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Original Research Article

Controlling soil surface crust formation using Nanosized sulfonated polyaniline

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Agricultural expansion and desert reclamation are considered the most important projects influencing the development agenda in Egypt. Most of the new reclaimed lands are located in arid and semi-arid regions, which suffer from crusting. This phenomenon is a process by which a compact layer or thin mantle of consolidated soil particles is formed at the soil surface. They result in water loss, soil erosion, seedling emergence difficulties and water infiltration problems into the soil. Crust formation leads to deterioration in soil characteristics and productivity. Nanotechnology is a new area of research with the potential to contribute to various areas of scientific investigation, including natural resources and soil conservation. The objectives of this research were selection and synthesis of suitable nanomaterial for use as a soil conditioner for controlling soil surface crust formation. Additionally, this study aimed to determining of optimum application rate and examining the toxicity of this material on Earthworm and mice. The result showed appropriate use of Sulfonated polyaniline (SPANI), for the first time, as a soil conditioner for controlling soil surface crust formation from the use of polyaniline (PANI). The optimum rate of (SPANI) was 0.678%, which gave the lowest values of the soil resistance to penetration. The germination rate of corn after 5 days of sowing was 100% for SPANI treatment, but in the case of control treatment the same percentage was achieved after 12 days from sowing. This means that the rate of occurrence was 20% for SPANI compared with control treatment which was11% .On the other hand, using the proposed rate of SPANI provided a germination rate of wheat by 60% and increased the rate of occurrence to 22.8% compared to the control treatment which was 13.5%. The toxicity test showed that the concentration of a substance that is (LC50) lethal to 50% of the earthworm was 1.13%. This indicates that using sulfonated polyaniline (SPANI) at the optimum rate would be safe. The oral LD50 of SPANI was 206.64 mg / kg body weight of mouse which classified as moderately toxic.

INTRODUCTION

Soil crusting is a worldwide problem that occurs under a wide range of soils and climatic conditions. This problem affects seedling emergence and reduce soil infiltration rate causing loss of water and crop yield (Kebede et al., 2012).

A soil crust is a thin, dense, hard layer at the soil surface. Crusts are characterized by greater density and shear strength than regular soil. Also, soil crusts have finer pores and lower saturated hydraulic conductivity than the underlying soil. As a result, soil crusts interfere with seedling emergence, hamper gas exchange between soil and the atmosphere, reduce infiltration and encourage runoff and erosion. Because of their role in sealing the soil surface to water infiltration, crusts are often referred to as seals when wet. There are no clear morphological or developmental criteria for distinguishing crusts from seal (Shainberg, 1992).

The capability of a soil to form a seal or surface crust depends on the aggregate stability (LeBissonnais, 1996). The aggregate stability is affected by the complex interaction of different internal soil properties and also by external factors (Amezketa, 1999; Barthes et al., 2008; Martínez-Gamiñoand Walthall, 2000; Pagliai, 2003; Six et al., 2004). Among the internal factors are: soil organic matter (SOM), texture, clay mineralogy, cations, moisture content, salinity, oxides and hydroxides of Fe and Al, $CaCO_3$, Mg and gypsum (Amezketa, 1999;Lado et al., 2007; Wakindiki and Ben-Hur, 2002). External factors that have received attention include: the intensity of rainfall, the gradient and length of slopes, electrolyte concentration, and type of cation of the rainwater, in

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addition to the soil management practices (AssoulineandBen-Hur, 2006; Pagliai, 2003).

Several methods were studied and implemented to minimize the effects of soil surface crust with varying degrees of success. These methods include changing characteristics of the irrigation system by using smaller sprinklers that require lower operating pressure, resulting in, smaller water droplets, and relying on overlapping of water jets to increase irrigation uniformity (Silva et al., 2007). Other approaches include, reducing intervals between irrigations (Bradford and Huang, 1992), maintaining crop residues on the soil surface (Al-Kaisi et al., 2009), applying minimum tillage techniques (Soil Quality Indicators, 2008), breaking soil surface crust (Minnesota crop eNews, 2007) and using soil conditioners (Wu et al., 2010). A new approach to minimize crusting, which has not been fully investigated yet, is the use of nanoparticles.

Nanotechnology is a promising field of interdisciplinary research. It opens up opportunities in various applications such as agriculture and natural resources management. For instance, ahydro gel based Nano-clay for use as growth media additive in pot plants and small scale cultivation (Boroghani et al., 2011and RamPrasad et al., 2014). In natural resources, nanotechnology has numerous applications for the synthesis of materials to stabilize sandy soil to maintain water and control erosion (Oztas et al., 2002).

Conducting polymers (CPs) with their unique properties have been incorporated into various applications (Shirakawaet al., 1977, MacDiarmidet al., 1993, Minet al., 2000 and Kollaet al., 2005). In the bio medical field, CPs combine the attractive properties of plastics, i.e., easy processing, adjustable physical and chemical properties (adhesion, wettability, surface charge, etc.), with the electrical properties of metals. They also offer a more biocompatible choice than conventional metals (Kamaleshet al., 2000).Moreover, by incorporating certain biomolecules (growth factors, enzymes, antibodies, etc.) as dopants, cellular activities can be further controlled (Hodgsonet al., 1994 and Hodgsonet al., 1996).

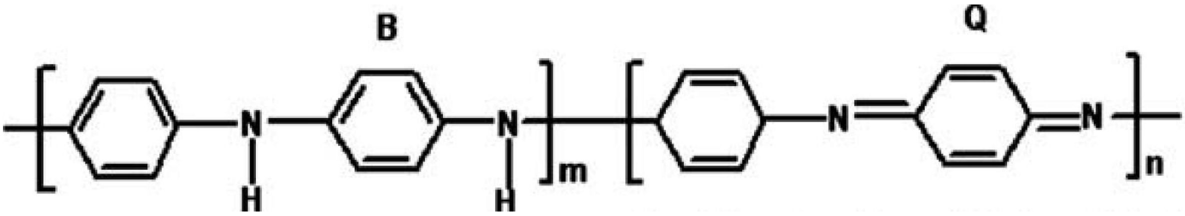
Polyaniline (PANI) is a very popular conductive polymer, which has been rediscovered in recent years. Detailed studies revealed its chemical structure and the different oxidation states it can assume under different conditions (Shirakawaet al., 1977 and Kollaet al., 2005).Our interest in SPANI and its properties is attributed to the fact that introducing -SO_3H improves SPANI solubility without substantially sacrificing conductivity. In the meantime the conductivity of SPANI is independent of external protonation in a broad pH range. Additionally, the covalent bonded -SO_3H dopant will not be released to affect the bio- medium. Furthermore existence of -SO_3H on the phenyl rings improved the environmental stability of polyaniline (PANI) due to its strong electron-withdrawing properties.

It has been shown that SPANI has better thermal stability than PANI doped with HCl (Yueet al., 1990;Yueet al., 1991;Weiet al., 1996 and Shimizuet al., 1997). There are many ways to synthesize SPANI, by utilizing either chemical or electrochemical oxidation, or simply exposing the emeraldine base form of PANI to fuming sulfuric acid (Mavet al., 1999). Biological applications of CPs are still a relatively new area of research. Our main aim is to understand the effects of introducing CPs as soil conditioner for controlling soil surface crust formation with good cytocompatible and easy processing into this area.

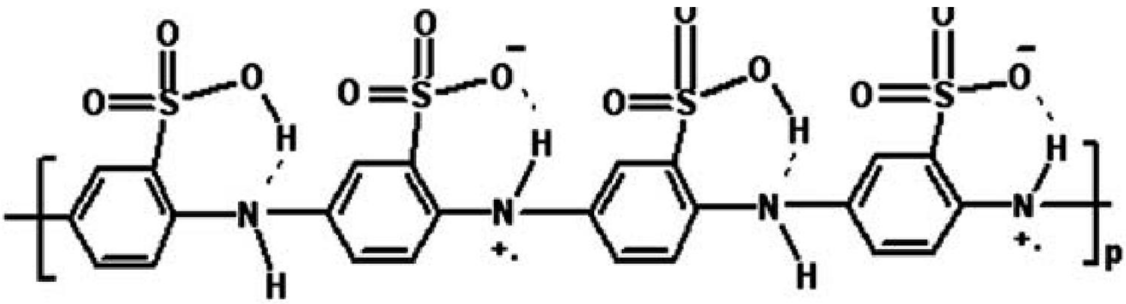
MATERIALS AND METHODS

Selection and synthesis of suitable nanomaterial

Two types of organic polymers namely; polyaniline and sulfonated polyaniline were tested for use as a soil conditioner that reduced soil surface crust formation.



Polyaniline



Polyaniline sulfate

Synthesis of polyaniline

High molecular weight PANI can be produced by room temperature oxidation of aniline with ammonium persulfate, in agreement with the method reported in Ref. (US Patent, 1996). Aniline (37.2 g, 0.40 mol) was added under mechanical stirring to a 400 ml solution of 1 M HCl. separately, 91.2 g (0.40 mol) of ammonium persulfate $[(NH_4)_2S_2O_8]$ were dissolved in 240 ml of distilled water. The persulfate solution was added to the aniline solution. The reaction mixture turned blue and became very viscous with a weak evolution of heat. It was mechanically stirred for one day and then it was filtered, washed with water, de doped with an excess of 37% ammonia solution followed by water and acetone. After drying the yield was quantified.

Synthesis of sulfonated polyaniline

The PANI synthesized using the earlier methodology was placed into a beaker with excess fuming H_2SO_4, and the mixture was stirred with a magnetic stirrer for 6 h at room temperature (25 ^oC). The mixture was then slowly poured into ice water (75: 25), and a green precipitate was then filtered and washed several times with ice water until a constant pH was achieved (to remove excess acid). The residue was then dried in a vacuum oven at 60^{o}C for 48 h. Finally, the dried powder was rewashed using methanol and dried in a vacuum oven at 60^{o}C for 48 h. This sulfonated PANI is designated as SPANI.

Soil Properties

Soil samples were collected from El-Hammam agricultural experiment station located at west of Alexandria. The soil was collected from the top layer, 10 cm depth, using a shovel transported handled in heavy-duty polyethylene bags(1.6 mm thick) before transported to the soil laboratory for the study.

The soils mechanical analyses were carried out using the hydrometer method. Calgon (37.5 gm sodium hexametaphosphate + 12.5 gm sodium carbonate) was used as a dispersing agent (Piper, 1950). The soil texture was classified using the soil-texture triangle according to FAO (1970). Soil physical properties,such as bulk density (B.D), permanent welting point (P.W.P), field capacity (F.C), saturated hydraulic conductivity (ks) and basic infiltration rate (I), were determined according to (Black et al. (1982) and Klute (1986)).Table (1) has shown some soils physical analyses.

Table (1) soils physical analyses

Depth cm	Particle size distribution%			Texture	BD gm/cm^3	P.W.P% m^{3}m^{-3}	F.C % m^{3}m^{-3}	k_s mmh^{-1}	I mmh^{-1}
	sand	silt	Clay						
0-10	70	8	22	Sandy Clay Loam	1.35	13.78	24.33	22.57	27.682

Chemical analysis of the soil was conducted in Soil and Water Science Department, Faculty of Agriculture, Alexandria University. Some soluble cations (Ca++, Mg++, Na+, and K+) and anions (Hco_3-, So_4- - and Cl-) were measured in the soil extract according to (Page, 1982) as well as pH and electrical conductivity (EC). Total Calcium carbonate content ($CaCo_3$%) was determined using the volumetric calcimeter method (Black, 1965). Organic matter content (O.M %) was determined using Walklay- Black method (Walklayet al. (1934),as shown in table (2).

Table (2) soils routine analyses

Depth Cm	PH	Ec Ds/m	Cations(meq/l)				Anions(meq/l)			O.M %	O.C %	$CaCo_3$ %
			Ca^{++}	Mg^{++}	Na^{+}	K^{+}	Hco_3^{-}	So_4^{--}	Cl^{-}			
0-10	7.15	4.57	12.4	7.4	36.96	1.82	2.4	17.6	25	1.03	0598	19.619

A series of laboratory experiments were conducted at Soil Laboratory, Agricultural Engineering Department, Faculty of Agriculture, Alexandria University, to investigate the effects of adding of polyaniline (PANI) and sulfonated polyaniline (SPANI) on soil surface crust formation.

Determine the suitability of PANI and SPANI for controlling soil surface crust formation and determine of the optimum application rate

Preliminary testing of PANI and SPANI polymers

Four mixing ratios of PANI and SPANI were used (1%- 1.5% - 2% - 2.5%) in addition a control treatment with no mixing.The application rates were determined, by weight, using the weight of the soil placed in the container by using the value of bulk density 1.35 gm/ cm3 as measured in the field and the volume of the soil in the container.

Soil penetration force measurements were conducted after 1, 2, and 3 days from irrigation by aneedle penetrometer with a cylindrical flat- tip, 1.59 mm diameter (1/16 in.) (Rolston et al., 1991).The result showed that all PANI levels increased soil penetration force. On the other hand, SPANI decreased soil penetration force and the minimum value was between zero and 1%, accordingly, the experiment was repeated with another 7 mixing ratios of SPANI to determine the mixing optimum rate (No mixing, 0.485%, 0.582%, 0.679 %, 0.776%, 0.873%, and1 %). The measurements were performed after1,2, and 3 days from irrigation.

Germination and seedlings occurrence rates

Laboratory experiments were conducted in soil without treatment and soil treated by 0.679% SPANI. The tests were conducted in cylindrical containers, 12 cm diameter and 10 cm height. The containers were planted with corn and wheat seeds at 2 cm depth from the surface. The containers were placed in a horizontal position before they were irrigated.
Gupta and Yadav (1978) proposed the following equation for determining the rate of occurrence of seedling emergence:

$$C_V = \frac{A_1 + A_2 + A_3 + --- + A_n}{A_1 \times T_1 + A_2 \times T_2 + A_3 \times T_3 + --- + A_n \times T_n}$$

where

C_v : the rate of occurrence of emergence.

A_1 : the number of seedling marked on first day , A_2,……,An the number of additional seedling marked on subsequent days.

T_1 : the time in days after sowing till the first day of seedling emergence , and T_2, …..,Tn represent the time after sowing till days when seedling emergence

Toxicity Testing

Toxicity tests were performed by determining the oral dose that kills 50 of the test mice, (LD50), and the concentration that is lethal to 50% of earthworm (LC50). The exact LD50 and LC50 were interpolated from the plotted concentrations and the corresponding mortality percentages were determined.

LC50 TEST

LC50 was using earthworm. Eight mixing ratios: (0.25, 0.5, 0.75, 0.8, 0.9, 1, 1.25, and 1.5 %) of SPANI in addition to the control were mixed with the soil. The mortality percentage was measured every day for 3 days and the relationship between different concentration and the mortality percentage was plotted to determine LC50 according to Finney, 1952.

LD50 TEST

Twenty mice were selected for the test based on health and initial body weights (BW). Individual oral doses were calculated based on BWs., three doses: (100, 250 and 400 mg / kg body weight)in addition to the control were tested using stainless steel ball-tipped gavage needle attached to an appropriate syringe. After administration, each animal was returned to its designated cage. Feed was replaced approximately 3 hours after dosing. The animals were observed for mortality, signs of gross toxicity and behavioral changes at approximately one hour after dosing and at least once daily for 3 days. The relationships between different doses and the mortality percentages was plotted to determine LD50 according to Finney, 1952.

RESULT AND DISCUSSION

Soil penetration force

The effect of different levels of PANI on soil penetration force is presented in figure (1). The data showed soil penetration force increased exponentially when increases interval after irrigation due to decreases water content. None of the PANI polymer levels reduced soil penetration force below the control. On the other hand, SPANI addition has shown to have an adverse effect on the soil penetration forces presented in figure (2).

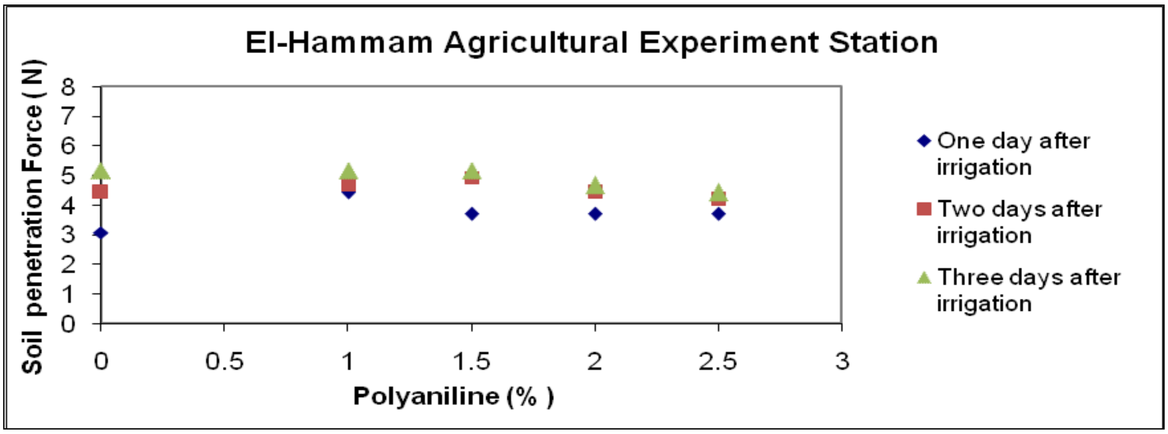


Figure (1) The effect of different levels of PANI on soil penetration force

Figure (2) show the effect of SPANI on soil penetration force. The data showed that adding 1% SPANI decreased the penetration force by 33.2%, 21.15%, and 19.15after 1, 2, 3 days from irrigation compared with the control treatment. However, increasing the SPANI ratio increased soil penetration force.

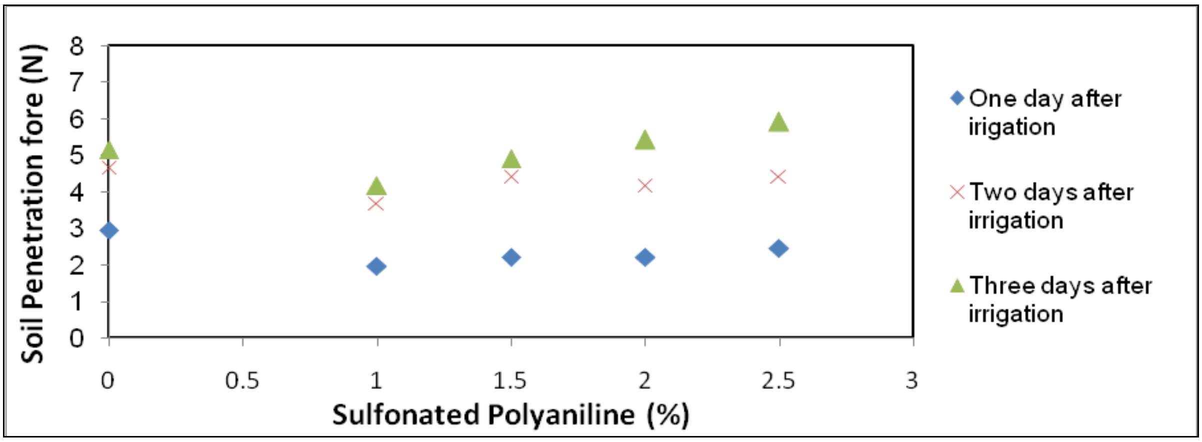


Figure (2) The effect of different levels of SPANI on soil penetration force

Figure (3) showed that, between the levels tested, the optimum rate of SPANI mixing was 0.678% which decreased the penetration force by 91.5% , 79%, and 33.2% after 1, 2, 3 days from irrigation compared with the control treatment.

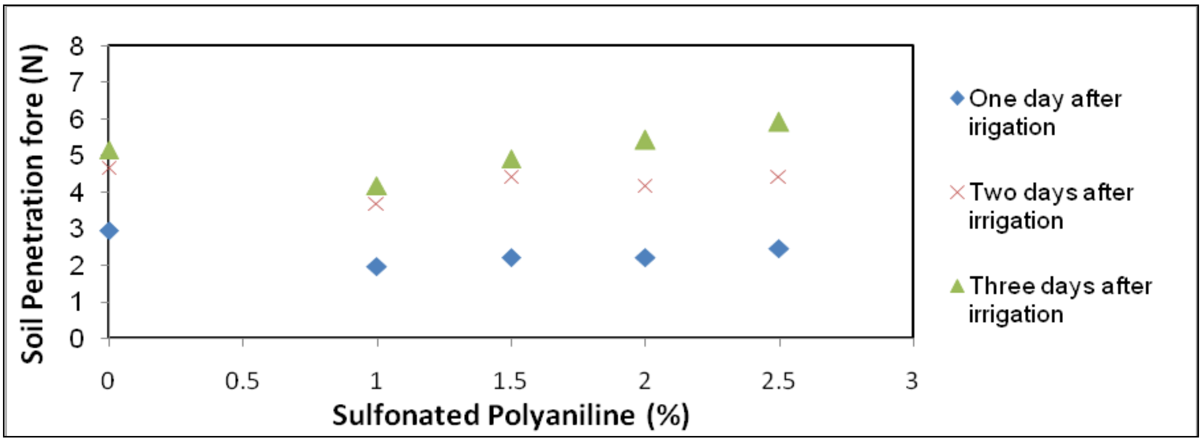


Figure (3) The effect of different levels of SPANI on soil penetration force

Germination and seedlings occurrence rates for corn and wheat

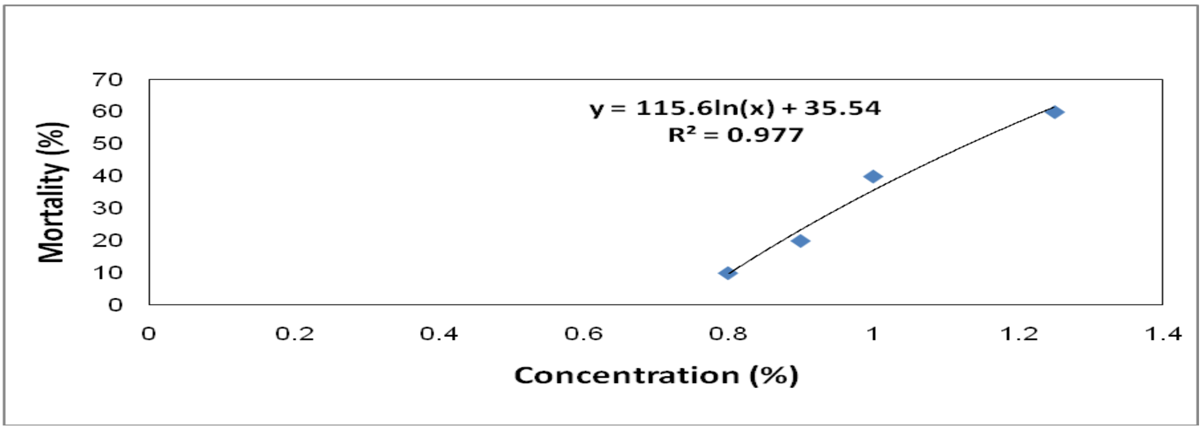
Table (3) shows the effect of mixing SPANI, at the optimum rate of 0.678%, on the germination and seedlings occurrence rates for corn and wheat as compared to the control (no SPANI). The germination rate of corn were 100% for both control and the SPANI pots, but the rate of occurrence increased from 11% in the control to 50% for the SPANI pots. On the other hand, the germination rate of wheat was 50% for control and 80% for SPANI pots. Also, the rate of occurrence increased from 13.5%in the control to 22.8% for the SPANI pots.

Days After Sowing	Corn		wheat	
	The Number of Seedling Marked		The Number of Seedling Marked	
	No Treatment	0.678% SPANI	No Treatment	0.678% SPANI
1	-	-	-	-
2	-	-	-	-
3	-	-	-	-
4	-	-	1	6
5	-	5	1	1
6	-		-	1
7	1		-	
8	1		1	
9	2		-	
10	-		2	
11	-			
12	1			
Germination Rate	100%	100%	50%	80%
Rate of Occurrence	11%	20%	13.5%	22.8%

Table (3) The effect of the optimum adding rate of SPANI (0.678%) on the germination rate and rate of occurrence for corn and wheat.

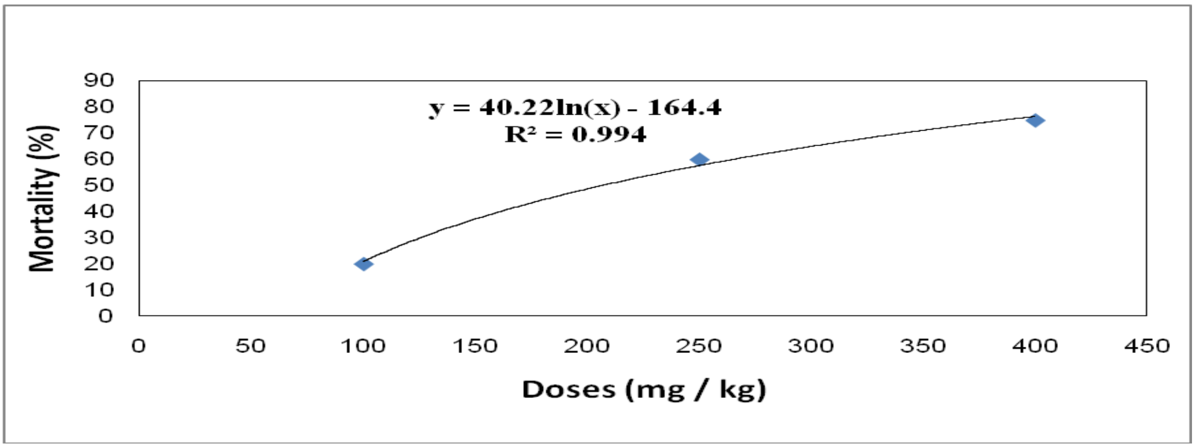
Toxicity Test

Figure (4) shows the different concentrations tested and the corresponding mortalities. These data points were used to determine the LC50 for SPANI through curve fitting. The LC50 was found to be 1.13%. This indicates that using sulfonated polyaniline (SPANI) at the optimum rate of 0.678% would be effective for controlling soil surface crust and also safe for use.



Extrapolation beyond the covered range is not recommended
Figure (4) determine the concentration of a substance that is lethal to 50% of the earthworm (LC50)

Similarly, figure (5) shows the different SPANI doses and the corresponding mortalities. The oral LD50 of SPANI was determined, as described earlier, to be 206.64 mg / kg_{BW}. It is classified as moderately toxic.



Extrapolation beyond the covered range is not recommended
Figure (5) determine the oral LD50

CONCLUSIONS

In general, we can conclude that the use of sulfonated polyaniline (SPANI) as a soil conditioner for controlling soil surface crust is appropriate from the use of polyaniline (PANI). The optimum rate of (SPANI) was 0.678%, which gave the lowest values of the soil resistance to penetration. The germination rate of corn after 5 days of sowing was 100% for SPANI treatment, but in the case of control treatment the same percentage was achieved after 12 days from sowing. This means that the rate of occurrence was 50% for SPANI compared with control treatment which was11% .On the other hand, using the proposed rate of SPANI provided a germination rate of wheat by 60% and increased the rate of occurrence to 22.8% compared to the control treatment which was 13.5%. The toxicity test showed that the concentration of a substance that is (LC50) lethal to 50% of the earthworm was 1.13%. This indicates that using sulfonated polyaniline (SPANI) at the optimum rate would be safe. The oral LD50 of SPANI was 206.64 mg / kg body weight of mouse which classified as moderately toxic. Finally, it may be recommended that more work is needed to be done for obtaining the absorbing rate of SPANI in the plant to determine the rate of toxicity to plants and human.

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