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STUDY OF SOIL STRUCTURAL PROPERTIES UNDER THE EFFECT OF COMPOSITE ADDITIVES (BASED ON INDUSTRIAL WASTE)

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Abstract. *This study investigates the regulation of the structural properties of soil using composite additives based on water-soluble polyelectrolytes and an industrial wastewater-treatment residue referred to as "Bioshlam." Poly (methacrylic acid) (PMAA) was synthesized by radical polymerization and chemically modified with amines of different hydrocarbon radical lengths to obtain compositionally different structure-forming materials. In parallel, Bioshlam generated during water treatment at Uz-Kor Gas Chemical was examined as a potential biologically active and mineral-containing additive. The study compared the physicochemical behavior of PMAA and amine-modified PMAA systems with the effects of Bioshlam on water absorption and soil swelling. Elemental analysis of the Bioshlam sample showed substantial contents of oxygen, silicon, calcium, aluminum, potassium, and phosphorus, with a measured pH of 7.6–7.8. The swelling degree of the soil after treatment with PMAA, PMAA–diethylamine (PMAA–DEA), and Bioshlam increased from an initial value of 34.04% to 42.18%, 53.28%, and 65.86%, respectively, under the conditions reported in the study. The results indicate that industrial wastewater-treatment residues can be considered as a resource for preparing soil-structuring and organic–mineral additives, while also contributing to waste reduction and green-chemistry-oriented agricultural applications.*

Keywords: *soil structure; water-soluble polymer; poly(methacrylic acid); polyelectrolyte; amine modification; Bioshlam; industrial waste; swelling; water absorption; soil fertility.*

1. INTRODUCTION

Dispersed systems exhibit diverse structural and mechanical properties because of differences in composition, nature, aggregate state, particle size, and conformational behavior in different solvent environments. These characteristics create a need for natural and synthetic water-soluble polymers capable of modifying the properties of dispersed systems in a controlled manner.

One of the important theoretical and practical problems of modern colloid chemistry is therefore the study of natural and synthetic systems in the presence of high-molecular-weight compounds containing polyfunctional groups, particularly water-soluble polymers, and the purposeful modification of their properties [1].

Soil is a natural dispersed system forming the upper fertile layer of the Earth's land surface. In addition to mineral and organic constituents, soil contains water and air in varying amounts. Because structural and mechanical properties strongly influence the physical, chemical, and biological processes occurring in soil, considerable attention has been devoted to controlling these properties [2,3]. The use of organic and organomineral fertilizers, humic substances, and other soil conditioners has been associated with changes in nutrient availability and crop productivity [4-11]. Previous studies cited in the source manuscript report, for example, that combining organic fertilizers with mineral fertilizers can increase yield, while bacterially treated organomineral fertilizers based on humic substances can improve nutrient-use efficiency and reduce the required amount of mineral fertilizer [12–16].

The present work focuses on the preparation of structure-forming additives from water-soluble polyelectrolytes and an industrial residue from wastewater treatment. Particular attention is given to poly (methacrylic acid) and its amine-modified derivatives, as well as to Bioshlam obtained at the Uz-Kor Gas Chemical facility. The study aims to compare these systems with respect to their interaction with soil and their ability to influence water-related structural properties.

2. MATERIALS AND METHODS

2.1. Experimental design

The study investigated chemical and biological approaches for regulating the properties of soil as a natural dispersed system and for increasing its productive potential. In the chemical approach, methacrylic acid (MAA) was polymerized by a radical polymerization method to obtain poly (methacrylic acid) (PMAA). The synthesized polymer was subsequently used to prepare composite samples modified with amines having hydrocarbon radicals of different lengths. In the biological/industrial-waste approach, a wastewater-treatment residue called “Bioshlam” was obtained from the Uz-Kor Gas Chemical plant and evaluated as a soil-conditioning component.

The central experimental objective was to determine changes in macromolecular behavior as a function of the medium and solvent environment and to evaluate the effect of amine modification on PMAA. The resulting polymer systems and Bioshlam were then studied in relation to their interaction with soil, with emphasis on water absorption and swelling behavior.

2.2. Materials

Technical-grade methacrylic acid was purified by redistillation at 68 °C and 15 mm Hg and separated from the solution using NaCl or CaCl2. Methylamine (CH3NH2), diethylamine ((C2H5)2NH), and triethylamine ((C2H5)3N) were used as organic bases for modification. Potassium persulfate (K2S2O8) and potassium metabisulfite were used as initiator components for the oxidation–reduction initiation of the polymerization reaction. The polymer was purified by precipitation in ethanol. The source manuscript states that the main physical properties of the reagents were summarized in Table 1; however, the numerical table itself was not preserved in the provided document text and is therefore not reproduced here.

Bioshlam was obtained as an industrial wastewater-treatment residue from Uz-Kor Gas Chemical in the Republic of Karakalpakstan under an industrial cooperation arrangement. The material was mixed with soil at different ratios for comparative experiments. According to the source description, microorganisms are used at the facility to oxidize organic contaminants during industrial water treatment, with aerobic and anaerobic stages involved in the treatment process.

2.3. Analytical methods

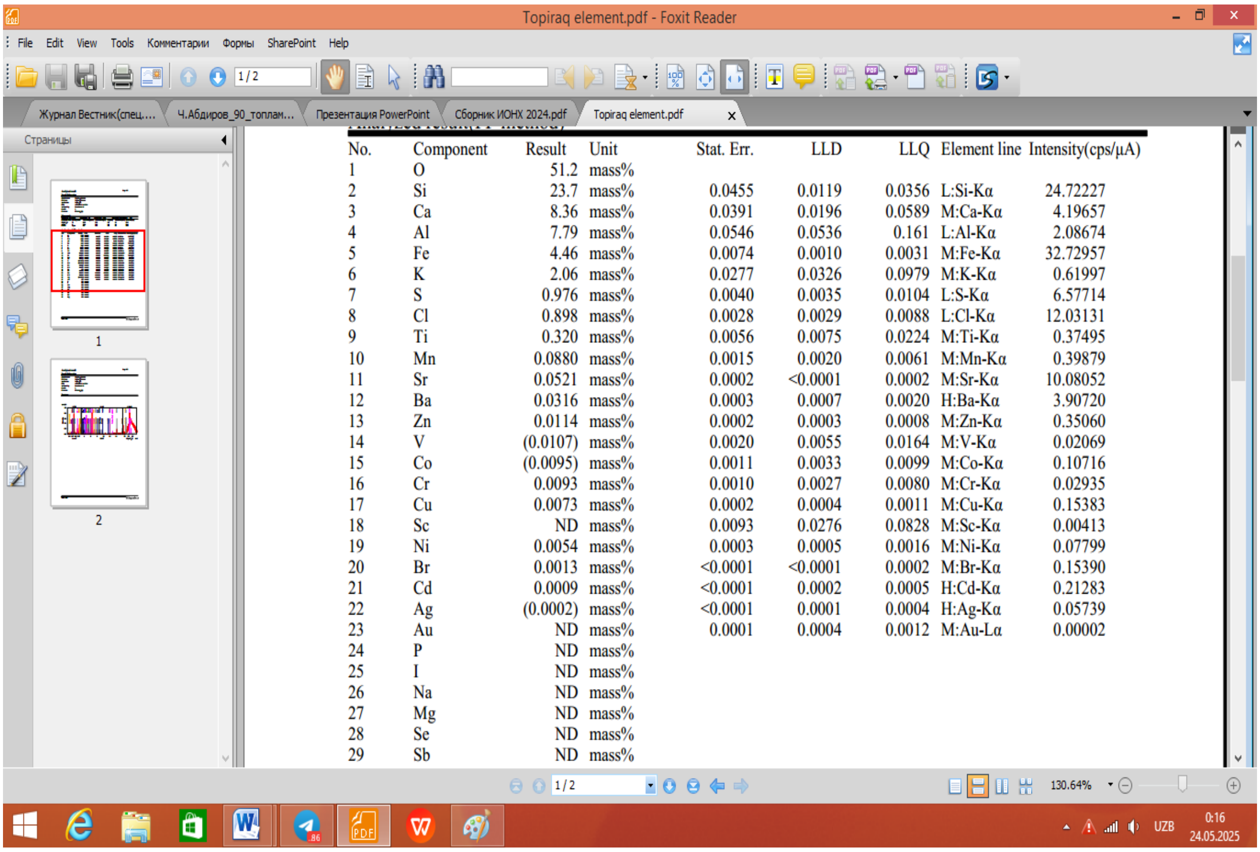
A combination of physicochemical and colloid-chemical techniques was used to characterize the synthesized structure-forming samples and their interactions with soil. These included viscometry, conductometry, potentiometry, calorimetry, infrared spectroscopy, X-ray phase analysis, energy-dispersive elemental analysis, and colloid-chemical methods.

The experimental work was conducted in laboratories of Karakalpak State University and related research facilities in Karakalpakstan. Soil samples were collected from a cultivated area associated with the IICAS auxiliary experimental farm in the Samanbay agricultural area of Nukus district.

2.4. Composite-system concept

The polymer–Bioshlam system was treated as a composite material. A composite is understood in the study as a system containing two or more phases, one of which forms a continuous dispersion medium (matrix), while the remaining phases are distributed within the matrix as particles, fibers, or films.

The dispersed phase can function as a filler or reinforcing component. When a polymer is used as the matrix, it serves as the binding component of the composite.



No.	Component	Result	Unit	Stat. Err.	LLD	LLQ	Element line	Intensity(cps/µA)
1	O	51.2	mass%					
2	Si	23.7	mass%	0.0455	0.0119	0.0356	L:Si-Kα	24.72227
3	Ca	8.36	mass%	0.0391	0.0196	0.0589	M:Ca-Kα	4.19657
4	Al	7.79	mass%	0.0546	0.0536	0.161	L:Al-Kα	2.08674
5	Fe	4.46	mass%	0.0074	0.0010	0.0031	M:Fe-Kα	32.72957
6	K	2.06	mass%	0.0277	0.0326	0.0979	M:K-Kα	0.61997
7	S	0.976	mass%	0.0040	0.0035	0.0104	L:S-Kα	6.57714
8	Cl	0.898	mass%	0.0028	0.0029	0.0088	L:Cl-Kα	12.03131
9	Ti	0.320	mass%	0.0056	0.0075	0.0224	M:Ti-Kα	0.37495
10	Mn	0.0880	mass%	0.0015	0.0020	0.0061	M:Mn-Kα	0.39879
11	Sr	0.0521	mass%	0.0002	<0.0001	0.0002	M:Sr-Kα	10.08052
12	Ba	0.0316	mass%	0.0003	0.0007	0.0020	H:Ba-Kα	3.90720
13	Zn	0.0114	mass%	0.0002	0.0003	0.0008	M:Zn-Kα	0.35060
14	V	(0.0107)	mass%	0.0020	0.0055	0.0164	M:V-Kα	0.02069
15	Co	(0.0095)	mass%	0.0011	0.0033	0.0099	M:Co-Kα	0.10716
16	Cr	0.0093	mass%	0.0010	0.0027	0.0080	M:Cr-Kα	0.02935
17	Cu	0.0073	mass%	0.0002	0.0004	0.0011	M:Cu-Kα	0.15383
18	Sc	ND	mass%	0.0093	0.0276	0.0828	M:Sc-Kα	0.00413
19	Ni	0.0054	mass%	0.0003	0.0005	0.0016	M:Ni-Kα	0.07799
20	Br	0.0013	mass%	<0.0001	<0.0001	0.0002	M:Br-Kα	0.15390
21	Cd	0.0009	mass%	<0.0001	0.0002	0.0005	H:Cd-Kα	0.21283
22	Ag	(0.0002)	mass%	<0.0001	0.0001	0.0004	H:Ag-Kα	0.05739
23	Au	ND	mass%	0.0001	0.0004	0.0012	M:Au-Lα	0.00002
24	P	ND	mass%					
25	I	ND	mass%					
26	Na	ND	mass%					
27	Mg	ND	mass%					
28	Se	ND	mass%					
29	Sb	ND	mass%					

Figure 1. Elemental analysis of the soil sample (source analytical record).

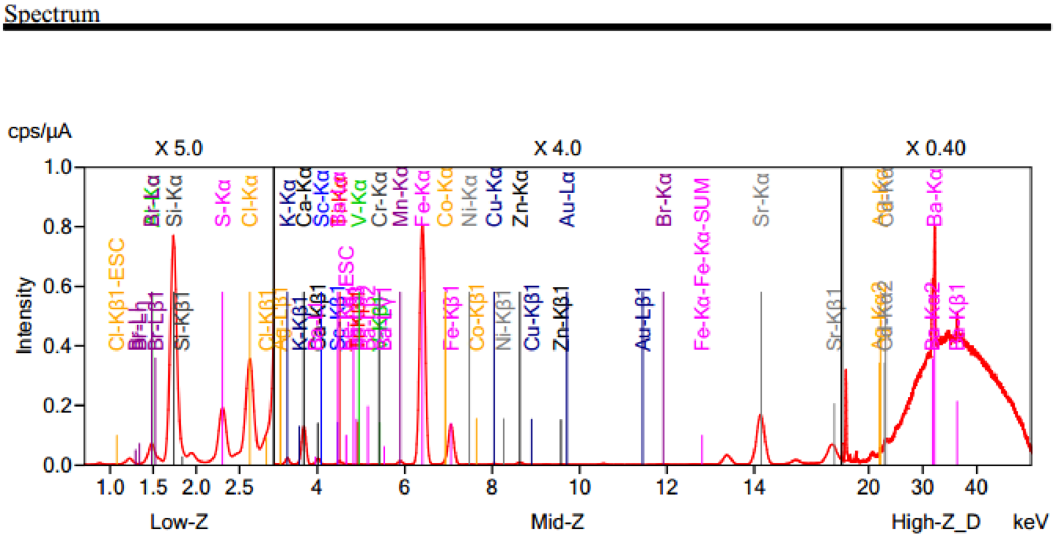


Figure 2. Spectrum of the analyzed soil sample.

Analyzed result(FP method)

No.	Component	Result	Unit	Stat. Err.	LLD	LLQ	Element line	Intensity(cps/µ
1	O	70.1	mass%					
2	Si	15.2	mass%	0.0341	0.0102	0.0307	L:Si-Kα	17.68669
3	Ca	6.13	mass%	0.0310	0.0149	0.0446	M:Ca-Kα	3.92867
4	Al	3.69	mass%	0.0379	0.0496	0.149	L:Al-Kα	0.98307
5	Fe	1.98	mass%	0.0044	0.0008	0.0025	M:Fe-Kα	19.77917
6	K	1.24	mass%	0.0205	0.0289	0.0866	M:K-Kα	0.46677
7	S	0.739	mass%	0.0030	0.0026	0.0077	L:S-Kα	6.21698
8	P	0.364	mass%	0.0046	0.0094	0.0282	L:P-Kα	1.02055
9	Cl	0.220	mass%	0.0013	0.0022	0.0067	L:Cl-Kα	3.71054
10	Ti	0.167	mass%	0.0038	0.0059	0.0177	M:Ti-Kα	0.25623
11	Mn	0.0626	mass%	0.0011	0.0015	0.0045	M:Mn-Kα	0.38437
12	Sr	0.0409	mass%	0.0001	<0.0001	0.0001	M:Sr-Kα	11.88374
13	Zn	0.0148	mass%	0.0002	0.0002	0.0006	M:Zn-Kα	0.67950
14	Ba	0.0118	mass%	0.0002	0.0005	0.0015	H:Ba-Kα	2.01902
15	Cu	0.0068	mass%	0.0002	0.0003	0.0008	M:Cu-Kα	0.21362
16	V	(0.0050)	mass%	0.0014	0.0041	0.0123	M:V-Kα	0.01272
17	Co	(0.0045)	mass%	0.0007	0.0020	0.0060	M:Co-Kα	0.06957
18	Ni	0.0030	mass%	0.0002	0.0004	0.0012	M:Ni-Kα	0.06423
19	Cr	(0.0030)	mass%	0.0007	0.0021	0.0062	M:Cr-Kα	0.01238
20	Br	0.0021	mass%	<0.0001	<0.0001	0.0002	M:Br-Kα	0.36883
21	Ag	(0.0001)	mass%	<0.0001	<0.0001	0.0003	H:Ag-Kα	0.03628

Figure 3. Elemental analysis of the soil + Bioshlam sample by the FP method.

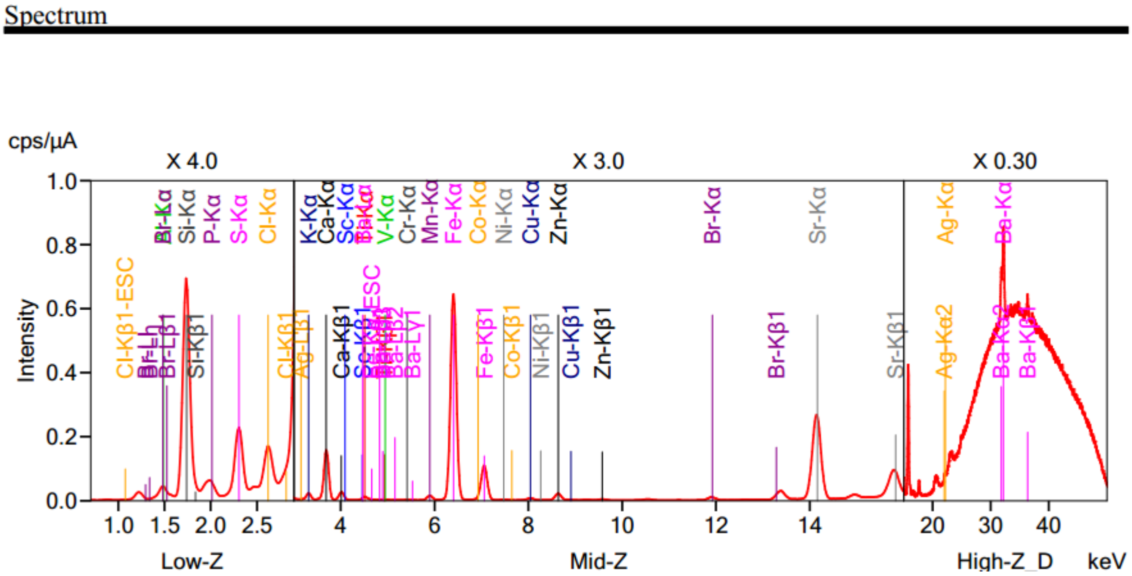


Figure 4. Spectrum of the soil + Bioshlam sample.

3. RESULTS AND DISCUSSION

3.1. Elemental composition of Bioshlam

Elemental analysis of the Bioshlam-containing sample showed a composition dominated by oxygen and silicon, with substantial contributions from calcium and aluminum. The principal values reported in the analytical record were 70.1 mass% O, 15.2 mass% Si, 6.13 mass% Ca, 3.69 mass% Al, 1.24 mass% K, and 0.364 mass% P. The measured pH was reported as 7.6–7.8. The analytical record also identified smaller amounts of Fe, S, Cl, Ti, Mn, Sr, Zn, Ba, Cu, V, Co, Ni, Cr, and Br, while several elements were recorded at very low levels or as not detected.

Table 1. Principal components detected in the soil + Bioshlam sample

Sample Information

Sample name	Soil + Biosludge_Oxide	
File name	Soil + Biosludge_Oxide	
Application	Fertilizer_Oxide	
Date	11/20/2025 1:56 PM	
Analyzed by	Utepbergenova A.	
Counts	1	
Comment Meas. cond.	Oxide_Qiy	

Diaphragm DE-10mm	Atmosphere Air		Sample spin None	Meas. order optimization Yes		
Condition name	Primary filter	Tube voltage (kV)	Tube current (µA)	ST (µsec)	Meas. Time (sec)	Dead time (%)
High-Z_D	D	60.0	200	1.6	60	18.3
Mid-Z	C	35.0	342	1.6	60	31.8

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Low-Z Open 6.5 Analyzed result (FP method)				378	1.6	60	37.3
No.	Component	Result	Unit	Stat. Err.	LLD	LLQ Element line	Intensity(cps/μA)
1	SiO2	55.7	mass%	0.0928	0.0298	0.0893 L:Si-Kα	23.33226
2	CaO	14.4	mass%	0.0653	0.0312	0.0935 M:Ca-Kα	4.20443
3	Al2O3	14.3	mass%	0.110	0.117	0.351 L:Al-Kα	1.74552
4	Fe2O3	7.11	mass%	0.0125	0.0020	0.0059 M:Fe-Kα	28.32598
5	SO3	3.20	mass%	0.0124	0.0104	0.0313 L:S-Kα	7.11367
6	K2O	2.83	mass%	0.0395	0.0505	0.151 M:K-Kα	0.58196
7	Cl	0.950	mass%	0.0032	0.0036	0.0107 L:Cl-Kα	10.44003
8	TiO2	0.603	mass%	0.0115	0.0162	0.0486 M:Ti-Kα	0.33048
9	P2O5	0.547	mass%	0.0141	0.0354	0.106 L:P-Kα	0.44502
10	MnO	0.151	mass%	0.0025	0.0034	0.0102 M:Mn-Kα	0.41232
11	SrO	0.0894	mass%	0.0003	<0.0001	0.0003 M:Sr-Kα	11.29410
12	BaO	0.0297	mass%	0.0004	0.0009	0.0027 H:Ba-Kα	2.57659
13	ZnO	0.0261	mass%	0.0004	0.0004	0.0013 M:Zn-Kα	0.49951
14	V2O5	(0.0253)	mass%	0.0045	0.0125	0.0376 M:V-Kα	0.02139
15	Cr2O3	0.0158	mass%	0.0019	0.0051	0.0152 M:Cr-Kα	0.02659
16	CuO	0.0155	mass%	0.0004	0.0006	0.0019 M:Cu-Kα	0.20112
17	Co2O3	(0.0140)	mass%	0.0019	0.0057	0.0171 M:Co-Kα	0.08676
18	NiO	0.0089	mass%	0.0004	0.0009	0.0027 M:Ni-Kα	0.07849
19	PbO	0.0029	mass%	0.0002	0.0005	0.0014 M:Pb-Lα	0.07537
20	Br	0.0028	mass%	<0.0001	<0.0001	0.0003 M:Br-Kα	0.25561
21	As2O3	0.0020	mass%	0.0001	0.0003	0.0008 M:As-Kα	0.09039
22	Sc2O3	ND mass%		0.0183	0.0555	0.167 M:Sc-Kα	0.00000

The source manuscript interprets the presence of these mineral components as evidence that Bioshlam has potential for use as an organic–mineral soil amendment. In the original interpretation, the measured concentrations of several trace heavy metals were considered to be within ranges regarded by the authors as non-harmful to plant production. This interpretation is reported here as part of the source study and should be distinguished from an independent environmental-safety assessment.

3.2. Water absorption and swelling behavior

Comparative experiments were performed for PMAA and PMAA–DEA samples, as well as for Bioshlam. During a two-hour period, the soil water-absorption and swelling characteristics increased after addition of the structure-forming materials. For the PMAA-treated system, the swelling degree increased from 34.04% to 42.18%, whereas for the PMAA–DEA system it increased from 34.04% to 53.28%.

Under the reported experimental conditions, the soil treated with Bioshlam exhibited the highest swelling range, reaching 65.86%. The source manuscript relates this behavior to the organic polymeric and protein-rich character attributed to Bioshlam and its ability to retain moisture.

These observations support the concept that modification of soil with polymeric or organic–mineral components can alter the water-retention behavior of the dispersed system. At the same time, the differences between the modified polymer systems indicate that the chemical structure of the polyelectrolyte is important for controlling the resulting soil–water interaction.

3.3. Conformational behavior of modified polyelectrolytes

The study associates the observed changes in polymer behavior with the degree of neutralization of functional groups. As neutralization increases, electrostatic interactions within and between polymer chains can change, which affects the conformation of the polyelectrolyte.

The resulting conformational expansion can increase solution viscosity and modify the interaction between the polymer and dispersed soil particles. The source results further indicate that the relative electrical conductivity changes with polymer concentration: as polymer concentration increases, the reported reduced specific conductivity decreases.

The comparative order of the specific-solubility parameter reported for the aqueous medium was PMAA < P*TEA < P*MA < P*DEA, while the structure-forming ability of the chemically modified samples followed PMAA < P*MA < P*TEA < P*DEA. PMAA–DEA was therefore identified in the source study as the most effective of the tested modified polymers and was selected for comparison with Bioshlam.

3.4. Structure-forming effect and practical significance

The combined results indicate that purposeful use of additives can regulate the formation of soil aggregates and modify their physicochemical properties. Bioshlam, obtained as a residue from wastewater treatment, displayed a measurable mineral component together with organic constituents and therefore has potential as a soil-conditioning material. Its comparatively high effect on swelling and water-related behavior suggests that the residue may contribute to the development of moisture-retaining soil structures under the tested conditions.

From a technological perspective, the use of an industrial wastewater-treatment residue as a component of a soil amendment may simultaneously address two objectives: improving the functional properties of soil and redirecting a production residue toward a potentially useful application. The study therefore places the proposed approach within the broader framework of resource recovery and green chemistry. However, field-scale validation, agronomic trials, long-term environmental monitoring, and standardized safety testing would be required before large-scale agricultural application.

4. CONCLUSIONS

- Composite structure-forming systems based on water-soluble poly(methacrylic acid) modified with organic amines and on the industrial wastewater-treatment residue Bioshlam were investigated for their ability to influence the structural and water-related properties of soil from the Aral Sea region.

• The polymer systems showed different behavior as a function of medium, concentration, and pH. The reported order of structure-forming ability was PMAA < P*MA < P*TEA < P*DEA, with PMAA–DEA identified as the most effective modified polymer among the systems tested.

• Addition of Bioshlam increased the soil swelling degree under the reported experimental conditions. The initial value of 34.04% increased to 65.86% in the Bioshlam-treated system, compared with 42.18% for PMAA and 53.28% for PMAA–DEA.

• Elemental analysis of the Bioshlam-containing sample showed 70.1 mass% O, 15.2 mass% Si, 6.13 mass% Ca, 3.69 mass% Al, 1.24 mass% K, and 0.364 mass% P, with a reported pH of 7.6–7.8. These characteristics support the possibility of using Bioshlam as a component of an organic–mineral soil amendment, subject to further safety and field evaluation.

• The investigation demonstrates a potentially useful green-chemistry pathway for converting an industrial wastewater-treatment residue into a value-added material for soil conditioning and for improving moisture-related structural characteristics.

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