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Author: Ali Kabeya Ilunga Reinout Meijboom



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Synthesis of narrowly dispersed silver and gold nanoparticles and

their catalytic evaluation for morin oxidation

Ali Kabeya Ilunga and Reinout Meijboom

Department of Chemistry, University of Johannesburg, PO Box 524, Auckland Park 2006,

Johannesburg, South Africa. Tel: +27(0)11 559 2367; *fax.:* +27(0)115592819; *e-mail:*

rmeijboom@uj.ac.za

Dedicated to Professor Cedric Holzapfel on the occasion of his 80th birthday

Graphical abstract



Dendrimer encapsulated metal nanoparticles

HIGHLIGHTS

- Dendrimer encapsulated Ag and Au nanoparticle were synthesized in aqueous solution.
- Oxidation of morin was performed as a catalytic model reaction.
- The catalytic oxidation was modeled to the Langmuir-Hinshelwood equation.
- Effect of temperature and concentration were investigated.
- Kinetic and thermodynamic parameters were determined.

Abstract

We present a study on the synthesis of narrowly dispersed silver and gold nanoparticles using generation five amino-terminated poly(amidoamine) dendrimers as a template. UV-vis spectrophotometry was performed to monitor the synthesis process and to characterize the metal nanoparticles. Infrared (IR) spectroscopy, and transmission electron microscopy (TEM) were also used to characterize the metal nanoparticles. A catalytic oxidation of morin (quercetin) in the presence of hydrogen peroxide was performed as a model reaction to evaluate the metal nanoparticle activities. Ultra high performance liquid chromatography analysis was performed to identify the reaction products. The kinetic data obtained were modeled to the Langmuir-Hinshelwood equation. The encapsulated silver and gold nanoparticles show high activity which confirm the passive interaction with the dendrimer.

Keywords: Dendrimer; Langmuir-Hinshelwood; Oxidation; Silver nanoparticles; Gold nanoparticles; Morin.

Introduction

Since the commercialization of poly(amidoamine) (PAMAM) dendrimers, their use in biology, medicine, and chemistry, particularly catalysis, are increasing considerably. A number of key features make PAMAM dendrimers interesting; notably the well-defined molecular composition, size, and shapes. Their high density of nitrogen ligands along with the potential of interaction with metal ions allows the use of dendrimers as templates for the synthesis of metal nanoparticles [1, 2]. The use of metal nanoparticles increased due to the fact that they show electronic, optical, catalytic, and biological activity different from their bulk materials [3, 4]. The ability of metal nanoparticles to lower the activation energy of a reaction, and thus increase the rate of reaction and yield desired products, could be attributed to their high surface-area to volume ratio, amongst a number of other explanations. Metal nanoparticles as catalysts result in higher turnover frequencies, per weight, as well as a potential increase in selectivity [5-8].

Around 15% of dyes is lost in the textile industry during the dyeing process and is released into the wastewater. The major techniques of removing these dyes in wastewater are oxidation, adsorption, and flocculation or precipitation. Those approaches are used in bleaching processes and the chemical oxidation applied in organic dye degradation can be performed as pre- or posttreatment [9-11]. Hydrogen peroxide, a high potential oxidizing agent, generates radicals which leads to degradation of organic dyes [12, 13].

Morin, a bioflavonoid dye present in tea, fruits, and vegetables, is used in here as model compound to evaluate the catalytic activity of silver and gold nanoparticles in an oxidation process using hydrogen peroxide as oxidizing agent [14].

The synthesis of silver and gold nanoparticles encapsulated into dendrimers is well known and their catalytic activities were reported in many reaction types. It was established that the catalytic activities described was related to their surface area and concentration [15-17].

Here, we report the synthesis of NH₂ terminated generation five dendrimer (PAMAM) encapsulated silver and gold nanoparticles. The characterization of these metal nanoparticles were performed by UV-vis spectroscopy, Fourier transform infrared spectroscopy, and high-

resolution transmission electron microscopy. The balance between metal ions and dendrimer or template was established by spectrophotometric titration monitored via UV-vis spectroscopy.

A full kinetic evaluation of silver and gold nanoparticles was performed on the oxidation of morin by hydrogen peroxide. The binding energy of the reactants onto the nanoparticle surfaces was determined. Thus, modeling the kinetic data to the Langmuir-Hinshelwood mechanism is described. [18, 19]. To the best of our knowledge, this is the first full kinetic elucidation of a liquid phase oxidation reaction catalyzed by Ag and Au nanoparticles.

Experimental

Materials and instruments

All chemicals were commercially available and used without further purification. Fifth generation amine-terminated poly(amido-amine) dendrimer, obtained as 5 wt.% solution in methanol was purchased from Sigma-Aldrich. The volatiles were removed *in vacuo* at room temperature. Morin hydrate ($C_{13}H_{10}O_7 \times H_2O$, $\geq 98.0\%$), silver nitrate (AgNO₃, $\geq 99.0\%$), chloroauric acid (HAuCl₄·3H₂O, $\geq 99.9\%$), and sodium borohydride (NaBH₄, $\geq 98.0\%$) were purchased from Sigma-Aldrich. Sodium hydroxide pellets (NaOH, $\geq 99.86\%$), hydrochloric acid 30% (HCl, $\geq 31.79\%$), and hydrogen peroxide 30% (H₂O₂, 30-35%) were purchased from Promark Chemicals. Sodium hydrogen carbonate (NaHCO₃, $\geq 99.86\%$), and anhydrous sodium carbonate (Na₂CO₃, $\geq 99.5\%$) were obtained from Merck Laboratories. Deionized water was acquired from an in house Milli-Q system (18.2 MΩ·cm) was used as solvent in all solutions prepared. All chemicals used in this work were of analytical-reagent grade.

Micropipettes from Physiocare concepts (Eppendorf Research Plus) were used to transfer all aqueous solutions. An Orion pH meter model 420A was applied to determine the solution pH at room temperature. Atomic Absorption Spectrometry (Perkin Elmer Precisely, A. Analyst 400, made in Germany) was used to determine the metal ion and nanoparticle concentration. UV-vis (Shimadzu UV-1800 spectrophotometer) was applied to monitor the synthesis process and the reaction, and characterize the nanoparticle synthesis. FT-IR spectroscopy was performed on a Bruker Tensor 27. HR-TEM analysis was performed on a JOEL JEM-2100F electron microscope with accelerating voltage of 200 kV using a copper grid. The average size of the nanoparticles

was determined using Image-J software [20]. All catalytic data were recorded and fitted using Kinetic Studio and Origin Pro 8.5 graphing and modeling software [21, 22]. An Ultra High Performance Liquid Chromatography UHPLC (Nexera Series (8030) Triple Quadrupole Instrument) from Shimadzu was used to identify the reaction products.

Synthesis of nanoparticles

The interaction of tertiary amino groups located inside the dendrimer with metal ion is an important aspect in the synthesis of dendrimer encapsulated nanoparticles. Spectrophotometric titration reported in previous work was conducted to determine the loading capacity of the dendrimer [23, 24]. Aliquots of 0.5 mM of both salt solutions were added successively into 3 mL of dendrimer solution (10 μ M, 3×10⁻⁵ mmol), to investigate the interaction between the inner amino group and metal ion. The titrations were performed in triplicate.

The synthesis of a colloidal solution of dendrimer encapsulated silver and gold nanoparticles were adapted from the literature [25, 26]. Two solutions of 5 μ M dendrimer in 50 mL (2.5×10⁻⁴ mmol), acidified with hydrochloric acid (0.2 M, pH~2), were prepared as template for each metal nanoparticle. Exactly, 231 μ L of silver nitrate (1.08 M, 2.5×10⁻² mmol) or 306 μ L of chloroauric acid (0.08 M, 2.5×10⁻² mmol) were added to each dendrimer solution. The metal nanoparticle formation from the individual metal ions was performed by a chemical reducing process. An aqueous solution of 1 M sodium borohydride (250 μ L, 0.25 mmol) was used as solvent in the preparation of 1 M sodium borohydride (0.3 M) was used as solvent in the preparation of 1 M sodium borohydride (250 μ L, 0.25 mmol), used as reducing agent for the synthesis of gold nanoparticles. All the catalytic studies were performed using the same stock solution.

Catalytic oxidation of morin

A set volume of catalyst, 300 μ L of AgDENs (0.49 μ M, 1.47×10⁻⁶ mmol) or 400 μ L of AuDENs (0.62 μ M, 1.86×10⁻⁶ mmol), was used to evaluate the catalytic oxidation of morin. A UV-vis spectrophotometer was used to monitor the process by recording the absorbance at λ 410 nm, the maximum morin absorbance, for three hours. Exactly, 180 μ L of hydrogen peroxide (24 mM, 4.32×10⁻³ mmol) was used as oxidant. A volume of 300 μ L of carbonate buffer solution (50 mM, 0.15 mmol) was used to assure the stability of hydrogen peroxide by maintaining the pH at 10

[27]. A freshly prepared solution of 1 mM morin was diluted to 0.05-0.15 mM for all evaluations. A required volume of deionized water was added unto each cuvette to the total of 3 mL. At least 15 minutes were allocated for temperature equilibration of the reactants into the UV-Vis compartments and morin solution was added last. For the uncatalyzed reaction, the nanoparticle solution was replaced with a dendrimer solution of the same concentration. The stability of the colloidal catalysts was investigated by three recycle runs of 5 mL of both silver and gold nanoparticles, $(0.49 \ \mu\text{M}, 2.45 \times 10^{-6} \ \text{mmol})$ and $(0.62 \ \mu\text{M}, 3.10 \times 10^{-6} \ \text{mmol})$ respectively. The catalyst solutions were dialyzed against 50 mL of aqueous solution of all reactants (morin (0.05 mM, $2.5 \times 10^{-3} \ \text{mmol})$, hydrogen peroxide (24 mM, 1.2 mmol), and carbonate buffer (50 mM, 2.5 mmol)) at room temperature.

Kinetic analysis

Previous work reported the use of dendrimers as template in synthesis of metal nanoparticles, and the catalytic activity related to the metal nanoparticles was demonstrated, as well as the fact that the dendrimer does not present a diffusion barrier to the diffusion of reactant to the metal nanoparticle surface [28]. To evaluate catalytic activity of silver and gold nanoparticles, the oxidation of morin has been used as a model reaction. The catalytic oxidation of morin was monitored using time resolved UV-vis spectroscopy by recording the relative decrease of adsorption at λ 410 nm which is directly proportional to the concentration. The kinetic analysis of the catalytic oxidation reaction is mathematically described by equation 1.

$$-\frac{d[Morin]}{dt} = k \cdot [Morin]^n \cdot [H_2O_2]^m \cdot [Cat]^l = k_{obs} \cdot [Morin]^n \quad (1)$$

Where, k_{obs} is the observed rate constant of the reaction, and n, m, and l are order of the reaction. By using a large concentration of the hydrogen peroxide compared to the morin, we assume that the concentration of hydrogen peroxide remains constant. It is also assumed that the catalyst concentration remains constant. Therefore, the reaction appeared to be *pseudo*-nth order (n=1) [29-31] with the absorbance versus time, as measured at λ 410 nm, being perfectly described by equation 2.

$$-ln\frac{A_t - A_{\infty}}{A_0 - A_{\infty}} = k_{obs} \cdot t \tag{2}$$

The basic buffer system has been used to assure the adsorption of morin on the catalyst surface and to maintain stable hydrogen peroxide while the reaction is proceeding. A study of acid and alkaline buffer systems on morin oxidation catalyzed by manganese oxide nanoparticles resulted to the same observed rate constants [32]. Therefore, the carbonate buffer system was applied to maintain the solution pH at 10. The equilibrium between hydrogen carbonate and hydrogen peroxide forms the peroxocarbonate ion which is more active than hydrogen peroxide [33, 34]. The formation of the peroxocarbonate ion results in a small increase of observed rate constant.

The adsorption of the reactant on the catalyst surface is necessary for the reaction. The active surface area may be calculated by considering the average diameter of the nanoparticles based on the assumption that they are spherical. The catalyst concentration is directly proportional to the observed rate constant. That may be explained by the fact that the k_{obs} is directly related to both the concentration and total surface area of the nanoparticles. Thus equation 1 could be expressed as equation 3.

$$-\frac{d[Morin]}{dt} = k \cdot S \cdot [Morin]$$
(3)

Where k, and S are surface area normalized rate constant per unit volume of solution, and total surface area of the system, respectively.

A main prerequisite of the above analysis is that the rate-determining step is the reaction on the catalyst surface. This means that the diffusion of the reactants to and from the nanoparticle surface should be much faster than the chemical reaction on the surface. Diffusion limitation of the process can be ruled out by calculating the second Damköhler number (*DaII*), which assesses the competition between the chemical reaction and mass transport (equation 4) [28, 35, 36].

$$DaII = \frac{reaction \, rate}{diffusion \, mass \, transfer \, rate} = \frac{k_{obs} \cdot [Morin]^{n-1}}{\beta \cdot a} \tag{4}$$

Where k_{obs} is the observed rate constant, [Morin] is the morin concentration, n is the reaction order (here, *pseudo*-first order), β is the mass transport coefficient, and a is the total area of the interface. The mass transfer coefficient is obtained by the diffusion coefficient divided by characteristic length scale, δ , over which mass transfer occurs [37]. For estimation of β , it is expedient to use the diameter of the generation five amino terminated PAMAM dendrimer as the

magnitude ($\delta = 5.4$ nm) [38], and the diffusion coefficient reported for morin is 5.45×10^{-10} m²/s [39]. Hence, β is given as 0.101 m/s. The observed rate constant for silver and gold nanoparticles, 1.51×10^{-4} s⁻¹ and 1.53×10^{-4} s⁻¹, respectively, which were derived from 0.1 mM of morin (3 mL, 3×10^{-3} mmol) and 24 mM (3 mL, 7.2×10^{-2} mmol) of hydrogen peroxide at 25 °C (pH=10). The value calculated for the total area interface is 315.87 m⁻¹ and 277.83 m⁻¹ for silver and gold nanoparticles, respectively. The estimated values for *DaII* were 4.74×10^{-7} and 5.49×10^{-7} for silver and gold nanoparticles, respectively. Those values are far below unity, indicating that the oxidation of morin is conducted in the kinetic domain.

The liquid phase chromatographic analysis was conducted in order to identify the product formation pathway. Exactly, 0.1 mM of morin $(1 \times 10^{-3} \text{ mmol})$, 50 mM of carbonate buffer $(2.5 \times 10^{-2} \text{ mmol})$, 30 mM of hydrogen peroxide $(1.5 \times 10^{-2} \text{ mmol})$, and 0.62 μ M of gold nanoparticles $(0.31 \times 10^{-7} \text{ mmol})$ were mixed and the mixture was diluted to 50 mL with deionized water. After 45 minutes, a mixture was sampled for investigation. The UHPLC trace at 7.567 tR (MS heat block temperature 300 °C) shows the intermediate product (2-(2,4-dihydroxyphenyl)-2,5,7-trihydroxychroman-3,4-dione) which decomposes to 2,4-dihydroxybenzoic acid (β -resorcyclic acid), and 2,4,6-trihydroxybenzoic acid (phloroglucinol carboxylic acid). These benzoic acids can undergo further oxidation processes [40-42]. Figure 1 shows the MS spectrum and oxidation pathway of morin oxidation. However, the first stage of the morin oxidation (λ 410 nm) is of interest for our kinetic study.

The kinetic analysis was investigated in terms of the Langmuir-Hinshelwood model, which consist of the adsorption of the reactant to the catalyst surface in order to form the active species. The catalyst surface presents the active sites, which could occupy one reactant and there is no interaction between adsorbate species on adjacent sites [43-45]. Figure 2 displays the essential assumption of this model. A competitive adsorption takes place between the reactants to occupy the active sites. Therefore, the rate-determining step of the catalytic oxidation occurs on the surface of the metal nanoparticles. The process has been investigated in detail by measuring two different sets of reactions. By maintaining constant concentration of hydrogen peroxide, k_{obs} was measured while varying the concentration of morin. Inversely, morin concentration was kept constant while the concentration of hydrogen peroxide was varied.

The interaction of the reagents with the surface of the metal nanoparticles can be expressed in terms of a Langmuir adsorption isotherm [46]. The adsorption of the reactants modeled in terms of the Langmuir-Hinshelwood mechanism can be expressed mathematically by

$$-\frac{d[Morin]}{dt} = k \cdot S \cdot \theta_{Morin} \cdot \theta_{H_2 O_2}$$
(5)

Where θ_{Morin} and $\theta_{H_2O_2}$ are the surface coverage of the nanoparticles by the reactants, morin and hydrogen peroxide, respectively. The surface coverage of the metal nanoparticles is given by

$$\theta_{Morin} = \frac{(K_{Morin} \cdot [Morin])^n}{1 + (K_{Morin} \cdot [Morin])^n + (K_{H_2O_2} \cdot [H_2O_2])^m}$$
(6)

$$\theta_{H_2O_2} = \frac{\left(K_{H_2O_2} \cdot [H_2O_2]\right)^m}{1 + (K_{Morin} \cdot [Morin])^n + (K_{H_2O_2} \cdot [H_2O_2])^m}$$
(7)

Here, K_{Morin} , [Morin]; and K_{H2O2} , [H₂O₂] are the adsorption equilibrium constant and concentration of each reactant, morin and hydrogen peroxide, respectively. Sips exponents n and m (not order) relate to the heterogeneity of the sorbent [47]. Those express the adsorption isotherm which is reduced to a linear adsorption isotherm when both exponents equal to unity [47].

Thus equation 1 can be rewritten as equation 8.

$$-\frac{d[Morin]}{dt} = \frac{k \cdot S \cdot (K_{Morin} \cdot [Morin])^n \cdot (K_{H_2O_2} \cdot [H_2O_2])^m}{\{1 + (K_{Morin} \cdot [Morin])^n + (K_{H_2O_2} \cdot [H_2O_2])^m\}s^2} = k_{obs} \cdot [Morin] (8)$$

And thus, k_{obs} can be written as equation 9.

$$k_{obs} = \frac{k \cdot S \cdot (K_{Morin})^n \cdot [Morin]^{n-1} \cdot (K_{H_2O_2} \cdot [H_2O_2])^m}{\{1 + (K_{Morin} \cdot [Morin])^n + (K_{H_2O_2} \cdot [H_2O_2])^m\}^2}$$
(9)

Equation 9 demonstrates that the observed rate constant, k_{obs} , is related to the rate constant on the metal nanoparticles' surface; k, a normalized surface area of particles; S, and the concentration and equilibrium constant of each reactant, morin and hydrogen peroxide.

The dependency of the rate constant k and k_{obs} on the temperature, T, can be expressed through the Arrhenius equation (10)

$$k = k_0 \cdot e^{\frac{-E_A}{R \cdot T}} \tag{10}$$

Where, k_o is the frequency factor of the surface reaction and E_A describes the activation energy of the surface reaction. The Erying equation was used to determine the thermodynamic parameters (enthalpy and entropy) on the catalyst surface and for the reaction process (both the kinetic rate on the surface and the observed rate constant) [48]. The Eyring equation is written in equation 11.

$$k_n = 2 \cdot 10^{10} \cdot T \cdot e^{\frac{\Delta S^{\#}}{R}} \cdot e^{\frac{-\Delta H^{\#}}{R \cdot T}}$$
(11)

Where the rate constant of the reaction, k_n , related to temperature, $\Delta H^{\#}$ and $\Delta S^{\#}$ are the enthalpy and entropy of activation of process, R is the universal gas constant.

The dependency of the equilibrium constant of both reactants on temperature can be evaluated from the application of Van't Hoff's equation. This application leads to obtaining the enthalpy and the entropy of both reactants of the process. Van't Hoff's equation is given in equation 12, where $\Delta G^{\#}$ is the Gibbs energy of activation of the reactants.

$$\ln K = -\frac{\Delta G^{\#}}{R \cdot T} = \frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{R \cdot T}$$
(12)

Results and Discussion

The spectrophotometric titration performed highlights that the internal amino group interacts with silver and gold cations by coordination. Table 1 presents the value of number internal amino groups, and the equilibrium constant established, figure 3 shows the absorbance for each interaction and the data plotted using the binding isotherm equation reported previously [24]. The synthesis of metal nanoparticles encapsulated in dendrimers can be subdivided at three steps. All these steps can be monitored by UV-vis spectrophotometry. Figure 4 shows the spectra for the silver and gold nanoparticle synthesis. Initially, the spectrum of dendrimer solution was recorded, no absorbance peaks were detected. The second step is the interaction of inner amino group with metal ions. The UV-vis spectra illustrate this interaction by showing the absorbance at λ 290 nm and λ 315 nm for silver and gold ions respectively. A final step, is the formation of encapsulated metal nanoparticles using a chemical reducing agent. The formation of metal nanoparticles was detected by UV/vis spectroscopy by recording the maximum absorbance at λ

420 nm and λ 519 nm for silver and gold nanoparticles, respectively. The shift of colorless solution to light yellow indicates the formation of silver nanoparticles. Similarly, a shift of light yellow solution to red solution indicate gold nanoparticle formation. The molar ratio of dendrimer-metal nanoparticles synthesized was 100 equivalents of metal ions. The purification of the nanoparticles was performed by dialyzing against deionized water overnight [49, 50]. The concentration of the purified nanoparticles was determined by atomic absorption spectroscopy analysis as 4.893 ± 0.034 and $4.652 \pm 0.081 \mu$ M of silver and gold nanoparticles, respectively.

FTIR analysis was conducted to assess the interaction of metal cations with internal amino groups [51]. The coordination of silver ions with tertiary amine groups was ascertained by shifts of adsorption bands observed from v 1368-1457 cm⁻¹ to v 1363-1443 cm⁻¹, whereas gold ion coordination was detected from v 1355-1373 cm⁻¹ to v 1372-1395 cm⁻¹ and from v 1127 cm⁻¹ to v 1137 cm⁻¹. The carbonyl group interaction was observed from v 1616 cm⁻¹ to v 1625 cm⁻¹, and v 1590 cm⁻¹ to v 1614 cm⁻¹ for silver ion and gold ion respectively (see supporting information, figures S1).

Three trials were performed for each titration. The binding isotherm parameters were determined by fitting the data of each trial individually. The number of internal amino group of dendrimer (N), and the equilibrium constant (*K'*) were determined. Equilibrium constant values are in units of 10 μ M⁻¹ dendrimer. The average of three trials ± the standard deviation is obtained for each data set.

High-resolution transmission electron microscopy analysis was performed to determine the size distributions of both nanoparticles, EDX analysis (on copper gird) was also performed to confirm the metal nanoparticle presence in colloidal solution. Figure 5 presents the micrograph obtained for each catalyst, and the average size was determined using Image J software. The average size calculated for silver and gold nanoparticles was 3.8 ± 0.5 and 2.8 ± 0.4 nm, respectively. A minor amount of chlorine, possibly from the HCl used during the first step of the synthesis, was detected in both catalyst solutions, and copper detected was from the copper grid (see supporting information, figure S2).

The specific surface area for the catalytic reaction involving both catalysts was calculated using the size distribution. The primary amine group, located on the periphery of the dendrimer, controls the solubility and the diffusion of compounds into the dendrimer. Those attributes allow the use of dendrimers as template for nanoparticles. A low concentration of catalyst was considered in each catalytic run which prevented Ostwald ripening and maintained the catalytic activity of total surface area, and additionally increased the stabilization provided by the dendritic structure.

The UV-vis spectra, figure 6, illustrate the catalytic oxidation of morin by describing the absorbance decrease at λ 410 nm and the kinetics of oxidation of morin by recording the relative adsorption at λ 410 nm as a function of time. The rate for the catalyzed and the uncatalyzed reaction demonstrated that the oxidation without any catalyst does not proceed in the time frame of the experiment. To evaluate the molecular oxygen interference during the catalytic process, air was used as an oxidizing agent. The UV-vis spectra of the catalytic oxidation of morin by air performed for 2 h 50' show no significant decrease of absorbance at λ 410 nm (see supporting information figure S3).

The evaluation of catalyst stability during the course of reaction was determined using three consecutive runs performed on the gold nanoparticle catalyst and demonstrated that the metal nanoparticles remain active after the first run. Note that these runs were performed inside a dialysis membrane, and thus the rates are significantly lower than during kinetic runs. The catalyst located inside a dialysis bag did not undergo additional purification for the next run. The observed rate constant calculated was $(2.27 \pm 0.05) \times 10^{-4} \text{ s}^{-1}$, $(1.72 \pm 0.04) \times 10^{-4} \text{ s}^{-1}$, and $(1.38 \pm 0.04) \times 10^{-4} \text{ s}^{-1}$ for the first, second, and third run respectively (Figure 7). In addition, no metal was observed outside the membrane bag, as determined by AAS. The observed rate constant is the slope obtained by constructing the plot of relative absorption recorded at λ 410 nm as function of time using equation 2. The atomic adsorption on the solution outside the bag showed no appreciable gold concentration. We therefore conclude that leaching and/or Ostwald ripening does not occur during catalysis and the catalysts remained stable.

The linear relationship between k_{obs} and catalyst concentration indicates that the catalytic process occurs on the surface of the nanoparticles and depends on the total surface area of the nanoparticles. This observation assesses the reliability of the rate constant data and proves that the metal nanoparticles play the role of a true catalyst in the catalytic oxidation of morin. The dependency of observed rate constant on the catalyst concentration was evaluated at 25 °C with an aqueous solution of 0.1 mM of morin (3 mL, 3×10^{-4} mmol), 24 mM of hydrogen peroxide (3 mL, 7.2×10^{-2} mmol), and 50 mM of carbonate buffer (3 mL, 0.15 mmol). Figure 8 shows the linear relationship between the observed rate constant and the catalyst concentration. A diffusion limitation zone was detected in case of silver nanoparticles, whereas no diffusion limitation zone was observed for gold nanoparticles. These experiments also support the conclusion drawn from the calculated values for the second Damköhler number, namely that the following kinetic investigation takes place in the kinetic domain, for the chosen catalyst and substrate concentrations, and that there is no interference from diffusion.

Two sets of experiments were performed at three different temperatures for the kinetic investigation. First, the influence of morin concentration was evaluated by varying the concentration from 0.05 mM to 0.125 mM at two constant concentrations of hydrogen peroxide (24 mM and 48 mM). In the second set of experiments, the effect of hydrogen peroxide concentration was analyzed, varying the hydrogen peroxide concentration (from 4-60 mM) at constant concentration of morin (0.05 mM and 0.1 mM). The observed rate constant as function of the concentration of either morin (a, b) or hydrogen peroxide (c, d) is shown in figures 9 and 10 for each catalyst involved. The data points were fitted using the Langmuir-Hinshelwood model (eq. 9). The determined parameters are summarized in Table 2. We found that an increase of morin concentration leads to a decrease in the observed rate constant, whereas an increase of hydrogen peroxide results in an increase of the observed rate constant, which levels off at higher concentrations. Those observations can be explained by assuming that both reactants compete for the same site on the catalyst, and only the absorbed species participate in the reaction. If most of the active sites are occupied by one of the reactants, the observed rate constant will decrease.

The accuracy of catalytic oxidation of morin modeled by the Langmuir-Hinshelwood mechanism was assessed in more detail by plotting k_{obs} . [Morin] versus the product of θ_{Morin} . θ_{H2O2} according to equation 9. The slope of the straight lines provides the product of rate constant and the

normalized surface area of the metal nanoparticles involved. Given the error propagation through the calculations of both adsorption isotherms leading to errors in θ_{Morin} and $\theta_{H_2O_2}$, respectively,

The kinetic analysis at different temperatures leads to an investigation of activation energy on catalyst surface and of the reaction. The adsorption constant for morin onto the catalyst surface is related on each catalyst involved. The dependency of the adsorption constant of morin onto the silver nanoparticle surface is inversely proportional to the temperature. The adsorption constant of morin onto the gold nanoparticle surface shows a direct proportional relationship. The adsorption constant of hydrogen peroxide for both catalysts is directly proportional to the temperature. The rate constant and thermodynamic constant of morin onto manganese oxide nanoparticles surface reported by Ballauff group show the same thermal dependency as the silver nanoparticle. Table 3 summarizes the kinetic parameters, and the thermodynamic parameters calculated for the reactants.

The uncatalyzed oxidation of morin by hydrogen peroxide in carbonate buffer solution describes the activity due to formation of the peroxocarbonate ion, the activation energy calculated using equation 10 is 73.41 kJ/mol. The activation energy obtained for the catalyzed process, as determined from the observed rate constants is much higher than the activation energy obtained with the rate constant on the catalysts surfaces (table 3). That can be explained by the fact that the observed rate constant is related to the rate constant on the catalyst surface, and the adsorption constant of all reactants. Figure 12 shows the Arrhenius plots, the observed rate constant versus temperature (A), and the rate constant on catalyst surface versus temperature (B). The thermodynamic parameters were calculated through the relationship between rate constant and thermodynamic parameters established by utilization of the Erying equation. The enthalpy in the uncatalyzed process is higher than the catalyzed process.

The enthalpy and entropy of the reactions were determined through equation 12. The adsorption enthalpies of morin and hydrogen peroxide on silver nanoparticles describes an exothermic and endothermic process for each of the reactants. The adsorption enthalpies on gold nanoparticles for both reactants are endothermic. Figure 13 shows the graph of adsorption constant versus temperature of each reactant constructed using the Van't Hoff's equation. The hydrogen

peroxide adsorption on the surface of the metal catalyst is a complicated process that involves several steps, the thermodynamic parameters determined therefore need further analysis.

Conclusions

This study consists of the evaluation of catalytic activity of silver and gold nanoparticles encapsulated into dendrimer cavities. The catalytic oxidation of morin by hydrogen peroxide in aqueous solution was performed as a model reaction and the analysis of the kinetic data suggests that the rate-determining step occurs on the catalyst surface. The use of dendrimers as a template for the synthesis of monodisperse metal nanoparticles did not exhibit a diffusion barrier for the reactant to adsorb onto the catalyst surface. The Langmuir-Hinshelwood model was evaluated to understand the adsorption of reactants onto the catalyst surface. The surface reaction and adsorption process of reactants are described by the kinetic constant, and thermodynamic adsorption constants for both reactants. The adsorption process of morin onto the metal nanoparticle surface is related to the type of nanoparticles involved. The encapsulated silver nanoparticles (-27.54 kJ·mol⁻¹) show a similar thermal adsorption process (exothermic) as manganese oxide nanoparticles (-19.8 kJ·mol⁻¹), whereas the adsorption of morin onto encapsulated gold nanoparticle surface is an endothermic process. The lower activation energy of the surface rate k, by both encapsulated metal nanoparticles, compared to the manganese oxide nanoparticles (45.8 kJ·mol⁻¹) [32], indicated the passivity of the dendrimer and high activity of the encapsulated nanoparticles.

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Figure 1: (A) The MS spectrum of reaction intermediate in catalytic oxidation of morin, and (B) the morin oxidation pathway as suggested by Colombini and coworkers [40].



Figure 2. Langmuir-Hinshelwood mechanism of the catalytic oxidation of morin by hydrogen peroxide on the surface of the encapsulated metal nanoparticles. Hydrogen peroxide reacts on the catalyst surface to form the adsorbed active species. Concomitantly, morin adsorbs onto unoccupied sites of the nanoparticles surface. The adsorption/desorption of both reagents on the metal nanoparticle surface is assumed to be a fast process.



Figure 3. Spectrophotometry titration of metal ions into dendrimer. UV/vis spectra of silver ions (A), and gold ions (B) titrated into G5-PAMAM dendrimer. Best fit using a binding isotherm equation of silver ions (C) and gold ions (D) interacting with internal amino functionalities. The data points represent the average of three independent runs.



Figure 4. UV/vis spectra of dendrimer encapsulated nanoparticle syntheses. Figure A presents encapsulated silver nanoparticle and figure B encapsulated gold nanoparticle syntheses. (1) The dendrimer solution spectrum. (2) Spectra of the metal precursor's solution. (3) Absorbance of interaction of internal amino groups versus metal ions in each case. (4) Metal encapsulated nanoparticles.



Figure 5. HRTEM micrograph of dendrimer encapsulated metal nanoparticles and the corresponding histogram for the size distribution. (A), and (B) silver nanoparticles micrograph and their average diameter ($3.8 \pm 0.5 \text{ nm}$) obtained by counting ≥ 140 particles. (C), and (D) presents the micrograph and average diameter ($2.8 \pm 0.4 \text{ nm}$) of gold nanoparticles by counting ≥ 150 particles.



Figure 6. The UV-vis spectra of catalytic oxidation of morin (0.1 mM) by hydrogen peroxide (24 mM) with pH stabilized at 10 using carbonate buffer (50 mM) using gold nanoparticle (0.62 μ M) as catalyst at 25 °C. The spectrum shows a decrease in characteristic absorption maximum at λ 410 nm of morin with time (A). The relative adsorption recorded at 410 nm as function of the reaction time (B).



Figure 7. Stability of metal nanoparticles evaluated using oxidation of morin at room temperature. The evaluation performed on three recycle runs of catalyst contained in a dialysis bag.



Figure 8. (A) The influence of silver nanoparticle concentration (0.49 μ M) on morin oxidation at 25 °C. (B) The influence of gold nanoparticle concentration (0.62 μ M) in same reaction and temperature. The green star in both plots indicates the catalyst concentration used for the kinetic investigation, and red triangle in (A) shows the diffusion limitation zone domain.



Figure 9. Dependence of the observed rate constant, k_{obs} , for the silver catalyzed reaction, on the concentration of morin at constant concentration of hydrogen peroxide (24 mM in a, 48 mM in b) and on the concentration of hydrogen peroxide at constant concentrations of morin (0.05 mM in c, 0.1 mM in d) at different temperatures. The lines represent the best fits of the Langmuir-Hinshelwood model.



Figure 10. Dependence of the observed rate constant, k_{obs} , for the gold catalyzed reaction, on the concentration of morin at constant concentration of hydrogen peroxide (24 mM in a, 48 mM in b) and on the concentration of hydrogen peroxide at constant concentrations of morin (0.05 mM in c, 0.1 mM in d) at different temperatures. The lines represent the best fits of the Langmuir-Hinshelwood model.



Figure 11. The accuracy of the data fitted to the Langmuir-Hinshelwood model at constant morin concentration (A) for Ag and (B) for Au, as well as constant peroxide concentration (C) for Ag and (D) for Au. The straight line is the product of rate constant of catalyst surface and normalized surface of catalyst.



Figure 12. The thermal dependency of the observed rate constant (A), and the rate constant on the catalyst surface (B).



Figure 13. The adsorption constant of morin and hydrogen peroxide versus the temperature established for the thermodynamic parameter determination.

PAMAM-NH ₂	(M ⁺ⁿ) _x	Binding isotherm parameters		
pH=2.3		N	K' (× 10 ⁻³)	
G5	$(Ag^{+})_{140}$	109 ± 11	0.91 ± 0.06	
	$(Au^{+3})_{140}$	115.02 ± 0.02	8 ± 1	

Table 1. Total loading capacities of the 0.5-1 ANIANI-1012	Table	1. Tota	l loading	capacities	of the	G5-PAMAM-NH ₂
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Table 2. Summary of the rate constant, k, and the adsorption constant of morin and hydrogen peroxide (K_{Morin} and K_{H2O2}) at different temperatures by fitting the experimental data to the Langmuir-Hinshelwood model for silver nanoparticles and gold nanoparticles shown in figure 9 and 10, respectively.

Catalyst	T(°C)	Parameters					
Catalyst		$\boldsymbol{k} \; (\text{mol/m}^2 \cdot \text{s})$	<i>K_{Morin}</i> (L/mol)	$K_{H_2O_2}(L/mol)$	n	m	
	10	$(0.63 \pm 0.29) \times 10^{-10}$	90+66	0.03 ± 0.01	1.00 ±	0.91 ±	
	10	5	9.0 ± 0.0	0.05 ± 0.01	0.01	0.07	
AgDENs	20	$(0.75 \pm 0.01) \times 10^{-10}$	26+16	0.15 ± 0.11	1.00 ±	0.96 ±	
		5	2.0 ± 1.0	0.15 ± 0.11	0.02	0.03	
	30	$(1.25 \pm 0.53) \times 10^{-10}$	26 ± 20	0.23 ± 0.17	1.00 ±	0.99 ±	
		5	2.0 ± 2.0	0.25 ± 0.17	0.01	0.01	
AuDENs	10	$(0.98 \pm 0.52) \times 10^{-10}$	11 + 05	0.15 + 0.07	1.00 ±	0.99 ±	
		5	1.1 ± 0.5	0.15 ± 0.07	0.01	0.01	
	20	$(1.24 \pm 0.39) \times 10^{-10}$	32 + 20	0.10 + 0.09	1.00 ±	0.99 ±	
	20	5	5.2 ± 2.0	0.17 ± 0.00	0.02	0.01	
	30	$(1.29 \pm 0.53) \times 10^{-10}$	35+17	0.26 ± 0.12	1.00 ±	0.93 ±	
		5	5.5 ± 1.7	0.20 ± 0.12	0.01	0.06	
MnO _x NP a	T(°C)	$k S (\text{mol}\cdot\text{m}^2/\text{L}\cdot\text{s})$	<i>K_{Morin}</i> (L/mol)	$K_{H_2O_2}(L/mol)$	n	m	
	15	$(14+03)\times10^{-6}$ 3866 + 1	3866 + 1157	7 242 ± 20	1.00 ±	0.87 ±	
		(1.1 ± 0.5)×10			0.04	0.03	
	20	$(1.9 \pm 0.4) \times 10^{-6}$	3434 + 1174	34 ± 1174 255 ± 24	1.00 ±	0.86 ±	
			0101 - 1111		0.04	0.02	
	25	$(2.5 \pm 0.8) \times 10^{-6}$	3145 + 1623	175 ± 18	1.00 ±	0.90 ±	
					0.07	0.04	
	30	$(3.5 \pm 1.3) \times 10^{-6}$	2631 ± 1529	165 ± 17	1.00 ±	0.86 ±	
					0.07	0.04	

^a: Manganese oxide nanoparticles [32].

Catalyst	Parameters	E_A (kJ·mol ⁻)	$\Delta H^{\#} (kJ \cdot mol^{-1})$	$\Delta S^{\#}(J \cdot mol^{-1})$	$\Delta \mathbf{G}^{\#(b)} (kJ \cdot mol^{-1})$
Uncatalyzed	k obs (mol/L.s)	73.41 ± 0.05	70.98 ± 0.07	-81.41 ± 0.24	94.84
AgDENs	k _{obs} (mol/L.s)	57.77 ± 6.31	55.82 ± 6.27	-132.58 ± 21.41	94.67
	k (mol/m ² s)	24.78 ± 7.43	21.93 ± 7.52	-218.84 ± 25.69	86.05
	K _{Morin} (L/mol)	-	-27.54 ± 14.31	-84.09 ± 47.21	-2.90
	<i>K</i> _{H202} (L/mol)	-	59.03 ± 24.95 ±	183.35 ± 83.89	5.31
AuDENs	k obs (mol/L.s)	63.26 ± 3.29	61.10 ± 3.29	-113.06 ± 11.23	94.23
	$k(mol/m^2s)$	9.99 ± 3.88	7.52 ± 3.86	-265.98 ± 13.19	85.59
	K_{Morin} (L/mol)	-	48.46 ± 13.31	172.13 ± 47.00	-1.97
	<i>K</i> _{H202} (L/mol)	-	19.94 ± 1.94	54.52 ± 6.58	3.97
MnOxNP ^a	$\frac{k}{(\text{mol}\cdot\text{m}^2/\text{L}\cdot\text{s})}$	45.8 ± 7.0	-	-	-
	K_{Morin} (L/mol)	-	-19.8 ± 8.7	0.2 ± 29.6	-
	<i>K</i> _{H202} (L/mol)	-	-20.8 ± 3.1	-26.1 ± 10.7	-

Table 3. Summary of the temperature dependence of the rate constants and adsorption constants.

^(b): at 0.1 mM Morin and 48 mM H₂O₂ (20 °C)