

Effects of nano iron oxide powder and urban solid waste compost coated sulfur on chemical properties of a saline-sodic soil

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Abstract

The main limiting factors in saline-sodic soils are high amounts of salts, low soil organic matter (SOM) and low availability of macro and micro-nutrients. The effect of different amounts of nano iron oxide powder and urban solid waste compost coated sulfur (USWCS) on the chemical properties of a saline-sodic soil was investigated. The experiment was conducted using a randomized complete block design with factorial arrangement and three replications, in a farm near Qom city. Treatments used in this study included USWCS (0 and 15 ton/ha) and nano iron oxide powder (0 and 20 mg/kg); treatments were applied to treated plots of 4 m² and sunflower seeds were sown. The results show that 20 mg/kg of nano-iron oxide, significantly ($P < 0.05$) increased electrical conductivity of saturation extract (ECe), availability of nutrient elements (5.26, 30, 18.18% for phosphorous (P), iron (Fe), and copper (Cu), respectively) in soil, while nitrogen (N), pH and sodium adsorption ratio (SAR) in soil decreased significantly ($P < 0.05$). Fifteen (15) tons/ha of USWCS significantly increased soil ECe (6.1%), micro and macro-nutrients amounts (8.3, 21.1, 46.6, 45.5, and 14.9% for N, P, Fe, Cu, and Manganese (Mn) respectively), but significantly ($P < 0.05$) decreased the soil pH and SAR, compared to the control. The combined effect of 20 mg/kg of nano iron oxide and 15 ton/ha of USWCS increased micro-nutrient availability, but decreased soil pH and SAR significantly. It was concluded that the combined application of USWCS and nano iron oxide increased the availability of nutrients in saline-sodic soil.

Keywords: Sodicity; Salinity; Nutrient element; Compost; Nano material

1. Introduction

Soil degradation due to the salinity and sodicity of irrigation water, and improper management of lands threaten agricultural lands (Astarai and Chauhan, 1992a, b; Astarai and Chauhan, 1994). Although the low fertility of saline/sodic soils is attributed to high amounts of salts, low soil organic matter (SOM) and low availability of nutrients especially nitrogen (N), phosphorous (P), potassium (K), and micro-nutrients, are the main limiting factors in saline/sodic soils (Astarai and Chauhan, 1992a, b; Astarai and Chauhan, 1994). Therefore, salinity/sodicity risks and deteriorating

of agricultural ecosystems is needed to develop specific management practices for improving soil fertility and productivity. In many parts of Iran, the deficiency of micro-nutrients especially iron (Fe), due to high pH values, high soil calcium carbonate, poor irrigation water, and low SOM in soils have been reported (Mohajer Milani, 1996). Ehtesham Nia (2008) reported that with increasing soil salinity, the uptake and transport of most nutrients (including micro-nutrients) by plants decreased. Page *et al.* (1990) found that the maximum availability of micro-nutrients depends on pH, electrical potential of soil solution, and adsorption sites on the surface of organic and inorganic particles. In saline-sodic soils, the degree of solubility of micro-nutrients, especially Fe and zinc (Zn), is low and plants growing in these soils often

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show deficiency of these nutrients (Astarai and Chauhan, 1994).

Waste iron oxide powder resulted in a decrease in soil pH, thereby increasing the availability of micro-nutrients (i.e. DTPA extractable elements) in soil (Foruhar, 1990). Nano-particles of iron oxide increase the surface area and enhance reactions with complexes such as OM, resulting in an increase in Fe availability for plants (Mazaheri Nia et al., 2010). Urban solid waste compost coated sulfur (USWCS) contains high OM and improves soil aggregates and structure (Emami and Astarai, 2012; Wong, 2008). In addition, it can provide high amounts of macro and micro-nutrients to plants growing in such soils. The organic matter in USWCS will decrease soil pH, and form soluble complexes, that will result in increasing micro-nutrients availability (De Hann, 1981; Astarai and Almasian, 2010; Mazaheri Nia et al., 2010). The supply of some nutrients, such as, N, P, and K for plant uptake, will be through the work of bacteria and fungi during plant growth. Melero et al. (2007) reported that the application of urban waste compost as an amendment to semi-arid Mediterranean soils, increased organic carbon, N, P, microbial biomass, and the activity of soil enzymes.

Beshrati (1998) reported that the use of sulfur powder with *Tiobacillus spp.* in soil, increased the availability of Fe and P elements in soil, due to reduction in soil pH. Higher uptake of Fe and P in plants, was recorded after treatment using sulfur powder with *Tiobacillus*, this resulted in the highest dry matter yield of the plants. Gyamati et al. (2009) studied the effects of four treatments (control soil, sulfur powder (1 ton/ha), urban solid waste compost (20 ton/ha) and urban solid waste compost (20 ton/ha) + sulfur powder (10% of USWC w/w) on soil properties and sugar beet crop. They reported that both sulfur powder and USWC treatments reduced soil pH significantly, compared to the control soil. Sulfur powder treatment reduced soil E_c significantly by 36.6% compared to USWC + Sulfur powder treatment. Also, this treatment reduced Na concentration in soil solution significantly by about 71%, compared to USWC treatment. USWC and Sulfur powder treatments showed higher amount of total nitrogen and available P in soil.

Iran has both arid and semi-arid regions and most of the soils are deficient in SOM, (being the main problem under these conditions), it is therefore essential to apply organic materials to

improve sustainable agriculture. Urban and industrial wastes are usually used to supply the nutrients and increase crop yield (Astarai and Almasian, 2010; Mazaheri Nia et al., 2010). This research aimed to study the effects of USWCS and nano iron oxide on soil chemical properties as well as the fertility status of saline-sodic soil.

2. Material and methods

The study area is located in the agricultural field of Qanavat part, Qom Province (Iran) with longitude 50° 59' and latitude 34° 37'. A field experiment was conducted using a randomized complete block design with a factorial arrangement and three replications during the year 2010 and USWCS was considered as the main factor while nano iron oxides were considered as subfactors. USWCS was prepared from Mashhad municipal solid waste factory. Two levels of USWCS (0 and 15 ton/ha) and nano iron oxide (0 and 20 mg/kg), were considered as experimental treatments. Iron wastes were obtained from iron sheets during the acid-washing process (Zobeahan Factory of Isfahan, Iran), having particle sizes ranging from 0.02-0.06 mm in diameter, and were treated by a mechanical method (ball mill) for 48 h to produce nano iron oxide. The diameter of prepared nano iron oxide powder was determined using a Transmission Electron Microscope (TEM) in the Central Research Laboratory of Ferdowsi University of Mashhad. The diameter range of nano iron oxide obtained by TEM was between 80 to 250 nm. The chemical properties of nano iron oxide are presented in Table 1. Experimental treatments were mixed at 0-30 cm soil depth in 4 m² plots and 20 sunflower seeds (*Record cultivar*) were sown in two rows 70 cm apart, in each plot (5000 plants per ha) in June 2010 (Ghodsi et al., 2012). Before the application of treatments, soil samples were collected from 0-30 and 30-60 cm soil depths and their properties were measured (Table 2). Soil bulk density was determined by core samples (10 cm in diameter, and 10 cm in height) (Blake and Hartge, 1986). The Beerkan infiltration method was used for measuring the final infiltration rate (Lassabatere et al., 2006). Saline-sodic irrigation water was used for this study and the chemical properties analyzed are presented in Table 1.

After sunflower harvest, soil samples were collected from 0-30 cm depths from each treatment, and analyzed for chemical properties. pH was determined from saturated paste, electrical

conductivity of saturation extract (ECe) (Page *et al.*, 1982), soluble calcium (Ca^{+2}) and magnesium (Mg^{+2}) concentrations by titration method with EDTA (Rayan *et al.*, 2001), soluble sodium (Na^+) and K^+ by Flame photometer apparatus (JENWAY PFP 7 Model), soluble carbonate (CO_3^{-2}) and bicarbonate (HCO_3^{-}) by titration method with 0.01 N sulfuric acid (Klute *et al.*, 1986), soluble chloride (Cl^-) by titration method with 0.01 N AgNO_3 (Klute *et al.*, 1986) and soluble sulfate by turbidometry method (Patel *et al.*, 1996) were used. Also, total N by Kjeldal method (Patel *et al.*, 1996),

available P (Olsen, 1954) and available K by Ammonium Acetate (Klute, 1986) were determined in soil samples. In addition, DTPA extractable micro-nutrients (Zn, Fe, Mn, and Cu) were measured by atomic absorption apparatus (Shimadzu AA-670) in soil samples (Lindsay and Norvell, 1978).

The data obtained were analyzed in SAS 9.1 software, and treatment means were compared, using Duncan's Multiple Range Test (DMRT) at P 0.05.

Table 1. Chemical structure of studied nano iron oxide and properties of urban solid waste compost coated sulfur

Nano iron oxide	Fe ₂ O ₃	FeO	CaO	Na ₂ O	Zn	Mn	Cu	L.O.I ^{a*}	
	(%)								
	0.78	0.005	0.16	0.0022	0.14	0.04	1.4	94.7	
USWCS	pH	EC (1:5 Water : USWCS)	N	P	K	Fe	Mn	Zn	Cu
	-	dSm ⁻¹	-----(-)-----			----- (mgkg ⁻¹)-----			
	6.5	4.7	1.3	0.2	0.2	7.7	201.95	8.3	212.3

*:Loss on ignition (%)

Table 2. Properties of surface (0-30 cm) and subsurface (30-60 cm) of studied soil before cultivation and irrigation water

properties	Soil depth (cm)		Irrigation water
	0-30	30-60	
Texture	Clay Loam	Clay Loam	-
pH	8.2	8.2	8.0
ECe (dS/m)	8.6	9.3	7.1
SAR	15.4	16	14.6
Organic Carbon (%)	0.81	0.65	-
N (%)	0.09	0.08	-
P _{ava} (mg/kg)	15	10	-
K _{ava} (mg/kg)	305	298	-
Fe (mg/kg)	5.5	4.5	-
Mn (mg/kg)	11.7	13.7	-
Cu (mg/kg)	0.64	0.86	-
Zn (mg/kg)	1.8	2.1	-
CO ₃ ⁻² (mmol/l)	-	-	-
HCO ₃ ⁻ (mmol/l)	4.4	4.3	4.2
Cl ⁻ (mmol/l)	51	51.4	52.4
SO ₄ ⁻² (mmol/l)	42.5	38	31.3
Ca ⁺² +Mg ⁺² (mmol/l)	52.8	32.1	34.1
Na ⁺ (mmol/l)	79.13	64.1	60.29

3. Results and discussion

Application of 20 mg/kg nano iron oxide decreased soil pH significantly (P 0.05) compared to the control (Table 3), and the same result was recorded for the 15 ton/ha USWCS treatment (Table 4). Application of nano iron oxide powder with a strong acidic nature- pH=2.4 (1:100 nano iron oxide to distilled water suspension) into soil, resulted in soil pH decrease (Mazaheri Nia *et al.*, 2010). Mohamadi Nia (1995) found that SOM decomposition produces organic acids such as citric and malic acids, that decreases soil pH. Application of 20 mg/kg nano iron oxide increased

soil ECe significantly (P 0.05) compared to the control (Table 3). A similar result was obtained with 15 ton/ha USWCS application (Table 4). Application of 20 mg/kg nano iron oxide decreased SAR significantly (P 0.05) compared to the control (Table 3). Since the studied soil was alkaline (pH=8.2), and due to the acidic nature of nano iron oxide, the solubility of Ca-compounds increased, and the activity of CO₃⁻² and HCO₃⁻¹ ions in soil solution also decreased, due to the precipitation of low soluble constituents. Similar results were reported by Mashhadi and Rowell (1978). The increasing soil acidity due to nano iron oxide increased the concentrations of Ca⁺² and

Mg⁺² ions leading to decrease in Na⁺ concentration, thereby lowering soil SAR.

The interaction between 15 ton/ha USWCS and 20 mg/kg nano iron oxide resulted in a significant (P 0.05, Fig. 1) decrease in soil pH. The acidic nature of nano iron oxide coupled with the decomposition of USWCS in the studied soil, produced organic acids because of sulfur oxidation from USWCS and resulted to a decrease in soil pH (Mazaheri Nia *et al.*, 2010). The interaction of 15 ton/ha USWCS and 20 mg/kg nano iron oxide increased soil ECe significantly (P 0.05, Fig. 2), probably due to high concentration of salts in

USWCS along with nano iron oxide, similar results were reported by Mazaheri Nia *et al.* (2010). They observed that nano iron oxide increased the availability of soil nutrients and solubility of inorganic compounds, concentration of soluble salts, thereby, leading to higher soil ECe. Also, USWCS have many soluble constituents and its application leads to higher soil ECe (Astarai and Almasian, 2010). Vazquez Montiel (1996) reported that increase in soil ECe because of compost addition, depends on the total amounts of dissolved salts present in compost and addition of compost results in the accumulation of soluble salts in soil.

Table 3. Effect of Nano iron oxide on soil chemical properties

Nano iron oxide (mg/kg)	pH	ECe (dS/m)	SAR
0	7.9	9.8	10.25
20	7.8	10.05	9.95
P value	0.0001	0.0001	0.02

Table 4. Effect of urban solid waste compost coated sulfur on soil chemical properties

USWCS (ton/ha)	pH	ECe (dS/m)	SAR
0	7.9	9.8	10.25
15	7.6	9.2	9.9
P value	0.0001	0.0001	0.0004

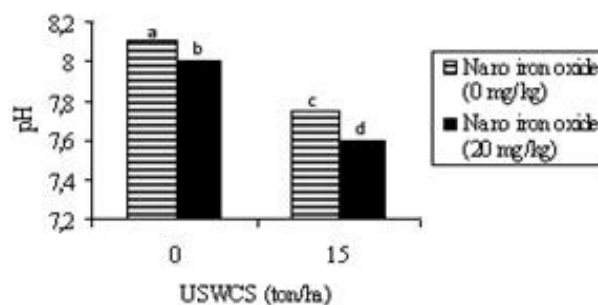


Fig. 1. Interaction effects of nano iron oxide and urban solid waste compost coated sulfur on soil pH

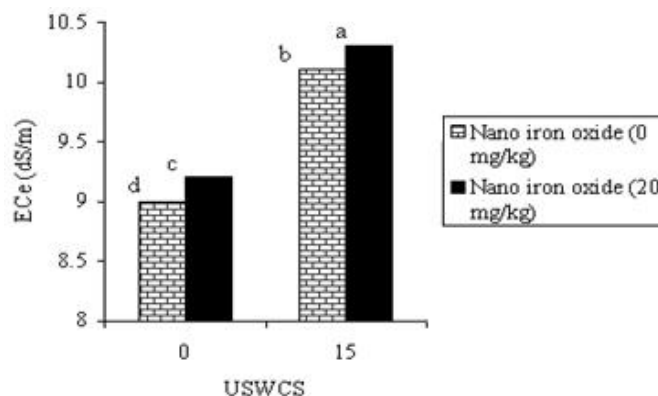


Fig. 2. Interaction effects of nano iron oxide and urban solid waste compost coated sulfur on ECe (Same letters are not significant at $P < 0.05$)

The interaction of 20 mg/kg nano iron oxide and 15 ton/ha USWCS decreased SAR significantly ($P < 0.05$, Fig. 3). The addition of OM to soil for reclaiming soil physico-chemical properties and to increase the availability of nutrients in sodic soils should be regarded after considerable reduction of Na and pH in these soils (Gupta *et al.*, 1984). Sodic soils due to high pH and high calcium carbonate

can release more Ca into soil solution, thereby reducing the harmful effects of Na (Chorom and Rengassamy, 1997). Therefore, the simultaneous application of USWCS and nano iron oxide to soil, in addition to increasing acidic strength and higher solubility of Ca-compounds, increased infiltration rate and Na-leaching and as a result, decreased SAR in the studied soil.

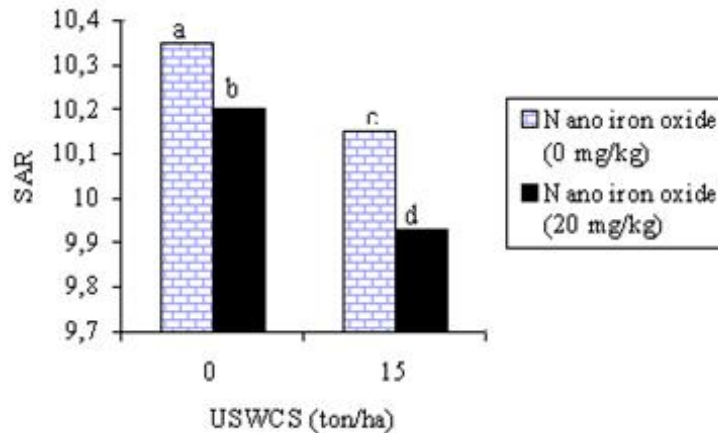


Fig. 3. Interaction effects of nano iron oxide and urban solid waste compost coated sulfur on SAR (Same letters are not significant at $P < 0.05$)

Application of 20 mg/kg nano iron oxide increased concentrations of soil micro-nutrients, soil available P and K, while total N concentration in the soil (Table 5) decreased significantly ($P < 0.05$). Mazaheri Nia *et al.* (2010) reported that application of nano iron oxide powder increased micro-nutrients concentrations in calcareous soils. By acidifying soil media, nano iron oxides

increased the solubility of micro-nutrients. Soil P availability is strongly affected by pH, and maximum availability of P is found in pH range of 6.5-7 (Engelstand and Terman, 1980). Therefore, with decreasing soil pH (Tables 3 and 4) after addition of USWCS and nano iron oxide, P availability increased in soil (Tables 5 and 6).

Table 5. Effect of Nano iron oxide on concentration of nutrients in a studied soil

Nano iron oxide (mg/kg)	N	P	K	Fe	Zn	Cu	Mn
	(%)	(mg/kg)					
0	0.12	19	320	7.0	4.3	1.1	16.8
20	0.11	20	321	9.1	4.7	1.3	17.5
P value	0.004	0.0001	0.004	0.0001	0.0001	0.0001	0.0001

Table 6. Effect of urban solid waste compost coated sulfur on concentration of nutrients in a studied soil

USWCS ton/ha)	N	P	K	Fe	Zn	Cu	Mn
	(%)	(mg/kg)					
0	0.12	19	320	7.3	4.3	1.1	16.8
15	0.13	23	324	10.7	5.8	1.6	19.3
P value	0.0001	0.0001	0.001	0.0001	0.0001	0.0001	0.0001

The concentrations of nutrients in soil increased significantly ($P < 0.05$) with the addition of USWCS (Table 6). Increasing the concentrations of N, K, and P in soil, after USWCS addition is probably due to the high concentrations of these nutrients in

USWCS (Astarai and Almasian, 2010). The results of Engelstand and Terman (1980) show that P availability increased by applying OM into soil. Muhammad *et al.* (2007) also found that by application of 1% compost to soil, soil P

extractable by Na-bicarbonate increased. During the decomposition of organic matter, probably humic acid is produced and unavailable P is transformed to available forms. Application of OM to soil increases microbial biomass and activity, thereby increasing the availability of urease, -Glycosidase, and phosphatase alkaline enzymes in the soil (Liang *et al.*, 2005). Lakhar (2008) reported that the application of compost into saline-sodic soils increased the concentrations of micro and macro-nutrients in rhizosphere and reduced the negative interaction effects among nutrients. Khoshgoftar Manesh and Kalbasi (2000) reported that urban waste compost containing organic and inorganic acids; decreases soil pH because of their acidity, thereby indirectly increasing the availability of micro-nutrients.

The interaction between 15 ton/ha USWCS and 20 mg/kg nano iron oxide increased the concentrations of DTPA extractable micro-nutrients (Table 7) significantly ($P < 0.05$). The results show that the combined application of nano iron oxide and USWCS had significantly higher effect on availability of micro-nutrients, than when each treatment was applied alone. Therefore, the concentrations of Fe, Mn, Cu, and Zn in soil

increased by 24, 4, 14, and 10%, respectively as a result of the combined application of nano iron oxide and USWCS, compared to separated application of USWCS (Table 6). Compost can provide a source of nutrients and releases them gradually for plant uptake, about 10% of N in compost is available for plants in the first year, after its application (De Hann, 1981). Igleis and Alvarez (1993) reported that 21% of N in compost as NH_4NO_3 was available for plants to utilize after 6 months. Crowley *et al.* (2001) found that by applying OM, the concentration of siderophores increased in the soil and as a result, Fe solubility also increased. Tombacz and Rise (1999) reported that OM is able to form soluble complexes with micro-nutrients, thereby increasing their solubility in soil. In addition, the application of compost containing soluble P to soil, considerably increased soil available P (Perez, 2007). Rahimi *et al.* (1992) found that the application of urban waste compost to some soils in Isfahan, Iran, resulted in an increase in available N and P. Furthermore, the use of urban waste compost in Mediterranean semi-arid lands, increased N, P, K, and organic carbon in the rhizosphere (Melero *et al.*, 2007).

Table 7. Interaction effects of nano iron oxide and urban solid waste compost coated sulfur on concentration of nutrients in a studied soil

USWCS (ton/ha)	Nano iron oxide (mg/kg)	N (%)	P	K	Fe	Zn	Cu	Mn
		----- (mg/kg) -----						
0	0	0.09 ^c	16 ^d	318 ^d	5.4 ^d	3.4 ^d	0.9 ^d	15.2 ^d
	20	0.08 ^b	17 ^c	319 ^c	7.4 ^c	3.8 ^c	1.0 ^c	15.8 ^c
15	0	0.13 ^a	22 ^b	322 ^b	8.6 ^b	5.1 ^b	1.4 ^b	18.4 ^b
	20	0.13 ^a	23 ^a	324 ^a	10.7 ^a	5.6 ^a	1.6 ^a	19.1 ^a

Same letters in each column are not significant at $P < 0.05$

4. Conclusion

The results of this research show that the application of nano iron oxide to soil increased the concentrations of Fe, Mn, Cu, and Zn to 30, 4, 18, and 9% respectively, compared to the control. Most Iranian soils are deficient in micro-nutrients especially Fe, as a result of different reasons such as salinity, alkalinity, calcareous and low contents of SOM. Therefore, the application of nano iron oxide can play an important role towards increasing the availability of micro-nutrients. Application of USWCS increased the amounts of Fe, Mn, Cu, and Zn to 32, 20, 60, and 45% respectively, compared to the control. In addition, the interaction effect of USWCS and nano iron oxide resulted in maximum availability of micro-nutrients in the studied saline-sodic soil, as the

concentrations of Fe, Mn, Cu, and Zn increased by 94, 39, 86, and 160%, respectively, compared to the concentrations before sunflower sowing. In addition, the application of USWCS increased the concentration of N, P, and K by 44, 43, and 2% respectively, compared to the control. The application of USWCS increased SOM, improved soil structure and due to improved micro and macro-nutrients availability, increased crop yield. Based on the results obtained, the combined application of USWCS and nano iron oxide, even with the use of saline-sodic irrigation water, can be used to increase the availability of nutrients in saline-sodic soil for plant uptake and increase the yield of sunflower.

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