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Purified monoammonium phosphate fertilizer promotes the yield and reduces heavy metals accumulation in tomato (*Lycopersicon esculentum* L.)

Y. Ben Salah^{1,2} · H. Oudadesse³ · B. Lefeuvre³ · S. Tounsi² · H. El Feki¹

Abstract

Monoammonium phosphate is a commonly used fertilizer for better crop production. However, its repeated application causes the accumulation of harmful metals levels in plants and soil over time. Here, the impact of the purification of monoammonium phosphate fertilizer on vegetative growth and yield of tomato plants (*Lycopersicon esculentum* L.), and the heavy metals accumulation in both soil mix and tomato fruits was investigated through a pot experiment on three different concentrations of purified and unpurified monoammonium phosphate fertilizer. This study showed that the purification of monoammonium phosphate led to a significant enhancement on vegetative growth and yield attributes, mainly for 1 g/L of purified fertilizer. Importantly, the physicochemical investigations showed a significant reduction in heavy metals accumulation (Pb, Cr, Cd, Ni, and V) in the fruits and the soil mix treated with purified monoammonium phosphate. This study confirms that the use of purified monoammonium phosphate fertilizer improves the fruit yield and at the same time reduces the impact of toxicity of heavy metals present in the environment, which can be classified as a part of an environmental management systems.

Keywords Tomato · Monoammonium phosphate fertilizer · Heavy metals · Purification · Soil mix

Introduction

In agriculture, the use of chemical fertilizers is necessary to improve production yield (Achary et al. 2017; Cordell et al. 2009; Tomlinson 2013). In particular, phosphate (PO₄) fertilizers are frequently used worldwide (Hartley et al. 2013; Taliman et al. 2019) as it supplies one of the most crucial nutrients with regard to crop production, i.e., globally about 150 million tons of phosphate rock are extracted each year for PO₄ fertilizers production (Bhat et al. 2019; Cordell et al. 2009; Jasinski 2008; Valadares et al. 2017). However, the extensive use of chemical fertilizers with higher PO₄

strength in agriculture is becoming a serious problem to deal with, due to the toxicity of many naturally occurring metals present in phosphate rock (Gupta et al. 2014; Jiao et al. 2012; Walsh et al. 2018). Once deposited in the ground, plants can easily absorb metals from the soil and introduce them into food chains, which increases consumers metal toxicity risks (Bücker-Neto et al. 2017; Roy and McDonald 2015). Subsequently, PO₄ fertilizers such as monoammonium phosphate (MAP), di-ammonium phosphate (DAP) and triple superphosphate (TSP) are allowed to have higher heavy metals (Pb, Cr, Cd, Ni, and V) levels, and the environmental risks of trace elements in agro-ecosystems pertaining to P₂O₅ fertilization are commonly known as previously discussed and reviewed (Chen et al. 2007; Grant et al. 2013; Hartley et al. 2013; He et al. 2005; Jiao et al. 2012). However, repeated applications of unpurified phosphate rock containing fertilizers will cause harmful heavy metals to accumulate in cropland soils and cause a vast deterioration in soil health and micro-flora needed for continuation of crop growth (Tripti et al. 2015). Note that the presence of heavy metals, characterized by non-biodegradability and persistence in the environment, can reach toxic levels in vegetables and function as stressors resulting in physiological constraints

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that decrease both yield and quality (Chibuiké and Obiora 2014; Shekar et al. 2011). On the other hand, MAP is a world widely recognized fertilizer product (Gargouri et al. 2012), that, when applied as a fertilizer in agriculture, causes potentially toxic trace elements such as Pb, Cr, Cd, Ni and V (Schipper et al. 2011; Zhang et al. 2017). As a preventive use of MAP fertilizer in an alternative agricultural system like that of organic farming, an effective approach is required to eliminate impurities. Our previous preliminary results (Gargouri et al. 2012; Nasri et al. 2014) showed that the purification of MAP successfully reduced the concentration of heavy metals, which could be considered by farmers as an alternative way to improve crop yield and avoid toxic metals at the same time. Unfortunately, the distribution of metals in tomato is still relatively unexplored (Lombi et al. 2011; Trebolazabala et al. 2017) and thus prompted us to conduct in vivo studies on tomato culture as model for heavy metal uptake by the tomato plant.

Here, we report the positive effect of the purification of industrial MAP fertilizer on *Lycopersicon esculentum* L. (tomato) plant growth, fruit yield, and the reduction in toxic heavy metals in fruits and soil mix. *Lycopersicon esculentum* L. tomatoes were used as a test crop, as it is one of the most well-recognized and commonly grown crops in the world, with a global production of ~159 million tons, as of 2011 (Heuvelink 2018). Furthermore, it consists of nutrients such as folate (vitamin B), P, vitamins A and C, carotenoids, and flavonoids (Ouzounidou et al. 2008; Wold et al. 2004) and are generally associated with the reduced risk of several diseases (cancer, prostate, heart diseases, etc.) (Cantore et al. 2016; Li et al. 2016). Moreover, it is well-known that the tomato is a strong accumulator of heavy metals, which poses a great risk to human health (Khan et al. 2015). In this study, the application of MAP before and after purification was performed to compare its effects on plant growth, tomato yield, and heavy metals accumulation in fruits and soil mix. Accordingly, the physicochemical properties of the fruits were deeply investigated through inductively coupled plasma atomic emission spectroscopy (ICP-OES), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM).

The current study was carried out between 2017 and 2019 in Rennes, France and Sfax, Tunisia.

Materials and methods

Crystallization of industrial MAP and analytical methods

The crystallization experiments of the starting product, MAP, were carried out in a batch reactor at 60 °C, under 400 rpm stirring rate over 1 h (Gargouri et al. 2012). The

phosphorus (P₂O₅) content in the solution was analyzed via a gravimetric method, involving molybdate precipitation. The nitrogen (N) content was determined using the Kjeldahl method (Bradstreet 1954), and the heavy metals levels (Pb, Cr, Cd, Ni, and V) were analyzed using ICP-OES.

Experimental design and treatments

A hybrid tomato, known as Rio Grande, was used as a test crop. A greenhouse experiment with tomato plants was conducted during the drier season. The growth conditions inside the greenhouse were day/night, the temperature 32/15 °C, and the light period 12/12 h. Four-week-old germinated seedlings were transplanted into 20 L pots, containing a mixture of peat moss and soil (the mixture is called soil mix) in a ratio of 1:3. The physicochemical properties of the soil mix are presented in Table 1. Tomato plants were treated by purified and unpurified MAP fertilizer at three different concentrations of 0.5, 1, and 2 g/L. The experiments consisted of seven different treatments, including a control (control: 0 g/L unpurified MAP + 0 g/L purified MAP, T1: 0.5 g/L of unpurified MAP, T2: 0.5 g/L of purified MAP, T3: 1 g/L of unpurified MAP, T4: 1 g/L of purified MAP, T5: 2 g/L of unpurified MAP, and T6: 2 g/L of purified MAP). Each treatment had nine replicates. The purified and unpurified MAP fertilizers were applied five times during the experiment, i.e., at the start of the experimental treatments and afterward at 3, 5, 7, and 9 weeks. The applied dose was 0.5, 1, and 2 g per plant on each occasion, respectively. To prepare the treatments, 0.5 g, 1 g, and 2 g of purified and unpurified MAP were dissolved separately in 1 L of water and the suspension was added to each pot. During the growing period, the tomato plants were irrigated based on their water demand and water quantities were equal for all treatments.

Determination of growth parameters, tomato yield, dry matter, and chlorophyll content

During the entire growing season, measurements of plant height, number of leaves, and stem diameter were taken

Table 1 Physicochemical properties of experimental soil mix

Soil mix properties	Values
pH	6.3
EC ^a (mS/m)	0.44
OM ^b (%)	68
<i>Soil texture</i>	
Sand (%)	64.28
Silt (%)	20.43
Clay (%)	15.29

^aElectrical conductivity

^bOrganic matter

every seven days. The days of 50% flowering and 90% first fruit picking were recorded, i.e., when around 50% of the plant population of each treatment started flowering and 90% of these plants reached their first crop harvest (Mengistu et al. 2017). At 60 days after transplantation (DAT), the number of clusters per plant was recorded, while at 90 DAT the number of flower clusters per plant was determined.

At harvest (180 DAT), the fruits number was measured for each plant and separated into green and red. Only ripen tomatoes were weighed and the yield data were estimated in gram per plant. Three fruits per treatment were chosen to determine their transversal diameters (width) and longitudinal diameters (length). At 60, 120, and 180 DAT, three plants from each treatment were gently uprooted from the pots for total dry biomass measurements. Then, all samples were washed using water and then oven-dried at 70 °C for 72 h.

The total chlorophyll content of the leaves was also determined at 60, 120, and 180 DAT (Porra 2002). A sample of 0.5 g of the youngest fully expanded leaves was ground with 80% acetone for chlorophyll extraction. The absorbance at 663 and 646 nm was measured using a PerkinElmer Lambda 14UV/Vis Spectrometer.

Determination of metals accumulation in soil mix

The collection of initial soil mix samples took place before the layout of treatments (T0) to assess heavy metals accumulation. Moreover, soil mix samples were also collected after the harvesting of the crop (180 DAT) to measure its heavy metals content. Soil mix samples were first dried overnight at 80 °C, then 0.25 g of each sample was digested with 4 mL concentrated hydrochloric acid and 1 mL concentrated nitric acid. The quantification of Pb, Cr, Cd, Ni, and V was performed using ICP-OES on a Ciros Spectro Analytical Instrument (Germany). Standard solutions of Pb, Cr, Cd, Ni, and V were employed to prepare the working standard solution and the blank solution.

Characterization of tomato fruits

Tomato fruits were characterized using ICP-OES, FTIR, and SEM techniques. Heavy metals accumulation in dry tomato fruit was measured using ICP-OES. After harvesting, tomato fruits were dried over 72 h at 60 °C. Dried tomatoes were ground into a powder of which 0.2 g were placed in a microwave tube and acid-digested with 1 mL of plasma pure nitric acid and 4 ml of 30% hydrogen peroxide in a microwave system (Packer et al. 2007). Moreover, to identify the nature of chemical bonds between atoms, FTIR measurements were performed in 4000–400 cm⁻¹ range using a JASKO FT/IR 420 spectrometer. Tomato fruits powders were mixed with KBr then pellets on 0.5 cm in diameter. The morphology and

microstructure of dried fruits were also examined by SEM imaging using a JEOL JSM 6301F (Japan).

Results and discussion

Characterization of MAP fertilizer before and after purification

The ICP-OES results of heavy metals analysis of MAP fertilizer before and after purification are summarized in Table 2. Pb, Cr, Cd, Ni, and V rates of purified MAP show a significant decrease compared to those of unpurified MAP. The rate of decrease, following purification, was 52.66%, 29.72%, 68.34%, 33.03%, and 72.92% for Pb, Cr, Cd, Ni, and V, respectively. Moreover, as shown in Table 2, after purification, the percentages of P₂O₅ and N increased by 15.93% and 3.15% compared to those of the unpurified MAP. The obtained values are in good agreement with previous study (Gargouri et al. 2012).

Effect of treatments on growth and yield attributes

The morphology of plants was monitored throughout the culture period for different treatments. The effect of treatments on leaf numbers, plant height, and stem diameter of tomato plants at 60, 120, and 180 DAT are summarized in Table 3. Overall, both purified and unpurified MAP significantly improved the growth parameters compared to the untreated plants. These results confirm that MAP fertilizer exerts a great improvement on plant growth and development compared to that obtained without fertilization, which is in line with the previous report of Groot et al. (de Groot et al. 2003). Interestingly, these findings revealed that the purified MAP led to higher plant height, stem diameter, and leaf numbers as compared to unpurified MAP. As shown in Table 3, at 120 DAT, the highest number of leaves was

Table 2 Physicochemical properties of MAP fertilizer before and after the purification, measured by ICP-OES technique

Properties	MAP fertilizer	
	Unpurified MAP	Purified MAP
pH	4.8	4.8
<i>Heavy metal (ppm)</i>		
Pb	4.5	2.13
Cr	70.51	49.55
Cd	6.76	2.14
Ni	38.29	25.64
V	3.04	0.39
Total N (%)	11.67	12.05
Total P ₂ O ₅ (%)	50.92	60.57

Table 3 Leaf numbers (leaf/plant), plant height (cm) and stem diameter (mm) at 60, 120, and 180 DAT, under different fertilization

Treatments	Leaf numbers (leaf/plant)	Plant height (cm)	Stem diameter (mm)
<i>60 days after transplanting</i>			
Control	12±0.4a	46.4±6.2a	5.9±0.7a
T1	12±0.86a	51.7±5.76abc	6.77±0.61ab
T2	13±1.64a	51.9±3.32abc	7.25±0.57b
T3	13±0.52a	56.3±7.78bc	7.38±0.66b
T4	13±0.92a	59.4±4.54c	7.55±1b
T5	12±1a	48.5±3.88ab	6±0.58a
T6	12±0.48a	50.7±5.51ab	6.22±0.71a
<i>120 days after transplanting</i>			
Control	18±0.59a	81.5±6.05a	7.34±0.35a
T1	21±0.86bc	93±5.32bc	8.41±0.87abc
T2	21±1.56bc	95.6±10.01bc	8.84±0.72bcd
T3	21±0.86bc	95.6±5.8bc	9.25±1.58 cd
T4	22±1.61c	99.4±6.58c	9.88±0.31d
T5	20±1b	86.4±5.97ab	7.43±0.44a
T6	21±1.74bc	92.7±6.46bc	8.07±0.57ab
<i>180 days after transplanting</i>			
Control	21±0.4a	91.7±4.54a	7.82±0.38a
T1	25±0.92c	105.1±8.16bcd	9.47±0.77b
T2	26±1c	109.3±6.46 cd	9.67±0.86b
T3	28±0.97d	112.6±6.65de	10.93±0.22c
T4	32±1.64e	118.6±5.98e	11.58±0.9c
T5	22±0.48ab	96.3±5.4ab	8.18±0.52a
T6	23±0.88a	100.9±6.09bc	8.69±0.64a

Data are means of nine replicates, with standard errors. Means followed by a common letter in columns are not significantly different ($p \leq 0.05$)

obtained by T4 (22 leaves), while T5 increased the latter by only 10% over the control treatment. Moreover, the purified MAP at 1 g/L significantly improved the plant height at 60 DAT, 120 DAT, and 180 DAT by 21.88%, 18%, and 22.68%, respectively, compared to the control. Similarly, the maximum stem diameters 7.55, 9.88, and 11.58 mm were obtained by T4 treatment at, 60, 120, and 180 DAT, respectively.

On the other hand, as shown in Table 4, the analysis of variance for days to 50% flowering (DTF) and 90% first fruit picking (DTP) displayed a significant difference ($p > 0.05$) between treated (with purified and unpurified MAP) and untreated plants (control). A retardation in fruits maturity was observed in all unpurified treatments, which clearly confirms that the purification of MAP fertilizer led to an enhancement of the performance of tomato. The fastest flowering (56 DTF) and maturation (119 DTP) were observed in plants treated with 1 g/L of the purified MAP (T4). None of the treatments altered the number of

Table 4 Effect of different doses of purified and unpurified MAP fertilizer on selected phenological of tomato

Treatments	DTF*	DTP**	No of cluster Plant-1	No of flowers Cluster plant-1
Control	91±2f	181±1 ^c	6±0.77a	4±3.98a
T1	64±0b	133±0c	7±0.52ab	16±2.42b
T2	64±1b	133±2c	8±1.16ab	16±2.33b
T3	63±3b	126±1b	8±1bc	17±3.08b
T4	56±2a	119±1a	10±1.81c	18±4.94b
T5	84±1 ^c	174±0d	6±1.11a	5±2.5a
T6	78±1c	172±2d	7±0.97ab	8±1.8a

*Days to 50% flowering

**Days to 90% first fruit picking

Data are means of nine replicates, with standard errors. Means followed by a common letter in columns are not significantly different ($p \leq 0.05$)

clusters per plant, except for T3 and T4, which significantly increased the number of clusters by 25% and 40% compared to control. Contrary to T5 and T6, T1, T2, T3, and T4 markedly increased the number of flower clusters per plant by 75%, 75%, 76.47%, and 77.77%, respectively, over the control.

The fruits number (green and red) and sizes are shown in Table 5. Compared to the untreated plants, all the treated plants showed an increase in total fruits number and size. Interestingly, the lowest green fruit number (6) and the highest red fruit number (21) were observed by purified MAP at 1 g/L (T4). All treatments significantly increased the width and the length of fruits, compared to the control. Plants treated with purified MAP exhibited high average fruits sizes compared to those treated with unpurified MAP fertilizer. The most important width (33.27 mm), length (37.6 mm), total fruits number per plant (27 fruits), and yield per plant (176.66 g) were recorded for (T4). This increase in yield can be attributed to the high number of clusters and flowers per plant recorded for (T4).

On the other hand, this increase in growth and yield parameters may be ascribed to the difference in the rate of N and P₂O₅ supplied with purified MAP (Cantore et al. 2016; Fandi et al. 2010; Giuliani et al. 2018; Kirimi et al. 2011). Several reports observed that the use of N and P₂O₅ is required for better root formation, growth, and yield of plants (Kushwaha et al. 2001; Troeh and Thompson 2005). Note that the highest reported values of various growth and yield parameters were clearly recorded for the most favorable treatment (T4), which is assigned to the use of higher percentage of P₂O₅ and N conferred by purified MAP. Beside, supplying the essential nutrients, the positive effect of purified MAP on the growth and yield of tomato plants might also be related to the role of microbiota in improving organic matter, mineralization of soil, solubilization of soil

Table 5 Green, red, and total fruit as well as size and yield of fruits harvested from tomato plants at 180 DAT under different fertilization

Treatments	No of fruits plant ⁻¹			Size of fruits		Yield plant ⁻¹ (g)
	Green	Red	Total	Width (mm)	Length (mm)	
Control	15 ± 1c	1 ± 1a	16 ± 4.5a	19.91 ± 2.91a	23.27 ± 1.27a	95 ± 5a
T1	10 ± 2abc	9 ± 1bcd	19 ± 6ab	25.15 ± 1.97bc	30.64 ± 0.64bc	143.33 ± 3.6 cd
T2	10 ± 1abc	10 ± 0 cd	20 ± 6.5b	26.7 ± 1bc	31.38 ± 2bc	148.33 ± 0.33d
T3	9 ± 1ab	14 ± 2d	23 ± 7.81b	28.7 ± 1.7c	34.82 ± 0.82 cd	148.88 ± 0.88d
T4	6 ± 0a	21 ± 1e	27 ± 9.87b	33.27 ± 0.27d	37.6 ± 2.6e	176.66 ± 0.66e
T5	15 ± 3c	3 ± 4.04ab	18 ± 9.61ab	23.22 ± 0.22ab	27.54 ± 1.54ab	131.25 ± 1.25b
T6	14 ± 3.46bc	5 ± 0abc	19 ± 7.25ab	25.07 ± 0.07bc	30.22 ± 1b	139.44 ± 4.44bc

Data are means of three replicates, with standard errors. Means followed by a common letter in columns are not significantly different ($p \leq 0.05$)

mineral, and chelation of ions (Janzen et al. 1995), giving rise to improved biological function of the plant.

These investigations showed that despite the amount of MAP fertilizer was similar in the purified and unpurified treatments, the purified MAP had an additive effect in enhancing the growth and fruits yield of tomato. It is well-known that soil pollution, due to metals, deteriorates soil productivity and hydrophobicity, as well as water capacity. This deterioration is linked to a decreased trend of cellular volume, fruit size, and tomato yield (Gangwar et al. 2010; Ivanov et al. 2016; Mathur et al. 2016; Soinnie et al. 2014; Wu et al. 2010). Kelling et al. (2000) reported that most heavy metals are toxic to plants with the first result of toxicity being the reduction in plant growth, subsequently leading to the reduction in yield. Therefore, the negative effects on growth and yield of tomato plants can be assigned to the presence of higher heavy metals levels in unpurified MAP (Table 2).

Water content of tomato plants

The effect of purified and unpurified MAP on total dry biomass of tomato plants is presented in Fig. 1a. At 60, 120 and 180 DAT, plants treated with purified and unpurified MAP fertilizer displayed a significant improvement in their dry biomass compared to the untreated plants. Furthermore, the use of purified MAP (T2, T4 and T6) for tomato cultivation led to a higher dry weight compared to unpurified treatments (T1, T3 and T5). As expected, the most remarkable improvement was recorded for the purified MAP used at 1 g/L (94.93 g) after 180 DAT. The minimum percent increase (1.4% over the control treatment) in total dry weight was recorded using unpurified MAP at 60 DAT. This is due to high heavy metals accumulation in unpurified MAP which can affect the plasma membrane permeability and causes a reduction in water content (Costa and Morel 1994). It has been also reported that water content decreased in the different organs of plants grown in solutions containing toxic levels of heavy metals (Rucińska-Sobkowiak 2016).

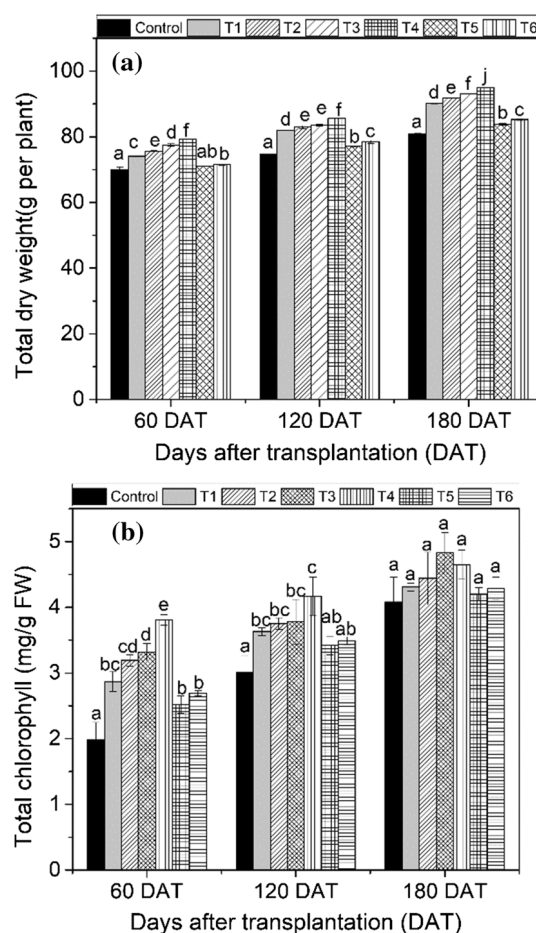


Fig. 1 a Total dry weight and b chlorophyll content of (*Lycopersicon esculentum* L.) harvest at cultivation under different treatments and harvest at 60, 120, and 180 days after transplantation. Each value is represented by the mean ± SD. Values with different superscripts; a–j are significantly different at $p < 0.05$ (means of three replicates)

Leaf pigments analysis

Figure 1b shows the effect of purified and unpurified MAP fertilizer on total chlorophyll. At 60 DAT, an improvement

was obtained with all the treatments, compared to the control. Overall, the chlorophyll content is higher in purified treatment. Particularly, T4 showed the most important improvement, 48.03% over the control. Similarly to dry biomass results, the low level of chlorophyll content in treated plants with unpurified MAP is mainly due to the high levels of heavy metals present in MAP fertilizer before purification, which can damage the photosynthetic apparatus (Hourri et al. 2020). However, at 120 and 180 DAT, cultivated plants

based on purified MAP displayed approximately similar chlorophyll content compared to unpurified MAP, confirming that its application had no negative effect on the photosynthesis of plants.

Heavy metals accumulation in soil mix

The mean values of heavy metals in soil mix are summarized in Fig. 2. A significant increase in heavy metals

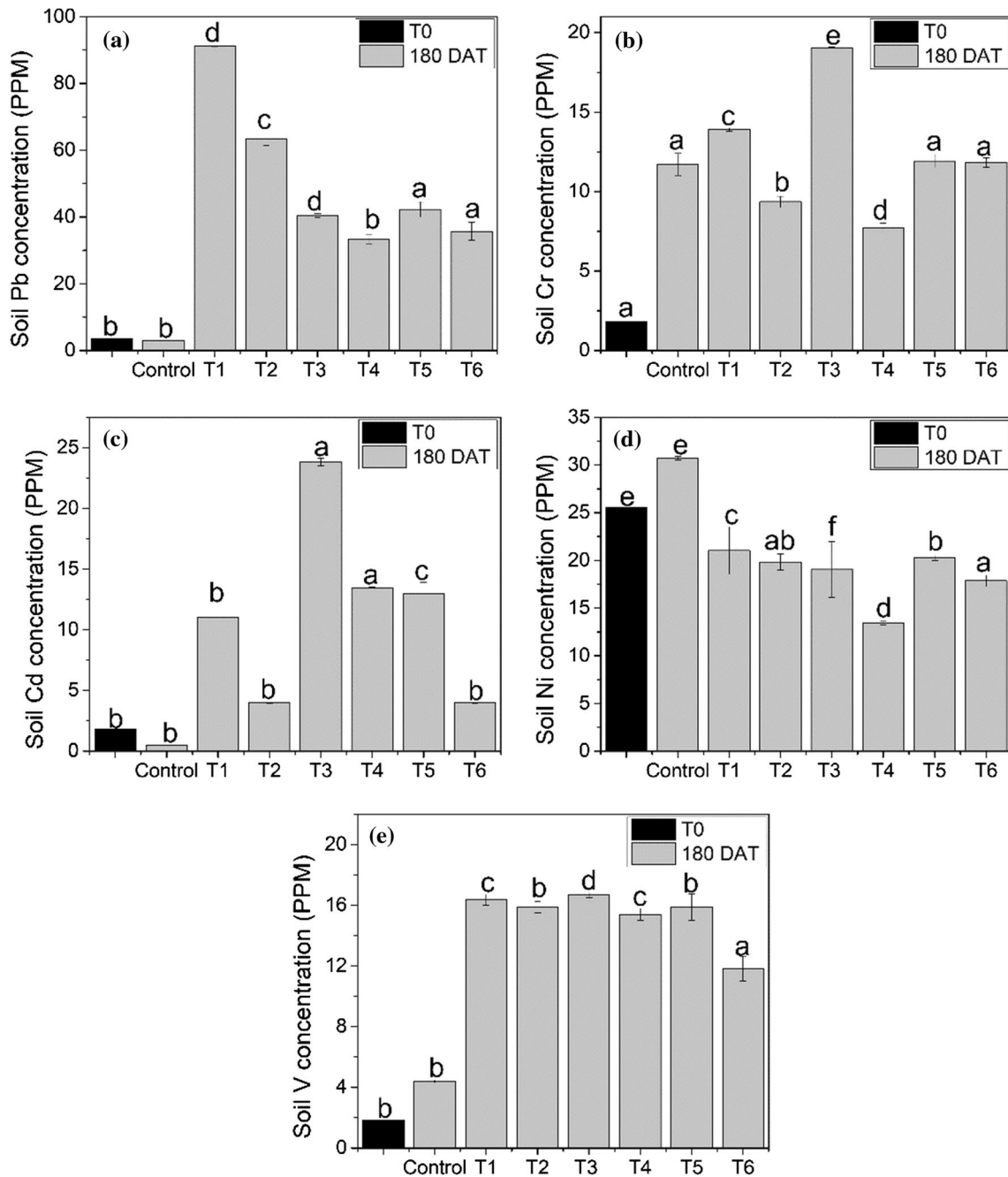


Fig. 2 Effect of different treatments on heavy metals concentration in soil mix before transplantation (T0) and at 180 DAT. Each value is represented by the mean \pm SD. Values with different superscripts; a–f are significantly different at $p < 0.05$ (means of three replicates)

accumulation in soil mix (in both purified and unpurified treatment) compared to the control treatment was observed. This result is in accordance with data obtained by previous studies (Oyedele et al. 2006; Thomas et al. 2012). Indeed, the soil mix treated with purified MAP (T2, T4, and T6) accumulated fewer heavy metals compared to that treated with unpurified MAP (T1, T3, and T5). Particularly, the accumulation of heavy metals in soil mix was more accentuated at 180 DAT, compared to those determined before transplantation (T0). These results are in good matching with those of Khan et al. (2015), showing that the associated health hazard of toxic metal depends on exposure times. Furthermore, the high levels of Pb, Cd, and V of the treated soil mix reported after the experiment (180 DAT) compared to the initial values in both purified and unpurified MAP compounds are the result of the high contribution of PO_4 fertilizer applied five times during the experiment. This fact was already reported (Grant and Sheppard 2008). They found that the Cd accumulation not only depends on the concentration of Cd in the fertilizer, but also on the application rate of chemical fertilizer. Moreover, De Vries et al. (2002) reported that high-fertilizer applications may cause a decrease in pH and thus increase heavy metal availability. Another study (Levy et al. 1992) suggested that the presence of high heavy metals concentrations in the soil could be attributed to their reactions in the soil such as mineral precipitation and dissolution, ion exchange, adsorption, desorption, aqueous complexation, biological immobilization and mobilization, and plant uptake.

Heavy metals accumulation in tomato fruits

Figure 3 shows the heavy metals concentration in tomato fruits treated with different doses of purified and unpurified MAP fertilizer. A higher bioavailability of Pb, Cr, Cd, Ni, and V in the unpurified treatment T1, T3, and T5 was observed as compared to the purified treatments T2, T4, and T6, respectively. The concentration of Pb and Cd decreased with all treatments of purified MAP (T2, T4, and T6), compared to their respective purified concentration of unpurified MAP. Interestingly, plants treated with T4 scored the lowest values (1.67 PPM and 1 PPM for Pb and Cd, respectively). The concentration of Cr in fruits significantly decreased by increasing the rate of purified and unpurified MAP, compared to the control. The lowest accumulation of Cr (0.04 PPM) was recorded in fruits receiving 2 g/L of the purified MAP (T6). Moreover, purified and unpurified treatments decreased significantly the Ni accumulation in fruits compared to control. Ni accumulation was significantly lower in plants exposed to purified treatments by 49.89% for T2, 44.31% for T4, and 12.97% for T6, compared to plants treated with unpurified MAP (T1, T3, and T5, respectively). Furthermore, for V metal accumulation, T4 treatment exhibited the lowest

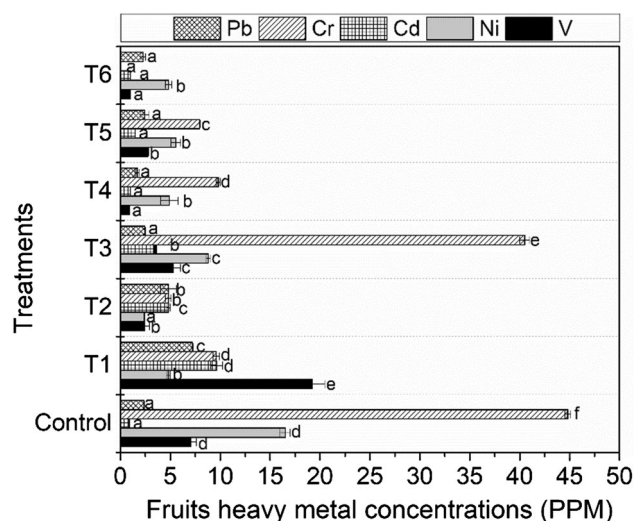


Fig. 3 Heavy metals concentrations in tomato fruits harvest, from grown tomato plants to full maturity (180 DAT) in soil mix amended with different concentrations of purified and unpurified MAP

concentration, while T1 increased the V accumulation by 63.18% compared to the control.

These investigations showed that tomato plants grown in the soil mix under purified MAP (T2, T4 and T6) lost higher concentrations of heavy metals compared to those grown in the soil mix under unpurified MAP (T1, T3, and T5). This fact is attributed to the low heavy metals concentration after the purification of MAP fertilizer. Moreover, we also found that, after purification, the percentage of P_2O_5 and N was increased compared to the unpurified MAP (Table 2), which can be at the origin of the low heavy metal level in fruit treated with purified MAP. Several studies (Anjum et al. 2008; Carranca et al. 2018; Liedschulte et al. 2010; Sarwar et al. 2010; Zechmann and Müller 2010) reported that N is an essential nutrient, responsible for protein and glutathione synthesis by providing defensive mechanisms for heavy metals tolerance. Furthermore, Iqbal et al. (2012) reported that P_2O_5 fertilizer is capable of reducing the concentration of heavy metals in plants through the fixation process between heavy metals and PO_4 .

The results showed that all analyzed heavy metals were most readily absorbed by tomato plants, and their accumulation in the fruits verifies their presence in soil mix (Fig. 3). The concentration of heavy metals in the fruits decreased as compared to soil mix but remain still high compared to their presence in purified and unpurified MAP fertilizer. This fact is commonly associated with the increased heavy metals accumulation in soil mix since soil composition and soil-root interactions are widely known to determine the status of aboveground plants organs (Adams et al. 2004). It has been evidenced that the mobility of metals from soil to plant is a function associated with the physical and chemical

properties of the soil and vegetable species (Kabata-Pendias 2010; Pogrzeba et al. 2017; Zurera et al. 1987). Furthermore, numerous studies showed that the mobility of heavy metals is influenced by the activity of microorganisms, which could increase their mobility and their uptake from the rhizosphere (Hanc et al. 2012; Kozdrój et al. 2007; Pogrzeba et al. 2017).

Fruits characterization by Infrared spectroscopy

Figure 4 shows the FTIR spectra of tomato fruits of plants treated differently. For the control fruit, FTIR spectrum shows the presence of several vibration modes of different groups. The modes located at 620 and 2928 cm^{-1} correspond to OH^- which are not displaced, and that of 777 cm^{-1} also corresponds to the OH^- , which is displaced (El Feki et al. 2000, 1991). Moreover, the vibration modes of 821 and 1403 cm^{-1} represent the carbonate groups (H_2CO_3) (Ścibisz et al. 2011), and those observed at 1058 and 1247 cm^{-1} are

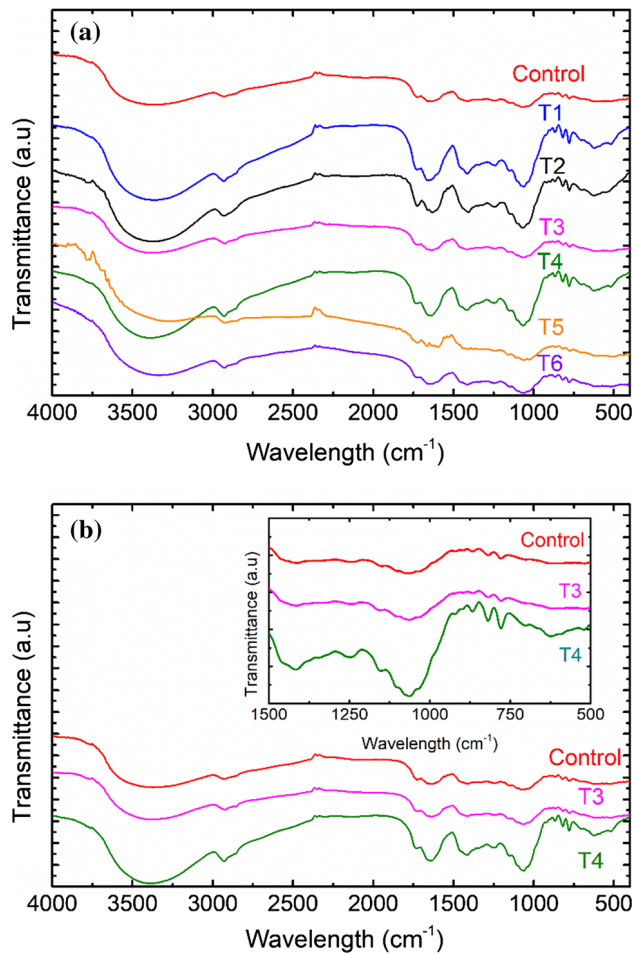


Fig. 4 FTIR spectra of tomato fruits; **a** treated differently and **b** of the control tomato fruits and those of the fruits treated with unpurified MAP (T3) and purified MAP (T4). The inset of **b** shows the magnification of the low wavelength range

attributed to PO_4 groups. Two modes were observed around 1625 and 722 cm^{-1} and assigned to the oxides of organic molecules such as CO_2 (Paradkar et al. 2002). We also noted the disappearance of the OH^- band on the FTIR spectrum of fruits treated with unpurified MAP and its presence in the spectrum of fruits treated with the purified MAP. The disappearance of the OH^- vibration mode illustrated the elimination of phenol groups present in fruits treated by unpurified MAP. Kamil et al. (2011) observed that polyphenolic compounds, carotenoids, and lycopene are vital in tomato as these components are vital for consumer nutrition owing to their antioxidant activity via chelating redox-active metal ions, which inactivate lipid-free radical chains and prevent hydroperoxide conversion into reactive oxyradicals. This can be elucidated by the existence of certain chemical reactions between the polyphenol groups and the heavy metals that are already present in the crude MAP, hence the stabilization of these groups in the soil mix and thus their absence in the fruits. Moreover, we noticed that the intensity of the displaced OH^- mode (777 cm^{-1}) decreased in the case of the unpurified fruit compared to the control fruit (see Fig. 4). However, the intensity of the same mode of the fruit treated with the purified MAP remains constant compared to that of the control. Furthermore, by considering the H_2CO_3 and PO_4 groups in the FTIR spectrum of the control fruit, we observed the displacement of the 1247 cm^{-1} (control) PO_4 mode at 1230 cm^{-1} for the unpurified MAP and at 1249 cm^{-1} for the purified MAP, leading to displacement rates of 1.37% and 0.16%, respectively. Similarly, we noted a displacement of 1.14% of the 1403 cm^{-1} H_2CO_3 mode to 1419 cm^{-1} for the fruit treated with unpurified MAP, this displacement is lower ($\sim 0.35\%$) in the case of the purified MAP. These displacements of certain FTIR vibration modes highlight the disturbing phenomenon of heavy metals in fruits. Bai et al. (2014) reported that the FTIR spectrum of metal-loaded bacteria displayed a highly significant shift of certain peaks as compared to those of bacteria before biosorption of Pb, and Mallampati and Valiyaveetil (2012) reported that significant differences were detected in the positions of the peaks in the FTIR spectrum before and after the absorption of the heavy metals.

Scanning electron micrograph (SEM)

Scanning electron microscopy images of tomato fruits treated with MAP are presented in Fig. 5. The SEM image of the control fruit showed the existence of pores with irregular shapes and sizes (Fig. 5g). However, SEM images of tomato fruits treated with MAP (Fig. 5a–f) show larger pores compared to the untreated fruits. Interestingly, tomato treated with unpurified MAP (Fig. 5a–c) possess larger pores comparable to those treated with purified MAP (Fig. 5d–f). These results showed that the application of unpurified

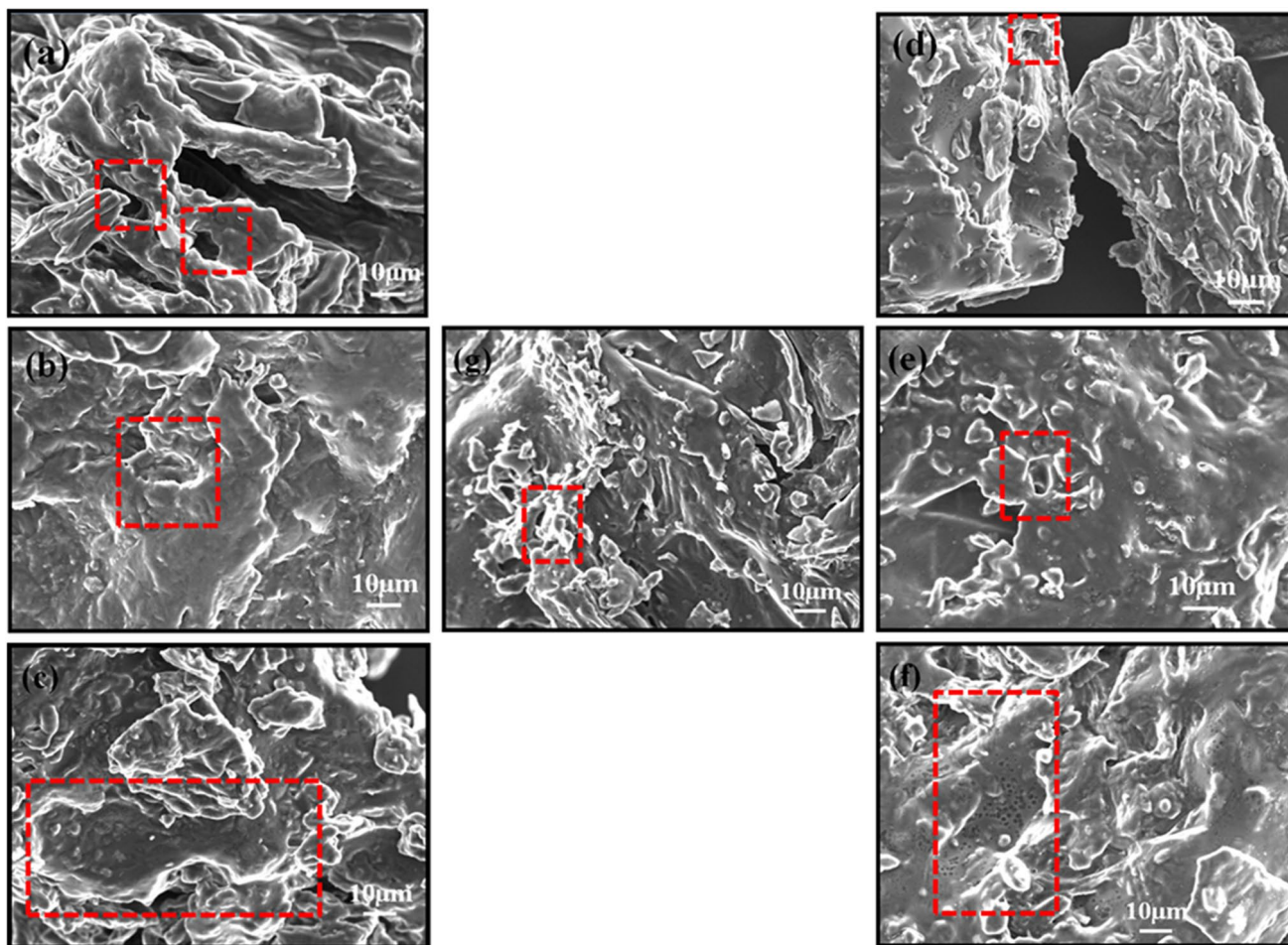


Fig. 5 SEM images ($\times 1000$) of tomato samples treated at different concentrations with **a–c** unpurified MAP and **d–f** purified MAP compared to **g** that of control tomatoes

MAP effectively modified the microstructure of the fruit by increasing the pore size as compared to the control and purified fruits, which could be attributed to the chemical links established by the insertion of heavy metals into the fruit structure, which are advantageously present due to the application of unpurified MAP.

Conclusion

In summary, this study reported that purified MAP provides a good-quality fertilizer that can improve tomato growth and productivity and reduce the impact of toxicity of heavy metals present in the environment. The aim of this study is to optimize the use of purified MAP to fertilize tomato plants which will help to maintain fruit yield and soil potential. By considering all the measured parameters, we conclude that the purified MAP with 1 g/L concentration (T4) is the most efficient fertilizer. ICP-OES analyses show a decrease in heavy metals concentrations

in fruit and soil mix, which is revealed by disturbances in FTIR, and supported by SEM images. Importantly, the reported purified MAP fertilizer plays a dual role, i.e., the first being an efficient fertilizer and the second being a heavy metal chelator by the complexation of the impurities in the soil mix, as compared to the unpurified MAP fertilizer. Finally, the use of purified MAP showed that Ni and Cr heavy metals are well below the concentration limit for tomato consumption. However, some heavy metals concentration remains higher than the concentration limit for tomato consumption, which can be associated to the high heavy metal accumulated in the used soil mix.

As a perspective of this study, we will work on the optimization of the purification process to approach the heavy metals concentration limit for tomato consumption and we will also focus on the distribution of heavy metals in roots, stems, and leaves of tomato to assert whether they exceed the safe toxicity level limits for human consumption and we will investigate the role of soil microorganisms in influencing the bioavailability of heavy metals in MAP fertilizer for

tomato growth. These results will be reported in a forthcoming paper.

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