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BIOREMOVAL OF TOXIC CHROMIUM(VI) VIA DARK HYDROGEN FERMENTATION OF MULTICOMPONENT ORGANIC WASTE

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Thermodynamic calculations allow determining optimal metabolic pathways for microbial extraction of toxic soluble hexavalent chromium compounds from contaminated sewage.

The purpose was to predict theoretically and confirm experimentally the possibility of hazardous Cr(VI) removal by hydrogen producing microbiome with simultaneous destruction of multicomponent organic waste and hydrogen synthesis.

The gas composition was determined by the standard gas chromatography method. The redox potential (Eh) and pH of the medium were measured potentiometrically. The Cr(VI) concentration was measured by a photocolorimetric method.

The multicomponent organic waste was effectively destroyed by hydrogen producing microbiome at the absence of chromium. The hydrogen fermentation cycle was not significantly inhibited by addition of Cr(VI). After complete microbial reduction of soluble CrO_4^{2-} to insoluble $Cr(OH)_3 \cdot nH_2O\downarrow$ the metabolic parameters returned to initial values.

The optimal pathway of microbial detoxification of toxic Cr(VI) compounds was thermodynamically predicted and experimentally confirmed. The high efficiency of Cr(VI) removal by strict anaerobic hydrogen producing microbiome via dark hydrogen fermentation of multicomponent organic waste was demonstrated. The obtained results can be used for development of novel environmental biotechnology of chromium-containing sewage purification and simultaneous destruction of environmentally hazardous organic waste as well as obtaining of eco-friendly energy carrier biohydrogen.

Key words: thermodynamic prediction, environmental biotechnologies, hydrogen fermentation, biohydrogen synthesis, toxic chromium(VI) compounds, microbial reduction of chromate, multicomponent organic waste destruction.

Chromium (VI) is one of the hazardous contaminant of the water and soil environment [1]. Human activity has caused the widespread distribution of chromium compounds in natural and man-made ecosystems [1–3]. Chromium is widely applied in the chemical and metallurgic industry, including production of refractory materials, electroplating, stainless steel formation, tanning agents and pigments production [4]. The environmental pollution by toxic chromium compounds is steadily increasing due to the accumulation of huge volumes of chromium-containing industrial sewage. For example, sewage from electroplating facilities contains toxic forms of hexavalent chromium — chromate and dichromate [5]. Ingestion of toxic sewage to natural ecosystems causes death of living organisms and drastic effects on human health [1, 6]. Chromium(VI) compounds have been found in different industrial sewage. The concentration of chromium(VI) in sewage ranges from 0.2 to 0.65 ppm [7]. The Cr(VI) concentrations were in the range of 0.00190 ± 0.0020 and 0.0010 ± 0.0006 ppm in the influent and effluent sewage samples respectively collected from Nacogdoches

Waste Water Treatment Plant (East Texas, USA) [8].

The toxicity of Cr(VI) for plants, animals, microorganisms as well as human is caused by high oxidizing potential and solubility of chromium, mobility across the membranes in living organisms with effects such as loss of membrane integrity or inhibition of the electron transport chain [1, 9]. Therefore, the development of effective methods for purification of aquatic and soil ecosystems from hexavalent chromium compounds is of a great interest to modern science and industry. Physico-chemical techniques of chromium containing sewage purification such as flotation, chemical precipitation, coagulation–flocculation, ion exchange and membrane filtration are efficient and rapid, but often require considerable economic costs and are environmentally hazardous [10]. The biotechnological techniques are industrially promising, cost-effective and environmentally friendly alternative ones. They are based on the microbial reduction of soluble chromium(VI) to non-toxic insoluble chromium(III) in the form of $Cr(OH)_3 \cdot nH_2O\downarrow$ [9]. For the first time, the possibility of microbial reduction of hexavalent chromium was shown for *Pseudomonas* spp. by Romanenko and Korenkov over 42 years ago [11]. It is known that microorganisms isolated from polluted industrial sites are able to reduce Cr(VI). The strain Cellulosi microbium cellulans DQ-4 (EU816697) isolated from metallurgical plants of Bagnoli (Naples, Italy) reduced Cr(VI) with high efficiency (92%) at the initial concentration of 50 ppm and was resistant to 150–250 ppm Cr(VI) [9]. Despite the considerable interest to the microbial methods of chromium extraction, scientists have not yet been able to develop biotechnology to completely purify contaminated sewage at high chromium(VI) concentration.

The accumulation of huge amount of organic waste is another global environmental problem today. First of all, they are hazardous due to the accumulation of toxic products of decay (hydrogen sulfide, mercaptans, NH_3, fatty acids) and proliferation of pathogenic microorganisms. Physico-chemical methods such as incineration, pelletisation, deposition at the landfill sites [12] are not capable to destroy enormous volumes of organic waste [13], since their rate of accumulation far exceeds the duration of their decomposition.

Herein, we propose the novel methodological approach for rapid and effective microbial purification of chromium-containing sewage and simultaneous destruction of multicomponent organic waste (MOW) with obtaining of high-energy carrier — biohydrogen. Biohydrogen is defined as molecular hydrogen obtained via the fermentation of organics.

Thus, the purpose of our study was to predict theoretically and confirm experimentally the possibility of hazardous chromium(VI) removal by hydrogen producing microbiome via dark anaerobic fermentation of multicomponent organic waste.

Materials and Methods

Thermodynamic prediction as a universal method to justify the possibility of microbial interaction with metals. Thermodynamic prediction was applied as the theoretical background to justify the possibility of Cr(VI)removal from sewage by hydrogen-producing anaerobic microbiome. It allows substantiating the most effective mechanisms of soluble toxic chromium(VI) ions detoxification by microbial reduction to insoluble chromium(III) in the form $Cr(OH)_3 \cdot nH_2O\downarrow$. The Pourbaix diagram (the diagram of the stability of the elements as aqueous electrochemical system in "pH-Eh" coordinates) was used as a basis for thermodynamic prediction of microbial interaction with chromium(VI) compounds [14].

Bioremoval of 50 ppm Cr(VI) during fermentation of model multicomponent organic waste. Effectiveness of chromium(VI) removal during hydrogen fermentation of MOW was determined using glass bioreactor (0.5 L). We used a spore-forming anaerobic hydrogen-producing microbiome (HPM) as the low-potential donor system. For this purpose, MOW were prepared as follows: 25 g of potato peels, 5 g of tomato tops, 5 g of apple peels, 10 g of rotten apricots, 5 g of meat (Fig. 1) waste and 10 g of granular microbial preparation (GMP) were mixed in a sterile bioreactor (0.5 L).

The GMP was developed as granular preparation containing selected from the digested sludge of methane tank community of spore-forming anaerobic hydrogen-producing microorganisms as well as nutrients and regulators of microbial metabolism.

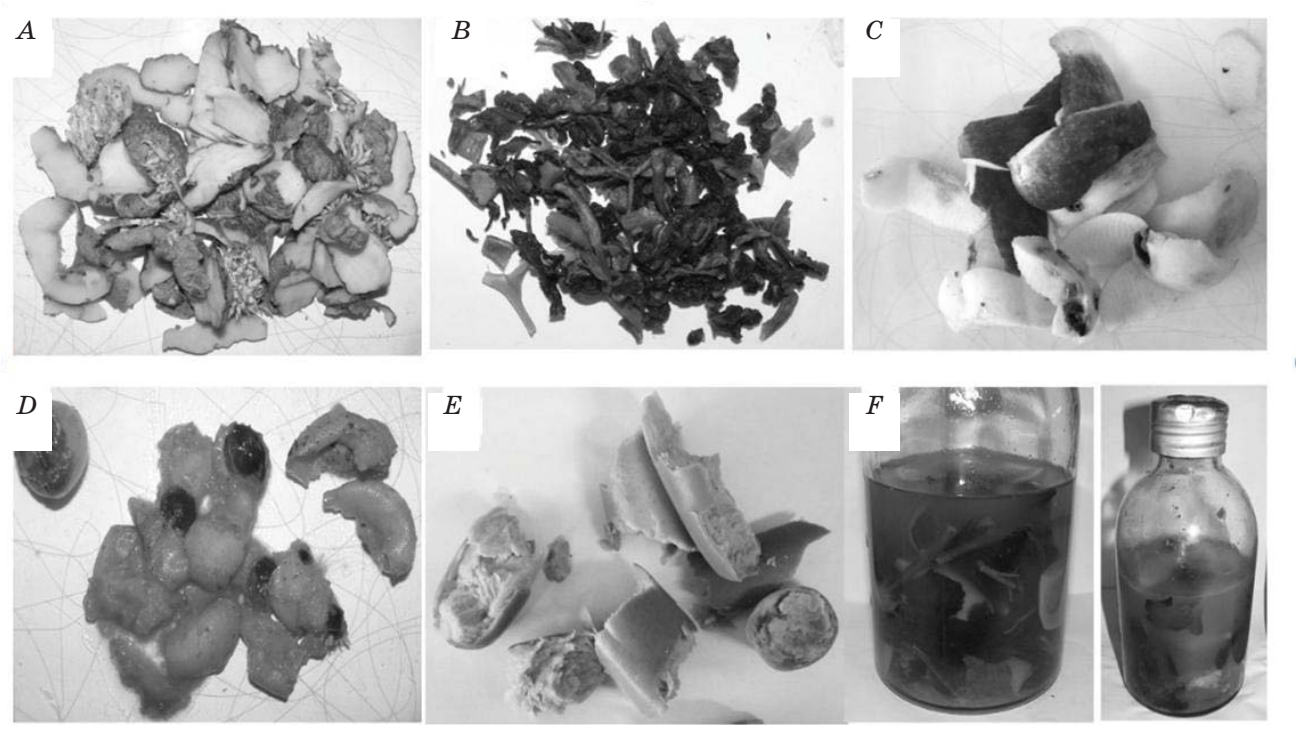

Fig. 1. **Mixture of model multicomponent organic waste for hydrogen fermentation:**
A — the potato peels; *B* — the tomato tops; *C* — the apple peels; *D* — the rotten apricots;
E — the meat; *F* — the glass bioreactor after waste loading

All components of model waste were also heated up for 20 minutes on water bath at 90 °C to eliminate of non-spore forming microorganisms and mixed with 250 ml of boiled tap water. Bioreactors were sealed by rubber stoppers with metal securers and cultivated at 30 °C during four days. The gas synthesized in the fermentation process was collected in the gas-holder. For this purpose, we used the gas-holder with rubber pipe and a needle. The rubber stopper of the bottle was pierced by the needle and the gas was transferred to gas-holder through the pipe, connected to the needle (Fig. 2).

Air was the initial gas phase in the bottles. Solution of $NaHCO_3$ was added to the reactor to provide values of pH close to pH = 7.0 for optimal pathway of fermentation of MOW.

Chromium(VI) solution was added to the glass bioreactor (500 ml) when microorganisms reached the final stage of metabolic activity. It was estimated by the decrease of hydrogen yield (concentration of H_2 in the gas phase of bioreactor decreased from 36% to 19%) and the redox potential began to rise. After that chromium solution was added to the bioreactor to the final concentration 50 ppm Cr(VI) in the form of K_2CrO_4 salt. The experiment was carried out in triplicate. Statistical analysis was carried out using Excel and Origin 8.5.1. software.

Bioremoval of 100 ppm Cr(VI) from liquid phase during final stage of fermentation of MOW. To investigate the possibility of microorganisms to remove 100 ppm Cr(VI) (in form of K_2CrO_4 salt) the liquid phase of anaerobic batch bioreactor (240 L) was collected [15]. The metabolically active culture liquid containing fermented MOW was sampled in the final phase (80 hours) of fermentation and used to investigate the dynamics of Cr(VI) removal.

For this purpose, 300 ml of culture liquid with low metabolic activity (the Eh increased to −120 mV, the H_2 concentration in the gas phase of bioreactor decreased) was sampled from the bioreactor (240 L) and transferred to the laboratory glass bioreactor (0.5 L). The gas phase (0.2 L) of the bioreactor was replaced by argon. The bioreactor was hermetically closed and cultivated at 30 °C during 12 hours to provide strict anaerobic conditions for optimal growth of hydrogen producing microorganisms. After that, chromium solution was added to the cultivation system to the final concentration 100 ppm Cr(VI).

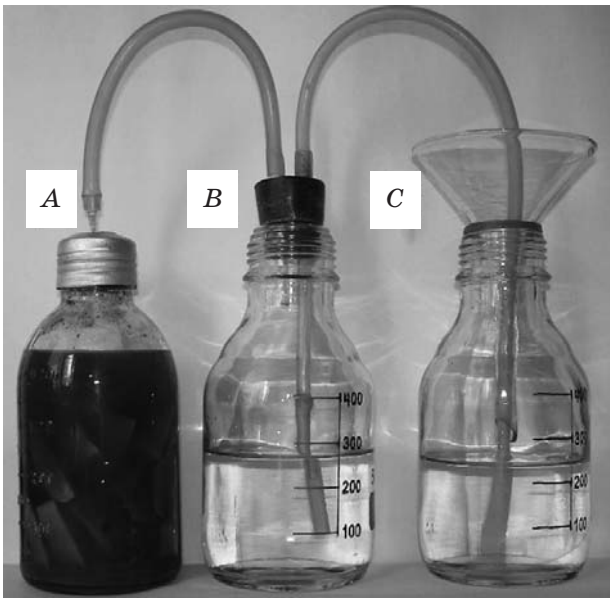

Fig. 2. **The measurement of the gas volume:**
A — the bioreactor; *B* — the gas-holder;
C — the water seal

The preparation of chromium solution and determination of Cr(VI) concentration. The solution of 30 000 ppm Cr(VI) was used as a stock. It was prepared by K_2CrO_4 salt dissolution in distilled water in the volumetric flask. The Cr(VI) concentration was determined by a colorimetric method with 1,5-diphenylcarbazide (DPC) in the range of 1.0–25.0 ppm Cr(VI). The method is based on the formation of colored violet complex caused by the interaction of chromium(III) compounds with DFCat the pH ≤ 1.0 [16].

The control of metabolic parameters of fermentation process. The concentration of hydrogen in the gas phase was analyzed by the standard gas chromatography method [17]. The chromatograph equipped with two steel columns — one (I) for the analysis of N_2, O_2, N_2 and CH_4, the second (II) — analysis of CO_2.

Parameters of column: I — l = 3 m, d = 3 mm, molecular sieve 13X (NaX); II — l = 2 m, d = 3 mm, with carrier Porapak-Q; column temperature — 60 °C, the temperature of evaporator — +75 °C, detector (katharometer) — +60 °C, the current detector — 50 mA. Carrier gas — argon, gas duct velocity — 30 cm^3/min.Volume of gas samples was: the first column — 2.5 cm^3, the second — 1 cm^3.

The redox potential (Eh) and pH of the medium were measured potentiometrically. For this purpose, the determination of pH and Eh was performed using an EZODO MP-103 universal ionomer with remote electrodes and a temperature sensor. To measure pH and Eh, we used the combined electrodes with BNC connectors — PY41 and PO50 models, respectively. Before the measurement the electrodes were tested by convention standard buffer solutions. For pH check conventional pH-buffer solutions were used: solution of $KHC_2O_4H_2C_2O_4{\cdot}2H_2O$ (pH = 1.68); mixture of NaH_2PO_4 and K_2HPO_4 (pH = 6.86); $Na_2B_4O_7{\cdot}10H_2O$ (pH = 9.18). Standart pH-buffers were prepared according to the producer's manual (OJSC "Kyiv plant RIAP"). For the validation of Eh measurement three buffer solutions were used. The first one was ferricyanide, with Eh = +273 mV (13.5 g/l $K_3[Fe(CN)_6]$ and 3.8 g/l $K_4[Fe(CN)_6].3H_2O$), The first one was Fe(II) citrate (10.0 g/l with Eh = –150 mV and the third one was Ti(III) citrate (15.0 g/l) with Eh = –440 mV [18].

The following metabolic parameters of MOW fermentation were controlled: 1) duration of fermentation period (*T*, days); 2) biohydrogen yield (L); 3) coefficient of waste destruction (*Kd*) meaning the ratio of initial and final weight of waste [19].

Results and Discussion

The following theoretical positions are the basis for the development of novel biotechnologies of chromium containing sewage purification. All metabolic oxidation-reduction processes are carried out by microorganisms in

the field of thermodynamic stability of water (Fig. 3). In neutral conditions (pH = 7.0) water is stable in the range of standard values of the redox potential E_o' from −414 to +814 mV. The lower limit of water stability is determined by the reversible reaction of proton reduction to molecular hydrogen: $2H^+ + 2\bar{e} = H_2$; $E_o' = -414$ mV. The upper limit of water stability is determined by the reversible oxidation reaction of water oxygen to molecular oxygen: $2H_2O = O_2 + 4H_+ + 4\bar{e}$; $E_o' = +814$ mV (Fig. 3, *a*). In case when the redox potential of the aqueous solution is higher than +814 mV, the oxygen of the water acts as a reducing agent. It is oxidized to O_2, and the Eh returns to the initial value +814 mV. In case if the potential is lower than −414 mV, the proton of water acts as an oxidizing agent. It is reduced to H_2 (Fig. 3, *b*). Water acts as a binary redox buffer that is stable in the range of the standard redox potentials from −414 to +814 mV [14, 16]. In accordance with our hypothesis microbial growth in the presence of the oxidized forms of toxic metals and interaction with them are theoretically permissible if the redox potential of the system formed by the metal and its reduced form is inside of the field of thermodynamic stability of water [16].

Herein, our methodological approach is based on the thermodynamic justification of the optimal microbial metabolic pathway to reduce high potential CrO_4^{2-} ($E_o' = +555$ mV) to insoluble non-toxic $Cr(OH)_3 \cdot nH_2O\downarrow$ and low potential ($E_o' = -414$ mV) anaerobic destruction of organic waste with obtaining high-energy carrier — biohydrogen.

The oxidation levels of soluble form of chromium are +6, +3 and +2 (Fig. 3). Chromium in the +2 level is the reducing agent. It reduces H^+ of water to molecular H_2

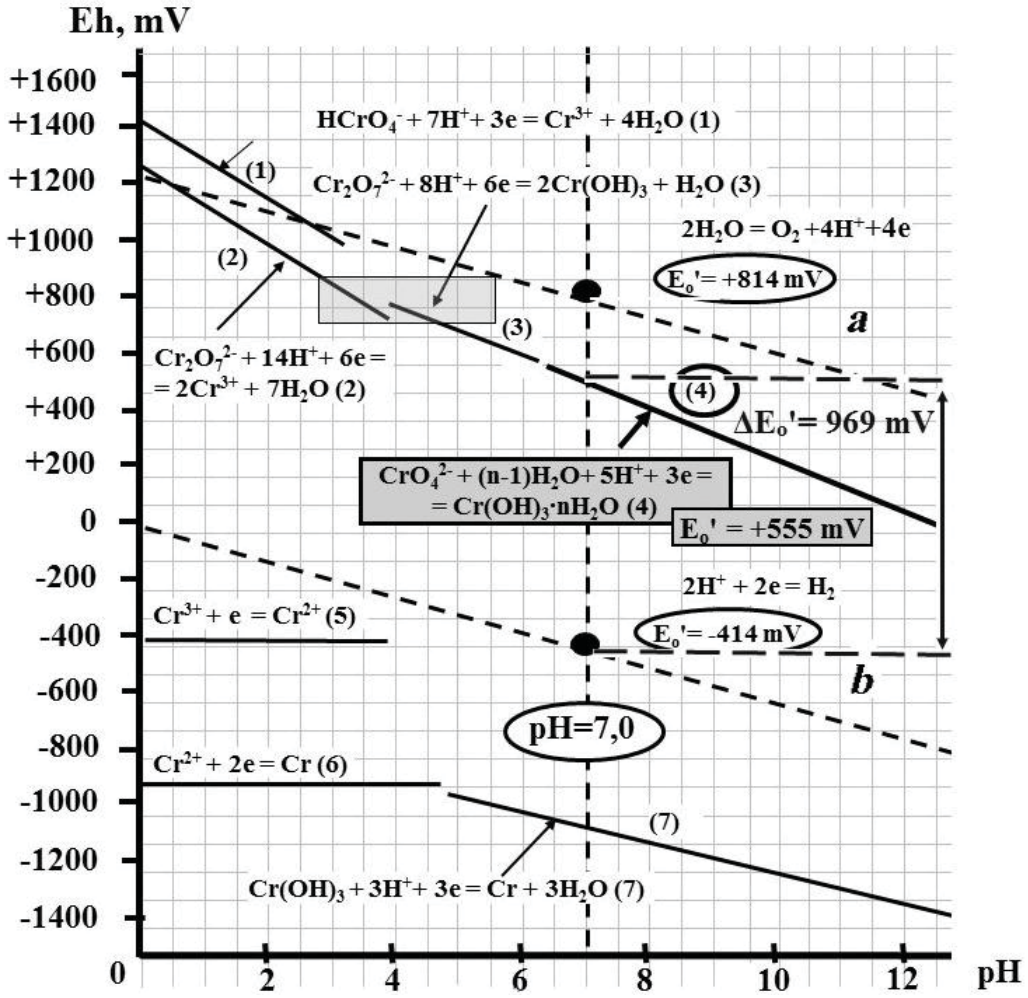

Fig. 3. **The Pourbaix Diagram showing thermodynamic stability of chromium redox-forms in solutions: upper and lower limits of stability are determined by reactions *a* and *b***

(Fig. 3, No. 5). In the +6 state it is a powerful oxidizing agent, because the redox potential of hexavalent chromium compounds is very high (Fig. 3, reactions No. 1–4) [20]. For example, the standard redox potential (E_0') of the reduction of Cr(VI) to Cr(III) is +555 mV (Fig. 3, reaction No. 4).

Chromium in the +6 level is considerably important due to its carcinogenicity and toxicity to living organisms [9]. In aqueous solutions Cr(VI) can exist in different forms ($HCrO_4^-$, $Cr_2O_7^{2-}$,CrO_4^{2-}) depending on the value of pH (Fig. 3, reactions No. 1–4). The precipitation of chromium(VI) by microorganisms is impossible, because the insoluble chromium(VI) compounds do not exist. Therefore, the reduction of CrO_4^{2-} to insoluble $Cr(OH)_3 \cdot nH_2O\downarrow$ is theoretically acceptable and suitable microbial pathway of toxic chromium(VI) removal from solutions. The Eh of this reaction is +555 mV and it takes place within the field of water stability. This reaction (Fig. 3, reaction 4) is limited by pH value that should not be lower than 6.5 (Fig. 3) [16]: $CrO_4^{2-} + (n-1)\cdot H_2O + 5H^+ + 3e = Cr(OH)_3\cdot nH_2O\downarrow$, $E_o'(pH \geq 6{,}5) = +555$ mV (Fig. 3, reactions No. 4).

Thus, the redox potentials of the reaction underlying the microbial removal of chromium(VI) is inside thermodynamic stability of water field (Fig. 3).

As it follows from our theoretical positions, microorganisms can realize only those reactions of interaction with metals which redox potential is inside of the field of thermodynamic stability of water (Fig. 3). Consequently, the reactions No. 1, 2, 3, and 4 are theoretically acceptable, and reactions No. 5, 6, and 7 are inaccessible to microorganisms. Thus, microorganisms can reduce chromium(VI) compounds only to Cr(III). Further reduction of Cr(III) to Cr(II) and Cr(0) by microorganisms is impossible. All compounds of Cr(VI) are the strongest oxidizing agents that explains their high toxicity to microorganisms (Fig. 3, reactions No. 1–4). Detoxification of chromium(VI) compounds is possible only via their removal from aqueous solutions by microorganisms. It is known that the removal of metals is possible both via the formation of insoluble compounds (hydroxides, carbonates, sulfides, etc.) without changing their valence as well as via the reduction to insoluble compounds [16, 21]. However, insoluble chromium(VI) compounds do not exist. All Cr(VI) compounds are stable in the form of anions $HCrO_4^-$ (pH = 0.0...3), $Cr_2O_7^{2-}$ (pH = 0.0...6.0), CrO_4^{2-} (pH = 6.0...12.0) and do not precipitate in the form of sulphides, carbonates in a wide range of pH (0.0... 12.0). This clearly implies that removal of Cr(VI) anions from solutions is possible only via reduction to insoluble compounds, for example, $Cr(OH)_3\cdot nH_2O\downarrow$ (Fig. 3, reaction No. 4). This mechanism of chromate removal is possible only in neutral or slightly alkaline conditions, because under acidic conditions (pH ≤ 4.0), the Cr(VI) compounds will be reduced to soluble Cr^{3+} cation (Fig. 3, reaction No. 5). It is known that the effectiveness of redox reactions is proportional to the potential difference between the donor and acceptor systems [22]. Obviously, the hydrogen producing strict anaerobic microorganisms create the lowest redox potential (Eh) of the donor system. Thus, microorganisms create $\Delta E_o' = -414$ mV via hydrogen fermentation of carbohydrates (starch, etc.). The redox potential difference between the donor and acceptor systems is maximum ($\Delta E_o' = 969$ mV) in the related redox reaction:

$$H_2 = 2H^+ + 2e; (E_0' = -414 \text{ mV})$$

$$CrO_4^{2-} + (n-1)\cdot H_2O + 5H^+ + 3e =$$

$$= Cr(OH)_3\cdot nH_2O\ (E_0' = +555 \text{ mV}).$$

According to the thermodynamic calculations dark hydrogen fermentation is shown to be the most effective pathway of soluble Cr(VI) detoxification. Therefore we suggest the removal of toxic CrO_4^{2-} via fermentation of model multicomponent organic wastes by anaerobic hydrogen producing microbiome as the most effective pathway.

Our model organic waste is multicomponent and simulates real municipal waste because it contains substrates of both plant and animal origin. The microbiome that produces hydrogen includes microorganisms of the genus *Clostridium* [23], *Bacillus, Enterobacter, Enterococcus* [24, 25], *Escherichia* [26–28], etc. The GMP was used as the inoculum, the fermentation of the waste and CrO_4^{2-}bioremoval occurred by spore-forming microbiome. Most likely, it consisted mainly of two genus of microorganisms — *Clostridium* and *Bacillus*.

In our investigation, HPM have carried out rapid and effective MOW fermentation in 0.5 L bioreactor in control conditions (without chromium) with simultaneous regulation of microbial metabolism (Fig. 4, *A*). This was evidenced by the redox-potential (Eh) decrease from +325 mV to −320 mV

during the first 32 hours of MOW fermentation and high concentration of H_2 (36%) in the gas phase of the bioreactor. The pH value was decreased from 7.15 to 5.0 after 24 hours of cycle. Then it was adjusted and stabilized in the range 6.5–7.3 to preserve optimal conditions for MOW destruction and simultaneous hydrogen production (Fig. 4, *A*). The MOW was effectively destroyed by hydrogen producing microbiome in control conditions at the absence of chromium(VI). The following parameters were obtained: biohydrogen yield was 81 L/kg of solid organic waste, coefficient of waste destruction $Kd = 92$.

change after addition of 50 ppm Cr(VI). It was in the range 25–26% after complete chromium(VI) bioremoval (Fig. 6, *A*). Under these conditions, the H_2 yield was 75 L/kg of solid food waste, coefficient of waste destruction $Kd = 83$. Thus, the process of fermentation was not significantly inhibited by 50 ppm Cr(VI) (Fig. 4, *B*, Fig. 6, *A*). The H_2 yield and efficiency of waste destruction (Kd) were decreased on 7% and 10% consequently. The duration (T) of fermentation cycle in both variants of the experiment was 82 hours (Fig. 4).

The active synthesis of gas, the formation of foam, as well as the intensive destruction of

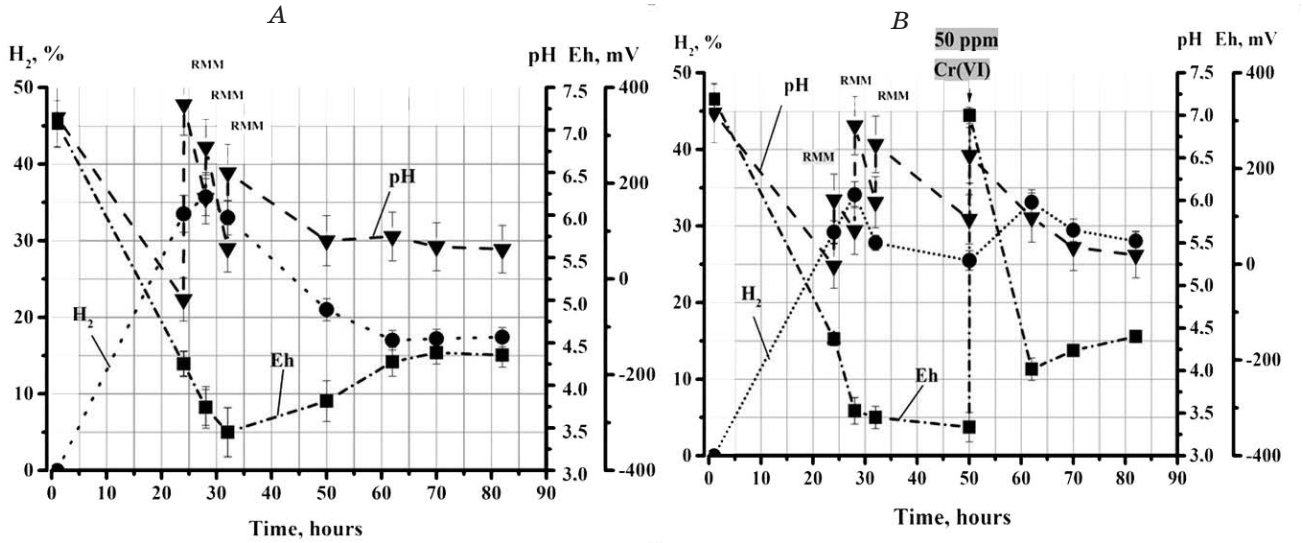

Fig. 4. **The efficiency of solid waste fermentation in control conditions without Cr(VI) (*A*) and at the presence of 50 ppm Cr(VI) (*B*)**
(RMM — the points indicate when the regulators of microbial metabolism were added)

As it was expected, the addition of 50 ppm of Cr(VI) in the form of $K_2Cr_2O_4$ at the beginning of the final phase of fermentation (50 hours) caused a rapid increase of the Eh from −320 mV to +311 mV (Fig. 4, *B*; Fig. 6, *A*). However, the redox-potential was autoregulated by HPM and decreased from +311 mV to −5 mV after 1.5 hours of 50 ppm Cr(VI) addition (Fig. 6, *A*). It should be noted that microorganisms overcame the negative effect of high-potential CrO_4^{2-}. Hydrogen fermentation resumed after Cr(VI) reduction.

The pH increased from 5.7 to 6.5 immediately after the addition 50 ppm of Cr(VI), but the medium was acidified to 5.8 and 5.36 at 62 and 82 hours consequently during further fermentation (Fig. 4, *B*). The concentration of H_2 did not significantly

solid particles of waste in both variants of the experiment (Fig. 5) also indicated the absence of inhibition of the fermentation process by the addition of 50 ppm Cr(VI).

At the same time, the high efficiency of 50 ppm Cr(VI) removal by HPM was demonstrated in our study (Fig. 6, *A*). The concentration of soluble chromium(VI) was decreased from 50 ppm to 27 ppm after only one hour of fermentation. The efficiency of Cr(VI) bioremoval was 100% after 53 hours of waste fermentation (Fig. 6, *A*). The removal of Cr(VI) from the solution is suggested to take place due to its reduction. It is evidenced by the appearance of grey precipitate typical for Cr(III) hydroxide, i.e $Cr(OH)_3 \cdot nH_2O\downarrow$.

To investigate the effectiveness of Cr(VI) bioremoval during the final phase of hydrogen

fermentation of solid multicomponent organic waste by liquid phase (i.e. culture medium) was important issue of our research. The final parameters of the end fermentation process in large bioreactor (240 L) testified to the decrease of metabolic activity of microorganisms. The concentration of H_2 in the gas phase of the bioreactor decreased from 36% to 19%, the value of the Eh increased from −340 mV to −120 mV, as well as the gas volume increase was ended. After that the liquid phase was sampled (after 80 hours of fermentation of MOW) into the glass bioreactor (0.5 L) and cultivated for 12 hours at 30 °C to renew the partial metabolic activity of the HPM. Despite the weak metabolic activity, the microbiome showed high reductase activity and produced H_2. The initial parameters before the addition of Cr(VI) were as follows: Eh = −190 mV, 16% of H_2 (Fig. 6, *B*), the absence of gas volume synthesis as well as the complete destruction of solid particles of waste. The parameters indicated the final phase of dark hydrogen fermentation of MOW. As expected, the addition of 100 ppm of Cr(VI) causes the high potential stress for strict anaerobic hydrogen producing microorganisms (Fig. 6, *B*). The addition of 100 ppm Cr (VI) caused an increase of the redox potential from −190 to + 325 mV. Then, the concentration of Cr(VI) has decreased to analytical zero (over

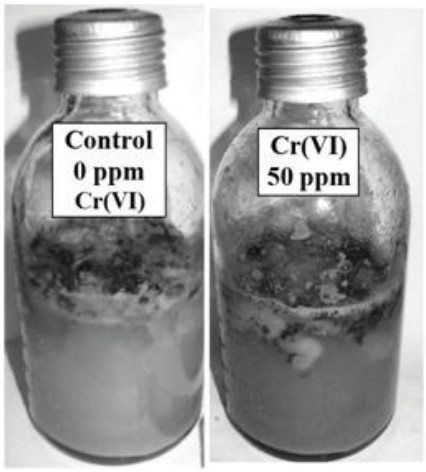

Fig. 5. **The absence of inhibition of MOW fermentation by toxic hexavalent chromium compounds (70 hours of fermentation)**

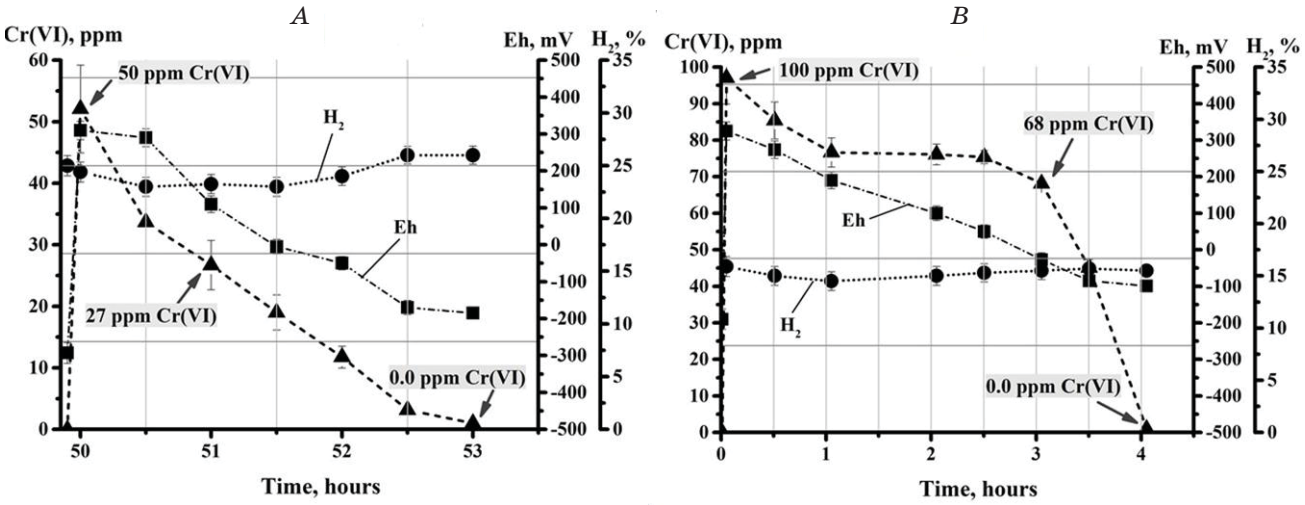

Fig. 6. **Bioremoval of Cr(VI) during final phase of hydrogen fermentation of multicomponent food waste:** *A* — addition of 50 ppm Cr(VI) to the glass bioreactor (0.5 L) after 50 hours of hydrogen fermentation; *B* — addition of 100 ppm Cr(VI) to the liquid phase sampled from bioreactor (240 L) after 80 hours of hydrogen fermentation

4 hours of fermentation). The decrease of Cr(VI) concentration correlated with the decrease of the Eh from +325 to −99 mV (Fig. 6, *B*). This result is quite natural, because the rate and efficiency of the reaction is determined by the potential difference between the donor and acceptor systems in accordance with the thermodynamic prognosis [16]. The standard redox potential of the chromate reduction reaction is +555 mV, and the potential of the investigated HPM was −190 mV. Microorganisms completely reduced the chromate in just 4 hours due to the high difference in redox potentials (745 mV).

To summarize, the effectiveness of chromium(VI) bioremoval from culture medium of bioreactor was 100% and continued 4 hours. The process of chromium removal correlated with the decrease of the redox potential (from +325 mV to −99 mV) (Fig. 6, *B*). The concentration of H_2 was not changed during the process of chromium(VI) bioremoval (Fig. 6, *B*). So, the toxic Cr(VI) did not significantly affect on the fermentation process.

Thus, we have experimentally confirmed the theoretical background of effective soluble Cr(VI) removal by hydrogen producing microbiome. The investigation of optimal microbial pathway of chromium-containing sewage purification from soluble hexavalent chromium compounds is of a great interest to modern science [5, 9, 29–31]. We suggested the novel methodological approach based on thermodynamic calculations to provide complete detoxification of contaminated environments from toxic chromium compounds.

The optimal pathway of microbial detoxification of toxic chromium(VI) compounds was thermodynamically predicted and experimentally confirmed. The high efficiency of Cr(VI) removal by strict anaerobic hydrogen producing microbiome via dark hydrogen fermentation of multicomponent organic waste was demonstrated. The obtained results can be used as a basis for development of novel environmental biotechnology of chromium-containing sewage purification and simultaneous destruction of environmentally hazardous organic waste as well as obtaining of eco-friendly energy carrier — biohydrogen.

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БІОВИЛУЧЕННЯ ТОКСИЧНОГО ХРОМУ(VI) В ПРОЦЕСІ ЗБРОДЖУВАННЯ БАГАТОКОМПОНЕНТНИХ ОРГАНІЧНИХ ВІДХОДІВ

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Термодинамічні розрахунки дають змогу визначити оптимальні метаболічні шляхи для мікробного вилучення токсичних розчинних сполук шестивалентного хрому з контамінованих стічних вод.

Метою дослідження було теоретично передбачити та експериментально підтвердити можливість вилучення небезпечного Cr(VI) за допомогою воденьсинтезувального мікробіому у процесі одночасної деструкції багатокомпонентних органічних відходів та синтезу водню.

Склад газу визначали, використовуючи стандартний метод газової хроматографії. Редокс-потенціал (Eh) та pH середовища вимірювали потенціометрично. Концентрацію Cr(VI) визначали фотоколориметричним методом.

Багатокомпонентні органічні відходи було ефективно зруйновано воденьсинтезувальним мікробіомом за відсутності хрому. Цикл водневого зброджування несуттєво інгібувався додаванням Cr(VI). Після повного мікробного відновлення розчинного CrO_4^{2-} до нерозчинного $Cr(OH)_3 \cdot nH_2O\downarrow$ метаболічні параметри повернулися до початкового рівня.

Оптимальний шлях мікробного вилучення сполук токсичного Cr(VI) термодинамічно обґрунтовано та експериментально підтверджено. Була показана висока ефективність вилучення Cr(VI) за допомогою облігатно анаеробного воденьсинтезувального мікробіому у процесі водневого зброджування багатокомпонентних органічних відходів. Отримані результати можна використовувати для розроблення новітніх природоохоронних біотехнологій очищення хроматвмісних стічних вод та одночасної деструкції екологічно небезпечних органічних відходів, а також з метою отримання екологічно чистого енергоносія — біоводню.

Ключові слова: термодинамічне прогнозування, природоохоронні біотехнології, водневе зброджування, синтез біоводню, сполуки токсичного хрому(VI), мікробне відновлення хроматів, деструкція багатокомпонентних органічних відходів.

БИОИЗВЛЕЧЕНИЕ ТОКСИЧНОГО ХРОМА(VI) В ПРОЦЕССЕ СБРАЖИВАНИЯ МНОГОКОМПОНЕНТНЫХ ОРГАНИЧЕСКИХ ОТХОДОВ

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Термодинамические расчеты позволяют определить оптимальные метаболические пути для микробного извлечения токсичных растворимых соединений шестивалентного хрома из контаминированных сточных вод.

Целью исследования было теоретически предсказать и экспериментально подтвердить возможность извлечения опасного Cr(VI) с помощью водородсинтезирующего микробиома в процессе одновременной деструкции многокомпонентных органических отходов и синтеза водорода.

Состав газа определяли, используя стандартный метод газовой хроматографии. Редокс-потенциал (Eh) и pH среды измеряли потенциометрически. Концентрацию Cr(VI) определяли фотоколориметрическим методом.

Многокомпонентные органические отходы были эффективно разрушены водородсинтезирующим микробиомом при отсутствии хрома. Цикл водородного сбраживания несущественно ингибировался внесением Cr(VI). После полного микробного восстановления растворимого CrO_4^{2-} до нерастворимого $Cr(OH)_3 \cdot nH_2O\downarrow$ метаболические параметры вернулись к исходному уровню.

Оптимальный путь микробного извлечения соединений токсичного Cr(VI) был термодинамически обоснован и экспериментально подтвержден. Была показана высокая эффективность извлечения Cr(VI) облигатно анаэробным водородсинтезирующим микробиомом в процессе водородного сбраживания многокомпонентных органических отходов. Полученные результаты могут быть использованы для разработки новейших природоохранных биотехнологий очистки хроматсодержащих сточных вод и одновременной деструкции экологически опасных органических отходов, а также получения экологически чистого энергоносителя — биоводорода.

Ключевые слова: термодинамическое прогнозирование, природоохранные биотехнологии, водородное сбраживание, синтез биоводорода, соединения токсичного хрома(VI), микробное восстановление хроматов, деструкция многокомпонентных органических отходов.