

EFFECT OF IONIC STRENGTH ON MORPHOLOGICAL CHARACTERISTIC AND THE STABILITY OF Ag/ALGINATE NANOPARTICLES: THEORETICAL REVIEW BASED ON THE ENERGY OF PARTICLE FORMATION

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ABSTRACT

This study evaluated the effect of ionic forces on morphological characteristics and stability of Ag/alginate nanoparticles. The ionic strength was varied by adding 0,17-12 mmol NaCl to the mixture before and after the formation of the Ag/alginate nanoparticles. The synthesis of Ag/alginate nanoparticles is carried out with the aid of microwave irradiation and utilizes sodium alginate as a reducing agent and stabilizer. The results showed that the addition of NaCl to the mixture of metal and alginate precursors before the formation of nanoparticles resulted in a decrease in particle size as NaCl concentration increases, due to a decrease in the rate of particle formation ($J/J_{\max}$) or an increase in the maximum Gibbs ($\Delta G(r^*)$) free energy of particle formation. Conversely, the addition of NaCl after the formation of nanoparticles resulted in an increase in particle size from about 10 nm to 150 nm due to aggregation. The addition of NaCl reduced the stability of the Ag/alginate nanoparticles both before and after the formation of the nanoparticles.

Keywords: Ag Nanoparticle, Alginate, Ionic Strength

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INTRODUCTION

Stabilization of nanoparticles in solution faces challenges because nanoparticles tend to be unstable due to high surface area, so they tend to increase the particle size to achieve lower energy levels.^{1,2} The driving force in the sintering process is associated with an increase in surface free energy compared to the free energy in the bulk system, which causes nanoparticles present in the metastable form and tend to aggregate to form larger nanostructures.³⁻⁵ To obtain nanoparticles with a small size and narrow size distribution, and which are stable for a long time, an effort is needed to prevent aggregation.

Various factors can affect the stability of the nanoparticles against aggregation, for example, experimental conditions (concentrations of metal precursors and reducing agents), pH and ionic strength.⁶ Park studied that the addition of NaCl can affect the particle size and stability of Fe₃O₄ nanoparticles.⁷ In general, according to the DLVO theory^{8,9}, an increase in ionic strength can reduce the stability of the colloid system and promote aggregation because it reduces the repulsion between charges on the surface of the particles.

Au and Ag nanoparticles synthesized with alginate are expected to have a high stability because the alginate has a structure that is bulky enough to allow it to cover the surface of the nanoparticles formed. The stability as a function of ionic strength will be tested in this study, and it is hoped that the presence of alginate as a capping agent can minimize the effect of ionic forces in destabilizing particles.

EXPERIMENTAL

Tools and Materials

Sodium alginate was obtained from Himedia, AgNO₃ p.a, NaOH, HCl, and NaCl were purchased from Merck. Double distilled water was used as solvent throughout the experiment. The optical extinction spectra were measured by an ultraviolet-visible (UV-Vis) spectrophotometer (UV-1700, Shimadzu) in a scanning range of 200 nm to 1100 nm. A particle size analyzer (Malvern Zetasizer, ZEN-1600 and

NanoZS) was used to measure particle size and its distribution. Transmission electron microscopy (JEM-1400, JEOL) was operated at 120 kV to evaluate the morphology of particles. The domestic microwave oven was used in the experiment for nanoparticle synthesis.

Procedures

A total of 1.0 mL of 0.01 M AgNO₃ solution was put into a 100 mL beaker, then 5 mL of 0.50% sodium alginate solution was added and diluted with aquabidest to obtain a solution of 20 mL. After being shaken until completely homogeneous, the solution is put into a high-pressure microwave oven, with a maximum power of 800 W. After being irradiated for several minutes with a power of 50% of the total power, the beaker is removed and cooled to room temperature, then centrifuged at a certain speed (3000 rpm) for 30 minutes. The effect of ionic strength was evaluated by adding NaCl to the precursor mixture (i.e. before the formation of nanoparticles) or by adding NaCl after the formation of the nanoparticles. The amount of NaCl mass was varied from 0.01 g to 0.70 g for the experiment in which NaCl was added before synthesis, and the volume of the 0.1 N NaCl solution was varied from 0.2 mL to 1.0 mL for the experiment in which NaCl was added after the synthesis.

The resulting Ag/alginate nanoparticles were analyzed using a UV-Vis spectrophotometer (at a wavelength range of 300-800 nm), particle size analyzer equipped with zeta potential measurements, and transmission electron microscope.

RESULTS AND DISCUSSION

Previous research has shown that alginate can act as both a reducing agent and a stabilizer for Ag nanoparticles.¹⁰ At optimum conditions, the stability of the Ag nanoparticles synthesized with the alginate can reach two months of storage without significant aggregation.

Addition of NaCl before Synthesis

When adding NaCl to a mixture of metal and alginate precursors (or before the formation of nanoparticles), it can be seen that the concentration of NaCl affects the characteristics of the nanoparticles obtained. The results obtained revealed that the colloid Ag/alginate nanoparticles color becomes thinner and the absorbance decreases drastically, as the volume of NaCl added to the mixture of Ag and alginate precursors increases. This phenomenon may be due to the possibility of Cl⁻ ions binding to Ag⁺ before Ag⁺ reacts with alginate molecules. Since the reaction of Ag⁺ with Cl⁻ produces AgCl which has very low solubility in water ($K_{sp} = 1.80 \times 10^{-10}$), the amount of Ag⁺ available to react with alginate is reduced.

According to the SPR spectrum obtained (Fig.-1A and B), it can be seen that above the NaCl volume of 0.50 mL, the wavelength is shifted towards a lower value. This indicates the formation of smaller particles, as supported by data from particle size testing using PSA (Fig.-1). The reduced particle size can be caused by the reduction of Ag⁺ ions in the system so that the concentration of Ag⁰ formed is not too large and the distance between the Ag⁰ nanoparticles is not too close together so that the probability of aggregation occurring is smaller. This is in accordance with the explanation discussed in the sub-chapter of the effect of Ag⁺ concentration.¹⁰ In this case, the addition of NaCl did not affect the shape of the nanoparticles obtained, as can be seen from the SPR spectrum which has a characteristic range of peak values for spherical Ag⁰ nanoparticles and does not show the formation of more than one peak. According to Park *et al*⁷ who studied magnetite nanoparticles, the decrease in particle size which is influenced by the increasing concentration of NaCl in the synthesis of nanoparticles has a relationship with the rate of nanoparticle formation. The rate of formation of these nanoparticles can be expressed in terms of Gibbs's free energy, and the value is directly proportional to the particle size. This is shown by eqns.-1 to 3.

$$\Delta G(r) = -\left(\frac{4}{3}\right)\pi r^3 \left(\frac{1}{V}\right) k_B T \ln(S) + 4\pi r \gamma \quad (1)$$

V , k_B , T , γ and S are the molecular volume (m³) of the Ag nanoparticles, Boltzmann constant (J/K), absolute temperature (K), face stress (N/m) and the value of saturation, respectively, defined by equilibrium equation between Ag⁺ and OH⁻, assuming that the formation of Ag nanoparticles bypasses interactions with hydroxides because they run in very alkaline conditions (pH 10). In this study, surface tension increased with the increasing concentration of NaCl added (Table-1). Since the values of V , k_B , T ,

and S are constants, over the range of r values studied, the curve pattern $\Delta G(r)$ has higher values at higher NaCl concentrations, as shown in Fig.-1D. The rate of nanoparticle formation (J) is expressed in terms of the maximum Gibbs free energy reached at a certain value of r ($\Delta G(r^*)$), as written in eqn.-2. The value of $\Delta G(r^*)$ can be obtained from the curve in Fig.-1D.

$$J = \frac{dN}{dt} = \left(\frac{2D}{3\delta}\right) \exp\left(\frac{-\Delta G(r^*)}{k_B T}\right) = J_{\max} \exp\left(\frac{-\Delta G(r^*)}{k_B T}\right) \quad (2)$$

$$d \approx Jq$$

q is the reaction time, which is estimated to be the same for every variation of NaCl concentration, assuming the solution is homogeneously dispersed. Thus d (particle size) depends only on the J value.

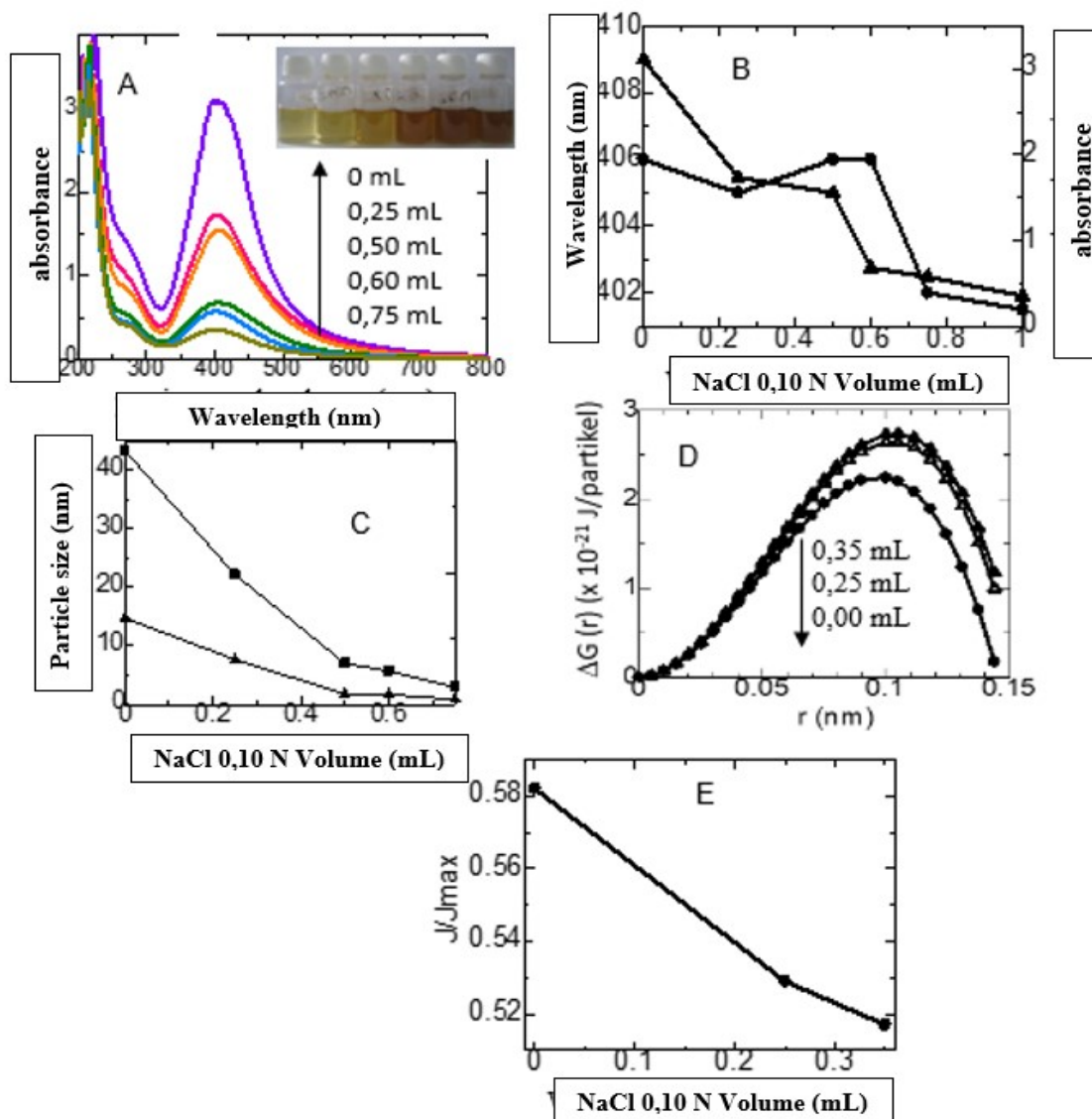


Fig.-1: (A) Corresponding Ag/alginate SPR spectrum (top to bottom). Inset: Colloid Ag/alginate at the addition of 0.10 N NaCl of 0; 0.25; 0.50; 0.60; 0.75 mL before synthesis (from right to left). (B) The relationship between the volume of 0.10 N NaCl with wavelength (▲) and absorbance (■) of the SPR spectrum of the Ag/alginate nanoparticles. (C) The relationship between particle size (■) and peak width (▲) and the volume of NaCl. (D) Gibbs free energy curve as a function of r at various concentrations of NaCl. (E) The $J/J_{\max}$ value as a function of NaCl volume.

Table-1: The Values of Surface Tension, $\Delta G(r^*)$, $\Delta G(r^*)/k_B T$ and $J/J_{\max}$ at Several Variations in NaCl Concentrations

Volume NaCl 0,1 N (mL)	γ (mN/m)	$\Delta G(r^*)$, J	$\Delta G(r^*)/k_B T$	$J/J_{\max}$
0.00	56.81	2.24×10^{-21}	0.540821256	0.582
0.25	59.98	2.64×10^{-21}	0.637173913	0.529
0.35	60.67	2.73×10^{-21}	0.660289855	0.517

By making a plot between $J/J_{\max}$ and the volume of NaCl, it can be seen that as the volume of NaCl increases, the value of $J/J_{\max}$ decreases so that based on eqn.-2 the particle size also decreases (Fig.-1E). This explains the curve pattern obtained in Fig.-1C.

The decrease of the rate of nanoparticle formation was also confirmed by another study in which the NaCl salt was used as a catalyst in the Ag nanoparticles synthesis. At higher concentrations of sodium chloride, AgNPs were formed in less time¹¹. Sharif and Dorrani¹² also found that at a certain concentration of NaCl (5-10 mM), the as-formed AgNPs were smaller than that produced in distilled water.

Addition of NaCl After Synthesis

The addition of NaCl after the formation of Ag^0 (which is coated with alginate) gave different results compared to the addition made simultaneously into the Ag and alginate precursor systems (before the reduction process). Based on visual observations, it can be seen that the greater the addition of NaCl into the Ag-NP/alginate colloid, the colloid color changes to dark brown and then dark green (Fig.-2A). The color change is also related to the intensification of the formation of the second SPR peak at a relatively large wavelength above 600 nm (Fig.-2B). The arrow in Fig.-2A shows that the first peak decreases and the second peak increases with an increasing amount of NaCl. The presence of the second SPR peak indicates the formation of larger particle size and/or the formation of particles other than spherical. By using the Gaussian fitting program, the second peak of the SPR can be shown. As the absorbance increases at wavelengths above 600 nm, the absorbance in the area around 400 nm decreases (Fig.-2C), indicating that the formation of aggregates and/or particles other than spherical is increasing.

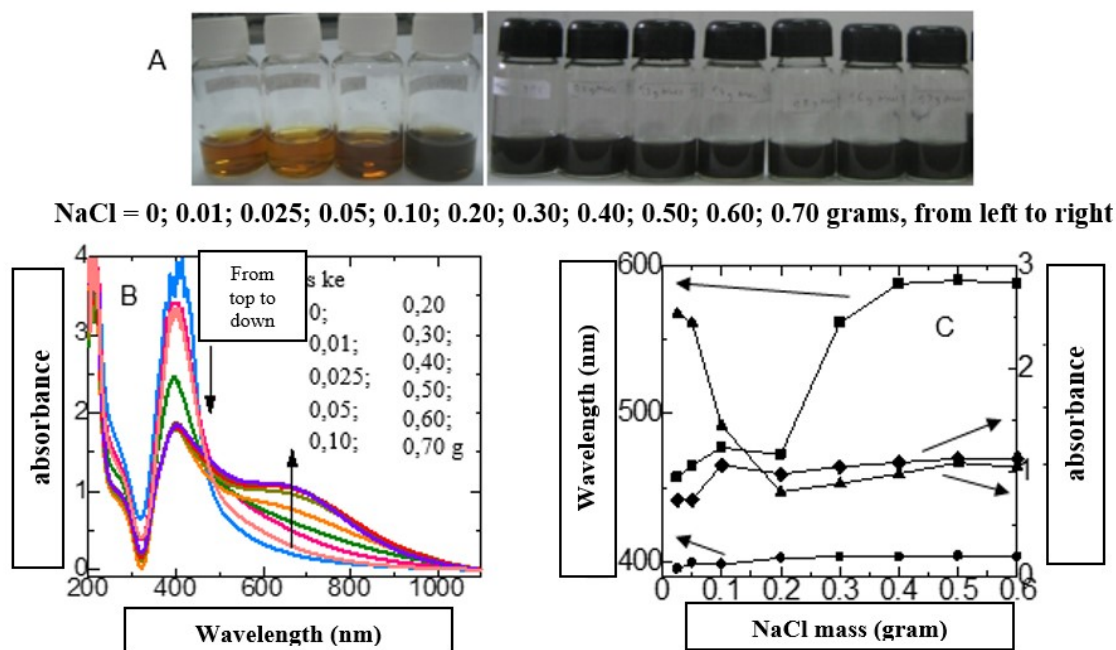


Fig.-2: Appearance of colloid (A) and SPR spectrum (B) of Ag/alginate nanoparticles added with NaCl of 0; 0.01; 0.025; 0.05; 0.10; 0.20; 0.30; 0.40; 0.50; 0.60; 0.70 grams, from top to bottom ($[\text{Ag}^+] = 0.50 \text{ mM}$, $[\text{alginate}] = 0.0375\% \text{ w/v}$, pH 10). (C) Curve relationship between the mass of NaCl with the wavelength ($\bullet$) and the absorbance ($\blacktriangle$) of the SPR 1 peak and the wavelength ($\blacksquare$) and the absorbance ($\blacklozenge$) of the SPR 2 peak

The results of the particle size test using PSA showed that the greater the mass of NaCl added, the particle size increased significantly Fig.-3(A) without any change in terms of % amount. This means that the formation of aggregates goes through the coalescence mechanism. The aggregates formed are visible in the TEM image shown in Fig.-3(B). This is different from the addition of NaCl before synthesis which results in a decrease in particle size, in the addition of NaCl after synthesis there is no interaction between Ag^+ and Cl^- to form AgCl because all Ag^+ has been reduced to Ag^0 . Thus what happens is a decrease in electrostatic repulsion, leading to intense interactions between particles to form aggregates. TEM images also showed that under these conditions particles with shapes other than spherical were not produced. The effect of adding NaCl or increasing ionic strength on the stability of Ag nanoparticles is shown in Fig.-4(A). As more and more NaCl is added, the stability will decrease.

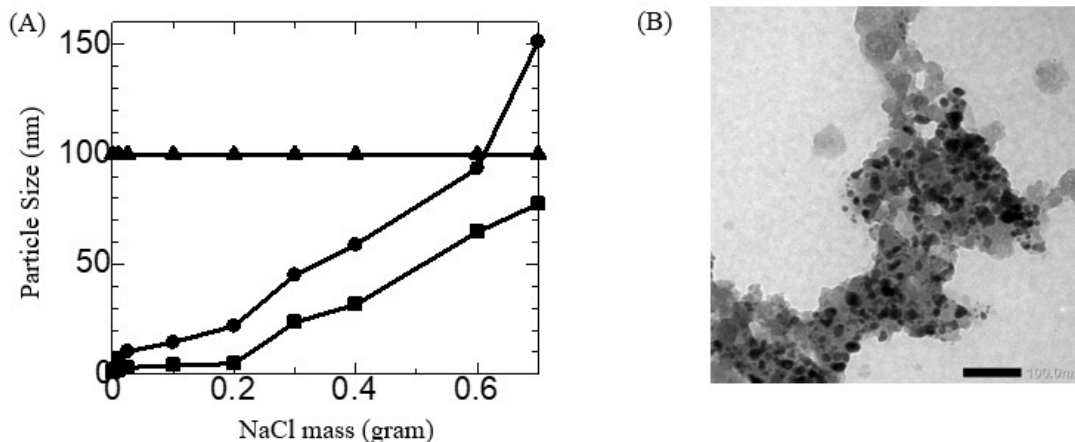


Fig.-3: (A). Relationship between particle size (●), % amount (▲), and peak width (■) for Ag-NP/ alginate added by NaCl. (B). TEM image of Ag-NP/alginate at an addition of 0.50 g NaCl

The effect of adding NaCl or increasing ionic strength on the stability of Ag nanoparticles is shown in Fig.-4(A). As more and more NaCl is added, the stability will decrease. The instability of the nanoparticles observed in a certain storage time can be observed visually from the disappearance of the yellowish color characteristic of Ag nanoparticles. This can be seen in Fig.-4(A). At a fairly small amount of NaCl (0.01 grams), the effect of NaCl on optical characteristics (color, SPR spectra) was relatively small so there was no significant change after being stored for 2 months. However, with the addition of ten-fold NaCl initial concentration, changes began to occur, i.e the yellow color began to fade, and at a larger amount of NaCl, the destabilization of the nanoparticles became more intensive so that the colloid turned clear. The same pattern was also obtained for the addition of NaCl before synthesis.

The destabilization of the Ag nanoparticles can be explained by the zeta potential value at various variations in the amount of NaCl added. Based on Fig.-4(B), with the increasing mass of NaCl added, both before and after the synthesis of Ag nanoparticles, the zeta potential value becomes less negative. Similar results were also obtained in the synthesis of Ag nanoparticles synthesized with sodium citrate in a colloid system at NaCl concentration of 150 mM¹³ and as a monolayer layer on the mica surface¹⁴. A decrease in the value of zeta potential (to be less negative) was also found in sodium alginate biomolecules, in the absence of metal nanoparticles.¹⁵

The difference between the addition of NaCl before and after synthesis can be observed from the magnitude of the change in zeta potential. In the addition of NaCl after synthesis, a relatively small concentration of NaCl (≤ 0.05 M) can also significantly reduce the zeta potential, but a fairly low zeta potential value of around -9 mV is obtained at a much larger NaCl concentration (0.34 M). The zeta potential value can be used to estimate the repulsion energy between Ag nanoparticles using classical DLVO theory. Based on this theory, energy repulsion between nano colloids decreases with decreasing ionic strength, resulting in decreased colloid stability¹⁶. This zeta potential experiment revealed the role of NaCl in modifying surface charge, leading to the attraction between nanoparticles. The influence of

surface charge on the stability of nanoparticles was also explained by a previous study, in which the pH, instead of NaCl, was the cause of the alteration of surface charge.¹⁷

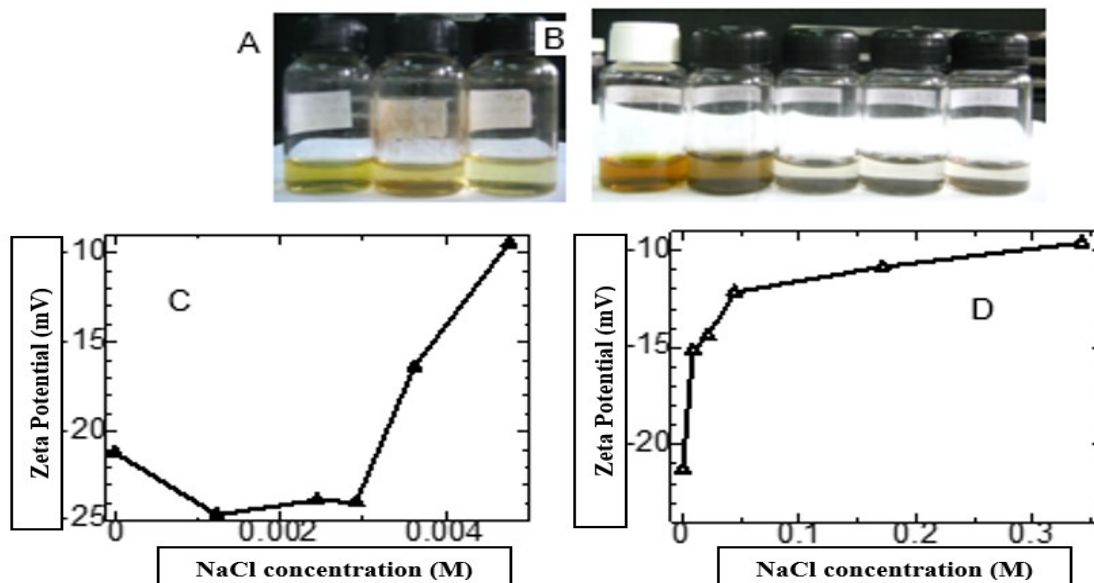


Fig.-4: Colloidal Ag/alginate nanoparticles added with NaCl after synthesis (A) at various masses of 0.01; 0.10; 0.20; 0.30; 0.40 gram, from left to right, at a storage time of 2 months. The zeta potential of Ag/alginate nanoparticles at various mass variations of NaCl added after synthesis (B)

CONCLUSION

The addition of NaCl to a mixture of Ag and alginate precursors which increased in ionic strength resulted in a decrease in the size of the Ag/alginate nanoparticles due to the decreasing rate of formation or the increasing maximum Gibbs free energy. The addition of NaCl after the formation of the Ag/alginate nanoparticles resulted in an increase in particle size due to aggregation but did not produce a particle shape other than spherical. The addition of NaCl also affects stability, the greater the concentration of NaCl or the increase in ionic strength, the lower the stability of the nanoparticles due to decreased electrostatic repulsion.

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