium hydroxide (Fluka, ≥99% purity) solution. All samples were prepared using Milli-Q water.

Methods. Micelle Immobilization Experiments. The incorporation of surfactant micelles within the supramolecular complex was followed by fluorescence correlation spectroscopy (FCS). Experiments were performed on a Leica TCS SP5 II confocal microscope. Calibration of the confocal volume and its anisotropy was performed using Alexa Fluor 488 as a reference dye with a known diffusion coefficient of 435 μm² s⁻¹.³⁸ An argon laser was used as the light source (λ = 488 nm), delivered at the sample through an apochromatic 63×, 1.2 NA water immersion objective. The fluorescence light was collected through the same objective, the beam was split into two equal parts, and the intensities were detected using two single-photon avalanche photodiodes. The intensity cross-correlation function $G(\tau)$ was obtained on a PicoHarp 300 correlator and was described as

$$G(\tau) = G_0(1 - T + T e^{-\tau/\tau_i}) \left[A(1 + \tau/\tau_{\text{fast}})^{-1} \left(1 + \frac{\tau/\tau_{\text{fast}}}{k^2} \right)^{-0.5} + (1 - A)(1 + \tau/\tau_{\text{slow}})^{-1} \left(1 + \frac{\tau/\tau_{\text{slow}}}{k^2} \right)^{-0.5} \right] \quad (1)$$

with G_0 , T , A , τ_i , τ_{fast} , and τ_{slow} being the intercept, the fraction of dyes in the triplet state, the relative amplitude of the fast mode, and the triplet, fast, and slow decay times, respectively. The parameter k is the anisotropy of the confocal volume and is defined as the ratio of the vertical (z_0) and lateral (ω_0) extension of the confocal volume $k = z_0/\omega_0$. For the description of the pure surfactant solutions, A was fixed to 1, resulting in a monomodal decay.

The diffusion coefficients relative to the fast and slow modes are obtained as

$$D_i = \frac{\omega_0^2}{4\tau_i} \quad (2)$$

The hydrodynamic radii associated with the diffusion modes observed are calculated using the well-known Stokes–Einstein relation:

$$Rh_i = \frac{k_B T}{6\pi\eta D_i} \quad (3)$$

with k_B , T , and η being the Boltzmann constant, the temperature, and the solvent viscosity, respectively.

Recovery Experiments. The recovery of hydrophobic (Sudan red) and hydrophilic (methylene blue) dyes by means of centrifugation was investigated by UV–vis spectroscopy. Spectra were recorded on a Varian Cary 50 UV–vis spectrophotometer using water as the reference. The contribution of scattered light from the supramolecular complex in the absorption spectrum was accounted for using a power law background subtraction:

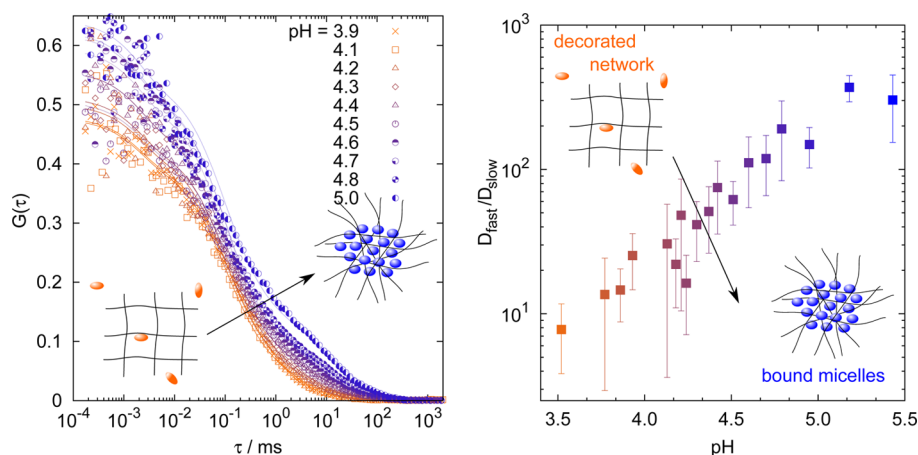


Figure 2. Left: fluorescence autocorrelation functions recorded for chitosan– $C_{18:1}E_9Ac$ mixtures containing 5 nM Nile red, with $Z = [-]/[+] = 0.2$, a constant chitosan concentration of ~ 0.3 wt %, and variable pH. Full lines are best fits according to a bimodal decay model. Right: ratio of fast and slow diffusion coefficients as a function of the pH.

$$\text{bkg}(\lambda) = a\lambda^{-b} + c \quad (4)$$

A saturated Sudan red solution in 2 wt % $C_{18:1}E_9Ac$ was obtained by homogenizing dye, surfactant, and ethanol. Ethanol was evaporated overnight under vacuum. After the addition of an acetic acid buffer solution and vigorous stirring, the solution was centrifuged. The supernatant was used for the preparation of complexes with chitosan. The final concentration of Sudan red was 10 μM , as determined from its peak maximum at 506 nm using an adsorption coefficient of $3.14 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$.³⁹ A concentrated aqueous solution of methylene blue was then added to achieve a final concentration of 10 μM .

The recovery of copper and iron ions by means of centrifugation was investigated by inductively coupled plasma optical emission spectrometry (ICP-OES). Experiments were carried out on a ICP-OES 715 ES (Varian Inc., USA). Copper was detected at the 327.395 and 324.754 nm emission lines and iron at the 238.204 and 259.94 nm emission lines. The initial concentration of metal ions was $10^{-3} \text{ mol kg}^{-1}$, and that of ammonium pyrrolidine dithiocarbamate was $4 \times 10^{-3} \text{ mol kg}^{-1}$.

RESULTS AND DISCUSSION

Chitosan and alkyl oligoethylene ether carboxylic acids self-assemble into very versatile structures that are strongly pH-responsive.²⁴ The pH responsiveness of these mixtures arises from a delicate balance of structure-determining forces acting in the system, with the most significant being the stiffness of the chitosan chains and their electrostatic interaction with the surfactant micelle. While the former can be considered to be unaffected by the pH at the experimental conditions, the latter strongly depends on the degree of ionization of the micelle, and, accordingly, on the pH.²⁴ All experiments were done in a 0.2 mol kg^{-1} acetate buffer, close to physiological conditions, but a similar behavior of the complexes is also seen at lower ionic strength.

From a physicochemical perspective, the two extreme cases are particularly interesting: at low pH, a chitosan network, which extends throughout the solution, is randomly and loosely decorated by small charged surfactant micelles. In contrast, at high pH, a core–corona superstructure is formed, with charged surfactant micelles densely packed within the core surrounded by a stabilizing chitosan corona. These aggregates have an average core diameter of ca. 250 nm, and ca. 2000–5000 micelles per aggregate are present.²⁴ Similar structures are commonly found in mixtures of double hydrophilic polymers and charged macroions.^{40,41} According to Figure 1, it should be

possible to switch the state of aggregation (and thereby also the properties of the system) largely for $Z = 0.2$ by switching the pH from 3.6 to 5.0, thereby compacting or freeing micelles. This concept then can be exploited for control of the mobility and the state of solubilizates (active agents).

pH-Triggered Immobilization of Surfactant Micelles.

We probed the mobility of the surfactant micelles using FCS and Nile red as a hydrophobic dye, which is solubilized within the micelles with an equilibrium constant of $1.5 \pm 0.2 \mu\text{M}^{-1}$ [see the Supporting Information (SI) for further information]. In Figure 2, the correlation functions recorded for chitosan– $C_{18:1}E_9Ac$ mixtures with constant mixing ratio $Z = [C_{18:1}E_9Ac]/[\text{glucosamine}]$ and variable pH are shown (further curves are shown in Figure S2 in the SI). The gradual change in the pH allows one to cross the phase diagram reported in Figure 1, therefore probing the mobility of the micelles before and after complexation with chitosan. At pH ~ 4.0 , an additional slow mode in the correlation function becomes visible, characteristic of the large complex aggregates. Accordingly, $G(\tau)$ is described using a bimodal decay (eq 1). To increase the reliability of the fit parameters, the fast decay time $\tau_{\text{fast}} = 0.1$ ms, the fraction of dyes in the triplet state $T = 0.19$, and the triplet decay time $\tau_t = 2 \times 10^{-3}$ ms were fixed and kept equal to the average value found for the pure surfactant solutions at the same concentration. The shift in $G(0)$ with the pH is ascribed to a simple dilution effect arising from the addition of a concentrated NaOH solution (see the Experimental Section for the sample preparation procedure).

From τ_{fast} and τ_{slow} , the ratio of the diffusion coefficients $D_{\text{slow}}/D_{\text{fast}}$ is obtained (eq 2), with D_{fast} and D_{slow} being the fast and slow diffusion coefficients, respectively. They are shown in Figure 2, and one observes a large increase of D_{slow} in the pH range of 3.6–5.0, where for the highest pH values this effect levels off, which indicates that here the transformation is complete. The reduced mobility of the surfactant micelles at low pH can be ascribed to short-life interactions with chitosan. The hydrodynamic radii, which can be calculated according to the Stokes–Einstein relation (eq 3), are ~ 2 and ~ 10 –400 nm for the fast and slow modes, respectively. This supports the idea that at high pH diffusion of the micelles incorporated into the large complexes is observed. The relative amplitudes of the slow and fast modes are reported in the SI.

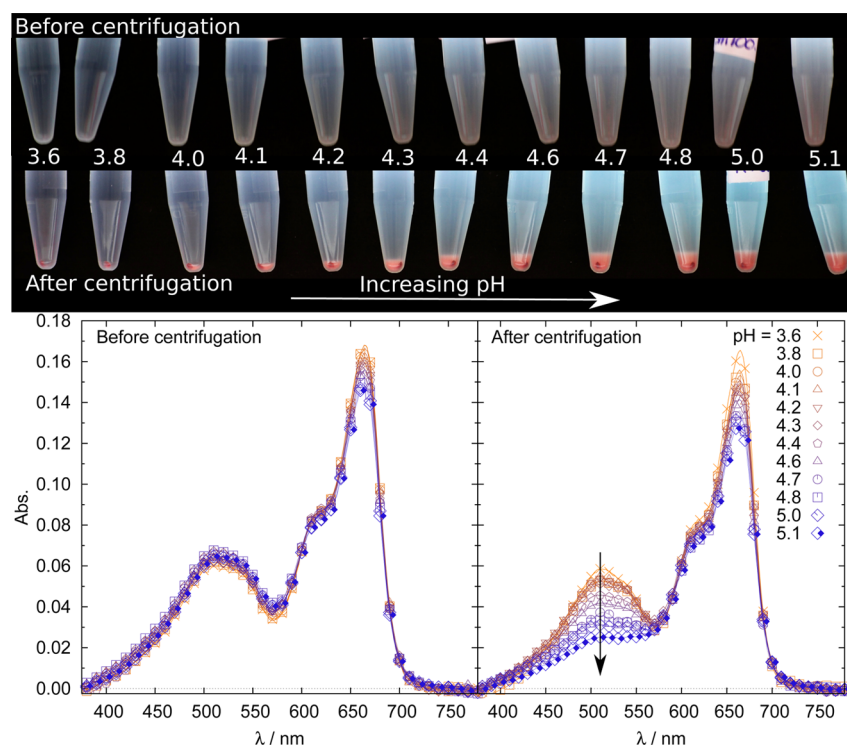


Figure 3. Top: photographs of chitosan- $C_{18:1}E_9Ac$ solutions containing Sudan Red ($10 \mu M$) and methylene blue ($10 \mu M$) with $Z = [-]/[+] = 0.2$, a chitosan concentration of ~ 0.3 wt %, and variable pH before and after centrifugation. Bottom: UV-vis spectra of the solution before centrifugation and the supernatant solution after centrifugation. Spectra were corrected for scattering contributions (eq 4; the parameters are summarized in Table S4 in the SI). See the text for more details.

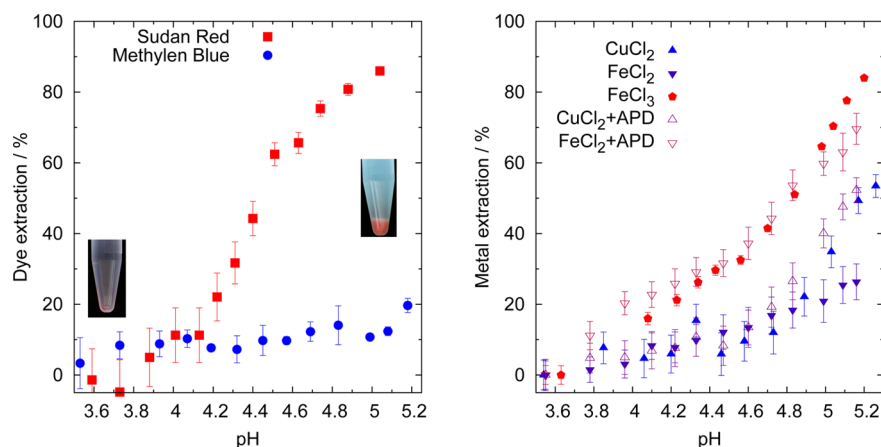


Figure 4. Removal efficiency of chitosan- $C_{18:1}E_9Ac$ complexes with respect to Sudan red and methylene blue (left) and different metal salts (right) as a function of the pH. The chitosan concentration was ~ 0.3 wt %, $Z = [-]/[+] = 0.2$, and the pH was variable. The metal-ion concentration obtained at pH ~ 3.6 (ca. 1×10^{-3} mol kg^{-1}) was used as a reference value. The initial ligand (APD) concentration was 4×10^{-3} mol kg^{-1} .

While at low and intermediate pH a continuous increase for D_{slow}/D_{fast} is observed, which levels off at pH ~ 5.0 , the relative amplitude of the slow mode can be divided into three regions: (i) below pH 4, where its value is constant; (ii) between pH 4 and 5, where a moderate increase in the importance of the slow mode is observed; (iii) above pH 5, where there is a strong increase of the slow-mode amplitude. This information, together with the structural picture described in ref 24, leads to the following conclusions: the surfactant micelles first decorate the polymer network, with the interaction becoming stronger and therefore increasing the lifetime of the micelle-polymer complex and involving more micelles with increasing pH. A further increase in the pH causes the collapse of the

polymer network into the core-corona structure, in which the micelles are tightly bound, i.e., with a lifetime within the complex larger than the experimental time.

Selective Removal of Pollutants from Aqueous Solutions. This demonstrated that the pH-responsive coassembly of chitosan and $C_{18:1}E_9Ac$ micelles can be exploited for the controlled recovery of pollutants from an aqueous solution. In the following, we address the question of whether chitosan-surfactant complexes can be used for pH-triggered, selective removal of dye molecules and heavy-metal ions from an aqueous solution. As previously shown, supramolecular aggregates of chitosan and surfactant micelles are formed upon an increase of the pH. These complexes are colloidally stable

but can be separated from an aqueous solution by centrifugation. In Figure 3, the selective removal of an hydrophobic dye, Sudan red, in the presence of an hydrophilic dye, methylene blue, is depicted. Both dyes show a pH-independent spectrum within the investigated range. Before centrifugation, the solutions appear purple and become increasingly turbid with increasing pH. After centrifugation, a red precipitate and clear blue supernatant solution are obtained, indicating both the high selectivity of this method and its efficiency. The spectrum of the supernatant solution shows a strongly decreasing peak at ca. 500 nm, characteristic of Sudan red, while the adsorption band of methylene blue at ca. 650 nm remains unaffected (Figure 3).

The removal of methylene blue was quantified from the absorption peak maximum ($\lambda = 665$ nm) before and after centrifugation. The quantitative extent of the removal of Sudan red was determined from the absorption peak maximum ($\lambda = 515$ nm) considering the methylene blue contribution (UV-vis spectrum given in Figure S5 in the SI). A more precise determination was performed in a separate experiment in the absence of methylene blue (see Figure S4 in the SI) from the adsorption peak area between 370 and 600 nm (see Figure S3 in the SI). The results from both procedures are in good agreement (see Figure S6 in the SI). The removal efficiency of chitosan complexes with respect to both dyes is reported in Figure 4. The removal of methylene blue is about 10% and independent of the pH, which is probably because of unspecific interactions of the dye with chitosan. In contrast, Sudan red can be efficiently removed from the solution (up to 90% within the investigated pH range) because it is incorporated in the surfactant micelles that are centrifuged out of the solution.

However, this concept is not just restricted to organic compounds of different polarities. Alkyl oligoethylene carboxylic acids were also shown to effectively bind metal cations with large potential in wastewater treatment.^{30–32} In particular, it was shown that, because of the different binding affinities of the carboxylic headgroup toward metal cations, this class of surfactant can be employed for the separation of different species by mean of micellar-enhanced ultrafiltration.³² The removal efficiency of the complexes with respect to CuCl_2 , FeCl_3 , and FeCl_2 is reported in Figure 4. The efficiency follows the order $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Fe}^{2+}$, as expected from the binding affinities of the carboxylic headgroup.^{32,42} Moreover, the removal efficiency can be improved with the addition of an appropriate ligand, which renders the ions more hydrophobic.

The removal of soluble iron(II) salts is rather low (<30%, even at pH \sim 5) but can be largely enhanced by the addition of APD as an appropriate ligand. In contrast, the removal of copper(II) and iron(III) chloride is rather effective, >60% and >80%, respectively, and in good agreement with the previous results on copper filtration using micellar-enhanced ultrafiltration with $\text{C}_{18:1}\text{E}_9\text{Ac}$ as the surfactant.^{30,32} The efficiency is expected to further increase with increasing pH, at the cost of the colloidal stability of the complexes.

The examples reported in this work serve as a demonstration for the ability of this biofriendly system to be employed for the selective removal of pollutants, with the selectivity either arising from the solubility of the target in the micellar hydrophobic core or, in the case of metal ions, given by the binding constant toward the carboxylic headgroup. Moreover, light-scattering experiments shown in the SI demonstrate that the addition of metal ions to the solution does not affect the self-assembly of $\text{C}_{18:1}\text{E}_9\text{Ac}$ and chitosan.

CONCLUSIONS

In this work, we demonstrate the ability of mixtures of the chitosan and oppositely charged alkylethoxy carboxylates to release and/or recover hydrophobic cargos upon small pH changes. This property, arising from the strong structural changes taking place at pH \sim 3.8–5.0, can be exploited for the formulation of selective pollutant recovery systems.

FCS experiments revealed that the coassembly of surfactant micelles and biopolysaccharide chitosan leads to an effective incorporation of the solubilized cargo, e.g., a hydrophobic molecule, within the supramolecular complex. The formed core–corona structure, whose formation and dissolution options can be controlled within a few tens of pH units, is a highly promising carrier with a pH-switchable release option.

We demonstrated that the pH-triggered complex formation can be used for the selective removal of pollutants from aqueous solutions, for both organic molecules and metal ions or metal/ligand complexes. As a case study, the removal of the hydrophobic dye Sudan red in the presence of the hydrophilic dye methylene blue is reported. This process was shown to be highly selective and effective, with the removal of ca. 90% of the hydrophobic dye while only 10% of the hydrophilic one is coprecipitated. Further decontamination experiments showed that metal ions having a strong affinity with the carboxylated surfactant headgroup can be effectively removed from solution. Also, metal ions with low affinity can be recovered, provided they are contained in a hydrophobic and charge-neutral metal/ligand complex.

The reported examples are based on the principle of solubilizing a hydrophobic compound in the micellar core (Nile red and Sudan red) or binding to the micellar headgroups (metal/APD complexes), where binding to the supramolecular complex is a pH-triggered process. The complexes, with their cargo, can then be removed from solution by centrifugation. It is worth noting that the centrifuged complex can become resolubilized by acidification and therefore can be employed for successive treatments, which then leads to a sustainable process using biofriendly components of low toxicity.

All of the reported examples are of high practical relevance. Chitosan is a biomaterial of high interest in the medical, cosmetic, food, and agricultural industries,⁴³ and its combination with alkyl ethoxy carboxylates, a biofriendly surfactant, opens up the path for the formation of versatile and biocompatible complexes. For instance, the complexes presented in this work can be employed for improved wastewater treatment, where chitosan is already largely used.^{26,27,44} Finally, the presented systems can be of interest for the cosmetic industry, where hydrophobic molecules, e.g., pheromones, sebum components, etc., can be solubilized and bound to the complex after the application of acidic cosmetic formulations such as skin toners, deodorants, or conditioners. Last but not least, the compounds used are cheap, nontoxic, and available in large quantities, which renders them suitable for large-scale applications, thereby allowing one to reduce their environmental impact.

ASSOCIATED CONTENT

Supporting Information

Additional FCS curves, fit parameters, Nile red–surfactant binding constant determination, UV-vis scattering contribution corrections, additional centrifugation experiments, and

light scattering experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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