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Biodegradable electrospun fibers enriched with struvite crystal seeds for the recovery of phosphorous and nitrogen

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ABSTRACT. One of the greatest global challenges of the 21st century is facing the depletion of phosphorous reserves, widely used in fertilizers. One possibility is to recover the phosphorous discharged in the water by human activities, with the consequent additional benefit of improving water quality by limiting eutrophication. In this work, biodegradable poly(L-lactic acid) (PLLA) nonwovens produced by electrospinning are proposed as highly porous fibrous materials characterized by high surface-to-volume ratio for promoting the crystallization of struvite crystals as a means to recover both phosphorus and nitrogen from a nutrient rich solution. To this aim, PLLA fibers were intentionally loaded with a small amount of struvite crystals (3,7 wt%) by applying different preparation procedures, including sonication steps, single-nozzle and coaxial electrospinning. PLLA fibers containing struvite crystals were immersed in a synthetic solution of suitable ions to investigate the occurrence of struvite accumulation through the analysis of the soaked nonwovens with several techniques, i.e. Scanning and Transmission Electron Microscopy, Wide Angle X-Ray Diffraction, Thermogravimetric analysis and Atomic Emission Spectrometry. We demonstrated that struvite loaded in the PLLA fibers successfully acted as crystal seeds and enabled the precipitation of struvite crystals firmly attached to fiber surface. Results showed that the quality of crystal seeds dispersion in PLLA fibers as well as their location along the fiber section heavily affect struvite recovery. Prospectively, these materials can be directly used, after being in contact with wastewater and enriched with struvite, as ready-to-use fertilizers.

KEYWORDS. Electrospinning; Polylactic acid; Nutrients; Wastewater; Struvite.

Introduction

Modern agriculture is highly dependent on the use of phosphorus and nitrogen as key fertilizer constituents. In 2001 Tilman et al. [1] forecasted that by 2050th the industrial production of fertilizers containing nitrogen will be 2.7 times the amounts of 2000th, while the production of those containing phosphorous will be 2.4 times. Phosphorus is derived from phosphate rock, a non-renewable resource whose global reserves are being depleted by the increasing demand of this element [2]. In addition, phosphorus and nitrogen-containing substances deriving from human activities and associated industrialization are discharged in water bodies or infiltrates onto the groundwater, causing eutrophication and consequent impacts on the aquatic ecosystem [3]. Phosphorus recovery would thus provide a double benefit, as clearly described by Mayer et al. [4] on minimizing the shortage of P supply and, at the same time, on improving the quality of the aquatic ecosystem.

Numerous techniques to recover phosphorous from various waste streams were developed, such as struvite and calcium phosphate precipitation [2]. Struvite is a white crystalline substance consisting of magnesium, ammonium and phosphate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) whose precipitation in aqueous environment is controlled by pH and ion concentration [5]. Precipitation occurs when the concentrations of Mg^{2+} , NH_4^+ , and PO_4^{3-} exceed the struvite solubility product constant and it increases with increasing pH. Struvite is a common scale deposit causing blockage of pipes in wastewater treatment plants and it has been considered mainly as a problem to eliminate rather than a product of economic interest [6-8]. Notably, it is a marketable product with excellent fertilizer qualities [9-12]. A number of lab-, pilot- and industrial-scale processes have been specifically developed to elicit struvite precipitation and recovery from wastewater and sludge [13,14]. Most of them are based on the chemical precipitation approach, generally characterized by high efficiency, energy saving and low costs [14], and use of fluidised bed reactors [15], which

consist of a standard columnar reactor containing a suspension of seed material acting as nucleating agent that accelerates struvite precipitation [16].

In this work the concept of struvite precipitation with the help of crystal seeds is applied by loading the seeds on a solid support intended to facilitate the accumulation of N and P by collecting struvite crystals. Since struvite crystals are supposed to grow on the surface of struvite seeds directly exposed to nutrient-rich aqueous solutions, the specific surface area displayed by the solid support is expected to play a major role in process efficiency. For this reason, we used electrospun nonwoven polymeric fibers as support. Electrospun nonwoven meshes are characterized by high porosity, pore interconnectivity, microscale interstitial spacing, and a large surface-to-volume ratio. Thanks to these particular features they are considered highly attractive materials for a wide range of special applications, such as (e.g. filtration, sensors, catalytic systems, structural composites and in biomedical field) [17-20]. Moreover, either functional nanofibers or multi-component nanofibers can be prepared by spinning polymers blended with additional compounds such as nanoparticles, carbon nanotubes and ceramics [21]. Electrospun materials have been also proposed in agriculture applications for the release of nutrients incorporated in the fibers during their permanence in contact with the soil [22,23].

In this work struvite crystal seeds were added to the polymeric solution before spinning to produce fiber loaded with struvite crystal to promote the harvesting of struvite from an aqueous environment (Figure 1A). Poly(L-lactic acid) (PLLA), a well-known biodegradable and bio-based polymer was used to produced fibers. PLLA electrospun fibers loaded with struvite crystals were produced by different methodologies involving solution sonication prior to electrospinning and a coaxial needle to control the struvite seeds distribution along fiber section. The capability of PLLA fibers to promote struvite accumulation was assessed by using a supersaturated synthetic solution of Mg^{2+} , NH_4^+ and PO_4^{3-} ions. This study is a proof-of-concept to provide a ready-to-use

electrospun product that, in contact with nutrient-rich wastewaters, can collect struvite and be directly applied in agriculture as fertilizer. Indeed, the high surface area of electrospun materials combined with their easy-to-use, good mechanical properties in terms of flexibility and the possibility to be used as breathable barrier films make them the ideal supports for the recovery of nutrients for agriculture.

Experimental Section

Materials

Poly(L-lactic acid) (PLLA Lacea H.100-E, $M_w = 8.4 \times 10^4$ g/mol, PDI = 1.7) was supplied by Mitsui Fine Chemicals (Dusseldorf, Germany). Dichloromethane (DCM), dimethylformamide (DMF), struvite crystal seeds ($MgNH_4PO_4 \cdot 6H_2O$), labeled as MAP (acronym of Magnesium Ammonium Phosphate), magnesium hydroxide ($Mg(OH)_2$), ammonium chloride (NH_4Cl) and dipotassium hydrogen phosphate (K_2HPO_4) were purchased from Sigma-Aldrich and used without further purification. Crystal seeds of MAP were purchased by Sigma-Aldrich (SEM images in Figure S1).

Preparation of electrospun mats

A single-nozzle electrospinning apparatus was used (Spinbow Lab Unit, Spinbow S.r.l. Italy), equipped with a grounded aluminum plate positioned 15 cm away from the tip of the needle. The polymer solution was dispensed at a flow rate of 0.9 ml/h, through a PTFE tube, to the needle, that was vertically placed over the collector. Electrospinning was performed at room temperature (RT) and a relative humidity of 40-50 %. The applied voltage was 18 kV. PLLA and MAP were dissolved at a concentration of 13% (w/v) and 0.5% (w/v), respectively, in a solvent mixture of DCM:DMF=65:35 (v/v) (MAP final concentration in the fibers was 3,7 wt%). The polymeric

solutions containing MAP were prepared by following three different procedures (Figure 1B), and the obtained mats were labelled P1, P2 and P3. Briefly, all procedures consisted in dispersing MAP in DCM, followed by PLLA dissolution and DMF addition.

In the P1 mat, MAP was dispersed in DCM by stirring; in the P2 mat, MAP dispersion in DCM was carried out through sonication in a water bath for 20 minutes (two steps of 10 min each to minimize temperature increase) before PLLA and DMF addition; and in the P3 mat, sonication (two steps of 10 min) was applied to the MAP loaded PLLA solution just before electrospinning. A pure PLLA mat was also produced as control from a 13% (w/v) PLLA solution in DCM:DMF=65:35 (v/v), based on a previously reported procedure [24]. Additional mats containing MAP were produced by using a coaxial spinneret (Spinbow, S.r.l., Italy) having an inner needle (i.d. 0.55 mm, o.d. 0.80 mm) concentrically mounted inside an outer needle (i.d. 1.50 mm, o.d. 1.20 mm). The inner capillary protrudes out of the external capillary of 0.1 mm. Two syringe pumps were used in this case to separately control the inner and outer flow rates that were set at 0.2 ml/h and 0.6 ml/h, respectively. Two different mats were produced as shown in Figure 1C: in MAPshell the struvite was loaded in the shell solution and the core was made of plain PLLA, while in MAPcore the struvite was loaded in the core solution and plain PLLA was loaded in the shell. In both types of fibers, the final content of MAP was 3,7 wt% and MAP was dispersed in the polymeric solutions according to P2 procedure. Electrospun mats were kept under vacuum over P_2O_5 at RT overnight in order to remove residual solvents.

Struvite accumulation on electrospun mats

Appropriate amounts of $Mg(OH)_2$, NH_4Cl and K_2HPO_4 were dissolved in deionized water according to literature [25] to get a synthetic solution with the following ion concentrations: Mg^{2+} 187 mg/L, NH_4^+ 140 mg/L and PO_4^{3-} 742 mg/L (corresponding to an equimolar ion concentration). The obtained synthetic solution had a pH of 9.40 ± 0.02 . Electrospun mats were fixed at

CellCrown® plastic rings (inner diameter = 29 mm, Scaffoldex, Tampere, Finland) and immersed in 100 mL of the synthetic solution (in a 250 ml container). Samples **in triplicate** were shaken at RT and after different time intervals (24 h, 48 h and 72 h) they were recovered, gently washed with deionized water to remove weakly adherent inorganic precipitate and dried at RT before characterization. The weight increment experienced by each sample was measured and the percentage amount of accumulated struvite was determined by applying Equation 1:

$$\text{struvite (wt\%)} = \frac{m_f - m_i}{m_f} \cdot 100 \quad [1]$$

Where m_i is the initial mass of the sample and m_f is the mass of the sample after soaking in synthetic solution. Mats fabricated by coaxial electrospinning were tested by following two different procedures: (i) direct immersion in the synthetic solution, as described above, and (ii) wetting in deionized water for 30 min followed by immersion in synthetic solution for 72 h.

Characterization techniques

Scanning Electron Microscope (SEM) observations were carried out using a Philips 515 SEM at an accelerating voltage of 15 kV, on samples sputter-coated with gold. The distribution of fiber diameters was determined through the measurement of about 250 fibers and the results were given as the average diameter \pm standard deviation. The one-way ANOVA was used to test the statistical significance of the difference between the mean values ($p < 0.05$). Electrospun fibers, supported on conventional copper microgrids, were observed by using a Philips CM 100 Transmission Electron Microscope (TEM) operating at 60 kV. Wide angle X-ray diffraction measurements (WAXD) were carried out at RT with a PANalytical X'Pert PRO diffractometer equipped with a fast solid state X'Celerator detector. CuK α radiation was used (40 mA, 40 kV). The 2θ range was from 5° to 50° with a step size of 0.033° and time/step of 20 s. Thermogravimetric analysis (TGA) was performed with a TA Instruments TGA2950 thermogravimetric analyzer from RT to 600°C (heating rate $10^\circ\text{C}/\text{min}$, purge gas air). Since PLLA completely degrades under these conditions

while struvite has a residual weight of 55% (Figure S2), the TGA residual weight is proportional to the amount of struvite contained in the samples after accumulation experiments and can be calculated as follows:

$$\text{struvite (wt\%)} = \frac{\text{wt\%}_{res}}{55} \cdot 100 \quad [2]$$

Microwave Plasma-Atomic Emission Spectrometer (MP-AES Agilent 4210) was used to determine the P and Mg contents in the samples retrieved from the synthetic solution, after microwave-assisted digestion in HNO₃. The struvite content either referred to Mg or P was then calculated by applying Equation 3 and 4 respectively:

$$\text{struvite (wt\%)} = \frac{\text{wt}_{Mg} \cdot 245.4}{24.3} \cdot \frac{100}{m_f} \quad [3]$$

$$\text{struvite (wt\%)} = \frac{\text{wt}_P \cdot 245.4}{31.0} \cdot \frac{100}{m_f} \quad [4]$$

where wt_{Mg} and wt_P are the mass of Mg and P measured by AES, respectively, 245.4 is the molecular weight of struvite, 24.3 and 31.0 are the atomic masses of Mg and P, respectively, and m_f is the final weight of the sample after soaking in synthetic solution.

Results and Discussion

Biodegradable PLLA fibers loaded with MAP were first prepared by means of a single-nozzle electrospinning apparatus starting from polymeric solutions where MAP was dissolved using three different procedures as explained in the Experimental Section (see Figure 1B). Figure 2 shows SEM and TEM characterizations of P1, P2 and P3 mats together with those of a plain PLLA mat used as a control. The latter is composed by bead-free fibers with average diameter of 530 ± 100

nm. The addition of MAP slightly decreased fiber diameters: (410 ± 90) nm for P1, (430 ± 100) nm for P2 and (440 ± 90) nm for P3, that were not statistically different. SEM inspection revealed that only in P1 (not sonicated solution) large aggregates were found within the nanofibrous layer (see representative SEM image in Figure 2B). Moreover, TEM images clearly show the presence of few large particles in P1, while P2 and P3 fibers contained several smaller particle aggregates, revealing that MAP sonication was useful to decrease particles dimension and improve their dispersion in the fibers. The presence of struvite in P1, P2 and P3 was also confirmed by WAXD analysis (Figure S3A) and affected the mechanical properties, as revealed by the stress-strain mechanical data (Table S1). In particular, in P1, where crystal seeds were added to the solution without applying sonication, a significant decrease of elastic modulus (E) and increase of stress at break (σ_b) was found compared to the plain PLLA. P2, where MAP sonication was applied before adding PLLA to the solution, showed the highest improvement of mechanical properties (both E and σ_b increased), while mechanical properties of P3, where sonication was applied to the polymer solution just before electrospinning, were similar to those of PLLA. These results can be explained by hypothesizing that the best MAP dispersion in the fibers was achieved in samples P2, in line with with SEM and TEM observations and are expected to have an important effect on the membrane performance in terms of nutrient recovery.

With the aim to investigate the effect of MAP loading and quality of MAP dispersion on struvite recovery, the mats produced by single-nozzle electrospinning were immersed in a synthetic solution containing a concentration of Mg^{2+} , NH_4^+ and PO_4^{3-} ions and presenting a pH that favors struvite precipitation [25]. SEM images of samples retrieved from the synthetic solution after 72 h are reported in Figure 3. Morphology of plain PLLA appeared unaltered (Figure 3A) while P1, P2 and P3 (Figure 3B-3D) contained several particles entrapped in the fibrous net with the typical elongated shape of orthorhombic struvite crystals [26-28]. SEM inspection revealed that the

highest accumulation of particles arranged in compact aggregates occurred in P2, followed by P1 and then P3, the latter containing only a few crystals. X-ray diffractograms of the retrieved samples are reported in Figure 3E and confirmed SEM observations since only P1, P2 and P3 showed struvite diffraction peaks (more intense in P2), while PLLA displayed only the polymer amorphous halo [24,29]. TGA curves of samples after soaking in synthetic solution are reported in Figure 3F and are characterized by a first weight loss below 100 °C, ascribable to the decomposition of struvite, a second weight loss around 300 °C, corresponding to PLLA degradation, and a residual weight that is proportional to the amount of struvite contained in the analyzed sample. The struvite accumulated on the different mats was quantified gravimetrically (Equation 1), by TGA (Equation 2) and by AES analyses (Equation 3 and 4) and data are reported in Figure 4. PLLA sample shows a small amount of inorganic content after experiments (among 5-10%) that is ascribable to struvite crystals precipitated from the synthetic solution that remained after sample washing. Among the samples produced by single-nozzle electrospinning, P2 is the mat capable of recovering the highest amount of struvite with a final content of inorganic phase between 40-50 wt%, followed by P1 and P3. In practice, it turns out that 1 g of P2 is able to recover about 1 g of struvite from the synthetic solution after 72 h of soaking. These results demonstrate that MAP crystal seeds in the fibers are necessary for promoting struvite accumulation on fiber surface. Moreover, sonication applied to crystal seeds suspension before the addition of the polymer (case P2) leads to higher accumulation of struvite, probably as a consequence of a better dispersion of MAP inside the fibers, that in turns increases seed surface area, as previously hypothesized to explain the mechanical properties of this sample. Sample P2 was also tested in the synthetic solution at different times of soaking (24 h, 48 h and 72 h), showing a clear increase of struvite crystal on fiber surface with time (Figure S4).

To further demonstrate the action of the MAP contained in the fibers as crystal seed for the struvite crystallization on PLLA, a coaxial spinneret was used to prepare fibers where MAP particles were preferentially located either on the surface (MAPshell) or in the core (MAPcore) of the fibers (Figure 2, right column). To this aim, PLLA solution containing MAP was loaded either in the outer or in the inner needle of the coaxial spinneret, respectively (Figure 1C). It is pointed out that both core and shell solutions consisted of PLLA dissolved in the same solvent mixture while its concentration was varied to gain a final MAP content of 3,7 wt% in the fibers. Therefore, a partial mixing between the inner and the outer solutions during electrospinning cannot be excluded, and fibers with a defined core-shell structure are not expected. Nevertheless, TEM images acquired before immersion in synthetic solution confirmed that in MAPshell the inorganic particles were preferentially located close to the fiber surface (Figure 2F, highlighted with circles), differently from the MAPcore where seeds were mostly found in the fiber core (Figure 2E, highlighted with circles).

SEM images showed that after soaking in the synthetic solution for 72 h, fibers containing MAP crystal seeds in fiber core promoted a higher accumulation of struvite when compared to MAPshell (Figure 5A and 5B vs Figure 5C and 5D). Accordingly, WAXD analysis showed more intense struvite peaks in MAPcore compared to MAPshell (Figure 5E). These qualitative results were confirmed by struvite quantification (Figure 4). In particular, after 72 h soaking MAPcore contained about 70 wt% of struvite while MAPshell only 20 wt%, meaning that 1 g of nonwoven fibers can recover about 2.3 g in the first case and only 0.25 g in the second case.

Although in MAPcore crystal seeds were preferentially located in the bulk of the fibers, thus in principle less available for promoting struvite crystallization, this sample showed the best performance among all the tested mats (see Figure 4). This unexpected result can be justified by a partial dissolution of crystal seeds located at fiber surface of MAPshell sample, once in contact

with the synthetic solution. To verify this hypothesis, in a further experiment samples produced by coaxial electrospinning were immersed in deionized water for 30 min before incubation in the synthetic solution for 72 h. This preliminary wetting treatment is expected to dissolve the MAP seeds weakly embedded into the polymeric fibers. SEM images and WAXD analysis reported in Figure 6 show that fibers, originally containing MAP crystal seeds in the core, were still able to collect struvite crystals from the synthetic solution, even after the pre-immersion in deionized water; conversely, the struvite accumulation on MAPshell was very low. Therefore, in MAPcore crystal seeds better resist to water dissolution, in line with literature evidences reporting the capability of core-shell structures to protect the structural integrity of the encapsulated substances [30,31].

Conclusions

In this work we proposed a biodegradable and bio-based product, in contact with nutrient-rich wastewaters, can collect struvite and be directly applied in agriculture as fertilizer. Electrospinning was used as polymer processing technology to produce highly porous nonwovens characterized by high surface-to-volume ratio. To induce the precipitation of P and N in form of struvite on PLLA, the fibers were loaded with MAP crystals. We thoroughly demonstrated that MAP is capable of acting as crystal seed for struvite crystallization at the fiber surface and, by controlling its dispersion and distribution along the fiber (i.e. preferentially located at the surface, in the core or homogeneously distributed along fiber section), it is possible to modulate the amount of struvite accumulation in the fibrous net. Prospectively, this information can be exploited to engineer a biodegradable mat made up of several layers with different MAP loading and distribution along the fibers that enable the selective accumulation of struvite along its thickness.

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Declaration of Competing Interest

None

Data availability statement

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Appendix A. Supplementary material

SEM of commercial struvite, TGA of struvite and PLLA, WADX analysis of as-spun samples, stress-strain tests, and struvite accumulation experiments on P2 over time.

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Figure captions

Figure 1. A) Sketch describing the mode of action of the electrospun PLLA loaded with MAP: MAP incorporated in the fibers acts as crystal seeds for the recruitment of Mg^{2+} , NH_4^+ , and PO_4^{3-} from the solution. B) Single-nozzle electrospinning: in P1 MAP was added to DCM and stirring was applied for 1 hour (step a), PLLA was added and after 1 hour stirring the polymer was completely dissolved (step b), finally DMF was added (step c); in P2, 20 min of sonication (two steps of 10 min each with 2 minutes between them) were applied between step a and b; in P3 sonication (two steps of 10 min each with 2 minutes between them) was performed just before electrospinning. C) Coaxial-nozzle electrospinning: details on the preparation of MAPcore (MAP was loaded in the inner solution) and MAPshell (MAP was loaded in the outer solution).

Figure 2. As-spun mats obtained from single-nozzle electrospinning (left) and coaxial-nozzle electrospinning (right). SEM and TEM micrographs of PLLA (A), P1 (B), P2 (C), P3 (D), MAPcore (E and G) and MAPshell (F and H) mats. Scale bars: 2 μm (SEM); 200 nm (TEM, A, B, C and D); 500 nm (TEM, E and F). **Circles in TEM images highlight the struvite particles.**

Figure 3. Mats produced by single-nozzle electrospinning after soaking in synthetic solution for 72 h. SEM micrographs of PLLA (A), P1 (B), P2 (C) and P3 (D) (Scale bar: 10 μm). E) X-Ray diffraction patterns and F) TGA curves of PLLA (a, black), P1 (b, blue), P2 (c, red) and P3 (d, green).

Figure 4. Weight percentage of struvite contained in electrospun samples after soaking in synthetic solution for 72 h quantified by different methods: by mass (Equation 1, blue); by TGA (Equation 2, grey); by AES (Mg determination, Equation 3, red); by AES (P determination, Equation 4, green).

Figure 5. SEM micrographs of MAPcore (A-B) and MAPshell (C-D) samples after soaking in synthetic solution for 72 h. Scale bar: 20 μm (A,C) and 10 μm (B,D). E) X-Ray diffraction patterns of MAPcore (a) and MAPshell (b) samples after soaking in synthetic solution for 72. F) TGA curves of MAPcore (a, red) and MAPshell (b, black) samples after soaking in synthetic solution for 72.

Figure 6. Mats produced by coaxial electrospinning and immersed in deionized water before soaking in synthetic solution for 72 h: SEM micrographs (scale bars = 20 μm) of MAPcore (A) and MAPshell (B) and X-Ray diffraction patterns of MAPcore (a) and MAPshell (b).