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Silver Nanoparticles Functionalized with Sodium Mercaptoethane Sulfonate to Remove Copper from Water by the Formation of a Micellar Phase

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Abstract: This work presents a novel procedure for the removal of Cu^{2+} from water, an essential element in human nutrition considered toxic in high concentrations, based on a microextraction technique involving the formation of a micellar phase. To achieve the total elimination of copper from aqueous samples, a Cu^{2+}-complexing reagent based on silver nanoparticles functionalized with sodium mercaptoethane sulfonate (AgNPs@MESNa) was used. The complex formed by Cu^{2+} and the reagent was extracted into a micellar microphase formed by Triton X-114, a harmless surfactant. Volumes of 200 µL of the 10^{-4} mol L^{-1} suspension of AgNPs@MESNa and 100 µL of a solution of Triton X-114 at 30% m/m were employed to successfully remove 10 mg L^{-1} of Cu from 20 mL of water samples. The time and temperature needed to achieve 100% microextraction efficiency were 10 min and 40 °C, respectively. The procedure is considered environmentally friendly due to the low volume of the extracting phase and the simple experimental conditions that achieve total removal of Cu^{2+} from water samples.

Keywords: copper removal; mercaptoethane sulfonate; micellar phase; microextraction; remediation; silver nanoparticles

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1. Introduction

Copper is considered an essential element in human nutrition because it is involved in many enzymatic reactions, being one of the indispensable micronutrients. At least 30 copper-containing enzymes are known, whose functions include redox catalysis (cytochrome oxidase, nitrate reductase) or oxygen transportation (hemocyanin) [1,2]. High levels of copper are considered toxic, being of paramount importance for natural ecosystems [3]. The form that this metal presents (ionic, compound, or precipitated) depends on environmental factors, such as pH, redox potential, soil and type of sediment, and water hardness and organic content, which could vary depending on the ecosystem [3,4].

The levels of copper accessible in the environment greatly increase in areas with human activities that enhance its abundance [5], including smelting; mining; industrial activities; and the application of fertilizers, algaecides, and fungicides containing copper [6,7], which allow copper to pass through the soil. As a consequence of the contact of water with the earth's crust, copper salts can be found dissolved in surface water and in underground mantles due to industrial activity, usually in concentrations lower than 20 µg L^{-1} [8]. However, at high concentrations, copper is toxic to organisms, its effect becoming stronger for plants and fish [9]. These higher concentrations can be found at points of water use as a result of corrosion of brass and copper pipes [10].

For these reasons, nowadays, the study and development of new techniques to eliminate copper from water is of capital importance. In the recent literature, numerous ways of eliminating Cu^{2+} from water and other matrices are found. Some of these techniques are based on oxidation processes [11–15], precipitation [16–20], and adsorption procedures that employ different materials as adsorbents [21–26].

Liquid–liquid extraction techniques are widely used to remove Cu^{2+} from water or soil due to their simplicity [27–30]. However, generally, these procedures require large volumes of solvents and sequential treatment, which significantly increases the cost and time employed to remove small amounts of copper. In recent years, interest in the use of nanoparticles to remove Cu^{2+} from water has grown [31–34], being most of the methods employed based on adsorption techniques which involve tedious procedures that do not achieve 100% adsorption efficiency.

In this work, we present a novel approach for the removal of Cu^{2+} from water samples combining the use of silver nanoparticles functionalized with sodium mercaptoethane sulfonate (AgNPs@MESNa) with a microextraction technique that uses a small volume of Triton X-114. This harmless surfactant forms a small micellar phase that allows the microextraction of Cu^{2+} by complexing with AgNPs@MESNa. After centrifuging, the microvolume is placed in the bottom of the flask, allowing its total separation. The experimental conditions to achieve the total elimination of Cu^{2+} from aqueous solutions are easy to achieve, being optimal at pH close to 3, achieved by employing an appropriate amount of nitric acid, and preheating at 40 °C for 10 min. The volumes of AgNPs@MESNa suspension and Triton X-114 solution necessary to eliminate 10 mg L^{-1} of Cu^{2+} from 20 mL of water are small (200 µL of a 10^{-4} mol L^{-1} suspension of AgNPs@MESNa and 100 µL of a solution of Triton X-114 at 30% m/m), which makes this procedure a cost-effective and environmentally friendly technique.

The method offers a novel alternative for the removal of Cu^{2+} from aqueous samples to adsorption techniques and classic extraction processes, which require large volumes of solvent and successive removals to totally eliminate Cu^{2+}, leading to environmental issues and higher costs.

2. Experimental Section

2.1. Materials and Instrumentation

The solutions were prepared using deionized water purified with a Millipore system (Millipore, Bedford, MA, USA). The Cu(II) solution was prepared daily from 1 g L^{-1} of standards from Panreac (Barcelona, Spain) by adequate dilution. The surfactant Triton X-114 employed as the extractant medium was purchased from Fluka (Buchs SG, Switzerland) and used to prepare a 30% m/m solution in ultrapure water and then kept in the refrigerator until use. The 10^{-4} mol L^{-1} solution of sodium 2-mercaptoethane sulfonate (MESNa; Sigma-Aldrich, Steinheim, Germany) was prepared before use in ultrapure water. Silver nitrate from Merck (Darmstadt, Germany) was used for the synthesis of silver nanoparticles. The reducing agent $NaBH_4$ was obtained from Fluka and used in the solid state for the generation of silver nanoparticles.

A Perkin-Elmer Model 600 atomic absorption spectrometer equipped with Zeeman correction, a graphite furnace atomizer (ETAAS), and an AS-800 autosampler (Perkin-Elmer, Shelton, WA, USA) were used. The tubes equipped with the L'Vov platform were made of pyrolytic graphite and obtained from the same manufacturer. Argon was used as the inert gas, with a flow rate of 250 mL min^{-1} in all stages, except for the atomization stage, where the flow stopped. Copper and nickel hollow cathode lamps (Perkin-Elmer, Shelton, USA) operating at 15 and 25 mA, respectively, were used.

A 50 W ultrasound bath (ATU, Valencia, Spain) with temperature control was used for the thermal treatment of the solutions and the degassing of the samples. The solutions were centrifuged in the Unicen 21 Centrifuge (Madrid, Spain) with a rotor and an adapter for 50 mL conical-bottom tubes up to 4000 rpm.

2.2. Preparation of Silver Nanoparticles Functionalized with Sodium 2-Mercaptoethanesulfonate (AgNPs@MESNa)

Silver nanoparticles (AgNPs) were prepared by the reduction of Ag (I) [35]. For this purpose, 100 mL of 10^{-4} mol L^{-1} silver nitrate solution was placed in a flask. Under vigorous stirring, 0.012 g of solid $NaBH_4$ was added. After 10 min of stirring, the mixture acquired a pale-yellow color. Afterward, 2 mL of a 10^{-4} mol L^{-1} aqueous solution of MESNa was added, stirring for 30 min until the suspension turned reddish. The prepared AgNPs@MESNa suspension was stable for several days at room temperature. After this process, the suspension of silver nanoparticles functionalized with MESNa was transferred to a topaz-colored bottle and stored in the refrigerator for better conservation.

2.3. Proposed Procedure for the Removal of Cu^{2+} from Water

Next, 20 mL of a water sample with a Cu^{2+} concentration of 10 mg L^{-1} was placed in a conical-bottom centrifuge tube. The pH was adjusted to 3 with the addition of 0.1 mol L^{-1} of commercial nitric acid at 70% w/w (approximately 200 μL) and preheated to 40 °C. Then, 50 μL of the AgNPs–MESNA solution and 100 μL of the 30% m/m aqueous Triton X-114 solution were added. The mixture was stirred manually and heated at 40 °C for an additional 10 min. Afterward, the dispersion was centrifuged at 3500 rpm for 10 min and the extractant phase (Triton X-114) was separated, remaining at the bottom of the tube, and removed using a chromatographic syringe.

The Cu^{2+} content of the aqueous sample was determined by ETAAS before and after the microextraction process, showing that all the Cu^{2+} was removed in the micellar phase. In addition, to check that there were no traces of silver in the water sample, after removing the copper from the solution, the silver content was measured by ETAAS, showing no traces.

3. Results and Discussion

3.1. Selection of the Functionalizing Reagent

Modifying the surface of metallic nanoparticles with molecules containing functional groups is an appropriate way to alter their properties, making them suitable for use in various processes. A representative example is the functionalization of nanoparticles with biomolecules [36,37]. Nanoparticles exhibiting a protective monolayer surface can be obtained directly from precursors [38] by means of an exchange reaction with a suitable ligand [39] or by coupling with a suitable functional group [40]. Alkanethiols are the most widely studied monolayer ligands in the case of gold and silver nanoparticles because of the ability to attach to the surface through a metal–sulfur bond, leaving their carbon chains directed outward. Less studied is the use of bifunctional ligands that, on the one hand, associate with the surface of the nanoparticles and, on the other hand, act as complexing agents for metallic species. The coupling of metals on their surface expands the possibilities of their use in catalysis processes, sensors, and biomolecules [41]. In this work, MESNa was chosen as a bifunctional reagent since it contains an S atom to bind with the nanoparticle, while the sulfonate group would be responsible for the interaction with metal ions.

In a previous study on the use of MESNa-functionalized AgNPs for the determination of Hg^{2+} by surface-enhanced Raman scattering spectroscopy, it was manifested that the removal of mercury took place by means of its interaction with sulfur belonging to the thiol groups of MESNa [42]. Moreover, some other studies have revealed strong interactions between elements, such as copper, and sulfonate groups [43–46]. Therefore, in this work, the mechanism was driven by the same kind of interactions.

In the absence of AgNPs@MESNa, the extraction of Cu^{2+} in the condensed micellar phase was not observed. However, when MESNa was used at high concentrations (10^{-4} mol L^{-1}), a low extraction of Cu^{2+} (22%) was obtained. This clearly indicates MESNa's ability to complex with metal ions. When a small concentration of AgNPs@MESNa was added instead of a high concentration of MESNa, a considerable increase in extraction was achieved. It is therefore evident that a strong interaction takes place between metal ions and functionalized silver nanoparticles, in addition to MESNa, thus reinforcing the role of silver nanoparticles.

3.2. Effect of pH on Cu^{2+} Removal

The pH of the medium had a strong effect on the extraction of the Cu^{2+} retained in the AgNPs@MESNa in the condensed micellar phase of Triton X-114, as shown in Figure 1. Error bars are smaller than the symbol size. The pH values were adjusted with the use of nitric acid, sodium hydroxide, and 0.001 mol L^{-1} of phosphate regulators. The maximum extraction efficiency was achieved at pH close to the zero-charge potential of AgNPs [47]. Although the potential of zero charge changes with the functionalizing species [48], a pH value lower than 3 is not advisable, because AgNPs can dissolve in the media. In view of the results obtained, the most suitable value was pH = 3, adjusted with the use of dilute nitric acid.

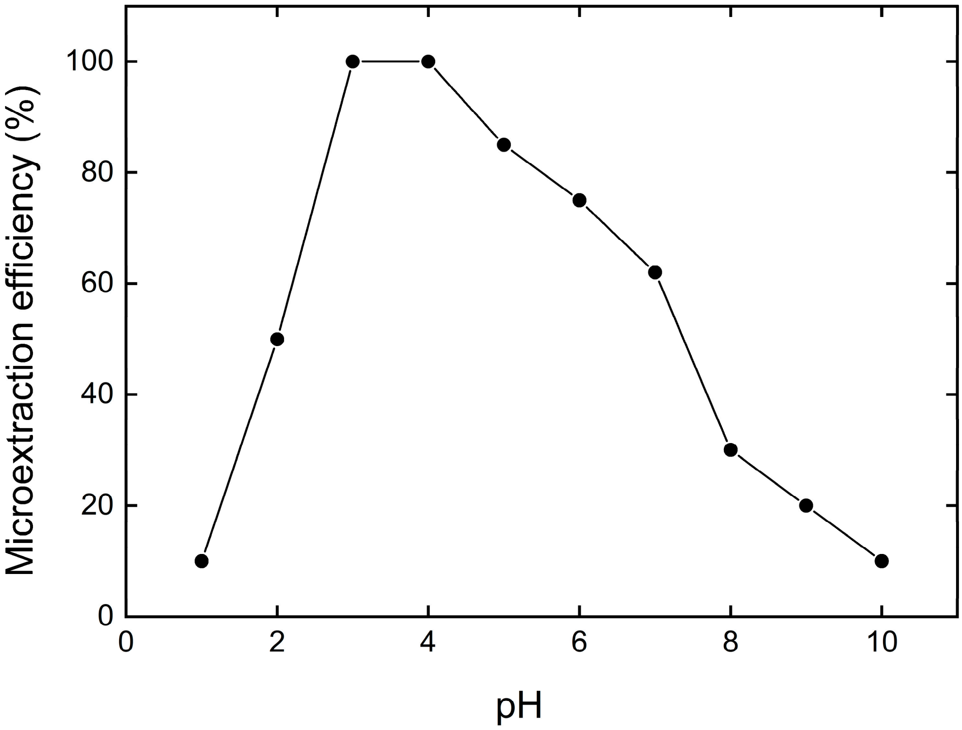

Figure 1. Dependence of microextraction efficiency on pH for the removal of Cu^{2+}. The maximum efficiency was achieved at pH around 3. The straight line shows spline connectors.

3.3. Effect of Triton X-114 Concentration

The concentration of Triton X-114 plays an important role as it must be high enough for the cloud to form in the solution (3×10^{-4} mol L^{-1}) [49], characterized by a cloudy appearance or scattering, while removing 100% of the Cu^{2+}. In this work, we studied the effect of the concentration of Triton X-114 ranging from 0.02% to 0.5% v/v, measuring Cu^{2+} by ETAAS both in the extract and in the aqueous phase. For an aqueous phase volume of 20 mL, an increase in the microextraction efficiency with the concentration of Triton X-114 was observed, reaching the maximum for values between 0.05% and 0.1% v/v. Higher concentrations unnecessarily increased the volume of the condensed phase, thus reducing the cost-effectiveness and making this technique less environmentally friendly. The addition of 100 µL of Triton X-114 at 30% v/v to 20 mL of the aqueous phase was selected as the amount of surfactant that leads to the best results. In this way, approximately 38 µL of the condensed phase was obtained.

3.4. Effect of Temperature on the Microextraction Efficiency of Cu^{2+}

The temperature at which the Triton X-114 cloud began to form was determined to be between 23 and 25 °C, although it changes according to the environmental conditions [50] since it depends on the interactions between the additives and the micelles. The effect of temperature and incubation time of the solution containing Triton X-114 was studied. Figure 2 shows the dependence of the microextraction efficiency of Cu^{2+} in the condensed phase on the temperature, between 25 and 70 °C, after 15 min of a temperature bath. Error bars are smaller than the symbol size. Below 40 °C, the condensed phase volume obtained reduced, causing the Cu^{2+} not to be removed. From 40 °C, this effect disappeared and all Cu^{2+} was eliminated up to 70 °C. The optimal temperature was selected as 40 °C, since for higher values, more energy would need to be provided, thus reducing the cost-effectiveness of the process. Moreover, at 40 °C, the critical micellar concentration was reached, resulting in a reduction in the hydration of the hydrophilic group. This effect produces the cloud point of non-ionic surfactants and therefore favors micellization [8].

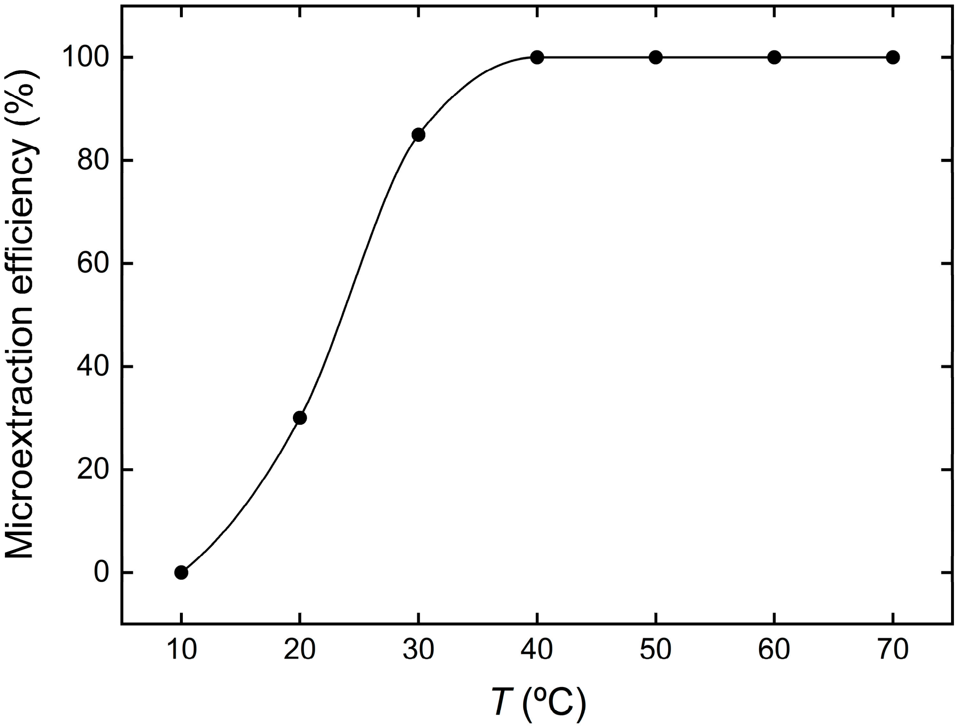

Figure 2. Dependence of Cu^{2+} removal efficiency on temperature. The optimal value was chosen as 40 °C. The straight line shows Akima spline connectors.

3.5. Contact Time Effect

Regarding the time necessary for the extraction to take place, it was observed that from 15 min onward, the extraction of Cu^{2+} was complete, operating at 40 °C. However, if the sample containing the analytes and AgNPs@MESNa was preheated at 40 °C prior to the addition of Triton X-114, the microextraction time reduced to 10 min and all Cu^{2+} was removed, as shown in Figure 3. Error bars are smaller than the symbol size. Therefore, it is recommended to incubate the sample for 10 min at 40 °C after the addition of Triton X-114 to accelerate the removal process.

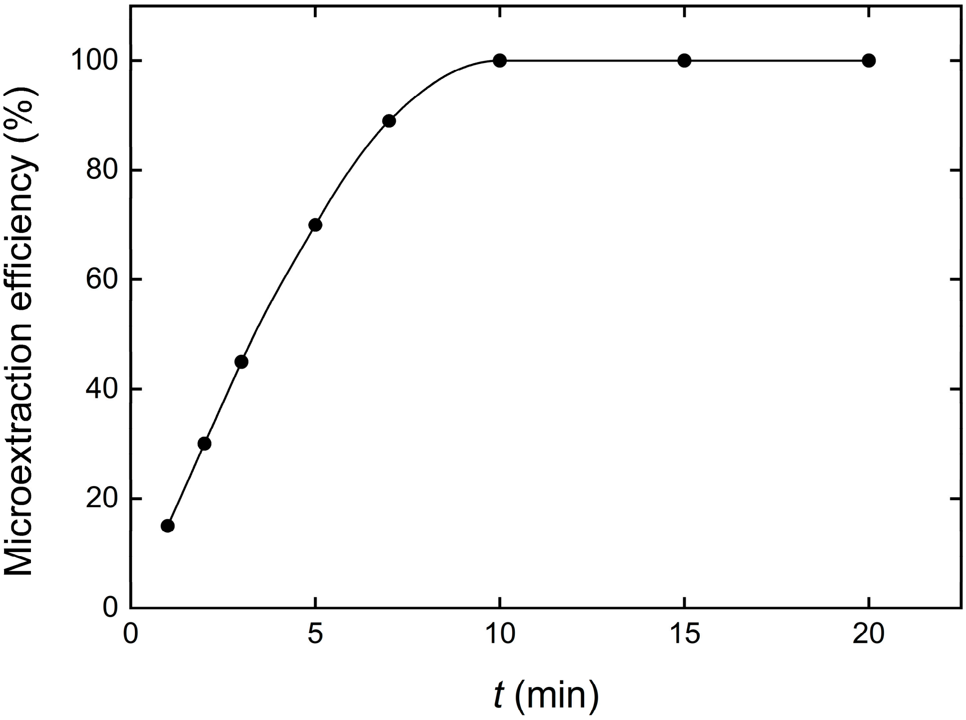

Figure 3. Dependence of microextraction efficiency on incubation time for the removal of Cu^{2+}. The maximum efficiency was achieved in 10 min when the sample was preheated at 40 °C. The straight line shows Akima spline connectors.

3.6. Effect of Other Ions Present in the Medium

In the aquatic environment, there are numerous ions commonly present, such as Pb^{2+}, Cd^{2+}, Cr^{3+}, Cr^{6+}, $SO_4{}^{2-}$, $PO_4{}^{3-}$, $NO_3{}^{-}$, and $CO_3{}^{2-}$. To determine how they influence the proposed copper elimination process, the procedure has been applied in the presence of high concentrations of the indicated ions. The results reveal that for concentrations even 100 times higher than the concentration of copper, the removal of the latter is not affected.

In addition, to verify that the process could be suitable for real water samples, it was applied to four real water samples, two taken from the sea and two from the tap, all doped with a concentration of Cu^{2+} of 10 mg L^{-1}. After applying the proposed procedure, all the copper was eliminated, proving this approach is applicable to real water samples.

4. Conclusions

This work introduced a novel procedure using silver nanoparticles functionalized with sodium 2-mercaptoethane sulfonate (AgNPs@MESNa) as an effective reagent for the retention and removal of the cationic form of Cu^{2+} from water samples. The nanoparticles were completely separated from the solution by their entrapment in the Triton X-114 micelles generated under appropriate experimental conditions. The high partition coefficient between both phases and a high-volume ratio of the aqueous-to-micellar phase allowed the removal of all Cu^{2+} present in water samples, proving this procedure as a novel alternative to traditional techniques for the elimination of high concentrations of Cu^{2+}. This new procedure removes up to 10 mg L^{-1} of Cu^{2+} from 20 mL of water in 10 min without using high volumes of solvent and under mild experimental conditions. Additionally, the approach is fast, cost effective, and environmentally friendly.

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Validation, Y.V.-M., M.C.G., M.d.C.G.-O. and A.S.-M.; Visualization, Y.V.-M., M.C.G., M.d.C.G.-O. and A.S.-M.; Writing—original draft, Y.V.-M., M.C.G., M.d.C.G.-O. and A.S.-M.; Writing—review & editing, Y.V.-M., M.C.G., M.d.C.G.-O. and A.S.-M. All authors have read and agreed to the published version of the manuscript.

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