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Letter to Editor

Removal of Heavy Metal Ions on Smectite Ion-Exchange Column

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Abstract

The present work is a continuation of studies on the use of ion-exchanging properties of smectite raw material from Męcinka mine to the recovery of chromium from waste water.

In this work the smectite ion-exchange column was used for removal of other heavy metals: Zn (II), Cd (II), Pb (II). The effect of ion exchange Zn (II), Cd (II), Pb (II) from model solutions prepared out of nitrate salts of these metals was examined under dynamic conditions. The efficiency of ion-exchange column with smectite bed was determined by measuring in the column efflux till the moment when the concentration of metals in efflux is equal to concentration in influx. For measurement of concentration of metals the voltamperometric method was used. The ion-exchanging column was determined by stating the following parameters: sorption capacity of exchanger, volume of solution till the moment of column breakthrough (V_{max}) and column dynamics, which means the relative concentration of metal ions c/c_0 in the efflux as a function of efflux volume. Out of the model waste water containing three heavy metals, the best eliminated is Pb (II) and subsequently Zn (II). The efflux volume classified to the 1st and 2nd category of water cleanness amounts to about 1/3 V_{max}. Worse results are observed for ions Cd (II), which have the least ion exchange ability. The obtained results of studies on removal of ions of heavy metals: Zn (II), Cd (II), Pb (II) out of model waste water confirm, similar to the Cr (III) studies, the possibility of application of the raw smectite adsorbent as the column packing within the process of removal of heavy metals.

Keywords: smectite, ion exchange column, removal of heavy metals, recovery Cr(III)

Introduction

The raw smectite material in basalt layers in Męcinka mine belongs to loamy mineral from the smectite (montmorillonite) group with a content of smectite between 70-95%. The smectite material has a characteristic tendency to form isomorphic substitution that determines specific cation exchanging properties. Subsequently, big dispersity of smectite material increases its sorption properties.

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The previous investigations on sorption and ion exchanges properties of this mineral state it in the group of the raw mineral sorbents [1, 2]. This smectite, as the column packing removes out of the model waste water Cr (III), in the amounts giving the effluent of column, classifying these effluents as the 1st category of water cleanness [3, 4]. The studied surface properties of this raw material (CEC = 60 mval/100g; S = 50 m^2/g) and elaborated parameters of the smectite ion exchanging column, used for the cleaning of Cr (III) out of water, suggest extending these investigations to other heavy metals.

The aim of this work is to investigate the usefulness of

smectite mineral from the Męcinka mine as a raw mineral sorbent for removal of chosen heavy metal ions out of water solutions. This aim was realised by studies of dynamic ion exchange process of the model solution of ions Zn (II), Cd (II), Pb (II) on the column with smectite filling. The effects of removal from the solution of investigated ions were shown as effluent concentration histories, which means that the concentration of ions of investigated metals in the column efflux as a function of the column efflux volumes (so called – dynamics of column). The values characteristic for ion exchange column, such as sorption capacity of exchanger, solution volume flowing through the column until the moment of column breakthrough and also amounts of metals recovered from solution, were also calculated.

Table 1. The mean chemical composition of smectite from Męcinka mine.

Composition	Content % by weight
loss of calcinaty	16.78
Al_2O_3	16.12
SiO_2	39.35
Fe_2O_3	15.90
MgO	2.48
CaO	2.70
BaO	0.08
MnO	0.08
TiO_2	3.26
K_2O	0.71
Na_2O	0.36
P_2O_5	1.08
Total:	99.03

Table 2. Composition of the ion exchange complex of smectite from Męcinka mine. (CEC).

Fraction [mm]	Miliequivalents per 100 g sample [mval/100 g]				
	Ca^{2+}	Mg^{2+}	Na^+	K^+	CEC
0 ± 0.2	42.40	16.20	0.20	0.78	59.58
0.4 ± 0.6	40.15	15.40	0.19	0.76	56.50

Table 3. Difraction pattern of smectite material from Męcinka mine.

I	d_{hk} [nm]	Mineral
93	0.448	M Il K
57	0.405	Kr
46	0.376	Sk
58	0.368	Fe
76	0.321	Sk
86	0.270	Fe
91	0.252	Fe
43	0.221	Fe

I – intensity, d_{hkl} – interplanar spacing, M – montmorillonite, Il – illite, Sk – feldspar, K – kaolinite, Kr – kristobalite, Fe – hematite.

Experimental

Within this project the Zn (II), Cd (II), Pb (II) process of ion exchange in the model waste water solution, made up out of the salts nitrate of these metals, having concentration of 0.01 M after mixing, was studied. In these investigations, the procedure analogous to the procedure of removal of Cr (III) was used, applying the ion exchange in dynamic conditions on the ion exchange column with raw smectite mineral filling from Męcinka mine [1, 5].

The physicochemical properties of this material are presented in Tables 1-3.

The dynamic sorption of ions was performed at a temperature of 298 K on the columns with smectite filling of parameters analogous to the parameters of columns used for removal of ions of Cr (III) [1]. Such procedures enable drawing a comparison of effects of simultaneous removal out of solution of three metals (Zn, Cd, Pb) to the effect of removal of ions of Cr (III), which was investigated earlier, columns I and III, and also II and IV, respectively. For comparison, there were also presented the results of removal of ions Cr (III) on the column with cation exchanging resin Wofatite KS 10 filling (column V).

The parameters of column are presented in Table 4.

Usefulness of the column was stated by measuring the concentration of ions of investigated metals in the column efflux. The characteristic values of the ion exchange process in the dynamic conditions were determined:

z – sorption capacity of exchanger [mval/g];
$V_{1/2}$ – volume of efflux until the moment when concentration of efflux equals 0.5 c_0 [cm^3];
V_{max} – entire volume of efflux until the moment when concentration of efflux equals concentration in influx (column breakthrough) [cm^3].

Sorption capacity of ion exchanger is calculated on the formula:

$$z = \frac{V_{1/2} \cdot c_0}{m} \tag{1}$$

c_0 – concentration of ions of metal in influx [mval/cm^3]
m – mass of bed of column [g].

These results are presented in Tables 5 and 6.

The ion column dynamics (Table 7) was shown on example of column I, III (the similar column dynamics

Table 4. Parameters of the column.

Number of column	Kind of bed	Metal sorption	Mass of bed [g]	Volume of bed [cm^3]	High of column [cm]	Diameter of column [cm]
I	Smectite	Zn, Cd, Pb	35	39	22	1.5
II	Smectite	Zn, Cd, Pb	35	46	6.5	3.0
III	Smectite	Cr	35	42	24	1.5
IV	Smectite	Cr	35	46	6.5	3.0
V	Wofatite	Cr	35	46	6.5	3.0

Table 5. Sorption capacity of exchanger [mval/g sorbent].

Number of column	Exchanging ion of metal				Total	Calculated from CEC [mval/g]
	Zn(II)	Cd(II)	Pb(II)	Cr(III)		
I	0.277	0.270	0.568	–	1.115	0.565 ÷ 0.60
II	0.276	0.337	0.457	–	1.070	0.565 ÷0.60
III	–	–	–	1.073	1.073	0.565 ÷ 0.60
IV	–	–	–	0.857	0.857	0.565 ÷ 0.60
V	–	–	–	1.890	1.890	–

Table 6. The volume of efflux related to the parameters of column.

Number of column	Tested ion of metal	$V_{1/2}$ [cm^3]	$V_{w_{1/2}}$ [cm^3/cm^3]	V_{max} [cm^3]	$V_{w_{max}}$ [cm^3/cm^3]
I	Zn(II) Cd(II) Pb(II)	484 421 995	12.4 10.8 26.0	700 500 1250	18.0 12.8 32.0
II	Zn Cd Pb	480 590 800	10.5 12.8 17.4	700 700 1000	15.2 15.2 21.8
III	Cr	1252	29.8	1700	40.5
IV	Cr	1000	21.8	1400	31.1
V	Cr	2200	47.8	3000	65.2

$V_{1/2}$, V_{max} – Volume of efflux till the moment when level of metals of efflux equals and subsequently: $0.5c_0$; $c_{max} = c_0$; $V_{w_{1/2}}$, $V_{w_{max}}$ – as above, related to the unit bed volume.

was observed for columns II and IV), in the form of function $c/c_0 = f(V_w)$ of the column efflux volume V_w, related to the unit bed volume V_z.

$$V_w = V/V_z \qquad (2)$$

V – solution volume in the column efflux [cm^3]; V_z – bed volume [cm^3].

These results are presented in Table 7 and in the Fig. 1.

The mass of metal recovered on the column was calculated from value V_{max}, specific for each metal. These results are presented in Table 8.

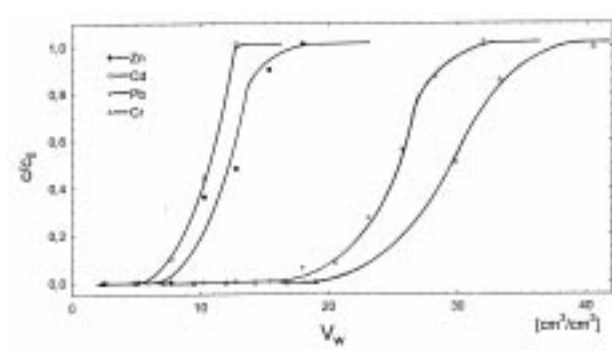

Fig. 1. Effluent concentration histories. Column I (Zn, Cd, Pb); Column III (Cr).

Table 7. Dynamic of column I i III (Cr).

Number of efflux	Volume of efflux V_w [cm^3/cm^3]	Relative concentration c/c_0			
		Zn(II)	Cd(II)	Pb(II)	Cr(III)
1	2.6	$2.7x10^{-4}$(I)	$0.7x10^{-4}$(III)	$0.13x10^{-4}$(I)	$2.3x10^{-5}$(I)
2	5.1	$8.9x10^{-4}$	$7.6x10^{-4}_{max}$	$0.26x10^{-4}$(II)	$3.4x10^{-5}$(I)
3	7.7	$13.0x10^{-4}_{max}$	0.1	$0.22x10^{-4}$(III)	$4.6\ x10^{-5}$(I)
4	10.3	0.36	0.44	$1.4x10^{-4}$	–
5	12.8	0.48	1.01	0.005_{max}	$7.3\ x10^{-5}$(I)
6	15.4	0.90		0.06	$9.4\ x10^{-5}$(I)
7	18.0	1.01		0.27	$1.7x10^{-3}_{max}$
8	23.0			0.56	–
9	25.6			0.87	–
10	28.2			–	
11	29.8			1.02	0.51
12	32.0				–
13	33.3				0.85
14	40.5				1.00

I, II, III, max – subsequently: the 1st, 2nd, 3rd category of water cleanness; maximum permissible concentration in wastewater.

For measurement of concentration of metals in the effluents the voltamperometric method was used.

Discussion of Results, Conclusions

The effluent concentration histories (Fig.1, Table 7) show that all the ions of metal are removed out of the modelling solution in different degrees. The tests carried out showed that lead is removed most efficiently from a model solution containing three heavy metals (Zn, Cd, Pb), resulting in effluents which can be classified as 1st class cleaness water [3, 4]. Worse results were obtained for cadmium and zinc.

The ion column dynamics are similar: the level of tested metal ions in the column effluents gradually increase until the point of inflection on the curves (Fig. 1) and, sequently, the value c_0 (the column breakthrough) are obtained quickly. Thus, it can be stated that various values V_{max} and $V_{1/2}$ are determinated by ion exchange capacity, dependant on each metal. The biggest values of efflux volumes V_{max} and $V_{1/2}$ are for lead, lower for zinc and subsequently the lowest values are for cadmium.

The obtained results as well as those presented in other works on the sorption in static condition [6] indicate that ion exchange capacity for Pb (II) is higher than for Zn (II) and Cd (II). Total sorption capacity of exchanger (smectite column) for sorption performed simultaneously out of solution of three metals (Zn, Cd, Pb) is of the value similar to the sorption capacity of exchanger for sorption performed out of solution of chromium. These results correspond to the calculated values of mass of metals removed on ion exchange smectite column (Table 8). The total mass of metals calculated as miliequivalents of metal ions, related to the mass of exchanger, is comparable to the mass of chromium removal.

Table 8. Recovery of metal on the column [mval/35g sorbent].

Number of column	Tested ion of metals	Amount of recovered metal	Amount of recovered metal calculated from CEC
I	Zn(II) Cd(II) Pb(II)	14.0 10.0 25.0	
Total		49.0	21
II	Zn Cd Pb	14.0 14.0 20.0	
Total		48.0	21
III	Cr(III)	51.0	21
IV	Cr	42.0	21
V	Cr	90.0	–

The efficiency of Cr (III) removal on the column of the Wofatite KS 10 is about twice higher than on the smectite column.

The mass calculated from the value of ion exchange complex (CEC = 56-60 mval/100g) of sorption for metal ions is about twice lower than mass obtained in the experimental way (Table 8). The above discrepancy means that parallel to the ion exchange process, the physical adsorption on a well-developed surface of smectite weathering and participation of Fe_2O_3, dispersed in the

smectite structure, are of important weight. This fact was confirmed in [1, 7].

It was found that by using dynamic ion exchange treatment with column with filling of smectite minerals, a high degree of efficiency of harmful heavy metal removals can be achieved, especially for Pb (II) and Cr (III) ions from waste water model solutions. These effects may be reached when adopting this method for raw solutions.

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