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Enhanced Adsorption Capacity and Photo-Catalytic Oxidative Activity of Dyes in Aqueous Medium by Hydrothermally Treated Titania Pillared Clay

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Abstract. Titania pillared montmorillonite clay was prepared by two different routes viz. 1) conventional ion exchange method and 2) modified method wherein the post hydrothermal treatment after ion-exchange was employed. The influence of the post hydrothermal treatment on the textural properties of titania-pillared clays was studied. The calcined clay was characterized by different physico-chemical techniques such as XRD, EDX, low temperature (77 K) nitrogen adsorption and UV-Vis diffuse reflectance spectroscopy. The content of pillared titania remained unchanged irrespective of the method of preparation. The method of preparation and severity of the conditions employed for the hydrothermal treatment resulted in alteration of the crystallinity and crystallite size of the anatase. The changes in the average pore diameter was found to comensurate with the changes in crystallite size of anatase phase. The increase in total pore volume as a function of the severity of the post hydrothermal treatment resulted in the decrease in micropore volume. The severity of the post hydrothermal treatment governed the extent of the blue shift in UV-Vis DRS spectra.

The behaviour of titania pillared clays in adsorptive capacity and in photo-catalytic oxidation of methylene blue and victoria pure blue in aqueous medium was studied as a function of their physico-chemical characteristics. The titania pillared clays prepared by post hydrothermal route has shown enhanced adsorption capacity and photo-catalytic oxidation.

Keywords: titania pillared clay, hydrothermal treatment, anatase, photo-oxidation, methylene blue, victoria pure blue

Introduction

The pillared clays have created tremendous potential for adsorption and catalysis because of high surface area and permanent localised porosity in the larger micropore region. Also introduction of Bronsted and Lewis acidity, improved thermal stability and increased pore width open a wide scope for the pillared clays in its utility in various organic transformations and adsorption. Since last two decades, the photo-catalytic removal of trace contaminants from air and water is recognized as a growing research area. Organic compounds such as phenol, trichloroethylene, di-Bu phthalate in water, also toluene, benzaldehyde associated with pharmacaeutical and perfume industries (Vincenzo et al., 1999; Alemany et al., 1997;

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Ooka et al., 2000), dyes from dye industries (Zheng et al., 1997), discharged effluent from the textile dyeing and finishing industry are important pollutants usually found in air and or/wastewater (Arslan et al., 2000; Yiqun et al., 1999; Guangming et al., 1999). Studies on treatment of the wastewater containing organic pollutants is one of the important needs today. Few adsorption (Correia et al., 1994; Houas et al., 1999; Mall and Upadhyay, 1998; Khattri and Singh, 1999) as well as photo-oxidation (Arslan et al., 2000; Yiqun et al., 1999; Yoshida et al., 1999; Lavson et al., 1994) methods are reported for their removal. The catalytic activity of titanium dioxide to degrade air borne pollutants has led to the utility of TiO_2 in paints, papers etc. But the use of TiO_2 for purification of water is found not much useful as that for treating air. The textile dyeing and finishing industry is one of the major polluters of effluent water from industry. Appreciable amount of reactive azo dyes remain in waste water. So it is essential to study photocatalytic degradation of pollutants on more eco friendly basis. Zheng et al. (1997) has studied the photoremoval of Acid Red 2B dye by TiO_2 suspension solution and found that catalytic activity depends on crystalline form of the catalyst and adsorption ability of the catalyst for Acid Red 2B. Though photo-oxidation by titania is well known documented, the use of titania pillared clay as a photocatalyst for removal of organic pollutants has not been exhaustively reported in view of the method of their preparation and its influence on the efficiency in photocatalysis. In view of this, attempts were made to investigate the performance of titania pillared clay in photo-catalysis of dyes as a function of method of its preparation and their physico-chemical characterization.

In the present communication, we are reporting the performance of titania pillared montmorilionite prepared by conventional ion exchange method, with and without post hydrothermal treatment in adsorption and photo-catalytic degradation for removal of basic dyes like methylene blue and victoria pure blue in aqueous medium.

Experimental

Titania pillared clay was synthesized by following the procedure reported by Yamanaka et al. (1987) using Kunipia-F montmorillonite clay (Na form, Kunimine Industries) with a cation exchange capacity 1.28 meq. g^{-1} and having structural formula ($Na_{0.35}K_{0.01}Ca_{0.02}$) ($Si_{3.89}Al_{0.11}$) ($Al_{1.60}Fe_{0.08}Mg_{0.32}$)-$O_{10}(OH)_2 \cdot nH_2O$. Titanium tetraisopropoxide was added to 1 M HCl solution under vigorous stirring at 323 K keeping HCl to alkoxide molar ratio 1. The resulting slurry was peptised till clear TiO_2 sol was obtained. The TiO_2 sol was mixed with aqueous clay slurry (1%) keeping molar ratio of TiO_2/CEC of the clay 30. The suspension was stirred for 3 h at room temperature. The product was washed several times with water and separated by centrifugation technique. For hydrothermal treatment the intercalated pillared clay was dispersed in water resulting into slurry containing 2% solid. Then it was further hydrothermally treated at 433, 473 and 523 K for 24 h, 2 h and 1 h respectively under autogeneous pressure and at static condition. The hydrothermally treated product was centrifuged and washed till effluent showed no sodium and then dried in air-oven maintained at 373 K for 4 h. All the intercalated clay samples synthesized with/without hydrothermal treatment were further calcined in an air-oven at 773 K for 3 h. The calcined clay was characterized by powder XRD (Rigaku 3070E using Cu K_α radiation). The % crystallinity due to anatase phase in pillared clay sample was evaluated by taking ratio of areas under (101) reflection of the test sample to the reference sample which was prepared by mixing clay homogeneously with pure anatase which contributes 57.3% part (w/w) of the mixture. The crystallite size of the anatase in pillared clay was determined by applying Scherrer equation to XRD data. From low temperature nitrogen adsorption (BELSORP 28SA automatic Gas adsorption apparatus) isotherms BET surface area, pore diameter, total pore volume and pore size distribution curve was determined. Prior to the determination of adsorption isotherm, the sample was evacuated at 10^{-2} torr and at 423 K to remove all of the physi-sorbed species from the surface of the adsorbent. The samples were further characterized by EDX (HORIBA MESA-500NA) and UV-Vis diffuse reflectance spectroscopy (Perkin Elmer UV-Vis spectrometer attached with labsphere RSA-PE-18 reflectance spectroscopy accessory) techniques. The specifications of the pillared clays are listed in Tables 1 and 2.

For photo-catalytic oxidation of the methylene blue (M.B.) and victoria pure blue (V.P.B.) Xenon short arc lamp (Ushio Inc. Japan) was used for photo-irradiation. 50 mg of the calcined sample was dispersed in 50 ml of 10 ppm dye (M.B./V.P.B.) (aqueous) solution in a beaker and stirred magnetically in dark for 10 minutes. The absorbance measurement was done at $\lambda_{max} =$ 665 nm and 615 nm for M.B. and V.P.B. respectively

Table 1. Preparation conditions and details regarding titania phase in pillared clays.

Sample designation	Preparation conditions			% anatase crystallinity[a]	Crystallite size of TiO_2[b] (Å)	% TiO_2 content[c]
	Method	Temp. (K)	Time (h)			
S-1	UT[d]	–	–	38	19.5	57.80
S-2	HT[d]	433	24	66	34.0	57.20
S-3	HT	473	2	60	34.0	57.10
S-4	HT	523	1	85	40.0	57.15
Clay	–	–	–	–	–	–

[a]% Anatase crystallinity $= \frac{\text{Area under the (101) reflection of the test sample}}{\text{Area under the (101) reflection of the reference sample}} \times 100$.
[b]Calculated from diffraction peak of anatase (101) using Scherrer equation.
[c]Estimated by EDX.
[d]UT, HT-hydrothermally untreated and hydrothermally treated.

Table 2. Detailed data derived from analysis of low temperature nitrogen adsorption.

Sample	Specific BET surface area[a] ($m^2\ g^{-1}$)	Average pore diameter[b] (Å)	Total pore volume[c] ($cm^3\ g^{-1}$)	Micropores volume[d] ($cm^3\ g^{-1}$)
S-1	216	22.0	0.1581	0.1286
S-2	152	36.0	0.1845	0.0804
S-3	147	36.0	0.1814	0.0737
S-4	140	38.8	0.2147	0.0187
Clay	21	–	–	–

[a]Determined from N_2 adsorption isotherm.
[b]Determined from pore size distribution curve of N_2 adsorption isotherm.
[c]Calculated from N_2 adsorption isotherm.
[d]Calculated from 't' plot of N_2 adsorption isotherm.

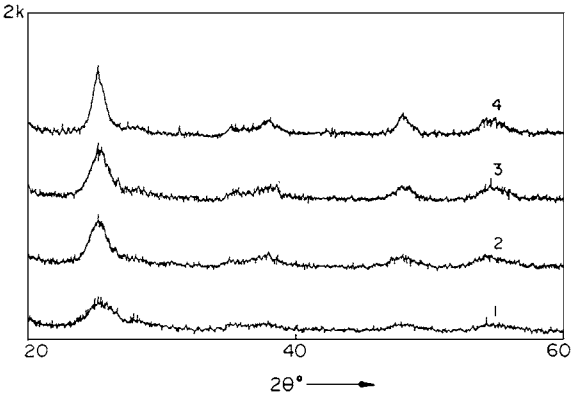

Figure 1. Powder XRD profiles of pillared clay samples (1) S-1, (2) S-2, (3) S-3 and (4) S-4.

using UV spectrometer, Hitachi U-3200. The mixture of sample and dye solution was then photo-irradiated/ not irradiated at room temperature for 10 minutes, and absorbance of clear solution was measured. This procedure was consecutively repeated 6 times without changing the concentration of reaction mixture.

Results and Discussion

The sample designations, preparation conditions and product characterization including textural properties are listed in the Table 3.

It is clearly evident from the table, that the pillared clays prepared with and without hydrothermal treatment routes showed almost the same amount of TiO_2 (57.5 ± 0.4%). Thus the method of preparation was found no influence on the extent of inclusion of TiO_2.

Figure 1 shows powder XRD profiles of the pillared clays prepared with (S-2, S-3 and S-4) and without (S-1) hydrothermal treatment in the 2θ range from 20 to 60°. S-1 sample has shown a broad, less intense (101) reflection due to anatase phase at around $2\theta \sim 25°$. The samples S-2, S-3 and S-4 have exhibited the sharp and more intense (101) reflection as compared to S-1. Comparing any XRD profile of hydrothermally treated sample with untreated sample, the crystallinity of anatase phase has found to depend on the method of preparation. With increase in anatase crystallinity, the main peak of anatase $2\theta \sim 25°$ sharpened with appearance of additional anatase peaks at ∼37, 48 and 55°. The more intense (101) reflection with reduced FWHM may attribute to the long range order in the pillared clay. A prominent peak appeared at 7° (not shown in XRD) for the original clay has been found to be absent in all the pillared clays indicating that the pillaring has

been successfully occured, irrespective of the method of preparation. The crystallinity and crystallite size of anatase determined from XRD profiles are included in Table 1. The analysis of the XRD data shows that the % crystallinity and crystallite size of anatase phase depend upon preparation method and conditions employed for preparation. Furthermore, it is seen that, at higher temperature the transformation of amorphous titania to anatase is faster resulting in the larger crystallite size at comparatively less period. The crystallite size of anatase in all the pillared clay samples was found to be in the range of 19–40 Å.

Figure 2 depicts the nitrogen adsorption-desorption isotherms at 77 K of the samples S-1, S-3, S-4 and the original clay. Sharp increase in the adsorbed N_2 volume at relative pressure below 0.02 followed by steady increase in the range of 0.1 to 0.5 of relative pressure indicated the bimodal pore size distribution in S-1 sample. Moreover, the presence of micropores in these samples was confirmed by analysing the same data in terms of t-plot. Hence, the preparation without post hydrothermal treatment may be operative in the formation of a pillared clay wherein micropore contribution is greater than the mesopore. The influence of the post hydrothermal treatment on the formation of the pillared clay containing essentially mesopore can be clearly evident from the adsorption isotherms of S-2 (not shown in figure), S-3 and S-4 samples. The original clay showed slight hysterisis indicating some porosity.

The analysis of the data on low temperature adsorption for the pillared clays is summarized in Table 2. All the pillared clay samples exhibited an increase in, BET surface area. Eventhough, the pillared clays S-2, S-3 and S-4 showed increased surface area than the original clay, the extent of increase was found much less as compared to S-1. The post hydrothermal treatment parameters such as temperature and time seem to be operative in lowering the specific BET surface area on account of increased extent of disorder in the oriented silicate layers. It is interesting to note, eventhough, the specific BET surface area decreases due to post hydrothermal treatment, the total pore volume was found to increase depending upon the preparation conditions. The increase in total pore volume as a function of the severity of the post hydrothermal treatment was found to be associated with the decrease in micropore volume. Micropore volume was determined by plotting the amount of N_2 sorbed/cm^3 g^{-1} at S.T.P. against the thickness (nm) of the sorbed layer. Extrpolation of the curve to the ordinate gives the positive intercept from which micropore volume of the sample was determined.

Figure 3 shows the pore size distribution curves of S-1, S-2 and S-4 samples calculated using Cranston-Inkley (Cranston and Inkley, 1957) method using the adsorption isotherm. S-1 sample shows the presence of both micropores and mesopores which supports its bimodal shaped nitrogen adsorption curve. The contribution due to micropore however, is higher as compared to mesopore. It is clearly evident from the figure, that by employing hydrothermal treatment only presence of mesopores were observed in case of S-2

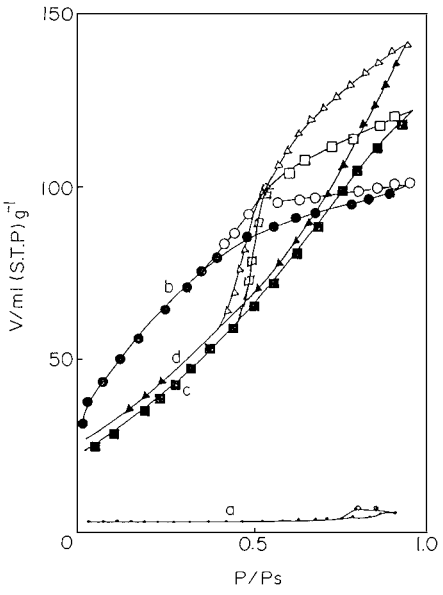

Figure 2. Nitrogen adsorption-desorption isotherms of the samples (a) clay (adsorption (•), desorption (◦)), (b) S-1 (adsorption (●), desorption (○)), (c) S-3 (adsorption (■), desorption (□)) and (d) S-4 (adsorption (►), desorption (▻)).

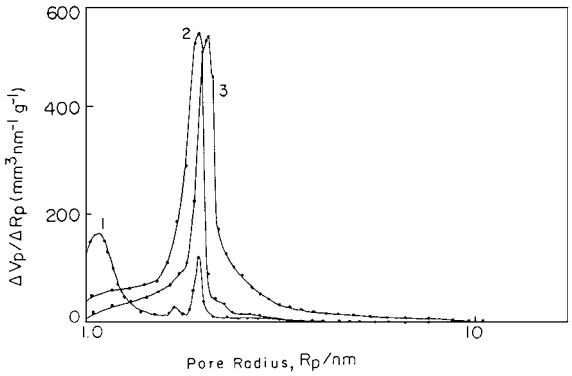

Figure 3. Pore size distribution curve of pillared clay samples (1) S-1, (2) S-2 and (3) S-4.

and S-4 samples. As hydrothermal conditions became more severe, the pore size distribution curve shifted to larger pore size region. Since during the preparation of S-2, S-4 samples, the step by which S-1 is prepared was initially followed before subjecting to hydrothermal treatment, it can be concluded that mesopores are formed at the cost of micropores. Formation of mesopores due to hydrothermal treatment may be due to the orientation of silicate layer structure. The severity of the hydrothermal treatment was found to influence the average pore size diameter of the pillared clay samples, determined from nitrogen adsorption isotherm and in turn anatase crystallite and the crystallite size in the TiO_2 pillars.

The charge transfer transition of Ti in anatase with octahedral configuration was reported (Grohmann et al., 1994) at 333.3 nm. Figure 4 illustrates the UV-Vis diffuse reflectance spectra of all calcined titania pillared clays in the range of 300–450 nm including pure anatase phase. It is evident from the figure, irrespective of the method employed for the synthesis, all the calcined titania pillared clay samples have shown the blue shift when compared with pure anatase. However, the extent of the blue shift was found greater in case of hydrothermally untreated sample. The changes in the hydrothermal treatment were found to influence the crystallinity and size of the anatase phase. Hence both the crystallinity and crystallite size are the prominent responsible factors for the extent of blue shift in an optical transition. The S-4 sample possessing higher crystallinity and crystallite size was found to exhibit the least extent of blue shift in the present studies.

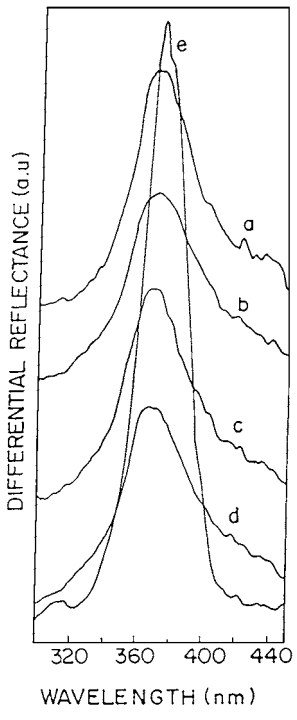

Figure 4. UV-Vis DRS spectra of pillared clay samples (a) S-4, (b) S-3, (c) S-2, (d) S-1 and (e) pure anatase.

Adsorption Capacity and Photo-Oxidative Activity of Dyes

In the present studies, it is well established that not only the method of preparation but also preparation parameters such as temperature and time play a prominent role in modifying the physico-chemical properties of the titania pillared clay samples. Ooka et al. (1999) had also reported similar results during preparation of Ti pillared clay by hydrothermal treatment and without hydrothermal treatment by changing different preparation parameters. The comparison was made in view of examining the performance of the titania pillared clays in adsorption and photo-catalytic oxidation in relation to these properties. Original clay, calcined S-1 and calcined S-4 samples were selected for the adsorption and photo-oxidation studies on the basis of the considerable differences in physico-chemical characteristics. Figure 5(A) depicts the results on the adsorption and photo-catalytic oxidation test using M.B. Period 'a' is the initial time (10 minutes for all samples) for which the mixture of sample and dye solution is stirred in dark. Period 'b', denotes the results obtained after regular interval of 10 minutes' time subjecting the mixture for exposure with/without UV irradiation. The purpose of undertaking the photo-catalytic runs without exposing UV irradiation, was to confirm whether further adsorption or photo-oxidation were responsible for the decrease in relative concentration of M.B. to initial state. In Fig. 5, the dotted line represents the results obtained without subjecting to UV irradiation whereas the solid line represents the results obtained with UV irradiation. It is clearly evident from the Fig. 5(A) that original clay has shown 20% adsorption in dark and remained unchanged in period 'b' with and without UV irradiation. Both S-1 and S-4 samples have shown the adsorption of M.B. in dark, during timeframe of 10 minutes to different extent yielding 50% and 82% drop in the initial concentration respectively. The original clay sample has shown only adsorptive capacity for M.B. with no further photo-oxidative capability by

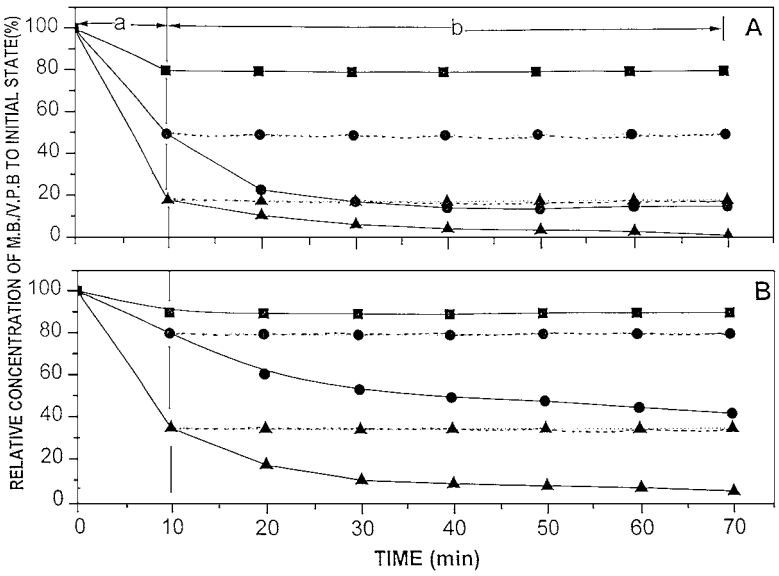

Figure 5. Relative concentration of (A) M.B. and (B) V.P.B. to initial state (%) by Clay (■), S-1 (●) and S-4 (▲) samples with time on stream.

UV irradiation. Thus, the presence of titania seems to promote the photo-oxidative and also adsorptive property in pillared clays to considerable extent. Higher adsorptive capacity and photo-oxidative activity of S-4 as compared to S-1 indicates that the hydrothermal treatment provides a novel route to improve the surface quality favouring enhanced ability for adsorption of M.B. When exposed to photo-irradiation, the continuous drop in the initial concentration of M.B. was observed with increase in time on stream. However, at the end of 60 minutes' exposure, S-1 and S-4 samples have shown 85% and 99% drop in concentration of M.B. respectively. The catalytic runs without exposing to UV irradiation (shown by dotted lines), no further drop was observed evenif the time on stream was extended upto 60 minutes in case of S-1 and S-4 samples. This indicates that the decrease in relative concentration of M.B. to initial state must be due to photo-oxidation and not due to further adsorption. For all pillared clay samples as well as original clay, the slurry of 50 mg of the catalyst per 50 ml of water was used for adsorption as well as photo-catalytic oxidation of dyes.

Similar investigations were made for adsorption and photo-catalytic oxidation of V.P.B. using clay, S-1 and S-4 (Fig. 5(B)) samples. Original clay has shown 9% adsorption in dark and remained unchanged in period 'b' with and without UV irradiation. Samples S-1 and S-4 exhibited more or less identical behavior except the extent of adsorption and photo-oxidation activity. The adsorption of V.P.B. in dark was found to result in decrease by 20% and 66% of the initial concentration when S-1 and S-4 sample was used respectively. Furthermore, at the end of 60 minutes' photo-irradiation exposure, S-1 sample showed 58% drop in initial concentration of V.P.B. whereas 93% drop was observed in case of S-4 sample. Without exposing to UV irradiation, S-1 and S-4 samples showed no further drop in concentration indicating that decrease in relative concentration of V.P.B. to initial state was due to photo-oxidation and not due further adsorption.

When summarized, it is clear that even though S-1 has higher specific BET surface area as compared to S-4, the adsorptive and photo-oxidative property of the latter is higher than that of the former. The higher adsorptive property of S-4 may be attributed to the higher pore volume whereas higher photo-oxidative property depends on higher utility of the active sites of S-4 for the interaction of the basic dyes like M.B. and V.P.B. In addition to this, the higher interaction between preadsorbed dye molecule and incoming molecule seems to be responsible for higher packing efficiency yielding more occupancy of the available pore volume.

The higher adsorption and photo-oxidation activity of M.B. may be attributed to mode (Galbraith et al., 1958) of adsorption (edge-on type) and smaller dimension ($16 \times 8 \times 4$ Å) as compared to V.P.B. which has high coverage factor (Galbraith et al., 1958) on account

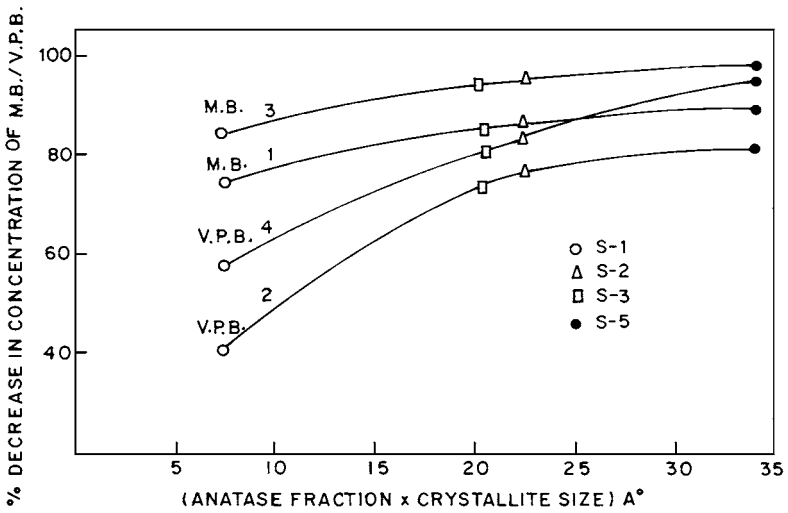

Figure 6. Decrease in concentration (%) due to adsorption and photo-oxidation of methylene blue (curves 1 and 3 respectively) and victoria pure blue (curves 2 and 4 respectively) as a function of [Anatase fraction × crystallite size, Å] in titania-pillared clays.

of its larger dimension ($18 \times 16 \times 5$ Å) and end-on mode of adsorption.

From the above evidences, it can be concluded eventhough, S-1 and S-4 samples possess the same amount of titania, the higher contribution of anatase phase with larger crystallite size in S-4 sample improves both adsorptive and photo-oxidative capability. Thus at identical level of titania content, not only the extent of crystallite phase contribution but also crystallite size play an important role in the adsorptive and photo-oxidative performances. The extent of crystalline titania and crystallite size can be controlled by governing the severity of the hydrothermal treatment.

Since in all the samples, the anatase contribution is $\leq$85% with the variations in the crystallite size in the range of 19 to 40 Å, it was rather difficult to conclude whether both the fraction of anatase and the crystallite size are important or one of them is important for adsorptive and photo-oxidative capability. Therefore, the combined effect of both [anatase fraction × crystallite size, Å] was considered to elucidate the performance of the samples with identical titania content obtained by different methods and hydrothermal conditions. Figure 6 illustrates the performance of S-1, S-2, S-3, S-4 samples at the end of period 'a' in dark and period 'b' with UV irradiation and presented to establish the above said correlationship. It is seen from the figure that as the [anatase fraction × crystallite size, Å] increases, the concentration of M.B. is found to decrease at the end of both the periods. Similar trend was also observed in case of V.P.B. Thus the sample with higher value of product [anatase fraction × crystallite size, Å] was found to yield better performance in photo-oxidative capability. It is also interesting to note that eventhough S-2 and S-3 possess identical crystallite size, S-2 has exhibited the better performance in photo-oxidative degradation.

Conclusion

The method of preparation of titania pillared clay was found to have an impact on the performance in adsorptive and photo-oxidative characteristics. From EDX study, the content of pillared TiO_2 was found to be unchanged irrespective of the method of preparation. % anatase crystallinity, crystallite size and homogenity in pillaring of the clay was determined by XRD studies. Improved anatase crystallinity and higher crystallite size was achieved by modified method wherein the post hydrothermal treatment after ion-exchange was employed for the preparation of titania pillared clay. The preparation method and parameters employed during the hydrothermal treatment were found to affect the contribution and crystallite size of anatase phase. The severity in hydrothermal treatment seems to be operative for alteration in the surface area, the crystallite size and crystallinity of the anatase phase in the pillared clays. Both the crystallinity and crystallite size of anatase are the prominent factors responsible for the extent of blue shift in UV-Vis DRS spectra. The higher

adsorptive property of the samples is attributed to the higher pore volume. Sample with higher value of product [anatase fraction × crystallite size, Å] was found to yield better performance in photo-oxidative capability of dyes. Titania pillared clay obtained by hydrothermal treatment route proved its superiority in the adsorption and photo-oxidation of basic dyes such as methylene blue and victoria pure blue (99 and 93% respectively) as compared to sample obtained by conventional method (85 and 58% respectively) thereby exhibiting its potentiality as efficient economic and environmental friendly photocatalyst.

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References

Alemany, L.J., M.A. Banares, E. Pardo, F. Martin, M. Galan-Fereres, and J.M. Blasco, "Photodegradation of Phenol in Water Using Silica-Supported Titania Catalyst," *Appl. Catal. B*, **13**(3–4), 289 (1997).

Arslan, I., I.A. Balcioglu, and D.W. Bahnemann, "Heterogeneous Photocatalytic Treatment of Simulated Dyehouse Effluents using Novel TiO_2-Photocatalyst," *Applied Catal B: Environmental*, **26**, 193–206 (2000).

Correia, V.M., T. Stephenson, and S.J. Judd, "Characterization of Textile Wastewater—a Review," *Environ. Technol.*, **15**, 917–929 (1994).

Cranston, R.W. and F.A. Inkley, "The Determination of Pore Structures from Nitrogen Adsorption Isotherms," *Adv. Catal.*, **9**, 143–154 (1957).

Galbraith, J.W., C.H. Giles, A.G. Halliday, A.S.A. Hassan, D.C. Mcallister, N. Macaulay, and N.W. Macmillan, "Adsorption at Inorganic Surfaces III. The Mechanism of Adsorption of Organic Solutes, including Dyes, by Graphite," *J. Appl. Chem.*, **8**, 416–424 (1958).

Grohmann, I., W. Pilz, G. Walther, H. Kosslick, and V.A. Tuan, "XPS-Investigation of Titanium Modified MFI-type Zeolites," *Surf. Interface Anal.*, **22**(1–12), 403–406 (1994).

Guangming, C., P. Jingjun, H. Buxing, and Y. Haike, "Adsorption of M.B. on Montmorillonite," *J. Dispersion Sci. Technol.*, **20**(4), 1179–1187 (1999).

Houas, A., I. Bakir, M. Ksibi, and E. Elaloui, "Removal of M.B. from Aqueous Solution by CECA40 Commercial Activated Charcoal," *J. Chim. Phys. Phys.-Chim. Biol.*, **96**(3), 479–486 (1999).

Khattri, S.D. and M.K. Singh, "Colour Removal from Dye Wastewater using Sugar Cane Dust as an Adsorbent," *Adsorpt. Sci. Technol.*, **17**(4), 269–282 (1999).

Larson, S.A. and J.L. Falconer, "Characterization of TiO_2 Photocatalysts used in Trichloroethene Oxidation," *Applied Catalysis B: Environment*, **4**, 325–342 (1994).

Mall, I.D. and S.N. Upadhyay, "Studies on Treatment of Basic Dyes bearing Wastewater by Adsorption Treatment using Flyash," *Indian J. Environ. Health*, **40**(2), 177–188 (1998).

Ooka, C., S. Akta, and Y. Ohashi, "Photocatalytic Character on Pillared Clay with Hydrothermally Crystallized TiO_2," *Nagoya-shi Kogyo Kenkyusho Kenkyu Hokoku*, **85**, 13–17 (2000).

Ooka, C., S. Akta, O.Y. Ohashi, T. Horiuchi, K. Suzuki, S. Komai, H. Yoshida, and T. Hattori, "Crystallization of Hydrothermally Treated TiO_2 Pillars in Pillared Montmorillonite for Improvement of the Photocatalytic Activity," *J. Mater. Chem.*, **9**(11), 2943 (1999).

Vincenzo, A., C. Salvatore, L. Vittorio, M. Leonardo, M. Gianmario, P. Leonardo, and S. Mario, "Photocatalytic Oxidation of Gaseous Toluene on Anatase TiO_2 Catalyst: Mechanistic Aspects and FT-IR Investigation," *Applied Catal B: Environmental*, **20**, 15–27 (1999).

Yamanaka, S., N. Tatsuo, and M. Hattori, "Preparation and Properties of Titania Pillared Clay," *Materials Chemistry and Physics*, **17**, 87–101 (1987).

Yiqun, F., S. Zaifeng, N. Xu, and S. Jun, "Degradation of M.B. using Photocatalytic Membrane Reactor," *Nanjing Huagong Daxue Xuebao*, **21**(5), 49–52 (1999).

Yoshida, H., T. Kawase, Y. Miyashita, C. Murata, C. Ooka, and T. Hattori, "Effect of Hydrothermal Treatment of Titania-Pillared Montmorillonite for Photocatalytic Degradation of Dibutyl Phthalate in Water," *Chemistry Letters*, 715–716 (1999).

Zheng, S., Q. Huang, J. Zhou, and B. Wang, "A Study on Dye Photoremoval in TiO_2 Suspension Solution," *J. Photochem. Photobiol. A*, **108**(2–3), 235 (1997).