

# Kinetics of copper(II) and metal complex dye adsorption on activated carbon in the single and binary systems

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The kinetics of adsorption of Lanasyn Navy M-DNL (LN) metal complex dye and Cu(II) by granular activated carbon Norit PK 1–3 in single and binary adsorption systems has been investigated. The activated carbon has been characterized by scanning electron microscopy, Boehm titration, and pH drift method. The studies showed that interaction of Norit PK 1–3 activated carbon surface structures with aqueous solution leads to changes in pH of the solution. The initial pH value changed considerably during the experimental period in the single Lanasyn Navy M-DNL dye solution. The presence of copper(II) in the solution leads to the lower change in solution pH when compared to the single dye adsorption system. The experimental data was analyzed using various adsorption kinetic models (pseudo-first-order, pseudo-second-order and intraparticle diffusion). The results show that the pseudo-second-order equation fitted the experimental data well. Also, the diffusion model fitted the experimental data well, indicating that the process of Cu(II) and Lanasyn Navy M-DNL metal complex dye adsorption was diffusion-controlled. Relative adsorption  $A_r$  of LN dye and Cu(II) in the adsorption system was calculated. For both pollutants, LN dye and Cu(II) ions, the presence of another compound has a slight positive effect on adsorption kinetics with the exception of the initial period of 5 min for Cu(II).

**Key words:** metal complex dye, copper(II), activated carbon, adsorption, kinetics

## INTRODUCTION

Dyes are widely used in industries, such as dyestuff, textiles, leather, paper, plastics, etc., to color their products. The metal complex dye group is one of the most important and widely used groups in the textile dyeing industries [1]. Adsorption of dye molecules is an efficient and cost effective process for colour removal from wastewater. The removal of metal complex dyes, Metal Complex Blue and Metal Complex Yellow, from aqueous solutions by pine sawdust has been studied in single component sorption systems [2]. Kinetics of removing chromium complex dye from acidic aqueous solutions by

commercially available anion exchangers Purolite A 845 and Purolite A 500P has been investigated [3]. Kinetic and thermodynamic modelling of copper-phthalocyanine dye Gemazol turquoise blue-G adsorption by waste sugar beet pulp has been reported [4].

Heavy metal ions are dangerous constituents of wastewaters because of their toxicity to living systems even at low concentrations. Thus, removing of heavy metal ions from sewages, before their release to the environment, is a key problem of modern wastewater treatment [5]. Heavy metals constitute a family of contaminants that may be found coexisting with dyes in wastewater.

There is extensive literature covering multiple aspects of the adsorption of a number of different dyes [6–8] and heavy

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metals [9–11] on activated carbons. However, most of the research focused on the removal potential of a single type of dye or heavy metal ions and the amount of studies on adsorption processes in multicomponent systems is rather limited. In reality, wastewater from textile and dyeing industries contains not only dye materials, but also other pollutants, such as heavy metals [12]. Consequently, the multi-component approach is obviously required in order to understand and predict the performance of the activated carbons in the treatment of real wastewater. Malachite green and  $\text{Pb}^{2+}$ , as typical dye and heavy metal ions, have been chosen to compare their adsorption in single and binary systems on the natural zeolite [12].

The interaction between dyes and adsorbents may vary in the presence of heavy metals. Similarly, the existence of dyes may change the adsorption behaviors of adsorbents towards heavy metals. So far, little is known about the interaction between dye and heavy metal in binary adsorption systems. The competitive adsorption of congo red and copper by chitosan hydrogel beads in a binary adsorption system has been investigated [13]. It was determined that chitosan hydrogel beads show better adsorption performance towards congo red and copper in single adsorption systems. The addition of copper caused a 25% reduction in congo red adsorption capacity, while copper adsorption was enhanced slightly by the presence of congo red. The adsorption of acid blue 25,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  on a physically activated bituminous carbon and a phosphoric activated carbon from wood was studied using single and binary (dye / metal) solutions, at 30 °C and pH 5 [14]. Results showed a synergic effect of acid blue 25 in the adsorption of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ . A batch mode was applied to study the behaviour of  $\text{Cu}^{2+}$  and methylene blue (MB) adsorption in single and binary systems on wheat straw [15]. In the binary system,  $\text{Cu}^{2+}$  and MB exhibited competitive adsorption. The adsorption of  $\text{Cu}^{2+}$  or MB was considerably reduced with an increasing concentration of the other. Visa et al. [16] studied the simultaneous removal of MB and  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  in multicomponent systems using fly ash modified with NaOH. High removal efficiencies were obtained at low heavy metal concentration while the uptake of the metal ions was affected by competitive adsorption processes as their concentrations increased.

The adsorption capacity is one of the most important parameters of the adsorbent characteristics. Nevertheless, high values of sorption capacities are not sufficient in broad application areas and it is important to be able to predict the rate at which a pollutant is removed from an aqueous solution in order to design appropriate sorption treatment systems [2, 17].

The goals of the present work were to study the mutual effect of metal complex dye and copper(II) ions on their removal by adsorption and make a comparison of different kinetic models which can describe the adsorption of these pollutants on granular activated carbon.

Lanasyn Navy M-DNL, a member of anionic azo dyes, and copper(II) were selected as a typical dye and heavy metal. Adsorption kinetics in single and binary adsorption systems was conducted.

## EXPERIMENTAL

### Adsorbent

Commercial granular activated carbon (AC) Norit PK 1–3 supplied by Norit Company (AC Amersfoort, Netherlands) was used as the adsorbent without further activation. Scanning electron microscopy (SEM) analysis was conducted to study the surface texture of AC and the development of porosity. The SEM used was EVO 50EP (Carl Zeiss SMT AG). The surface functional groups were determined by Boehm titration [18, 19]. The titration of various acidic surface groups was effected using 0.05 M  $\text{NaHCO}_3$ , 0.05 M  $\text{Na}_2\text{CO}_3$ , and 0.05 M NaOH solutions. Boehm titrations quantify the basic and acidic surface groups on ACs. The total number of basic groups was measured with 0.05 M HCl solution. The number of basic sites was calculated from the amount of hydrochloric acid that reacted with the carbon. The  $\text{pH}_{\text{PZC}}$  (pH at the point of zero charge) of AC was determined by the so-called pH drift method [20] by adding 0.1 g of AC in aqueous 0.1 M  $\text{KNO}_3$  solutions. The pH of the solutions was adjusted to successive initial values between 2 and 12 with 0.1 M  $\text{HNO}_3$  or 0.1 M KOH. The suspensions were stirred for 48 h and the final pH was measured and plotted versus the initial pH. The  $\text{pH}_{\text{PZC}}$  is the value at which  $\text{pH}_{\text{final}} = \text{pH}_{\text{initial}}$ .

### Adsorbates

Lanasyn Navy M-DNL (LN) metal complex dye ( $\lambda_{\text{max}} = 616 \text{ nm}$ ) supplied by Clariant (Switzerland) was chosen as the adsorbate. Chemically, it is a 1 : 2 chromium monoazo complex dye (trisodium bis [3-hydroxy-4 [(2-hydroxy-1-naphthyl) azo] naphthalene-1-sulphonato (3-)] chromate (3-)) with the molecular mass of 834 g/mol. The chemical structure of the dye is presented elsewhere [21]. A stock solution (1 mmol/L) was first prepared by dissolving the necessary amount of Lanasyn Navy M-DNL dye in deionized water. UV-visible spectrometry (Varian Cary 50, Varian Australia Pty Ltd) was employed to measure the concentration of the dye at  $\lambda_{\text{max}}$  using a standard calibration curve.

The Cu(II) solution was prepared from a 10 mmol/L stock solution of copper chloride (Merck). The concentration of copper was determined by inductively coupled plasma emission spectrometry (Optima 7000 DV, Perkin Elmer, USA). For the single adsorption systems, 0.05 mmol/L Lanasyn Navy M-DNL and 2.25 mmol/L  $\text{CuCl}_2$  solutions were obtained by diluting stock solutions with deionized water. In a binary adsorption system, Lanasyn Navy M-DNL and copper(II) chloride solutions were mixed to get solution (100 mL) containing 0.05 mmol/L LN and 2.25 mmol/L Cu(II). The pH value of the initial dye and/or copper(II) solutions was adjusted using a 0.1 M HCl or NaOH solution.

### Batch adsorption experiments

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 ( $20 \pm 1 \text{ }^\circ\text{C}$ ) and at constant agitation

speed of 190 rpm. The sample solution was withdrawn at different time intervals (5–180 min). A fixed volume (0.001 L) of solution was taken out from the system, and later on, each sample was analyzed to determine the concentration of the copper. Subsequently, an aliquot of the supernatant was used for determination of the remaining dye concentration, and the remainder was poured back into the original solution. The pH value in all experiments was adjusted to pH 5.0 before the sorption process but the solution was not buffered in order to simulate the real situation in wastewater [22]. In all cases, the working pH was the natural value of the solutions measured at different time intervals.

### Kinetic modeling in batch system

Three simplified models were adopted to examine the sorption kinetics of metal complex dye and copper(II) ions on the activated carbon.

#### Lagergren irreversible pseudo-first-order model

The first-order rate expression of Lagergren [23], based on solid capacity, is generally expressed as follows:

$$dq/dt = k_1(q_e - q). \quad (1)$$

Integration of Eq. (1) with the boundary conditions  $q = 0$  at  $t = 0$  and  $q = q$  at  $t = t$  gives

$$q = q_e(1 - e^{-k_1 t}). \quad (2)$$

The linear form of the first-order equation is given as Eq. (3):

$$\log(q_e - q) = \log q_e - k_1 \cdot t/2.303, \quad (3)$$

where  $q_e$  and  $q$  are the amount of solute sorbed at equilibrium and time  $t$ , respectively. The first-order constant  $k_1$  and the calculated  $q_e$  values were determined from the plot slopes and intercepts of  $\log(q_e - q)$  versus  $t$ .

#### Pseudo-second-order model

The pseudo-second-order equation [24, 25] is also based on the sorption capacity of the solid phase. If the rate of sorption is a second-order mechanism, the pseudo-second-order chemisorption kinetic rate equation is expressed as

$$dq/dt = k_2(q_e - q)^2. \quad (4)$$

After integration of Eq. (4) with the boundary conditions  $q = 0$  at  $t = 0$  and  $q = q$  at  $t = t$  Eq. (4) becomes

$$q = t/(1/k_2 q_e^2 + t/q_e). \quad (5)$$

Its mostly used form is the linear dependence  $t/q$  vs  $t$ :

$$t/q = 1/k_2 q_e^2 + t/q_e, \quad (6)$$

where  $k_2$  is the pseudo-second-order rate constant. When this model is applicable, the plot of  $t/q$  against  $t$  gives a linear relationship, from which  $k_2$  and calculated  $q_e$  could be determined from the intercept and slope of the plot.

#### Intraparticle diffusion model

Weber and Morris [26] developed a widely accepted kinetic-based model that represents the time dependent intra-particle diffusion of components and shows that the sorption process is diffusion controlled if the rate is dependent upon the rate at which adsorbate and adsorbent diffuse towards one another. The model equation (7) is shown as follows:

$$q = k_{id} t^{1/2} + C, \quad (7)$$

where  $q$  (mg/g) is the adsorbate loading on the solid phase at time  $t$ ,  $k_{id}$  (mg/min<sup>1/2</sup>/g) is the intraparticle diffusion rate constant, and  $C$  (mg/g) is the constant that is proportional to the thickness of the boundary layer; the larger the value of  $C$ , the greater the boundary layer thickness.

## RESULTS AND DISCUSSION

### Characterization of activated carbon

Adsorption properties of activated carbons are determined by their textural characteristics and surface chemistry. Adsorption of organic and inorganic compounds from aqueous solutions strongly depends on the nature of carbon surface, and the size and shape of pores in the adsorbent. Norit PK 1–3 activated carbon is built of small grains the effective size of which is 1.2 mm according to the data provided by the manufacturer. The SEM image with a magnification of 2 000x shows a relatively heterogeneous surface of AC as illustrated in Fig. 1. Pores of different size and different shape could be observed in this figure.

The surface chemistry of AC is strongly determined by the presence of heteroatoms such as oxygen or nitrogen. Oxygen functional groups are the most common ones and they are reported to exhibit both basic and acidic character [18]. The

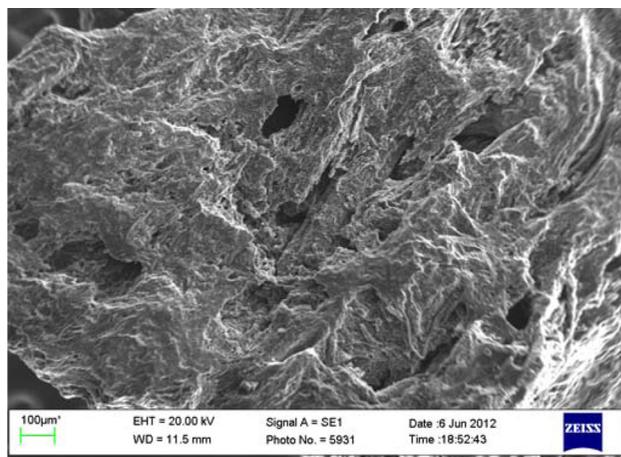


Fig. 1. SEM image of plain Norit PK 1–3 activated carbon. Magnification 2000x

Table 1. Characteristics of the Norit PK 1–3 activated carbon

Parameter	Value
Specific surface area*, m <sup>2</sup> /g	875
Effective size*, mm	1.2
Apparent density*, kg/m <sup>3</sup>	290
pH <sub>PZC</sub>	8.5
Ash content*, mass-%	8
Total acidic groups, mmol/g	0.13
Total basic groups, mmol/g	1.25

\* According to the manufacturer's specification.

acidity/basicity and pH<sub>PZC</sub> are important chemical characteristics of the adsorbent as they determine the net charge of the adsorbent surface in the solution [27]. The surface chemistry of AC was analyzed by Boehm method and pH of the point of zero charge (pH<sub>PZC</sub>). The contents of functional groups obtained by titration are reported in Table 1. The results showed that AC contains both acidic and basic groups. The amount of various basic groups referred to the unit mass of the adsorbent is substantially higher as presented in Table 1. Mineral impurities also have an influence on the surface chemistry of AC. The ash content for the Norit PK 1–3 activated carbon is equal 8 mass-%. The combined effect of all functional groups determines pH<sub>PZC</sub>. Experimental results of the pH<sub>PZC</sub> determination are illustrated in Fig. 2. It can be seen that PZC of AC in KNO<sub>3</sub> aqueous solutions is at pH 8.5 (pH level where a common plateau is obtained). The Norit PK 1–3 activated carbon is rather a basic carbon.

The chemical properties of the adsorbent affect the attractive or repulsive interactions between the adsorbent surface and the adsorbate. It is well known that adsorption of heavy metal ions is enabled when the surface of the adsorbent is negatively charged and then it is capable for electrostatic binding the metal cation. The surface charge of the adsorbent and the ionic charge of the dye molecule play an important role in adsorption as well. The positive charge developed at the surface of the activated carbon serves as active sites and facilitates the diffusion and adsorption process of anionic dye. The studies showed that interaction of AC surface structures leads to changes in pH of the solution (Fig. 3). The initial pH value changed considerably during the experimental period in the single dye solution. It is evident that the presence of copper(II) in the solution leads to the lower change in solution pH when compared to the single dye adsorption system. These results can be explained by the specific adsorption of Cu(II) cations on the basic carbon surface sites [28]. At pH < pH<sub>PZC</sub> ~ 8.5 electrostatic attraction favoured the adsorption between the positively charged surface and the negatively charged dye molecules. Though electrostatic repulsion between the Cu(II) ions and AC at pH 5.0–5.8 should not favour adsorption, the uptake of copper(II) takes place. The possible mechanism of copper(II) adsorption could be dipole-dipole ( $\pi$ -d) interactions between graphene layers and copper(II) ionic species. The surface groups influence the amount of adsorbed copper(II) and dye both by direct interaction and by the modification of external solution pH [29].

### Adsorption kinetics

Information on adsorption kinetics is needed to select optimum operating conditions for industrial applications and is helpful for determining the adsorbate uptake rate and thus the time needed to attain equilibrium. 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 the 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,

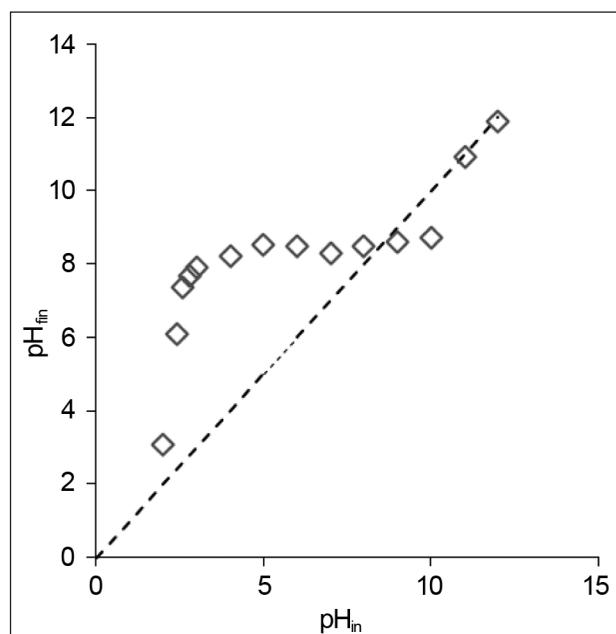


Fig. 2. Determination of pH<sub>PZC</sub> of Norit PK 1–3 activated carbon in KNO<sub>3</sub> solutions (pH<sub>in</sub>, initial value; pH<sub>fm</sub>, final value)

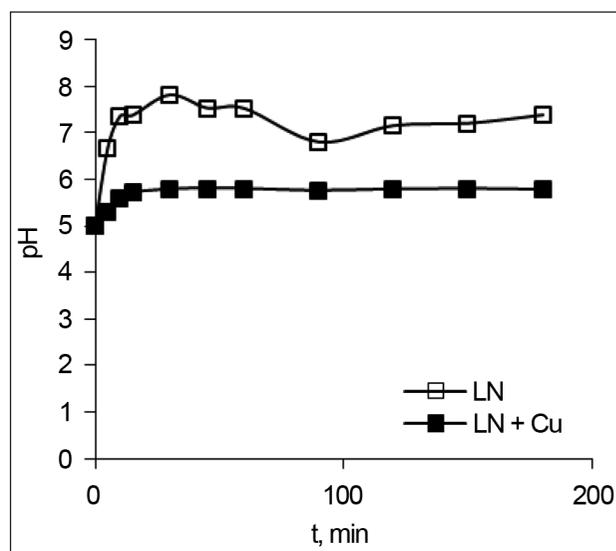


Fig. 3. Effect of the contact time on single Lanasyne Navy M-DNL dye and binary solution pH. Initial pH 5.0, liquid / solid ratio = 250, agitation 190 rpm

pH, temperature, and adsorbent dosage). Contact time experiments provided the kinetic data in the form of LN dye and Cu(II) concentration decay vs time curves. The performance of single and binary adsorption systems is illustrated in Fig. 4.

Figure 5 shows the results of the simultaneous adsorption of LN dye and copper(II) on 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 the 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.

The pH of the aqueous solution is an important controlling parameter in the adsorption process. pH of a single LN solution increases from 5.0 to 7.4 within 10 min of contact with AC whereas it changes from 5.0 to 5.8 in a two-component solution. The lower value of the binary solution pH is favourable for anionic dye adsorption. In general, the results show that the LN dye adsorption onto AC is not signifi-

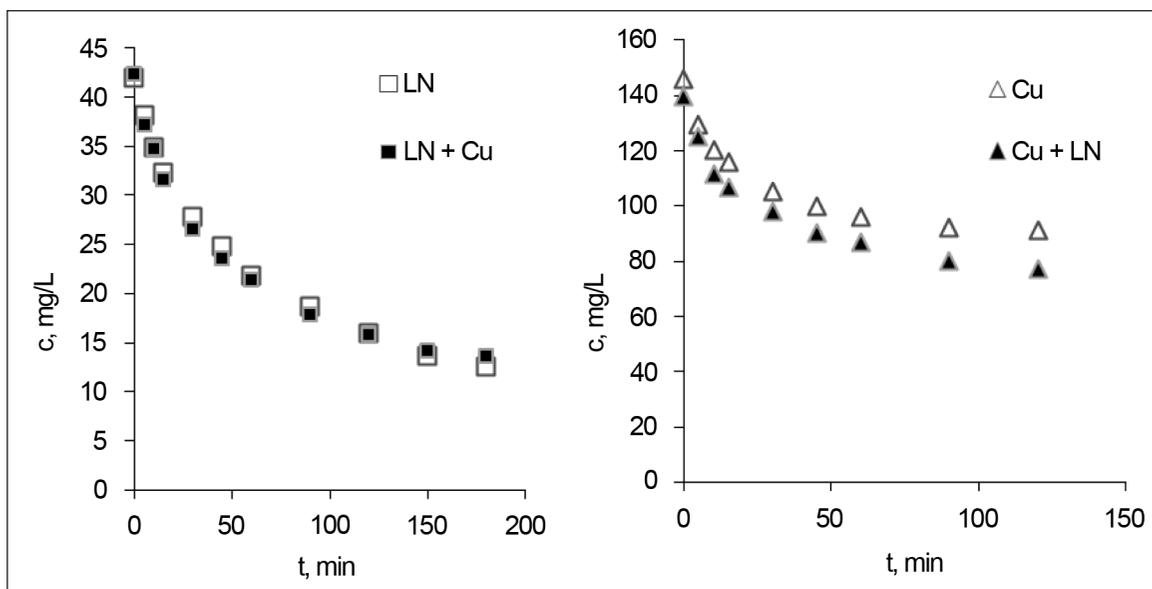


Fig. 4. Lanasy Navy M-DNL dye (left) and Cu(II) (right) concentration decay vs time curves. Liquid / solid ratio = 250, agitation 190 rpm

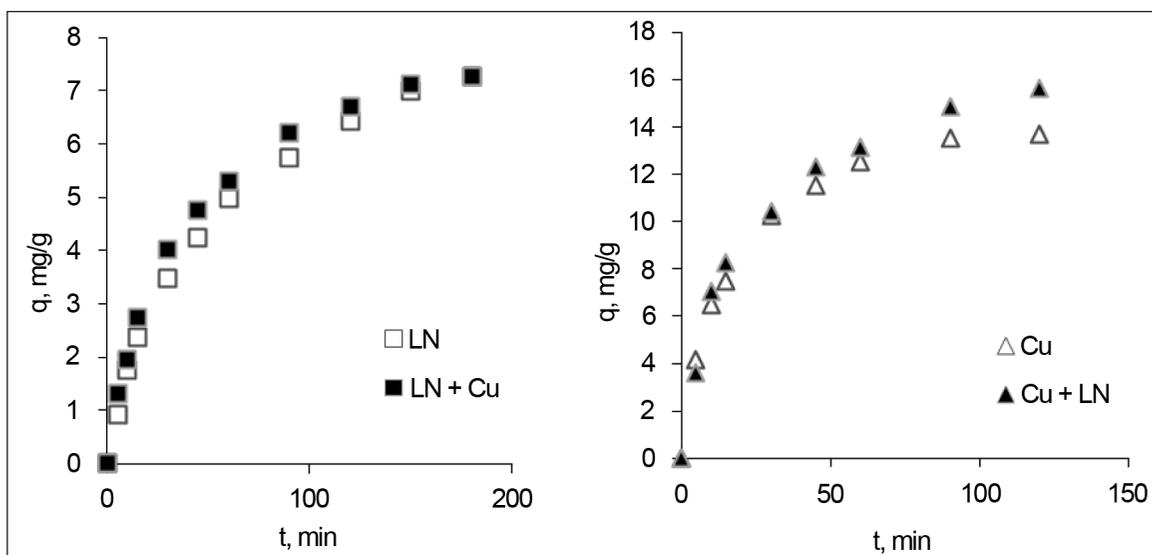


Fig. 5. Adsorption kinetics of Lanasy Navy M-DNL dye (left) and Cu(II) (right) on Norit PK 1-3 activated carbon. Initial pH 5.0, liquid / solid ratio = 250, agitation 190 rpm

cantly affected by the presence of copper(II) in the binary solution.

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. The 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 a non-uniform pore structure or a complicated pore network [30]. During the initial period of adsorption the presence of LN dye in the 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 the adsorption process of Cu(II) and LN dye on AC: the

pseudo-first-order, the pseudo-second-order, and the intraparticle diffusion. The overall sorption process may be controlled by film diffusion, intraparticle diffusion or sorption on the surface. In order to gain a better understanding of the sorption process, various kinetic models should be used to test the experimental data.

The curves by plotting  $\log(q_e - q_t)$  versus  $t$  for different adsorption systems did not show straight lines during the whole adsorption progress. Fig. 6 shows that the pseudo-first-order equation fits well for the first 30 min and thereafter the data deviate from theory. Thus, the model represents the initial stages where rapid adsorption occurs well but cannot be applied for the entire adsorption process. Table 2 lists the results of the rate constants  $k_1$  studies for different adsorption systems by pseudo-first-order model. 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

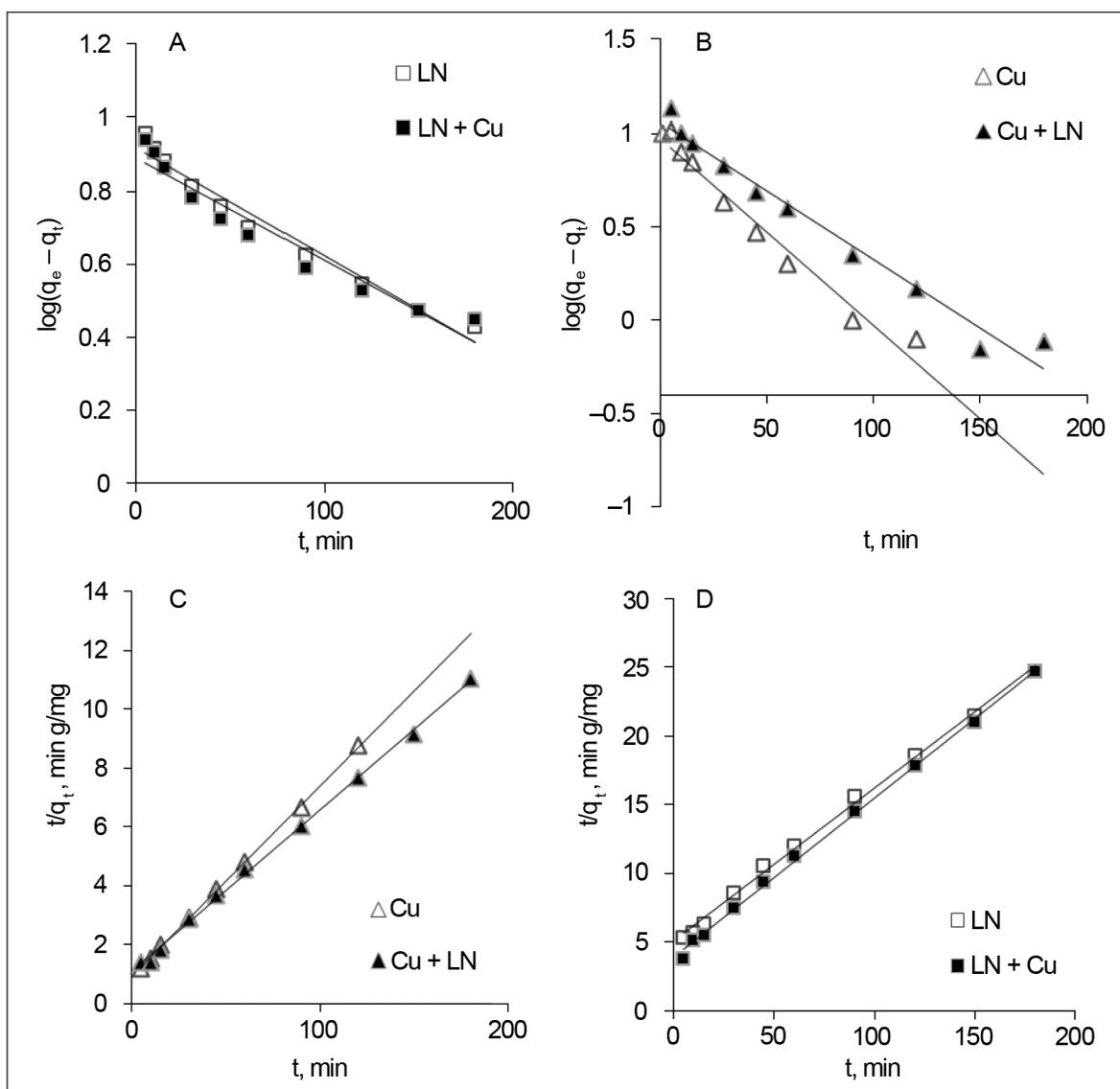


Fig. 6. Tests of the pseudo-first-order (top) and pseudo-second-order (bottom) model for the adsorption of LanasyN Navy M-DNL dye and Cu(II) in single and binary adsorption systems

Table 2. Kinetic parameters for the Lanasin Navy M-DNL dye and Cu(II) in single and binary adsorption systems

Adsorbate	$q_e$ (mg/g) experimental data	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			Intraparticle diffusion model		
		$q_e$ (mg/g) theoretical	$k_1$ (1/min)	$R^2$	$q_e$ (mg/g) theoretical	$k_2$ (g/mg · min)	$R^2$	$k_{id}$ (mg/g · min <sup>0.5</sup> )	C (mg/g)	$R^2$
LN	10.46	8.33	$6.9 \cdot 10^{-3}$	0.9701	8.97	$2.46 \cdot 10^{-3}$	0.9966	0.4490	1.5009	0.9997
LN + Cu(II)	10.03	7.81	$6.4 \cdot 10^{-3}$	0.9393	8.60	$3.49 \cdot 10^{-3}$	0.9981	0.4293	1.9760	0.9882
Cu(II)	14.50	9.43	$2.3 \cdot 10^{-2}$	0.9662	15.46	$4.46 \cdot 10^{-3}$	0.9993	0.9931	4.8388	0.9991
Cu(II) + LN	17.10	11.51	$1.7 \cdot 10^{-2}$	0.9737	18.22	$2.76 \cdot 10^{-3}$	0.9985	1.2437	3.4537	0.9880

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.

The linear plots of  $t/q$  versus  $t$  (Eq. (6)) indicates the applicability of the pseudo-second-order kinetics and good agreement with obtained experimental results. Regression coefficients ( $R^2$ ) of pseudo-second-order reaction kinetics were much better than those of pseudo-first-order reaction kinetics. The values of the correlation coefficient  $R^2$  for the pseudo-second-order adsorption model for both adsorbates are relatively high ( $>0.99$ ), and the adsorption capacities calculated by the model are also close to those determined by experiments. Therefore, it has been concluded that the pseudo-second-order adsorption model is more suitable to describe the adsorption kinetics of the LN dye and Cu(II) in single and binary adsorption systems. All kinetic data for the adsorption of LN dye and copper(II) ions onto AC, calculated from the related plots, are summarized in Table 2. In the binary solution,  $k_2$  for Cu(II) is reduced when compared to the single one. Contrary to Cu(II),  $k_2$  values for LN dye are higher in the binary adsorption system. This finding can be attributed to higher net positive charge on the surface of AC after contact with the binary solution. Hence, the electrostatic attraction also increased between LN dye and the surface of AC.

The adsorption process of an adsorbate usually takes place through several consecutive steps: bulk solution transport, film diffusion, pore diffusion, and adsorption on the surface or pores. The lowest step limits the overall adsorption rate. According to the literature, film diffusion and diffusion into particle pores (intraparticle diffusion) often control an adsorption process [31]. 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 (7). The amounts of LN dye and / or Cu(II) adsorbed versus  $t^{0.5}$  plots are shown in Fig. 7. The results show that the plots present 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) is 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

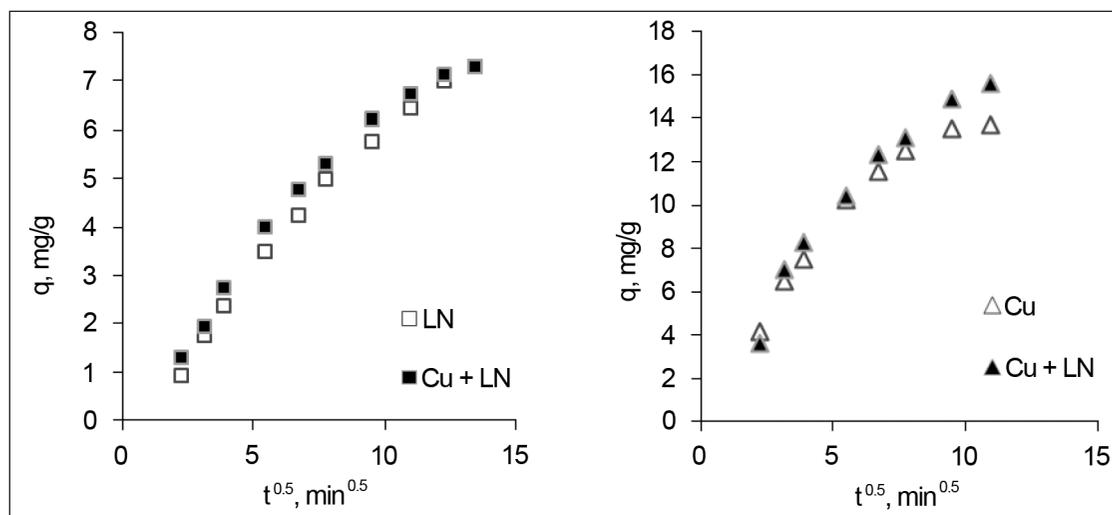


Fig. 7. The intraparticle diffusion kinetics model for the adsorption of Lanasin Navy M-DNL dye and Cu(II) in single and binary adsorption systems

size of LN, thus making it difficult to diffuse into the pores of the activated carbon [12]. Finally, the final equilibrium adsorption starts after the second stage. The values of the model intercepts,  $C$ , are higher for Cu(II) than for LN dye. Therefore, the effect of film diffusion on Cu(II) ion adsorption is probably more considerable.

Relative adsorption  $A_r$  of LN dye and Cu(II) in the adsorption system was calculated using the following equation [12]:

$$A_r = [q]_B / [q]_S, \quad (8)$$

where  $[q]_B$  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 the pollutant is promoted by the presence of another pollutant in the two-component system, if  $A_r = 1$ , the adsorption capacity of the pollutant in the two-component system is not affected by another compound, and if  $A_r < 1$ , the presence of another contaminant reduces the adsorption of the pollutant. Fig. 8 shows the variation of relative adsorption of LN dye and Cu(II) with time in the adsorption system. As can be seen from Fig. 8, the relative adsorption of LN dye was high in the initial 5 min of adsorption (1.4), indicating that the 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 the relative adsorption of Cu(II) slightly increases. The presence of LN dye in the binary solution enhances the adsorption of Cu(II) on commercial AC. Fig. 8 reflects that for both pollutants, LN dye and Cu(II) ions,

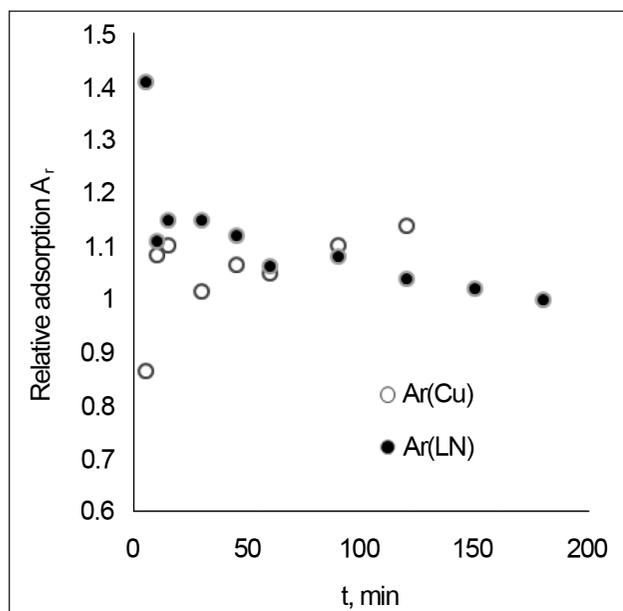


Fig. 8. Variation of the relative adsorption of LanasyN Navy M-DNL dye and Cu(II) with time

the presence of another compound has the positive effect on adsorption kinetics with the exception of the initial period of 5 min for Cu(II).

## CONCLUSIONS

The pH of the aqueous solution is an important controlling parameter in the adsorption process.

The studies showed that interaction of Norit PK 1–3 activated carbon surface structures with an aqueous solution leads to changes in pH of the solution. The initial pH value changed considerably during the experimental period in the single LanasyN Navy M-DNL dye solution. The presence of copper(II) in the solution leads to lower change in solution pH when compared to the single dye adsorption system. At  $\text{pH} < \text{pH}_{\text{PZC}} \sim 8.5$  electrostatic attraction favoured the adsorption between the positively charged carbon surface and the negatively charged dye molecules. Though electrostatic repulsion between the Cu(II) ions and activated carbon at pH 5.0–5.8 should not favour adsorption, the uptake of copper(II) takes place.

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 LanasyN Navy M-DNL dye adsorption occurred within 60 min of contact with the adsorbent.

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. During the initial period of adsorption, the presence of LanasyN Navy M-DNL dye in the binary adsorption system was not favourable for Cu(II) ions uptake. Later on, the positive effect of the dye on Cu(II) adsorption prevailed and it increased with time. The pseudo-second-order adsorption model is more suitable than the pseudo-first-order adsorption model to describe the adsorption kinetics of the LanasyN Navy M-DNL dye and Cu(II) in single and binary adsorption systems. In the binary solution,  $k_2$  for Cu(II) is reduced when compared to the single one. Contrary to Cu(II),  $k_2$  values for the dye are higher in the binary adsorption system.

The first stage in the adsorption process, the external surface adsorption, is observed from 0 to 20 min for Cu(II) and from 0 to 45 min for LanasyN Navy M-DNL 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 the dye, respectively. The diffusion rate of Cu(II) is higher than that of LanasyN Navy M-DNL dye in both single and binary adsorption systems.

The relative adsorption of LanasyN Navy M-DNL dye was high in the initial 5 min of adsorption (1.4), indicating that the adsorption of the 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 the dye shows a decreasing trend and approaches a constant value of 1 while the relative adsorption of Cu(II) slightly increases.

## ACKNOWLEDGEMENTS

The authors thank Clariant Product AG (Switzerland) for the Lanasyn Navy M-DNL dye. Thanks also belong to Norit Company (Netherlands) for providing the activated carbon.

Received 8 January 2013

Accepted 29 January 2013

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**CU(II) IR METALO KOMPLEKSINIO DAŽIKLIO ADSORBCIJOS AKTYVINTOSIOMIS ANGLIMIS KINETIKA VIENKOMPONENTĖSE IR BINARINĖSE SISTEMOSE**

*Santrauka*

Metalo kompleksinio dažiklio Lanasyn Navy M-DNL ir Cu(II) adsorbcijos aktyvintosiomis anglimis Norit PK 1–3 kinetika tirta vienkompomentėse ir binarinėse adsorbcijos sistemose. Aktyvintosios anglys apibūdintos skleidžiančiosios elektroninės mikroskopijos, Boehm'o titravimo ir pH slinkio metodais. Tyrimai parodė, kad dėl aktyvintųjų anglių paviršiaus sąveikos su vandeniniais tirpalais pakinta tirpalų pH vertė. Eksperimento metu iš esmės pakito vienkompomentės dažiklio Lanasyn Navy M-DNL tirpalo pH vertė. Binarinėje adsorbcijos sistemoje, kurioje yra Cu(II) jonų, tirpalo pH vertė pakinta mažiau. Eksperimentiniai duomenys buvo analizuojami taikant įvairius adsorbcijos kinetikos modelius: pseudopirmojo laipsnio, pseudoantrojo laipsnio ir vidinės difuzijos. Rezultatai rodo, kad eksperimentiniai duomenys tenkina pseudoantrojo laipsnio lygtį. Difuzijos modeliui taip pat paklūsta eksperimentiniai duomenys, tai rodo, kad dažiklio Lanasyn Navy M-DNL ir Cu(II) adsorbcijos procesą riboja difuzija. Adsorbcijos sistemoms nustatytos dažiklio ir Cu(II) santykinės adsorbcijos  $A_r$  vertės.

Abiems teršalams (ir dažikliui Lanasyn Navy M-DNL, ir Cu(II) jonams) antrasis tirpale esantis junginys turi nedidelį teigiamą poveikį, išskyrus pradinį Cu(II) adsorbcijos etapą, trunkantį 5 min.