SYNTHESIS SILVER NANOPARTICLES AND ITS APPLICATION FOR WASTEWATER TREATMENT: CATALYTIC AND PHOTOCATALYTIC DEGRADATION METHYLENE BLUE

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Abstract

This paper aims to propose a simple, eco-friendly method for obtaining colloidal solutions of silver nanoparticles (Ag NPs) by using of contact non-equilibrium low-temperature plasma in presents carboxymethyl cellulose (CMC) as a stabilizing agent and investigation on the decolorization of representative cationic phenothiazine dye in presence of nanocatalysts. Silver nanoparticles were prepared in aqueous AgNO₃ solution by using of contact non-equilibrium low-temperature plasma in the present of carboxymethyl cellulose as capping agent. Ultraviolet–visible (UV) spectroscopy, X-ray diffraction, zeta potential, DLS analysis and SEM were used to study the formation and properties of silver nanoparticles. Measurements of optical spectra showed that the surface plasmon resonance was localized around 410-418 nm when the reaction mixture exposed to plasma for 1-5 min. The nanoparticles exhibited a good catalytic reduction for methylene blue dye in the presence of NaBH₄. It followed pseudo-first order kinetics with a rate constant of 0.16 min⁻¹. The catalytic degradation reaction was completed (98-99%) within 25 min. The photocatalytic activity of the synthesized silver nanoparticles was examined by degradation of methylene blue under sunlight irradiation. Synthesized silver nanoparticles were effectively degrading the dye nearly 98% at 70-72 h of exposure time.

Key words: carboxymethyl cellulose; degradation; dye; catalytic; photocatalytic; nanocatalysts; silver nanoparticles; wastewater.
Materials and equipment for water treatment

**Introduction**

The last advances in material science and technology have converted nanotechnology as one of the most promising emerging technologies of the twenty-first century, improving industrial products and processes. Within this broad area of research, metal nanoparticles are one of the most studied nanostructures due to their excellent properties such as large surface area and high surface reactivity, which are useful in a wide variety of application fields (Hess 2012). Silver (Ag) NPs have generated substantial interest not only in fundamental research and development but also at the industrial scale owing to their excellent properties (Nowack, Krug and Height 2011).

Recently, metal nanoparticles (MNPs) have attracted attention for the treatment of wastewaters due to their number of active sites, strong electron transfers abilities, large specific surface area, high thermal stabilities and excellent activity and efficiency (Wijnhoven, S. et al., 2009, Dontsova, T. et al., 2020). Different approaches have been applied for the fabrication of Ag NPs such as chemical, physical, electrochemical, biological, etc (Kassaee, M. et al., 2008, Abdelghany, T. et al., 2017).

However, there is a growing interest to develop eco-friendly techniques to avoid the use of toxic and hazardous chemicals as well as toxic and hazardous waste. In this sense, the known plasma-assisted synthesis method to obtain nanoparticles is one of the innovation and studied processes in the last decade. Plasmas can reduce silver ions and have the potential of generating AgNPs without any harmful byproducts. Many experimental setups of plasma in liquid generation have been reported, in which the liquid medium, electrode material, electrode configuration, electric power source, and other parameters were varied (Saito and Akiyama, 2015). Among plasma-chemical discharges, contact non-equilibrium low-temperature plasma (CNP) is a promising option from the point of view of practical application (Skiba et al., 2018). Plasma discharge generated between the electrode in the gaseous phase and solutions AgNO₃ is a rich source of high-energy electrons \( (e^-_g) \) that bombard the solution surface. After thermalization (energy loss through multibody interactions with water molecules) of the \( e^-_g \) from the gas phase, solvated electrons \( (e^-_aq) \) are formed in the liquid phase. Redox reactions mediated by the \( e^-_aq \) and other reactive species, such as hydrogen radicals (H), hydrogen peroxide (H₂O₂), singlet oxygen (O) and hydroxyls (OH), result in particle nucleation and the growth of AgNPs in the solution. In order to prevent precipitation and make stable colloidal silver nanoparticles, we evaluated the effect of different protective agents or stabilisers such as (sodium alginate, citrate, PVA, grape pomace waster) are demonstrated in other published works (Pivovarov O.A. et al., 2017; Skiba et al., 2019, Skiba M. et al., 2020). Therefore, this synthesis technique seems to have potential for metal nanoparticles synthesis.

Sodium carboxymethyl cellulose (CMC), a nontoxic and biodegradable cellulose derivative, has been used widely in biotechnology, medicine hydrogels, and other materials. Recently, CMC has
been used as a good stabilizer in the synthesis of metal nanoparticles in an aqueous medium (Chen J. et al., 2008, Hebeish et al., 2010). Therefore, studying of the process of obtaining silver nanoparticles in the presence of CMC stabilizing reagent, under the action of plasma discharge, is of scientific and practical interest.

Dyes, one of the most important industrial pollutants, inhibit sunlight penetration into the stream and affect aquatic ecosystem (Rani and Shanker, 2017, Valter, K. et al., 2019). It is well known that some dyes and their degradation products cause poisoning, allergy, skin irritation and cancer in humans. Thus, the removal of dyes from effluents is very important because of their esthetic impacts on the environment. MB dye, otherwise known as methylthioninium chloride, is a basic dye used in various areas such as biology, chemistry and medicine. Moreover, the increasing demand for clothing has brought adverse effect to the environment whereby textile industries have been dubbed as one of the largest contributors of pollutants in surface water: chemicals, dyes, and heavy metals. Conventional wastewater treatment methods fail to degrade MB because of the heterocyclic aromatic structure, hydrophilicity and good stability against many chemicals and physical parameters. In recent years, catalytic and photocatalytic degradation of MB by AgNP has been studied by many researchers because of low activation energy requirement of the kinetically feasible process.

The main goal is to investigate synthesis of silver nanoparticles and its application for catalytic and photocatalytic degradation methylene blue.

Materials and Methods

All the chemicals and reagents used in this study were of analytical grade. Silver nitrate (99.8%, Kishida), carboxymethyl cellulose (Mw =90 000 g/mol), sodium borohydride, MB were purchased from Merck Co. Ltd. (Darmstadt, Germany). Aqueous solutions of silver nitrate at different concentration were prepared using ultrapure water (Direct-Q UV, Millipore) and were utilized as starting materials without further purification

Synthesis of silver nanoparticles AgNPs

A simple one-step reaction was used to synthesize AgNPs. Silver nanoparticles were synthesized using synthesis reactor (Skiba et al. 2018). AgNO₃ was dissolved in double distilled water to give a solution of fixed concentration (mmol/L). CMC was dissolved in double distilled water to obtain a solution of 1.25–2.5 g/L at heating to 90 °C. Then fixed volume of CMC was added to 40 ml solution AgNO₃ under stirring 0.1 min. The resulting reaction mixtures were 1.25%; 2.5% CMC. No other additives were used either to promote the reaction or to protect growth Ag particles. The resulting reaction mixture was treated in the reactor with the discharge of contact non-equilibrium
low-temperature plasma with fixed parameters (pressure, current strength, voltage). The parameters of plasma I=120 mA, P=0.08 MPa.

**Characterization techniques**

Spectra of colloidal solutions were obtained by means of spectrophotometer UV-5800PC using quartz cuvettes in the wavelength range of 190-700 nm (FRU, China). Dynamic light scattering (DLS) and zeta potential (ZP, ζ-potential) analyses were performed using zetasizer (Malvern Instruments Ltd., Malvern, England). Disperse phase of the solution obtained as a result of plasma-chemical treatment of the solution and dried in the air 25°C was studied with the use of X-ray diffractometer Ultima IV Rigaku. Microphotographs of nanoparticles were obtained on scanning electron microscope JEOL JSM-6510LV (JEOL, Tokyo, Japan).

**Catalytic degradation of Dye**

In order to assess the catalytic action of the AgNP, the MB dye was subjected to degradation using NaBH₄. 10 mmol/L stock solution of MB were mixed with 3 mL of 1 mmol/L freshly prepared NaBH₄ solution. The fixed amount (0.05 mL, Ag⁺ = 3.0 mmol/L, CMC 2.5%) of as-synthesized colloidal AgNPs was further added into previously made mixture of MB/NaBH₄. The final volume of reaction mixture in all three samples was adjusted to 16 mL by adding ddH₂O. The remnant MB was estimated at regular time intervals by determining the absorbance at 664 nm.

**Photocatalytic Degradation of Dye**

In typical experiment about 9 mg of synthesized silver nanoparticles was added to 100 mL of methylene blue dye solution (10 mg/1000 mL). A control samples was without addition of silver nanoparticles. Then the dispersion was put under the sunlight and monitored. At specific time intervals, aliquots suspension were used to evaluate the photocatalytic degradation of dye. Concentration of dye during degradation was calculated by the absorbance value at 664 nm.

**Results and discussion**

UV-Vis spectrophotometric technique was applied to confirm the formation of silver nanoparticles in the CNP plasma-irradiated AgNO₃/CMC solution. The effect of the different variables on the one-pot plasma-induced synthesis of silver nanoparticles was investigated under normal laboratory conditions following different experimental protocols.

Figure 1 (a, b) shows the UV–vis spectra of the AgNPs obtained using CMC in different concentration (1.25–2.5%) at the fixed concentration of silver nitrate (3 mmol/L AgNO₃) and at various time intervals of the reaction medium treatment with plasma discharge (the parameters of plasma I=120 mA, P=0.08 MPa).
Fig. 1. UV–Vis spectra of aqueous solution AgNO$_3$/CMC treated with plasma at different discharge durations for various concentrations of CMC (a) 1.25%; (b) 2.5%.

The data in Fig. 1 reveals several important findings which can be presented as follows:

(i) treatment of the silver nitrate/CMC solution by low-temperature plasma discharge on the spectrum results in the SPR absorption peak ($\lambda_{\text{max}}$) to 408–418 nm, characterizing the formation of silver nanoparticles;

(ii) As a result of gradual increase in plasma exposure time from 0.1 to 5.0 min, the Ag$^+$/CMC solution evenly and gradually gets darker in color through concurrent formation of the silver nanoparticles. For all samples at the early stage reaction duration (<1 min.), the plasmon band is broad and weak indicating low conversion of Ag$^+$ to AgNPs at this irradiation duration; Further increase in the irradiation time to 5 min there is a gradual increase in the absorption intensity; This observation is accompanied by a regular blue shift in the range of 408–410 nm. The blue shift is indicative of the
formation of smaller silver nanostructures according to increase in reducing efficiency of Ag⁺ ions to metallic Ag afforded by the plasma activated CMC;

(iii) the increase in intensity of UV absorption spectra indicates increase in number of silver nanoparticles with increasing concentration of CMC from 1.25 % to 2.5 %. CMC is a salt of strong acid and weak base, so CMS solution presents alkalescent. Therefore, CMS with high concentration will promote the forming of Ag₂O from AgNO₃, which will disturb the growth of silver nanoparticles. So CMC concentration should not be too higher. Experimental results have revealed that the CMS concentration cannot be higher than 2.5%.

Figure 2 shows the UV–Vis spectra for AgNPs/CMC produced with AgNO₃ concentrations varying from 0.1 to 3.0 mM, a constancy of CMC concentration at 2.5% and plasma exposure time of 5 min. Similar absorption spectra were obtained at wavelength 420 nm, and the peaks intensity increases with increasing AgNO₃ concentration. However, while the concentration of silver nitrate altered from 0.1 to 0.5 mmol/L, the intensity of SPR peaks was changed slightly. This may be explained by the exhaustion of the precursor Ag⁺. With the increase in Ag⁺ concentration up to 1.0–3.0 mmol/L, the peaks intensity increases to 2.7. Thus, in order to achieve better stability and efficient reduction for conversion of Ag⁺ ions to silver nanoparticles with extremely small sizes, certain ratio of silver nitrate to CMC in the reaction medium must be ascertained.

![Absorption spectra of obtained colloidal solutions of AgNPs/CMC using plasma-chemical method.](image)

**Fig. 2.** Absorption spectra of obtained colloidal solutions of AgNPs/CMC using plasma-chemical method.

Figure 3 shows the change in the Ag⁺/CMC aqueous solution pH as a function of discharge duration. It is shown in Fig. 3 that the initial pH value of Ag/CMC solution is 6.4 and the solution
pH steadily decreased during the treatment from 5.37 to 2.28. After the rapid decrease in pH to 2.74-3.39, the pH value is stabilized and maintained. The intense reduction of the solution acidity is likely to be due to the consumption of OH radicals to form hydrogen polyoxides and transfer of electrons of H radicals to the solution. The CMC is an interesting pH-sensitive polyelectrolyte similar to poly-(acrylic acid) and at these experimental condition CMC chains can collapse and aggregate to form micropheres at low pH in aqueous solution which leads to good stability for AgNPs in the system.

![Graph showing pH change](image)

**Fig. 3.** The change in the AgNO₃/CMC aqueous solution pH as a function of discharge duration at concentration of AgNO₃= 1.0 mmol/L.

To further characterize the AgNPs in the colloidal water systems, dynamic light scattering (DLS) was used, which essentially consists of a technique that can be used to determine the size distribution profile of small particles in suspensions. It can be seen from the table 1 the average particle size is about 27-36 nm. The SEM images of the prepared Ag/CMC (same sample 2.5 % CMC) are shown in Figures 4. The synthesized nanoparticles were generally found to be spherical in shape.

In recent past development of silver nanoparticles and their application in the treatment of wastewaters is becoming a major area of research. It is mainly applicable to the removal of three major pollutants.

The catalytic activity of plasma synthesized Ag NPs was analyzed for degradation of an organic dye, MB. The catalytic property of plasma-synthesized Ag NPs for MB dye degradation was studied at present NaBH₄ and the results are presented in Fig. 5. After the addition of NaBH₄ to MB no reaction took place up to 25-60 min. After addition of synthesized AgNPs to MB, the absorbance was gradually decreased which indicated the ability of NaBH₄ to degrade MB in the presence of catalytic amount of Ag NPs. The absorbance of MB decreased to minimum (~ 90-100% reduction)
after 20-25 min. The results indicate that Ag NPs cause substantial structural changes and the removal of chromophoric group from dye molecules.

**Table 1.** The particle size and polydispersity index of obtained silver nanoparticles

<table>
<thead>
<tr>
<th>C (\text{AgNO}_3), mmol/L</th>
<th>Average particle size (d_{\text{AgNPs}}), nm</th>
<th>Polydispersity index</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>27.0</td>
<td>0.21</td>
</tr>
<tr>
<td>0.5</td>
<td>28.6</td>
<td>0.26</td>
</tr>
<tr>
<td>1.0</td>
<td>30.0</td>
<td>0.27</td>
</tr>
<tr>
<td>3.0</td>
<td>33.1</td>
<td>0.35</td>
</tr>
<tr>
<td>6.0</td>
<td>36.0</td>
<td>0.38</td>
</tr>
</tbody>
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**Fig. 4.** SEM-image of AgNPs/CMC prepared by discharge plasma.
From the kinetic studies (Fig. 6), the results showed that the degradation of MB satisfactory followed a pseudo-first order kinetics. That is, a rate constant $k$ was derived from the equation $\ln \left( \frac{A_t}{A_0} \right) = kt$, where $A_t$ and $A_0$ are the absorbance of the dye at time $\tau$ and 0 min, respectively, and are proportional to the real time concentrations of the dye. The plot of $\ln \left( \frac{A_t}{A_0} \right)$ versus reaction time was fairly linear (Fig. 6), supporting the first-order nature of the kinetics, and the $k$ value was subsequently estimated to be 0.167 min$^{-1}$. Therefore, for the degradation of MB the synthesized AgNPs may act as effective catalyst. Here, electron transfer between AgNPs and reducing agent plays an important role in the degradation of MB. AgNPs can demonstrate the ability to function as nanoelectrode. When AgNPs surface was charged by the addition of reducing agent, the stored electrons in AgNPs were discharged to the MB as electron acceptor. In this case, the electrons were transferred from AgNPs until most of the stored electrons in AgNPs were extracted. Here, AgNPs acted as an electron relay point that behaved alternatively as acceptor and donor of electrons.
Photocatalytic activity of silver nanoparticles on degradation of dye was demonstrated by using the dye methylene blue. The degradation of methylene blue was carried out in the presence of silver nanoparticles at different time in the sunlight. The absorption spectrum showed the decreased peaks for methylene blue at different time intervals. Initially, the absorption peaks at 664 nm for methylene blue dye were decreased gradually with the increase of the exposure time and that indicates the photocatalytic degradation reaction of methylene blue. The completion of the photocatalytic degradation of the dyes is known from the gradual decrease of the absorbance value of dye approaching the base line. The percentage of degradation efficiency of silver nanoparticles was calculated as 95.3% at 72 h (Fig. 7).

Fig. 6. The plot of ln(A_t/A_0) versus time for the reduction of MB in the presence of CMC-AgNPs.
Conclusions

A straightforward and environmentally benign method for the synthesis of silver nanoparticles (AgNPs) is reported. A sustainable and nontoxic polysaccharide carboxy methyl cellulose (CMC) was used as stabilizer in the process of synthesizing AgNPs. Silver nanoparticles were prepared in aqueous AgNO₃ solution by using of contact non-equilibrium low-temperature plasma. Measurements of optical spectra showed that the surface plasmon resonance was localized around 410-418 nm when the reaction mixture exposed to plasma for 1-5 min. According to the results of our findings, introduction of stabilizer promotes the increase in intensity of formation of silver nanoparticles. The increase the silver nitrate concentration does not increase the particle size that are formed. The catalytic degradation reaction under solar irradiation was completed (98-99%) within 25 min. The photocatalytic activity of the synthesized silver nanoparticles was examined by degradation of methylene blue under sunlight irradiation. The catalytic degradation of MB by sodium borohydride in the presence of silver nanoparticles/CMC as catalyst.

Conflict of interests

The authors declare that they have no conflict of interest.

Acknowledgment

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References


В роботі запропоновано простий, екологічно чистий спосіб отримання колоїдних розчинів наночастинок срібла (НЧС) із використанням контактної нерівноважної низькотемпературної плазми в присутній карбоксиметилцелюлози (КМЦ) як стабілізуючого агента та досліджено знибрання барвника катіонного типу у присутності НЧС, як нанокаталізатора. Наночастинки срібла одержано у водному розчині AgNO₃, використовуючи розряд контактної нерівноважної низькотемпературної плазми в присутності карбоксиметилцелюлози як стабілізатора утворених часток. Дослідження одержаних НЧС та їх властивості здійснювали із використанням наступних методів: спектрофотометрія, рентгеноскопія, динамічне світлорозсіювання та скануюча мікроскопія. Одержані спектральні залежності показали, що поверхневий плазмонний резонанс НЧС спостерігається при 410-418 нм, при обробці реакційної суміші розрядом плазми протягом 1-5 хв. Вміст наночасток срібла зростає при збільшенні тривалості дії плазми на розчин; обробка протягом 5 хв. забезпечує формування стабільних колоїдних розчинів НЧС. Середній розмір утворених НЧС визначений методом динамічного світлорозсіювання та скануючої мікроскопії становить 27-36 нм. Проблема очищення стічних вод з вмістом органічних барвників нині є актуальною. Саме тому розглянуто каталітичні та фотокаталітичні властивості одержаних НЧС в моделних умовах для розкладання барвника метиленового синього (МС). Одержані НЧС продемонстрували каталітичну активність по відношенню до барвника метиленового синього (МС) в присутності NaBH₄. Процес характеризується реакцією псевдо першого порядку з константою швидкості ~0,16 хв⁻¹. Розкладання МС через 25 хв. у присутності нанокаталізатора становить 98-99%. Фотокаталітичну активність синтезованих НЧС досліджували також шляхом розкладання МС під дією сонячного світла. Встановлено, що ступінь розкладання на рівні 98,0 % досягається за 70-72 год.

Ключові слова: карбоксиметилцелюлоза; деградація; барвник; каталітичний; фотокаталітичний; нанокаталізатор; наночастинки срібла.