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Research article

Mechanochemical conversion of chrysotile/K_2HPO_4 mixtures into potential sustainable and environmentally friendly slow-release fertilizers

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ABSTRACT

Chrysotile fibers pose a threat to public health due to their association relation to respiratory malignant lung disease such as cancer. For this reason, they must be stored and discarded appropriately, including after treatment, which raises costs. In the present study, insoluble chrysotile fibers were milled in solid state with highly soluble K_2HPO_4, destroying both structures, making the chrysotile nontoxic and generating a new material with potential use as sustainable slow-release fertilizer (SSRF) containing mainly K and P. Based on the mills, milling conditions and chrysotile/K_2HPO_4 molar ratios used, Mg originating from chrysotile fibers reacted with K and P from dibasic potassium phosphate and were transformed into $MgKPO_4 \cdot H_2O$, $MgKPO_4 \cdot 6H_2O$ and probably a mixture of amorphous SiO_2/MgO. In this study, a zirconia planetary mill and high-energy ball mill were used, both of them produced SSRF. In conclusion, it was possible to synthesize high-value and extremely useful materials for agriculture using a harmful waste. The release rate can be tailored by controlling chrysotile/K_2HPO_4 molar ratios, grinding speed and time, which makes the process even more promising for farming applications.

1. Introduction

Chrysotile, or white asbestos, is a fibrous hydrated magnesium silicate with the ideal formulation $Mg_3Si_2O_5(OH)_4$, a mineral of the serpentine group whose structure is formed by octahedral brucite-like ($Mg(OH)_2$) sheets covalently bonded with tetrahedral tridymite-like (SiO_2) sheets, forming nanotubes, which are packed in bundles in the macroscopic fibers (Lafaya et al., 2012; Korytkova et al., 2004; Bales and Morgan, 1985). Chrysotile's use has been banned in many countries due to the risk to health, since it is linked with lung diseases such as cancer (Korytkova et al., 2004; Donaldson and Tran, 2004; Bernstein et al., 2015; Gualtieri et al., 2009). Products containing chrysotile can release their fibers into the environment when being handled or just by weathering, contaminating the soil, watercourses, animals and the human beings. Considering that chrysotile is used in thousands of different products, including roofing tiles and containers to store drinking water, which need to be replaced periodically, there is a consensus that these end-of-life materials need to be discarded properly or destroyed.

The literature reports many different methods to destroy or detoxify asbestos containing wastes, including chrysotile (Spasiano and Pirozzi, 2017). The method combining hydrated oxalic acid and silicates such as tetraethoxysilane ($SiH_{20}C_8O_4$), although efficient, takes at least 30 days to complete the reaction (Turci et al., 2007; Valouma et al., 2017). Thermal and hydrothermal treatments are the most efficient and commonly applied methods, but since high temperatures and/or strong acids are used, it is costly and in the last case, the excess acid needs to be neutralized before disposal in the environment (Kusiorowski et al., 2013; Nam et al., 2014; Anastasiadou et al., 2010; Belardi and Piga, 2013). Artificial carbonatization can produce useful nontoxic materials from chrysotile such as hydromagnesite ($Mg_5(CO_3)_4(OH)_2$) and magnesite ($Mg(CO_3)$), but, once more, this process requires high temperatures and long treatment times (Radvanec et al., 2013). Mechanochemical activation has also been successfully used to treat some wastes (Li et al., 2017), including materials containing chrysotile, leading to amorphous inert materials that can be used for other purposes like construction (Plescia et al., 2003; Guo et al., 2010).

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Based on this brief description, and concerning about the development of methodologies and products which respect the state of socio-ecological resilience (Farley and Voinov, 2016), the present study aimed to destroy chrysotile fibers to eliminate their toxicity, and also to produce value-added products, specifically a sustainable slow-release fertilizer (SSRF). The mechanochemical method used consists basically of milling chrysotile and K_2HPO_4 mixtures in the solid state, with the objective of producing amorphous and/or crystalline materials, which can slowly release nutrients from insoluble chrysotile (Mg and Si source) and from soluble K_2HPO_4 (K and P source). Expected products were potassium struvite ($MgKPO_4.6H_2O$) and Dittmarite ($MgKPO_4.H_2O$), reported to be possible products from magnesium-containing matrices (Graeser et al., 2008; Borges et al., 2017), as well as being a source of P, K and Mg, essential nutrients for plants in general. To investigate the effects of milling conditions such as chrysotile:K_2HPO_4 molar ratio (MR), milling time and speed and pretreatment processes, the release behavior was systematically studied by an experimental design and the residual materials were analyzed after contact with water, using inductively coupled plasma atomic emission spectroscopy (ICP-OES).

The samples were also characterized by several instrumental techniques, like X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and thermogravimetric analysis (TGA).

2. Materials and methods

K_2HPO_4 was purchased from Neon Química – Brazil (99%) and chrysotile fiber with length below 2.0 mm (SAMA7ML) (idealized formula – $Mg_3Si_2O_5(OH)_4$) was donated by SAMA S/A – Minerações Associadas (Minaçu - GO, Brazil). As already described (Wypych et al., 2003, 2005), the used chrysotile presents some contamination of talc ($Mg_3Si_4O_{10}(OH)_2$) and traces of iron oxides/hydroxides (goethite, hematite and magnetite).

Two types of mills were used, the first one (Z mill) (Table 1) a planetary Fritsch Pulverisette 2, consisting of a zirconium vessel with 10.5 cm diameter and zirconium disk attached to the mill by an attachment rod, working at a fixed speed of 70 rpm.

The second investigated mill, (HE Mill) (Table 2) was a Fritsch Pulverisette high-energy ball mill, with a 250 ml agate bowl containing 15 agate balls with 10 mm diameter.

In the Z mill, the pretreatment time (6, 9 or 12 h), milling time (6, 9 or 12 h) and molar ratios (MR) (chrysotile:K_2HPO_4 - 1:2, 1.5:1.5 or 2:1) were investigated according to a 2^3 experimental design with central point (ZCCP) evaluated in triplicate. The pretreatment consisted of previous chrysotile milling in 10 ml of double distilled water and then drying. This process facilitates the disaggregation

Table 1
2^3 experimental design for the Z mill.

Sample code	Levels			Conditions		
				Pre-treatment (h)[a]	Milling time (h)	MR[b]
ZC1	−	−	−	6	6	1:2
ZC2	+	−	−	12	6	1:2
ZC3	−	+	−	6	12	1:2
ZC4	+	+	−	12	12	1:2
ZC5	−	−	+	6	6	2:1
ZC6	+	−	+	12	6	2:1
ZC7	−	+	+	6	12	2:1
ZC8	+	+	+	12	12	2:1
ZCCP	0	0	0	9	9	1.5:1.5

[a] Chrysotile grinding in 10 ml of double distilled water.
[b] Chrysotile:K_2HPO_4 molar ratio; ZCCP - Central point.

Table 2
2^3 experimental design for the HE mill.

Sample code	Levels			Conditions		
				Milling time (h)	Rotation (rpm)	MR[a]
HEC1	−	−	−	6	200	1:2
HEC2	+	−	−	12	200	1:2
HEC3	−	+	−	6	600	1:2
HEC4	+	+	−	12	600	1:2
HEC5	−	−	+	6	200	2:1
HEC6	+	−	+	12	200	2:1
HEC7	−	+	+	6	600	2:1
HEC8	+	+	+	12	600	2:1
HECCP	0	0	0	9	400	1.5:1.5

[a] Molar ratio chrysotile:K_2HPO_4; HECCP – Central point.

the chrysotile bundles into fibers or occasionally single fibrils (nanotubes). In the HE mill, the milling time (6, 9 or 12 h), rotation (200, 400 or 600 rpm) and molar ratio (chrysotile:K_2HPO_4 - 1:2, 1.5:1.5 or 2:1) were also investigated according to a 2^3 experimental design with the central point, evaluated in triplicate (HECCP).

Subsequent to the milling process, some samples, free of chrysotile fibers (ZC2 and HEC4), were treated in solid state at 100 °C for 6 h in a laboratory oven to investigate the possibility of maximizing the crystalline phases to help the characterization.

The X-ray diffraction (XRD) measurements were performed using a Shimadzu XRD-6000 diffractometer, with CuKα radiation source of λ = 1.5418 Å, current of 30 mA and tension of 40 kV. The samples were placed in glass sample holders. The diffraction patterns were acquired using the θ/2θ Bragg Brentano geometry, with a dwell time of 2° min^{-1}, step of 0.02° and 2θ range from 3 to 40°.

The scanning electron microscopic (SEM) images were obtained using a Cambridge Scan 360 SEM operating at 1 kV and a Zeiss supra 55 FEG-VP operating at 3 keV. For these observations, the samples were mounted on conductive carbon adhesive tabs and submitted to gold sputtering.

Thermogravimetric analysis (TGA) was performed with a 4000 TGA Perkin Elmer equipment, using 150 μL alumina crucibles and a temperature ramp of 10 °C/min at a synthetic air flow of 35 mL/min, in the temperature range of 25° C-1000 °C.

Transmission electron microscopy (TEM) and selected area electron diffraction were performed by depositing the sample material on a 3 mm Formvar coated copper grid in a JEOL JEM EX-II microscope, at 80 kV. Gold was used as internal standard for indexation of the samples.

The release studies were performed to verify the influence of the grinding conditions using 25 mg of each sample in 10 ml of deionized water, where initial tests were performed at 1 and 168 h release and the percentage release between these two assays was also considered. As already mentioned, to quantify the nutrient release, the ICP-OES technique was used. The spectrometric

Table 3
Characteristics and operating conditions used for analysis by ICP-OES.

Parameter	Characteristics
Radiofrequency	40 MHz
Radiofrequency power	1150 W
Plasma gas flow	12.0 L min^{-1}
Auxiliary gas flow	1.0 L min^{-1}
Gas flow in the nebulizer	0.7 L min^{-1}
Torch	Quartz for axial view
Nebulizer	Concentric
Replicates	3
Analytical lines	K (I): 766,490 nm; Mg (II): 280,270 nm P (I): 213,618 nm

(I) Atomic line, (II) Ionic line.