Highly Efficient Removal of Silver-Containing Nanoparticles in Waters by Aged Iron Oxide Magnetic Particles

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Supporting Information

ABSTRACT: Methods for the removal of silver nanoparticles (AgNPs) and their transformation products, silver-containing nanoparticles (AgCNPs), are important, because of their potential risks to the general population and the environment. In this study, aged iron oxide magnetic particles (IOMPs) were synthesized by a simple solvothermal reaction and used for the removal of AgCNPs. The prepared IOMPs exhibit a high adsorption capacity toward AgCNPs in aqueous medium. Kinetic studies indicated that the adsorption of AgCNPs is a pseudo-second-order process. The experimental data for the adsorption of AgCNPs follow the Langmuir isotherm model, and their maximum adsorption capacities were 19.9–62.8 mg/g at pH 6.2 and 298 K. The sorption mean free energy calculated by the Dubinin–Radushkevich isotherm was 4.09–5.17 kJ/mol, indicating the occurrence of physisorption, which was mainly due to the electrostatic interactions. The IOMP adsorbents maintained high removal efficiencies after four cycles of adsorption–desorption, suggesting good reusability of the developed IOMPs. Moreover, good removal efficiencies (63.3%–99.9%) and recoveries (67.1%–99.9%) were obtained from the real samples spiked with AgCNPs at levels of 10 µg/L, showing that the aged IOMPs could be used as efficient and low-cost adsorbents for the removal and recovery of AgCNPs from real waters.

KEYWORDS: Aged iron oxide magnetic particles, Adsorption, Silver-containing nanoparticles, Removal, Waters

INTRODUCTION

Because of the excellent electro-optical, antimicrobial, and catalytic properties, silver nanoparticles (AgNPs) have many applications in sensing,¹ catalysis,² antimicrobial products,³ and water treatment.⁴ However, the growing use of consumer products incorporated with AgNPs leads to their increasing release into the environment.^{5–7} Since AgNPs are far from being chemically inert, once they entered the environment, they have been shown to react with Ag-complexing ligands (i.e., organic matter, sulfur, chlorine) to form various Ag-containing NPs (AgCNPs), such as AgCl NPs and Ag₂S NPs.^{8–10} There are many studies on toxicity and environmental safety of AgCNPs to various aquatic organisms in different trophic levels, such as microorganisms,^{11–13} algae,¹⁴ macrophytes,^{15,16} and fishes.¹⁷ *In vitro* studies demonstrated that AgCNPs can damage mammalian cells and their DNA.¹⁸ Also, *in vivo* studies with AgCNPs showed their bioaccumulation in important body organs, including the lungs, liver, kidneys, and brain, which has adverse impacts and hazards on mammals.¹⁹ Moreover, several studies have demonstrated the transfer and biomagnification of AgCNPs in a food chain.^{20–22} At present, AgCNPs have been considered as one of the most important pollutants, and the related researches are becoming hotspots in the field of

environmental science.^{23,24} Thus, the issue of environmental remediation of AgCNPs must be urgently addressed.

A variety of approaches have been available for the removal of NPs, including chemical coagulation,²⁵ membrane filtration,^{26,27} biological processes,²⁸ and cloud point extraction.²⁹ Adsorption is a very promising method for the removal of NPs from environmental waters, because of its simplicity and cost-effective nature. However, limited adsorbents including polymers,^{30,31} carbon spheres,³² hybrid material,³³ and metal oxides³⁴ have been proposed for the removal of AgNPs from various water samples. Magnetic particles are excellent adsorbents for the removal of pollutants from waters, because they can be easily separated after binding and require little energy.³⁵ Iron oxide magnetic particles (IOMPs) have been widely used in the purification, because of their cost-effective preparation, large surface area, good biocompatibility, and low toxicity.^{36,37} However, the use of IOMPs for the removal of AgNPs has not been reported.

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In our previous work, aged IOMPs (Fe_3O_4 magnetic particles) were used for speciation analysis of Ag_2S NPs in environmental waters.³⁸ The optimum conditions for AgCNP extraction were obtained by investigating the factors, including pH, extraction time, amount of humic acid, the coatings, and sizes of the AgCNPs. While pristine IOMPs can also effectively extract AgCNPs from water, the stability and oxidation capability of the adsorbents was significantly increased after aging. Meanwhile, the high saturation magnetization ensured their separation within ~ 1 min after extraction. Therefore, the aged IOMPs show promise as a potential new adsorbent for the removal of AgCNPs. However, whether the aged IOMPs can serve as an adsorbent for the removal of AgCNPs in practical applications is still determined by the adsorption performance in engineering point of view, including the adsorption capacity and adsorption rate, which are crucial factors for designing adsorption reactors, and controlling the cycle period of a fixed bed adsorption process, as well as optimizing working conditions. In addition, to cut the costs during practical wastewater treatment, high desorption ability after adsorption and good reuse performance are required for an excellent adsorbent. In our previous work, the key issues of the adsorption kinetics, adsorption isotherm, and regeneration of the adsorbents have not been studied yet. Moreover, the applicability in removal of AgCNPs from real waters with complex matrices remains to be verified.

The objective of this work is to study the use of aged IOMPs for the removal of AgCNPs from waters. Using the four most predominant AgCNPs in the environment (AgNPs , $\text{Ag}\&\text{Ag}_2\text{S}$ NPs, Ag_2S NPs, and AgCl NPs) as models, the sorption kinetics were analyzed using pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Elovich models, while the adsorption isotherm was identified using Langmuir, Freundlich, and Dubinin–Radushkevich isotherms. The reusability and applicability of the aged IOMPs in real waters were also investigated.

■ EXPERIMENTAL SECTION

Chemicals and Materials. Aqueous dispersions of AgNPs with unknown coating were obtained from Shanghai Huzheng Nanotechnology Co. Ltd. (Shanghai, China). A series of citrate-coated and poly(vinylpyrrolidone) (PVP)-coated AgNPs with nominal sizes of 10 (± 2), 30 (± 3), 40 (± 4), 60 (± 4) nm, respectively, were obtained from nanoComposix (San Diego, CA). NiO (< 30 nm) and ZnO NPs (30 nm) with unknown coatings were purchased from Sigma–Aldrich (St. Louis, MO) and Aladdin Chemistry Co., Ltd. (Shanghai, China), respectively. Their zeta potentials measured by dynamic light scattering (DLS) were 34.3 mV (ZnO NPs) and 32.6 mV (NiO NPs), respectively (Table S1 in the Supporting Information). Silver nitrate and bis(*p*-sulfonatophenyl)phenylphosphane dehydrate dipotassium salt (BSPP) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Thiourea was obtained from Sigma–Aldrich (St. Louis, MO). All other chemicals were obtained from Beijing Chemicals (Beijing, China). All chemicals were used as received without additional purification. Ultrapure water (18.2 M Ω) from a Milli-Q Gradient System (Millipore, Bedford) was used in the entire experimental process.

$\text{Ag}\&\text{Ag}_2\text{S}$ NPs (transformed from AgNPs with S^{2-} , containing mostly Ag_2S NPs and some $\text{Ag}\&\text{Ag}_2\text{S}$ NPs with a Ag core and Ag_2S shell), Ag_2S NPs, and AgCl NPs, were prepared according to the details described in the Supporting Information.

Synthesis of IOMPs. The IOMPs were prepared through a solvothermal reaction with minor modification.^{39,40} Briefly, 2.7 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was vigorously stirred in 100 mL of ethylene glycol to form a clear solution. Then, 7.2 g of sodium acetate was all added at once and stirred at 1500 rpm for 20 min. The obtained solution was transferred into a Teflon-lined stainless-steel autoclave, sealed, and

heated at 200 °C for 10 h. The products were collected using a permanent magnet and washed sequentially with ethanol and ultrapure water several times to remove nonmagnetic byproducts, and the clean products were dried under vacuum at 60 °C for 6 h. Finally, the dried microspheres were aged at 90 °C overnight. Note that, although the solvothermal reaction must be carried out under high temperature and high pressure, it has been widely applied in the large-scale industrial production of various functional nanoparticles, such as TiO_2 NPs and graphene.^{41,42}

TEM Characterization. Transmission electron microscopy (TEM) was conducted with a TEM system (Model H-7500, Hitachi, Japan) operated at 80 kV. TEM samples were prepared by dripping 5 μL of the NP sample solution onto a carbon-coated TEM grid (Cu, 200 mesh, Zhongxingbairui Technology Co. Ltd., Beijing, China) and drying at room temperature under vacuum. The particle number size distribution was calculated by counting at least 160 particles with Nano Measurer 1.2 software.

SEM Characterization. Field-emission scanning electron microscopy (FE-SEM) (Model SU8010, Hitachi) was conducted for surface morphology and size investigations. Powders were loaded on silicon slices, and SEM images were recorded at an operation voltage of 3.0 kV.

DLS Characterization. The hydrodynamic diameters and polydispersity index of each NP sample were measured by dynamic light scattering (DLS) with a Malvern Nano ZS instrument (Malvern Instruments, Ltd., U.K.) using 2 mL of 1 mg/L NP suspension in a macrocuvette (pass length = 1 cm). The scattering angle was 173°, and the temperature was maintained at 25 °C. The refractive index (RI) for the NPs was 1.07 and the adsorption value was 0.01. Each DLS measurement was performed for 30 acquisitions and the DLS characterization of each sample was repeated three times. The same instrument was used to determine the zeta potential of each sample.

XRD Characterization. The crystal structure of pristine and aged IOMPs was examined with a MSAL-XD2 X-ray diffractometer (X'Pert Pro instrument, Panalytical) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.1541$ nm) ranging from 10° to 90° (2θ) at 30 kV and 30 mA.

Adsorption Kinetic Study. Kinetic studies were conducted by adding 20 mg of the as-prepared aged IOMPs (0.2 mL of 100 mg/mL aqueous dispersions) into 100 mL of 20 mg/L AgCNP solution. At scheduled time (5–90 min), 0.2 mL of water sample was collected for the determination of the residual AgCNP concentration. The adsorption capacity at time t , Q_t (mg/g), was calculated by⁴³

$$Q_t = \frac{(C_0 - C_t)V_0 - \sum_{i=1}^{t-1} C_i V_s}{m} \quad (1)$$

where C_0 (mg/L) is the initial AgCNP concentration, C_t (mg/L) is the AgCNP concentration at time t , V_0 (L), and V_s (L) are the respective volume of the AgCNP solution and the AgCNP solution collected for analysis, and m (g) is the mass of the aged IOMPs.

Adsorption Isotherm Study. AgCNP working solutions (100 mL) with initial concentrations in the range of 0.01–15 mg/L were prepared by serial dilution of a stock solution. The pH then was adjusted to 6.2 with HAc/NaAc buffer solution (1M) and the Ca^{2+} concentration was adjusted to 10 mM with 1 M $\text{Ca}(\text{NO}_3)_2$. Finally, 20 mg of the as-prepared aged IOMPs (0.2 mL of 100 mg/mL aqueous dispersions) was added. Experiments were carried out at room temperature in covered polyethylene terephthalate (PET) bottles and shaken using a platform shaker (IKA KS501) at 300 rpm for 20 min. The aged IOMPs were then separated from the AgCNP solution using a permanent magnetic. The concentration of silver in supernatant was determined by inductively coupled plasma–mass spectrometry (ICP-MS) (Model 7700cs, Agilent). The adsorption capacity (Q_e , mg/g) can be expressed as eq 2:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

Figure 1. Characterization of IOMPs: (A) SEM image of aged IOMPs, (B) TEM image of aged IOMPs, and (C) XRD patterns of pristine and aged IOMPs.

Figure 2. Fitting of different kinetic models to AgCNP adsorption by aged IOMPs: (A) pseudo-first-order, (B) pseudo-second-order, (C) intraparticle diffusion, and (D) Elovich.

where C_0 is the initial Ag concentration (mg/L), and C_e is the equilibrium Ag concentration (mg/L), V is the volume of the AgCNP solution (L), and m is the mass of the aged IOMPs (g).

Desorption and Reuse of Aged IOMPs. The reuse of IOMPs as adsorbents was evaluated by testing the adsorbents over four adsorption–desorption cycles. For each adsorption cycle, 20 mg of aged IOMPs was used per 100 mL of 1 mg/L AgCNP solution and the mixture were shaken at 300 rpm for 20 min. For desorption, the IOMPs were then shaken in 1 mL of an aqueous solution containing 10 mM thiourea and 2% HAc at 300 rpm for 30 min. The removal efficiency (Removal, %) and recovery (Recovery, %) were calculated by

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (3)$$

and

$$\text{Recovery (\%)} = \frac{C_d V_d}{C_0 V_0} \times 100 \quad (4)$$

where C_0 is the initial Ag concentration (mg/L), C_e is the equilibrium Ag concentration (mg/L), C_d is the equilibrium Ag concentration of the desorption solution (mg/L), V_d is the volume of the desorption solution (L), and V_0 is the volume of the AgCNP solution (L).

Effect of Metal Oxide NPs on Removal of AgCNPs. Model dispersions of AgNPs, ZnO NPs, and NiO NPs in real waters were prepared as follows: 0.5 mL of AgNPs (20 mg/L), ZnO NPs (100 mg/L) and NiO NPs (100 mg/L) were spiked into 98.5 mL of lake water and wastewater treatment plant (WWTP) influent, and then shaken at 300 rpm for 1 h. The removal and desorption process then were performed following the above-mentioned procedures.

RESULTS AND DISCUSSION

Characterization of AgCNPs. As observed under TEM, the size distribution of all the studied AgCNPs were in the range of 2–48 nm in diameter (Figure S1 in the Supporting Information). The hydrodynamic size, polydispersity index (PDI), and the zeta potential values of the AgCNPs were determined by DLS (Table S2 in the Supporting Information). All NP samples had a polydispersity index (PDI) range of 0.167–0.387, indicating that the AgCNPs were well-dispersed. The zeta potentials of the AgCNPs indicated that all samples were negatively charged.

Characterization of IOMPs. According to our previous study, aging has little impact on the size and morphology.³⁸ Here, the size and morphology of the aged IOMPs were investigated with TEM and SEM. Results showed that size

Table 1. Adsorption Kinetic Parameters of Various Models for the Adsorption of AgCNPs by aged IOMPs

Pseudo-First-Order					
AgCNPs	$Q_{e,exp}^a$ (mg/g)	$k_1 (\times 10^{-3} \text{ min}^{-1})$	$Q_{e,cal}^b$ (mg/g)	R^2	
AgNPs	47.4	86.7	43.3	0.9856	
Ag&Ag ₂ S NPs	67.9	80.3	13.3	0.5472	
Ag ₂ S NPs	21.5	90.7	6.25	0.8473	
AgCl NPs	42.2	65.5	6.73	0.6924	
Pseudo-Second-Order					
AgCNPs	$Q_{e,exp}^a$ (mg/g)	$k_2 (\times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1})$	$Q_{e,cal}^b$ (mg/g)	R^2	
AgNPs	47.4	3.15	51.5	0.9987	
Ag&Ag ₂ S NPs	67.9	12.0	68.5	0.9996	
Ag ₂ S NPs	21.5	71.5	21.3	0.9997	
AgCl NPs	42.2	21.4	44.6	0.9999	
Intraparticle Diffusion					
AgCNPs	k_{p1} (mg g ⁻¹ min ^{-0.5})	R^2	k_{p2}	R^2	k_{p3} (mg g ⁻¹ min ^{-0.5})
AgNPs	8.42	0.9852	1.88	0.9932	0.20
Ag&Ag ₂ S	9.70	0.9925	0.95		
Ag ₂ S NPs	2.80	0.9411	0.85		
AgCl NPs	4.77	0.9936	0.89		
Elovich Equation					
AgCNPs	α (mg g ⁻¹ min ⁻¹)		β (mg g ⁻¹ min ⁻¹)		R^2
AgNPs	22.87		0.105		0.9396
Ag&Ag ₂ S	2289		0.144		0.8008
Ag ₂ S NPs	109199		0.719		0.8043
AgCl NPs	33113		0.313		0.7883

^aExperimental Q_e ; ^bCalculated Q_e .

ranges from 150 nm to 330 nm in diameter, and that the aged IOMPs were well dispersed and had a rough surface (Figure 1). Furthermore, the structure of as-synthesized pristine and aged IOMPs was characterized by XRD (Figure 1C). Six characteristic peaks at 30.1°, 35.4°, 43.1°, 53.4°, 56.9°, and 62.5°, corresponding to planes (220), (311), (400), (422), (511), and (440) of magnetite (JCPDS File No. 19-0629), respectively, were observed for both pristine and aged IOMPs. This result revealed that the IOMPs are polycrystalline with a short-range mesoscopic ordering structure, and no phase change of Fe₃O₄ was observed, even though the IOMPs are aged.

Adsorption Kinetics. The solute uptake rate governs the equilibrium of the sorption reaction at the solid/solution interface. The AgCNP adsorption by the aged IOMPs was studied by determining the variation of the AgCNP concentration (mg/L) in aqueous phase at pH 6.2 from 5 to 90 min. A significant color fading with time was observed in the optical image of AgNP dispersion (Figure S2 in the Supporting Information). The AgCNP adsorption occurs rapidly during the first 15 min (Figure S3 in the Supporting Information), which may be ascribed to the abundant amount of available active sites on the aged IOMPs. Then, the active sites in the system gradually decreased and the adsorption equilibrium was reached.

To examine the adsorption mechanisms, the pseudo-first-order model, pseudo-second-order model, and intraparticle diffusion model were used to analyze the adsorption data, respectively. The fitting precision between the experimental data and model-predicted value was evaluated with the correlation coefficient R^2 .

The pseudo-first-order and pseudo-second-order models are linearly expressed as eqs 5 and 6, respectively:^{44,45}

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (5)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} \quad (6)$$

where Q_e (mg/g) and Q_t (mg/g) are the respective amount of AgCNPs adsorbed per unit weight of aged IOMPs at equilibrium and at time t (min), and k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) are the respective rate constants for the pseudo-first-order model and pseudo-second-order model. Figures 2A and 2B showed the fitting of the experimental data to the two models, and the obtained kinetic parameters are shown in Table 1. The calculated Q_e from the pseudo-second-order model agreed with the experimental value. In addition, significantly higher correlation coefficients were observed for the pseudo-second-order model (0.9987–0.9999) than the pseudo-first-order model (0.5472–0.9856). These results indicated that the adsorption of AgCNPs onto aged IOMPs agrees well to the pseudo-second-order model and the adsorption process may be controlled by intraparticle diffusion and weak interactions.⁴⁶

Intraparticle diffusion model was used to interpret the movement of the species from the surface of the adsorbents to the inner pores. The model is linearly expressed as⁴⁶

$$Q_t = k_d t^{1/2} + C \quad (7)$$

where k_d ($\text{mg g}^{-1} \text{ min}^{-1/2}$) is the intraparticle diffusion rate constant or rate factor, and C (mg/g) is the intraparticle diffusion rate constant, which is related to the boundary layer thickness. As shown in Figure 2C, the plots of Q_t vs $t^{1/2}$ are nonlinear over the studied time range, indicating a multistage adsorption process.^{47,48} A close examination revealed the existence of three regions for the AgNPs. In stage I, the

Figure 3. Adsorption isotherm for AgCNPs at room temperature: (A) AgNPs, (B) Ag&Ag₂S NPs, (C) Ag₂S NPs, and (D) AgCl NPs. Initial concentration of AgCNPs: 0.01–15 mg/L.

external diffusion and adsorption was rapid at the surface. In stage II, a slow intraparticle diffusion occurs. Finally, in stage III, a much slower intraparticle diffusion occurs toward the final part of the adsorption process. However, only two regions were observed for the Ag&Ag₂S, Ag₂S NPs, and AgCl NPs. The first stage is defined by rapid external diffusion and adsorption at the surface, and the second stage has a slow intraparticle diffusion that occurs toward the final part of the adsorption process.

The multistage adsorption process was further verified by the presence of three respective diffusion rate constants k_{p1} , k_{p2} , k_{p3} for regions I, II, and III (Table 1). Among all of the AgCNPs, the maximum k_{p1} value indicated that the AgCNPs transferred fastest from the aqueous solution to the aged IOMP surface. Interestingly, k_{p1} for the Ag&Ag₂S NPs was higher than that for the AgNPs, suggesting the sulfidation of AgNPs increases the intraparticle diffusion rate, and then results in a positive effect on AgCNP adsorption. This can be due to the reduction of stability caused by the change in physicochemical properties, such as the zeta potential (Table S2 in the Supporting Information).

The Elovich equation is typically used to describe the kinetics of chemisorption on highly heterogeneous sorbents, which can be linearly expressed as⁴⁹

$$Q_t = \frac{\ln(\alpha\beta)}{\beta} + \frac{\ln t}{\beta} \quad (8)$$

where Q_t (mg/g) is the adsorption capacity for the AgCNPs at time t , α ($\text{mg g}^{-1} \text{min}^{-1}$) is the initial adsorption rate, and β ($\text{mg g}^{-1} \text{min}^{-1}$) is the desorption rate. A weak linear relationship between Q_t and $\ln t$ was observed for all of the AgCNPs (Figure 2D). In addition, the values for the α calculated from the slope deviate significantly with the experimental Q_e (shown in Table 1), especially for Ag₂S NPs ($1.09 \times 10^5 \text{ mg g}^{-1} \text{min}^{-1}$) and AgCl NPs ($3.13 \times 10^4 \text{ mg g}^{-1} \text{min}^{-1}$). These results suggested that the adsorption processes are not controlled by chemisorption.

Adsorption Isotherms. Adsorption isotherms and the equilibrium adsorption capacity (Q_e), as a function of equilibrium concentration (C_e) at constant temperature, were studied. The parameters obtained from the different models reflect the surface characteristics of the adsorbents. The equilibrium data were fit with the Langmuir, Freundlich, and Dubinin–Radushkevich isotherm models, respectively. Figure 3 presents the Langmuir and Freundlich plots for the removal of various AgCNPs at room temperature.

The Langmuir model assumes that the adsorption occurs at specific homogeneous sites on the adsorbents, and has been successfully applied in monolayer adsorption process. The equation can be linearly expressed as⁵⁰

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \quad (9)$$

where C_e (mg/L) is the equilibrium AgCNP concentration in the water sample, Q_e the equilibrium adsorption capacity of the AgCNPs, Q_m (mg/g) the maximum adsorption capacity for the AgCNPs, and K_L (L mg^{-1}) the Langmuir isotherm constant. The maximum adsorption capacities of the aged IOMPs for different AgCNPs are shown in Table 2.

In addition, a nondimensional constant (R_L), known as the equilibrium parameter, was used to predict the type of adsorption process, and is expressed as⁵⁰

$$R_L = \frac{1}{1 + K_L C_0} \quad (10)$$

where C_0 is the initial AgCNP concentration (mg/L). When the isotherm is linear or irreversible, R_L is 1 or 0, respectively. Furthermore, the isotherm is favorable when $0 < R_L < 1$ and unfavorable when $R_L > 1$. The parameters derived from the Langmuir isotherm are shown in Table 2.

The Freundlich isotherm assumes a heterogeneous adsorption of pollutants onto the adsorbent, and the equation is expressed as⁵¹

Table 2. Langmuir, Freundlich, and Dubinin–Radushkevich Parameters for Various AgCNP Adsorption by Aged IOMPs

AgCNPs	Langmuir			
	Q_m (mg/g)	b (L/mg)	R_L	R^2
AgNPs	39.5	11.3	0.0055–0.8831	0.9789
Ag&Ag ₂ S NPs	62.9	8.53	0.0048–0.6311	0.9650
Ag ₂ S NPs	19.9	12.0	0.0052–0.8776	0.9923
AgCl NPs	42.8	6.41	0.0079–0.0509	0.9477
AgCNPs	Freundlich Equation			R^2
	K_F (mg ^{1-(1/n)} L ^{1/n} g ⁻¹)	n		
AgNPs	3.16	29.3		0.8429
Ag&Ag ₂ S NPs	3.46	49.3		0.7876
Ag ₂ S NPs	3.68	15.0		0.9004
AgCl NPs	3.37	31.4		0.8580
AgCNPs	Dubinin–Radushkevich Equation			
	Q_m (mg/g)	β (mol ² kJ ⁻²)	R^2	E (kJ/mol)
AgNPs	47.7	23.9×10^{-3}	0.9762	4.57
Ag&Ag ₂ S NPs	59.6	18.7×10^{-3}	0.9596	5.17
Ag ₂ S NPs	43.4	22.5×10^{-3}	0.9838	4.71
AgCl NPs	43.9	29.9×10^{-3}	0.9199	4.09

$$\ln Q_e = \ln K_F + \frac{\ln C_e}{n} \quad (11)$$

where Q_e is the equilibrium adsorption capacity of the AgCNPs (mg/L), and K_F (mg^{1-(1/n)} L^{1/n} g⁻¹) is the Freundlich constant, which is related to the adsorption capacity. n is the adsorption intensity, representing the favorability of adsorption, where $n < 1$ shows that a favorable adsorption occurs in the concentration range studied, and $n > 1$ suggests the adsorption is favorable at only high concentrations. The parameters derived from the Freundlich isotherm are shown in Table 2.

According to the correlation parameters (R^2) of these two models, the Langmuir isotherm model better describes the adsorption mechanism than the Freundlich isotherm model. R_L values (Table 2) indicate that favorable adsorption occurs between the aged IOMPs and various AgCNPs. In addition, analysis of the Langmuir Q_m values of the AgNPs (39.5 mg/g) and Ag&Ag₂S NPs (62.9 mg/g) shows that the maximum adsorption capacity can be greatly improved by transforming the AgNPs into Ag₂S NPs. It is noteworthy that the physicochemical properties of NPs are dependent on the size and surface coating. Therefore, the maximum adsorption capacities are different for AgCNPs with the same chemical composition but different dimensions and coatings.^{34,52} As shown in Figure 4, a marked increase in the adsorption capacity was observed for both citrate-coated and PVP-coated AgNPs with sizes in the range of 10–60 nm. Meanwhile, it was found that the adsorption capacities for citrate-coated AgNPs were normally higher than those for PVP-coated AgNPs with similar sizes, which is mainly due to the higher negative surface charges of citrate-coated AgNPs (Table S1 in the Supporting Information).

The sorption data was further analyzed using a Dubinin–Radushkevich isotherm model to distinguish between physical and chemical adsorption of the AgCNPs. The equation can be expressed as⁵³

$$\ln Q_e = \ln Q_m - \beta \epsilon^2 \quad (12)$$

where Q_e is the equilibrium adsorption capacity (mol g⁻¹), Q_m is the maximum adsorption capacity (mol g⁻¹), β is an activity

Figure 4. Effect of NP sizes and coatings on the adsorption capacities of the aged IOMPs for AgNPs. Initial concentration of AgNPs: ~15 mg/L.

coefficient related to the mean free energy of adsorption (mol² kJ⁻²), and ϵ is the Polanyi potential, which is expressed as⁵³

$$\epsilon = RT \left(1 + \frac{1}{C_e} \right) \quad (13)$$

where R is the gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the temperature (K). C_e (mg/L) is the equilibrium AgCNP concentration in the water sample.

By plotting $\ln Q_e$ against ϵ^2 , the equilibrium data fit the Dubinin–Radushkevich isotherm model well. Q_m and β can be calculated using the intercept and slope of the fit. The mean free energy of adsorption is described as⁵³

$$E = \frac{1}{\sqrt{2\beta}} \quad (14)$$

The process is chemical adsorption when $8 \text{ kJ/mol} < E < 16 \text{ kJ/mol}$, and physical adsorption dominates when $E < 8 \text{ kJ/mol}$.⁵⁴ The parameters derived from the Dubinin–Radushkevich equation and E are shown in Table 2. The values of E (4.09–5.17 kJ/mol) indicate that the adsorption of AgCNPs by aged IOMPs is a physisorption process. This agrees well with that obtained in our previous study, where electrostatic interactions between positively charged aged IOMPs and negatively charged AgCNPs at pH 6.2 play key roles in the extraction of AgCNPs.³⁸

Desorption and Reuse of Aged IOMPs. Cost should be taken into consideration for new adsorbents used in water treatment. To this end, the reusability of the aged IOMPs was evaluated by subjecting the adsorbents to four consecutive adsorption–desorption processes. The desorption of the AgCNPs from the aged IOMPs were performed in 10 mM thiourea in 2% (v/v) HAc, followed by shaking at 300 rpm for 30 min, which is a procedure that was verified in our previous study.³⁸ Figure 5 indicates that the aged IOMPs exhibited excellent performances of adsorption and desorption throughout the cycles tested, while the recoveries of the AgCNPs decreased by <16.9%, compared to the first cycle, indicating that the aged IOMPs are stable during the desorption and the materials can be reused.

Effect of Metal Oxide NPs on Removal of AgCNPs. Considering the great diversity of particles in the industrial nanowastes and real environmental waters, potential interferences from other particles in the removal of AgNPs were studied. Metal oxide NPs (MO NPs) as another widely

Figure 5. (A) Removal and (B) recovery amounts of AgCNPs over four adsorption–desorption cycles. Initial concentration of AgCNPs: 1 mg/L.

Figure 6. Removal and recovery of AgNPs, ZnO NPs and NiO NPs in real waters spiked with a mixture of 100 $\mu\text{g/L}$ AgNPs, 500 $\mu\text{g/L}$ ZnO NPs, and 500 $\mu\text{g/L}$ NiO NPs: (A) lake water and (B) wastewater treatment plant (WWTP) influent.

produced NPs, whose isoelectric points (IEPs) were >7.1 ,⁵⁵ were exemplarily selected. Here, ZnO NPs and NiO NPs were used as models. As shown in Figure 6, the removal and recovery efficiencies in lake water and WWTP influent spiked with a 1:5:5 mixture of Ag/ZnO/NiO NPs were $>90.4\%$ and $>92.3\%$ for AgNPs, respectively, while $<15.4\%$ of ZnO NPs and NiO NPs were removed. These results indicated the promise specificity of the aged IOMPs as adsorbents for AgCNPs, even in the WWTP influent with complex matrixes, which is essential for the practical application in removal of AgCNPs from the nanowastes and real environmental waters.

Comparison with Other Adsorbents. As shown in Table 3, the maximum adsorption capacities of the aged IOMPs are comparable to that of other adsorbents for the removal of

AgNPs from environmental waters. However, the adsorption time is much less (<20 min) than those reported previously. Furthermore, the aged IOMPs are also effective for the removal of other AgCNPs, such as Ag&Ag₂S NPs, Ag₂S NPs, and AgCl NPs.

Effect of Real Water Matrix. To evaluate the practical use of aged IOMPs, five real environmental waters spiked with 10 $\mu\text{g/L}$ each of the studied AgCNPs were subjected to the typical NP removal and recovery process. The characterization information for the waters are shown in Table S3 in the Supporting Information, all the samples were weakly alkaline (pH 7.94–8.49), and contained a considerable concentration of common cations (4.6–135.1 mg/L Na⁺, Mg²⁺, K⁺, and Ca²⁺) and DOM (5.3–46.8 mg C/L). The removal efficiencies and recoveries of the water samples were in the range of 63.3%–99.9% and 67.1%–99.9% (Table S4), respectively, indicating that the matrix has limited influence on the removal of AgCNPs, and therefore the aged IOMPs could be utilized for the removal of AgCNPs from real waters. Note that, although AgCNPs could be removed in a conventional wastewater treatment process,⁵⁷ most of them entered the activated sludge, resulting in secondary environmental pollution.²³ Since the precious metal Ag is horribly difficult to recover, further processing is often needed to recycle Ag in wastewater treatment processes.

In conclusion, aged IOMPs were shown to be promising adsorbents for the removal and recovery of various AgCNPs including AgNPs, Ag&Ag₂S NPs, Ag₂S NPs, and AgCl NPs. The adsorption kinetics and adsorption isotherm of AgCNPs on aged IOMPs fit well to the pseudo-second-order kinetic model and Langmuir isotherm model, respectively. The agreement to Dubinin–Radushkevich model verified that the AgCNPs were physisorbed onto the aged IOMPs. In comparison to other adsorbents in literatures, IOMPs showed

Table 3. Comparison of the Removal of AgCNP by IOMPs with Other Absorbents

adsorbents	AgCNPs	maximum adsorption capacity (mg/g)	adsorption equilibrium time	ref
surface-modified electrospun PVA nanofibers	AgNPs	23.8–55.8	3 h	30
cellulose-based nanofibers	AgNPs	13.1	6 h	31
PVA/gluten nanofibers	AgNPs	31.84	2 h	33
biomimetic metal oxides	AgNPs	5.0–54.8	3 h	34
plasma-treated nanofiber membranes	AgNPs	38.62	3 h	56
aged IOMPs	AgNPs, Ag&Ag ₂ S NPs, Ag ₂ S NPs, and AgCl NPs	19.9–62.8	20 min	this study

much shorter adsorption equilibrium time and comparable maximum adsorption capacities. Moreover, the removal and recovery of the AgCNPs remained nearly unchanged after four adsorption–desorption cycles, and the aged IOMPs could remove 63.3%–99.9% of the AgCNPs from real water samples, demonstrating the applicability of aged IOMPs as renewable and efficient adsorbents for the removal of AgCNPs from polluted waters.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.7b00797.

Details about synthesis of NPs, water collection and additional references (Figure S1–S3 and Tables S1–S3) (PDF)

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Notes

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