

Chitosan-Sodium Lauryl Ether Sulfate Particles and Their Use for Adsorption of Cu(II) Ions

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ABSTRACT: The synthesis of small particles through the interaction between chitosan (CS) and sodium lauryl ether sulfate (SLES) was studied. Depending on working condition, microparticles at atmospheric pressure and ultrafine particles at high pressure have been obtained. At atmospheric pressure, the microparticles were formed instantaneously when the CS solution was dripped into the SLES aqueous solution. To obtain ultrafine particles, the surfactant solution in contact with high pressure carbon dioxide was sprayed into chitosan solution. Fourier Transform Infrared Spectroscopy proves the interaction between the sulfate groups of SLES and the amino groups of CS. The Scanning Electron Microscopy reveals that the microparticles are quasi-spherical, but some of them can take the form of pellets depending on preparation conditions. The obtained microparticles were successfully used to uptake Cu(II) ions from aqueous solutions. The adsorption of Cu(II) depends on pH being maximum at pH = 5.5. The kinetic experiments demonstrated that Cu(II) adsorption onto CS/SLES microparticles obeys the Langmuir model. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40059.

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INTRODUCTION

In recent years, the synthesis methods of small particles have been diversified. One of these methods derives from the interaction between polymers and surfactants due to their special properties, particle size control, and multiple applications in environmental protection, pharmacy, and medicine. Interactions between polymers and surfactants in aqueous solutions have been a subject of intensive research as well as fundamental scientific studies.^{1–3}

One of the basic approaches used to obtain information about these interactions is the determination and analysis of the binding isotherm. The binding of ionic surfactants to polyelectrolytes of opposite charge has been reported as a co-operative process.^{4–6} Interaction between a charged polymer and an oppositely charged surfactant usually lead to phase separation owing to strong electrostatic forces. These forces may induce precipitation of polymer–surfactant complex, provided that a certain surfactant concentration range is reached.⁷

The polymer–surfactant complexes can be present in the system as clear solution, as colloidal particles or as gels with good

mechanical properties.^{8,9} The interaction between ionic polymers and oppositely charged surfactants is dominated by electrostatic forces, causing the association at a very low surfactant concentration, known as the critical aggregation concentration (CAC), usually a few orders of magnitude lower than the critical micelle concentration (CMC) of the surfactant.¹⁰

In this study, we used sodium lauryl ether sulfate (SLES) as anionic surfactant, which unlike sodium lauryl sulfate (SDS) possesses ethylene oxide groups (EO) between the hydrophilic moiety and dodecyl hydrophobic group, which increase the overall hydrophilicity of the surfactant. SLES is an anionic surfactant which is widely used in shampoos, detergents and other commercial cleaning products.¹¹

Chitosan (CS) is widely used for the synthesis of polymer–surfactant complexes due to its properties, biocompatibility, biodegradability and non-toxicity. Chitosan is a partially deacetylated chitin with following chemical structure: 2-amino-2-deoxy-(1→4)- β -D-glucopyranan.

Chitin can be obtained from the shells of crustaceans such as lobsters or shrimps. The protonation of amino groups makes

chitosan water soluble and the two hydroxyl groups can be chemically modified to formulate useful products for different applications.^{12,13} As compared to many other natural polymers, chitosan can acquire positive charges and acts as a chelating agent that selectively binds trace metals,¹⁴ being used as coagulant in wastewater treatment,¹⁵ or in fabrication of composite materials.¹⁶ Different methods such as emulsion cross-linking,¹⁷ coacervation or precipitation,¹⁸ spray-drying,¹⁹ and anionic surfactant gelation,²⁰ have been used to prepare chitosan particulate systems.

The discharge of residues containing heavy metals from industrial and mining processes into the environment is one of the main pollution sources of surface and ground waters. Copper is toxic for the human body and concentrations above 1.3 mg/L can cause gastrointestinal, kidney, or liver damage.²¹ Copper is also toxic to aquatic organisms even at very low concentrations.²² Studies performed until now report various adsorbents for Cu(II) including chitosan,²³ CS-cross-linked,²⁴ CS-cross-linked immobilized on bentonite,²⁵ or CS adsorptive membrane.²⁶ According to our knowledge, there are no studies of adsorption capacity of Cu(II) on CS/surfactant complex in the form of microparticles.

The aim of this study is to obtain small particles by interaction between chitosan and SLES at different pressures and also to characterize them. The obtained microparticles will be used for the removal of copper ions from aqueous solutions.

MATERIALS AND METHODS

Materials

Chitosan (CS) with medium molecular weight ($M_w = 120 \pm 70$ kDa) from shrimp shell and a deacetylation degree of 85% was supplied by Aldrich (Germany) and used without purification. Sodium lauryl ether sulfate (SLES) 70% was purchased from Rhodia Novacare Company Co., Romania. All experiments were performed on dried substance by lyophilization with the following composition: 99% SLES, 1% water and possible remaining contaminants NaCl, Na₂SO₄. Copper sulfate pentahydrate CuSO₄ · 5H₂O 99 % was purchased from Merck (Germany). Carbon dioxide (CO₂) with 99.9% purity was purchased from Linde Gas Romania. The pH of the solutions was adjusted to the required value with acetic acid (CH₃COOH) 0.5% (w/v) and NaOH 0.1 N solutions. The water used in the experiments was Milli-Q water. This water was obtained using a MILLIPORE Simplicity UV Lab System, France (18.2 mΩ cm resistivity at 25°C ultrapure water).

Synthesis of Particles at Atmospheric Pressure

The chitosan stock solution was prepared by dissolving 2 g of chitosan in 100 mL of aqueous CH₃COOH solution 0.5% (w/v) under magnetic stirring at 300 rpm for 24 h at room temperature. The CS/SLES microparticles are instantaneously formed by spraying 20 mL chitosan solution of 0.00174–0.00347 M preheated for 1 h at 40°C through a syringe needle of 20 mm length and 0.3–0.4 mm diameter, into 20 mL SLES aqueous solution of 0.0025–0.025 M. The distance from the needle to the surface of polymer solution was of about 20–30 mm. The obtained particles were separated by centrifugation. They are

washed 4–5 times with 100 mL Milli Q water on a microporous filter, then with ethanol to remove traces of surfactant. Finally, the wet particles were freeze dried using an ALPHA 1–2 LD plus apparatus. The dried microparticles were kept in a desiccator at room temperature for later use.

Synthesis of Particles at High Pressure

In order to obtain ultrafine particles, an experimental apparatus equipped with a high pressure cell was used. The surfactant was sprayed using high pressure CO₂, into biopolymer solution bath, through a stainless steel capillary nozzle. Carbon dioxide was used as propelling gas because it is nontoxic, nonflammable, inexpensive, environmentally benign, and does not react with chitosan or with sodium lauryl ether sulfate.²⁷ The obtained particles were collected from the solution through centrifugation at 10,000 rpm for 40 min. Supernatant was discarded, and the CS/SLES ultrafine particles were extensively rinsed 4–5 times with Milli Q water, and then with ethanol to remove any trace of surfactant, followed by freeze-drying process at –55°C for 26 h.

Synthesis of Particles by Dropping and Mixing the Reactants at High Stirring

Using this original method, a solution of anionic surfactant SLES 0.01 M was dropped into a mixture of polymer chitosan (0.00347 M) and acetic acid (0.5% wt/v) at weight ratio 1 : 1, under vigorous stirring at 11,500 rpm for 40 min using an ultra-turRax IKA T25. The obtained particles were washed 4–5 times with Milli Q water, centrifuged, separated from the liquid phase, and freeze-dried.

Characterization Techniques

The Fourier Transform Infrared (FTIR-ATR) spectra were recorded on a Nicolet iN10 FT-IR microscope with iZ 10 external module, Thermo Scientific, in the 550–4000 cm⁻¹ wavenumber range, at a spectral resolution of 4 cm⁻¹. The size and morphology of particles were determined by Scanning Electron Microscopy (SEM) using a Quanta 3D FEG 200/400 apparatus. Measurements for determination of mean diameters and zeta potential of the particles by dynamic light scattering (DLS) were performed using a Zetasizer Nano from Malvern. SLES analysis was made using a ¹H-NMR 300 MHz (Varian Gemini 2000), solvent D₂O and DMSO-D₆, integration error ±5%, at 60°C.

Copper Ions Adsorption

Standard Cu (II) solutions were prepared by dissolving copper sulfate pentahydrate in Milli Q water. Batch adsorption experiments were conducted in 50 mL conical flasks filled with 25 mL aliquots of CuSO₄ solutions in the range of 0.002–0.012 M, and equilibrated with feasible amount of CS/SLES dried microparticles (25 mg) at room temperature (25°C), for different values of pH.

The amount of Cu(II) adsorbed on the microparticles, q_e (mg/g dried), was calculated as follows:²³

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where V (L) is the volume of the Cu(II) solution, m (g) the weight of the dried microparticles, C_0 (mg/L) the initial Cu(II) concentration, and C_e (mg/L) the Cu(II) concentration at equilibrium.

Table I. Variation of Particle Diameter (D_p) Depending on Preparation Conditions

D_p^a (μm)	Diameter of needle (mm)	Distance needle – surface of surfactant solution (mm)	Drip rate (drops/min)
4.0	0.3	20.0	30
4.0	0.3	30.0	35
5.0	0.4	20.0	30
5.0	0.4	30.0	35

^aMeasured by SEM microscopy.

The concentrations of Cu(II) were determined at different interval of times by using a UV–Vis spectrophotometer (Varian Cary 100-Bio), and the pH values were measured by using an Orion pH-meter model 402A.

RESULTS AND DISCUSSION

Relation Between Particle Size and Conditions of Synthesis

Two types of particles were obtained: microparticles, at atmospheric pressure, and ultrafine particles, at high pressure.

Particles Synthesis at Atmospheric Pressure

A complex gel is formed at atmospheric pressure when chitosan solution droplets reach the surface of the surfactant solution, thereby forming microparticles. Their size can be controlled by: (a) varying the diameter of the syringe needle; (b) varying the distance between the needle and the surface of the surfactant solution; (c) control of drip rate (Table I).

The obtaining of insoluble membrane of CS/SLES complex at the surface of polymeric drop occurs as result of electrostatic interactions between anionic surfactant and cationic polymer. Further, surfactant diffuses inside the microcapsule leading to microparticle formation. The formation of the CS/SLES complex depends on the weight ratio between the structural units of chitosan and the surfactant there are several existence domains in the phase diagram (Figure 1). Namely we observed: (a) homogeneous solutions, monophasic, and clear within domain C; (b) precipitates, preceded by the appearance of an advanced

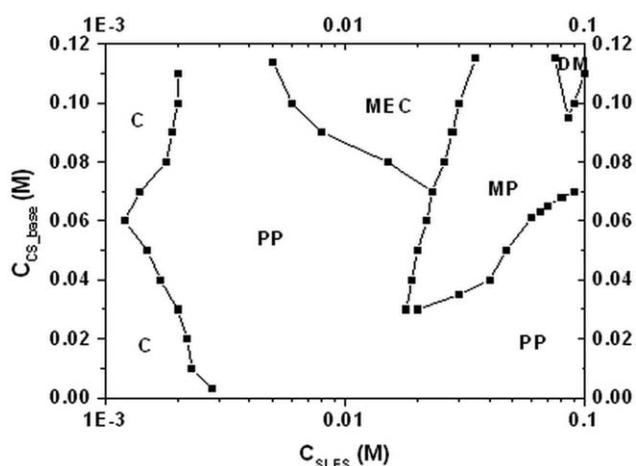


Figure 1. Domains of complex-gel CS/SLES.

turbidity within domain PP; the formation of precipitates was followed both visually and by using UV–Vis method; and (c) formation of gel-type membranes within domains MEC (microcapsule that expels its content), MP (spherical microcapsule) and DM (deformed microcapsule).

At low surfactant concentrations (0.005–0.03M), in the MEC domain, the droplets tend to expel the liquid from the outside and form an excrescence, while at high surfactant concentrations (0.075–0.1M), in the DM domain, the droplets shrink.

Within the MP Domain the Formed Particles Are Quasi-Spherical and Have Maximum Stability

We found that in the MP domain the obtained capsules keep their spherical shape, they do not deform, do not appear floaters on the surface. To determine the stability, daily measurements of the particles diameter were made by using SEM microscopy (Figure 2). The dimensions were maintained fairly unchanged for a measurement period of 30 days, namely $5 \pm 0.1 \mu\text{m}$.

The microcapsules have low mechanical strength because of the formed film's has low thickness. During the manual handling of microparticles (when they are prepared for SEM

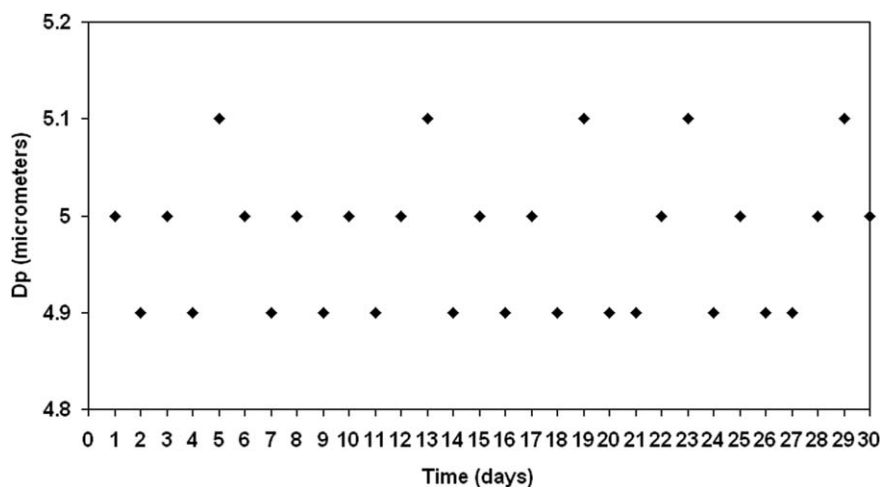


Figure 2. Stability determinations at long-time experiments for CS/SLES particles.

Table II. Effect of Pre-Expansion Pressure on the Particle Average Diameter and Zeta Potential

Pressure (MPa)	D_p (nm)	Zeta potential, mean charge (mV)
2	510	+34.6
3	463	+30.2
4	428	+28.0
5	418	+19.6

determinations) we found they are soft, elastic and retains its spherical shape due to external film.

One possible explanation for the obtaining of microparticles is based on the important role of the surfactant micelle shape in the physical binding of chitosan to form insoluble complex. SLES concentration of 0.018M at which stable microparticles (MP domain) start to form is noticeably higher than 0.0008M, the CMC of SLES in water.²⁸ Therefore, at concentration of 0.018M, SLES is in micellar form, which favors the cross-linking with chitosan molecules.

Particles Synthesis by Spraying-Pressure Method

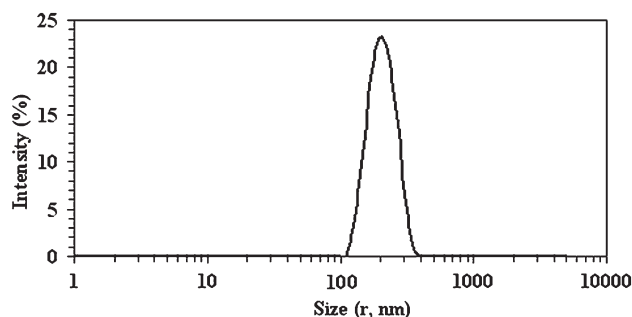
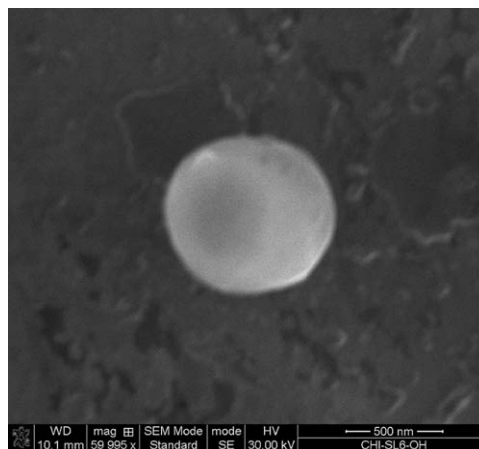
Depending on pre-expansion spraying pressure of SLES solution, ultrafine particles of different sizes were obtained. The average diameter and zeta potential of CS/SLES particles determined by dynamic light scattering (DLS) depend of the spraying pressure of SLES solution (Table II).

The CS/SLES particles are positively charged. Both, size and zeta potential decrease with increasing the spraying pressure of surfactant solution.

Depending on the spraying pressure (2–5 MPa), ultrafine particles of diameters ranging between 418 and 510 nm were obtained. Thus, for a series of measurements performed at 5 MPa, the size of the particles in solution ranges between 345–510 nm, with an average diameter of 418 nm (Figure 3).

The optimum concentration domain where ultrafine articles were obtained falls in range of 0.00174–0.00347M for CS, and 0.0025–0.025M for SLES.

SEM microscopy revealed that the ultrafine particles have quasi-spherical shape, with diameters around 500 nm, close to those obtained by DLS measurements (Figure 4).

**Figure 3.** Size distribution for CS/SLES ultrafine particles prepared at 5 MPa.**Figure 4.** Microphotograph of ultrafine particles obtained by spraying.

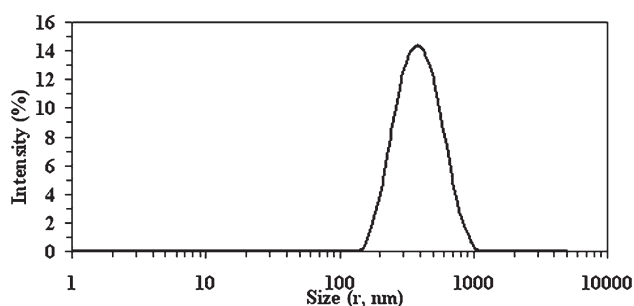
Particles Synthesis by Dropping and Mixing the Reactants at High Stirring

Ultrafine particles were also obtained by dropping SLES solution in vigorously shaken CS solution. The DLS measurements show that these particles are larger than those synthesized by the high-pressure method, but their size distribution is narrow (Figure 5). These particles are monodisperse with diameters around 800–900 nm, having an average size of 825.5 nm. A typical SEM picture is given in Figure 6.

The SEM Investigations Confirmed the Average Dimensions Obtained by DLS Measurements and Have Revealed a Pellet Shape for the Particles

The interaction between chitosan and sodium lauryl ether sulfate was studied on lyophilized samples by using FTIR spectroscopy, and the resulting data is presented in Figure 7. The FTIR spectra suggest that the interactions between CS and SLES have occurred during the CS/SLES complex formation. It may be possible that the protonated CS in the acetic acid solution is neutralized by the dissociated negative SLES ions through electrostatic interaction, with obtaining CS/SLES complexes as particles.

It is noteworthy that the characteristic peaks of CS at 1642 cm^{-1} for the $-\text{NH}$ bending vibration and at 1585 cm^{-1} for the $-\text{NH}$ deformation vibration of the amino groups were affected and shifted to 1633 and 1548 cm^{-1} , respectively, in the spectrum of the CS/SLES complex, which shows that the amino

**Figure 5.** Size distribution for CS/SLES ultrafine particles prepared at high stirring.

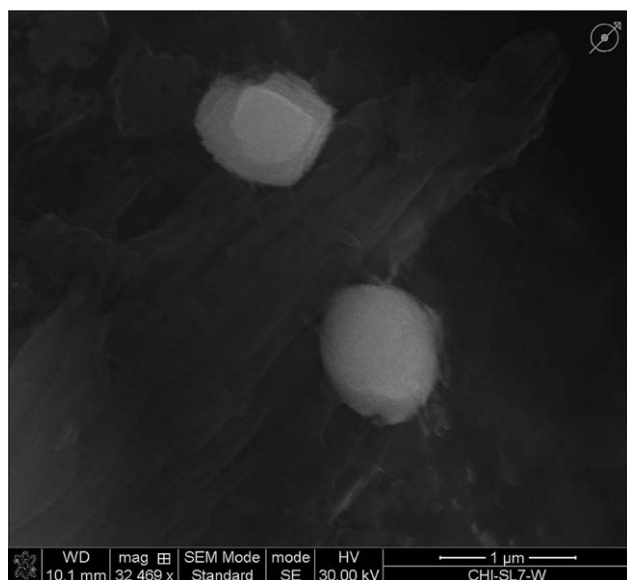


Figure 6. Microphotograph of CS/SLES ultrafine particles prepared at high stirring.

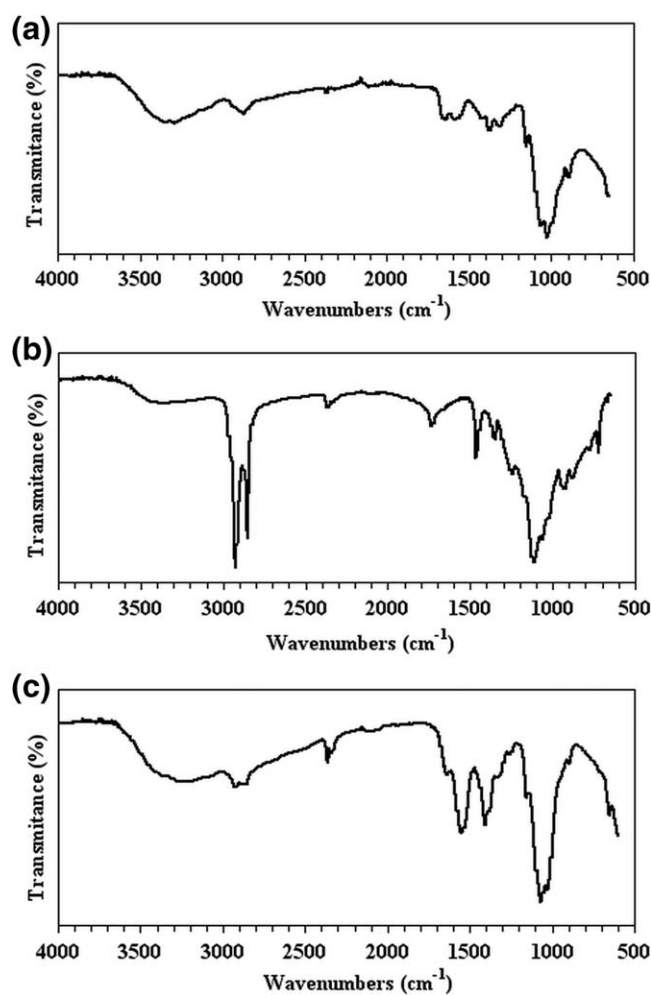


Figure 7. FTIR spectra of (a) CS, (b) SLES, and (c) CS/SLES microparticles.

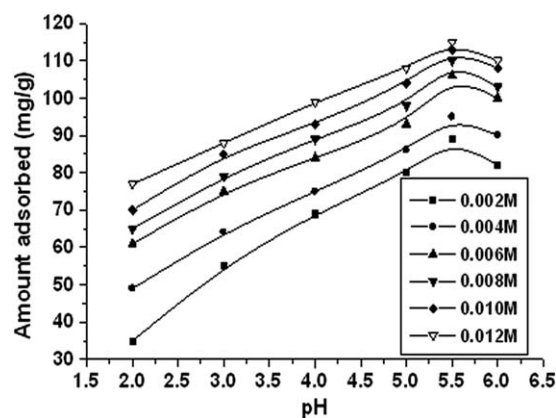


Figure 8. Effect of pH on the amount adsorbed onto CS/SLES microparticles at different Cu(II) initial concentrations.

groups are crosslinked by sulfate groups of SLES. On the other hand, the characteristic peaks of SLES at 1116 cm^{-1} for $-\text{SO}_3$ vibrations were affected and shifted to 1065 cm^{-1} in the spectrum of the CS/SLES complex, and the 1244 cm^{-1} for $\text{S}=\text{O}$ vibrations were affected and shifted to 1255 cm^{-1} in the spectrum of the CS/SLES complex. The strong and broad band centered at 1116 cm^{-1} which exists as multiple band structures in SLES spectrum, could be assigned to sulfate free anion absorptions.

Therefore, the FTIR data support the existence of electrostatic interactions between anionic sodium lauryl ether sulfate and positively charged chitosan.

Adsorption Experiments of Cu(II) Ions

The CS/SLES complex poses reactive functional groups on its surfaces, including sulfate, and amino groups that can bond the targeted substances through specific interactions such as surface complexation or ion exchange.²⁹

We have chosen to use only micrometer-sized particles obtained at atmospheric pressure, as they have the advantage of easy handling during phase adsorption of copper ions, decantation, filtration, and a high specific surface area, optimal for adsorption processes.

The adsorption performance was studied in terms of the effect of pH, adsorption kinetics, and isotherms.

Effect of pH on the Adsorption Process

One of the most important parameters which influence the adsorption capacity is the pH of pollutant solution. We have studied the effect of pH on the adsorption of Cu(II) ions on CS/SLES microparticles for several initial concentrations of the pollutant and the results are summarized in Figure 8. One may observe that the adsorbed amount increases with pH and the maximum uptake of Cu(II) ions is at $\text{pH} = 5.5$.

We assume that at pH values of 2.0–4.0, the amine groups of chitosan are protonated which induces an electrostatic repulsion and prevents the approaching of Cu(II) ions. Increasing the pH above 6.0, the Cu(II) ions in the solution can form copper hydroxide, which prevents the adsorption process. Taking into

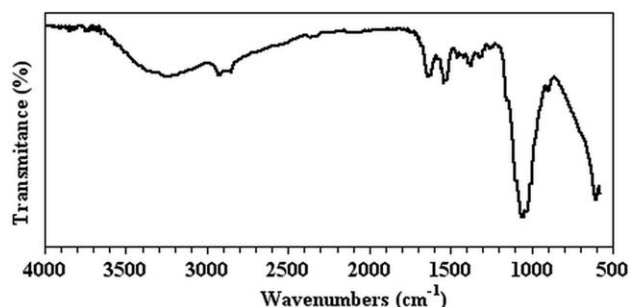


Figure 9. FTIR spectra of CS/SLES microparticles after Cu(II) adsorption.

account these data, the optimum pH value for Cu(II) adsorption is found at about 5.5.

Evidence of Cu(II) Adsorption

The FTIR spectra of CS/SLES dried microparticles, before and after Cu(II) adsorption, were recorded over a frequency range of 550–4000 cm^{-1} and are shown in the Figure 9. The peaks in the FTIR spectra of CS/SLES microparticles after Cu(II) adsorption corresponding to the $-\text{NH}_2$ vibration of amino groups, become wider and are shifted from 1548 to 1540 cm^{-1} , and $-\text{SO}_3$ vibrations are shifted from 1065 to 1057 cm^{-1} . They indicate that the functional groups amino are involved in the complexation of copper ions. We observe that the adsorption of Cu(II) on CS/SLES microparticles leads to apparition of a new band at 606 cm^{-1} which can be due to stretching vibrations of Cu–N bonds.

The microparticles used for Cu(II) adsorption have 4–5 μm average diameters and after the adsorption, the mean diameters is approximately 6 μm , as can be seen from Figure 10. On the other hand, the surface of CS/SLES microparticles before adsorption has a mean charge of +11.8 mV. After the Cu(II) adsorption onto the CS/SLES microparticles, the mean charge increases to +23.6 mV, as shown in the Figure 11.

Kinetics of Cu(II) Ions Adsorption

The kinetics of Cu(II) adsorption on CS/SLES microparticles was spectrophotometrically studied at 25°C, pH = 5.5 and the results are shown in Figure 12.

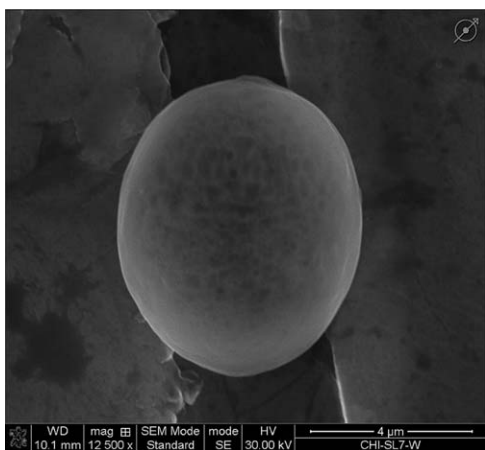


Figure 10. SEM microphotograph of CS/SLES microparticles after Cu(II) adsorption.

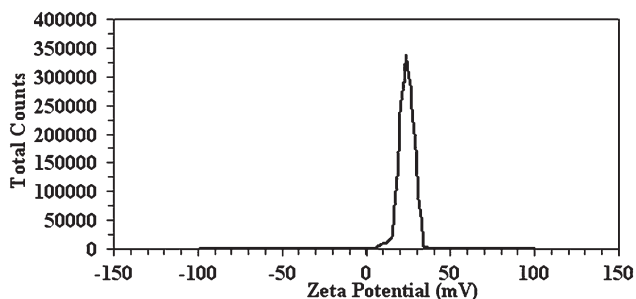


Figure 11. Zeta potential of CS/SLES microparticles after Cu(II) adsorption.

The amount of Cu(II) ions adsorbed on CS/SLES microparticles increases with the contact time for all the initial pollutant concentrations. One may observe that the adsorption is stronger in the first 200 min, after which the process slows, and reaches an equilibrium value after about 800 min. We consider that the adsorption capacity is related to the binding sites, the amino groups, for binding of Cu(II) ions. This statement comes along with previous data showing that the adsorption capacities depend on the binding sites and porosity.³⁰

The equilibrium adsorption is usually described by an isotherm characterized by specific parameters, which express the surface property and affinity of the adsorbent. The adsorption of Cu(II) ions onto CS/SLES microparticles prepared at atmospheric pressure was investigated, and the experimental data were analyzed with classical Langmuir and Freundlich models.

We have used for the adsorption studies only microparticles prepared at atmospheric pressure, having size of 4–5 μm , which allows us to approximate the surface area per gram of particles with certain accuracy.

One of the most used equations for modeling the adsorption process is the Langmuir isotherm.³¹ The Langmuir model assumes monolayer sorption on a surface with a finite number of identical adsorption sites.²⁹

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (2)$$

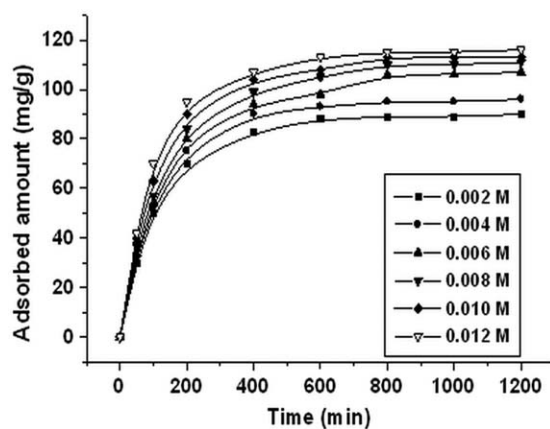


Figure 12. Effect of contact time and initial Cu(II) concentration on the adsorbed amount onto CS/SLES microparticles, at pH = 5.5.

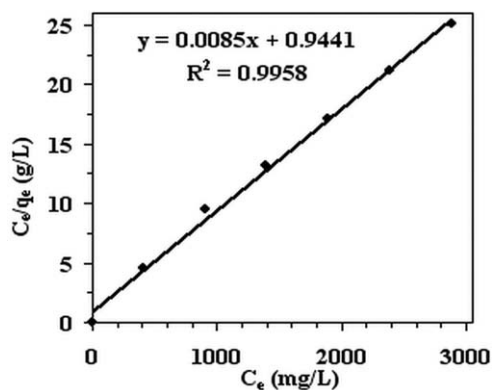


Figure 13. Langmuir plot for Cu(II) ions adsorption onto CS/SLES microparticles.

where: C_e is the equilibrium Cu(II) concentration, K_L is the Langmuir isotherm constant, and q_m represent the maximum adsorption capacity. Equation (2) can be rearranged to the following form:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (3)$$

The values of Langmuir constants (q_m and K_L) are calculated from the plot of C_e/q_e versus C_e . For CuSO_4 adsorbed on CS/SLES microparticles the plot is shown in Figure 13, and the values for the Langmuir constants are $q_m = 117.65$ mg/g and $K_L = 9.1$ L/mg respectively. These results are comparable to those obtained by adsorption of Cu(II) ions onto crosslinked or non-crosslinked CS beads,³² or on CS hollow fiber membranes.²⁹

The Langmuir isotherm was found to be linear over the studied concentration range and the correlation coefficient was of $R^2 = 0.9958$, which shows that the adsorption of Cu(II) ions to CS/SLES microparticles is in agreement with Langmuir equation.

Freundlich equation was also applied to the adsorption data and the correlation coefficient R^2 was found to be 0.8517. This low value indicates that the adsorption is not consistent with Freundlich model.

CONCLUSIONS

The interaction between the cationic chitosan and the anionic surfactant sodium lauryl ether sulfate leads to obtaining of micro and ultrafine particles depending on the spaying pressure. At atmospheric pressure the complex CS/SLES can exist as homogeneous and clear solutions, precipitate or can form stable or deformed microparticles, depending on the chitosan/surfactant weight ratio. The CS/SLES complex in the form of ultrafine particles was obtained by spraying surfactant solution at high pressure in chitosan solution. The obtained ultrafine particles have positive electrical charges and the SEM microphotographs show that these particles have nanometric size around 500 nm. The FTIR spectra reveal interactions between the sulfate group of sodium lauryl ether sulfate and amino group of chitosan. The CS/SLES microparticles were successfully used to uptake Cu(II) ions from aqueous solutions. The FTIR data prove that

amino groups are involved in complexation of Cu(II) ions. The experiments showed that the adsorption of copper ions occurs in accordance with the Langmuir model.

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