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INDCRO-9226; No. of Pages 9
ARTICLE IN PRESS
Industrial Crops and Products xxx (2016) xxx–xxx
Contents lists available at ScienceDirect
Industrial Crops and Products
journal homepage: www.elsevier.com/locate/indcrop

Synthetic nanozeolite/nanohydroxyapatite as a phosphorus fertilizer for German chamomile (*Matricariachamomilla* L.)

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ARTICLE INFO

Article history:
Received 18 June 2016
Received in revised form 10 October 2016
Accepted 28 October 2016
Available online xxx

Keywords:
Nanohydroxyapatite
Nanoclinoptilolite
Chamomile (*Matricaria chamomilla* L.)
Phosphorus fertilizer
Calcareous soil

ABSTRACT

Some regular P fertilizers are less effective in supplying the nutrient P. Thus, a greenhouse experiment was carried out to assess the fertilizing effect of synthetic nanozeolite (nCp)/nanohydroxyapatite (nHA) on agro-morphological characteristics, Chamanzulene and phosphorus up take of chamomile (*Matricariachamomilla* L.). Treatments consisted of (A) control, (B) saturated nano zeolite with ammonium sulfate (nCp-NH_4^+), (C) rock phosphate (RP), (D) saturated nano zeolite with ammonium sulfate plus rock phosphate (nCp-NH_4^+ + RP), (E) nanohydroxyapatite(nHA), (F) saturated nano zeolite with ammonium sulfate plus nanohydroxyapatite(nCp-NH_4^+ + nHA) (G) triple superphosphate (TSP) (H) saturated nano zeolite with ammonium sulfate plus triple superphosphate (nCp- NH_4^+ + TSP) were applied in this study. The nanohydroxyapatite (nHA) particles, with diameters of 25–50 nm, were produced by wet chemical process, in order to compare its ability in P solubility with that of a natural fertilizers (as Triple Superphosphate (TSP) and rock phosphate (PR). The results revealed that application of both nCp/nHA particles and conventional P fertilizer (TSP) could enhance the growth of chamomile. Both Cp-NH_4^+ + nHA and Cp-NH_4^+ + TSP showed the highest mean values for most of the measured traits including plant height, branch number, sub-branch number, Chamanzulene, flower number, soil, root and shoot phosphorous content, flower fresh and dry weight, and also shoot fresh weight and dry weight. On the contrary, no significant differences were observed among applied treatments regarding total nitrogen content and sulfate. The overall results point out that using nCp/nHA as a new class of P fertilizer can potentially enhance agronomical yield and reduce risks of water eutrophication.

1. Introduction

According to the World Food Organization (FAO) applying chemical fertilizers is the most important factor toward increasing global agricultural production in the past three decades. It is stated that out of 3900000 tons increase in demand of P_2O_5 between 2014 and 2018, 58 percent is belongs to Asia, 29 percent to America, 9 percent to Europe, 4 percent to Africa and finally 0.5 percent to Oceania (Lin et al., 2013; FAO, 2015). Although it is established that the amount of total P in the soil is relatively high, its availability to plants is often low (Mahanta et al., 2014; Smith et al., 2011). The difficulty in increasing P availability is due to the strong interaction of phosphates with many inorganic and organic soil components (Driessen et al., 2001). In calcareous and alkaline soils, phosphate is usually associated with Ca^{2+} in apatite minerals so that it generates an insoluble form of phosphate (Aziz et al., 2006). Phosphate rock (PR) is the precursor of many P fertilizers, since there are many natural resources and mines worldwide. PR effectiveness as a fertilizer by its very low solubility is limited (Hamdali et al., 2008; Meck et al., 2010; Koppelaar and Weikard, 2013) which is due to large size of these particles and thus restricting phosphate from reaching the root plants (Liu and Lal, 2014). On the other hand, water soluble P fertilizers are easily dissolved in the soil solution and it would be easily available to the plants. Overuse of phosphorus fertilizers cause occurrence of surface water pollution and eutrophication (Fageria, 2009). To resolve this problem, modifiers, such as zeolites, have been recently added to P fertilizers (Bernardi et al., 2010). Liu and Lal, (2014) reported the impact of nanohydroxyapatite (nHA) as a new class of P fertilizer to enhance the growth and yield of soybean (*Glycine max*) through a greenhouse study (Liu and Lal, 2014). Furthermore, Jiang et al. (2014) stated that the only way of passing nHA through cell membrane in to the cytoplasm to inhibit the

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http://dx.doi.org/10.1016/j.indcrop.2016.10.054
0926-6690/

growth of the mung bean (*Vigna radiate*) sprouts is when the size of nHA is small enough (Jiang et al., 2014).

Iran's climate is mostly arid and semi-arid (Baghalian et al., 2008) and water deficiency is increasingly becoming a serious problem in agricultural areas of Iran (Salami et al., 2009). Introducing and distinguishing different types of plant which can tolerance water deficit conditions in such situations could be a way to overcome low water availability. Chamomile (*Matricariarecutita* L.), as medical plant is allegedly compatible with a wide range of climates and soils (Das et al., 1998) changing conditions thatappears to be existing in the West, North West and South of Iran (Podlech 1986; Baghalian et al., 2011). In addition to water deficit conditions, this plant is also suitable for planting in saline soils (Baghalian et al., 2008), sodic (Balak and Misra, 2004; Razmjoo et al., 2008).

Chamomile, is annual, aromatic, herbal plant and belongs to the Asteraceae family (Baghalian et al., 2008). It is widely distributed in Europe, Asia, Africa and America, and it has (Alibabaei et al., 2014) both autumn and spring varieties (Singh et al., 2011). About 0.2–1.9% of its essential oil is usually extracted from flower' head (Baghalian et al., 2008; Singh et al., 2011). These essential oils contain bisabolol oxide, bisabolon oxide, farnesol, farnesen and chamazulene (Esmaeili et al., 2011; Murti et al., 2012; Ghaedi Jeshni et al., 2015). Chamazulene is the origin of the blue German chamomile essential oil and its determinants oil prices (D'Andrea, 2002; Roby et al., 2013; Bessada et al., 2015). A double-loop hydrocarbon consist of with between 1 and 11 wt% of the total oil (Franke, 2005). Chamomile has medicinal properties, anticonvulsant, anti-inflammatory, antispasmodic, relaxing, anti-rheumatic, carminative, antiseptic bandages, anti-bacterial, treatment of acne, insomnia, gastric ulcer prevention and treatment. It is used along with moisturizers, anti-aging and sunscreen (McKay and Blumberg, 2006; Mohammad et al., 2010; Formisano et al., 2015). It has been reported that alzheimer's disease (AD) (Alibabaei et al., 2014) knee (Buono-Core et al., 2011; Shoara et al., 2015; Ghaedi et al., 2015) anti-inflammatory and regenerative wound is attributed to chamazulene content (Karami et al., 2009).

Since Phosphorus (P) has a key roles during developing and extending stages of flowering and reproduction (Kumar et al., 2006), and also the most important part of chamomile plants used economically and in pharmaceutical industries is its yellow flowers; therefore, study the effect of different kind of phosphorous fertilizers and their impact on its performance is crucial. Hence, the present study was implemented to compare nano-compound fertilizer regarding different morphological and chemical characteristics of chamomile. This work can provide promising and effective way to prepare phosphorus for plants.

2. Materials and methods

The study was conducted at the Research Fields in Esfahan, Iran, in 2015. Before fertilizing, soil samples (0–30 cm) were taken from each block and analyzed according to standard procedures. Soil analysis were measured as follows: pH (Jackson, 1967), cation exchange capacity (CEC) (Jackson, 1958), calcium carbonate ($CaCO_3$) (Caglar, 1949), texture and organic matter (Black, 1965), total N (Bremner, 1965), extractable P (Olsen and Sommer, 1982), extractable potassium (K), calcium (Ca), sodium (Na) and magnesium (Mg) (Pratt, 1965; Thomas, 1982) in addition to extractable iron (Fe), zinc (Zn), copper (Cu), manganese (Mn), and boron (B) (Lindsay and Norvell, 1978). The characteristics of the soil in this study are given in Table 1.

2.1. Preparation of materials

The zeolite (Cp) applied in this research was originated from a zeolite mine in Semnan province, Iran. Elemental composition of Cp was determined by X-ray fluorescence (XRF) (Table 2). Nano scaled Cp was prepared by grinding the mineral to the size of 31–65 nm then saturated with NH_4^+, using soaking the samples in a 1 M sulfate for 10 days (Perrin et al., 1998). Rock phosphate (PR) was used from Esfordi deposit, Yazd province, Iran. It was grounded to 0.1–0.2 mm and elemental composition of PR was calculated by XRF technique (Table 3).

The nHA was synthesized by the wet chemical precipitation method, using calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) as the source of calcium, diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) and P source. Ca $(NO_3)_2{\cdot}4H_2O$ and $((NH_4)_2HPO_4)$ were dissolved sequentially, in distilled water. Ethanolamine (EA) was used as a dispersant to prevent the products from aggregating during the synthesis process. In a typical procedure (for sample), $Ca(NO_3)_2$ and $((NH_4)_2HPO_4)$ were dissolved in distilled water, and their initial pH values were adjusted to 10.00 with aqueous ammonia. The concentration of the calcium and phosphoric ions were both 0.3 M. Calcium nitrate $Ca(NO_3)_2$ solution (50 ml) was added to 250 ml three necked flask, and 3 wt.% of EA was added as a dispersant to the solution of $Ca(NO_3)_2$. The mixture was stirred at a speed of 400 r/min, and the temperature was controlled at 40 °C. Then, 30 ml of $(NH_4)_2HPO_4$ solution was added drop by drop into the mixture, at a speed of 2 ml/min. The mixture was stirred continually for 1.5 h and then gradually cooled to room temperature. The resulting suspension was aged for 24 h at room temperature and then filtered. The product was washed with water to remove residual impurities and then washed with ethanol to remove water and improve the dispersibility. The final product was atmospheric–dried at 70 °C for 5 h and then calcined at 700 °C for

Table 1
Properties of the calcareous soil studied.

Depth (cm)	pH	EC (ds/m)	Olsen P (ppm)	Ca (ppm)	Mg (ppm)	K (ppm)	OC (%)	Cu (ppm)	Zn (ppm)	Mn (ppm)	Fe (ppm)
0–30	7.8	0.722	7.45	48	14.4	155	0.27	0.9	1.46	9.46	3.64

Table 2
Chemical composition of zeolite.

SiO_2 (%)	SO_3 (%)	Cl (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	Br (%)	K_2O (%)	P_2O_5 (%)	SrO (%)	TiO_2 (%)
82.7	0.6	0.27	8.64	1.7	1.77	0.7	0.12	2.03	0.28	0.3	0.32

Table 3
Chemical characteristics of the rock phosphate (PR).

P_2O_5 (%)	Fe_2O_3 (%)	CaO (%)	SiO_2 (%)	MgO (%)	Al_2O_3 (%)	Na_2O (%)	K_2O (%)	SO_3 (%)	CO_2 (%)	F (%)	Cl (%)	Cd (ppm)
37 ± 1	3.5± 1	50 ± 4	3.50 ± 1	1 ± 0.5	0.25	0.26	0.04	0.05	1 ± 0.5	2 ± 1	0.18 ± 0.03	10 ± 5

Please cite this article in press as: Mikhak, A., et al., Synthetic nanozeolite/nanohydroxyapatite as a phosphorus fertilizer for German chamomile (*Matricariachamomilla* L.). Ind. Crops Prod. (2016), http://dx.doi.org/10.1016/j.indcrop.2016.10.054