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Efficiency of removal of anionic dye and copper(II) from aqueous solutions by activated carbon: effect of temperature and solution composition

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The removal efficiency of anionic metal complex dye Lanasyn Navy M-DNL (LN) and Cu(II) ions has been studied in single and LN dye-Cu(II) binary solutions using the commercial activated carbon. To determine the removal process and properties, the effects of various operating parameters, the 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 the 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.

Key words: metal complex dye, copper(II), activated carbon, removal, temperature

INTRODUCTION

Industrial development and human activities have increased the discharge of industrial wastes containing heavy metals and dyes. Since heavy metals are nonbiodegradable, they accumulate in the environment and subsequently contaminate the food chain. The treatment of textile wastewater comprising dyestuffs also poses considerable problems in the wastewater treatment industry [1]. The metal complex dye group is one of the most important groups of dyes used in the textile dyeing. The chemical and biological stability of metal complex dyes to conventional water treatment methods and the growing need for high quality treatment have made adsorption a very favourable treatment process [2]. Colour removal from aqueous solutions of metal complex dyes by biosorption using *Posidonia oceanica* leaf sheaths, different kinds of fungi and bacterial cells was investigated [3–5]. The adsorption 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. The effect of the pine sawdust dose, initial pH and concentration has been determined [2]. Adsorption is also a cost-effective and user-friendly technique for the removal of metallic pollutants from water. Activated carbon, prepared from an agricultural solid waste by-product, has been studied for the removal of copper and cadmium ions [6].

Adsorption capacity depends on the temperature, it may increase or decrease with increasing temperature.

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Adsorption of three dyes, methylene blue, malachite green, and crystal violet, from effluent solutions by activated carbon prepared from waste apricot increased with an increase in temperature, indicating that the process is endothermic [7]. A novel $KMnO_4$ modified bamboo charcoal was used for the adsorption of Pb(II) from aqueous solutions at different temperatures (288, 298 and 308 K) [8]. The thermodynamic parameters indicated that the adsorption was spontaneous and exothermic. The adsorption of Pb(II), Cu(II) and Cd(II) onto functionalized mesoporous silica was strongly dependent on temperature, and the adsorption capacity decreased with increasing the temperature, indicating the exothermic nature of adsorption [9]. The performance of activated carbon has been investigated for the adsorption of eosin dye dissolved in water. It was observed that with an increase in temperature, adsorption capacity decreased [10].

Kinetic modelling of the adsorption is important in order to design appropriate treatment systems. Kinetic analysis of the four models (pseudo first- and second-order equations, intraparticle diffusion equation and the Elovich equation) has been used to test experimental data for the adsorption of metal complex dyes by pine sawdust [2]. Removal of hexavalent chromium and methylene blue, taken as representative species for heavy metals and dyes, from one-component aqueous solutions, using pine sawdust, has been studied. The high applicability of the pseudo-first and pseudo-second order kinetic equations has been determined [11]. The rate of eosin dye adsorption by activated carbon was successfully explained by a pseudo second-order kinetic model [10].

In the water treatment, the water in most cases contains many species; they can be metal ions as well as organic substances. It is therefore important to study the competitive effects on the adsorption [12]. A multicomponent solution may exhibit three possible types of adsorption effects under competitive conditions: synergism, antagonism and non-interaction. The adsorption of Acid Blue 25, Basic Blue 9, Basic Violet 3, Pb^{2+}, Ni^{2+}, Zn^{2+}, and Cd^{2+} ions has been studied in single and dye-metal binary solutions using two mineral materials: clinoptilolite and erionite. In the multicomponent adsorption experiments an antagonistic effect was observed in the removal of basic dyes and heavy metals [13]. Effect of sodium dodecyl sulphate (SDS) on the adsorption of Zn(II) and Ni(II) on carbon derived from mustard oil cake was investigated. Addition of SDS favoured the adsorption process [14].

The aim of this work was to ascertain the reciprocal effect of metal complex dye Lanasyn Navy M-DNL (LN) and copper(II) on their uptake from a binary solution by activated carbon. Comparative studies of Cu(II) ions and anionic dye removal from their single solutions have also been carried out using the same adsorbent. The effects of the important factors, such as temperature, pH, copper(II) ion concentration, and competitive effects were discussed in this study.

EXPERIMENTAL

Adsorbent and adsorbates

Commercial granular activated carbon (AC) Norit PK 1–3, supplied by Norit Company (AC Amersfoort, Netherlands), was used as the adsorbent without further activation. The physical and chemical properties of the adsorbent are presented elsewhere [15].

Lanasyn Navy M-DNL (LN) metal complex dye (λ_{max} = 616 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 molar mass of 834 g/mol. The chemical structure of the dye is presented elsewhere [16]. 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 λ_{max} using a calibration curve. Additionally, special calibration curves were also obtained for binary LN dye and Cu(II) solutions.

The Cu(II) solutions were 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 $CuCl_2$ solutions in the range of 1–4 mmol/L 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 1–4 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

Batch adsorption experiments were carried out in 250-mL Erlenmeyer flasks by agitating 0.1 L of solution with 0.4 g activated carbon at three different temperatures (20, 40 and 60 °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 the 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 [17]. In all cases, the working pH was the natural value of the solutions measured at different time intervals.

Two simplified models (pseudo-second-order equation [18, 19] and intraparticle diffusion model [20]) were adopted to examine dependence of the sorption kinetics of metal complex dye and copper(II) ions on temperature and copper(II) ions concentration.

The removal efficiency (RE) of adsorbate and adsorption capacity (q_t) was calculated using the following relationships [21]:

$$\% \text{ RE} = [(C_0 - C_t)/C_0] \cdot 100, \quad (1)$$

$$q_t = (C_0 - C_t) \cdot V/m, \quad (2)$$

where C_0 is an initial concentration of adsorbate (mg/L), C_t is an adsorbate concentration (mg/L) at time t, V is the volume of the solution (L), m is the mass of the adsorbent (g).

RESULTS AND DISCUSSION

Adsorption experiments for copper(II) and LN dye removal were conducted using both the single component and two component solutions. The performance of adsorption treatment depends on the interactions between the solute–solvent, solute–sorbent, and solvent–sorbent. In an aqueous solution, the LN dye (a salt consisting of a medium strong acid and a strong base) was dissolved, and the medium strong sulfonate groups of the metal complex dye were dissociated and converted to anionic dye ions [22]:

$$R(SO_3)_2Na_2 \rightarrow R(SO_3)_2^{2-} + 2Na^+. \quad (3)$$

The speciation of copper(II) in the aqueous solution depends on solution pH. It has been assumed that metal ion removal by activated carbons is due to the adsorption of free metal ions (M^{m+}) and their hydroxides ($M(OH)_l^{(m-l)+}$). However, an additional metal chloride ($MCl_l^{(m-l)+}$) could be formed when chloride salts are used [23]. The interaction between activated carbon and aqueous solutions involves all the species dissolved in water. The adsorption process can be considered as a network of parallel-consecutive adsorption reactions with the ionic species and the active sites as reagents and the adsorbed species as products. The possible adsorption pseudo-reactions for the cations are as follows [24]:

$$\sigma H + P^+ = \sigma P + H^+, \quad (4)$$

$$\sigma H + P^+ = \sigma HP^+, \quad (5)$$

$$\sigma_n + P^+ = \sigma_n P^+, \quad (6)$$

where σH denotes the CO_xH_y functional groups with acid (4) or base (5) behaviour, σ_n are the Lewis base ones, P^+ stands for metallic cations, H^+ ions and all other cations present in the solution.

The possible adsorption pseudo-reactions for the anions are the following:

$$\sigma H + H^+ = \sigma H_2^+, \quad (7)$$

$$\sigma H_2^+ + Q^- = \sigma H_2^+ Q^-. \quad (8)$$

The presence of surface heteroatoms and the structure of the graphitic layer, as well as the ashes properties, determine the occurrence of active sites acting as Lewis acids or bases [25]. Ash content for Norit PK 1–3 activated carbon is equal 8 mass-%, the amount of various basic groups referred to the unit mass of the adsorbent is substantially higher than acidic ones, 1.25 and 0.13 mmol/g, respectively [15]. The combined effect of all functional groups and mineral impurities determines the surface chemistry of the adsorbent and the adsorption process of Cu(II) and LN dye, which may be described by equations (4)–(8).

Dependence of pH on the solution composition and temperature

The pH value is one of the most important parameters affecting the adsorption process since the surface charge of an adsorbent could be modified by changing pH of the solution [26]. The study has showed that interaction between the activated carbon and the binary or single component solution leads to changes in pH of the solution. The increase of the contact time to 180 min is accompanied by a simultaneous increase of the solution pH (Figs. 1, 2). This pH evolution may be assigned to the adsorption of hydrogen ions from the solution and dissolution of some impurities from the granules of activated carbon [27]. The change of solution pH was observed at all the temperatures investigated. It decreases with the increasing Cu(II) concentration, for both single and binary adsorption systems. At constant Cu(II) concen-

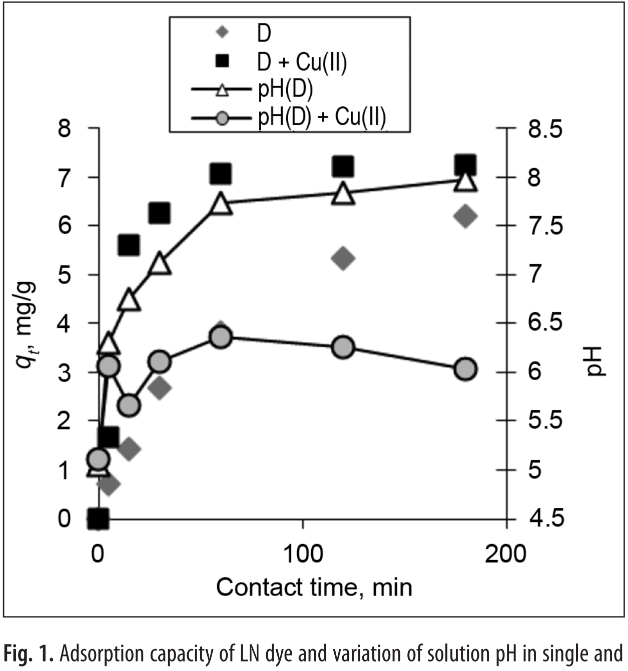

Fig. 1. Adsorption capacity of LN dye and variation of solution pH in single and binary systems with increasing contact time. Initial pH 5.0, C_0 ($CuCl_2$) = 1 mM, liquid / solid ratio 250 : 1, agitation 190 rpm, temperature 60 °C

tration the change in solution pH decreases with increasing temperature. At the temperature of 60 °C, when the contact time was 15–60 min, the increased pH value drops down, after that it slowly increases again (Figs. 1, 2). The same trend was observed at 40 °C (not shown). It might be suggested that there is possibly a hydrolysis reaction producing H^+ ions and increasing the solution acidity.

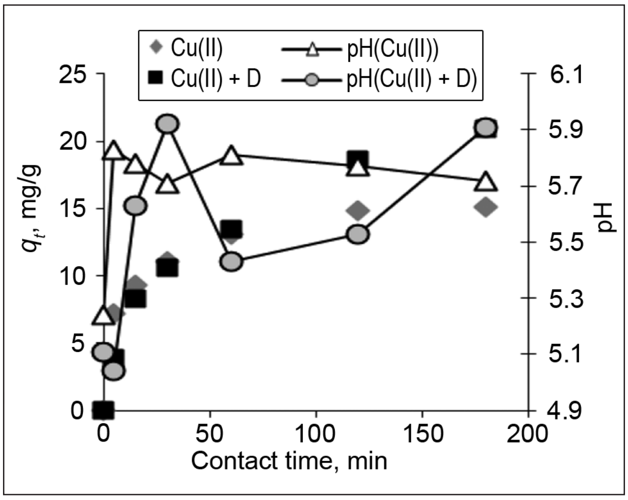

Fig. 2. Adsorption of copper(II) and variation of solution pH in single and binary systems with increasing contact time. Initial pH 5.0, C_0 ($CuCl_2$) = 2 mM, liquid / solid ratio 250 : 1, agitation 190 rpm, temperature 60 °C

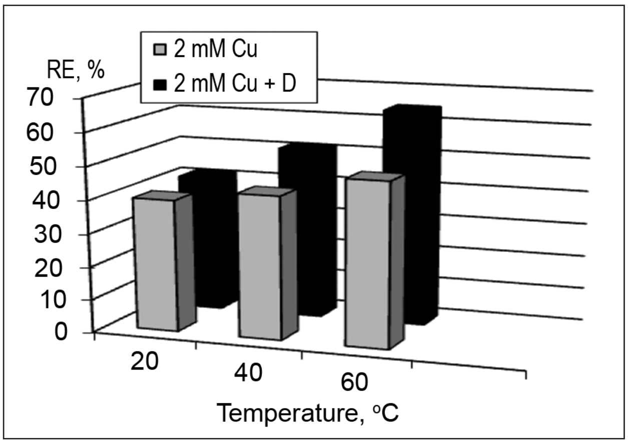

Fig. 3. Effect of temperature on the Cu(II) removal percentage. Conditions: initial pH 5.0, agitation speed 190 rpm, contact time 180 min

For the single LN dye solutions pH value gradually increases and after the period of 180 min it changes from the initial pH 5.0 to the final pH 7.4–8.0 (Fig. 1). At room temperature (20 °C) the difference between the pH values of the single LN dye solution and mixtures with Cu(II) salt is lower than that at higher temperatures. The lower pH values of binary solutions are favourable for the adsorption of anionic LN dye. The higher pH values (pH > 5.6) of low concentration Cu(II) solutions affect the removal efficiency of the contaminants from both single and binary systems because of the precipitation reactions. When pH is increased, more hydroxyl ions will be presented in the solution, resulting in surface precipitation [28].

Effect of temperature

The effect of temperature on the adsorption rate and removal efficiency of LN dye and Cu(II) was investigated at 20, 40 and 60 °C. The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate [29].

Removal efficiency of Cu(II) from the one component solution of 2 mM increases from 40 to 50% with the increase in temperature from 20 to 60 °C (Fig. 3) whereas it increases from 52 to 97% when the 1 mM Cu(II) solution was used (Table 1). 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 the 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 the 2 mM solution has been determined (Fig. 3).

Table 1. **Removal efficiency of copper(II) and LN dye from single and binary systems. Contact time 180 min**

Adsorption system			Removal efficiency, %		
Adsorbate	**Single (s) or binary (b)**	**C_0 (Cu(II)), mmol/L**	**20 °C**	**40 °C**	**60 °C**
Copper(II)	s	1	52.4	82.2	96.6
	b	1	50.4	64.5	90.1
	s	2	39.9	43.1	49.4
	b	2	41.2	51.6	64.7
	s	4	30.3	–	38.7
	b	4	25.1	–	40.1
Lanasyn Navy M-DNL	s	–	62.2	41.4	50.9
	b	1	59.8	55.6	71.2
	b	2	54.9	63.9	65.1
	b	2.6	–	66.3	–
	b	4	54.0	56.1	63.0

The dependence of the 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 (Fig. 4). 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. The capacity of activated carbon for the dye sorption was enhanced by 15–20% (Table 1).

Effect of contact time and Cu(II) concentration

In order to establish time for maximum uptake and to know the kinetics of adsorption process, the adsorption of Cu(II) on activated carbon was studied as a function of contact time and the results are shown in Fig. 5. 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 the 2 mM solution in the beginning is more rapid in the binary adsorption system when compared to single one and 70% of the total adsorption is completed within 1 h. Figure 6 summarizes the removal of LN dye by activated carbon as a function of contact time. It is clear that the removal of the dye increased with increase in agitation time. As seen in Fig. 6, the presence of copper(II) salt has a clear positive effect on the LN dye adsorption rate. 1–4 mM Cu(II) concentrations were used to elucidate the influence of initial copper(II) salt concentration on the LN dye and Cu(II) removal. At room temperature the effect of Cu(II) on the removal efficiency of LN dye is inappreciable at all Cu(II) concentrations used (Table 1). 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 the single solute system, presumably because of lower solution pH (Fig. 6). 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 (Table 1). 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 the 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 (Table 1). Sufficient adsorption sites are available at lower initial concentration, but at higher concentration metal ions are greater than adsorption sites [26]. The higher surface coverage resulting from the increase of metal ion concentration raises the activation energy for reaction, thereby making it more difficult for the surface to bind metal ions [23]. Although, the adsorption

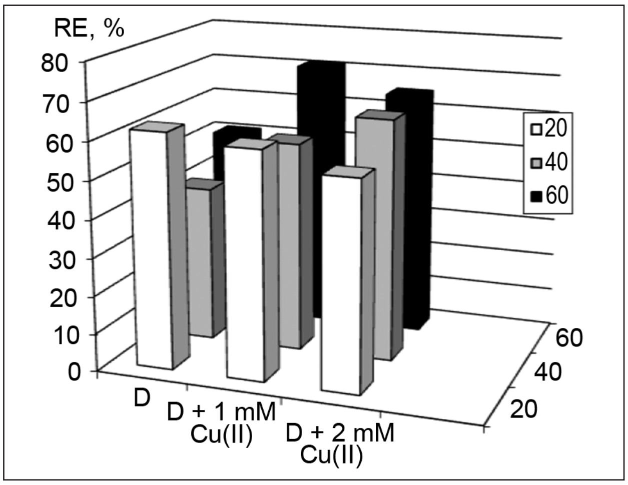

Fig. 4. Effect of temperature and solution composition on the LN dye removal percentage. Conditions: initial concentration of LN dye 0.05 mM, initial pH 5.0, agitation speed 190 rpm, contact time 180 min

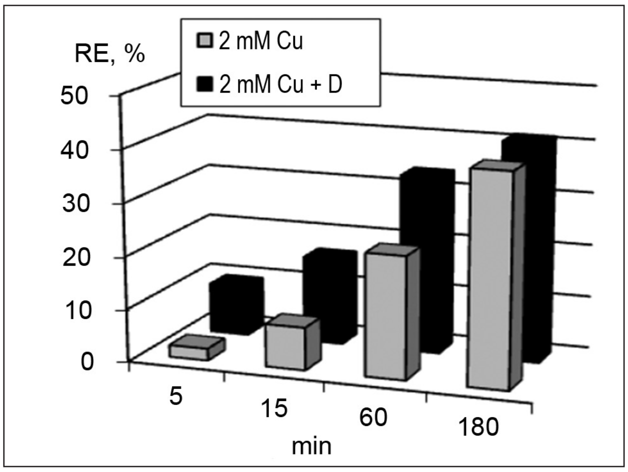

Fig. 5. Effect of contact time and LN dye on the removal efficiency of Cu(II). Conditions: initial concentration of LN dye 0.05 mM, initial pH 5.0, agitation speed 190 rpm, temperature 20 °C

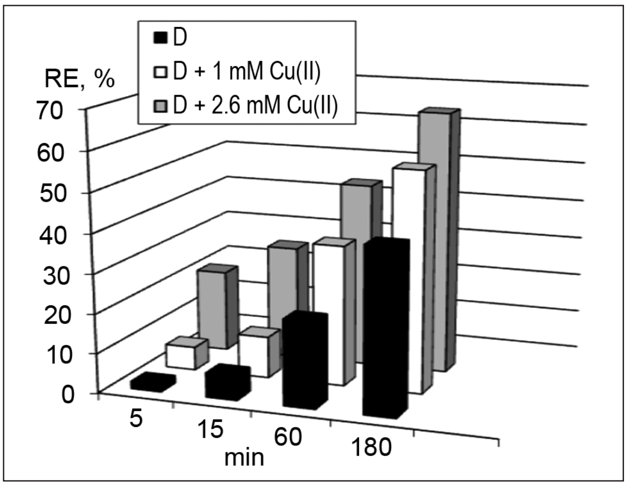

Fig. 6. Effect of contact time and Cu(II) concentration on the removal efficiency of LN dye. Conditions: initial concentration of LN dye 0.05 mM, initial pH 5.0, agitation speed 190 rpm, temperature 40 °C

studies revealed that higher temperature enhances Cu(II) uptake.

Effect of LN dye on Cu(II) removal

The influence of the LN dye on Cu(II) removal was analyzed in terms of adsorption rate (adsorption kinetics) and removal efficiency. Metal complex dye adsorbed by activated carbon changes the hydrophobicity and hydrophylicity character of the surface of the sorbent. At room temperature the mutual effect of LN dye and Cu(II) on their adsorption is insignificant. At higher temperatures the positive effect of LN dye on Cu(II) removal was determined when the Cu(II) concentration was 2–4 mM. On the other hand, this concentration of Cu(II) was also favourable for the removal of LN dye (Table 1). The removal efficiency values are found in the range of 90.1–25.1% for Cu(II) removal from the two component solution. The presence of LN dye in the adsorption system enhanced Cu(II) uptake from the solution of 2 mM in the range of temperature 20–60 °C.

Kinetics of adsorption

Kinetic tests were used to characterize the adsorption rates and the process dynamics of adsorption reaction. For the examination of the controlling mechanisms of adsorption process, such as chemical reaction and diffusion control, the pseudo-second order and intraparticle diffusion models were used for the description of experimental data, covering a wide range of working conditions. Data were applied to the Ho and McKay's pseudo-second-order kinetic rate equation [18, 19]. To understand the applicability of the model, linear plots of t/q_t versus t under three different temperatures (20, 40 and 60 °C) and various Cu((II) ions concentrations from 1 to 4 mM for the adsorption of Cu(II) and LN dye were obtained. The k_2, q_e and correlation coefficients were calculated from these plots and are given in Tables 2 and 3. The plots of t/q_t vs t show a linear relationship for LN dye as well as for Cu(II). The correlation coefficients (R^2) are high, in the ranges of 0.9547–0.9974 and 0.9675–0.9965 for LN dye and Cu(II), respectively. Equilibrium adsorption capacities of activated carbon for LN dye and Cu(II) have been calculated using the pseudo-second-order sorption model. In addition, the initial sorption rates h (mg/g min) also have been obtained from the model, which can be defined as follows [2]:

$$h = k_2 \cdot q_e^2, \tag{9}$$

where k_2 is the rate constant of pseudo-second-order adsorption (g/mg min), q_e is the amount of the adsorbate adsorbed at equilibrium (mg/g).

The values of pseudo-second-order rate constants k_2 have a tendency to increase with temperature increase, thereby confirming that the process is endothermic. Endothermic nature of the adsorption process might be due to the chemical interaction between the adsorbate and the chemical functional groups on the surface of the adsorbent [30]. The values of k_2 for Cu(II) adsorption from the 2 mM solution increases from $1.40 \cdot 10^{-3}$ to $5.86 \cdot 10^{-3}$ g/mg min with increase in temperature from 20 to 60 °C. The equilibrium adsorption capacity q_e for Cu(II) adsorption also increases (Table 2). As seen in Table 2, the value of k_2 depends on the initial Cu(II) concentration. When the initial Cu(II) ions concentration increases from 1 to 4 mM, the pseudo-second-order constants diminish from $3.57 \cdot 10^{-3}$ to $6.92 \cdot 10^{-4}$ g/mg min at 20 °C temperature and from $2.56 \cdot 10^{-3}$ to $7.10 \cdot 10^{-4}$ g/mg min at 60 °C temperature. While the initial sorption rate, h, increases with an increasing of initial Cu(II) concentration (Table 2).

The pseudo-second-order rate constant k_2 for LN dye adsorption on activated carbon indicates an increase with

Table 2. **Kinetic parameters for copper(II) in single and binary adsorption systems**

Temperature, °C	Solution composition	Pseudo-second-order kinetic model				Intraparticle diffusion model	
		q_e, mg/g	k_2, g/mg min	h, mg/g min	R^2	k_{id}, mg/g min$^{0.5}$	R^2
20	1 mM Cu(II)	9.24	$3.57 \cdot 10^{-3}$	0.3050	0.9828	0.5922	0.9974
	1 mM Cu(II)+D	11.30	$1.15 \cdot 10^{-3}$	0.1468	0.9745	0.5957	0.9998
	2 mM Cu(II)	14.20	$1.40 \cdot 10^{-3}$	0.2823	0.9887	1.0981	0.9988
	2 mM Cu(II)+D	15.48	$2.86 \cdot 10^{-3}$	0.6853	0.9986	1.5101	0.9781
	4 mM Cu(II)	29.15	$6.92 \cdot 10^{-4}$	0.5883	0.9909	1.5747	0.9923
	4 mM Cu(II)+D	26.11	$1.91 \cdot 10^{-3}$	1.3012	0.9965	1.5399	0.9942
40	1 mM Cu(II)	14.88	$1.89 \cdot 10^{-3}$	0.4190	0.9723	0.9617	0.9953
	1 mM Cu(II)+D	12.18	$1.79 \cdot 10^{-3}$	0.2656	0.9757	0.7982	0.9982
	2 mM Cu(II)	14.60	$3.22 \cdot 10^{-3}$	0.6864	0.9940	1.2749	0.9963
	2 mM Cu(II)+D	19.72	$1.23 \cdot 10^{-3}$	0.4783	0.9869	1.4353	0.9986
	2.6 mM Cu(II)	27.03	$8.99 \cdot 10^{-4}$	0.6566	0.9675	1.6479	0.9749
	2.6 mM Cu(II)+D	29.76	$1.81 \cdot 10^{-3}$	1.6010	0.9965	1.7819	0.9924
60	1 mM Cu(II)	17.15	$2.56 \cdot 10^{-3}$	0.7515	0.9886	0.9176	0.9954
	1 mM Cu(II)+D	16.53	$2.17 \cdot 10^{-3}$	0.5923	0.9809	0.9273	0.9824
	2 mM Cu(II)	15.72	$5.86 \cdot 10^{-3}$	1.4481	0.9881	1.0609	0.9903
	2 mM Cu(II)+D	24.33	$1.18 \cdot 10^{-3}$	0.6985	0.9857	1.4468	0.9964
	4 mM Cu(II)	35.98	$7.10 \cdot 10^{-4}$	0.8920	0.9908	1.7471	0.9935
	4 mM Cu(II)+D	33.67	$2.42 \cdot 10^{-4}$	0.2745	0.9726	1.7349	0.9978

Table 3. **Kinetic parameters for the Lanasyn Navy M-DNL dye in single and binary adsorption systems**

Temperature, °C	Solution composition	Pseudo-second-order kinetic model				Intraparticle diffusion model	
		q_e, mg/g	k_2, g/mg min	h, mg/g min	R^2	k_{id}, mg/g min$^{0.5}$	R^2
20	D	9.49	$2.28 \cdot 10^{-3}$	0.2052	0.9878	0.4236	0.9755
	D +1 mM Cu(II)	9.95	$7.23 \cdot 10^{-4}$	0.0716	0.9642	0.4905	0.9958
	D +2 mM Cu(II)	8.00	$1.54 \cdot 10^{-3}$	0.0986	0.9651	0.4595	0.9868
	D +4 mM Cu(II)	9.11	$2.30 \cdot 10^{-3}$	0.1909	0.9567	0.4162	0.9945
40	D	8.84	$5.69 \cdot 10^{-4}$	0.0445	0.9547	0.3623	0.9979
	D +1 mM Cu(II)	8.27	$1.48 \cdot 10^{-3}$	0.1012	0.9625	0.5529	0.9921
	D +2 mM Cu(II)	7.81	$3.36 \cdot 10^{-3}$	0.2050	0.9816	0.6278	0.9932
	D +2.6 mMCu(II)	8.60	$4.81 \cdot 10^{-3}$	0.3557	0.9868	0.5659	0.9952
60	D	8.29	$1.88 \cdot 10^{-3}$	0.1292	0.9904	0.4875	0.9998
	D +1 mM Cu(II)	7.72	$1.39 \cdot 10^{-2}$	0.8283	0.9950	0.5093	0.9985
	D +2 mM Cu(II)	7.75	$4.68 \cdot 10^{-3}$	0.2811	0.9974	0.5204	0.9861
	D +4 mM Cu(II)	9.47	$2.96 \cdot 10^{-3}$	0.2655	0.9780	0.5832	0.9993

an increase in binary solution temperature (Table 3). When the temperature increases from 20 to 60 °C, the k_2 values for LN dye adsorption increase from $7.23 \cdot 10^{-4}$ to $1.39 \cdot 10^{-2}$ g/mg min in the binary adsorption system with 1 mM Cu(II) and from $1.54 \cdot 10^{-3}$ to $4.68 \cdot 10^{-3}$ g/mg min in that with 2 mM Cu(II). The k_2 value is the highest at 20 °C temperature when the adsorption of LN dye takes place in the single component system. The dependence of q_e values for LN dye adsorption on adsorption temperature is inappreciable.

The activation energy of Cu(II) and LN dye adsorption onto the adsorbent can be calculated by the Arrhenius relationship [31]:

$$\ln k_2 = \ln k_0 - E_\mathrm{a}/RT, \tag{10}$$

where k_2 is the pseudo-second-order constant, k_0 is the Arrhenius factor, E_a is the activation energy of adsorption (J/mol), R is the gas constant (8.314 J/mol K), T is the solution temperature (K). Plotting of ln k_2 against the reciprocal temperature gives a reasonably straight line (not shown), the gradient of which is $-E_\mathrm{a}/R$. The magnitude of activation energy gives an idea about the type of adsorption. Low activation energies (5–50 kJ/mol) are characteristics for physical adsorption, while higher activation energies (60–800 kJ/mol) suggest chemical adsorption.

The activation energies were found to be 29.76 kJ/mol for the Cu(II) in the single component solution of 2 mM and 23.24 kJ/mol for the LN dye in the 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 physisorption. Therefore, the affinity of Cu(II) and LN dye for activated carbon may be ascribed to electrostatic attractions and Van der Waals forces between the adsorbates and the surface of the carbon particles. This value is consistent with the value in the literature where the activation energy was found to be 18.54 kJ/mol for the adsorption of methylene blue from the aqueous solution using carbon nanotubes [32].

The possibility of intraparticle diffusion resistance affecting adsorption was explored by using the intraparticle diffusion model [20]. According to this model, the plot of uptake q_t versus $t^{0.5}$ should be linear if intraparticle diffusion is involved in the adsorption process. The plots of q_t against $t^{0.5}$ for LN dye and Cu(II) adsorption on activated carbon are multi-linear (not shown), indicating that the sorption process consists of two or more steps. The first, sharper portion (about 5–10 min), is external surface adsorption. The second portion is a gradual adsorption stage in which the intraparticle diffusion is rate-controlling. The slope of this portion was used to derive the values of the intraparticle diffusion rate parameter k_i, given in Tables 2 and 3 for Cu(II) uptake and LN dye adsorption, respectively. The correlation coefficients (R^2) for the intraparticle diffusion model are between 0.9781–0.9998 for Cu(II) and 0.9755–0.9998 for LN dye. This indicates that Cu(II) and LN dye adsorption may be followed by the intraparticle diffusion model up to 60–90 min. As can be seen from the results, the rates of LN dye and Cu(II) diffusion into the granules of activated carbon depend on the temperature. An increase in temperature leads to an increase in the rate of diffusion of the adsorbed particles into the internal pores of the adsorbent. The same trend was observed in both single and binary adsorption systems (Tables 2, 3). Additionally, the intraparticle diffusion coefficient values for Cu(II) adsorption obtained at different temperatures increases with increase in Cu(II) concentration.

CONCLUSIONS

A synergic effect may be attained when carrying out the adsorption process at higher temperatures of 40–60 °C. An increase in both Cu(II) and LN dye removal percentage was found for binary adsorption systems when compared to that for single solute systems. In binary adsorption systems, the most efficient removal of the LN dye is that obtained under the following optimal conditions: Cu(II) concentration equal to 1–2.6 mM, and a sorption temperature of 40–60 °C. At higher temperatures of 40 and 60 °C the removal percentage of the dye increases by 15–20% in the presence of Cu(II) salt. The uptake of Cu(II) also increases by 10% in the presence of LN dye. The adsorbed amount of LN dye 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. An increase in Cu(II) removal was found with increasing temperature for both single and binary systems. When the initial Cu(II) concentration was increased, the metal removal percentage decreased.

The change of solution pH during the adsorption process was observed at all temperatures investigated, thus Cu(II) and LN dye removal was affected. Cu(II) salt, present in the solution, was able to maintain lower pH value, consequently, to develop the positive charge at the surface of the adsorbent. This may facilitate anionic dye adsorption. On the other hand, anionic dye adsorbed on activated carbon can act as a cation exchanger and affect the uptake of Cu(II).

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ANIJONINIO DAŽIKLIO IR VARIO(II) ŠALINIMO IŠ VANDENINIŲ TIRPALŲ AKTYVINTOSIOMIS ANGLIMIS EFEKTYVUMAS: TEMPERATŪROS IR TIRPALO SUDĖTIES ĮTAKA

Santrauka

Anijoninio metalo kompleksinio dažiklio Lanasyn Navy M-DNL (LN) ir Cu(II) jonų šalinimo efektyvumas tirtas naudojant vienkomponenčius ir dvikomponenčius tirpalus bei komercines aktyvintąsias anglis Norit PK 1–3. Šalinimo proceso ypatybėms nustatyti statinėmis sąlygomis buvo tiriama įvairių veiksnių (pradinės Cu(II) jonų koncentracijos (1–4 mM), sąveikos laiko (5–180 min.) ir temperatūros (293–333 K)) įtaka. Viename litre tirpalo naudojant 4,0 g aktyvintųjų anglių nustatyta, kaip bėgant laikui kinta 0,05 mM dažiklio LN ir Cu(II) jonų koncentracija tirpale. Tirpalo sudėtis turi didelės įtakos šalinimo procesui ir tirpalo pH kitimui. Adsorbcijai vykstant aukštesnėse temperatūrose, nustatytas sinergizmas. 40 ir 60 °C temperatūroje dažiklio pašalinama 15–20 % daugiau iš tirpalo, kuriame yra Cu(II) druskos. Cu(II) jonų pašalinama taip pat 10 % daugiau tuo atveju, kai tirpale yra dažiklio LN. Adsorbuoti dažiklio LN ir Cu(II) jonų kiekiai šiek tiek mažesni iš mišrių tirpalų 20 °C temperatūroje, tačiau Cu(II) pašalinama beveik tiek pat, kai pradinė Cu(II) koncentracija 2 mM. Adsorbcijos procesas vyksta kaip pseudoantrojo laipsnio reakcija, tai būdinga abiems adsorbentams esant skirtingoms pradinėms Cu(II) koncentracijoms. Kylant temperatūrai didėja adsorbuotų dalelių difuzijos į vidines adsorbento poras greitis.