



Utilization and biodegradation of wastes

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Conversion of household solid waste organic ingredients into fertilizers containing organic and mineral constituents

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Abstract – The article is devoted to the problem of solid household waste disposal. A procedure is proposed for converting the organic part of solid household waste into fertilizers containing both organic (~40%) and mineral (~60%) components, i.e. representing an analogue of organomineral fertilizers. Due to the presence of pathogenic microflora in raw household waste, it seems unreasonable to use it without preliminary detoxication. A possibility is considered of using geothermal waters of Azerbaijan, coming to the ground surface with a temperature of 25–75°C and containing hydrogen sulfide, for disinfection of the pathogenic microflora of the organic ingredients of the solid household waste. The method involves treating the organic part of the waste with geothermal water followed by introducing natural additives of the local origin. For introducing micronutrient elements, a phonolite is added to the organic component of the waste, and a local shell limestone is used for regulating pH level of the resulting fertilizer. The influence of H₂S presence in the geothermal waters on the efficiency of disinfection of the raw materials is studied. The role of hydrogen sulfide dissolved in the geothermal waters in increasing the efficiency of disinfection is substantiated.

Keywords: solid household waste, organic ingredients, analogue of organomineral fertilizers, disinfection, geothermal water, hydrogen sulfide.

Трансформация органической составляющей твердых бытовых отходов в удобрения органо-минерального типа

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Аннотация – Статья посвящена актуальной проблеме утилизации твердых бытовых отходов (ТБО). Предложен способ переработки органической части ТБО в удобрения, содержащие в своем составе как органические (~40%), так и минеральные (~60%) компоненты, т.е. представляющих собой аналог органо-минеральных удобрений. Ввиду наличия в сырых бытовых отходах патогенной микрофлоры невозможно их использование без предварительного обезвреживания. Рассмотрена возможность использования геотермальных

вод Азербайджана, выходящих на поверхность с температурой 25–75°C и содержащих сероводород, для борьбы с патогенной микрофлорой органической составляющей ТБО. Способ предусматривает обработку органической части ТБО геотермальными водами и введение природных добавок местного происхождения. Для внесения микроэлементов к органической составляющей ТБО добавляют фонолит, для регулирования pH полученного удобрения используют ракушечник. Изучено влияние присутствия H₂S в геотермальных водах на эффективность обеззараживания используемого сырья. Обоснована роль растворенного в геотермальных водах сероводорода в повышении эффективности обеззараживания.

Ключевые слова: твердые бытовые отходы, органическая составляющая, аналог органоминеральных удобрений, обеззараживание, геотермальные воды, сероводород.

INTRODUCTION

The accumulation, storage and processing of solid household waste is an urgent environmental problem since it causes significant pollution of the atmosphere and soil, as well as contributes to human health impairment [1].

This problem is of great concern in many countries and increasingly gains a global character [2–4]. Based on experts estimates, by 2025 the total number of urban population in the world will likely increase to 4.3 billion people generating about 1.42 kg/capita/day of municipal solid waste (2.2 billion tonnes per year) [4].

The problem's solution should be based on developing safe technologies for processing of solid waste and finding ways to use household waste as secondary raw materials.

One of the efficient ways for solving this problem is using various types of waste as raw materials for production of organomineral fertilizers [5–7].

The effectiveness of using organomineral fertilizers is beyond any doubt, since they combine the advantages of both organic and mineral fertilizers. Mineral fertilizers are known to compensate only 25-30% of nutrients extracted by plants from the soil. Depending on the climate zone and seasonal changes, municipal solid waste may contain up to 30-60% of food waste. Organic ingredients can contribute up to 70% of the total volume of food waste [8].

In nature, organic waste is routinely decomposed which does not pose any threat. However, due to the fact that the household solid waste may contain pathogenic microorganisms, this type of waste poses a significant sanitary hazard. Therefore, when using raw household waste for the preparation of fertilizers, it should be preliminarily disinfected and detoxified [9].

The microbial cells can be destroyed by means of a physical thermal procedure when a processed material is heated at a temperature of 50–80°C [10]. In this case, about 90% of pathogenic microorganisms are killed. Thermal disinfection of food waste in the sterilizer for 40–50 minutes at 100–110°C is sufficient to inactivate all pathogenic microorganisms [11]. However, this procedure requires certain energy costs.

The reason for choosing a method for disinfection of pathogenic microflora when developing a technology for processing solid household waste was the presence of numerous geothermal sources with various properties in the territory of the Republic of Azerbaijan.

Therefore, the aim of this work was to study a feasibility of processing solid household waste into fertilizers using the geothermal waters of Azerbaijan for disinfection of the raw materials, with introducing other materials of local origin to produce a product containing organic and mineral components suitable for use the end product in agriculture.

EXPERIMENTAL

For the experimental study of a possibility of using geothermal waters for the disinfection of solid household waste, three types of geothermal water samples were collected from wells drilled in the territory of the Lerik region of the Azerbaijan Republic. Thermal water from these open wells comes to the ground surface with a temperature of 25–75°C. The average content of the main chemical ingredients of the thermal waters of the indicated region is presented in Table 1. Three types of sources were distinguished depending on the pH value of the water: acidic, neutral and alkaline.

Table 1. Average content of chemical components in geothermal waters of Azerbaijan used in this study, mg/l

Geothermal source type	Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻
Acidic (pH = 5.7)	0.287	0.189	0.051	0.743	1.32	0.261
Neutral (pH = 7.4)	0.578	0.243	0.019	1.05	0.457	0.302
Alkaline (pH = 9.2)	0.502	0.199	0.021	0.796	0.334	0.223

A characteristic feature of these types of water is that the water contains 28–31% of the maximum possible concentration of dissolved hydrogen sulfide, in the absence of carbon dioxide.

Procedure for preparation fertilizers from solid household waste

Before carrying out the experiments, all inorganic inclusions consisting of bones, glass, metal, plastic, building materials, etc., were removed from municipal solid waste. The remaining organic component of the waste consisted of food waste of animal and vegetable origin, wood, paper residues, etc. and was characterized by the following chemical composition (% of dry wt.):

Organic ingredients – 56–73;

N_{total} – 0.7–1.7;

Phosphorus – 0.5–0.7;

Potassium – 0.3–0.7;

Calcium – 3.91–5.6;

Sulfur – 0.2–0.3;

Carbon – 28–34.

Humidity – 33–48% of the total wt.;

pH = 6.5–7.5.

The experiments were carried out in two steps. At the first step, before developing the technology for producing fertilizers of organomineral type, the effect of H_2S present in the geothermal waters on the degree of disinfection of the organic component of solid waste was studied. To conduct the experiments, geothermal waters with a wide pH spectrum and similar mineralization degree were used to exclude the possible effect of mineralization on the solubility of the hydrogen sulfide present.

Portions of 100 g of the organic component of the solid waste prepared as described above, were placed in seven containers. Then 20 ml of geothermal water samples with $pH = 7.2$, containing 0.25 mg/l of dissolved H_2S (28%) was poured into the each vessel. The geothermal water samples poured into containers differed from each other with a temperature value corresponding to 25, 30, 40, 50, 60, 70, 75°C, which corresponded to the temperature of the geothermal water from the wells with similar mineralization degrees. The contents of the containers were mixed for 10 min. Samples of the suspension taken from each container were tested for the presence of pathogenic microflora. The microbial suspension was sown in a liquid non-selective medium, the media were incubated and the number of colonies formed, typical for a certain type of bacteria, was determined. The degree of disinfection was calculated as the difference between the indications of the presence of pathogenic microspheres in the feedstock and in the samples after their treatment with geothermal water.

Similarly, using the same procedure, the disinfection process was repeated with the use of geothermal water with an acidic ($pH = 5.5$) and alkaline ($pH = 9.1$) medium with the same salt content and the content of dissolved hydrogen sulfide.

At the second step of the experiments, 100 g of the organic component of the solid household waste was placed in a container with a volume of 600–800 ml, and 20 ml of an alkaline solution of geothermal water with a H_2S content of 15% was added. The mixture was stirred for 10 min, then 15 g of grinded phonolite (a volcanic rock, composition is shown below) was added with stirring. The resulting mixture was placed in an oven and kept at a temperature of 100°C for 1.2 h. Then, the resulting mass was cooled for 30 min for ripening. After ripening, 2.4 g of crushed limestone was added to the resulting mixture with stirring, adjusting the pH of the medium to 6.5. The obtained fertilizer after granulation had the following composition (% wt.):

$N_{total} - 0.55;$
 $P_2O_5 - 0.45;$
 $K_2O - 6.1;$
 $MgO - 1.66;$
 $Na_2O - 0.93;$
 $CaO - 19.2;$
 $Al_2O_3 - 9.9;$
 $SiO_2 - 17.81;$
Oxides of Fe, Mn, Ti – 2.4;
Organic ingredients – the rest (41).

A phonolite sample of the local origin was taken from Azerbaijan mineral assets and used for the preparation procedure of the fertilizer. The phonolite belongs to the phonolites of medium SiO₂ content and has the following chemical composition (% wt.):

SiO₂ – 59÷79;
 TiO₂ – 0.85;
 Al₂O₃ – 16.98;
 Fe₂O₃ – 3.25;
 FeO – 2.76;
 MnO – 0.09;
 MgO – 2.51;
 CaO – 1.69;
 Na₂O – 1.93;
 K₂O – 9.6;
 P₂O₅ – 0.55.

To neutralize the resulting intermediate product, we used a local shell limestone of the coastal zone of the Absheron Peninsula with a porosity of 27–31%, water absorption of 0.9–1.2%, having the following composition (wt.%):

CaO – 51÷57;
 MgO – 1.33;
 CO₂ – 38÷48;
 Al₂O₃ – 2.04;
 Fe₂O₃ – 0.3;
 K₂O – 1.2;
 Na₂O – 0.5.

RESULTS AND DISCUSSION

The effectiveness of using hot geothermal water for disinfection of pathogenic microflora is fully substantiated by the well-known fact of thermal exposure. Nevertheless, it was interesting to identify the effect of the presence of hydrogen sulfide in geothermal waters on the degree of disinfection of the crude organic component of the solid waste.

For this purpose, experiments were carried out with prepared samples of neutral, acidic and alkaline saline solution, identical in composition to geothermal waters, but without the presence of H₂S (blank solution).

The results were compared with that for the real geothermal water mediated disinfection of the organic part of the solid household waste. The comparative experimental data are presented in Figure 1.

Comparison of the temperature dependence curves of the degree of disinfection (Fig. 1a) and b)) reveals the identity of the curves character with a slight upward shift relative to the x-axis when using alkaline and neutral geothermal waters containing H₂S. However, in the presence of H₂S, the position of the curve for the acidic solution is preserved; meanwhile, a change in the position of the curve for the neutral solution is observed, while the distance between them decreases. At the same time, the distance between the curve for the acidic solution and alkaline solution significantly

increases. The change in the position of the curves may be due to the difference in the conditions of the disinfection process, and thus can be attributed to the presence of hydrogen sulfide.

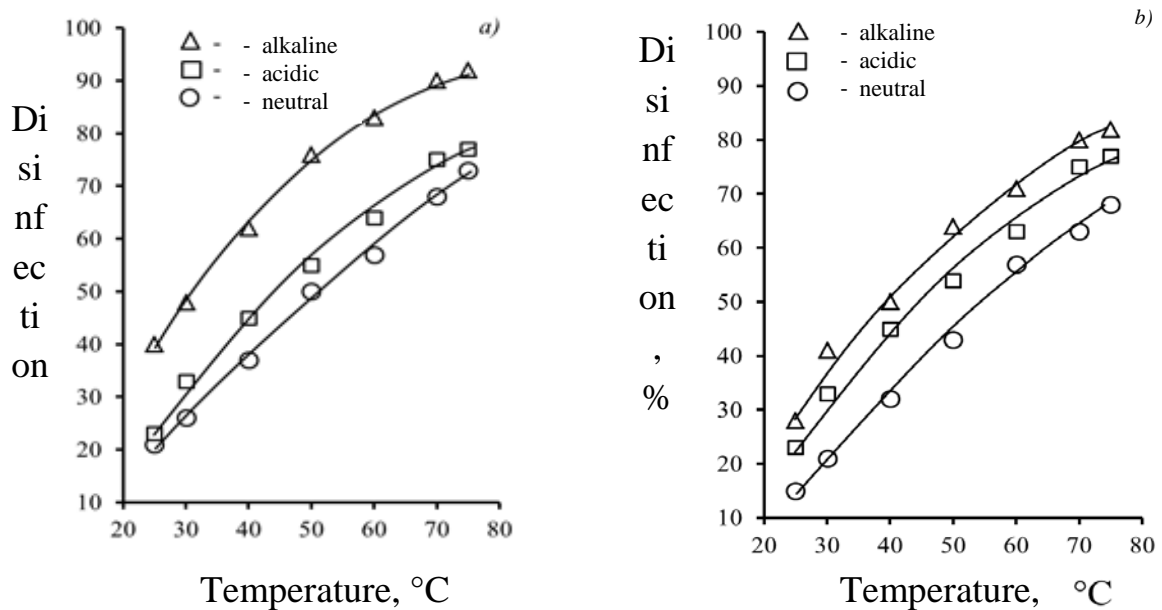


Fig. 1. Dependence of degree of disinfection on temperature of saline solution: a) geothermal water containing H₂S; b) blank solution.

As for the numerical values of the disinfection efficiency, the degree of disinfection is 92% in the studied temperature range in the presence of H₂S in the alkaline solution at the temperature of 75°C, whereas the degree of disinfection corresponds to 83% in the blank solution at the same temperature.

To explain this difference, it seems reasonable to consider the following known facts.

On the first hand, the total amount of hydrogen sulfide dissolved in the water is distributed between the concentrations of undissociated molecules of gaseous H₂S, hydrosulfide ions HS⁻, and, very seldom, sulfide ions S₂⁻. Moreover, the ratio of these components is determined mainly by the pH of the aqueous solution, to a lesser extent, it is affected by temperature and mineralization degree, this distribution can be expressed as follows [12]:

at pH ≤ 6 – H₂S;

at pH = 6–7 – H₂S = HS⁻;

at pH = 8–11 – HS⁻;

at pH = 12 – S₂⁻.

Thus, it is clear that the presence of hydrogen sulfide will affect the changes in the acidity of geothermal waters, which can be characterized by the data presented in Table 2.

As can be seen from the Table 2, the presence of hydrogen sulfide in geothermal waters changes the distribution of the chemical composition of the solution compared to the blank solution. In the acidic solution, definitely, no changes will occur.

Table 2. Effect of the presence of hydrogen sulfide in the chemical composition of geothermal waters at different acidity levels

Solution type	Solution medium		
	Neutral	Acidic	Alkaline
Blank solution	$H^+ = OH^-$	H^+	OH^-
Geothermal water, containing H_2S	$H^+ = OH^-$, $H_2S = HS^-$	H^+ , H_2S	OH^- HS^-

As for the neutral medium, even with the existing equilibrium of the undissociated H_2S molecules and HS^- species, the presence of the HS^- ions, which is responsible for hydrolysis of anions, will increase the pH of the solution by a certain degree depending on the concentration of the dissolved hydrogen sulfide. As for the alkaline environment, a noticeable increase in alkalinity can occur in the solution. According to the available literature data, at typical groundwater pH values 6–9, a relatively small change in pH (even by 1) can result in a 5–10-fold change in the ratio of the dissolved H_2S molecules and dissolved HS^- ions.

At $pH > 8$, more than 90% of hydrogen sulfide species will be in the form of the hydrosulfide ion HS^- [13].

On the second hand, referring to the microbiological factor, it is important to keep in mind that, in addition to the temperature effect, the vital activity of microorganisms depends on the concentration of proton (H^+) or hydroxyl (OH^-) ions in the substrate on which they are growing. The influence of the pH of the medium on the activity of microbes is due to the interaction of H^+ protons with enzymes located in the cytoplasmic membrane and in the cell wall. It is known that a change in pH levels disrupts the catalytic activity of enzymes located in the cytoplasmic membrane and cell wall [14, 15]. As for the hydroxyl group, it causes alkaline hydrolysis of the outer layer of the cell walls of pathogenic bacteria, which consists of complex proteins. This results in protein cleavage under alkaline hydrolysis conditions which leads to cell death.

Thus, summing up the both of the abovementioned factors, it becomes obvious that the effectiveness of the process of disinfection of pathogenic microflora is affected by the quantitative characteristics associated with the presence of both proton (H^+) and hydroxyl (OH^-) ions in the solution, which determine the conditions of pathogenic microflora exposure.

Turning back to the results of our experiments, shown in Figure 1, and taking into consideration the two factors discussed above, it can be stated that the change in the position of the curves resulting in an increase in the disinfection efficiency, depends directly on the presence of dissolved H_2S in geothermal water.

The applied alkaline solution of geothermal water containing H_2S not only disinfects the organic ingredients of the waste, but also contributes to the hydrolytic destruction of the pulp formed after mixing the organic component with geothermal waters. Conditioning the pulp at the temperature of 100–105°C for 1.2–1.5 h will accelerate the destruction process, enhancing transformation of the fat contained in the food waste into low molecular weight carboxylic acids, and proteins – into amino acids and peptides. Polysaccharides contained in cellulosic waste are hydrolyzed to

monosaccharides, followed by their degradation and formation of organic acids and carbon dioxide. Lignin, which is one of the components of plant material contained in food residues, undergoes hydrolysis with the formation of benzene polycarboxylic acids. At this step, the pH values of the resulting pulp decrease to 3.4–3.6 due to the formation of acids. It should be noted that when the pulp is kept in an oven at a temperature of 100–105°C, only evaporation of moisture occurs, and the remaining mass is a mixture of organic acids, the boiling point of which is much higher.

Cooling and curing the pulp for 30–40 min is necessary to complete the destruction of the constituents of food waste, as well as to release carbon dioxide formed during fermentation.

At the end of ripening step, the pH value of the pulp reaches the values in the range of 2.6–2.8. Such acidity level would worsen the growth and branching of the plant roots, reducing the permeability of the root cells and leading to a decrease in the access of water and nutrients absorbed from soil and fertilizers. Therefore, taking into account chalking as an important condition for intensification of agricultural plant production, the crushed limestone was added to the resulting mass of the fertilizer.

CONCLUSION

A procedure has been developed for processing the organic ingredients of municipal solid waste into fertilizers containing both organic (~40%) and mineral components (~60%), i.e. representing an analogue of organomineral fertilizers. The proposed technology for the production of fertilizers of organic-mineral type will make it possible to utilize solid household waste with the involvement of natural resources of Azerbaijan in the process of waste disposal. The use of phonolite as an additive provides introduction of additional micronutrient elements into the composition of the fertilizer, while the introduction of shell limestone would allow to adjust the acidity level of the fertilizer for its use under a specific soil.

To disinfect pathogenic microorganisms in the organic ingredients of the solid household waste, it is proposed to use hot geothermal waters containing hydrogen sulfide. The presence of hydrogen sulfide in geothermal waters contributes to a change in the pH of the solution (pH shifting to the alkaline range), thereby increasing the efficiency of the process of disinfection. It is assumed that the greatest disinfection efficiency achieved using alkaline geothermal waters is due to the presence of HS⁻ hydrosulfide ions in the solution, which are responsible for the hydrolysis of anionic type.

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