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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Silver Ion Reduction with Peat Fulvic Acids

D. S. Sal'nikov[a], A. S. Pogorelova[b], S. V. Makarov[a], and I. Yu. Vashurina[a]

[a] *Ivanovo State Chemicotechnological University, Ivanovo, Russia.*
[b] *Institutes of Solution Chemistry, Russian Academy of Sciences, Ivanovo, Russia*

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Abstract—Formation of silver nanoparticles in chemical reduction of $AgNO_3$ with peat fulvic acids in an aqueous alkali solution was studied spectrophotometrically. The size of the resulting nanoparticles and their stability were examined in relation to the reaction temperature and time,and concentrations of fulvic acids and silver nitrate.

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Nanotechnologies represent one of the key directions in development of science and technology, which yield materials with unique physical, chemical, and biological properties [1]. Increased interest in nanosize silver is dictated by the promises of its antibacterial and antiviral applications [2, 3]. There exist several methods of preparation of silver nanoparticles, in particular, chemical reduction [3–7].

Today, a topical issue is the search for new reducing agents to prepare nanosize silver. The preference among these agents is given to natural environmentally safe compounds like arabinogalactan (polysaccharide) [8] and quercetin (flavonoid) [9]. These compounds owe their reducing power to the aldehyde and phenolic groups in their molecules, respectively.

Here, we demonstrate that reducing agents for preparation of nanosilver can be found in environmentally safe natural biopolymers, peat fulvic acids. The corresponding method of preparation of the nanomaterial is simple and easily implemented. Combined with physiological activity of fulvic acids proper [10, 11], this offers promise for synthesis of new bactericides for various technical and medicinal applications.

EXPERIMENTAL

We used chemically pure-grade silver nitrate and an aqueous solution of fulvic acids isolated from high-type cotton grass-sphagnum peat by alkaline extraction with sodium hydroxide by a standard procedure [12]. The alkaline extract of peat, containing humic and hymatomelanic acids along with fulvic acids, was acidified to pH 1. This caused precipitation of humic and hymatomelanic acids, which were subsequently separated from fulvic acids by filtration. The concentration of fulvic acids in solution was determined gravimetrically. The solutions of fulvic acids were alkalized with chemically pure-grade sodium hydroxide to pH 6.5, in which medium the reduction reaction was run. The temperature was varied within 25–90°C. The absorption spectra were recorded on a Specord M-40 spectrophotometer.

Fulvic acids belong to one of the fractions of humus acids, along with humic and hymatomelanic acids. Structurally, humus acids are distinguished by a broad spectrum of groups and moieties they contain. Of greatest value among them are oxygen-containing groups, specifically phenolic, carboxy, alcoholic, and aldehyde, as well as ketone and quinone groups. Also, the molecules of humus acids contain amino acid and carbohydrate residues, as well as flavonoid moieties [11, 13].

Fractionation of humus acids is underlain by the difference in the solubility of fulvic, humic, and hymatomelanic acids in acids and alkalis [11–13]. Fulvic acids represent a fraction soluble both in alkalis and acids. Compared to humic acids, fulvic acids have a lower molecular weight, a less aromatic molecular structure, and increased content of oxygen-containing groups. Fulvic acids actively participate in diversified interactions, including redox processes [14–17]. Thus, simple preparation technology and readily accessible inexpensive raw material, as well as nontoxicity, environmental safety, and broad spectrum of properties of peat fulvic

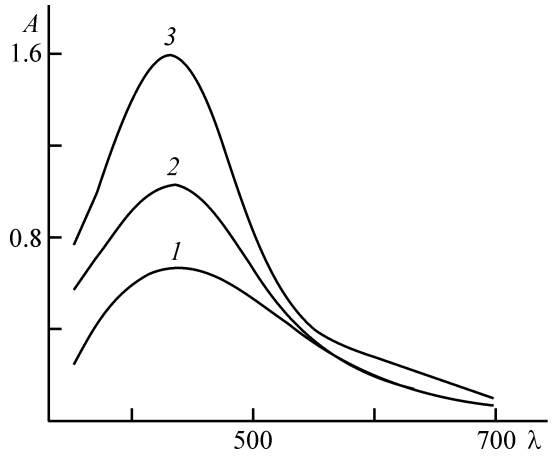

Fig. 1. Absorption spectra of silver sols at different temperatures of silver nitrate reduction with peat fulvic acids. [$AgNO_3$] = 1×10^{-3} M, [fulvic acids] = 0.5 g l^{-1}, reaction time 300 min. (*A*) Optical density, and (λ) wavelength, nm; the same for Figs. 2 and 3. Reaction temperature, °C: (*1*) 70, (*2*) 80, and (*3*) 90.

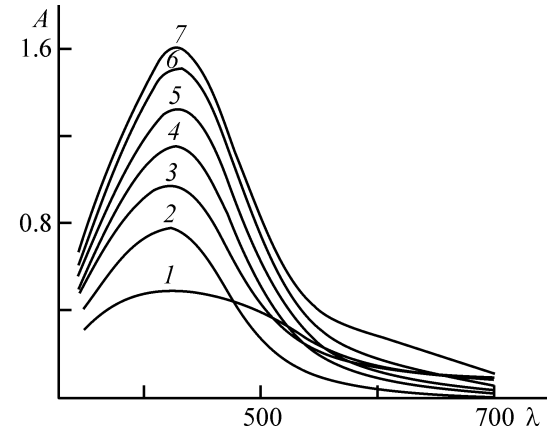

Fig. 2. Absorption spectra of silver sols at different reaction times in silver nitrate reduction with peat fulvic acids. [$AgNO_3$] = 1×10^{-3} M; [fulvic acids] = 0.5 g l^{-1}; reaction temperature 90°C. Reaction time, min: (*1*) 25, (*2*) 40, (*3*) 60, (*4*) 120, (*5*) 180, (*6*) 240, and (*7*) 300.

acids motivated their investigation as candidate reducing agents for preparation of silver nanoparticles.

It was found that the reaction of Ag(I) with fulvic acids proceeds at temperatures above 50°C. In the absorption spectrum (Fig. 1), a band with a maximum at 430–438 nm, depending on the reaction temperature, appears. This band is associated with light absorption by conductivity electrons (surface plasmons) of colloid silver [18]. It should be noted that, with increasing temperature, both the rate and extent of silver reduction tend to grow. The final absorption spectrum of the silver sol is modified: The absorption maximum exhibits a hypsochromic shift from 438 to 430 nm.

Published data suggest that the major reducing groups in fulvic acids are the phenolic groups which are oxidized to quinine groups in the reaction with silver ions

$$FA(CO–H) + Ag^+ + OH^–$$
$$\rightarrow FA(C=O) + 1/2\ Ag_2 + H_2O,$$

where FA is the part of the molecule of fulvic acids, unchanged in the reduction reaction.

Along with phenolic groups, aldehyde groups also can act as reducing agents.

Figure 2 demonstrates evolution of the absorption spectrum of silver plasmons during reduction of silver ions with fulvic acids at 90°C. At the initial moment small silver cluster are formed, as confirmed by the peak at λ = 364 nm (Fig. 2, curve *1*) [19]. With increasing reaction time, clusters tend to aggregate as manifested in a gradual bathochromic shift of λ_{max} (from 420 to 430 nm), as well as in the appearance of a shoulder near 625 nm (Fig. 2, curve *7*).

According to the Mie-Drude theory [20, 21], the position of the absorption band maximum for surface plasmons in metal is determined by the equation

$$\lambda^2_{max} + (2\pi c)^2 m(\varepsilon_0 + 2n)/4\pi N_e e^2,$$

where *c* is the light velocity; *m*, effective mass of electron; e, electron charge; ε_0, dielectric permittivity of the metal; *n*, refractive index of the medium; and N_e, free electron density in the metal.

This equation shows that a decrease in N_e causes a shift to longer waves of the absorption band of the plasmons in the metal. Hence, the observed changes in λ_{max} of the silver sols during the reaction suggest a decrease in the electron density in the metal.

The correlation between the nanoparticle size and spectral characteristics of various metals are the subject of much investigation [4, 18, 19, 22–24]. It was found that silver particles with the size of 2–5, 7–16, and 20–30 nm are characterized by λ_{max} of 390, 410–420, and 425–435 nm, respectively [4, 8, 9, 18, 19, 22–24]. Thus, peat fulvic acids are suitable for preparation of silver particles with the size from 7 to 30 nm, depending on the reduction conditions (temperature, time).

The appearance of a shoulder in the longwave region of the spectrum is most probably associated with formation of fractal structures in the metal [4]. The reason is that

the resulting silver nanoparticles are typical lyophobic colloids which tend to aggregate because of excessive surface energy they possess.

The next stage consisted in examination of the size and stability of the resulting metal nanoparticles in relation to the concentrations of fulvic acids and Ag^+ ions. First, we varied the fulvic acids concentration from 0.1 to 1.0 g l^{-1} at a constant initial concentration of silver nitrate ($[AgNO_3] = 1\times10^{-3}$ M, 90°C, experiment time 300 min):

[Fulvic acids], g l^{-1}	0.1	0.25	0.5	0.74	1.0
λ_{max}, nm	418	420	429	440	453

These data suggest that, with increasing fulvic acids concentration in solution, the resulting metal nanoparticles tend to grow in size, as evidenced by a bathochromic shift of λ_{max}. The reason is that, at higher concentrations of fulvic acids, silver nanoparticles are formed in a larger amount and rapidly aggregate. Hence, at high concentrations of silver nanoparticles, there is a need in additional introduction into solution of a stabilizing agent. Despite formation of small silver nanoparticles at fulvic acids concentration of 0.1 g l^{-1}, the reduction reaction did not receive extensive development in this case, and the metal nanoparticles are formed in a not very large number. With 0.25 g l^{-1} fulvic acids in solution, the smallest, 7–16-nm, silver nanoparticles are formed.

Figure 3 characterizes the reduction of silver nitrate with fulvic acids in relation to the initial concentration of silver nitrate $[Ag^+]_0$ in solution. With increasing $[Ag^+]_0$ not only absorption is enhanced, which suggests an increase in the number of the metal particles, but also the latter vary in size, as manifested in the bathochromic shift of the plasmon peak (from 415 to 440 nm). Interestingly, with the silver nitrate concentration increasing within $(0.5–2)\times10^{-3}$ M the bathochromic shift and the optical density at 400–450 and 600–700 nm tend to increase. However, further increase in $[Ag^+]_0$ causes the optical density at 400–450 nm to decline, in parallel with enhancement of absorption at 600–700 nm (Fig. 3, the crossing point of curves *6* and *4*). Evidently, this suggests destabilization of the colloid solution of silver and an increase in the contribution from the fractal structures. Indeed, further increase in $[Ag^+]_0$ is accompanied by rapid formation of a silver precipitate. Our experiments revealed the best conditions of the reaction, at which the maximal number of the smallest silver particles (7–20 nm) is formed: temperature 90°C; time 300 min; fulvic acids concentration 0.25 g l^{-1}; and silver nitrate concentration $(1.0–1.5)\times10^{-3}$ M.

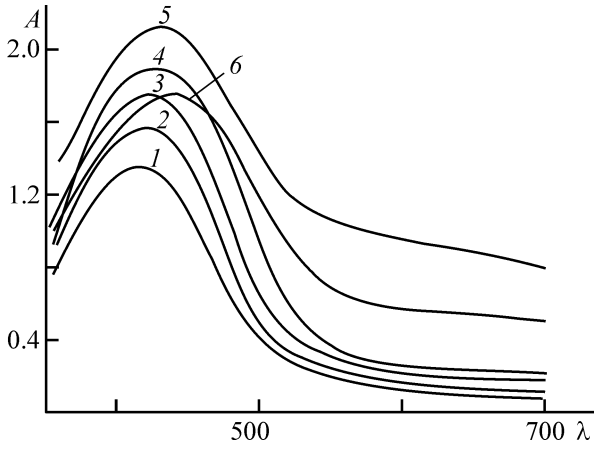

Fig. 3. Absorption spectra of the silver sols at different initial concentrations of silver nitrate in solution in reduction with peat fulvic acids. Reaction temperature 90°C; reaction time 300 min; [fulvic acids] = 0.25 g l^{-1}. $[AgNO_3]\times10^3$, M: (*1*) 0.5, (*2*) 0.75, (*3*) 1.0, (*4*) 1.5, (*5*) 2.0, and (*6*) 3.0.

We examined the stability of the silver sol prepared under the above-described conditions and found the following. In the first 7 days reduction proceeded, but the optical density at the absorption maximum changed by no greater than 5% of the value recorded 300 min since the synthesis was begun. The final absorption spectrum of the silver sol remained unchanged for 30 days, which was followed by gradual aggregation of the metal nanoparticles, accompanied by decline of the optical density at the absorption maximum. Within 40 and 50 days, the absorption intensity decreased by ca. 25 and 45%, respectively, and after 70 days the sol was completely degraded.

In this context, of key importance is preparation of fulvic acids having reproducible properties, when repeatedly isolated from a natural source. Here, we examined fulvic acids of high-type cotton grass-sphagnum peats from three deposits. As established previously [25], basic properties (elemental composition, content of functional groups, molecular weight) of the fulvic acids isolated by the standard technique from similar sources, e.g., high-level peats, vary within a very narrow range, i.e., are reproducible. This suggests that the established relationships adequately describe the interaction of silver ions with fulvic acids prepared from high-level peats.

CONCLUSION

It was demonstrated for the first time that inexpensive and environmentally safe peat fulvic acids are suitable in principle for preparation of silver nanoparticles. The optimal conditions for the corresponding reduction reaction were identified.

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