Interactions of Ag nanoparticles with humic acid present in surface water

Srijita Basumallick

Original Article

Abstract

The present paper reports aggregation behaviour of humic acid (HA) in the presence of silver nanoparticles. Aggregation behaviour has been studied from dynamic light scattering (DLS) measurement, in the presence of silver nanoparticle. Silver nanoparticle has been prepared through chemical route and characterized by plasmon resonance spectroscopy. HA used in the study has been characterized by UV–Vis and fluorescence study; its charged state has been evaluated from the study of its interaction with a cationic dye ruthenium bipyridine. It has been found that HA forms small–medium- and large-sized aggregates in the presence of silver nanoparticle as obtained from DLS diameter. The result has been explained in terms of Langmuir–Hinshelwood adsorption model. It has been proposed that hydrogen bonding and hydrophobic interaction play an important role in the formation of aggregates of HA.

Keywords Humic acid · Silver nanoparticles · DLS · Langmuir–Hinshelwood

Introduction

According to the WHO report (Drinking water 2017; Banik and Basumallick 2017), globally 2 billion people uses a contaminated water source for drinking water. Again, about 144 million people use surface water (Drinking water 2017) without any treatment. Thus, purification of water for a safe drinking purpose is a major challenge of the day. Recently, Inamuddin et al. have nicely reviewed (Mashkoor et al. 2020) the use of carbon nanotubes for the removal of dyes from contaminated water. Inamuddin et al. also recommended the use of organic–inorganic composite exchanger (Mohammad and Inamuddin 2015), Inamuddin (2010) for water purification. Banik and Basumallick 2017; Basumallick and Santra 2017) reported a cost-effective method of removal of humic acid (HA) from surface water using ZnO nanoparticles and sun light using photo-Fenton-type reaction. Santra and Basumallick Banik and Basumallick (2017), Basumallick and Santra (2017) designed a fluorescence sensor for the detection of ppm level HA in surface water.

In the present paper, we have studied the interactions of HA with Ag nanoparticles. The motivation comes from the fact that both HA and Ag nanoparticles are present in contaminated surface water. Surface water is contaminated with HA through plant sources or from the soil. It is a complex bio-degradable product of bio-mass. Chemically it is mainly a complex poly-nuclear hydrocarbon with different hydrophilic groups, but neither its chemical structure nor its configuration in solution is clearly known (Abbt-Braun et al. 2004; Kerner et al. 2003; Šmejkalová and Piccolo 2008). Chemical structure and physical state of HA in solution are not fully understood. Model structure of HA has been proposed. It is known that HA contains different oxygen-containing groups like –OH, –COOH, –CHO, ethoxy on its aliphatic and aromatic skeleton. Due to the presence of these hydrophilic as well as hydrophobic groups, it often behaves like a surfactant. It is reported that it forms micelle in aqueous environment (Kerner et al. 2003). But reported CMC values of HA range from 1 to 10 mg per ml of solutions. This indicates that HA undergoes aggregation in solution. It also forms supra-molecular aggregation (Šmejkalová and Piccolo 2008). If HA-contaminated water is chlorinated in water treatment plant, it forms highly carcinogenic organic chloro-compounds (Kerner et al. 2003). Thus, the removal of HA from surface water is prerequisite before water treatment.

* Srijita Basumallick
  srijitabasumallick@gmail.com

1 Department of Chemistry, Asutosh College, Calcutta University, Kolkata, India
Interestingly, surface water is often found to contain trace amount of Ag nanoparticles. Source of these Ag nanoparticles is consumer products like sanitizers, equipments like washing machines and refrigerators and drinking water purifier. Ag nanoparticles from these products are finally released (Farkas et al. 2011) to different water bodies. Thus, the study of interactions of Ag nanoparticles with HA is expected to help revealing the aggregation behaviour of HA in the presence of Ag nanoparticles, although metal ion-assisted aggregation behaviour of HA has been studied earlier (Adegboyega et al. 2013; Chen et al. 2012). To the best of our knowledge, there is no systematic report on aggregation behaviour of HA by Ag nanoparticles. Here, aggregation of HA has been studied by the DLS method.

**Experimental**

**Materials and methods**

All chemicals used in this study were of analytical reagent grade and were used without further purification. Silver nitrate (AgNO3), sodium borohydride (NaBH4), trisodium citrate were purchased from Sigma-Aldrich. Ethanol and conc. HCl were purchased from Merck and used as received. Double distilled water was used for preparation and spectroscopic studies. All the glassware was washed thoroughly with distilled water and dried in an oven.

**Preparation of silver nanoparticles**

Silver nanoparticles were prepared by following our earlier method (Choudhury et al. 2016). Briefly, a solution of NaBH4 0.01 M and a separate solution of AgNO3 0.01 M were prepared. 0.2 mg of tri sodium citrate was weighted to which 45 ml of ice-cooled 0.01 M NaBH4 was added at the stirring condition. After 20-min stirring at ice bath, 2 ml of 0.01 (M) AgNO3 was added drop by drop (1 drop per sec); after addition, the electronic absorption spectra of the yellow solution were taken at the range of 200–800 nm.

Sodium salt of HA (Loba Chemicals) was used as supplied, and its dilute aqueous solutions were prepared using double distilled water. The HA solution was characterized by its prominent fluorescence spectra. A solution of 0.1 mg/ml of HA was used for DLS study. Dilute solutions of Ag nps (0.1% and 1.0%) were used for agglomeration study. DLS diameters of the solutions were taken exactly after 30 min of mixing. The electronic absorption spectra of the reactants and products were recorded in the region 1100–200 nm using a Shimadzu UV–Vis- 1800 spectrophotometer with a quartz cell of 1.0 cm path length. Fluorescence spectra were recorded by using a PerkinElmer LS 55 spectrofluorometer in the range 0–1000 nm. Unicon rectangular water bath was used for reaction as well as concentrating various samples to their desired value.

**Results and discussions**

Unlike biogenic synthesis of nanoparticles (Choudhury et al. 2016; Inamuddin. 2020), Ag nanoparticles have been prepared by usual chemical route using borohydride as reducing agent and citrate as capping agent. It has been characterized by plasmon resonance spectra as shown in Fig. 1. The
observed sharp peak at 409 nm indicates (Choudhury et al. 2016) the presence of spherical nanoparticles with average diameter of 50 nm.

Ag nanoparticle and HA used in this study have been characterized by their UV–visible (Fig. 1) and fluorescence spectra (Fig. 2). As it is well known that HA obtained from different sources has different compositions (Banach-Szott et al. 2021; Qin et al. 2020), the observed spectra cannot be compared. It is seen from Fig. 2 that the observed spectra depend on the concentration of HA. This is owing to the fact that HA undergoes self-aggregation at higher concentration. The nature of this aggregation is not clearly known. However, hydrophobic interaction and hydrogen bonding among different groups present in HA are supposed to play an important role. It is reported (Šmejkalová and Piccolo 2008) that HA forms supra-molecular aggregates at higher concentration.

The objective of the present study is to understand the influence of Ag nanoparticles to the aggregation behaviour of HA. In this connection, it should be mentioned that aggregation of cyanine dye (Chen et al. 2012; Shimidzu et al. 1985) is strongly influenced by Ag nanoparticles. Cyanine dyes are negatively charged, so it is desirable to elucidate the charge state of HA used in this study. For this purpose, we have used Rubipy (Shimidzu et al. 1985) a cationic dye, with a prominent fluorescence spectra (Fig. 3) when excited at 455 nm. Now we have gradually added HA solution to this Rubipy solution. Fluorescence quenching of Rubipy is noted (Fig. 3), indicating that HA used in this study is likely to be negatively charged.

In this experiment, we have taken Rubipy (500 micromolar) and its fluorescence spectra as depicted in Fig. 3.

To study the aggregation behaviour of HA in aqueous environment and in the presence of Ag nanoparticles, we have determined DLS diameters of aqueous dispersion of 0.1 mg/ml HA 30 min after its preparation. The DLS curve is shown in Fig. 4a; trimodal distribution comprises of relatively smaller particles with diameters around 100 nm (Fig. 4a), 500 nm and larger particles of diameter around 1100 nm with overall average diameter of 1034 nm.

But in the presence of 0.1% Ag nanoparticles, DLS diameter value changes; it remains trimodal distribution comprising of small, medium and large particles; the diameter of the large particles is found to be slightly less than 10,000 nm with overall average diameter of 2240 nm.

In the presence of 1.0% Ag nanoparticles, the trimodal distribution patterns retain, but diameters of larger particles exceed 10,000 nm with overall average diameter 3300 nm. All the measurements have been taken after 30 min of mixing. From DLS study, we conclude that Ag nanoparticles accelerate probably through adsorption of HA onto its surface. Citrate-capped Ag nanoparticles are positively charged (Bhattarai et al. 2011); therefore, they easily adsorb HA which are of negatively charged.

We proposed Langmuir–Hinshelwood type of adsorption (Vincent and Gonzalez 2001) (Fig. 5) of HA that takes place onto Ag surface as follows:

\[ \text{Ag} (\text{HA})_{\text{adsorbe}} + \text{Ag}(\text{HA})_{\text{adsorbe}} \leftrightarrow (\text{HA})_2 + \text{Ag} \]

\[ \text{Ag}(\text{HA})_2_{\text{adsorbe}} + \text{Ag} (\text{HA})_{\text{adsorbe}} \leftrightarrow (\text{HA})_3 + \text{Ag} \]

Once these Ag-assisted HA dimers and trimmers are formed, they undergo usual coagulation forming different aggregated HAs. This is supported from DLS data, where we have observed small, medium and large sizes of aggregated HA. It is reported (Tan et al. 2018) that the COOH group and OH group present in HA play an important role in the aggregation process of the HA probably through forming hydrogen bond. Apart from hydrogen bonding, hydrophobic interaction also plays an important role.

Finally, we have applied this method for the removal of HA from water. We have taken a very dilute solution of HA (132 ug/ml) to which we have added 1% of Ag nanoparticles solution, and we have found that after keeping them for 90 min and then filtering through 0.2-um filter paper about 50% of HA are removed in the filtrate as seen in the UV spectra shown in Fig. 6.

![Fig. 3 Fluorescence quenching of $5 \times 10^{-6}$ (M) Rubipy in different concentrations of HA](image-url)
Conclusions

In the present study, we have shown that in the presence of Ag nanoparticles HA undergoes rapid coagulation as indicated in its increased DLS diameter. The concentration of Ag nanoparticles also plays an important role. This can be explained with initial adsorption of HA onto Ag nanoparticles followed by Langmuir–Hinshelwood-type desorption. This method may be applied for rapid removal of HA from surface water.

Fig. 4 DLS diameter of HA at different concentrations: a only HA, b 0.1% Ag nanoparticles, c 1% Ag nanoparticles

Fig. 5 Langmuir–Hinshelwood type of adsorption
Funding The author(s) received no specific funding for this work.

Acknowledgements The authors sincerely acknowledge the Principle of Asutosh College and HOD of Department of Chemistry, Asutosh College, Kolkata, for providing necessary support for this work.

Declarations

Conflict of interest This work does not have any conflict of interest.

Ethical statement This work does not require any animal/similar species for experiment.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

Abbt-Braun G, Lankes U, Frimmel F (2004) Structural characterization of aquatic humic substances? The need for a multiple method approach. Aquat Sci 66:151–170
Adegboyega NF, Sharma VK, Siskova K, Zbofil R, Sohn M, Schultz BJ et al (2013) Interactions of aqueous Ag+ with fulvic acids: mechanisms of silver nanoparticle formation and investigation of stability. Environ Sci Technol 47(2):757–764
Banach-Szott M, Debska B, Tobiasova E (2021) Properties of humic acids depending on the land use in different parts of Slovakia. Environ Sci Pollut Res 28(41):58068–58080
Bank J, Basumallick S (2017) Nanoparticle-assisted photo-Fenton reaction for photo-decomposition of humic acid. Appl Water Sci 7(7):4159–4163
Basumallick S, Santra S (2017) Monitoring of ppm level humic acid in surface water using ZnO–chitosan nano-composite as fluorescence probe. Appl Water Sci 7(2):1025–1031
Bhattarai N, Khanal S, Pudasaini PR, Pahil S, Romero-Urbina D (2011) Citrate stabilized silver nanoparticles: study of crystallography and surface properties. Int J Nanotechnol Mol Comput 3:15–28
Chen Z, Campbell PGC, Fortin C (2012) Silver binding by humic acid as determined by equilibrium ion-exchange and dialysis. J Phys Chem A 116(25):6532–6539
Choudury R, Majumder M, Roy DN, Basumallick S, Misra TK (2016) Phytotoxicity of Ag nanoparticles prepared by biogenic and chemical methods. Int Nano Lett 6(3):153–159
Drinking water (2017) Available from: https://en.wikipedia.org/wiki/Drinking_water.
Farkas J, Peter H, Christian P, Gallego Urrea JA, Hassellöv M, Tuoriniemi J et al (2011) Characterization of the effluent from a nanosilver producing washing machine. Environ Int 37(6):1057–1062
Inamuddin IY (2010) Synthesis and characterization of electrically conducting poly-o-methoxyaniline Zr(IV) molybdate Cd(II) selective composite cation-exchanger. Desalination 250:523–529
Inamuddin, (2020) Biogenic synthesis of selenium nanoparticles with edible mushroom extract: evaluation of cytotoxicity on prostate cancer cell lines and their antioxidant, and antibacterial activity. Bioninterface Res Appl Chem 10:6629
Kerner M, Hohenberg H, Ertl S, Reckermann M, Spitz T (2003) Self-organization of dissolved organic matter to micelle-like microparticles in river water. Nature 422(6928):150–154
Masikhoo F, Nasar A, Inamuddin, (2020) Carbon nanotube-based adsorbents for the removal of dyes from waters: a review. Environ Chem Lett 18(3):605–629
Mohammad A, Inamuddin, Hussain S (2015). Poly (3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS) Zr(IV) phosphate composite cation exchanger: sol-gel synthesis and physicochemical characterization. Ionics, 21(4):1063–71
Qin S, Xu C, Xu Y, Bai Y, Guo F (2020) Molecular signatures of humic acids from different sources as revealed by ultrahigh resolution mass spectrometry. J Chem 2020:7171582
Shimidzu T, Iyoda T, Izaki K (1985) Photoelectrochemical properties of bis(2,2’-bipyridine)(4,4’-dicarboxy-2,2’-bipyridine) ruthenium(II) chloride. J Phys Chem 89(4):642–645
Šmejkalová D, Piccolo A (2008) Aggregation and disaggregation of humic supramolecular assemblies by NMR diffusion ordered spectroscopy (DOSY-NMR). Environ Sci Technol 42(3):699–706
Tan L, Tan X, Mei H, Ai Y, Sun L, Zhao G et al (2018) Coagulation behavior of humic acid in aqueous solutions containing Cs+, Sr2+ and Eu3+: DLS EEM and MD simulations. Environ Pollut 236:835–843
Vincent MJ, Gonzalez RD (2001) A Langmuir-Hinshelwood model for a hydrogen transfer mechanism in the selective hydrogenation of acetylene over a Pd/C-AI2O3 catalyst prepared by the sol–gel method. Appl Catal A 217(1):143–156

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.