Journal of Electrostatics 71 (2013) 717–727

Contents lists available at SciVerse ScienceDirect

Journal of Electrostatics

journal homepage: www.elsevier.com/locate/elstat

Fabrication of micro–nanocapsules by a new electrospraying method using coaxial jets and examination of effective parameters on their production

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ARTICLE INFO

Article history:
Received 21 November 2012
Received in revised form
14 March 2013
Accepted 17 April 2013
Available online 2 May 2013

Keywords:
Microencapsulation
Electrospray
Coaxial nozzle
Morphology
Particle size

ABSTRACT

This paper considers a new method related to the micro and nanocapsules production by using coaxial jets electrospray. The produced micro–nanocapsules were characterized on their structure, mean particles size and morphology by optical and scanning electron microscope. The effects of different operating parameters on the size of the particles were investigated. The obtained results showed the efficiency of the mentioned method in micro–nanocapsules fabrication. The average diameter of fabricated capsules was variable from 80 nm to 900 μm by adjusting different parameters of process.

1. Introduction

Electrospraying is a process of synchronous production of droplets and their charging using electrical forces. In this technique, a conducting liquid is gradually fed through a needle forming a meniscus. It adopts an almost conical-like shape (Taylor cone) from whose vertex a slender microthread is issued. It finally breaks up into an aerosol of highly charged droplets [1,2].

In 1600, William Gilbert's observations placed the first stone in the path of understanding the electromagnetic influence on fluids. He observed that a spherical droplet of water could be drowning up into a cone by holding a piece of rubbed amber above it [3]. Centuries later, Lord Rayleigh demonstrated that a charged spherical droplet of charge (Q), droplet radius (a) and surface tension (σ) would remain stable in return for $x < 1$. This amount can be expressed as $x = Q^2/(64\pi^2\varepsilon\sigma a^3)$ [4].

Taylor carried out experiments on the disintegration of water drops in strong electrical fields and fluid jets emerging from the tip of a capillary. He demonstrated that an electrostatic charge applied to a fluid could cause a predictable deformation, finally distorting the spherical drop into a cone (known as a Taylor cone) (Fig. 1). According to Rayleigh's observations, Taylor notified that if the electrostatic field increases a fluid jet, it will be exiting from the tip of the cone. These experiments formed the basis of electrospray processing [4,5]. Various forms of electrospraying can be classified into two principal categories: dripping and jet methods that were systematically evaluated by Hayati et al., in 1987 [6], Cloupeau and Prunet-Foch in 1994 [7], Shiryaeva and Grigor'ev in 1995 [8], Jaworek and Krupa in 1999 [9] and Loscertales et al., in 2002 [10].

Electrospray is a well-known phenomenon which has different applications such as fabrication of inorganic nanoparticles, deposition of nano-thin films, deposition of nanoparticles, aerosolization, generation of micro–nanocapsulation, etc. [11,12]. Encapsulation technology is a gaseous bubble as a core material in a polymer shell covering. The objective of this technology is to protect the active core material such as pharmaceutical materials, enzymes, dyes, flavors, etc. from the external environment. The shell polymer may consist of carbohydrates proteins, herbaceous gums or synthetic polymers. Micro–nanocapsules are applied in pharmaceutical, cosmetic, food industries etc. [13,14].

Recently, many authors have optimized the electrospray process due to its application in encapsulation. In one study, Watanabe et al. evaluated the immobilized enzyme gel particles using electrostatic atomization technique and the corresponding catalytic performance of immobilized enzyme [15]. Electrostatic droplet generation was used by Nedovic et al. for microbeads loaded with the

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http://dx.doi.org/10.1016/j.elstat.2013.04.001

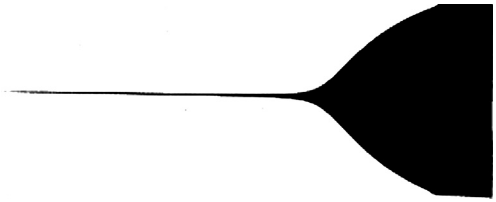

Fig. 1. Image of the Taylor cone.

brewing yeast production. Their purpose was to investigate internal mass transfer limitations in microbeads with diameters in the range of 0.3–2 mm that were loaded with yeast cells. The other purpose was to determine conditions for controlled production of optimal size beads [16]. In the other study, Xie and Wang studied whether it was possible to stabilize a high-flow rate electrospray process by imposing an ancillary electric field to achieve micro-encapsulation of Hep G2 living cells with controllable size [11].

In this study, we used electrohydrodynamic forces to produce capsules in the nano-micrometer range by changing electrospray equipment and using coaxial nozzles. This technique was utilized for encapsulating essential oil with natural sodium alginate biopolymer. The effect of various vehicles parameters and the ones based on solution on the form and size of the encapsulated particles were investigated and the optimized conditions for micro–nano-capsules production with suitable construction were determined. With the help of photographs taken by optical and electronical microscope, the morphological changes of produced micro–nano-capsules were studied and evaluated.

2. Materials and methods

2.1. Materials

The polymer used for micro–nanocapsules preparation was sodium alginate from Sigma–Aldrich (Germany). Calcium chloride from Merck (Germany) was obtained as the cation used for the ionic gelation. Essential oil as core material was purchased from Barij Essence Pharmaceutical Co (Iran).

2.2. Experimental setup and capsules formation

In the present work, alginate micro–nanocapsules were prepared using an encapsulation device that was based on electrostatic atomization. An experimental approach for the preparation of micro–nanocapsules was using electrospraying via coaxial jets. Fig. 2 shows the experimental apparatus. This system includes two high voltage generators, syringe pump and two simple plastic syringes. The one with smaller size (2 ml) remains constant in the one (60 ml) in which they are placed coaxially.

Two needles with different gauge size were arranged coaxially so that two different solutions of core and shell exited eventually in an orifice. Alginate solution with determined concentration was used as wall polymer that was arranged inside the external syringe. An emulsion (o/w) of essential oil was prepared as the core material and poured in the internal syringe. Both two solutions were pumped using a syringe pump (GV-BZ:02/m-014, Germany) with control the flow rate. In order to prevent to disperse the particles in environment due to applied voltage, a ring electrode with 4 cm diameter was utilized in the system that placed in 1 cm from the nozzle.

Positive voltages for the nozzle and ring electrode were also applied. As can be seen in Fig. 2, V_1 and V_2 were defined as the potential difference between the nozzle and gelling bath and potential difference between the ring electrode and gelling bath,

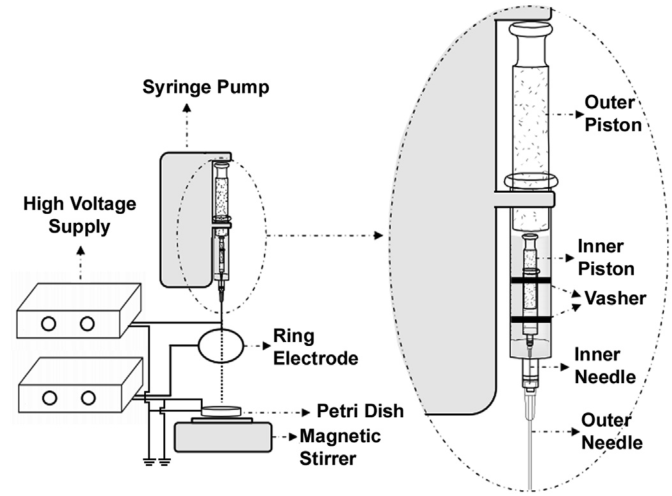

Fig. 2. Schematic description of the encapsulation system using a coaxial jets electrospray.

respectively. When the electrostatic force was induced by the charge potential, a strong electric field was built up at the nozzle outlet that overcame the surface tension of the polymer solution. In both liquids flowing out from the coaxial nozzles, one solution was dripped into the other one in which an outer liquid coated an inner one, disintegrating into droplets due to electrical forces. The formed droplets were dripped into calcium chloride aqueous solution placed at 10 cm from the nozzle. The plate including $CaCl_2$ solution was kept on a magnetic stirrer with a continuous stirring speed. However, the gelification process was between Ca^{2+} ions and guluronate blocks of alginate chain and the mentioned capsules were formed. After the formation of micro–nanocapsules, they were collected using a centrifuge at 2000 rpm for 5 min and washed twice again with deionized water. Drying of samples was done by freezing dryer (Heto Holten, Denmark). The capsules, however, were first frozen at −20 °C for 12 h and then transferred to freeze dryer at −20 °C under vacuum with pressure less than 0.61 kPa. They were left for 5 h during which their water was vaporized completely.

2.3. Evaluation of effective parameters on capsules formation

In order to investigate the effect of coaxial jets electrospraying parameters on capsules size, different calcium alginate micro–nanocapsules were produced by changing the experimental operating parameters. Voltage, flow rate, nozzle diameter, distance, magnetic stirrer rate, concentration of $CaCl_2$ solution and alginate type and concentration were the investigated parameters.

The morphology of alginate micro–nanocapsules was examined by optical (Nikon, CSM, Japan) and electron (SEM; SORON Technology ALS-2100, South Korea) microscopes. A sample of 40 microcapsules was taken from each experiment and the average diameters of them were measured with an accuracy of 200 μm under a microscope observation. The obtained nano-capsules were measured with SEM, based on the experimental optimized condition.

3. Results and discussion

Examining the possibility of electrospray process stabilization was successfully done by two coaxial nozzles to achieve encapsulation of essential oil with controllable size. Using the new method of coaxial jet electrospray in the present study allowed generating