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Effect of Co(II) ions adsorption in the hydroxyapatite/aqueous $NaClO_4$ solution system on particles electrokinetics

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Abstract: The study of the kinetics and statics of cobalt adsorption at the hydroxyapatite/electrolyte interface using radioactive isotope ^{60}Co was conducted. The course of adsorption kinetics indicates that at the beginning adsorption proceeds quickly and then slowly. Such adsorption kinetics is best described by a multiexpotential equation. The analysis of cobalt adsorption as a function of pH and the results of H^+ ions desorption/adsorption confirmed that cobalt adsorption proceeds due to ion exchange with calcium ions in the crystal lattice and hydrogen ions in the surface groups of hydroxyapatite. Cobalt ions adsorption results in the increase of the electrokinetic potential but for the solution of the initial concentration of 0.001 mol/dm^3 at pH = 8.17 a reversal of the charge due to overloading of the compact layer (edl) is observed.

Keywords: *hydroxyapatite, adsorption Co(II), electrokinetic properties*

1. Introduction

This is our privilege and pleasure to be part of the Festschrift to honor Professor Kazimierz Małysa, the outstanding scientist in the area of physical surface chemistry and his great contributions to the understanding the bubble motion in solution and its interactions with surfaces.

Hydroxyapatite based materials are widely applied in practice. Besides the studies of hydroxyapatite application as a biomaterial, many papers were devoted to studies on adsorption of ions at the hydroxyapatite/electrolyte solution interface system. The presence of microchannels in the crystalline structure of hydroxyapatite causes that it adsorbs partially irreversibly, some cations of the transition metals and anions adsorbing partially irreversibly (Madhavi et al., 2005, Leyvaet et al., 2001, Ma et al., 1994). Studies of transition metal cations adsorption are carried out using hydroxyapatite for removal and immobilization of the ions present in waters and waste waters (Bailliez et al., 2004, Hea et al., 2013). Furthermore, these studies include interactions of ions with hydroxyapatite as a mineral component of bones and teeth (Jones et al., 2001). The hydroxyapatite samples with the transition metal ions (among others cobalt ions) substituted in the lattice were studied as catalysts for chemical syntheses (Venugopal et al., 2003; Elkabouss et al., 2004; Crosmana et al., 2004; Jun et al., 2006; Jaworski et al., 2013; Riad et al., 2013).

Cobalt is a microelement which plays an important role in functioning of human and animal organisms. However, consumption of a too large dose of cobalt is harmful (Siminsen et al., 2012). Cobalt occurs naturally in soil, seawater and atmospheric dusts. Besides it is released into the environment from the metallurgical industry and combustion of coal and oil (Kabata-Pendias et al., 2011). Investigations were also carried out on adsorption of Co^{2+} for samples of biogenic hydroxyapatite considering its efficiency of cobalt ^{60}Co and ^{90}Sr removal from nuclear wastes (Handley- Sidhu et al., 2011). It was proved that the optimal loss of Co^{2+} and Sr^{2+} ions was obtained for the sample of large specific surface area and small sizes of crystals. The studies of mineralization in the hydroxyapatite (HAP)/collagen system in the solution containing transition metal ions showed that Co^{2+} ions are favorable for hydroxyapatite crystallization on collagen sponge (Jia et al., 2013).

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Substitution of cobalt in the crystal lattice instead of calcium causes that hydroxyapatite, being a diamagnetic material, becomes a paramagnetic material, so it can be applied for drug delivery medical imaging and hypothermal treatment of tumors (Kramer et al., 2014). Moreover, hydroxyapatite containing cobalt in the crystal lattice possesses properties which can be useful for production of gas sensors (Mahabole et al., 2013).

Studies of Co^{2+} adsorption, in the range of the initial concentrations from 1×10^{-4} to 1×10^{7} mol/dm^3 at the hydroxyapatite/electrolyte solution interface, carried out by Gomez Del Rio et al. (2004) show that the equilibrium time of kinetics of Co^{2+} adsorption was below 24 hours and that the it proceeds by both ion exchange and adsorption on the surface of the phosphate groups of hydroxyapatite. Studies on Co^{2+} adsorption carried out by Smicklas et al. (2006) stated that adsorption kinetics is well described by the second order equation, with some contribution of the intermolecular diffusion model, whereas the dependence of cobalt adsorption on concentration can be well described by the Langmuir and Dubinin-Kaganer-Radushkevich models. Analysing the dependence of cobalt adsorption as a function of pH function and also from the XRD pattern of HAP with adsorbed Co^{2+}, they found that adsorption proceeds due to exchange of both Ca^{2+} ions from the HAP crystal lattice and H^+ ions from the surface groups of hydroxyapatite. As follows from the studies of Co^{2+} adsorption on hydroxyapatite obtained from bones, kinetics of Co^{2+} adsorption is well described by the second order equation, next by the Freundlich isotherm, and then by the Langmuir one (Pan et al., 2009). They proved that in the studied Co^{2+} concentration range i.e. 7 $\times10^{-3}$ to 1.7 $\times10^{-2}$ mol/dm^3 exchange with Ca^{2+} ions is responsible for adsorption.

The paper presents the results of studies on adsorption kinetics of cobalt ions at the hydroxyapatite/electrolyte solution interface as a function of pH. The experiments were carried out for the following initial concentrations of ions/hydroxyapatite of Co (II): 1×10^{-6}, 1×10^{-5}, 1×10^{-4} and 1×10^{-3} mol/dm^3. Additionally, potentiometric titration of the suspension for determination of Co(II) ions adsorption taking into account the H^+ ions balance in the system as well as measurements of zeta potential using the electrophoresis method were conducted.

2. Experimental

2.1 Materials

Hydroxyapatite was obtained according to the Liu et al. (2003) procedure. A sample of 0.25 mol·dm^{-3} of $(NH_4)_2HPO_4$ (prepared from the analytically pure reagent from POCh was added to 0.5 mol·dm^{-3} of Ca $(NO_3)_2$ solution (prepared from analytically pure $Ca(NO_3)_2{\cdot}4H_2O$ from POCh) with the rate of 1 dm^3 per hour. Such amount of the reagents was used to obtain Ca/P = 1.67. The reaction proceeded at constant temperature and constant pH equal 12 (the pH value was maintained by adding the NH_4OH solution) with continuous stirring. After the addition of the whole amount of ammonium hydrophosphate, the solution was boiled, and then left for another 10 minutes. The obtained precipitate was left for 24 hours, then washed and dried at 60–100 °C. Next, it was calcined at 200 °C. The XRD analysis showed that the obtained sample possessed a crystalline structure of hydroxyapatite. The specific surface area, calculated by the BET method based on the nitrogen adsorption/desorption data, was 158 m^2/g and the average pore radius was 17.03 nm.

2.2 Methods

Adsorption of Co(II) ions was studied by means of the radioactivity loss method using radioactive isotope $^{60}Co^{2+}$. Based on the radioactivity changes before and after adsorption, there was calculated sorption of ions (Γ) on the surface of oxides from the equation:

$$\Gamma = \frac{c_0 V}{m S_w}\left(1-\frac{N_r}{N_0}\right) \tag{1}$$

and

$$c_r = c_0 \frac{N_r}{N_0} \tag{2}$$

where:
c_0 – the initial concentration [mol/dm^3],
V – the volume of solution sample [dm^3],
m – the hydroxyapatite sample weight [g],
S_w –the specific surface area [m^2/g],
N_r – the number of counting's from the source taken up during adsorption,
N_0 - the number of counting's from the source taken up from solution before adsorption,
c_r – the equilibrium concentration [mol/dm^3].

Radioactivity of gamma sources was measured in the scintillation counter Gamma 5500 with the crystal NaI thallium activated. The zeta potential was measured by the electrophoretic method using Zetasizer 3000 of Malvern. In the zeta potential calculations, there was also applied the Henry equation because of $\kappa a \sim 74$. The potentiometric titration method was used to determine the effect of Co(II) ions hydrocomplexes adsorption on the balance of H^+ ions in the hydroxyapatite/ $NaClO_4$ + Co(II) solution system. The potentiometric titration of background electrolyte and suspension was conducted in the Teflon cell equipped with a propeller mixer. The temperature of 25±0.1 °C, was provided by the Lauda RE204 thermostat. The inert atmosphere over the solutions was provided by passing nitrogen free of CO_2. Measurements of pH were made using the Radiometer PHM-240 pH-meter with the indicator pHG201-8 electrode and REF 451 calomel electrode, as the reference. The titrant (NaOH solution) was dosed by means of the Metrohm Dosimat 665 automatic burette. Both devices were connected with a computer which collected the data from the pH meter and burette and steered the burette.

The electron binding energies for the elements were measured with an ultrahigh-vacuum (UHV) setup Prevac, equipped with the hemispherical Scienta R4000 analyser.

3. Results and discussion

3.1 Kinetics of Co(II) adsorption process

Adsorption of Co(II) ions on hydroxyapatite, similarly to that of other ions of transitions metals is a complicated process from the point of view of concentration changes kinetics because it depends on the transport of ion to the solid surface transport in pores and the process of ion exchange in the crystal structure or hydrogen ions in the surface groups of hydroxyapatite. As adsorption is dependent on Ca^{2+} and H^+ ions concentration, which is connected with the dissolution reactions, the description of the process kinetics is complicated. As mentioned above, the adsorption kinetics was described by the second order equation and a intramolecular diffusion equation.

Figure 1 presents the kinetics of Co(II) ions adsorption from the solution of the initial concentration 1×10^{-3} mol/dm^3 on hydroxyapatite. As can be seen, the best fit to the experimental data of Co(II) adsorption was obtained using the multiexponential model (Marczewski, 2007; Deryło-Marczewska et al., 2010):

$$\frac{c}{c_0} = A_0 + \sum_{i=1}^{n} A_i \exp(-k_i t) \quad where \;\; A_0 + \sum_{i=1}^{n} A_i = 1\,, \tag{3}$$

$$\frac{a}{a_{eq}} = 1 - \frac{\sum_{i+1}^{n} A_i \exp(-k,t)}{\sum_{i+1}^{n} A_i} = 1 - \frac{\sum_{i=1}^{n} A_i \exp(-k,t)}{1-A_0} = 1 - \sum_{i=1}^{n} \frac{A_i}{1-A_0} \exp(-k_i t), \tag{4}$$

where:
a - the adsorption,
a_{eq} - the equilibrium adsorption,
c_0 - the initial concentration,
A_0 - the relative equilibrium concentration,
A_i - describes the part of the i-th process characterized by the coefficient k_i.

The dependences shown in Fig. 1 indicate that for the initial concentration of Co(II) ions 1×10^{-3} mol/dm^3 the adsorption process does not reach equilibrium during 100 min, contrary to the system of the initial concentration 1×10^{-4} mol/dm^3, where the equilibrium was reached after 30 min. For the initial concentration 1×10^{-4} and 1×10^{-3} mol/dm^3 of Co(II) ions the dependence of adsorption as a function of time is the best described by the multiexponential model. This proves that the adsorption process is a multistage one: after fast adsorption, a slow one follows which is connected with penetration and exchange of Co(II) ions in the crystal lattice of hydroxyapatite

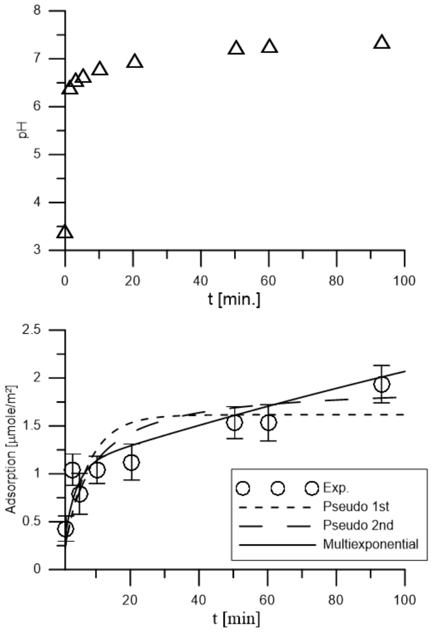

Fig. 1. Kinetics of changes of suspension pH and Co(II) ions adsorption on hydroxyapatite from the solution of the initial Co(II) ions concentration 0.001 mol/dm^3. The points indicate the experimental data, the short-dashed line - the first order model for $q_e = 0.285$ and $k_1 = 0.857$, the long-dashed line – the second order model for $q_e = 0.298$ and $k_2 = 5.423$, the continuous line – the multiexponential model: a_e=0.307, $A_0 = 0.0057$, $k_1 = 1.370$, $A_1 = 0.790\times10^{-5}$, $k_2 = 0.0029$, $A_2 = 0.132$

3.2 Adsorption of Co(II) ions

Adsorption of Co(II) ions on hydroxyapatite as a pH function is limited to the pH range from 6 to 10 due to significant solubility of hydroxyapatite beyond this pH range. On the other hand, Co(II) ions in aqueous solutions have the hydroxycomplex forms (Martel et al., 1989), of which two in the studied pH range play a dominant role. Up to pH = 9.3 simple Co(II) ions are the dominant from in the solution and above this value the main soluble form is $Co(OH)_2$ (Smiciklas et al., 2006). Simple Co(II) ions can adsorb on the functional groups of hydroxyapatite (-OH or -PO_4H) and exchange Ca^{2+} ions in the crystal structure of hydroxyapatite. The undissociated form of cobalt hydroxide, which is dominant above pH = 9.3, can undergo physical adsorption or adsorb specifically on the surface groups. The studies of electrokinetic potential as a function of pH show that above $pH_{iep} = 5$, the hydroxyapatite surface is negatively charged (Janusz et al., 2016) and therefore the electrostatic interaction of simple ions of cobalt and surface charge will promote adsorption of these ions.

The dependences of Co(II) ions adsorption from the solutions of the concentrations 1×10^{-6} and 1×10^{-3} mol/dm^3 which are presented in Figures 2 and 3, respectively, as a function of pH at the hydroxyapatite solution 0.001 mol/dm^3 $NaClO_4$ interface show a different course. Adsorption from the solution of the lowest initial concentration i.e. 1×10^{-6} mol/dm^3 depends on pH to a small extent and the whole amount of Co(II) is practically adsorbed from the solution. As follows from the diagram of hydroxyapatite solubility in the studied pH range 7.5-10, Co(II) ions concentration decreases (Pan et al., 2009). If the adsorption proceeded by the ion exchange of Co^{2+} from the solution and Ca^{2+} from hydroxyapatite, then the adsorption increase should be observed in the studied pH range. The observed adsorption dependence can be related to the exchange of H^+ ions in the surface (hydroxyl and phosphate) groups of hydroxyapatite as above pH = 7 the concentration of H^+ ions is many-fold lower than that of Co(II). The adsorption of Co(II) ions from the solution of the initial concentration 1×10^{-3} mol/dm^3 (Fig. 3) increases in the pH range from 7.5 to 9.5. The dependence shape reminds the edge of cations adsorption on metal oxides but at the lowest pH value is equal to 6.8 that is about 30%

of the initial number of Co(II) ions adsorbs, but at pH = 9.5 about 4% of ions remains in the solution. Taking into account the OH groups concentration on the hydroxyapatite surface (Skartsila et al., 2007), in the case of combination the surface concentration of the $\equiv SO^-Co^{2+}$ groups, it corresponds to the coverage with a monolayer (4.27 μmol/m^2), however for the $(\equiv SO^-)_2Co^{2+}$groups (with the adsorption of one Co(II) ion on two surface hydroxyl groups) it is 2.14 μmol/m^2. Thus in the case of Co(II) adsorption on one surface hydroxyl group of hydroxyapatite, according to the site binding theory more Co(II) ions should adsorb above pH = 9.5. If adsorption proceeded on two OH groups, then the coverage corresponding to the adsorption monolayer would be larger and other mechanisms would be responsible for the adsorption process. Additionally, hydroxyapatite has phosphate groups which concentration is 5.12 μmol/m^2 and Ca^{2+} ions with concentration of 8.51 μmol/m^2 (Kurkura et al., 1972). Co^{2+} ions may exhibit great affinity for phosphate groups and undergo ion exchange with calcium ions on the hydroxyapatite surface. Thus, the number of adsorption sites accessible on the hydroxyapatite surface is significantly larger at pH above 9.5 from the solution of the initial concentration 1×10^{-3} mol/dm^3. Adsorption on surface groups and ion exchange adsorption were proposed by Gomez del Rio et al. (2004).

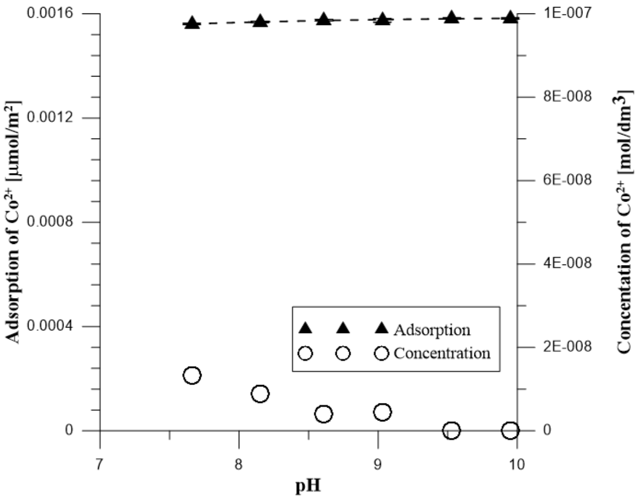

Fig. 2. Adsorption of Co(II) ions/hydroxocomplexes from the solution of the initial Co(II) ions concentration 1×10^{-6} mol/dm^3 as a function of pH at the hydroxyapatite/0.001 mol/dm^3 $NaClO_4$ solution

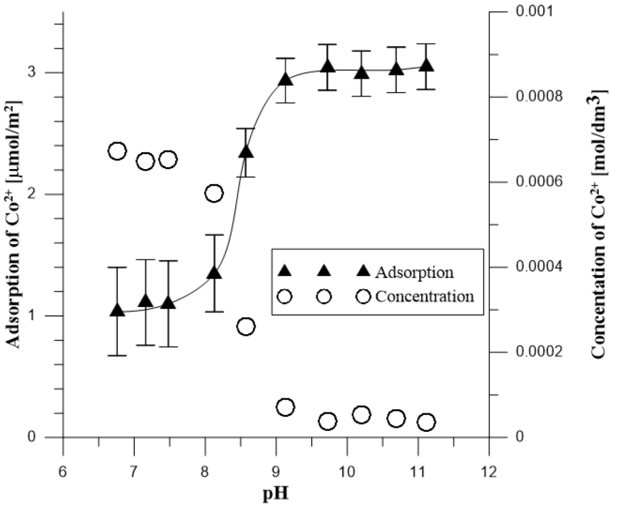

Fig. 3. Adsorption of Co(II) ions/hydroxycomplexes from the solution of the initial Co(II) ions concentration 1×10^{-3} mol/dm^3 as a function of pH at the hydroxyapatite/0.001 mol/dm^3 $NaClO_4$ solution

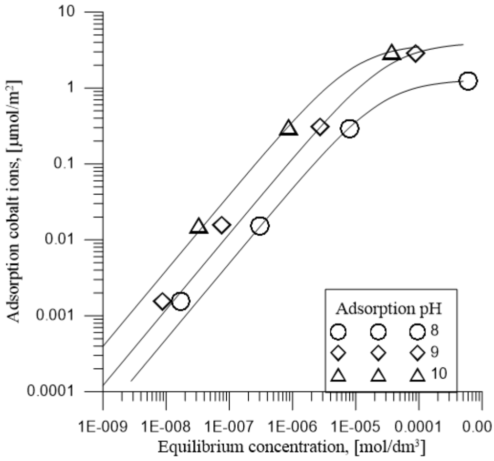

Fig. 4. Adsorption of Co ions on hydroxyapatite from the 0.001 mol/dm^3 $NaClO_4$ solution as a function of equilibrium concentration of Co (II) ions. The points indicate the experimental data of adsorption and the lines show the course of Langmuir isotherms

Figure 4 shows the isotherm of Co(II) ions adsorption on hydroxyapatite for the three values of pH (8, 9 and 10). In the studied range of concentrations the tendency of cobalt ions for saturation of adsorption site on the hydroxyapatite surface was observed. Linear Langmuir isotherm is characterized by a high correlation coefficient for the lowest pH but with its increase the correlation coefficient slightly decreases. In the range of low concentrations, the log-log adsorption vs. concentration plot has a linear course and the direction coefficient indicates that the adsorption proceeds on the surfaces of energetically heterogeneous adsorption sites (Stumm et al., 1992). The formal coverage with a monolayer for pH 8, 9 and 10 calculated from the Langmuir isotherm is 1.31, 3.62 and 3.47 µmol/m^2, respectively.

The effect of cobalt adsorption on the dependence of hydrogen ions consumption/release is presented in Fig. 5. As can be seen cobalt adsorption from the solutions of the initial concentration smaller or equal 1×10^{-4} mol/dm^3 does not cause significant changes in consumption/release of hydrogen ions. Just cobalt ions adsorption from the solution of the cobalt initial concentration 1×10^{-3} mol/dm^3 results in the significant ions release. Comparison of Co(II)ions adsorption from the solution of the Co ions initial concentration 0.001 mol/dm^3 (Fig. 3) with H^+ ions desorption (Fig. 5) shows that at pH = 8.5 each adsorbing Co^{2+} ion releases statistically 0.2 H^+ ion. The amount of released ions increases with the increasing pH and reaches the value 0.84 for pH = 10.2. If follows that at lower pH values adsorption proceeds mainly due to the Co^{2+}/Ca^{2+} ion exchange. Every fifth Co^{2+} ion takes part in adsorption on the hydroxyapatite surface groups. The situation is reversed in a more alkaline medium.

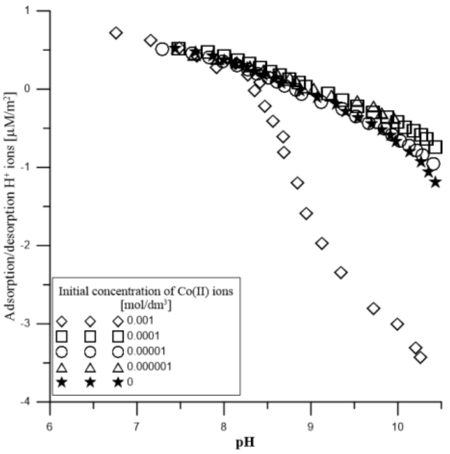

Fig. 5. Balance of bound or released H^+ ions due to Co ions adsorption on hydroxyapatite

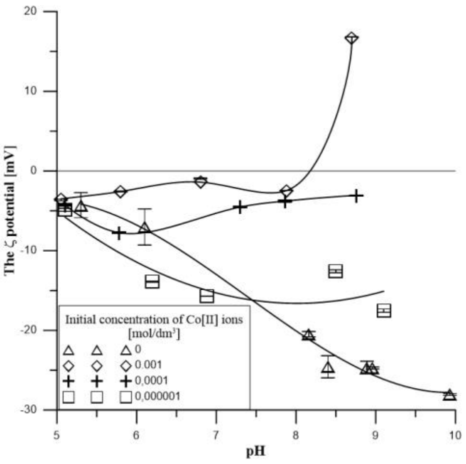

Fig. 6. Influence of cobalt adsorption on the dependence of zeta potential on pH in the hydroxyapatite/aqueous solution 0.001 mol/dm³ $NaClO_4$ system

Figure 6 presents the effect of cobalt ions adsorption on the dependence of zeta potential as a function of pH. A significant effect of cobalt adsorption in the zeta potential increase was observed in the systems of the initial concentrations 0.0001 and 0.001 mol/dm³ of the cobalt ions/hydroxycomplexes. For the highest concentration, the charge reversal from negative to positive is found at pH=8.17. This can be a result of overcharging of the compact layer of the double electrical layer by the adsorption of Co^{2+} ion on the surface group while forming the $\equiv O^{-}Co^{2+}$ type group (Scindler, 1981).

The high resolution XPS method was applied to study the hydroxypapatite sample with the absorbed Co(II) ions from solution of the initial concentration 0.001 mol/dm³ of cobalt ions. The survey of the XPS spectrum revealed the presence of C, O, Ca, P and Co. Figure 7 shows the spectrum of Co 2p3/2 and its analysis reveals peaks at 781.3, 783.1, 786.9 and 791.3 eV. The peak position is in good agreement with the literature data (Biesinger et al., 2011) The peak 781.3 corresponding to Co^{2+} exchanging into Ca^{2+} in the HAP lattice.

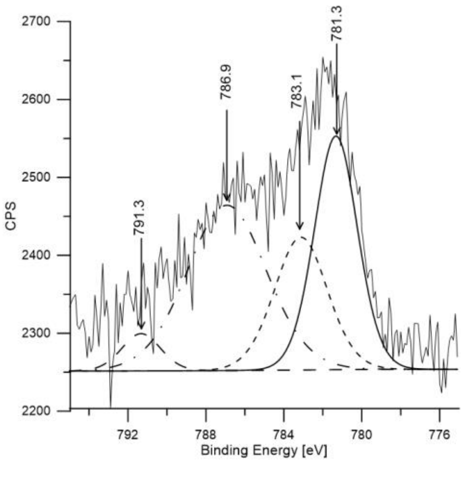

Fig. 7. XPS spectrum of Co 2p 3/2 region of hydroxyapatite with Co^{2+} adsorbed from solution of initial concentration of 0.001 mol/dm³

4. Conclusions

The time of equilibrium time of Co^{2+} ions adsorption on hydroxyapatite for 0.0001 mol/dm³ solution is 30 min and increases with the increasing cobalt initial concentration. For the solution of the concentration of 0.001 mol/dm³ adsorption is established after 100 min. The course of process kinetics indicates that at the beginning adsorption proceeds quickly and then slowly. Such adsorption kinetics is best described by a multiexpotential equation. The analysis of cobalt adsorption as a function of pH and the results of H^+ ions desorption/adsorption confirm that cobalt adsorption proceeds, due to ion exchange with calcium ions in the crystal lattice and hydrogen ions in the surface groups of hydroxyapatite. Cobalt ions adsorption results in the increase of electrokinetic potential but for the solution of the initial concentration of 0.001 mol/dm^3 at pH=8.17, reversal of the charge due to overloading of the compact layer edl is observed.

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