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Effect of the Reactor Configuration on the Production of Silver Nanoparticles

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The main aim of this work is to show the effect of the reactor configuration on the production of silver nanoparticles by chemical synthesis. Silver nanoparticles were produced in batch mode using the chemical precipitation method. Different reactor-precipitation set-up were adopted: a stirred tank reactor (STR) with a three blade marine propeller or a turbine impeller, and a spinning disc reactor (SDR) coupled with an STR. It was shown that the intensification of the mixing process, provided by the turbine impeller and the use of the SDR, leads to a decrease of the nanoparticles average size from 31 down to 16 nm. On the contrary, the yield was affected by both the mixing effectiveness and the reactor residence time. At the optimal condition a value of yield equal to 93 % was obtained. The purity of the obtained nanoparticles was in all the cases quite satisfactory in the range 89 – 96 % of silver.

1. Introduction

Silver nanoparticles (SNP) are applied in multidisciplinary research fields due to their excellent optical, chemical electronic properties and widely known antimicrobial functionality, moreover they are used for semiconductor applications for their remarkable electrical conductivity (Pol et al., 2002). It is well-known that nanoparticles exhibit size and shape-dependent properties that are of interest for applications in wide research fields. For this purpose the main task in the production of nanoparticles is to optimize the synthesis process with respect to its specific application. A typical chemical precipitation method to produce SNP involves the reduction of silver nitrate by means of a reducing agent such as formaldehyde, N,N-dimethylformamide, or ascorbic acid (Chou et al., 2000). In this work, SNP were produced in batch mode by using the green chemical precipitation method proposed by Raveendran et. al (2003) in which β-D-glucose and starch, both nontoxic and inexpensive, were used as reducing and capping agents, respectively, for silver nitrate. The precipitation stage takes place very quick and is largely affected by the degree of the local mixing, that is the micromixing, as noticed by Chen et al. (1996). In order to intensify the micromixing recently Chee Meng Ng et al. (2012) applied the Raveendran method for the SNP production by using a rotating packed bed reactor by obtaining at optimal operating conditions values of SNP size between 28 and 72 nm and a maximum silver yield of 91 %.
In this work, after some preliminary runs, the reduction process of silver nitrate was carried out by using two kind of reactors: a stirred tank reactor fitted with a three marine propeller and a rotating disc reactor. This latter technique allows the achievements of a complete micromixing of the reagents over the disc surface (Baffi et al., 2002), (Stoller et al., 2009). The experimental investigation has concerned the effect of the different reactor configurations on the SNP size and purity, and on the process yield.

2. Experimental

2.1 Materials

All chemicals were used as received. Silver nitrate $AgNO_3$, soluble starch $(C_6H_{10}O_5)_n$ and β-D glucose $C_6H_{12}O_6$ were purchased from Sigma-Aldrich; sodium hydroxide NaOH was purchased from Carlo Erba.

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2.2 Characterization

The images of the SNP samples have been obtained by a scanning electron microscopy (SEM, Jeol JSM-767 F). Scanning was performed in LEI mode at an accelerating voltage of 15 kV and a working distance of 4.5 mm. Energy dispersive micro-X-ray analysis was performed using the device X-Max 50 (Oxford Instruments), fitted in the used SEM.

2.3 Synthesis of silver nanoparticles

The adopted recipe of the chemical synthesis is that proposed by Chee Meng Ng (2012). Two reagent solutions A and B were mixed giving rise to a reaction followed by precipitation at room temperature. The solution A was composed by the two following aqueous solutions:

0.01 M silver nitrate ($AgNO_3$) aqueous solution;

1% starch aqueous solution. This solution was obtained by dissolving starch in bidistilled water at a temperature of 85 °C for more than 3 hours under stirring.

The second solution (solution B) consists of:

0.07 M sodium hydroxide (NaOH) aqueous solution;

0.02 M glucose aqueous solution.

It should be noted that the soluble starch is used both as a reducing agent and as stabilizer. The aldehyde component of starch undertakes the reduction of silver ions, while the starch component acts as a stabilizer. Sodium hydroxide (NaOH) acts as an accelerator, while the glucose is a reducing agent. The main factors affecting the nanoparticles size and the yield were respectively the L_A/L_B flow rate ratio and the starch/Ag nitrate ratio. Minimum nanoparticles size values, around 28 nm, were attained for an optimal value of the L_A/L_B flow rate ratio equal to 1, whereas the maximum value of the yield around 90 % was obtained for the starch/Ag nitrate ratio equal to 2. It has to be noticed that a big increase of the yield was obtained by increase this latter parameter from 1.5 to 2.0. In this work the experimental runs were performed at the following values of the key operating parameters: flow rate ratio L_A/L_B equal to 1 and starch/Ag nitrate ratio equal to 3.

In this work we investigated the effect of the intensification of the mixing process on the nanoparticles size by carrying out a series of runs by using a spinning disc reactor, which is a very effective equipment to realize the micromixing between two reagent solutions over the disc surface. A further series of runs were carried out with a more traditional reactor, that is a stirred vessel fitted with a three blade marine propeller. The performances of each run was evaluated in terms of the produced SNP average size, nanoparticles chemical composition and of the silver yield, calculated as follows:

$$Yield = \frac{actual\ amount\ of\ silver\ produced\ (mg\ per\ ml)}{maximum\ possible\ amount\ of\ silver\ (mg\ per\ ml)} 100\% \quad (1)$$

The reaction scheme consists of two steps. The first one leads to the oxidation of silver and the release of hydroxyl, that is:

$$2\ AgNO_3 \rightarrow Ag_2O + 2HNO_3 \quad (2)$$

$$2NaOH \rightarrow 2Na^+ + 2OH^- \quad (3)$$

During the second step OH- ions, produced by the dissociation of NaOH, can react with starch in accordance with the following equation:

$$Starch + 2OH^- \rightarrow Oxidized\ starch + 2H_2O + 2e^- \quad (4)$$

$$Ag_2O \rightarrow 2Ag^+ + O^{-2} \quad (5)$$

$$2Ag^+ + 2e^- \rightarrow 2Ag^0 \quad (6)$$

The electrons O_2- produced by the dissociation of Ag_2O (eq.5) may then reactwith the ions 2Na + (eq.3).

2.4 Synthesis of silver nanoparticles by using a mechanical mixer

The set up in this case is a stirred tank reactor (STR) which consists of a glass beaker 1 l in capacity fitted with a three blade marine propeller or a turbine impeller, both rotating at a quite high speed. Initially, the solution B was put into the vessel, then the run started by feeding the solution A through a tube immersed under the liquid surface close to the impeller periphery. 100 ml of the solution A was fed in 146 sec. The mixture was maintained under stirring for 5 minutes. Along this period of time the color of the solution continuously changed from a transparent to a dark color according to the reaction progress. For the same

period of time, i.e. 5 minutes, Cheen Meng Ng et al. (2012) operated the packed bed reactor. However, in this latter work the yield was measured only after a further stirring of the suspension of 30 minutes. It has to be noticed that in all the runs the dissolution of the starch was undertaken at 95°C for 30 minutes, then the clear solution was cooled down to 40°C. At the end of each experiment, the separation of the nanoparticles from the mother liquor was carried out by centrifugation at 8000 rpm for 60 minutes. Then the SNP were submitted to 5-7 cycles of washing with a mixture bidistilled-water acetone 1:1 and finally dried in an oven at 105 °C for 18 hours.

2.5 Synthesis of silver nanoparticles by using a spinning disc reactor

The lab spinning disc adopted is shown in Fig. 1.

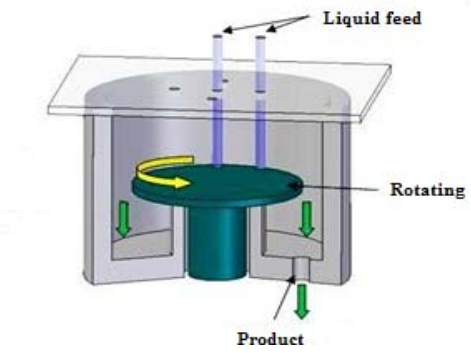

Figure 1: the experimental spinning disc reactor

The disc and the case were made by PVC. The case was provided by a cover fitted with some holes to inject the two reagent solutions in a precise point of the disc surface. The disc was 9 cm in diameter. The operating conditions and the obtained results for all the experimental runs are reported in Table 1. The ratio between the volumes of solution A and the solution B has been chosen equal to 1, while the speed of rotation was equal to 900 rpm. Each reagent solution was poured over the disc surface at a distance from the center of 2 cm and at a flow rate of 65 cm^3 per minute. SNP precipitated over the surface of the SDR. From preliminary runs a very low silver yield results by using only the SDR, because of the very short time of the liquid suspension over the disc. Thus it was decided to perform the process by using two reactors in sequence: the SDR and a cylindrical vessel fitted with a turbine, and to recycle the suspension out letting from the STR back to SDR during 5 minutes. The SDR outlet suspension was treated in a centrifuge rotating at 17000 rpm for 30 minutes. Afterwards, the SNP were submitted to a washing process, using a solution water-acetone 1:1. The washing was repeated 7 times, then the nanoparticles were maintained for 18 hours in an oven at 105°C for drying.

3. Results and discussion

The operating conditions and the results of all the experimental runs are reported in Table1. The experimental work plan was focused to evaluate the effect of the type of the impeller for the runs 1 and 2 performed at the same operating conditions whereas run 3 was finalized to evaluate the influence of the ratio starch/silver nitrate. The images of the SNP obtained in the runs by using the mechanical stirrers are shown in Fig. 2 and Fig 4 (left) for the runs 1 and 2, and 3, respectively . Finally, Fig. 3 reports the energy dispersive spectrum (EDS) of silver nanoparticles produced in run 2. A similar spectrum was measured for the run no. 1 and 3, thus we may conclude that for both these runs silver was produced at a quite high purity of more than 90 % .

Table 1: Experimental results: operating conditions and obtained results

	Run 1	Run 2	Run 3	Run 4
Configuration	Mar. Propeller	Turbine	Turbine	SDR+Turbine
pH	13.5	13.0	13.0	13.2
Starch (ml)	150	150	100	300
$AgNO_3$ (ml)	50	50	100	100
NaOH+glucose (ml)	200	200	200	400
Rotationsl speed (rpm)	600*	700*	700*	900**/600*
Size range from SEM (nm)	21-42	14 - 28	17-29	12.2 – 20.1
Yield (%)	72	93	67	72
Silver content weight %	91.4	93.6	96.0	88.8

* rotational speed of the impeller of the STR, ** rotational speed of the SDR

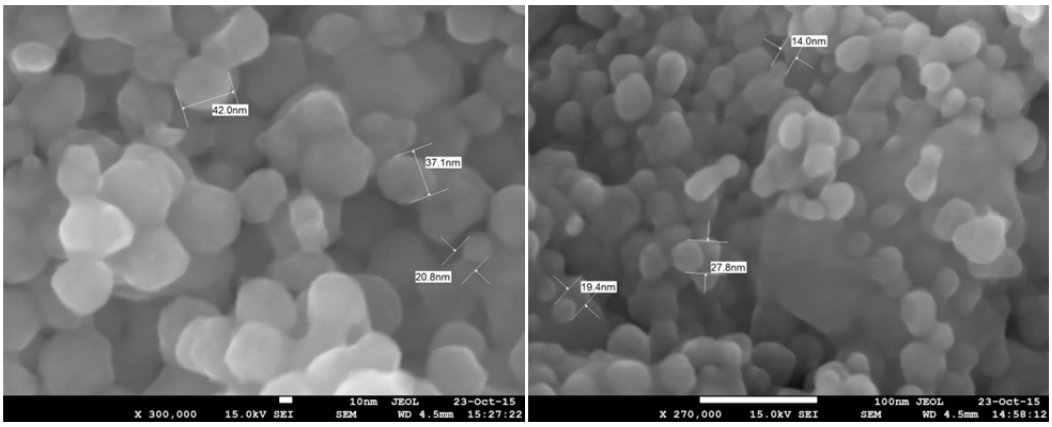

Figure 2: SEM images of the SNP produced in runs 1 (left) and 2 (right)

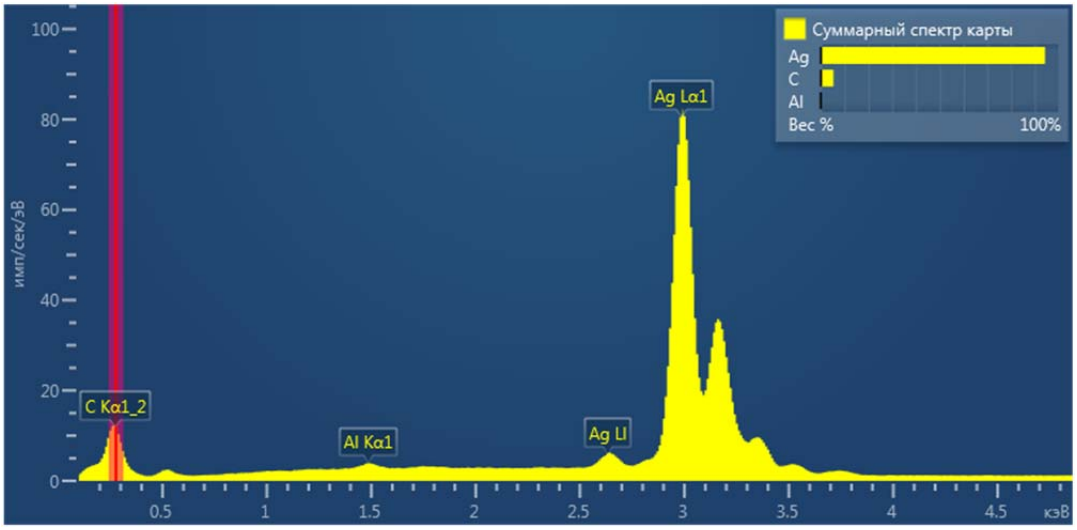

Figure 3.Energy dispersive spectrum (EDS) of silver nanoparticles produced in run 2.

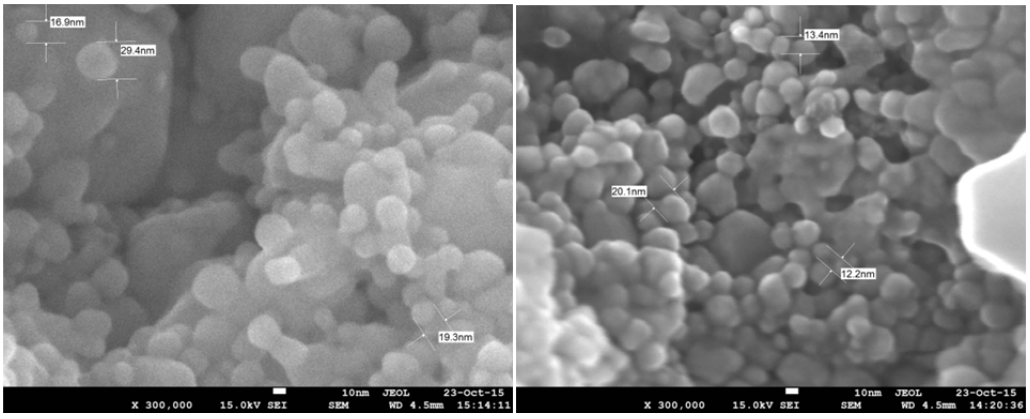

Figure 4: SEM Images of the SNP produced in runs 3 (left) and 4 (right)

The SEM image and the EDS spectrum of the particles produced in run 4 performed by the SDR + STR fitted with turbine are reported Fig. 4 (right) and Fig. 5, respectively.

In the SEM image only minor agglomeration of nanoparticles can be observed. The small percentages of big or agglomerated particles is quantitatively shown in Figure 6 by the histogram of the silver nanoparticles produced in run 1. It has to pointed out that in Table 1 it is reported the range of the average size of the SNP.

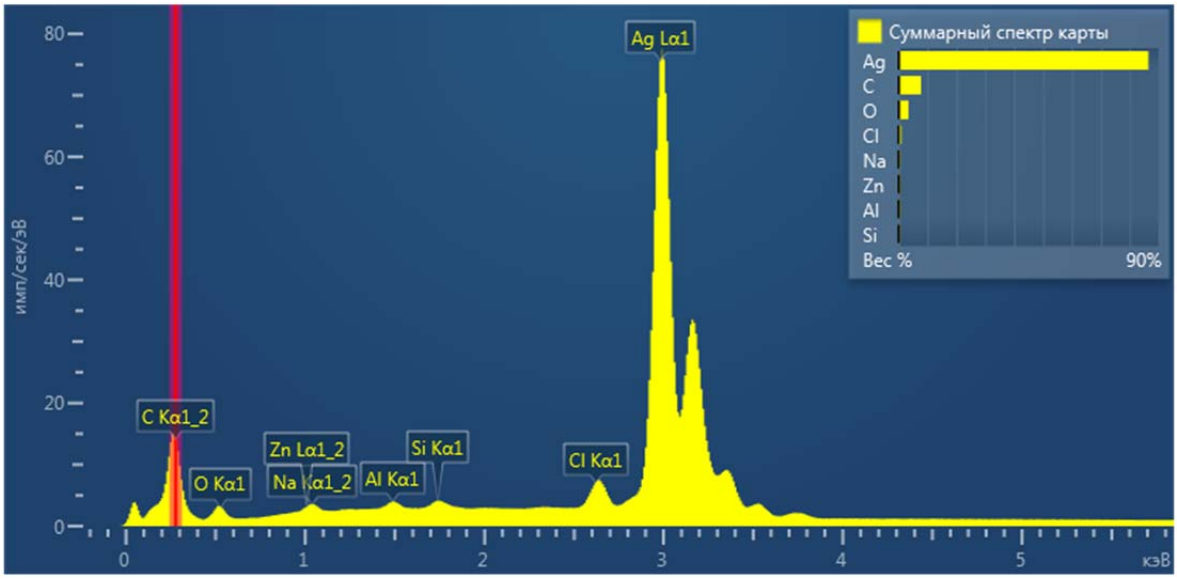

Figure 5.Energy dispersive spectrum (EDS) of silver nanoparticles produced in run 4.

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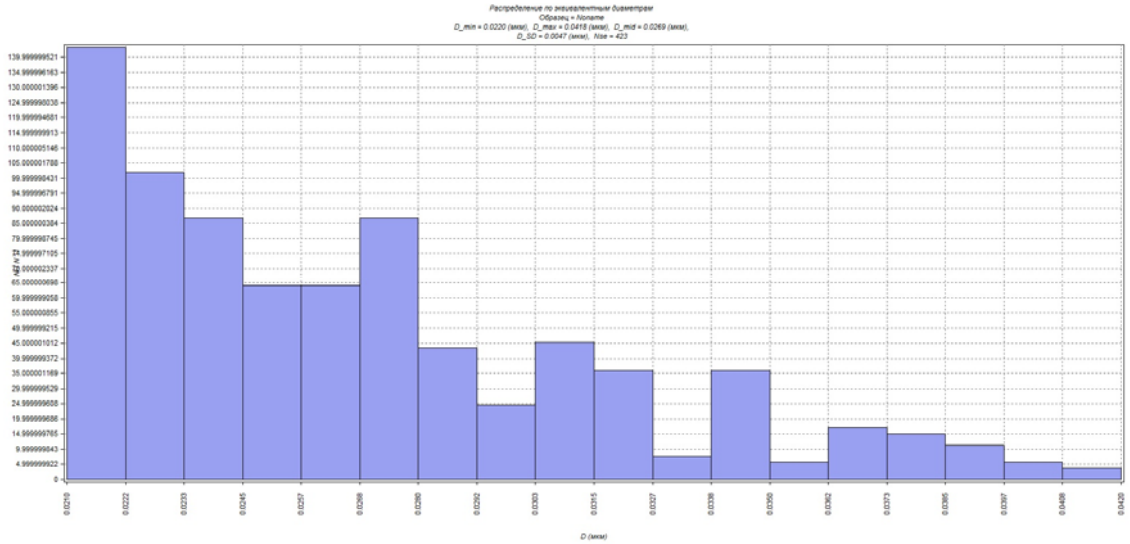

Figure 6. Histogram of distribution of silver nanoparticles in size.

The EDS spectrum shows that the impurities present in the nanoparticles mainly consist of carbon and oxygen elements. The reason of such a presence should be an inclusion of glucose or starch in some agglomerates of nanoparticles. Other minor inorganic impurities as Al, Zn, Si elements may depend on some residues of nanoparticles previously produced over the SDR itself.

In this work the performances of the green process in terms of size, yields and purity of the produced SNP have been studied by changing the ratio starch/silver nitrate and the reactor configuration (see runs 2 and 3). The decrease of the ratio starch/ silver nitrate affected negatively the yield. This could be justified by a lower rate of the oxidation reaction of the starch, expressed by eq. 4. On the contrary the mentioned ratio was beneficial for the nanoparticles purity, probably because of a smaller inclusion of organic products into the precipitated silver. A wider experimental work was devoted to the comparison of the performances attained in correspondence of different reactors configurations, characterized by a different grade of micromixing between the two reagent solutions. The runs 1,2 and 4 were performed at same operating conditions, but by using

reactors configurations leading to a different micromixing. In fact, it is well known that the SDR is very effective to produce complete micromixing over its surface (de Capraris et al., 2012) and turbine impeller produces a higher turbulence at his periphery with respect to three blade marine propeller. The obtained results in terms of SNP's size confirms the importance of micromixing, in fact the minimum detected size was equal 21, 14 and 12 nm by using the marine propeller, turbine and spinning disc, respectively, which provides in order an increasing micromixing. The minimum average nanoparticles size obtained by the configuration SDR+STR with turbine is around 16 nm, thus less than the minimum average value reported by Chee Meng Gu et. al (2012) of 26 nm. It has to be noticed that in runs 2 and 3 where only the turbine impeller was used some big nanoparticles, some hundreds of nm in size were detected. This is because turbine cannot provide a good macromixing and in some parts of the vessel volume, at the bottom and near the liquid surface, a relatively low supersaturation persists throughout the whole run, leading to a continuous growing of some nanoparticles.

The best performance in terms of yield was shown by the STR with turbine impeller, i.e. 93% in run 2. This valuable result was due to the very effective attained micromixing together with a suitable residence time. On the contrary a relatively low value of yield was obtained by coupling the SDR with the STR, regardless of the high micromixing expected by the use of the SDR, however in this case the residence time was probably not enough long because of the increasing volume of the overall reaction mixture.

4. Conclusions

In this work,it was investigated the effects ofthe ratio starch/silver nitrate and some reactor configurations on the production of silver nanoparticles using the green synthesis process. In spite of the explorative aspect of the experimental study, some interesting results have been obtained in particular on the influence of the mixing intensification between the reagent solutions. In fact, it has been shown that by adopting mixing devices, which improves the micromixing, the SNP's size should be decreased down to an average value of 16 nm. Such SNP size resulted less than those ones reported in recent works in literature, even when an intensified mixing reactor, as the rotating bed, was adopted.

By assuming a suitable residence time as that one in the run 2 a relatively high yield value of 93 % was obtained. Finally good purity values, higher than 90 % was observed.

In conclusion, It seems that the green synthetic process to produce SNP may lead to satisfactory performances also by using a simple reactor as an STR provided by a turbine, but better results should be expected in a future work by using the SDR coupled with a following STR and by assuring a suitable residence time for the completion of the reaction.

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