Continuous production of KNO₃ nanosalts for the fertilization of soil by means of a Spinning Disk Reactor

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Abstract

In this study the production of high soluble material nanoparticles was successfully performed by means of a spinning disk reactor (SDR). This result was possible due to the use of a potassium nitrate saturated solution, which was continuously recycled back to the reactor after removal of the produced solid nanoparticles.

Several process configurations were checked. It appears to be mandatory that the recycled saturated solution must be free of residual nanoparticles since their presence would lead to heterogeneous nucleation. In this respect, a small amount of nitric acid was added to the stream to permit the residual nanoparticle dissolution. Moreover, a spiral wounded piping system was developed in order to increase both the contact time and the mixing condition of the saturated solution with the added acid before entering the SDR.

Keywords: SDR, nano-salts, continuous-production, process-intensification, DLS.

1. Introduction

The history of potassium nitrate goes deep back for thousand years, in fact according to Thorwald KNO₃ is mentioned in an ancient Sumerian clay tablet, dated from about 2200–2100 B.C.E. and in the Ebers papyrus from Egypt, dated about 1500 B.C.E. Potassium nitrate is also known as ''saltpeter'', because for many years, rocks and their minerals were the only sources of KNO₃. Its main use was as preservative in several aliments, in medicine and for cooling wine (probably because its dissolution in water is a strongly endothermic process and reduces the water temperature) (Partington, 1962). Only after the discovery that employing potassium nitrate in the combustion of organic matter caused a remarkable acceleration of the oxidation process, this salt was used almost only for the production of gunpowder, the well-known ''black powder'' (Barnum, 2003). The gunpowder is an explosive mixture of saltpeter (75%), charcoal (15%) and sulphur (10%) used for the production of explosives, fireworks and propellants (Gray *et al*., 1982). Besides in the black powder production, KNO₃ has been used in Concentrated Solar Power Systems (CSP technology) due to its low hygroscopicity (Bauer *et al*, 2011) with respect to other nitrate salts, and as a fertilizer (Glauber, 1656). Several studies demonstrated that the nitrate salt of potassium is a more suitable K source for several crops, like tobacco and potato (McCants, 1960). With regards to the latter crop, these studies have shown in general, that the chloride source of potassium, as compared to the sulfate or nitrate source, resulted in a decrease in the dry matter and starch content of the tubers. As a result of the effects of chlorides on quality of potatoes, in many of the commercial potato growing areas it is recommended that the potassium be added as the sulfate. However, when large amount of K₂SO₄ is used, the quantity of sulfate sulfur, which is applied to the soil, is in excess of that needed by the plants (Jacob, 1963). The world supply of potassium nitrate was formerly derived from incrustations on the soils around habitations in tropical countries, such as Egypt and India and derived from the decomposition of organic matter in K-rich soil by nitrifying bacteria (Mehring *et al*., 1929). Much of the potassium nitrate of commerce is manly produced by top-down approaches starting from the relevant salt or by bottom-up approach trough crystallization processes. The latter case has gained more interest in the last decades to produce pure potassium nitrate suitable for the industrial applications, but has a limit in the minimum particle size that can be obtained, that is in the order of 10 microns (Linnikov *et al*., 2013). Through mechanical size reduction some authors achieved nanometric dimension of KNO₃, to produce nano-flash powders (Azhagurajan *et al*., 2014).

Spinning Disk Reactor (SDR) represents a successful bottom-up technology for the continuous production of nanoparticles by wet chemical synthesis and precipitation, granting the production of particles characterized by a narrow and uniform size distribution (de Caprariis *et al*., 2012). SDR has been already used for the production of titanium dioxide (Stoller *et al*., 2009) and hydroxyapatite nanoparticles (Parisi *et al*., 2011; de Caprariis *et al*., 2015). Regarding the production of slightly soluble salts by means of a SDR, several authors have already reported the precipitation of BaSO₄ (Cafiero *et al*., 2002) and CaCO₃ (Burns and Jachuck, 2005), whereas the production of soluble salt, as KNO₃, has to our knowledge not been investigated yet. In this work three different equipment set-up based on the use of a SDR were developed, to aim the production of nanocrystals of potassium nitrate.

2. Materials and Methods

2.1 Materials

The chemical reagents used in the study (K_2CO_3, HNO_3 and KNO_3) are of analytical grade from Sigma-Aldrich (Milan, Italy) and were used without further purification.

2.2 Synthesis and experimental procedure

Among the several synthesis ways of potassium nitrate (Joshi *et al*., 2015) the carbonate-nitric acid way was selected for this work. The production follows the stoichiometry reported below (equation 1):

$$K_2CO_3 + 2HNO_3 \rightarrow 2KNO_3 + H_2CO_3 \qquad (1)$$
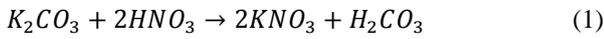
In each tests the molar ratio HNO_3/K_2CO_3 was set equal to 2.5, slightly larger than the stoichiometric ratio, in order to dissolve completely the potassium carbonate, which could cause interferences during the DLS (Dynamic Light Scattering) measurements.

Three test series were set during the experimentation. The first consisted in the production of potassium nitrate in a thermo-regulated batch reactor, without stirring, in order to investigate the possible spontaneous precipitation. The test was conducted at 20°C and a solution of 1.6 M of potassium carbonate was used with HNO_3 4 M in order to produce a saturated KNO_3 solution (3.17 M), according to the following equation (Rolfs *et al*., 1997):

$$S_{\frac{gKNO_3}{100\ g\ H_2O}} = 13.767 + 0.5588T + 0.0178T^2 \qquad (2)$$

where T(°C) was set to 20°C. After the reaction, a sample of 50 mL was withdrawn for the measure of the mean size d (nm) of the nanoparticles by a DLS Plus 90 supplied by Brookhaven and the solution refractive index n by a refractometer. In each tests the estimation of the concentration of potassium nitrate nano-crystals was carried out after a filtration through a PTFE Whatman filter (0.2 mm) of the already characterized sample (in terms of mean size, n and NO3- concentration) and a subsequent re-dissolution of the collected crystals in 50 mL of deionized water, mixed at 30°C at 200 rpm. The presence of nitrates in the solution was measured by ion chromatography (Dionex ICS—1100), the difference of [NO_3^-], before and after the crystals separation, was compared with that one measured after the dissolution of the crystals collected on the filter. The second and third series of test were conducted by means of a SDR, adopting two different set up (2IP, two injection points, and 3IP, three injection points). In the former test series, according to the 3IP configuration (Figure 1, where the geometry of the SDR is also reported) the two reagents were added at a distance from the disk center equal to 2 cm, at 50 mL min⁻¹, whereas the third solution was added at the centre of the disk at 80 mL min⁻¹. The third solution initially was the product of the batch experiments, whereas in a second moment a pure KNO_3 saturated solution was employed. As regards the 2IP configuration, the only difference from the 3IP one was that the HNO_3 and the third solutions (batch experiments product or pure saturated KNO_3 solution) were added together at the disk center. The rotational velocity $\square$ was set to the maximum possible value for the disk, equal to 142.5 rad s⁻¹, in order to favor the micro-mixing conditions (De Caprariis *et al*., 2015).
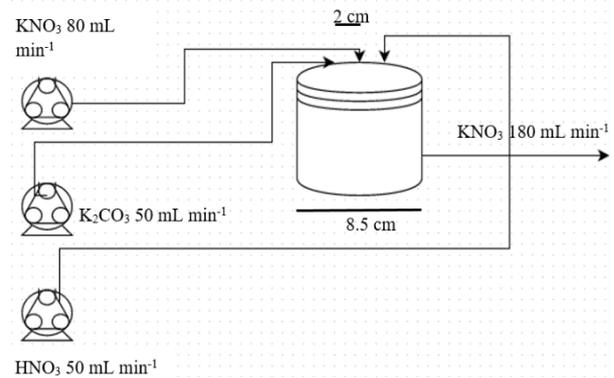
Figure 1. Second test series: experimental set-up (3IP).

The potassium carbonate concentration was varied in the range 0.05-0.2 M, whereas the nitric acid in the range 0.125-0.5 M, fixing the HNO_3/K_2CO_3 molar ratio equal to 2.5. The optimum concentrations, according to the minimum crystals size obtained, were adopted for the third test series.

In the last test series, the same reagents flow-rates and configurations were adopted, but only the pure saturated KNO_3 was added as third reagent. In these experiments the produced solution was recirculated at the disk center in the 3IP, whereas it was recirculated in the HNO_3 line in the 2IP configuration (Figure 2).
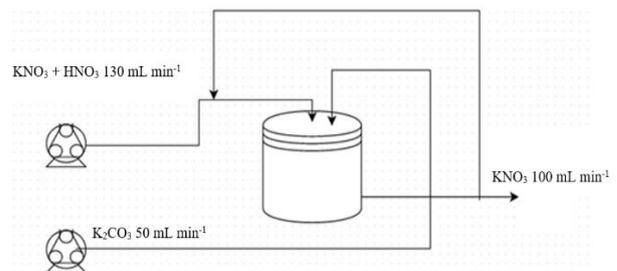
Figure 2. Third test series: experimental set-up (2IP).

The samples were collected in a beaker linked to the conical flask, endowed of a spillway, linked directly to the out-flow of the SDR. Twelve samples, one sample per minute of production, were collected in each experiment of the third series and the same characterization procedure followed in the other tests was adopted. To improve the stability and reduce the d of the crystals, a fourth experimental set-up was developed, using a spiral wounded piping system, granting a larger contact time between the nitric acid and the produced solution, in order to dissolve all the remained crystals.

3. Results and Discussion

3.1 Batch production

Three runs in batch mode were carried out, varying the reagents concentrations. Before starting the synthesis, the refractive indexes of K_2CO_3, KNO_3 and HNO_3 solutions were measured, varying the initial concentration of the reagents. In Table 1 the results obtained are reported.

Table 1. n values of different solutions at different concentrations.

Reagent	Concentration			
	8.1 M	4.05 M	2.03 M	0.5 M
K_2CO_3	1.42	1.39	1.36	1.35
	3.17 M	1.59 M	0.79 M	0.2 M
KNO_3	1.35	1.35	1.34	1.33
	2 M	1 M	0.5 M	0.125 M
HNO_3	1.35	1.34	1.33	1.32

In Table 1 it is possible to observe that the refractive index of potassium carbonate and potassium nitrate solutions are very similar. Moreover, a solution of K_2CO_3 and KNO_3 together was prepared (1 M for both salts) and an n value equal to 1.33 was measured. This implies that the n measurement could not be used to validate the presence of potassium nitrate in the product, thus only the ionic chromatogram of the re-dissolved crystals was taken into account in order to estimate the concentration of potassium nitrate nano-crystals production. It appears that batch mode is not capable to give rise to nanoparticles since none were observed in all samples. In detail, no light scattering of the solution was observed by DLS and no differences in the NO_3^- concentration were observed before and after the filtration of the produced solution, by ionic chromatography. As a consequence, the solution produced during the batch tests ($[NO_3^-] = 4$ M) was employed to subsequent tests in continuous mode.

3.2 SDR production without recirculation

The results obtained by DLS of the products exiting the SDR are reported in Figure 3, as a function of the mean value of diameter d (nm), by varying the initial reagent concentrations and the set-up configuration, adopting as a third reactant the saturated solution produced in the previous batch experiments.
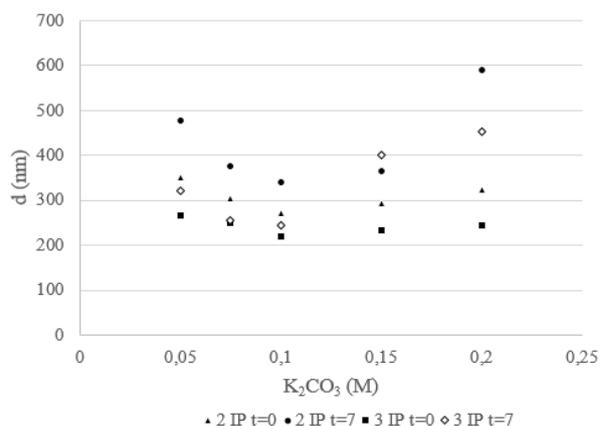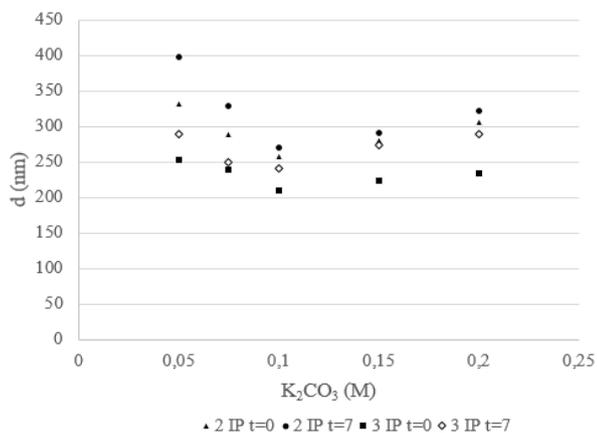

Figure 3. Mean nanopartilces diameter obtained during the first experimental run.

İt is possible to observe that for both configurations, the optimum potassium carbonate concentration was 0.1 M and the nano-crystal concentration was measured. Among the two configurations, the one labeled 3IP seems to be that one which grants the best performance, considering th obtained mean diameter and crystal production. In fact, as reported in Table 2, the concentration of nano-crystals obtained by using the 3IP configuration was 1.5-fold larger respect to that obtained adopting the 2IP one. Similar results were obtained in the tests where a pure potassium nitrate saturated solution was employed (Figure 4).

Table 2. KNO_3 crystals concentration in the SDR-production without recirculation.

|	SDR first run		SDR second run	
	3 IP	2 IP	3 IP	2 IP
$[NO_3^-]_b$	1.481 M	1.481 M	1.481 M	1.481 M
$[NO_3^-]_a$	1.457 M	1.466 M	1.452 M	1.462 M
$[NO_3^-]_d$	0.023 M	0.015 M	0.029 M	0.019 M
$[NO_3^-]_b$-$[NO_3^-]_a$	0.023 M	0.015 M	0.029 M	0.019 M

Figure 4. Mean nanopartilces diameter obtained during the second experimental run.

In Table 2 $[NO_3^-]_b$, and $[NO_3^-]_a$ represent the nitrate concentration of the produced solution before, and after the filtration, whereas $[NO_3^-]_d$ represents the nitrate concentration of the collected crystals. Through the adoption of pure KNO_3 solution a remarkable stability of the nano-crystals was achieved: after 7 days (t) of solution storage at 20°C the samples still contain nanoparticles at slighlty increased size. Moreover, it appears that all produced KNO_3 nanoparticles have a signficant tendency to agglomerate. For instance, in the 2IP test, with 0.2 M K_2CO_3, the agglomeration produced crystals characterized by a mean size 1.83-fold larger than those measured at t=0. On the contrary, the second SDR run produced smaller and more stable crystals.

3.3 SDR-production with recirculation

These productions were conducted by adopting the optimum reagent concentrations, i.e. 0.1 K_2CO_3 M and 0.25 HNO_3 M, and adding a recirculation line of produced solution to the nitric acid one. Figure 5 shows the obtained results of the 12 samples collected in 12 minutes and then stored for 7 days.
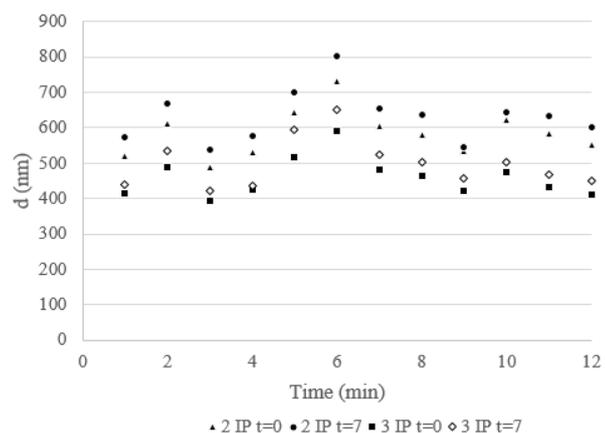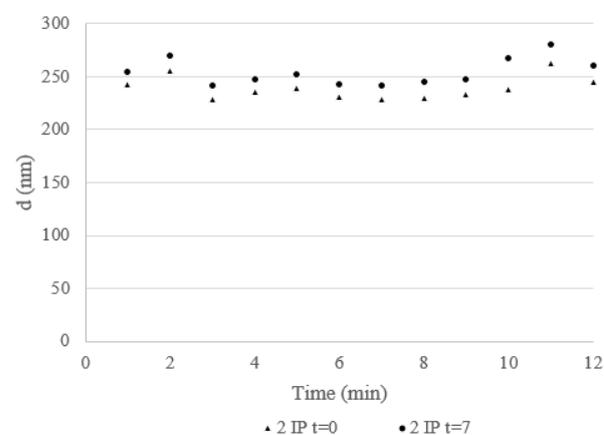

Figure 5. Mean nanopartilces diameter obtained during the third experimental run.

The crystals produced showed a remarkable stability but their mean size is larger with respect to those produced during the previous experiments, carried out with no recirculation of the product. A possible justification may be the short contact time between the product and the nitric acid, not enough to dissolve again the produced crystals. As a consequence, the latter ones may become preferential secondary nucleation sites, advantaging agglomeration and crystal growth phenomena. A difference observed by comparison of the previous tests is that the 2IP configuration exhibited increased performances in respect to the 3IP one. This fact may be the consequence of the presence of a larger surviving crystal number in the recirculated solution in case of 3IP configuration, since this stream is not added beforehand to the acid line before entering the SDR. In order to guarantee almost complete crystal dissolving in the recirculated stream, an increase of the contact time with acid is desirable: for this reason, a spiral wounded piping system was developed (Figure 6), and new runs were carried out, by adopting the 2IP configuration only.
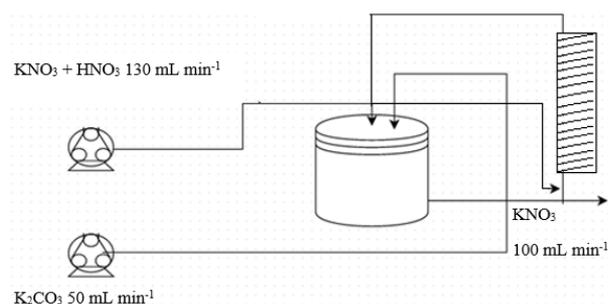
Figure 6. Wounded piping system configuration.

Figure 7 reports the obtained results.

Figure 7. Mean nanopartilces diameter obtained during the fourth experimental run.

As expected, by increasing the contact time between the produced solution and the nitric acid, the crystals were efficiently dissolved thus granting the disappearance of possible agglomeration sites; moreover, a sensible increase of the process performances, considering mean size and stability, was achieved. In detail, the mean size in the same run is almost constant as a function of time, if compared to the third run, where the d value almost doubles after one minute: the produced crystals exhibit a mean size of 584±66 nm and 460±55 nm for 2IP and 3IP configuration, respectively. On the contrary, the fourth run produced nano-crystals, characterized by a mean size of 239±11 nm.

Table 3 reports the concentration of the produced nano-crystals, similar to that obtained after the other experimental runs.

Table 3. KNO_3 crystals concentration in the SDR-production with recirculation.

	SDR third run		SDR fourth run
	3 IP	2 IP	2 IP
$[NO_3^-]_b$	1.481 M	1.481 M	1.481 M
$[NO_3^-]a$	1.453 M	1.461 M	1.462 M
$[NO_3^-]d$	0.028 M	0.017 M	0.019 M
$[NO_3^-]_b$-$[NO_3^-]_a$	0.024 M	0.020 M	0.019 M

4. Conclusions

The present study reports the applicability of SDR for the production of nano-crystals of highly soluble salts. In particular, various set-up configurations were investigated to achieve a stable, nanosized potassium nitrate crystal solution, that may be used for the subsequent production of nano-fertilizers. The reaction between potassium carbonate and nitric acid in batch systems does not produce any precipitate on nano scale, whereas the use of the SDR granted the production of nano-crystals with a mean size below 300 nm and a significant stability in respect to agglomeration or crystal growth over time. The best configuration, exhibiting a wounded piping system capable to increase the contact time between the recirculated produced solution and the adopted nitric acid, sensibly improved the performances of the process, achieving a mean size of the particles in all cases lower than 250 nm.

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