ENHANCED ADSORPTION AND PHOTO DEGRADATION OF PHYSICALLY MIXED TiO_2 BASED PHOTOCATALYSTS

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Abstract— A variety of single, bi and tri metal doped TiO_2 nanoparticles were prepared by sol-gel method and analysed for their adsorption and photocatalytic abilities using Methylene Blue (MB) as target pollutant. The materials were characterised using XRD, ESD, SEM, FT-IR, FL microscopy and DRS. A very simple, low cost, efficient and robust physical heterostructure of Ag_3PO_4/TiO_2 was also successfully developed. The composition, optical properties and morphology of the prepared nanomaterials were controllable by adjusting the mixing ratios. The physical mixture exhibited much higher photocatalytic performance under the visible light as well as adsorption capacities. The coupling of Ag_3PO_4 particles with UV light active TNPs simultaneously could utilize the larger part of solar spectra and less consumption of metals. The heterostructure is quite appealing for their practical use in environmental issues. Further, this provides an easy, rapid and low cost adsorbent and a good photocatalyst which otherwise is costly and time consuming when synthesised chemically.

Keywords— Adsorption, Methylene blue, Mixture, Photocatalysis, Titania.

I. INTRODUCTION

Industries in the developing countries, mostly being water inefficient, use around 22% of the total world water consumption. Over 70% of the resulting wastewater ends up in open environment without any treatment or processing [1]. These wastewaters may also contain harmful chemicals which can cause various health problems to flora and fauna and pose environmental challenge [2]. Treatment of such wastewater is costly and difficult due to quality and composition [3].

A variety of techniques has been proposed to treat the complex wastewater including thermal, membrane separation, ultra filtration, coagulation, flocculation, reverse osmosis, activate carbon adsorption microfiltration and sand filters [4]. "However, none of these treatment methods is effective enough to produce water with acceptable levels of the most persistent pollutants within a reasonable time" [5].

Advanced oxidation processes (AOPs) have gained considerable attention due to its high efficiency in relatively short period of time. Photocatalysis using TiO_2 (titania) has been widely investigated for the environmental problems due to its low cost, easy availability, non-toxicity, high photocatalytic activity, chemical stability, and its ability to completely mineralize the organic pollutants to carbon dioxide and water [6]. Photocatalytic activity of the titania can be greatly influenced by a variety of parameters such as titania preparation conditions, doping of metal or nonmetal ions, surface area and porosity, band gap energies, dispersion in the aqueous system, quality and quantity of target pollutant, light source and intensity and electron hole recombination rate. Particularly, TiO_2 doped with lanthanides ions posses higher photocatalytic activity than that of pure TiO_2 [7].

The application of titania nanoparticles (TNPs) for the photocatalysis is also limited due to low adsorption of the target organic pollutants on the surface of TNPs [8]. Since, photocatalytic degradation of organic pollutants involving TNPs mainly happen on the surface of the catalyst hence, mass transfer of the organic pollutants to the surface of the TNPs must be facilitated for the better efficiency of the photocatalysis reactions [9,10]. Enhanced adsorption by TiO_2 does not necessarily improve the photo-activity [11]. The removal of a variety of species by adsorption on titanate nanotubes has been previously investigated [9]. However, physical mixtures of TiO_2 based photocatalysts, for adsorption capacities, are more economical, easy to prepare, require less sophisticated equipment for synthesis, these have not been satisfactorily explored yet.

In the present paper, chemical and physical mixtures of metal doped titania have been evaluated as adsorbents for their potential to uptake Methylene Blue (MB) from synthetic solution. The effect of various operating conditions, including initial MB concentration, adsorbent dose and pH, was investigated on the adsorption process in batch adsorption experiments. Physical mixtures were also prepared and compared with the chemical mixtures of the same titania materials under the same operating conditions.

II. EXPERIMENTAL DETAILS

2.1. Preparation of photocatalysts

A typical sol-gel method was used to prepare pure and metal doped TNPs. In a typical method, 100 mg of surfactant (P-123) was dissolved in 10 mL of distilled water (DW) while stirring at 50 C. pH of the solution was adjusted at 3-4 using 0.5 M HCl. After

10 min stirring 3 mL of titanium tetra isopropoxide (TTIP) was drop wise added to the above solution while vigorous stirring. The reaction mixture was then sonicated for one hour followed by stirring of 4 h. Resultant mixture was allowed to stand for 24 h and the white precipitates were centrifuged at 20,000 rpm and washed with distilled water (DW) 4 times. Prepared TNPs were dried at 80 C for 12 h and calcined at 500 C for 6 h. Metal doped TNPs were prepared using the same method with addition of desired amount of metal salt in the first step.

For the synthesis of Ag_3PO_4/TiO_2 hybrid was prepared typically, TiO_2 nanoparticles were dispersed in 50 mL of de-ionized (DI) water and 0.6 mmol of $AgNO_3$ was added and continuously stirred to form a homogeneous suspension. Designated amounts of Na_2HPO_4 solution (0.02 M) was added to the above suspension slowly. The reaction mixture was further kept stirring for 1 h at room temperature in dark. "Finally, the resulting Ag_3PO_4/TiO_2 hybrid composite was collected by centrifugation, washed repeatedly with ethanol and DI water, and then dried at 60 ˚C overnight" [12]. Pure Ag_3PO_4 particles were synthesized under similar reaction conditions in the absence of TiO_2 nanoparticles [12].

2.2. Photocatalytic setup

Prepared photocatalysts were evaluated for their adsorption ad photocatalytic efficiencies using Methylene Blue (MB) as target pollutant. Photocatalytic experiments were conducted in the 15 mL pyrex glass tubes. Ten milliliter MB solution and desired amount of photocatalysts were added to the glass tube and sonicated for 5 min to disperse TNPs. Test tubes were shaken on an orbital shaker for 20 min in the dark to achieve the adsorption desorption equilibrium. These test tubes then were then exposed to 50 W LED light and samples were collected at regular time intervals. Residual MB was measured by UV-Vis spectrophotometer (Schimadzu, 3600) at 665 nm.

2.3. Adsorption experiments

Adsorption experiments for MB were evaluated by shaking a mixture of MB solution with various as-prepared TiO_2 based materials at 25 C for desired time period. The suspension was centrifuged at 13000 rpm for 5 min. The supernatant was analyzed by the UV–Vis spectrophotometer (Schimadzu, 3600) at 665 nm to evaluate the adsorption capacity of TiO_2 [13].

The adsorption rate R (%) and the amount of dye molecules adsorbed onto the as-prepared photocatalysts q_e (mg/g), in a certain time t, were calculated from Eqs. (i) and (ii), respectively,

$$R\ (\%) = \frac{(Ct - Co) \times 100}{Co} \quad \text{(i)}$$

$$qe\ (mg/g) = \frac{Ct - Co}{M} \quad \text{(ii)}$$

where C_o is the initial dye concentration (mg/L), C_t is the residual dye concentration (mg/L) at time t (min) and m is the mass of an adsorbent (g/L). Rate constants of decoloration was determined using exponential relation (Eq. iii)

$$\ln\left(\frac{C}{Co}\right) = -kt \quad \text{(iii)}$$

Where C was concentration of dye, time t and Co was initial dye concentration. A plot of $\ln C/C_o$ versus t without intercept yields slope equals to k.

2.4. Characterization and analysis

Various analytical techniques were employed to characterize the prepared titania nanoparticles (TNPs) and PE films. The crystal structure of the titania nanoparticles was studied using X-ray diffraction (XRD) spectroscopy using JEOL JDX-II with Cu-Kα radiation (voltage: 40 kV; current 20 mA). The range of diffraction angles (2θ) was 20^o - 80^o and the scanning rate was 0.05^o 2θ/s.

Rutile content in the TNPs was calculated based on the intensities of rutile and anatase peaks in the XRD patterns using following formula,

$$X_R = \frac{\left(\frac{I_R}{I_A}\right)0.79}{1+\left(\frac{I_R}{I_A}\right)0.79} \quad \text{(iv)}$$

here XR shows the fraction by weight of the rutile phase TNPs, and IA and IR are the integrated X-ray intensities of the reflection of anatase at 2θ = 25.4◦ and the rutile at 2θ = 27.5◦, respectively.

Scherrer's formula was applied to calculate the particle size (L) using XRD data,

$$L = \frac{0.89\lambda}{\beta \cos\theta} \quad \text{(v)}$$

Where L is the particle size, λ is X-ray wavelength, β is the full width at the half maximum of the diffraction peak and θ is the diffraction angle.

Scanning electron microscopy (SEM) was used after Au coating by a sputtering method to investigate the surface morphology of the TNPs using JEOL JSM-6460

III. RESULTS AND DISCUSSION

3.1. Characterization and analysis

Pure and metal doped TNPs were prepared by sol gel method and characterized using XRD, EDS, SEM, FT-IR and UV-Vis spectroscopy. The XRD pattern shows peaks of 2θ at 25.2, 36.9, 37.8, 38.5 and 48.1 were corresponding to the lattice plane of (101), (103), (004), (112) and (200) in anatase, respectively [14]. Prepared TNPs were primarily in the anatase form with an average particle diameter of 25 nm. Metal doping slightly increased the particle size. Similar finding were reported when Mn-doped concentration was higher than 0.2%, the peak intensity was stronger than the pure TiO_2. This indicating that high Mn^{2+} concentration helps to increase the particles size [15]. All the tested TNPs were in dominantly in the anatase phase except the Mn-doped TNPs. With the increase of Mn content, the formation of the anatase phase needs higher

temperature, but obviously the phase-transition temperature from anatase to rutile decreases. Whereas, if Mn content is higher than 8%, the rutile phase became the dominant phase [16].

For the metal doped TNPs, "the positions of all diffraction peaks shifted to lower angle and the peak intensity is relatively low, mainly because of lattice distortion and the low degree of crystallinity, respectively" [17].

Metal doping has also produced a red shift in the UV-Vis absorption of TNPs. Mn doped TNPs showed the maximum red shift compared to the pure TNPs whereas, Zn doped TNPs generated least fluorescence signal when excited at wavelength of 316 nm showing the least recombination of electron hole pair. The EDS spectra of pure TNPs showed no impurity whereas SEM image showed the particles are spherical in shape.

3.2. Adsorption capacities of TNPs

As prepared TNPs and commercially available TNPs were evaluated for their abilities to adsorb MB dye molecules. Adsorption of dye molecules on to the photocatalyst is the first foremost step to achieve complete mineralization of dye. Generally, more the adsorption of dye molecules more will be the degradation. Metal doping (1%) increased the adsorption of MB compared to the pure TiO_2. The highest adsorption of MB was shown by the Mn-TiO_2 followed by Ce-TiO_2 and Zn-TiO_2.

Whereas, TNPs, modified with H_2O_2 showed higher adsorption compared to pure TNPs, possibly due to increased surface hydroxyl groups. Modification with H_2O_2 also reduced the aggregation of TNPs making more sites available for anchoring dye molecules resulting in highest adsorption capacity. Di and tri metal doping did not show significant difference in the adsorption capacity.

Interestingly, the physical mixtures of singly doped metal TNPs showed better adsorption capacities compared to the chemically mixed counter parts. The metal doped TNPs were physical mixed in 1:1 ratio, grounded and evaluated for their adsorption and photocatalytic efficiencies. A 1:1 physical mixture of separately doped with Zn and Mn TNPs showed the highest adsorption of MB. "The strong adsorptive phenomenon could be attributed to the modification of TiO_2 by cationic metal doping which can provide amount of positive sites to the surface charges of the samples" [18,19]. Zeta potential results show that the metal doped TNPs are positively charged (Data not shown). MO molecules possess negatively charged ions in aqueous solutions and thus could be adsorbed by samples through electrostatic interactions [19]. More positive sites could have been produced by physically mixing Mn and Zn doped TNPs which could help to increase the adsorption of MO anions considerably. "Oxygen vacancies on the surfaces of TiO_2 due to incomplete crystallization, the existence of surface functional groups can interact with MB molecules via hydrogen bonds and/or electrostatic forces can also promote the adsorption of dye molecules" [20].

However, in case of chemically combined and calcined metal doped TNPs, the samples could have transformed to negatively charge upon calcination in air at 400 ˚C resulting in weak adsorptive ability and possibly better photoactivity. "The adsorption surpassing photodegradation was rarely discussed clearly in some related literatures" [19].

3.3. Photocatalytic efficiency of TNPs

Photocatalytic efficiencies of as-prepared TNPs were evaluated by exposing to a variety of light sources. Emission spectra of these light sources are shown in. The results of LED and UV-254 lights are presented in this paper. It can be seen that LED light (50 W) showed broad emission peaks at 450 and 540 nm while UV-254 lamp emits multiple sharp peaks of high intensity.

Among the single metal doped TNPs, Mn-TNPs showed highest degradation (70%) of MB followed by the Ce (67%) and Zn (65%) doped TNPs respectively. Whereas, di and tri metal doped TNPs showed very less MB removal when compared to the pure TNPs (Fig. 1). Zn, Mn and Ce doped

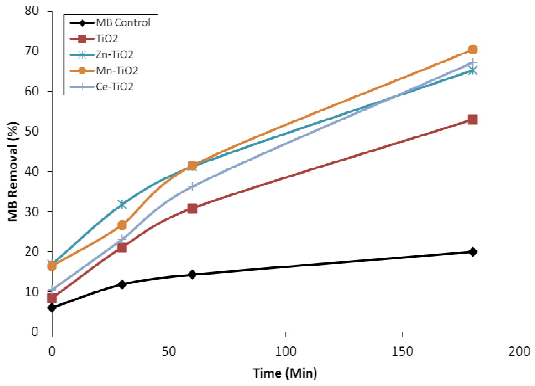


Fig. 1. Photocatalytic degradation of MB using pure, single and multi doped TNPs under LED light

TNPs showed better degradation compared to the pure TNPs and hence used for further investigations. Interestingly, photocatalytic degradation of MB under UV-254 light using pure and single metal doped TNPs showed no significant difference. This could be attributed to the high intensity emission from the UV-254 lamp which easily excites the TNPs making the photocatalytic reactions possible. However, bi and tri metal doped TNPs showed significantly lower degradation compared to the pure TNPs. The possible reason could be the high recombination of electron-hole pair resulting from the quenching of electrons/holes by the metals.

Physical mixtures of metal doped TNPs were further tested to the degradation of MB under the LED as a visible light source. A 1:1 mixture of Zn and Mn doped TNPs showed 91% degradation of MB after 240 min of LED exposure. It is important to note that

the chemically combined bi metallic doped TNPs were less effective than the physical mixture. Synthesis of physical mixtures is very inexpensive and require very less time compared to simple sol-gel process for metal doping which is an added advantage to use only the physical mixture.

3.4. Factor affecting efficiency of physical mixtures of TNPs

Physical mixture of Zn and Mn doped TNPs was further investigated to evaluate the effect of various factors, like pH, dose and initial dye concentration, for adsorption and photodegradation of MB capacities.

3.4.1. Effect of pH

The role of pH on photocatalytic degradation of MB was studied by keeping all other experimental conditions constant and varying the initial pH values by adding HCl and NaOH (Fig. 2). Effect of solution pH (4, 6.5, 10) was investigated on the adsorption and photocatalytic capacities of 50:50 physical mixture of Zn and Mn-TNPs.

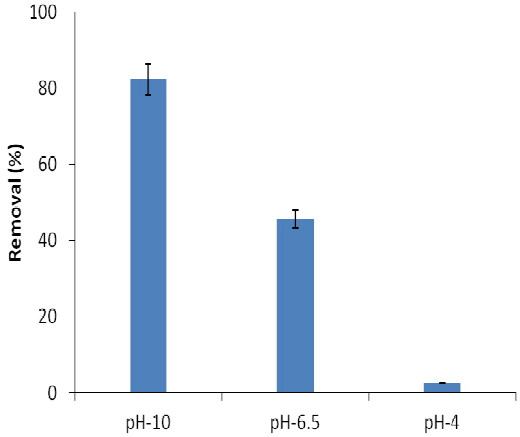


Fig. 2. Effect of pH on adsorption of MB using 1:1 Zn-TiO_2 and Mn-TiO_2, Dose: 1mg/mL

It was observed that the basic pH (10) showed a drastic increase in the adsorption capacity (83%) compared to the neutral pH (6.5) of the MB solution. Whereas, adsorption capacity of the sample was significantly reduced when the pH of the solution was 4. Photocatalysis of the MB solution having pH 10 was highest and 95% of MB was reduced after 120 min of LED exposure. Degradation of MB at pH 4 apparently goes to zero and same as with the adsorption. Obviously, "increasing the initial pH value of solution would result in an increase of degradation of rate and efficiency. It is well known that the surface of photocatalyst is positively charged in acidic solutions and negatively charged in alkaline solutions. As a result, it is not surprising to observe increase in the adsorption of dye molecules (with positive charge) on the surface of photo-catalyst in basic solutions and thus the increasing of degradation efficiency of dye" [13,19].

3.4.2. Effect of dose on adsorption and photocatalysis of MB

It is very important for a good adsorbent to remove the maxi-mum amount of adsorbate at a low adsorbent dose. Therefore, the effect of the concentration of adsorbent on the percentage adsorption of MB was studied at various concentrations in the range of 0.25 to 1.5mg/mL (Fig. 3). Adsorbent dose of 1mg/mL showed highest adsorption of 45% and photodegradation of 91% after 250 min of LED exposure. It was observed that the adsorption of MB increased with the increasing mass of mixture of TNPs up to 1mg/mL. However, with a further increase in the mass, a decrease in the adsorption efficiency was observed. "This may be linked to two factors. First, at a higher concentration, the surface area was decreased due to the aggregation of the adsorption sites and the increased diffusion path. Second, with the increased concentration, the decreased surface area limits the adsorption of MB on the surface" [21].

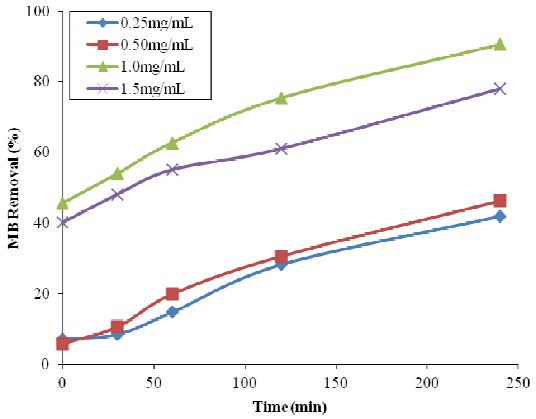


Fig. 3. Effect of photocatalyst dose on degradation of MB

3.4.3. Effect of initial dye concentration on adsorption and photocatalysis of MB

Effect of initial dye concentration was also evaluated using a fixed amount of photocatalyst dose (1 mg/mL) and pH (6.5). Increasing initial dye concentration showed increasing adsorption onto the adsorbent (Fig. 4). This is possibly due to equilibrium state in the solution and onto the adsorbent. Lower the concentration lower the surface adsorbed dye molecules because the system achieved the equilibrium faster and further molecules tend to remain in the solution phase. "It has been assumed that initially dye molecules were adsorbed on the exterior surface of TiO_2 resulting in the formation of a unimolecular layer that reflects in its higher adsorption rate. But, when the adsorption of the outer surface reached maximum, the dye molecules start to penetrate inside the pores of TiO_2 and were adsorbed by the interior surface of the particle which takes relatively long contact time" [22].

The photocatalytic degradation however, decreased with increase in the initial dye concentration possibly

due to less penetration of photons through the solution and the shielding effect of dye molecules to the photocatalyst particles.

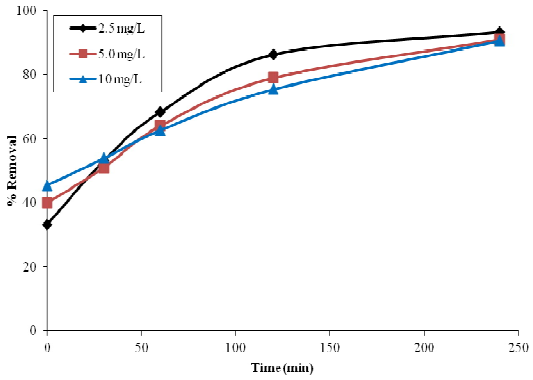


Fig. 4. Effect of initial dye concentration

3.5. Adsorption and photocatalytic efficiency of physical mixtures of TNPs and Ag3PO4

In this work the degree of enhancement in reaction activity from our Ag_3PO_4 based photocatalysts related to pure Ag_3PO_4 is quite limited, since the as-prepared Ag_3PO_4 product in our work shows significantly higher photocatalytic activity toward the degradation of MB under similar conditions and it would be more difficult to further improve its reaction activity through the formation of heterostructures. A set of physical mixtures of TNPs and Ag_3PO_4 was also investigated for their ability to adsorb dye molecules. As-prepared TNPs and the Ag_3PO_4 were mixed in different proportions and grounded before application (Table 1).

Table 1: Composition of the photocatalysts

Mixture No.	TiO_2	Ag_3PO_4
1	0	100
2	5	95
3	10	90
4	15	85
5	20	80
6	40	60
7	60	40
8	80	20
9	100	0

"Since the obtained Ag_3PO_4/TiO_2 hybrid composites are optically responsive in both UV and visible light regions, the photocatalytic activities of selected samples were investigated under visible light. Note that a further improved photocatalytic efficiency can be achieved for the Ag_3PO_4/TiO_2 hybrid composites, which is significantly higher than that of pure Ag_3PO_4 particles and pristine TiO_2" [12]. However, the synthesis process for Ag_3PO_4/TiO_2 is very complex, time consuming and expensive. We therefore have tested a physical mixture of Ag_3PO_4 and TiO_2 in various proportions for the adsorption and photodegradation of MB.

It was interesting to note that adsorption capacity of the mixture was increased with the increase in the TiO_2 content. Maximum adsorption of 56% was achieved with a mixture of 80% TiO_2 and 20% Ag_3PO_4. All the mixtures showed higher adsorption compared to the TiO_2 or Ag_3PO_4 alone. A strong correlation was seen (R^2=0.99) between TiO_2 content and the adsorption capacity of the resulting mixture (Fig. 5).

Taking the Ag_3PO_4/TiO_2 (20:80) mixture, the photocatalyst is observed to degrade more than 98% of the initial MB dye within 10 min under LED irradiation, which is quite appealing for the practical use of Ag_3PO_4/TiO_2 mixture as an efficient and green photocatalyst toward the decomposition of organic contaminants in water.

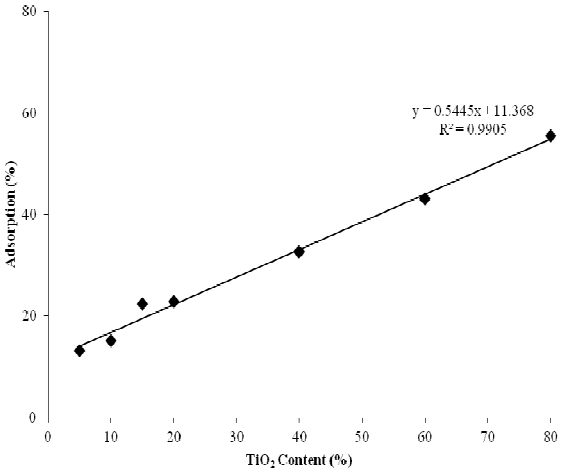


Fig. 5. Effect TiO_2 content on adsorption capacity of the physical mixture of Ag_3PO_4 and TiO_2

Besides the high adsorption capacities of mixtures, the photocatalytic efficiencies were also very high compared to only TNPs. Photocatalytic efficiencies of the mixtures were very high (>90%) till the TiO_2 content of 80%. A 20% mixture of photocatalysts showed highest degradation rate for MB removal.

CONCLUSIONS

A very simple, low cost, efficient and robust physical heterostructure of Ag_3PO_4/TiO_2 was successfully developed. The composition, optical properties and morphology of the prepared nanomaterials were controllable by adjusting the mixing ratios. The physical mixture exhibited much higher photocatalytic performance under the visible light as well as adsorption capacities. The coupling of Ag_3PO_4 particles with UV light active TNPs simultaneously could utilize the larger part of solar spectra and less consumption of metals. The heterostructure is quite appealing for their practical use in environmental issues. Further, this provides a easy, rapid, reusable and low cost adsorbent and a good photocatalyst which otherwise is costly and time consuming when synthesised chemically.

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