

Separation Cd²⁺ by Oxycelluloses and Active Pulp

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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 Cd²⁺ from polluted water by use of oxycellulose (OC) hydrocolloid fibrous form was compared with dissolved carboxyl methylcellulose (CMC).

Introduction

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) (Milichovský et al., 2014).

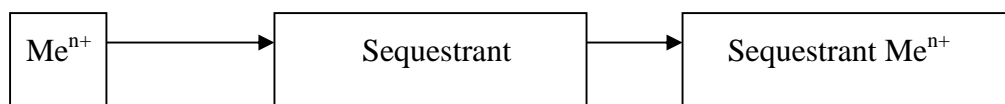
As known, a hopefully separation filtration process is improved by use of sorption filtration methods for cleaning of polluted water contains of cationactive substances predominantly heavy metals. The treatment of heavy metals is of special concern due to their recalcitrance and persistence in the environment. In recent years, various methods for heavy metal removal from waste water have been extensively studied (Fenglian & Wang 2011). Adsorption characteristic of polysaccharides, cellulose and its derivatives including oxycellulose in relation to cations, particularly (Burke et al., 2000) heavy metals, have drawn more attention recently. We have studied the following colloid-sorption methods:

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

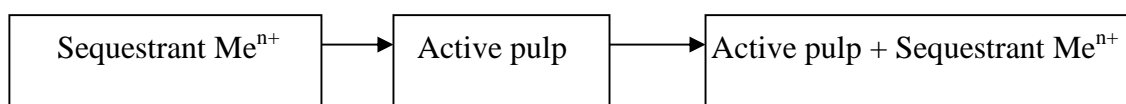
Theoretical

Separation with rheosedimentation (CSS)

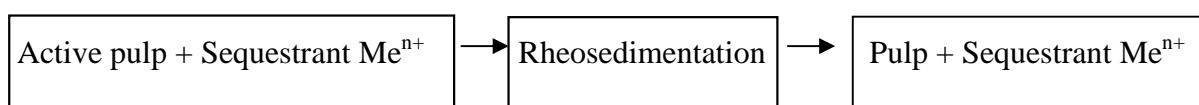
1. step: chemical reaction with colloidal part of oxycellulose - sorption



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



3. step: separation contaminated pulp by sedimentation



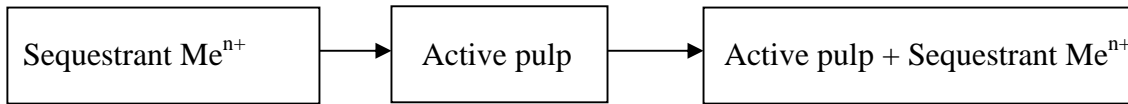
4. step: deposition bioactive fibre sediment with Meⁿ⁺

Separation by drainage of a fibre suspension (CSD)

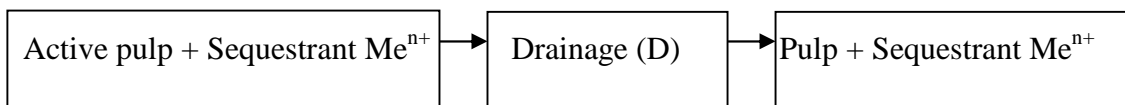
1. step: chemical reaction with colloidal part - sorption



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 (Fišerová, 2010).

A movement of rheosedimenting fibre network continuum is very well described (Milichovský et al., 1982) by general equation of continuity as similar as Smellie and La Mer (Smellie, & La Mer, 1956) 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 (Milichovský, & Češek, 2004).

Formerly was shown (Milichovský, & Češek, 2004) 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.

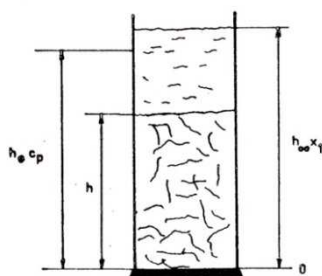


Fig. 1: Schematic presentation the principle of rheosedimentation.

Experimental

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 (Filipi & Milichovsky, 2015).

$$SE = \frac{100 * c_a}{c_p} = \frac{100 * (c_p - c_{rov.})}{c_p}, \quad (1)$$

where

$c_{rov.}$	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.

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 (Malát, 1973). 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 $61.32 \mu g$ Cd.

The amount of ions in the supernatant was then determined by use of spectrophotometry and standard addition method of quantitative analysis approach (Filipi & Milichovský 2014).

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 wood pulp from Biocel Paskov, Czech Republic – see Table 1

Table 1: The parameters of oxycellulose (Filipi & Milichovský 2008).

Sample	DP	X_{GA} , g/g	P_{DP}	X_{COOH} , %	X_{DS} , %	$X_{GA-PAGA}$, (mmol GA-PAGA/g oxycel.)
Okcel H-L 284/051/3	35.8	0.4557	0.8137	17.8	70.8426	0.6513

Carboxymethyl cellulose (CMC) was received from Fisher Scientific

Non-active pulp

Sulphite pulp (air-dry) was defibrillated 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 (Milichovský & Vodeničarová, 1999).

Carboxyl celluloses

Suspensions of oxycellulose were prepared by weighing 1.6 kg 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 CdCl₂ cooled to 15 °C in concentrations 0.5, 0.4, 0.3, 0.2 and 0.1g CdCl₂/l. The mixture was mixed 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 mixed again.

1.6g oxycellulose was added into five 250 ml beakers, then 100ml of the solution of CdCl₂ in concentrations 0.4, 0.3, 0.2, 0.1 and 0.05g CdCl₂/l were added. The mixture was mixed 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 mixed 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 CdCl₂/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 CdCl₂ in concentrations 0.4, 0.3, 0.2, 0.1 and 0.05 g CdCl₂/l were added. The mixture was mixed 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 mixed again and left to rest for 15 minutes.

1.6 g oxycellulose was added into five 250 ml beakers, 100ml of the solution of CdCl₂ in concentrations 0.4, 0.3, 0.2, 0.1 and 0.05 g CdCl₂/l were added again. The mixture was mixed 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 CdCl₂/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 Cd²⁺ in clear filtrate was determined again by use of the spectrophotometric dithizone method.

Result 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 on the Figs. 2 and 3.

Separation via rheosedimentation process (CSS)

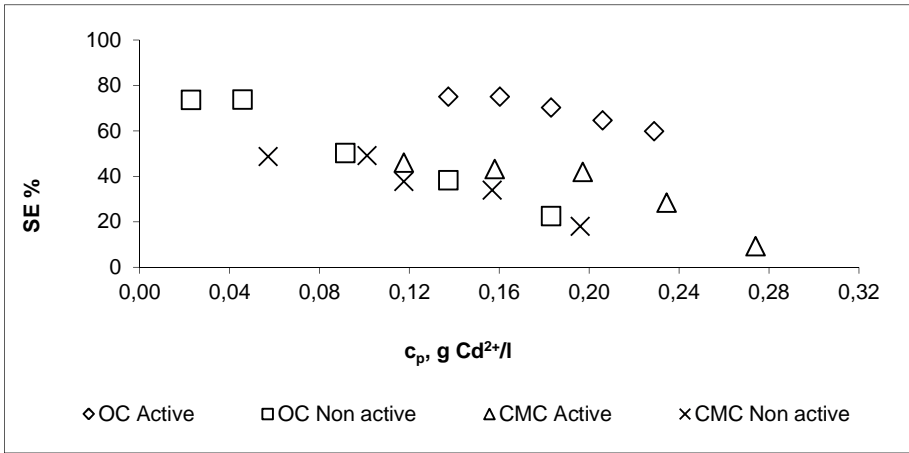


Fig. 2: Dependence of SE versus c_p , g Cd²⁺/l where SE and c_p are the separation efficiency and the total concentration of the Cd²⁺ in model water, respectively.

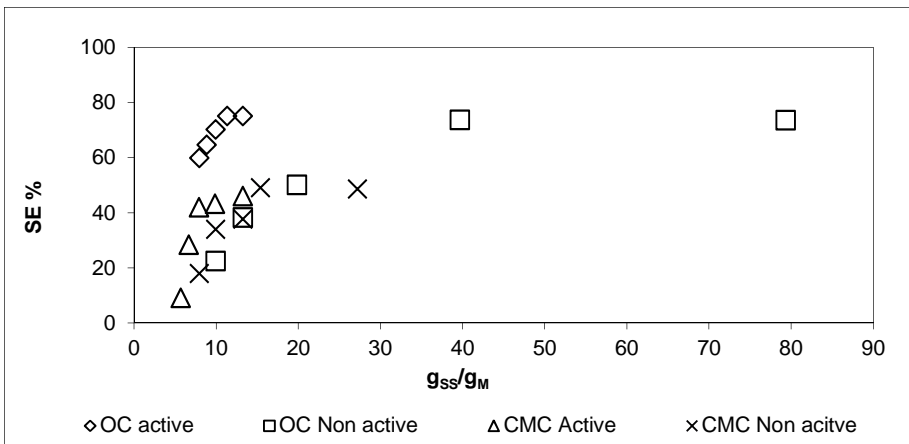


Fig. 3: Dependence of SE versus, g_{ss}/g_M where SE, g_{ss} and g_M are the separation efficiency, the amount of sequestrating aid and the amount of Cd²⁺, respectively.

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 on the Figs. 4 and 5.

Separation via drainage of a fibre suspension (CSD)

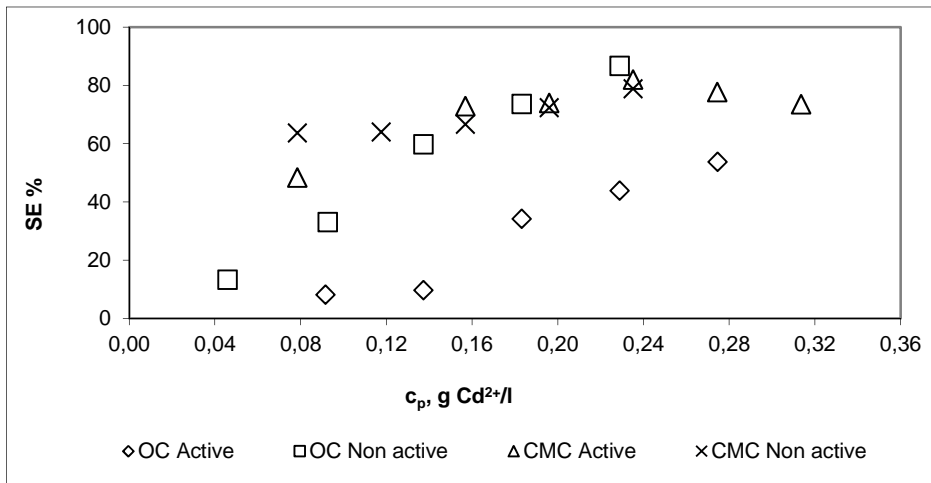


Fig. 4: Dependence of SE versus c_p , g Cd²⁺/l where SE and c_p are the separation efficiency and the total concentration of the Cd²⁺ in model water, respectively.

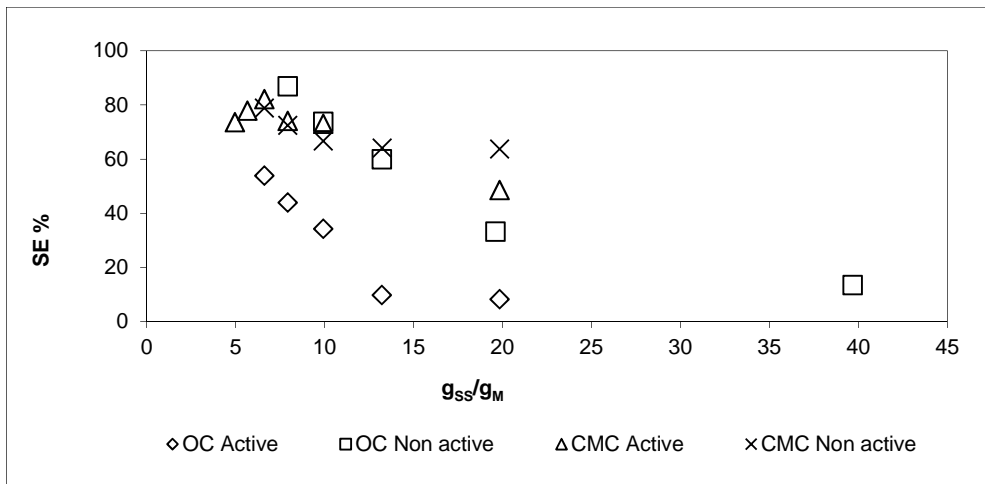


Fig. 5: Dependence of SE versus, g_{SS}/g_M where SE, g_{SS} and g_M are the separation efficiency, the amount of sequestering aid and the amount of Cd²⁺, respectively.

The separation efficiency (SE) expresses the amount of cadmium, which was captured on the pulp fibres by help of sequestering aids CMC and oxycellulose. It is given by the proportion of the captured (absorbed) amount of Cd²⁺ in the pulp fibre to the total amount of Cd²⁺ 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 Cd²⁺ 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.

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 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 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 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).

Conclusions

A separation of cadmium ions 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 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, 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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