

ADSORPTION OF Cu(II) FROM AQUEOUS SOLUTION ON WHEAT STRAW LIGNIN: EQUILIBRIUM AND KINETIC STUDIES

TATIANA TODORCIUC, LAURA BULGARIU and VALENTIN I. POPA

“Gheorghe Asachi” Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, 71A, D. Mangeron Blvd., 700050 Iasi, Romania

✉ *Corresponding author: Tatiana Todorciuc, todorciuct@yahoo.com*

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In this study, the adsorption of Cu(II) ions from aqueous solutions onto wheat straw lignin was investigated. The experiments were performed in a batch system, at room temperature (20 ± 0.5 °C), and the copper ions analysis was done after equilibrium was attained. Different experimental parameters (initial solution pH, sorbent dose, initial Cu(II) concentration and contact time) were varied in order to establish the optimum conditions for copper removal using wheat straw lignin. The experimental results were fitted using the Langmuir, Freundlich and Sips isotherm models, and the characteristic adsorption parameters were determined. Experimental data were also tested using two kinetic models: the pseudo-first-order Lagergren model and the pseudo-second-order Ho model. Based on these models, the kinetic parameters (rate constant and equilibrium adsorption capacity) for Cu(II) adsorption on lignin were calculated.

Keywords: wheat straw lignin, Cu(II), adsorption, equilibrium, kinetics

INTRODUCTION

Currently, industrial waste effluents are a severe environmental problem and require the implementation of new pollution control strategies.¹⁻³ Wastewater containing metal ions and black liquors resulting from the pulping process raises serious concerns and requires special attention.

Presently, the most common methods applied to remove metal ions from aqueous solutions are chemical precipitation, ion exchange, adsorption, flotation, the membrane-related process, the electrochemical technique and the biological process.⁴⁻⁷ However, many of these methods have been found to be very inefficient and/or very expensive. It is genuinely problematic when most of the above methods are used to treat huge volumes of aqueous effluents containing metal ions as they have low selectivity. Besides, these methods may also generate secondary wastes, which are difficult to discharge cleanly. To remove metal ions from wastewater, especially when the concentration is very low, the adsorption processes should be the preferred method.

The adsorption process implies the presence of an “adsorbent” that binds metal ions by physical attractive forces, ion exchange and chemical

binding. Even though the efficient removal of heavy metals can be successfully done by adsorption onto active carbon, this procedure is expensive and cannot be applied on an industrial scale.⁸⁻¹² For this reason, it is advisable to use an adsorbent that is available in large quantities, easily renewable and inexpensive. Considering this, lignin would appear to be an attractive solution.

The complex three-dimensional polymeric structure and the abundance of functional groups on the phenyl-propane structural units (Fig. 1) of lignin¹³ indicate that this material has the potential to be used as a possible adsorbent to remove metal ions from wastewater.

Being one of the major components of vascular plants, lignin has an important role in natural fibers ensuring structural strength. Lignin provides the waterproofing properties of plant cell walls. For a system conducting water,¹³ it must be removed in order to increase the flexibility and the brightness of paper fiber. About 90-95% of the reactive lignin biopolymer that results from the Kraft pulping process is soluble as compounds with lower molecular mass, and contributes to the dark brown colour and pollution load of the

effluents.¹⁴ Only some of the black liquors are burned in boilers in order to obtain thermal energy and recover chemicals.¹⁵⁻¹⁶ This procedure uses

only a part of the lignin from black liquors, the rest represents a profitable alternative that is currently being used by incineration.

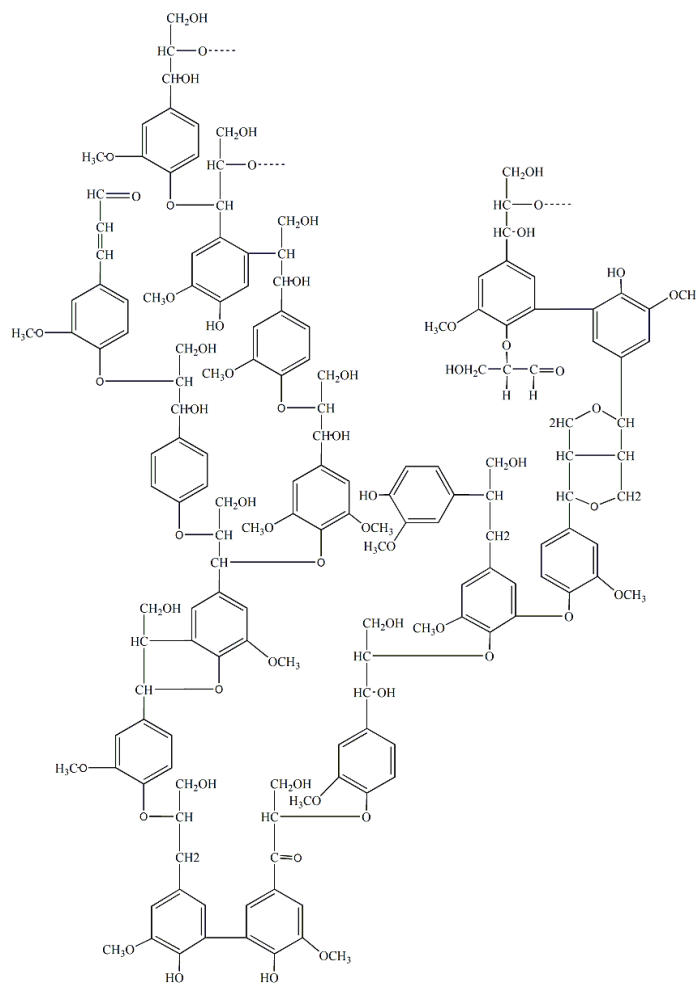


Figure 1: Schematic representation of a structural fragment from wheat straw lignin

In order to minimize the negative impact of black liquors and wastewater on natural soil ecosystems and aquatic life, the separation of lignin in several steps and transforming it into value-added products have been considered.¹⁷⁻¹⁹ Thus, the utilization of lignin as biosorbent for removing trace metals from wastewater^{14,20-27} or as a precursor for conversion into active carbon represents an attractive alternative, given the growing concern about heavy metals water pollution.^{6,27-29}

Adsorption has gained special attention in recent years because it offers an efficient and cost-effective alternative to traditional remediation and decontamination technologies for

large-scale wastewater treatment.³⁰⁻³¹ In particular, metal retention onto lignin, which is a very complex process, is affected by a couple of factors: the origin of the lignin (lignin from softwood, hardwood and from non-woody plants)³² and the method of extraction. The mechanisms involved in the retention process include chemisorption, complexation, adsorption-complexation on surface, ion exchange, micro-precipitation and heavy metal hydroxide condensation on surface.^{5,10}

Based on the published reviews,^{4-5,33} we have observed significant differences in the metal adsorption capacities of different types of lignin, the metal-binding mechanisms of lignin being still

difficult to predict. The statistical data concerning the depletion of wood resources have increased the interest in using non-wood products,³⁴⁻³⁶ for example agricultural residues. Wheat straw lignin properties have been thoroughly investigated. Our studies have been especially focused on establishing the optimum conditions for interactions with metal ions.

Our objective was to conduct detailed research of the adsorption of Cu(II) on wheat straw lignin. Generally, the adsorption process is affected by pH, sorbent dose, initial concentration of metal ion, and contact time. Using the batch technique, the experiments were performed by varying the aforementioned parameters to determine the optimum conditions for the adsorption process. The equilibrium and kinetic studies are presented in order to examine the affinity of Cu(II) for wheat straw lignin and to determine the efficiency of the adsorption process.

EXPERIMENTAL

Materials

The lignin used in the experiments, provided by Granit Company, Switzerland, was obtained from wheat straw by alkaline cooking. The stock solution of Cu(II), containing around 10^{-2} mol Cu(II)/L, was prepared by dissolving copper sulphate (Reactivul, Bucharest) in double-distilled water, followed by solution standardization by iodometric titration with sodium thiosulfate in the presence of starch. The working solutions were obtained by diluting the stock solutions with double-distilled water. The initial pH of the working solution was obtained by adding small volumes of 0.5 N HNO₃ (for pH 2.0 and 3.0) or acetate buffer (for pH 4.0 and 6.0). All chemical reagents were of analytical degree and were used without further purification.

Adsorption experiments

The experiments were all performed at room temperature (20 ± 0.5 °C). The batch experiments were performed by adding lignin powder to 25 mL solution containing Cu(II) ions in 150 mL conical flasks. A series of such conical flasks were intermittently shaken during 24 hours, in order to attain equilibrium conditions, and then the phases were separated by filtration. The Cu(II) content from the filtrate was spectrophotometrically analyzed (Digital JASKO 550 spectrophotometer equipped with 1 cm glass cells, with rubenic acid at $\lambda = 390$ nm) using a calibration curve. The Cu(II) adsorption efficiency was evaluated using the following parameters: the amount of Cu(II) retained on mass unit of lignin (q , mg/g) and the percent of copper adsorbed onto lignin, calculated as a retention yield (R , %), defined by the relations:

$$q = (C_i - C_e) \cdot \frac{V}{m} \quad (1)$$

$$R (\%) = \frac{(C_i - C_e)}{C_i} \cdot 100 \quad (2)$$

where C_i and C_e are the initial and equilibrium concentrations of Cu(II) ions in solution (mg/L), V is volume of metal ion solution used in adsorption experiments (L), m is mass of dry powder of wheat straw lignin (g).

In order to determine the optimum experimental conditions for Cu(II) adsorption onto lignin, different experimental parameters (initial solution pH, sorbent dose, Cu(II) initial concentration and contact time) were varied and analyzed. The influence of the initial solution pH on the retention capacity was investigated for two concentrations of Cu(II) (38.63 and 64.38 mg Cu(II)/L), in the pH range from 2.0 to 6.0, at a constant dosage of lignin. The effect of the lignin dose was evaluated by varying the lignin concentration from 1 to 40 g lignin/L, at optimum pH value (established in the previous experiment) and using an initial Cu(II) concentration of 64.38 mg/L. The influence of the initial Cu(II) concentration on lignin adsorption capacity was studied over the 25.75-257.54 mg Cu(II)/L concentration range, at pH 6.0 and a constant dosage of lignin (5 g/L). For the kinetics experiments, the lignin samples were mixed with 25 mL of 64.38 mg/L Cu(II) solution, at various time intervals from 5 to 180 min.

Isotherm models

The study of adsorption equilibrium is very important to determine the retention capacity of wheat straw lignin and to establish fundamental physical-chemical data of the adsorption process. Adsorption equilibrium is usually described by isotherm equations whose parameters express the surface properties and affinity of the sorbent, under given experimental conditions.

In this study, three models – Freundlich, Langmuir and Sips – were used to describe the experimental adsorption isotherm.^{4,9,14,27} The Freundlich isotherm is an empirical relationship, which can be expressed in a non-linear form (Eq. 3):

$$q_e = K_F \cdot C_e^{1/n} \quad (3)$$

where: K_F is the Freundlich constant, indicating the adsorption capacity, n is a constant that characterizes the affinity of metal ions towards the sorbent, q_e is the amount of metal ions adsorbed per weight unit of adsorbent (mg/g) at equilibrium, C_e is the equilibrium concentration of metal ions in solution (mg/L).

The Langmuir adsorption isotherm⁴ has been successfully applied to many adsorption processes, and is based on the assumption that adsorption takes place at specific homogeneous sites from the sorbent surface. In addition, it is assumed that once a metal ion occupies a site, no further adsorption can take place at

that site. The saturated monolayer isotherm can be represented as (Eq. 4):

$$q_e = q_{\max} \frac{K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (4)$$

where: K_L is the Langmuir constant related to the free energy of adsorption (L/mg), q_{\max} is the maximum amount of metal ion retained on sorbent (upon complete saturation of the surface) (mg/g); q_e is the amount of metal ion retained on mass unit of adsorbent (mg/g) at equilibrium, and C_e is Cu(II) concentration at equilibrium (mg/L).

Sips isotherm⁴ may provide more precisely the parameters for metal adsorption process, and is written as Eq. (5) in non-linear form:

$$q_e = q_{\max} \frac{(K_S \cdot C_e)^{n_s}}{1 + (K_S \cdot C_e)^{n_s}} \quad (5)$$

where: K_S is the Sips constant, C_e is Cu(II) concentration at equilibrium (mg/L), q_e is the amount of metal ion retained on mass unit of adsorbent (mg/g) at equilibrium, n_s is the Sips constant characterizing the system heterogeneity.³⁷

The Sips isotherm given by Eq. (5) has a similar form to that of the Langmuir isotherm (Eq. (4)). The distinctive feature between Eqs. (4) and (5) consists in the presence of an additional parameter, n_s , specific to the Sips isotherm and characterizing the heterogeneity of the adsorption system. When this parameter is unity, Eq. (5) is similar with Eq. (4).

Kinetic models

The kinetics of the adsorption process is very important to elucidate the adsorption mechanism and characterize the surface properties of the sorbent. The pseudo-first-order Lagergren and pseudo-second-order Ho are the most widely used kinetic models for this purpose.³⁸⁻³⁹

The Lagergren first-order rate equation for adsorption in a liquid-solid system is based on solid capacity, and can be written as (Eq. 6):

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (6)$$

and its linear form is (Eq. 7):

$$\lg(q_e - q_t) = \lg q_e - \frac{k_1}{2.303} t \quad (7)$$

The pseudo-second-order model is derived from the adsorption capacity of the solid phase, and can be expressed as (Eq. 8):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (8)$$

The linear form of this model is:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \quad (9)$$

where: k_1 and k_2 – pseudo-first order and pseudo-second order rate constants; q_e , q_t – adsorption capacity at equilibrium and at time t , respectively.

RESULTS AND DISCUSSION

The lignin used in this study was obtained from wheat straw,⁴⁰ and its characteristic functional groups and properties are presented in Table 1.

The essential characteristic of an adsorbent is its adsorption capacity, defined as the amount of metal ions retained by a mass unit of adsorbent. This characteristic is determined by a series of experimental parameters, such as solution pH, surface functional groups, pore and particle size distribution and specific surface area, and for this reason their study has a great importance.

Effects of experimental parameters on Cu(II) removal by adsorption on lignin

Initial solution pH

The solution pH is one of the most important parameters affecting metal ion adsorption on various adsorbents, because it affects both the dissociation degree of the functional groups from the adsorbent surface and the speciation/solubility of the metal ions. In this study, the initial solution pH was varied between 2.0 and 6.0. According to the copper speciation diagram,⁴¹ over this pH domain Cu(II) remains predominantly as divalent free ions (Cu^{2+}), and this species can be involved in chemical processes during adsorption on lignin. The effect of the initial solution pH on Cu(II) retention is illustrated in Fig. 2, for the two initial concentrations of metal ions. For both concentrations, similar behaviours have been observed, the effect being even more evident in the case of the higher concentration.

According to the data from Fig. 2, a pronounced dependence of metal adsorption on the initial solution pH may be noticed. At low pH values (pH 2.0), copper retention was almost negligible for both initial concentrations. By increasing the initial solution pH (from 2.0 to 6.0), the retention efficiency increased sharply, and at pH 6.0 the maximum retention was observed. Such retention tends to be attributed to the competition between Cu(II) ions and protons for the binding sites on the lignin macromolecule. At a low pH, the presence of proton excess may compete with Cu(II) ions for the binding sites on lignin, and the level of the metal ions retained is lower. Whereas at higher pH values, due to the dissociation of functional groups of lignin, the level of metal ions retained on lignin is evidently higher. The pH has not been further increased in order to avoid Cu(II) precipitation (which can take place at pH 6.2). Based on the results of this

experiment, pH 6.0 was selected to be used in further studies.

The important effect of initial solution pH on the adsorption efficiency suggests that copper ions are retained presumably due to the ion-exchange mechanism. Similar behaviour was observed and reported for other metal ions (Cr(III), Pb(II), Cd(II), Zn(II) and Ni(II)) on different types of lignin (softwood and hardwood lignin) and on active carbon.^{9,10,42}

Lignin dose

The variation of Cu(II) removal as a function of the lignin dose, at the optimum initial solution pH, is shown in Fig. 3. According to our obtained data, the removal of Cu(II) reaches the maximum efficiency (more than 90% of Cu(II) in solution being removed) at a relatively low lignin dose (5 g/L).

At low doses of lignin (1-5 g/L), the retention capacity increased from 66% to 90% due to the increase in the adsorption surface and in the number of possible binding sites. The increase of copper retention by nearly a half of the initial percentage value (66%) was earlier observed in the case of copper (II) adsorption onto chitosan (from 58% to 84%).⁴³

The increase of lignin dose over this value (10-40 g/L) did not improve the retention of Cu(II) from aqueous solution. At a higher lignin dose, particle agglomeration may occur on the adsorption sites, which leads to a decrease of the number of active sites, consequently the value of the retention yield decreases. Therefore, the lignin dose was maintained at 5 g/L in all the subsequent experiments and this value was considered as optimum for the removal of Cu(II).

Initial concentration of Cu(II)

Using a constant value of pH and the same dose of sorbent (5 g lignin/L), the increase of the initial Cu(II) ions concentration from 25.75 mg/L to 257.54 mg/L led to an improvement of the adsorption of metal ions by lignin (Fig. 4). Copper retention was calculated as the ratio of copper amount adsorbed (mg/L) to adsorbent dose (g/L); according to the graph in Fig. 4 (continuous line), the highest retention corresponds to the highest initial concentration of Cu(II) ions. However, analysing the percentage of the retention (Fig. 4, dotted line), which is independent of the sorbent mass, one can see that the values are high (over 90%) just for the interval 25.75 ÷ 77.26 mg/L of Cu(II).

Table 1
Characteristics of wheat straw lignin⁴⁰

Characteristics	Lignin	Characteristics	Lignin
M_w , g/mol	3510	Acid insoluble lignin, %	90
COOH, mmol/g	3.8	Acid soluble lignin, %	1
Aromatic OH, mmol/g	1.7-1.8	Solubility in alkali, pH = 12	98.5
OH/C9 (chemical method)	1.02	Ash, %	2.5
OH/C9 (FTIR)	1.06	T (softening), °C	170

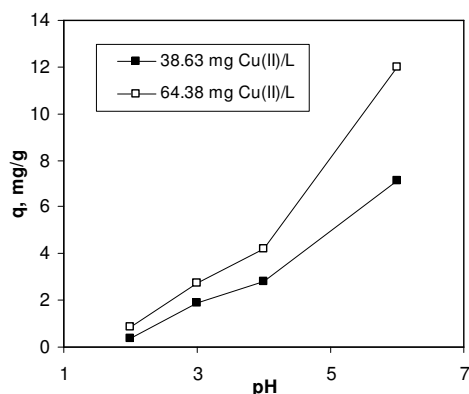


Figure 2: Effect of solution pH on Cu(II) ions adsorption by wheat straw lignin

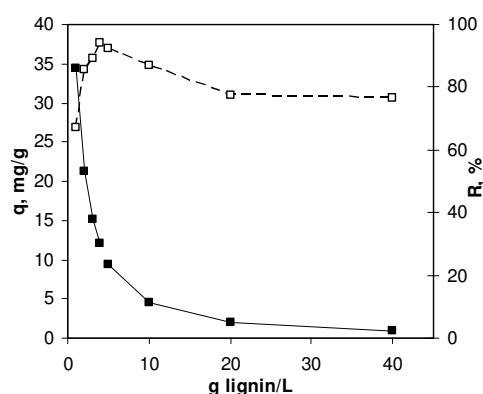


Figure 3: Effect of sorbent dose on the adsorption of Cu(II) by wheat straw lignin

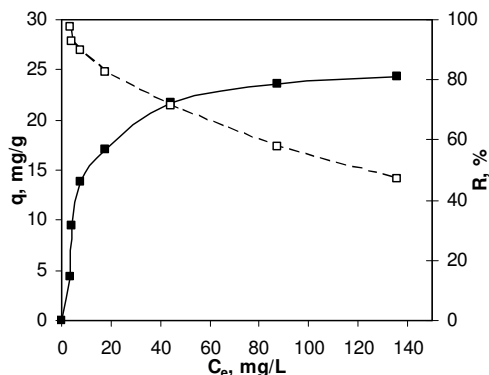


Figure 4: Effect of initial concentration of metal ions on the adsorption of Cu(II) by wheat straw lignin

The optimum calculated value of the initial concentration is 51.50 mg/L. This effect could be explained by the fact that at higher metal ion concentration, the available superficial groups of lignin are already occupied, and consequently, the diffusion of Cu(II) ions on the unreacted functional groups is inhibited.

Contact time

The contact time influence was investigated by varying the period of interaction between Cu(II) and lignin from 5 to 180 minutes, and maintaining the other parameters at the optimum values established (Fig. 5).

The results presented in Fig. 5 evidence a fast increase of the retention capacity in the first 20 minutes of contact time. This is probably due to the large number of available sites for the adsorption of Cu(II) ions. After this initial stage, the adsorption process reaches equilibrium and becomes slower. The equilibrium state is practically obtained after 90 min, when 95% of Cu(II) from the aqueous solution, is retained. A similar behaviour was observed in the case of Cu(II) ion retention on wheat bran.⁴⁴

These observations lead to the supposition that the adsorption process in the Cu(II)-lignin system is based on chemical interactions (ion-exchange and/or complexation) between metal ions (Cu^{2+}) and the superficial functional groups of the sorbent.

Adsorption isotherms

The adsorption isotherm, representing the equilibrium distribution of Cu(II) ions between the solid phase of the adsorbent and the aqueous solution, is represented in Fig. 6.

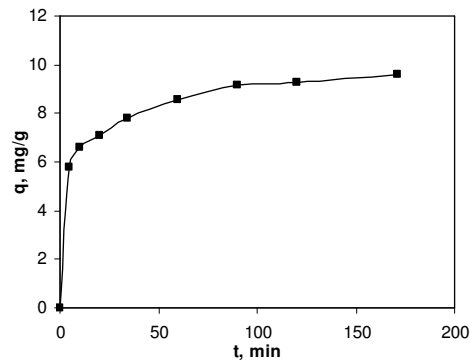


Figure 5: Effect of contact time on the adsorption of Cu(II) by wheat straw lignin

Although the linear representation and calculation method are preferred due to simplicity and convenience, the non-linear method provides more precise results. The non-linear curves fitting to our experimental data are also presented in Fig. 6. The parameters of the three isotherms were calculated based on Eqs. (3), (5) and (7) and are summarized in Table 2.

It can be observed that the regression coefficients obtained from the Sips and Langmuir isotherms are similar and higher than those of the Freundlich. This suggests that the mechanism of adsorption is complex and respects only partially the assumptions of each isotherm. Taking into consideration the fact that the linear calculation methods were not very accurate, the non-linear model is focused especially on the Sips isotherm model, which is a combination between the Langmuir and the Freundlich isotherms.

The first indication for the application of Sips model is its high correlation coefficient value, which confirms the precision of this model. However, nearly equal values of the correlation coefficients in the case of the Langmuir and Sips isotherms make necessary the comparison of the calculated values with the experimental ones. The experimental value of the maximum amount of metal ions adsorbed during the experiments is very close to the value calculated using the Sips non-linear isotherm ($q_{\text{max}} = 24.89$ mg/g). This concordance plays a decisive role in determining the proper isotherm model for the system.

Conversely, the n_s parameter, which characterizes the system heterogeneity, is very close to unity ($n_s = 1.16 \pm 0.32$), leading to the supposition that the adsorption of metal ions takes place at functional groups or binding sites on the surface of the sorbent, one mole of metal ion per

mole of binding site. In this situation, the use of the Langmuir isotherm may be considered also appropriate. Based on all these observations, the Sips isotherm model, which considers the

possibility of the existence of heterogeneous binding sites, seems to provide the most appropriate model for the system.

Table 2
Parameters for the adsorption isotherms according to the non-linear model equation

Freundlich isotherm	Langmuir isotherm	Sips isotherm
$R^2 = 0.9053$	$R^2 = 0.9660$	$R^2 = 0.9612$
$K_F = 6.5989 \pm 1.4136$	$K_L = 0.1117 \pm 0.0222$	$K_S = 0.1255 \pm 0.0309$
—	$q_{\max} = 26.0250 \pm 1.3788$	$q_{\max} = 24.8979 \pm 2.1106$
$n = 3.5401 \pm 0.6647$	—	$n_S = 1.1693 \pm 0.3280$

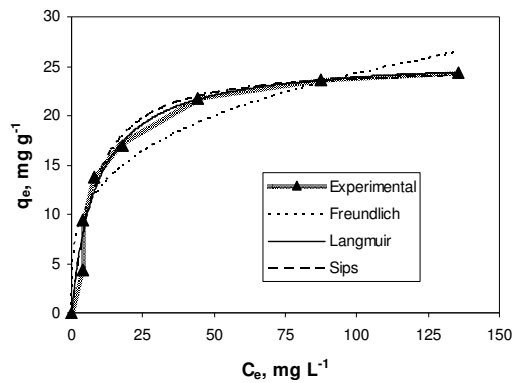


Figure 6: Adsorption isotherm of Cu(II) onto lignin

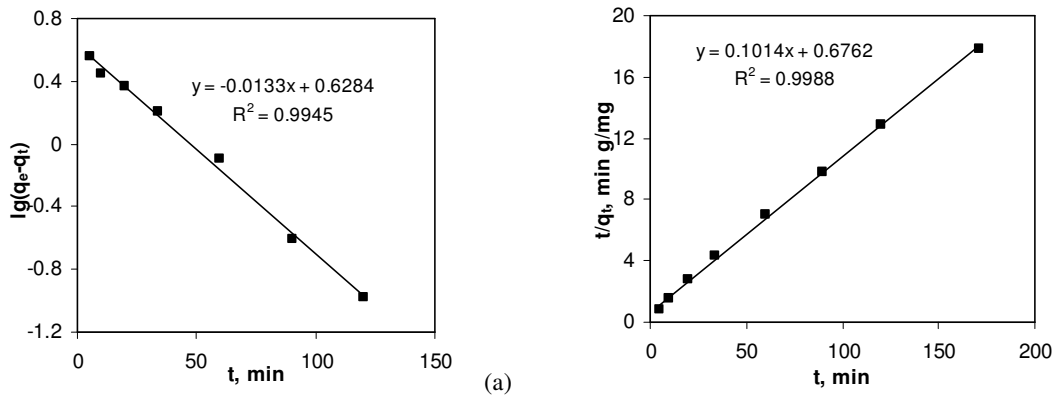


Figure 7: Application of the pseudo-first-order Lagergren model (a) and the pseudo-second-order Ho model (b) to Cu(II) adsorption on lignin

Table 3
Values of kinetic parameters obtained from linear dependences presented in Fig. 7

$q_e^{\text{exp}}, \text{mg/g}$	Lagergren model			Ho model		
	R^2	$q_e, \text{mg/g}$	k_1, min^{-1}	R^2	$q_e, \text{mg/g}$	$k_2, \text{g/mg min}$
9.5910	0.9945	4.2501	0.0306	0.9988	9.8619	0.1499

Kinetic studies

The prediction of the adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of

solute uptake is required for selecting the optimum operating conditions for a full-scale batch process. For this reason, two kinetic models have been tested to fit the experimental adsorption

data, in order to investigate the mechanism of adsorption and its potential rate-controlling steps.

The kinetic studies were carried out using the operating conditions and parameters that had proved to be optimum in previous experiments (pH = 6.0, 5.0 g/L lignin dose, 51.5097 mg/L Cu(II) initial concentration). In order to analyze the adsorption kinetics of Cu(II) on lignin, the pseudo-first-order Lagergren and the pseudo-second-order Ho models were applied to the experimental data. The graphical representation of the linear forms for the pseudo-first-order and pseudo-second-order kinetic models is presented in Fig. 7.

The rate constant k_1 was obtained by plotting $\lg(q_e - q_t)$ against the time and the rate constant k_2 was obtained from the intercept of the $t/q = f(t)$ dependence. The obtained data together with the rate constants (q_e) and correlation coefficients (R^2), calculated for each kinetic model, are summarized in Table 3.

It can be observed from Table 3 that both correlation coefficients (R^2) values obtained for the linear dependences from Fig. 7 are very close to unit. From another point of view, the adsorption capacity value, in the case of the Lagergren model, is much lower than the experimental one (9.59 mg/g), and as a consequence this model is non-adequate for describing the Cu(II) adsorption from aqueous solution on lignin. However, if a comparison is made between the adsorption capacity value calculated using the Ho model and the value obtained from the experimental data, it can be observed that these values are very close, leading to the assumption that the adsorption in the investigated system can be better represented by the pseudo-second-order Ho model.

The observations presented above come as an indication that the rate-limiting elementary process is the chemical interaction between metal ions and functional groups of the adsorbent and depends on the availability of both. In this case, the adsorption may be called chemisorption, which involves valence forces through sharing or exchanging electrons between the sorbent and the sorbate, complexation, coordination and/or chelation.

CONCLUSION

This study aims to establish the conditions for the retention of copper (II) ions on wheat straw lignin. The retention of Cu(II) on lignin increases with the increase of initial solution pH, indicating

that Cu(II) ions are retained mainly through the ion-exchange mechanism. The maximum retention (over 90% of Cu(II) from the initial quantity) appears at relatively low lignin dose (5 g/L), the optimum initial concentration of copper(II) was established to be 51.50 mg/L. The adsorption process attains the equilibrium in 90 minutes.

These results obtained from the analysis of the isotherms permit the hypothesis that a monolayer adsorption of Cu(II) on lignin occurs, with the observation that the adsorption sites on lignin surface are heterogeneous, when Cu(II) is adsorbed on the surface, different sorption sites have different affinity for Cu(II) ions and different adsorption energy. The Sips isotherm, which admits the possibility of the existence of heterogeneous binding sites, seems to provide the most appropriate model for the system.

From the kinetic point of view, the experimental data obtained in the case of Cu(II) adsorption on lignin are very well fitted by pseudo-second-order Ho model, which confirms the chemical nature of the rate-limiting process. In this case, the adsorption may be called chemisorption, which involves valence forces through the sharing or exchange of electrons between the adsorbent and sorbate, complexation, coordination and/or chelation and depends on the availability of functional groups of lignin. The value of the rate constant gives an indication that Cu(II) adsorption on lignin is a relatively fast process.

The availability of wheat straw and the good retention capacity of its lignin, which is a product resulting from pulp manufacture, make the use of lignin as a sorbent a sound option for the retention of copper ions from batch systems.

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