Adsorption of silver nanoparticles from aqueous solution on copper-based metal organic frameworks (HKUST-1)

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HIGHLIGHTS

- This study investigates the removal of AgNP colloids by Cu-(BTC) MOFs.
- Adsorption of AgNP on HKUST-1 was very fast and followed Freundlich isotherm.
- The efficient and complete removal of AgNP was affected by the type of water.
- SEM and EDX analysis showed that AgNP were adsorbed onto the MOFs.
- Very low amount of HKUST-1 (10 mg) are necessary to perform adequate adsorption of AgNP the range of environmental levels.

ARTICLE INFO

ABSTRACT

Silver nanoparticles (AgNP) are emerging pollutants. The use of novel materials such as Cu-(benzene 1,3,5-tricarboxylate, BTC) Metal-Organic Framework (MOFs), for AgNP adsorption and their removal from aqueous solutions has been studied. The effect of different parameters was followed and isotherm model was suggested. MOFs adsorbed fast and efficiently AgNP in the range $C_0 < 10$ mg L^{-1}, being Freundlich isotherm (R = 0.993) these data fitted to. Among studied parameters a remarkable effect of chloride on sorption was found, thus their possible interactions were considered. The high adsorption efficiency of AgNP was achieved and it was found to be very fast. The feasibility of adsorption on Cu-(BTC) was proved in spiked waters. The results showed the potential interest of new material as adsorbent for removing AgNP from environment.

1. Introduction

Sufficient, clean and safe drinking water is increasingly scarce in many parts of the world (Farahi et al., 2012; Batley et al., 2013; Bhatt and Bhumi, 2011). Emerging contaminants such as, for example hormones, anti-depressants and nanomaterials (materials less than 100 nm in at least one dimension) are becoming more common in wastewaters (Boxall et al., 2012; Rodrigues-Mozaz and Weinberg, 2010), and the production and application of engineered nano-materials (e.g., detergent disinfectants, wood preservatives, pesticides, cosmetics, sunscreen, textiles, medical delivery devices, sensors, solar cells and construction materials) continue to increase (Daughton and Ternes, 1999a; Panyala et al., 2008; Rocío-Bautista et al., 2015). The rapid growth in the commercial use of silver nanoparticles (AgNP) is inevitably increasing exposure to silver in the environment and among the general population. AgNP have numerous uses because of their desirable antimicrobial properties; however, the literature reports insufficient information about the effects of nanomaterials on ecosystems.

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Nanoparticles can enter the environment via wastewater, plant effluents, agricultural uses (e.g., in biosolids) or improper disposal (Li et al., 2012; Kulthong et al., 2010; Flores et al., 2010; Ecological Health and Hum, 2015; Fabrega et al., 2011a). AgNP entering surface waters are mostly associated with other natural colloids (e.g., fulvic and humic acids) and settle to become sequestered in the subaquatic sediments (Lowry et al., 2012). Unfortunately, little is known about the removal of these new types of pollutants using conventional or natural wastewater treatment methods; thus, nanoparticles (NPs) are present in drinking water sources (Abbott Chalew et al., 2013; Chaloupka et al., 2010; Reinfelder and Chang, 1999). Blaser et al. (Blaser et al., 2008) estimated that, in the worst-case scenarios, the predicted environmental concentrations of AgNP in rivers would be approximately 3 nM. Additionally, the estimated concentrations of AgNP in U.S. surface waters range to 10 μg/L. Chalew et al. (Abbott Chalew et al., 2013) evaluated the removal of different nanoparticles during drinking water treatment and emphasized the importance of applying the precautionary principle in considering AgNP as emerging drinking water contaminants. Silver is one of the most toxic metals, surpassed only by mercury and it is universally unstable (Reinfelder and Chang, 1999; Blaser et al., 2008; Benlanger et al., 2012).

Metal−organic frameworks (MOFs), essentially coordination polymers, are built up from clusters or chains of metal ions and organic linkers bearing multiple complexation functions (Hawes et al., 2014; Zhang et al., 2014). MOFs exhibit extra-high specific surface areas, highly ordered pore structures, and tunable pore sizes and shapes; they have been applied in fields related to gas storage and catalysis (Li et al., 2012). Their uniform molecular-scale pores have high surface areas and are insoluble and highly stable in common solvents, making them desirable for separations (Hawes et al., 2014). Adsorption is preferred over other techniques for the removal of emerging contaminants (e.g., membranes) (Lowry et al., 2012). To date, studies on the adsorption of inorganic contaminants from aqueous-phase using MOFs are limited to a few compounds, e.g. mercury(II), arsenic and fluoride. Effective sorption of either organic or inorganic pollutants from water relies on the specific interactions between the analytes and MOFs (Sohrabi, 2014; Meipeng et al., 2015; Baojian et al., 2014; Nobuko et al., 2011; Grunwaldt et al., 1999; Prestipino et al., 2006). Even if the use of MOFs as a sorbent in the gas phase is well known, their applicability in the liquid phase is much more complex and requires further exploration (Baojian et al., 2014; Nobuko et al., 2011). The pore structure, unsaturated coordinate sites, together with metal ions involved in MOFs, all play dominant roles in adsorption. Charge interactions with guest molecules improve the adsorption affinity of MOFs in the aqueous phase, and introducing functional groups into MOFs through post-synthetic modification enhances the adsorption affinity of MOFs toward solutes in the aqueous phase through electrostatic interactions.

The adsorption of NPs to substrates is sensitive to the physicochemical properties of the underlying substrate and to the external environment (Lowry et al., 2012; Fabrega et al., 2011b; Khan and Jhung, 2013; Daughton and Ternes, 1999b; Golovina and Kustov, 2013; Nowack and Bucheli, 2007). Some of the AgNP used in commercial products are likely to be coated with organic compounds to promote their dispersion, including citrate, cysteine, polyethylene glycol and starch. Capping materials surrounding the metal cores determine the manner in which the metal nanoparticles assemble and the properties of the resulting structures (Wagener et al., 2012; Song et al., 2015). The composition, structure, and surface properties of AgNP are altered after entering the environment as a result of changes in their physicochemical properties (Chaloupka et al., 2010; Chandra et al., 2012). Herein, we report the application of HKUST-1, Cu₃(BTC)₂ (H₂O)₃, as a possible novel adsorbent for the rapid adsorption and removal of AgNP from aqueous solution (tap and mineral waters).

2. Experimental

2.1. Reagents

All chemicals were of analytical grade. Silver nitrate ($AgNO_3$), trisodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), sodium nitrate, sodium hydroxide, magnesium chloride, calcium chloride, hydrochloric acid and Basolite C300® ($\approx$ HKUST-1) were purchased from Sigma−Aldrich. Nitric acid 65% (Suprapur® grade) was acquired from Merck (Darmstadt, Germany). Ultrapure water was prepared using a Milli-Q system (Millipore, Bedford, TX) and was used throughout the experiments. All glassware was first rinsed with nitric acid and then with Millipore water before use.

2.2. Synthesis of silver nanoparticles

Silver colloids were prepared by adding $AgNO_3$ (1.0×10^{-3} M) to a sodium citrate (2.0×10^{-3} M) solution in double-deionized water that had been heated until it began to boil. Silver nitrate was added dropwise to the sodium citrate solution at a ratio of 1:2 with stirring, for approximately 10 min at 100 °C until a pale yellow color occurred, indicating reduction of the Ag^+ ions to Ag^0 (AgNP). The color of the colloidal solution slowly turned greyish yellow Heating was continued for an additional 10 min, after the solution was allowed to cool to room temperature in dark. AgNP colloidal working solutions were prepared by pipetting a corresponding volume of stock suspension. Primary sizes of AgNP were estimated by scanning electron microscopy (SEM) and from the results of hydrodynamic diameter and zeta-potential measurements, which were performed via dynamic light scattering (DLS).

2.3. Adsorption experiments

The batch adsorption experiments were conducted at 298−313 K using a temperature-controlled shaker. Initially, the AgNP colloidal solutions (10 mL) at different concentrations (50−40 mM) and an appropriate amount of adsorbent (~10.0 mg, HKUST-1) were mixed with 10 mL solutions in a set of beakers. To ensure sufficient mixing, the beakers were stirred at ~500 rpm for 10 min to reach adsorption equilibrium. After adsorption, sediment containing the {AgNP, MOF} was separated by centrifugation. The supernatant was used to determine the residual non-adsorbed AgNP concentration by UV−Vis spectroscopy and/or *graphite-furnace atomic absorption* spectrometry (GF-AAS). The precipitate, {AgNP, MOF}, was dried and further analyzed by electron microscopy.

The amount of AgNP adsorbed was calculated using the Eq. (1):

$$q_t = \frac{\rho \, V(C_0 - C_t)}{m} \tag{1}$$

where q_t is the amount of AgNP adsorbed at time t (mg·g^{-1}), V is the volume of the solution (mL), C_0 and C_t are the initial and residue solute concentrations at time t or at equilibrium (mg·L^{-1}), m is the mass of adsorbent (g), and ρ is the density of water. To determine the effect of pH on the adsorption capacity of AgNP on HKUST-1, the pH of the AgNP solution was adjusted with 0.1 M HNO_3 and 0.1 M NaOH.

Data from experiments were used to study adsorption isotherms, either Langmuir or Freundlich fits by using Eqs. (2) and (3), respectively: