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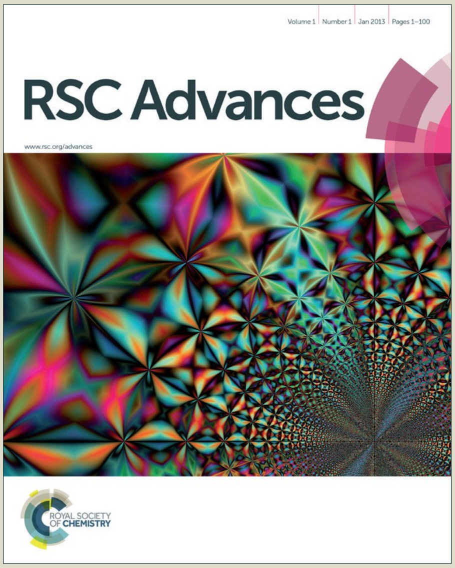

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Titanium aminophosphates : Synthesis, characterization and Orange – G dye degradation studies

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Abstract

Titanium aminophosphates are prepared by using titanium tetraisopropoxide, orthophosphoric acid and aliphatic amines. The synthesized TNPAP, TNOAP and TNDDAP titanium aminophosphates are characterized by various physicochemical techniques. The catalytic effect of TNPAP, TNOAP and TNDDAP has been studied for the degradation of orange G dye. TNDDAP is found to be most effective catalyst. The optimum conditions required for efficient orange G degradation have been found to be pH = 3.0, $[H_2O_2] = 1.0 \times 10^{-3}$ M, $[OG] = 1.0 \times 10^{-4}$ M and TNDDAP catalyst dosage of 150 mg. TNDDAP is efficiently catalyzes the degradation of orange G dye with 97.3% degradation in 250 min. These catalysts exhibit good reusability over five successive cycles. They have potential to be used as economical catalysts for dye degradation of industrial waste waters.

Keywords : Titanium aminophosphates; synthesis; characterization; orange G dye degradation

Introduction

Organic dyes are major pollutants released into water systems during their manufacturing and processing from the industries. These compounds are highly coloured and cause serious problem to the aquatic environment as they affect the photosynthetic activity by reducing light penetration. Their presence in low concentration as 1 mg L^{-1} in the effluent is considered to be undesirable and needs to be removed before the wastewater can be discharged into the environment [1]. In addition, their presence in drinking water constitutes a potential human health hazard. They are difficult to degrade due to their complex structure which makes them mutagenic and carcinogenic. Thus, efficient colour removal from wastewaters involving physical, chemical and biological methods has attracted the interest of environmentalists and researchers. Majority of the dyes consumed at industrial scale are having azo, anthraquinone, triphenylmethane, phthalocyanine, formazin or oxazine functional groups [2]. These dyes are used extensively in textile industries owing to their brilliant colour, high wet fastness, easy application and minimum requirement of energy during the process.

In specific azo dyes are non-degradable, carcinogenic, teratogenic and toxic [3]. Approximately 50 - 70% of the dyes available in the market are azo compounds [4]. They are very important pollutants; recalcitrant, even at low concentrations they can affect the water sources by imparting undesirable colour which reduces the light penetration through the water column [5]. Therefore, studies on decolourisation and detoxification of azo dye effluents have received increasing attention. Orange G (Fig. 1) is a synthetic azo dye used in histology in many staining formulations.

Synthetic dyes are recalcitrant to remove by conventional wastewater treatment technologies such as adsorption, photo degradation [6-13], coagulation, flocculation, chemical oxidation, electrochemical oxidation and biological process. Available physical and chemical treatment methods have limited use and are operationally expensive. Research efforts are needed to develop powerful techniques for the removal of azo dyes from aqueous medium to avoid their accumulation. Hence there is a need for efficient water treatment technologies to degrade hazardous contaminants present in the effluents and make water resources both safe and potable to human consumption.

Phosphate based materials are important in several industrial acid catalysed reactions [14]. In recent years inorganic phosphorous containing materials have received much attention on account of their ability to selectively uptake specific ions, resistance to oxidation, high thermal and chemical stability. In addition, the presence of phosphate in materials seems to enhance catalytic properties, stabilize surface area, crystal phase, improve surface acidity and make the material porous [15]. Research on phosphate based materials with open frameworks is currently in progress due to their applications in catalysis and gas separation [16]. Study of transition metals phosphates has received great attention in recent years. Phosphate frameworks stabilize reduced oxidation states, due to its high charge (PO_4^{3-}) and hence favour the formation of anionic frameworks with a high degree of chemical, mechanical and thermal stability.

Aminophosphates are amine and phosphorous based materials [17]. The organic functionality in aminophosphate framework enhances hydrophobicity and shows high activity in base catalysed reactions. Incorporation of transition metals such as titanium or vanadium or palladium in aminophosphates leads to novel materials with redox properties. In particular, titanium cation Ti^{4+} in framework positions is found to exhibit good activity in shape selective redox reactions. This manuscript deals with synthesis and characterization of a group of titanium aminophosphates. Owing to the presence of titanium that has redox site, Bronsted acid site, Lewis acid site, Lewis base nitrogen donor alkyl groups in titanium aminophosphates, the materials are expected to have peculiar catalytic properties. Titanium aminophosphates have been investigated for their catalytic applications towards the degradation of orange G dyes at room temperature using hydrogen peroxide as oxidant.

Experimental

Synthesis of titanium aminophosphates was carried out at room temperature. In typical synthesis n-propyl amine (10.9 mL) or n-octyl amine (22.0 mL) or n-dodecyl amine (30.6 mL) was added to 0.05 mL of titanium tetraisopropoxide and was stirred. To this mixture, 1.87 mL of orthophosphoric acid was added and stirred vigorously to yield solid products (0.02 TiO_2: P_2O_5: 8 RNH_2). The products thus obtained were thoroughly washed with ether, dried at 40 °C for about 30 min and ground to fine powder to obtain respective titanium aminophosphates.

Qualitative phase analysis of titanium aminophosphates have been studied using a Bruker AXS D8 Advance diffractometer at room temperature with Cu-Kα X-ray source of wave length 1.5406 Å using Si (Li) PSD detector. The morphology and surface elemental composition of the material was investigated using scanning electron microscopy (SEM/EDAX) on a JEOL Model JSM-6390LV. Fourier transform infrared spectroscopy (FT-IR) was recorded on Thermo Nicolet, Avatar 370 spectrophotometer equipped with a pyroelectric detector (DTGS type); a resolution of 4 cm^{-1} was adopted and provided with KBr beam splitter. Dispersive Raman spectroscopy was performed on Bruker senterra at a wavelength of 532 nm using laser radiation as source. The co-ordination and oxidation state of titanium was examined by diffuse reflectance UV-Visible spectrophotometer (UV-Vis DRS) on Varian, Cary 5000 in the wavelength range of 175 – 800 nm. X-ray Photoelectron spectroscopic analysis was carried out using ESCA-3000 (VG Scientific, UK) instrument. The ^{31}P magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy was performed at room temperature on a Bruker DRX-500 AV-

III 500(S) spectrometer, with a spinning rate of 10-12 KHz operating at 121.49 MHz using a 5 mm dual probe. The ^{13}C cross polarization magic-angle spinning (CP-MAS) nuclear magnetic resonance (NMR) spectroscopy was performed at room temperature on a DSX-300 Avance-III 400(L) NMR spectrometer with a spinning rate of 10-12 KHz operating at 75.47 MHz using a 5 mm dual probe.

The degradation of orange G dye (Fig. 1) using hydrogen peroxide as oxidant in presence of titanium aminophosphates have been studied at room temperature. A stock solution of dye having concentration of 1×10^{-3} M was prepared and solutions of desired concentrations have been obtained by the successive dilutions of stock solution. The degradation has been studied using UV-Visible spectrophotometer by measuring the decrease in absorbance of the dye solution with respect to time at the respective λ_{max} of dye, 476 nm for orange G. Effect of pH, concentration of the dye, concentration of oxidant H_2O_2 and amount of catalyst on the degradation has been studied. All the studies were carried out under room temperature.

Results and Discussion

Powder X-ray diffraction patterns of titanium n-propylamino phosphate (TNPAP), titanium n-octylaminophosphate (TNOAP) and titanium n-dodecylaminophosphate (TNDDAP) are shown in Fig. 2. TNPAP exhibits peaks at 2θ degrees of 22.9°, 24.1°, 26.1°, 27.9° and 30.7° indicates the presence of −Ti−O− linkage [18]. Similarly X-ray diffraction pattern of TNOAP and TNDDAP shows peaks at 2θ degrees of 5.6°, 8.2°, 8.3°, 13.7° and 18.7° corresponding to presence of –Ti–O– with a mesoporous structure [18-20]. TNOAP, TNDDAP exhibits low angle diffraction peaks at 4.1° and 4.2° characteristic of mesoporous structure.

The SEM-EDAX images of TNPAP, TNOAP and TNDDAP are shown in Fig. 3. The SEM images of TNPAP and TNOAP reveal that the materials possess micron sized irregular flakes throughout the surface of the materials. The SEM image of TNDDAP show the material has tubular like morphology. The EDAX analysis of TNPAP, TNOAP and TNDDAP shows the distribution of the constituent elements O, C, P, N and Ti.

The TG/DTA of TNPAP, TNOAP and TNDDAP shows that the thermogravimetric analysis exhibits continuous weight loss up to 400 °C. This may be due to removal of polymerized molecules. Thereafter, the weight remains constant which indicates the decomposition, combustion and crystallization of organic material present in titanium aminophosphates. DTA shows exothermic peaks for oxidative decomposition of organic amine and endothermic peaks which are due to dehydration and evaporation of a part of organic components.

The BET surface area analysis of titanium aminophosphates showed 50, 71 and 112 m^2/g for TNPAP, TNOAP and TNDDAP respectively (Table 1 & Fig. 4). The lesser surface area compared to that reported for zeolites is due to the blockage of pores by alkyl groups present in amines.

The FT-IR spectra of TNPAP, TNOAP and TNDDAP shows a broad absorption band at 3420 cm^{-1}, which corresponds to O−H or N−H stretching vibrations for TNPAP. The peaks in the range of 3020 - 2850 cm^{-1} corresponds to the alkyl symmetrical and asymmetrical stretching vibrations of amine groups in titanium aminophosphates [21]. Peaks in the range of 1640 - 1630 cm^{-1} are attributed to O−H bending vibrations of adsorbed water in titanium aminophosphates. Peaks observed at 1469, 1467 cm^{-1} is due to asymmetric deformation vibrations of alkyl group in

TNOAP and TNDDAP [22]. The bands at 1079, 1085 cm^{-1} in TNOAP and TNDDAP are attributed to P–O stretching vibrations [23, 24]. The bands at 1038 and 1034 cm^{-1} in TNPAP and TNOAP are due to Ti–O–P stretching vibrations. The bands around 980 cm^{-1} are attributed to vibrational frequencies of P–O group in titanium aminophosphates [33]. Peaks at 1240 and 1222 cm^{-1} in TNOAP and TNDDAP correspond to the characteristic absorbance of C–N bonds [25]. The peaks at 887 and 892 cm^{-1} in TNOAP and TNDDAP are due to asymmetric stretching vibrations of P–O–P groups. The peaks at 759, 758 cm^{-1} in TNPAP and TNOAP are attributed to non-bridging Ti–O bond vibrations [26, 27]. The peaks at about 725 and 723 cm^{-1} in TNOAP and TNDDAP are assigned to symmetric stretching vibrations of P–O–P groups. The peaks in the range of 700 - 400 cm^{-1} are attributed Ti–O and Ti–O–Ti vibrations in titanium aminophosphates. The peaks at 538, 492, 530 and 540 cm^{-1} in titanium aminophosphates are attributed to P–O bending vibrations [28, 29].

The Raman spectra of TNPAP, TNOAP and TNDDAP shows small peaks at 568 cm^{-1} and 939 cm^{-1} in TNPAP corresponds to stretching vibration of Ti−O bond [30,31]. The band at 1200 cm^{-1} in TNPAP is associated with asymmetric stretching vibration of P−O bond of phosphate group [32]. The week intensity of the peaks in other catalysts are due to the presence of low density of titanium.

The UV-Visible diffuse reflectance spectra of TNPAP. TNOAP and TNDDAP show peaks around 215 nm due to charge transfer transitions between empty 3d-orbital's of Ti (IV) cations and 2p-orbitals of oxygen anions (O^{2-}). The charge transfer transition infers the presence of titanium in tetrahedral co-ordination. TNPAP, TNOAP and TNDDAP show peaks at 343, 330 and 325 nm respectively. These can be attributed to the existence of titanium in tetrahedral co-ordination.

The X-ray photo electron (XPS) spectra of carbon, oxygen, nitrogen, phosphorous and titanium ion (TNPAP) show that the carbon 1s shows peak at 288.0 eV. This can be attributed to carbon bonded to oxygen, nitrogen and hydrogen respectively [33]. The peak around 534.0 eV corresponds to oxygen 1s binding energy. This is due to chemisorbed water and weakly adsorbed oxygen molecules on the surface. The binding energies of 534.2 eV and 532.4 eV are ascribed to oxygen co-contributed from Ti–O, P–O [34]. The peaks at 462 and 468 eV correspond to the binding energies of Ti $2p_{3/2}$ and $2p_{1/2}$ electrons, which is due to nitrogen doped interstitially into the titania matrix [31]. The higher binding energy value of titanium is due to different electronic interaction with nitrogen compared to oxygen. They suggest considerable modification of the lattice due to N substitution. Titanium binds to nitrogen or oxygen atoms in the lattice to form O–Ti–N or Ti–N–O [35]. The P 2p shows peak at 136.0 eV corresponding to the presence of phosphorous oxide (P_2O_5) in the TNPAP.

The ^{31}P MASNMR spectra of TNPAP, TNOAP and TNDDAP are show peaks at 4.654 ppm and -0.73 ppm with its side bands for TNPAP. The peaks are in 1:3 intensity ratios and suggest the existence of two crystallographically non-equivalent phosphorous atoms. The ^{31}P MASNMR spectra of TNOAP and TNDDAP show peaks at 5.824 and 1.924 ppm. The presence of only one peak in TNOAP and TNDDAP spectra indicates that there is a unique chemical environment of phosphorous atoms. The ^{31}P peaks in the range of -5 to 3 ppm corresponds to the presence of mesoporous crystalline titanium aminophosphate framework [36].

The ^{13}C MASNMR spectra of TNPAP, TNOAP and TNDDAP are shown in Fig. 5. They show peaks at 41.12 and 39.80 ppm, which corresponds to the C_1, carbon bonded to nitrogen atom of amine group. The peaks at 34.46 and 32.12 ppm in TNOAP can be assigned to the C_2 and C_3 carbons linked to C_1 carbon which is directly attached to nitrogen of amine group. The peak at 21.47 ppm in TNPAP can be assigned to the carbon of methylene ($-CH_2-$) group. The peaks at 29.93, 28.37 and 24.49 ppm in TNOAP can be assigned to the carbons of methylene ($-CH_2-$) groups. Peaks at 12.30 and 14.98 ppm in TNPAP and TNOAP can be attributed to the carbon of terminal $-CH_3$ group of amine molecules [22, 37]. Fig. 5c shows the characteristic peaks of dodecylamine carbon atoms.

Based on the above characterization, we have proposed the following plausible mechanism for titanium aminophosphate synthesis and basic structure of the catalysts (Fig. 6). This is a tetrafunctional catalyst due to the presence of titanium ion (redox, Lewis acid), amine (Lewis base) and exchangeable proton (Bronsted acid) sites. As the reaction is carried out in solvent free condition, there is no residue from the synthesis of catalyst (It means 100% yield). So all the input titanium and amine are present in the basic structure. The presence of solid acid sites are deduced from the proposed structure, which is confirmed by the NaCl ion exchange experiment.

In order to test the generality of titanium aminophosphates as catalysts for dye degradation purposes, degradation of orange G dye was also studied. The % degradation of orange G was evaluated by measuring the decrease in the absorbance of orange G solution with respect to time at 476 nm, the λ_{max} of orange G.

The effect of pH on the degradation of orange G by hydrogen peroxide in the presence of titanium aminophosphate catalysts has been studied at room temperature in the pH range of 2.0 to 7.0 at orange G dye concentration of 1.0×10^{-3} M and catalyst dosage of 150 mg. Degradation of orange G was found to increase with the increase of pH from 2.0 to 3.0 in the presence of all the three titanium aminophosphate catalysts (Table 2). Further increase in pH from 3.0 to 7.0 does not affect the percentage degradation. These results indicate that the degradation of orange G was significantly influenced by the pH of the solution and the maximum degradation of orange G dye was found to be at pH 3.0. Hence, pH 3.0 has been chosen as optimum for orange G dye degradation at room temperature.

Effect of varying concentration of hydrogen peroxide on the orange G dye degradation has been investigated at room temperature in the range of 1.0×10^{-3} M to 2.0×10^{-3} M of H_2O_2. The degradation of orange G dye increases up to H_2O_2 concentration, 1.0×10^{-3} M and further increase in concentration does not have appreciable effect on the degradation (Table 3). The increase in the degradation with increase in H_2O_2 concentration until 1.0×10^{-3} M shows the basis of availability of more hydroxyl radicals for the attack on adsorbed orange G. Further increase in H_2O_2 concentration may not be contributing to the increase in OH radicals due to scavenging effect. The % degradation of orange G was found to be maximum at 1.0×10^{-3} M of H_2O_2 after a period of 250 min with a % degradation of 97.1. Consequently all the other experiments on the degradation were carried out using 1.0×10^{-3} M of H_2O_2.

Effect of amount of catalyst on the degradation of orange G has been studied by varying the amounts of catalyst from 25 mg to 200 mg at pH 3.0 and keeping the concentrations of H_2O_2 & orange G as constant. It is observed that the percentage degradation of orange G increases from 39.8 to 97.3 with increase in the amount of TNDDAP catalyst from 25 mg to 150 mg (Table 4). Further increase in the amount of catalyst did not show much influence on % degradation. Hence, 150 mg of the TNDDAP has been chosen as optimum dosage to carry out all other investigations.

Degradation of orange G was studied in the presence of TNDDAP catalyst by varying concentration of orange G in the range of 1.0×10^{-3} M to 4.0×10^{-3} M at pH 3.0 and H_2O_2 concentration of 1.0×10^{-3} M and TNDDAP dosage as 150 mg. The % degradation of orange G at different initial concentrations of orange G is shown in Table 5. The conversion does not vary considerably with change in Orange G concentration in this range.

From the above studies, it can be concluded that titanium aminophosphates are efficient catalysts for the degradation of orange G with H_2O_2 as oxidant. Among the catalysts studied, TNDDAP was found to be more effective. We have also established the optimum conditions for the efficient degradation of orange G. Eeffect of various titanium aminophosphate catalysts on the degradation of orange G dye has been investigated using catalyst dosage of 150 mg, pH 3.0 and H_2O_2 concentration of 1.0×10^{-3} M. It has been observed that the degradation of orange G proceeds much more rapidly in the presence of TNDDAP compared to TNOAP and TNPAP. Increased catalytic activity of TNDDAP m attributed to the enhanced pore size and adsorption due to the bulkier dodecyl group than TNPAP and TNOAP. The percentage degradation was found to be 97.3 for TNDDAP whereas 77% for TNOAP and 71% for TNPAP in 250 min. The higher adsorption can be related to a higher affinity of the dye to the surface, which is affiliated with a higher number of active centres on the catalyst's surface. The surface nitrogen is also important for basic catalytic activity in these materials. Studies on the reusability (Fig. 7) of catalyst on the degradation of orange G have been carried out by using TNDDAP, the most efficient among the catalysts studied. The catalyst was separated by centrifugation after maximum % of dye gets degraded. It is thoroughly washed with water and then by ethanol. The recovered catalyst is reused in the next cycle under optimum reaction conditions. It is observed that TNDDAP effectively catalyzes the degradation of orange G without much loss of its activity for atleast five successive runs (Table 6).

The results presented above reveals that titanium aminophosphates act as efficient catalysts for the degradation of orange G dyes. The catalytic effect can be due to the tetrahedral co-ordination geometry of the titanium ion in the framework. Tetrahedrally co-ordinated metal ions in the framework being unsaturated, will activate oxidant species and create desirable transition states in the vicinity of active centres for subsequent activation of the substrates. On the other hand, six co-ordinated metal species have not been found to be as effective as that of four co-ordinate analogues as they are co-ordinatively saturated. As a result, the interaction of the oxidant with the catalyst is retarded making the system comparatively inactive [38]. TNDDAP is more effective in the case of orange G degradation, indicating the specificity of catalysts. This observation can be partly rationalized on the basis of the structural features of orange G (azo dye) which influence the binding forces between the dye molecules and titanium aminophosphate frameworks [39]. In orange G dye, the azo bonds are more active. The degradation of orange G may be due to the initial electrophilic cleavage of chromophoric azo group (−N=N−) by the reaction of peroxy radicals and generation of nitrosoaryl intermediates or C−N bond resulting in aniline as one of the intermediate products.

Conclusions

Titanium aminophosphates are prepared by using titanium tetraisopropoxide, orthophosphoric acid and aliphatic amines. The synthesized TNPAP, TNOAP and TNDDAP titanium aminophosphates are characterized by various physicochemical techniques. Powder XRD pattern of titanium aminophosphates suggests the presence of -Ti–O– phase. The % of titanium incorporated into the frameworks of titanium aminophosphates has been confirmed from EDAX analysis. The infrared and Raman spectra infers the presence of peaks due to vibrational bands of Ti–O, P–O and Ti–O–P linkages. The UV–Vis diffuse reflectance spectra reveal the presence of tetrahedral co-ordination of Ti in the framework. The XPS spectra suggest the presence of −O–Ti–N− or −Ti–N–O− framework in TNPAP. The ^{31}P MASNMR spectra of titanium aminophosphates indicate the presence of crystalline titanium aminophosphate framework. The catalytic effect of TNPAP, TNOAP and TNDDAP has been studied for the degradation of orange G dyes. TNDDAP is more effective in the case of orange G dye degradation, indicating the specificity of catalysts. The optimum conditions for the efficient degradation of orange G have been found to be pH = 3.0, $[H_2O_2] = 1.0 \times 10^{-3}$ M, $[OG] = 1.0 \times 10^{-3}$ M and TNDDAP catalyst dosage of 150 mg. TNDDAP efficiently catalyzed the degradation of orange G dye with 97.3% degradation in 250 min. These catalysts exhibited good reusability over five successive cycles. They have potential to be used as economical catalysts for dye degradation of industrial waste waters.

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Table 1 : Surface properties of the titanium aminophosphates.

S. No.	**Catalyst**	**Surface Area (m^2/g)**	**Pore volume (cm^3/g)**	**Pore size (Å)**	**Horvath-Kawazoe pore width (Å)**
1.	**TNDDAP**	112	0.55	239	301
2.	**TNOAP**	71	0.51	178	231
3.	**TNPAP**	50	0.32	138	198

Table 2: Effect of pH on the degradation of orange G

$[H_2O_2] = 1.0 \times 10^{-3}$ M, $[OG] = 1.0 \times 10^{-3}$ M, Catalyst dosage = 150 mg

pH	**% Degradation**		
	TNPAP	**TNOAP**	**TNDDAP**
2.0	43.8	47.9	72.6
3.0	71.9	77.1	**97.3**
4.0	57.1	67.3	96.4
5.0	56.2	65.4	95.1
6.0	56.4	64.1	94.2
7.0	55.7	63.8	92.8

Table 3: Effect of hydrogen peroxide concentration on the degradation of orange G

[OG] = 1.0 × 10^{-3} M, pH = 3.0, Catalyst dosage = 150 mg

[H_2O_2] × 10^4 M	**% Degradation**		
	TNPAP	**TNOAP**	**TNDDAP**
0.1	26.8	38.9	38.7
0.2	42.2	47.1	42.9
0.5	53.7	58.2	54.4
0.75	61.5	68.6	78.3
0.100	**71.9**	**77.1**	**97.3**
0.150	70.8	76.5	96.4
0.200	69.1	75.7	95.8

Table 4: Effect of catalyst dosage on the degradation of orange G

$[H_2O_2] = 1.0 \times 10^{-3}$ M, [OG] $= 1.0 \times 10^{-3}$ M, pH = 3.0

Catalyst Dosage (mg)	% Degradation		
	TNPAP	TNOAP	TNDDAP
0	13.9	13.9	13.9
25	28.2	31.7	39.8
50	34.1	36.4	45.4
75	46.5	41.3	49.6
100	53.3	57.4	74.8
150	71.9	77.1	**97.3**
175	70.2	76.9	96.1
200	69.3	76.1	95.2

Table 5: Effect of concentration of orange G on its degradation in the presence of TNDDAP catalyst

$[H_2O_2] = 1.0 \times 10^{-3}$ M, pH = 3.0, TNDDAP = 150 mg

S.No	$[OG] \times 10^{-3}$ M	% Degradation
1	1.0	**97.3**
2	2.0	97.0
3	3.0	96.7
4	4.0	96.3

Table 6: Reusability of TNDDAP towards the degradation of orange G

[OG] = 1.0×10^{-3} M, [H_2O_2] = 1.0×10^{-3} M, pH = 3.0, TNDDAP dosage = 150 mg

Catalyst	**Fresh**	**Recycled 1**	**Recycled 2**	**Recycled 3**	**Recycled 4**	**Recycled 5**
% Degradation	97.3	96.8	95.7	95.0	94.9	94.9

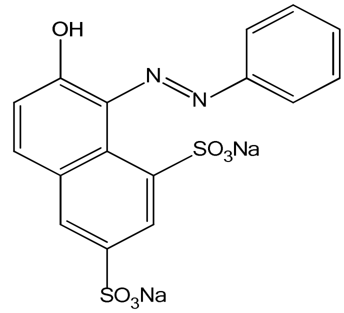

Fig. 1 : **Structure of orange G dye.**

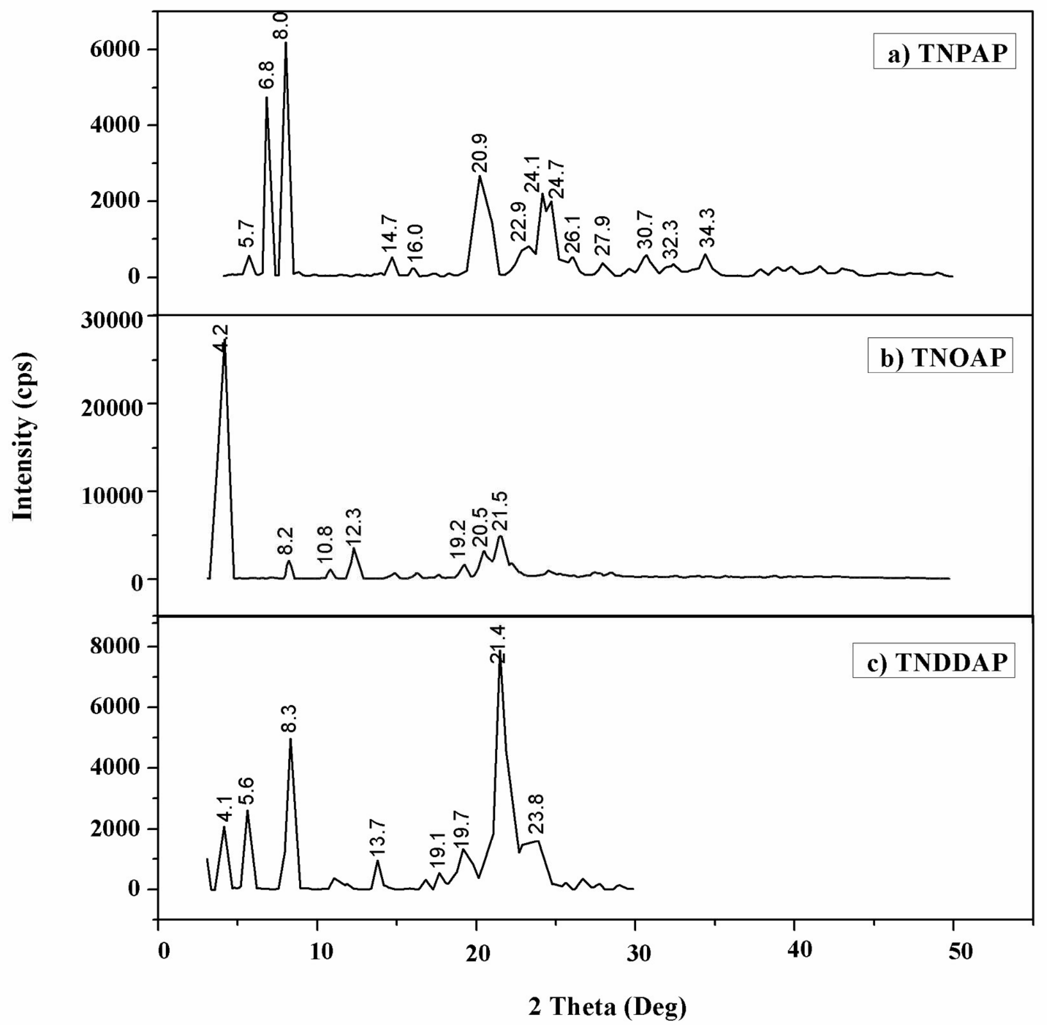

Fig. 2: **Powder XRD patterns of a) TNPAP, b) TNOAP and c) TNDDAP.**

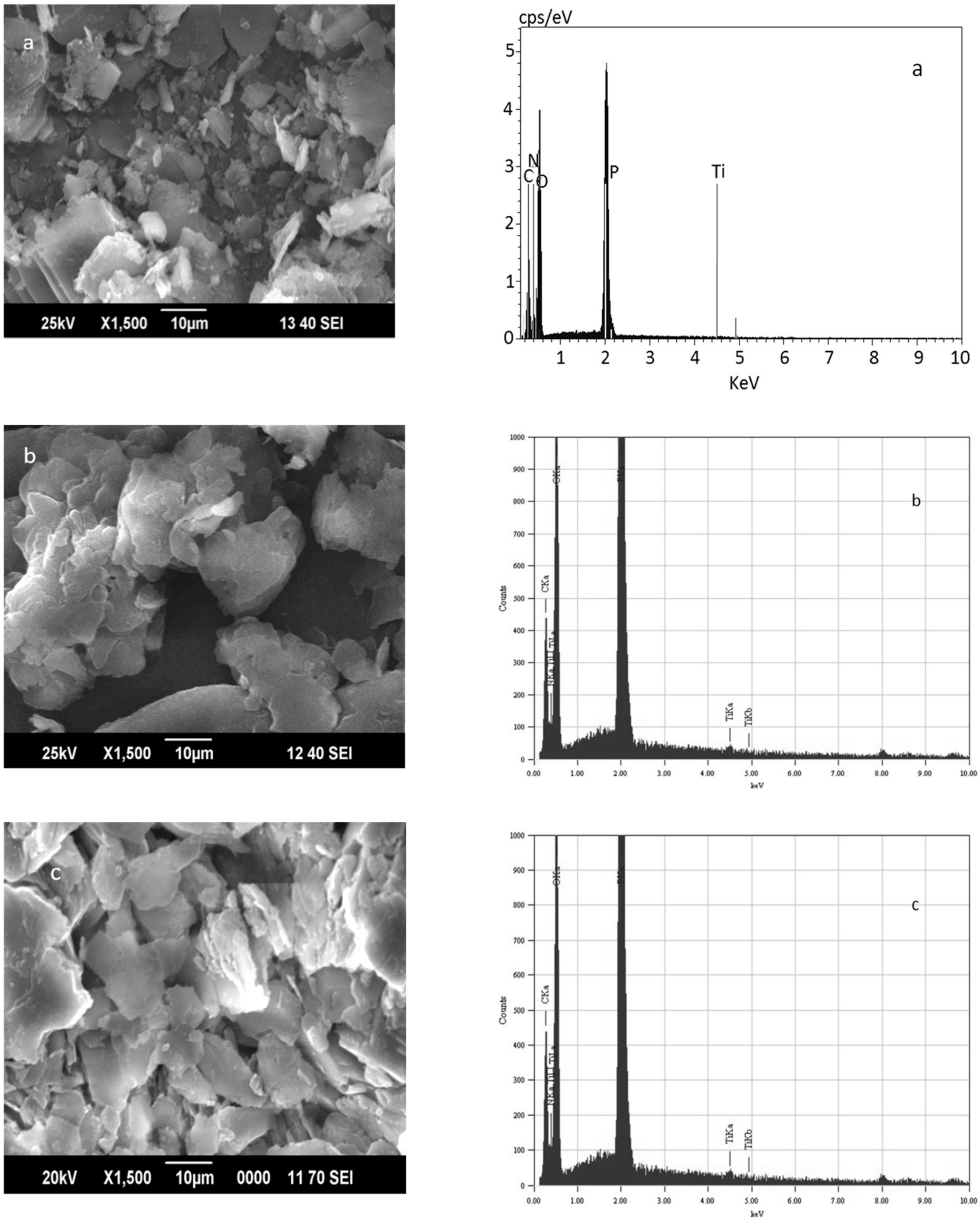

Fig. 3: **SEM-EDAX images of a) TNPAP, b) TNOAP and c) TNDDAP.**

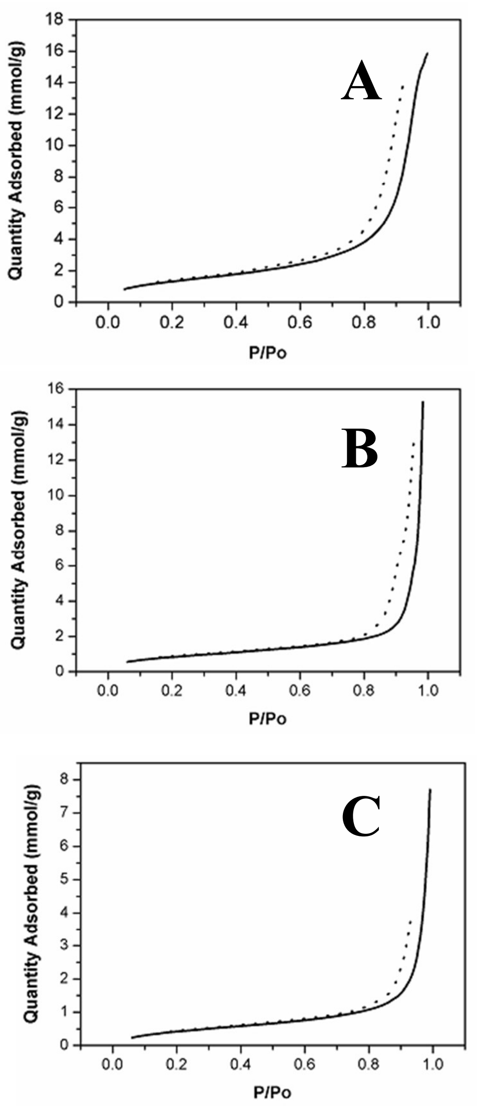

Fig. 4 BET – Adsorption isotherm of A) TNDDAP, B) TNOAP and C) TNPAP.

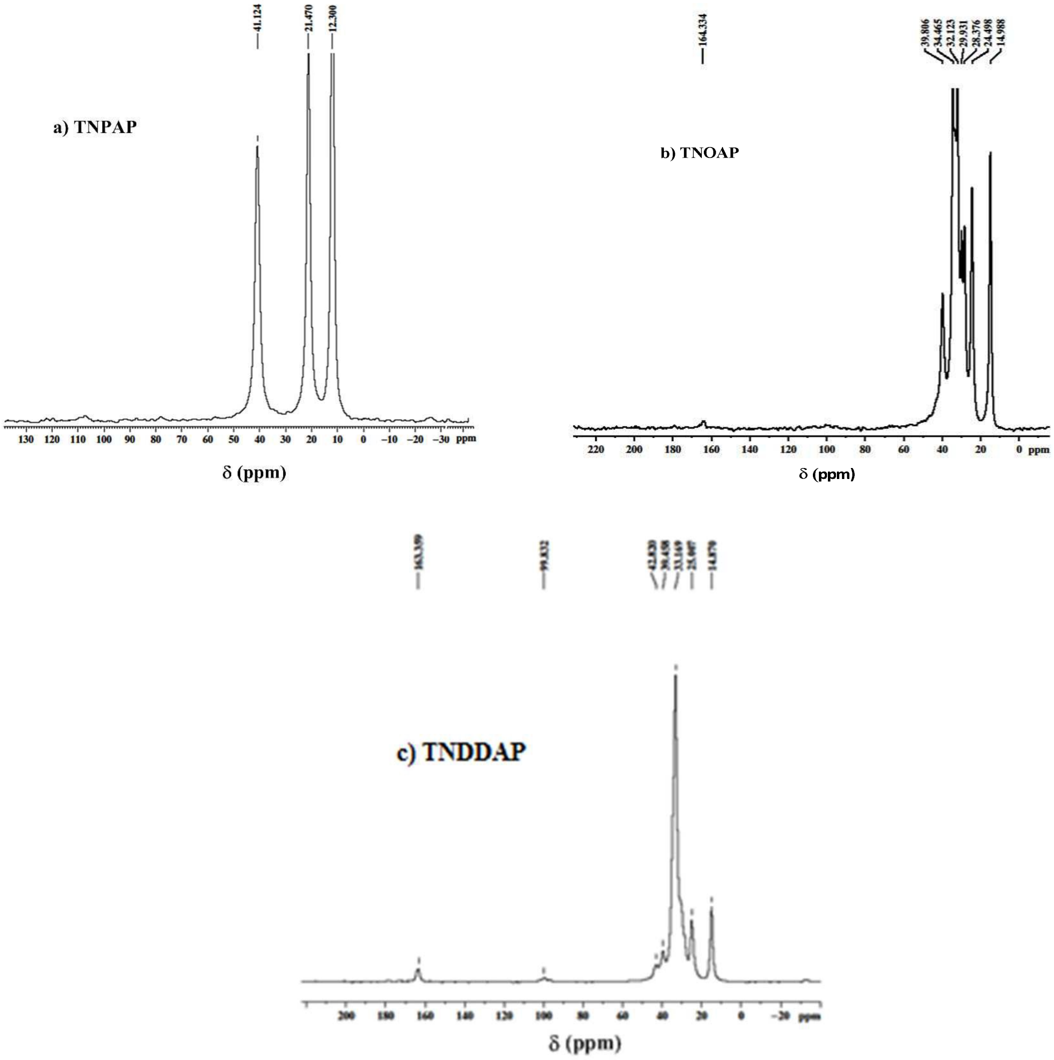

Fig. 5 : ^{13}C MASNMR spectra of a) TNPAP, b) TNOAP and c) TNDDAP.

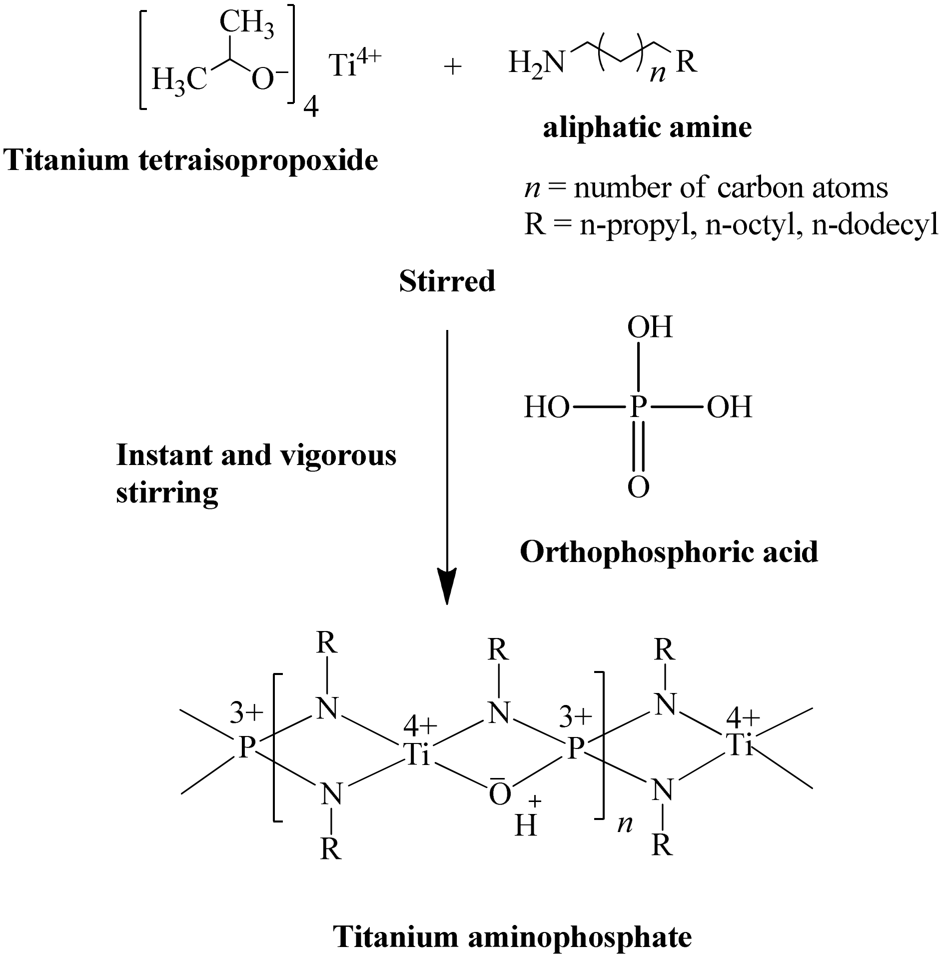

Fig. 6 : **Schematic synthesis mechanism and proposed basic structure of titanium aminophosphates.**

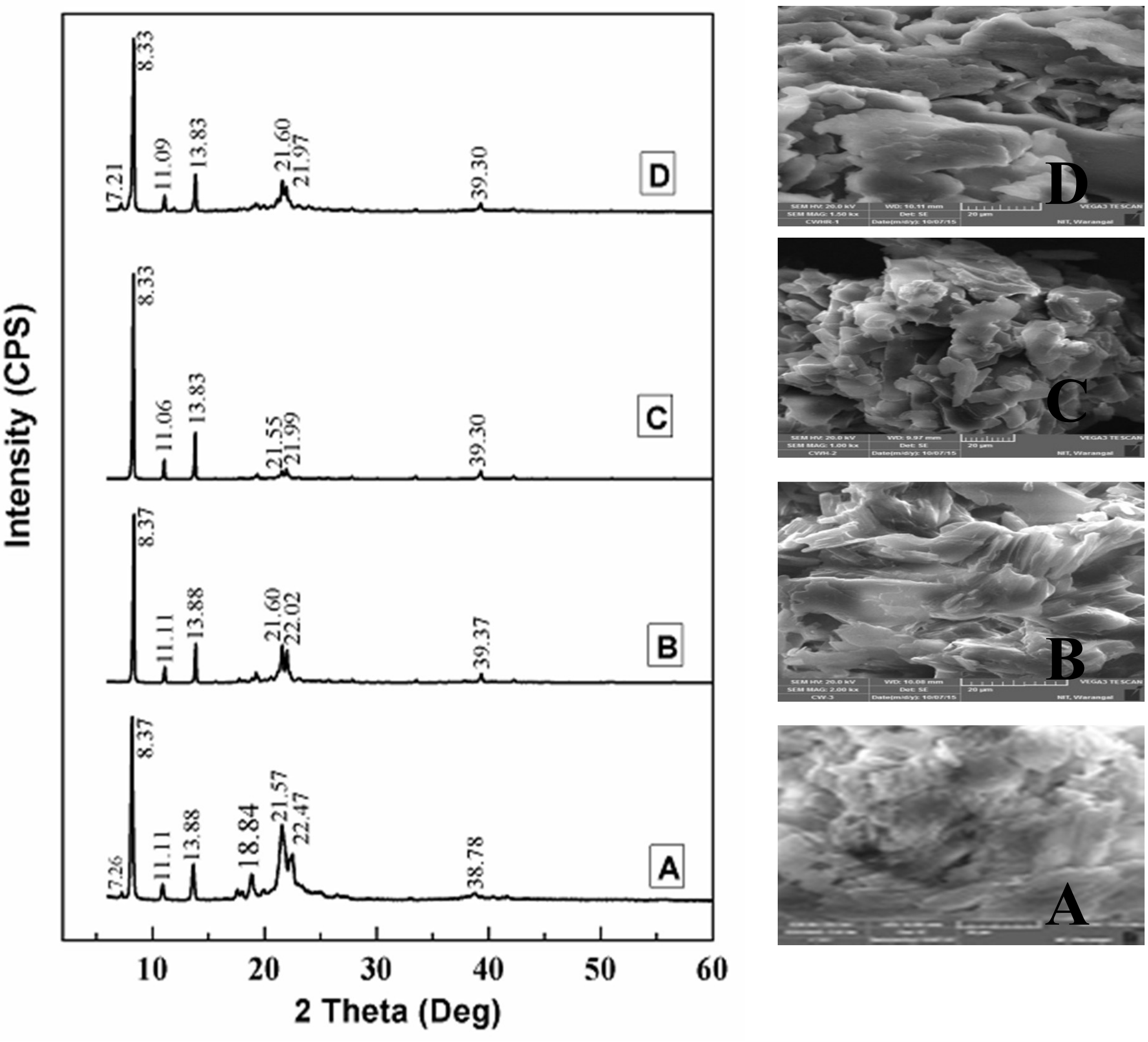

Fig. 7: **Scanning electron microscopic picture / Powder X-ray diffraction pattern of A) Titanium do-decylaminophosphate, B) Water treated (2 hrs) Titanium do-decylaminophosphate, C) H_2O_2/H_2O (1:1) treated (2 hrs) Titanium do-decylaminophosphate and D) H_2O_2/H_2O/Orange – G dye (1:1:1) treated (2 hrs) Titanium do-decylaminophosphate.**

Titanium aminophosphates : Synthesis, characterization and Orange – G dye degradation studies

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A group of titanium aminophosphate catalysts are synthesized, characterized in detail and their catalytic application towards Orange G dye degradation are studied.