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## The effect of hydrothermal modification of titanium phosphate on the adsorption affinity towards cadmium ions

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**Abstract:** The effect of hydrothermal treatment of the gel or xerogel of titanium phosphate (TiP) sample on the surface properties was studied using the EDS and FTIR ATR methods. The results show that the hydrothermal treatment of initial titanium phosphate decreases the amount of physically adsorbed water but increases the surface concentration of phosphate groups. Supplementary measurements of electrokinetic properties of modified and hydrothermally modified titanium phosphate samples confirmed an increase of the concentration of acidic groups on the TiP surface. The adsorption affinity of titanium phosphate towards cadmium ions was discussed. It was found that at a low initial concentration of cadmium ions adsorption affinity increases as a result of hydrothermal treatment of TiP gel.

**Keywords:** titanium phosphate, FTIR ATR, hydrothermal treatment, adsorption, cadmium ions

### 1. Introduction

Removal of heavy metal ions from industrial wastewaters is still a growing problem due to the rapid development of industries that manufacture these elements and then discharge them into the environment (Atkowska et al., 2018; Fu et al., 2011). Among them there are potentially toxic elements like cadmium ions, that can enter the food chain and accumulate in the human body causing serious diseases including cancer (Bernard, 2008). The methods used to remove heavy metal ions from wastewaters include chemical precipitation, ion exchange, reverse osmosis, coagulation, extraction, adsorption, membrane filtration and electrochemical treatment (Hua et al., 2012; Wang et al., 2012). Adsorption, in most cases, is considered as one of the methods that is characterized by high efficiency, low cost, multiple use and easy operation (Hua et al., 2012). On the other hand, this method is sometimes confined to removal of heavy metal ions due to low sorption capacity of adsorbents (Wang et al., 2012). Therefore, extensive studies of new adsorbents are carried out to find materials with strong adsorption affinity and sorption capacity. Another aspect is related to the development of new, low cost adsorbents originating from agricultural wastes, natural materials or polymers (Bakarat, 2011). The tetravalent metal phosphates exhibit very interesting properties as adsorbents due to their high cation exchange capacity, ions selectivity, chemical stability and temperature resistivity (Parida et al., 2004). Their adsorption properties were studied for several heavy metal ions (Parida et al., 2004; Sahu et al., 2002; Jia et al., 2008; Chowdhury et al., 2016).

This paper presents the comparison of the acidity of surface groups and Cd<sup>2+</sup> ions adsorption study on hydrothermally and mechanically modified titanium phosphate (TiP) which belongs to the most efficient ion exchangers (Sahu et al., 2002; Jia et al., 2008; Chowdhury et al., 2016). However, the effect of hydrothermal treatment (HTT) of TiP, on its adsorption properties with respect to cations was studied previously. The composition, porous and crystalline structure of the studied titanium phosphate samples were discussed in our previous paper in details (Janusz et al., 2019).

## 2. Materials and methods

### 2.1. Materials

The amorphous titanium phosphate sample (denoted as initial) prepared by means of precipitation from titanyl sulfate, was modified and characterized using the earlier experimental procedure (Janusz, 2019). The sample, hydrothermally treated in the form of a wet gel at 200 °C was designated as HTT-gel-200 and the samples hydrothermally modified in the form of dried xerogel at 200 °C or 300 °C were designated as HTT-xero-200 and HTT-xero-300, respectively. The full surface characteristics of the adsorbents tested can be found in Janusz et al., 2019.

### 2.2. EDS analysis

The titanium samples were covered with a conductive carbon coater, mounted in the specimen holder and transferred to the Quanta 3D FEG scanning electron microscope, FEI Company. The qualitative and quantitative surface analysis of the main elements of titanium phosphate samples were conducted from the EDS spectra collected using the FEI Quanta 3D FEG scanning electron microscope equipped with the EDS spectrometer.

### 2.3. FTIR ATR analysis

The FTIR ATR spectra of the samples were recorded using FTIR Nicolet 8700A Thermo Scientific with the Smart Orbit TR diamond ATR attachment, at room temperature in the region 400-4000 cm<sup>-1</sup>. Graphical deconvolution of the complex spectral bands into their components was performed using the Origin program.

### 2.4. Electrophoretic measurements

The electrophoretic measurements of initial and modified TiP samples in the 0.001 mol/dm<sup>3</sup> NaCl solution were performed using Zetasizer Nano-ZS, Malvern. The zeta potentials for all samples (except HTT-xero-300) were calculated according to the recommendation IUPAC Technical Report (Delgado et al., 2007) by means of the Smoluchowsky equation because of  $\kappa a > 150$  (where;  $a$  is the particle radius and  $\kappa$  is the Debye-Huckel parameter). Due to a small diameter of HTT-xero-300 particles (Janusz, 2019), the Henry equation for the zeta potential was used. The pH value of titanium phosphate suspension was adjusted using 0.1 mol/dm<sup>3</sup> HCl or 0.1 mol/dm<sup>3</sup> NaOH solution and controlled using pHM-240 with the connected glass and calomel electrodes.

### 2.5. Adsorption of Cd<sup>2+</sup> ions

Adsorption of Cd<sup>2+</sup> ions was studied by means of the radioactivity loss method using the radioactive isotope <sup>133</sup>Cd<sup>2+</sup>. Based on the radioactivity changes before and after sorption of Cd<sup>2+</sup> ions on the surface of titanium phosphate samples efficiency of adsorption was calculated, the details of the method are described in the literature (Janusz, 2018). To compare the adsorption affinity, 0.275, 0.306, 0.593, 0.118, 0.281 g of the initial samples (HTT-gel-200, HTT-xero-200, HTT-xero-300), was added to the 50 cm<sup>3</sup> of cadmium ions solution, so that the ratio of the adsorbent surface area to the solution volume was the same. Radioactivity of the solutions before and after adsorption processes was measured using the liquid scintillation counter LS 5000 TD Beckmann.

## 3. Results and discussion

The hydrothermal treatment of the initial titanium phosphate sample leads to transformation of the amorphous structure to the crystalline one as it was shown earlier. The XRD analysis results show the presence of two crystalline phases of titanium phosphates (titanium oxide phosphate hydrate and titanium oxide phosphate) with titanium dioxide of anatase structure (Janusz et al., 2019). It should be noted that interfacial properties of titanium phosphates primarily depend on the surface layer composition and the presence of surface groups that may have different adsorption affinity for the metal (cadmium) ions. The results of the EDS analysis of the studied samples are presented in Table 1. As it

can be seen, besides O, P and Ti there is a small amount of Si as impurity, because synthesis and hydrothermal treatment were carried out in a glass or quartz vessels. The hydrothermal treatment of the initial gel sample at 200 °C leads to an increase of phosphorous content but to a decrease of titanium content, the sample designated HTT-gel-200. Whereas after hydrothermal treatment of the dried initially samples, at 200 °C or 300 °C (designated HTT-xero-200 or HTT-xero-300, respectively), the P content increases and that of Ti changes slightly. However, at 200 °C it decreases but at 300 °C it increases of a few decimal percent. The observed increase of P content on the surface of titanium phosphate sample should enhance the acidic properties of the surface titanium groups.

Table 1. The results of EDS analysis of titanium phosphate samples

Element	Concentration (%)			
	Initial	HTT-gel-200	HTT-xero-200	HTT-xero-300
O	40.2	43.9	40.0	37.5
Si	0.1	0.2	0.3	0.1
P	16.8	19.1	19.6	20.4
Ti	40.7	36.7	40.1	41.9

The normalized FTIR-ATR spectra of the initial sample, the gel sample hydrothermally modified at 200 °C and xerogel titanium phosphate sample hydrothermally modified at 200 °C and 300 °C are shown in Fig. 1. One can observe an evolution of the bands in the regions of 3700-2500  $\text{cm}^{-1}$ , 1300-500  $\text{cm}^{-1}$  and 1800-1300  $\text{cm}^{-1}$  as the effect of the hydrothermal treatment of TiP samples. Significant changes in the FTIR spectrum of the TiP samples are observed in the regions of 3700-2500  $\text{cm}^{-1}$  and 1800-1300  $\text{cm}^{-1}$ , and are associated with the stretching and bending modes of surface hydroxyl groups and adsorbed water molecules, respectively (Benmokhtar et al., 2007; Stanghellini, 2004; Bao et al., 2011). Analyzing the hydroxyl groups and water adsorbed on the anatase surface (a broad band in the range of 3700-3000  $\text{cm}^{-1}$ ), Soria et al. found several overlapped bands that may be assigned to the weakly adsorbed water – the second layer water bonded to that coordinated to  $\text{Ti}^{4+}$  cations (Soria et al., 2007). The baseline correction and curve fitting analysis of the broad band of titanium phosphate samples in the range of 3700-2400  $\text{cm}^{-1}$  were performed using the Origin program. Deconvolution using the Gauss function revealed four overlapped bands for the initial, HTT-gel-200 and HTT-xero-200 samples and three bands for HTT-xero-300 (Fig. 2). Table 2 presents the information about the number of curves, peak position and peak area. For the HTT-xero-300 sample (Fig. 2), instead of the peaks at  $\sim 3450 \text{ cm}^{-1}$  and  $\sim 3550 \text{ cm}^{-1}$ , two small bands at 3698  $\text{cm}^{-1}$  and 3728  $\text{cm}^{-1}$ , were observed. They correspond to the vibrations of isolated OH groups that may be formed due to the dehydroxylation of HTT-xero-300 surface during the hydrothermal treatment. The hydrothermal treatment of the initial gel or xerogel of titanium phosphate samples leads to a significant decrease of peak areas at  $\sim 3033 \text{ cm}^{-1}$  and  $\sim 3300 \text{ cm}^{-1}$  (Table 2), which is connected with the loss of physically adsorbed water in the form of multilayer. Water desorption during the hydrothermal treatment can be also proved by a decrease of an intensity of the band at  $\sim 1627 \text{ cm}^{-1}$  (Fig. 1). For the initial xerogel sample hydrothermally treated at 300 °C, dehydroxylation causes formation of the surface Ti-O-Ti groups with a characteristic band at 1526  $\text{cm}^{-1}$ . Figure 3 illustrates the comparison of the peak area at  $\sim 3300 \text{ cm}^{-1}$  (peak no. 2) with the mass loss noted in TG curve at 300 °C. The TG data taken from (Janusz et al., 2019). There is a linear relationship which was observed for the other systems, where physical adsorption of water takes place (Gallego-Gomez et al., 2011). The interception of the linear course ( $\sim 36 \text{ au}$ ) is connected with crystalline water not desorbed at 300 °C and remaining in the solid phase (structure).

The hydrothermal treatment of the initial gel and xerogel of titanium phosphate samples changes the FTIR ATR spectra in the range from 1300 to 700  $\text{cm}^{-1}$  (Fig. 1). The deconvolution of the spectra in this range reveals several peaks characteristic for phosphate groups (Figs. 4a-d and Table 3). Thus, the hydrothermal treatment of gel or xerogel at 200 °C leads to small changes in the vibration and bending bands characteristic for phosphate groups. The sharp band in the range of 1100-800  $\text{cm}^{-1}$  consists of 3 peaks (peaks No. 5, 6 and 7) associated with the asymmetric vibrations of  $(\text{O}_3\text{POH})^-$  and  $(\text{O}_2\text{P}(\text{OH})_2)^-$  groups. An increase of their area can be observed for the HTT-gel-200 and HTT-xero-200 samples in comparison to that of the peaks for the initial titanium phosphate sample. For the xerogel sample

hydrothermally treated at 300 °C the band at 1100-800  $\text{cm}^{-1}$  is a little wider and it is composed of 5 peaks also associated with the asymmetric vibrations of phosphate groups. This effect may result from a higher degree of crystallinity of the sample (Stanghellini et al., 2004). The analysis of the XRD pattern of HTT-gel-200, HTT-xero-200 and HTT-xero-300 in the  $2\theta$  range of 20-34°, using the Watsfix software developed by Rabiej (2003), reveals the following crystallinity degrees: 0.56, 0.61 and 0.93, respectively. The initial sample of titanium phosphate was amorphous. The difference in crystallinity degree of HTT-gel-200 and HTT-xero-200 samples is small. As a result, the spectra in the 1300-500  $\text{cm}^{-1}$  range do not differ much for these samples.

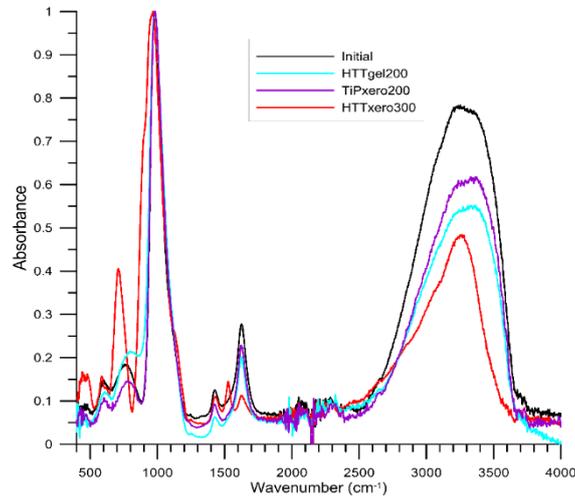


Fig. 1. FTIR ATR spectra of the initial and hydrothermally modified titanium phosphate samples

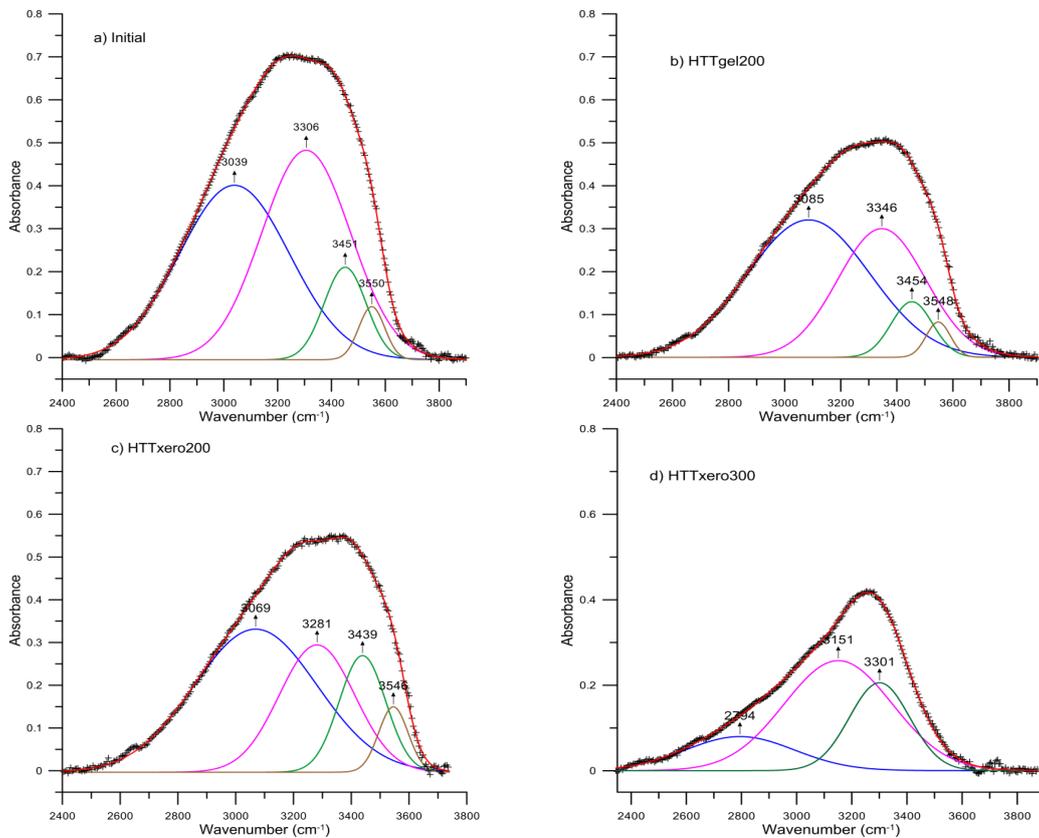


Fig. 2. Curve fitting results for the FTIR ATR spectra in the range of 3850-2400  $\text{cm}^{-1}$ : a) initial titanium phosphate sample, b) HTT-gel-200, c) HTT-xero-200, d) HTT-xero-300. The red line represents the sum of peaks, symbols 1 of 10 the experimental points of spectrum

Table 2. The wavenumbers of peak center (xc) and surface area (A) in the range of 3700-3000  $\text{cm}^{-1}$  read from the FTIR ATR spectra of the titanium phosphate samples

Peak no.	Initial		HTT-gel-200		HTT-xero-200		HTT-xero-300		Initial sample heated at 300 °C	
	xc ( $\text{cm}^{-1}$ )	A	xc ( $\text{cm}^{-1}$ )	A						
1	3039	208.2	3085	176.0	3069	178.6	3151	126.2	3033	10.5
2	3306	201.5	3346	117.3	3281	97.5	3301	56.2	3234	49.4
3	3451	42.3	3453	24.0	3439	55.2			3477	31.0
4	3550	1.6	3548	8.9	3546	19.5				

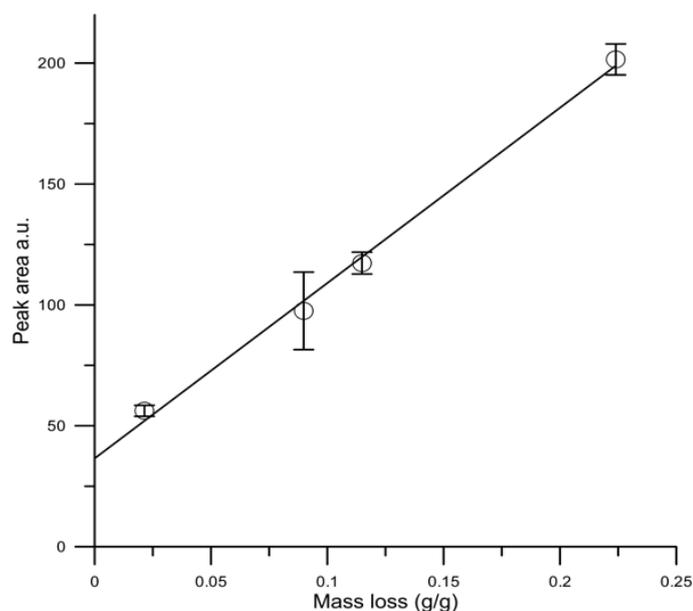


Fig. 3. The area of peak at  $\sim 3300 \text{ cm}^{-1}$  as a function of the mass loss of titanium phosphate samples at 300 °C

Table 3. The wavenumbers of peaks center (xc) and surface area of peaks (A) in the range of 400-1350  $\text{cm}^{-1}$  read from the FTIR ATR spectrum of titanium phosphate samples

Peak no.	Sample								Vibrational character (Stanghellini et al., 2004)	Unit (Stanghellini et al., 2004)
	Initial		HTTgel200		HTTxero200		HTTxero300			
	xc ( $\text{cm}^{-1}$ )	A								
1	600	5.4	595	5.2	604	3.5	591	3.7	$\delta(\text{P-O-H})$	$(\text{O}_2\text{P}(\text{OH})_2)^-$
2	761	21.1	806	44.7	783	18.5	718	30.4	$\nu(\text{Ti-O})$	Ti-O
3							887	27.2	$\delta(\text{P-O-H})$	$(\text{O}_2\text{P}(\text{OH})_2)^-$
4							937	2.1	$\nu_{\text{as}}(\text{P-O})$	$(\text{O}_3\text{POH})^-$
5	967	26.3	968	22.3	968	30.6	965	96.4	$\nu_{\text{as}}(\text{P-O})$	$(\text{O}_3\text{POH})^-$
6	1001	59.4	1007	93.4	1005	61.8	1052	33.0	$\nu_{\text{as}}(\text{P-O})$	$(\text{O}_2\text{P}(\text{OH})_2)^- + (\text{PO}_4)$
7	1088	28.7	1118	19.3	1088	35.4	1142	14.0	$\nu_{\text{as}}(\text{P-O})$	$(\text{O}_2\text{P}(\text{OH})_2)^-$

The electrokinetic potential vs. pH, measured in 0.001  $\text{mol}/\text{dm}^3$  aqueous solution of NaCl, for initial and hydrothermally modified titanium phosphates is presented in Fig. 5. As it can be seen, the initial sample of titanium phosphate, above  $\text{pH}=4.03$  ( $\text{pH}_{\text{iep}}$ ), exhibits negative values of the zeta potential which decrease with increasing pH values. For the initial and HTT-xero-300 samples the  $\text{pH}_{\text{iep}}$  may be

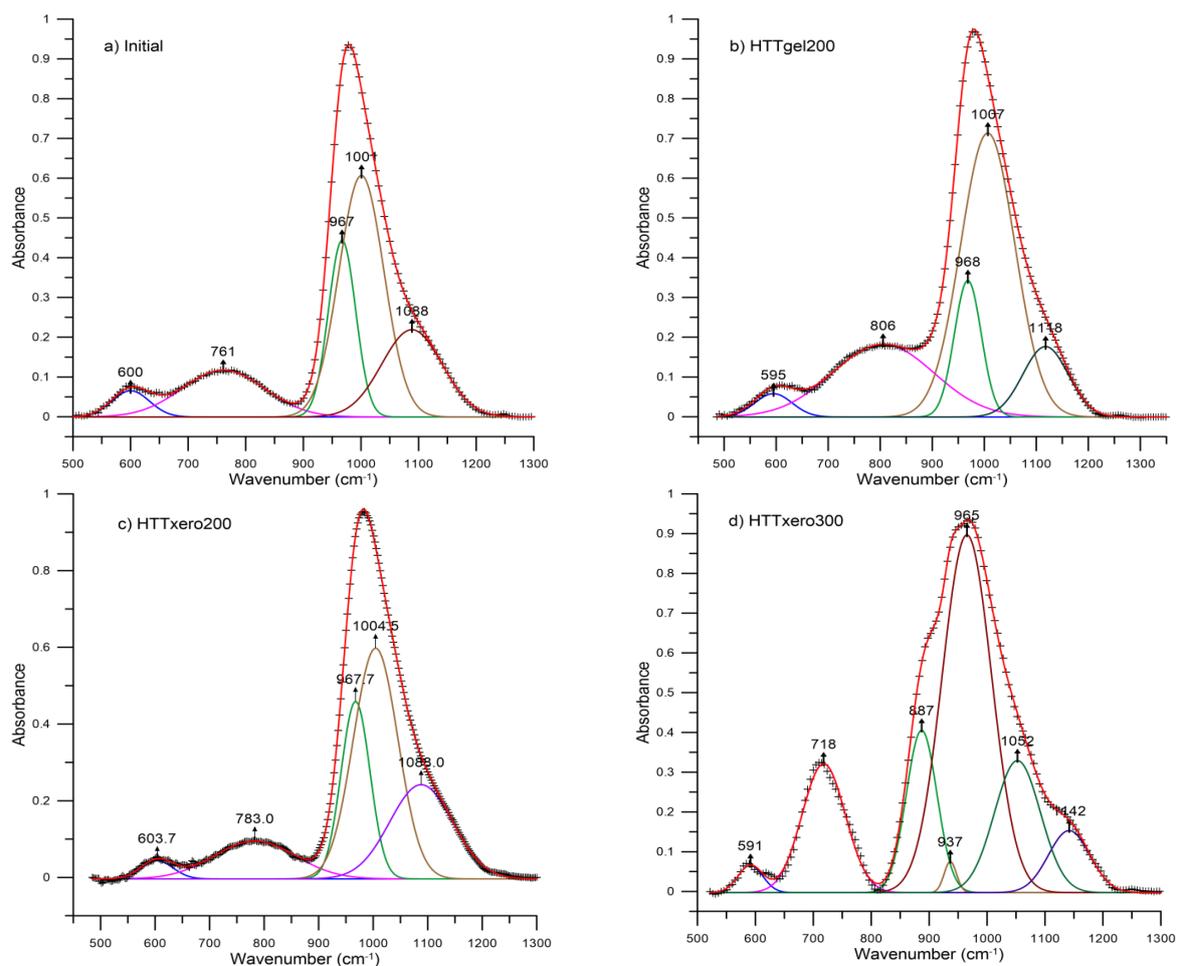


Fig. 4. Curve fitting results for the FTIR ATR spectrum in the range of 400-1350  $\text{cm}^{-1}$ : a) the initial titanium phosphate sample, b) HTT-gel-200, c) HTTxero-200, d) HTTxero-300. The red line represents the sum of peaks, symbols 1 of 10 the experimental points of spectrum

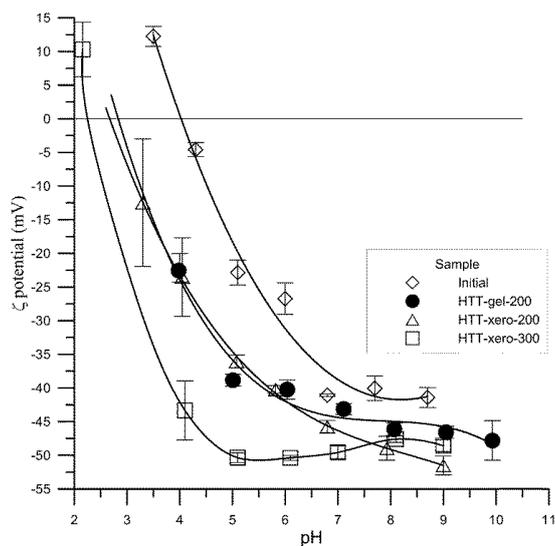
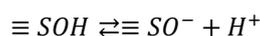


Fig. 5. The electrokinetic potential as a function of pH for the hydrothermally modified initial titanium phosphate sample

easily determined because besides negative values of the zeta potential also positive ones were noted. For the others, only extrapolation of zeta potential as a function of pH allows to estimate  $\text{pH}_{\text{iep}}$ . The

values of  $\text{pH}_{\text{iep}}$  for initial, HTT-gel-200, HTT-xero-200 and HTT-xero-300 are 4.0, 2.8, 2.7 and 2.3, respectively. The hydrothermal treatment of titanium phosphate samples also affects the shift of zeta potential towards lower values of pH. This is due to the presence of more acidic groups on the surface of hydrothermally treated titanium phosphate samples. According to the EDX data, they can be additional P-OH groups. Based on the zeta potential vs. pH data, the values of ionization constants of groups on the surface of titanium phosphate in 0.001 mol/dm<sup>3</sup> NaCl, were calculated applying the method proposed by Sprycha (1984). The obtained values of  $\text{pK}_{\text{a}2}$  for initial, HTT-gel-200, HTT-xero-200 and HTT-xero-300 are 7.5, 5.8, 5.9 and 5.9, respectively. The values of the ionization constants  $\text{pK}_{\text{a}2}$  of the reaction:



increase for the samples subjected to hydrothermal treatment as compared to the initial one. This indicates that, according to the above-mentioned reaction, the ionization of surface groups will be favoured for these sample (Table 4).

Table 4. The values of the isoelectric point and the ionization constant  $\text{pK}_{\text{a}2}$  of the surface groups determined applying the Sprycha method (Sprycha et al., 1984)

	Sample	$\text{pH}_{\text{iep}}$	$\text{pK}_{\text{a}2}$
1	Initial	4.0	7.5
2	HTT-gel-200	2.8	5.8
3	HTT-xerogel-200	2.7	5.9
4	HTT-xerogel-300	2.3	5.9

The study concerning adsorption of  $\text{Cd}^{2+}$  ions on the titanium phosphate surface was carried out up to  $\text{pH}=8$  because up to  $\text{pH}=9.5$  the  $\text{Cd}^{2+}$  ions are a predominant form of cadmium species in the aqueous solution at the highest initial concentration of  $\text{Cd}^{2+}$  ions i.e. 0.001 mol/dm<sup>3</sup>. At pH above 9.5 the precipitation of cadmium hydroxide can take place. Adsorption of  $\text{Cd}^{2+}$  ions on the titanium phosphate surface may result from the interactions of cadmium ions with the hydroxyl groups bonded to titanium atoms and with hydrophosphate groups. In both cases the adsorption of cadmium ions proceeds via release of protons so it should increase with increasing pH values. However, affinity of cadmium ions for the hydroxyl and hydrophosphate groups should be different.

The effect of hydrothermal treatment of initial titanium phosphate on its affinity towards  $\text{Cd}^{2+}$  ions is presented in Figs. 6-7 (initial concentration of  $\text{Cd}^{2+}$  ions equal to 0.000001 mol/dm<sup>3</sup>, 0.00001 mol/dm<sup>3</sup>, 0.0001 mol/dm<sup>3</sup> and 0.001 mol/dm<sup>3</sup>, respectively). As it can be seen from Figs. 6a and b, the hydrothermal treatment of the initial titanium phosphate samples increases cadmium ions adsorption affinity for the titanium phosphate samples –  $\text{Cd}^{2+}$  ions adsorb strongly from the solution of  $\text{pH}<4$  – ~95% of  $\text{Cd}^{2+}$  ions were adsorbed at  $\text{pH}\sim 4$  on the HTT-xero-200 from the solution in the initial concentration of 0.000001 mol/dm<sup>3</sup> whereas for the initial titanium phosphate sample adsorption wasn't higher than ~4%. This significant difference can be associated with the presence of hydrophosphorous groups on the surface, characterized by strong affinity towards cadmium ions. For the initial  $\text{Cd}^{2+}$  ions concentration of 0.00001 mol/dm<sup>3</sup> the adsorption affinity towards hydrothermally modified titanium phosphate is also strong – adsorption of cadmium ions is higher than 90%.

For the initial concentration of cadmium ions equal to 0.0001 mol/dm<sup>3</sup> and 0.001 mol/dm<sup>3</sup>, the course of the adsorption curve as a function of pH for the HTT-xero-200 sample is below one for the initial titanium phosphate sample (Figs. 7a and b). The hydrothermal treatment of a gel and a xerogel doesn't only create a small number of adsorption sites characterized by strong affinity towards cadmium ions (effect observed at a low initial concentration of the ions) but also deactivates some adsorption sites of the initial sample (this effect is observed at a high initial concentration of cadmium ions). The formation of active adsorption sites can result from generation of hydrophosphate groups that have stronger acidic properties than those of hydroxyl groups. Whereas deactivation of surface groups may result from surface dehydration during hydrothermal treatment, and formation of Ti-O-Ti groups as mentioned above.

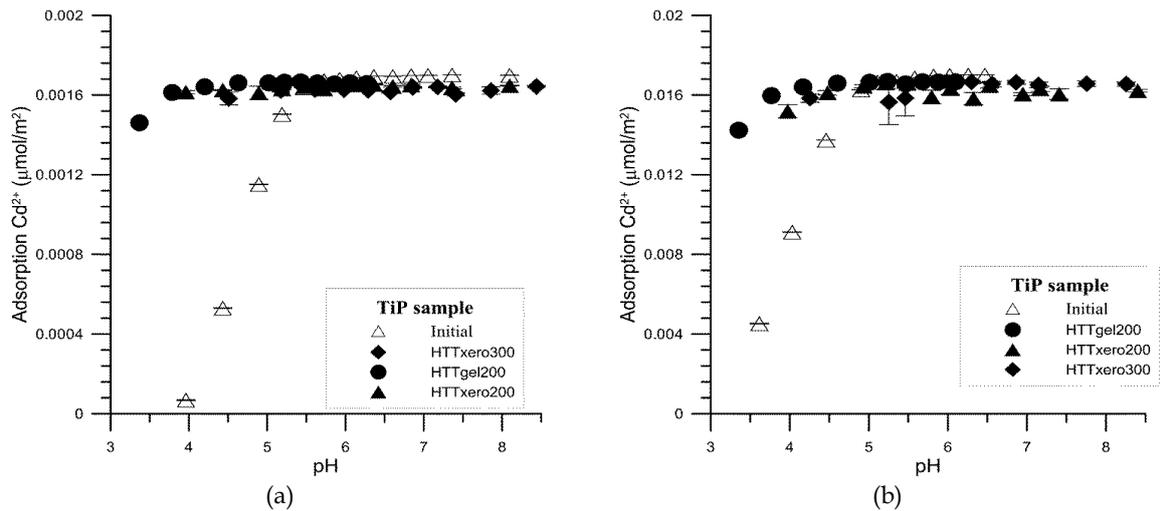


Fig. 6. Adsorption of Cd<sup>2+</sup> ions from the solution in the initial ions concentration of (a) 0.000001 mol/dm<sup>3</sup> and (b) 0.00001 mol/dm<sup>3</sup>, as a function of pH, at the titanium phosphate samples, 0.001 mol/dm<sup>3</sup> NaCl solution interface

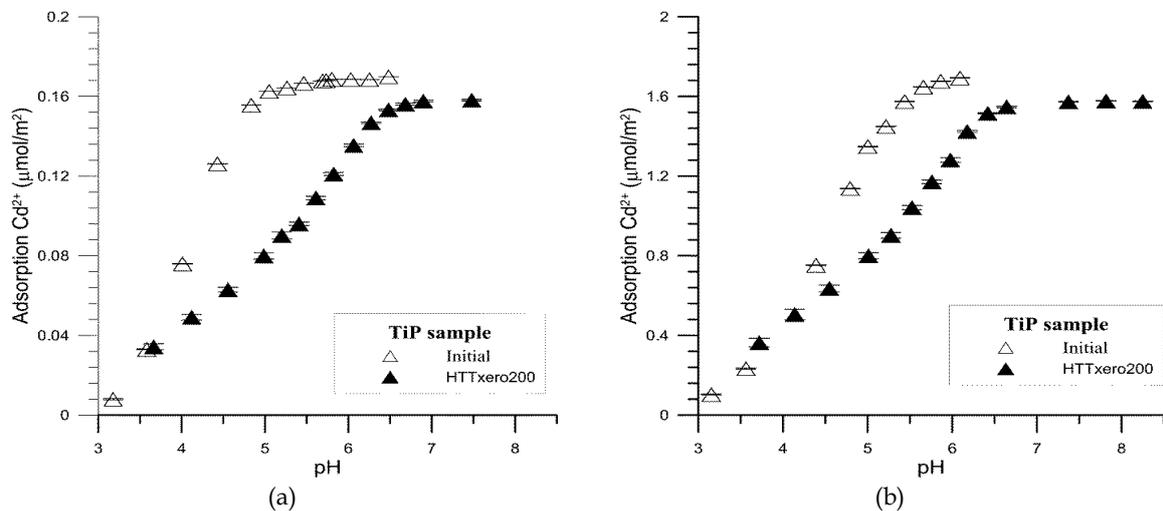


Fig. 7. Comparison of adsorption of Cd<sup>2+</sup> ions from the solution in the initial ions concentration of (a) 0.0001 mol/dm<sup>3</sup> and (b) 0.001 mol/dm<sup>3</sup>, as a function of pH, at the initial titanium phosphate or HTT-xero-200 samples, 0.001 mol/dm<sup>3</sup> NaCl solution interface

#### 4. Conclusions

The EDS analysis shows that the hydrothermal treatment of titanium phosphate samples in the form gel or dried xerogel enriches the surface sites with phosphorous groups and the concentration of Ti changes slightly. The increase in concentration of phosphorous groups on the hydrothermally treated titanium phosphate results in the increases of acidic character of their surface.

As follows from the FTIR ATR analysis the hydrothermal treatment of the initial titanium phosphate samples decreases the amount of physically adsorbed water on the surface. Therefore, the band characteristic for Ti-O-Ti groups was observed for the samples treated at 300 °C. The hydrothermally treated samples reveal several peaks characteristic for the vibrations of phosphate groups in the range of 1100-800 cm<sup>-1</sup>. The presence of phosphate groups on the hydrothermally treated titanium phosphate results in predominance of the groups possessing acidic properties and in the shift of the pH<sub>Iep</sub> to lower values of pH.

The adsorption affinity of cadmium ions for hydrothermally treated titanium phosphate changes in a more complicated way as compared to the initial sample. At low, initial concentration of Cd<sup>2+</sup> ions (<=0.00001 mol/dm<sup>3</sup>) the adsorption affinity increases for the hydrothermally treated sample, but decreases at the higher concentration. These changes are due to the creation of phosphorous groups on

the surface which intensifies cadmium ions adsorption. On the other hand, the dehydration of the HTT-xero-200 surface decreases the number of adsorption sites.

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