Chapter 5

Selective Separation of Titanium Chloride and its Conversion to TiO$_2$ Powders
Solvent extraction of tetravalent titanium has been extensively investigated using commercially available acidic organophosphorus extractants such as DEHPA, EHEHPA and BTMPPA from acidic chloride solutions (Biswas and Begum 1998a; Reddy and Saji 2002; Saji et al. 2000; Saji and Reddy 2003). The major disadvantage with these reagents is the relatively slow kinetics of extraction (60-120 min). This has been attributed to the slow rate at which the \((-\text{Ti}–\text{O–})_n\) polymeric chains are broken down prior to being extracted as simple ions (Biswas and Begum 1998a). Hence, longer residence time would be necessary to operate these systems on a commercial scale for the separation of titanium from leach liquors. However, better selectivity can be achieved by employing acidic organophosphorus extractants between titanium and other associated multivalent metal ions present in the waste chloride liquors of titanium minerals processing industry. On the other hand, neutral organophosphorus extractants such as TRPO exhibit rapid extraction kinetics (couple of min) but poor selectivity for the extraction of titanium(IV) from the waste chloride liquors of titanium minerals processing industry (Remya and Reddy 2004, Duyvesteyn et al. 2002). Although
preliminary studies on the extraction of titanium(IV) from hydrochloric acid with TBP are known (Narita et al. 1983), systematic efforts have not been made to employ TBP for the extraction and separation of titanium(IV) either from the leach liquors of titanium minerals processing industry or from titania waste chloride liquors. Hence, in the present work, TBP has been chosen as an extractant for the separation of titanium(IV) from the waste chloride liquors of titanium minerals processing industry. In the present study efforts have also been made to recover titanium as phase-pure titania powders by adopting a low temperature hydrothermal synthesis route.

5.1 Experimental

The preparation of stock solutions of metal ions, apparatus used and solvent extraction and analytical procedures followed in this work are the same as described in chapter 3. Preliminary experiments showed that the extraction equilibrium was attained within couple of min.

*Hydrothermal synthesis procedure*

The hydrothermal synthesis of TiO₂ powders was performed in a pressure reactor with monel alloy as the material of construction and with a teflon liner (600 cm³). The autoclaving temperatures were varied between 413 to 453 K (under autogeneous pressure corresponding to its temperature) with constant stirring (200 r.p.m.). The precursor amorphous titania powder was prepared by the following procedure: The amorphous titania was prepared from the TiCl₄ loaded organic phase (2.5 mol/dm³ TBP in kerosene containing
0.2 mol/dm³ TiCl₄) obtained from solvent extraction process by precipitation-stripping by the addition of sodium hydroxide (2.0 mol/dm³) with constant stirring. The white amorphous precipitate was then separated from the organic phase, washed with deionised water and acetone, respectively. The amorphous titania precipitate was then dispersed in deionised water (100 cm³), adjusted the pH of the suspension to the desired value (4-7) and autoclaved for varying lengths of time (60-180 min) and temperatures (413-453 K). After the completion of the autoclaving treatment, the powders were filtered, washed with water and acetone, respectively, dried at 353 K and then stored in a desiccator. The powders were characterized by X-ray diffraction analysis (XRD), thermogravimetry (TG), differential thermal analysis (DTA) and FT-IR. Scherrer's equation \( D = \frac{0.9 \lambda}{\beta \cos \theta} \), where \( D \) is the crystallite size, \( \lambda \) is the wavelength of X-ray used, \( \beta \) and \( \theta \) are half width of XRD diffraction lines and half diffraction angle 2\( \theta \), respectively, was applied to determine the crystallite size of the anatase TiO₂ to find out the effects of various preparation parameters on the crystal growth. The specific surface area of the powders was measured via nitrogen adsorption, using a surface area analyzer (Micromeritics, Gemini, USA). The average particle size, \( d_{BET} \) was calculated based on the BET specific surface area analysis. The morphological analysis was performed using scanning electron microscopy.

**Photocatalytic activity**

The photocatalytic activity of the synthesized anatase TiO₂ was assessed by photocatalytic degradation of methyl orange. The synthesized anatase TiO₂ (1.0 g/dm³) was suspended in aqueous solution of methyl orange (250 cm³
containing $50 \times 10^{-6} \text{ mol/dm}^3$ methyl orange) and photoirradiated using 450W medium pressure mercury lamp under air oxygen at $303 \pm 1.0 \text{ K}$ with vigorous magnetic stirring. The samples were withdrawn at different time intervals and centrifuged at 6000 r.p.m. to remove the TiO$_2$ powders. The absorbance of the methyl orange was measured at 462 nm using a Shimadzu scanning spectrophotometer, UV-3101 PC UV-VIS-NIR. There was no loss of dye observed when the irradiation was carried out in the absence of TiO$_2$. On the other hand, some loss of dye occurred due to the adsorption of TiO$_2$ in the unirradiated blank solution.

5.2 Results and Discussion

**Effect of hydrochloric acid concentration**

The extraction of titanium(IV) ($0.03 \text{ mol/dm}^3$) and other associated metal ions, viz., magnesium(II) ($0.04 \text{ mol/dm}^3$), aluminium(III) ($0.03 \text{ mol/dm}^3$), chromium(III) ($0.01 \text{ mol/dm}^3$) and manganese(II) ($0.03 \text{ mol/dm}^3$) present in the waste chloride liquors of titanium minerals processing industry was investigated as a function of hydrochloric acid concentration (4.0-10.0 mol/dm$^3$) using 1.47 mol/dm$^3$ TBP in kerosene as an extractant. The results are depicted in Fig. 5.1. The extraction of titanium(IV) was found to be negligible at hydrochloric acid concentrations below 6.0 mol/dm$^3$. On the other hand, the extraction efficiency increases with increasing acidity in the aqueous phase at hydrochloric acid concentrations above 6.0 mol/dm$^3$. The investigations also reveal that magnesium(II), aluminium(III), chromium(III) and manganese(II), present in the raffinate stream after the removal of
iron(III) and vanadium(V) (as described in chapters 3 and 4, respectively) were not extracted under the present experimental conditions.

![Graph showing the effect of hydrochloric acid concentration on the extraction of titanium(IV) using 1.47 mol/dm$^3$ TBP in kerosene.](image)

**Figure 5.1.** Effect of hydrochloric acid concentration on the extraction of titanium(IV) (0.03 mol/dm$^3$), magnesium(II) (0.04 mol/dm$^3$), aluminium(III) (0.03 mol/dm$^3$), chromium(III) (0.01 mol/dm$^3$) and manganese(II) (0.03 mol/dm$^3$) using 1.47 mol/dm$^3$ TBP in kerosene.

The effect of hydrogen ion concentration on the extraction of titanium(IV) was studied using 1.47 mol/dm$^3$ TBP in kerosene as an extractant at constant chloride (8.0 mol/dm$^3$) and metal (0.03 mol/dm$^3$) ion concentrations using HCl + CaCl$_2$ mixtures and the results are depicted in Fig. 5.2. The extraction of titanium(IV) was found to be independent of hydrogen ion concentration under the present experimental conditions. It is evident from the above results (Figs. 5.1 and 5.2) that the extraction efficiency of titanium(IV) was dependent only on the chloride ion concentration in the aqueous phase. It can be concluded from the slope of the plot Log D versus Log $a_{HCl}$ that (Fig. 5.3) four chloride ions are involved in the extracted
complex. The activity coefficients of the species H⁺ and HCl in the aqueous phase were calculated using Bromley's formulation (Bromley 1973).

**Effect of metal ion concentration**

The effect of metal ion concentration ($5.0 \times 10^{-4}$ to $4.0 \times 10^{-2}$ mol/dm³) on the extraction efficiency of titanium(IV) was investigated from 8.0 mol/dm³ HCl by employing 1.47 mol/dm³ TBP in kerosene as an extractant. The Log–Log plot (Fig. 5.4) of equilibrium organic-phase titanium(IV) concentration against aqueous-phase titanium(IV) concentration is linear with a slope of unity, indicating that only mononuclear species are extracted into the organic phase.

**Effect of extractant concentration**

The effect of concentration of TBP (0.7-1.8 mol/dm³) on the extraction of titanium(IV) was studied at constant metal ion (0.03 mo/dm³) and hydrochloric acid (8.0 mol/dm³) concentrations and the results are shown in Fig. 5.5. The extraction efficiency of titanium(IV) increases linearly with increasing TBP concentration in the organic phase. From the slope of the plot of Log D versus Log [TBP], it can be inferred that two molecules of TBP are involved in the extracted complex.

**IR spectra of titanium(IV) - TBP complex**

The IR spectrum of the extracted complex shows that the stretching frequency of P=O was shifted from 1276 cm⁻¹ in TBP to 1265 cm⁻¹ in TiCl₄.
2TBP, indicating the interaction between the oxygen of the P=O group in TBP with the metal ion (Fig. 5.6).

**Figure 5.2.** Effect of hydrogen ion concentration on the extraction of titanium(IV) (0.03 mol/dm³) at constant chloride ion concentration. [Cl⁻] = 8.0 mol/dm³, [TBP] = 1.47 mol/dm³ in kerosene.

**Figure 5.3.** Effect of HCl concentration on the extraction of titanium(IV) (0.03 mol/dm³), [TBP] = 1.47 mol/dm³ in kerosene.
Figure 5.4. Effect of metal ion concentration on the extraction of titanium(IV). [HCl] = 8.0 mol/dm$^3$, [TBP] = 1.47 mol/dm$^3$ in kerosene.

Figure 5.5. Effect of TBP concentration on the extraction of titanium(IV) (0.03 mol/dm$^3$), [HCl] = 8.0 mol/dm$^3$. 

Extraction equilibrium

Based on the above results, the extraction equilibrium of titanium(IV) using TBP as an extractant can be represented as:

\[
\begin{align*}
Ti^{4+}_{aq} + 4Cl^-_{aq} + 2TBP_{org} & \rightleftharpoons TiCl_4 \cdot 2TBP_{org} \\
K_ex & = \frac{[TiCl_4 \cdot 2TBP]_{org}}{[Ti^{4+}]_{aq} [Cl^-]_{aq}^4 (TBP)^2_{org}}
\end{align*}
\]

where \( K_{ex} \) is the equilibrium constant. Similar extraction equilibrium was proposed for the extraction of titanium(IV) from hydrochloric acid solutions with various alkyl phosphine oxides (Kakade and Shinde 1995; Saji et al. 1999; Allal et al. 1997). On the other hand, the involvement of two or three molecules of TBP in the extracted complex of titanium(IV) was also reported elsewhere at different HCl and TBP concentrations (Narita et al. 1983). The co-extraction of HCl along with the metal complex by TBP is also known (Narita et al. 1983; De et al. 1970; Marcus and Kertes 1967).

Effect of nature of the diluent on the extraction of titanium(IV)

The extraction efficiency of titanium(IV) from 8.0 mol/dm\(^3\) hydrochloric acid solutions was studied using 1.47 mol/dm\(^3\) TBP in various diluents. The results are shown in Table 5.1. The results demonstrate that diluents such as benzene, xylene, toluene and kerosene, which have low dielectric constants, show higher extraction efficiency for titanium(IV). On the other hand, diluents having higher dielectric constants, such as chloroform, exhibit poor extraction. This may be due to the strong interaction between TBP and chloroform through hydrogen bonding (Sekine and Hasegawa 1997). In view of the
commercial availability and good extraction efficiency, kerosene was chosen as the diluent in the present study.

Figure 5.6. IR spectra of pure TBP, \( \text{TiCl}_4 \cdot 2\text{TBP} \) complex and TBP after precipitation-stripping.

**Loading Capacity**

Aliquots of 10 cm\(^3\) of 1.47 mol/dm\(^3\) TBP in kerosene were repeatedly extracted at 303 ± 1 K for 10 min with equal volumes of the aqueous phase containing 1.44 g/dm\(^3\) of titanium(IV) in 8.0 mol/dm\(^3\) hydrochloric acid. The
aqueous phases were analysed for titanium(IV) after each stage of extraction and the cumulative titanium(IV) content transferred into the extractant phase was calculated. The plot of cumulative titanium(IV) in the organic phase per 100 g of TBP versus the number of stages of contact is presented in Fig. 5.7. It shows that the loading capacity of TBP in kerosene for the extraction of titanium(IV) from hydrochloric acid solutions is 0.9 g of titanium(IV) per 100 g of TBP.

**Table 5.1.** Effect of nature of diluent on the extraction of titanium(IV) (0.03 mol/dm$^3$). [HCl] = 8.0 mol/dm$^3$, [TBP] = 1.47 mol/dm$^3$ in kerosene.

<table>
<thead>
<tr>
<th>Diluent</th>
<th>Dielectric constant ($\varepsilon$)</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kerosene</td>
<td>2.00</td>
<td>1.23</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>2.02</td>
<td>1.40</td>
</tr>
<tr>
<td>Xylene</td>
<td>2.24</td>
<td>1.58</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.26</td>
<td>1.58</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.28</td>
<td>1.58</td>
</tr>
<tr>
<td>Chloroform</td>
<td>4.90</td>
<td>0.95</td>
</tr>
</tbody>
</table>

**Extraction isotherm**

The extraction isotherm for a typical feed solution containing 1.44 g/dm$^3$ of titanium(IV) and 8.0 mol/dm$^3$ hydrochloric acid using 1.47 mol/dm$^3$ TBP in kerosene as an extractant was generated and the results are depicted in Fig. 5.8. The McCabe–Thiele plot for a feed solution containing 1.44 g/dm$^3$ of
titanium(IV) showed that almost quantitative extraction of titanium(IV) is possible in four counter-current stages using an A : O ratio of 1 : 2.

![Cumulative T[IV] concentration vs. number of stages](image)

**Figure 5.7.** Loading capacity of TBP by titanium(IV). $[\text{HCl}] = 8.0 \text{ mol/dm}^3$, $[\text{TBP}] = 1.47 \text{ mol/dm}^3$.

**Effect of hydrochloric acid concentration on the stripping behavior of titanium(IV)**

The effect of HCl concentration on the stripping behaviour of titanium(IV) from a loaded organic solvent system consisting of 1.47 mol/dm$^3$ TBP in kerosene and 0.72 g/dm$^3$ titanium(IV) was investigated and the results are shown in Fig. 5.9. It is clear from the results that quantitative stripping of titanium(IV) is possible in a single stage with hydrochloric acid concentration in the range 1.0 to 5.0 mol/dm$^3$. Thus in the present study, 1.0 mol/dm$^3$ hydrochloric acid was chosen as a stripping agent for the recovery of titanium(IV) from the loaded organic phase.
The McCabe-Thiele plot (Fig. 5.10) for a loaded organic phase containing 0.72 g/dm³ of titanium(IV) showed that quantitative stripping of titanium(IV) is possible in a single stage of counter-current stripping using 1.0 mol/dm³ hydrochloric acid as the stripping agent (O : A = 1 : 1).

\[ [\text{Ti(IV)}]_{\text{aq}}, \text{g/L} \]
\[ 0 \quad 0.5 \quad 1 \quad 1.5 \quad 2 \]

\[ [\text{[Ti(IV)]}]_{\text{org}}, \text{g/L} \]

\[ 0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1 \]

**Figure 5.8.** McCabe-Thiele plot for titanium(IV) extraction. \([\text{Ti(IV)}] = 1.44 \text{ g/dm}^3, [\text{HCl}] = 8.0 \text{ mol/dm}^3, [\text{TBP}] = 1.47 \text{ mol/dm}^3 \) in kerosene.

*Extraction and separation of titanium(IV) from simulated waste chloride liquors of titanium minerals processing industry*

Based on the above results, a simulated waste chloride liquor consisting of magnesium(II) (0.04 mol/dm³), aluminium(III) (0.03 mol/dm³), titanium(IV) (0.03 mol/dm³), chromium(III) (0.01 mol/dm³) and manganese(II) (0.03 mol/dm³) in 8.0 mol/dm³ hydrochloric acid, similar to the raffinate stream of the solvent extraction process II (after the removal of vanadium(V)), was prepared and subjected to a batch-type counter-current
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extraction process using 1.47 mol/dm$^3$ TBP in kerosene as an extractant (A : O = 1 : 2; Number of stages = 4). Batch type counter-current extraction and stripping studies were performed at laboratory scale using separatory funnels of suitable volume at 303 $\pm$ 1 K. The loaded organic phase was then subjected to counter-current stripping by employing 1.0 mol/dm$^3$ hydrochloric acid as a stripping agent at an O : A phase ratio of 1 : 1 (Number of stripping stages = 1).

![Graph showing the stripping behaviour of titanium(IV) from the loaded TBP phase using hydrochloric acid. Strip feed = 1.47 mol/dm$^3$ TBP in kerosene containing 0.72 g/dm$^3$ titanium(IV).]

*Figure 5.9.* Stripping behaviour of titanium(IV) from the loaded TBP phase using hydrochloric acid. Strip feed = 1.47 mol/dm$^3$ TBP in kerosene containing 0.72 g/dm$^3$ titanium(IV).

Typical results of the process are given in Table 5.2. The above results demonstrate that titanium(IV) chloride can be selectively separated from the waste chloride liquors of titania manufacturing industry by employing TBP as an extractant.
Figure 5.10. McCabe-Thiele plot for titanium(IV) stripping. Strip feed = 1.47 mol/dm³ TBP in kerosene containing 0.72 g/dm³ titanium(IV). Stripping agent = 1.0 mol/dm³ HCl.

Table 5.2. Extraction and separation of titanium(IV) from simulated waste chloride liquor using 1.47 mol/dm³ TBP in kerosene. Extraction: Number of stages = 4; A : O = 1 : 2, Stripping: Number of stages = 1; Stripping agent = 1.0 mol/dm³ HCl; O : A = 1 : 1.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Feed (mol/dm³)</th>
<th>Raffinate (mol/dm³)</th>
<th>Strip liquor (mol/dm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(II)</td>
<td>0.036</td>
<td>0.036</td>
<td>N.D.</td>
</tr>
<tr>
<td>Al(III)</td>
<td>0.035</td>
<td>0.035</td>
<td>N.D.</td>
</tr>
<tr>
<td>Ti(IV)</td>
<td>0.028</td>
<td>N.D.</td>
<td>0.014</td>
</tr>
<tr>
<td>Cr(III)</td>
<td>0.014</td>
<td>0.014</td>
<td>N.D.</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>0.031</td>
<td>0.031</td>
<td>N.D.</td>
</tr>
<tr>
<td>HCl</td>
<td>8.050</td>
<td>6.260</td>
<td>1.895</td>
</tr>
</tbody>
</table>
Chapter 5

Hydrothermal synthesis of TiO₂ powders and characterization

The preparation of TiO₂ powders comprises the steps of:

- Precipitation of amorphous titania from the TiCl₄ loaded TBP phase by employing sodium hydroxide (2.0 mol/dm³);
- Separation of amorphous titania from the TBP phase and washing with deionized water and acetone, respectively, to remove excess alkali, chloride ions and organic solvent impurities;
- Dispersion of amorphous titania powders in deionized water and adjustment of the pH of the reaction suspension to the desired value;
- Hydrothermal synthesis of titania powders by using the above precursor;
- Separation of the synthesized products by filtration or centrifugation, washing with deionized water and acetone, respectively, and drying at 353 K.

The schematic diagram of the process is shown in Fig. 5.11. The products were characterized by XRD and FT-IR. The morphological analysis was performed by SEM. The thermal studies were carried out by TG/DTA analysis. The specific surface area of the powder was measured using the three point BET method. Photocatalytic activity of the titania powders was also investigated.

**Effect of pH on the hydrothermal synthesis**

It is evident from the XRD patterns (Fig. 5.12c) that phase-pure anatase TiO₂ powders having crystallite size 15 nm (Table 5.3) was formed when the pH of the reaction suspension was 7.0 (at 453 K for a reaction time of 120
Figure 5.11. Schematic representation of the process for the preparation of TiO\textsubscript{2} powders.
Further, it is clear from the XRD patterns that neither rutile nor brookite phases are present. The results demonstrate that the presence of water in the reaction atmosphere catalyses the crystallization step for the formation of anatase. This is in good agreement with the previous results published for anatase, crystallized from amorphous titania using the hydrothermal technique (Yanagisawa and Ovenstone 1999).

On the other hand, at pH = 4.0 poor crystal growth with small crystallite size (5 nm) was observed (Fig. 5.12b). The chloride ions present in the amorphous powder at pH = 4.0 (HCl has been used for the adjustment of the pH of the reaction suspension from pH = 7.0 to pH = 4.0) of the reaction suspension may be bound to the surface of the powders. These chemisorbed species will cause certain amount of disorder in the lattice due to the differing charge and size between the oxygen and chloride ions (Yanagisawa and Ovenstone 1999). Amorphous TiO$_2$ was observed at pH = 9.0 (Fig. 5.12a). At higher pH values, the amorphous TiO$_2$ could not be separated well due to less protonation, and TiO$_6$ units would be still in the aggregate form via hydrogen bonding. This finding is consistent with the earlier reports that the formation of amorphous phase TiO$_2$ under mild basic hydrothermal conditions (Yin et al. 2001).

Fig. 5.13 shows the morphology of TiO$_2$ powder synthesized at pH = 7.0 of the reaction suspension. The particles are found to be very fine and highly agglomerated. In a solvent with a high dielectric constant such as water, precipitates with high surface potentials are stable for relatively small particle sizes (Park et al. 1997).
Figure 5.12. XRD patterns of TiO$_2$ powders synthesised at various pH values of the reaction suspension. Reaction temperature = 453 K; Reaction time = 120 min. a) pH = 9.0, b) pH = 4.0, c) pH = 7.0.

Effect of temperature on the hydrothermal synthesis

It is clear from Fig. 5.14 that the growth of the titania particles with anatase phase increases with increasing hydrothermal reaction temperature from 413 to 453 K (crystallite size increases from 6 to 15 nm). The changes in the crystallite size suggests that a shift in the growth mechanism from solid-state epitaxy to dissolution precipitation, since in this region the ionic product...
of the crystallization medium increases rapidly, allowing for greater solubility of the amorphous titania as well as faster transport kinetics. On the other hand, the specific surface area of the anatase powders decreases drastically with increase in the reaction temperature as shown in Table 5.3. Similar behaviour has also been reported elsewhere (Yanagisawa et al. 1997). Hence it could be concluded that crystallization was prompted by increasing the autoclaving temperature under the present experimental conditions. The remarkable decrease in surface area with an increase in reaction temperature from 413-453 K indicates that a large amount of amorphous content remained in the compacts at 413 K, as evidenced by the negligible increase in Vickers hardness with increase in reaction temperature.

Table 5.3. Effect of various hydrothermal reaction conditions on the surface area, particle size and crystallite size of the anatase powder.

<table>
<thead>
<tr>
<th>Hydrothermal reaction conditions</th>
<th>Surface area (m²/g)</th>
<th>Particle size (nm)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 4.0 453°C 120 min</td>
<td>291</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>pH 7.0 453°C 120 min</td>
<td>85</td>
<td>18</td>
<td>15</td>
</tr>
<tr>
<td>pH 9.0 453°C 120 min</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>pH 7.0 413°C 120 min</td>
<td>247</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>pH 7.0 433°C 120 min</td>
<td>167</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>pH 7.0 453°C 60 min</td>
<td>88</td>
<td>17</td>
<td>13</td>
</tr>
<tr>
<td>pH 7.0 453°C 180 min</td>
<td>84</td>
<td>18</td>
<td>15</td>
</tr>
<tr>
<td>pH 7.0 453°C 120 min (calcined)</td>
<td>40</td>
<td>38</td>
<td>19</td>
</tr>
</tbody>
</table>
Figure 5.13. SEM micrograph of anatase TiO$_2$ powder synthesised from a reaction suspension of pH = 7.0; Reaction temperature = 453 K; Reaction time = 120 min.

Figure 5.13c. SEM micrograph of calcined (773 K) anatase TiO$_2$ powder. Reaction temperature = 453 K; Reaction time = 120 min; Reaction suspension pH = 7.0.
Figure 5.14. X-ray diffraction patterns of TiO$_2$ powders synthesised at various reaction temperatures. pH = 7.0; Reaction time = 120 min. a) 413 K, b) 433 K, c) 453 K.

Effect of hydrothermal reaction time on the hydrothermal synthesis

It is evident from Fig.5.15 that a marginal increase in crystallite size occurs with increasing autoclaving time from 60 to 180 min. This is also
consistent with the results obtained from the BET surface area analysis as can be seen from Table 5.3.

Figure 5.15. X-ray diffraction patterns of TiO$_2$ powders synthesised at various reaction times. pH = 7.0; Reaction temperature = 453 K by a) 60 min b) 120 min c) 180 min.
TG/DTA analysis of the synthesized TiO$_2$ powders

The peak at 553 K in the DTA curve (Fig. 5.16) indicates the removal of absorbed water (Lee and Zuo 2004). This is also consistent with the loss of weight (2.5%) as can be seen from the TG analysis data (Fig. 5.17). Further, it is also evident from the TG/DTA data that no phase transformation was observed for anatase phase TiO$_2$ in the temperature range from 313 to 1273 K.

![Figure 5.16 Differential thermal analysis of TiO$_2$ powders. Reaction temperature = 453 K; Reaction time = 120 min; Reaction suspension pH = 7.0.](image)

The broad absorption peak at 3400 cm$^{-1}$ and the peaks at 1627 cm$^{-1}$ and 650 cm$^{-1}$ present in the FT-IR spectrum of the synthesized anatase powder.
(Fig. 5.18) corresponds to the absorbed molecular water present in the anatase powder. The absence of P=O stretching frequency of TBP (at 1276 cm\(^{-1}\)) clearly indicates that the synthesized powder is free from contamination by the extractant used for the preparation of the precursor.

\[\text{Figure 5.17} \quad \text{Thermogravimetric analysis of TiO}_2 \text{ powders. Reaction temperature} = 453 \text{ K; Reaction time} = 120 \text{ min; Reaction suspension pH} = 7.0.\]

\textit{Mechanism of anatase crystallization}

Anatase consists of TiO\(_6\) octahedra, which share faces, and the phase transformation is accomplished by the rearrangement of these octahedra. For anatase, the rearrangement under hydrothermal conditions of these octahedra from the amorphous state proceeds by a solid-state reaction, where water
molecules form bridges between surface OH groups of different octahedra which share only one common vertex, using the two lone pairs of electrons on oxygen. Due to the size of the water bridges, it is possible for two bridges to form between the two octahedra, thus linking them by triangular face. Having thus aligned the octahedra correctly, dehydration occurs, and the original two water molecules are lost, along with two further water molecules, leaving the two titanium ions linked by two further oxygen ion vertexes, thus sharing a face (anatase). Several investigators have proposed the similar mechanism for anatase crystallisation (Yanagisawa and Ovenstone 1999; Yin et al. 2001).

Figure 5.18 IR spectrum of TiO₂ powders. Reaction temperature = 453 K; Reaction time = 120 min; Reaction suspension pH = 7.0.
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Photocatalytic activity

The excellent photocatalytic activity of titania has been well documented (Fox and Dulay 1993) and is well known that it is the anatase polymorph rather than the brookite or rutile polymorph that has the highest photocatalytic activity. The most active commercially available photocatalyst (Degussa P25) has an anatase content of 75% and 25% of rutile content (Sudhadevi et al. 2003). The difficulty in producing an extremely active phase-pure anatase photocatalyst stems from the fact that rutile is the thermodynamically stable polymorph, and although anatase is kinetically stable, it is readily converted into rutile phase in the temperature range of 873-1273 K. It is therefore desirable to find a low-temperature route for the synthesis of anatase phase to avoid conversion to rutile. Furthermore, control of the physical properties of anatase itself is important in determining its photocatalytic activity. It is widely regarded that anatase powder with a high surface area and also with high degree of crystallinity, with a large crystallite size is desirable to enhance the photocatalytic activity, since such a powder will have relatively few disruptions in its electronic band structure. Hence, in the present study, an attempt has been made to test the photocatalytic activity of the synthesized phase-pure anatase titania by investigating the photocatalytic degradation of methyl orange. For comparison, studies also have been performed with commercially available photocatalysts, Degussa P25 (consists of 75% anatase and 25% rutile with a specific BET surface area of 50 m²/g and particle size 30 nm) and Hombikat UV 100 (consists of 100% pure anatase with a specific BET surface area of 250 m²/g and particle size of 5 nm).
Fig. 5.19 shows the change in the absorption intensity on irradiation of an aqueous solution of methyl orange (50.0 x 10^{-6} \text{ mol/dm}^3) containing 1.0 g/dm^3 TiO_2 (hydrothermally synthesized anatase at 453 K for 120 min at pH = 7.0) in the presence of air oxygen using 450W medium pressure mercury lamp. Control experiments were carried out by employing unirradiated blank solution. It is evident from the results that the absorption intensity decreases with increasing irradiation time and nearly total decolourisation was observed within 180 min. On the other hand, total decolourisation of methyl orange was obtained within 30 min in the presence of Degussa P25 and within 60 min in the presence of Hombikat UV 100 (Fig. 5.20). The more time required for the decolourisation of methyl orange with the synthesized anatase TiO_2 may be due to the presence of absorbed water in titania powder, as is evident from the TG/DTA analysis data. To achieve the full photocatalytic potential of the synthesized sample, calcination of the powder may be required as documented in the literature (Kominami et al. 1995; Kominami et al. 1999).

Hence the synthesized anatase powder (at 453 K for 120 min at pH = 7.0) has been subjected to calcination at 773 K for 120 min with a view to improve its photocatalytic property. It is evident from the XRD pattern (Fig. 5.21) that the calcined anatase powder contains neither rutile nor brookite phases. Enhancement in the crystallite size (15 nm to 19 nm) and decrease in the BET specific surface area (85 to 40 m^2/g) was noticed for the calcined anatase TiO_2 powder. The typical SEM micrograph of the calcined sample is shown in Fig. 5.13c. The particles are found to be very fine and highly agglomerated. The DTA analysis of the calcined sample indicates the absence of absorbed water molecules (Fig. 5.22).
**Figure 5.19** Change in absorption spectrum on irradiation of aqueous suspension of the synthesised TiO₂ (1.0 g/dm³) (Reaction temperature = 453 K; Time = 120 min; Suspension pH = 7.0) containing methyl orange (50.0 × 10⁻⁶ mol/dm³). a) blank, b) 5 min, c) 10 min, d) 20 min, e) 30 min, f) 90 min, g) 180 min.

**Figure 5.20** Change in intensity at 462 nm versus irradiation time for the aqueous solution of methyl orange (50.0×10⁻⁶ mol/dm³). a) in presence of Degussa P25 ((1.0 g/dm³). b) in presence of Hombikat UV 100. c) in presence of calcined TiO₂ at 773 K. d) in the presence of TiO₂, (Reaction Temperature = 453 K; Time = 120 min; Suspension pH = 7.0).
Figure 5.21. X-ray diffraction pattern of calcined (773 K) TiO$_2$ powder. Reaction temperature = 453 K; Reaction time = 120 min; Reaction suspension pH = 7.0

Figs. 5.20c and 5.23 show the change in the absorption intensity on irradiation of an aqueous solution of methyl orange (50.0 x 10$^{-6}$ mol/dm$^3$) containing 1.0 g/dm$^3$ calcined TiO$_2$ anatase powder. The photocatalytic activity of the calcined sample was significantly improved as compared to the uncalcined sample.

The results demonstrate that phase-pure anatase TiO$_2$ nanocrystallites can be synthesized hydrothermally at relatively low temperatures (413-453 K) and reaction times (1-2 hr) as compared to the earlier reports (reaction time 12-48 hr; reaction temperature 473-623 K). Further, the results also reveal that photocatalytic anatase powders can be prepared without the addition of mineralizers and additives.
Figure 5.22 Differential thermal analysis of calcined (773 K) TiO$_2$ powders. Reaction temperature = 453 K; Time = 120 min; Suspension pH = 7.0.

Figure 5.23. Change in absorption spectrum on irradiation of aqueous suspension of calcined (773 K) TiO$_2$ ((1.0 g/dm$^3$) (Reaction Temperature = 453 K; Time = 120 min; Suspension pH = 7.0) containing methyl orange ($50.0 \times 10^{-6}$ mol/dm$^3$). a) blank, b) 30 min, c) 60 min, d) 90 min.
Chapter 5

Recycling capacity of the solvent

The recycling capacity of the extractant was tested, first by extracting titanium(IV) using 1.47 mol/dm$^3$ TBP from 8.0 mol/dm$^3$ of hydrochloric acid solutions containing 0.03 mol/dm$^3$ titanium(IV) and then stripping with 2.0 mol/dm$^3$ sodium hydroxide in an org : aq. phase ratio of 1 : 2. The stripped organic phase was reused for extraction. The extraction efficiency was found to be the same as that of fresh extractant. Further, the recycling capacity was also confirmed by IR spectral data (Fig. 5.6). It is clear from the IR data that the P=O stretching frequency of TBP was not changed even after precipitation-stripping. The results revealed practically insignificant change in the extraction efficiency of the solvent even after five cycles of extraction and stripping processes.