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Physico-Chemical Characterization and Interfacial Electrochemical Properties of Nanoparticles of Anatase-TiO_2 Prepared by the Sol-Gel Method

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Abstract: In this work, we prepared by the sol-gel method titanium dioxide nanoparticles having a large specific area (S_{BET} = 218 m^2/g). The isotherm of N_2 adsorption-desorption at 77K revealed that it concerns a mesoporous solid with a maximum pore diameter of 43 Å. The X-ray diffraction showed that the solid is constituted of the anatase phase. The transmission electron microscopy revealed us that the synthesized grains of TiO_2 are of nanometric sizes (diameter between 8 and 20 nm) and manifest under agglomerated shape. The study of its solubility in dispersing phase, by conductometric titrations, showed that the prepared solid is totally insoluble in all the domain of the studied pH. The measured inter-facial electrochemical properties, based on the isotherms of ionic adsorption and the conductometric titrations, are: the point of zero charge found equal to 6,2±0,1, the total number of sites of surface found equal to 5,8 OH/nm^2 and the nature of action of the dispersed phase on the dispersing phase which is found organizer of the structure of water. Besides, the difference of the ionization constants ΔpK is found superior to 4 for all the adsorbed ions and the constants of surface complexation are independent from the nature of the adsorbed ion.

Key words: Nanoparticles, Anatase-TiO_2, Sol-gel, Interfacial electrochemical properties.

Introduction

Currently, the titanium dioxide (TiO_2) under the form of nanoparticles appears to be the material of the future for the resolution of the environmental problems such the organic and mineral pollution of the water and the air and the storage of the energy because of its photo-catalytic and photo-electrochemical properties[1-4]. The titanium dioxide has various polymorphs such as rutile, anatase and brookite[5,6], but the anatase and rutile are thermodynamically the most stable at low temperature. There are several methods that can be used to prepare nanoparticles of titanium dioxide[7-14]; however, the sol-gel method is the most widely used because of its simplicity and its reproducibility. The aim of this work is to prepare, characterize by physico-chemical methods and determine the interfacial electrochemical properties of TiO_2 nanoparticles having high specific surface area.

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The physico-chemical characterization was made by Fourier Transformed Infra-Red Spectroscopy (FTIR), X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and N_2 sorption at 77K.

The determination of the inter-facial electrochemical properties of prepared TiO_2 was carried out at 298K by ionic adsorption measurements and conductometric titrations in the presence of different electrolytes alkali-halide type 1-1 and at different ionic strengths. These electrochemical properties are the state of insolubility of the dispersed phase in the dispersing phase, the pH at the point of zero charge (pH_{pzc}), the total number of surface sites (Ns), the ionization and the complexing constants and the nature of action of the dispersed phase on the dispersing phase.

The novelty of this work lies in the development in our laboratory of experimental methods based on the conductometric titrations. These techniques aimed at the determination of the pzc and the study of the solubility of TiO_2 nanoparticles in dispersing phase.

Experimental Section

Preparation of nanoparticles

The TiO_2 nanoparticles were prepared by the sol-gel method by using as precursor the titanium(IV) isopropoxide [$Ti(O\text{-}iPr)_4$] purchased from Sigma Aldrich (purity: 99,99 %). The precursor is dissolved in the isopropanol bought also at Sigma Aldrich (purity: 99,99 %). The mixture is maintained under constant stirring at room temperature. The pH of the mixture being 4,4 and the hydrolysis is made under constant agitation adding distilled water and respecting a molar ratio $r = \frac{[H_2O]}{[Ti(O\text{-}iPr)_4]} = 100$. The obtained mixture is passed in the centrifuge at 5000 rpm/min for 10 min to separate TiO_2. Finally, the obtained solid is washed with distilled water, filtered under vacuum and dried overnight in an oven at 373K. The TiO_2 prepared was calcined at 673K during 3 hours prior to characterization.

Characterization of nanoparticles

The FTIR spectra (400-4000 nm) of prepared solids were obtained using a spectrophotometer type JASCO 4100. Crystalline structures of the powders were characterized by X-ray diffraction with a X'PERT MPD_PRO diffractometer using Cu Kα radiation. The accelerating and the applied current were 45 kV and 40 mA respectively. The determination of the crystalline phases was carried out by applying the Bragg law where λ = 1,5406 Å. The size and morphology of as-prepared nanoparticles were determined by Transmission Electron Microscopy imaging (microscope Tecnai 12 from FEI Company). A Nitrogen sorption experiments were carried out at 77 K using a Micromeritics ASAP 2010 apparatus. The surface area was calculated according to Brunauer, Emmet and Teller (BET) in the P/P_0 range of 0,05 to 0,3 and the pore size distribution was determined according to Barrett, Joyner and Halenda (BJH) from desorption branch of the isotherms.

Potentiometric and conductometric titrations

Experimental device

The used experimental device is common to the potentiometric and conductometric titrations and allows measuring a surface charge of a solid having a volume fraction of minimal specific area of 5 m^2/g. It is constituted of the following: a thermostatic bath settled at 298K, of a unit containing the suspension to be studied, a ball of glass combined electrode,

of the conductivity measurement unit, of a pH-meter, of a conductometer, of a helix agitator activated by an engine, of a micro-burette and of nitrogen gas entrance to chase away the atmospheric carbon dioxide from the measurement unit.

It is important to indicate that before every potentiometric or conductometric titration, it is necessary to leave the solid in dispersing phase age for approximately 20 hours. This time represents the necessary duration for the ionic exchange, characterizing the experimental parameter pH, between both dispersed and dispersing phases.

The used salts in this work are NaCl (purity: 99,9 %), KCl (purity: 99,9 %), NaF (purity: 99,5 %), KI (purity: 99,5 %) and LiCl (purity: 99,9 %).They are supplied by the Sigma Aldrich Company.

The used water is distilled and passed on a column of mixed resin. Its specific conductivity at the column exit is of $0{,}510^{-6}$ ($\Omega^{-1}.cm^{-1}$).

Principle of determining the surface charge

The surface charge of metallic oxides such as TiO_2, results from the uneven ions adsorption determining the potential H^+ and OH^-[15]. The experimental measures of this charge are obtained by the potentiometric titrations of the solid suspensions prepared in the presence of a known constant concentration in electrolyte[16].

Results and Discussion

FTIR Spectroscopy

The FTIR spectrum of TiO_2 (**Figure 1A**) shows a broad band between 420 and 750 cm^{-1}. As displayed in **Figure 1B** (inserted), it is due to several bands overlapping and which are attributed to different modes of vibration of Ti-O[14,17-22]. The bands at 420 cm^{-1} and 450 cm^{-1} are related to the vibration of Ti=O and the stretching vibration of Ti–O in the anatase, respectively. The stretching vibration of Ti–O–Ti group appears at 544 cm^{-1} and the vibration at 629 cm^{-1} is probably associated to the vibrations of TiO_6 polyhedron. The shoulder at 839 cm^{-1} can be linked to the vibration of the anatase TiO_2.

The spectrum also shows the presence of the other bands of low intensities located at 1387 and 1620 cm^{-1}. The band at 1387 cm^{-1} can be attributed to the symmetric stretching vibration of CO_2 contained in the ambient air or to C–H deformation. The band at 1620 cm^{-1} is attributed to the bending vibration of the adsorbed H_2O on the surface of the solid. We also note the presence of a broad absorption band between 3000 et 3600 cm^{-1} (centred towards 3400 cm^{-1}) assigned to the stretching vibration of H_2O adsorbed on the surface of the solid [19,23,24].

X-Ray Diffraction

The XRD pattern of the prepared nanoparticles of TiO_2 and calcined at 673K for 3 hours is given in **Figure 2**. It shows that the solid crystallizes in the anatase phase (all peaks have been indexed in the anatase phase).

Transmission Electronic Microscopy

The TEM micrograph of the TiO_2 nanoparticles (**Figure 3)** shows that the solid consists of highly agglomerated fine particles which have a homogeneous shape. The size of the individual particles is between 8 and 20 nm.

Nitrogen adsorption/desorption isotherm at 77K

Figure 4A presents the nitrogen adsorption/desorption isotherm at 77K obtained for a prepared TiO_2 and calcined at 673K for 3 hours. The obtained isotherm is according to the IUPAC classification of type IV characteristic of mesoporous solids presenting a loop of hysteresis of type H2[25]. This hysteresis is characteristic of porous solids for which the size distribution and shape of the pores are not uniform.

The calculated specific area, using the BET method[25], is of 218 m^2/g. The pores size distribution was obtained using the BJH method from the desorption isotherm (**Figure 4B)**. It shows that the diameters of pores vary between 30 and 50 Å with a maximum distribution towards 43 Å, indicating the presence of mesopores.

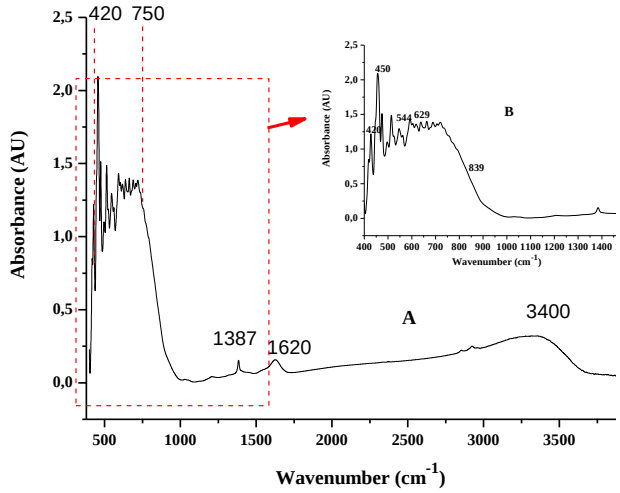

Figure 1. FTIR absorption spectra of TiO_2 nanoparticles

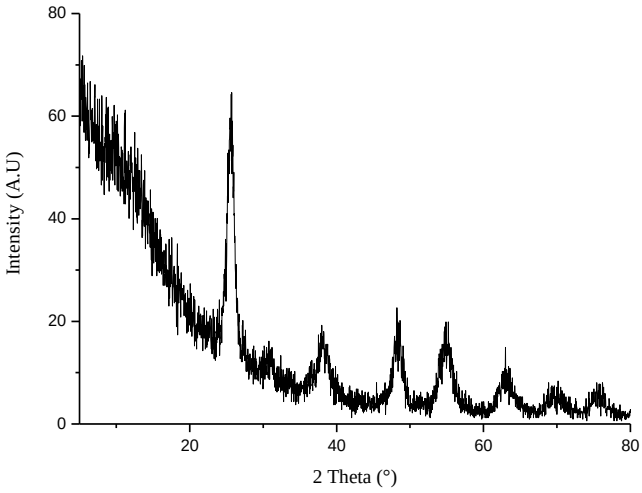

Figure 2. XRD spectrum of TiO_2 nanoparticles prepared and calcined at 673K for 3 hours

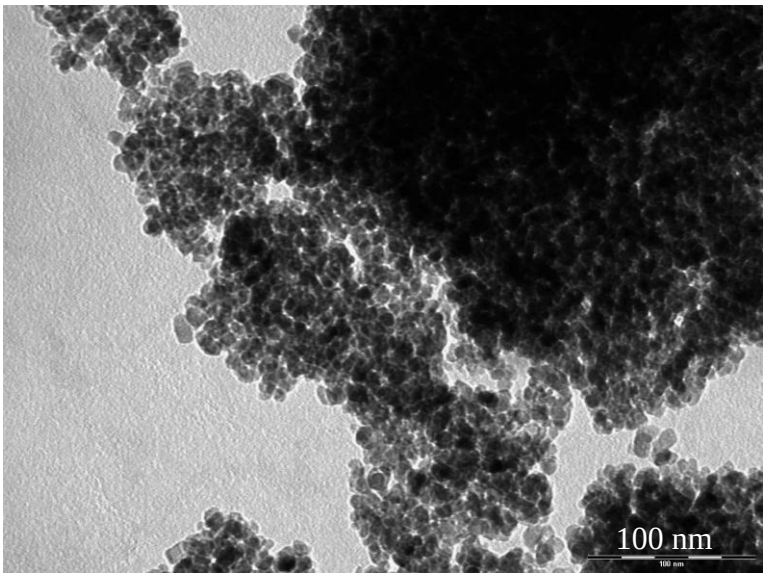

Figure 3. TEM micrograph of TiO_2 nanoparticles

Solubility of TiO_2 powder prepared in dispersing phase

We studied the solubility of TiO_2 nanoparticles in aqueous phase at a given ionic force and under the same operating conditions of surface charge measurements to determine de pH range where the TiO_2 nanopaticles are in a colloidal state or in ideal insolubility.

The principle of this study is based on the comparison of the conductometric titrations curves in absence (white titration) and in presence of the studied solid. At a given pH, the difference of specific conductivity between both conductometric titrations curves corresponds to the conductivity brought by the soluble ionic species in solution deriving from the solubility of solid nanoparticles studied in aqueous phase.

Figure 5 for example, shows the conductometric titrations curves obtained in absence and presence of the TiO_2 nanoparticles, in presence of LiCl at 10^{-3} mol/L. We notice that both conductometric titrations curves coincide perfectly translating a colloidal state or perfect insolubility of the solid in all the domain of studied pH. A similar behaviour was observed in the presence of the other studied salts.

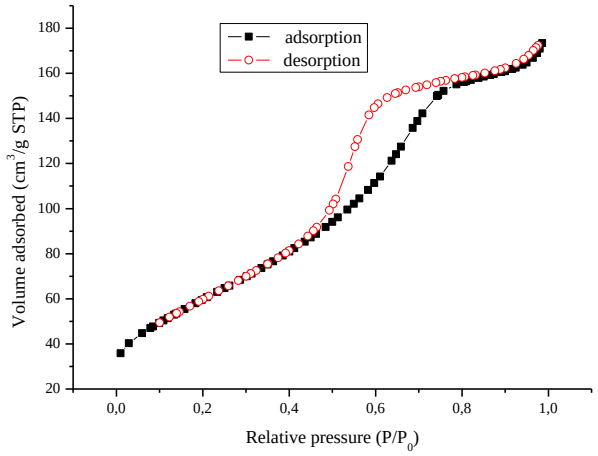

Figure 4A. Nitrogen adsorption/desorption isotherm at 77K

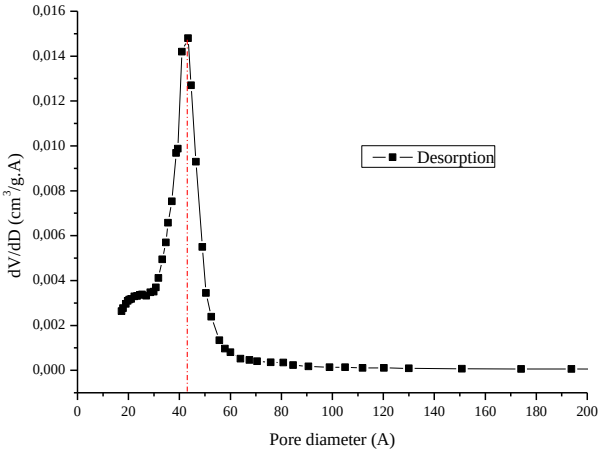

Figure 4B. BJH pores size distribution of nanoparticles of TiO_2

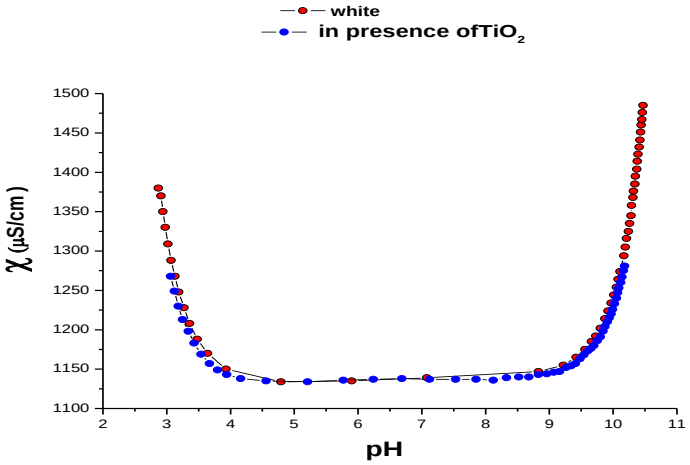

Figure 5. Specific conductivity curves in the absence (white titration) and in the presence of the TiO_2 nanoparticles prepared according to the pH of the salty aqueous suspension.

Electrochemical properties of the interface TiO_2 solid/dispersing phase

The point of zero charge (pzc)

The experimental determination of the pzc of a colloidal suspension can be made by several methods. If the potentiometric titrations are carried out in function of pH and salt concentration, the most used experimental approach is when the potentiometric curves intersect at a point. This point corresponds to the point of zero charge[26,27].

In this work, we present a new experimental method for the determination of the pzc based on the conductometric titrations. As for metallic oxides the surface charge results from the uneven ions adsorption determining the potential H^+ and OH^-, this method consists in following the consumption of these ions by various sites of surface.

The principle of this method consists in realizing conductometric titrations in absence and in presence of the solid at various ionic forces. The curves representing the difference of specific conductivity between those in absence (white titrations) and in presence of the solid according to the pH of the colloidal suspension and also according to the concentration of salt cross at a unique point which is the pzc.

Generally, in absence of specific adsorption, the net point of zero charge corresponds to the intersection of the isotherms of charge adsorption of measured surface at various ionic forces. **Figure 6A** shows the surface charge density variation of the titanium oxide prepared according to the pH and to the ionic force of the electrolyte KCl.

We clearly notice, that these surface charge curves cross at a unique point which is the pH at the pzc. For the titanium dioxide nanoparticles in the presence of a non specifically adsorbed electrolyte such as KCl, NaCl or KI, the measured value of the pH_{pzc} is 6,2±0,1. In pH above this point, the studied solid nanoparticles are negatively charged while at pH less than the pH_{pzc}, nanoparticles are positively charged.

The exploitation of the curves of the conductometric titrations in absence and in presence of the solid, led us to develop an original method of determination of the point of zero charge of a colloidal suspension. **Figure 6B** shows the application of this new technique of determination of the point of zero charge to the TiO_2 studied in presence of LiCl electrolyte.

We notice that the curve $\Delta\chi$ according to the measured pH at ionic force equals to 10^{-2} M, takes a form that is constituted of two branches with the tangents cross at a unique point which is the pH_{pzc}. The found value equals 6,2±0,1 which is similar to that measured when applying the potentiometric titrations technique.

The validity of this new method is confirmed by its application on another standard TiO_2, with different surface area (S_{BET} = 8 m^2/g), marketed by Sigma-Aldrich Company. **Figure 7A** shows the difference's variation of the specific conductivity ($\Delta\chi = \chi_{blanc} - \chi_{solide}$) according to the pH and the concentration of LiCl in the solution.

We notice that these curves measured at various ionic forces are all formed by two branches which meet at a unique point which is the point of zero charge equal to 6,7±0,1. This measured value for TiO_2 commercial in the presence of the electrolyte LiCl is similar to that found by the potentiometric titrations method **(Figure 7B).**

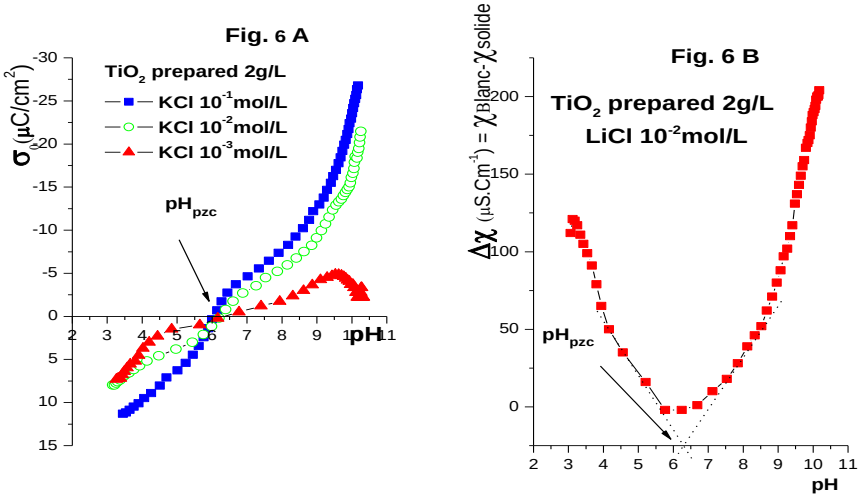

Figure 6. Determination of the pH_{pzc} of TiO_2 nanoparticles prepared from potentiometric (A) and conductimetric (B) titrations

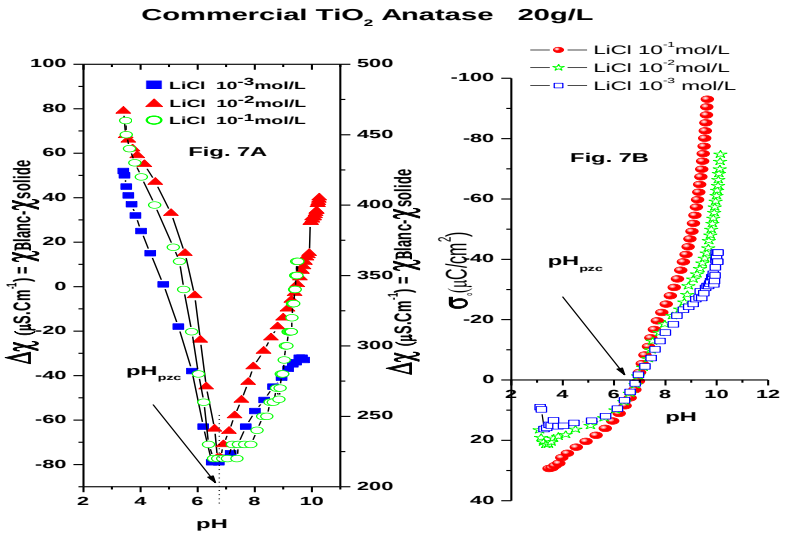

Figure 7. Determination of the pH_{pzc} of the commercial TiO_2 from the conductometric (A) and potentiometric (B) titrations

Nature of action of the dispersed phase on the dispersing phase

The knowledge of the nature of action of the dispersed phase on the dispersing phase is essential in the study of the stability of a colloidal suspension. In fact, the presence of a permanent hydration layer on the surface of particles increases considerably the stability of the studied hydrosol[17].

The ionic adsorption on the prepared titanium oxide is studied in pH superior to the pzc in the presence of alkaline cations Li^+, Na^+ and K^+ and with pH inferior to the pzc in the presence of halides anions F^-, Cl^- and I^-.

Figure 8A shows the sequence of ionic adsorption observed on the anatase TiO_2 solid prepared in the domain of pH superior to the pzc with ionic force 10^{-3} mol/L.

In a given pH, the more an ion is adsorbed on a surface the bigger the developed surface charge density becomes. On the basis of this definition, we can say that the sequence of adsorption observed on the studied solid with pH >pH_{pzc} is the following: **Li^+> Na^+> K^+**.

The same sequence of ionic adsorption is observed at ionic forces 10^{-2} and 10^{-1} mol/L. At pH inferior to the pzc, the **Figure 8B** shows the sequence of ionic adsorption observed on the TiO_2 oxide prepared at various ionic forces: $F^->Cl^-> I^-$. In other words, the ion F^- is more adsorbed than Cl^- which is also more adsorbed than the ion I^-. It is more practical to carry the charge of surface σ_0 according to ΔpH in order to eliminate the effect of the specific adsorption of the fluorine ion strongly adsorbed.

The interpretation of the sequence of ionic adsorption observed on the studied oxide requires the study of respective interactions between the surface of solids and water, between the ions and the surface, and between the ions and water. Frank, Evans, Gurney and Gierst's theoretical models[28,29] allow the study of all these interactions. The following important conclusion is drawn from the combination of these theoretical models: an ion is particularly adsorbed to an interface that its action on the structure of water is similar to the interface.

As the ion Li^+, which is the most adsorbed on the negative surface, and the ion F^-, which is the most adsorbed on the positive surface, are organizing ions of the structure of the water[30] then the TiO_2 nanoparticles prepared act in solution as organizer of the structure of the water.

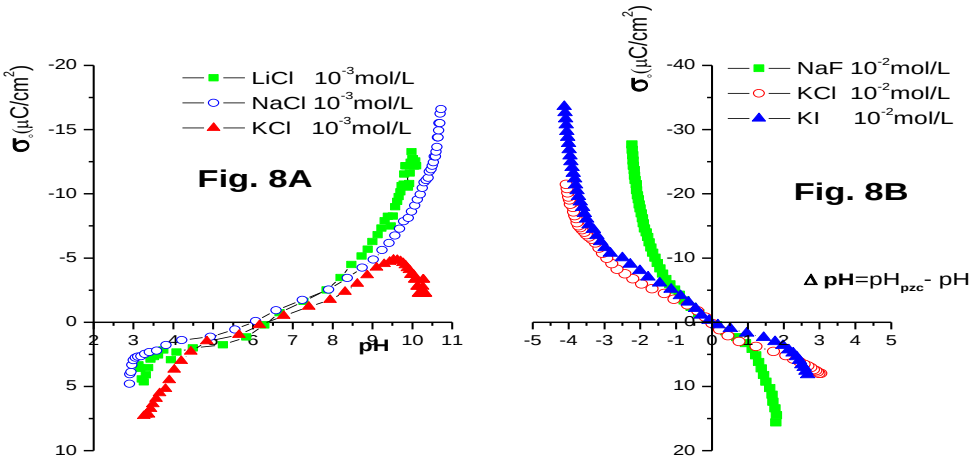

Figure 8. Sequence of ionic adsorption observed on the prepared oxide TiO_2. (A) with $pH>pH_{pzc}$ and (B) with $pH<pH_{pzc}$

Total number of surface sites Ns

The determination's principle of Ns by application of Stumm, Huang and Jenkins's graphic extrapolation technique[31,32] is based on the choice of the electrolytes which depends on the nature of the solid action on the dispersing phase.

For the organizing oxides of the structure of the water, the case of the studied TiO_2 oxide, it is necessary to choose for the positive surface of the solid, the graphic extrapolation of the curve $\frac{1}{[H_s^+]}$ in function $(\frac{1}{\sigma_0})$ corresponding to the most electronegative anion of the periodic table, which is the anion F^-, and which is the most organizing and most adsorbed. For the negative surface of the solid, it is necessary to choose the graphic extrapolation of the curve $[H_s^+]$ in function $(-\frac{1}{\sigma_0})$ corresponding to the most electropositive alkaline cation Li^+ of the periodic table and which is the most adsorbed on the studied solid.

The graphic extrapolation corresponding to the anion F^- allows the determination of number of positive sites N_s^+ and the one corresponding to the ion Li^+ gives the number of negative sites N_s^-. The total number of sites is $N_s = N_s^+ + N_s^-$

The determination's principle of the total density of sites of surface for the disorganizing oxides is opposite to that of the organizing surfaces.

Figures 9A and **9B** show the obtained straights and their corresponding equations respectively in the adsorption of the ion F^- and the ion Li^+. The calculated value of N_s^+ is in the order of 43,22 µC/cm^2 and that of N_s^- is in the order of 50 µC/cm^2. The value of the total density of sites of surfaces Ns of the solid prepared TiO_2 is:

$$N_s = N_s^+ + N_s^- = 93\ \mu C/cm^2$$

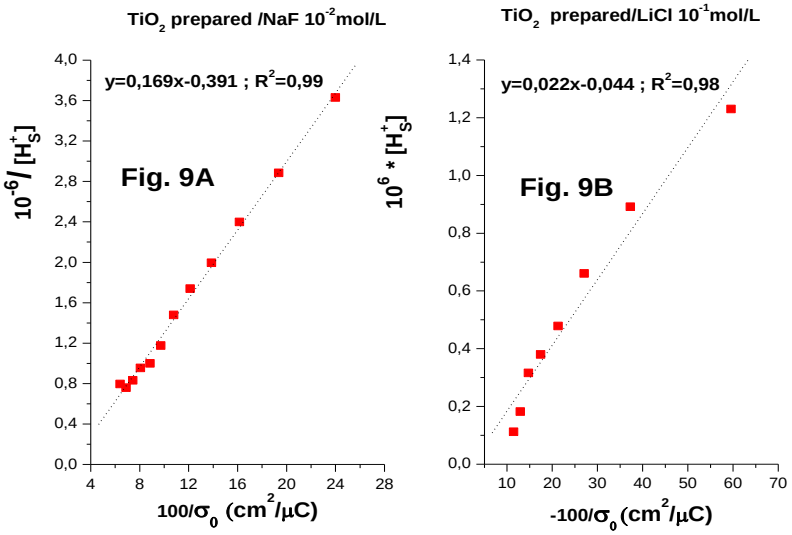

Figure 9. Curves of determination of the total density of sites of surface Ns of TiO_2 oxide prepared by the graphic extrapolation method.

The found value for Ns in µC/cm^2 does not exactly translate the maximal exchange capacity adsorbat-adsorbing of the prepared titanium oxide. It is necessary to convert Ns in number of OH group per nm^2 called sites density by unit of surface, and noted Ds[33].

$$D_s = \frac{\text{numbre of surface sites}}{\text{unit of surface}} = \frac{n_s \cdot N_{Av}}{A \cdot m_s}$$

A: the solid specific surface.

m_s: mass of the studied solid.

n_s: equivalent number of mole of titrated sites

N_{Av} : Avogadro number

$$D_s = 6{,}24.10^{-2}.Ns\ \ (OH/nm^2) = 5{,}8\ (OH/nm^2)$$

Constants of ionization and of complexation of the prepared TiO_2 nanoparticles

The determination of the constants of ionization and of complexation by the application the site-binding model of Davis, James and Leckie[34,35], is essentially based on the following equations:

*** Ionization constants**

- With pH below the pH_{pzc} where the particles surface is positively charged

$$pK_{int}^{+} = pH + \log\left(\frac{\alpha^{+}}{1-\alpha^{+}}\right) + \frac{e\psi_0}{2{,}303kT} - \log\left\{1 + K_{int}^{An}\left[An^{-}\right]\cdot\exp\left(\frac{e\psi_\beta}{2{,}303kT}\right)\right\}$$

$$pK_{int}^{+} = pQ^{+} + \frac{e\psi_0}{2{,}303kT} - \log\left\{1 + K_{int}^{An}\left[An^{-}\right]\cdot\exp\left(\frac{e\psi_\beta}{2{,}303kT}\right)\right\}$$

If we take pQ^{+} according to $10\ \alpha^{+} + \sqrt{C_s}$, the constant pK_{int}^{+} can be determined by a double graphic extrapolation until $\alpha+ = 0$ and C_s=0 mol/L.

- At pH above the pH_{pzc} where the particles surface is negatively charged

$$pK_{int}^{-} = pH - \log\left(\frac{\alpha^{-}}{1-\alpha-}\right) + \frac{e\psi_0}{2{,}303kT} + \log\left\{1 + K_{int}^{Ca}\left[Ca^{+}\right]\cdot\exp\left(-\frac{e\psi_\beta}{2{,}303kT}\right)\right\}$$

$$pK_{int}^{-} = pQ^{-} + \frac{e\psi_0}{2{,}303kT} + \log\left\{1 + K_{int}^{Ca}\left[Ca^{+}\right]\cdot\exp\left(-\frac{e\psi_\beta}{2{,}303kT}\right)\right\}$$

If we take pQ^{-} according to $10\ \alpha^{-} + \sqrt{C_s}$, the constant pK_{int}^{-} can be determined by a double graphic extrapolation until $\alpha^{-} = 0$ and $C_s = 0$ mol/L

The values of constants pK_{int}^{-} and pK_{int}^{+} of the prepared TiO_2 solid in the presence of studied electrolytes, determined by D.J.L's double extrapolation graphic method[34,35], are summarized in the table 1.

Table 1. The ionizations constants values $\mathbf{pK_{int}^{-}}$ and $\mathbf{pK_{int}^{+}}$ of the prepared TiO_2 determined by the double extrapolation graphic method

Nature of electrolyte	LiCl	NaCl	KCl	KI
$\mathbf{pK_{int}^{-}}$	8,4	8,5	9	8,4
$\mathbf{pK_{int}^{+}}$	3,7	3,7	3,5	3,3
$\mathbf{pH_{pzc}=1/2(pK_{int}^{+}+pK_{int}^{-})}$	6,1	6,1	6,2	5,9
$\mathbf{\Delta pK = pK_{int}^{-} - pK_{int}^{+}}$	4,7	4,8	5,5	5,1

- Interpretation of the $\mathbf{pK_{int}^{-}}$ values

We notice for the values related to the adsorbed cations Li^{+}, Na^{+} of the NaCl and K^{+} of KCl electrolyte: $\mathbf{pK_{int}^{-}(Li^{+}) = 8{,}4 < pK_{int}^{-}(Na^{+}) = 8{,}5 < pK_{int}^{-}(K^{+}) = 9}$

The explanation of this order of constants pK_{int}^{-}, requires the intervention of the ionic adsorption sequence observed on the prepared TiO_2 solid with pH superior to pH_{pzc}.

In fact, the constant pK_{int}^{-} corresponds to the following reaction:

$$MOH \rightleftharpoons MO^{-} + H_s^{+} \qquad K_{int}^{-} \frac{\left[MO^{-}\right]\left[H_s^{+}\right]}{\left[MOH\right]}$$

The more an ion is adsorbed on a solid the bigger the density of charge or the concentration of $[MO^{-}]$ becomes. In that case, the value of K_{int}^{-} is big and consequently pK_{int}^{-} is small.

As the sequence of ionic adsorption observed on the studied solid is in the order $Li^+ > Na^+ > K^+$, we must expect the following order of pK_{int}^-: pK_{int}^- **(Li^+)** < pK_{int}^- **(Na^+)** < pK_{int}^- **(K^+)** Which is in accordance with the found values of pK_{int}^- of the prepared TiO_2 nanoparticles.

- Interpretation of the pK_{int}^+ values

Concerning the pK_{int}^+ values related to the adsorbed anions at the surface positively charged with the prepared TiO_2 nanoparticles, the comparison can only be made between the pK_{int}^+ related to the anion Cl^- of the salt KCl and the anion I^- of the salt KI:

$$pK_{int}^+ \textbf{(Cl}^-\textbf{)} > pK_{int}^+ \textbf{(I}^-\textbf{)}$$

However, the constant K_{int}^+ is related to the following reaction:

$$MOH_2^+ \rightleftharpoons MOH + H_s^+ \qquad K_{int}^+ = \frac{[MOH]\,[H_s^+]}{[MOH_2^+]}$$

The more an anion is adsorbed on the surface, the bigger the concentration of the positive sites $[MOH_2^+]$, and consequently σ_0 is big. In that case, K_{int}^+ is small and consequently pK_{int}^+ is big. As the sequence of ionic adsorption observed on the studied TiO_2 solid is in the order: **Cl^- > I^-**. Therefore, we have to expect that: pK_{int}^+ **(Cl^-)** > pK_{int}^+ **(I^-)**; which is in agreement with the obtained experimental results.

The ionization constants values pK_{int}^- and pK_{int}^+ obtained for the prepared TiO_2 can be interpreted as follows:

- The comparison of the measured experimental value of the intrinsic pzc of the solid and the one due to the specific adsorption with the value calculated from the expression of $pH_{pzc}=1/2(pK_{int}^+ + pK_{int}^-)$.

- The comparison of the values of ΔpK calculated with those of the literature corresponding to organizing oxides[35,36]. ΔpK is a surface property intrinsic to every colloidal suspension.

We notice that the values of pzc measured in the presence of LiCl, NaCl, KCl and KI salts are the same as those calculated from the ionization constants. It is thus important to indicate that the double extrapolation graphic method used to determine the ionization constants, also detects the specific adsorption which occurs in the case of the ion adsorption Li^+.

We also notice that the ΔpK values related to all the adsorbed ions on the prepared TiO_2 solid are superior to the value 4. This is in accordance with several works[37-39] stating that the oxides having a relatively weak density of sites Ns, as in the case of the studied TiO_2 nanoparticles, are characterized by a high ΔpK, superior to 4.

*** Complexation Constants**

- With pH inferior to pH_{pzc} where the surface of particles is positively charged

$$p^*K_{int}^{An} = pK_{int}^+ - pK_{int}^{An} = pH + \log\left(\frac{\alpha^+}{1-\alpha^+}\right) - \log[An^-] + \frac{e\,(\psi_0 - \psi_\beta)}{2{,}303kT}$$

$$= p^*Q^{An} + \frac{e\,(\psi_0 - \psi_\beta)}{2{,}303kT}$$

If we take p^*Q^{An} according to $10\alpha^+ - \log C_s$ using also the data of surface charges corresponding to high ionic forces 10^{-2} and 10^{-1} M, the constant of complexation $p^*K_{int}^{An}$ can be determined by a double graphic extrapolation until $\alpha^+=0$ and C_s=1mol/L.

- With pH superior to pH_{pzc} where the surface of particles is negatively charged:

$$p^*K_{int}^{Ca} = pK_{int}^{+} + pK_{int}^{Ca} = pH - \log\left(\frac{\alpha^-}{1-\alpha^-}\right) + \log[Ca^+] + \frac{e\,(\psi_0 - \psi_\beta)}{2{,}303kT}$$

$$= p^*Q^{Ca} + \frac{e\,(\psi_0 - \psi_\beta)}{2{,}303kT}$$

If we p^*Q^{Ca} according to $10\alpha^-$ - $\log C_s$ using also the data of surface charges corresponding to high ionic forces 10^{-2} and 10^{-1} M, the constant of complexation $p^*K_{int}^{Ca}$ can be determined by a double graphic extrapolation until $\alpha^+ = 0$ and C_s=1mol/L.

To determine the intrinsic constants of complexation, Davis-James and Leckie[34,35] were based on the approximation that at high concentrations of electrolyte (strictly superior to 10^{-3} mol/L), the oxides surface charge is essentially due to the formation of the complexes on the surface. For this reason, we were limited only to the data of surface charge corresponding to the ionic forces 10^{-2} and 10^{-1} mol/L of the studied electrolyte.

Table 2 summarizes the values of the constants $p^*K_{int}^{Ca}$ and $p^*K_{int}^{An}$ determined by a double graphic extrapolation until $\alpha^+ = 0$ or $\alpha^- = 0$ and Cs =1 mol/L for all the studied electrolytes.

Table 2. Complexation constants' values $p^*K_{int}^{Ca}$ and $p^*K_{int}^{An}$ of the prepared TiO_2 oxide determined by the double graphic extrapolation method.

Nature of electrolyte	**LiCl**	**NaCl**	**KCl**	**KI**
$\mathbf{p^*K_{int}^{Ca}}$	8	8,2	8,5	8,3
$\mathbf{p^*K_{int}^{An}}$	3,7	3,7	3,7	3
$\mathbf{\log\,(K_{int}^{Ca}) = pK_{int}^{-} - p^*K_{int}^{Ca}}$	0,4	0,3	0,50	0,1
$\mathbf{\log(K_{int}^{An}) = p^*K_{int}^{An} - pK_{int}^{+}}$	0	0	0,2	0,3

Table 2 also contains the values of K_{int}^{Ca} and K_{int}^{An} which really translate the phenomenon of complexation at the particles' surface. These values are deduced from those of the ionization constants pK_{int}^{-} and pK_{int}^{+} and complexation constants $p^*K_{int}^{An}$ and $p^*K_{int}^{Ca}$.

Constants $p^*K_{int}^{An}$ and $p^*K_{int}^{Ca}$ have no physical sense, and it is the constants K_{int}^{Ca} and K_{int}^{An} that really translate the phenomenon of complexation which occurs at the surface of the studied solid.

The comparison of the constants values $\log(K_{int}^{Ca})$ for studied electrolytes LiCl, NaCl, KCl and KI shown in table 2, shows clearly similar values. The same remark can be made for the $\log(K_{int}^{An})$ values.

The found result shows clearly that for the prepared TiO_2 solid, the phenomenon of complexation on a positive or negative surface is not specific in a given ion, but is of a purely electrostatic nature.

Conclusion

In this work, we prepared mesoporous titanium dioxide nanoparticles with a large specific area (S_{BET} = 218 m^2/g). The maximal diameter of pores is 43 Å. The X-rays diffraction reveals that the solid is constituted of the anatase phase. The TEM observation revealed to us that the synthesized TiO_2 is formed of agglomeration of nanoparticles. The study of its solubility in dispersing phase, by conductometric titrations, showed that the prepared solid is totally insoluble in the range of pH studied.

The interfacial electrochemical properties of TiO_2 oxide are mainly the pH_{pzc}. It can be determined both by the classical method of the potentiometric titrations and by a method developed in this work based on the conductometric titrations.

The value of the intrinsic pH_{pzc} measured by both methods is the same and it is equal to 6,2±0,1. The total number of sites of surface Ns, determined by extrapolation graphic method**,** found equal to 5,8 OH/nm^2 .

The study of the ionic adsorption sequence at different ionic forces showed a structuring action nature of the prepared solid particles on the dispersing phase. The application of triple layer model on the realized surface charge density measures gave a difference of the ionization constants ΔpK superior to 4 for all the adsorbed ions, characteristics of organizing oxides, and the constants of surface complexation are independent from the nature of the adsorbed ion.

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