

Silver Nanoparticles Synthesised within the Silica Matrix in Hyperstoichiometrical of Mercury from Aqueous Solutions

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Abstract. Mercury adsorption of silver containing silica-based nanocomposites was evaluated. Maximum adsorption capacity of 0.4 mmol g^{-1} was achieved at silver loading of 0.5 mmol g^{-1} . Nevertheless, if to calculate in respect to silver content the mercury adsorption capacity was generally elevated along with decreasing silver nanoparticle diameter. It has been demonstrated that silver particle diameters and loading should collectively be taken into consideration in designing the optimal mercury removal process. Further recommendations have been proposed with the aim of increasing the mercury removal efficiency using silver nanoparticles deposited on the surface of silica with lower silver loading, while achieving similar or even higher efficiencies due to observed hyperstoichiometry effect.

1. Introduction

Mercury and its compounds are persistent, highly bio-accumulative in to people and the environment [1] originates from natural and anthropogenic processes into environment in elemental, organic and inorganic forms [2]. They are classified as one of 13 priority hazardous substances (PHS) in accordance with the Water Framework Directive (WFD) and its daughter directives as for example the Environmental Quality Standards Directive (EQSD) which has been adopted recently [3, 4]. The maximum permissible concentrations (MPC) for mercury is $1.0 \text{ }\mu\text{g/L}$ [5]. According to the current legislation, the EU will have had to stop using mercury in all the products and processes by 2020 [3]. Although this strategy will eventually lead to the desired result, i.e. a reduction of mercury pollution and achievement of new levels of MPC, but this unlikely occur soon. None of the existing commercially available technologies for mercury removal can reduce the level of mercury below the level of 50 ng/l [5]. Mercury exists in environment mainly in form of elemental mercury (Hg^0), inorganic (Hg^+ , Hg^{2+}) and as organic species (MeHg^+ , MeHg^{2+} , EtHg^+ and etc.) [6]. The constant redistribution of mercury species accrues in water as a function of temperature changes, evaporation and changes in the concentration of various inorganic and organic compounds, the speed and nature of water movement, the absorption of mercury by soil, plants and living organisms, etc. Water bed sediments acts as buffer media and depending on environmental conditions can accumulate or liberate mercury [7]. Due to the enormous toxicity of mercury and ability to accumulate in organisms, particularly in fish, it is a dangerous pollutant and one of the most studied. Nevertheless, there is a very incomplete understanding of the factors that control the bioconcentration and turnover of mercury in the living organisms.

Silver-mercury amalgamation is a process well known in a precious metal mining [8] and a formed amalgam alloy is the extremely inert chemically. The ability of silver nanoparticles to form such stable compound might be useful in a mercury extraction from aqueous solution. In this work, silver



nanoparticles of narrow size distribution were produced upon chemical redox transformation on a non-porous silica surface that was grafted with redox active silicon-hydride Si-H groups[9]; the only variable parameter was the metal salt concentration. The ligand free metal nanoparticles are converted to metallic nanoparticles and bound to silica surface via strong bonding interaction between the surface atoms of the nanoparticle and the Si-H groups of the SiO₂ matrix. Owing to its large specific surface area of 300–350 m²/g and thermal stability, the fumed silica is an attractive material for utilization as a noble metal NP support [10]. Obtained silver NPs/SiO₂ composites were used in extraction of mercury from aqueous solutions.

2. Materials and Methods

2.1. Chemicals

AgNO₃ (>99.9%), SiO₂ (395 m²/g), Triethoxysilane (TEOS, 95%), HgCl₂ (≥99.5%), acetic (glacial) and nitric (70.0%) acids, acetone and ethanol (all from Sigma-Aldrich) were used as received. Ultrapure water with resistivity of 18.3 MΩ·cm was obtained by reversed osmosis followed by ion-exchange and filtration (Millipore).

2.2. Silver metal nanoparticle synthesis

The silver NP/SiO₂ composites were prepared by *in-situ* redox reaction method. Silica surface was modified with TEOS in glacial acetic acid as described elsewhere[9] in order to create redox-active silicon-hydride functional groups. The common procedure for silver NPs/SiO₂ preparation was as follows: 1.0 g of TEOS-modified SiO₂ sample was immersed in 0.1 M aqueous solution of AgNO₃ with an appropriate volume to create metal NPs loading of 0.05, 0.2, 0.3, 0.4 and 0.5 mmol per gram of silica. The mixture was stirred in the dark for 1 h to the reaction completion. The mixture was then rinsed to remove unreacted salt, filtered and dried in a bench oven at 105 °C for 8 h.

2.3. Mercury adsorption

All solutions were prepared using ultra-pure water. Briefly, mercury solution was prepared by dilution of 1000 mg L⁻¹ Hg stock solution (HgCl₂). The adsorption of Hg²⁺ on AgNP/SiO₂ nanocomposite was studied by batch technique. All batch adsorption experiments were performed by mixing a 1.0 g of nanocomposite sorbent into a HgCl₂ solution (8.5 mg/L, 100 mL) with stirring (120 r/min) at room temperature for 120 min. Hg solutions were adjusted to pH 6 by adding 0.1 M HNO₃. Then, the supernatant was separated from the mixture solution by filtration with 0.22 μm MF membrane. The concentration of Hg²⁺ ions remaining in solution was measured by mercury analyzer (RA-915+, Lumex). The amount of Hg²⁺ ions adsorbed by nanocomposite q_t (mg/g) is calculated using the following Eq. (1):

$$q_t = \frac{(C_0 - C_t) \cdot V}{m} \quad (1)$$

where C_0 and C_t are the initial and a time t liquid-phase Hg²⁺ concentrations (mg L⁻¹), V is the volume of the solution (mL), and m is the mass of dry adsorbent used (g).

2.4. Characterization of materials

Wide-angle X-ray diffraction (XRD) was used to characterize the noble metal NP diffraction patterns. All measurements were collected over the 2θ range from 10° to 70° on a Rigaku SmartLab diffractometer equipped with a CuK α radiation source (0.1549 nm). A Nicolet 6700 FT-IR spectrometer (Thermo Scientific) with attenuated total reflection (ATR) attachment was used to collect IR spectra from silica samples after chemical modification. Transmission electron microscopy (TEM) analysis was carried out using a JEOL-JEM2100 instrument operated at 200 keV. All samples were ultrasonically dispersed in isopropyl alcohol at room temperature, and then a portion of the solution was placed onto a Cu grid for TEM measurements. Zeeman Mercury analyser (Lumex RA-915+ atomic absorption (AA) spectrometer coupled with a PYRO-915 pyrolysis attachment, Lumex Instruments) was used to analyse total mercury (THg) concentration [4].

3. Results and Discussion

Silica surface modified with TEOS contained Si-H surface groups which reduces silver ions when contacted with in aqueous solution of AgNO_3 . According to the FTIR analysis (Figure 1, a) the chemical composition of the TEOS modified silica surface contain silicone-hydride groups (absorption band at 2240 cm^{-1} [11]). Iodometric titration results (not shown here) revealed the presence and total number of silicone hydride groups (0.83 mmol/g). Disappearance of the 2240 cm^{-1} band after reaction with Ag^+ (Figure 1, b) confirms consumption of those groups in reaction of silver reduction.

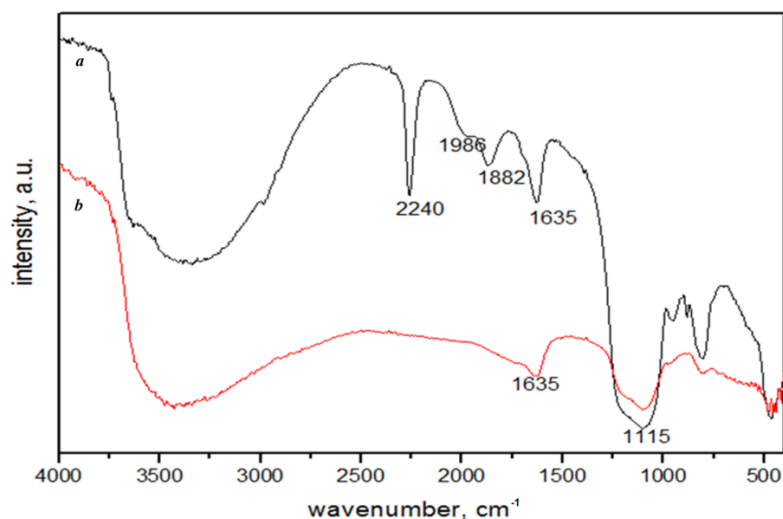


Figure 1. FTIR spectra of silica modified with triethoxysilane (a) and sample after interaction with silver ions (b).

After reduction of silver ions the original white silica sample gain a colour ranging from light yellow to dark ochre with increasing NP size and loading of samples from 0.05 mmol/g to 0.5 mmol/g . As shown in Figure 2b, virtually monodisperse nanoparticles were obtained at 0.05 mmol/g of Ag NPs loading. Their mean diameter was estimated by using the XRD spectra and the Debye–Scherrer formula to be 11 nm .

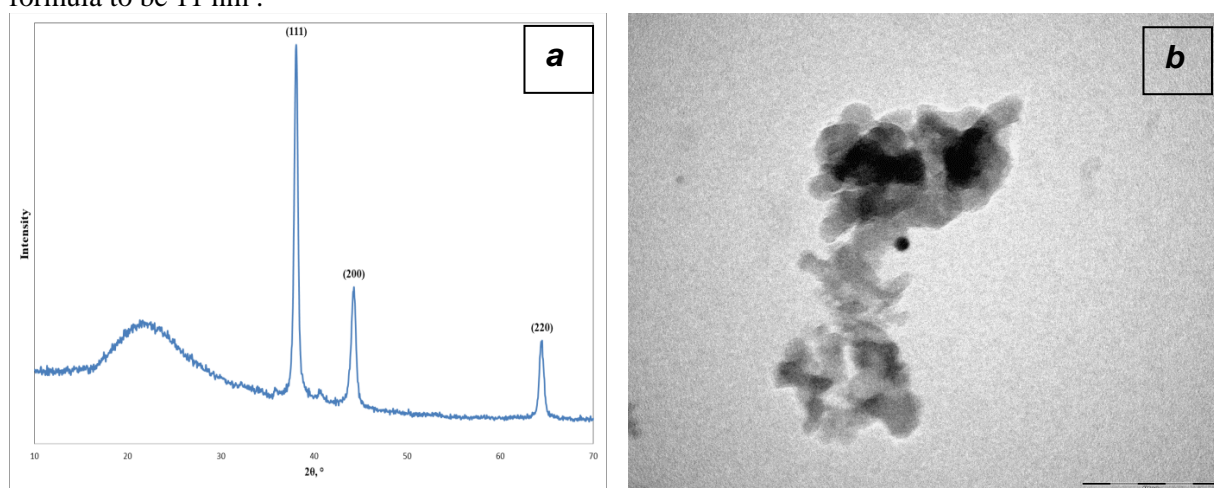


Figure 2. XRD spectra (a) and TEM image (b) of silver nanoparticles in silica matrix prepared with Ag NPs loading of 0.05 mmol/g .

XRD analysis of non-porous silica decorated with silver nanoparticles (Figure 1a) revealed a clear pattern of bands at 2θ values of 38.05° , 44.3° and 64.5° that correspond to (111), (200) and (220) planes of cubic Ag crystals, respectively. All the peaks in XRD pattern can be readily indexed to a structure of nanocrystalline silver (JCPDS, File No. 4-0783) [12]. The crystal structure of Ag NPs is well defined. A large halo at $22.5^\circ 2\theta$ originates from the amorphous structure of silica. No peaks of

other crystalline phases have been detected. All XRD spectra are similar to one presented in Figure 1, a.

According to the mercury adsorption experiments, nanocomposite samples reach equilibrium in 120 min (in whole range of silver loading). Therefore the time allowed for establishing equilibrium was 120 min with constant agitation. The values of Hg^{2+} adsorption uptake (Table 1) increased with the increase in silver content in composite, however if calculate mercury/silver ratio the composites with smallest AgNPs diameters – sample **1** (AgNPs/SiO₂_0.05) were found to have greater adsorption capacities than silica's with higher silver content under the experimental condition used. Samples of silica modified with TEOS and unmodified pristine silica showed no affinity for mercury in tested conditions.

In order to prove applicability of silver containing silica in adsorption of mercury from “real” samples of water collected from heavily contaminated site – Lake-Reservoir Bulkyldak (Pavlodar city) the following experiment was designed: 1.0 g of AgNP/SiO₂_0.05 sample was introduced to the 100 mL of “real” mercury containing sample (14.84 ppb of total mercury analysed by RA-915+; pH adjusted to 6, by 0.1 M HNO₃) with stirring (120 r/min) at room temperature for 120 min. After 120 min of extraction the mercury concentration in supernatant was – 0.77 ppb (which is below of the MPC for mercury [5]), and extraction rate is 94.81%.

Table 1. Mercury adsorption results.

Sample	Ag content (mmol of Ag/g SiO ₂)	Average AgNPs diameter (nm)	Hg uptake (mmol of Hg/ g of composite)	Hg/Ag ratio
1	0.05	11	0.1	2.0
2	0.2	24	0.2	1.0
3	0.3	37	0.25	0.83
4	0.4	63	0.3	0.75
5	0.5	90	0.4	0.8

4. Conclusions

This work demonstrated that the mercury adsorption characteristics of the silver decorated silica sample were influenced significantly by the size of silver nanoparticles. Amount of mercury adsorbed (mmol g⁻¹) in samples was deviated from stoichiometry, i.e. hyperstoichiometry was observed. The sample of silver containing composite demonstrated hyperstoichiometry effect was used in mercury extraction from “real” aqueous sample; reduction of mercury concentration below the MPC level was achieved. These findings demonstrate the need for further investigation on mercury adsorption mechanism in order to assess potential application in mercury removal from the aqueous solution.

5. References

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