

Recovery and reuse of TiO₂ photocatalyst from aqueous suspension using plant based coagulant - A green approach

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(Received 4 November 2015 • accepted 22 February 2016)

Abstract—Separation of TiO₂ from aqueous suspension is a major constraint in heterogeneous photocatalytic water treatment. As an alternative for existing less effective immobilization techniques, the application of plant based coagulant for the recovery and reuse of TiO₂ was investigated for the first time. Aqueous extract derived from seeds of *Strychnos potatorum* was found to be an effective coagulant for the sedimentation of TiO₂. Further, the potential for recovery and reuse of the sedimented photocatalysts TiO₂, was investigated by photocatalytic degradation of rhodamine B and terephthalic acid tests. The photocatalytic degradation experiments with recovered catalyst obey pseudo first-order kinetics with enhanced photocatalytic activity than that of the pure TiO₂. The investigation of recovered catalysts with XRD, BET, SEM etc., suggests that there is no change in surface and morphological properties when compared with pure TiO₂ and the recovered catalysts are highly suitable for recycle and reuse.

Keywords: Titanium Dioxide, Flocculation and Coagulation, Plant Coagulants, Reuse of Photocatalyst, *Strychnos potatorum*

INTRODUCTION

Semiconductor oxide mediated photocatalysis is emerging as a promising technology for water treatment. Of all the photocatalysts tried so far, Titanium dioxide (TiO₂) is found to be most suitable as it is very effective, easy to use, inexpensive, less toxic, leads to complete mineralization of the pollutants and also has the potential to work with solar-energy [1-5]. Typically, in photocatalytic experiments, when aqueous solution (sample) along with catalyst (TiO₂) in suspension is illuminated with light of appropriate wavelength, charge separation process is initiated, leading to the formation of various reactive oxygen species (ROS), which plays a vital role in the degradation of organic contaminants [6-11]. Heterogeneous photocatalysis in suspension is far superior to the immobilized as the latter reduces the photocatalytic efficiency by a combinatorial factor such as reduction in the active surface area, introduction of ionic species and difficult exchange with the solution. Presently, several studies report the immobilization of the catalysts to different media. However, the efficiency of the photocatalyst is reduced to a large extent as a result of immobilization. But the separation of the used catalyst from the suspension is difficult, energy intensive and cumbersome [12-14]. To overcome this, we report a novel green route to separate the TiO₂ photocatalysts from its aqueous suspensions by using a plant coagulant derived from *Strychnos potatorum*.

There are few previous reports on the separation of TiO₂ from its slurry by using chemical coagulants such as aluminium chloride [12], grafted cationic polyelectrolytes [15], polyferric sulfate,

ferric chloride, poly aluminium chloride, alum [16] and also using chitosan [17]. However, the application of plant-based coagulants for the separation of suspended TiO₂, and its recycling potential is explored for the first time. Most of the chemical coagulants are expensive, effective only on extreme pH and may have a detrimental effect on the environment. Moreover, the catalysts recovered by means of chemical coagulation are unfit for reuse as the inorganic ions present in the coagulant influence the photocatalytic activity by inhibiting the active sites present in it. Hence, application of plant based coagulant *Strychnos potatorum* is studied for sedimentation and recovery of TiO₂ used in suspended batch reactors.

Strychnos potatorum is a dry deciduous species belonging to the family Loganiaceae, and its seeds are used by indigenous communities to clarify turbid water in arid regions of South India. Ancient Indian texts like Sushruta Samihita report that 'nirmali' seeds (*Strychnos potatorum*) could be used to clarify turbid water [18]. These seeds were known to possess antidiarrheal, diuretic and coagulant properties. Hence this species was selected for our studies.

We tested the aqueous extract derived from the seeds of *Strychnos potatorum* to sediment TiO₂ from its aqueous suspensions under standardized optimal experimental conditions. The work also reports the reuse of TiO₂, recovered after the sedimentation process. The sedimented TiO₂ is recovered and tested for its potential reuse by determining its photocatalytic activity through photoluminescence spectroscopy and dye degradation experiments. The optimum conditions for coagulation, flocculation and sedimentation of TiO₂ suspensions in tap water with this plant coagulant were also evaluated.

EXPERIMENTAL SECTION

1. Materials

Commercial-grade TiO₂ procured from Merck India Ltd. was

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Table 1. Physiochemical parameters of tap water used in the experiment

Parameters	Value
pH	6.9
EC	272 $\mu\text{sm}/\text{cm}^2$
TDS	176.8
Turbidity	1.5 NTU
Total Hardness	84
Alkalinity	60
Calcium	20
Magnesium	9
Sulphate	6
Chloride	37
Iron	3.4
Sodium	32.2
Potassium	2.5

All units are expressed in mg/l except pH, EC and Turbidity

used in the experiments. The TiO_2 used here was of anatase phase having a surface area of $11.03 \text{ m}^2/\text{g}$, and the size of the particle was approximately 50-200 nm. TiO_2 stock suspensions of desired concentrations were prepared and sonicated for 30 minutes prior to each experiment, which was sufficient for the TiO_2 particles to remain in suspension for long durations [21]. Since the system should be applicable in actual field, tap water was used to prepare TiO_2 suspensions, and distilled water was used in determining the effect of pH and ionic strength in coagulation. The quality of tap water used in our experiments was determined as per the standard methods APHA 20th ed. [22] and is given in Table 1.

2. Preparation of the Coagulant

Seeds of *Strychnos potatorum* were powdered and sieved through 0.4 mm membrane, and the sieved fraction was used for preparing the crude extract. The coagulant solution (1% w/v) was prepared by dissolving 1 g of the sieved fraction in 100 ml distilled water and stirred using a magnetic stirrer for 30 minutes. The suspension was then filtered through Whitman No. 1 filter paper and the filtrate was used in the experiments.

3. Jar Tests

The coagulation/flocculation experiments involved a jar test apparatus consisting of multiple stirrer units with stainless steel paddles (TECHNICO, India). The details of experimental conditions are as follows. The required quantity of coagulant was added to TiO_2 suspension of desired concentration. The coagulant was loaded at different concentrations ranging from 1 mg/L to 20 mg/L. After the addition of the coagulant, the test suspensions were placed on the stirrer unit and rapidly mixed for 1 minute at a speed of 300 rpm, then at a speed of 150 rpm and 50 rpm each, for 15 minutes, respectively. Then, the unit was switched off and the flocs were allowed to settle for 30 minutes. Finally, the samples were withdrawn 2 cm below the solution surface using a pipette for each turbidity measurement. Turbidity was measured with a digital nephelo turbidity meter (ELICO India), using standard formazine suspensions (1 g/L) as per standard methods (APHA 20th edition). All experiments were repeated thrice for consistency, and the results were

averaged. The effects of pH and ionic strength were also evaluated to determine their influence in the coagulation/flocculation processes. All experiments were at ambient conditions and pH was adjusted using 1 M NaOH or 1 M HCl. The same tests which were done without coagulant as control were denoted as T_c , and the tests done with coagulant were denoted as T_s . The coagulation performance was evaluated as

$$\text{Coagulation activity \%} = \frac{(T_c - T_s)}{T_c} \times 100$$

4. Characterization of the Recovered Titanium Dioxide

After sedimentation of TiO_2 , the solution was decanted and the sedimented TiO_2 samples were collected and air dried followed by calcination at 500°C in muffle furnace for four hours. The samples were cooled and powdered for further characterization and reuse.

XRD, an essential requisite in determining the crystalline structure and crystallinity of the TiO_2 , was done using PAN Analytical XRD using a Cu target $K\alpha$ radiation. Scherrer's formula was used to determine its crystal grain size. The BET surface area was determined by nitrogen adsorption desorption by Micromeritics Gemini VII 2390 model. The surface area of the sample was determined from adsorption isotherm by Brunauer-Emmett-Teller (BET) method, and pore size was calculated from desorption isotherm by Barrett-Joyner-Halenda (BJH) method. Average pore size was calculated by t-plot method. The surface morphology of the TiO_2 particles was resolved using Hitachi S-3400NSEM operated at 15 kV. For measuring the optical properties, diffuse reflectance spectra (DRS) and absorbance were recorded with UV-Vis. NIR spectrophotometer-Varian Cary 5000. BaSO_4 was used as the reference. The photoluminescence spectrum was measured for determining the rate of electron hole recombination by flurospectrophotometer (JY Fluorolog - FL3-11), with xenon lamp as an excitation source.

5. Reuse of the Recovered TiO_2 after the Sedimentation

5-1. Dye Degradation Experiments

Rhodamine B was selected as the model organic compound to evaluate the photocatalytic efficiency of the recovered TiO_2 . The experiments were carried out in open borosilicate beakers of 250 ml capacity filled with 100 ml dye solution (10 mg/l). TiO_2 (100 mg/l) was added to the dye solution and sonicated for 15 minutes. Then, the samples were kept in a water bath for temperature regulation and exposed to solar irradiation. Required quantities of samples were withdrawn at regular time intervals, centrifuged, and the supernatant was analyzed by using UV spectrophotometer at 553 nm.

5-2. Analysis of Hydroxyl Radicals by Terephthalic Acid Probe Test

When aqueous suspension of TiO_2 is irradiated, hydroxyl radicals are produced and play an important role in the degradation of pollutants. The formation of hydroxyl radicals in water can be detected by photoluminescence technique, using terephthalic acid as the probe molecule. Terephthalic acid reacts with hydroxyl radicals to produce a fluorescent product, 2-hydroxyterephthalic acid. The intensity of the photoluminescence (PL) peak of 2-hydroxyterephthalic acid is directly proportional to the amount of hydroxyl radicals produced in water. The PL signal at 425 nm refers to the hydroxylation of terephthalic acid with hydroxyl radical formed at the water/ TiO_2 interface [23]. We used this terephthalic acid probe

test to check the photocatalytic efficiency of the recovered TiO₂ in comparison with pure TiO₂.

A total of 0.5 mM terephthalic acid was prepared by dissolving it in 2 mM NaOH. Ten milligrams of pure and recovered TiO₂ was separately added to 100 ml of terephthalic acid and sonicated for 15 minutes. The samples were then kept under solar radiation for 30 minutes and 5 ml of sample was withdrawn, centrifuged at 10,000 rpm to settle the particles. Then the supernatant was excited at 320 nm in spectrofluorometer to evaluate the intensity of photo-generated hydroxyl radicals.

RESULTS AND DISCUSSION

1. Coagulation of TiO₂ in its Aqueous Suspensions

Our investigation to test the possibility of using a plant coagulant for settling TiO₂ photocatalyst in suspension gave good results. The results showed that about 92% of TiO₂ in suspension rapidly settled through this method at a neutral pH of 7.5. The data indicated in Fig. 1 shows that maximum settling efficiency of the coagulant was 64.4%, 84.0%, 84.4% and 92.8%, respectively, for 50 mg/l, 100 mg/l, 500 mg/l and 1,000 mg/l of TiO₂ concentration within a coagulant dosage of 10-15 mg/L. The residual turbidity receded from 4000 nephelometric turbidity unit (NTU) to less than 10 NTU. Since maximum settling of TiO₂ was observed at 1 g/l suspension with a minimum coagulant dosage 10 mg/l, further experiments were conducted at this concentration. Santos et al. [26] observed nearly 98% turbidity removal in 500 mg/l TiO₂ suspension using aluminium sulphate. Wang et al. [16] also reported average settling efficiency of 55% and 77% for FeCl₃ and Poly ferric sulphate (PFS) respectively for 30 mg/L TiO₂ suspension with 0.03 mM coagulant dosage. The use of chemical coagulants to sediment TiO₂ has drawbacks, as it is effective only at extreme pH and the inorganic ions may influence the surface morphology of the TiO₂ particles rendering it unfit for reuse [24]. With the addition of the natural coagulant, there is no significant change in the pH and alkalinity of water, whereas using chemical coagulants like FeCl₃

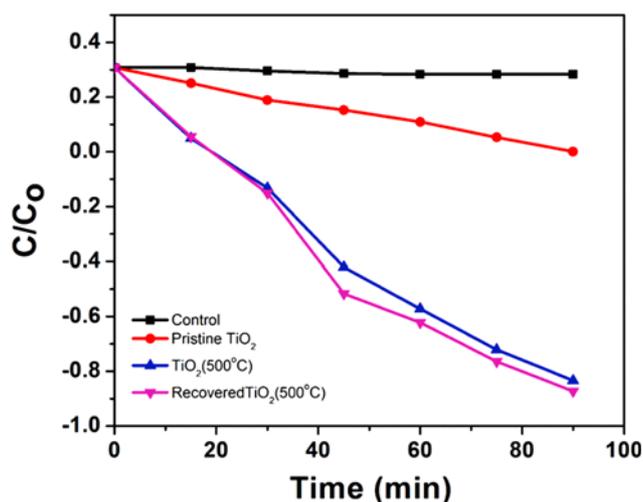


Fig. 1. Effect of varying coagulant concentrations on TiO₂ turbidity removal.

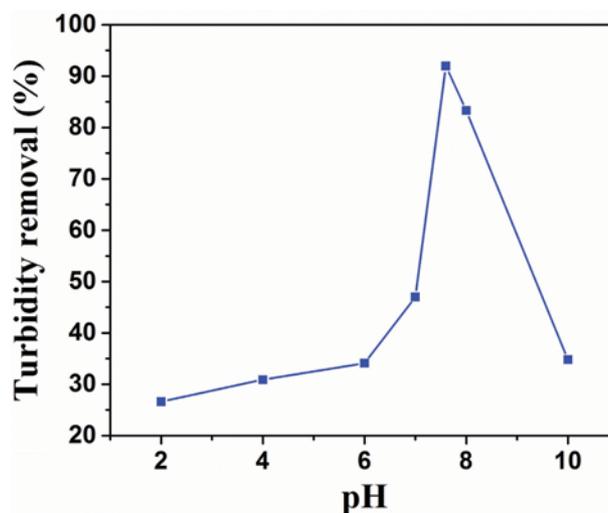


Fig. 2. Effect of pH on TiO₂ turbidity removal from water using plant coagulant (10 mg/Lin 1 g/LTiO₂ suspension).

possessing hydrolyzing property alters the pH drastically from 8.60 to 2.63 [25]. The effect of pH was tested at initial pH values of 5, 6, 7, 8, 9 and 10 (Fig. 2). The lowest residual turbidity value was observed between pH 6 and 8, and in subsequent experiments, maximum coagulation efficiency was attained at pH 7.5 where the nephelometric turbidity unit receded below 10 NTU. Hence, further investigations were carried out at this optimum pH. Though titanium dioxide particles get easily settled at a pH below 3 and above 10, the higher chemical consumption for neutralizing makes it infeasible [26].

Similarly, the increase in ionic strength can influence the effect of coagulation in aqueous medium [27]. So, NaCl was adopted as the typical electrolyte to study the influence of ionic strength on flocculation and coagulation in distilled water with 1 g/L TiO₂ suspension. A jar test without NaCl was taken as control. It is evident (Fig. 3) that flocculation rate increased with the addition of the

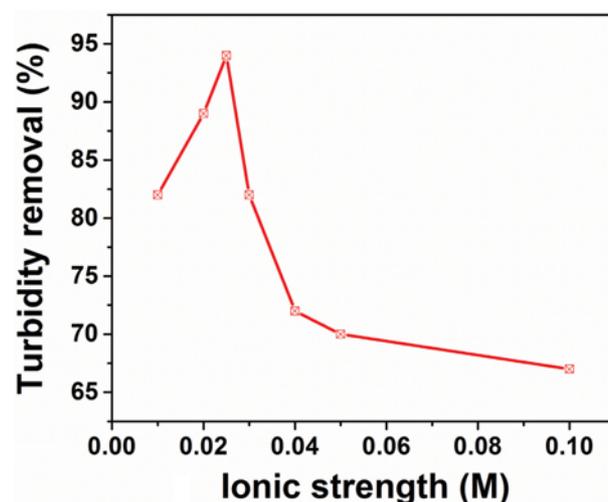


Fig. 3. Effect on ionic strength on TiO₂ turbidity removal with optimum coagulant dosage of 10 mg/l in 1 g/LTiO₂ suspension.

electrolyte, and the optimum concentration was found to be 0.025 M for NaCl. The addition of electrolyte like NaCl enhanced the solubility of the active coagulant component present in the biomass leading to better turbidity removal. The flocs settled could be easily recovered and annealed for reuse. The anionic polyelectrolytes or polysaccharide fraction containing galactan and galactomannan present in this plant coagulant may be responsible for destabilizing the particles present in the water medium by means of inter particle bridging, thus enhancing settling [18,20,28]. Further, the plant coagulant used here is non-toxic and biodegradable compared to its chemical counterparts. Whereas, various reports suggest that inorganic salts used as coagulants may influence the photocatalytic activity by inhibiting the active sites and hydroxyl radical scavenging [24].

2. Experiments to Test the Reuse Potential of the Recovered Catalysts

To investigate the possibility of reusing the recovered TiO_2 after coagulation and flocculation, the samples were calcined at 500°C to remove the organic content from the catalysts. The photophysical properties and surface morphology of the calcined samples were studied to determine the stability of the particles for its reuse. The reuse efficiency was also tested by photocatalytic degradation experiments and terephthalic acid tests.

3. Characterization of the Recovered Catalyst

3-1. X Ray Diffraction Studies

XRD patterns of the pure and recovered TiO_2 particles were compared to investigate the change in phase structure. As depicted in Fig. 4 they almost resemble each other by exhibiting peaks at 25.4° , 37.8° , 48.07° , 54° , 55° , 62.7° , 75.09° , which is attributed to the anatase phase of TiO_2 . It is clear from the diffractogram that there is no phase transition, but slight sharpening of the peaks suggesting the growth of anatase crystallites [29]. The crystalline sizes of

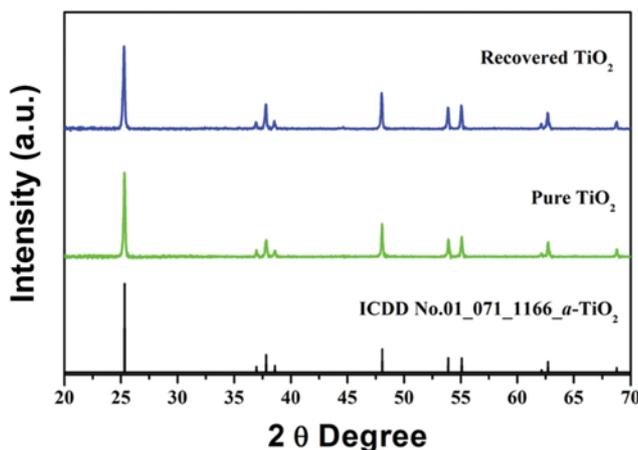


Fig. 4. XRD pattern of the pure and recovered titanium dioxide particles.

the particles were determined to be 47.5 nm and 66.5 nm for the pure and recovered TiO_2 , respectively. The increase in crystalline size could be attributed to the sintering process. The calcination of the recovered TiO_2 influences a significant change in the crystalline size due to minimization of interfacial energy [30].

3-2. Surface Morphological Properties

Pore volume and BET surface area are the key properties in understanding the structure and catalytic property of the photocatalysts. To characterize the specific surface area and porosity of the samples, nitrogen sorption isotherm studies were carried out. From Fig. 5, it is evident that the nitrogen sorption of the pure and recovered photocatalysts can be classified as type II according to IUPAC classification [31]. Also, hysteresis approaches towards P/

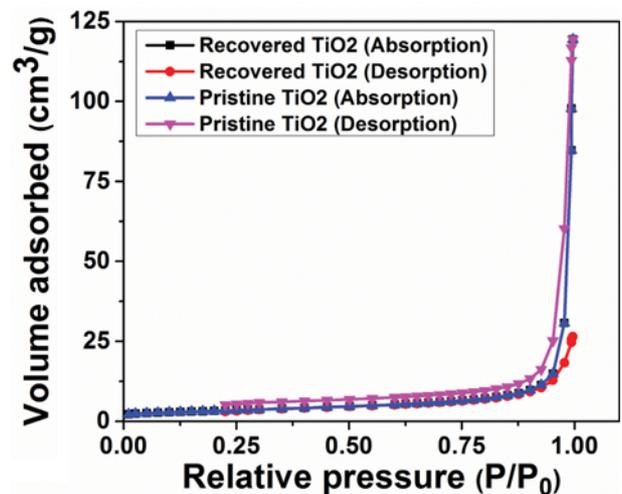


Fig. 5. Adsorption-Desorption isotherm of pristine and recovered titanium dioxide particles.

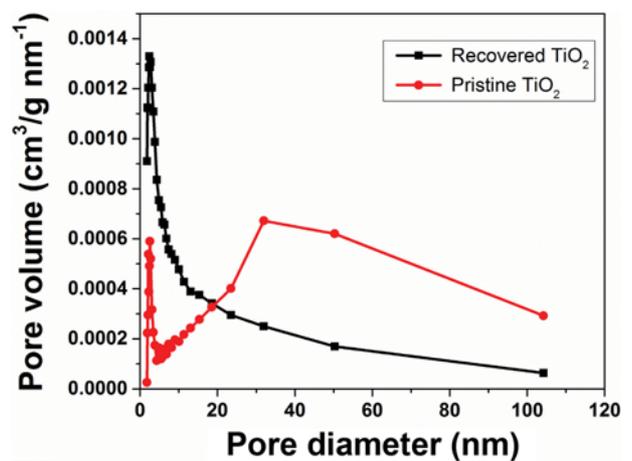


Fig. 6. Pore size distributions of the recovered and pristine titanium dioxide particles.

Table 2. Physical properties of the pristine and recovered TiO_2

Sample	Phase content	Crystalline size (nm)	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Pristine TiO_2	Anatase	55.5	11.414	0.1847	0.647
Recovered TiO_2	Anatase	66.5	11.003	0.0409	0.148

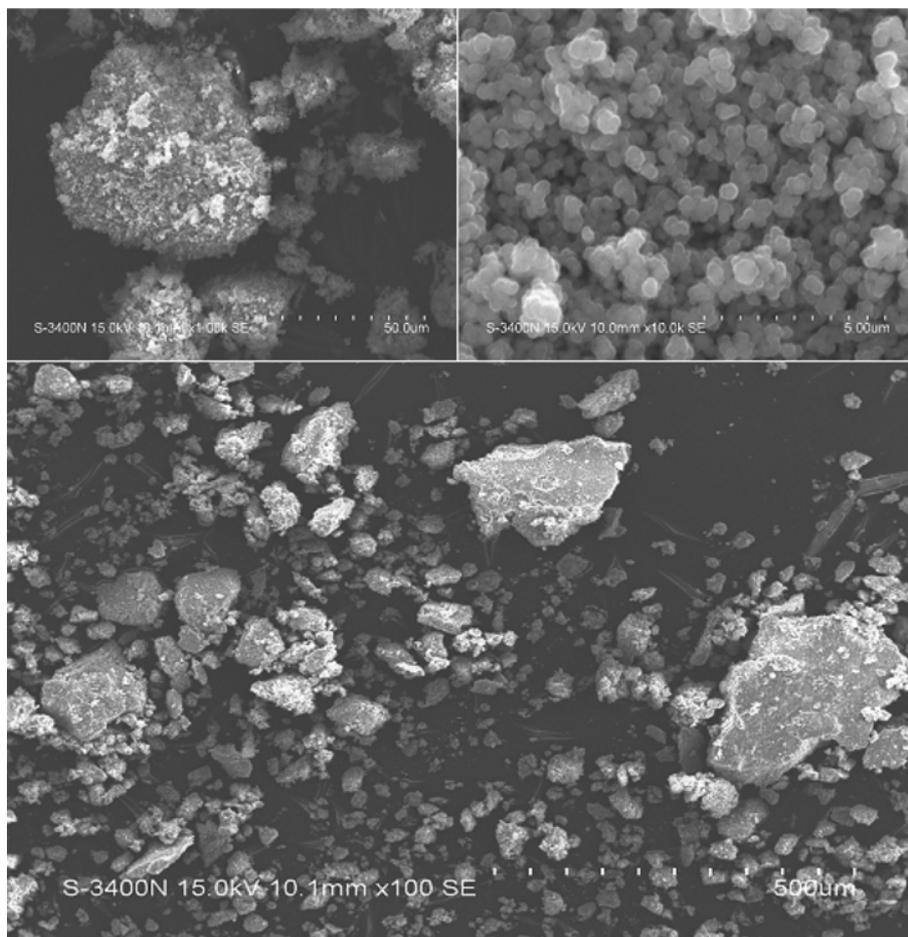


Fig. 7. SEM image of recovered TiO₂.

Po=1, suggesting the presence of macroporous structure with large pores (>50 nm) [32]. From Table 2 and Fig. 6, it could be inferred that both the samples possessed almost same surface area (SBET > 11 m²/g), while the pore volume and pore size decreased slightly, which may be attributed to the combination of factors like calcination or adsorption of polyelectrolytes onto the pores of the catalysts. Our results are in good agreement with Drisko et al. [33] and Mishael et al. [34] who propose that the polyelectrolytes adsorbed will affect the pore volume, as the polyelectrolytes coil and loop into the void spaces present in the pore rather than lying flat on the support of surface. These agglomerated macroporous structures could be directly observed in SEM images, as shown in Fig. 7. Rough spherical surface morphology with the agglomerated macroporous framework is also observed. The surface morphological properties of TiO₂ almost remained the same even after the coagulation and calcination process, except for their pore volume. Optical properties of the pure and recovered TiO₂ showed no remarkable changes, which was confirmed with DRS and PL spectra (Fig. S1 and S2).

3-3. Evaluation of Photocatalytic Efficiency of the Recovered Photocatalysts

Rhodamine B, a highly soluble basic dye of xanthene class, was used to test the photocatalytic activity of the recovered TiO₂ particles. An attempt was also made to determine whether the calcina-

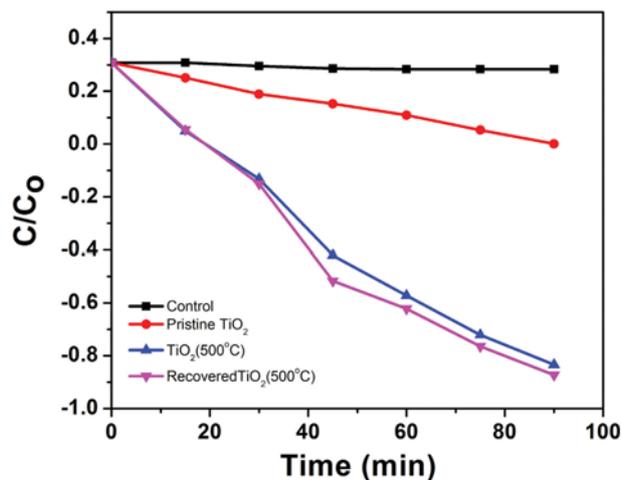


Fig. 8. Comparison of photocatalytic efficiency of pristine and recovered titanium dioxide particles.

tion process has any influence on the photocatalytic efficiency. Fig. 8 shows the comparative photocatalytic activity of the particles, and it can be clearly inferred that recovered TiO₂ is superior in efficiency than that of calcined and noncalcined pristine TiO₂ particles. With an increase in irradiation duration, the decolorization

of Rhodamine B progressed in a steady manner and complete decolorization was observed in 90 minutes. The rate constants were calculated to be for 0.33×10^{-3} , 1.288×10^{-3} and 2.37×10^{-3} for pure, calcined and recovered particles, respectively. The enhanced photocatalytic activity in the recovered and calcined titanium dioxide particles could be attributed to a comparatively higher surface volume ratio due to calcination [35]. The sintering process would have contributed to the dispersion of the particles, resulting in high surface volume ratio accessing more light during photocatalytic reaction. Our results of an increase in crystalline size are in accordance with the work of Yu et al. [29] and also justify the enhanced photocatalytic activity. Still, the recovered TiO_2 is found to be slightly more effective than calcined sample, which might be due to adsorption of polyelectrolytes onto the pores present in photocatalyst as evident from our BET analysis. This may reduce the electron-hole recombination, thereby increasing the photocatalytic degradation of Rhodamine B.

Furthermore, to understand the involvement of active species in the enhanced photocatalytic activity of the recovered TiO_2 particles, a terephthalic acid test was carried out at ambient conditions to determine the formation of hydroxyl radicals. The spectrum (Fig. 9) shows identical shape and peak position with subtle change

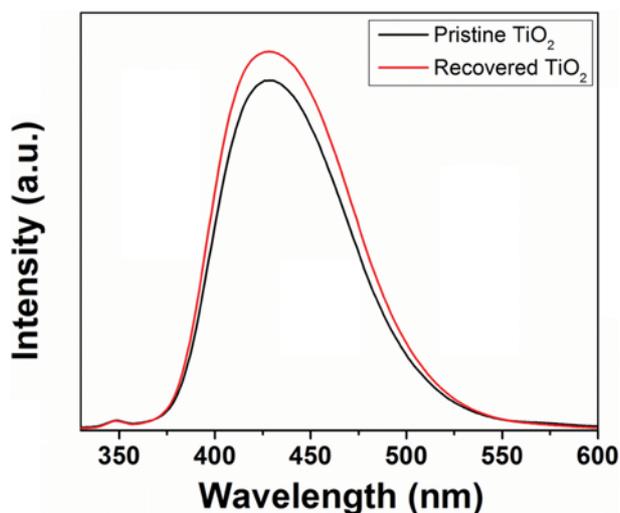


Fig. 9. Fluorescent spectral change of TiO_2 particles in terephthalic acid.

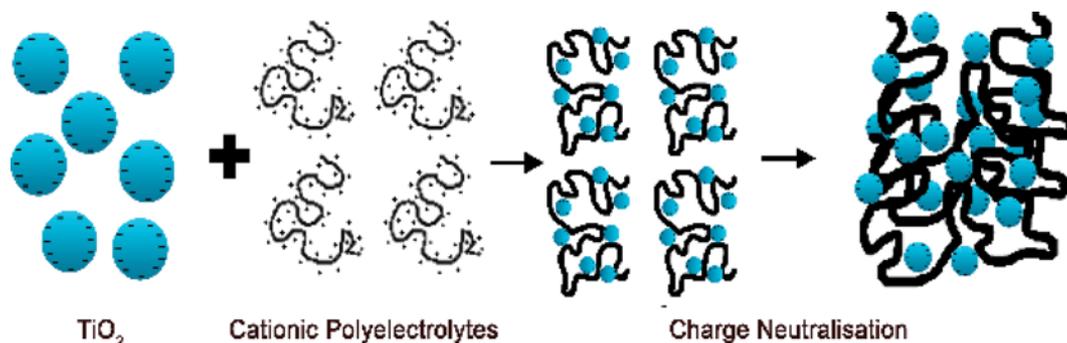


Fig. 10. Plausible mechanism in coagulation of TiO_2 in aqueous suspension.

for the recovered particles, exhibiting higher intensity than that of pure TiO_2 . The slight increase in the intensity peak position of the recovered TiO_2 particles may be due to reduction in recombination rate, positively correlating with enhanced photocatalytic activity (Fig. 8). The increase in crystalline size would have ultimately contributed to the increase in OH radical production, enhancing the photocatalytic activity. Further detailed investigation is required in this aspect.

3-4. Plausible Mechanism of Coagulation

The adsorption of TiO_2 depends to a great extent on the surface charge, which varies according to the pH of the solution. The plant coagulant used in the coagulation flocculation experiment consisted of ampholytic polyelectrolytes containing both the cationic and anionic groups. The negatively charged surface of the TiO_2 readily adsorbs with the cationic polyelectrolytes present in the suspension, leading to neutralization favoring the coagulation-flocculation process. The dispersed TiO_2 particles flocculate readily with the presence of electrolytes by interacting with each other forming aggregates as illustrated in the Fig. 10. The other factors which influence the flocculation of TiO_2 particles are the presence of cations, anions and NOM present in the tap water. As mentioned earlier, TiO_2 in distilled water does not readily flocculate because of the underlying fact that the presence of charged ions and NOM influences the coagulation flocculation process. The traces of NOM particles present in tap water covered by a sheath of humus encircle the TiO_2 particles and enhance the adsorption at the neutral pH, whereas in alkaline and acidic pH, coagulation does not occur. In our experiments, the optimum pH for coagulation flocculation process was found to be 7.5. Hence, pH of the water is an important factor in influencing the coagulation flocculation. Accordingly, the coagulation of TiO_2 suspensions using *Strychnos potatorum* is presumed to be due to the destabilization of the negatively charged aggregates by the cationic polyelectrolytes present in the coagulant.

CONCLUSION

A novel and greener method was developed using seed extracts of *Strychnos potatorum* for the recovery and reuse of TiO_2 photocatalyst from its aqueous suspension. The optimum dose of 10 mg/L of the plant coagulant can settle ninety percent of TiO_2 suspension at neutral pH. The potential reuse efficiency of the recovered

catalysts validated with dye decolorization experiment, and terephthalic acid test shows more enhanced photocatalytic activity than pure TiO₂. Therefore, this method could be translated as a probable alternative for the separation of TiO₂, a major bottleneck in photocatalytic water treatment.

ACKNOWLEDGMENTS

We gratefully acknowledge the UGC, New Delhi, Govt. of India for funding the research project (F.No. 40/146/2010 (SR) and F 7-237/2009 (BSR) for providing a fellowship for authors b and a, respectively. We also thank the Central Instrumentation Facility, Madanjeet School of Green Energy Technologies and Department of Earth Sciences, Pondicherry University for providing instrumentation facilities for the characterization studies.

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

REFERENCES

1. K. Nakata and A. Fujishima, *J. Photochem. Photobiol. C*, **13**, 169 (2012).
2. C. Pagnout, S. Jomini, M. Dadhwal, C. Caillet, F. Thomas and P. Bauda, *Colloids Surf., B*, **12**, 315 (2012).
3. A. G. Rincon, C. Pulgarin, N. Adler and P. Peringer, *J. Photochem. Photobiol. A: Chem.*, **139**, 233 (2001).
4. A. R. Khataee, *Environ. Technol.*, **30**, 1155 (2009).
5. P. K. Robertson, J. Robertson and D. W. Bahnemann, *J. Hazard. Mater.*, **211**, 161 (2012).
6. Y. Kikuchi, K. Sunada, T. Iyoda, K. Hashimoto and A. Fujishima, *J. Photochem. Photobiol. A*, **106**, 51 (1997).
7. D. M. Alrousan, P. S. Dunlop, T. A. McMurray and J. A. Byrne, *Water Res.*, **43**, 47 (2009).
8. A. L. Linsebigler, G. Lu and J. T. Yates Jr., *Chem. Rev.*, **95**, 735 (1995).
9. J. Kim and W. Choi, *Energy Environ. Sci.*, **3**, 1042 (2010).
10. S. Devipriya and S. Yesodharan, *Sol. Energy Mater. Sol. Cells*, **86**, 309 (2005).
11. H. Sun, Y. Bai, Y. Cheng, W. Jin and N. Xu, *Ind. Eng. Chem. Res.*, **45**, 4971 (2006).
12. S. Kagaya, K. Shimizu, R. Arai and K. Hasegawa, *Water Res.*, **33**, 1753 (1999).
13. A. Fernandez, G. Lassaletta, V. M. Jimenez, A. Justo, A. R. Gonzalez-Elipse, J. M. Herrmann and Y. Ait-Ichou, *Appl. Catal. B: Environ.*, **7**, 49 (1995).
14. A. Rachel, M. Subrahmanyam and P. Boule, *Appl. Catal. B: Environ.*, **37**, 301 (2002).
15. D. Li, S. Zhu, R. H. Pelton and M. Spafford, *Colloid. Polym. Sci.*, **277**, 108 (1999).
16. H. T. Wang, Y. Y. Ye, J. Qi, F. T. Li and Y. L. Tang, *Water Sci. Technol.*, **68**, 1137 (2013).
17. R. Divakaran and V. S. Pillai, *Water Res.*, **38**, 2135 (2004).
18. P. N. Tripathi, N. Chaudhuri and S. D. Bokil, *Indian J. Environ. Health*, **18**, 272 (1976).
19. S. Biswas, T. Murugesan, K. Maiti, L. Ghosh, M. Pal and B. P. Saha, *Phytomedicine*, **8**, 469 (2001).
20. M. Adinolfi, M. M. Corsaro, R. Lanzetta, M. Parrilli, G. Folkard, W. Grant and J. Sutherland, *Carbohydr. Res.*, **263**, 103 (1994).
21. J. Qi, Y. Y. Ye, J. J. Wu, H. T. Wang and F. T. Li, *Water Sci. Technol.*, **67**, 147 (2013).
22. APHA, 20th Ed. *American Public Health Association*, Washington (1998).
23. Y. Yang, T. Zhang, L. Le, X. Ruan, P. Fang, C. Pan and J. Wei, *Sci. Rep.*, **4**, 7045 (2014).
24. C. Guillard, E. Puzenat, H. Lachheb, A. Houas and J. M. Herrmann, *Int. J. Photoenergy*, **7**, 1 (2005).
25. W. P. Cheng, *Chemosphere*, **47**, 963 (2002).
26. J. M. Santos, J. P. Valente, S. M. A. Jorge, P. M. Padilha, M. J. Saeki, G. R. Castro and A. O. Florentino, *Orbital: Electron. J. Chem.*, **5**, 233 (2013).
27. R. A. French, A. R. Jacobson, B. Kim, S. L. Isley, R. L. Penn and P. C. Baveye, *Environ. Sci. Technol.*, **43**, 1354 (2009).
28. M. M. Corsaro, I. Giudicianni, R. Lanzetta, C. E. Marciano, P. Monaco and M. Parrilli, *Phytochemistry*, **39**, 1377 (1995).
29. J. Yu, H. Yu, B. Cheng and C. Trapalis, *J. Mol. Catal. A: Chem.*, **9**, 135 (2006).
30. H. K. Shon, S. Vigneswaran, I. S. Kim, J. Cho, G. J. Kim, J. B. Kim and J. H. Kim, *Environ. Sci. Technol.*, **41**, 1372 (2007).
31. K. S. Sing, *Pure Appl. Chem.*, **57**, 603 (1985).
32. Y. Wang, L. Zhang, K. Deng, X. Chen and Z. Zou, *J. Phys. Chem. C*, **111**, 2709 (2007).
33. G. L. Drisko, L. Cao, M. C. Kimling, S. Harrisson, V. Luca and R. A. Caruso, *ACS Appl. Mater. Interfaces*, **1**, 2893 (2009).
34. Y. G. Mishael, P. L. Dubin, R. de Vries and A. B. Kayitmazer, *Langmuir*, **23**, 2510 (2007).
35. J. F. Porter, Y. G. Li and C. K. Chan, *J. Mater. Sci.*, **34**, 1523 (1999).

Supporting Information

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(Received 4 November 2015 • accepted 22 February 2016)

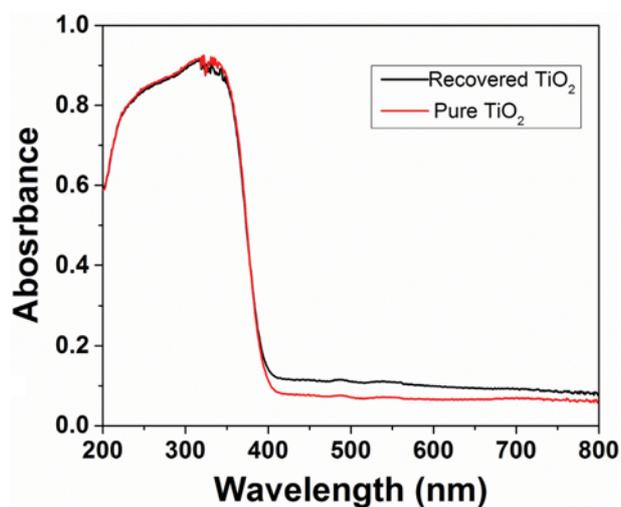


Fig. S1. Diffuse Reflectance spectra of pristine and Recovered TiO₂.

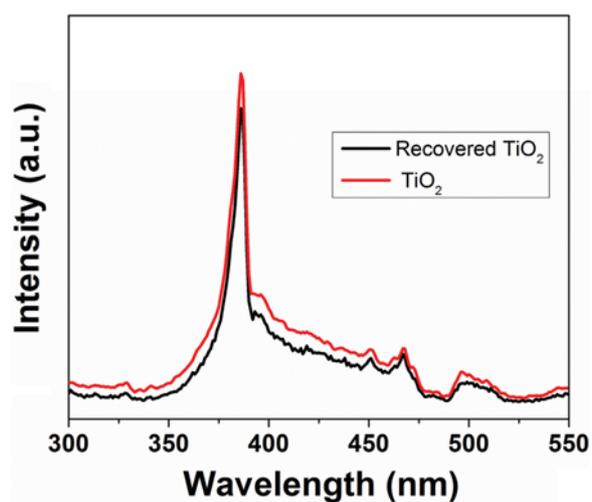


Fig. S2. PL spectra of pristine and recovered TiO₂.