Sulphur efficiency in rising of pollution soil by heavy metals qualification under conditions of lettuce plant cultivation

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Abstract: Pot experiment was established in green house at National Research Centre, Dokki, Egypt, in polluted soil from industrial wastes by heavy metals. Sulphur elemental was used at different rates (100, 200 and 300 ppm). Lettuce plant of class (lactuca sativa var. Capitata). Loamy sand soil type from Helwan region at south of Egypt. Some parameters in fresh plant were performed. From plant analysis showed existence positive relationships between sulphur concentrations were added and chlorophyll concentrations, (N,P and K) and (Fe, Mn, Zn and Co) while a negative contact between sulphur rates were added and (Cd, Ni, Pb and (Cu) contents by comparison with control. Water filtering from water irrigation was analyzed and shown that heavy metals were leached from soil. Soil was analyzed at experiment end shown that nonexistence heavy metals in soil except slight traces. All the differences between treatments were significantly.

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Introduction

Pollution soils problems came great rate in modern time and dangerous as a result to several reasons as wastes human industries and heavy metals by different sources, it now scientists are trying in modern time finding solutions to this deteriorate through their researches until not happen decrease in foods, may occur world catastrophe as a result that and thus it give vegetable production is not healthy for human and animal to take extent, toxicity for them and may lead to death. Some modern researches, it found some solutions to this problem, such as cultivation of some plants species leaves plants specially to it high ability to absorption this heavy metals then using it at other purposes unlike the food, such as industries and vital fuel or using some amendments and conditioners or chemical materials to equal of charges this heavy metals and transformation to salts then leaching it from soil but this methods require to good drains to soil. Pollution and exces of salinity its main reason at decrease of soils fertilization in Egyptian soils. Accumulation of heavy material represents dangerous threat to vegetable production and animals.

These element important as pb. Zn, Cu, Ni, Hg and Cd six of the heavy metals, namely Ni, Zn, Cu, pb, Hg and Cd have been shown by many researchers to reach toxic levels in soils. their hazard extend to plants, animals and human being. In Egyptian soils the extent of pollution due to Cd and / or Hg accumulation is relatively limited (Hilal 1994). This study is important as only pb, Ni, Cd and Cu while others elements that find it with high concentrations in Egyptian soils are little ereas of soils.

Materials and Methods

Pot experiments were established under green house condition using pollution soil by industrial wastes from (Helwan) as Cairo south to evaluation effect of sulphur as amendment to improving soil properties under conditions lettuce plant cultivation and evaluation effect of sulphur on soil pollution and plants.

Soil textural was loamy sand. Table (1), shown some physical and chemical characteristics. Pot contents as 8kg of soil and pot diameter 40 cm, soil pot height 40 cm with position good drain system and receiving of filtering from pot after each irrigation to determination of heavy metals concentrations. Lettuce plant of class (lactuca sativa var capitata) were cultivated as indicator to treatments under study. Three replicates were taken to determination some macronutrients (N, P and K), some micronutrients (Fe, Mn, Zn and Co) and some heavy metals (Cd, Ni, pb. And Cu) that's after 60 days it growing period to lettuce plant. Nitrogen was added at a rate 100 ppm as a form ammonium suphate (NH_4SO_4) at one dose after plantation stage, di-hydrogen potassium phosphate KH_2PO_4 was added at a rate 200 ppm as a source for each of potassium and phosphours. There levels of sulphur were added as elemental sulphur, it (100,200 and 300) ppm uniformly mixed with soil surface layer. The moistur content of the pot was maintained 100% of saturation capacity along the experiment period plants were harvested on 60 days.

Table (1): Some chemical and physical properties of the studied soil.

Site	Clay%	Texture	PH (1:2.5)	E.C (dSm-1)	Cations mq/L				Anions mq/L			
					Ca++	Mg++	Na+	K+	HCO3-	Cl-	SO4--	
Helwan	17.3	Loamy sand	8.5	0.31	11.2	38.0	38.2	44.3	7.6	151	1.45	
	O.M%	CaCO3%	O.W.		DTPA Available heavy metals (μg/g)				Total heavy metals (μg/g)			
					Cd	Ni	Pb	Cu	Cd	Ni	Pb	Cu
	0.39	1.35	1.37		0.47	13.90	3.92	0.31	0.7	25.2	10.2	0.35

Fresh plants were divided to many parts to fresh weight, after that plant samples were dried to constant weight at 70°C in aventilated oven, dried plant material was anlysed for total nitrogen was determined by using microkjeldahel distillation (Jakson, 1985). Phosphours, potassium, heavy metals (Cd, Ni, pb) and micronutrients (Fe, Mn and Zn) as according (Jakson, 1985). (chlorophyll concentration fresh leaf was determined according to (Licheloem and weilburn, 1983).

Results and discussion

Sulphur of main amendments to different soil types clay, calcareous and sandy soils as decreasing of soil pH which increase available of nutrients to plants and thus increasing mobility of elements in soil of what contribute to get ride of high concentrations harmful elements by leaching during of soil irrigation. (Abd-Elfattah et al.., 2005) indicated that a drop in soil pH as a function of applied sulphur which dependent upon soil type, rates of sulphurs application and inoculated period of soils with sulphur oxidizing bacteria. (Tyler and Mc Bride, 1982). They reported that the soil chemical properties had generally a larger effect on the mobility of metals than did the properties of the metal themselves. The least mobility of metals was observed in a mineral soil with a relatively high pH, CEC and exchangeable base content. The order of mobility of the metals in the used soils was: Cu $\leq$ Z $\leq$ Ni $\leq$ Cd. This work was used sulphur to evaluation effect on behavior of some heavy metals (Cd, Ni, pb and Cu under conditions of lettuce plants cultivation. Table (2) shown that some parameters of lettuce plant in harvest period end. Sulphur treatments were at a positive relation with the determination parameters by comparison control as increasing of sulphur concentration.

Increase of all parameters (Fresh plant weight, fresh roots weight and number of leaves) . Fresh weight increased by rate (18.5 ,29, and 68.3) % with sulphur concentrations (100.200 and 300) ppm respectively comparative control,

Table (2): Some parameters in lettuce plant as affected by sulphur additions and pollution soil by heavy metals.

Sulphur treatments	Fresh plant weight gm	Fresh root weight gm	No of leaves
Control	109	24.3	46.0
100	131	28.7	58.0
200	149	39.6	68.0
300	194	45.7	77.0
L.S.D.0.05	12.6	5.43	7.32
L.S.D.0.01	16.9	7.66	9.15

Fresh roots weight took the same of previously trend increasing in the fresh roots weight comparative control (18.1, 63 and 88) % pursuant to sulphur concentrations respectively. Number of leaves were in the order (26, 48 and 67)% pursuant to sulphur concentrations respectively. In this results shows that sulphur increase plant ability in keeping of the water, and it increase of dry weight to plant.

(Abd-El Fattah et al, 2005). Found that the yield of garlic increased from 4 to 5.7 t by application of 2t per acre of suplphur alone.

Dry matter status:

Data in table (3) shows that dry plant weight was in a positive connection with sulphur concentrations addition as whenever increased of sulphur concentrations. Increased of dry plant weight pursuant

to the following order head value of dry plant weight (36.4 gm) was with sulphur concentration (300 ppm) while among value (23.8 gm) was with (200ppm) of sulphur concentration, the least value (16.7 gm) was found with (100 ppm) of sulphur concentration. Increasing rates in comparison control as following (22, 74 and 166) % pursuant to sulphur concentrations respectively. All differences between the treatments were significantly almost to each of two significant levels.

Dry roots weight took the same previos trend as was found a positive contact between sulphur concentrations and dry matter weight to roots as whenever increased of sulphur concentration increased of dry roots weight. Increasing rates were estimated comparative control as following (61, 176 and 227)%, this results indicated that sulphur is play important role in life plants as that's increase plant uptake of macro micronutrients and its lead to structure of sulphureous amino acids which lead to structure of proteins which foundation plant growing, in addition to improving of soils physicals and chemicals properties. Some treatments were significantly under. L.S.D. 0.05 level and some the other were significantly under L.S.D. 0.01 level. (Graines and phatak 2002). Found that increases sulphus levels significantly increased the dry weight of corn, soybean, tomato, cowpea lops and soybean roots. They also stated that total N/S ratio in soybean were greatly reduced by increased sulphur rates, whereas protein N/S and (N/S): P ratio were constant and less affected. (Hilal and Abd El-Fattah. 1987) stated that the yield of barly dry matter per pot was shown to respond greatly to sulphur application in clay loam soil (Brazozowska et al., 1994). Reported that sulphur deficient plants of ground nut (Arachis hypogeal L.) had less protein N in all plant organs. There was an accumulation of arginine and a decrease in cyctine, cyctein and methonine contents. .

Nitrogen contents status:

Data in table (3) showed that sulphur elemental treatments by different concentrations in a positive connection with nitrogen contents in lettuce plants. Whenever sulphur concentrations increased nitrogen contents is increase amounts of increasing of nitrogen contents comparative control as following (29, 107 and 134)% this mean's that the sulphur stimulate of plant uptake to nitrogen because of constitution sulphureous amino acids which lead to structure of the proteins. (Thomas et al., 1991; Frgle and Eaton 1994). Showed that (N/S) / P ratio of cotton leaves increased from 13 to 17 when sulphur was applied at rates varying between 1 to 10 ppm . (Spencer, 1990) found that sumptoms of sulphur deficiency did not appear until second growth period, when plants without added sulphur developed chlorotic leafiest. (McNaught and chrisloffels, 1991) indicated that sulphur addition enhanced nodulation, sulphur may have increased nodulation by increasing growth and nitrogen demand.

Phosphours contents status:

Phosphorus was found in a positive contact with sulphur concentrations, that's mean available phosphorus was continuing.

Table (3): Dry weight and some macronutrients (%) content in lettuce plant as affected by sulphur additions and pollution soil by heavy metals.

Sulphur treatments ppm	Dry plant weight gm	Dry root weight gm	N	P	K
Control	13.7	3.42	1.76	0.63	0.13
100	16.7	5.52	2.27	0.74	0.17
200	23.8	9.44	3.65	0.78	0.21
300	36.4	11.2	4.11	0.92	0.26
L.S.D.0.05	5.56	1.05	0.82	0.092	0.026
L.S.D.0.01	5.63	1.78	1.11	0.128	0.038

To plant a long the experiment period despite existence some bad properties in soil similar pH raising presence of calcium carbonate and bicarbonate, this properties contribute to phosphorus fixed as converted to unavailable form to plants, that's means the elemental sulphur was improved of soil properties. Increasing rates of phosphours contents compartive with control as following (17.5, 24.0 and 46.0)% with sulphur concentrations (100,200 and 300) ppm respectively. Previously results indicated that sulphur elemental increasing of phosphours available form and is protect's of soil phosphours from the fixation, it also improvement of soil properties.

(Khater, 1981) showed that application of sulphur generally increased available P in alluvial soil. (Shadfan and Hussein, 1985) found a significant increase in NaHCO3 extractable P from 10-13.5 ppm by applying 500 ppm S and 8 weeks of incubation in a loamy sand soil. (Heter, 1985) indicated that most of the added P to calcareous soil will be fixed as unavailable form for plants uptake due to the alkalinity reaction of the soil. He found that the addition of sulphur and H2SO4., through their effect on soil pH,

are expected to increase the availability of P by increasing the solubility of the Ca compound he also found that the effect was more evident in the case of low CaCO3 content of soil and the available P was found to be correlated with the extracted SO4-S.

Potassium contents status:

Potassium was found in a positive relation with sulphur concentrations (100, 200 and 300) ppm as whenever sulphur concentrations increasing potassium content in lettulce plant increases. Increasing rates of potassium contents comparative with control as following (31, 62 and 100)% respectively, this results showed that sulphur concentrations was contribute at potassium available to plants may be due to low of soil pH thus it protects of potassium of fixation between soil minerals layers and following turn unavailable to plants as a potassium element is needful for plants life also it enter in structure plant of dry matter. All differences between the treatments were significantly under each of two levels.

(Vijayapriya et al. 2009) showed that addition of 30 kg S h-1 in a clay loam soil at form gypsum in the presence bradyrhiobium inoculation with soybean resulted nutrient uptake and availability of nutrients were significantly by the addition of S % and Rhizobium compared to the control. The nutrient uptake and availability were significantly higher in plant inoculated with Rhizobium compared to uninoculated plants. The uptake of N, P, K and S by soybean and their availability in soil. increased with S levels and the highest values were recorded at 30 kg S h-1.

Chlorophyll contents status:

Data in table (4) indicated that chlorophyll was found in a positive contact with sulphur concentrations (100,200 and 300) ppm. Also its in a positive contact with all micronutrients under study (Fe, Mn, Zn and Co) where as all this trace elements under study were found in a positive contact with sulphur concentrations under study also. Chlorophyll is nutrition factory to plants of during sunlight as perform light constructive process to industrialization carbohydrate matters especially. Chlorophyll is require to micro and macro nutrients at structure it is necessary, that's presence at available form in soil. Sulphur is play important role in available form abundance micro-macro nutrients in soil. Chlorophyll concentration increases with increasing of sulphur concentrations.

The increasing rates of chlorophyll concentrations comparative with control and due to sulphur concentrations were as (11.3, 17,8 and 58)% respectively. Head value of chlorophyll concentration was found with 300 ppm of sulphur concentration, among value with 200 ppm and least value with 100 ppm of sulphur concentrations from previously results show that sulphur is amendment conditions to polluted soils. (Rending and Mc comb, 1991) indicated that the chlorotic condition of leaves in sulphur deficient plants was visual evidence of disturbance in photosynthesis. They suggested that sever deficiency enough to disrupt normal photosynthesis would ultimately be reflected on the changes in the kinds and amounts of carbohydrates.

Table (4): Chlorophyll and some micronutrients (ppm) contents in lettuce plant as affected by sulphur additions and pollution soil.

Sulphur treatments (ppm)	Chlorophyll mg/g	Fe	Mn	Zn	Co
Control	0.62	163	98	25	39
100	0.69	189	124	32	48
200	0.73	211	152	37	75
300	0.98	305	173	46	89
L.S.D.0.05	0.063	14.7	11.2	3.52	5.43
L.S.D.0.01	0.088	19.6	14.1	4.59	7.05

Micronutrients contents status:

Table(4) contents shown that also some trace elements concentrations (Fe, Mn, Zn and Co) in lettuce plants as affected by polluted soil by heavy metals and different rates of elemental sulphur (100,200 and 300) ppm was added. Trace elements contents were found in appositive relationship with all off sulphur concentrations. Head values of (Fe, Mn, Zn and Co) were found with 300 ppm of sulphur concentrations while among values were found with 200 ppm and the least values with 100 ppm of sulphur concentrations increasing rates of trace elements contents comparison with control as to Fe (16, 29 and 87) %, as for Mn (27, 55 and 77)%, as to Zn (24, 48 and 84)% as for cobalt Co (23, 92 and 128)%. From previously results were recorded that sulphur of soil amendment under pollution conditions that's may be due to decreasing of soil pH and of rising of solubility rate to trace elements which lead to abundant available form for plant. (Abd El-Fattah and Hila., 1985) they suggested that the use of sulphur as a soil amendment would in case of Fe, Mn and Zn deficient soils, increase the availability of

these elements and evok a plant response, if, however, the amount of applied sulphur exceeded the soils basicity, large quantities of Fe, Mn and Zn would be dissolved and may thus became toxic to both plants and animals and its probable that toxic level of Al would also occur under the conditions of high sulphur application.

Heavy metals contents status:

Data in Table (5) indicated of some heavy metals contents in lettuce plant as affected by different rates of elemental sulphur applications (100,200 and 300) ppm and pollution soil by heavy metals (Cd, Ni, Pb and Cu). Heavy metals contents were noticed in a negative relationship with sulphur concentrations applications. This's sulphur effect success in a slight of heavy metals concentrations in plants as its very harmful to human and animals health. Head value of heavy metals was found with sulphur concentration of 100 ppm, among value with 200 ppm and the least value with 300 ppm respectively.

Decreasing rates by comparison with control as following (34, 51 and 75.4)% as for Cd element respectively, as to Ni element (51, 65 and 89) % respectively, as to pb element (60, 63 and 65) % respectively and Cu element as (56,76 and 88)% respectively. This results may be due to the repetition leaches to soil in each once was irrigated soil as moisture reach to a rate 100% saturation capacity then was taken of the leaky as was determined heavy metals at every once as reached a times number of irrigation or leaches were twelve of time also it incourages aspossibility dilulion of to heavy metals from soil pollution to become useful to cultivation (Tyler and Bride, 2005). They reported that the soil chemical properties had generally a larger effect on the mobility of metals than did the properties of the metal themselves the least mobility of metals was observed in a mineral soil with a relatively high pH. CEC and exchangeable bas content. The order of mobility of the metals in the used soils was: Cu $\leq$ Zn $\leq$ Ni $\leq$ Cd. (Biddappa et al., 2002) found that the pb and Cu ions were less mobil than that of Zn and Cd. Nickel has exhibited greater mobility than other heavy metals under the leaching stress in two typical soils of Jappan.

The specific migration properties of each metal ion varied depending on the nature of the ion and of the leaching solution.

Heavy metals status in drain water:

Data in table (6) shown that heavy metals concentrations in irrigation water to evaluation heavy metals concentration in every leaching then added up to total at harvest season and under different rates (100, 200 and 300) ppm of elemental sulphur applications and lettuce plant cultivation. Results indicated that to presence a positive contact between amounts of heavy metals were leached in the filtrating water of the irrigation water and sulphur concentrations applications (100,200 and 300) ppm. Head values of heavy metals were found with sulphur rate 300 ppm, while among values were found 200 ppm and the least values were found with 100 ppm from sulphur rates were added, that's to all of heavy metals under study (Cd, Ni, pb and Cu) whenever increased of sulphur rate was added heavy metals concentrations in filtrating water were increasing. The increasing a mounts of heavy metals by comparison with control as (53, 67 and 93)% as for cadmium (Cd) element with sulphur rates were added (11,200 and 300) ppm respectively.

Table (5): Some heavy metals contents in lettuce plant as affected by sulphur additions and pollution soil by heavy metals.

Sulphur treatments (ppm)	Cd	Ni	Pb	Cu
	ppm			
Control	0.65	6.53	2.86	0.25
100	0.43	3.17	1.15	0.11
200	0.32	2.29	1.07	0.06
300	0.16	0.75	1.00	0.03
L.S.D.0.05	0.055	0.255	0.234	0.010
L.S.D.0.01	0.072	0.331	0.304	0.024

As to nickel element as (907, 2009 and 2973)% respectively.

As for lead (pb) element (1200, 1254 and 1319)% with sulphur rates were added (100,200 and 300) ppm respectively and copper element Cu (23, 154 and 169)% respectively.

From previous results shown that sulphur is play role very important in increasing of heavy metals elements mobility and it raising of solubility product.

All differences between the treatments were significantly on both of two levels.

Herms and Brümmer (2007) found that at pH 7 and 8 Zn and Cd show a very low solubility. Which increase strongly with decreasing pH. The concentration of Ni also rises with dropping pH. The concentration of Ni also rises with dropping pH. The concentrations of Cu and pb increases. When pH values decrease below 4 to 5. at pH 6 to 8 solubility of pb and Cu rises due to increasing solubility of complexing organic substances. The soil reaction influences the heavy metal solubility in the order Cd ≥ Zn>Ni<pb. Compared with mineral soil components

Residua effect of heavy metals in soil:

Data in table (7) reveal that residual effect in soil of heavy metals under study after of yield harvest as found that the soil became devoid of the heavy metals pollution, that's due to elemental sulphur which confirmed of good efficiency at get rid of heavy metals from soil therefore necessary using it on wide range in soil pollution, through generally look on table (7) was found that not residual of heavy metals except slight traces, it not harmful.

Table (6): Heavy metals concentrations in irrigation water after each leaching under cultivation of lettuce plants and sulphur applications.

ppm																
Sulphur treatments / No of Irrigation	Control				100				200				300			
	Cd	Ni	Pb	Cu	Cd	Ni	Pb	Cu	Cd	Ni	Pb	Cu	Cd	Ni	Pb	Cu
1	0.00	0.01	0.01	0.01	0.02	0.03	0.01	0.00	0.01	0.02	0.03	0.01	0.02	0.03	0.03	0.02
2	0.00	0.02	0.01	0.00	0.03	0.02	0.01	0.02	0.01	0.02	0.05	0.03	0.02	0.05	0.02	0.02
3	0.00	0.04	0.02	0.01	0.03	0.05	0.01	0.01	0.02	0.03	0.05	0.01`	0.02	0.14`	0.07	0.03
4	0.01	0.03	0.05	0.00	0.02	0.05	0.02	0.01	0.02	1.15	0.11	0.02	0.02	1.87	0.61	0.03
5	0.02	0.07	0.03	0.00	0.02	0.17	0.04	0.01	0.02	1.12	0.12	0.05	0.02	1.19	0.55	0.03
6	0.01	0.06	0.05	0.02	0.04	0.22	0.03	0.01	0.02	2.14	0.09	0.07	0.02	2.47	0.45	0.03
7	0.02	0.02	0.07	0.01	0.02	0.15	0.15	0.01	0.02	1.22	0.13	0.06	0.02	1.33	0.76	0.03
8	0.01	0.05	0.01	0.00	0.01	0.21	0.18	0.01	0.03	1.15	0.15	0.03	0.03	2.36	0.53	0.03
9	0.02	0.10	0.01	0.02	0.01	1.15	0.20	0.02	0.02	1.24	1.12	0.01	0.02	2.35	0.67	0.03
10	0.02	0.07	0.06	0.03	0.01	1.10	2.06	0.02	0.02	1.28	1.06	0.02	0.03	1.47	0.58	0.04
11	0.02	0.03	0.02	0.02	0.01	1.17	1.03	0.02	0.03	1.11	1.03	0.01	0.04	1.36	0.03	0.03
12	0.02	0.05	0.03	0.01	0.01	1.22	1.07	0.02	0.03	1.14	1.07	0.01	0.03	2.24	0.95	0.03
Total	0.15	0.55	0.37	0.13	0.23	5.54	4.81	0.16	0.25	11.6	5.01	0.33	0.29	16.9	5.25	0.35
L.S.D.0.05	0.002	0.007	0.004	0.002	0.003	0.07	0.06	0.002	0.003	0.14	0.06	0.004	0.003	0.20	0.06	0.003
L.S.D.0.01	0.003	0.009	0.005	0.003	0.004	0.09	0.08	0.003	0.004	0.18	0.08	0.005	0.004	0.26	0.08	0.004

Table (7): Residual effect of heavy metals in soil under study after harvest of lettuce plants.

Sulphur treatments ppm	ppm			
	Cd	Ni	Pb	Cu
Control	0.02	0.01	0.22	0.01
100	0.02	0.02	0.25	0.02
200	0.03	0.01	0.43	0.03
300	0.02	0.02	0.69	0.02
L.S.D.0.05	0.003	0.002	0.04	0.002
L.S.D.0.01	0.004	0.003	0.05	0.003

Summary and Conclusion:

The aims of this work study and evaluate to elemental sulphur efficiency at rising fertilization of soil pollution by heavy metals (Cd, Ni, pb and Cu) under lettuce plant cultivation conditions. Sulphur was used at three rates (100, 200 and 300) ppm. All the parameters and determinations confirmed existence a positive effects to sulphur applications especially with rate 300 ppm of sulphur was added. Sulphur effects due to decreasing of soil pH, oxidation reduction reaction, availability of macro-micronutrients and increasing of mobility and solupility product to the elements, in the

experiment end not reisual of heavy metals except slight traces therefore was recommended by using of sulphur especially of high concentration with soil leaching.

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