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ADSORPTION OF HEAVY METAL IONS AT THE Al$_2$O$_3$-SiO$_2$/NaClO$_4$ ELECTROLYTE INTERFACE

The study on adsorption of heavy metals (Cd(II), Ni(II) and Pb(II)) at the Al$_2$O$_3$-SiO$_2$/electrolyte solution interface is presented in this paper. The influence of ionic strength, pH, background electrolyte (NaClO$_4$) concentration and composition of metal oxide on adsorption of Cd(II), Ni(II) and Pb(II) from solution of initial concentration ranged from 1×10^{-6} to 1×10^{-3} mol/dm^3 in the mentioned system was investigated. The adsorptions edge parameters (pH$_{50\%}$ and ΔpH$_{10-90\%}$) for different concentrations of electrolyte were presented. The adsorption measurements were complemented by the potentiometric titration of Al$_2$O$_3$-SiO$_2$ suspensions and electrophoretic measurements. Charge reversal point (CR2) can be observed for solution concentration of 10^{-3} mol/dm^3 as a result of Cd(II), Ni(II) and Pb(II) ions adsorption.

key words: cation specific adsorption, heavy metals, Cd(II), Ni(II) and Pb(II), electrical double layer, Al$_2$O$_3$-SiO$_2$, zeta potential

INTRODUCTION

Most studies of cations adsorption at metal oxide/electrolyte interface concern the systems where the solid phase is a pure compound. Such systems are convenient for theoretical study, however they differ significantly from real dispersed systems where as a rule, both phases are multicomponent. The adsorption affinity of ions to the surface depends on the basic–acidic properties of the surface hydroxyl groups of metal oxide. Metal atoms surrounding them in the crystal lattice determine the properties of hydroxyl groups. It is known that even simple metal hydroxyl groups change their

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properties with the number of metal atoms in the vicinity of a given surface hydroxyl group. Mixed –two component oxides create greater opportunity of changing properties due to the diversity of metal atoms in the hydroxyl group's surroundings. The adsorption of heavy metal ions at the solid/electrolyte solution interface has been studied to describe processes taking place in environmental systems and for technological purpose to prepare catalysts (Hayes and Katz 1961). Significant amount of anthropogenic heavy metal ions is found in wastewaters from many industries e.g. mining, metallurgical, metal plating, tanneries (Karvelas et al., 2003, Bailey et al.,1999) and in urban inputs like sewage business effluents, atmospheric deposition, and traffic related emissions (Alloway 1995). Because heavy metals are not biodegradable and have a tendency to accumulate in living organisms causing various diseases and disorders, they must be removed from wastewaters. One of the efficient methods of water treatment in order to remove heavy metal is their adsorption at adsorbents type of the metal oxide.

The multivalent ions can be adsorbed specifically on the metal oxide surface on one or two surface sites (hydroxyl groups) via hydrogen exchange, but number of sites usually occupied by a single ion is smaller than two (Schindler et al.,1981) Adsorption such ions may lead to inner-sphere complexes or outer-sphere complexes (when adsorbed cation is separated from surface by water molecule). Usually sharp increase of the cation adsorption from 0% to 100%, with on increase of pH of the electrolyte, is observed. This relationship is called "edge of adsorption" and Robertson and Leckie (1997) have proposed very useful parameters to characterize it, as shown in Table 1.

Table 1. Parameters of adsorption edge

Parameters	Parameters of adsorption edge
$pH_{50\%}$	The value of pH when 50% of initial concentration of cation adsorbs, this parameter characterizes the position of adsorption edge on the pH scale.
$pH_{10-90\%}$	The range of pH where the adsorption changes from 10% to 90%, it characterizes the slope of the edge.
$d\text{pMe}/d\text{pH}$	Parameter that shows the activity of cations; must vary when pH of the solution changes to maintain the constant adsorption of the cation.

Metal cations belong to ions having a great adsorption affinity to mixed oxide surface and create inner-sphere complexes. DLM and TLM models may describe specific adsorption of ions. According to DLM model, specific adsorption of ions is possible with the creation of inner-sphere complexes, where ions take place inside surface plane. According to TLM (model SCM, *site binding*), also the adsorption of background electrolyte ions may be considered as a specific and nonspecific adsorption. Ions taking part in ionization and complexation reactions, increase the surface charge density on the oxide and adsorb specifically, but ions in diffusion part of edl are adsorbed nonspecifically (Hayes and Katz 1996). In this paper we report the changes of

adsorption affinity Cd(II), Ni(II) and Pb(II) ions with composition of adsorbent and subsequent changes of the parameters of the electrical interfacial layer (EIL) change at the mixed alumina-silica/electrolyte interface.

EXPERIMENTAL

The Al$_2$O$_3$-SiO$_2$ systems were prepared according to the fumed procedure (Gun'ko et al., 2000). The percentage of Al$_2$O$_3$ in the samples was as follows: 8, 3 and 1% are denoted as AS8, AS3 and AS1, respectively. Nitrogen adsorption – desorption isotherms in temperature 77,35 K was used to determine the specific surface area and pore radius of studied materials. These parameters are summarized in Table 2.

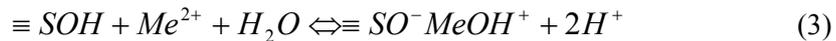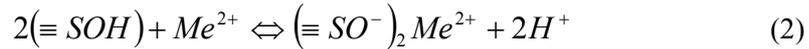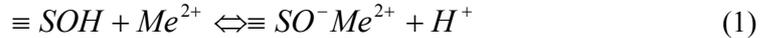Table 2. Specific surface area and pore radius of AS samples (Janusz et al.,2007)

Sample	AS1	AS3	AS8
Al$_2$O$_3$ [wt %]	1.3	3	8
S$_{BET}$ [m^2/g]	207	188	308
R$_p$ [nm]	3.7	3.8	3.8
pH$_{PZC}$	4	4	4
pH$_{IEP}$	<3	<3	<3

The specific adsorption of Cd(II), Ni(II) and Pb(II) ions at Al$_2$O$_3$-SiO$_2$ interface was determined by the means of radioisotope method as a function of Cd(II), Ni(II) and Pb (II) concentration, NaClO$_4$ as a background electrolyte concentration and pH. The initial concentration of the cations ions was ranged from 1×10^{-6} to 1×10^{-3} mol/dm^3, pH was changed from 3 to 10. The NaClO$_4$ solution was used of concentrations 0.1, 0.01, 0.001 mol/dm^3. The adsorption measurements were complemented by the potentiometric titration of Al$_2$O$_3$-SiO$_2$ suspensions and electrophoresis measurements. To remove ionic type contaminations, which might influence the ion adsorption measurements, the Al$_2$O$_3$-SiO$_2$ was washed with double distilled water until conductivity of the supernatant was constant (~2 μS/cm). The adsorption and the surface charge measurements were performed simultaneously in the suspension of the same solid content, to keep the identical conditions of the experiments in a thermostated Teflon vessel at 25°C. To eliminate the presence of CO$_2$ all potentiometric measurements and adsorption experiments were carried out under the nitrogen atmosphere. The pH values were measured using a set of glass REF 451 and calomel pHG201-8 electrodes with Radiometer assembly. Surface charge density was calculated from the difference of the amounts of added acid or base to obtain the same pH value of suspension as for the background electrolyte. The zeta potential of the Al$_2$O$_3$-SiO$_2$ dispersions was determined by electrophoresis with Zetasizer 3000 by Malvern. The measurements followed the ultrasonication of the suspension containing 100 ppm of the solid.

The adsorption of Cd(II), Ni(II) and Pb(II) ions was determined by radiotracer method using [61]Ni, [115]Cd, ^{210}Pb radioisotopes respectively. The radioactivity of an electrolyte solution before and after adsorption was measured using liquid scintillation counter LS5000D by Beckman for [61]Ni, [115]Cd radioisotopes, and using Gamma Counter 5500 for [210]Pb.

RESULTS AND DISCUSSION

The surface charge at a mixed metal oxide/electrolyte interface is formed as a result of acid-base reaction of the surface hydroxyl groups (-SOH) and specific interactions these groups with the background electrolyte ions (Wiese et al.,1976, James, Parks 1982). The acid – based properties of hydroxyl groups at the mixed silica-alumina/electrolyte interface are results of type and number of metal surrounding the oxygen in surface hydroxyl groups. Besides, the surface of the mixed oxide may be composed of patches of pure silica or alumina. Table 2 presents all values pH_{PZC} and pH_{IEP} for the electrical double layer at the Al_2O_3-SiO_2/electrolyte solution interface. As it was mentioned above the properties of hydroxyl groups at the surface of mixed oxides depend on a kind of surrounding metal atoms as well as on their number. In the studied adsorbents the surface hydroxyl groups are coordinated by two atoms that might be the same (two Si or two Al) or different ones (one Si atom and one Al atom). Then the properties of these surface hydroxyl groups should differ and therefore the adsorption affinity of cations should also differ. The following reactions are responsible for the adsorption of bivalent cations at the oxide/electrolyte interface:

$$\equiv SOH + Me^{2+} \Leftrightarrow \equiv SO^- Me^{2+} + H^+ \tag{1}$$

$$2(\equiv SOH) + Me^{2+} \Leftrightarrow (\equiv SO^-)_2 Me^{2+} + 2H^+ \tag{2}$$

$$\equiv SOH + Me^{2+} + H_2O \Leftrightarrow \equiv SO^- MeOH^+ + 2H^+ \tag{3}$$

As may be noticed from Eq 1 and 2 the adsorption of cations releases the hydrogen ions from hydroxyl groups, so the increase of pH in the system will favor the adsorption of cations at the metal oxide/electrolyte interface.

Figures 1 (a) and (b) show the adsorption of Cd(II), Ni(II) and Pb(II) ions at the SA1/0.001M NaClO$_4$ system interface for an initial ion concentrations of 1×10^{-6} and 1×10^{-3} mole/dm^3 respectively. Similar dependences of adsorption as a function pH for other studied samples (of different composition) were also observed. The plot of adsorption as a function of pH called as the adsorption edge is characterized by $pH_{50\%}$ and $\Delta pH_{10-90\%}$ parameters. Basing on the adsorption data, parameters characterizing the adsorption edge ($pH_{50\%}$ and $\Delta pH_{10-90\%}$) were calculated. Figures 2 a and b present

these parameters as a function of an initial concentration of Cd(II), Ni(II) and Pb(II) ions. As it can be seen, the adsorption edge shifts towards higher pH values with an increase of an initial concentration of measured ions. For all studied samples of mixed oxide the following sequence of adsorbed metals was observed:Pb(II)>Cd(II)>Ni(II).

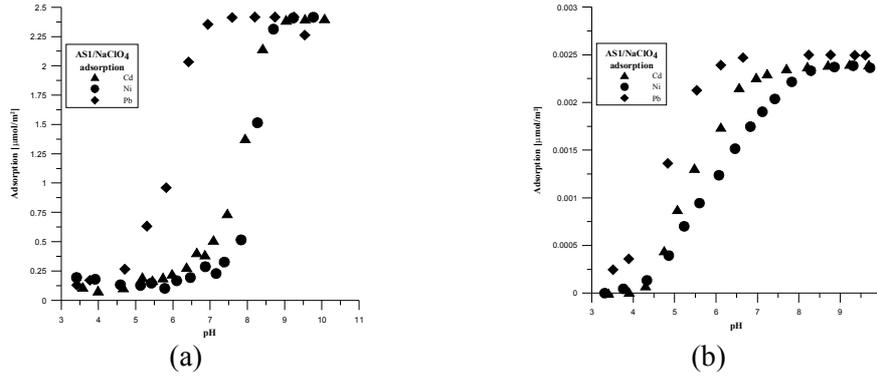(a)   (b)

Fig. 1. The adsorption density of Cd(II), Ni(II) and Pb(II) ions as a function of pH in the AS1/0.001M NaClO$_4$ system; the initial ion concentration: (a) 1×10^{-3}; (b) 1×10^{-6} mol/dm^3.
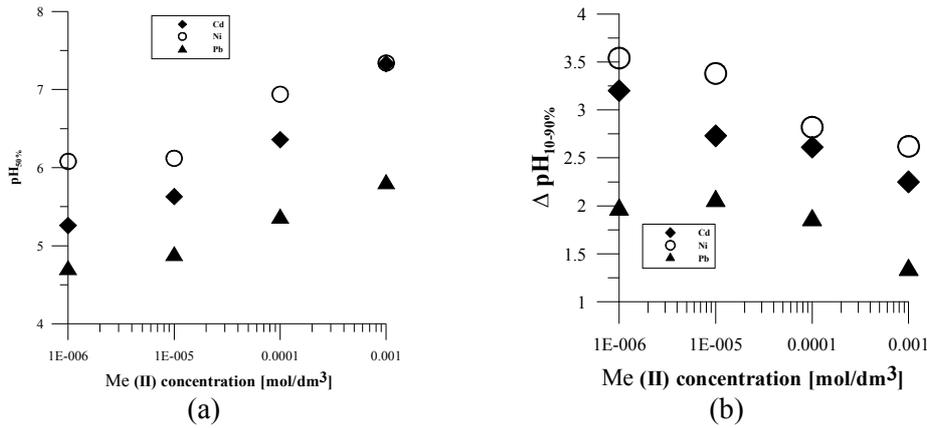

(a)   (b)

Fig. 2. The parameters of adsorption edge as a function of initial concentration of Cd(II), Ni(II) and Pb(II) for AS1 oxide: (a) pH$_{50\%}$; (b) ΔpH$_{10-90\%}$.

The sequence of the adsorption affinity of cations is in an agreement with selectivity series of heavy metal and transition metal ions on the simple metal oxide/electrolyte interface (Hayes and Katz 1996). As it was mentioned above, heavy metal and transition metal cations create inner sphere complexes on the metal oxides. The ability to form inner sphere complexes is connected with the formation of hydrated complexes by respective ions. One can notice certain analogy between the reactions (Hayes and Katz 1996):

$$Me^{2+} + H_2O \leftrightarrow Me(OH)^+ + H^+ \tag{5}$$

$$Me^{2+} + \equiv SOH \leftrightarrow SOMe^+ + H^+ \tag{6}$$
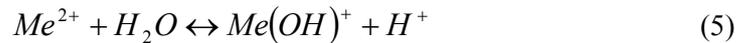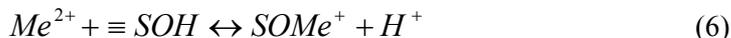
It is assumed that there is a correlation between the complexation reactions of surface hydroxyl groups and the ability to formation hydrated complexes by metal cations. In Table 3 the values of the first constant of hydrolysis for selected metal cations are presented.

Table. 3. The values of the 1st hydrolysis constant
for selected bivalent metal cations (Hayes and Katz 1996).

Cation	pK value
Pb(II)	7.7
Ni(II)	9.9
Cd(II)	10.1

However we observed that the adsorption affinity of Cd(II) ions is higher that Ni(II) ions at low initial concentrations, only for the 0.001 mol/dm^3 adsorption edges cover, so only for this case the correlation discussed above may have place. The parameter charactering the slope of adsorption edge, $\Delta pH_{10-90\%}$, decreases with an increase of the Cd(II), Pb(II) and Ni(II) ions concentration, which means that the adsorption edge becomes steeper.

Table. 4. The adsorption constants for Cd(II), Ni(II), Pb (II) ions
for AS/electrolyte solution system

Concentration [mol/dm^3]	AS1		AS3		AS8	
	Cd (II)					
	pK$_1$	pβ$_2$	pK$_1$	pβ$_2$	pK$_1$	pβ$_2$
10^{-6}	3.45	9.89	4.00	9.95	4.49	9.94
10^{-5}	3.77	9.98	4.34	9.45	4.05	9.84
10^{-4}	3.62	9.56	4.51	9.99	4.15	9.95
10^{-3}	4.00	10.16	6.79	8.89	9.00	9.55
	Ni(II)					
10^{-6}	3.01	9.44	4.44	7.22	3.88	8.15
10^{-5}	3.42	8.96	4.30	8.34	4.00	8.72
10^{-4}	4.72	9.99	4.17	9.33	4.74	9.54
10^{-3}	3.05	8.72	4.00	9.71	4.42	9.99
	Pb(II)					
10^{-6}	2.50	10.5	3.38	10.50	2.90	10.77
10^{-5}	2.42	10.49	3.76	10.90	3.14	9.97
10^{-4}	3.10	10.5	4.31	6.35	3.45	10.88
10^{-3}	3.60	10.5	4.02	6.92	3.86	10.9

We suppose that this phenomenon is caused by influence of increased content of alumina in successive, other samples. According to the reaction 1 and 2, adsorption of metal ions proceeds via exchange of hydrogen ions from one or two surface hydroxyl

groups. For the data presented in Figures 2 the values of adsorption constant of Ni(II), Cd(II) and Pb(II) ions were determined by numerical optimization, using the TLM model. These values are collected in Table 4. For AS1 and AS8 samples the predominant part plays reaction of Pb(II) with one surface hydroxyl group, according reaction 1, while reaction with two surface hydroxyl groups brings a small contribution into adsorption. For higher initial concentration of Pb(II) for AS3 samples the part of reaction 2 in the adsorption process is larger.

Such adsorption mechanism of bivalent metal cations at the high adsorption densities would lead to the overcharging of the compact part of edl and to the presence of the charge reversal point(CR2) on the ζ potential as a function of pH dependence.
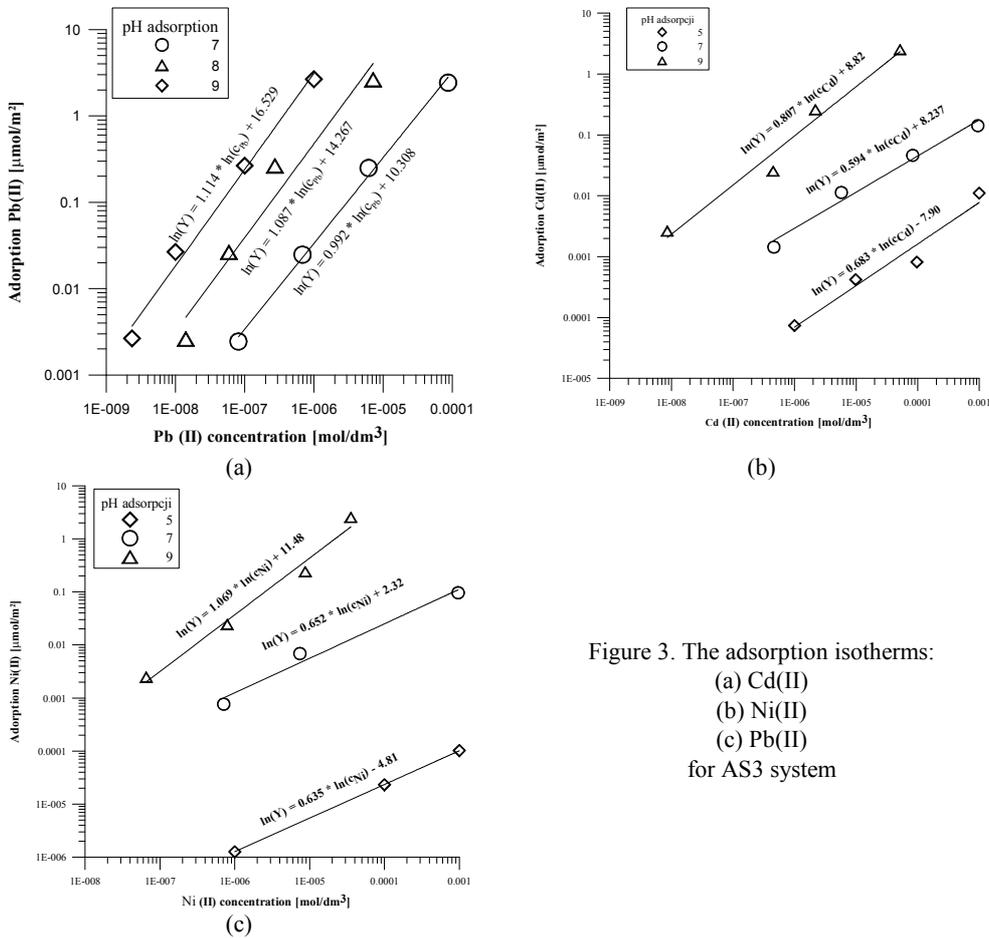

(a)

(b)

(c)

Figure 3. The adsorption isotherms:
(a) Cd(II)
(b) Ni(II)
(c) Pb(II)
for AS3 system

On the basis of Cd(II), Ni(II) and Pb(II) adsorption data the isotherms adsorption were calculated and they are presented in Figure 3 as the Kurbatov plots (log adsorption – log concentration). A linear fitting can be observed for these systems. The same relationship was observed for oxides AS1 and AS8.

The presence of metal ions leads to an increase in the number of negatively charged sites at the metal oxide surfaces. The most significant influence was observed for the highest metal concentration of (10^{-3}M, see Figures 4 (a), (b) and (c)).
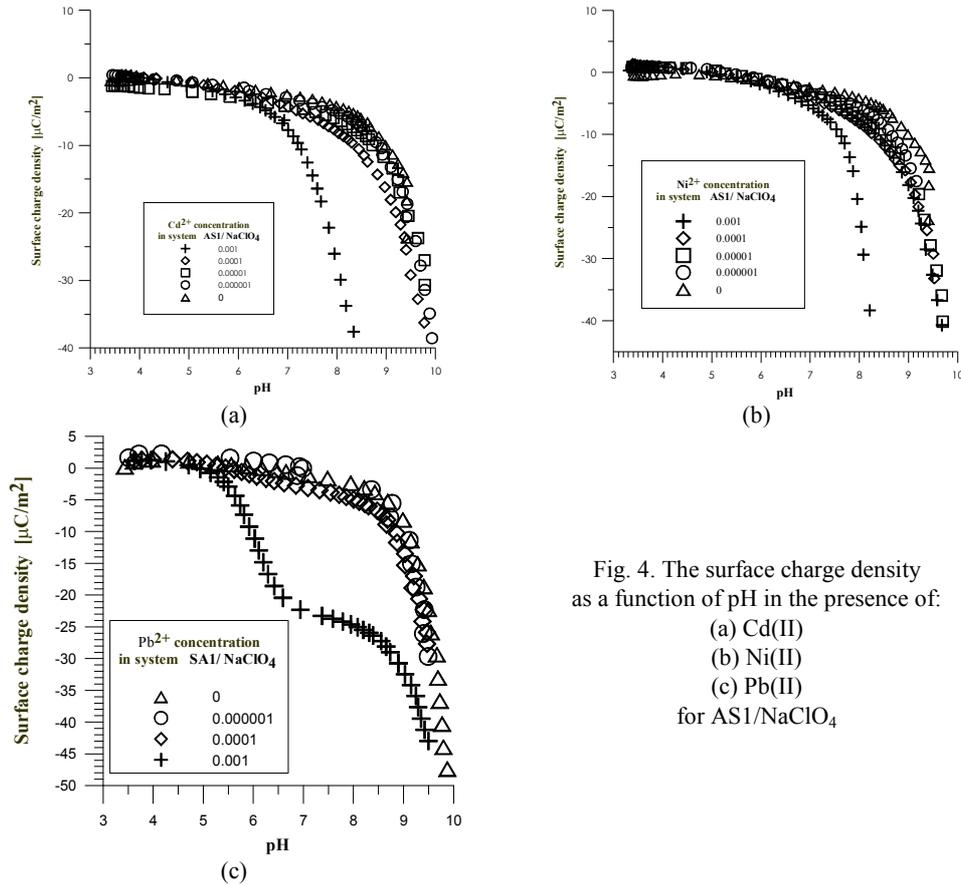

(a)

(b)

(c)

Fig. 4. The surface charge density
as a function of pH in the presence of:
(a) Cd(II)
(b) Ni(II)
(c) Pb(II)
for AS1/NaClO$_4$

The presence of Cd(II), Ni(II) and Pb(II) cations causes changes of ζ potential in the studied systems. Such influence is shown in Figure 5. For the highest concentration of metal ions a charge reversal point was observed (CR2). This phenomenon is characteristic for the overcharging of the compact part of the edl as a result of specific ion adsorption. As it is seen this point (CR2) is at pH about 6.0 for Pb(II) ions and at pH about 8.0 for Cd(II) and Ni(II) ions. Dependence for cadmium and nickel was observed and it can be explained with a mentioned ability of these ions to hydrolysis, and therefore a small difference between their hydrolysis constant.
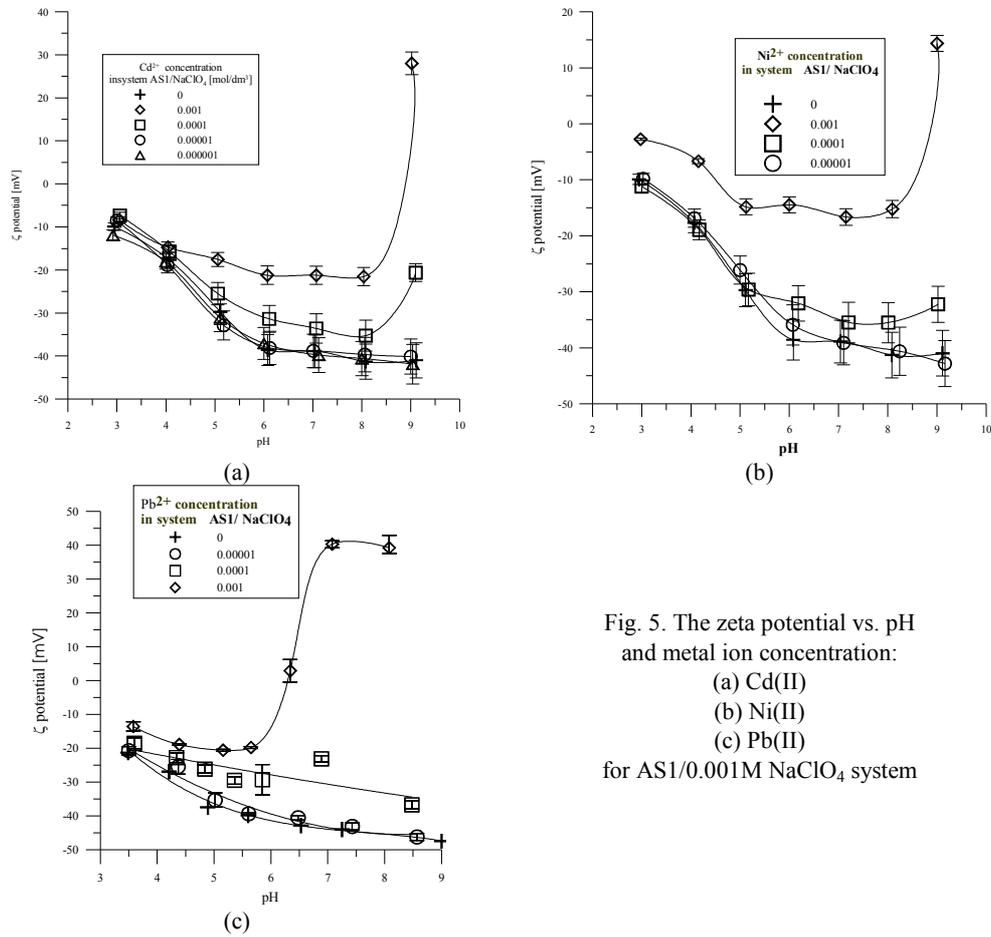
(a)

(b)

(c)

Fig. 5. The zeta potential vs. pH
and metal ion concentration:
(a) Cd(II)
(b) Ni(II)
(c) Pb(II)
for AS1/0.001M NaClO₄ system

CONCLUSIONS

The samples of mixed alumina/silica oxides with a content of alumina ranging from 1 to 8% have the same pH_{pzc}. Adsorption of Cd(II), Ni(II) and Pb(II) ions can be described by the TLM model of electrical double layer. The shape of Cd(II), Ni(II) and Pb(II) ions adsorption as a function of pH on mixed alumina/silica oxides are similar to one on clean metal oxides. The adsorption process can be characterized by the adsorption edge, which can be described by two parameters: $pH_{50\%}$ and $\Delta pH_{10-90\%}$. The parameter characterizing the position of adsorption edge ($pH_{50\%}$) shifts towards higher pH values with the increase of the initial metal concentration for majority of samples. The adsorption isotherms of Cd(II), Ni(II) and Pb(II) ions as a function of log adsorption – log concentration are linear. For all mixed oxides the metal adsorption can be fitted by a Freudlich isotherm. The specific adsorption of bivalent cations

causes a shift of the pH_{iep} towards alkaline pH values and an increase of the ζ potential. The high concentration of adsorbing bivalent cations (Cd, Ni and Pb) causes the overcharging of the compact part of edl and appearance of CR2 point. The presence of bivalent cations causes an increase of the negative surface sites and shifts pH_{pzc} towards lower pH values.

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Kadm, ołów i nikiel są toksycznymi metalami ciężkim, który stanowią wciąż poważne zagrożenie dla organizmów żywych. W środowisku naturalnym oraz w wielu procesach technologicznych mamy do czynienia ze skomplikowanymi układami gdzie występują obok siebie tlenki typu Al$_2$O$_3$-SiO$_2$ oraz jony metali ciężkich. Przeprowadzono badania adsorpcji jonów niklu, kadmu i ołowiu dla różnych stężeń początkowych, w funkcji pH dla układów AS1, AS3, AS8/roztwór NaCl. Kształt krzywych adsorpcji w funkcji pH ma postać krawędzi adsorpcji. Wzrost stężenia początkowego jonów metali ciężkich, powoduje przesunięcie krawędzi w kierunku zasadowym skali pH. Wyznaczono charakterystyczne parametry krawędzi

adsorpcji tj. pH$_{50\%}$ i ΔpH$_{10\text{-}90\%}$, w oparciu o zależność adsorpcji od pH stosując model TLM, obliczono również stałe reakcji adsorpcji jonów Ni(II), Cd(II), Pb(II) metodą optymalizacji numerycznej. Zależność gęstości ładunku powierzchniowego od pH w obecności jonów metali ciężkich, jest w dobrej korelacji z zależnością adsorpcji jonów Ni(II), Cd(II), Pb(II) od pH. Adsorpcja badanych jonów na powierzchni AS1, AS3, AS8 prowadzi do wzrostu stężenia grup ujemnie naładowanych.

słowa kluczowa: adsorpcja kationów, metale ciężkie, Cd(II), Ni(II), Pb(II), podwójna warstwa elektryczna, Al$_2$O$_3$-SiO$_2$, potencjał dżeta