Oxidized Cellulose: An Application in the Form of Sorption Filter Materials

Marcela Foglarova,[1] Jiri Prokop,[1] Miloslav Milichovsky[2]

[1]Hobra-Skolnik Společnost S Ručením Omezeným, Smetanova Ulice, CZ 550 01 Broumov, Czech Republic
[2]Department of Wood, Pulp, and Paper, Faculty of Chemical Technology, University of Pardubice, Studentska 95, CZ 530 10 Pardubice, Czech Republic

ABSTRACT: Oxidized cellulose (oxycellulose) was very effectively used in the form of filter sheets to remove some metal ions from water and from aqueous solutions. Furthermore, oxycellulose was applied in an ion-exchange column and in a batch process. The mechanisms of the sorption process inside oxycellulose as well as the kinetics of sorption were studied. A comparison of oxycellulose and other adsorption components such as zeolites and ion-exchange resins was made. The affinity of oxycellulose to metal ions was determined to be in the following order: Cd^{2+}, Zn^{2+} > Ni^{2+} ≫ Ca^{2+} > Mg^{2+} ≫ Na^+. The use of oxycellulose was very effective, especially in the form of sorption filters, because this allowed us to use a simple filtration process. Moreover, the specific loading amount of the filter cake was higher for filtration than for the column process under comparable conditions. Oxycellulose in a glass column behaved similarly to an ion-exchange resin. It showed approximately constant efficiency until the sorption capacity of the adsorbent was exhausted, and then it suddenly dropped. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 669–678, 2009

Key words: biofibers; biomaterials; composites; diffusion; separation techniques

INTRODUCTION

The standard method of water filtration has been viewed for a long time merely as a mechanical process of straining out solid particles. In this way, turbid water has been clarified. The filter media must allow the fluid, commonly water or another aqueous system, to pass through while holding back particulate contaminants. This retention of the contaminants is accomplished by an operation within the porous media by one or both of two distinctly different filtration mechanisms: mechanical sieving and electrokinetic particle capture. In the case of mechanical sieving, a particle is removed by mechanical entrapment when it attempts to pass through a pore smaller than itself. Within this mechanism, filtration efficiency is controlled by the relative size of the contaminant and the filter pore diameter. The efficient removal of very small particles, including colloid particles (e.g., <0.1 μm in diameter), therefore requires filter media with very small pore sizes for removal by mechanical sieving. Such finely pored filter sheets (FSs) tend to have the undesirable characteristics of a high-pressure drop across the FSs and shorter filter lives. In the case of the electrokinetic capture mechanism, the surface of particle colloids is interfaced with the porous filter media and retained on the surface by short-range attractive electrostatic forces.[1]

However, these filters are not able to separate dissolved substances. In this case, the best solution is using sorption filters: particles or molecules of colloidal or dissolved substances are adsorbed by pore surfaces and micropores of the sorption filter, respectively. For this reason, sorption filters are functional for the retention of both dispersed and dissolved contaminants.[2] In previous years, improved filters have been developed, such as filters with modified surface charge characteristics. These filters capture and concentrate colloidal particles around the filter pore nanocenters by electrokinetic interactions followed by their surface coagulation or flocculation.[3,4] These filters have mainly positively charged pore surfaces.[2]

Recently, studies have focused on the development of anion-active sorption FSs that will be able to capture metal ions, cationic colloids, or other positively charged particles. Cellulose and its derivates are potentially suitable materials because cellulose is insoluble in water, renewable, biodegradable, and

biocompatible. Because of its abundance in nature, cellulose is a very suitable material for cost-effective technologies in ion-exchange, affinity-chromatography, and membrane applications.[5] However, pure cellulose does not have a sufficient number of functional groups for effective metal removal efficiency. For this reason, various modified celluloses have been used as ion-exchange or chelation agents because they are hydrophilic and more advantageous for such applications.[4–6] One of the possible functional groups that can be introduced into the cellulose molecule is the COOH group, which is formulated by the process of cellulose oxidation. Being oxidized by an inexpensive technology, oxycellulose (OC) could be the material of choice for various industrial applications in separation technologies. Moreover, OC is, unlike minerals and synthetic resins, a fully biodegradable material. Typically, OC in an unregenerated natural form has a complicated cell wall morphology with different degrees of erosion due to acid hydrolysis during its preparation.[7]

This study deals with the sorption and ion-exchange properties of OC used especially in the form of an FS. This application appears to have the best potential for the removal of metal ions from aqueous solutions because no reversibility or returnability to its original state is needed.

The aim of this study was to determine the mechanism of the adsorption process, to show the selective ability of OC for individual ion capture, and to compare this with similar mineral and synthetic nonbiodegradable products. The standard characteristics of sorption materials are described too.

EXPERIMENTAL

Hydrogen peroxide bleached magnesium bisulfite softwood pulp (Biocel, Paskov, Czech Republic) was used as the raw material for an acid process of N_2O_4-mediated oxidation. The resulting hydrogen form of OC in a fibrous form and in the form of hand-made sheets was used in all sorption and filtration experiments, that is, for batch and column experiments and for filtration, respectively. OC or an alternative sorption material was added to a mixture of sulfite pulp, deionized water, and a wet-strength agent (to ensure the required wet strength of the FS), and the fibrous slurry was intensively stirred. The slurry was stirred until no large clusters were present in the mixture. Small FSs were made on a Buchner funnel and were dried at a temperature of $100°C$ in a laboratory dry kiln for 8 h. Small, circular segments (60 mm in diameter) were cut out from these FSs with a circular mechanical cutter and used for the experiments.

In addition to laboratory-scale preparation, some of the FS preparation was carried out on a produc-

tion-scale paper machine (Hobra Školník, Broumov, Czech Republic). For the machine-made sheets, N_2O_4-oxidized cellulose with approximately 1% COOH and tap water were used. The drying temperature was $120°C$. Both the laboratory and production-scale manufactured FSs showed a satisfactory wet strength (>150 kPa) and thickness uniformity. The color was unchanged despite drying at $120°C$. Hand-made samples with a higher COOH content (9.3%) were used for sorption experiments.

Qualitative character of OC

The qualitative character of OC was determined by a titration method, by a viscosimetric method determining the degree of polymerization (DP), and by ultraviolet–visible spectroscopy[11] of a cadoxen solution:

- Content of COOH groups: 9.3%.
- DP: 65.
- Polydispersion of DP: 0.3.1 (with increasing DP polydispersion values, the DP distribution became more polydisperse).
- Content of free glucuronic acid (GA) in OC (w/w): 0.2.4.
- Share of COOH groups in poly(1,4-β-D-anhydroglucuronic acid) (PAGA): 50.2%.
- Content of destabilizing components in OC: 0.1.22 (mmol of GA–PAGA/g of OC).

Wood pulp with a low COOH content (1.3. %) was used only for the preparation of FSs on a production machine. This pulp was obtained by careful N_2O_4-mediated oxidation of a wood bleached pulp in the form of a fibrous slurry. FSs were made on a standard paper machine with the addition of a poly(amide amine) epichlorohydrin wet-strength resin (Giluton, BK Giuliny GmbH, Ludwigshafen, Germany).

Other materials

Some natural adsorbents from the zeolite group were used for a comparison of the sorption properties of OC:

- Zeolite from Slovakia SlovZeolite (Presov, Slovakia) with an average grain size of 200 μm (60% clinoptilolite, 18% amorphous glass, 12% alkali feldspar, quartz, cristobalite, and mica).
- Sepiolite (Tolsa, Spain; grain size = 250 um).
- Clinoptilolite (Enlimining, Turkey; grain size = 250 μm).

Also, the synthetic ion-exchange resin Dowex 50 WX4 (Serva Electrophoresis GmbH, Heidelberg, Germany) with 4 mmol of acid groups/g was used.

High-purity chemicals [CdCl$_2$·2H$_2$O (*pro analysis*), ZnCl$_2$ (*pro analysis*), NiCl$_2$·6H$_2$O (*pro analysis*), CaCl$_2$ (*pro analysis*), and NaCl (*pro analysis*)] from HiChem (Brea, California) were used for the preparation of solutions.

The pH of the fibrous slurries was adjusted by small additions of either 1 mol/L HCl or 1 mol/L NaOH and was held constant at pH 6 in all experiments. The stirring speed of the laboratory blender was 500 rpm in all experiments, and the temperature was kept constant at 22.5. ± 1°C.

Deionized water was prepared with reverse-osmosis and ion-exchange methods (Aqua Osmotic, Tisnov, Czech Republic).

Methods

Adsorption isotherms were measured in a batch mode for experiments with 2 g of OC fibers dispersed in 1 L of water. The initial concentration of all Cd^{2+}, Zn^{2+}, and Ni^{2+} solutions in deionized water varied from 2 to 280 mg/L. After 30 min, the fibrous OC was filtered out, and the concentrations of residual metal ions were determined by means of atomic absorption spectroscopy (AAS) with a Solar S4 AAS instrument (Thermo Electron, Waltham, MA). As a control experiment, the sorption of cadmium ions on sulfite pulp was studied.

For ion-exchange experiments, a glass column (Kavalier, Sazava, Czech Republic) with sintered glass (S1), a tap diameter of 22 mm, a height above the sintered glass of 300 mm, and a 19/17 ground joint was used. Two grams of OC (which was previously stirred in deionized water) was placed into the column in such a way that no empty spaces were left, and the OC formed a compact mass. The thickness of the OC bed was about 50 mm. An aqueous solution of metal ions in deionized water was driven through the column with OC, and separate fractions were collected. The concentration of metal ions in the supernatant was determined by AAS. All filtration experiments were carried out on a small plate filter (Minicol, Hobra Školník) with a filtration area of 20 cm^2. The pH of the solution was measured with a pHep 5 pH meter (Hanna Instruments, Ann Arbor, Michigan). The flow rate through the samples and the resulting pressure drop were measured with an FLR 1011 flow meter (Newport Electronics, San Francisco, CA) and with a GPE81/0–10 bar electronic pressure converter (Bartex), respectively.

An aqueous solution of the ions in deionized (or drinking) water was placed in a container with a volume of about 50 L. The solution was pumped from this container to the Minicol filtration equipment, in which the FS was placed. The filtrate was collected at exact time intervals, and the residual concentration of metal ions was measured by the AAS method. The ion concentration in the solution after passage through the OC FS was compared with the ion concentration from a control experiment with a pure sulfite pulp.

FSs containing OC, pulp, zeolites, and a wet-strength agent were used in all filtration experiments. A standard-range FS (S 150N, Hobra Školník) containing unrefined pulp and a wet-strength resin was used as a control sample.

All measurements of residual metal ions in the supernatant were conducted three to five times. Data in graphs represent average values with a mean relative quadratic deviation equal to 5.3%.

RESULTS AND DISCUSSION

Kinetics of the sorption processes

To determine the sorption capacity of the used OC, a preliminary kinetic study was necessary. First, the sorption kinetics of nickel, zinc, and cadmium ions of various initial concentrations (0.7 mmol/L Ni^{2+}, 1.5 mmol/L Zn^{2+}, and 0.5 mmol/L Cd^{2+}) were determined. In the following experiments, the initial concentration of cadmium ions was varied from 0.1 to 2 mmol/L Cd^{2+} (0.1, 0.2, 0.5, 1, and 2 mmol/L). OC (2 g) was added to every liter of the sample solution, and the slurry was stirred gently for 60 min. Some solution (50 mL) was withdrawn and filtered through laboratory-grade filter paper at defined intervals. It was verified that the paper filter had no ion-exchange or sorption activity. The filtrate was analyzed by means of AAS, and the Cd^{2+} concentration was plotted as a function of time (Fig. 1). Consequently, the time of 30 min was used for the measurement of adsorption isotherms.
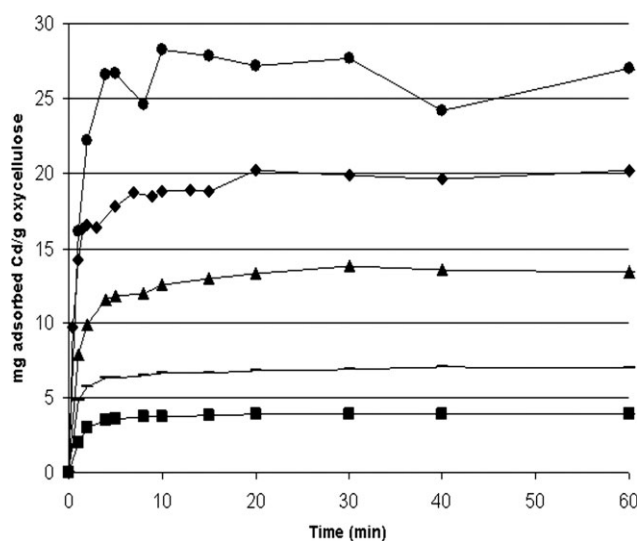

Figure 1 Sorption kinetics of OC for five different initial concentrations of Cd^{2+}: (■) 0.1, (—) 0.2, (▲) 0.5, (◆) 1, and (●) 2 mmol/L.

Furthermore, the kinetics of these sorption processes were satisfactorily verified with the following theoretical function (see Fig. 2) predicted by a simple diffusion model:

$$c_a = \frac{n_a \cdot t}{(K.n_a + t)} \qquad (1)$$

where n_a and c_a are the concentrations of the adsorbed components retained by OC, pulp, and so forth at time $t \to \infty$ and at time t, respectively, and D is the diffusion coefficient of the measured component in the cell wall of the fibrous pulp and OC (m^2/s). The parameter K is proportional to the reciprocal value of D for metals adsorbed into the cell wall of OC because $K = k/D$. Obviously, as it follows eq. (1), $\lim_{t \to \infty} c_a(t) = n_a$.

The values of the slopes of the linear dependence of t/c_a versus t in Figure 2 satisfactorily prove this behavior because these values increase with the reciprocal values of n_a for Cd^{2+}, and the resultant values of n_a from kinetic measurements are in satisfactory agreement with the results of adsorption measurements presented later in Figure 4. This behavior confirms that the diffusion into the microthin surface layers of the cell wall of natural OC is the dominant process controlling the adsorption kinetics. Moreover, verification of the kinetic measurements enables us to characterize the mechanism of the sorption process. The intercepts of these linear
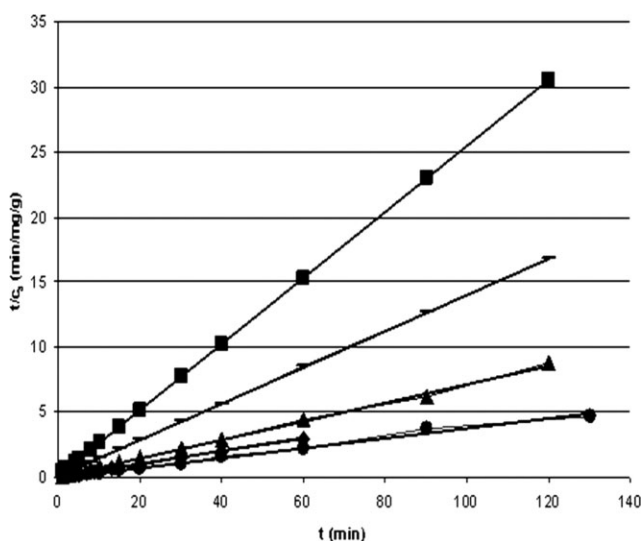

Figure 2 Verification of the sorption kinetics of OC for different initial concentrations of Cd^{2+}: (■) 0.1 mmol/L ($y = 0.2532x + 0.140$, $R^2 = 1$, $x_{ra}^2/D = 0.55$ min, $n_a = 3.95$ mg of Cd/g of OC), (—) 0.2 mmol/L ($y = 0.1394x + 0.112$, $R^2 = 0.999$, $x_{ra}^2/D = 0.80$ min, $n_a = 7.17$ mg of Cd/g of OC), (▲) 0.5 mmol/L ($y = 0.0713x + 0.073$, $R^2 = 0.999$, $x_{ra}^2/D = 1.02$ min, $n_a = 14.02$ mg of Cd/g of OC), (◆) 1 mmol/L ($y = 0.0494x + 0.032$, $R^2 = 0.999$, $x_{ra}^2/D = 0.65$ min, $n_a = 20.24$ mg of Cd/g of OC), and (●) 2 mmol/L ($y = 0.0381x + 0.011$, $R^2 = 0.992$, $x_{ra}^2/D = 0.28$ min, $n_a = 26.25$ mg of Cd/g of OC).

dependences (K) are proportional to the distance in the cell wall to which the adsorbed component has penetrated in the steady state [the mean depth of penetration (x_{ra})] and to the reciprocal value of n_a because k is equal to x_{ra}^2/n_a (more details later).

Therefore, it is possible to conclude that the adsorption process does not take place strictly on the surface of OC but instead is followed by diffusion to a limited depth of its cell wall. Obviously, if D is constant, then the steady-state depth of diffusion in the eroded cell walls of OC (i.e., x_{ra}; cf. the values of x_{ra}^2/D in the legend of Fig. 2) is independent of the metal-ion concentration in an aqueous solution.

Theoretical description of the kinetics of sorption processes

Given that the rate-limiting step of the sorption process is predominantly the one-dimensional diffusion of molecules in the radial direction of the fiber into microthin surface layers of the cell wall of natural OC, this process is described by Fick's well-known first law with the following formula:

$$- i_d = -D \times \mathrm{grad}\, c = c \times v$$

where i_d is the one-dimensional diffusion flow of the component molecules; grad c is equal to dc/dx; v is equal to dx/dt; x is the distance achieved by molecules penetrating the eroded cell wall at time t (measured perpendicularly to the interface); and c is the concentration of the measured component in the solution (mol/L). By simple rearrangement of this equation, a basic differential equation can be obtained:

$$- D \cdot \frac{dc}{dt} = c.\left(\frac{dx}{dt}\right)^2 \qquad (2a)$$

or

$$D \cdot \frac{dc_a}{dt} = c_a.\left(\frac{dx}{dt}\right)^2, \qquad (2b)$$

The concentration of the diffusing component is in reality the concentration of the adsorbed component in the surface layers of the cell walls; in other words, dc_a is obviously equal to $-dc$.

Because of infinitesimal distances in the surfaces of multistratified cell walls, it is possible to suppose that grad c is constant:

$$- \frac{dc}{dx} = \frac{n_a}{x} = \frac{c_o}{D} \cdot \frac{dx}{dt} \qquad (3a)$$

or

$$- \frac{dc}{dx} = \frac{c_a}{x} = \frac{c_o}{D} \cdot \frac{dx}{dt}, \qquad (3b)$$

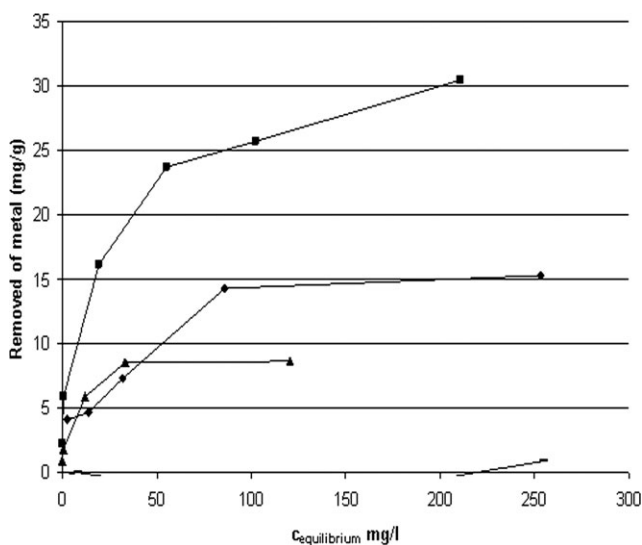where n_a and c_a are the steady-state concentrations of the adsorbed component at time $t \to \infty$ and time

Figure 3 Isotherms for the adsorption of metal ions onto OC and cellulose: (■) Cd^{2+} (OC), (◆) Zn^{2+} (OC), (▲) Ni^{2+} (OC), and (—) control cellulose ($c_{equilibrium}$ = equilibrium concentration).

t, respectively. Moreover, the condition of a constant total concentration of the diffused components must be realizable at any time of the sorption process:

$$c_a + c = c_0 \text{ and } n_a + c_r = c_o$$

where c and c_r are the steady-state concentrations of the measured components in the supernatant at time t and time $t \to \infty$, respectively, and c_o is the total concentration of the dosed component.

By the integration of eq. (3), we obtained x_{ra} for the adsorbed component in the cell wall of OC at time t in the following forms for n_a and c_a:

$$x_{ra}^2 = 2D(n_a/c_o)t \tag{4a}$$

$$x^2 = 2D(c_a/c_o)t \tag{4b}$$

By the connection of these two equations, we obtained eq. (5), which describes the mutual dependence of these depth distances on the adsorbed concentrations:

$$x^2 = x_{ra}^2(c_a/n_a) \tag{5}$$

If we assume that the velocity of penetration of the adsorbed components into infinitesimally small depths of the eroded cell walls is constant, this equation follows:

$$dx/dt = x/t$$

For this reason, the differential equation [eq. (2b)] can be connected with eq. (5). Then, we can obtain a simple differential equation:

$$D \cdot \frac{dc_a}{dt} = \frac{x_{ra}^2}{n_a} \cdot \left(\frac{c_a}{t}\right)^2 \tag{6}$$

By the integration of eq. (6) under the given boundary conditions and with x_{ra} constant

$$\int_{c_a}^{n_a} (1/c_a^2)\, dc_a = K \int_t^\infty (1/t^2)\, dt$$

Equation (1) can be obtained in a verifiable form:

$$t/c_a = K + (1/n_a)t \tag{7}$$

where K is equal to $x_{ra}^2/(D \times n_a)$.

Adsorption isotherms

The ion-exchange behavior of OC was studied for Cd^{2+}, Ni^{2+}, and Zn^{2+} ions, and it was compared with adsorbents from the group of zeolites under the same conditions used in these experiments.

The curves in Figure 3 and 4 represent adsorption isotherms. This is described by the use of the Langmuir isotherm.

Studying the cadmium-ion uptake onto sorbents from the group of zeolites, we compared zeolites with OC under the same conditions. A comparison was also made with the commercially available ion-exchange resin Dowex (see Fig. 4 and Table I).

The Langmuir isotherm is described by this dependence:
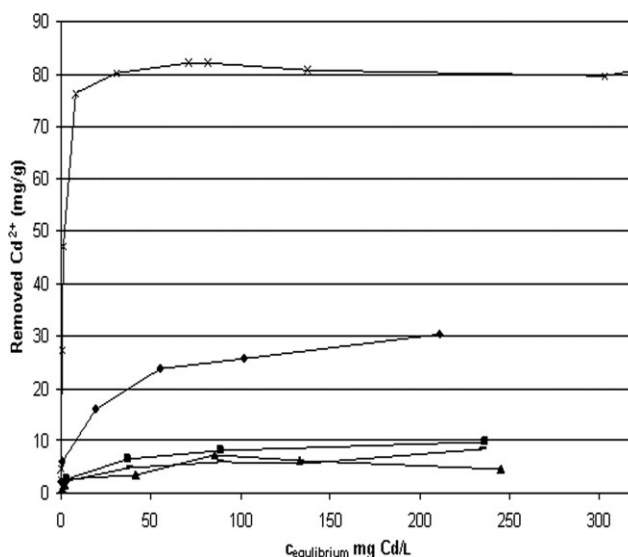
$$n_a = bc_r Q^0/(1 + bc_r) \tag{8}$$

Figure 4 Adsorption isotherms of Cd^{2+} on (◆) OC, (■) sepiolite, (▲) clinoptilolite, (—) zeolite, and (×) Dowex ($c_{equilibrium}$ = equilibrium concentration).

TABLE I
Comparison of the Parameters of the Langmuir Isotherm for the Mineral Sorbents, Synthetic Resin, and OC

| Adsorbent (ion exchange) | Langmuir's parameter | | | |
| | Q^0 [mg/g (mmol/g)] | | | b (L/mg) |
	Cd^{2+}	Ni^{2+}	Zn^{2+}	
OC	30.86 (0.275)	9.58 (0.16)	16.89 (0.258)	0.099
Zeolite	9.26 (0.082)	—	—	0.037
Clinoptilolite	4.97 (0.044)	—	—	0.32
Sepiolite	10.39 (0.092)	—	—	0.063
Dowex	83.3 (0.742)	—	—	0.39

where n_a is the amount of the adsorbed component per unit of mass of the adsorbent and is calculated as the difference between the original amount of metal ions in the solution and the amount of metal ions in the supernatant after contact with OC (mg/g); c_r is the equilibrium solution-phase concentration (mg/L); and Q^0 and b are Langmuir parameters related to the maximum adsorption capacity corresponding to complete coverage of the available adsorption sites (mg/g) and the energy/intensity of adsorption, respectively.

The Langmuir parameters were obtained through the fitting of the experimental data to the linear form of eq. (8).

$$1/n_a = (1/Q^0 b)1/c_r + 1/Q^0$$

The experimental data indicated a good fit and the applicability of the Langmuir isotherm model.

The Langmuir parameters for OC and other sorbents are listed in Table I.

The adsorption capacity of OC is approximately 2 times lower for Ni^{2+} and Zn^{2+} than for Cd^{2+}. We have no exact explanation for this behavior. Likely, it is additionally evoked by greater coordinative bonding ability of OC and Cd^{2+} versus Ni^{2+} and Zn^{2+}. Pure sulfite pulp with zero COOH group content was used as a control experiment, and it was shown that its ion-exchange capacity could be considered zero as well (Fig. 3).

As can be seen from Table I and Figure 4, OC has a higher sorption capacity for Cd^{2+} in comparison with the other natural sorbents. In comparison with the ion-exchange resin Dowex, the capacity of OC is more than 2 times lower. However, we obtained different results by using a more exact comparison of the isotherms for the OC and ion-exchange resin. The adsorbed amount of cadmium ions was recalculated per millimole of acid groups of the adsorbent (see Fig. 5). The adsorption capacity of OC is similar to that of Dowex, but its adsorption isotherm increases more slowly with the equilibrium concentration of cadmium ions in solution. The reason is that the ion-exchange resin contains strong ion-exchange

—SO_3H groups, whereas OC has only weak —COOH groups. The ion-exchange resin has explicitly defined particles with an exactly defined surface area, whereas OC is available in a fibrous form with stratified cell walls of a complicated morphology.

Analysis of adsorption capacities by the column method in deionized water

The ion-exchange behavior of an OC bed in a glass column was studied with the help of its uptake ability for nickel ions. For better comparison with FSs, the same method of data interpretation was used (see Fig. 6). Obviously, the efficiency of separation is higher in the column experiment than in the filter experiments at a small specific loading of filter cake (FC). At a higher specific loading, this efficiency curve drops abruptly only in the column experiment. This difference in behavior is caused by the different characters of the homogeneous supernatant flow across FC in the column method and the more channeling flow in the filtration experiment. The results imply that filtration is a process in which a supernatant flows mainly through big, continual pores and slowly in small pores; that is, the adsorption sites are predominantly in the big pores, and step-by-step occupation of the small pores follows.

This different behavior can be seen better in Figure 7. The results of column and filter experiments with the OC and ion-exchange resin are shown. Again, different behavior is observed with a reduction of the separation efficiency for Ni^{2+} with a prolonged specific loading amount of the column and FS. The curves of the efficiency of Ni^{2+} versus the specific loading amount of FC show a tendency of
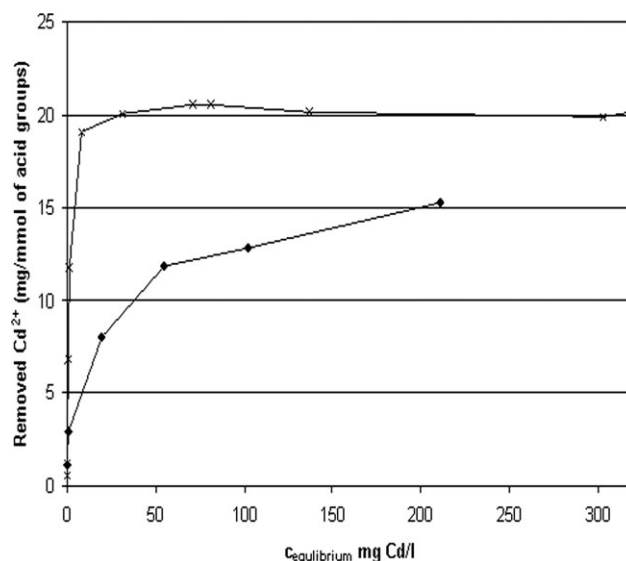
Figure 5 Comparison of adsorption isotherms of Cd^{2+} on OC and an ion-exchange resin: (×) Dowex and (◆) OC ($c_{equilibrium}$ = equilibrium concentration).
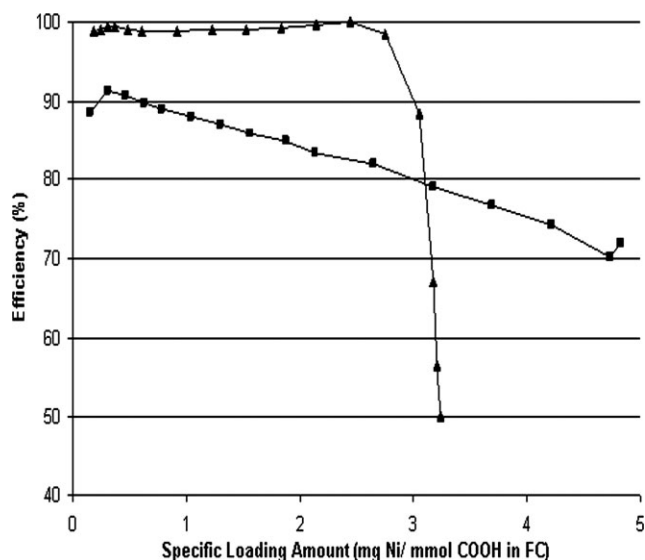
Figure 6 Comparison of the removal efficiency of Ni^{2+} by the column and filter method: (■) 2.23 (46.5% OC in an FS) and (▲) 2.5673 mg of Ni^{2+}/L (100% OC in a column).

slowly decreasing in FSs and a sharper drop in column cakes after crossing their specific loading limit. However, in comparable column experiments, this drop is logically sharper for the more homogeneous structure of the ion-exchange resin Dowex (because of its spherical shape and equal particle size) than for OC. As Figure 7 indicates, the separation efficiency in column experiments under comparable conditions decreases with an increased specific loading amount more slowly for OC than for Dowex.
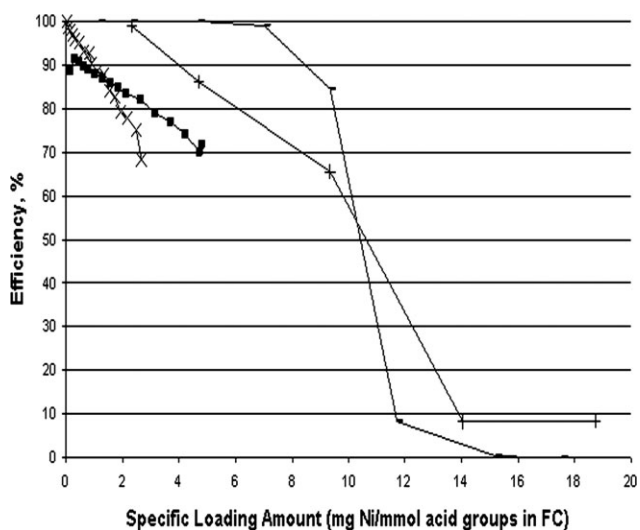

Figure 7 Comparison of the removal efficiency of Ni^{2+} by the column and filter method: (■) 2.23 (46.5% OC in an FS), (×) 1.7 (3.0 g of OC and sepiolite in an FS), (+) 98.3 (2.1 g of OC in a column), and (—) 98.3 mg of Ni^{2+}/L (2.1 g of Dowex in a column).

Separation efficiency of OC FSs in the filtration process with deionized water

The filtration experiments with deionized water with different concentrations of heavy metal ions were performed to verify the separation efficiency of sorption FSs prepared from different mixtures of OC and pulp. The applied metal ions were Cd^{2+} and Ni^{2+}. The efficiency of separation (%) is defined as follows:

$$(\text{Metal concentration in input water}$$
$$- \text{Metal concentration in effluent})$$
$$\times 100/(\text{Metal concentration in input water}) \quad (9)$$

The separation efficiency is defined by eq. 9 in every stage of the filtration process.

This observation indicates that the sorption capability of OC during filtration is effectively independent of the time of adsorption and of the shear rate of the filtrate at relatively low concentrations of metal ions. It has been shown that, at a relatively low concentration and short contact time (ca. 1 s), the flow rate has no influence on the removal efficiency of Ni^{2+} in the range of 100–500 L/m². As illustrated in Figure 8, with an increasing filtrate flow rate, that is, with the shear rate increasing and the contact time decreasing, the separation capability of FS is practically unchanged.

With respect to the kinetics of the sorption process described by eq. 1, an explanation for this behavior is possible only as long as $x_{ra}^2/D \ll t$. Either the diffusion coefficient of Ni^{2+} is high or the adsorption takes place strictly only at the surface layers of the cell walls; that is, the depth of the diffusion layer (i.e., x_{ra}) is very small. More likely, both these
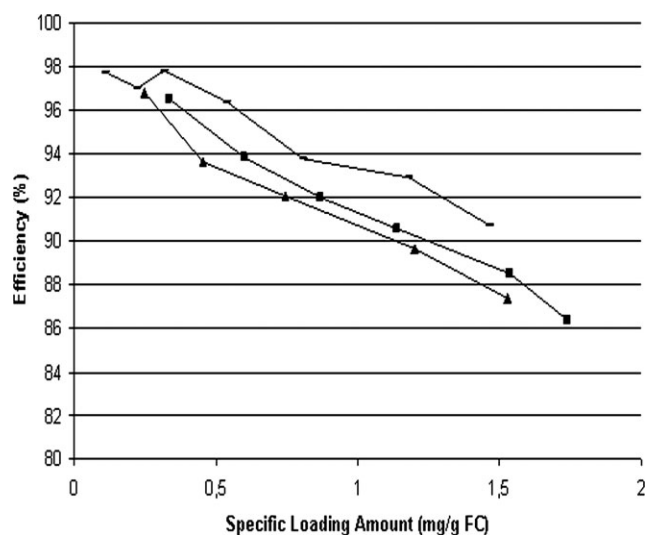

Figure 8 Separation efficiency of the filtration of a 0.033 mmol/L Ni^{2+} aqueous solution versus the specific loading amount of the FS at different filtrate flow rates.

processes are present because of the low influence of the shear rate. Unfortunately, we have no exact data for x_{ra} and D to make a definitive conclusion. Nevertheless, a difference between filtration and batch sorption processes has been confirmed.

Filtration experiments with various concentrations of Cd^{2+} in deionized water solutions but with high specific loading amounts of FS were performed. The results are presented in Figure 9. The curves for the removal efficiency of Cd^{2+} by OC from solution versus the specific loading amount of FS are practically the same for both cadmium concentrations in filtered solutions. However, the efficiency dependences versus the specific effluent volume (L/m^2 of FS) are logically different (see Fig. 10) because with an increase in the Cd^{2+} concentration, the specific loading amount of FS is increased as well. This fact implies that with an increasing specific filtrate volume, the efficiency of cadmium separation decreases much faster for a more concentrated Cd^{2+} solution containing 0.058 mmol of Cd^{2+}/L. The removal efficiency of the control FS can be considered zero.

An experiment with the same molar ratio of Ni^{2+} and Cd^{2+} mixed together was also carried out. As illustrated in Figure 11, the molar concentrations of Ni^{2+} and Cd^{2+} being the same, the uptake of cadmium is higher than the uptake of nickel. The difference is not too significant at the beginning of filtration, but as the experiment continues, the curves are more and more different. Thus, this experiment confirms the previous finding: the affinity of OC is much better for cadmium than for nickel (see Fig. 3).
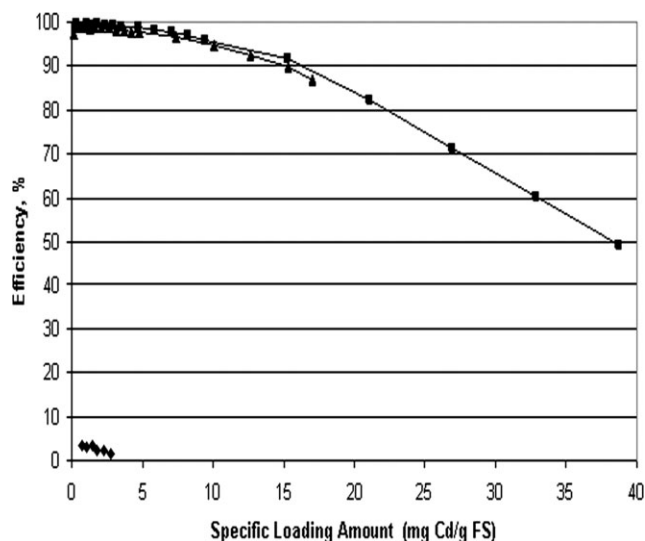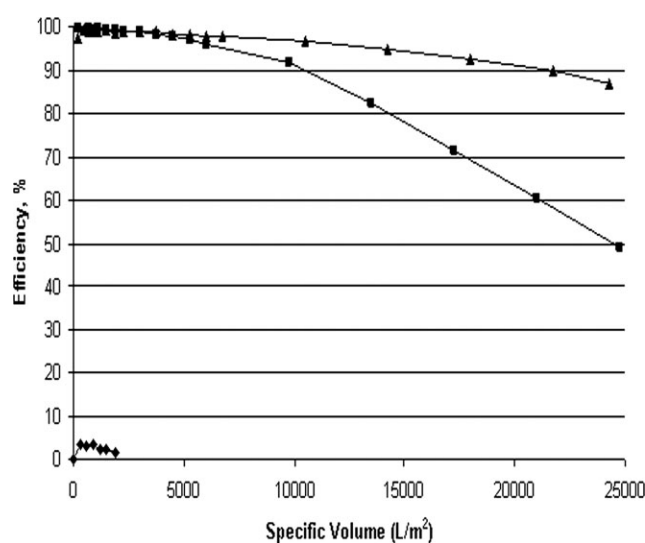

Figure 10 Filtration experiments with different concentrations of cadmium ions versus the specific filtrate volume: (■) 0.058 (OC, 9 mmol of COOH), (▲) 0.026 (OC, 9 mmol of COOH), and (◆) 0.032 mmol/L Cd^{2+} (control pulp).

Separation efficiency of OC FSs in the filtration process with mineral water

The filtration experiments showed the better capability of sorption FSs for removing Ni^{2+} or Cd^{2+} from mineral water containing a mixture of other ions (Ca^{2+}, Mg^{2+}, Fe^{2+}, Na^{2+}, etc.). The concentration of ions in mineral water were as follows: 66 mg/L Ca^{2+}, 8 mg/L Mg^{2+}, and 0.0.6 Fe^{2+} mg/L (according to the water supplier, VaK, Nachod, Czech Republic).

In the first batch of experiments, Cd^{2+} was added to the mineral water, in which the concentrations of alkaline earth metal ions (eventually other metal
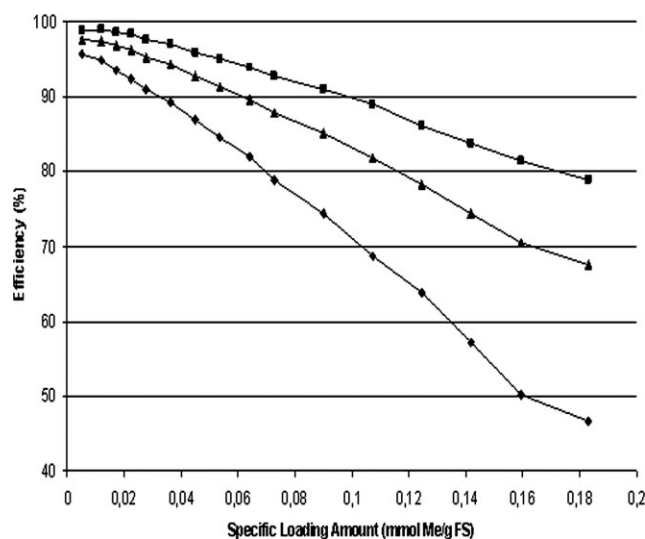

Figure 9 Filtration experiments with different concentrations of cadmium ions versus specific loading amounts of the FS: (■) 0.058 (OC, 9 mmol of COOH), (▲) 0.026 (OC, 9 mmol of COOH), and (◆) 0.032 mmol/L Cd^{2+} (control pulp).

Figure 11 Removal of nickel and cadmium from their mixture (5.6 mmol of COOH groups in FSs): (■) 0.034 mmol/L Cd^{2+}, (◆) 0.034 mmol/L Ni^{2+}, and (▲) 0.068 mmol/L metal-ion mixture.
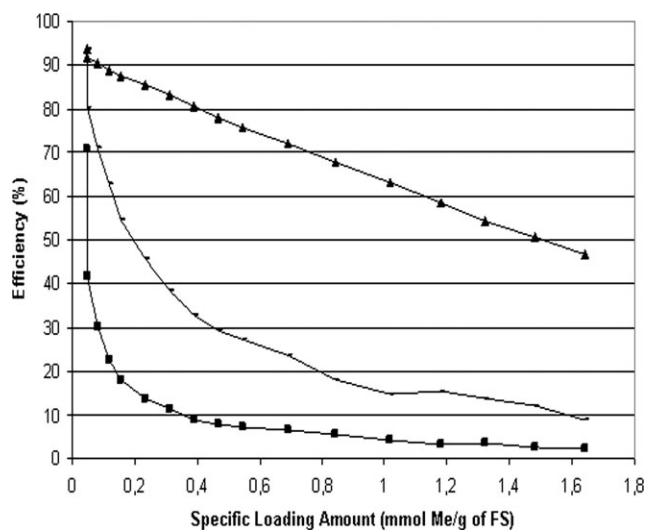
Figure 12 Removal of Cd^{2+} from mineral water (8.8 mmol of COOH groups in FSs): (▲) 0.03 mmol/L Cd^{2+}, (—) 1.6 mmol/L Ca^{2+}, and (■) 0.33 mmol/L Mg^{2+}.

ions are present in drinking water) were about 60 times higher than the Cd^{2+} concentration. The ion concentrations of cadmium, calcium, and magnesium were measured again by means of the AAS method. As can be seen in Figure 12, Cd^{2+} is preferentially withdrawn from drinking water as well. The affinity of Cd^{2+} is higher even though some COOH groups are occupied by alkaline earth metals or other metals present in mineral water. Obviously, the preferred affinity of Cd^{2+} to OC is produced not only by the ionic bond between Cd^{2+} and OC but also by their strong coordinative complex formation.

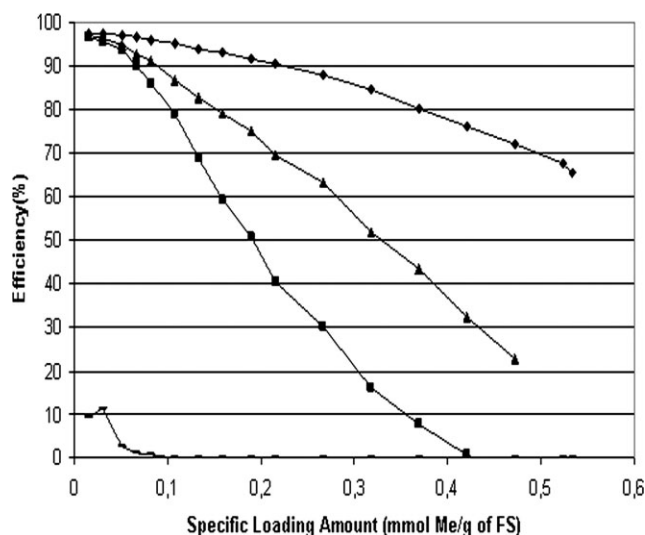Subsequently, we mixed together ions of cadmium, calcium, magnesium, and sodium in approxi-

Figure 13 Removal of Cd^{2+} from deionized water containing a mixture of ions (5.6 mmol of COOH groups in FSs): (◆) 0.046 mmol/L Cd^{2+}, (▲) 0.06 mmol/L Ca^{2+}, (■) 0.067 mmol/L Mg^{2+}, and (—) 0.18 mmol/L Na^+.
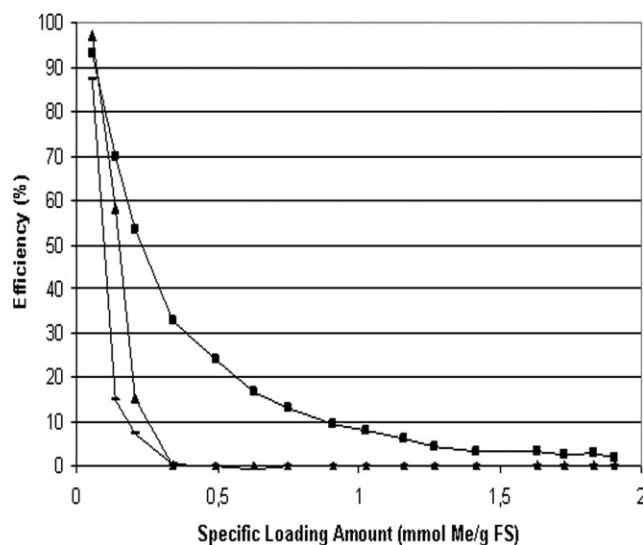

Figure 14 Removal of Ni^{2+} from mineral water (5.6 mmol of COOH groups in FSs): (■) 0.039 mmol/L Ni^{2+}, (▲) 1.6 mmol/L Ca^{2+}, and (—) 0.38 mmol/L Mg^{2+}.

mately the same ratio. This experiment proved the following finding: the lower the concentration of the co-ions (calcium, magnesium, iron, manganese, etc.), the greater the removal of cadmium from the solution. The affinity of ions to OC is in the following order: $Cd^{2+} > Ca^{2+} > Mg^{2+} \gg Na^+$. These findings are in full agreement with ion-exchange batch experiments published in the literature.[9] It is logical that the uptake of monovalent cations is much lower than the uptake of divalent cations. The affinity of Na^+ to OC is nearly zero in the presence of divalent cations (see Fig. 13).

Finally, experiments with nickel ions added to mineral water were performed. As in the case of cadmium, even though the concentrations of the other ions present in mineral water were more than 60 times higher, the nickel was removed preferentially (see Fig. 14). Again, this observation is in accordance with published results for batch experiments.[10]

CONCLUSIONS

The high sorption activity of OC in the form of an FS for metal ions, especially for heavy metals (Cd^{2+}, Zn^{2+}, and Ni^{2+}), was documented. The affinity of OC to metal ions was determined to be in the following order: Cd^{2+}, $Zn^{2+} > Ni^{2+} \gg Ca^{2+} > Mg^{2+} \gg Na^+$.

A verification of the kinetic measurements enabled us to characterize and better understand the mechanism of the sorption process in OC. We concluded that this adsorption process, in contrast to homogeneous synthetic resins, is not taking place strictly on the surface of OC. The adsorption process in OC is complicated because of its morphology and stratified

cell wall characteristics. Therefore, in the case of OC adsorbents, metal ions also diffuse into deeper inner parts of eroded fibrous stratified cell walls. It is a fundamental difference in comparison with synthetic homogeneous ion-exchange resins with simple spherical particles with only surface anionic groups. During filtration with OC FSs, the metal ions are taken more and more into the inner parts of cell walls. Because of this fact, the separation efficiency of this filtration process has a monotonously decreasing character with an increasing specific loading amount of FS or a specific filtrate amount.

It was shown that the application of OC in the form of an FS is a very effective way of removing metal ions (Cd^{2+}, Zn^{2+}, and Ni^{2+}) from aqueous solutions. In the case of low-concentration nickel-ion solutions, the filtrate flow rate through the FS has no influence on the efficiency of Ni^{2+} removal in the range of 100–500 L/m^2.

Moreover, the separation activity of OC used in a batch or column process is different in comparison with OC used in the form of an FS. OC applied in the form of an FS shows a gradual decrease in the separation efficiency caused by the specific character of the filtrate flow through this FS. OC applied in a glass column, similarly to an ion-exchange resin, shows approximately constant removal efficiency until the sorption capacity of the adsorbent has been exhausted, and then it suddenly drops. However, the separation curves obtained during column filtration have a more decreasing character in the case of OC than in the case of ion-exchange resins.

NOMENCLATURE

AAS	atomic absorption spectroscopy
c	concentration of the measured component in an aqueous solution (mmol/L or mg/L)
c_o	complete concentration of the separated component (mg/L or mmol/L)
c_r	equilibrium solution-phase concentration (mg/L or mmol/L)
D	diffusion coefficient of the measured component in the cell wall of fibrous pulp and oxycellulose (m^2/s)
DP	degree of polymerization
FC	filter cake
FS	filter sheet
GA	glucuronic acid
i_d	one-dimensional diffusion flow of component molecules (mmol m/L s or mg m/L s)
n_a and c_a	concentrations of adsorbed components retained by oxycellulose, pulp, and so forth at time $t \to \infty$ and t, respectively (mg/L or mmol/L)
OC	oxycellulose
PAGA	poly(1,4-β-D-anhydroglucuronic acid)
Q^0 and b	parameters of the Langmuir adsorption isotherm related to the maximum adsorption capacity corresponding to complete coverage of available adsorption sites (mg/g or mmol/L and L/mg, respectively)
t	time
v	dx/dt
x	distance achieved by penetrated molecules into the eroded cell wall at time t measured perpendicularly to interface of this one (m)
x_{ra}	mean depth of penetration of the adsorbed component into the cell wall (m)

References

1. Pall, D. B.; Degen, P. J.; Joffee, I. B.; Foss, W. M.; Gsell, T. C. U.S. Pat. 4,734,208 (1988).
2. Milichovsky, M. Proceedings of the 15th International Congress of Chemical and Process Engineering, Prague, Czech Republic, 2002.
3. Vodenicarova, M.; Milichovsky, M.; Cesek, B. Cellul Chem Technol Czech Society of Chemical Engineering 2001, 35, 59.
4. Milichovsky, M.; Cesek, B. Adsorption Sci Technol 2002, 20, 883.
5. Ghanshyam, S.; Chauhan, R. Desalination 2000, 130, 85.
6. Hirato, M. Developments of Functional Celluloses; CMC: Tokyo, 1985; Chapter 5.3.
7. Milichovsky, M.; Sopuch, T.; Richter, J. J Appl Polym Sci 2007, 106, 3641.
8. Gert, E. V.; Torgashov, V. I.; Yubets, O. V.; Kaputskij, F. N. Cellulose 2005, 12, 517.
9. Saito, T.; Isogai, A. Carbohydr Polym 2005, 61, 183.
10. Saliba, R.; Gauthier, H.; Gauthier, R.; Petit-Ramel, M. Cellulose 2004, 9, 183.
11. Milichovsky, M.; Milichovska, S. J Appl Polym Sci 2008, 107, 2045.