Project 10

Title: Water Treatment and Waste-to-Energy Conversion by Plasma and Nanoparticles synergetic action on pollutant in water

PI: Anatoly Maltsev, Drexel University

Need and Relevance: Need to new approaches to solve existing technological problems in wastewater deep and cost-effective treatment from toxic inorganic pollutant (like heavy metal ions, etc.) and/or high concentrated organics (like landfill leachate) with waste-to-energy conversion. Current solutions are too expensive and have low effectiveness. Market niche for these solutions is extensive - estimated as more than \$1 Bln/year.

Goals: Development of effective and low-cost technologies for Water Treatment (WT) and Waste-to-Energy Conversion (WTEC) in selected directions.

Approach: Heavy hydrocarbons and other organics direct destruction by hard electrons using ADRE (corona, DB, gliding forms); AP/NP (generated inside water) synergetic action on pollutant with byproducts sorption by NP, following NP coagulation and treated water ultra-filtration.

Outcomes/Deliverables: ADRE/NP action study results/New technologies description and evaluation for toxic ions/organics removing, as well as for WTEC.

Project Duration, Budget: 24 months / \$100,000.00







Need and Relevance

Conventional wastewater treatment and waste-to-energy conversion technologies used on the market at present are not effective enough for some of types of wastewater.

For example – there are no technologies on the market for dissolved toxic ions (heavy metal ions, arsenic, fluoride, etc.) deep (down to residual concentration on the level of 0.05 mg/l and less) and low-cost (operation cost less than \$1/ton) removal from wastewater with chelating agents or with high concentration of some of organics (like in landfill leachate).

There is an extensive market niche (more than \$1Bln/year) for these solutions in the US and many other countries.

Conventional types of atmospheric plasma generated inside or nearby/through the treated water can sometimes result in effective plasma-chemical conversion of different pollutants in water (including pollutant molecules, atoms or ions partial oxidation) by chemical oxidation process or stimulation of some plasma catalytic processes. But, as a rule, such a pollutant conversion by conventional plasma is not effective enough for highly polluted water deep treatment.

As a result, there is an actual need for new approaches to solve existing technological problems in wastewater deep and cost-effective treatment from toxic inorganic pollutant (like HMI, etc.) and/or high concentrated organics (like landfill leachate) with waste-to-energy conversion.







Goals

The mentioned above, need and relevance is the reason to develop new effective and low-cost technologies for some types of wastewater treatment and waste-to-energy conversion to decrease energy consumption (operation cost) by wastewater treatment or even to generate net energy by such a process. These are our goals in the frame of the present project.

To reach these goals, we have formulated the following tasks:

- 1. Special Research Installation development, manufacturing, and assembling for a study of synergetic action on pollutant in water by different atmospheric plasma and nanoparticles generated inside air bubbles in water.
- 2. Landfill leachate BOD/COD ratio increasing (from 0.1 to 0.3 and higher) mechanisms investigation by atmospheric discharge of different types (corona, DBD, and gliding DRE, spark in air bubbles inside water) action on leachate.
- 3. Heavy metal ions removal mechanism investigation from water with high concentration of organic pollution (landfill leachate analogs).
- 4. The comparison of heavy hydrocarbons destruction effectiveness by discharges with runaway electrons and by oxidation using hydroxyl radicals. Evaluation of the approach to use any of DRE types for heavy hydrocarbon molecules conversion into syngas.







Discharge with **Runaway Electrons (DRE)** in dense gas. Corona type volumetric discharge.





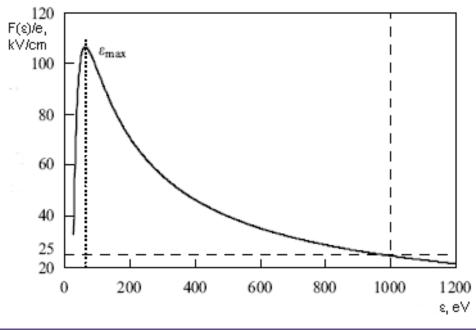




Runaway electrons in gas discharge

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 $d\varepsilon / dx = eE - F(\varepsilon)$ (1) $F(\varepsilon) = 2\pi e^{4}ZN \ln(2\varepsilon/\varepsilon_{i})/\varepsilon$ (2) $E_{c} = e^{3}ZN / (4\pi\varepsilon_{0}^{2}2.72\varepsilon_{i})$ (3)



- ε electron energy;
 x electron coordinate along the electric field with intensity E;
 - e electron charge;
 - N gas molecules concentration;
 - Z atom number;
 - ϵ_0 dielectric constant;
 - ϵ_i average energy of inelastic losses.





References

- 1. Korolev V S, Maltsev A N *Izvestiya VUZov, Series "Physics"* 2 7 1992
- 2. Korolev V S, Maltsev A N *Izvestiya VUZov, Series "Physics"* 6 67 1993
- 3. Korolev V S, Maltsev A N All-Russia conference "Physics and engineering of plasma ", Ryasan, Russia 1994
- 4. Korolev V S, Maltsev A N *SPIE Proceedings Series* 2619 94 1995
- 5. Maltsev A N Patent of RF # 2274923 by 01.09.2003



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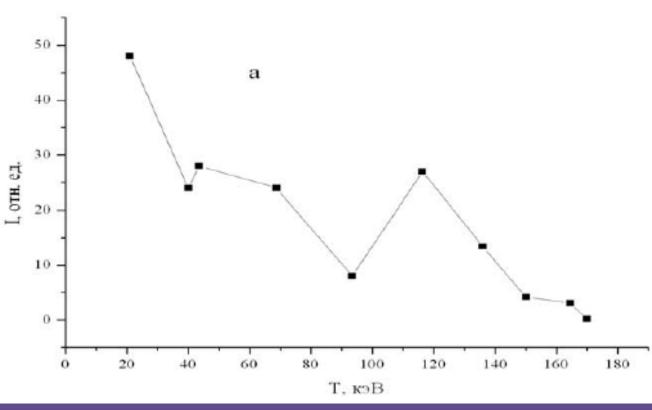






washington,

ELECTRON ENERGY DISTRIBUTION IN ADRE



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Electron energy distribution. High voltage pulse generator RADAN – 303, voltage amplitude on the gap is about 150 kV. (Tarasenko, et al, 2009).





Discharge with Runaway Electrons (DRE) in dense gas

Dielectric Barrier Discharge with Runaway Electrons

Gliding Discharge with Runaway Electrons

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Some results for the Approach # 1

Application for spore bacteria decontamination

Samples 1-7. ADRE-plasma with low current of runaway electrons and high average power shows good enough effectiveness of SA decontamination after 90 seconds of treatment. But for spore form bacteria (7) the same parameters made the unsterile result only.

The sterilization of spore form bacteria after 15 min treatment was made by ADREplasma with low average power but high specific current of runaway electrons (samples #8-10).

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First 5 samples have been seeded by vegetative form bacteria Staphylococcus Aureus with concentration 1 Mln/ml. The samples # 6-10 have been seeded by spore form of bacteria Licheniformis Subtilis with the same concentration (standard level for medical sterilization verification).

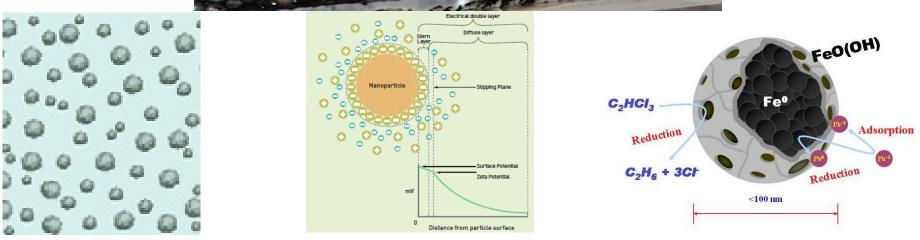
Nº of the ample	Type of the bacterium	Treatment duration, sec	Sterility result
	Staphylococcus		
1	Aureus	0 (control sample)	unsterile
	Staphylococcus		
2	Aureus	30	unsterile
	Staphylococcus		
3	Aureus	60	unsterile
	Staphylococcus		
4	Aureus	90	sterile
	Staphylococcus		
5	Aureus	180	sterile
6	Licheniformis Subtilis	0 (control sample)	unsterile
7	Licheniformis Subtilis	600	unsterile
8	Licheniformis Subtilis	900	sterile
9	Licheniformis Subtilis	1800	sterile
10	Licheniformis Subtilis	2700	sterile





Synergetic action of atmospheric discharge and nanoparticles generation in air bubbles inside water on pollutant (CONAP process)



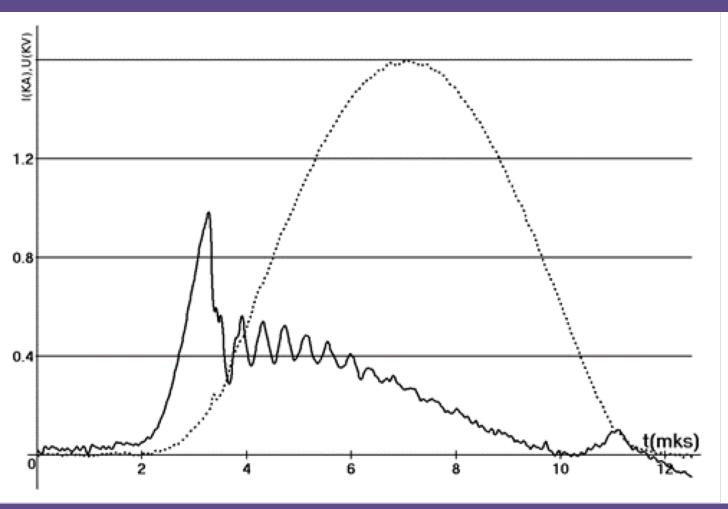


Hydrosol with nanoparticles (NP) Structure of layers around a NP in water Structure of a ferrum NP typical layers









Oscillograms of voltage between electrodes (positions 7, 8 on the WR picture, kV, solid line) and (kA, current stroked line) between these electrodes in WR at the average power consumption from power supply line 2.4 kW and pulse repetition frequency 700 Hz.







Formation of unsolvable iron chromate can be descend on reaction

$$2Fe(OH)_2 + Cr_2O_7^{2-} = 2FeCrO_4 + H_2O + 2OH^{-}$$
(4).

Cr(OH)₃ formation is possible by the following reactions

$$CrO_4^{2-} + Fe + 4H_2O = Cr(OH)_3 + Fe(OH)_3 + 2OH^-$$
 (5),

$$2CrO_4^{2-} + 3Fe + 8H_2O = 2Cr(OH)_3 + 3Fe(OH)_2 + 4OH^{-}$$
(6)

Hexavalent chromium ion reduction to trivalent ion is possible on reactions

$$Cr_{2}O_{7}^{2-} + 14H^{+} + 3Fe = 2Cr^{3+} + 3Fe^{2+} + 7 H_{2}O$$
(7),

$$Cr_{2}O_{7}^{2-} + 14H^{+} + 2Fe = 2Cr^{3+} + 2Fe^{3+} + 7 H_{2}O$$
(8),

$$Cr_{2}O_{7}^{2-} + 14H^{+} + 6Fe^{2+} = 2Cr^{3+} + 6Fe^{3+} + 7 H_{2}O$$
(9).

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Some results by the Approach #2

Results of the CONAP process application for heavy metal ions removing from water

- \mathcal{N}_{2} 3 (at the left) initial wastewater with ion concentration $[Cr^{6+}] = 49.6$ g/m^{3}
- N_{2} water # 3 treated by the CONAPprocess (before filtration);
- \mathcal{N}_{2} 1 (at the right) water # 2 after filtration. $[Cr^{6+}] = 0.01 \text{ g/m}^{3}$
- Effectivity of chromium removing is 99.98%. Maximal Permitted Level of $[Cr ^{6+}] = 0.05 \text{ g/m}^3$ for water reservoirs of communities.









Some results by the Approach #2

Results by the Approach # 2 application for heavy metal ions removing from wastewater



At the left – Initial wastewater with ion concentration $[Cr^{6+}] = 148 \text{ g/m}^3 + [Zn^{2+}] = 417 \text{ g/m}^3$ At the right - Treated wastewater. $[Cr^{6+}] = 0.015 \text{ g/m}^3 + [Zn^{2+}] = 0.010 \text{ g/m}^3$ Effectivity of Chromium removing is 99.99 %. Maximal Permitted Concentration of $[Cr^{6+}] = 0.05 \text{ g/m}^3$ for water reservoirs of communities. Effectivity of Zinc removing is 99.998 %. Maximal Permitted Concentration of $[Zn^{2+}] = 1.0 \text{ g/m}^3$ for water reservoirs of communities. c.oeap

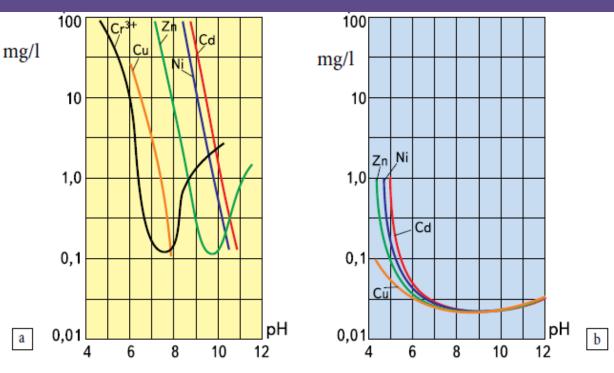




Some results by the Approach #2

The advantages of the CONAP process in comparison with conventional chemical reagent technology of treatment of without high water concentrations of organics:

1. The ability to remove all HMI by treated water pH of 8-9 from initial concentration level of 100-300 g/m³ to necessary 0.1- 0.03 g/m^3 .



Curves of heavy metal ions sedimentation from wastewater :

a)traditional CR technology; b) water treatment by hydrosol with Nano-Particles

The ability to reach residual concentration of HMI less than a precipitable product dissolved

concentration and less than Maximal Permitted Concentration for water discharge to a nature reservoir.



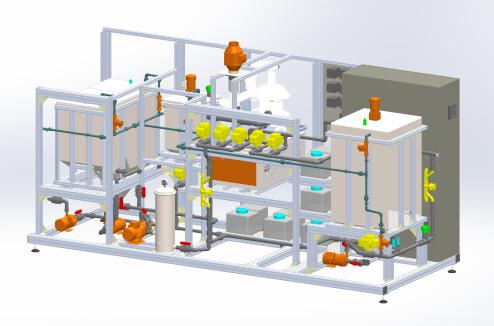


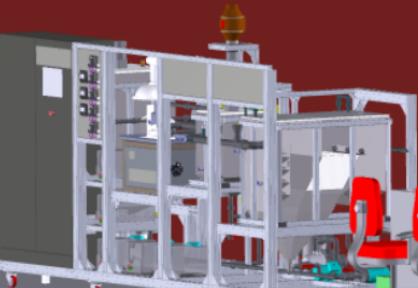




Outcomes/Deliverables

Task 1. First planned intermediate result is the Research Installation developed for the study of synergetic action of different type of plasma and different type of nanoparticles on pollutant in water.





Research Installation Development

3D model of a Research Installation (for Plasma and Nanoparticles synergetic action on pollutant in water) developed for heavy metal ions and organics removal from wastewater and landfill leachate. Automatic remote control of all processes





Outcomes/Deliverables

Task 2. The results of a landfill leachate BOD/COD ratio changing mechanism investigation by action on leachate with corona, DBD, and gliding DRE, as well as with spark in air bubbles inside water. 3D model development of pilot installation for leachate processing by most effective atmospheric plasma type.

Task 3. The results of physical and chemical mechanism investigation of heavy metal ions removing from water with high concentration of organic pollution (landfill leachate analogs). Technical description and economical evaluation of an optimal technological (industrial scale) installation for heavy metal ions removing down to residual concentration less than Maximal Permitted Level for water discharge into natural reservoir.

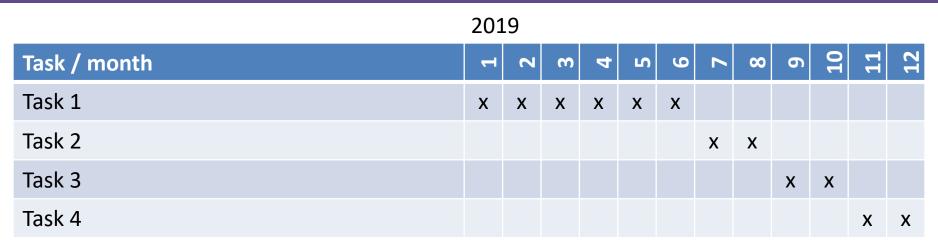
Task 4. The results of some heavy hydrocarbons destruction effectiveness measurement by atmospheric discharges with runaway electrons and its comparison with such a destruction effectiveness by oxidation using hydroxyl radicals. Technical description and economic evaluation of optimal technological line for heavy hydrocarbon or some other organic molecules conversion into syngas by the ADRE.







Project Timeline and Duration



2020

Task / month	H	2	M	4	Ŋ	9	2	∞	σ	10	11	12
Task 1												
Task 2	х	х	х	х								
Task 3					х	Х	Х	х				
Task 4									х	х	х	Х









Project Budget

Item	Cost			
Student stipend	\$ 0.00*			
Supplies	\$ 15,000.00			
Purchased services	\$ 10,000.00			
Equipment	\$ 60,000.00			
Travel	\$ 15,000.00			
Project total*	\$ 100,000			

*Stipends planned to be paid from some other sources





