Hybrid Sorption and Microfiltration Characteristics of Zeolite

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Abstract. Industrial wastewater treatment and reuse is one of the principal tasks of present. For this purpose several physical, chemical and combined methods have been used. This paper deals with the study of sorption behaviour of natural zeolite with respect to Zn(II) and Cu(II) followed by cross-flow membrane microfiltration. The conducted experiments were aimed at the verification of effectiveness of ion exchange of selected metals from wastewater using zeolite – with the main component of clinoptilolite. The obtained experimental data were fitted using Langmuir and Freundlich isotherms. The sorption capacity was studied for zinc and copper uptake, followed by a study of microfiltration of zeolite suspension using a cross-flow microfiltration device with tubular ceramic membrane. According to experimental results the basic parameters of microfiltration process were evaluated. In comparison with other processes, the hybrid membrane microfiltration offers more effective way of water treatment.

Introduction

Many industrial wastewater streams contain heavy metals which are of great environmental concern and must be removed prior to water discharge or water recycling. The development and application of effective treatment processes is necessary.

The association of conventional water treatment unit operations (such as coagulation, softening, sorption, ion exchange, and flotation) with membrane processes can be a way, how to increase performance and product quality. They are many examples of hybrid (or combined) processes utilization at water treatment observed [1-3]. Some of the combined processes have been used for a number of years. MF and UF have been traditionally used as a RO pretreatment, an adsorption or a coagulation accordingly with membrane processes have been parts of the complex water treatment [4, 5]. On the other hand, there are some new techniques utilizing membrane modules and conventional separation methods, such as membrane bioreactors or RO/NF and ion-exchange hybrid processes [2, 3, 5, 6]. The combined membrane processes can be carried out in both cross-flow and dead-end configurations and they can use different types of membranes, inorganic (ceramic) membranes, polymeric and ion-exchange membranes.

This article deals with the study of sorption behavior of natural zeolite with respect to Zn(II) and Cu(II) ions [7] removal followed by cross-flow membrane microfiltration.

Materials and Methods

In the experiments natural zeolite - clinoptilolite (Zeocem a.s., Bystre, Slovakia) was used. The particle size distribution was determined by Mastersizer (Malvern Instruments, UK).

The isotherms of zeolite for Zn(II) and Cu(II) ions at 22°C were determined by batch experiments. A flask was filled with 500×10^{-6} m^3 of salt solution in water (concentration c_0), weighed amount of zeolite (m_z) was suspended in the solution and stirred. After 30 minutes the solution was filtered through microfilter and then the concentration of metal ions (c_{eq}) was

determined. To ensure that 30 minutes period was long enough to reach the equilibrium state, preliminary experiments were carried out with longer (2 hours) sorption process performed.

The experiments were performed for several initial concentrations of the salt. The samples with concentrations over $5x10^{-3}$ kg.m^{-3} of metal ions were diluted before analyzing.

The Cu(II) and Zn(II) ions concentrations in samples were analyzed by AAS spectroscopy.

From batch experiments, the data set was obtained of concentration – sorptive capacity dependency. The metal ions concentration retained in the adsorbent phase, a_{eq}, was calculated according to Eq. 1

$$a_{eq} = \frac{(c_o - c_{eq}).V}{m_z} .$$ (1)

From these data, the parameters of Langmuir isotherm [8]

$$a_{eq} = \frac{a_\infty k_L c_{eq}}{1 + k_L c_{eq}}$$ (2)

and Freundlich isotherm [9]

$$a_{eq} = K_f c_{eq}^{1/n}$$ (3)

were determined by nonlinear least squares analysis. In order to quantitatively compare the applicability of isotherm equations in fitting to data, non-linear correlation coefficient (R^2) was calculated.

Experimental

Microfiltration experiments were performed on cross-flow microfiltration system consisting of membrane module, feed container, pump with regulation valve, electronic balance, flowmeter, temperature and pressure sensors and computer which recorded the measured data. The used tubular ceramic membrane (Membralox, France) was a membrane with pore diameter $50x10^{-9}$ m, effective length 0.225 m and active surface $4.948x10^{-3}$ m^2.

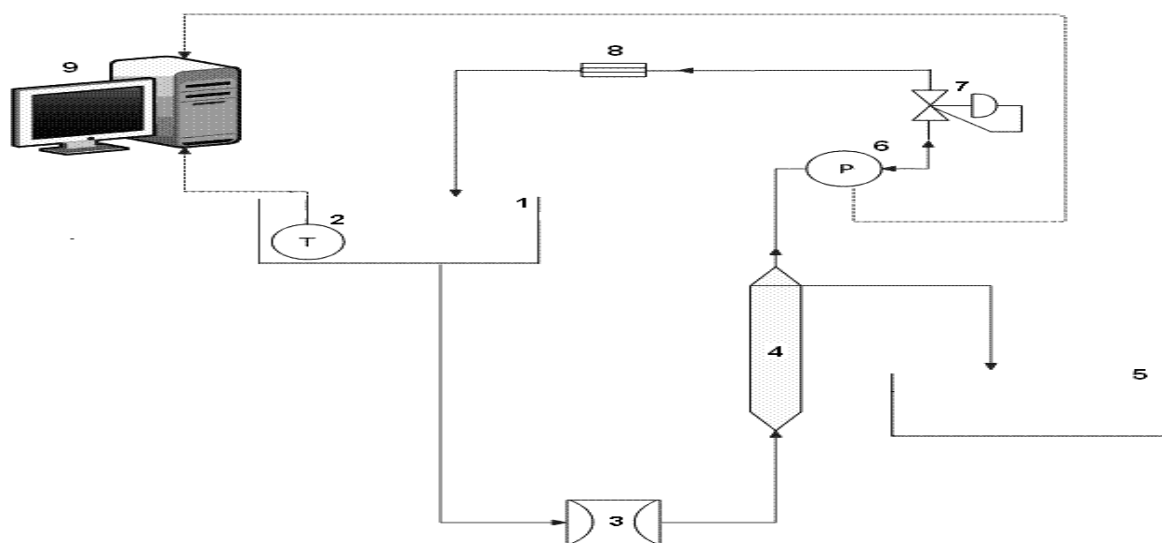Schematic drawing of the experimental system is given in Fig.1.

Fig. 1. Cross-flow microfiltration unit.
Key: 1 – container; 2 – thermometer; 3 – pump; 4 –membrane module; 5 – membrane module; 6 – pressure sensor; 7 – flow control valve; 8 – flowmeter; 9 – computer.

The first set of experiments measured the permeate flux depending on time at different zeolite concentrations. To ensure experiments running below critical value of permeate flux, preliminary

experiments were done when the system was tested at pressure increasing and decreasing. It was found that the critical pressure was 100,000 Pa at the retentate flow rate of 2.20 $m.s^{-1}$.

Results and Discussion

Zeolite sorption capacity. The experimental data for copper and zinc sorption equilibrium on zeolite are shown in Fig. 2 and Fig. 3, respectively. Both the Langmuir (Eq.2) and Freundlich (Eq.3) isotherms approximate the experimental data similarly in the concentration range studied, the correlation coefficients are close (Table 1). The sorption capacity of zeolite is higher for Cu (II) than for Zn (II) by about 58%.
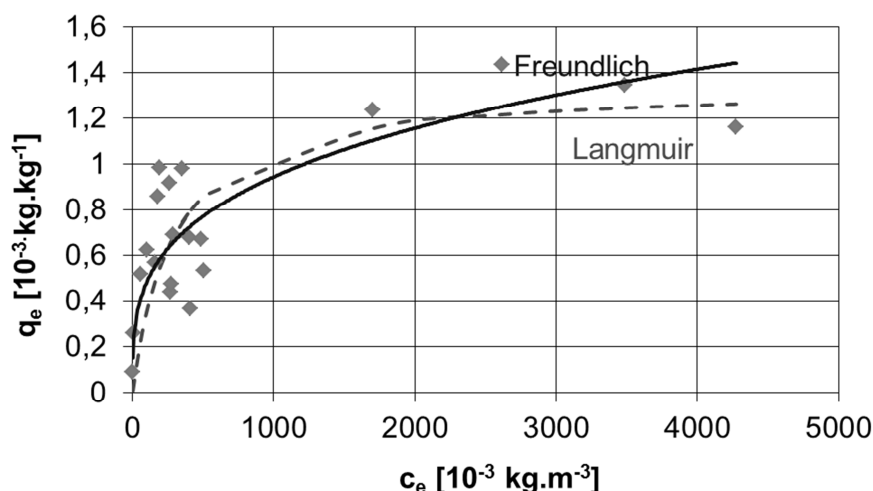

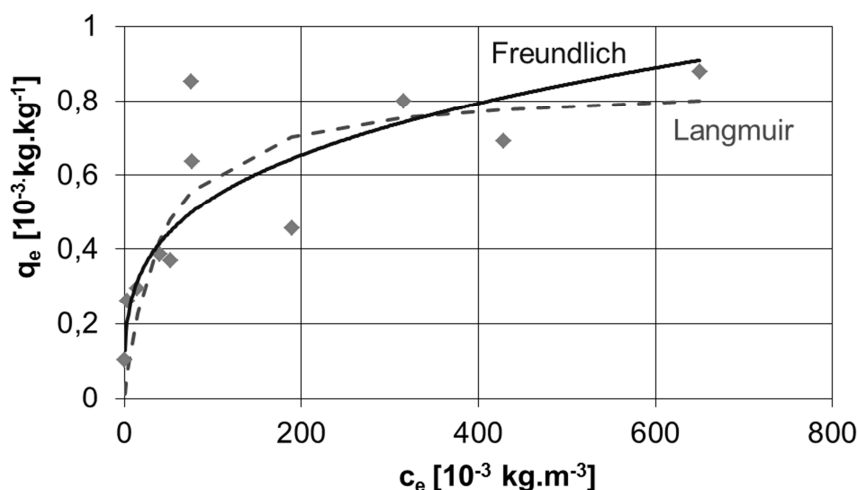Fig. 2. Zeolite sorption capacity for Cu(II) ions removal.

Fig. 3. Zeolite sorption capacity for Zn(II) ions removal.

Zeolite sorption kinetics. The experimental data for copper and zinc ions sorption kinetics on zeolite are shown in Fig. 4 and Fig. 5, respectively. According to the presented data in the figures the sorption process is relatively fast.

Table 1. Isotherms parameters.

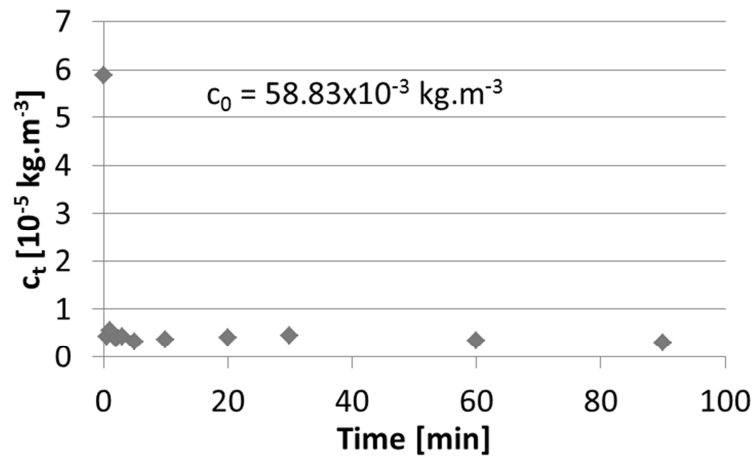| Metal	Langmuir isotherm			Freundlich isotherm		
	a_∞ [10^{-3} kg.kg^{-1}]	k_L [10^3 m^3.kg^{-1}]	R^2	K_f [10^3 m^3.kg^{-1}]	$1/n$ [-]	R^2
Cu(II)	1.3459	0.0035	0.873	0.1262	0.2914	0.832
Zn(II)	0.8512	0.0247	0.851	0.2867	0.0427	0.847

Fig. 4. Experimental data for Cu(II) sorption kinetics on zeolite.
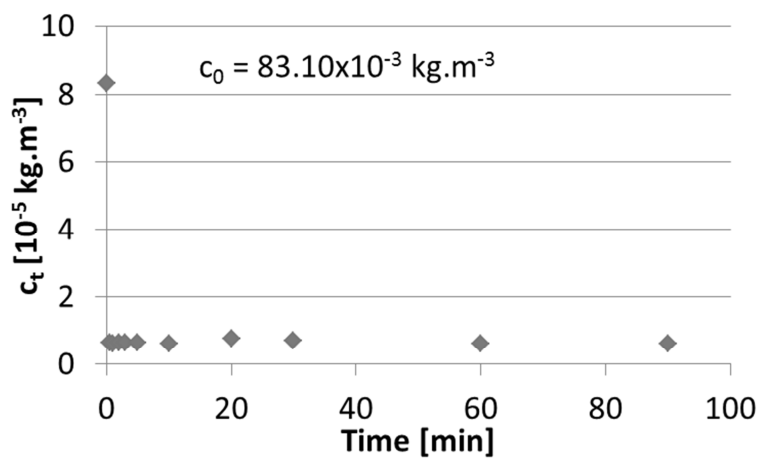

Fig. 5. Experimental data for Zn(II) sorption kinetics on zeolite.

Zeolite microfiltration. Microfiltration measurements were made to determine the stability of the microfiltration system under various conditions – i.e. under various pressures and concentrations of the zeolite suspension – to find the stable flux. Used zeolite particle size was 20×10^{-6} m on average. Microfiltration experiments with suspensions of zeolite of 3, 6, and 9 $kg.m^{-3}$ and a pressure of 100,000 Pa are shown in Fig. 6. The figure shows that the permeate flux through the membrane after the addition of zeolite (after about 20 minutes from the start of the experiment) declined sharply to a value of 8.61×10^{-5} $m^3.m^{-2}.s^{-1}$ in all the three cases. The decline did not stop only slowed down and continued throughout the experiment. This drop in flux indicates that certain fouling of the membrane occurs under these conditions.
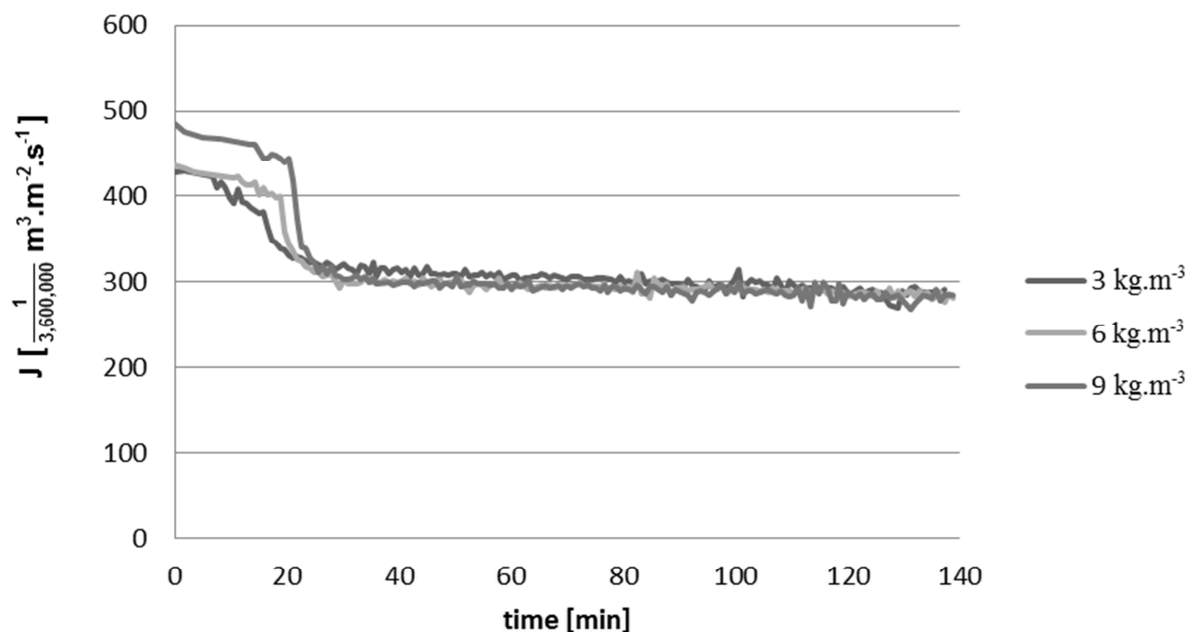
Fig. 6. Flux at a pressure of 100,000 Pa, flow rate of permeate of 2.2 $m.s^{-1}$ and various concentrations of zeolite suspension.
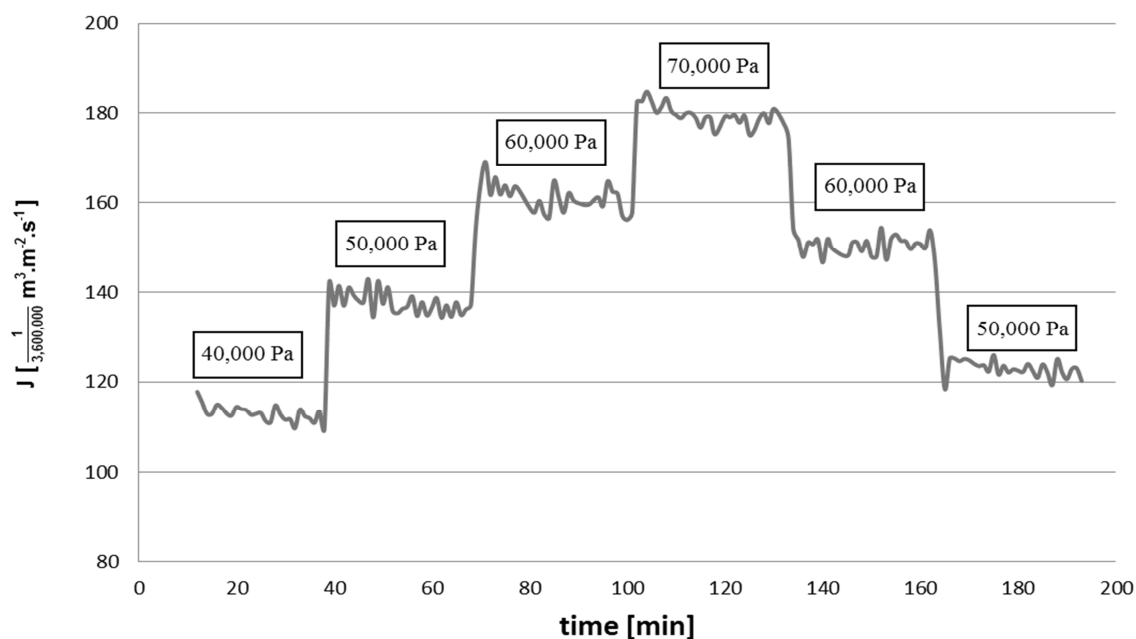

Fig. 7. Microfiltration experiment with gradual increase and decrease of pressure at low rate of permeate of 1.5 $m.s^{-1}$ and concentration of zeolite suspension of 3 $kg.m^{-3}$.

An experiment with a gradual increase and subsequent decrease of pressure (Fig. 7) has been carried out to determine the optimum pressure for microfiltration process. The pressure was increased in the range from 40,000 to 70,000 Pa and then was decreased to 60,000 and 50,000 Pa for a comparison. From the figure it can be concluded that certain decrease in membrane flux occurs after reaching the pressure of 70,000 Pa and the subsequent decrease of the pressure. Therefore it is appropriate to use lower operating pressures than 70,000 Pa.

Fig. 8 shows the microfiltration experiments with pressure of 50,000 Pa and with various concentrations of the zeolite in the range from 1 to 30 $kg.m^{-3}$. At lower concentrations of zeolite the system was very stable. At higher concentrations of zeolite suspension after an initial decrease the flux was stabilized at the value of 4.17×10^{-5} $m^3.m^{-2}.s^{-1}$ and did not drop further.
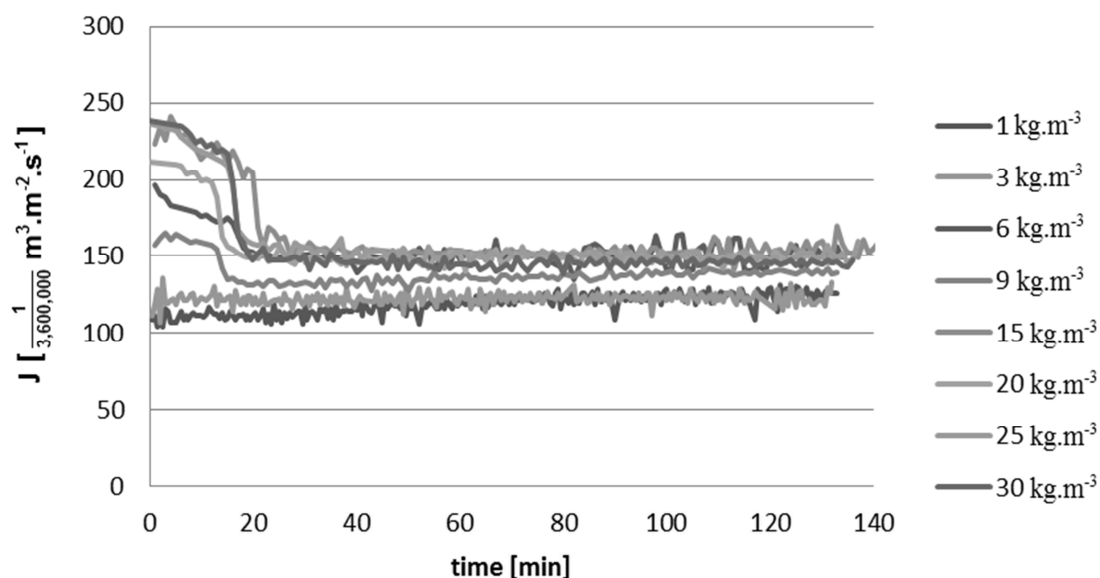
Fig. 8. Flux at a pressure of 50,000 Pa, flow rate of permeate of 2.2 m.s^{-1} and various concentrations of zeolite suspension.

Summary

From experiments conducted it can be concluded that the best results can be obtained at lower operating pressures, i.e. 40,000 to 60,000 Pa. At higher pressures membrane fouling has occurred even at low concentrations of the zeolite suspension. On the contrary, at the applied pressure of 50,000 Pa very good conditions for the microfiltration of the zeolite suspension over a wide range of values (from 1 to about 30 kg.m^{-3}) have been proven.

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