Green nanoparticle production using micro reactor technology

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Green nanoparticle production using micro reactor technology

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Abstract. The importance and potential of nanoparticles in daily life as well as in various industrial processes is becoming more predominant. Specifically, silver nanoparticles are increasingly applied, e.g. in clothes and wipes, due to their antibacterial properties. For applications in liquid phase it is advantageous to produce the nanoparticles directly in suspension. This article describes a green production of silver nanoparticles using micro reactor technology considering principles of green chemistry. The aim is to reveal the potential and constraints of this approach and to show, how economic and environmental costs vary depending on process conditions. For this purpose our research compares the proposed process with water-based batch synthesis and demonstrates improvements in terms of product quality. Because of the lower energy consumption and lower demand of cleaning agents, micro reactor is the best ecological choice.

1. Introduction

The number of mass products that contain nanoparticles is increasing and so is the interest in greener industrial production of these materials. So far, gas phase processes are often used to synthesize aggregates of nanoparticles in ton-scale [1]. For some applications, however, well-defined nanoparticles in suspension of a (non-toxic) solvent are required, e.g. monodisperse iron oxide particles with a certain diameter is required for magnetic resonance imaging [2]. Commonly, these product characteristics can be obtained by wet chemical procedures using a solvent as a medium. When organic solvents are used, shape and size of nanoparticles can be consistently controlled. However, the cost of ensuring safety in this process can prove costly. In contrast the usage of water as green solvent results to a poor shape and size control, if the synthesis is performed in a batch reactor (table 1). The key to overcome this dilemma of defined particle size and environmental friendliness is **safer micro reactor technology**. This paper features this process by a case study, the production of silver nanoparticles, which are a mass product due to a continuously increasing application in different daily products, such as clothes and wipes. In contrast to the common batch production technology, micro reactor systems allow for continuous production improved operational safety, and, due to the highest heat and mass transfer rates, well-defined synthesis conditions in tailored reaction zones.

Table 1. Comparison of the advantages (highlighted) and disadvantages of batch reactor and a micro reactor in case of using water based synthesis or synthesis including organic solvents.

	Batch process	Micro reactor
Synthesis (water-based)	• **Environmentally friendly** • Discontinuous • Poor shape & size control • Little ton-scale (below 6 t/a)	• **Environmentally friendly** • **Continuous** • **Good shape & size control** • **Middle ton-scale (6-15 t/a)**
Synthesis (organic solvent)	• **Good shape & size control** • Discontinuous • Not environmentally friendly • Little ton-scale (below 6 t/a)	• **Continuous** • **Good shape & size control** • **Middle ton-scale (6-15 t/a)** • Not environmentally friendly

Moreover, combinations of environmentally friendly synthesis and micro reactor technology should include as many of the 12 principles of green chemistry as possible (Prevention, Atom Economy, Less Hazardous Chemical Syntheses, Designing Safer Chemicals, Safer Solvents and Auxiliaries, Design for Energy Efficiency, Use of Renewable Feedstock, Reduce Derivatives, Catalysis, Design for Degradation, Real-time analysis for Pollution Prevention, Inherently Safer Chemistry for Accident Prevention) [3]. These principles were outlined to give reference points to design new chemicals and chemical processes.
This work answers these four following leading questions.

1. Is it possible to avoid the disadvantages of aqueous synthesis by using a micro reactor?
2. From the ecological point of view: Is it beneficial to use micro reactor technology?
3. From the economic point of view: Is it efficient/ cost effective to use micro reactor technology?
4. Are there further advantages in terms of using micro reactors?

2. Product Quality

In most cases nanoparticles including organic solvents are used to get well-defined single particles because of the high shape and size control [4]. But actually these ways of producing nanoparticles are not sustainable, neither in a batch process nor in a continuous micro reactor process. Alternatively, water-based syntheses are more environmentally friendly, but the size and shape control are very poor [5]. So the aim is to avoid these disadvantages by using micro reactor technology caused by well defined reaction conditions. To survey the product quality of both processes, the analytic method of dynamic light scattering is used (DelsaNanoC, Beckmann Coulter). In the following paragraph both plants are described.

The flow sheet of the batch reactor system, figure 1a), shows a stirred tank reactor, where the first solution is placed, including the pump which transports the second solution. After the pump the tube is divided into ten smaller tubes to reduce the local gradient of concentration. The stirred tank reactor can be heated, if necessary. In figure 1b) the flow sheet of the micro reactor plant is shown. The three solid dosing feeders carry the solid reactants into the corresponding mixing tanks, where the two required starting solutions are prepared. After preparing the reactants the solutions are pumped to the entrances of the micro reactor (T-shaped micro mixer). The 2 micro reactor intakes end at the small reaction capillary, where the reaction takes place. This is called the production mode. The production mode is followed by the cleaning mode, where the cleaning agents (first HNO_3- solution; second H_2O) were pumped through the micro mixer and the capillary. The thermostat offers the possibility of heating the micro mixer.

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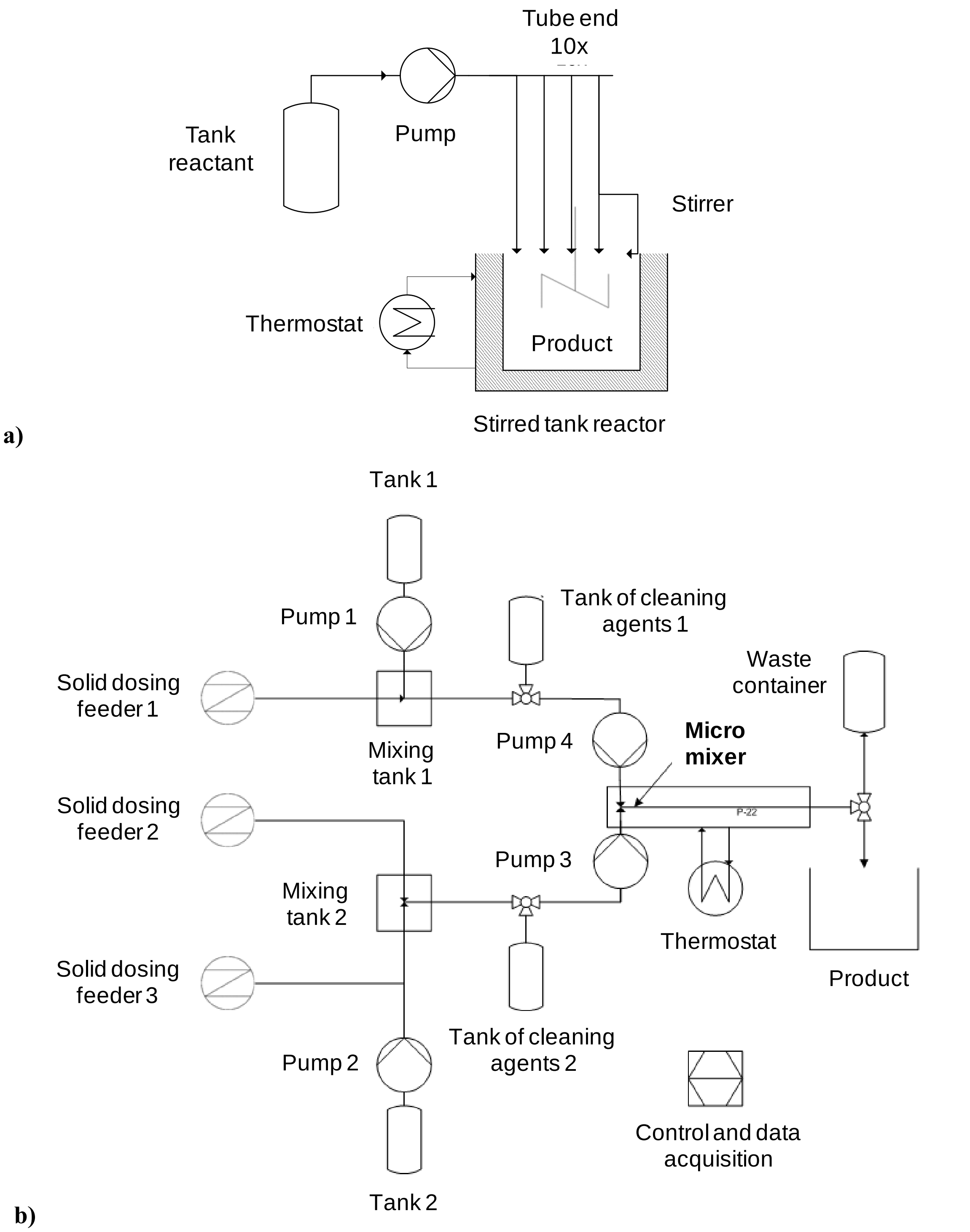


Figure 1. Flow sheet of the compared processes. (a) Batch reactor system. The first reactant solution is placed in the stirred tank reactor, while the second solution is pumped to the first solution. (b) Micro reactor plant. The reactants are automatically prepared and pumped to the micro mixer, where the silver nanoparticles are synthesized.

Our findings demonstrate that the product quality can be increased. In figure 2 a typical size distribution for batch-nanoparticles and for a micro reactor-curve are shown. Distributions were obtained by Non Negative Least Square Method. The diameters of micro reactor-nanoparticles are small and the size distribution narrower, that means a higher product quality. The small peaks, which appear in both cases, are often artefacts coming from the particle rotation [6]. Also, the shape is clearly defined as spherical particles as shown in the representative TEM (transmission electron microscope) picture, figure 2.

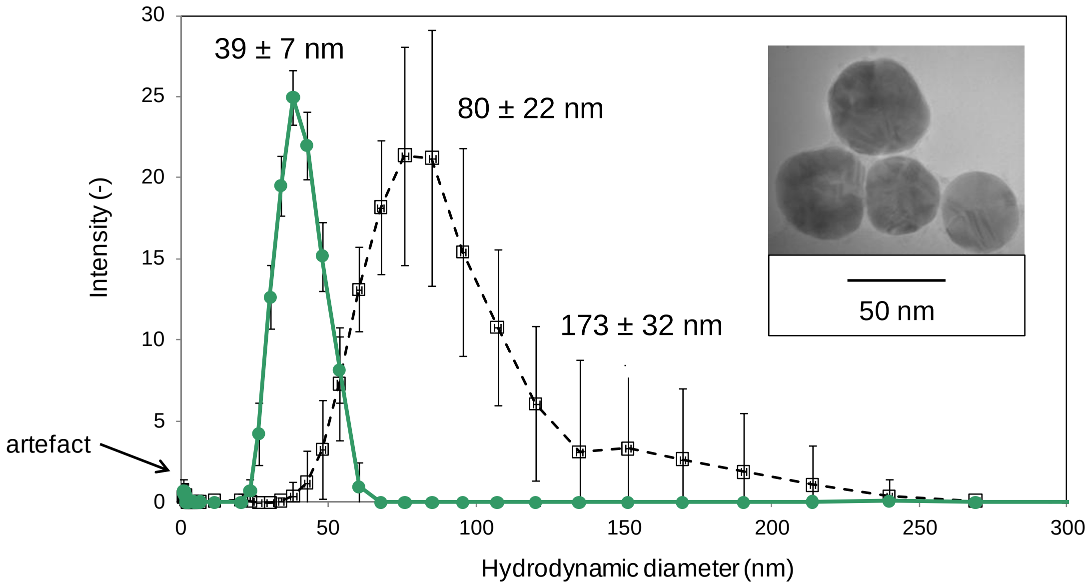


Figure 2. Particle size distributions of samples produced in a batch reactor (open squares) and a micro reactor (solid circles). Particles of the latter micro reactor-nanoparticles are smaller, and the size distribution is narrower.

3. Ecological Analysis

To determine the ecological benefit of a micro reactor a cumulative energy demand (CED) analysis is done. To realize a comparison of a batch reactor and a micro reactor the data are standardized of one year or one production cycle. So the two processes are comparable independent of the operational time.

A silver nanoparticle synthesis, which is accomplished in a standard flask, acts as a case study for obtaining a benchmark by computing the energy demand and the amount of chemicals required for a higher scale process. To accelerate the feed-in of the second reactant solution the tube is subdivided into ten tube parts. To clean the reactor the product suspension is collected and the cleaning agent (nitric acid) is filled in. After the cleaning with nitric acid the reactor is rinsed with pure water twice. The resulting energy demand is listed in table 2.

The electrical energy demand of a micro reactor is generated during the process. The measured data are shown in table 2. The different modes are mentioned in section 2.

Table 2. Process data of the two types of processes investigated.

Process	Apparatus	Power (W)	Time required	Effective consumption of electricity (Wh)
Batch reactor process				
Preparing of the solutions			20 min	manual
Production mode	Pump	15		22.5
	Stirrer	20	1h 15 min	30
	Thermostat	200		300
Further stirring	Stirrer	200	10 min	33.3
drawdown/ cleaning			20 min	manual
Sum			**2h 05min**	**385.8**
Micro reactor process				
Production mode	Solid dosing feeder 1	0.2	50 min	0.167
	Solid dosing feeder 2	1		0.833
	Solid dosing feeder 3	0.8		0.667
	Pump 1	5		4.167
	Pump 2	15		12.5
	Pump 3	5		4.167
	Pump 4	15		12.5
	Thermostat	60		50
	Control-PC	12.5		10.417
Cleaning mode (H_2O/HNO_3)	Pump 3	5	5 min	0.417
	Pump 4	5		0.417
	Control-PC	12.5		1.042
Cleaning mode (H_2O)	Pump 4	5	5 min	0.417
	Control-PC	12.5		1.042
Sum			**1 h**	**98.75**

Table 3. Cumulative energy demand of each component of both processes.

Process	Apparatus	Energy demand (Wh)	Primary energy demand (MJ)
Batch reactor process			
Production	Pump	22.5	0.23
	Stirrer	30	0.3
	Thermostat	300	3
Further stirring	Stirrer	3.3	0.33
	Sum	**385.8**	**3.86**
Micro reactor process			
Production mode	Solid dosing feeder	1.667	0.017
	Pump	33.334	0.333
	Thermostat	50	0.5
	Control-PC	10.417	0.104
Cleaning mode	Pump	1.251	0.013
	Control-PC	2.084	0.021
	Sum	**98.75**	**0.988**

The cumulative energy demand of both processes is calculated to describe the production of silver nanoparticles without the preproduction. This is considered in the analysis using **Umberto** software. Because of the same reactants and end use of both processes, further line sections of life time cycle are neglected. The degree of efficiency (energy production) is g = 36 % as average of the power plants in Germany [7]. To produce nanoparticles in a batch reactor fewer components, which need electrical energy, are required than in a micro reactor: one pump, one stirrer and one thermostat. After the actual reaction, a second stirrer mode takes place due to an improved mass flow and a higher yield. The data of each component is shown in table 3. Calculation of the CED including added end energy demand per production cycle (EEV) using equation 1 with NEV (non energetic consumption) = 0, SEI (material bounded energy content) = 0, g = 0.36) results to an energy demand of 3.87 MJ.

$$CED = \sum \frac{EEV_i}{g_i} + \sum \frac{NEV_j}{g_j} + \sum \frac{SEI_k}{g_k} \quad (1)$$

The batch reactor produces 0.096 g silver nanoparticle per production cycle (worst case: 100 µM silver, yield = 60%), that takes 2.083 h. To achieve a comparable value the energy demand is divided by the amount of produced silver nanoparticles. This quotient is called comparative quotient CQ: **CQ_{batch} = 37.29 MJg^{-1}**. For the industrial production designed micro reactor system consists of nine components, which need electrical energy: three solid dosing feeders, four pumps, one thermostat and one PC. The required power and the duration are described above. The CED is computed according to equation 1 (NEV = 0, SEI = 0, g = 0.36). Together with the production amount of 0.086 g silver nanoparticles per hour (worst case: 100µM silver, yield = 60 %) the comparative quotient for the micro reactor calculates to: **CQ_{micro} = 11.48 MJg^{-1}**. Figure 3 demonstrates the effect of “Numbering-Up”. “Scaling-Up” is not computed in this article because the data is incomplete. Accomplishing a “Numbering-Up” the CQ reaches the lowest point of energy demand per gram product at a six times “Numbering-Up”. Because further “Numbering-Ups” were performed a second or even more thermostat or other compounds are required, so that the CQ will increase.

Furthermore, an eco-efficiency analysis using Umberto software is done. Now the preproduction of the reactants and cleaning agents are considered. These data are taken from the **ecoinvent** (Umberto) data bank. The comparison here is not only the batch reactor versus the micro reactor. Also are compared different silver concentrations and amounts of cleaning agents (nitric acid). Figure 4 shows that the CO_2-eqivalent depends strongly on the amount of nitric acid and the electro energy production.

Using CED the CQ of the micro reactor is approximately three times lower than the CQ of the batch reactor. This result is achieved mainly due to the high heating energy. The micro reactor is also the better choice, when the CO_2- equivalents are compared because of the higher need of cleaning agents and the higher demand of electro energy.

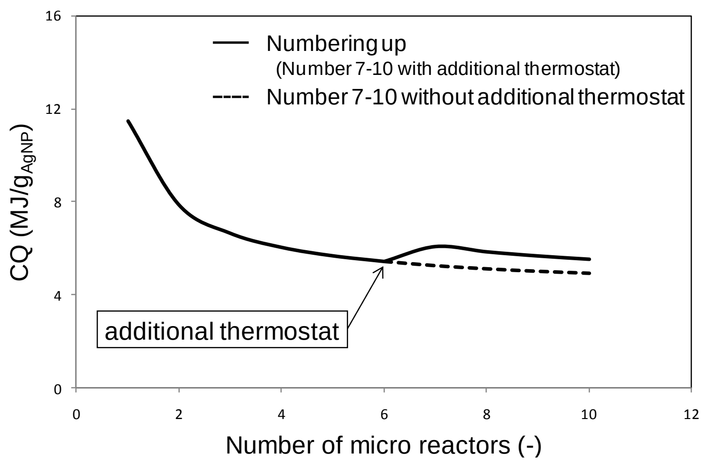
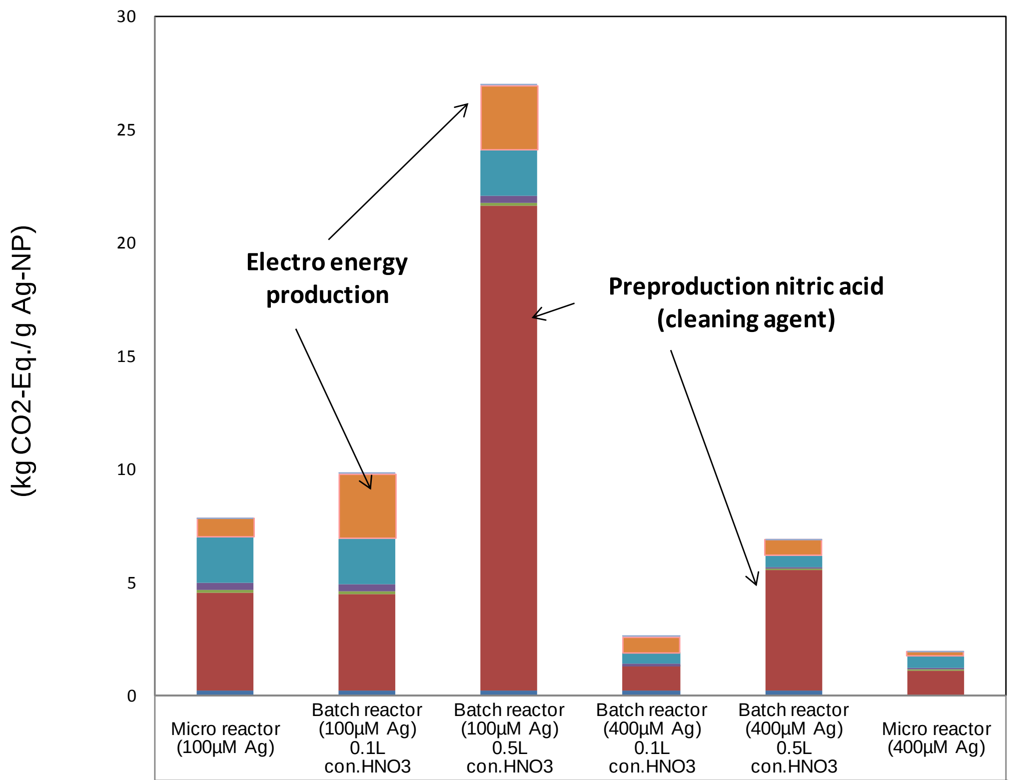


Figure 3. Dependence of the comparative quotient (CQ) on the number of parallel micro reactors determining the turnover.



	Micro reactor (100µM Ag)	Batch reactor (100µM Ag) 0.1L con.HNO3	Batch reactor (100µM Ag) 0.5L con.HNO3	Batch reactor (400µM Ag) 0.1L con.HNO3	Batch reactor (400µM Ag) 0.5L con.HNO3	Micro reactor (400µM Ag)
Wastewater treatment	0.00	0.01	0.01	0.00	0.00	0.00
Electro energy production	**0.82**	**2.84**	**2.84**	**0.71**	**0.71**	**0.20**
Preproduction, starch	2.02	2.01	2.01	0.50	0.50	0.51
Preproduction, sodium hydroxide	0.31	0.31	0.31	0.08	0.08	0.08
Preproduction, pure water	0.10	0.14	0.14	0.03	0.03	0.03
Preproduction, nitric acid	**4.37**	**4.30**	**21.47**	**1.07**	**5.37**	**1.09**
Preproduction, silver	0.17	0.17	0.17	0.17	0.17	0.17

Figure 4. CO_2- equivalent per gram silver nanoparticle (AgNP) of a batch and a micro reactor process (column 1 and 2) including different amounts of cleaning agents for the batch reactor (column 3). CO_2- equivalent is calculated for a higher concentration of silver (column 4- 6).

4. Economic Analysis

To find out if the micro reactor is cost effective or not the comparative cost method and the period payback rule are used. Table 4 shows the data for the batch reactor and the micro reactor. The economic examination is based on the service life and therewith the depreciation and amortization, the imputed interest rate, the operational costs and the investment costs. Besides the investment costs, the operational costs present makes a significant part of the incoming costs and are calculated separately for every process. The service life for each type of reactor is appointed for five years. An imputed interest rate of 4% per year is assumed. That is the average annual rate of return of the government bond of the Federal Republic of Germany. The proceeds, which can be achieved, depend on the current price of silver. For our calculations, the prices of *PlasmaChem GmbH* are applied. 312 € are estimated or 500 mL of suspension with a silver content of 0.1 mg/mL [8]. This assumed value is recalculated for each product. For our calculations the average data for electricity cost [9], personnel costs [10] and the material costs of chemicals [11] are used.

The investment costs of the batch reactor are established according to an offer of *AP-Miniplant GmbH & Co KG* (23,354 €). The operational costs consist of the demand of chemicals, need of electrical power and working hours. The initial solutions for the batch process are manually prepared. Also the removal of the product and the cleaning of the batch reactor after every production cycle are not automatically done. For each cycle of the batch process, 0.66 h of man hours is required. It is possible to perform four cycles per 8 hour work day. Our average product exhibits a silver content of 100 µM (yield = 60%). These add up to a computed proceed of 41.60 €/L and an annual production amount of 15,000 L (250 days, one-shift operation). The investment costs of the micro reactor plant (71,910 €) are calculated by addition of every single component of our prototype plant, see figure 1. The operational costs comprise the electrical demand, material costs of the chemicals and man hours. Because of high automation, only one manual working hour per day is required. This hour is necessary to adjust the operation and inspect the production process. Per day (8 working hours) 8 production cycles may be realized. Our average product exhibits a silver content of 100µM (yield = 60%). The computed proceeds of the micro reactor add up to 41.60 €/L and an annual production amount of 26,800 L (250 days, one-shift operation).

Table 4. Data base of the batch and the micro reactor for economic analysis.

	Micro reactor	Batch reactor
Production amount per cycle	13.4 L (8 cycle/ d)	15 L (4 cycle/ d)
Operational costs/ year	128.97 €	315.58 €
Investment costs	71.91 €	23.35 €
Service life/ year	5	5
Imputed interest rate	4 % p. a.	4 % p. a.

Table 5. The costs per production unit of the micro and the batch reactor.

	Micro reactor	Batch reactor
Annual production	26 800 L	15 000 L
Annual operational costs	32 241 €	49 750 €
Annual accrual	14 382 €	4 670 €
Annual interest rate	1 438 €	467 €
Total annual costs	**48 061 €**	**54 887 €**
Costs/ production unit	**1.79 €/L**	**3.66 €/L**

Comparative cost method: Due to significantly higher investment costs of the micro reactor, the annual interest rates and the annual accrual is also very high. This mostly affects the costs per production unit, see table 5. For the batch reactor the costs per production unit depend primarily on the operational costs. The largest part of the total costs constitutes the operational costs. That is directed to both processes. In the context of the **period payback rule** the profit should be considered by the investment costs to the profit. Thus the amortization of the investment costs can be calculated for each process. The profit contribution is due to the difference of the proceeds and the operational costs per production unit, that means for 37.22 €/L the micro reactor and 37.94 €/L for the batch process. The equations E_{BR} and E_{MR} mentioned in figure 5 are for calculations beyond investment costs (BR= batch reactor, MR= micro reactor). The comparative cost method shows lower production costs per production unit using a micro reactor resulting from the higher production amount and lower man hours. The results of the period payback rules shows that the investment costs for the batch process are paid back after 10 days and after 18 days for the micro reactor, see figure 5. Higher productivity and lower operational costs affect the overall costs on micro reactors.

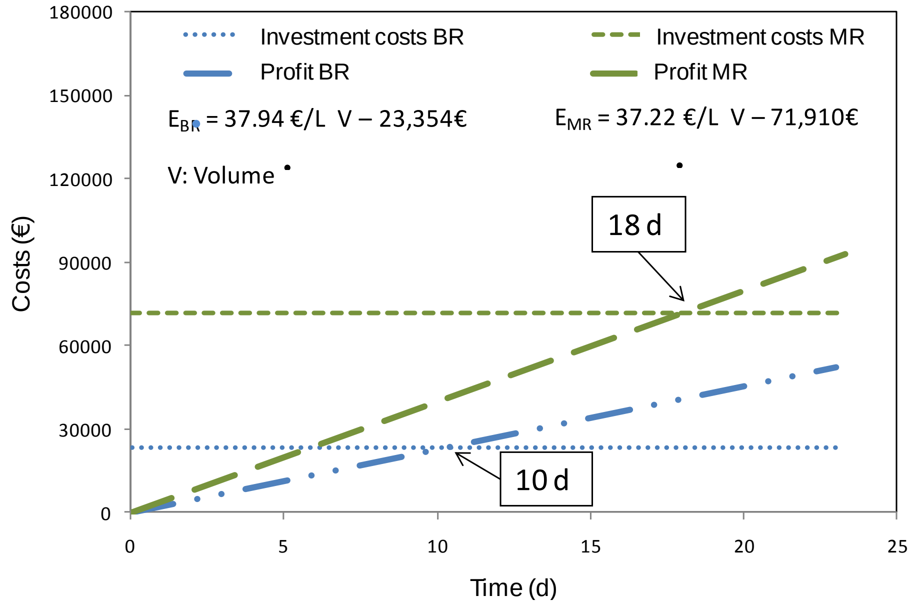


Figure 5. Payback period of micro reactor (MR) and batch reactor (BR).

For BR the payback period is 44 % shorter.

5. Advantages of micro reactors

Because of the high surface to volume ratio the thermal conditions of a process can be controlled very well. That results in a fast and intensive mass and heat transfer. Also a quick mixing can be realized by special structures in or of the micro reactor. One prime example of the advantages of the micro reactor is the prevention of a runaway, which sometimes happens in a batch reactor. Due to the high surface to volume ratio and accordingly to the quick and intensive heat transfer, the temperature profile is a steady state instead of a runaway.

6. Conclusion

The micro reactor is suitable to compensate for disadvantages of aqueous nanoparticle synthesis produced in batch reactor. At a scale of one ton per year allows for a drastically improved particle size distribution and reduced cumulative energy demand compared to a conventional production in a 15 L stirred-tank reactor. The improved environmental performance is caused by the smaller dimension of the micro reactor (*e.g.* less heating energy is required) and the low demand of cleaning agents. The eco-efficiency analysis additionally shows that also CO_2- emission is reduced in the case of a micro reactor. Furthermore, the micro reactor approach follows all relevant recommendations of the twelve principles of green chemistry.

Despite higher investment costs of a micro reactor plant compared to a batch reactor process, producing silver nanoparticles in a micro reactor system can be economically favorable. This is due to higher production amount and lower labour costs. Furthermore, efficient heat control, small reactor volume, excellent process control, and a high level of safety are possible. To sum it up micro reactor technology provides a promising avenue for sustainable production of silver nanoparticles.

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