

# SEPARATION OF Cd<sup>2+</sup> FROM WATER BY USE OF OXYCELLULOSES AND ACTIVE PULP

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**Abstract:** Natural cellulose and carboxyl celluloses are highly hydrated substances with interesting sorption behaviour. They have the similar chemical composition, but different size of molecules and representation of COOH groups organized into a complex of supramolecular structure. Separation of Cd<sup>2+</sup> from polluted water by use of oxycellulose (OC) hydrocolloid fibrous form was compared with dissolved carboxyl methylcellulose (CMC). The carboxyl celluloses adsorption capacity of Cd<sup>2+</sup> ions increases with increasing of -COOH group content and distinctly increases with other competitive ions in the aqueous solution. The dissolved and hydrocolloid fibrous forms of carboxyl celluloses were separated from water by use of pulp fibre in both activated and inactivated form as a scavenger. It was revealed that for factual separation efficiency static (i.e. rheosedimentation) or dynamic (i.e. drainage fiber suspension) conditions of the scavenger application evoking counter character of the separation behavior are most important.

**Keywords:** oxycellulose, linters, adsorption, rheosedimentation

## 1 INTRODUCTION

Properties and interactions of cellulose surfaces and its derivatives are of a great interest for wide variety of applications including paper, textiles, and pharmaceutical products. In many applications the cellulose products are in contact with aqueous solutions or humid environment. In these cases the formation of active groups, e.g. carboxylic groups, determine adsorption phenomena of polymer/solution interface as occurring in sorption filtration and textile production or washing.

The most widely spread separation procedures include filtration working on various spatial levels (common filtration, microfiltration, ultrafiltration, nanofiltration and more and more important sorption filtration) [1].

As known, a hopefully separation filtration process is improved by use of sorption filtration methods for cleaning of polluted water contains of cationactive substances predominantly heavy metals. The treatment of heavy metals is of special concern due to their recalcitrance and persistence in the environment. In recent years, various methods for heavy metal removal from waste water have been extensively studied [2]. Adsorption characteristic of polysaccharides, cellulose and its derivatives including oxycellulose in relation to cations, particularly [3] heavy metals, have drawn more attention recently. Distribution of heavy metal depends on the existence of natural sources and human's activity [4, 5, 6]. Heavy metals at trace levels are difficult to metabolise in human body and very harmful; hence, research on the determination of heavy metals in food and environmental samples are very popular for healthy life of human [7, 8, 9].

We have studied the following colloid-sorption methods:

- colloid-sorption separation with inactivated fibre /CSS separation/
- colloid-sorption separation with activated fibre /ACSS separation/.

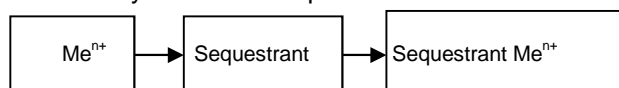
The main tested separation component (Sequestrant) was the H-form of oxycellulose (OC) of various compositions in the fibrous form and nano-form and its sequestration effect was compared with carboxyl methylcellulose (CMC). Carboxymethyl cellulose (CMC) is an anionic polysaccharide obtained from the carboxymethylation of natural cellulose. In contrast to the cellulose, CMC is a kind of hydrophilic polymers which is easily solubilized in water and has excellent water swelling ability [10].

Also sorption capacities of the fibrous oxycellulose were measured. The tested metal was cadmium Cd<sup>2+</sup> in model water containing competitive ions of calcium and magnesium with pH = 11,5. For separation of the activated and inactivated papermaking pulp fibers from the water suspension two following methods were then utilized.

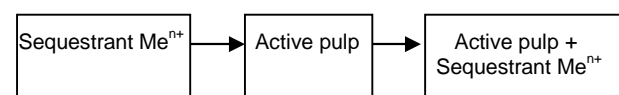
### 1.1 Theoretical

#### Separation with rheosedimentation (CSS)

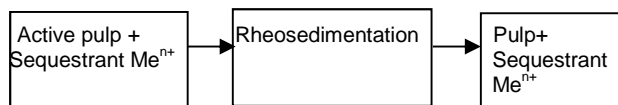
1. step: chemical reaction with colloidal part of oxycellulose - sorption



2. step: : surface flocculation with pulp (F) in active (ACSS) or no-active (CSS) form



3. step: separation contaminated pulp by sedimentation



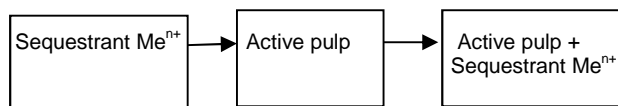
4. step: deposition bioactive fibre sediment with  $Me^{n+}$

### Separation by drainage of a fibre suspension (CSD)

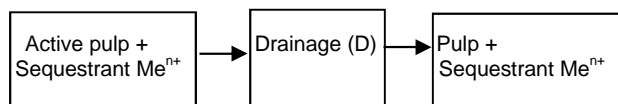
1. step: chemical reaction with colloidal part - sorption



2. step: surface flocculation with pulp (F) in active (ACSS) or no-active (CSS) form



3. step: separation contaminated pulp by its drainage



4. step: deposition of bioactive fibre cake with  $Me^{n+}$

### Rheosedimentation

A control of papermaking process is possible by measurement of strength and bonding properties of pulp fibres. These properties are possible to estimate by rheosedimentation method. This method is based on sedimentation of fibre network [11].

A movement of rheosedimenting fibre network continuum is very well described [12] by general equation of continuity as similar as Smellie and La Mer [13] used this equation to description of subsidence of uraniferous phosphate slime. As showed in Fig. 1, the observation of a proper rheosedimentation is very simple because rheosedimenting fibre network is characterized by high of this fibre network in cylindrical vessel [14].

Formerly was shown [14] that rheosedimentation is strongly dependent on intensity of pulp beating, i.e., with increasing a degree of beating the rheosedimentation gets slowly, and the standard rheosedimentation velocity can be used for determination of character the beating process. It was found theoretically and proved by experiments that with increasing of pulp beating, the standard velocity of rheosedimentation is decreasing markedly faster for fibrillation than for fibre cutting. Further it was found that the course of the initial velocity of rheosedimentation is different

for dried and never dried pulps, i.e. dried pulp rheosediments at comparable condition more rapidly than never dried pulp. This phenomenon was also depending on the degree of delignification, i.e., on a composition of tested the cellulosic material. The more the pulp was delignified, the deeper the phenomenon.

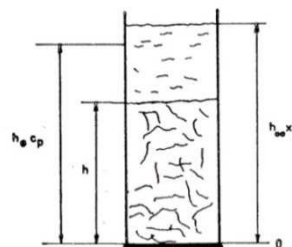


Figure 1 Schematic presentation the principle of rheosedimentation.

## 2 EXPERIMENTAL

### 2.1 Separation efficiency

Separation efficiency SE expresses a quantity of metal  $M^{n+}$ , which has been trapped on the fibres of cellulose suspension. It is given by ratio of sorbed amount of metal  $M^{n+}$  to total initial amount of metal  $M^{n+}$  which has been used in the experiment [15].

$$SE = \frac{100 * c_a}{c_p} = \frac{100 * (c_p - c_{rovn.})}{c_p},$$

	where
$c_{rovn.}$	equilibrium concentration of $Cd^{2+}$ in model water after separation process (g/L)
$c_a$	equilibrium concentration of the $Cd^{2+}$ sorbed onto the pulp (g/L),
$c_p$	total concentration of the $Cd^{2+}$ in model water (g/L),
SE	separation efficiency %.

The metal tested was cadmium  $Cd^{2+}$  in model water containing competitive ions of calcium and magnesium of pH 11.5.

### 2.2 Spectrophotometric determination of $Cd^{2+}$ ions

The concentration of  $Cd^{2+}$  in the supernatant was determined spectrophotometrically with the help of dithizone extract (0.005% solution of dithizone in chloroform) of alkalized supernatant (by use of 10% solution of NaOH with the ratio 1:1) at  $\lambda = 515$  nm [16]. The same measurements were conducted at this wavelength against the reference solution (solution with chemicals without  $Cd^{2+}$ ).

The basic cadmium solution was prepared by dissolution of 0.1 g in  $CdCl_2$  and refilling with

distilled water up to the 1 litre volume. 1ml of the solution thus contained 61.32  $\mu\text{g}$  Cd.

The amount of ions in the supernatant was then determined by use of spectrophotometry.

### 2.3 Materials

As native cellulose was used commercial cotton linter. Oxycelluloses OKCEL H-L were prepared by nitroxide-mediated oxidation of linters in Synthesia, Pardubice-Semtin, Czech Republic and pulp is commercial bleached MgBi-sulphite spruce pulp from Biocel Paskov, Czech Republic – see Table 1.

**Table 1** The parameters of oxycellulose

Sample	DP	$X_{\text{GA}}$ , g/g	$P_{\text{DP}}$	$X_{\text{COOH}}$ , %	$X_{\text{DS}}$ , %	$X_{\text{GA-PAGA}}$
Okcel H-L 284/051/3	35.8	0.455	0.813	17.8	70.842	0.6513

$X_{\text{GA-PAGA}}$  (mmol GA-PAGA/g oxycel.)

Carboxymethyl cellulose (CMC) was received from Fisher Scientific.

$$\text{DS} = 0.7$$

$$M_{\text{CMC}} = 250000$$

$$M_{\text{ACMG}} = 242$$

$$M_{\text{AG}} = 162$$

$$M_{\text{COONa}} = 67$$

#### Non-active pulp

Sulphite pulp (air-dry) was defibrated in laboratory pulper for 10 minutes, so that 3% suspensions could be obtained. 30 g of pulp was added into the pulper vessel with 1 litre of distilled water and was left to swell for 2 minutes. Then the pulp suspension was stirred at 600 revolutions.

Parameters of the pulper are: vessel volume 3 liters, vessel height 0.19 m, and internal diameter of the vessel 0.155 m. The mixer is from steel with the diameter 9 cm with three rectangular blades situated vertically in the axis of the vessel. The vessel has 4 spiralled stops on its walls.

#### Active pulp

A 3% sulphite pulp suspension was cationized by oligomeric cationic component Refaktan K (trade mark of Chemotex, Decin CR, prepared by the reaction between dimethylamine and epichlorhydrine), which was activated by dissolving NaOH in Refaktan K at a mass ratio of Refaktan K: NaOH of 1:0.05. The reaction of cationization were as follows: temperature 50-60 °C, reaction time 30 min, pH 7-8, 10% addition of activated Refaktan K calculated upon a.d. pulp [17].

### Carboxyl celluloses

Suspensions of oxycellulose were prepared by weighing 1.6 g in 100ml of the model mixture. 5 mg of carboxyl methylcellulose were added into 500ml of distilled water.

#### Colloid-sorption separation by rheosedimentation (CSS separation)

1.6 g carboxyl methylcellulose (CMC) was added into five 250 ml beakers, i.e. the calculated amount of 1% solution CMC (24 ml) was measured out and added 100 ml of the solution of  $\text{CdCl}_2$  cooled to 15 °C in concentrations 0.5, 0.4, 0.3, 0.2 and 0.1g  $\text{CdCl}_2/\text{l}$ . The mixture was stirred by application of a glass stick, left to rest for 30 minutes, then 32.4ml of activated pulp was added to each beaker and the content was stirred again.

1.6g oxycellulose was added into five 250 ml beakers, then 100ml of the solution of  $\text{CdCl}_2$  in concentrations 0.4, 0.3, 0.2, 0.1 and 0.05g  $\text{CdCl}_2/\text{l}$  were added. The mixture was stirred with the use of a glass stick, left to rest for 30 minutes – sorption took place. The measuring flask was used to add 32.4ml of activated pulp into each beaker, it was stirred and left to rest for 15 minutes – surface flocculation occurred.

The same experiment as in case of activated pulp was made for the inactivated pulp for concentrations 0.5, 0.45, 0.4, 0.35 and 0.3 g  $\text{CdCl}_2/\text{l}$ . Blend experiments without carboxyl celluloses sequestrants were gained by similar way.

After the solution cleared above the rheosedimenting pulp, a pipette was used to gauge an amount of 10 ml of supernatant to determine Cd content by using of (0,005% solution of dithizone in chloroform) spectrophotometric method.

#### Colloid-sorption separation by drainage of a fibre suspension (CSD separation)

1.6 g CMC was added into five 250 ml beakers, i.e. the calculated amount of 1% solution of CMC (24 ml) was measured out and added. 100 ml of the solution of  $\text{CdCl}_2$  in concentrations 0.4, 0.3, 0.2, 0.1 and 0.05 g  $\text{CdCl}_2/\text{l}$  were added. The mixture was stirred with the use of a glass stick, left to rest for 30 minutes – sequestration, 32.4 ml of activated pulp was added to each beaker and the content was stirred again and left to rest for 15 minutes.

1.6 g oxycellulose was added into five 250 ml beakers, 100ml of the solution of  $\text{CdCl}_2$  in concentrations 0.4, 0.3, 0.2, 0.1 and 0.05 g  $\text{CdCl}_2/\text{l}$  were added again. The mixture was stirred thoroughly with a glass stick, left to rest for 30 minutes – sorption took place. The measuring flask was used to add 32.4 ml of activated pulp into each beaker, it was mixed and left to rest for extra 15 minutes – surface flocculation occurred.

The same evaluation as in case of activated pulp was made for the inactivated pulp for

concentrations 0.5, 0.45, 0.4, 0.35 and 0.3 g CdCl<sub>2</sub>/l. By similar way took place the blend experiments without carboxyl celluloses sequestrants.

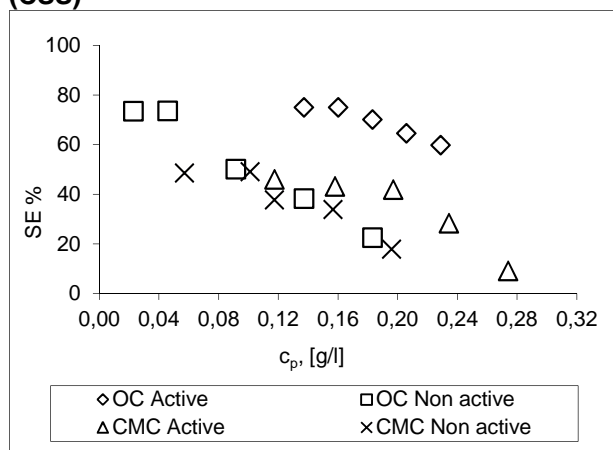
The content of the beaker was filtered through the Büchner funnel without the filter sheet; the filtrate containing remnants of fibres was poured again over the created filter cake on the Büchner funnel. This pouring was always performed 3 times for all samples – the filtrate did not contain any fibres.

Content of Cd<sup>2+</sup> in clear filtrate was determined again by use of the spectrophotometric dithizone method.

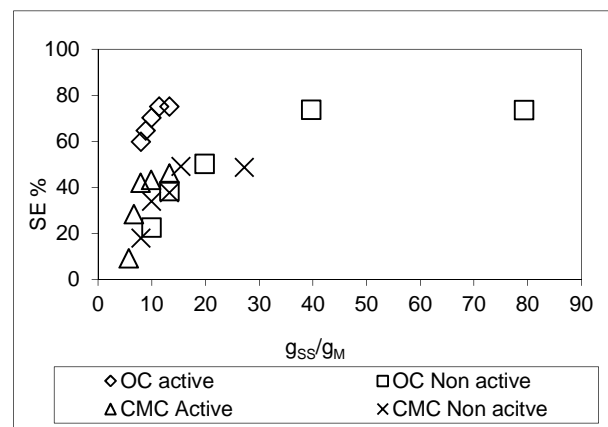
### 3 RESULTS AND DISCUSSION

Separation of cadmium from water via sequestration agents OC and CMC with the use of rheosedimenting fibre pulp suspensions in both activated and inactivated forms is illustrated in the Figs. 2 and 3.

#### Separation via rheosedimentation process (CSS)



**Figure 2** Dependence of SE versus  $c_p$ , g Cd<sup>2+</sup>/l where SE and  $c_p$  are the separation efficiency and the total concentration of the Cd<sup>2+</sup> in model water, respectively.

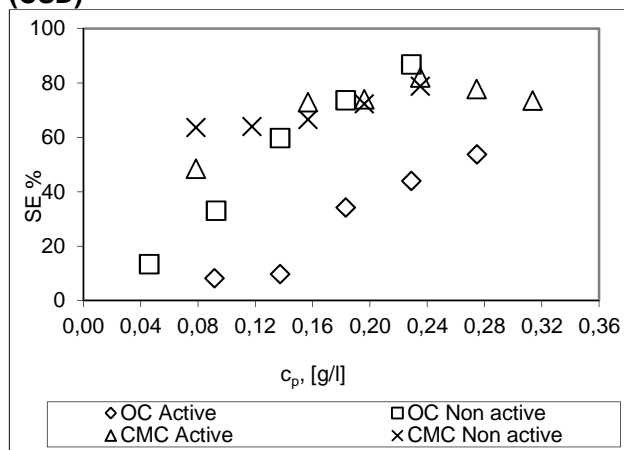


**Figure 3** Dependence of SE versus,  $g_{ss}/g_M$  where SE,  $g_{ss}$  and  $g_M$  are the separation efficiency, the

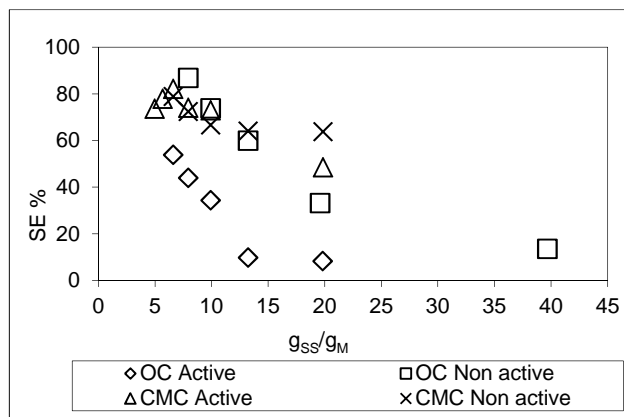
amount of sequestering agent and the amount of Cd<sup>2+</sup>, respectively.

A separation of cadmium from water via sequestration agents OC and CMC with the use of separation by drainage of a fibre pulp suspension in both activated and inactivated forms is illustrated in the Figures 4 and 5.

#### Separation via drainage of a fibre suspension (CSD)



**Figure 4** Dependence of SE versus  $c_p$ , g Cd<sup>2+</sup>/l where SE and  $c_p$  are the separation efficiency and the total concentration of the Cd<sup>2+</sup> in model water, respectively.



**Figure 5** Dependence of SE versus,  $g_{ss}/g_M$  where SE,  $g_{ss}$  and  $g_M$  are the separation efficiency, the amount of sequestering agent and the amount of Cd<sup>2+</sup>, respectively.

The separation efficiency (SE) expresses the amount of cadmium, which was captured on the pulp fibres by help of sequestering aids CMC and oxcellulose. It is given by the proportion of the captured (absorbed) amount of Cd<sup>2+</sup> in the pulp fibre to the total amount of Cd<sup>2+</sup> in the separation mixture. Received results document that logically dependences SE vs.  $c_p$  have opposite character the dependences SE vs.  $g_{ss}/g_M$  (compare Figs. 2 – 3

and Figs. 4 – 5). However, a controversial character of CSS and CSD separation process is important. During CSD process the separation efficiency increases with increase of  $\text{Cd}^{2+}$  ion concentration in model water to the contrary of rheosedimentation CSS process. Moreover, in comparison with CMC, by use of oxycellulose as sequestering aid was achieved better separation efficiency at CSS than the CSD separation process. Reversely, the CSD process is more efficiency for use of CMC as sequestering aid. Further, also the effect of activated and inactivated pulp is manifested here in a great extent. In comparison with active pulp, the inactivated pulp shows better separation effect if it is use at drainage separation process (CSD) than at the rheosedimentation separation process (CSS). Also, the received results reveal significant counter differences in a separation mechanism of both processes. Obviously, an explanation of these counter differences it is necessary to look for on difference in hydrodynamic shear forces during CSS separation process – low shear forces – and during CSD separation process – high shear forces.

It was confirmed that the separation effect of the colloid-fiber form of oxycellulose is high. It was also positive to find out that the colloid-fiber form of oxycellulose has a high affinity to the common ligno-cellulose fibrous material – pulp. This affinity can be further increased by modifying the pulp through introducing oligomer cation-active groups. The result is, unlike the CSS process, an increasing separation effect of the CSD process with an increase in the concentration of cadmium cations, or potentially with a decrease of the dose of SS/M.

Unlike the CSD process, as it can be seen from the Figs. 2 - 3, the separation efficiency of the CSS separation decreases with an increasing concentration of  $\text{Cd}^{2+}$ , i.e., or it increases with the growing amount of COOH groups of sequestration agents with regard to the amount of metals in the model water (see Fig. 3). It is completely inverse behaviour to CSD separation where, on the contrary, the activated pulp negatively affects the separation efficiency of  $\text{Cd}^{2+}$ , especially in case of OC (see Figs. 4 -5). This confirms a significant colloidal-stability effect of cadmium ions on the agglomeration of hydrocolloids of sequestration agents of the anion-active character, especially OC.

This behaviour can be explained by means of the classical stability theory of of colloid systems and their electro-kinetic behaviour. The colloid system of hydrocolloid sequestrants with cadmium and other ions is thus destabilised only by the increasing concentration of cadmium in model water, or more precisely by its hydrated forms. Unlike the CSD separation, virtually no shear forces are applied in rheosedimentation (CSS) separation. This means that the thickness of the adjacent part of the electric double layer of pulps is relatively

wide and it probably also includes the protruding oligomer cation-active groups. These then serve to apply during colloid interactions and only the resulting hydrated surface interface of the fibre characterised with its Zeta potential is applied here. Due to this effect, the Zeta potential of active pulp is positive but drawing closer zero and a negative Zeta potential of oxycellulose colloid-fibres, theirs surface behave as anion-active, is depressed by interaction with  $\text{Cd}^{2+}$  ions. Moreover, taking into account a low thickness of the diffuse part of the electric double layer given by the high ionic force of model water, the applied electrostatic interactions are only very little. In the case of fully dissolved CMC, these small electrostatic inter-particle forces are practically not applied.

At high-shear hydrodynamic condition of CSD separation is another situation, because the high shear hydrodynamic forces decrease the thickness of the adjacent part of the electric double layer of the hydrated pulp interfaces, expose more active hydrate pulp groups and the oligomer cation-active groups on the pulp are more active. As a result of action the intermolecular and shear hydrodynamic forces, in comparison with oxycellulose colloid-fibres, the hydrated macromolecules of CMC are practically quantitatively captured in drained pulp bed. Obviously, the further intermolecular forces are important beside the classical colloidal forces (see relatively high separation efficiency of non-active pulp in Fig. 4). In addition to classical electrostatic forces of electrokinetic character, the hydration forces are predominantly important too [18]. In simple terms, that controversy differentia between drainage (CSD) and rheosedimentation (CSS) separation processes is possible in the raw to characterize as the interactions of more naked (CSD) and more clothed (CSS) hydrated interfaces of mutually interacted subjects, respectively.

#### 4 CONCLUSION

A separation of cadmium ions  $\text{Cd}^{2+}$  was performed from the model mixture, which contained both cadmium ions and chemicals for modification of the pH environment, under the presence of activated and inactivated pulp and sequestration agents, i.e. oxycellulose and carboxyl methylcellulose. It was apparent from all evaluated experiments that the separation of  $\text{Cd}^{2+}$  from polluted water can be made by means of sequestrants and pulp. The efficient component of the fibre suspension (pulp + sequestrant) was the sequestration agent.

Two steps took place in the reaction mixture. First,  $\text{Cd}^{2+}$  reacted with the sequestration agent and secondly, this one interacts with hydrated interfaces of porous fiber walls of the rheosedimenting or drained pulp fibers functioning as scavengers of the sequestrants. If the sample

contained only pulp, the separation effect was small.

However, most important are static (i.e. rheosedimentation) or dynamic (i.e. drainage fiber suspension) conditions of scavenger application evoking counter character of the separation behavior. A higher separation effect was achieved by rheosedimentation method in the cases where oxycellulose with cation-activated pulp were applied but more effective results were received by application of CMC and cation-activated pulp fiber for the drainage separation method.

Rheosedimentation is in fact a static process, when compared with drainage dynamic process, during which shearing forces revealing the oligomer cation-active groups in micro-interfaces of the activated pulps are not applied. However, they also release the captured hydrocolloid particles from microspheres of these fibrous scavengers. That is why a significant colloid behaviour, which is only slightly apparent in case of CSD method, is clearly apparent in the case of the rheosedimentation method (CSS).

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