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LIFE AND SCIENTIFIC PRIORITIES OF PROFESSOR MYROSLAV MALOVANYY

Nataliya Vronska

Lviv Polytechnic National University 12, S. Bandery Str., Lviv, 79013, Ukraine; dvnata81@gmail.com

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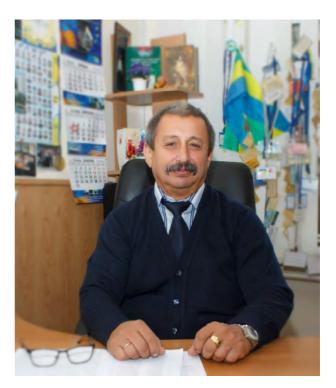
Abstract. This article describes the life and scientific priorities of professor Myroslav Malovanyy. It also provides details and results of a joint research with his students of a liquid media treatment from different types of pollution. The main research and its results are illustrated, as well as environmental technologies that were developed by using the archived results.

Key words: research, natural sorbents, adsorption, environmental technology, integrated processes.

Myroslav Malovanyy is an editor-in-chief of the "Environmental Problems" journal. He was born on August 13, 1957 in the town of Pidvolochysk, Ternopil region. In 1979 he graduated from Lviv Polytechnic Institute with a major in "Mechanical equipment for building materials plants". In 1984 he graduated from a postgraduate study at the "Processes and equipment of chemical plants" department of Lviv Polytechnic Institute, and in 1992 he defended his PhD on "Kinetics of phosphate leaching by a solution of nitric acid" - field of specialization 05.17.08 -Processes equipment of chemical and and petrochemical technologies. In 1997 he defended his Doctoral thesis on "Theoretical foundations of autocatalytic dissolution of sulphur processes and sodium polysulfide technology development": field of specialization 05.17.08 - Processes and equipment of chemical technology and 05.17.01 - Technology of inorganic substances.

After the graduation he was appointed to All-Union Scientific Research Institute of Sulphuric Industry (later, the Institute of Mining Industry, Lviv), where he worked his way through from the engineer to the head of the research department. In 1999 he was appointed the director of subsidiary JSC "Institute of Mining Industry" – "EKOHIMSERT", and in 2001 started to work as Professor at the department of "Chemical Engineering and Industrial Ecology" of Lviv Polytechnic University. In 2002 he was appointed the head of the "Ecology and Environment Protection" department (now Department of Ecology and Sustainable Environmental Management) where he is working up to this day.

Myroslav Malovanyy is a scientist and a public figure, his area of interest lies in the restoration and conservation of natural resources of Ukraine. Myroslav is an experienced teacher who is committed to training highly qualified scientific personnel. He takes a leading role in the environmental protection events: he also organized four international scientific congresses "Environment Protection", "Energy Saving", "Sustainable Environmental Management". He was a consultant for 3 Doctoral theses and a supervisor for 23 PhD theses.



Professor Malovanyi's scientific area is "The use of natural dispersed sorbents in environmental technologies". The results of his research were published in 611 scientific articles and presented at more than 160 international conferences; he also published 8 textbooks and 5 monographs on the topic of "Environmental Protection", developed and registered 28 patents.

Myroslav Malovanyy is a member of two Specialized Academic Councils for PhD and Doctoral theses in the field of specialization 21.06.01 "Environmental Security". He was also a member of the Presidium of the Commission of "Ecology, Environmental Protection and Sustainable Use of Natural Resources" of Ministry of Education and Science of Ukraine. He was among the developers of 3 standards of higher education in Ukraine.

Myroslav is the editor in chief of the journal "Environmental Problems", member of the editorial board of several international ecological journals "Sustainable Development" (Bulgaria), "Chemistry & Chemical Technology" and "Technology Audit and Production Reserves" (Ukraine), and also a number of Ukrainian scientific professional journals "Environmental Safety", "Environmental Safety and Sustainable Use of Resources", "EKOinform", "Journal of Lviv Polytechnic National University, edition "Chemistry, Technology of Materials and their Application".

Myroslav, together with his postgraduate students Zoriana Odnorig, Mykola Sannikov, Nedal Hussen Musalm Al Hasanat, Galyna Leskiv, Oksana Kyrychenko, Oleh Stokaliuk, Nazarii Ripak, Oksana Chaika, Vasyl Bunko, Natalia Holets, Natalia Tymchuk and Chornomaz, Ivan postdoctoral researchers Igor Petrushka and Halyna Sakalova studied aspects of natural sorbents in environmental technologies. Other aspects of environmental and chemical technologies were studied together with his Valerii postgraduates and students Chernov, Viyacheslav Larin, Eugen Dmitriev, Volodymyr Zarechenyi, Yurii Yatchyshyn, Roman Bat, Serhii Huhlych, Olena Kharlamova, Andrii Malovanyi, Mykola Basov, Maria Korbut, Vira Shandrovych, Natalia Vronska, Oleksandr Synelnikov, Kateryna Petrushka, Yurii Tulaidan, Andrii Sereda, Yurii Balandiuh and doctoral students Vasyl Diachko and Sergii Vakal.

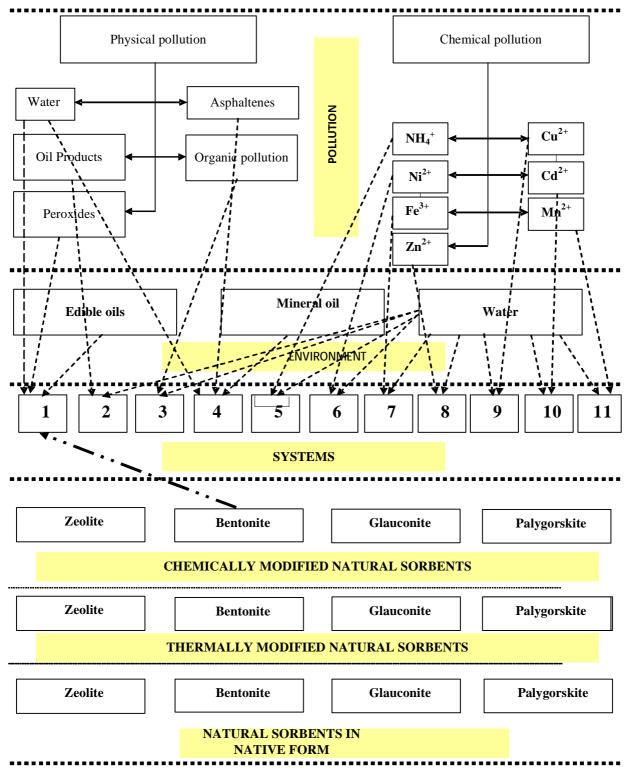
Myroslav Malovanyy's main scientific area is studying environmental technologies by using systems with natural sorbents. Based on the monitoring analysis of contaminated liquid systems formation, structural content, properties and methods of modifying natural dispersed materials, a structural and logic chart of contaminated liquid systems formation and possible ways of their treatment with the use of natural and modified dispersed sorbents was proposed [1] (Fig. 1). The chart is divided into 2 classifications that are combined by the lines showing possible and best connections. The top part of Figure 1 reflects the mechanism of polluted medium emerging; that is actually "breaks down" the studied medium into components: liquid medium vs components of contamination.

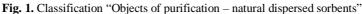
It should be noted, that for illustrational purposes the provided classification shows only simple cases, where the medium is polluted mainly by a single pollutant (excluding the known system 1, where purification of waste oils contaminated by water and asphaltenes were investigated, which corresponds to real conditions of contamination; and system 4, where cooking oil treatment from water and peroxide compounds was researched). The lower part of Figure 1 reflects the classification of the most widespread natural dispersed sorbents in native and modified form, which can be used to treat contaminated systems.

It should be noted, that for treating liquid mediums, the thermal modification is advisable to apply only in the case where the non-aqueous system should be treated, and the water itself acts as a contaminant. In the case of water systems purification, the use of thermal modification is not applicable. At the bottom of Figure 1, only one functional line is displayed and it corresponds to the use of chemically modified bentonite for cooking oil refining. Other researchers have proposed this functional line; and the optimal conditions for the treatment process were defined throughout many studies The optimal conditions for modification of Ukrainian bentonites with the aim of producing a high quality absorbent were determined.

In many cases, the treatment process can be implemented in several functional lines. The required degree of purification is achieved either through equivalent kinetic parameters and similar values of sorption capacity, or when the difference in these parameters is relatively small. In this case, the choice of a particular functional line for the process should be made taking into account the economic indicators (sorbent's cost for a particular location, which is mainly defined by a cost of sorbent preparation and transportation cost).

The suggested classification allowed to further develop theoretical and methodological foundation for effective treatment of liquid mediums by the adsorption method, including selection of sorbents and methods for their modification.





For the mathematical description of acid bentonite modification in the reactor with a mixer a mathematical model of the process was developed with consideration of the reagent concentration at any given time and the dynamics of the surface contact phase change. The identification of the research data of the developed mathematical model has confirmed its correctness and allowed to determine the value of the coefficient of linear correlation, which in its turn was used to determine the mass transfer coefficients and kinetic coefficient of surface contact phase change. The values of these coefficients are provided in Table 1.

Adsorption of hexane by natural sorbents (bentonite, glaukonite and paligorskite) was studied experimentally

[1, 3]. Adsorption kinetics curves and adsorption isotherms for 25 °C were built. It was found out that the adsorption process can be explained by the Henry isotherms. Using experimental data the Henry constants for the studied systems were calculated. The dependence of mass transfer coefficient from mixing intensity was found out. The methodology for calculation of the mass transfer coefficient was proposed. This methodology can be applied to evaluate its experimental value and calculate industrial processes. The methodology of determining the effective coefficients of inside diffusion during hexane sorption by natural sorbents and their numerical values have been developed. Using the methodology the coefficients were calculated for different sorbents at 25 °C: for bentonite $D = 4.52 \cdot 10^{-10} \text{ m}^2/\text{s}$; for paligorskite $D = 5.96 \cdot 10^{-10} \text{ m}^2/\text{s}$; for glaukonite $D = 1.08 \cdot 10^{-10} \text{ m}^2/\text{s}$.

Some aspects of the technology of wastewater treatment from organic dyes by adsorption of natural dispersed sorbents, – glaukonite and paligorskite,– have been studied [1, 4]. Based on theoretic analysis, a methodology for kinetic equation processing, which is based on integration method, has been developed. The kinetics of adsorption of the organic dye "anion green 8C" by natural dispersed sorbents, – glaukonite and paligorskite, – has been studied at different temperature and different starting concentration of the dye in synthetic wastewater. The analysis of the experimental data by using the known theoretical models has been conducted. Statistical coefficients of identification were calculated the analyses of which allows to make a conclusion that the adsorption on glaukonite is best explained by Redrich-Petersson, Tosa, Dubinin-Radushkevych and Langmuir-Freundlich models. The adsorption on paligorskite is best explained by Dubinin-Radushkevych and Langmuir-Freundlich models. The kinetic constants of adsorption of the "anion red 8C" dye on glaukonite and paligorskite were calculated and the fundamental technological scheme of wastewater treatment from dyes was developed.

Treatment of wastewater, groundwater and surface water from ammonium ions, oil and heavy metals was investigated by analyzing treatment technology from a point of an integrated process [5], which is the result of combining and optimizing of several successive processes. Based on combining treatment processes and and optimization of integrated processes, a methodological approach to research and development of economically feasible and environmentally safe technologies for wastewater and surface water treatment using natural sorbents was developed.

Adsorption properties of natural and modified sorbents for removal of ammonium, heavy metals and petroleum products were investigated and experimental data was fitted to theoretical adsorption models; the composition of environmentally safe and economically feasible natural and synthetic sorbents, to be used in the processes of surface water and wastewater treatment were justified. The combined processes of complex technologies for wastewater treatment by natural sorbents are illustrated in Table 2.

Table 1

Kinetic coefficients	Temperature °C	Number of revolutions of the reactor with a mixer, 1/s		
		1,6	4,2	5,8
Mass transfer coefficient (m/s)	60	6.0472 ⁻ 10 ⁻⁶	4.6688 ⁻ 10 ⁻⁶	11.659 [.] 10 ⁻⁶
	75	6.9368 ⁻ 10 ⁻⁶	9.5959 [.] 10 ⁻⁶	12.771 ⁻ 10 ⁻⁶
	90	11.1312 [.] 10 ⁻⁶	$16.9841^{-}10^{-6}$	19.278 ⁻ 10 ⁻⁶
Kinetic coefficient of surface contact phases change (1/s)	60	0.073	0.064	0.063
	75	0.047	0.053	0.054
	90	0.019	0.024	0.041
The coefficient of determination, R^2	60	0.8801	0.9219	0.9046
	75	0.8778	0.8846	0.8531
	90	0.9538	0.8608	0.9622

Results of calculations of bentonite modification kinetic parameters

Table 2

Processes which are combined in complex technologies of wastewater treatment using natural sorbents

	Treatment system combined of	Stage of the process				
	several stages	1st stage	2nd stage	3rd stage		
1	Treatment of surface water and wastewater from petroleum products by sorbents	Surface modification of natural sorbents	Hydrophobization of sorbents surface	Petroleum products sorption		
2	Ammonium removal from wastewater by adsorption on natural sorbents	Sorption on natural sorbents	Settling of used sorbents			
3	Ammonium removal from wastewater with pre- concentration by natural sorbents	Pre-concentration by ion exchange on natural sorbents	Regeneration of sorbents and eluate collection	Application of eluate for fertilizer production or treatment of it biologically with anammox process		
4	Heavy metals removal by adsorption on natural sorbents	Adsorption on natural sorbents	Flocculation and removal of used sorbents by settling			

Aiming at removal of pollutants to reduce the maximum allowed levels with a minimal cost of treatment, the main stages of the technology and the parameters of the processes were established.

Based on the experimental data on treatment of wastewater and surface water from petroleum products by natural sorbents the decrease of sorption capacity is decreasing in the series of the sorbents: iron containing modified clay, coquina and natural clay. The optimal parameters of oil and petroleum products on these sorbents were determined:

• Sorbent dose for iron containing sorbent ≥ 1 g/L; for coquina ≥ 4 g/L; for natural clay ≥ 10 g/L;

• Optimal contact time 1 h

• Optimal temperature range: for modified clay 20–40 °C; for coquina 10–30 °C

Sorption of petroleum products by hydrophobized sorbents was studied [5, 6]. Optimal content of hydrophobizing agent, dependence of sorption capacity from particle size and the most effective content of clay sorbent was determined. It was found out that the sorption process is best explained by three-parameter models, which are based on the theory of monomolecular adsorption and the removal of oil and diesel is best explained by multiparameter model of Marchevsky-Yaronc, which characterizes more complex sorption processes. Based on experimental investigations a fundamental technological scheme of treatment of water, polluted with petroleum products by particulate sorbents was proposed. The use of multi-stage sorption scheme with mechanical mixing allows to considerably decrease the dose of a sorbent due to better utilization of its adsorption capacity.

A technology of treatment of surface waters by application of hydrophobized clay sorbents was proposed. The first step of the technology is to separate the oil spill by floating containment booms in order to avoid further spreading of oil spill. If the spill volume is considerable, the oil should be collected mechanically before sorption process application. After that, the sorption treatment is applied by spreading a hydrophobized sorbent on water surface during 5-10 min. After oil sorption the sorbent creates agglomerates on the water surface, which should be mechanically removed from the water. The content and performance of natural, modified and hydrophobized sorbents with the aim of their application in the processes of treatment of wastewater polluted by oil were justified. It was shown that bentonite clay modified by iron (III) chloride is the most efficient sorbent for treatment of surface water from oil. The sorption capacity of the sorbent with a orisil content of 20 % is 2 g of petroleum product per 1 g of the sorbent. The most efficient hydrophobization is achieved when using oricil as a hydrophobizing agent in concentration of 10 % of the sorbent weight.

Lab- and pilot-scale studies of ammonium adsorption by natural sorbents (glaukonite, zeolite and paligorskite) were investigated [5, 7]. It was determined that sorption by zeolite and glaukonite could be explained by the linear part of the isotherm (Henry isotherm). Values of kinetic coefficients for these experiments were determined. Experimental data for adsorption of ammonium by paligorskite was analyzed by the developed program for identification of data by the known theoretic isotherms. Fitting of the experimental data showed that the process is best explained by the Langmuir isotherm. The maximum constants of ion exchange for the process of ammonium sorption by different types of sorbents were determined to be: for natural zeolite -3.61×10^{-5} 1/s; for paligorskite - 1.11×10^{-5} 1/s; for glaukonite – 0.278×10^{-5} 1/s. Based on the analysis of the performed investigations the optimal method of the used sorbent separation by gravitation was chosen. The optimal parameters of the settling process were determined.

The main processes of the integrated wastewater treatment technology of ammonium removal from wastewater by application of three stages – ammonium removal from wastewater by ion exchange, regeneration of the sorbents with concentrated ammonium solution production, and ammonium removal from the concentrate by either chemical precipitation with mineral fertilizer production or removal by the biological Anammox process [8] were investigated.

Ammonium removal from synthetic wastewater with the content similar to municipal wastewater was shown to be done most efficiently by cation exchange KU-2-8 resin, which is recommended for application for pre-concentration of ammonium from wastewaters with a high ratio of ammonium ions to hardness ions. It is recommended to apply natural zeolite to wastewater with low value of this ratio. The possibility and the expediency of application of the reagent method were confirmed for removing ammonia nitrogen from the reagent based on chemical interaction between ammonium ions with magnesium salts and orthophosphorus acid with its further removal from wastewater as poorly soluble magnesium ammonium orthophosphate MgNH₄PO₄· $6H_2O$ (struvite), which can be applied as a fertilizer. It was determined that the chemical method can be applied for simultaneous ammonium and phosphate removal reaching cleaning efficiency of 96.9 % an 99.7 %, respectively.

Results of the investigation of integrated processes of surface water treatment from heavy metals [5] have proven that maximal removal of chromium, nickel and zink ions by adsorption on bentonite is achieved during 30 min and almost complete removal after 8 h in constantly mixing conditions. Dosage of the flocculant – solution of polyacrylamide allows decreasing settling time by 20 min and increasing the level of settling by 30 % and, therefore, reaching the required level of environmental safety.

The recent research of Myroslav Malovanyy and his pupils (Vira Shandrovych, Natalia Vronska, Oleksandr Synelnikov, Kateryna Petrushka, Andriy Sereda, Yurii Balandukh) are focused on combination of biological treatment processes with sorption, physical and chemical treatment, investigation of prospects for biological degradation of organic substances with biogas production, search for effective ways of utilization of cyanobacteria and other biological and organic material pollution. The objects of investigation are municipal wastewater, landfill leachate, cyanobacteria, collected during vegetation period, organic waste. The goal of these investigations, which are the scientific goals of Myroslav Malovanye, is improvement of the state of environment, minimization of ecological risks and contributing to sustainable development of Ukraine.

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