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Humics-based interpolyelectrolyte complexes for antierosion protection of soil: Model investigation

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Abstract

The aim of this article is to demonstrate a novel polymer-based technique for stabilization of soil against wind and water erosion. Conventional approaches deal with individual water-soluble polymers, which, being deposited on the soil, are removed from the soil surface after rewatering. Here, we describe an elegant way for soil stabilization via deposition of interpolyelectrolyte complexes formed by two oppositely charged water-soluble polymers. Electrostatic complexation in an aqueous solution of a cationic poly(diallyldimethylammonium chloride) with an excess of water-soluble anionic biopolymers, humic acids, results in formation of a negative non-stoichiometric interpolyelectrolyte complex (NIPEC). Upon deposition of a NIPEC aqueous solution over soil and drying out, a protective layer (crust) forms on the surface, composed of NIPEC and soil particles, resistant to wind and water erosion. After destruction, the crust is completely restored by rewatering. The high stability of the NIPEC-soil crust is due to a NIPEC block structure with hydrophilic free anionic units and hydrophobic mutually neutralized anionic/cationic units, which ensures optimum adsorption on the surface of soil particles and binds them to bigger aggregates. The NIPEC treatment retains the porous structure of soil that favors seed germination and plant development. Being effective absorbent of heavy metals, the NIPEC formulation ensures a normal seed germination in the presence of toxic Cu^{2+} ions. Thus, the humics-based NIPECs ensures antierosion protection and detoxification of soil. Additionally to ecological and agricultural applications, the NIPEC formulations have potential for immobilization of moving sands, conservation of mining dumps, treatment of road slopes, and so forth.

KEYWORDS

antierosion protection, heavy metal ions, interpolyelectrolyte complex, polymer-soil crust, potassium humate

1 | INTRODUCTION

Soil health is one of the basic conditions of human existence and human health (Brevik, Burgess, & Cerdà, 2018; McBratney, Field, & Koch, 2014). It stems from a multitude of soil functions including accumulation and transformation of basic nutrient substances and energy, regulation of biogeochemical cycles, and protective and filtering ability

of the soil (Keesstra et al., 2016; Stavi, Bel, & Zaady, 2016). Natural erosion of the soil is reinforced by the imprudent human activities: breach of agrotechnical requirements, excessive (uncontrolled) grazing, felling of protective forests, use of fertile soil for industrial developments, results in degradation, and destruction of fertile land. This problem is relevant all over the world and especially concerns developing countries. In order to solve the problem, cooperation of

scientists from various fields of science is strongly required: physical geographers and soil scientists, ecologists, biologists, and chemists, for joint development of rational strategies for soil protection in different natural and climatic zones (Brevik et al., 2015; DeJong et al., 2011; Haney, Haney, Smith, Harmel, & White, 2018).

Chemical reagents silicates (Moayed, Huat, Kazemian, & Daneshmand, 2012), calcium carbonate (Krajewska, 2017), epoxy resin polymer (Naeini & Ghorbanalizadeh, 2010), polymer mulch and films (Kasirajan & Ngouajio, 2012), latex formulations (Al-Khanbashi & Abdalla, 2006), and so forth have shown themselves as fast and effective techniques for agrotechnical soil conservation; among which, the polymer-based approaches are of particular interest. It was shown in particular that water-soluble polymers, being deposited over soil, glue soil particles into larger aggregates (Homauoni & Yasrobi, 2011; Maghchiche, Haouam, & Immirzi, 2010; Mamedov, Beckmann, Huang, & Levy, 2007). As a result, a composite polymer-soil crust is formed in the topsoil layer, which is resistant to erosion processes, on the one hand, and permeable to growing plants, on the other (Chang, Im, & Cho, 2016; Xia et al., 2012). The crust protects the soil against drying out and washing away seeds and nutrients (Kabiri, Omidian, Zohuriaan Mehr, & Doroudiani, 2011; Lee, Shah, Awad, Kumar, & Ok, 2015; Orts et al., 2007). However, commonly used water-soluble polymer binders are quickly removed from the soil with rainwater and artificial irrigation (Chang et al., 2016; Sepaskhah & Bazrafshan-Jahromi, 2006). The stability of the crust can be significantly increased when replacing a polymer by an interpolyelectrolyte complex (IPEC), the product of interaction between two oppositely charged polyelectrolytes (PEs) (Zezin et al., 2015). IPECs contain both hydrophilic and hydrophobic areas that allow them to adsorb effectively onto various particles and surfaces (Müller, 2013; Shaikh et al., 2017).

Earlier, we have described the preparation of IPEC from two synthetic PEs, anionic poly(acrylic acid), and cationic poly(diallyldimethylammonium chloride) (PDADMAC), in which only 20 mol% of anionic units was neutralized by cationic units (Panova et al., 2017). In the lab experiments, a suspension of such non-stoichiometric interpolyelectrolyte complex (NIPEC) demonstrated the colloidal stability within at least within 3 months after preparation and formed the stable to wind erosion polymer-soil crust. Additionally, because of free anionic groups, the NIPEC was shown to bind heavy metal ions that made it promising for stabilization of soil contaminated with toxic metals.

The next step could be the use of natural PEs instead of synthetic ones for the preparation of NIPECs. The natural PEs are renewable and cheap (Dove, Bradley, & Patwardhan, 2016); in addition, they are nontoxic and harmless, so that natural polymers can be considered "environmentally friendly" alternatives of synthetic polymers for soil stabilization (Hataf, Ghadir, & Ranjbar, 2018; Latifi et al., 2016). In the present work, anionic natural polymers, potassium salts of humic acids (PHum), were used for complexation with cationic PDADMAC and NIPEC formations. Commercially available PHum, obtained by extraction from coal, compost, or peat (Asing, Wong, & Lau, 2009), are used for improving agriculture soils with low organic matter content (Calvo, Nelson, & Kloepper, 2014).

Humic substances are macroligands, consisting of condensed aromatic and heterocyclic compounds and peripheral branches with

oxygen-containing groups (de Melo, Motta, & Santana, 2016; Sutton & Sposito, 2005). In water surrounding, PHum form colloidal dispersions with pronounced surface-active properties; such colloids can bind toxic species like heavy metal ions, radionuclides, and pesticides (Bahemmat, Farahbakhsh, & Kianirad, 2016; Chaab, Moezzi, Sayyad, & Chorom, 2016). Finally, humic acids are known to stimulate plant growth and can be used as fertilizers (García et al., 2016; Ouni, Ghnaya, Montemurro, Abdely, & Lakhdar, 2014). We discuss composition of the negative PDADMAC/PHum NIPECs and their stability against aggregation in aqueous solutions, complexation of NIPEC with dispersed particles and heavy metal ions, and morphology of the NIPEC-soil crusts. Additionally, we give a few examples of the protective (antierosion) properties of the crusts and the positive effect of NIPEC on seed germination made in a laboratory conditions.

2 | MATERIALS AND METHODS

PDADMAC with $M_w = 400\text{--}500$ kDa and tris(hydroxymethyl)aminomethane (Tris; both from Sigma-Aldrich, USA), 25% aqueous ammonia and CuSO_4 (both from Chimmed, Russia), and PHum (Humintech GmbH, Germany) were used as received. M_w of PHum, determined by size-exclusion chromatography (Perminova et al., 1998), was of 9.9 kDa.

A sample of retisol (sod-podzolic soil) was collected in the Moscow region (Russia). An upper 10-cm layer of soil was used with pH 5.8 and a moisture content of 3 wt%. The soil was dried at 100°C to constant weight, additionally milled, and sifted through a 1.5-mm sieve. The sieved sample was fractionated by sequential passing through a set of sieves followed by weighting each fraction. The granulometric composition of the soil sample is shown in Figure 1.

Concentration of Cu^{2+} ions was determined via their precomplexation with ammonia. Optical densities of Cu/ammonia complex solutions were measured spectrophotometrically at 590 nm and recalculated to Cu^{2+} ion concentrations using a corresponding calibration curve.

Dynamic light scattering measurements were performed with an ALV-5 laser light scattering photometer (Germany).

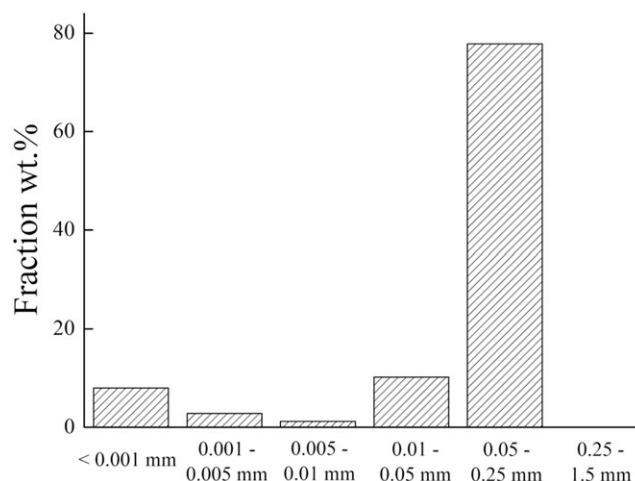


FIGURE 1 Granulometric composition of the soil sample (wt%)

Electrophoretic mobility (EPM) of particles was controlled by means of laser microelectrophoresis with a Brookhaven Zeta Plus (USA).

The UV spectra and the optical density of the dispersions were recorded with Hitachi UV-mini 1240 spectrophotometer (Japan).

Scanning electron microscopy images were obtained in the electron microscopy laboratory of Moscow State University Biology Department using a JEOL JSM-6380LA microscope.

All experiments were performed with threefold repeats. Statistical data processing was carried out with the Excel program; the confidence interval was of 95%.

3 | RESULTS AND DISCUSSION

Acidic groups in the PHum sample was quantified by potentiometric back-titration (Cooke, Hamilton-Taylor, & Tipping, 2007). Five milligrams of PHum was dissolved in 4 ml of a 0.1 M NaOH aqueous solution, and then 2 ml of deionized water and 5 ml of a 0.1 M HCl aqueous solution were added. Thus, obtaining a 0.008-wt% PHum solution with pH 2.6 was titrated by the 0.1 M NaOH aqueous solution to pH 11; pH values were detected with a pH meter (Curve 1 in Figure 2). In parallel, the potentiometric titration of a control mixture, 4 ml of 0.1 M NaOH solution + 2 ml of deionized water + 5 ml of 0.1 M HCl solution, by the 0.1 M NaOH aqueous solution was carried out (Curve 2). Concentration of PHum acidic was determined by a difference between titration Curves 1 and 2 at pH 7 (see dashed line in Figure 2). At this pH, only carboxylic groups of PHum were titrated, no phenolic groups with $pK \sim 8.4$ nor aliphatic alcoholic groups with $pH \sim 13$ were detected. Experimental data showed a 0.008-wt% aqueous PHum solution corresponded to a 2×10^{-4} M carboxylic groups. Further, in the text, the concentrations of PHum solutions are given in moles of carboxylic groups per liter.

Dynamic light scattering showed that PHum aqueous solutions with concentrations from 2×10^{-6} to 6.2×10^{-4} M contained particles with a mean hydrodynamic diameter of 130 ± 10 nm with a wide size distribution, which did not sediment within a year. EPM of PHum

particles were found to be -4 , -3.6 , and -3.4 ($\mu\text{m/s}/(\text{V}/\text{cm})$) at pH 9, 7, and 5, respectively.

The complexation between cationic PDADMAC and anionic PHum was studied in a Tris buffer aqueous solution with pH 7. A series of mixed solutions with the same PHum concentration 2.6×10^{-4} M but different PDADMAC concentrations were prepared, and the EPM values of the resulting PDADMAC/PHum complexes were measured by laser microelectrophoresis. As expected, binding of PDADMAC to PHum resulted in neutralization of the negative charge of the PHum particles and in a decrease of their EPM (Figure 3a); the $\text{EPM} = 0$ point is achieved at $[\text{PDADMAC}] = 2.6 \times 10^{-4}$ M. Further addition of PDADMAC gave a positive charge the complex particles.

The cationic PDADMAC contains quaternized amino groups whose total charges do not depend on pH of solution. It means all cationic PDADMAC groups participated in electrostatic complexation with PHum in a pH 7 solution. This in turn allowed the concentration of PHum carboxylic groups involved in the complexation with the PDADMAC amino groups at $\text{EPM} = 0$: $[\text{PHum}]_{\text{EPM} = 0} = [\text{PDADMAC}] = 2.6 \times 10^{-4}$ M, whereas the latter is equal to the concentration of carboxylic groups in the initial PHum solution. Thus, all PHum carboxylic groups electrostatically interacted with the PDADMAC amino groups in a pH 7 solution, and the composition of

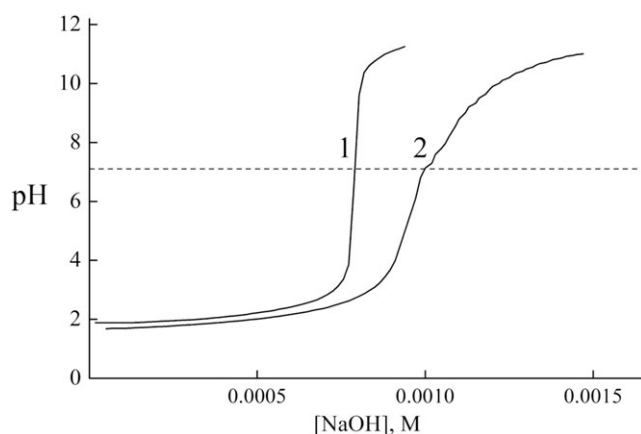


FIGURE 2 Potentiometric titration of a 0.008-wt% PHum solution (1) and the control mixture (2) by a 0.1 M NaOH aqueous solution. See details in the text

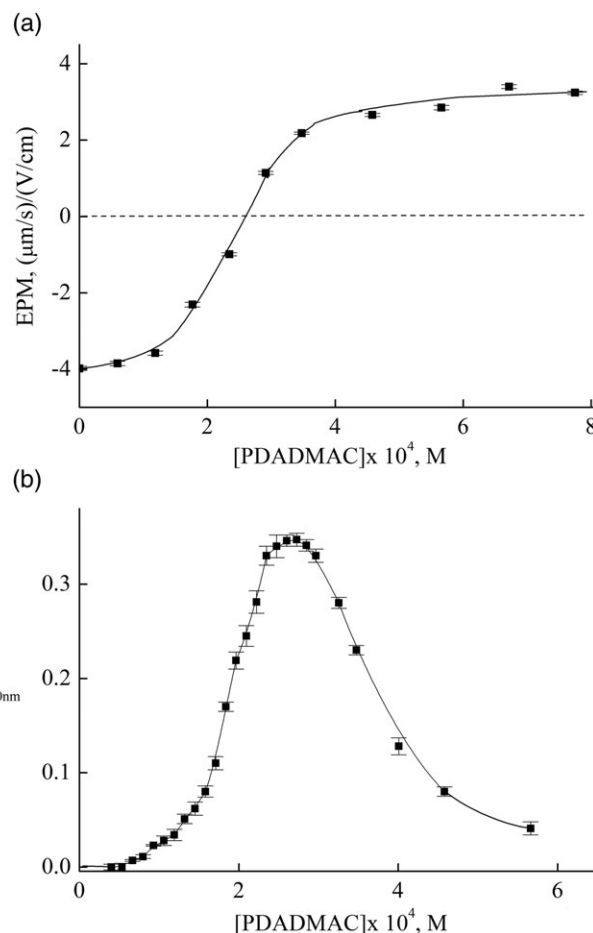


FIGURE 3 EPM of PDADMAC/PHum complexes (a) and turbidity of PDADMAC/PHum complex suspensions (b) versus PDADMAC concentration. $[\text{PHum}] = 2.6 \times 10^{-4}$ M; 10^{-3} M Tris buffer with pH 7

the saturated PDADMAC/PHum complex $Q_{\text{sat}} = [\text{PDADMAC}]/[\text{PHum}] = [\text{PHum}]_{\text{EPM} = 0}/[\text{PHum}] = 1$.

Mutual neutralization of the PE charges leads to a loss of the aggregation stability for the resulting IPECs (Müller, 2013) that could be detected by measuring the turbidity of the complex suspension (Izumrudov & Sybachin, 2006). In accordance to this scheme, we observed the maximum turbidity for the saturated PDADMAC/PHum complex suspension at EPM = 0 and lower turbidities for either negative or positive NIPECs left and right of the maximum, respectively (Figure 3b).

The negative PDADMAC/PHum NIPECs are of the greatest interest, because the abundant negative charges of NIPECs can catch heavy metal cations (Abdillahi, Mohamed, Lakard, & Fatin-Rouge, 2015; Panova et al., 2017), thus restricting their migration in soil. For this reason, the aggregation stability of the negative NIPECs with $Q = [\text{PDADMAC}]/[\text{PHum}] \leq 0.4$ was studied in more detail by using dynamic light scattering. The data of Table 1 show that the sizes (hydrodynamic diameters) of freshly prepared complexes were from 130 up to 200 nm (column 3) and did not change within a year after preparation (column 4). The stability of the complex particles was obviously due to their high negative charges (column 5), which suppressed the interaction of particles and their subsequent aggregation and precipitation.

A solution of CuSO_4 was used as a source of heavy Cu^{2+} cations interacting with the negative PDADMAC/PHum NIPECs and free PHum (control). The complexation was quantified as follows. A series of mixed solutions with the same concentration of PHum and different concentrations of CuSO_4 were prepared and left for a day at room temperature. After that, the polymer- Cu^{2+} complexes were separated by centrifugation, and concentrations of unbound Cu^{2+} ions in the supernatants were determined spectrophotometrically via precomplexation of Cu^{2+} ions with ammonia. The unbound Cu^{2+} concentration versus total Cu^{2+} concentration plot is given in Figure 4 (Curve 1). Then the experiment was repeated with $Q = 0.2$ NIPEC and $Q = 0.4$ NIPEC instead of PHum, and concentrations of PHum in both NIPECs was equal to the concentration of PHum in the first experiment (Curves 2 and 3 in Figure 4).

The spectrophotometric data allowed the experimental estimation of the ultimate concentration of Cu^{2+} ions capable of binding to PHum and two NIPECs (Table 2). On the other hand, it follows from the literature (Boamah et al., 2015; Zhao, Wang, Zhang, Gu, & Gao, 2018) divalent metal ions typically form two ionic bonds with carboxylic groups of water-soluble polymers. This offers another way to calculate the saturating Cu^{2+} concentration (column 5).

The table shows different results for the two approaches. Although in both cases, the capacity of polymers to Cu^{2+} ions

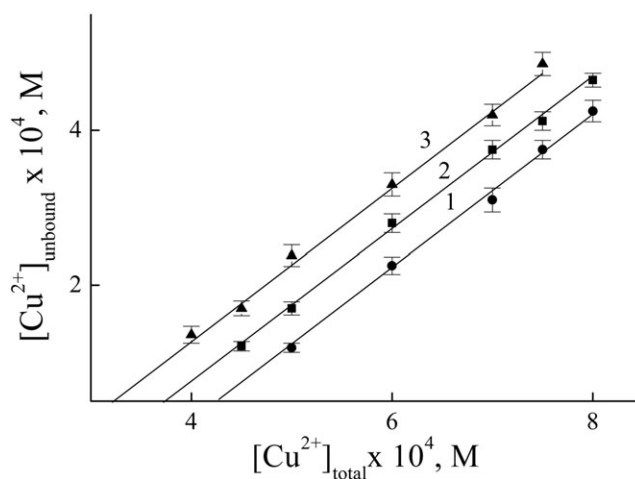


FIGURE 4 Concentration of unbound Cu^{2+} ions versus total Cu^{2+} ions in the system. Cu^{2+} + PHum (1), Cu^{2+} + PDADMAC/PHum NIPEC with $Q = 0.2$ (2), and Cu^{2+} + PDADMAC/PHum NIPEC with $Q = 0.4$ (3). $[\text{PHum}] = 4 \times 10^{-4}$ M; 10^{-3} M Tris buffer with pH 7

decreases when increasing the $Q = \text{PDADMAC}/\text{PHum}$ value, the experimental data are always higher than the calculated. Assumingly, the binding of small Cu^{2+} ions to PHum and NIPECs is not only due to electrostatic but also due to coordination and van der Waals interactions in which minor hydroxyl and amino groups of PHum could be involved. In addition, it was reported (Kabanov, Kokorin, Rogacheva, & Zezin, 1979) that at high concentrations of copper ions, each of them could form an electrostatic bond with one carboxylic group of an anionic polymer. Such arrangement of the final NIPECs could also contribute to their abundant capacity toward Cu^{2+} ions found in the experiment.

This means that we can prepare PDADMAC/PHum/ Cu^{2+} complexes "oversaturated" with respect to Cu^{2+} -cations. Based on the calculated binding model, 4×10^{-4} M PHum solution can ultimately bind 2×10^{-4} M Cu^{2+} (Table 2), thus giving the saturated PHum/ Cu^{2+} binary complex with a degree of PHum carboxylic group electrostatically bound to copper ions $M_{\text{sat}} = 2 \times (2 \times 10^{-4} \text{ M}) / (4 \times 10^{-4} \text{ M}) = 1$ (each copper ion can bind two carboxylic groups). The experimentally detected oversaturated $Q = 0.2$ PDADMAC/PHum/ Cu^{2+} complex shows $M_{\text{over}} = 2 \times (3.2 \times 10^{-4} \text{ M}) / (4 \times 10^{-4} \text{ M}) = 1.6$. So, in practice, the composition of the $Q = 0.2$ PDADMAC/PHum/ Cu^{2+} complex ternary complex can be varied within a $0.2 \leq M \leq 1.6$ interval.

The next step was to study the NIPEC interaction with a synthetic hydrophilic colloid regarded as a simple soil model. A cationic polystyrene latex (Lat), whose particles was approximately 90 nm in diameter, was mixed with different amounts of the $Q = 0.2$ PDADMAC/PHum NIPEC suspension, and the aggregation stability of Lat/NIPEC

TABLE 1 Size and charges of the negative PDADMAC-PHum NIPECs in a 10^{-3} M Tris buffer with pH 7

No.	Q	Hydrodynamic diameter 10 min after preparation, nm	Hydrodynamic diameter 1 year after preparation, nm	EPM, ($\mu\text{m/s})/(\text{V/cm})$
1	2	3	4	5
1	0.2	135 ± 10	130 ± 10	-3.4 ± 0.05
2	0.3	140 ± 10	145 ± 10	-3.3 ± 0.05
3	0.4	190 ± 10	195 ± 10	-3.1 ± 0.04

TABLE 2 Concentrations of Cu^{2+} ions ultimately bound to polymers (the capacity of polymers to Cu^{2+} ions)

No.	Q	[PHum] $\times 10^{-4}$ M	$[\text{Cu}^{2+}]_{\text{bound}} \times 10^4$ M (experiment)	$[\text{Cu}^{2+}]_{\text{bound}} \times 10^4$ M (calculation)
1	2	3	4	5
1	0	4	3.7 ± 0.1	2
2	0.2	3.2	3.2 ± 0.1	1.6
3	0.4	2.4	2.7 ± 0.15	1.2

Note. 10^{-3} M Tris buffer, pH 7.

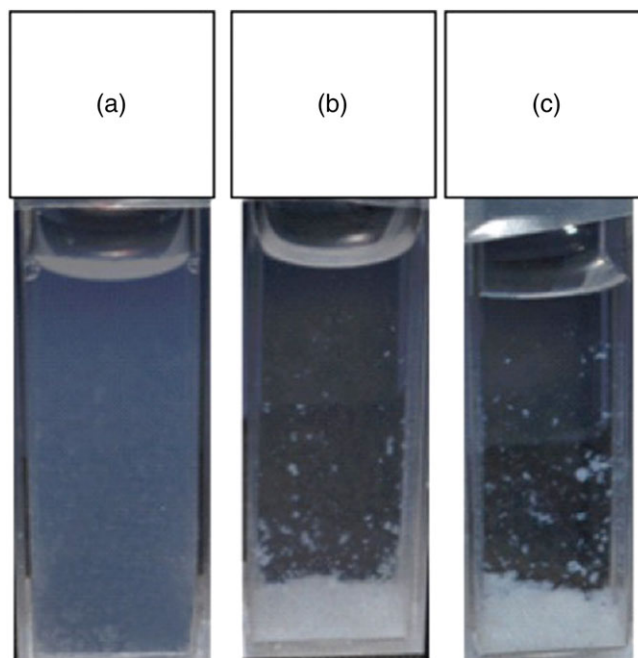


FIGURE 5 Lat/NIEC complex suspensions 7 days after preparation. Lat conc. 0.017 wt%; Q = 0.2 PDADMAC/PHum NIEC with [PDADMAC] = 7×10^{-6} M (a) 10^{-5} M (b) and 1.5×10^{-5} M (c) [Colour figure can be viewed at wileyonlinelibrary.com]

complexes was visually controlled. At a low NIEC concentration, the resulting complex did not precipitate within 7 days (Figure 5a); higher NIEC concentrations induced complex aggregation (Figure 5b,c).

More detailed information about the composition of the Lat/NIEC complex was obtained with the microelectrophoresis. Electrophoretic titration of the latex suspension by an PHum suspension (Figure 6, Curve 1) consistently reflects a decrease in the latex surface charge, its complete neutralization, and an appearance of the negative surface charge at higher NIEC concentrations. The EPM = 0 point was achieved at 0.95×10^{-5} M PHum carboxylic group concentration.

Then the Lat suspension with the same concentration of carboxylic groups was titrated with a Q = 0.2 NIEC suspension. The EPM of Lat/NIEC complex particles versus PHum concentration plot is given in Figure 6, Curve 2. The neutralizing PHum carboxylic group concentration is now 0.76×10^{-4} M. It follows from there that a degree of the PHum carboxylic groups involved in the complexation with Lat is $(0.76 \times 10^{-5} \text{ M}) / (0.95 \times 10^{-5} \text{ M}) = 0.8$. The remaining degree of 0.2 refers to the carboxylic groups, which were included in the initial NIEC. In other words, the Q = 0.2 PDADMAC/PHum NIEC did not dissociate when interacting with Lat, and only free PHum carboxylic groups formed electrostatic bridges with the latex cationic groups.

Finally, we modelled the situation when the NIEC first interacted with the heavy metal ions, and then with soil particles. The question was whether the NIEC can simultaneously perform two functions: immobilize toxic metals and form the polymer-soil crust. A negative Q = 0.2 PDADMAC/PHum NIEC was prepared, and a CuSO_4

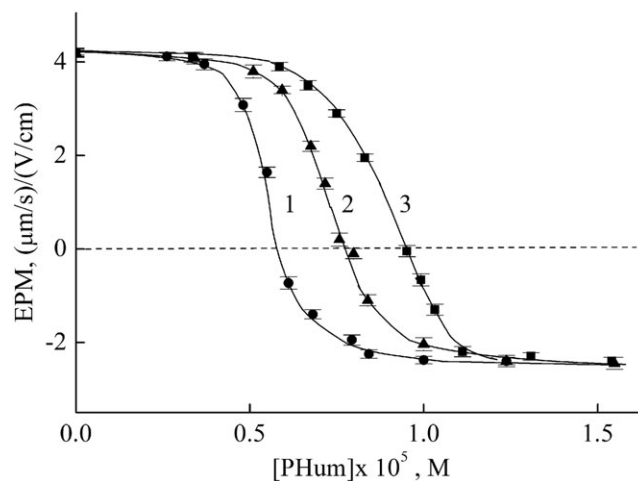


FIGURE 6 EPM of Lat particles in the presence of PHum (1), PDADMAC/PHum complex with Q = 0.2 (2), and PDADMAC/PHum complex with Q = 0.2 and M = 0.2 (3). 10^{-3} M Tris buffer, pH 7

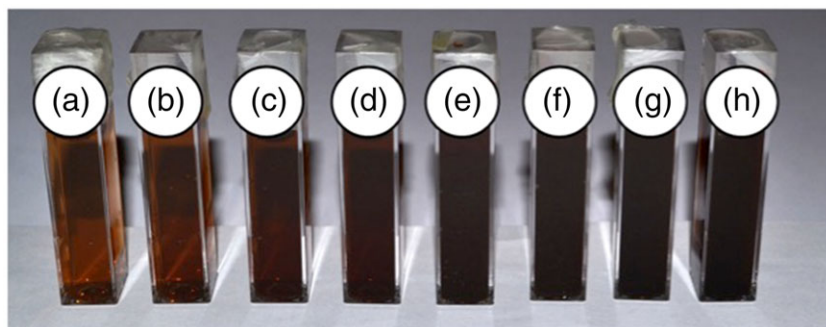


FIGURE 7 $Q = 0.2$ PDADMAC/PHum complex suspensions 2 weeks after preparation. Complex conc. 0.03 (a) 0.05 (b) 0.75 (c) 1 (d) 1.25 (e) 1.5 (f) 1.75 (g), and 2 wt% (h). 10^{-3} M Tris buffer with pH 7 [Colour figure can be viewed at wileyonlinelibrary.com]

solution was then added so that a NIPEC/ Cu^{2+} ternary complex with $M = 0.2$ was formed, which was stable against aggregation for at least 3 months. A suspension of thus prepared ternary complex was used for an electrophoretic titration of a Lat suspension (Figure 6, Curve 3). The $\text{EPM} = 0$ was achieved at 0.57×10^{-5} M carboxylic group concentration, corresponded to a $(0.57 \times 10^{-5} \text{ M}) / (0.95 \times 10^{-5} \text{ M}) = 0.6$ degree of PHum carboxylic groups. It is these groups that remained free after PHum complexation with PDADMAC ($Q = 0.2$) and Cu^{2+} ($M = 0.2$). This allowed to conclude that only free carboxylic groups in the PDADMAC/PHum/ Cu^{2+} ternary complex were involved in electrostatic complexation with Lat; no replacement of Cu^{2+} ions from the ternary complex was observed.

An important question concerns the limiting NIPEC concentration at which the aggregation stability of NIPEC suspension is still observed. In Figure 7, a series of photos is shown with different concentrations of the $Q = 0.2$ PDADMAC/PHum NIPEC in 10^{-3} M Tris buffer, pH 7. In the photos, taken 2 weeks after sample preparation, it is seen that the stable colloids were formed up to 2-wt% NIPEC concentration. No precipitation neither formation of insoluble sediments was detected. The 1- to 2-wt% NIPEC suspensions are of special

interest for the practical use: It is these concentrations that have been earlier recommended for the soil-stabilizing polymer formulations (Zezin et al., 2015).

In order to study the protective properties of the NIPEC formulation, the model approach was used with glass Petri dishes filled by 60 g of sod-podzolic soil each. The first dish (Control 1) was tilted by 60° that caused the soil partially to spill from the dish on the table (Figure 8a). The second dish (Control 2) was treated by 26 ml of deionized (DI) water (this minimum amount of water was found experimentally) and then left to dry for 5 days in the air and tilted by 60° . As a result, soil spilled from the dish again (Figure 8b) thus showing no protective properties of the topsoil treated by water. The third dish was treated by 26 ml of a $Q = 0.2$ 1% NIPEC formulation and then left to dry for 5 days in the air and put the dish upright. In this dish, no loss of soil was detected (Figure 8c). The sample treated with NIPEC was also exposed to a hot airflow (50°C) generated by a hair dryer at a flow rate of 10–12 m/s that did not induce defects in the surface layer. Finally, the NIPEC-soil crust was mechanically damaged by pressing it with the end of the pencil (Figure 8d). After that, 26 ml of DI water was deposited over the damaged crust, and the dish was left to dry for

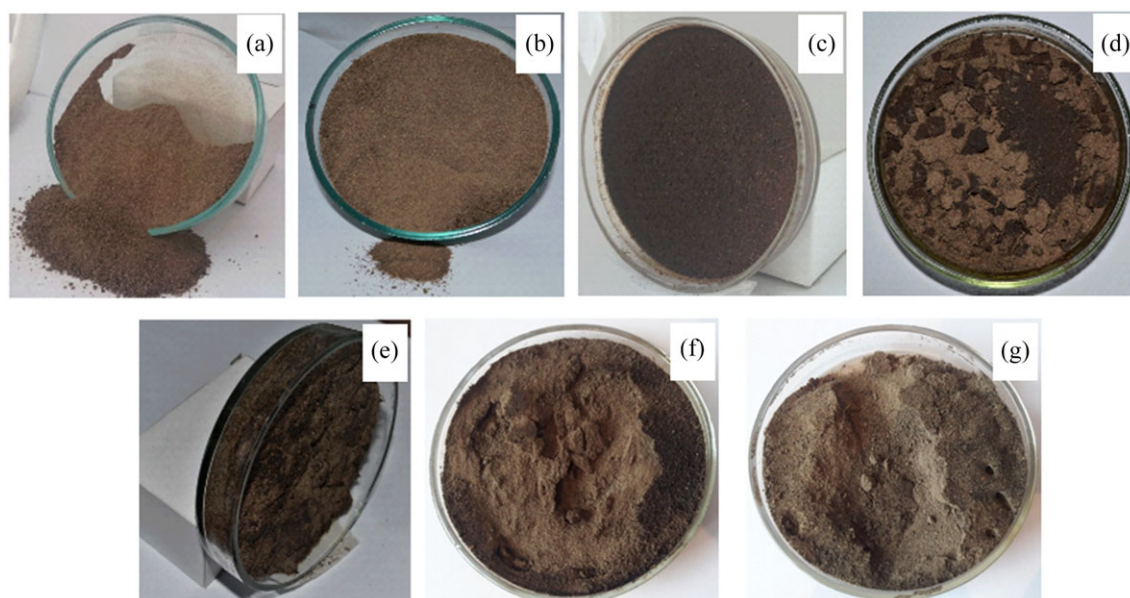


FIGURE 8 Petri dishes with soil: tilted by 60° (a) treated by water and then dried and tilted by 60° (b) treated by a $Q = 0.2$ NIPEC formulation and then dried and put upright (c) treated by a $Q = 0.2$ NIPEC formulation, dried, and mechanically damaged (d) then rewatered, dried, and put upright (e) treated by a PHum and then dried and treated with air flow for 20 s (f) treated by a PDADMAC and then dried and treated with air flow for 20 s (g) See details in the text [Colour figure can be viewed at wileyonlinelibrary.com]

5 days in the air and put upright. It was found that rewatering led to restoration of the protective properties of the NIPEC-soil covering (Figure 8e). In other words, being rewatered, the NIPEC-soil crust demonstrated self-healing properties.

The soil samples treated by solutions of individual polymers, PHum and PDADMAC, showed a different behavior. After the dried samples were exposed to a 50°C airflow for only 20 s, they lost 13 ± 2 g of soil that was an evidence of a very poor protection effects of both formulations (Figure 8f, g).

The next step was to examine whether the NIPEC-soil crust is able to resist water erosion. The Petri dishes were filled with 60 g of soil each again. The first dish was tilted by 15°, sprayed with 175 ml of DI water, dried for 5 days, and weighted. The dish was found to lose 8 ± 0.5 g of the soil (Figure 9a). The waste water was collected in a glass vessel where a fast sedimentation of soil particles was detected (Figure 9'). The second dish was treated with 26 ml of 1-wt% NIPEC formulation and left to dry for 5 days for the NIPEC-soil crust to be formed. Then the dish was tilted by 15°, sprayed with 175 ml of DI water, dried for 5 days, and weighted. In this case, only 0.2 ± 0.05 g of the soil was lost (Figure 9b). The waste water, collected in a glass vessel, showed a light brown solution with a small amount of soil on the bottom (Figure 9b'). Finally, the experiment was done again but using two dishes with soil, treated by 1% solutions of individual polymers, PHum and PDADMAC. Both dishes lost 7.6 ± 0.6 g of soil, comparable with the loss of soil from the first dish without polymer treatment (Figure 9c,d). In the wastewater from these samples, a fast phase separation and formation of dense precipitates were detected (Figure 9c',d').

The mechanism of the soil stabilization by NIPECs has been described previously (Panova et al., 2017; Zezin et al., 2015). The NIPECs, block copolymers with hydrophilic free anionic units and hydrophobic mutually neutralized anionic and cationic units, permeate into the porous of soil, find—due to an ability of polycomplexes to

adjust their blocks to complementary surface areas—the optimum adsorption sites (electrostatic and hydrophobic) on the surface of soil particles, and bind (glue) them to bigger aggregates. Upon drying, a polymer-soil crust (Figure 10) is formed on the soil surface resistant to wind and water destruction.

Figure 11 shows the morphology of the initial soil and the soil treated by the NIPEC formulation (the polymer-soil crust). Before the treatment, small soil particles with sharply contoured edges are seen in Figure 11a, which became rounded after the treatment due to their covering by NIPEC (Figure 11c). The treatment caused the particles to enlarge and glue together via polymer bridges (cf. Figure 11a and Figure 11c, and Figure 11b and Figure 11d), and the voids between the individual particles are clearly visible in the crust microphotograph.

The presence of pores in the polymer-soil crust, permeable for water, was also shown as follows. Eight samples of the crust,



FIGURE 10 Fragments extracted from NIPEC-soil crust [Colour figure can be viewed at wileyonlinelibrary.com]

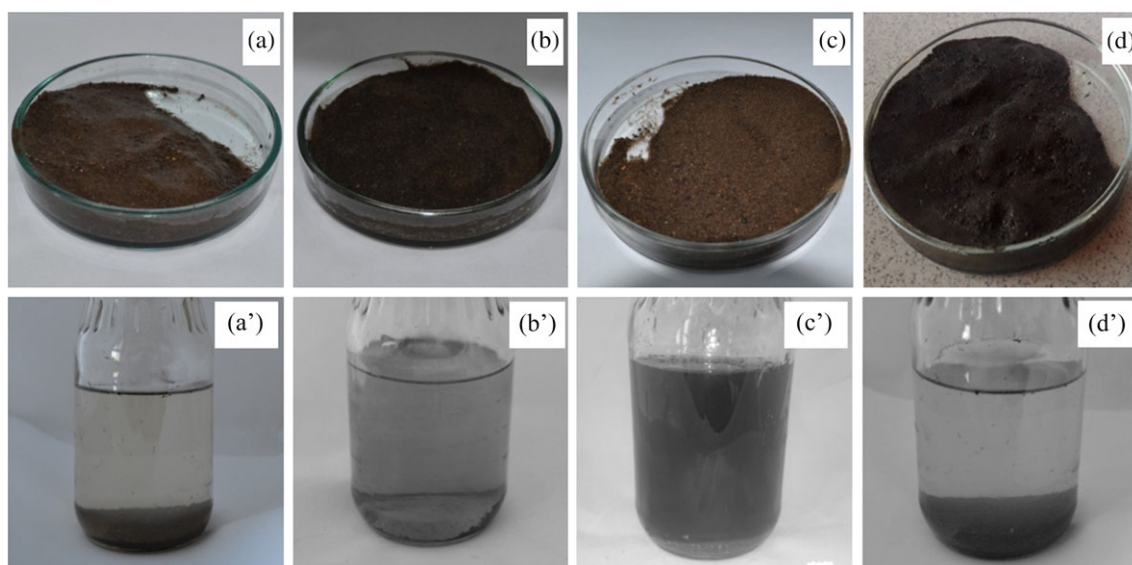


FIGURE 9 Petri dishes with soil (resistance to water): sprayed with DI water (a) and collected waste water (a') treated by a Q = 0.2 PDADMAC/PHum NIPEC formulation, dried and sprayed with DI water (b) and collected waste water (b') treated by a PHum, dried and sprayed with DI water (c) and collected waste water (c') treated by a PDADMAC, dried and sprayed with DI water (d) and collected waste water (d') [Colour figure can be viewed at wileyonlinelibrary.com]

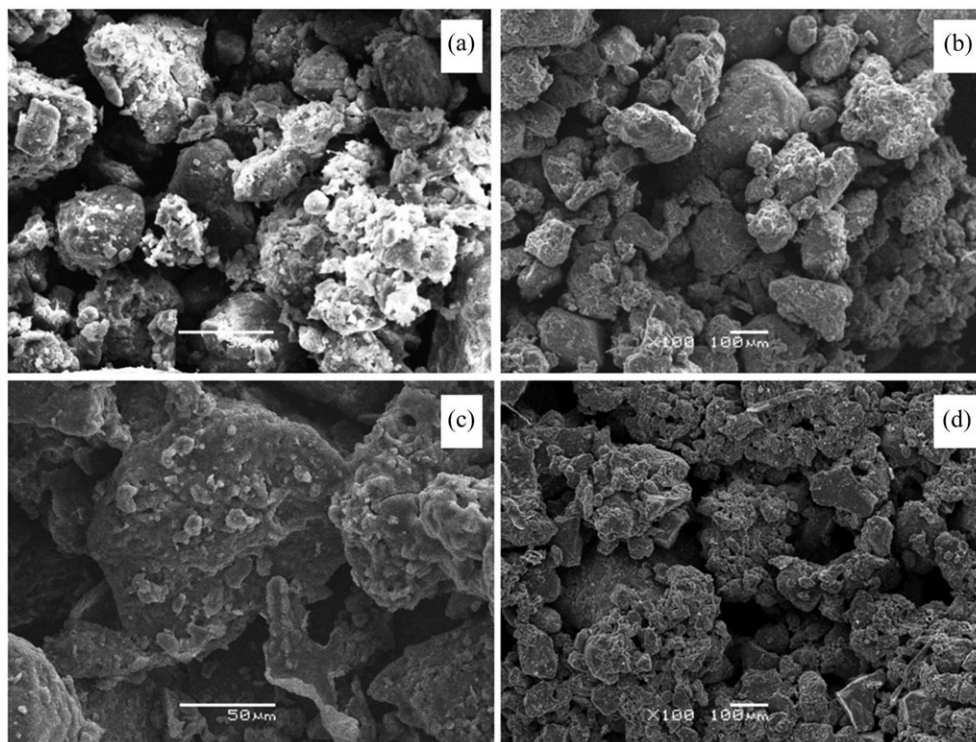


FIGURE 11 Microphotographs of soil samples before (a,b) and after treatment (c,d) by $Q = 0.2$ NIPEC formulation. White bar 50 μm (a,c) and 100 μm (b,d)

approximately 3 cm^3 each, were placed over a filter paper at the bottom of Petri dishes, after that the filter papers were slowly moistened with water. Petri dishes were covered with plastic wrap and left for 1 hr for water sorption. The porosity was estimated as $f = (W_{\text{water/crust}} - W_{\text{crust}})/W_{\text{crust}}$, where $W_{\text{water/crust}}$ is a weight of the crust with absorbed water and W_{crust} is the weight of the initial crust sample. The f value was found to be 0.25 ± 0.03 showing a high absorption power (porosity) of the NIPEC-soil crust. Thus, NIPEC treatment retained the porous structure of soil, which is a key agricultural requirement.

The suitability of the NIPEC-treated soil for agricultural use was demonstrated in the course of a simple visual experiment. Four plastic boxes were filled with soil; after that, approximately 100 cress salad seeds were evenly distributed over the soil in each box, and the seeds

were covered with 1-cm soil layer. Sixty-three milligrams of DI water was added to the first, 63 ml of $Q = 0.2$ NIPEC formulation to the second, 63 ml of 1 wt% PHum solution in the third, and 63 ml of 1 wt% PDADMAC solution in the fourth. Next 3 days, the soil in both boxes were watered, 150 ml per each. On the photos, taken 7 days after planting the seeds (Figure 12), is shown the same development of plants in all four boxes: treated with water (Figure 12a), NIPEC (Figure 12b), and individual polymers (Figure 12c,d). Thus, the polymer-soil crust in the second box did not prevent seed germination and plant development, obviously because of the air/water permeability of the polymer-soil crust.

Finally, the effect of NIPEC on the germination of cress salad seeds was examined in the presence of Cu^{2+} ions. The latter in trace amounts is necessary for growth and development of plants but in

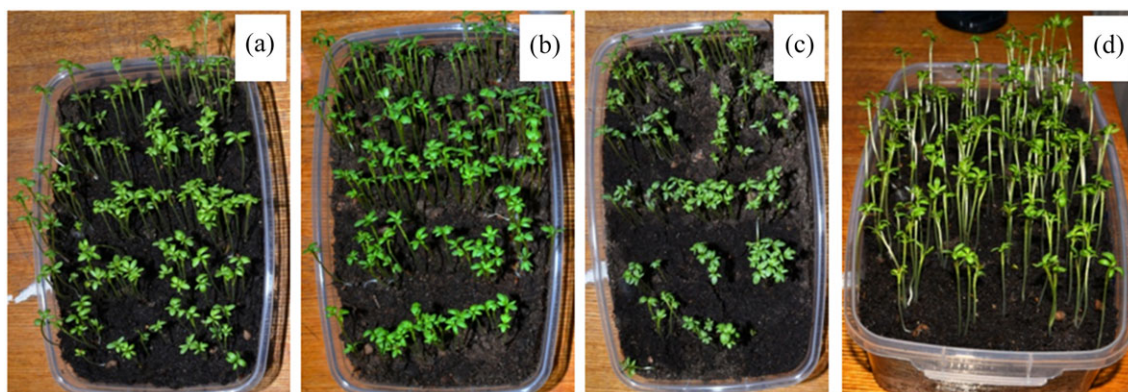


FIGURE 12 Development of cress salad in the boxes with water (a) NIPEC with $Q = 0.2$ NIPEC (b), PHum (c) and PDADMAC (d) [Colour figure can be viewed at wileyonlinelibrary.com]

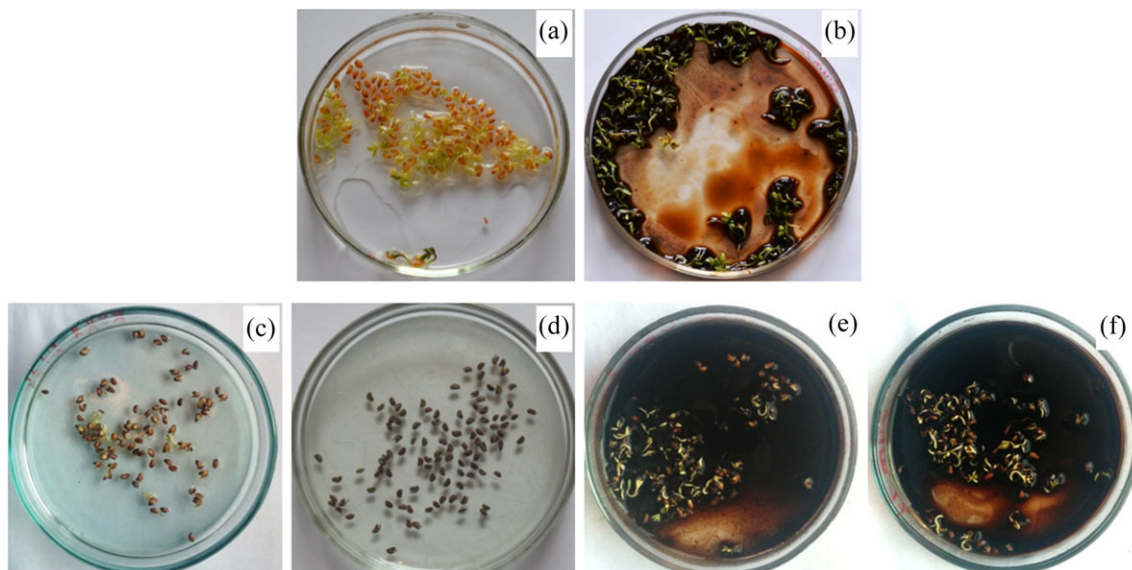


FIGURE 13 Petri dishes with cress salad seeds treated by DI water (a) $Q = 0.2$ NIPEC formulation (b) and 0.03 M CuSO_4 aqueous solution (c) as well as combinations of 0.03 M CuSO_4 aqueous solution and 1 wt\% PDADMAC solution (d) 1 wt\% PHum solution (e) and $Q = 0.2$ NIPEC formulation (f) [Colour figure can be viewed at wileyonlinelibrary.com]

the excess shows a strong toxic effect (Adrees et al., 2015). Different combinations of cress salad seeds, water or a polymer aqueous formulation, and a 0.03 M CuSO_4 water solution were tested in the experiment. The photos taken on the third day after the experiment started are shown in Figure 13. Water stimulated seed germination (Figure 13 a), and addition of the NIPEC formulation did not suppress the stimulation process (Figure 13b). Contrastingly, the CuSO_4 solution completely stopped the seed germination (Figure 13c). The cationic PDADMAC could not reverse the process and stimulate the germination because of its inability to bind Cu^{2+} ions (Figure 13d). At the same time, both PHum and negative NIPEC neutralized the toxic effect of Cu^{2+} ions and ensured a normal seed germination (Figure 13e,f) due to electrostatic binding of Cu^{2+} ions by anionic carboxylic groups of PHum and PDADMAC/PHum NIPEC.

4 | CONCLUSIONS

Addition of an aqueous solution of a cationic polymer, PDADMAC, to an aqueous solution of an anionic polymer, a potassium salt of humic acids (PHum), results in formation of an IPEC, stabilized by multiple ionic contacts between both polymer components. In the excess of PHum, a negative NIPEC is formed, which do not dissociate in the presence of heavy metal ions and positive colloidal particles but bind the ions and colloids thus forming the NIPEC/metal/colloid ternary complex. When deposited over soil, a NIPEC aqueous suspension (a NIPEC formulation) gives a protective layer (crust) forms on the surface, composed of NIPIC and soil particles, resistant to wind and water erosion. After destruction, the crust is completely restored by rewatering. The mechanism of the soil stabilization by NIPEC is the permeation into the pores of soil and glue the soil particles together. However, the NIPEC treatment retains the porous structure of soil, which favors seed germination and plant development. Being effective absorbent of heavy metals, the NIPEC formulation ensures a normal

seed germination in the presence of toxic Cu^{2+} ions. Thus, the humics-based NIPECs ensures antierosion protection and detoxification of soil. Additionally to ecological and agricultural applications, the NIPEC formulations have potential for immobilization of moving sands (desertification control), conservation of temporarily unused mining dumps, treatment of road and railroad slopes, and so forth.

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