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ADSORPTION OF Ni(II) IONS AT THE Fe_2TiO_5/ELECTROLYTE SOLUTION INTERFACE – THE ELECTRICAL DOUBLE LAYER STRUCTURE

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Physicochemical properties of Fe_2TiO_5 (pseudobrookite structure) surface was studied and basic properties of electrical double layer of the Fe_2TiO_5/NaCl+Ni^{2+} solution system were described. The adsorption of Ni (II) at the pseudobrookite/aqueous solutions interface was studied over the pH range of 3 to 11. The influence of ionic strength, pH, and presence of ions was researched. ζ potential, surface charge density, adsorption density, $pH_{50\%}$ and $\Delta pH_{10\text{-}90\%}$ parameters for different concentrations of background electrolyte were presented. The adsorption constants of surface hydroxyl groups' reactions were determined using numerical optimization.

Key words: Fe_2TiO_5, electrical double layer, surface charge density, zeta potential, adsorption

INTRODUCTION

Titanium substituted iron oxides are widespread in nature and represent an important mineral resource for the commercial obtainment of both iron and titanium compounds. Pseudobrookite is recently considered as a non-terrestrial an oxygen source for lunar bases (Guo et al. 1999). Pseudobrookite, a natural mineral, is present in igneous and metamorphic rocks and has magnetic properties (Guo et al. 1999, Surowce 1985). Fe_2TiO_5 can be used as material for optical filters and for photo catalytic applications (Perkas et al. 2001, Misook 2003, Garcia et al. 2002).

In the resent years many papers been published that describe methods of preparation of Fe_2TiO_5 by means of the sol-gel method (Misook 2002, Kanga et al. 2001, Lee et al. 2001) or by mixing in stoichiometric amounts Fe_2O_3 and TiO_2 powders.

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The surface charge at the Fe_2TiO_5/NaCl aqueous solution interface results from similar reactions to the simple oxide/electrolyte interface e.g. acid-base dissociation of the amphoteric surface hydroxyl groups (-SOH) and reaction of complexation of hydroxyl groups.

The equilibrium constants that characterize these reactions according the site – binding theory are important physicochemical quantities that characterize structure of the electrical double layer. There are a few method of calculation of these constants e.g.: Davis et. al., modified Schwarzenbach's method, and numerical optimization methods.

James and Parks reviewed electrical double layer models at the metal oxide interface and their suitability for estimating the surface charges and zeta potentials under a wide range of conditions including those witch an adsorbing heavy metal species present in solution. They concluded that the simultaneous measurement of parameters such as surface charge, zeta potential and degree of heavy metal adsorption is desirable for precise description of edl at the metal oxide interface (James and Parks 1982).

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 strongly that there are no water molecules between the adsorbed ion and the surface, so–called inner-sphere, complexes are formed. If a water molecule is present between the adsorbed ion and the surface, then the outer-sphere complex is formed (Hayes and Katz 1996). Divalent ions may adsorb at the metal oxide surface on one or two surface sites (Schindler 1981). It is assumed that the following reactions are responsible for the adsorption of divalent 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, 2 and 3 the adsorption of cations releases 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 increase of pH of the electrolyte as much as 1, 2 units are observed. This relationship is called "edge of adsorption" and Robertson and Leckie (1997) have proposed very useful parameters to characterize it:

- *d*pMe/*d*pH – parameter that shows the activity of cations; must vary when pH of the solution changes to maintain the constant adsorption of the cations,

- $pH_{50\%}$ - the value of pH when 50% of initial concentration of cations adsorbs, this parameter characterizes the position of adsorption edge on the pH scale,
- $pH_{10\text{-}90\%}$ - the range of pH where the adsorption changes from 10% to 90%, it characterizes the slope of the edge,

$$^{*}K_1^S = \frac{[H^+][\equiv SO^- Me^{2+}]}{[Me^{2+}][\equiv SOH]}\frac{\gamma_H\gamma_1}{\gamma_{Me}\gamma_0}\times\exp\left(\frac{e(2\psi_1-\psi_H)}{kT}\right), \tag{4}$$

$$^{*}\beta_{21}^S = \frac{[H^+]^2[(\equiv SO^-)_2 Me^{2+}]}{[Me^{2+}][\equiv SOH]^2}\frac{\gamma_H^2\gamma_2}{\gamma_{Me}\gamma_0^2}\times\exp\left(\frac{e(2\psi_2-\psi_H)}{kT}\right), \tag{5}$$

$$^{*}K_{MeOH}^S = \frac{[H^+]^2[\equiv SOMeOH]}{[Me^{2+}][\equiv SOH]}\frac{\gamma_H^2\gamma_1}{\gamma_{Me}\gamma_0}\times\exp\left(\frac{e(\psi_1-\psi_H)}{kT}\right), \tag{6}$$

where:

γ_1, γ_2 – activity coefficients of $\equiv SOH^{(z-1)+}$ and $(\equiv SO)_2H^{(z-2)+}$ groups, ψ_1, ψ_2 – means potentials in the planes of adsorption of Me^{2+} bounded to $\equiv SOH^{(z-1)+}$ and $(\equiv SO)_2H^{(z-2)+}$ 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 value of reaction constants may be determined by numerical optimization procedures. Results of specific adsorption of ions at electrical double layer structure may be described by means of DLM (double layer model) and TLM (triple layer model).

The influence of ionic strength, pH and presence of ions on adsorption of Ni (II) on the electrical double layer structure – at the Fe_2TiO_5 (pseudobrookite structure)/electrolyte interface was investigated. This study can help to understand the distribution process of Ni (II) ions between the solid phase and a solution during the enrichment processes because Ni occurs in some titanium/iron ores. Their purpose was to describe the process of adsorption of Ni (II) ions at Fe_2TiO_5/electrolyte interface. Adsorption measurements were complemented by surface charge density and determinations of ζ potential. The effect of Ni (II) adsorption on the properties of the edl is discussed. To determine the constants of surface reaction by numerical optimization, the ion adsorption data were used following the triple layer model of the edl.

EXPERIMENTAL

Experiments were performed on a commercial Fe_2TiO_5 sample from Alfa Aesar. The specific surface of the Fe_2TiO_5 sample, determined by nitrogen desorption, was 1.45 m^2/g. BJH analysis of the isotherm obtained by adsorption-desorption of nitrogen did not reveal microspores, only mezopores of the size of 35 Å in the examined Fe_2TiO_5 sample were detected. Roentgen diffraction analysis revealed that crystallographic structure of measured substance is pseudobrookite. Nickel ions adsorption was performed with ^{63}Ni isotope as a tracer. The specific adsorption of Ni (II) ions at Fe_2TiO_5 interface was investigated by the means of radioisotope method as a function of Ni (II) ions concentration, NaCl concentration and pH. The initial concentration of Ni (II) ions ranged from $1x10^{-6}$ to $1x10^{-3}$ $mol \cdot dm^{-3}$, pH was changed from 3 to 10. As a background electrolyte NaCl solution was used of concentrations 0.1, 0.01, 0.001 $mol \cdot dm^{-3}$. The adsorption measurements were complemented by the potentiometric titration of Fe_2TiO_5 suspensions and electrophoresis measurements.

To remove ionic type contaminations, which might influence the ion adsorption measurements, the pseudobrookite was washed with double distilled water until constant conductivity about 2 μS/cm was achieved. Adsorption and 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 in 25^oC. To eliminate the influence of CO_2 all potentiometric measurements were performed under nitrogen atmosphere. 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 pseudobrookite dispersions was determined by electrophoresis with Zetasizer 3000 by Malvern. The measurements were performed at 100 ppm solid concentration ultrasonication of the suspension.

RESULTS AND DISCUSSION

Figure 1 presents the surface charge density of pseudobrookite as a function of pH for two concentrations of NaCl solution as a background electrolyte. Figure 2 presents the ζ potential of Fe_2TiO_5 vs. pH for three concentrations of NaCl solution.

One may see that the pH_{IEP} and pH_{PZC} values differ.. The pH_{iep} value is below pH=4.2, whereas the pH_{PZC} for Fe_2TiO_5 is near 8.9. The difference between pH_{PZC} and pH_{IEP} may results form different part of interacting surfaces of metal oxide that is accessible in potentiometric titration and electrophoresis experiments. A part of pores may be smaller then 3nm and assuming that slipping plane is 1.5 nm away from the solid surface. Then, such pores might be blocked during electrophoresis and surface properties for this part of solid will not be reflected during electrophoresis.

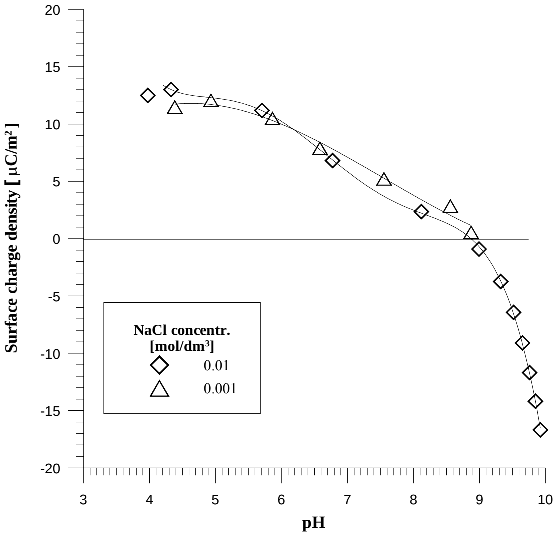

Fig. 1. Surface charge density at the Fe_2TiO_5/NaCl solution interface as a function of pH

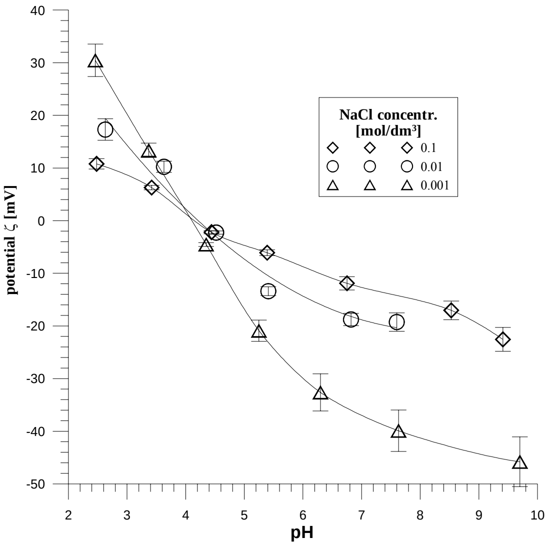

Fig. 2. The ζ potential as a function pH at the pseudobrookite particles in solution NaCl

Great part of surface charge may be compensated inside of particle pores and only the part created by ionized groups on the oxide surface is responsible for electrophoresis mobility. The difference in the position of pH_{IEP} and pH_{PZC} may also indicate the specific anion adsorption, because $pH_{PZC} > pH_{IEP}$. However, due to so low background electrolyte concentration this effect could not lead to such significant difference between pzc and iep.

The ionization and complexation constants of the surface hydroxyl groups were calculated according to the Davies et al. (1978), modified Schwarzenbach (Janusz 1991), and numerical optimization (Janusz 1994) methods, from surface charge density versus pH and electrolyte concentration data. The calculated values of the equilibrium constants are collected in Table 1.

Table 1. The values of surface ionization and complexation constants for Fe_2TiO_5/NaCl solution system

Constants	Method		
	Davis *et al.*	Modified Schwarzenbach's	Numerical Optimization
pK_{a1}	5.99	5.66	5.50
pK_{a2}	10.31	9.86	10.57
pK_{Cl}	3.94	3.98	3.50
pK_{Na}	10.84	10.12	10.79

One can see a good agreement of the constants with the values calculated by various methods. Fe_2TiO_5/NaCl system is characteristic for a relative big difference (ΔpK) between pK_{a1} and pK_{a2} ionization constants. Analysis of these constants indicates that there is a larger number of anionic surface groups than cationic ones, especially for the Fe_2TiO_5 system.

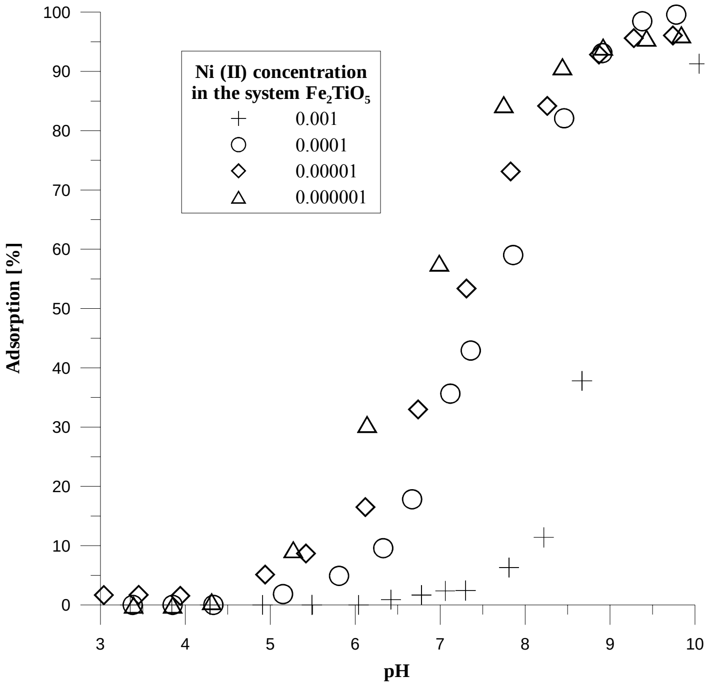

Fig. 3. Adsorption of Ni (II) ions at Fe_2TiO_5 / 0.001 mol dm^{-3} NaCl interface vs pH

The adsorption density of Ni(II) ions as a function of pH in the Fe_2TiO_5/NaCl solution system is presented in Fig. 3. The adsorption edge of the nickel ion adsorption plot in the studied system is characteristic for adsorption of divalent cations on the oxides. With increasing initial concentration of nickel ions the adsorption edge shifts toward higher pH values. At pH≈10 the adsorption reaches 100% that means that almost all nickel ions are bond by solid phase.

Table 2. The values of $pH_{50\%}$ and $\Delta pH_{10\text{-}90\%}$ parameters of Ni(II) adsorption edge for the system of Fe_2TiO_5 /0.001 mol dm^{-3} NaCl solution

Parameters of adsorption edge	$C_{Ni(II)}$ mol dm $^{-3}$			
	0.001	0.0001	0.00001	0.000001
$pH_{50\%}$	8.93	7.49	6.94	6.66
$\Delta pH_{10\text{-}90\%}$	1.8	2.08	2.59	2.69

Characteristic parameters of adsorption edge, $pH_{50\%}$ and $\Delta pH_{10\text{-}90\%}$ are listed in Table 2. These data show the shift of the adsorption edge towards higher pH values with the increase of starting concentration of nickel ions. The adsorption edge slope is characterized by the $\Delta pH_{10\text{-}90\%}$ parameter. It increases when nickel ions initial concentration decreases in the system.

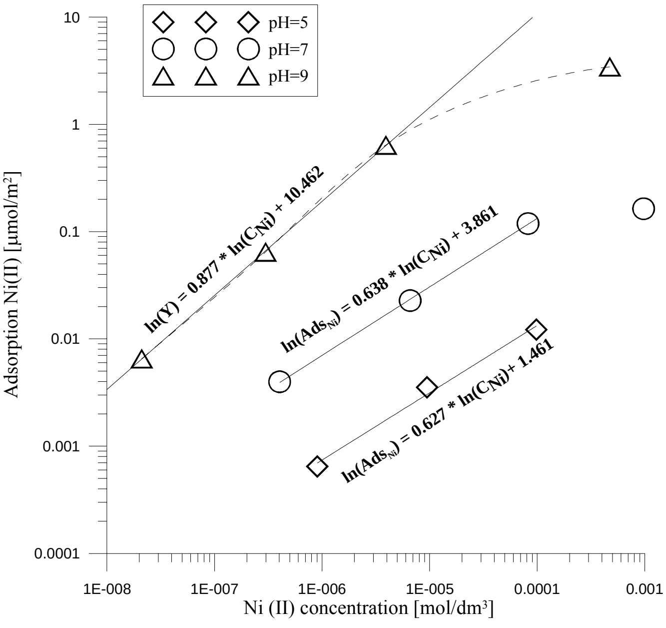

Fig. 4. Adsorption of Ni (II) at Fe_2TiO_5/0.001 NaCl solution interface as a function of equilibrium concentration for selected pH values (5, 7 and 9)

Figure 4 shows the adsorption isotherms of Ni(II) ions for selected pH values (pH=5.7 and 9). For the low concentrations of Ni ions the log-log plot of the isotherm is linear and is characterized by smaller than one slope coefficient. As can be noticed, increase of pH accompanies the increase the slope of the isotherms. Dependence: log number of adsorbed ions nickel vs. log concentration of these ions in solution is called the *Krurbatow plots*. For small concentration of ions it has a linear character, and it is usually described by the Freundlich isotherm.

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 3.

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

Constants	$C_{Ni(II)}$ mol dm^{-3}			
	0.001	0.0001	0.00001	0.000001
pK_1	7.80	5.45	7.27	7.70
$p\beta_2$	9.53	11.65	10.85	11.40

The results of the numerical optimization of Ni ions adsorption at the Fe_2TiO_5/NaCl solution interface as a function of pH show that part of Ni ions is adsorbed by one or two hydroxyl groups.

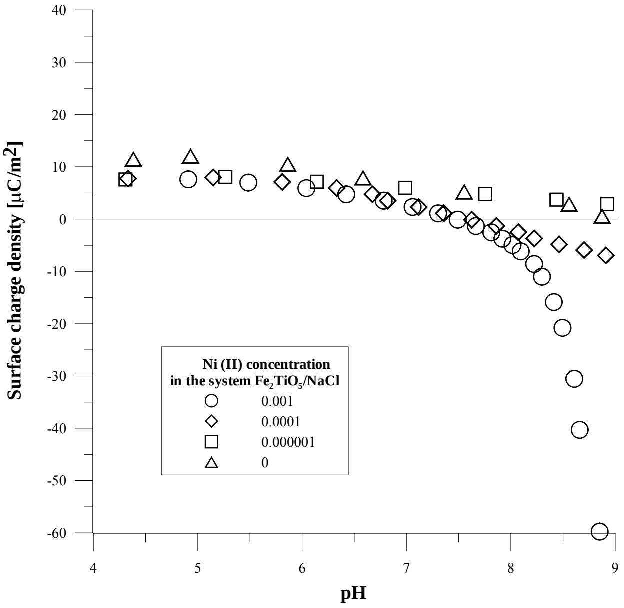

Fig. 5. The surface charge density Fe_2TiO_5 /NaCl solution interface as a function of pH

The surface charge density vs. pH in the presence and absence of Ni (II) ions is shown on Fig. 5. As it can be seen, the surfaces charge density plot for the lowest concentrations of Ni (II) is the same as for the system without nickel ions. The data in Fig. 5 shows that the value of pH_{pzc} is shifted towards lower pH values with the increase of initial concentration of Ni(II) ions. For 0.001 mol/dm^3 concentration of Ni (II) of pH_{pzc} is about one pH unit lower than in Ni (II) free electrolyte solution. For this concentration the adsorption of Ni(II) produces the sharp increase of concentration of negatively charged groups above pH=8. This decrease of surface charge agrees with "adsorption edge" of nickel (II) ions in this pH range (Fig. 3). Assuming that one Ni^{2+} ion exchanges on Fe_2TiO_5 surface one hydrogen atom in one hydroxyl group, for pH=9 recorded adsorption of Ni^{2+} ions is 3.44 μmol/m^2 and should give surface charge density decrease by about 33.2 μC/cm^2. Adsorption of Ni^{2+} ions on two surface hydroxyl groups will cause the decrease twice higher and change of the surface charge density. Because the concentration of negatively charge groups increases about 60 μC/cm^2 as result of adsorption, that means that Ni ions adsorbs mainly on two hydroxyl groups.

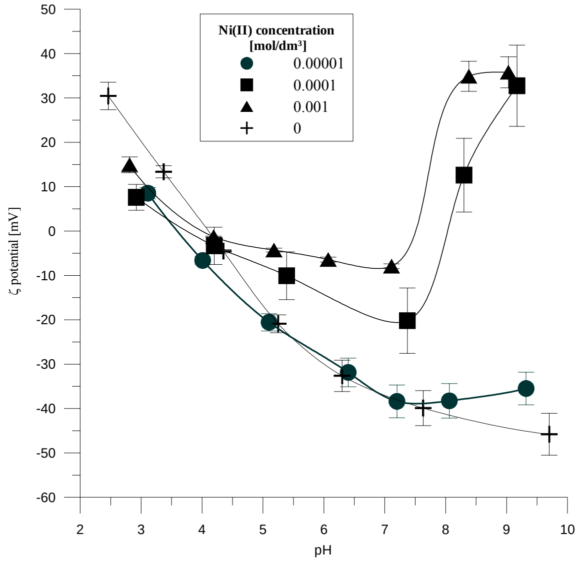

Fig. 6. ζ potential at Fe_2TiO_5 / NaCl solution interface as a function pH

Adsorption of Ni cations leads to the change of the surface hydroxyl group concentration onto the pseudobrookite surface and influences the ζ potential vs pH dependence (Fig. 6). As one can see, the ζ potential decreases with the increase of Ni(II) concentration. For 0.0001M Ni(II) concentration a charge reversal point (CR2) at pH=8.03 is observed. For the highest Ni(II) concentration (0.001M) the CR2 points shifts to pH=7.54.

CONCLUSIONS

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.
2. The adsorption of Ni(II) ions as a function of pH on Fe_2TiO_5 runs similarly as on simple metal oxides. The adsorption process can be characterized by the adsorption edge, which can be described by two parameters: $pH_{50\%}$ and $\Delta pH_{10\text{-}90\%.}$ The parameter characterizing the position of adsorption edge ($pH_{50\%}$) shifts towards higher pH values with the increase of the initial metal concentration.
3. The adsorption isotherms of Ni(II) ions as a function of log adsorption – log concentration are linear. For pseudobrookite the metal adsorption can be fitted by a Freundlich isotherm.
4. The specific adsorption of divalent cations causes a shift of the pH_{IEP} towards alkaline pH values and an increase of the ζ potential. The high concentration of adsorbing Ni(II) cations causes the overcharging of the compact part of edl and position of CR2 point.

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Związki tytanu występujące w postaci dyspersji są stosowane w wielu gałęziach przemysłu. Wśród nich właściwości powierzchniowe zostały dobrze opisane dla ditlenku tytanu, natomiast niektórych związków tytanu są nieznane, należy do nich Fe_2TiO_5 występujący w przyrodzie jako pseudobrukit. Przeprowadzono pomiary adsorpcji jonów niklu, dla jego różnych stężeń początkowych, w funkcji pH dla układu Fe_2TiO_5/roztwór NaCl. Kształt krzywej adsorpcji w funkcji pH ma postać krawędzi adsorpcji. Wzrost stężenia początkowego jonów Ni(II), powoduje przesunięcie krawędzi w kierunku zasadowym skali pH. Wyznaczono charakterystyczne parametry krawędzi adsorpcji tj. $pH_{50\%}$ i $\Delta pH_{10\text{-}90\%}$. W oparciu o zależność adsorpcji od pH stosując model TLM, obliczono również stałe reakcji adsorpcji jonów Ni (II) metodą optymalizacji numerycznej. Zależność gęstości ładunku powierzchniowego od pH w obecności jonów Ni (II), jest w dobrej korelacji z zależnością adsorpcji jonów Ni (II) od pH. Adsorpcja jonów niklu na powierzchni Fe_2TiO_5 prowadzi do wzrostu stężenia grup ujemnie naładowanych.