Cent. Eur. J. Chem. • 9(3) • 2011 • 437-445
DOI: 10.2478/s11532-011-0021-y

VERSITA

Central European Journal of **Chemistry**

Competitive adsorption of toxic metals on activated carbon

Research Article

Marek Šváb*[,1], Kateřina Sukdolová[1], Martina Švábová[2]

[1]*Department of Gas, Coke and Air Protection, Institute of Chemical Technology, 166 28 Prague, Czech Republic*

[2]*Institute of Rock Structure and Mechanics, Academy of Science of the Czech Republic, 182 09 Prague, Czech Republic*

Received 1 November 2010; Accepted 30 January 2011

Abstract: Competitive adsorption of zinc and copper on activated carbon is studied in this article. Main aim was to suggest an advanced model for competitive adsorption of both metals considering pH influence and precipitation. A surface-complexation approach was employed for the modeling. Two models were considered: simple adsorption and ion exchange. System "The Geochemists Workbench" was used for calculation of both static and dynamic adsorption tasks. From the batch experiments, concentration of four types of sorbing sites on the carbon surface and its protonation and sorption constants were deduced. Then, batch competitive adsorption experiments were compared with the models' results. Finally, a column experiment (fixed bed adsorption) was carried out. It was observed that the model of ion exchange can satisfyingly predict both chromatographic effect and increase of zinc concentration in effluent over its initial value, although a quantitative agreement between the model and the experiment was not totally precise.

Keywords: *Surface complexation • Adsorption • Activated carbon • Toxic metals • Modeling*

1. Introduction

Adsorption represents an important process used in a number of applications (gas and water treatment, industry, *etc.*). In the past, researchers spent their effort on solution of the complex sorption tasks through various inventive methods including a number of empirical or semi-empirical equations which allow achieving at least partial and strictly applied successes (*i.e.*, apparatus design). In concrete terms, we can name, for instance, equation for calculation of width of adsorption zone in sorption filter from the results of column experiment [1], various adsorption isotherms (Langmuir, Freundlich, Sips, BET *etc.*) and its combinations [2-4], empirical or semi-empirical equations for designing of fixed-bed adsorption filters (Bohart-Adams, Thomas) [5,6]. However, if we would look more deeply on such traditional approaches, we will recognize that a number of them originate, in fact, from the beginning of the last century: from the age in which a logarithmic rule was the only commonly available calculation instrument. For example, Irvin Langmuir deduced his well-known equation in 1916.

Nevertheless, such traditional, and still frequently used approaches consist of measuring experimental adsorption data (static or dynamic) and its subsequent interpolation by suitable mathematical formulas allowing at least limited transfer of results as well as elementary calculations. The advantage of such an approach is incorporation of all complicated particular process running during the overall adsorption resulting in semi-empirical interpolation; however, a serious disadvantage consists in minimal results transferability [7].

At present time, existing calculation instruments are incomparable with those from the beginning of the last century and make it possible to solve really complicated tasks. Therefore, it is possible to proceed conversely in comparison with above mentioned traditional approaches and to obtain outputs having wider validity. Such a recently applied approach consists of a suggestion of modeled process mechanism (even with awareness of its simplification and limits). Then, (if possible) generally valid input data are measured that provides wider validity of the model results.

In our paper, we would like to present possibilities of a calculation system "The Geochemists Workbench" (GWB), to model a competitive sorption task in a liquid

* *E-mail: Marek.Svab@vscht.cz*

phase: sorption of zinc and copper on granulated activated carbon. pH changes and its influence on sorption surface including precipitation of both metals in neutral or alkali pH will be taken into consideration.

2. Theory

Ionic sorption will be further considered in this study since it has the most important role in processes running on surfaces of solid phases in natural systems as well as in water treatment [8]. During ionic sorption, one type of ion is bound, and the sorption surface gains a corresponding charge. In this way, the internal part of an electrical double-layer is formed. Charge of the internal layer is balanced by adsorption of reverse-charged ions which form the external part of the double-layer (Stern double layer) [8]. This sketch is named "two layer surface complexation model" [9].

Description of particular adsorbate sorption onto a surface is done through the sorption reaction equilibrium constant between adsorbate and adsorption site creating a surface complex. Furthermore, concentration of adsorption site(s) must be known as well. Sorption of various dissolved species can be described including its competition; however, data requirements are high. This concept has been widely applied mainly in the case of sorption on hydrated iron oxides [10] because it is a process of great importance in natural environments as well as in water treatment technologies. Finally, a good database for such sorption reactions is available (many researchers and a lot of effort was used to measure it).

The above mentioned approach can be, in principle, applied to nearly any sorption process for which a suggestion of the particular reaction mechanism is possible. For all that, application of the double layer surface complexation concept is not common (yet), and we can find a number of actual sorption studies employing the traditional approaches. The reasons for that can probably be found in the complexity of the problem, totally different approach, and necessary usage of the correct advanced calculation instruments. In addition, agreement between results and experiments which is often worse in traditional methods can be compensated by the wider validity of the model. Such a model, then, can help with totally new outputs and results.

2.1. Modeled task

We used the system "The Geochemists Workbench" (GWB) for our purpose. GWB is an advanced calculation instrument for bio-hydro-geochemical modeling which has been developing for 20 years by the team of Prof. Bethke from the University of Illinois. General information is available on the web site of the software supplier. If more particular information is needed, scientific background of the system is available as well [9]. High quality and wide thermodynamic databases are supplied with the system including patterns for creation of individual datasets for sorption reactions.

The adsorbent we used was granulated activated carbon, Silcarbon K835, which is suitable for water treatment. Activated carbon was chosen as an example of a material with a complicated structure where precise description of sorption interaction chemistry is problematic. Hydroxyl, carbonyl and carboxyl groups are usually considered the active sites responsible for sorption capacity of activated carbon towards ionic adsorbates [11].

Zinc and copper were chosen as suitable toxic metals for demonstration of competitive adsorption. Their chemical behavior is similar and therefore their sorption properties might be considered as close [6].

Model description is based on the following basic facts: activated carbon K835 is alkalic (1), predominant surface charge depends on pH (2), zinc and copper cations will adsorb preferentially in neutral/alkali pH (negative surface charge) (3) and precipitation of both metals in the form of hydroxo-oxides will be the cooperating effect (4). These outlined assumptions can be transferred into a basic model concept consisting of the existence of definite number of adsorption sites present on the adsorbent surface which must be able to react with protons and both metals. In this way, both the dependence of surface state on pH and the mutual competition of both metals and protons are ensured. More types of adsorption sites with different reactivity may exist on the surface. In the first approximation, two basic adsorption mechanisms can be assumed: simple adsorption and ion exchange. Because both mechanisms are considered in this study, their comparison is also presented. Models do not consider electrostatic effects occurring near the adsorption surface which is a usual approach in the case of similar tasks [12].

Oversimplifications assumed in the models are obvious. As the most significant factors affecting the models result in comparison with experiments, we can name: simplification of complex system with activated carbon into a form of solid phase having only a few types of the sorption sites which react with adsorbate in the ratio of 1:1 (1), problems with formation of solid phases – kinetics and morphology of precipitates including its collateral sorption properties (2), other aqueous forms of metals (*i.e.*, complexes) and its sorption reactions are not considered in the models (3), calculation counts with thermodynamic equilibrium state, although fixed-bed sorption is non-equilibrium process (4), effects influenced

by the adsorbing particles' shape and size (placement of particular adsorbing site on the surface, pore diffusion *etc.*) are not assumed (5). Nevertheless, in defiance of above described simplifications, the models are able to fulfill the basic requirements.

2.1.1. Model 1 – simple adsorption

The simplest model considers adsorption of either metals or protons in a ratio of 1:1 on the adsorbing site, without ion exchange. General equations can be written:

$$AC + H+ = AC\text{-}H^{+} \quad (1)$$
$$AC + Zn^{2+} = AC\text{-}Zn^{2+} \quad (2)$$
$$AC + Cu^{2+} = AC\text{-}Cu^{2+}, \quad (3)$$

The "AC" denotes further non-specified adsorbing sites on the activated carbon surface. The model assumes that more types of active sites, AC, can exist on the surface and they may differ in both the concentration and reactivity. The basic imperfection of the model is the assumption of competitive reactions running without ion exchange and charge changes. This is why the second model was suggested.

2.1.2. Model 2 – ion exchange

Adsorption process run similarly as in the model 1, however, the ion exchange is employed:

$$AC\text{-}OH + H^{+} = AC\text{-}OH_2^{+} \quad (4)$$
$$AC\text{-}OH + Zn^{2+} = AC\text{-}OZn^{+} + H^{+} \quad (5)$$
$$AC\text{-}OH + Cu^{2+} = AC\text{-}OCu^{+} + H^{+}, \quad (6)$$

The "AC-OH" denotes the adsorbing site on the activated carbon surface which is capable of ion exchange of the proton and other cation. Denotation "AC-OH" is used with respect to expected chemistry of the reactions; however, it must be understood only as a suitable symbol for a possible structure of the site not as known and exact expression of the mechanism. Other assumptions are the similar to the case of model 1.

2.1.3. Input data and its determination

The input data for the models include the number of adsorption sites types (and their concentration on the adsorbent) and the equilibrium constants of all mentioned reactions.

The number of sorption site types and concentrations can be deduced from the titration curve of the activated carbon aqueous suspension. For the correct distribution of total concentration of the sorption sites (*i.e.*, ionic exchange capacity) on the particular types of the sites, as well as their protonation equilibrium constants, a good agreement between experiment and calculation must be achieved. For this purpose, the free software "Protofit" has already been developed (it can be downloaded from the web) or an individual solution can be prepared.

The second goal is to know the equilibrium constants of the sorption reactions with metals for each adsorbing site type. It is again the multi-parameter optimization task which is based on agreement between calculation and results of batch sorption experiments under various pH values (separated experiments for each metal). The experiments must be carried out in slightly acidic pH in order to prevent precipitation of the metal. Software solution for the best combination of equilibrium constants is used: individual solution can be prepared or commercial software "FITEQL" is also available. The above described method is often used for similar purposes in the literature [12].

3. Experimental Procedure

The first aim of the experimental part was to find input data for both adsorption models through the set of the batch experiments. Secondly, a column experiment was carried out (competitive adsorption of both metals). The results were compared with the calculation based on both models in the system, GWB, using input data deduced from batch experiments.

The granulated activated carbon Silcarbon K835 used as adsorbent is steam-activated with bulk density of 55 kg m^{-3} and size diameter of 0.5-2.5 mm. The activated carbon was used as received. As the source of metals, zinc nitrate (hexahydrate, Penta, P.a.) and copper sulphate (pentahydrate, Penta, P.a.) was used. For acidification and alkalization of the samples, hydrochloric acid (35-38%, Penta, P.a.) and sodium hydroxide (Penta, P.a.) were used. Analysis of metal concentrations was carried out with AAS (SensAA Dual, GBC). Except for the AAS, common laboratory equipment was used (pH-meter, shaker, peristaltic pump, data collection unit *etc.*).

A titration curve of activated carbon aqueous suspension was carried out with 6.06 and 5.998 g of K835 in 150 mL of distilled water. The suspension was titrated with hydrochloric acid solution (0.2265 M) and sodium hydroxide solution (0.2516 M). Equilibration time was 30 minutes (before next addition). Protonation parameters (concentration of the sites and their protonation constants) were deduced using the Protofit software.

Batch adsorption experiments were carried out with approximately 1 g of activated carbon and 100 mL of zinc or copper solution with concentrations

of 50 or 100 mg L^{-1}. The mixture was then acidified by addition of small amount of concentrated hydrochloric acid in order to achieve the equilibrium pH between 3–6 (copper) and 3–7 (zinc). Equilibration time was 24 h on the shaker. Because, in the case of zinc, within the first set the pH range was not satisfactory covered, two additional experiments were carried out. The necessary input data were sorption equilibrium constants of both metals on all sorption sites for which the best average agreement between the results of experiments and model has been achieved. The criterion was the average deviation of calculated results from the experiments for whole set of sorption data (*e.g.* at various pH). This optimization was done by Visual Basic software developed in Microsoft Excel environment. Finally, a control calculation was carried out using the GWB which is giving more precise results thanks to consideration of activities instead of the concentrations. For the purpose of all subsequent model calculations, the input data deduced from above described single-metal experiments were not modified further.

In order to verify the model results of batch adsorption, a set of batch experiments were carried out with a mixture of both metals. The experiments were carried out in the same way as in the above described single-metal tests.

Finally, a continuous fixed-bed column adsorption experiment was carried out. Basic parameters are presented in Table 1 and experimental scheme is illustrated in Fig. 1.

Column filling by the activated carbon was done by adding small amounts of the carbon under low water level in order to prevent formation of bubbles or non-homogeneities within the layer. Inlet solution was supplied from a storage beaker through a peristaltic pump. Effluent was conducted through the low-volume measuring cell equipped with a glass electrode for the on-line data collection. Collected samples were immediately stabilized by addition of one drop of concentrated nitric acid.

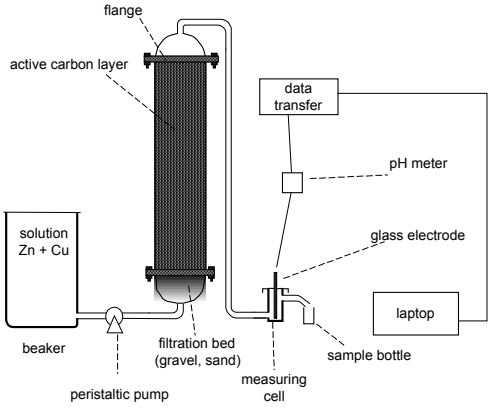

Figure 1. Scheme of the column experiment.

The course of the column fixed-bed adsorption process was then calculated by GWB using previously deduced input data from batch single-metal experiments. Except the sorption and protonation data (disclosed below in the Table 3), further parameters important for calculation of the continuous process were the diffusion coefficient and coefficient of hydrodynamic dispersion. For the model calculation, the usual values of these parameters were used [9]. Both can be defined precisely, if needed, by the other experiments such as by the tracer. As the possible solid phases formed in neutral/alkali pH, oxides or hydroxides of both metals were considered. Calculations were carried out for both variants. The input data used for the model calculation are summarized in the Table 2.

4. Results and Discussion

In the first step, the input data for the models were determined. The measured titration curve of activated carbon K835 is displayed in Fig. 2, from which a significant exchange capacity of the activated carbon is obvious. Calculation from the curve (pH 2.5 – 11) indicated that total concentration of the active sites should be about 0.441 mol kg^{-1}. The curve for pure water is also marked in the Fig. 2. It is obvious that pH 2.5 and 11 correspond to the beginning of the buffering capacity of pure water.

For the deduction of the models input data, it was desired to achieve good agreement between calculation and experiment in the pH range 2.5 – 10.3 (initial value) because higher values of pH do not have practical importance. It was found that the best agreement can be achieved by the use of four types of active sites on the surface with following concentrations (in mol kg^{-1}): 0.125, 0.15, 0.0833 and 0.0833. The sum of the concentration 0.4416 mol kg^{-1} corresponds to the value achieved simply from the titration curve. Equilibrium constants of protonation reactions of the four identified sites are listed in Table 3. The acidic titration curve achieved by calculation with disclosed input data is illustrated in Fig. 2.

Table 1. Basic parameters of the column experiment.

bed height	30 cm	retention time	36 min
bed diameter	5 cm	total time	9 h
bed volume	589 mL	effluent volume	2650 mL
bed mass	278 g	inlet concentration (Zn)	25 mmol L^{-1}
porosity (estimate)	0.3	inlet concentration (Cu)	25 mmol L^{-1}
solution flow rate	4.9 mL min^{-1}	pH of initial solution	3.68
linear flow rate	0.84 cm min^{-1}		

Table 2. Input data for the model calculation of the column experiment.

layer height	30 cm
layer cross-section diameters	4.43 cm × 4.43 cm (square)*
porosity (estimate)	0.3
activated carbon mass in bed	278 g
Discharge	0.004176 cm s^{-1} (4.9 mL min^{-1})
diffusion coefficient	10^{-6} cm^2 s^{-1}
longitudinal dispersivity	0.3 cm
inlet concentration (Zn^{2+})	25 mmol L^{-1}
inlet concentration (Cu^{2+})	25 mmol L^{-1}
inlet concentration (NO_3^-)	50 mmol L^{-1}
inlet concentration (SO_4^{2-})	25 mmol L^{-1}
charge balance calculated on	H^+
number of nodal blocks (for numerical solution)	60 (1 block = 0.5 cm)
solid phases allowed	hydroxides / oxides

** - for the purpose of model calculation in the system GWB, the cross section must be square; the area is equal to the laboratory column with circular cross-section.*

Table 3. Summary of all considered reactions with their equilibrium constants used for both models; Reactions are written in the direction of decomposition of adsorbed complex because in this form are used in the thermodynamic dataset of the GWB system. In the parenthesis, the total content of the site on the activated carbon surface is written.

model 1 reaction	Log K
(1)AC-H^+ = (1)AC + H^+ (0.125 mol kg^{-1})	-8.90
(2)AC-H^+ = (2)AC + H^+ (0.15 mol kg^{-1})	-7.30
(3)AC-H^+ = (3)AC + H^+ (0.0833 mol kg^{-1})	-4.80
(4)AC-H^+ = (4)AC + H^+ (0.0833 mol kg^{-1})	-2.80
(1)AC-Zn^{2+} = (1)AC + Zn^{2+}	-5.35
(2)AC-Zn^{2+} = (2)AC + Zn^{2+}	-3.30
(3)AC-Zn^{2+} = (3)AC + Zn^{2+}	-0.50
(4)AC-Zn^{2+} = (4)AC + Zn^{2+}	-3.20
(1)AC-Cu^{2+} = (1)AC + Cu^{2+}	-6.00
(2)AC-Cu^{2+} = (2)AC + Cu^{2+}	-4.74
(3)AC-Cu^{2+} = (3)AC + Cu^{2+}	-0.10
(4)AC-Cu^{2+} = (4)AC + Cu^{2+}	-3.40
model 2 reaction	**Log K**
(1)AC-OH_2^+ = (1)AC-OH + H+ (0.125 mol kg^{-1})	-8.90
(2)AC-OH_2^+ = (2)AC-OH + H+ (0.15 mol kg^{-1})	-7.30
(3)AC-OH_2^+ = (3)AC-OH + H+ (0.0833 mol kg^{-1})	-4.80
(4)AC-OH_2^+ = (4)AC-OH + H+ (0.0833 mol kg^{-1})	-2.80
(1)AC-OZn^+ + H^+ = (1)AC-OH + Zn^{2+}	8.25
(2)AC-OZn^+ + H^+ = (2)AC-OH + Zn^{2+}	8.50
(3)AC-OZn^+ + H^+ = (3)AC-OH + Zn^{2+}	3.50
(4)AC-OZn^+ + H^+ = (4)AC-OH + Zn^{2+}	3.50
(1)AC-OCu^+ + H^+ = (1)AC-OH + Cu^{2+}	9.00
(2)AC-OCu^+ + H^+ = (2)AC-OH + Cu^{2+}	9.00
(3)AC-OCu^+ + H^+ = (3)AC-OH + Cu^{2+}	2.25
(4)AC-OCu^+ + H^+ = (4)AC-OH + Cu^{2+}	2.15

Fig. 3 displays calculated distribution of the active sites (non-protonated forms - *i.e.*, forms available for positive ion binding) on activated carbon according to pH. It was calculated for 1 L of water with 10 g of activated carbon. As expectated, it is obvious that

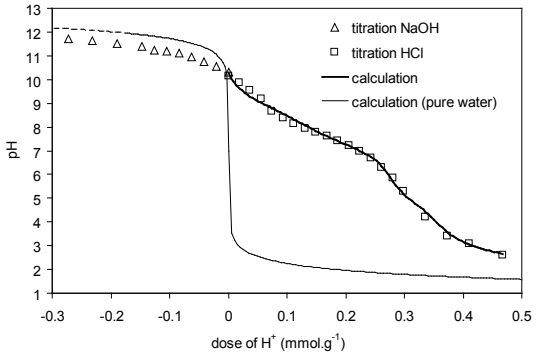

Figure 2. Titration curve of activated carbon K835 in aqueous suspension; Curve in acidic solution is interpolated by calculation in the system GWB. For comparison, the curve for water without the carbon is also presented (values on X-axis are relative to the same theoretical dose of carbon to make curves directly comparable).

sorption capacity of the sorbent towards positively charged ions increases with the increasing pH up to the maximal pH value between 10–11 (and higher).

In the next experiments, batch adsorption of both metals was measured for various pH in order to deduce sorption constants for all active sites. The results of experiments and calculations after models calibration are displayed in Fig. 4, which also shows average values of differences, in %, between experimental and model results. It was found that in the case of model 2, the agreement can be improved when only results for pH higher than 5.77 (Zn) and 5.17 (Cu) are considered. It might be also acceptable from the practical point of view to focus on the good agreement close to the neutral pH rather than the good agreement in whole pH range, but with the worse, practically, in the more interesting neutral area. This is why the model 1 was calibrated for the whole pH range covered by the experiment, while model 2 only for the data achieved with pH higher than above mentioned values. All adsorption data are summarized in Table 3.

Fig. 5 shows the results of experiments and model calculations for competitive adsorption of both metals. The principle of the experiments as well as of the graphical expression was identical as in the case of the Fig. 4. Worse agreement between calculations and experiments in comparison with the single metal adsorption is obvious. However, the calculations were carried out using data disclosed in Table 3 without any modification. Nevertheless, the models provide particular description of the metals behavior in case of their competition.

Looking at Fig. 5 for zinc, model 2 seems to provide slightly better results when we consider non-acidic pH (for example looking on results for pH 5.88 and 5.96), while model 1 seems to be better for the copper within

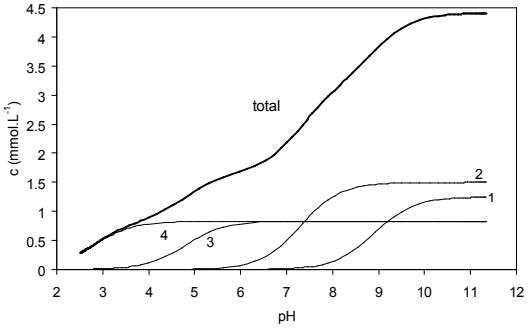

Figure 3. Calculated distribution of the active sites (non-protonated forms) on the surface of activated carbon (for 1 L of water and 10 g of activated carbon) = adsorption capacity towards positive charged ions at various pH values.

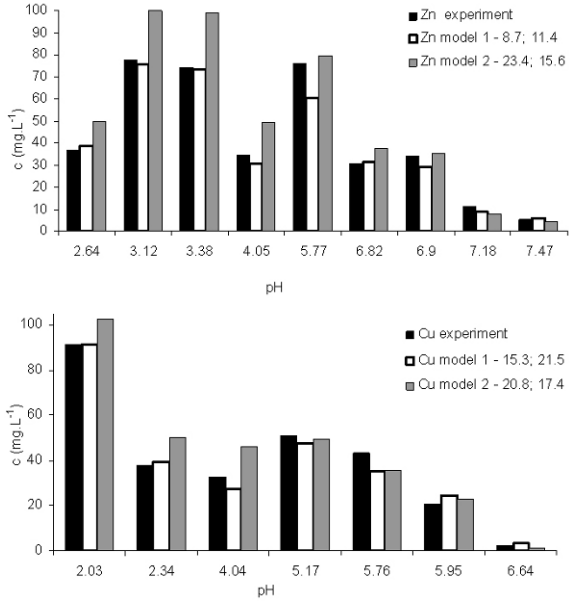

Figure 4. Concentrations of both metals in the solution after adsorption for various values of pH: experimental data in comparison with models results after calibration by finding of suitable combinations of the sorption equilibrium constants. There are average deviations (%) between experiment and model for all data (first value) and for data with pH > 5.77 (Zn) and pH > 5.17 (Cu) marked in the legend (single metal experiments).

the whole pH range. However, considering that the model 2 was calibrated only for the higher pH values, the agreement for pH > 5.25 is also acceptable (for copper). But, differences between the models results are not too conclusive, so it is not possible, based on such results, to simply conclude which model is closer to the reality. The results for copper with pH > 7 are not presented due to precipitation. In case of zinc and pH of 7.76, precipitation perhaps occurred as well, although it was not visually detected. It resulted in the quite low zinc experimental concentration in this sample. Formation of the solid phases always represents a very complicating effect which is influenced by a number of factors. So, the calculation with available thermodynamic data may not be reliable in all cases. Nevertheless, more significant adsorption (and perhaps precipitation as well) of the copper in lower pH values in comparison with the zinc is obvious from both the experiments and the calculations where the values of the sorption constants reflect the stronger adsorption of copper (see Table 3).

Two deviations in the trend of the residual concentrations of both metals decrease with increasing pH are visible: pH 6.86 (zinc) and 5.88 (copper). In these cases, the deviations are caused either by fortuitous mistakes in experiments (or analysis), or by further running processes which are not considered (for example by change of the chemistry of interaction between the metal and the activated carbon surface).

Henceforth, two model calculations are demonstrated in order to show the GWB possibilities using the models prepared. Each task can be deeply studied including detail information about all aqueous components speciation in the system, all forms of each adsorption site *etc.* For the purpose of the demonstration, only several types of the outputs will be selected. We used the model 2 for the demonstration, but similar results would be achieved for the model 1.

Fig. 6 shows calculated adsorption isotherms of copper for various pH. According to the theoretical expectations it is obvious that both sorption capacity and affinity of the sorption surface towards copper increases with pH. For pH of 6 and higher, the isotherm can not be calculated due to the copper precipitation from the definite concentration (copper oxide was considered in this example as a solid phase).

Fig. 7 shows the results of calculation of the alkalization of the mixture of water with activated carbon having an initial pH of 4 and initial concentration of both metals of 100 mg L^{-1}. In the beginning, both metals are present mostly in the solution. Concentrations of both metals in the solution decrease as alkalization continues with copper adsorbed preferentially. From pH of approximately 6.5, copper becomes precipitated and thus, it disappears from the solution faster, and it's desorption from the surface occurs as well (the key equilibrium is the precipitation while adsorption is considered as a reversible process). The copper precipitation results in increased zinc adsorption. From the pH of about 7.7, zinc beginns to precipitate as well. It is further obvious that, in spite of the precipitation, a substantial portion of the metals remain in the adsorbed form, mainly in case of zinc.

Such calculations can help with getting at least partial insight into the relatively complicated processes running in the similar kind of systems. Variability of the calculations is not limited.

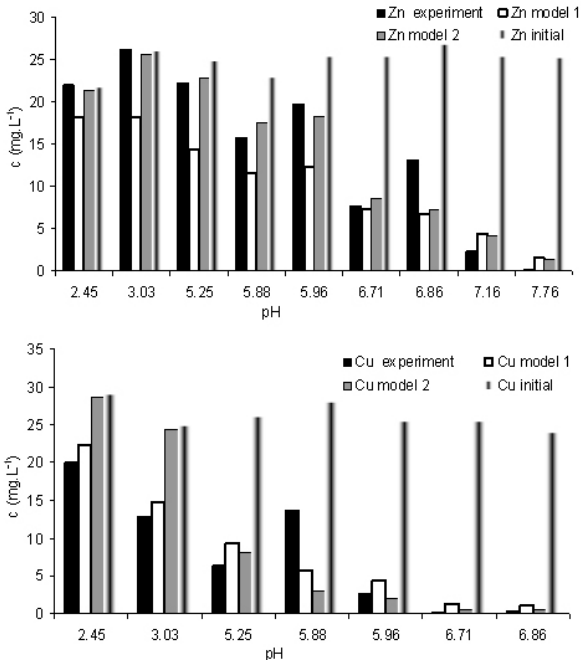

Figure 5. Results of models calculations in comparison with the experiments (competitive adsorption); Calculations were carried out using the data disclosed in Table 3, without any modifications.

Competitive adsorption was also tested and modeled in the flow-through process simulating fixed-bed adsorption. Model calculations were carried out using both models, each with two variants according to the considered solid phases (hydroxides/oxides). Evaluated/compared parameters were concentrations of both metals and pH in the column effluent during the process. It was found that better results of the calculations were achieved for oxides considered as the possible solid phases; however, the difference from the results achieved for hydroxides was low.

Fig. 8 shows the course of effluent pH during the experiment in comparison with the results of both models.

Before the results discussion, it might be useful to briefly specify the complex processes running simultaneously in the activated carbon layer. During the solution flow, the following processes occur in each cross-section of the layer (simplified):

- solution alkalization caused by the protons adsorption on the carbon surface;
- adsorption of both metals (competitively, with protons);
- both metals precipitation;
- lowering of pH by inflow of further portions of inlet solution, protons and metals adsorption/desorption;
- solid phases dissolution;
- metals desorption from the sorption surface.

During the flow-through process, an active zone in which above mentioned processes occur is formed. This zone is moving towards the end of the layer. For each parameter of interest, the two-variable function (time and position) is an output from the experiment.

Fig. 8 discloses the effluent pH over time (in fact it is a slice for constant time of the pH function in the last part of the layer). First, pH decrease corresponds to the saturation of the layer neutralization capacity by the flowing solution. Over time at the pH of about 6.7, equilibrium with precipitated zinc oxide is reflected. After its dissolution, the first portion of copper inflow from previous portions of the layer and copper precipitates (copper oxide): it corresponds to pH of about 5 (related to the calculated curve). After longer period of calculation time, copper precipitate would be dissolved and then, composition of effluent will be identical with the inlet. Precipitation of the solid phases can provide explanation of the qualitative differences between final pH measured and calculated (within disclosed time period). The cause of the difference may converge with fact, that the model calculation considers precipitated solid phases as immobile (remaining in the place of their formation independently on the solution flow), while in reality, the precipitates can partially migrate with the solution towards the end of the layer. This assumption supports the observation of solution turbidity in the measuring cell especially between first and third hour of the experiment. Thus, during the final phase of the experiment, precipitated copper was probably already flushed out resulting in decreased pH on the inlet value. On the contrary, the model calculation assumed solid phase presence in the layer until its entire dissolution (after substantially longer period). It can be stated that the model 2 provided better agreement with the experiment especially when comparing the first decrease of the pH and its subsequent delay. In addition, the difference in this delay duration may also cohere with the partial movement of the formed solid phase through the layer in the experiment (see above). With respect to the system complexity and input data obtained from the above described batch experiments which were used without any modifications, the agreement with the experiment can be understood as very good.

The concentrations of both metals in the column effluent during the time is shown in the Fig. 9. It is clear that chromatographic effect occurs in the sorbent layer, and effluent concentrations of zinc predominate during the definite period of the initial concentration. Considering the above discussed effect, this behavior can be expected. Zinc is due to weaker interaction with the adsorbing surface (see sorption constants

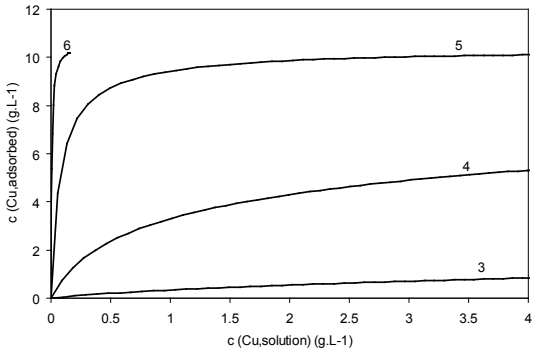

Figure 6. Calculated adsorption isotherms of copper for various pH using the model 2

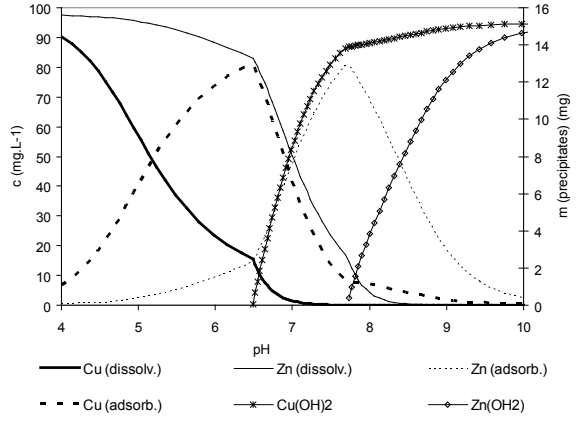

Figure 7. Results of calculation of the alkalization of mixture of water with activated carbon (100 mL, 1 g) with initial pH of 4 and initial concentration of both metals of 100 mg L^{-1} (using the model 2)

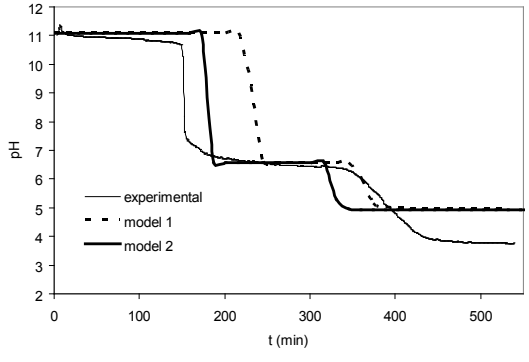

Figure 8. Effluent pH during the column experiment in comparison with the results of both models (oxides were considered as possible solid phases).

in the Table 3) forced out from the active sites by the copper. So, zinc is, in fact, pushed by the copper in the front of the adsorption zone in the layer. Both effects (chromatography and zinc concentrating above its initial content in the solution) were qualitatively correctly predicted by both models. Quantitative differences in both time of concentration increase and shape of curves

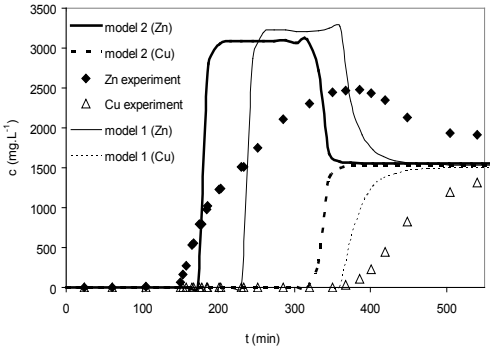

Figure 9. Metals concentrations in the column effluent during the time: comparison of experimental and models results.

can be also explained by above mentioned problems with migration/non-migration of precipitates. Further effects as diffusion/dispersion can also be named as possible responsible factors for such differences. Although such parameters can be, if desired, more specified by the tracer experiment. Nevertheless, the models (probably model 2 better) provided quite definite estimate of fixed-bed continual adsorption including pH and concentrations of metals in the effluent without the necessity of carrying out the column experiment. Finally, it is obvious that models can be used for a number of purposes – designing laboratory or pilot-scale experiments, optimization of the process, understanding of mechanisms *etc*. It is very important to remember, that input data now can be used for calculation of any systems of the same (or similar) composition: *i.e.*, geometry, concentrations and technical layout do not play a role for the data validity. Thus, the data validity is in the frame of activated carbon K835 universally. So, processes running in different geometry or concentrations can be calculated with the expectation of the results with similar reliability as presented in this paper.

5. Conclusions

An advanced approach to the modeling of competitive adsorption task using modern calculation instruments was introduced in this study. It is important to remember that all models of such kind are still a strong simplification of the reality which is much more complex.

Both models of competitive sorption of zinc and copper were suggested. In batch experiments, both models provided comparable agreement with the experiments. However, in the case of fixed-bed flow-through adsorption processes, slightly better agreement between calculation and experiments was achieved in the case of model 2 which is based on ion exchange. This observation relates especially to the pH changes

of the column effluent. Finally, the results indicate that the particular mechanism is more complicated: a model combining both types (model 1 and 2) as well as a model considering other interactions might be assumed. One limiting factor can be identified in the use of GWB: the system does not consider with particle size (for example size of activated carbon pieces) and diffusion towards its surface, although this parameter is relatively simple to obtain. It is important to remember such facts during results analysis and conclusion-making process.

Although the agreement between model and experimental results was not perfect, it was good in term of basic qualitative criteria. Considering the complexity of the continual flow-through system, the model calculation provides valuable results for further tasks: experimental design, process optimization, mechanism understanding *etc.*

The most important finding is that modern hydro-geochemical calculation instruments may be effectively used for the systems for which the input data are not generally known, but are deduced from the suitable experiments. Such data are then valid for a particular system, but are independent of concentrations, process parameters and geometry. This is the main difference from traditional approaches discussed in the theoretical part of the study. In addition, complexity of the modeled system is not, in principle, limited. For example, more complicated chemistry of the adsorption interaction can be suggested (for example reaction of various aqueous species with the active sites, reaction in different ratio than 1:1 *etc.*). Finally, such approaches to the modeling of competitive adsorption tasks look to be really promising.

Acknowledgements

This work was supported by the Research Plan grant MSM 6046137304, from the Ministry of Education, Youth and Sports of the Czech Republic.

References

[1] A.P. Sincero, G.A. Sincero, Physical-Chemical Treatment of Water and Wastewater (CRC Press, Boca Raton, 2002)
[2] P.Y. Kumar et al., J. Hazard. Mater. B137, 1246 (2006)
[3] Ch. Yan, J. Hazard. Mater., in press
[4] A.E. Ofomaja et al., Bioresour. Technol. 101, 3844 (2010)
[5] H.Ch. Khim, J. Hazard. Mater. 177, 1006 (2010)
[6] B. Salamatinia, Chem. Eng. J. 145, 259 (2008)
[7] M. Svab, L. Wimmerova, Groundwater: Modelling, Management And Contamination (Nova Science Publishers Inc., New York, 2008) 133-147
[8] E. Eriksson, Principles and applications of hydrochemistry (Chapman and Hall, London, 1985)
[9] C.M. Bethke, Geochemical Reaction Modelling (Oxford University Press, New York, 1996)
[10] D.A. Dzombak, F.M.M. Morel, Surface Complexation Modelling (J.Wiley&Sons, Hoboken, 1990)
[11] R.T. Yang, Adsorbents: Fundaments and Application (J. Wiley&Sons, Hoboken, 2003)
[12] X. Guo et al., J. Hazard. Mater. 151, 134 (2008)