

## Intensification of copper and chromium (VI) removal from solutions in magnetic field

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Possibility to replace mechanical stirring by the magnetic field induced one was shown for considerable intensification of Cu (II) and Cr (VI) ion biosorption by the yeast *Saccharomyces cerevisiae* 1968. Combined method of metal ion recover, including Cu (II) and Cr (VI) ion sorption by yeast *Saccharomyces cerevisiae* and Cu (II) and Cr (VI) cementation on a surface of a steel matrix, is tested in case of magnetic field induced stirring.

Рассмотрена возможность использования магнито-гидродинамического перемешивания (вместо механического перемешивания) для интенсификации биосорбции ионов Cu (II) и Cr (VI) при помощи дрожжей *Saccharomyces cerevisiae* 1968. В работе проверяется комбинированный метод извлечения ионов металла, который состоит из сорбции ионов Cu (II) и Cr (VI) дрожжами *Saccharomyces cerevisiae* и цементации ионов Cu (II) и Cr (VI) на поверхность стального элемента в случае перемешивания индуцированным магнитным полем.

The development of novel, cheap and efficient methods for waste water purification from heavy metal ions takes more and more importance recently in connection with the environment pollution. So, the hexavalent chromium compounds (chromic acid and salts thereof) are used in chemical treatment (etching, passivation) of steel and copper alloy surface, zinc-coated and cadmium coated steel, in electrochemical processing (anodization) of aluminum, in electrical polishing of steel as well as in galvanic works where most of protective coatings are the chromium ones [1]. Chromium content in washing sewages of machine building plants amounts up to 600 mg/L (as  $\text{Cr}_2\text{O}_7^{2-}$ ) [2]. In the production of building materials where portland cement is used (e.g. of asbestos, concrete, and reinforced concrete articles), the wastewater is also saturated

with Cr(VI) ions [3]. The waste waters of all these works may contain both a single component, e.g., chromium, and multiple components, e.g., chromium, copper, zinc, cadmium, nickel, iron, etc. [4]. These wastes make a considerable ecological danger, in particular, due to Cr(VI), since it is highly toxic and is known as a carcinogenic and mutagenic toxin for humans [1]. To date, there are numerous methods to purify the waste water from heavy metal ions, including chemical, mechanical, physicochemical, biological ones, etc. The physicochemical methods of waste water purification draw more and more the attention of researchers. The existing physicochemical methods, however, include multiple stages and are expensive, as requiring large amounts of reagents [4]. In this connection, the high-gradient magnetic separation using sorbents, includ-

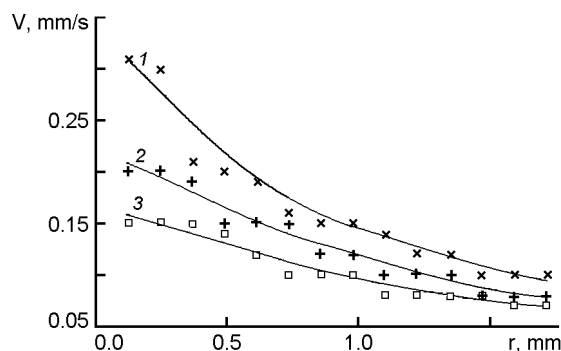


Fig. 1. Dependences of the solution flow rate  $V$  in the vicinity of a checker element on the distance  $r$  from the checker surface in the 1st (1), 3rd (2) and 5th minute after the magnetic field switching-on.

ing biosorbents, become more and more popular [5]. When developing biosorbents, a special attention is given to the yeast biomass that is a sorbent of good prospects relative to heavy metals [6]. The yeast grows rapidly, the cells thereof are convenient to operate with at genetic and morphology levels, it is able to grow at high concentrations of heavy metals and accumulate those in the biomass. The yeast biomass can be produced easily in sufficiently large amounts as a by-product of numerous fermentation processes [6, 7]. So, the commercial ion exchange resins being used in the waste water purification are 10 times so expensive as the biosorbents, thus, the latter are quite competitive [5].

In this work, we have studied the Cr(VI) removal process from a solution in magnetic field (MF) using the magneto-hydrodynamic mixing (MHDM) of electrolytes near the steel elements in a MF. We have studied also the combined Cr(VI) and copper removal method from a solution using cementation onto a steel element and the chromium and copper sorption with biomass of yeast (*Saccharomyces cerevisiae* 1968) in combination with MHDM.

To study the Cr(VI) removal efficiency, a  $K_2CrO_4$  solution of pH 2 with the initial Cr(VI) concentration 100 mg/L was used. The solution was placed in a glass cell provided with a checkerwork. The checker consisted of 40 identical elements shaped as carbon steel (GOST 1050-88) rods of 525  $\mu$ m diameter and 3000  $\mu$ m length arranged uniformly in the cell volume and fixed by a non-magnetic holder inert to the solution. The element spacing was equal to threefold element diameter, thus taking into account that at larger distances, the flow rate and

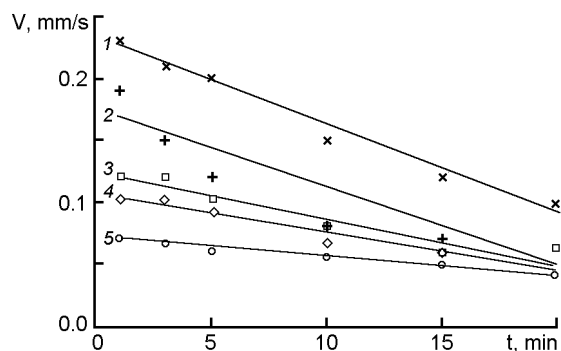


Fig. 2. Time dependences of the solution flow rate  $V$  in the vicinity of a checker element at the solution pH values: 1(1), 1.5 (2), 2 (3), 3 (4), 5 (5).

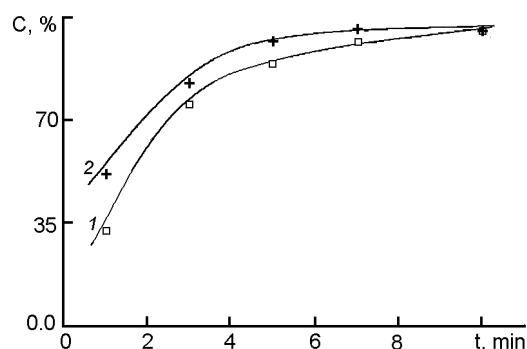


Fig. 3. Magnetic field effect on the Cr(VI) cementation; the process without (1) and with MF (2).

thus the mixing intensity is lowered at the specified system parameters (Fig. 1).

The solution pH was adjusted at 2 using nitric acid. At that pH value, the yeast does not lose its viability [8] while the liquid flow rate in the vicinity of the checker elements is sufficient for intense mixing (Fig. 2). The cell with the checker was placed in a constant MF of 240 kA/m and kept for 1 to 15 min. The studies were done in MF directed both in parallel and perpendicular to the axes of the checker rods.

The control experiments were made with the same  $K_2CrO_4$  solution and the checker but without MF. The residual Cr(VI) in the solution was determined by diphenyl carbazide method [9].

The study of chromium ion cementation has shown that 100 % of the ions were removed from the solution in the MF during 6 min. In control experiments, 10 min were required to attain 100 % removal of Cr(VI) by cementation without MF. In Fig. 3, presented is the Cr(VI) cementation process from the solution onto the steel element in MF and without it. It is seen that the MF intensifies considerably the chromium ion

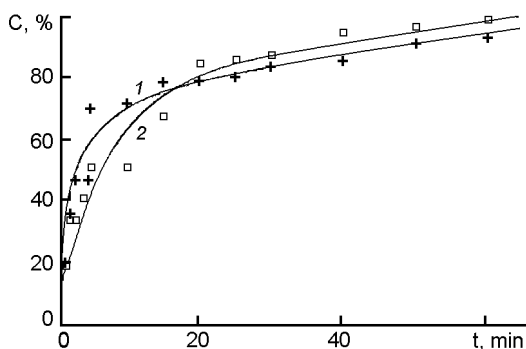


Fig. 4. Copper ion removal at parallel (1) and perpendicular (2) system geometry due to biosorption/cementation process.

cementation during the initial few minutes of the experiment.

We have studied also the biosorption of Cr(VI) and Cu(II) with *Saccharomyces cerevisiae* 1968 yeast using steel elements (checkerwork) in the constant MF. In this case, the biosorption process is intensified also due to the use of magneto-hydrodynamic mixing of electrolytes near the steel rods in the MP instead of mechanical stirring [10-12].

To obtain the biomass, the *S. cerevisiae* 1968 yeast was grown on mineral Ridder medium of the following composition (g/L):  $(\text{NH}_4)_2\text{SO}_4$ , 3.0;  $\text{MgSO}_4$ , 0.7; NaCl, 0.5;  $\text{K}_2\text{HPO}_4$ , 0.1;  $\text{KH}_2\text{PO}_4$ , 1.0; glucose, 10.0; yeast autolysate, 1.0, without copper ion admixture, in aerobic conditions, at 28°C. The yeast was cultivated in 250 ml conical flasks on shakers, the rotation frequency of stirrer being 220 rpm. The one-day culture (the stationary growth phase onset) was centrifuged and washed twice with sterile saline.

To study the copper removal efficiency,  $\text{CuSO}_4$  solution was prepared at pH 2 and the initial copper ion concentration of 50 mg/L. That solution was loaded with the *S. cerevisiae* 1968 yeast (0.1 g dry substance per 100 ml). The control experiments were done with the same  $\text{CuSO}_4$  solution but yeast-free, with the checkerwork, in and without the MF. After the experiments, the yeast was filtered off and the residual copper amount in the solution was determined using a C-115-M1 atomic adsorption spectrophotometer. The studies were done in MF directed both in parallel and perpendicular to the axes of the checker rods (in parallel and perpendicular system geometry, respectively).

In Fig. 4, compared are the Cu ion fractions (C, %) removed from the solution at

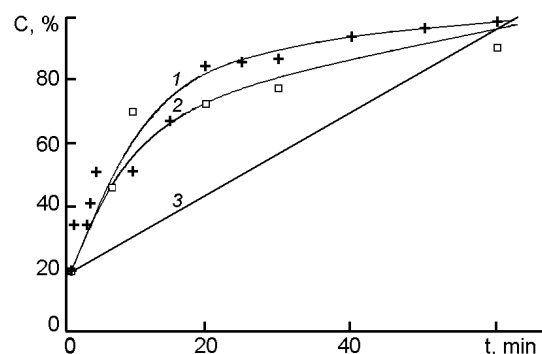


Fig. 5. Copper ion removal at parallel (1) and perpendicular (2) system geometry in MF and without MF (3) due to cementation.

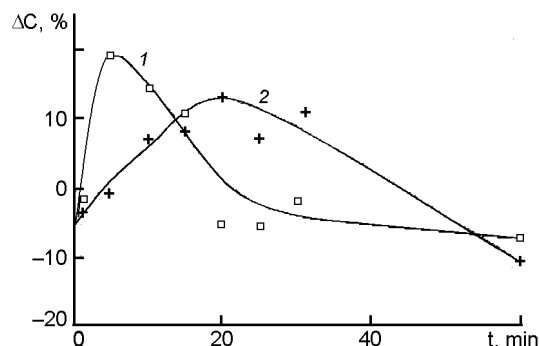


Fig. 6. Contribution of copper ion biosorption from a solution at parallel (1) and perpendicular (2) system geometry.

the parallel and perpendicular system geometry. It is seen that at the parallel geometry, about 70 % of the copper ions are removed during the first 5 min due to biosorption and copper cementation onto the checkerwork while after 1 h, the removed copper fraction is 92 %. At the perpendicular system geometry, the removed copper amounts are 49.2 and 97 %, respectively. Thus, the copper removal characteristics depend only slightly on the system geometry.

Fig. 5 illustrates the Cu ion fractions (C, %) removed from the solution at different MF directions due only to cementation. At the parallel geometry, 51 % of the copper ions are removed during the first 5 min and 99 % during 1 h; at the perpendicular geometry, the removed copper amounts are 46 and 90 %, while without MF, 36.7 % and 93 % are removed, respectively. From those results, taking into account the copper fraction removed due to cementation, curves have been obtained (Fig. 6) characterizing the biosorption contribution to the copper removal process from the solution.

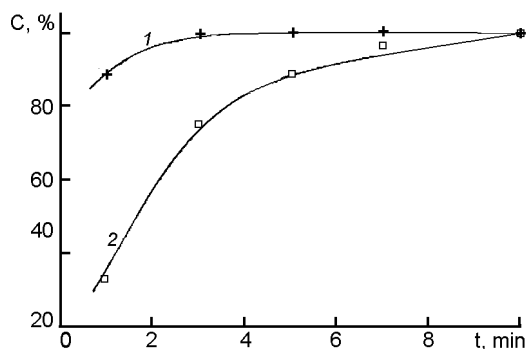


Fig. 7. Combined method of Cr(VI) removal from a solution without MF using cementation/biosorption (1) and cementation only (2).

Similar experiments were carried out to study the sorption of Cr(VI) ions with yeast biomass in MF. The  $K_2CrO_4$  solution was loaded with the *S. cerevisiae 1968* yeast (0.1 g dry substance per 100 ml). The results obtained show that at any system geometry, about 100 % of Cr ions were removed from the solution during 1 min due to combined cementation/sorption process. In control experiments without MF, the cementation and biosorption have provided the removal of about 89 % chromium during the first minute and about 100 % in 5 min. The results obtained are compared in Fig. 7. From those results, taking into account the chromium fraction removed due to cementation only, a curve has been obtained (Fig. 8) characterizing the biosorption contribution to the Cr(VI) removal process from the solution. In control experiments made at Institute for Microbiology and Virology, National Academy of Sciences of Ukraine, using traditional mechanical stirring, the initial chromium concentration being the same, the *S. cerevisiae 1968* yeast have sorbed up to 15 % of Cr(VI) and 37 % of Cu ions for 3 h.

Therefore, for waste water containing only Cr(VI) ions, it is expedient to remove the impurity by cementation onto steel elements in a constant magnetic field. But in purification of multicomponent waste water, justified is the use of combined Cr(VI) and Cu(II) removal method, i.e., the sorption with yeast under simultaneous cementation onto steel in MF, since the MF intensifies both cementation and biosorption processes. The biosorption in MF has been

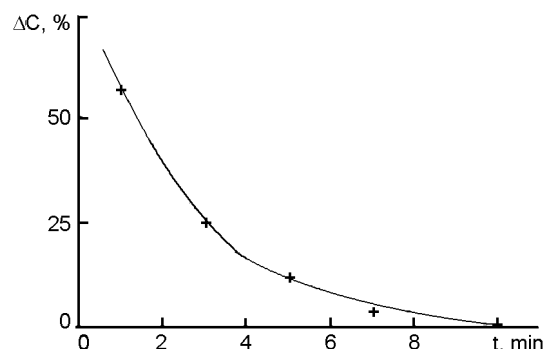


Fig. 8. Contribution of chromium ion biosorption at combined purification without MF.

found to be of a particular efficiency for copper removal. Thus, this work offers a substantial intensification of the heavy metal ion removal methods, such as biosorption and cementation, by using constant magnetic fields that provide the MHDM of solutions in the vicinity of steel elements.

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## **Інтенсифікація процесу вилучення іонів міді та шестивалентного хрому із розчинів у магнітному полі**

***С.В.Горобець, О.Ю.Горобець, І.Ю.Гойко, Т.П.Касаткіна***

В даній роботі розглядається можливість використання магніто-гідродинамічного перемішування (замість механічного перемішування) для інтенсифікації біосорбції іонів Cu (II) та Cr (VI) за допомогою дріжджів *Saccharomyces cerevisiae* 1968. В даній роботі перевіряється комбінований метод видалення іонів металу, який включає в себе сорбцію іонів Cu (II) та Cr (VI) дріжджами *Saccharomyces cerevisiae* та цементацією іонів Cu (II) та Cr (VI) на поверхню сталюого елемента, у випадку перемішування індукованого магнітним полем.