

# MODERN APPROACH TO AUTOMATIC CONTROL OF ENZYMIC HYDROLYSIS OF TANNERY WASTE\*

by

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## ABSTRACT

Total recycling of chromium-containing waste from tanning industry forms a compact technology that is aimed at solving the problem of the presence of chromium in both solid and liquid wastes generated during the leather manufacturing processes. If the technology is to provide a compact system usable in industrial practice it is necessary to provide a complex control system based on advanced technical and software tools that enable the use of modern automatic control methods. For that purpose, a decentralized computer control system has been constructed in laboratory conditions at Tomas Bata University in Zlín, the properties of which allow its relatively easy transformation into industrial scale. The system consists of two main parts: a control system of the key technological processes—hydrolysis, filtration, evaporation, total de-chroming of both the filtration cake and spent liquor; and a superior central control unit which ensures supervision of the entire process. The control system is designed alternatively with respect to the use of various types of technical components and communication paths, which allows designing the final industrial system with the use of a selected automation and information technology.

## RESUMEN

El reciclado total de residuos de la industria del cuero que contienen cromo, forma una tecnología compacta que está dirigida a resolver el problema de la presencia de cromo en desechos sólidos y líquidos generados durante los procesos de fabricación de cuero. Si la tecnología es proporcionar un sistema compacto que puedan utilizarse en la práctica industrial, es necesario establecer un complejo sistema de control basado en técnicas avanzadas y herramientas de software que permitan el uso de métodos modernos de control automático. A tal efecto, un sistema informático de control descentralizado se ha construido en condiciones de laboratorio en la Universidad Tomas Bata en Zlín, cuyas propiedades permiten su transformación relativamente fácil a escala industrial. El sistema consta de dos partes principales: un sistema de control de los procesos tecnológicos fundamentales—la hidrólisis, filtración, evaporación, total de descromado tanto de la torta de filtración como del licor usado, y una unidad central de control superior que garantice la supervisión de todo el proceso. El sistema de control ha sido diseñado alternatively con el uso de varios tipos de componentes técnicos y vías de comunicación, que permite diseñar el sistema industrial final con el uso de un sistema seleccionado de automatización y tecnología de la información.

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## INTRODUCTION

Chromium still remains the most used agent for hide-tanning in the tanning industry even though one of its variants – hexavalent chromium – is highly toxic and is proved to cause cancer.<sup>3</sup> Attempts to find a substitute that would give comparable results with respect to the quality of the products and production costs have not been successful so far, thus it seems unlikely that in the near future chromium in the tanning industry would be replaced. Therefore it is important to focus on the development of methods dealing with clean and effective disposal of chrome-tanned waste.

The amount of waste generated by the tanning industry is very high. Only about 20 percent of raw hide is transformed into the final product; the rest ends up as various forms of waste. The portion of this waste which contains chromium presents great burden for the environment and as a result, due to high disposal costs, significantly affects the effectiveness of the production. As already mentioned, it seems unlikely that chromium in the tanning process will be replaced and therefore it is useful to look for options of effective disposal of chromium containing waste or, even better, methods for recycling chromium from this waste. The main problem nowadays is not the technological solution for chromium recycling from the tannery waste, but the economical side of the issue. It is required that the process is as effective as possible. At our institute, a method was proposed for hydrolyzing chromium waste which produces valuable protein hydrolyzates and also chrome sludge.<sup>1</sup> If any new method is to be successfully implemented in industry it needs to be optimized in the means of investment and operating costs. For this reason the method was tested in small scale in our laboratory. Recently, when the laboratory has been moved into a new building, it has been decided to completely upgrade the equipment of this laboratory with a new control technology.

## PROBLEM FORMULATION

Enzymatic hydrolysis appears to be the best method for processing chromium-containing tannery waste both from the economic and environmental point of view. The procedure yields protein hydrolyzates that contain virtually no chromium while the dose of expensive enzyme is less than 1% and the filter cake can be recycled. The complete process for tannery waste recycling can be divided into the following four workplaces: hydrolyse, filtration, evaporation and dechromation. The principle of the method can be seen in Fig. 1.

The first step of the process is a chemical reaction—hydrolysis.<sup>2</sup> Product of this reaction is then filtered and the resulting filtrate (valuable protein hydrolyzate) is concentrated in a vacuum evaporator. The obtained filter cake containing

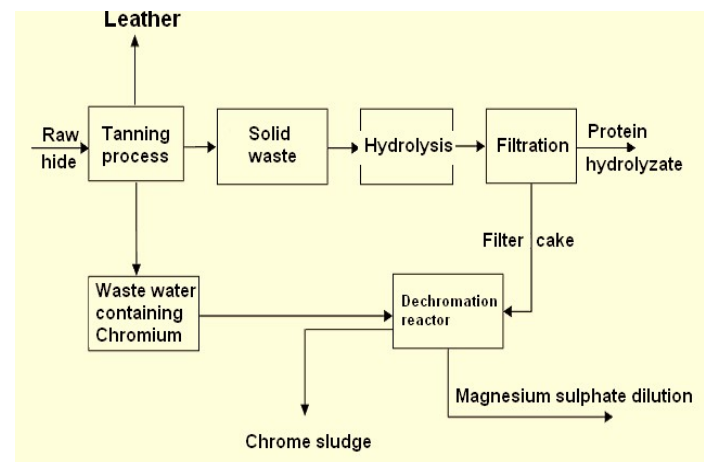


Figure 1. Principle of the technology.

magnesium hydroxide (material used in enzymatic hydrolysis) reacts in the dechromation reactor with spent liquor which contains chromium. As a result, the wastewater is freed of chromium and moreover the chromium thus obtained can be used in other industrial applications. For all the said technological operations, microcomputer-based individual monitoring and control systems have been developed in the form of embedded systems. Together with a supervising computer they create a two-level control and monitoring system. In this article we will focus on the new control system for the dechromation reactor (filter press workplace).

The most important operation in the whole process of leather manufacturing is tanning during which basic complexes chromium salts form strong coordinating bonds between carboxyl groups of the collagen protein. However, this reaction goes to equilibrium, i.e. some of the available chrome does not link to the collagen protein by tanning reaction and thus, according to the specific technological procedure, outgoing liquid contains 0.2–0.4 % of chromium ions. General practice is to use alkaline precipitator to remove chromium from this “spent” liquor. In our process the chromium sludge isolated after enzymatic dechromation of tanned solid scraps contains 10–15 % of magnesium oxide (on the free moisture base) and also a small amount of organic base. This fact allows us to explore the possible utilization of chromium sludge in removal and recovery of chromium ions in spent tanning liquors. Thus, we are suggesting that the sludge from enzymatic dechromation can be effectively used as a sacrificial chrome exhaust agent chrome precipitator for spent tanning liquors.

For good reasons, the application of automatic control of technological processes and computer technique in the leather industry has been increasing in recent years. The proposed model of the technology was used for a simulation test and optimum calculation in relation to minimization of the processing costs of the recycling technology in the connection of a kinetic precipitation represented kinetic speed constant (k) (See Fig.2). Details can be found in.<sup>2</sup>

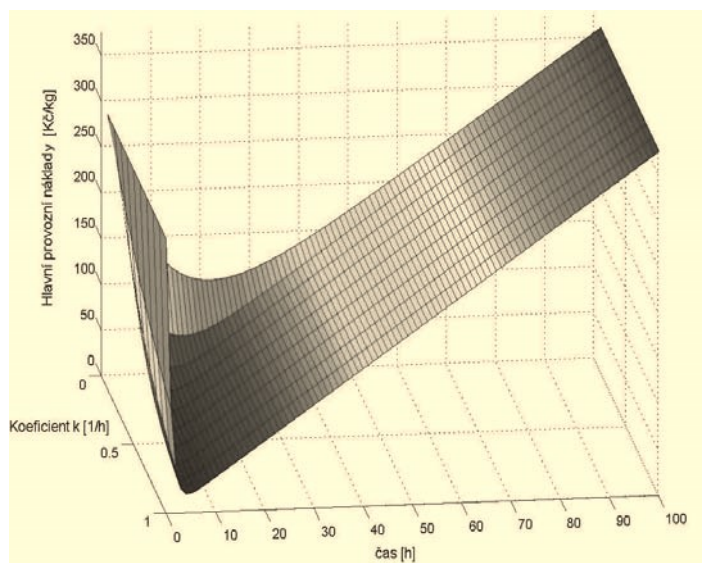


Figure 2. Cost curves for variable speed constant  $k$ .

## CONTROL SYSTEM

Because the equipment in the laboratory has been built over a period of years and many of the original devices became outdated, it was decided to rebuild the laboratory. The aim of the modernization was to equip the laboratory with modern computer systems and other means of automatic control<sup>7</sup>. The equipment had to be chosen not only with respect to the technology, but also to its helpfulness in demonstrating of the automatic control equipment to students of our university. The aims were defined as follows:

- Introduction of modern computer technologies for the technology control
- Application of intelligent sensors where useful
- Connection of the components using industrial buses
- Connection of the technology with supervising system
- Use of modern programming equipment with visualization

In the following text the solution we propose will be described. Due to the complexity of the technology, we will limit the description only to basic information in general and focus on one, basic part of the technology in detail.

When searching for the solution of the control system it is necessary to find harmony between the requirements of the modern control algorithms and possibilities of the hardware and software properties of microcontrollers and applications requirements.

Microcontroller that we would like to utilize in process control should have the following input/output units, peripherals modules and software running possibilities<sup>6</sup>:

- For technological data scanning is suitable minimally 4 channel 8 bit A/D converter with linear successive approximation. For applications with greater dynamic range of measuring signals it is necessary to use at least 10 bit A/D converter.
- Number of digital inputs and outputs is not a limitation, because majority of microcomputers with 40-pin package offer sufficient quantity. The amount of the input and output ports may be further upgraded by external expander chips.
- It is necessary to choose microcontroller with largest possible internal RAM memory, because a lot of microcontrollers have no external bus for connecting standard RAM memories. Special RAM chips can be connected through synchronous serial interfaces called SPI, MICROWIRE/PLUS™, etc. Maximum speed of serial interface and software handling limit maximum speed of these memories.
- For safe operation of control system it is useful, if microcomputer is equipped with a watchdog system for detecting software failures. Reliability can be improved by monitoring of supply voltage (applications powered from battery or accumulator) and verification of crystal oscillator frequency.
- Control systems with self-tuning regulators mostly demand presence of non-volatile EEPROM memory, where identified parameters from regulated system are stored. In most cases complies memory with capacity at least 128B. CMOS SRAM chip backed up by battery can completely substitute EEPROM memory.
- System timers with input capture and output compare function is required by applications with fast changes of logical levels on digital inputs and outputs. Very useful can be hardware support of pulse width modulation.
- Real time operating systems and math libraries for computing with floating point numbers have greater demands on size of program storage. Therefore internal program memory should have capacity at least 24KB. Big advantage is if this memory is FLASH type, because it considerably shortens developing time of new software.

The scheme of the complete technology from the control equipment point of view can be seen in figure 3. The whole technology in the laboratory is divided into five workplaces, four of which are directly connected with the technology and

one is supervising. The conception is based on distributed structure with a supervising computer on the top, connected with the workplaces by industrial Ethernet and alternatively also using Wi-Fi or GSM. The main components of the system are based on devices manufactured by Advantech<sup>5</sup>. At the top level an industrial personal computer is used. This computer should work as a supervising place from which it is possible to watch all the technology in the lab. However, it should also be able to control any of the workplaces directly.

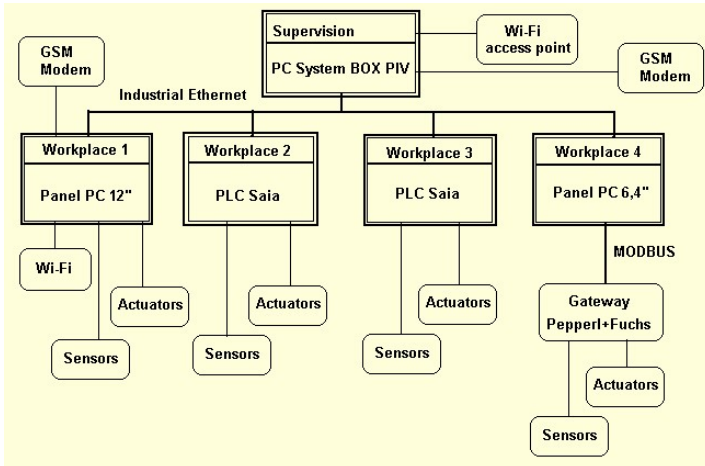


Figure 3. Scheme of the whole control system.

The supervising computer is connected with the workplaces via Ethernet, realized by Industrial switch ADAM 6520-B. The dechromation workplace is also connected via wireless LAN – the central computer creates an access point and the workplace can be connected to this access point. The computer at the dechromation workplace as well as the central computer are further equipped with a GSM modem so that it is possible to demonstrate also this communication option in practical application. The equipment of the dechromation workplace 1 will be described in detail further in the text. Workplaces 2 and 3 (for filtration and fermentation) use PLC SAIA PCD2 for direct control but are also connected to the supervising computer via RS232-Ethernet converter ADAM 4571. Workplace 4 (evaporator) is controlled by Advantech TPC650T-CE panel PC with 5.7” touch screen and Windows CE operating system. The sensors and actuators are connected with the computer via modular system made by Pepperl+Fuchs which includes gateway KSD2-GW2, relay modules KSD2-GW2 and analog input modules KSD2-CI-2. The gateway communicates with the computer via RS 485 line using MODBUS protocol and with the input/output modules using CAN protocol.

**DECHROMATION WORKPLACE CONTROL SYSTEM**

Fig. 4 depicts the technological schema of the dechromation workplace. The suspended filter cake obtained at the filtration workplace is transported from tank S3 to filter press FP. After

filling the FP, the tank M is filled with wastewater. The spent liquor is then circulated through the filter press until the concentration of chromium in the wastewater drops below the level where it is cheaper to precipitate the residual chromium using an alkali. The necessary amount of the alkali is then dosed from tank S2.

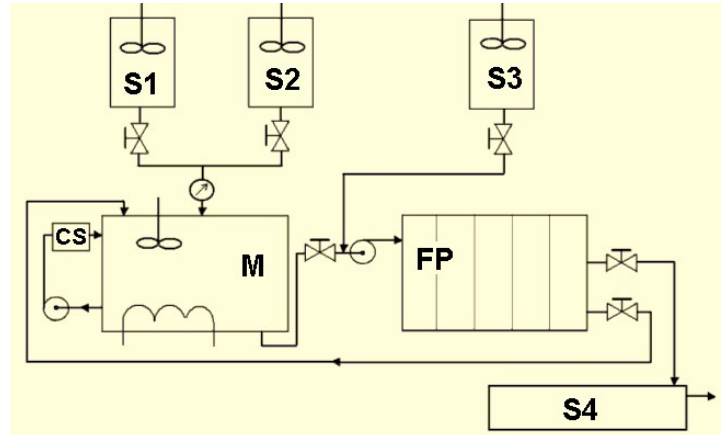


Figure 4. Schema of the dechromation workplace.

Fig. 5 shows the scheme of the control system of the dechromation workplace. At the heart of the system an industrial panel PC Advantech PPC-L126T-R70 is used. This computer with 12” touch screen and the Windows XP operating system allow comfortable control and visualization of the technology directly at the workplace. The computer is equipped with Via processor at 667 MHz with low power consumption and passive cooling which promises maintenance free operation for a long time. To connect the computer with the technology, we use Advantech ADAM modules. These modules form an RS 485 bus that is connected to the RS232 port of the panel PC through RS 232/485 converter ADAM 4520.

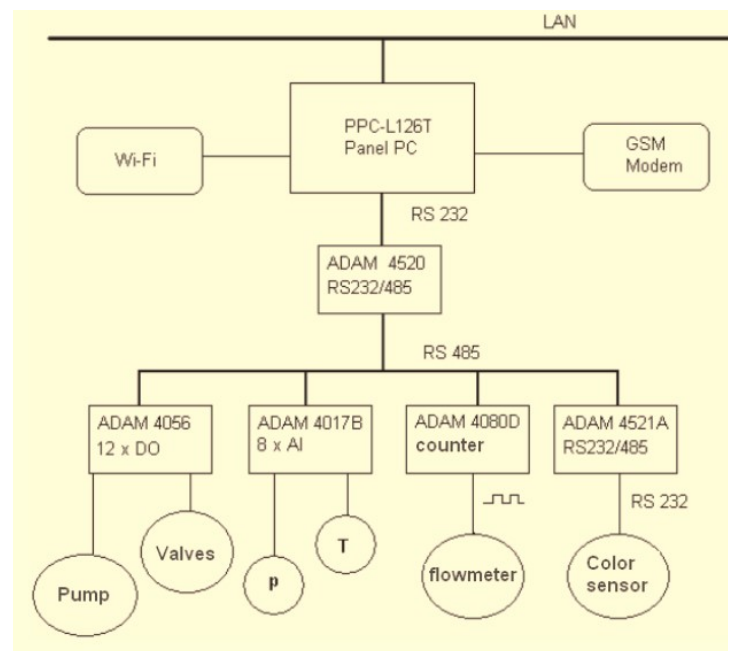


Figure 5. Schema of the control system for the dechromation workplace.

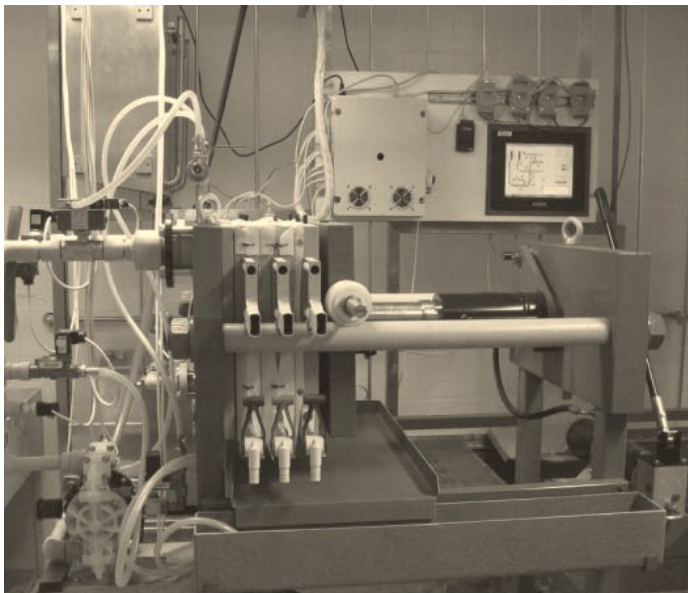


Figure 6. Filter press workplace—side view.

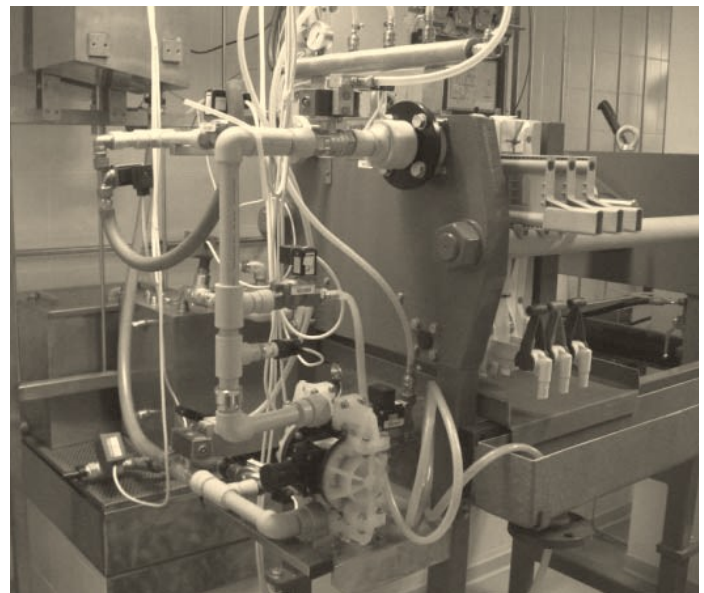


Figure 7. Filter press workplace—front view.

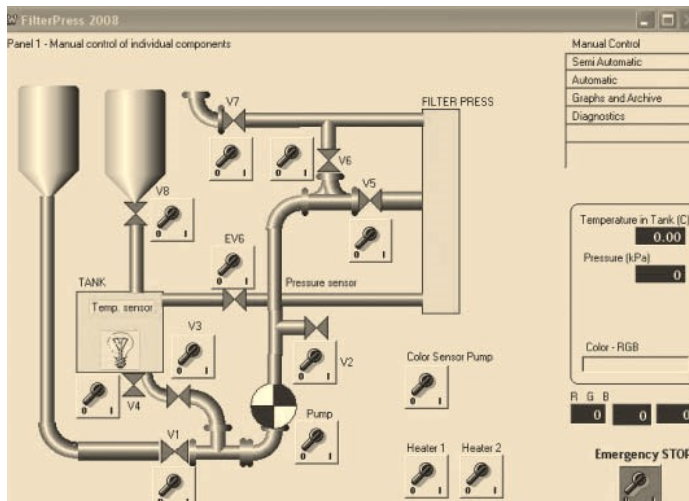


Figure 8. Main window of the control software.

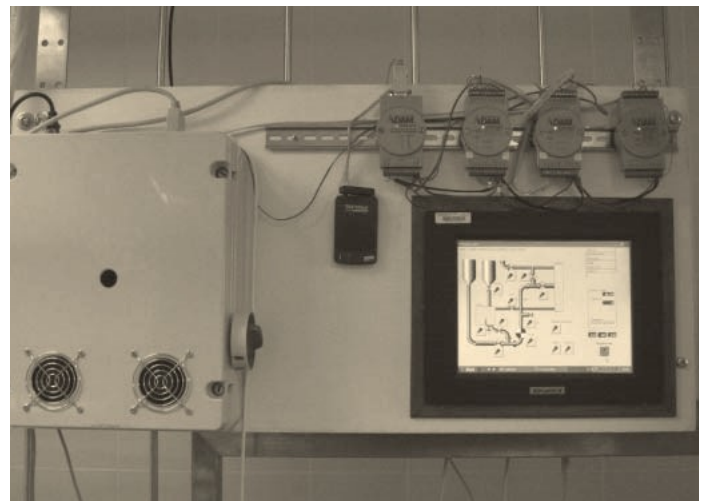


Figure 9. Control board with panel PC.

Based on the technology requirements, the following ADAM modules are used on the RS 485 bus:

- Digital output module ADAM 4056S—to control the actuators such as solenoid valves and pump. The module provides 12 outputs with open collector only, so the actuators are actually connected to a relay box controlled by the module.
- Analog-input module ADAM 4017B—used for sensors with current or voltage output.
- Input counter module ADAM 4080-D to connect flow meter.
- Converter module ADAM 4521-A (RS 232/485) used to connect the intelligent color sensor to the RS 485 bus.

For temperature measurement in the tank and pressure in the filter press, sensors with 4 to 20 mA current outputs are used. Special attention deserves the color sensor<sup>4</sup>. The color of the spent liquor circulating through the filter press is used as a measure of chromium concentration. We use an intelligent sensor HDSC16 which communicates with the computer via serial line and sends the color values directly in RGB<sup>4</sup>.

The following pictures (6 and 7) show the real equipment in the laboratory. The filter press itself can be seen in the front.

## SOFTWARE EQUIPMENT

Due to the variety of the devices and required flexibility in the programs we chose the Control Web development system to create the software for the technology. The Control Web is a

Rapid Application Development (RAD) system that allows easy development of control systems running in real time including visualization. The main advantage of such system is that the application is developed by putting together existing components and parametrizing them instead of writing all the required code from a scratch in lower level programming languages. This makes the development easy and quick. The Control Web supports many devices and basically all Windows platforms, including Windows CE.

For the dechromation workplace we use Control Web 5 runtime with an Advantech Adam driver.

In the following figures 8 and 9, the main window of the application for control of the dechromation workplace running on the Panel PC with Windows XP can be seen.

The program provides several tabs (windows) for different levels of the technology control. The most complex window is shown in figure 8, which allows switching on/off the individual components of the technology such as solenoid valves or pumps. It is also possible to control the technology at the level of phases such as filling the filter press with the filter cake, circulating the waste water through the filter press etc. It is also possible to review history of the measured values in one of the windows and also to archive the values into a database.

### CONCLUSIONS

This paper describes a control system for chromium recycling from tannery waste which is implemented in laboratory at our institute. The laboratory equipment has been recently updated with modern means of automatic control. The devices were chosen also with regard to the intended use of the laboratory for students as an example of modern automatic control in real applications. The complete technology is divided into five workplaces, four of which being directly attached to the technology and one supervising. The workplaces are connected together using an industrial Ethernet and optionally also via Wi-Fi and/or GSM modems. In this article we focused primarily on the main workplace—dechromation. This workplace is controlled with industrial panel PC Advantech PPC-L126T with touch screen that is connected to the process

via Advantech ADAM I/O modules. The components of the system have been assembled and tested. As the main programming system for the whole laboratory we use an RAD system Control Web. In this development environment, a program has been created which makes it possible to control the equipment either on elementary level or at level of phases of the process such as filling the filter press. The equipment is presently tested in real situation and then a fully automatic version of the program will be implemented.

### ACKNOWLEDGEMENT

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