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EVALUATION OF PYRITIC TAILINGS FROM A COPPER CONCENTRATION PLANT FOR CALCAREOUS SODIC SOIL RECLAMATION

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Abstract: This study was aimed to investigate the feasibility to use waste pyrite and sulphuric acid produced from waste pyrite for the reclamation of calcareous sodic soils. The final aim is to displace Na from an exchange complex and replace it with Ca, leading to a decrease in pH and exchangeable sodium percentage (ESP) and an improvement of soil structure. A fertility of the soil may also be enhanced by this technique since waste pyrite can be rich in several micronutrients. An additional advantage to this strategy is that waste pyrite is inexpensive and readily available in large quantities, by contrast to gypsum. In this study, column-leaching tests were carried out to evaluate a change in soil properties upon addition of gypsum and pyritic tailing amendments from a copper concentration plant. An availability of essential micronutrients for a plant growth (Fe, Cu, Zn and Mn) and hazardous potential of pyritic tailings in terms of heavy metal contamination were taken into account. Gypsum, powder waste pyrite and sulfuric acid produced from waste pyrite were applied to the soil with reference to the gypsum requirement (GR) of the soils. The results showed that application of waste pyrite with a dose of 44.74 megagrams per ha was superior to gypsum of 55.20 Mg/ha dose in terms of exchangeable sodium percentage (ESP) in 42 weeks. In addition, application of all the concentrations of sulfuric acid produced from waste pyrite also decreased the ESP values. The best values with sulfuric acid were obtained with a dose of 35.31 Mg/ha in 26 weeks. It was observed that the content of all micronutrients in the soil increased significantly ($P<0.01$) with waste pyrite and sulfuric acid applications. The levels of the micronutrients after treatments can be classified sufficient for the plant growth except for the iron level with the minimum dose of sulfuric acid application 17 Mg/ha. The heavy metal content in the soil after treatment with the pyritic tailings was found to be lower than the legal limit values. Thus, waste pyrite can be effectively used since rapid amelioration of calcareous sodic soils is possible with no deleterious heavy metal contamination.

***Keywords**: waste pyrite, gypsum, pyrite oxidation, column leaching test, sodic soil, reclamation*

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Introduction

The problem of soil sodicity (alkalisation) is extensively spread in many countries in the world. This is more vital for developing countries where a sodicity hinders agricultural production or even makes it impossible (Qadir et al., 2006; Brinck and Frost, 2009). Sodic soils contain sufficient exchangeable sodium to affect the plant growth adversely. According to the United States Salinity Laboratory these soils have an exchangeable sodium percentage ESP more than 15, pH of saturated soil paste (pHs) more than 8.5 and electrical conductivity of saturation extracts (ECe) less than 4 dS m^{-1} (Richards, 1954). Soil alkalisation frequently lead to deterioration and complete abandonment of agriculture and hence to a great economic damage.

Gypsum has been known to be an amelioration agent for sodic soil for more than 100 years; however, it has been used only rarely because of the high cost involved in the exploitation, transportation and crushing (Wang et al., 2008). Tailings from sulfide mines, on the other hand, usually contain large amount of pyrite (FeS_2) which is the main source of acid rock drainage and pollute the environment. Pyrite waste must be disposed off under strictly controlled conditions (Pulles et al., 1996; Jovanovic, 1998; Annandale et al., 1999). It has a great potential for restroring the productivity of calcareous sodic lands and improving the fertility of the soil. Oxidation of pyrite leads to the production of sulfuric acid, which reacts with native $CaCO_3$ to produce soluble Ca to replace adsorbed Na from the exchange complex of sodic soil and brings down to pH and ESP (Tiwari et al., 1988; Qadir et al., 1996; Qadir and Oster, 2004). The exchange of Ca with Na in the soil exchange complex results in flocculation of soil particles and the restoration of porous structure and high permeability of soil (Chun et al., 2001).

Pyrite can be also used as a source of micronutrients needed for a plant growth, particularly Fe, Cu, Zn and Mn. Therefore, it can be used as a fertilizer in calcareous sodic soils where these elements are deficient.

A comparison of gypsum vs. pyrite and sulfuric acid in reclamation of sodic soils indicated good possibilities of utilizing pyrite and sulfuric acid for sodic soil amelioration (Somani, 1994; Castelo Branco et al., 1999; Mace et al., 1999). This study was planned to compare the effectiveness of gypsum, waste pyrite from a copper concentration plant and suphuric acid produced from waste pyrite in reclaiming sodic soils. For this purpose, Na and sodium adsorption ratio (SAR) of the leachates, pH, ESP and heavy metal content of soils as well as essential micronutrient content of soil for the plant growth were investigated.

Materials and methods

Materials

The surface soil (0–15 cm) from Saraykoy, Ankara, Turkey was used in this study. The soil samples were air-dried, blended and ground to pass through a 2 mm sieve in a laboratory. Relevant properties of the as-received soil are presented in Table 1. This soil is classified as non-saline (EC = 2.85 dS m^{-1}), sodic (ESP = 83.33) (Richards, 1954), moderately calcareous ($CaCO_3$ = 9.18%) with low organic matter content (0.71%) (Ulgen and Yurtsever, 1974). The level of available micronutrients determined by a DTPA method was 1.75 mg kg^{-1} Fe, 0.29 mg kg^{-1} Cu, 0.07 mg kg^{-1} Zn and 3.53 mg kg^{-1} Mn. These levels of Fe, Zn and Mn are classified as marginal for the plant growth (Follet and Lindsay, 1970; Lindsay and Norwell, 1978; FAO, 1990). The heavy metal content of the soil is lower than the limit values set by Turkish Soil Contamination Regulation (2001) (Table 2).

Table 1. Relevant properties of calcareous sodic soil before the experiment

EC (dS m^{-1})	pH	Bulk density (g cm^{-3})	CEC (mmol$_c$ 100g^{-1})	$CaCO_3$ (%)	Organic matter (%)	Boron (mg kg^{-1})
2.85	9.27	1.22	38.52	9.18	0.71	8.87

	DTPA-extractable (mg kg^{-1})			
ESP (%)	Fe	Cu	Zn	Mn
83.33	1.75	0.29	0.07	3.53

Table 2. Heavy metal content of calcareous sodic soil

Element	Concentration (mg kg^{-1} soil)	Limit values[*] (mg kg^{-1} soil)
Cr	24.59	100
Co	3.20	20
Ni	20.78	75
Cu	14.40	140
Zn	61.32	300
Pb	20.89	300
Mo	2.19	10
Cd	0.12	3
Fe (%)	4.08	–

[*] according to Turkish Soil Contamination Regulation (2001)

Waste pyrite used as an amendment was taken from the tailings stream of Kure Copper Concentration Plant, Turkey. A sulfur content of pyrite was found to be 44% using the methods outlined in Turkish Standards Institution (1987). A heavy metal content of waste pyrite is given in Table 3.

Table 3. Heavy metal content of waste pyrite

Element	Cr	Co	Ni	Cu	Zn	Pb	Mo	Cd	Fe (%)
Concentration (mg kg^{-1} pyrite)	21.22	824	61.73	6886	781.25	202.54	<2.40	<0.54	40.70

The oxidation experiment of waste pyrite was performed by aerating a suspension of 400 g of waste pyrite in 15 dm^3 of water placed in a 25 dm^3 polypropylene container for 25 days at room temperature (22–24 °C). The suspension was stirred by injecting the air through a polyethylene container. Ferric iron (Fe^{3+}) from oxidation of pyrite precipitates as a solid ferric hydroxide and forms sulfuric acid from four H^+ generated for each iron atom initially present as pyrite (1) (Somani, 1994):

$$FeS_2 + 15/4O_2 + 7/2\ H_2O \rightarrow Fe\,(OH)_3 + 2H_2SO_4. \tag{1}$$

The sulfate concentration of sulfuric acid produced from waste pyrites is 10.02 g/dm^3 (Richards, 1954). The heavy metal content of sulfuric acid produced from waste pyrites is given in Table 4.

Table 4. Metal content of sulfuric acid produced from waste pyrite

Element	Cr	Co	Ni	Cu	Zn	Pb	Mo	Cd	Fe
Sulfuric acid solution (mg/dm^3)	0.55	9.10	0.95	81	35.70	0.86	<0.008	<0.003	2286

Pure powder gypsum ($CaSO_4 \cdot 2H_2O$) (Merck, 102161) was used as an amendment for the comparison of the effectiveness of waste pyrite.

Methods

Column leaching tests were carried out to estimate amount of leaching needed for the removal of excess soluble salts, to determine the response of soils to the addition of gypsum, waste pyrite and sulfuric acid, and to find the changes in the soil properties such as pH and ESP after leaching.

The leaching study was conducted with packed sodic soil columns treated gypsum, waste pyrite and sulfuric acid produced from waste pyrite. Polyvinyl chloride (PVC) columns with a diameter of 10 cm and a length of 35 cm were hand packed with air-dried and homogenized sodic soils (<2 mm) to a depth of 20 cm (Fig. 1).

Fig. 1. Photos of the column test set-up

The experimental layout was a randomized design with four doses of pyrite and sulfuric acid and one dose of gypsum with four replicates per dose. Gypsum, waste pyrite and sulfuric acid were applied to the soil on the basis of gypsum requirement (GR) of the soils (FAO, 1988). The minimum dose of pyrite addition level, 23.74 Mg/ha)(megagrams per hectare) (Pyrite 1 = GR) was calculated on the basis of gypsum requirement (GR), 55.2 Mg/ha, to reduce ESP to 15%. Randomly selected higher levels of pyrite addition, namely 31.96 Mg/ha (Pyrite 2), 39.63 Mg/ha (Pyrite 3) and 44.74 Mg/ha (Pyrite 4) (Table 5) were also applied to make up for the possible incomplete pyrite oxidation. In the application of sulfuric acid produced from waste pyrite, 31.46 Mg/ha of H_2SO_4 was assumed to be equivalent to 55.20 Mg/ha of gypsum (FAO, 1988). In this study, 17 Mg/ha (H_2SO_4–1), 19.62 Mg/ha (H_2SO_4–2), 23.54 Mg/ha (H_2SO_4–3), 26.15 Mg/ha (H_2SO_4–4) and 35.31 Mg/ha (H_2SO_4–5) of H_2SO_4 (Table 5) were tested to determine the effectiveness of sulfuric acid in reclamation of the calcareous sodic soil.

Table 5. Soil amendments and application rates

Soil Amendment	Application rate (t/ha)	Soil Amendment	Application rate (Mg/ha)
Gypsum	55.20	$H_2SO_4^{-}1$	17.00
Pyrite 1 (=GR)*	23.74	$H_2SO_4^{-}2$	19.62
Pyrite 2	31.96	$H_2SO_4^{-}3$	23.54
Pyrite 3	39.63	$H_2SO_4^{-}4$	26.15
Pyrite 4	44.74	$H_2SO_4^{-}5$	35.31

* GR: gypsum requirement of the soil

Pyrites undergo rapid oxidation when they are surface applied on the moist soils. Therefore, pyrite of predetermined doses was evenly spread on the moist soil surface as thinly as possible. In order to facilitate the oxidation of pyrite and ensure the supply of sufficient oxygen, the soil surface with pyrite was moistened until soaked by water spraying every 24 hours for 5 weeks in a similar way to Tiwari and Sharma (1989). The gypsum amendment was incorporated into the soil before packing. Sulfuric acid was applied onto the soil surface after packing. After the amendment applications, the columns were leached by a ponding method with tap water (EC = 1.21 dS m^{-1}, SAR = 1.66) with a hydraulic head of 10 cm (785 cm^3 water) in the columns at the certain intervals. Leaching dissolved and carried the amendments downward and removed the soluble salts. The leachate were collected and analyzed for Na and SAR to determine the effectiveness of amendments.

Analysis

The samples were air-dried and ground to pass a 2 mm sieve. The soil pH was measured in the saturated soil paste and EC was measured in the saturation extract (Richards, 1954; Rhoades, 1982a). A dry bulk density of soil was analyzed according to Tuzuner (1990). A cation exchange capacity (CEC) of the soil was determined by a Na acetate method (1M NaOAc at pH 8.2) (Rhoades, 1982b). A content of $CaCO_3$ was determined using a calcimeter (Nelson, 1982). Organic matter content was determined by a dichromate oxidation method (Nelson and Sommers, 1982). Boron was analyzed using a carmine solution (Richards, 1954). Soluble cations and anions, and exchangeable cations were determined using the methods described by Richards (1954). Fe, Cu, Zn and Mn were measured by an atomic absorption spectrophotometer after extraction using a DTPA solution (Lindsay and Norwell, 1978). The total trace elements in soils were determined by digestion with nitric acid using by an inductively coupled plasma mass spectrometry. ESP was calculated using the formula $(100 \cdot Na_x/CEC)$ (Na_x: exchangeable sodium (mmol 100 g^{-1})). SAR was determined using the formula $(Na/[(Ca+Mg)/2]^{1/2})$ (Na, Ca, Mg: soluble cations (mmol/dm^3)) (FAO, 1988). Statistical analyses were performed using MINITAB 15.1 software (Minitab Inc., 2007).

Results and discussion

Leachate properties

The leachate from the test columns were analyzed after full cycle (collection of 785 cm^3 leachate for each cycle) of the leaching tests. Na and SAR in the leachates of the soil were measured to evaluate the efficiency of the amendments.

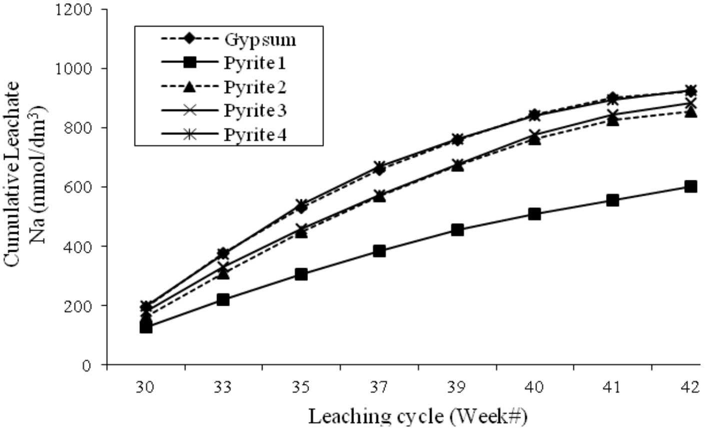

Fig. 2. Na in leachates from calcareous sodic soil columns treated with gypsum and waste pyrite

The solubility of salts enhanced removal of Na into the leachate of the calcareous sodic soil as a result of ion exchange. Exchangeable Na was replaced with Ca ions. Becoming soluble, it was removed from the soil during the leaching processes. For the soil treated with waste pyrite, the soil solution (leachate) was collected taking into account the SAR values of treated soils after 30, 33, 35, 37, 39, 40, 41 and 42 weeks after start of irrigation. The concentration of Na leaching, 926.17 mmol/dm^3, was the highest with the Pyrite 4 dose followed by 921.33 mmol/dm^3 with the gypsum application on the last leachate (Fig. 2). This result indicates that it is necessary to use almost twice the amount of pyrite than that calculated to be equivalent to minimum gypsum level.

For the soil treated with sulfuric acid, the leachates were collected after 15, 17, 19, 21, 23, 24, 25 and 26 weeks after the start of irrigation. The highest concentraton of Na leaching, 1096.25 mmol/dm^3, was observed for the H_2SO_4-5 application (Fig. 3).

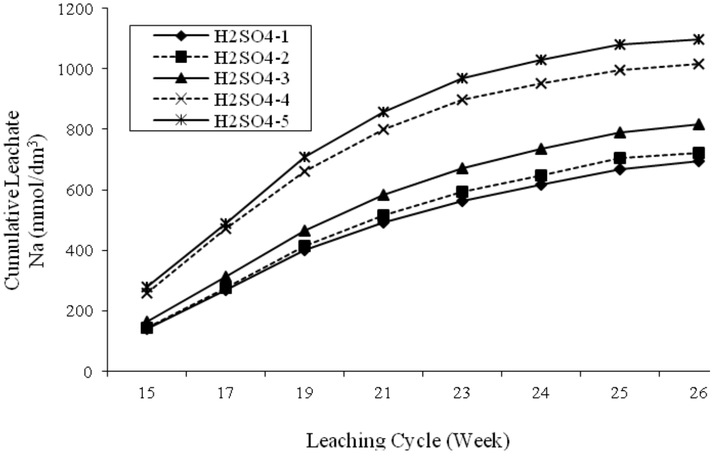

Fig. 3. Na in leachates from calcareous sodic soil columns treated with sulfuric acid

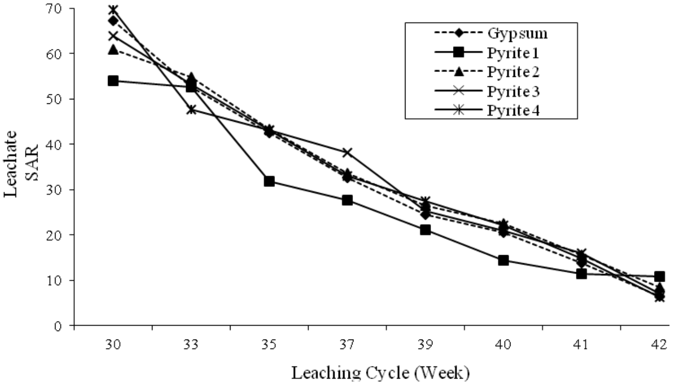

Fig. 4. SAR values in leachates from calcareous sodic soil columns treated with gypsum and waste pyrite

SAR is the ratio of sodium (detrimental element) to the combination of calcium and magnesium (beneficial elements). In the other words, SAR is the measure of the sodicity of soil and shows the efficiency of leaching process on soil remediation. After eight leaching cycles, SAR of all soils was lower than 12. This value separates the sodic soil from the non-sodic soils (Richards, 1954). For the soil treated with waste pyrite, SAR value 6.35, was the lowest with Pyrite 4 dose followed by 6.42 with the gypsum application on the last leachate (Fig. 4).

For the soil treated with sulfuric acid, the lowest SAR value 5.11 was observed for the H_2SO_4–5 application (Fig. 5).

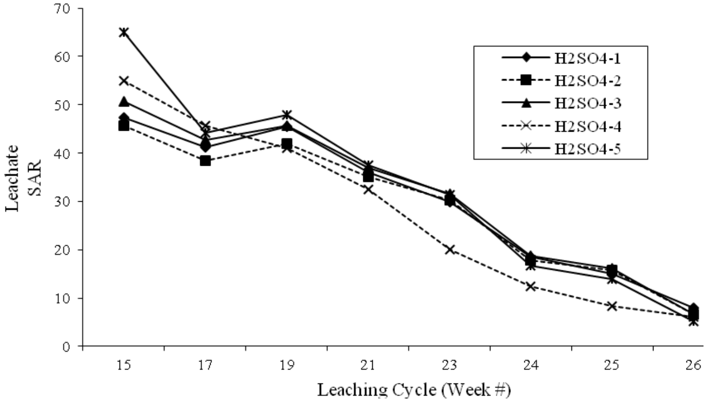

Fig. 5. SAR values in the leachates from calcareous sodic soil columns treated with sulfuric acid

Soil properties after leaching

The results indicated that gypsum for all application doses of waste pyrite and sulfuric acid produced from waste pyrite, had a significant effect on EC, ESP, $CaCO_3$, organic matter and boron content at the $P<0.01$ level in the soil treated with waste pyrite (Table 6) and had a significant effect on ESP, $CaCO_3$, organic matter at the $P<0.01$ level and boron at the $P<0.05$ level in the soil treated with sulfuric acid (Table 7).

Table 6. Physical and chemical properties of the soil before and after gypsum and waste pyrite treatment

Treatments	EC (**) (dS m^{-1})	pH (NS)	ESP (**)	$CaCO_3$ (**) (%)	O.M. (**) (%)	Boron (**) (mg kg^{-1})
Untreated Soil	2.85	9.27	83.33	9.18	0.71	8.87
Gypsum	2.05±0.02bc	7.78±0.07	12.26±0.04c	8.12±0.20a	0.76±0.03d	1.03±0.02c
Pyrite 1	2.27±0.02a	7.92±0.02	14.92±0.49a	7.59±0.07b	0.84±0.03d	1.63±0.03a
Pyrite 2	2.11±0.02b	7.87±0.08	14.63±0.15ab	7.14±0.05c	1.12±0.05c	1.30±0.01b
Pyrite 3	2.09±0.02bc	7.85±0.01	13.59±0.38b	6.27±0.05d	2.29±0.01b	1.26±0.08b
Pyrite 4	2.02±0.02c	7.77±0.05	11.77±0.22c	6.22±0.04d	2.65±0.04a	1.00±0.02c

Values represents means ± standard errors, same letter in each category were not different at $P < 0.01$(**) significant level
NS: not significant

Table 7. Physical and chemical properties of the soil before and after sulfuric acid treatment

Treatments	EC (NS) (dS m^{-1})	pH (NS)	ESP (**)	CaCO3 (**) (%)	O.M. (**) (%)	Boron (*) (mg kg^{-1})
Untreated Soil	2.85	9.27	83.33	9.18	0.71	8.87
H_2SO_4–1	2.06±0.01	7.51±0.08	14.34±0.33a	8.82±0.01a	1.11±0.01d	1.17±0.03a
H_2SO_4–2	2.05±0.01	7.46±0.09	13.65±0.33a	6.71±0.14b	1.12±0.01d	1.08±0.02ab
H_2SO_4–3	2.04±0.01	7.42±0.14	12.16±0.25b	6.00±0.14c	1.14±0.01c	1.06±0.03ab
H_2SO_4–4	2.04±0.01	7.34±0.04	9.39±0.03c	5.65±0.01c	1.30±0.01b	1.05±0.02ab
H_2SO_4–5	2.04±0.01	7.28±0.03	9.33±0.18c	5.65±0.14c	1.54±0.01a	1.00±0.03b

Values represents means ± standart errors, same letter in each category were not different at $P < 0.05$(*) and $P < 0.01$(**) significant levels. NS: not significant.

EC decreased in all the treated soil due to removal of salts by the leaching processes. The initial EC of untreated soil was 2.85 dS m^{-1}, which is well below the value of 4 dS m^{-1} separating the non-saline soils from the saline soils (Richards, 1954), and it was further reduced at the end of leaching (Table 6 and 7). The pH of untreated soil was 9.27 and higher than threshold value of 8.5 (Richards, 1954). Upon treatment the pH values of soil were reduced to 7.77–7.92 in the waste pyrite treated soil and 7.28–7.51 in the sulfuric acid treated soils.

All treatments had the ameliorative potential to lower the soil ESP below 15%. After leaching, ESP decreased from 83.33% down to 15% separating the sodic soils from the non-sodic soils (Richards, 1954). The maximum decrease of ESP was observed in Pyrite 4 dose (11.77%) and followed by gypsum (12.26%) applications in the waste pyrite treated soil (Table 6) and observed in H_2SO_4–5 (9.33%) and followed by H_2SO_4–4 (9.39%) applications in the sulfuric acid treated soil (Table 7).

Dissolution of $CaCO_3$ is clearly seen in the waste pyrite and sulfuric acid treated soils. The more the pyrite and sulfuric acid addition, the more $CaCO_3$ dissolution and therefore the less $CaCO_3$% in the soil was left. The organic content of soils increased after all applications. The soil organic matter content of less than 2% has a low infiltration and low productivity (Ulgen and Yurtsever, 1974). By adding increasing dose of waste pyrite and sulfuric acid, the organic matter content in the soil increased but only with Pyrite 3 (2.29%) and Pyrite 4 (2.65%) doses of waste pyrite applications the value reached above 2% (Table 6). Accumulation of boron in plants at toxic levels may result in plant injury or reduced growth and even death (FAO, 1988). The limit value of boron is 1.5 mg kg^{-1} in a saturated paste extract of soil for sensitive plants according to U.S. Salinity Laboratory (Richards, 1954). Boron decreased to well below 1.5 mg kg^{-1} with the all applications due to leaching except for the Pyrite 1 dose (1.63 mg kg^{-1}) application.

The heavy metal content of soils after treatment with gypsum, Pyrite 4 dose (maximum dose of waste pyrite) and H_2SO_4-5 (maximum dose of H_2SO_4) applications are given in Table 8. It was found that all values are within the tolerance limit of soil according to Turkish Soil Contamination Regulation (2001).

Table 8. Heavy metal content of calcareous sodic soil before and after treated with Pyrite 4 dose and H_2SO_4–5

Element	Untreated soil (mg kg^{-1} soil)	Pyrite 4 treatment (mg kg^{-1} soil)	H_2SO_4–5 treatment (mg kg^{-1} soil)	Limit values* (mg kg^{-1} soil)
Cr	24.59	32.40	62.70	100
Co	3.20	16.08	15.70	20
Ni	20.78	33.40	42.50	75
Cu	14.40	128.90	105.50	140
Zn	61.32	94.67	177.36	300
Pb	20.89	35.24	28.28	300
Mo	2.19	3.54	3.11	10
Cd	0.12	0.58	0.45	3
Fe (%)	4.08	8.04	6.28	-

*according to Turkish Soil Contamination Regulation (2001)

Table 9. Essential micronutrient content of soil for plant growth before and after waste pyrite and sulfuric acid treatment

	DTPA-extractable	Untreated soil	Pyrite 1	Pyrite 2	Pyrite 3	Pyrite 4	Sufficient level
Waste Pyrite Applications	Fe (mg kg^{-1})	1.75	8.55±0.09d	10.71±0.22c	14.86±0.40b	19.33±0.26a	> 4.5[1]
	Cu (mg kg^{-1})	0.29	1.45±0.07d	3.24±0.09c	6.68±0.11b	8.80±0.06a	> 0.2[2]
	Zn (mg kg^{-1})	0.07	1.70±0.04b	1.94±0.04ab	2.06±0.05a	2.08±0.12a	0.7 - 2.4[3]
	Mn (mg kg^{-1})	3.53	20.01±0.71cd	28.34±0.88b	22.16±0.80c	35.48±0.54a	14 – 50[3]
	DTPA-extractable	Untreated soil	H_2SO_4–1	H_2SO_4–2	H_2SO_4–3	H_2SO_4–4	H_2SO_4–5	Sufficient Level
Sulfuric acid Applications	Fe (mg kg^{-1})	1.75	3.61±0.09d	7.36±0.06c	7.25±0.10c	8.12±0.03b	11.07±0.20a	> 4.5[1]
	Cu (mg kg^{-1})	0.29	3.84±0.04e	8.19±0.06d	9.65±0.06b	9.21±0.04c	9.90±0.06a	> 0.2[2]
	Zn (mg kg^{-1})	0.07	1.14±0.04c	1.55±0.07b	1.97±0.04a	1.95±0.06a	2.10±0.30a	0.7 - 2.4[3]
	Mn (mg kg^{-1})	3.53	14.94±0.05d	17.35±0.27c	25.08±0.19b	25.42±0.87b	29.76±0.36a	14 – 50[3]

Values represents means ± standard errors, same letter in each category were not different at P < 0.01 significant level.

[1] Lindsay and Norvell, 1978, [2] Follet and Lindsay, 1970, [3] FAO, 1990.

The level of available micronutrients essential for the plant growth was determined by the DTPA method. It was observed that all the micronutrient in the soil increased significantly ($P < 0.01$) with waste pyrite and sulfuric acid applications (Table 9). The levels of the micronutrients after treatments can be classified sufficient for plant the growth except for the iron level with the minimum dose of sulfuric acid application, H_2SO_4–1 (Follet and Lindsay, 1970; Lindsay and Norvell, 1978; FAO, 1990). The micronutrient analysis was not done for gypsum tests because the gypsum material was a purified chemically.

Conclusions

All amendments tested in this study were effective in calcareous sodic soil reclamation. The application of waste pyrite with a dose of 44.74 Mg/ha (Pyrite 4) was superior to the gypsum of 55.20 Mg/ha dose in terms of ESP in 42 weeks. ESP decreased from 83.33% to 11.77% with the application of waste pyrite of 44.74 Mg/ha dose and from 83.33% to 12.26% with the application of gypsum of 55.20 Mg/ha dose. In addition, the application of all concentrations of sulfuric acid produced from waste pyrite also decreased the ESP values. The best values with sulfuric acid were obtained with a dose of 35.31 Mg/ha in 26 weeks. The application of waste pyrite or sulfuric acid to the soil resulted in the increased availability of DTPA-extractable Fe, Cu, Zn and Mn which are essential for the plant growth. The pyrite does not appear to lead to pollution or toxic problems in the soil. Thus, the use of pyrite, by the product or waste from the copper concentration plants may be the useful amendment and effective fertilizer in the calcareous sodic soils.

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