Preparation and evaluation of new hydrogels as new fertilizer delivery system

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Abstract

Four polymeric matrixes were prepared from hydroxyl ethyl cellulose (HEC) and crosslinked with borax. These matrixes were delivered with urea and liquid NP fertilizers. The evaluation of the release rate of the new fertilizers was studied by agricultural experiments. The dry , fresh weight and (%) seeds germination were determined after 30 days from planting, and then the dry weight and % N in soil were also determined after 90 days from planting. On the other hand, the new polymeric matrixes were used to stabilize the sandy loam soil. The efficiency of the new polymeric fertilizers as soil stabilizer was followed up by determining the diameter of the aggregates > 1 mm and (MWD) mean weight diameter (mm) of the aggregates formed by the treatment of the soil with solutions of new polymeric fertilizers.

الملخص

تم تحضير وإنتاج أربع أسمدة بوليمرية ذات الإطلاق البطئ بهيئة نظام الشبيكة من هيدروكسي اثيل سليلوز المتشابك بوساطة البوراكس وتحميله بسماد اليوريا و السماد السائل المتوي على النيتروجين والفسفور . تم دراسة وتقييم الاسمدة البوليمرية الجديدة من خلال تجربة زراعية وذلك بزراعة نبات الشعير مختبريا اذ تم ايجاد نسبة الانبات والوزن الطري والجاف للنباتات النامية بعد مرور30 يوم من بدء الزراعة وكذلك ايجاد الوزن الجاف للنباتات النامية وكمية النيتروجين المتاح في التربة بعد 90 يوم من الزراعة . من جهة اخرى تم تقييم الاسمدة البوليمرية الجديدة كمثبتات للترب الرملية وذلك بتعيين معدل القطر الموزون لتجمعات التربة وتجمعات التربة الاكبر من 1 ملم بعد معاملة التربة بمحلول 1% من الاسمدة البوليمرية واعطت النتائج المستحصل عليها كفاءة عالية للاسمدة الجديدة كمثبتات للتربة او باعتبارها اسمدة ذات انحلال بطئ .

Introduction

Hydrogels are crosslinked networks of hydrophilic polymer that readily absorb water. Hydrogels can absorb water many times of their weight. Cross linking prevent the dissolution of the hydrophilic polymer chains [W.Hennink .et .al. 2002] . Crosslinking can either occur by covalent bonds , ionic bonds or physical interaction between polymer chains . These physical interactions can be molecular entanglements or secondary forces , like hydrogen bonding or hydrophobic forces[A.Hoffman 2002] . It is common for a monomer or macromolecule with a single vinyl group to be covalently polymerized with a crosslinking agent containing two or more vinyl groups to create a hydrogel[N.Peppas et.al. 1993 , H.Kaur et.al. 1990] . Slow and controlled release fertilizers are fertilizers containing a plant nutrient in a form which either , delay it is availability for plant uptake and use after application or which is available to the plant significantly longer than a reference "rapid available nutrient fertilizer " such as ammonium nitrate or urea , ammonium phosphate or potassium chloride[AAPFCO 1995].There is no official differentiation between slow –release and controlled – release fertilizers . However , the microbially decomposed N products , such as urea – formaldehyde , are commonly referred to commercially as slow – release fertilizers which are coated or encapsulated products as controlled – release fertilizers[M .Trenkel 1997] . Controlled or slow nutrient release can be achieved through special chemical and physical characteristics. With controlled –release fertilizers the principle procedure is one whereby conventional soluble fertilizers are given a protective coating or encapsulated (water insoluble , semi permeable or impermeable with pores) , controlling water penetration and thus the rate of dissolution and nutrient release synchronized to the plants needs [M .Trenkel 1997]. The most important manufacturing routes can be described as :

* Materials releasing nutrients through low solubility due to a complex / high molecular weight chemical structure following microbial decomposition.

* Materials releasing nutrients through a coated surface (coated fertilizers).
* Materials releasing nutrients through a membrane which may or may not itself be soluble (encapsulation) .
* Nutrients - releasing materials incorporated into a matrix which itself may be coated. * Materials releasing nutrients in delayed form due to a small surface – to – volume ratio (super-granules , tablets , etc ….)[M .Trenkel 1997] .

Stabilization of soils using polymers has being widely applied . They represent a wide – range of materials from styrene – butadiene rubber to poly vinyl alcohol and many type of acrylic based polymers are also commonly employed [K .Newman et.al. 2004] .

Intensive irrigation is the source of severe damage to soils such as erosion , crust – formation and soil hardening . These naturally, water or wind erosions gradually strip uncovered soils of their nutrients . To preserve their natural components and to maintain their protection with a sustainable vegetation , polymers give the soil surface more stability , thus allowing better plant growth [R.Poupon 2000].

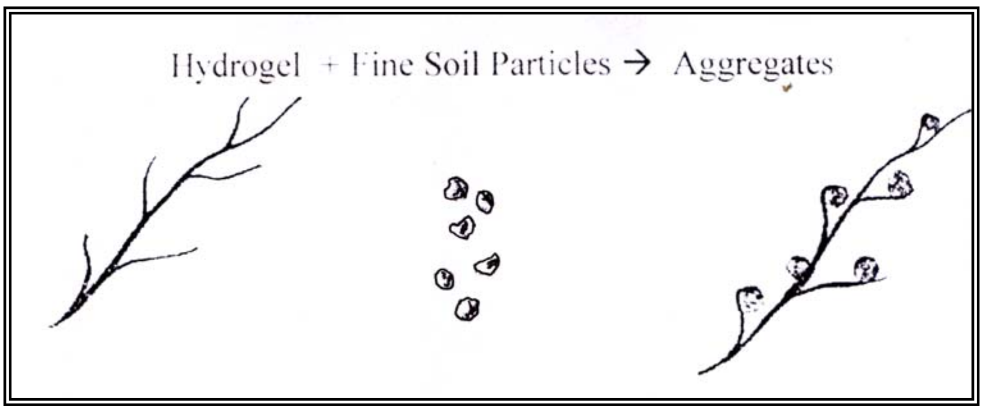


Fig.(1) : formation of soil aggregate

In this study , four hydrogel polymeric matrix fertilizers were prepared from cross linked hydroxyl ethyl cellulose with two conventional fertilizers , urea and liquid super phosphate .

Materials and Experiments

Materials

Urea was supplied by (B.D.H.Co.) , hydroxyl ethyl cellulose was supplied by (Aldrich Co.) , liquid NPK fertilizer was supplied by (Grow more Co. , USA) and borax was supplied by (Fluka Co.) .

Preparation of polymeric matrix fertilizers

20 g Hydroxy ethyl cellulose (HEC) and predetermined quantities of borax were dissolved in 500 ml distilled water then 100g urea in 200 ml water or 100 ml liquid NPK fertilizer in 200 ml water were mixed well with HEC solution with stirring for three hours at 70 ^{o}C . Table (1) shows the quantities of reactants used in the preparation of polymeric slow – release fertilizers .

Table (1) : The composition of the prepared polymeric matrixes as slow – release fertilizers

Sample	HEC (g)	Urea (g)	Liquid NPK (ml)	Borax (g)	H_2O ml)
HBU1	20	100	---	1	700
HBU2	20	100	---	2	700
HBP1	20	---	100	1	700
HBP2	20	---	100	2	700

Effect of polymeric matrixes as slow release fertilizers

Biological experiments were carried out to study and evaluate of polymeric matrixes as slow – release fertilizers .Seeding of Barely seed in pots with 18 cm diameter and 25 cm depth. 100 ml from the new polymeric fertilizers were mixed with 4 kg air dried soil and incubated at laboratory conditions for three days , then fifty seeds were planted in each pot . The complete randomized design was used in all experiments and finally the pots were irrigated to field capacity (once every three days) . All experiments were carried out with three replicates .Figures (2) and (3) show the results obtained for the tested plants. The plants were reduced to twenty five plants in each pot after 30 days of planting.

Fig (3) : The effect of new slow –release fertilizer (HBU1 and HBU2) comparison with control after 30 days from planting

The effect of the new polymeric fertilizers was tested via several parameters :

1- (% seed germination) : number of the growth seeds to the total seeds expressed as percentage .

2- Fresh and dry weight of the plant shoot part: the fresh weight of the plant shoot part was weighted (g / pot) after the plant had been cut directly after 30 day from planting . The dry weight of the plant shoot part was weighted after drying the plant shoot samples in oven at 52 ^{o}C for two days after 30 and 90 days from planting. Table (2) shows the data obtained from these measurements .

Table (2) : some agricultural parameters after 30 day from planting.

Treatments	% seeds germination	Fresh weight (g / pot)	Dry weight (g / pot)
HBU1	100	12.46	1.41
HBU2	100	11.73	1.33
HBP1	100	15.47	1.50
HBP2	100	12.74	1.45
Control	93	5.2	0.77

Water erosion resistance

The water erosion resistance for soil aggregate was determined by measuring the soil Mean Weight Diameter (MWD) by wet – sieving analysis [A.Page 1982] . The soil used in this study was characterized as sandy loam soil consisting of :

Sand = 655 g / Kg

Silt = 174 g / Kg

Clay = 171 g / Kg

$CaCO_3$ = 112.4 g / Kg

Organic matter (O.M) = 0.11 g / Kg

Electrical conductivity (E . C) = 2 ds/m

Cation exchange capacity (C.E.C) = 6.25 mole /Kg

pH = 8

100 g from air dry soil aggregates previously treated with 2g from (1% w / v)from the new polymeric fertilizers which have a diameter between (4-8 mm) were wetted by water for six minutes . The wetted samples were passed through shaking with sieves set (0.25 , 0.5 , 1 , 2 and 4 mm) for six minutes . The dry weight of soil aggregate was measured on different sieves. Finally the Mean Weight Diameter was determined. [R. Youker et.al. 1956] .

Wind erosion resistance

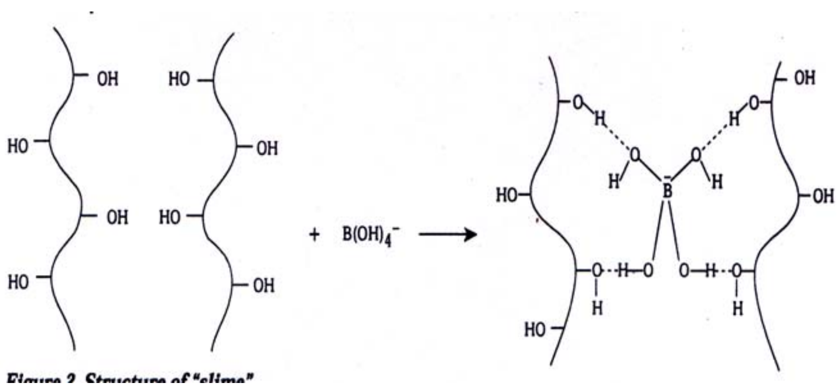
The aggregate stability of dry soils treated with new polymeric fertilizers was determined by dry - sieving method[D. Zachar 1982] . Thus 100 g of air dry soil samples previously treated with 2g from (1% w / v) new polymeric fertilizers were passed through the shaking set of sieves (0.25 , 0.5 , 1 , 2 and 4 mm) for ten minutes . The percentage of soil aggregates > 1 mm diameter was measured.

Results and Discussion

The crosslinking between hydroxyl ethyl cellulose and borate ion was occurred by hydrogen bonding . In water , the borax hydrolyzes to form a borate – boric acid system

$$B(OH)_3 + 2H_2O \rightleftharpoons B(OH^-)_4 + H_3O^+$$

The $B(OH^-)_4$ ion is believed to cross- link the polymer chains as shown in following equation [M. Orna 1994] :



The agricultural parameters investigation experiments listed in Table (2) after 30 days from planting showed that the application of the new polymeric fertilizers improves the plant growth conditions thus enhances % seeds germination , fresh and dry weight of the plant , this can be due to adequate available amount of N source to the plant .

The data represented in Fig. (4) showed that the plant dry weight which has grown in treated soil is significantly greater than control . The data also showed that the treated sample HBP1 has increased dry weight production (2.41 g / pot) relatively to the other samples . This may be due to the slow releasing of N nutrient from the tested polymers which have formed more net than other treatment and this can be related to increased gegree of crosslinking in HBP2 and HBU2 than HBP1 and HBU1 treatments which can lead to low swelling for hydrogel polymeric fertilizers which caused low nutrient diffusion from polymeric matrixes. This situation gave more time for the absorption of nitrogenous fertilizers which leads to increase of plant dry matter .

The ANOVA analysis (Table 3) showed significantly the differences between polymeric fertilizers treatment and control after 90 days from planting .

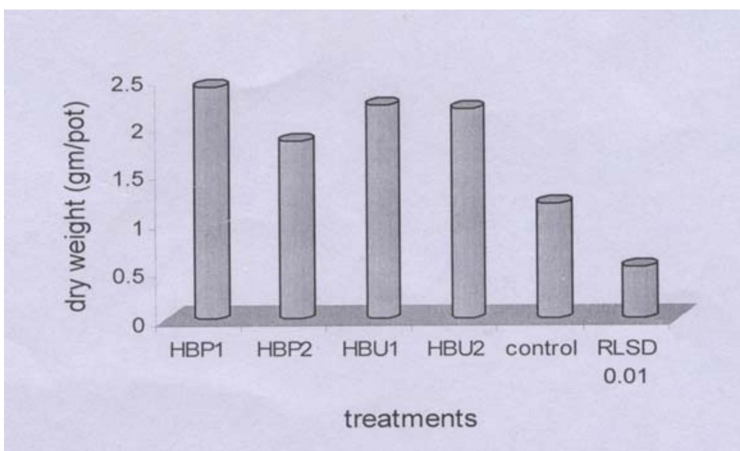


Figure (4) : The effect of treatments on dry weight of plant

Table (3) : ANOVA table for dry weight

Source	Df	Ms	F	Sig.
Treatment	4	0.676	9.036	**
Error	10	0.074		
Total	15			

The results of total N in the tested soil (Fig.5 and Table 4) showed that there is a significant differences in total N values . The data also showed that the treated HBP2 gave the highest effect due its high net formation which caused slow release of N and maintained the availability N to the end of the experiment.

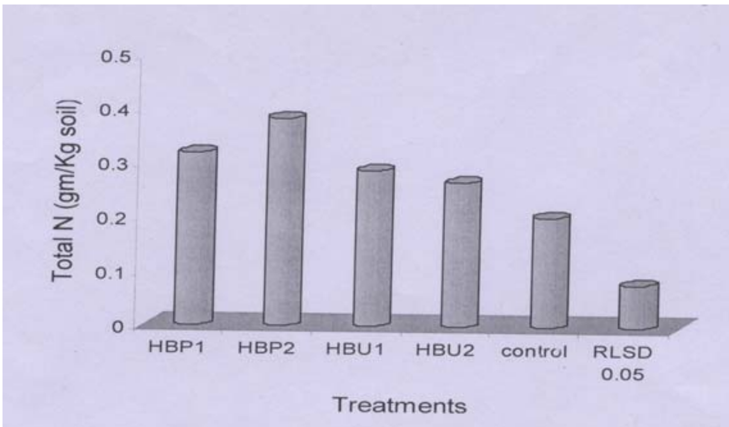


Figure (5) : The effect of treatments on total N in soil

Table (4) : ANOVA table for total N in soil

Source	Df	Ms	F	Sig.
Treatment	4	0.01311	5.767	*
Error	10	0.002273		
Total	15			

On the other hand , the data obtained from the soil stabilization experiments showed that the new polymeric fertilizers have a remarkable effects on improving the soil conditions for agricultural applications for sandy loam soil even at low concentration .

The results in fig.(6) and Table (5) showed the effect of the treatments on Mean Weight Diameter (MWD) . These results confirm that their is a significant differences among the tested treatments which reached the highest value for HBP1 and HBU2 treatments . The same effect can be noticed in determination of the percentage of soil aggregate > 1mm (Fig.7 and Table 6) . These result also show significant differences among the tested and control treatments.

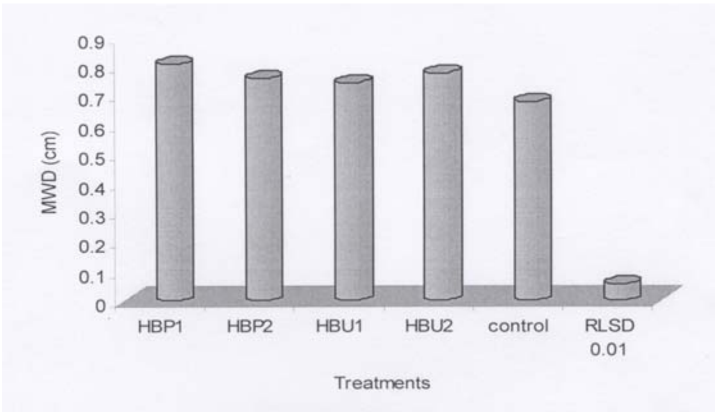


Figure (6) : The effect of treatments on MWD for sandy loam soil

Table (5) : ANOVA table for MWD in sandy loam soil

Source	Df	Ms	F	Sig.
Treatment	4	0.006741	12.43	**
Error	10	0.000542		
Total	15			

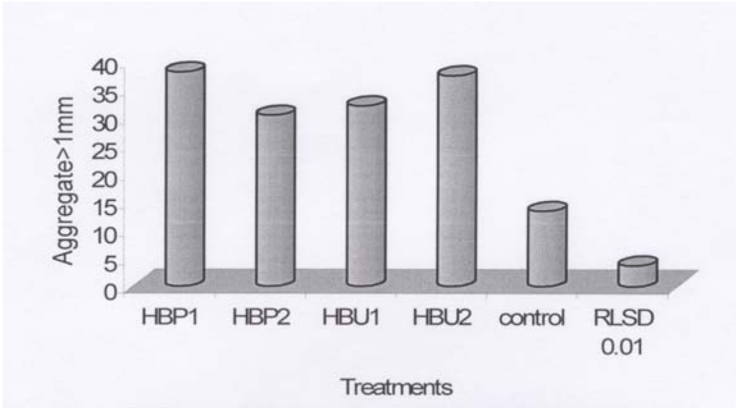


Figure (7) : The effect of treatments on soil aggregate>1mm for sandy loam soil

Table (6) : ANOVA table for soil aggregate>1mm for sandy loam soil

Source	Df	Ms	F	Sig.
Treatment	4	299.6	99.86	**
Error	10	3.0		
Total	15			

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