Purification of Waste Waters Containing Low Concentrations of Heavy Metals

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Abstract

Two types of brown coal, oxyhumolite and peat were studied with respect to their ability to remove heavy metals from waste waters. The results showed that the calcium loaded form of these materials can be effectively used for metal extraction by ion exchange with calcium. The proposed method can be recommended for concentrations of metals less than 10 mM.

INTRODUCTION

Purification of waste waters containing less than 500 mg/l of heavy metals is a rather complex problem. The common methods for removing metals are in this case either economically unfavourable (e.g. conventional ion exchange, electrolytic or liquid extraction, electrodialysis) or technically complicated (precipitation, cementation, reverse osmosis). The problem of the conventional ion exchange method is a rapid degradation of ion exchanger due to impurities contained in industrial waste waters. Coal-based materials seem to be a low cost ion exchanger alternative [1-4] .

In our previous paper[5] a possibility of using Czech low-rank brown coal for removing heavy metals from waste solutions was studied. It was shown that especially the calcium-loaded coal can be effectively used for extraction of heavy metals from aqueous solutions. The main advantage of the method is its simplicity and low costs. The objective of this contribution was (1) to test different coal-based materials with respect to their ion exchange capability with calcium, and (2) to determine the selectivity coefficients of the exchange reaction metals calcium for calcium-loaded sorbents.

MATERIALS AND METHODS

Four materials were used for the investigations: two types of brown coal from North-Bohemian brown coal fields Březová and Vřesová, oxyhumolite (a postsedimentary oxidized subbituminous coals containing humic substances capable of interacting with metal ions) and peat from Abertamy (West Bohemia). Properties of coals and oxyhumolite are given in Table 1 (particle size fractions of 0.3-1.0 mm were used for all three materials). The peat was used in as-received conditions regardless of   moisture   content   or   other characterization.

Table 1
Relevant properties of coals

Material	W_t^r %	A^d %	S_t^d %	Q_i^r MJ/kg
Coal 1: Březová	36.3	14.9	3.1	15.3
Coal 2: Vřesová	38.5	21.5	0.9	12.7
Oxyhumolite	9.6	24.6	0.8	17.6

W_t^r - total water content in raw coal, A^d - ash in dry coal

S_t^d - total sulphur content in dry coal, Q_i^r - calorific value of raw coal

The cation exchange capacity of coal materials with respect to Ca^{2+} ions was studied as follows: 200 ml of the solution of $Ca(OH)_2$ of a given concentration was contacted in a shaker with 2 g of media for 5 days after the equilibrium was established. The filtered solid phase was washed by distilled water and dried at 105°C for 3 hours. 1 g of the dry matter was boiled with 50 ml of HCl for 1 hour, the filtrate was made up to the 250 ml volumetric flask and the content of calcium was determined by atomic absorption spectroscopy. Simultaneously, pH was measured in aqueous phase.

Similar procedure was also used in metal ion exchange experiments: the contact of 2 g of calcium loaded materials with 200 ml of the solution containing metals ($CuCl_2$, $Pb(NO_3)_2$ or $ZnCl_2$) was carried out by shaking for 5 days and the contents of metals were determined by atomic absorption spectroscopy again.

A continuous mode was chosen to obtain a penetration curve of the calcium loaded coal. The solution of $CuCl_2$ flowed upwards through the bed of coal in a glass column of 10 mm i.d. The flow rate was 0.68 ml/min. The height of the bed was 0.18 m and it contained 7.7 g of coal (the content of calcium was 5.47%). The collected fractions of 25 and 50 ml were analysed by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

1. Calcium loading of media

The sorption isotherms of the studied materials are shown in Fig. 1 (subscripts s and w denote solid or water phase, resp.). A steep increase of the concentration of Ca^{2+} ions at higher calcium loadings indicates the saturation of the active carboxylic acid and phenolic hydroxyl groups. The cation exchange capacity (CEC) was estimated for each material as a point of intersection of the two linear parts of the sorption isotherms. The results are summarized in Table 2. It is obvious that coal 1, oxyhumolite and peat possess comparable capacities which are only slightly lower than those for commercial ion exchangers. The coal sample from Vřesová (coal 2) has a significantly lower CEC value, which can be explained by a lower number of active functional groups.

Also given in Table 2 are the values of pH of aqueous phase corresponding to a halfway point of saturation. These values indicate a certain acidity of the functional groups and should be taken into account to avoid the undesirable hydrolysis occuring during the extraction of metals at higher values of pH (see below).
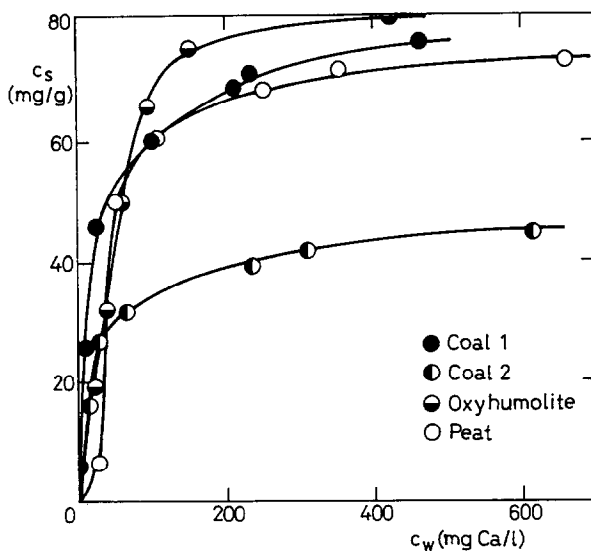
Figure 1. Sorption of Ca^{2+} ions from $Ca(OH)_2$ solutions

Table 2
The estimated values of CEC and values of pH at halfway saturation point

Material	Cation exchange capacity		pH
	mg Ca/g	mval/g	
Coal 1	65	3.3	9.0-9.5
Coal 2	32	1.6	8.0-8.5
Oxyhumolite	73	3.6	7.2-7.7
Peat	63	3.1	8.5-9.0

2. Extraction of metals with calcium loaded media

Due to the significantly lower value of CEC, the calcium loaded coal 2 was not used in our experiments. The results for the other materials are given in Figs. 2-4. The selectivity coefficients for the ion exchange reaction
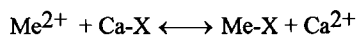
$$Me^{2+} + Ca\text{-}X \longleftrightarrow Me\text{-}X + Ca^{2+}$$

were computed from the relation

$$K_{Me,Ca} = \frac{[Me-X][Ca^{2+}]}{[Me^{2+}][Ca-X]}$$

where X denotes the sorbent, Me is a corresponding metal and the concentrations on the right-hand side are expressed in mol/l resp. mol/kg. Table 3 gives the values of the selectivity coefficients. It is obvious that selectivity increases in the order Zn<Cu<Pb and that there are no substantial differences among the materials. The values of K indicate high efficiency of the ion exchange procedure.

Similar experiments performed with unloaded materials showed much lower exchange efficiency: even at very high initial concentration of metal only 5-10% of it converts to Me-X form.
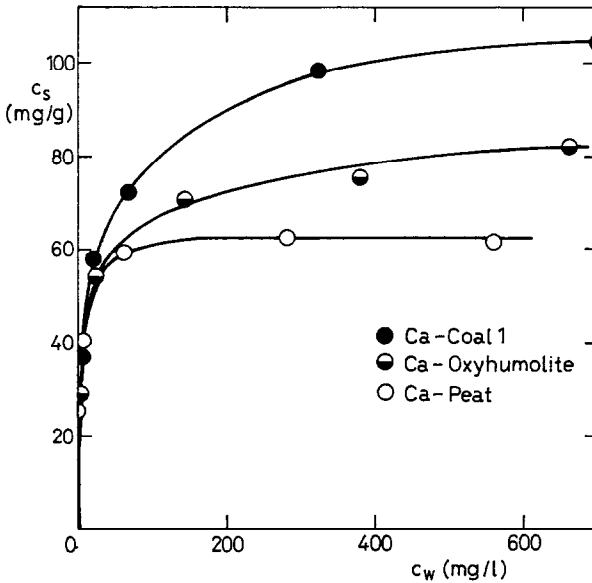
Figure 2. Distribution of Cu^{2+} ions between calcium-loaded materials and solution

Table 3
Values of selectivity coefficients $K_{Me,Ca}$

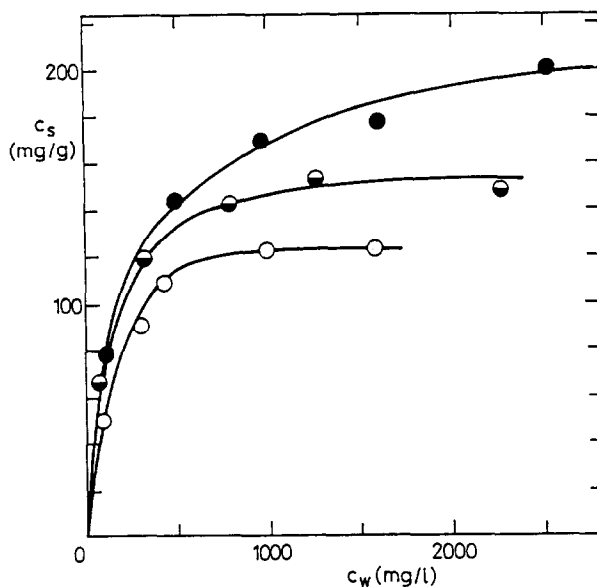| Material		Metal	
	Copper	Zinc	Lead
Ca-coal 1	30-50	4.0-5.6	125-150
Ca-oxyhumolite	45-65	8.8-10	>250
Ca-peat	130-170	5.8-7.0	150-200

Figure 3. Distribution of Zn^{2+} ions between calcium-loaded materials and solution (for symbols see Fig. 2)

3. Penetration curves

The process of penetration was studied with the calcium loaded coal 1. Three experiments were carried out with the different initial concentrations of $CuCl_2$: 20.7, 7.63 and 2.09 mmol $CuCl_2$ /l, respectively. The results for the highest and lowest concentrations are shown in Figs 5 and 6, where the dependence of concentrations of Cu^{2+} on the volume of the effluent are given together with the corresponding values of pH. Fig. 5 also shows the concentration of Ca^{2+} ions. It was found that before reaching the point of penetration, the concentration of Cu^{2+} ions is less than 0.01 ppm. Simultaneously, the equimolar amount of Ca^{2+} ions corresponding to the initial concentration of $CuCl_2$ was measured in the effluent. The penetration is well indicated by a steep decrease of the pH values.

The bed of adsorbent contained 10.5 mmol of calcium. Before reaching the point of penetration, the amounts of 1.6, 2.3 and 5.2 mmol of cupric ions were respectively retained by the bed for the three initial concentrations studied. These values corresponded to 15%, 22% and 50% of the saturation capacity of the bed. It can be seen that the sorption efficiency increases with decreasing metal concentrations. This fact can be explained by a partial hydrolysis of the cupric salt observed at higher concentrations. A fine suspension of the precipitated hydroxide was not quantitatively retained by the bed. On the other hand, no hydrolysis was observed for the lowest metal concentration.
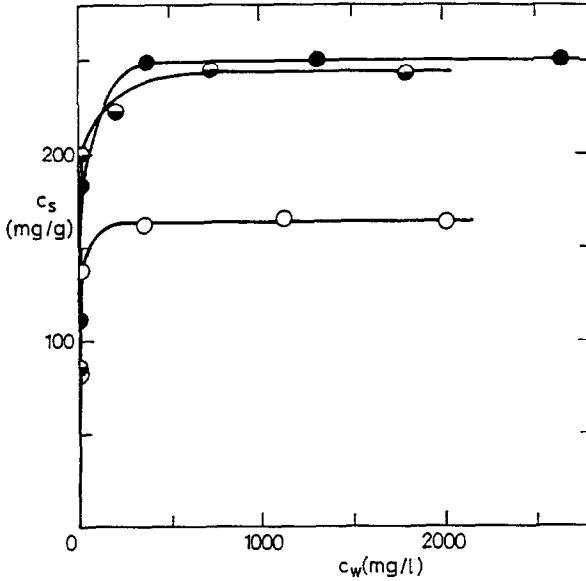
Figure 4. Distribution of Pb^{2+} ions between calcium-loaded materials and solution (for symbols see Fig. 2)

CONCLUSIONS

The cation exchange capacity of some Czech low rank brown coals and related materials is comparable with the values for usual commercial ion exchangers.

The calcium-loaded form of these materials have particularly high selectivity with respect to the extraction of heavy metals by ion exchange of the calcium.

The studied materials (coal, oxyhumolite and peat) have a similar selectivity for a given metal. From the practical point of view, however, the calcium-loaded coal can be recommended: oxyhumolite partially disintegrated in the contact with the solution and the utilization of peat is economically less favourable.

The method is limited by the pH values above which individual metals hydrolyse.

The proposed method can be recommended for lower concentrations of metals (~10mM).

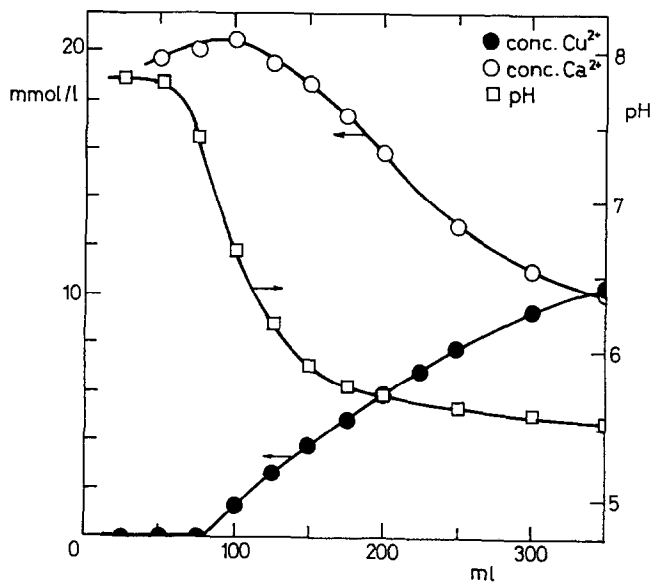For the process control in the continuous mode, the values of pH measured in the effluent can be effectively used.

Figure 5. Penetration curve of Cu^{2+} ions on calcium-loaded coal 1: initial concentration of $CuCl_2$ - $2 \cdot 10^{-2}$ M
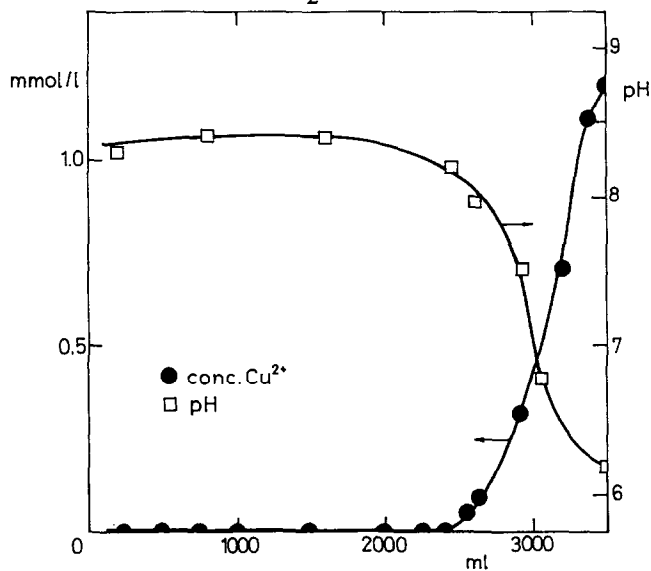

Figure 6. Penetration curve of Cu^{2+} ions on calcium-loaded coal 1: initial concentration of $CuCl_2$ - $2 \cdot 10^{-3}$ M

Acknowledgment

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