Dissolved Organic Matter-Capped Silver Nanoparticles for Electrochemical Aggregation Sensing of Atrazine in Aqueous Systems

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Dissolved Organic Matter-Capped Silver Nanoparticles for Electrochemical Aggregation Sensing of Atrazine in Aqueous Systems

Moustafa Zahran,* Ziad Khalifa, Magdy A.-H. Zahran, and Magdi Abdel Azzem

ABSTRACT: An electrochemical sensor based on silver nanoparticles (AgNPs) was developed by immobilizing dissolved organic matter (DOM) to interact with AgNPs on a glassy carbon electrode (GC), forming a DOM/AgNP/GC composite. AgNPs have been fabricated and characterized using ultraviolet−visible spectroscopy, fluorescence spectroscopy, and transmission electron microscopy. The immobilization efficiency and stability of the DOM/AgNP/GC composite have been optimized through studying the effects of electrode material type, immobilization technique, sticking duration, supporting electrolyte, and pH using square wave anodic stripping voltammetry. The detection of atrazine (Atz), a common herbicide, in aqueous systems has a great significance because of its toxicity to humans and other animals. The DOM/AgNP/GC composite has been used for Atz assessment under the optimized conditions based on the aggregated and nonaggregated AgNP-based sensors. The sensor linear range is between 20 and 220 μg/L for both aggregated and nonaggregated AgNP-based sensors. Atz could also be detected on the basis of its electrochemical oxidation at DOM/AgNP/GC with a linear range of 10−140 μg/L. Both sensors have been employed for the assessment of Atz in natural water with acceptable recovery values.

KEYWORDS: dissolved organic matter, silver nanoparticles, atrazine, electrochemical sensor, aggregation

INTRODUCTION

Atrazine (Atz) is considered as one of the most common pesticides that show effective herbicidal activities against several types of grassy weeds growing among various plants such as sugar cane, maize, sorghum, pinus, and pineapple. The prolonged utilization of Atz has resulted in its effluent to water streams, which leads to human health hazards because of its high toxicity and its side degradation outputs. Many analytical techniques have been utilized for the detection of Atz such as high-performance liquid chromatography, liquid chromatography, and gas chromatography−mass spectrometry. However, these sophisticated, time-consuming, and expensive techniques have shown both optimal sensitivity and selectivity for Atz detection and assessment. Recently, colorimetric sensors including surface plasmon resonance (SPR), fluorescence sensors, and electrochemical sensors have been developed for Atz determination.

Currently, the electrochemical technique is considered as an indispensable technique for organic pollutants assessment such as Atz, as opposed to other classical alternatives such as spectrophotometric, chromatographic, and colorimetric analytical techniques. This returns to its simplicity, optimized sensitivity, high efficiency, low cost, and ecofriendliness. Previously, bare and electrochemically modified electrodes such as gold (Au), platinum (Pt), and glassy carbon (GC) were used for Atz determination. Because of their capability of enhancing the sensitivity, multidetection ability, and detection limit of electrodes, electrochemical modification of electrodes and its composites with metallic nanoparticles has been considered as a potential technique for sensor applications. AgNPs have been used for electrochemical determination of organic molecules such as 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, metronidazole, chloramphenicol, azathioprine, pendenmethalin, and ethyl parathion. Reportedly, there are no published reports about the AgNP role in the electrochemical detection of Atz.

Because of their significant physicochemical features, AgNPs have been employed in enhancing the characteristics of many instruments such as catalysis, optical devices, electronic and electrochemical analysis. These peculiarities make AgNPs a
good candidate for many industrial, medical and environmental applications.\textsuperscript{19–23} AgNPs have been used as an electrocatalyst for methanol electrooxidation\textsuperscript{24} and the reduction of 4-nitrophenol\textsuperscript{25} as well. In addition, they have been suggested for the removal of some reactive dyes,\textsuperscript{26} determination of antioxidant flavonols isomers,\textsuperscript{19} and improvement of the anode material for lithium-ion batteries.\textsuperscript{27} Recently, our research group has prepared glassy carbon electrode (GC) modified with poly(1,8-diaminonaphthalene) coated with AgNPs for the electrochemical determination of cadmium, lead, and copper.\textsuperscript{28} AgNPs could be obtained by various preparation routes; in situ, ex situ, vapor phase deposition, ion implantation and direct chemical reduction.\textsuperscript{29} The direct chemical reduction method is considered as the most frequently used one in AgNP preparation.\textsuperscript{30} Biological macromolecules such as plant molecules, natural polymers, and dissolved organic matter (DOM) could be used in synthesis of highly stable AgNPs for medical and environmental applications.\textsuperscript{25,30–32} DOM is a multicomponent mixture of high-molecular-weight macromolecules that originates from debris of living organisms in aquatic ecosystems.\textsuperscript{33} Humic and fulvic acids are the major components of DOM in natural water. Humic acid concentration varies from 0.1 to 2 mg/L in treated water and from 1 to 60 mg/L in natural water.\textsuperscript{34} DOM and its most abundant constituents, humic and fulvic acids, have been appraised as a potential source for metal nanoparticles fabrication. This capability has resulted from the presence of phenolic and carboxylic groups in the structures of humic derivatives. These functional groups are known for their great bioreduction and stabilization capacity in metal nanoparticle fabrication.\textsuperscript{34} For instance, humic acid is prevalent for AgNP preparation and its stability.

AgNPs could be formed via direct addition of water samples containing humic acid or isolated humic acid without additional reagents, under environmentally relevant conditions. There are two possible mechanisms illustrating the reduction of Ag\textsuperscript{+} one is the complexation of silver by humic acid followed by ligand-to-metal charge transfer, and the other is the formation of free radicals of superoxide anion and oxygen/phenolic group interaction.\textsuperscript{35,36} AgNPs show a high stability in the presence of humic acid (1–20 mg/L) by inhibiting the Ag\textsuperscript{+} release that leads to the prolonged persistence of its nanoparticles in aquatic systems.\textsuperscript{37} The electrode modification with AgNPs represents an efficient tool for the determination of a number of targeted molecules based on AgNP stripping.\textsuperscript{38} In the present study, we report the optimization and preparation of novel electrochemical sensor based on DOM/AgNP/GC composite for Atz assessment in water utilizing electrochemical techniques.

DOM/AgNP/GC has been synthesized through a chemical reduction method and characterized using ultraviolet–visible (UV–vis) and fluorescence (FL) spectroscopy and transmission electron microscope (TEM) (Figure S2). The sensor has been fabricated by immobilizing DOM/AgNPs on GC. Different parameters such as modification technique, electrode material, exposure time, scan rate, and supporting electrolyte were tested for construction of highly stable AgNPs on the electrode material without any aggregation. AgNPs have been immobilized to the electrode surface via three different techniques: drop casting, sticking, and transfer sticking (Scheme 1).

The SWASV performance for DOM/AgNP/GC composite by utilizing the three techniques of electrode modification is illustrated in Figure 1. Sticking and transfer sticking modification techniques have led to a sufficient adherence of AgNPs without inducing any agglomeration of nanoparticles. Alternately, drop casting has led to the flocculation of AgNPs at the electrode surface. Moreover, in case of the sticking technique, the diluted AgNPs with phosphate buffer have been used to prevent aggregation of the nanoparticles. Both sticking and transfer sticking systems have led to the immobilization of nanoparticles. Clearly, the transfer sticking has been preferred because of its capacity to prevent agglomeration at higher nanoparticle concentrations.\textsuperscript{37} The sticking coefficients of AgNPs have a typical performance for different sizes of silver nanoparticles.\textsuperscript{38} The transfer sticking has been used for all subsequent voltammetric measurements.

The AgNP sticking coefficient has been correlated with the material of working electrodes under open circuit conditions. Immobilization of nanoparticles on the surface of Pt, Au and GC working electrodes have been tested using transfer sticking -the best modification technique-at the same voltammetric conditions (Figure 2). SWASV has been employed to detect the amount of adhered nanoparticles on the electrode surface. The three electrodes under investigation have shown a typical oxidation peak. AgNPs have been adhered efficiently at the GC electrode with the highest anodic current peak intensity. However, the Au electrode has shown a higher sticking
efficiency than the Pt electrode. In all, this leads to the aggregation of AgNPs. Because of the high affinity of GC for immobilization of the AgNPs, it has been employed for further studies.

The sticking duration is one of the most significant factors that affects the immobilization efficiency of AgNPs on the electrode surface. The oxidation peak current intensity of AgNPs on the GC electrode, at phosphate buffer pH 7.8, was correlated to the various exposure time intervals. Figure 3A shows a directly proportional relation between the exposure time intervals and the oxidation peak current intensity. The exposure time of 30 min has been used as the most optimized condition for silver nanoparticle immobilization. Alternatively, the relation between the scan rate and the number of immobilized nanoparticles has been studied by correlating the AgNP oxidation current peak intensity of with different scan rates: 0.025, 0.05, 0.075, and 0.1 V/s (Figure 3B). The peak current intensity of each scan has been recorded under the same electrolytic conditions in a phosphate buffer supporting electrolyte of pH 7.8, for an exposure time of 30 min. It is clear that the maximum oxidation peak current intensity has been recorded for a scan rate of 0.1 V/s.

The supporting electrolyte selection is a significant factor in electroanalytical studies because of its composition and the pH that affect the nanoparticle properties as well as the electrode—nanoparticle suspension interface. Subsequently, this affects the thermodynamics and kinetics of the charge transfer process. The effect of supporting electrolyte composition and pH on nanoparticle stability at the electrode surface has been investigated as shown in Figure 4. The effect of phosphate buffer, Britton–Robinson buffer, and acetate buffer of pH 7.8 on the stability of nanoparticles at the electrode surface has been studied. DOM/AgNP/GC composite in phosphate buffer at pH 7.8 has exhibited a single oxidation peak at 0.05 V, without causing any aggregation. However, both acetate and Britton–Robinson buffers have led to aggregation of some AgNPs at the GC surface. It is clear that the aggregation peak has shown a positive potential shift to 0.085 V, in comparison to the main oxidation peak at 0.05 V, as illustrated in Figure 4A. Acetate buffer increases the aggregation peak current intensity in comparison to the Britton–Robinson. Both buffers are not appropriate for AgNP stability at the defined pH. Besides, phosphate buffer solutions—the most suitable supporting electrolyte—with different pH values of 4, 6.2, and 7.8, have been investigated (Figure 4B). At pH 7.8, DOM/AgNP/GC composite has demonstrated a highly stable AgNPs with a single oxidation peak at 0.05 V. By decreasing the pH to 6.2, an aggregation of some AgNPs at the GC surface has been attained, comprising aggregated AgNPs with distinctive oxidation peak at positive potential 0.085 V. At pH 4, all AgNPs have been aggregated at the GC surface, exhibiting a single oxidation peak at 0.085 V. Thoroughly, the formation of highly stable silver nanoparticles has been resulted from the deprotonation of carboxylic and phenolic aromatic groups of both humic and fulvic acids of DOM. The carboxylate and phenolate groups have led to a high electrostatic repulsion between nanoparticles that improved its stability. Ultimately, phosphate buffer at pH 7.8 has been selected as the most suitable supporting electrolyte for further studies.

The aggregation of metallic nanoparticles and its nanocomposites have been studied extensively utilizing UV–vis spectroscopy. Conversely, there are few reports regarding the electrochemical behavior of aggregated metal nanoparticles. In this study, we report DOM/AgNP/GC composite as a novel electrochemical aggregation sensor to determine organic molecules such as Atz. This aggregation is dependent on the amount of added target molecule to the highly stable AgNPs, which makes it a new electroanalytical tool that shows high sensitivity and selectivity for Atz. This idea is based on the fact that each size of metallic nanoparticles
has a particular oxidation potential, which assists with determining the stability and monodispersity of metallic nanoparticles. This phenomenon makes the electrochemical route more sensitive and accurate than the colorimetric one because of the appearance of distinctive peak that represents the aggregated nanoparticles with a positive potential shift. The Atz effect on AgNP aggregation using SWASV has been investigated. The chemical structure of Atz shows its ability to bind with carboxylic and phenolic groups of DOM through the interaction of hydrogen bonding with NH groups of Atz. The atrazine chemical structure is shown (Figure S1). Eventually, this interaction has led to AgNP aggregation on the electrode surface. Scheme 2 shows the proposed mechanism of Atz determination at the DOM/AgNP/GC composite.

Previous studies explained the interaction mechanism between Atz and Humic substances.42 The results of SWASV analysis under optimized conditions have shown that there is a small oxidation peak (aggregation peak) around 0.085 V that represents the aggregated AgNPs with a positive potential shift from the main oxidation peak potential of stable AgNPs at 0.050 V. This positive shift could be attributed to diminishing of the surface area/volume ratio. In addition, previous studies have shown that the larger metallic nanoparticle oxidative peak intensity appeared with a positive potential shift, which confirms our results.40 Furthermore, SWASV results have been confirmed by UV–vis and TEM results (Figure S5). The UV–vis spectrum shows a broad SPR band with a red shift, which returns to the aggregation that has been induced by 100 μg/L atrazine. Moreover, the AgNP average size increased from 20 to 40 nm.

The SWASV results of DOM/AgNP/GC composite, in phosphate buffer of pH 7.8, upon addition of different Atz concentrations (20, 40, 60, 100, 140, 180, 220 μg/L) have been correlated to the corresponding calibration curves shown in Figure 6.

By the addition of different concentrations of Atz, a diminishing of the corresponding current intensity (of the main or nonaggregation peak −0.05 V) has been attained. This was accompanied by an increase in the current of the aggregation peak (0.085 V), simultaneously. The decrease in nonaggregation peak current returns to the AgNP (20 nm) consumption that form aggregated nanoparticles (40 nm). On the other hand, the increase in the aggregation peak current is due to the formation of aggregated nanoparticles by addition of different concentrations of Atz. The addition of the maximum amount of Atz (220 μg/L) has led to an aggregation of whole AgNPs that does not show any peak at the verified potential of main peak at 0.05 V. The aggregation peak current intensity has been increased by the increase in the Atz concentration, which shows a linear range between 20 and 220 μg/L with LOD and LOQ of 19.7 and 64.2 μg/L, respectively. Consequently, the nonaggregation peak (main peak) current has been decreased by increasing the Atz concentration with
LOD and LOQ of 28.1 and 93.6 μg/L, respectively (Table 1). Linear equations of both aggregated- and nonaggregated-based sensors are

\[ I_{Atz} = 0.0271C_{Atz} - 0.332 \] 

and

\[ I_{Atz} = -0.0393C_{Atz} + 10.897 \], respectively. The repeatability of this method has been studied using five replicates of 100 μg/L of Atz at the same electrolytic and voltammetric conditions. Relative standard deviation (RSD) of the five stripping peak currents has been recorded for aggregation and nonaggregation peak response with values of 2.75 and 2.79% respectively. This confirms the adequate repeatability of this method. Clearly, the aggregation peak response shows more sensitivity than the nonaggregation one (Table 1).

Atz could be determined through its oxidation at DOM/AgNP/GC. However, it was oxidized at the same conditions of the aggregation technique, and its oxidation peak attained a maximum intensity at pH 4 (Figure 7).

SWASV studies were employed in the presence of different concentrations of Atz (10, 20, 40, 80, and 140 μg/L) that have been correlated to its calibration curve as shown in Figure 8. The sensor shows good sensitivity for Atz determination with LOD and LOQ of 13.6 and 45.3 μg/L, respectively. Compared to aggregation-based sensor, it has shown a similar sensitivity and \( R^2 \) values with a lower LOD (Table 1). The regression equation is \( I_{Atz} = 0.0271C_{Atz} - 0.0035 \). The RSD of this sensor is accepted with a value of 2.15%. Recently, oxidation of Atz based on electrodes modified with CuO nanoparticles and Pt nanoparticles were investigated.1,43 To the best of our knowledge, AgNP-modified GC electrodes were not reported for the determination of Atz.

Different types of electrochemical- and non-electrochemical-based sensors were used for the detection of atrazine. For example, molecular-imprint-based quartz crystal microbalance (QCM) represents a non-electrochemical-based sensor for Atz determination with a good detection limit.44 A comparison between the analytical responses of our novel sensor toward Atz with other electrochemical methods is reported (Table 2). Previous studies reported the electrochemical reduction of Atz.

Table 1. Analytical Parameters for Atz Determination Using DOM-AgNP/GC Sensor

<table>
<thead>
<tr>
<th>sensor</th>
<th>linear range (μg/L)</th>
<th>( R^2 )</th>
<th>LOD (μg/L)</th>
<th>LOQ (μg/L)</th>
<th>sensi.</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgNP aggregation</td>
<td>20–220</td>
<td>0.983</td>
<td>19.3</td>
<td>64.2</td>
<td>0.03</td>
<td>2.75</td>
</tr>
<tr>
<td>AgNP non-aggregation</td>
<td>0.970</td>
<td>28.1</td>
<td>93.6</td>
<td>0.04</td>
<td>2.79</td>
<td></td>
</tr>
<tr>
<td>Atz oxidation</td>
<td>10–140</td>
<td>0.983</td>
<td>13.6</td>
<td>45.3</td>
<td>0.03</td>
<td>2.15</td>
</tr>
</tbody>
</table>
Table 2. Comparison of our Electrochemical Method with the Other Previous Reported Ones

<table>
<thead>
<tr>
<th>method</th>
<th>electrode material</th>
<th>linear range (μg/L)</th>
<th>LOD (μg/L)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>molecular imprinted QCM</td>
<td></td>
<td>0.017–0.323</td>
<td>0.006</td>
<td>44</td>
</tr>
<tr>
<td>electrochemical reduction</td>
<td>GC/Bi</td>
<td>2156–4313</td>
<td>3594.7</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>CuSAE</td>
<td></td>
<td>3.0</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>BIFE</td>
<td>144.5–4313</td>
<td>30.2</td>
<td>46</td>
</tr>
<tr>
<td>electrochemical oxidation</td>
<td>Au</td>
<td></td>
<td>927.4</td>
<td>52</td>
</tr>
<tr>
<td>electrochemical aggregated AgNP sensor</td>
<td>DOM/AgNP/GC</td>
<td>10–140</td>
<td>13.59</td>
<td>this</td>
</tr>
<tr>
<td>electrochemical non-aggregated AgNP sensor</td>
<td>GC</td>
<td>20–220</td>
<td>19.27</td>
<td>work</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>28.07</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Maximum Metal Ion Concentrations Maintaining DOM-Capped AgNP Stability

<table>
<thead>
<tr>
<th>metal ion</th>
<th>maximum acceptable concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺, K⁺</td>
<td>120</td>
</tr>
<tr>
<td>Ca²⁺, Mg²⁺</td>
<td>50</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>55</td>
</tr>
</tbody>
</table>
| Mg²⁺, Cu²⁺, and Cd²⁺ ions that do not induce any DOM-capped AgNP aggregation. Divalent metal ions have showed a complexing capacity more than monovalent ions ones, that returns to their high affinity to DOM. The interaction between metal ions Ca²⁺, Mg²⁺, Cu²⁺, and Cd²⁺ and the DOM to form a metal–DOM complex was previously reported.33,34 The complexing capacity of metal–DOM is significant at higher concentrations of DOM.33 It is highly recommended to use the DOM/AgNP/GC composite for the determination of organic pollutants such as Atz in water samples with moderate metal ion concentrations. However, dialysis is required for Atz determination in salt water samples.

Atz determination in natural water samples has been studied using DOM/AgNP/GC nanocomposite. This sensor has demonstrated a good recovery values for both aggregation and electrochemical oxidation techniques, as exhibited in Table 4. Aggregation techniques based on aggregated and non-

Table 4. Determination of Atz in River Water Samples

<table>
<thead>
<tr>
<th>sensor</th>
<th>added Atz (μg/L)</th>
<th>found Atz (μg/L)</th>
<th>recovery (%)</th>
<th>GC/MS (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>aggregation-based sensor</td>
<td>100</td>
<td>104 ± 1</td>
<td>104</td>
<td>99</td>
</tr>
<tr>
<td>non-aggregation-based sensor</td>
<td></td>
<td>109 ± 2</td>
<td>109</td>
<td></td>
</tr>
<tr>
<td>electrochemical oxidation</td>
<td></td>
<td>96 ± 2</td>
<td>96</td>
<td></td>
</tr>
</tbody>
</table>

*95% confidence interval calculated (n = 6).

CONCLUSION

This study reports the synthesis of AgNPs through direct chemical reduction techniques. The nanoparticles have been identified and characterized using UV–vis spectroscopy, FL, and TEM. DOM/AgNP/GC composite has been obtained by the GC electrode modification with DOM-capped AgNPs through transfer sticking for 30 min. The sticking coefficient and stability of AgNPs at the GC surface have been optimized. The modified electrode has been used as a potential sensor for Atz determination based on AgNP aggregation and the direct electrooxidation of Atz. Linear range, LOD, and LOQ, repeatability for the DOM/AgNP/GC composite have been determined. Additionally, the stability of the composite in different water samples has been investigated. The applicability of the sensor in real samples, such as natural water from water streams, has been studied. Our novel sensor opens the door for the determination of a variety of organic and inorganic molecules that are capable of inducing metallic nanoparticle aggregation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.0c00597.

Experimental details and results, including Figures S1 and S2 (PDF)

https://dx.doi.org/10.1021/acsanm.0c00597
Dedicated to Prof. H. M. Fahmy, Cairo University, on the occasion of his 70th birthday.

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