Adsorption of nickel ions at the pseudobrookite/NaCl and ilmenite/NaCl – the electrical double layer structure

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Basic parameters of the electrical double layer of the Fe_2TiO_5 (pseudobrookite)/NaCl and $FeTiO_3$ (ilmenite)/NaCl system are presented in this paper. The influence of ionic strength, pH, and presence of ions on adsorption of Ni(II) at the Fe_2TiO_5/NaCl and $FeTiO_3$/NaCl solution interface were investigated. Adsorption density, $pH_{50\%}$ and $\Delta pH_{10-90\%}$ parameters and constants of surface hydroxyl groups' reactions were presented.
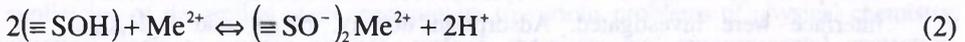
1. INTRODUCTION

Iron and titanium substituted oxides are widespread in nature and represent an important mineral resource for the commercial obtainment of both, iron and titanium compounds. The ilmenite ($FeTiO_3$) and pseudobrookite (Fe_2TiO_5) are the most widely used titanium minerals that play an important role in the titanium industry [1].

In his publication Jones suggested that transformation of ilmenite to the pseudobrookite phase was very fast, completing at 1000 °C in 5 min [2]. The results of Jones are consistent with the data obtained by Merk and Pickles [3].

Adsorption of heavy metal ions at the solid/electrolyte solution interface has been studied to describe processes having place in environmental systems and for technological purpose of preparing catalysts [4]. Most of the studies of cations adsorption at metal oxide/electrolyte interface concern the systems where the solid phases are pure compounds. Such systems are convenient for theoretical study; however, they differ significantly from real dispersed systems where as a rule both phases are multicomponent. Adsorption affinity of ions to

surface depends on basic-acidic properties of surface hydroxyl groups of metal oxide. These properties of hydroxyl groups are determined by metal atoms that surround it are in the crystal lattice. It is well known that even simple metal hydroxyl groups change their properties with the number of metal atoms in the vicinity of a given surface hydroxyl group. Mixed two component oxides create greater opportunity in changing properties due to the diversity of metal atoms in the hydroxyl group surroundings.

According to the site binding theory of edl the divalent ions can be adsorbed specifically on the metal oxide surface by forming the coordinate bonds between the surface oxygen atoms and the adsorbed cation. Some of them are adsorbed so intensely that there is no water molecule between the adsorbed ion and the surface. The so-called inner-sphere complexes are formed. The outer-sphere complex is formed when a water molecule is present between the adsorbed ion and the surface. Divalent ions may adsorb at the metal oxide surface on one or two sites [5]. It is assumed that the following reactions are responsible for the adsorption of bivalent cations at the oxide/electrolyte interface:

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

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

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. Consequently, the sharp increase of the cation adsorption from 0% to 100%, with a increase pH of the electrolyte as much as 1, 2 units are observed. This relationship is called the "edge of adsorption" [6] and Robertson and Leckie have proposed very useful parameters to characterize it in Table 1:

Tab. 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.
$dpMe/dpH$	Parameter that shows the activity of cations; must vary when pH of the solution changes to maintain the constant adsorption of the cation.

As discussed by Schindler [7] reaction (1) and (2) may be characterized by thermodynamic constants defined as follows:

$$^*K_1^S = \frac{[H^+][\equiv SO^-Me^{2+}]}{[Me^{2+}][\equiv SOH]} \frac{\gamma_H \gamma_1}{\gamma_{Me} \gamma_0} \times \exp\left(\frac{e(2\psi_1 - \psi_H)}{kT}\right) \tag{3}$$

$$^*\beta_{21}^S = \frac{[H^+]^2[(\equiv SO^-)_2 Me^{2+}]}{[Me^{2+}][\equiv SOH]^2} \frac{\gamma_H^2 \gamma_2}{\gamma_{Me} \gamma_0^2} \times \exp\left(\frac{e(2\psi_2 - \psi_H)}{kT}\right) \tag{4}$$

$$^*K_{MeOH}^S = \frac{[H^+]^2[\equiv SOMeOH]}{[Me^{2+}][\equiv SOH]} \frac{\gamma_H^2 \gamma_1}{\gamma_{Me} \gamma_0} \times \exp\left(\frac{e(\psi_1 - \psi_H)}{kT}\right) \tag{5}$$

where: γ_1, γ_2 – activity coefficients of $\equiv SOH^{(z-1)+}$ and $(\equiv SO)_2 H^{(z-2)+}$ groups, ψ_1, ψ_2 – potentials in the planes of adsorption of Me^{2+} bounded to $\equiv SOH^{(z-1)+}$ and $(\equiv SO)_2 H^{(z-2)+}$ surface species respectively, γ_0 – activity coefficients of $\equiv SOH$ group, γ_H – activity coefficients of H^+ ions, γ_{Me} – activity coefficients of metal cation, k – Bolzman constant.

The values of reaction constants may be determined by the use of numerical optimization procedures.

The multivalent ions can be adsorbed specifically on the metal oxide surface on one or two surface sites but the number of sites usually occupied by a single ion is fewer than two [5]. As it was mentioned above, the specific adsorption of ions may create inner-sphere complexes or outer-sphere complexes. 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 a surface plane. According to TLM (model SCM, *site binding*), also the absorption 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 [4].

The purpose of this paper was to study how the composition of adsorbent changes the adsorption affinity Ni(II) ions and how the parameters of the electrical interfacial layer (EIL) change at the ilmenite and pseudobrookite/electrolyte interface.

2. EXPERIMENTAL

Commercial ilmenite and pseudobrookite samples from Alfa Aesar were used in the experiments. XRF analysis of the ilmenite showed the presence of the following elements: 34.3% Fe and 27.7% Ti and pseudobrookite showed the presence of the following elements: 45% Fe and 17.63% Ti. The specific surface of $FeTiO_3$ was 1.28 m^2/g and Fe_2TiO_5 was 1.45 m^2/g. sample. A crystallographic structure of samples was determined by XRD using DRON-3 diffractometer using CuK_α radiation and nickel filters. Roentgen diffraction analysis revealed that crystallographic structures of the measured substance are ilmenite and pseudobrookite. Figures 1 and 2 show a typical structure for $FeTiO_3$, showing peaks 23.8 – 30%; 32.5 – 100%; 35.2 – 70%, 40.25 – 30%; 48.7 – 40%; 53 – 50%; 56.15 – 9%; 61.5 – 30% and a typical structure Fe_2TiO_5: 18.1 – 45%; 32.5 – 80%; 36.7 – 20%; 41.05 – 15%; 46.01 – 15%; 55.2 – 25%.
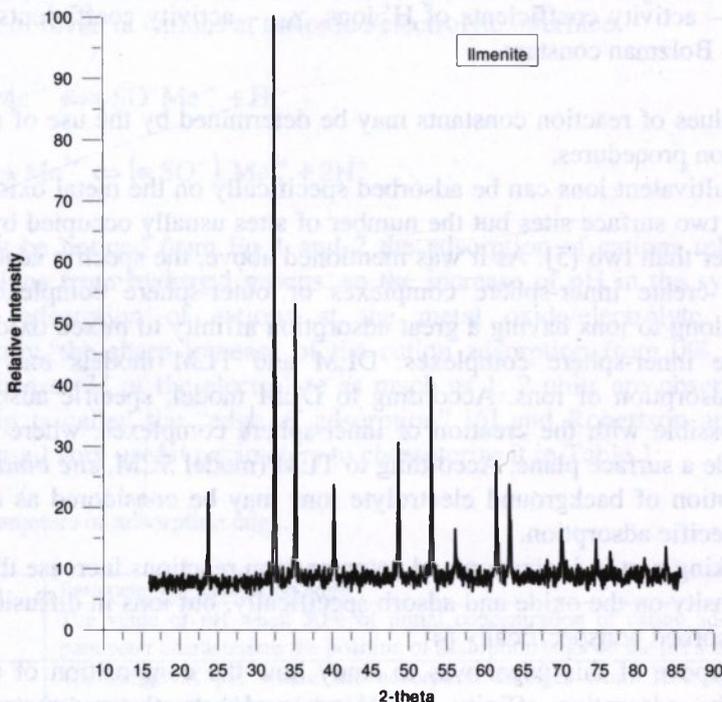

Fig. 1. Diffraction pattern of $FeTiO_3$.

Nickel ions adsorption was performed with [63]Ni isotope as a tracer. The specific adsorption of Ni(II) ions at substance interface was investigated by means of the radioisotope method as a function of Ni(II) concentration ions,

0.001M NaCl concentration and pH. The initial concentration of Ni(II) ions ranged from 1×10^{-6} and 1×10^{-3}M, pH was changed from 3 to 10 during adsorption of process. The zeta potential of the ilmenite and pseudobrookite dispersions was determined by electrophoresis with Zetasizer 3000 by Malvern. The zeta potentials were calculated using the Smoluchowski equation.
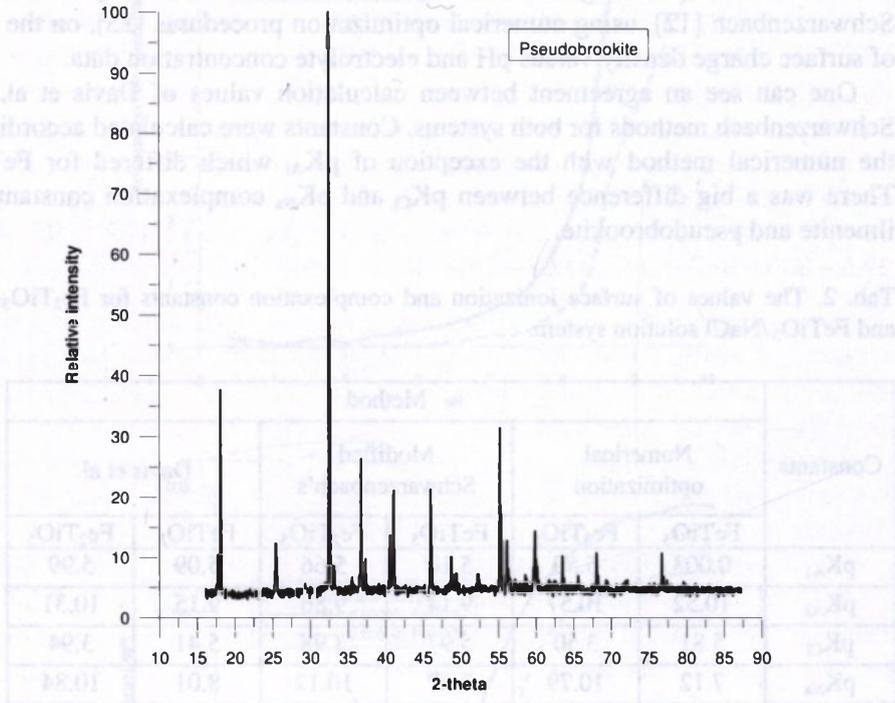

Fig. 2. Powder X-diffraction pattern of Fe_2TiO_5.

Surface charge density and zeta potential in concentration 0.1, 0.001, 0.001M NaCl were investigated. On the basis of these data pH_{PZC}, pH_{IEP}, the ionization and complexation constants were determined.

3. RESULTS AND DISCUSSION

In the references we can see only few papers about the structure of the electrical double layer in ilmenite/electrolyte system solution and pseudobrookite/electrolyte solution. In one of them the value for ilmenite pH_{PZC} is 6.3 and pH_{IEP} is 3.3 for pseudobrookite pH_{PZC} is 7 [8, 9, 10].The electrical double layer at the Fe_2TiO_5/NaCl solution interface is characterized by $pH_{PZC}=8.9$ and $pH_{IEP}=4.2$. The electrical double layer at the $FeTiO_3$/NaCl

solution interface is characterized by $pH_{PZC}=7.19$ and $pH_{IEP}=4$. A difference in pH_{PZC} value may be a result of a crystallographic structure. In the first case of ilmenite/electrolyte system it can be explained with the presence of mineral ilmenite, and in the second case, with the presence of mixed oxide.

The ionization and complexation constants of the surface hydroxyl groups were calculated according to the method of J.A. Davis et al. [11] modified by Schwarzenbach [12], using numerical optimization procedures [13], on the basis of surface charge density versus pH and electrolyte concentration data.

One can see an agreement between calculation values of Davis et al., and Schwarzenbach methods for both systems. Constants were calculated according to the numerical method with the exception of pK_{Al} which differed for $FeTiO_3$. There was a big difference between pK_{Cl} and pK_{Na} complexation constants for ilmenite and pseudobrookite.

Tab. 2. The values of surface ionization and complexation constants for $Fe_2TiO_5/NaCl$ and $FeTiO_3/NaCl$ solution system.

Constants	Method					
	Numerical optimization		Modified Schwarzenbach's		Davis et al.	
	$FeTiO_3$	Fe_2TiO_5	$FeTiO_3$	Fe_2TiO_5	$FeTiO_3$	Fe_2TiO_5
pK_{Al}	0.003	5.50	5.10	5.66	5.09	5.99
pK_{A2}	10.52	10.57	9.14	9.86	9.15	10.31
pK_{Cl}	5.81	3.50	5.97	3.98	5.41	3.94
pK_{Na}	7.12	10.79	7.67	10.12	8.01	10.84

The adsorption density of Ni(II) ions as a function of pH in the $FeTiO_3/NaCl$ and $Fe_2TiO_5/NaCl$ solution system is presented in Figure 3. The adsorption edge of the nickel ion adsorption plot in the studied system is characteristic of adsorption of divalent cations on the oxides. With an increasing initial concentration of nickel ions the adsorption edge shifts towards higher pH values. For pH≈10 adsorption reaches 100%, which means that almost all nickel ions are on the solid phase. The property surface hydroxyl groups on mixed oxides depend on the number and kind of metal atoms in the vicinity of hydroxyl group. In both cases hydroxyl groups would have different acid-base character [14]. One can see a small difference of adsorption edge for ilmenite and pseudobrookite in different electrolyte background concentration Figure 3 (A), (B). Consequently, there is a small difference in parameters $pH_{50\%}$ and $\Delta pH_{10-90\%}$.

(A)
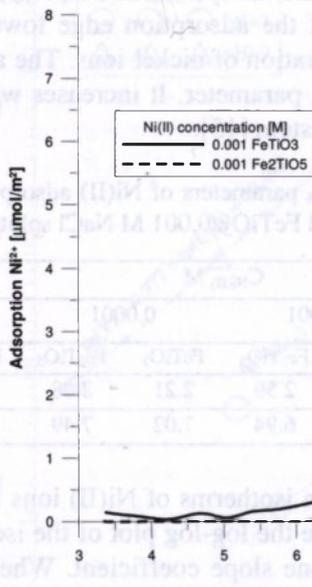
(B)
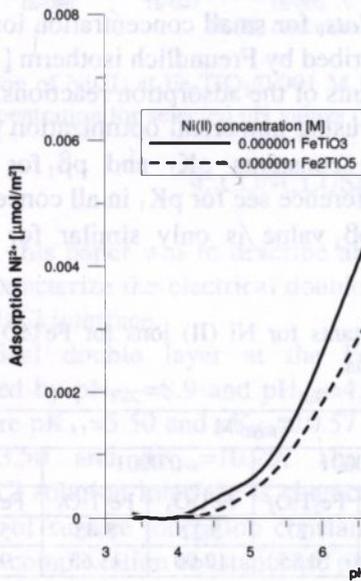

Fig. 3. Adsorption of Ni(II) ions at FeTiO₃/0.001M NaCl Fe₂TiO₅/0.001M NaCl interface vs pH.

Characteristic adsorption edge parameters $pH_{50\%}$ and $\Delta pH_{10-90\%}$ are listed in Table 3. These data show the shift of the adsorption edge towards higher pH values with the increase in the concentration of nickel ions. The adsorption edge slope is characterized by the $\Delta pH_{10-90\%}$ parameter. It increases when nickel ions initial concentration decreases in the system [15].

Tab. 3. The values of $pH_{50\%}$ and $\Delta pH_{10-90\%}$ parameters of Ni(II) adsorption edge for the system Fe_2TiO_5 /0.001 M NaCl solution and $FeTiO_3$ /0.001 M NaCl solution.

Parameters of adsorption edge	$C_{Ni(II)}$ M							
	0.000001		0.00001		0.0001		0.001	
	$FeTiO_3$	Fe_2TiO_5	$FeTiO_3$	Fe_2TiO_5	$FeTiO_3$	Fe_2TiO_5	$FeTiO_3$	Fe_2TiO_5
$\Delta pH_{10-90\%}$	2.58	2.69	2.43	2.59	2.21	2.08	2.14	1.8
$pH_{50\%}$	6.48	6.66	6.43	6.94	7.02	7.49	8.31	8.93

Figures 4 and 5 show the adsorption isotherms of Ni(II) ions for selected pH values (5, 7 and 9). In the low pH range the log-log plot of the isotherm is linear and is characterized by smaller than one slope coefficient. When pH increases the slope of the isotherms decreases.

The dependent log number of adsorbent nickel ions on log concentration ions in solution has carried *Krurbatov plots*, for small concentration ions has a linear character, from now on usually described by Freundlich isotherm [11, 12].

The values of equilibrium constants of the adsorption reactions, calculated on the basis of the TLM model of edl using numerical optimization procedure, are collected in Table 4. Comparing constants pK_1 and $p\beta_1$ for ilmenite and pseudobrookite we can see a big difference see for pK_1 in all concentrations with the exception of 0.0001M. For $p\beta_1$ value is only similar for concentration 0.001M.

Tab. 4. Values of the adsorption constants for Ni (II) ions for $FeTiO_3$ and Fe_2TiO_5 / 0.001 mol dm^{-3} NaCl solution, Ni(II) ions.

Constans	$C_{Ni(II)}$ M							
	0.000001		0.00001		0.0001		0.001	
	$FeTiO_3$	Fe_2TiO_5	$FeTiO_3$	Fe_2TiO_5	$FeTiO_3$	Fe_2TiO_5	$FeTiO_3$	Fe_2TiO_5
pK_1	4.29	7.70	4.00	7.27	5.22	5.45	5.00	7.80
$p\beta_1$	10.07	11.40	9.72	10.85	12.00	11.65	9.54	9.53

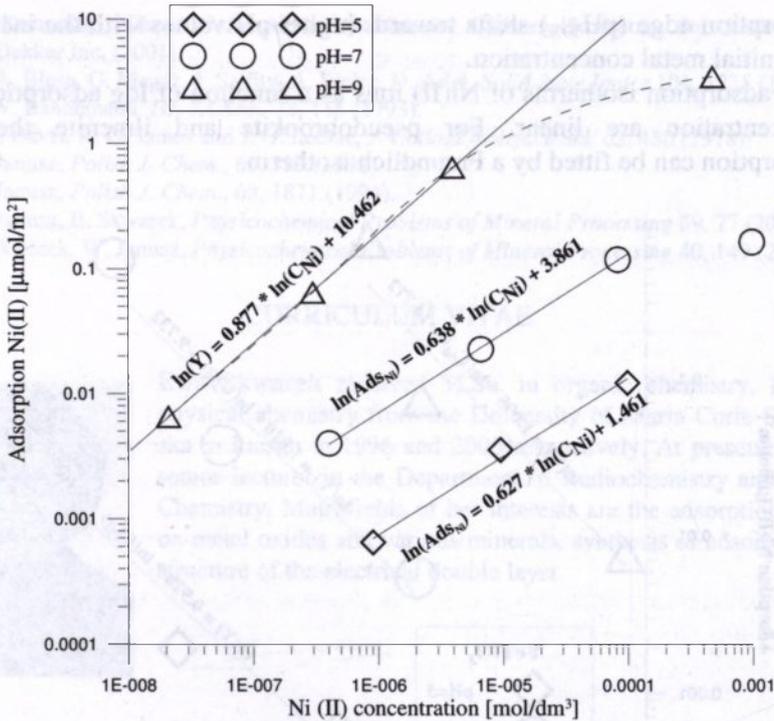Fig. 4. Adsorption of Ni(II) at Fe_2TiO_5/0.001 M NaCl solution interface as a function of equilibrium concentration for selected pH values (5, 7 and 9).

4. CONCLUSIONS

The aim of this paper was to describe and compare the adsorption of Ni(II) ions and to characterize the electrical double layer structure at the $FeTiO_3$/NaCl and Fe_2TiO_5/NaCl interface.

1. The electrical double layer at the Fe_2TiO_5/NaCl solution interface is characterized by pH_{PZC}=8.9 and pH_{IEP}=4.2. The values of surface ionization constants are pK_{A1}=5.50 and pK_{A2}=10.57 and surface complexation constants are pK_{Cl}=3.50 and pK_{Na}=10.79. The electrical double layer at the $FeTiO_3$/NaCl solution interface is characterized by pH_{PZC}=7.19 and pH_{IEP}=4. The values of surface ionization constants are pK_{A1}=0.003 and pK_{A2}=10.52 and surface complexation constants are pK_{Cl}=5.81 and pK_{Na}=7.12.

2. The adsorption of Ni(II) ions as a function of pH on Fe_2TiO_5 and $FeTiO_3$ runs similarly to the one on simple 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 in the initial metal concentration.
3. The adsorption isotherms of Ni(II) ions as a function of log adsorption – log concentration are linear. For pseudobrookite and ilmenite the metal adsorption can be fitted by a Freundlich isotherm.
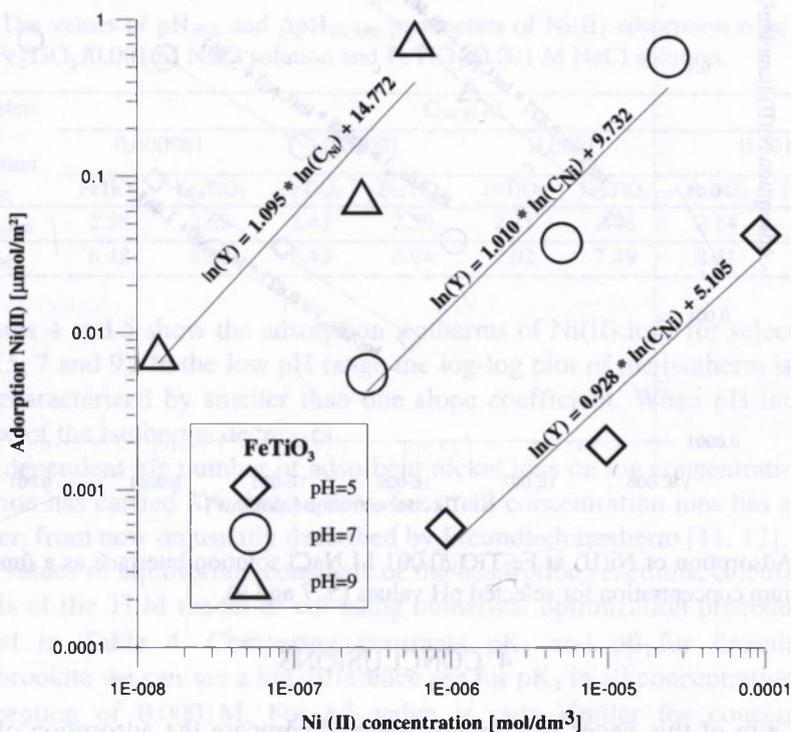

Fig. 5. Adsorption of Ni(II) at $FeTiO_3$ /0.001M NaCl solution interface as a function of equilibrium concentration for selected pH values (5, 7 and 9).

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CURRICULUM VITAE

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