Kinetic laws of the process of obtaining complex humic-organic-mineral fertilizers in the fluidized bed granulator

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Abstract

Introduction. The main part of wastes from the sunflower oil production is sunflower ash that contains useful substances. The aim of the work to determine kinetic laws of the process of obtaining complex organic-mineral granulated fertilizers using the sunflower ash.

Materials and methods. Dehydration and granulation of liquid heterogeneous systems that contained mineral, humic substances and sunflower ash were held in the fluidized bed apparatus equipped with a special gas distribution device for creating a jet-pulsating mode of fluidization by supplying gas heat carrier.

Results and discussion. A stable kinetics of granulation process of the humic-organic-mineral fertilizers which contain K:N:Ca:P:Mg:S:Hum.=23:9:5:2:6:15:2 with a coefficient of granule formation $\psi \geq 90\%$ was achieved with an average meaning of the heat carrier temperature difference at the entrence to the granulator and in fluidized bed $\Delta T=117^{o}C$. The obtained (resulting) product has a spherical shape, a uniform distribution of components at the micro level throughout the volume of granules, strength $\sigma \geq 35$ Newtons per granule that is more than 3 times higher than standard indicators. An increasing of the average specific load of bed's surface by moisture divided by the efficient temperature difference A_f =0,006–0,0066 $kg_{moisture}/(m^2 \cdot h \cdot deg)$ was achieved when applying a jet-pulsating hydrodynamic mode of fluidization.

The research results can be applied when creating an industrial equipment for production of humic-organic-mineral fertilizers with the use of mineral and organic nutrients. The use of sunflower ash in creating of new humic-organic-mineral fertilizers will provide rational usage of natural resources with the preservation of natural food chain and will improve the environmental safety as a result of recycling of wastes from fat and oil production.

Conclusions. The developed method allows to utilize wastes of sunflower oil production by their use in the producting of new complex humic-organic-mineral fertilizers.

Introduction

A dynamic development of food industry is accompanied by increasing of food products realization volumes, among which fat and oil industry occupies a special place [1] and is focused on the production of sunflower oil and allied products. Sunflower occupies more than 90% of the total oilseeds production in Ukraine and at least 10% of the sowing areas structure [2].

By-product of sunflower oil production is an oil meal and an oil cake that constitute 17–20% from the initial seed weight. However, in order to reduce an energy costs by the past 10 years almost all large oil and fat combines and oil-extraction plants of Ukraine have implemented technology of husk burning and pellets or briquettes from it, which is 80% or 312 tons per year.

Nevertheless, the quantity of residues (ash) after husk burning reaches up to 10% of the total volume – 31.2 thousand tons per year [3], which contains useful substances.

Thus, from an environmental point of view, the need for rational utilization of sunflower ash arises. The main components that belong to its composition, constitute 95.67% of the total mass, table 1, the rest (4,33%) are Zn, C, Co, Mn, Fe, Mo [4].

Table 1

The chemical composition of sunflower ash

Chemical compounds	K_2O	CaO	MgO	SO_3	P_2O_5
wt.%	31,40	19,07	18,58	13,68	10,94

Presence of potassium and phosphate components deficiency in soils, which increases significantly while growing sunflowers and ether-oil crops, stipulates an advisability of ash returning to an agricultural cycle in form of fertilizers. Moreover, a large removal of nutrients from the soils causes the necessity in restoration of their fertility. Therefore, one of the ways of using wastes from oil and fat industry after burning is the creation of organic-mineral fertilizers, into which structure nitrogen containing components and humic substances are additionally included.

There are known methods of a sunflower ash water solution granulation in rotating drum granulators [4–7]. However, the lack of nitrogen-containing components and humic substances reduces the effectiveness of of their use.

The firm "Ecoplant" [8] has organized a production of complex granulated fertilizers by pressing mixture, which is composed of sunflower ash, ammonium sulfate and humic-containing substance (brown coal). However, in this case the components distribution occurs at the macro level and the final product has a low strength and great ability to clumping. Furthermore, the addition of water causes the formation of calcium hydroxide, which reacts with ammonium sulfate or with carbamide and causes an intensive allocation of ammonia.

As world practice shows, the compensation of the soil fertility losses by means of using the mineral fertilizers with an increasing number of active substance up to 500 kg per hectare does not give desired results [9–12]. Therefore, the use of organic-mineral and especially humic-organic-mineral fertilizers, which contain nutrients of an organic origin refers to an effective ways of soil fertility preservation [13].

Materials and methods

To create a composite humic-mineral fertilizers containing NPK, macro and micro impurities of mineral and humic substances a method of obtaining solid humic and mineral fertilizers by dehydration of composite liquid systems in a fluidized-bed apparatus is developed [Patent of Ukraine 4465 IPC C05 G 1/01. A method for production of granulated organic-mineral fertilizers].

Thanks to a specially developed method and construction of the granulator realization of the granulation mechanism with a layer structure ensures a uniform distribution of mineral and organic components throughout the volume of granules [14].

The aim of experimental researches is determination of conditions of sunflower ash utilization and kinetic regularities of the process of obtaining granulated comprehensive organic-mineral fertilizers.

For studying the kinetics of a granule formation process was created the sample of an experimental-industrial equipment with a chamber of granulator size A×B×H = 0,1×0,3×1,5 m (Fig. 1), that was equipped with a special gas distribution device with sizes A×B = 0,1×0,3 m for creating a jet-pulsating regime of fluidization. [Patent of Ukraine 84680 IPC B01 J 8/44. Section of the fluidized bed apparatus].

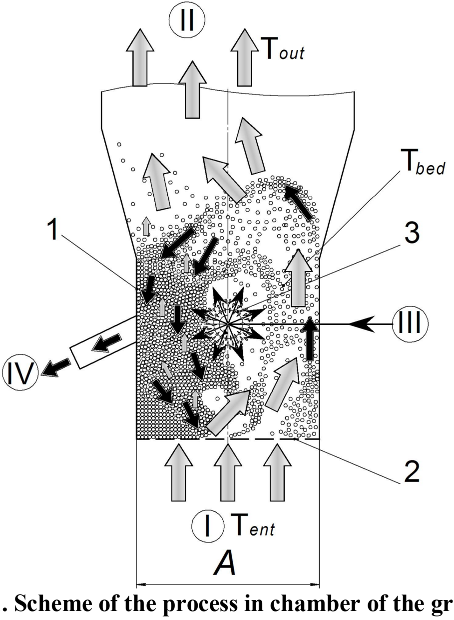
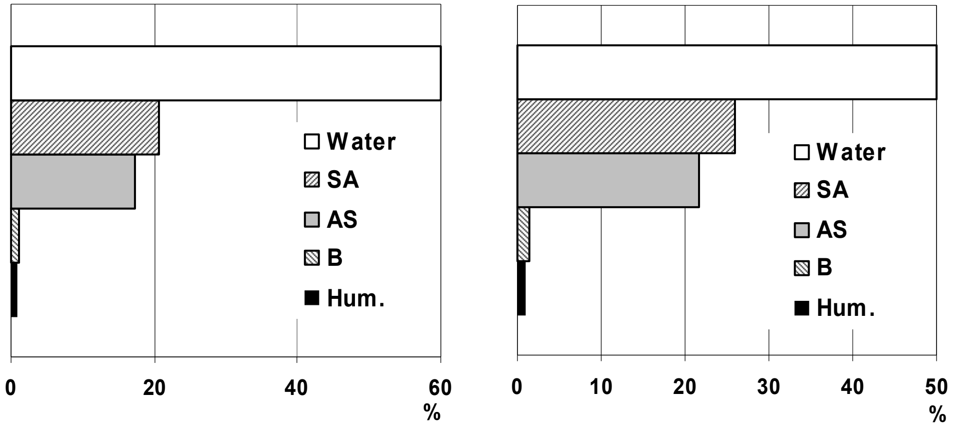


Fig.1. Scheme of the process in chamber of the granulator:
I – inlet heat carrier; II – outlet heat carrier;
III – initial solution; IV – granulated product;
1 – chamber of granulator; 2 – gas distribution device (GDD); 3 – dispergator;

As the heterogeneous liquid phase a water solution of ammonium sulfate (AS) with impurities of humates (H), sunflower ash (SA) and bentonite (B) was used.

All of the experiments were performed by the condition of keeping a constant bed mass in the chamber of granulator and was expressed by hydraulic resistance of bed ΔP_{bed}=1962 Pa (±50) which was fixed by indications of a differential manometer. Every excess of a granular material was unloaded from the bed of granulator.

An interaction of AS with a $Ca(OH)_2$ compound (which is formed when adding water to SA) in the initial solution causes the allocation of ammonia. To prevent this a certain amount of an acid must be added to it for the formation of useful calcium compounds. Beside this, in order to reduce deposition rate of the suspended particles of SA to the initial solution is added 15% of bentonite. Ratio of mass percent of dry components in the solution is [SA]:[AS]:[B]:[H]=25,6:21,4:1,5:1,0. The component composition of inlet liquid systems for dehidratation in apparatus with a fluidized-bed are given in Fig. 2.



a *b*

Fig. 2. Diagrams of the component composition of composite liquid systems:
a **– research №1;** ***b*** **– research №2**

Solids content in a liquid phase is determined by rheological properties of the initial solution and ensuring of the layering mechanism of granule formation with "onion" structure [15, 16].

From the point of view on dehydration efficiency of the process a water content must be reduced to its minimum (≤40%), but in this case there are difficulties with realization of the layering mechanism of granulation. Therefore, the influence of this parameter will be more thoroughly investigated in subsequent experiments, associated with development of a special unit of entering the initial solution.

As an initial granulation centers were used the granules with equivalent diameter D_e = 2,3 mm consisting of ammonium sulfate with impurities of humic substances [17].

Initial working solution III was injected in the fluidized bed by mechanical dispergator 3. Heat carrier temperature at the entrance to granulator ($T_{ent.}$) was maintained at the range $T_{ent.}$=200±10°C. The temperature of a layer of granular material (T_{bed}) was fixed by an electronic potentiometer and was holding in the set range $T_{bed} = 96 \pm 4$°C by injecting of a liquid phase III.

The coefficient of granule formation (ψ) was calculated by the equation, %:

$$\psi = G_{dry} / G_{g.p.} \cdot 100\%,$$

where $G_{g.p.}$, G_{dry} – productivity by a granulated product and by dry substances which are enjected to the apparatus with a liquid phase III respectively [18], kg/h.

Estimation of efficiency of the granule formation process when applying the hydrodynamic regime of fluidization is a value of specific load of the surface of bed by moisture [19] divided by the useful temperature difference (ΔT), $kg_{moist.}/(m^2 \cdot h \cdot deg)$:

$$A_f = G_{moist.}/(f_{bed} \cdot \Delta T),$$

where $G_{miost.}$ – moisture consumption enjected to the apparatus with an initial working solution III, $kg_{moist.}/h$; f_{bed} – the total surface of a bed of granular material, m^2; $\Delta T = T_{ent.} - T_{bed}$ – the useful temperature difference, °C.

A generalization of results of an experimental researches was carried out as a dependence of the coefficient of granule formation (ψ) from the complex $\Delta P_{bed}/(g \cdot D_e)$ and from the number of fluidization (K_w) – $\psi = f(\Delta P_{bed}/(g \cdot D_e); K_w)$, which allows to identify areas of rational realization of the process.

Results and discussion

Dynamics of changes of the equivalent diameter of granules D_e is shown in Fig. 3.

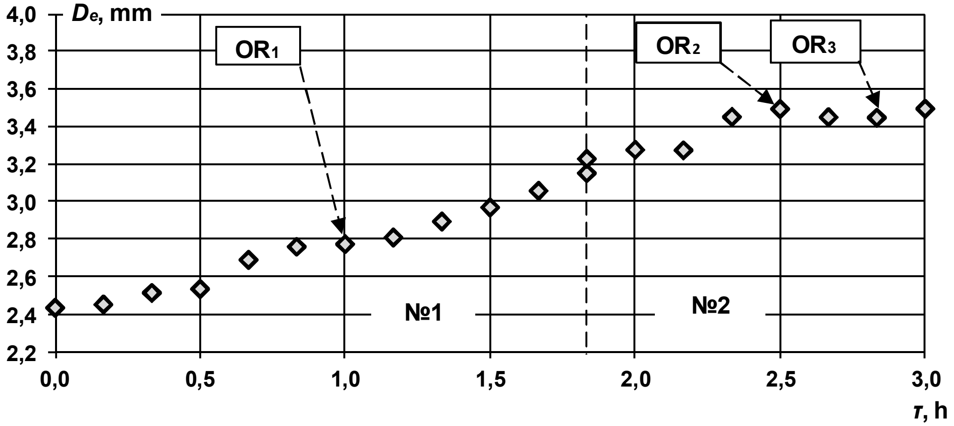


Fig. 3. Dynamics of changes of the equivalent diameter of granules $D_e = f(\tau)$: OR_1, OR_2, OR_3 – marks of the recycle ijection

When injecting a 40% initial water solution (research №1) there was a gradual increase of the granules diameter from D_e=2,43 mm to D_e=3,15 mm with a growth rate $+\frac{dD}{d\tau}$=0,35 mm/h, time $0,00 \le \tau \le 1,83$ h, which indicates a stable kinetics of granule formation, Fig. 3.

The layering mechanism of granule formation confirmed by the dynamics of changing of mass percent of certain fractions Fig. 4. Namely, in the considered time range a decrease of fraction +2,0 mm is accompanied by a corresponding increase of the next fraction by size – +3,0 mm.

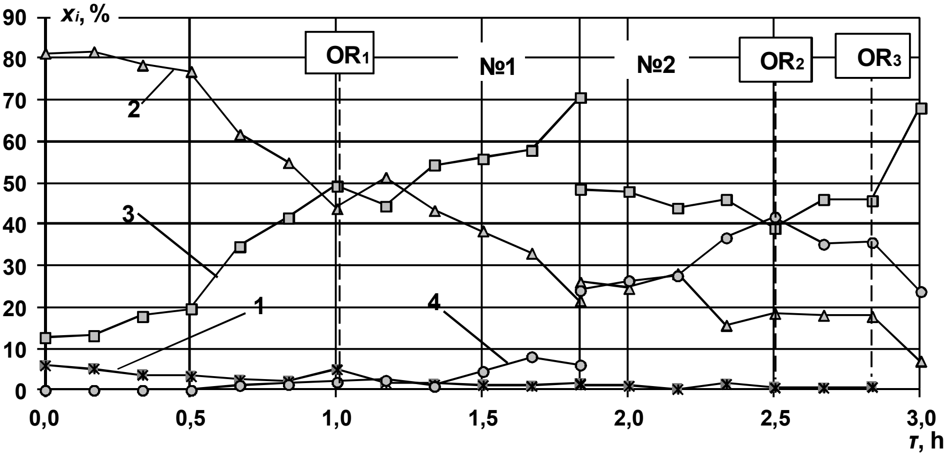


Fig. 4. Dynamics of changing in mass content percent of certain fractions $x_i = f(\tau)$ with the size of granules: 1 – +1,0 mm; 2 – +2,0 mm; 3 – +3,0 mm; 4 – +4,0 mm; OR_1, OR_2, OR_3 – marks of the recycle ijection

Injection of the outer recycle (OR) for stabilization of the dispersed composition at τ = 1,0 h (Fig. 3, 4) resulted the temporary increase of mass percent of the fraction +2,0 mm at τ = 1,17 h (OR_1). However subsequently, after τ = 1,17 h and to completion of the research №1 there was an increase of mass percent of fraction +3,0 mm to 70%, and the content of the fraction +2,0 decreased to 20%, Fig. 4. This gradual transition of granules from the smaller fractions to bigger ones demonstrates the layering mechanism of granule formation and the absence of crushing granules.

After τ=1,83 h D_e was instantly changed to 3,23 mm by injection of the outer recycle. A 50% initial water solution was injected for dehydration (research №2). However, further there was a gradual increase of the granules diameter from D_e = 3,23 mm to D_e = 3,49 mm with a growth rate $+\dfrac{dD}{d\tau}$ = 0,389 mm/h, time 1,83≤ τ ≤2,50 h, that increased proportionally with increasing concentration of the initial solution. After injection of OR_2 at time τ = 2,50 h was observed insignificant decrease of D_e to 3,45 mm was observed by increasing of a mass percent of fraction + 2,0 mm. A disperse composition of granules stabilized after τ = 2,66 h to D_e = 3,45 mm.

The feature of a granule formation process is that it was achieved a coefficient of granule formation $\psi \geq 90\%$ (Fig. 5) while was applying the jet-pulsating regime of fluidization with the number of fluidization $K_w \leq 1{,}43$ (Fig. 6).

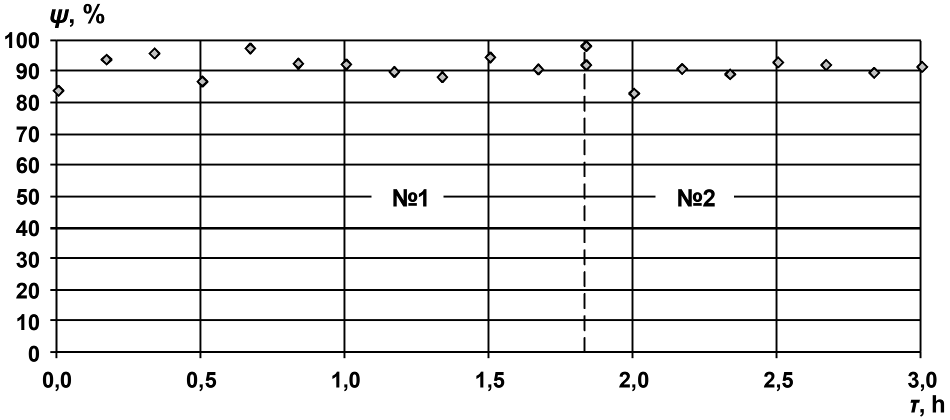


Fig. 5. Dynamics of changes of granule formation coefficient $\psi=f(\tau)$

Another advantage of application of the fluidization technology is possibility of injecting a heat carrier into the working area with a high temperature, which significantly exceeds the melting point of ammonium sulfate.

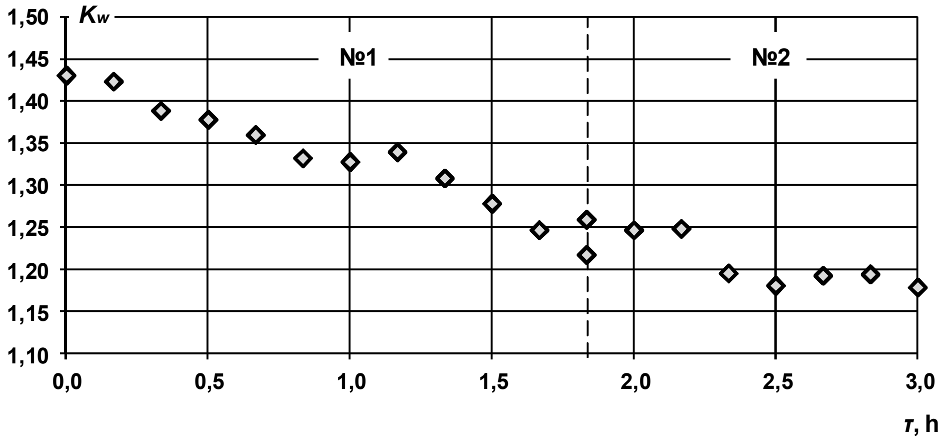


Рис. 6. Dynamics of changes of the number of fluidization $K_w=f(\tau)$

Dynamics of changes of a heat carrier temperature at the entrance to the apparatus, in a fluidized bed of granular material and the efficient temperature difference are shown in Fig. 7.

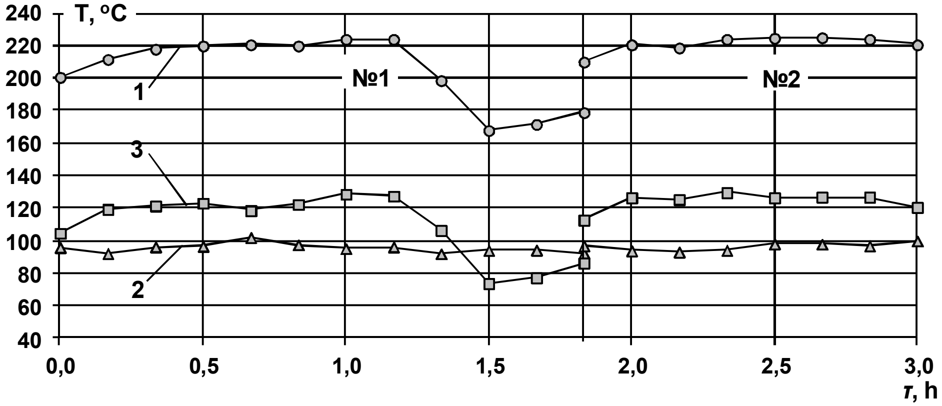


Fig. 7. Dynamics of temperature changes in the granulator:
1 – $T_{ent.}$ (temperature of heat carrier at the entrance to granulator); 2 – T_{bed} (temperature in a fluidized bed); 3 – ΔT (an efficient temperature difference ($\Delta T = T_{ent.} - T_{bed}$)).

The obtained values of the average specific load of the surface of bed by moisture divided by the efficient temperature difference A_f=0,006÷0,0066 $kg_{moist.}/(m^2 \cdot h \cdot deg)$ confirm the effectiveness of the applying of a jet-pulsating regime of fluidization (Fig. 8). However, it is necessary to repeat researches in future to confirm the results obtained in the research №2 in which the maximum value A_f is almost 2 times higher than a value thet ware obtained for the ordinary bubbling fluidization regime [20].

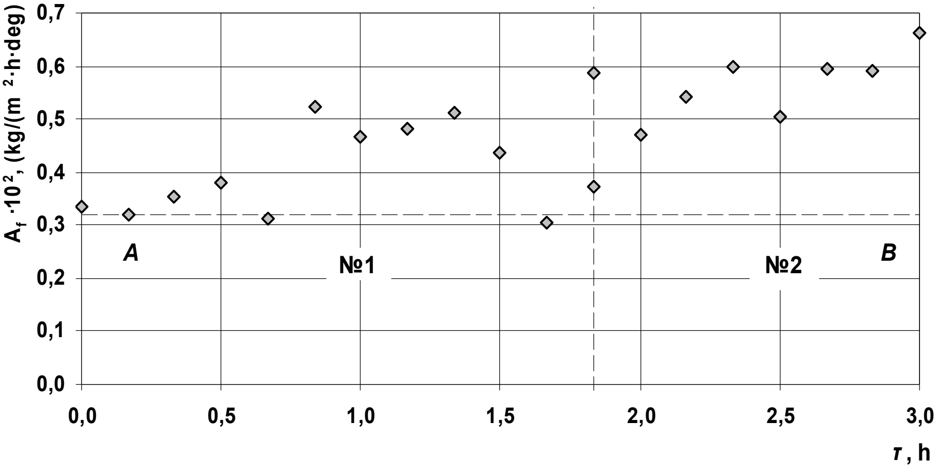


Fig. 8. Dynamics of changes of the average specific load of the surface of bed by moisture divided by the efficient temperature difference $A_f = f(\tau)$:
line *AB* – the maximum value of this parameter obtained for the bubbling regime of fluidization

A generalization of results of experimental researches was carried out as a dependence $\psi = f(\Delta P_{bed}/(g \cdot D_e); K_w)$, which allows to identify areas of rational realization of the process (Fig.9).

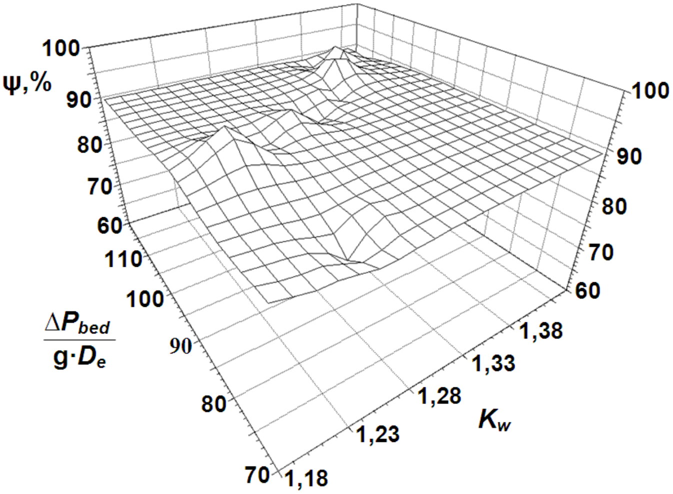


Fig. 9. Experimental dependence $\psi = f(\Delta P_{bed}/(g \cdot D_e); K_w)$

Thereby, values of the coefficient $\psi \geq 90\%$ achieves at $90 \leq \Delta P_{bed}/(g \cdot D_e) \leq 115$ with $2{,}43 \leq D_e \leq 3{,}15$ mm (research №1) and $68 \leq \Delta P_{bed}/(g \cdot D_e) \leq 75$ with $3{,}2 \leq D_e \leq 3{,}5$ mm (research №2) with value of the number of fluidization $1{,}2 \leq K_w \leq 1{,}4$.

A general view of the humic-organic-mineral fertilizers which contain K:N:Ca:P:Mg:S:Hum.=23:9:5:2:6:15:2 is shown in Fig. 10. A granular product has a spherical shape 2÷4% and strength $\sigma \geq 35$ Newtons per granule.

The granule cut is given in Fig. 11, which confirms the layering mechanism of granule formation.

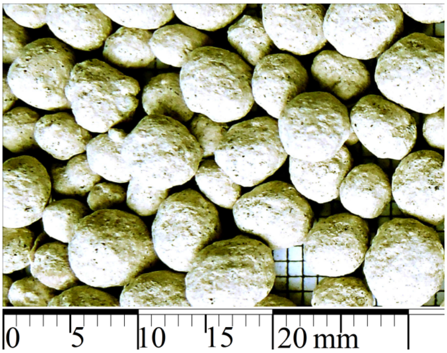


Fig. 10. A general view of the humic-phosphorus-calcium-nitrogen-potassium fertilizers with a stimulating action which contain: K:N:Ca:P:Mg:S:Hum.=23:9:5:2:6:15:2

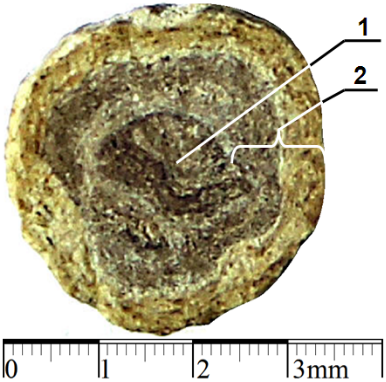


Fig. 11. The granule cut

In Fig. 11 is distinctly pronounced the center of granulation 1 (a nitrogenous-humic composite) with "onion" structure, around which is formed a multilayer structure from the new material 2 in the coaxial form.

Conclusions

The technological parameters of a stable kinetics of granulation process of the complex humic-organic-mineral fertilizers with a coefficient of granule formation $\psi \geq 90\%$ are established.

The obtained (resulting) product has a spherical shape with an equivalent diameter D_e=1,2÷4,5 mm, a uniform distribution of components at the micro level throughout the volume of granules and strength $\sigma \geq 35$ Newtons per granule that is more than 3 times higher than standard indicators.

Applying of the jet-pulsating hydrodynamic mode of fluidization allowed to increase an average specific load of the surface of bed by moisture divided by the efficient temperature difference to A_f = 0,006÷0,0066 $\text{kg}_{moist.}/(\text{m}^2\cdot\text{h}\cdot\text{deg})$, that allows to determine the area of an efficient mass transfer process.

For the first time completed studies for the first time allowed to determine the conditions of a sustainable process kinetics of the wastes recycling from the enterprises of fat and oil industry of Ukraine by continuous dehydration and granulation of fertilizers with set properties, obtained by dehydration of highly concentrated water solutions of sunflower ash and ammonium sulphate with impurities of humic substances.

References

1. (2015), Analiz pokazatelej hozjajstvovanija predprijatij maslozhirovoj otrasli Ukrainy, *Vestnik Plockogo gosudarstvennogo universiteta*, *Serija D – 2015*, pp. 74–79.
2. Derzhavna pidtrymka ukrayins'koho eksportu, available at: http://ukrexport.gov.ua/ukr/prom/ukr/156.html.
3. Michalik M. and Wilczynska-Michalik W. (2012), Mineral and chemical composition of biomass ash, *European Mineralogical Conference*, 1, pp. 423.
4. Paleckiene R., Sviklas A. M., Slinksiene R., Streimikis V. (2010), Complex Fertilizers Produced from the Sunflower Husk Ash, *Polish Journal of Environmental Studies*, 19 (№5), pp. 973-979.
5. Degrève J., Baeyens J., Van de Velden M., De Laet S. (2006), Spray-agglomeration of NPK-fertilizer in a rotating drum granulator, *Powder Technology*, 163, pp. 188–195.
6. Walker G.M, Holland C.R, Ahmad M.N, Fox J.N, Kells A.G. (2000), Drum granulation of NPK fertilizers, *Powder Technology*, 107, pp. 282–288.
7. Xue B.C., Hao Q., Liu T., Liu E.B. (2013), Effect of process parameters and agglomeration mechanisms on NPK compound fertiliser, *Powder Technology*, 247, pp. 8–13.
8. Ecoplant, available at: http://ecoplant.ua.
9. Romero-Díaz A., Marín-Sanleandro P., Ortiz-Silla R. (2012), Loss of soil fertility estimated from sediment trapped in check dams. South-eastern Spain, *CATENA*, 99, pp. 42–53.
10. Crusciol C.A.C., Artigiani A.C.C.A., Arf O., Filho A.C.A.C., Soratto R.P., Nascente A.S., Alvarez R.C.F. (2016), Soil fertility, plant nutrition, and grain yield of upland rice affected by surface application of lime, silicate, and phosphogypsum in a tropical no-till system, *CATENA*, 137, pp. 87–99.

11. Iqbal S., Guber A.K., Khan H.Z. (2016), Estimating nitrogen leaching losses after compost application in furrow irrigated soils of Pakistan using HYDRUS-2D software, *Agricultural Water Management*, 168, pp. 85–95.
12. Doan T.T., Tureaux T. H., Rumpel C., Janeau J.L., Jouquet P. (2015), Impact of compost, vermicompost and biochar on soil fertility, maize yield and soil erosion in Northern Vietnam: A three year mesocosm experiment, *Science of The Total Environment*, 514, pp. 147–154.
13. Korniyenko Y.M., Zahray Ya.M., Budzherak A.I. (2001), Zasady tekhnohennoyi bezpeky v ahropromyslovomu kompleksi Ukrayiny, Naukovi visti NTUU «KPI», 3, pp. 129-135.
14. Korniyenko Y.M., Hayday S.S., Semenenko D.S., Martynyuk O.V. (2013), Hranul'ovani azotno-kal'tsiyevo-huminovi tverdi kompozyty, modyfikovani bentonitom. Protses oderzhannya, Khimichna promyslovist' Ukrayiny, 5, pp. 46-51.
15. Vreman A.W., Lare V., Hounslow M.J. (2009), A basic population balance model for fluid bed spray granulation, *Chemical Engineering Science*, 64, pp. 4389-4398.
16. Srivastava S., Mishra G. (2010), Fluid Bed Technology: Overview and Parameters for Process Selection, *International Journal of Pharmaceutical Science and Drug Research*, 2(4), pp. 236-246.
17. Kornienko Y., Sachok R., Rayda V., Tsepkalo O. (2009), Mathematical Modeling of Continuous Formation Of Multilayer Humic-Mineral Solid Composites, *Chemistry & chemical technology*, 3 (№4), pp. 335–338.
18. Kornienko Y., Sachok R. (2008), Complex assessment of the efficiency of granulation process in dispersed systems, *Chemistry & chemical technology*, 2 (№3), pp. 217–220.
19. Kornienko Y., Sachok R., Tsepkalo O. (2011), Modelling of multifactor processes while obtaining multilayer humic-mineral solid composites, *Chemistry*, 20, pp. E19–E26.
20. Lim J.H., Bae K., Shin J.H., Kim J.H., Lee D.H., Han J.H., Lee D.H. (2016), Effect of particle–particle interaction on the bed pressure drop and bubble flow by computational particle-fluid dynamics simulation of bubbling fluidized beds with shroud nozzle, *An International Journal on the Science and Technology of Wet and Dry Particulate Systems*, 288, pp. 315–323.