

**VILNIUS UNIVERSITY  
CENTER FOR PHYSICAL  
SCIENCES AND TECHNOLOGY**

**RENATA ČESŪNIENĖ**

**ADSORPTION OF CHROMIUM COMPLEX DYE AND COPPER(II) IONS BY  
ACTIVATED CARBONS**

**Summary of Doctoral Dissertation  
Physical Sciences, Chemistry (03P)**

**Vilnius 2013**

The research has been carried out at the Institute of Chemistry of Center for Physical Sciences and Technology in the period of 2007-2013.

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The official discussion will be held on December 30, at 12 p.m. at the open meeting of the Evaluation board at the Assembly Hall of the Institute of Chemistry of Center for Physical Sciences and Technology.

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VILNIAUS UNIVERSITETAS  
FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRAS

**RENATA ČESŪNIENĖ**

**CHROMO KOMPLEKSINIO DAŽIKLIO IR VARIO(II) JONŲ ADSORBCIJA  
AKTYVINTOSIOMIS ANGLIMIS**

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Fiziniai mokslai, chemija (03P)

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## INTRODUCTION

In recent decades, more and more attention is paid to the environment protection because of the emission of large quantities of solid, liquid and gaseous waste from many manufacturing processes. They cause the environmental pollution and are harmful to human health. The commercial activated carbons (CAC) are widely used for drinking water and waste water treatment. Activated carbon is a form of graphite, which is characterized by irregular or amorphous structure, with varying sizes - from the visible to the naked eye to the molecular size of pores. They are derived from coconut shells, charcoal, lignin, petroleum coke, bone coal, peat, rice husks, peach pits, fertilizer waste, rubber waste, etc. Plain carbon is very different from activated, the latter is specially manufactured in order to adsorb harmful substances (dissolved organic matter, heavy metal ions, bacteria, etc.). Activated carbon is produced by varying the size of pores that are able to remove different sized particles. The efficiency of activated carbon is determined by the surface chemical and geometrical heterogeneity. Acidic and basic functional groups present on the surface of activated carbon allow to adsorb chemical compounds of diverse nature. Dyes are harmful chemicals, widely used in textile, rubber, paper, plastics and cosmetics industry. A metal complex dye group is one of the most important and widely used groups in the textile dyeing industries. It is known that every year about 2% of dyes release into the environment with wastewater from the production of dyes and 10 % from the textile and related manufacturing fields. Once released from the manufacturing processes to wastewater they give them color, which can reduce the amount of light reaching the surface water and disturb the photosynthesis processes. In order to prevent the environmental pollution, the water used must be cleaned. Heavy metals (Cu, Zn, Co, etc.) are pollutants found in the wastewater of various industries. They constitute a family of contaminants that may be found coexisting with dyes in wastewater. One of the effective methods for removal of metal ions is the adsorption on activated carbon, which has a large surface area and functional groups (active adsorption centers). The application of activated carbon for wastewater treatment requires a good understanding of the adsorption mechanism. So far, little is known about the interaction between metal complex dyes and heavy metals in binary adsorption systems. Lanasyne Navy M-DNL, a member of anionic azo dyes, and copper(II) were selected as a typical

dye and heavy metal. In this study, an attempt was made to find out whether the activated carbon used for the removal of organic compound metal complex dye Lanasyne Navy could be applicable for the adsorption of copper (II) ions. The goals of present work were to study the mutual effect of metal complex dye and copper(II) ions on their removal by adsorption. Consequently, the adsorption of the dye and metal ions from binary solutions has been investigated as well. The results of batch and column adsorption experiments have been obtained.

**The aim of the work** was to investigate the peculiarities of the simultaneous and consecutive (successive) adsorption of chromium complex dye and copper(II) ions by activated carbons under static and dynamic conditions.

**The following main tasks** were set to achieve the aim:

1. To investigate the chemical properties of the selected activated carbons and to determine the influence of modification (the treatment with the dye solution).
2. To study the copper(II) adsorption by activated carbons saturated with chromium complex dye under static and dynamic conditions.
3. To investigate the adsorption of chromium complex dye and copper(II) from binary solutions under static and dynamic conditions.
4. To determine the influence of various factors (solution pH, concentration of adsorbates, temperature, contact time) on the adsorption kinetics and equilibrium.
5. To evaluate the mutual effect of chromium complex dye and copper(II) ions for their removal under different conditions.

**Novelty and actuality of the work:**

Adsorption process of chromium complex dye and copper(II) ions by basic activated carbons using consecutive and simultaneous adsorption methods, to our knowledge, is not investigated. In the case of consecutive adsorption, the possibility to remove the copper(II) ions by activated carbons used for the adsorption of metal complex dye has been investigated. The influence of the adsorbent surface modification occurring during the dye removal for

the adsorption of copper(II) ions was examined. The search for optimal conditions for the removal of metal complex dye and copper(II) from single and binary solutions has been carried out. No data was found in the literature about the investigation of the system „activated carbon-aqueous solution of chromium complex dye and copper(II) chloride“. The work is actual from the practical point of view, because the industrial wastewater is usually the mixture of various materials – organic and inorganic, so it is important to clarify their mutual influence on the efficiency of water treatment. It is important to find out the opportunities and options for the removal of chromium complex dye and heavy metal, hence the copper(II) ions, by the universal adsorbent activated carbons.

## 1. EXPERIMENTAL

Commercial activated carbons Norit PK 1-3, Norit RB 0.8CC and AC-20 were used in this work. The surface morphology of the as received adsorbents was measured on a scanning electron microscopy (SEM). The SEM used was EVO 50EP (Carl Zeiss SMT AG). Elemental composition of activated carbon samples was examined using energy dispersive X-ray spectrometer (Oxford Instruments). Fourier transform infrared spectroscopy (Bomem FTIR spectrometer) was used to identify qualitatively the functional groups on the surface of adsorbents. Boehm's titration was used to calculate the number of surface functional groups. The pH values at the point of zero charge ( $\text{pH}_{\text{PZC}}$ ) of the activated carbon samples were measured using the pH drift method. The tested metal complex dye was the commercial textile dye Lanasyne Navy M-DNL obtained from Clariant (Schweiz).

The initial pH of the solutions was adjusted by adding either 0.1 or 1 mol/L HCl. The pH was measured using a Hanna Instruments pH-meter which was calibrated against buffer solutions of pH 4.0 and 7.1. The concentration of the dye after the sorption was measured spectrometrically (Varian Cary 50). Absorbance data were converted into concentration data using calibration relations. An inductively coupled plasma emission spectrometer (Optima 7000DV, Perkin Elmer) was used for copper ions determination.

The adsorption capacity of the sorbent and the removal efficiency of the ions was calculated using the following equations:

$$q = \frac{(C_0 - C_e)V}{W}$$

$$RE(\%) = \frac{(C_0 - C_e)}{C_e} \times 100$$

where  $q$  represents the adsorption capacity (mg/g),  $C_0$  and  $C_e$  are the initial and equilibrium solution concentration (mg/L),  $V$  is the volume of solution,  $W$  is the mass of sorbent, and RE is the removal efficiency (%).

A glass column was used as the fixed bed adsorber. The adsorbent bed was supported by glass beads that ensured uniform distribution of the solution. Each solution was passed through the column in a down flow mode. The parameters of a fixed bed column were as follows: adsorbent bed height 14 cm, inner column diameter 95 mm. A known quantity of the AC (2.0 g) was packed in the column to yield the desired bed height of the adsorbent. The number of the bed volumes ( $BV$ ) is defined as:

$$\text{Number of bed volumes} = \text{Volume of solution treated} / \text{Volume of carbon bed}$$

Kinetic experiments were carried out in 250-mL Erlenmeyer flasks by agitating 0.1 L of solution with 0.4 g activated carbon at room temperature ( $20 \pm 1$  °C) or higher temperatures of 40 and 60 °C and at constant agitation speed of 190 rpm. The sample solution was withdrawn at different time intervals (5-180 min).

## 2. RESULTS AND DISCUSSION

### 2.1. Investigation of the physical and chemical properties of activated carbons

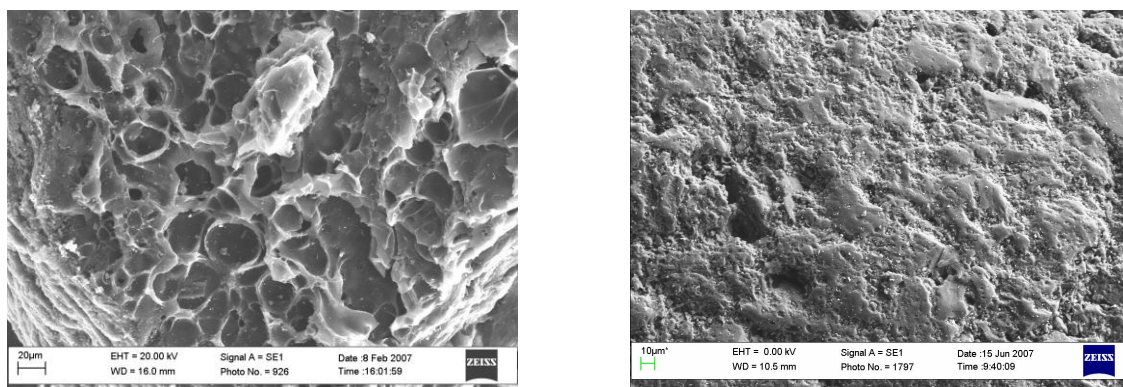
Activated carbons (AC) granulated Norit PK 1-3 and extruded Norit RB 0.8CC are commercially available non impregnated adsorbents, produced by Norit Ltd. Both carbons are basic in nature as shown by the values of their supernatant pH,  $pH_{PZC}$  and by Boehm's titration analyses. The surface chemistry of AC was analyzed by Boehm method and pH of the point of zero charge ( $pH_{PZC}$ ).

The functional groups contents obtained by titration have shown that activated carbons contain more basic than acidic groups. The amount of various basic groups



referred to the unit mass of Norit PK 1-3 activated carbon (1.25 mmol/g) is substantially higher as compared to acidic ones (0.13 mmol/g). Mineral impurities (7-8 %) also have an influence on the surface chemistry of AC.

SEM micrographs showed that the Norit PK 1-3 activated carbon had various irregular-shaped particles with macropores and micropores (Fig.1, left). In comparison, the Norit RB 0.8CC activated carbon appeared to have smoother surface (Fig. 1, right).



**Fig. 1.** SEM micrographs of activated carbons Norit PK 1-3 (left) and Norit RB 0.8CC (right).

A number of organic materials (Eriochrome Black, PAR, KHP, Chromazurol S, Lanasyne Navy M-DNL dye) have been selected as potential modifying agents. Modified activated carbons could be obtained by removing organic pollutants from aqueous solutions. In order to evaluate the applicability of the activated carbons saturated with commercial metal complex dye Lanasyne Navy M-DNL for the removal of Cu(II) ions the reuse of the spent sorbents was studied. The consecutive removal of two kinds of pollutants such as organic compounds and heavy metals is feasible by using the suitable adsorbent. According to the experimental results the percentage of Cu(II) removal was highest in the case of LN dye.

## **2.2. Consecutive adsorption of chromium complex dye and copper(II) ions**

In this study, the attempt was made to remove the two pollutants of different nature, namely, organic compound and heavy metal ions using the same portion of carbon adsorbent. In the first stage, during the adsorption of chromium complex dye surface

modification of activated carbon takes place, thus the adsorbents with a higher affinity towards Cu(II) ions are obtained. In the second stage, Cu(II) ions can be removed by the same portion of adsorbent. Our efforts have focused on the investigation of conditions favourable for the adsorption of two adsorbates, chromium complex dye and Cu(II) ions.

The activated carbon saturated with chromium complex dye from 0,1 mmol/l solution for 2-3 days was used for the removal of Cu(II) ions. The effects of several variables such as azo dye solution pH, Cu(II) concentration and solution pH on the removal efficiency have been evaluated. Optimization of removal process has been conducted by batch experiments. Adsorption of copper(II) on activated carbon was examined from external solutions of different pH covering the range from pH 3 to pH 5. Activated carbon surface chemistry influenced the amount of adsorbed copper(II) and dye not only by direct interaction but also by the modification of external solutions pH. Removal from the solutions with the same initial pH but with different initial copper(II) concentration causes the different changes in final pH of the solutions. The mechanism of copper(II) and dye uptake varies at various pH values since the pH affects the structure of the adsorbent surface and the form of adsorbate. The treatment of activated carbons with acidic LN dye solutions (pH 2) was not favourable for the removal of copper(II) (Table 1).

**Table 1.** Consecutive adsorption of chromium complex dye and copper(II) ions by activated carbon Norit PK 1-3

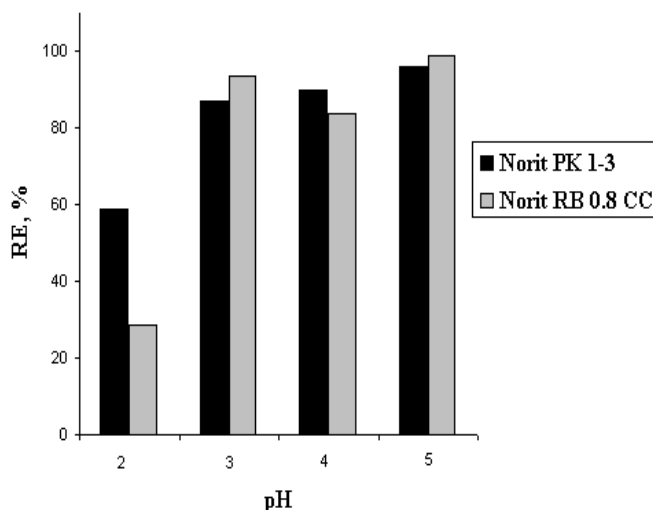
Sample number	First stage of adsorption				Second stage of adsorption			
	Solution	pH initial	pH final	q(LN), mg/g	Solution	pH initial	pH final	q(Cu(II)), mg/g
1	0.1 mM LN	6.16	8.28	13.51	4.5 mM CuCl <sub>2</sub>	3.0	5.45	13.46
2			10.55	12.08		4.0	5.50	17.21
3			8.89	12.27		5.0	5.50	14.73
1	0.1 mM LN + HCl	2.02	4.66	13.40		3.0	4.64	4.51
2			3.94	12.64		4.0	4.82	6.92
3			4.23	12.83		5.0	4.97	7.62
1	H <sub>2</sub> O	6.06	10.06			3.0	5.54	9.53
2			9.08			4.0	5.49	16.83
3			8.62			5.0	5.46	14.73
1	H <sub>2</sub> O + HCl	2.02	3.53			3.0	4.32	4.51
2			3.52			4.0	4.64	6.10
3			3.61			5.0	4.67	4.45

*Conditions:* mass of AC 0.2 g; volume of LN dye solution 50 ml, contact time 2 days; volume of CuCl<sub>2</sub> solution 25 ml, contact time 8 days.

The kinetics of consecutive adsorption of anionic dye Lanasyne Navy and copper(II) ions has been investigated. It was determined that activated carbon used for the removal of anionic dye from aqueous solution is capable to adsorb copper(II) ions. The influence of the time of activated carbon saturation with LN dye and of saturation degree for the adsorption of Cu(II) was evaluated. Experimental results have shown that the saturation period of 30 min is more favourable than that of 14 days. It was determined that the adsorption capacity of activated carbon saturated with anionic dye was higher when compared to untreated one: 1.125 and 0.06 mmol/g, respectively. The influence of initial copper(II) and adsorbent concentration has been evaluated. The increase in adsorbent concentration from 4 to 8 g/l leads to the increase in copper(II) removal efficiency for more than two times. The adsorption capacity of activated carbon for copper(II) ions increased with the initial metal ions concentration. The experimental kinetic data were fitted to the pseudo-first, pseudo-second and intraparticle diffusion models. It was found that the step which determines the overall removal rate is intraparticle diffusion. The rate of copper(II) ions diffusion was highest in the initial period of adsorption than gradually decreased and the adsorption equilibrium was attained.

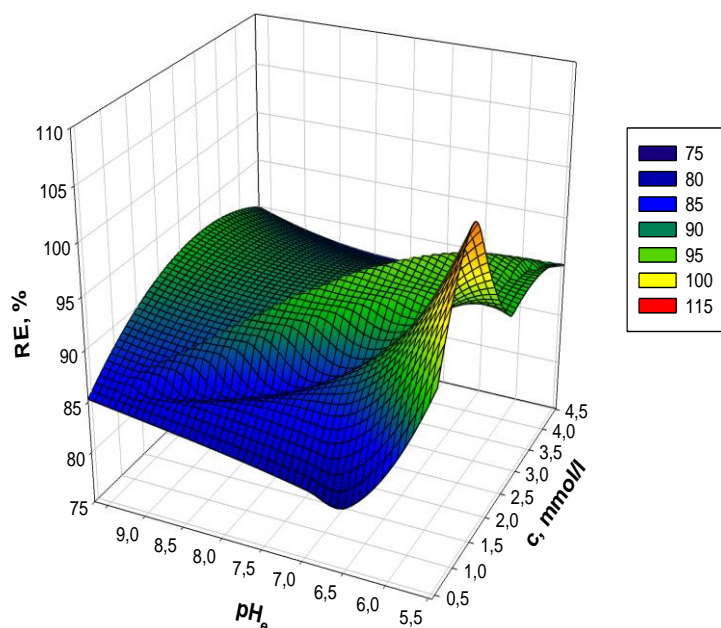
### **2.3. Simultaneous adsorption of chromium complex dye and copper(II) ions**

Batch sorption studies were performed at different pH values. Adsorption of Cu(II) and LN dye on activated carbon was examined from external solutions of different pH covering the range from pH 2 to pH 5 (Fig. 2). The uptake of Cu(II) decreased when initial pH was decreased from pH 5 to pH 2. The adsorptive decrease at pH below 3 was caused by the competition between H<sup>+</sup> and Cu<sup>2+</sup> ions for the negatively charged surface sites. Nevertheless even at low pH values the adsorption of LN dye and Cu(II) occurs. It was especially favourable for the adsorption of LN dye anions because the surface charge of the adsorbent was positive. During the removal process the solution pH increased from its lower initial value. For Cu(II) removal, the optimal pH was about 5.



**Fig. 2.** Effect of initial solution pH on the removal efficiency of Cu(II) ions from binary solution. Initial Cu(II) and LN dye concentrations  $5.5 \cdot 10^{-4}$  and  $6.7 \cdot 10^{-5}$  M, respectively

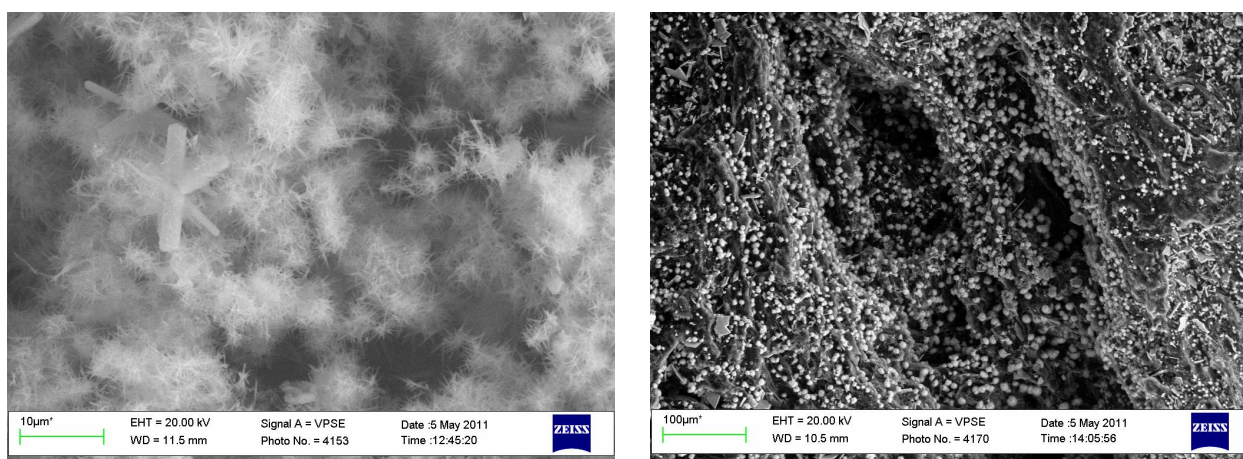
The results have shown that an increase in the initial copper(II) chloride concentration produced a reduction in the percentage removal of Cu(II) ions from the binary solution. The removal efficiency of Cu(II) ions decreased from 100 to 47 % with the increase of initial Cu(II) concentration from 0.4 to 4.5 mM, showing the process to be highly dependent on the initial concentration. Removal of chromium complex dye and Cu(II) from binary solutions with the same



**Fig. 3.** Variation of LN dye removal efficiency (RE) from binary solution with initial Cu(II) concentration. Initial LN dye concentration  $5.5 \cdot 10^{-4}$  M, initial solution pH 5

initial pH but with different initial Cu(II) concentration leads to different changes in pH value of the solutions. For example, when the batch adsorption experiments were carried out at initial pH 5 and initial Cu(II) ions concentration of 0.4 mM, the final (equilibrium) solution pH increased to 9.7. This increase caused surface precipitation reactions. Due to these reactions the removal of Cu(II) and LN dye was enhanced. The results of batch and column adsorption experiments showed higher removal efficiency at higher pH. For higher pH values the removal efficiency was influenced by the precipitation of copper(II) hydroxide. Elemental composition of carbon samples before and after interaction with binary solution was examined using energy dispersive X-ray spectrometer. Elemental analysis of carbon surface precipitate showed the presence of sulphur which can be attributed to  $-\text{SO}_3^-$  groups of anionic dye. The formation of precipitate results in the increased number of adsorption sites available for metal complex dye, so that the presence of Cu(II) in the mixture improved the LN dye uptake. The optimal conditions for the removal of LN dye at initial pH 5 was found to be at initial Cu(II) concentration of  $3 \cdot 10^{-3}$  mol/L (Fig. 3). When the initial concentration of

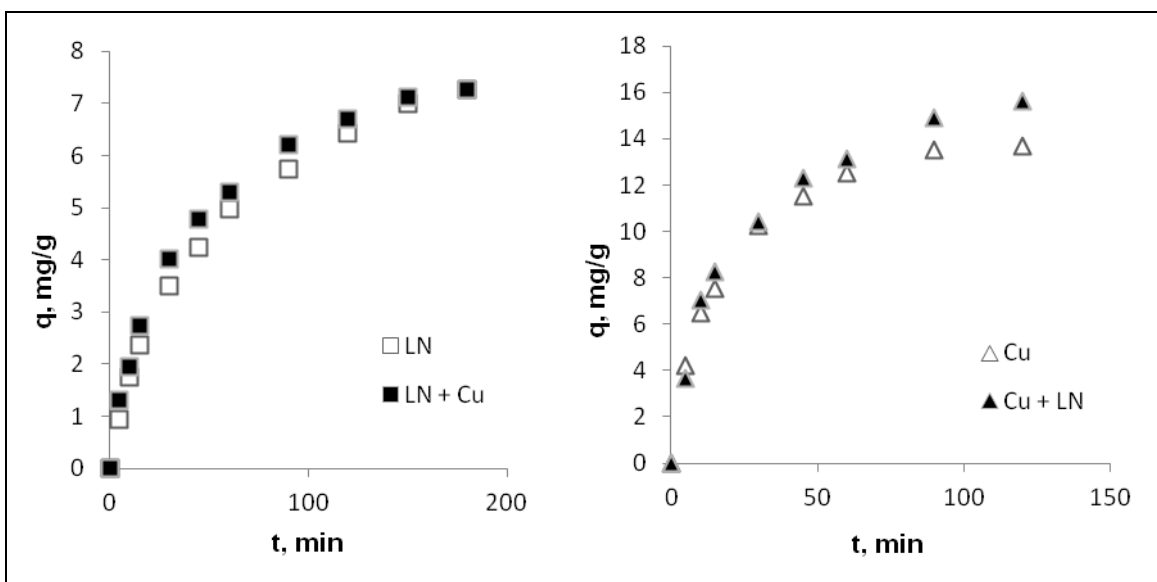
Cu(II) in the solution was lower than  $1 \cdot 10^{-3}$  mol/L, the pH value in equilibrium solution was high, and the precipitation in the bulk solution prevailed. The content of the precipitate in the solution decreased with increasing the concentration of Cu(II) ions. Under optimum conditions, the LN dye removal efficiency (RE) was higher than 93 %. Scanning electron microscopy (SEM) was used to characterize the copper compounds distribution on the carbon surface as a function of initial Cu(II) ions concentration and solution pH. SEM studies revealed the formation of copper compounds of various structures (nanosheets and flower-like aggregates) (Fig. 4). The structures formed depends on the mixed solutions parameters. Granulated Norit PK 1-3 and extruded Norit RB 0.8CC activated carbons appear to be suitable for the simultaneous capture of LN dye and Cu(II) ions.



**Fig. 4.** SEM micrograph of Norit PK 1-3 activated carbon after the interaction with binary LN dye and Cu(II) solution

In order to establish time for maximum uptake and to know the kinetics of adsorption process, the adsorption of chromium complex dye and Cu(II) on activated carbon was studied as a function of contact time. The kinetic studies showed that interaction of AC surface structures leads to changes in pH of the solution. The initial pH value changed considerably during the experimental period in the single LN dye solution. It is evident that the presence of Cu(II) in the solution leads to the lower change in solution pH when compared to single LN dye adsorption system. These

results can be explained by the specific adsorption of Cu(II) cations on the basic carbon surface sites. Kinetic experiments were conducted in binary adsorption systems to determine the rate-limiting adsorption process and the rate of adsorption of LN dye and Cu(II) on AC Norit PK 1-3. Cu(II) was excessive in binary adsorption system. For comparison, the capacities of the adsorbent when using mono-component solutions of LN dye or Cu(II) ions were also measured, at the same operating conditions (i.e., initial solution concentration, pH, temperature, and adsorbent dosage). Fig. 5 shows the results of the simultaneous adsorption of LN dye and Cu(II) on the AC. For comparison, the results of the adsorption of each pollutant in mono-component solutions are also included in this figure. It can be observed that the adsorption capacities ( $q$ , mg/g) increased along with contact time and eventually reached equilibrium. The uptake of LN dye on AC, as shown in Fig. 5, depicts that the adsorption is quite rapid initially, gradually slows down and then reaches the equilibrium. In both single and binary adsorption systems nearly 50 % of the ultimate LN dye adsorption occurred within 60 min of contact with AC. The decrease in amount of dye adsorbed with time may be due to saturation of adsorption sites, and resistance to diffusion of dye molecules in the adsorbent increases.



**Fig. 5.** Adsorption kinetics of LanasyN Navy M-DNL dye (left) and Cu(II) (right) on Norit PK 1-3 activated carbon. Initial pH 5.0, liquid/solid ratio = 250, ag n.

The amount of Cu(II) adsorbed increased linearly with time in the beginning (first 10 min), then non-linearly at a slower rate and finally attained saturation. Initial process within 10 min of contact with AC with fast Cu(II) adsorption rate is followed by a series of slower and slower processes. Such behaviour may be expected for porous adsorbents with non-uniform pore structure or a complicated pore network. During the initial period of adsorption the presence of LN dye in binary adsorption system was not favourable for Cu(II) ions uptake. Later on, as can be seen from Fig. 5, the positive effect of LN dye on Cu(II) adsorption was revealed and it increased with time.

Three kinetics models were applied to simulate the adsorption kinetics data in order to investigate the behavior of simultaneous adsorption process of Cu(II) and LN dye on AC: the pseudo-first-order, the pseudo-second-order, and the intraparticle diffusion. The values of  $R^2$  for the pseudo-first-order model are not satisfactory. Furthermore, the experimental  $q_e$  values do not agree with the calculated ones, obtained from the linear plots. Therefore, it has been concluded that the pseudo-first-order adsorption model is not suitable to describe the adsorption kinetics of both adsorbates LN dye and Cu(II) ions.

To identify the step possibly controlling the adsorption of LN dye and Cu(II) onto AC in single and binary adsorption systems, the experimental data were fitted with the Weber-Morriss equation. The amount of LN dye and/or Cu(II) adsorbed versus  $t^{0.5}$  plots present a multilinearity, illustrating that more than two steps are involved in the process. The first stage, the external surface adsorption, is observed from 0 to 20 min for Cu(II) and from 0 to 45 min for LN dye. Then the stage of intraparticle diffusion control is attained and continues from 20 to 90 min or from 45 to 150 min for Cu(II) and LN dye, respectively. The correlation coefficients of the Weber-Morriss model for this stage of diffusion are above 0.9, which indicate that the adsorption of LN dye and Cu(II) followed by intraparticle diffusion. Intraparticle diffusion rate constants  $k_{id}$  are presented in Table 2. The results show that the diffusion rate of Cu(II) is higher than LN dye in both single and binary adsorption systems. The difference in diffusion processes of Cu(II) and LN dye is probably due to a larger molecular size of LN dye, thus making it difficult to diffuse into pores of activated carbon. Finally, the final equilibrium adsorption starts after the second stage.



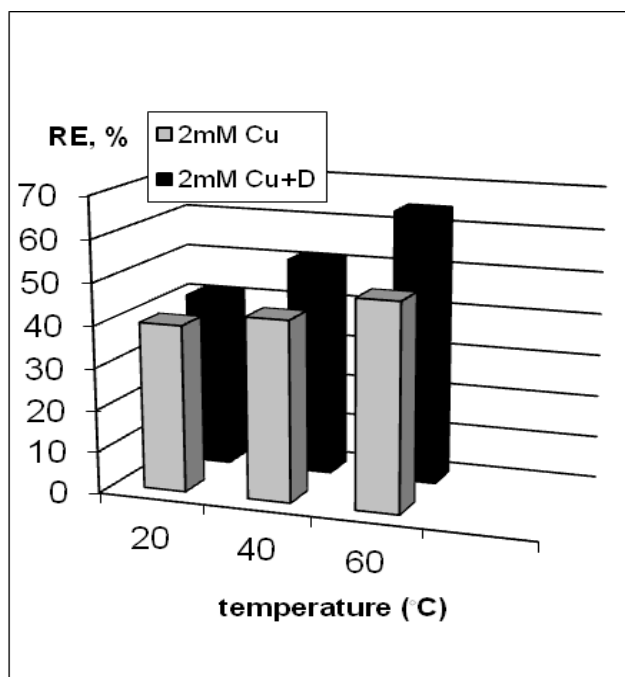
Relative adsorption  $A_r$  of LN dye and Cu(II) in the adsorption system was calculated using the following equation:

$$A_r = [q]_B/[q]_S$$

here  $[q]_B$  and  $[q]_S$  are the amounts of adsorption of specific adsorbate in the binary adsorption system and the single adsorption system at time  $t$ , respectively using the same initial concentration. If  $A_r > 1$ , the adsorption of pollutant is promoted by the presence of another pollutant in two-component system, if  $A_r = 1$ , the adsorption capacity of pollutant in two-component system is not affected by the other compound, and if  $A_r < 1$ , the presence of another contaminant reduces the adsorption of pollutant. The relative adsorption of LN dye was high in the initial 5 min of adsorption (1.4), indicating adsorption of LN dye in the binary adsorption system was promoted by the presence of Cu(II). Meanwhile, relative adsorption of Cu(II) exhibited a low ratio ( $<1$ ). Later on the relative adsorption of LN dye shows a decreasing trend and approaches a constant value of 1 while relative adsorption of Cu(II) slightly increases. The presence of LN dye in binary solution enhances the adsorption of Cu(II) on Norit PK 1-3 activated carbon. For both pollutants, LN dye and Cu(II) ions, the presence of another compound has the positive effect on adsorption kinetics with the exception of initial period of 5 min for Cu(II).

The removal efficiency of anionic metal complex dye Lanasyne Navy M-DNL (LN) and Cu(II) ions has been studied in single and LN dye-Cu(II) binary solutions using Norit PK 1-3 activated carbon. To determine removal process and properties, the effects of various operating parameters, initial concentration of Cu(II) ions (1–4 mM), contact time (5–180 min) and temperature (293–333 K) were investigated in a batch adsorption technique. The time profiles for 0.05 mM LN dye and Cu(II) have been obtained using 4.0 g of activated carbon per liter of the solution. The composition of the solution plays an important role in the removal process and the evolution of solution pH. A synergic effect was observed when carrying out the adsorption process at higher temperatures. At the temperatures of 40 and 60°C the removal percentage of the dye increases by 15-20 % in presence of Cu(II) salt. The uptake of Cu(II) also increases by 10 % in presence of LN dye. The adsorbed amount of LN and Cu(II) slightly decreased at 20°C temperature when the two solutes were present in the solution while the Cu(II) removal almost

remained unchanged when Cu(II) concentration was equal to 2 mM. The adsorption process is governed by the pseudo-second-order reaction, at various initial Cu(II) concentrations for the two adsorbates. An increase in temperature leads to an increase in the rate of diffusion of the adsorbed particles into the internal pores of the adsorbent.



**Fig. 6.** Effect of temperature on the Cu(II) removal percentage. Conditions: initial pH 5.0, agitation speed 190 rpm, contact time 180 min.

Fig. 6 reflects that the removal efficiency of Cu(II) from one component solution of 2 mM increases from 40 to 50 % with the increase in temperature from 20 to 60°C whereas it increases from 52 to 97 % when 1 mM Cu(II) solution was used. At 60°C, the maximum Cu(II) removal efficiencies were determined as 97, 50 and 39 % for 1, 2 and 4 mM Cu(II) solutions, respectively. The enhanced removal of Cu(II) from 1 mM solution may be attributed to precipitation of solid metal hydroxide. The same trend was observed using binary solutions with LN dye. At higher temperatures the positive effect of LN dye on Cu(II) adsorption from 2 mM solution has been determined (Fig. 6).

The dependence of removal efficiency of LN dye on solution temperature is more complicated. For single component solutions, the highest LN dye uptake was obtained at 20°C, but it was higher at 60°C when compared to 40°C. Whereas the positive effect of

temperature on LN dye removal from binary solutions was detected. A marked increase in the dye uptake capacity at 40–60°C temperature from two component solutions when compared to single dye solutions was observed.

At the initial stage, sorption takes place rapidly on the external surface of the adsorbent. It is seen that the rate of uptake of Cu(II) from 2 mM solution in the beginning is more rapid in binary adsorption system when compared to single one and 70 % of the total adsorption is completed within 1 h. The removal of the dye increased with increase in agitation time. The presence of copper(II) salt has a clear positive effect on the LN dye adsorption rate. At room temperature the effect of Cu(II) on the removal efficiency of LN dye is inappreciable at all Cu(II) concentrations used. Thus, it is reasonable to believe that the adsorption of Cu(II) and that of LN dye are individual and do not interfere with each other. At higher temperature of 40°C the removal efficiency of the dye from binary solutions was up to 15-20 % higher when compared to that from single solute system, presumably because of lower solution pH. The same trend was observed at 60°C temperature. The results also revealed that at 40°C temperature the maximum dye removal was attained at 2–2.6 mM Cu(II) concentration and was lower with higher Cu(II) amounts. Thus, this range of Cu(II) concentration appears to be the most favourable for LN dye adsorption.

Removal efficiency of Cu(II) decreases with increasing metal ions concentration. When the initial concentration of copper(II) ion in binary adsorption system was increased from 1 to 4 mM, the metal removal decreased from 50 to 25 % and from 90 to 40 % at 20°C and 60°C temperature, respectively.

The activation energy of Cu(II) and LN dye adsorption onto the adsorbent can be calculated by Arrhenius relationship:

$$\ln k_2 = \ln k_0 - E_a/RT$$

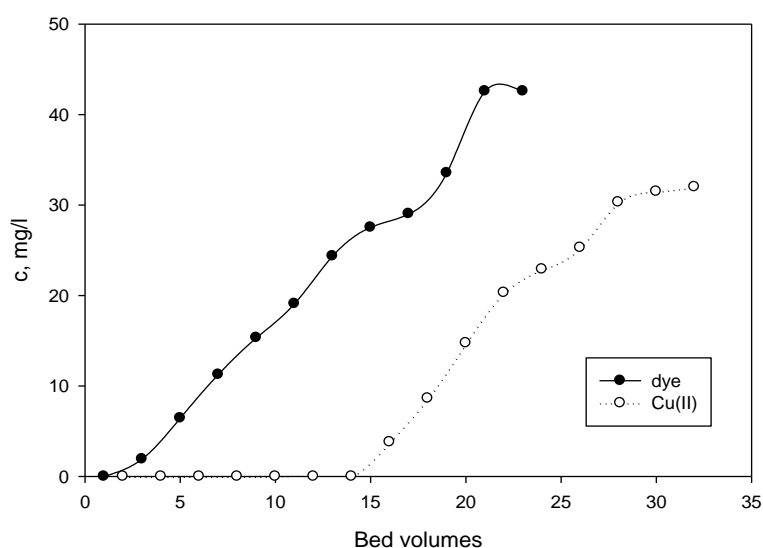
where  $k_2$  is the pseudo-second-order constant,  $k_0$  is the Arrhenius factor,  $E_a$  is activation energy of adsorption (J/mol),  $R$  is the gas constant (8.314 J/mol K),  $T$  is the solution temperature (K).

The activation energies were found to be 29.76 kJ/mol for the Cu(II) in single component solution of 2 mM and 23.24 kJ/mol for the LN dye in binary adsorption system with 2 mM Cu(II). The results obtained for the adsorption of Cu(II) and LN dye

onto activated carbon indicates that the predominant adsorption mechanism is a physisorption.

#### 2.4. Consecutive and simultaneous adsorption of chromium complex dye and copper(II) ions under dynamic conditions

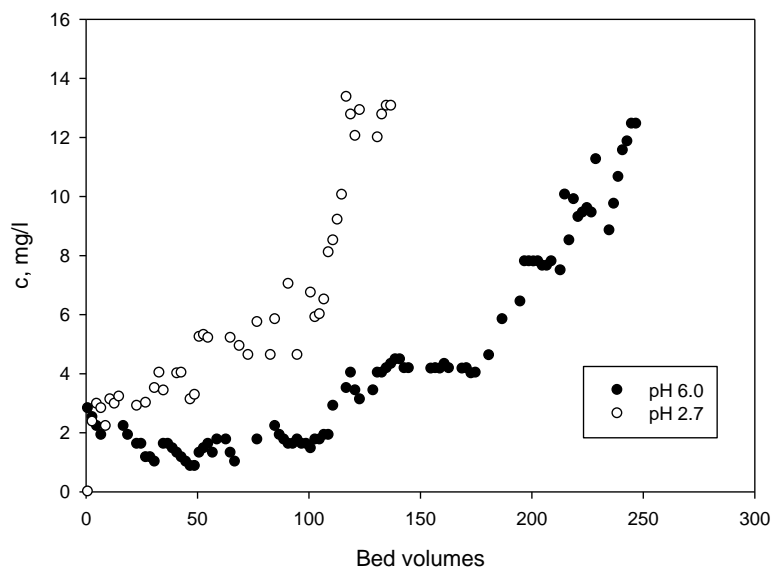
For the sake of comparison, consecutive and simultaneous adsorption of Cu(II) and LN dye was studied. In order to make the fixed-bed adsorption process economically more feasible, the spent activated carbon bed was used for the removal of copper ions. At the first stage, AC was saturated with anionic dye until 50% breakthrough was achieved (Fig. 7).



**Fig. 7.** Consecutive adsorption of anionic LN dye and Cu(II) in an Norit PK 1-3 activated carbon column. Initial concentration of the dye 0.1 mmol/L, pH 6.4. Initial concentration of copper(II) 1 mmol/L, pH 5.1.

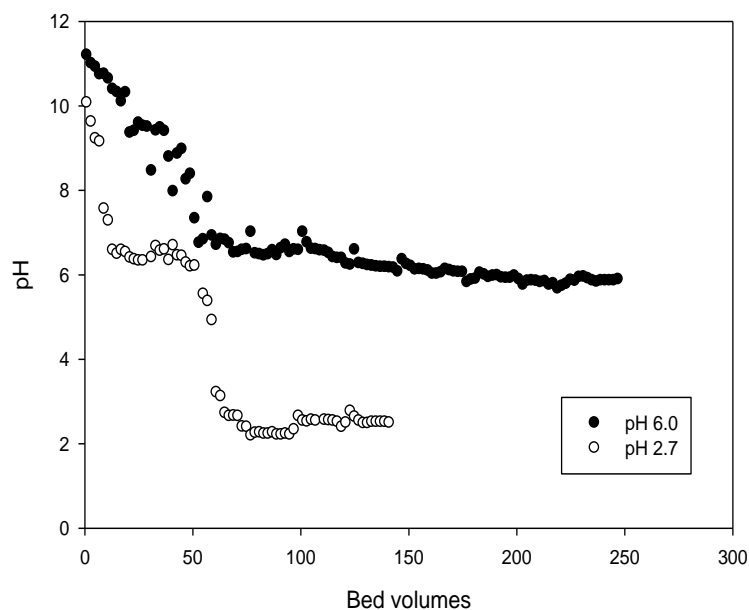
At the second stage, the removal of Cu(II) ions has been carried out using the same portion of adsorbent. LN dye-loaded AC retained > 95% of Cu(II) ions in the first 15 bed volumes (BV). The concentration of Cu(II) ions increased with time and attained 50% breakthrough after the treatment of 30 BV of 1 mmol/L copper salt solution (Fig. 7). The pH of copper(II) salt solution sharply increased from pH 5.1 to pH 9 in the first portions of effluent, later it gradually decreased and reached the constant value. The constant pH

value was achieved at the moment of 5% breakthrough. Binary solutions with initial pH 6.0 or pH 2.7, containing Cu(II) ions and anionic LN dye, were treated through the AC column. Adsorption in binary system is complicated due to the fact that many solute-surface and solute-solute interactions can be involved.



**Fig. 8.** Simultaneous adsorption of anionic LN dye and Cu(II) in an Norit PK 1-3 activated carbon column. Initial concentration of the dye 0.05 mmol/L, initial concentration of copper(II) 1 mmol/L.

Fig. 8 shows breakthrough curves of anionic dye at pH 6.0 and pH 2.7. As can be seen from the picture, the lower initial pH resulted in a shorter period to reach breakthrough point. Regardless of initial pH value, solution's pH sharply increased in the first period of saturation up to pH 10 and pH 11 during the treatment of acidic and nonacidic solution, respectively.



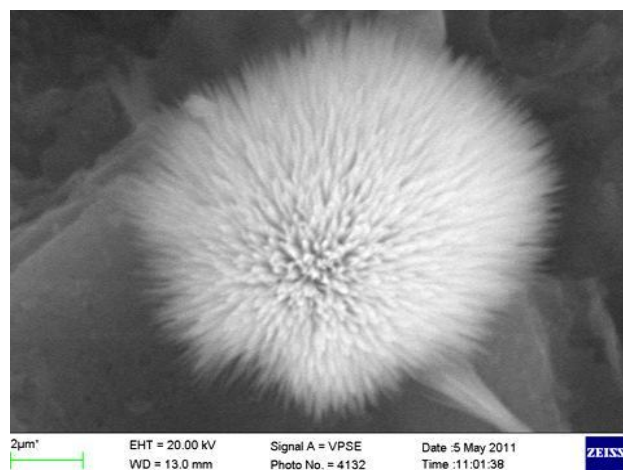
**Fig. 8.** Effluent pH curves for the simultaneous adsorption of anionic dye and copper in an activated carbon column. Flow rate 1 ml/min.

Later it decreased and reached the initial value. The 10% LN dye breakthrough in the acidic system was reached at the moment of the second sharp pH value decrease. Although for the adsorption of anionic dyes the acidic solution is more favorable, the removal of color in binary system was more effective at the initial solution pH 6.0. The copper ions may act as a supplementary agent, which, precipitated on the AC surfaces, causes an increase of surface area for the anionic dye adsorption.

Although for the adsorption of anionic dye the acid-ic solution is more favorable (Al-Degs *et al.* 2008), the results of column adsorption experiments showed the removal of color in binary system was more effective at the initial solution pH 6 (Fig. 7). The copper ions may act as a supplementary agent, which, precipitated on the AC surfaces, causes an increase of surface area for the metal complex dye adsorption.

Scanning electron microscopy (SEM) was used to characterize the copper compounds distribution on the carbon surface as a function of initial copper(II) ions concentration and solution pH. SEM studies revealed the formation of copper

compounds of various structure.



**Fig. 10.** SEM micrograph of Norit PK 1-3 activated carbon after the interaction with binary solution

Overall, it may be concluded that the removal of anionic LN dye and Cu(II) ions is possible in consecutive as well as simultaneous regime. The highest removal efficiency was achieved using combined solutions of anionic dye and copper(II) salt with initial pH 6. On the one hand, the presence of copper has positive influence on the removal of the dye, on the other hand, the presence of dye make the surface of carbon more hydrophilic with higher negative charge.

Granulated Norit PK 1-3 and extruded Norit RB 0.8CC activated carbons appear to be suitable for the simultaneous capture of dye and copper(II) ions.

### 3. CONCLUSIONS

1. The investigation using potentiometric titration and pH drift methods has shown that the Norit PK 1-3 and Norit RB 0.8CC activated carbons are materials with basic properties: the amount of basic functional groups is higher than that of acidic, according basicity the basic adsorption sites according basicity may be divided in two different groups.
2. During the process of consecutive or simultaneous adsorption the value of solution pH increases. The change in solution pH decreases with the decrease of initial solution pH and the increase of initial copper(II) concentration.
3. The adsorption capacity of activated carbons saturated with chromium complex dye towards copper(II) ions is comparable to that of unsaturated ones and it depends on the initial dye solution pH, saturation time as well as on the initial pH and concentration of Cu(II) solution.
4. Under the conditions of sufficient hydroxide ions concentration in the solution the adsorption process of chromium complex dye and copper(II) is accompanied by the formation of insoluble copper(II) compounds on the surface of activated carbon and in the bulk of the solution. The amount, the form and the distribution of the precipitate in the adsorption system depends on the initial copper(II) concentration and the initial pH of the solution.
5. The precipitate of the copper(II) compounds serves as the additional adsorption sites for chromium complex dye, their formation enhances the removal efficiency of copper(II) and the dye especially in the case of simultaneous dynamic adsorption.
6. The optimal conditions for the removal of copper(II) ions and chromium complex dye from single and binary solutions are as follows: LanasyN Navy solution



concentration 0.05-0.1 mM, and initial pH 5-6, 1-3 mmol/L copper(II) concentration and temperature of 40° C.

7. Kinetic study of the simultaneous and consecutive adsorption has shown that the chromium complex dye and copper(II) ions adsorption is governed well by the pseudo-second order and intraparticle diffusion models. An increase in temperature leads to an increase in the rate of diffusion.

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## **CHROMO KOMPLEKSINIO DAŽIKLIO IR VARIO(II) JONŲ ADSORBCIJA AKTYVINTOSIOMIS ANGLIMIS**

### **SANTRAUKA**

Disertacijoje nagrinėjami procesai, kurių metu tuo pačiu adsorbento aktyvintųjų anglių kiekiu bandyta pašalinti du skirtingos prigimties teršalus: organinį junginį chromo kompleksinį dažiklį ir vario(II) jonus. Pirmojoje, anijoninio dažiklio Lanasyn Navy M-DNL adsorbcijos pakopoje, įvyksta adsorbento paviršiaus modifikavimas. Antrojoje pakopoje gali būti pašalinti vario(II) jonai. Taip pat ištirtas vienalaikis dažiklio ir vario(II) jonų šalinimas iš mišrių tirpalų statinėmis ir dinaminėmis sąlygomis. Darbe naudotos aktyvintosios anglys Norit PK 1-3, Norit RB 0.8CC ir AC-20 (Purolite). Jos apibūdintos skenuojančios elektroninės mikroskopijos, Boehm'o titravimo ir pH slinkio metodu. Ištirta metalo kompleksinio dažiklio ir vario(II) jonų tarpusavio įtaka juos šalinant adsorbcijos metodu. Šalinimo procesui ir jo savybėms išnagrinėti, tirta įvairių veiksnių (pradinės vario(II) koncentracijos (0,4-10 mM), sąveikos laiko (5-180 min) ir temperatūros (293-333) įtaka. Vario(II) ir dažiklio adsorbcija aktyvintosiomis anglimis tirta naudojant tirpalus, kurių pH svyravo nuo pH 2 iki pH 6. Tyrimai parodė, kad dėl aktyvintųjų anglių paviršiaus sąveikos su vandeniniu tirpalu pakinta tirpalo pH. Pradinis tirpalo pH žymiai pakinta, kai adsorbcija vyksta iš vienkomponenčio dažiklio Lanasyn Navy M-DNL tirpalo. Kai tirpale yra vario(II), tirpalo pH pokytis yra mažesnis. Padidėjus tirpalo pH vyksta paviršinių nuosėdų susidarymo reakcijos. Dėl šių reakcijų iš

tirpalo pašalinama daugiau vario(II) ir dažiklio. SEM tyrimai parodė, kad adsorbento paviršiuje susidaro įvairios vario junginių struktūros (nanoplokštelės, gėlių žiedus primenantys agregatai). Eksperimentiniai duomenys buvo analizuojami taikant skirtingus adsorbcijos kinetinius modelius (pseudopirmojo, pseudoantrojo laipsnio bei vidinės difuzijos). Tyrimai, atlikti dinaminėmis sąlygomis, parodė, kad dvikomponenčio tirpalo spalva efektyviau pašalinama tuo atveju, kai tirpalo pradinė pH vertė pH 6. Iš gautų rezultatų matyti, kad granuluotos aktyviosios anglis Norit PK 1-3 ir presuotos Norit RB 0.8 CC tinka pakopinei ir vienalaikiai dažiklio ir vario(II) jonų adsorbcijai.

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