STUDY ON THE SEPARATION OF SURFACE-ACTIVE AGENTS IN THE AQUATIC ENVIRONMENT

Petru Spataru

Institute of Chemistry, Moldova State University, Chisinau, Republic of Moldova

Abstract

Laboratory simulations with surfactant-polluted water from the Dniester and Prut rivers initiated with NH_4^+ ions demonstrated an acceleration of the conversion to nitrates, approximately four to seven times faster than in reference samples, when granulated granite or expanded clay was applied. In contrast, $CaCO_3$ particles caused a visible inhibition for the same samples, while in the water of the Isnovat River, characterized by a higher organic matter content, the same procedure enhanced ammonium oxidation. UV spectral investigations were conducted using aqueous solutions of anionic, nonionic, and cationic surfactants individually and in mixtures at various ratios ($\sim 10^{-5}$ mol/L, near the critical micelle concentration), recorded with PerkinElmer Lambda 25 and UV 2005 SELECTA spectrophotometers. The UV spectra confirmed formation of SAA anionic–SAA cationic complexes. Cationic surfactant activity in natural waters depends on the organic matter index, reflecting the anionic character of the sample. Separation of cationic surfactants using $CaCO_3$ can be achieved by applying an excess of anionic surfactant (SAA An/SAA Ct > 1), while expanded clay completely adsorbs cationic surfactants. The expanded clay substrate adsorbs on its surface completely cationic AAS. The accelerated ammonium-to-nitrate conversion in the presence of expanded clay and granite suggests catalytic effects of mineral surfaces enhancing adsorption and oxygen transfer. These results provide insights into surfactant behavior and ammonium oxidation in natural waters.

Keywords Surfactants; laboratory simulations; ammonium oxidation; separation process; organic matter; calcium carbonate; expanded clay adsorbent

1. Introduction

Laboratory simulations using river or lake water have shown that specific substrates can accelerate ammonium oxidation (nitrification), while $CaCO_3$ particles inhibit it, raising interest in understanding these processes. Investigations on the Nistru and Prut rivers revealed a four- to sevenfold acceleration when small granite granules or expanded clay were added to water samples. Model experiments with river water contaminated by surfactants demonstrated varying inhibition of ammonium oxidation. Nitrite oxidation proved highly sensitive to environmental conditions; for example, the maximum nitrite concentration ratio in samples with and without $CaCO_3$ (Nistru River, Varancau) differed by nearly two orders of magnitude, indicating surfactant pollution. In contrast, ammonium oxidation in the Cunicea stream, free of synthetic surfactants, was unaffected by $CaCO_3$, confirming the system's sensitivity to surfactant presence, type, and concentration [1,2]. Heterotrophic bacteria showed distinct growth patterns: a single growth peak on days 30–35 with cationic surfactants alone, and two peaks (days 12 and 30) with both cationic and anionic surfactants, suggesting environmental toxicity or nutrient limitation influenced development [3]. Further studies in urban-polluted rivers demonstrated that $CaCO_3$ improved water quality, especially in samples with high organic matter, such as the Isnovat River (Ialoveni).

Anionic and nonionic surfactants were relatively non-toxic, whereas quaternary ammonium salts were more harmful. These findings highlight the need to consider anionic-to-cationic surfactant ratios and interactions with mineral substrates when evaluating environmental impacts. Mineral substrates and surfactant composition significantly influence ammonium oxidation dynamics. Clay and granite fractions accelerate oxidation via surface-mediated catalytic effects, while $CaCO_3$ inhibits the process. Surfactant contamination, particularly by cationic species, affects chemical equilibria and microbial activity, altering nitrification rates. Understanding these heterogeneous interactions is essential for designing water treatment strategies to minimize surfactant toxicity and enhance water quality.

2. Materials and Methods

Aqueous solutions containing anionic, nonionic, and cationic surfactants were prepared individually and in binary mixtures at various molar ratios. The total surfactant concentration was maintained near 10^{-5} mol L^{-1}, below the critical micelle concentration. The systems were analyzed spectrophotometrically to evaluate surfactant interactions and complex formation. UV spectra were recorded using Perkin Elmer Lambda 25 and UV-2005 SELECTA spectrophotometers under identical optical and temperature conditions.

3. Results and Discussion

UV spectra of N-CPy (N-cetylpyridinium) with LS (lauryl sulfate) showed consistent absorbance changes depending on the anionic-to-cationic surfactant ratio (SAA An/Ct) rather than total N-CPy concentration (Fig. 1). Adding LS increased absorbance to a maximum, then decreased with further anionic surfactant addition, identifying the optimal ratio for stable complex formation. For CTMA and TBA, the ratio effect persisted only when cationic surfactant exceeded the anionic amount; inverse ratios yielded similar spectral curves, indicating compact surfactant aggregation. After $CaCO_3$ sedimentation, most surfactant complexes were removed, except in the LS + 2N-CPy system, where some N-CPy remained in solution. This indicates that part of the anionic surfactant neutralizes $CaCO_3$ surface charges, forming stable SAA An·SAA Ct complexes, while leaving excess cationic surfactant in solution. Spectral data allow estimation of carbonate particle surface charge, and lower pH enhances LS dissociation and partial complex decomposition. Treatment with expanded clay demonstrated complete adsorption of cationic surfactants, confirming its potential for selective removal of charged organic compounds. These results highlight that surfactant–substrate interactions are governed primarily by electrostatics and adsorption. Preferential adsorption of cationic surfactants onto negatively charged substrates such as clay underscores the competitive nature of surface binding in heterogeneous aqueous systems.

4. Conclusions

UV spectra confirmed SAA An·SAA Ct complex formation, showing strong interactions between anionic and cationic surfactants in water. Cationic surfactant activity depends on the organic matter index, reflecting anionic content. Separation using $CaCO_3$ requires an anionic excess (SAA An/SAA Ct > 1), while expanded clay completely adsorbs cationic surfactants, highlighting its efficiency as a low-cost adsorbent.

These findings emphasize the importance of substrate type, surfactant ratios, and solution chemistry in controlling surfactant behavior in natural and engineered systems. Understanding these mechanisms supports the design of targeted remediation strategies for rivers, lakes, and wastewater systems, mitigating surfactant effects on ammonium oxidation and nitrification, and improving water quality.

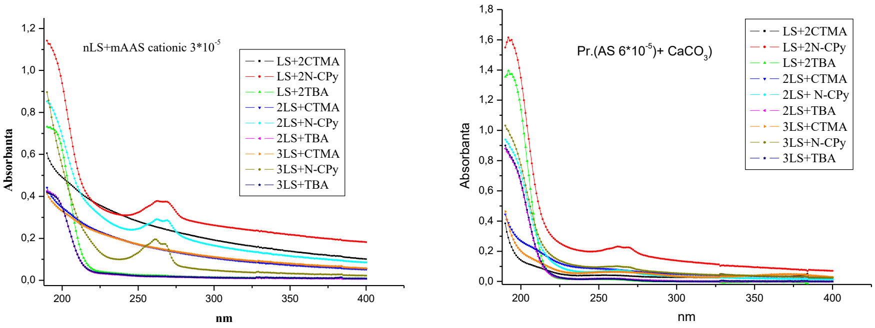

Fig. 1. UV spectra of solutions containing LS with CTMA, NCPy, or TBA at a concentration of $3 \cdot 10^{-5}$ mol/L, and of solutions containing LS with CTMA, NCPy, or TBA at a concentration of $6 \cdot 10^{-5}$ mol/L in the presence of $CaCO_3$.

References

1. Spataru P., Povar I., Mosanu E., Trancalan A. (2015) Study of stable nitrogen forms in natural surface waters in the presence of mineral substrates. *Chem J Moldova* 10:26–32
2. Spataru P., Fernandez Francisco, Povar I., Spataru T. (2019) Behavior of Nitrogen Soluble Forms in Natural Water in the Presence of Anionic and Cationic Surfactants and Mineral Substrates. *Advances in Sciences and Engineering* 11,2, p 70-77.
3. Spataru P. (2011) Transformations of organic substances in surface waters of the Republic of Moldova. PhD thesis (in Romanian)

SUSTAINABLE LOW ENERGY TREATMENT OF MUNICIPAL SLUDGE THROUGH MESOTHERMOPHILIC AEROBIC ANAEROBIC PROCESSING

Spataru Petru, Visnevschi Alexandru, Spinu Oxana, Povar Igor*

Institute of Chemistry, Moldova State University, Chisinau, Republic of Moldova
**Corresponding author: ipovar@yahoo.ca*

Abstract

The sustainable management of municipal wastewater sludge remains a critical environmental and operational challenge, especially in rapidly urbanizing areas. Conventional sludge treatment methods such as open air drying and chemical dewatering are increasingly unsustainable because of high energy use, odor emissions, and limited opportunities for resource recovery. This study introduces a meso-thermophilic aerobic anaerobic treatment (AAMT) process designed to improve sludge stabilization and dehydration with minimal energy input and without chemical additives. A pilot scale thermally insulated reactor was constructed to process mixtures of raw sediment and excess activated sludge in different ratios. Laboratory results showed that optimal mixtures containing 25 to 35 percent raw sediment and 65 to 75 percent activated sludge achieved more than 70 percent water separation efficiency. The process operated at 38-41 °C, sustained by its exothermic microbial activity, which significantly reduced external energy demand. The activity of nitrites and nitrates actually helps reduce odor by oxidizing hydrogen sulfide (H_2S) and organic thiols, while aeration mainly serves for mixing rather than oxidation. Chemical analyses confirmed that the solid fraction retained valuable nutrients such as nitrogen, phosphorus, and potassium while meeting the heavy metal limits specified in EU Directive 86/278/EEC, making it suitable for agricultural use as a soil conditioner or fertilizer. The AAMT process reduces the need for flocculants, decreases the volume of sludge for transport and disposal, and extends the service life of dewatering infrastructure. Overall, the proposed method provides a sustainable and environmentally sound solution for wastewater treatment facilities aiming to lower operational costs, recover useful resources, and minimize ecological impacts. It combines energy efficiency, nutrient recycling, and odor control into a single approach that supports circular economy and green technology goals.

Keywords Municipal sludge; Meso-thermophilic aerobic anaerobic treatment; Low energy process; Wastewater management; Resource recovery; Circular economy; Sustainable sludge stabilization

1. Introduction

The treatment and disposal of sewage sludge generated in municipal wastewater treatment plants represent a growing environmental and economic concern worldwide. The large volume and high moisture content of sludge make it difficult and costly to handle, transport, and dispose