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# **ORIGINAL ARTICLE**

# Synthesis of mesoporous TiO<sub>2</sub>/BMMs via hydrothermal method and its potential application toward adsorption and photocatalytic degradation of crystal violet from aqueous solution



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# KEYWORDS

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Abstract The novel mesoporous TiO<sub>2</sub>/BMMs nanocomposites using bimodal mesoporous silica (BMMs) as support and rutile-anatase mixed phase as active species were successfully synthesized via hydrothermal and subsequent calcination method. Their structural and physiochemical properties were characterized by X-ray diffraction, scanning/transmission electron microscopy, BET-isotherms, inductive coupled plasma optical emission spectroscopy, zeta potential, Fourier transform infrared and UV-visible spectroscopy. The results demonstrated that the photocatalytic degradation activity of the synthesized catalysts were extensively enhanced as compare to bare  $TiO_2$ , due to the highly uniform dispersion of mixed phases (Anatase and Rutile)  $TiO_2$  on the bimodal mesoporous surfaces. Particularly, the catalytic efficiency became increased as increasing the calcination temperature, showing the highest (98%) overall removal of CV dye using TBH5d as catalyst calcinated at 800 °C. Its most interesting finding is that the % adsorption of TBH5d was 46 %, more than that (26%) of TBH5c calcinated at 600 °C, however, its % degradation was 21 %, lower than that (39 %) of TBH5c for dye concentration of 20 ppm in 50 min. Meanwhile, the kinetic adsorption and degradation performances were followed the pseudo second and first order models, respectively, further proving the high degradation efficiency of TBH5c with high rate constant than that of TBH5d. Thermodynamic parameters ( $\Delta G_{ads}$ ,  $\Delta H_{ads}$ , and  $\Delta S_{ads}$ ) were calculated, suggesting the spontaneous and exothermic procedure with high entropy, while the adsorption equilibrium

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data was fitted to Dubinin-Radushkevich model. Both TBH5c and TBH5d showed an excellent stability and reactivity 71.2 and 61 %, respectively, even after 5th cycles. Thus, these results suggested that that TBH5c may be one of the suitable candidates in wastewater treatments.

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## 1. Introduction

Wastewater effluents from different industries, for example paints, textile, leather, tanning and printing, have various type of organic compounds, especially dyes, which cause severe problems to the environments (Barjasteh-Moghaddam and Habibi-Yangjeh, 2011; Gajbhiye, 2012). Dyes, such as crystal violet (CV), are very toxic organic pollutants mainly releasing from painting and textile industries (Houas et al., 2001; Adak et al. 2005; Akpan and Hameed, 2009), their most common effect on human are itching, sneezing, watery eyes, vomiting, diarrhea and symptoms of asthma (Hassaan and El Nemr. 2017). Beside the above toxic effects, the wastewater effluent (toxic) also causes death of soil microorganisms, which have a great effect on agricultural productivity (Salehi et al., 2012). Thus, the effectual removal of harmful organic dyes from industrial wastewater become an essential research goal. Presently, different technologies have been developed for effective wastewater treatment (decolonization and degradation), such as adsorption (Kandisa et al., 2016), ion exchange (Gregory and Dhond, 1972), reverse osmosis (Abdel-Hameed et al., 2017), chlorination and ozonation (Brik et al., 2004), membrane separation (Shawkya et al., 2020; Kotp, 2021), membrane filtration (Kotp, 2019; 2020), and aerobic and anaerobic treatments (O'neill et al., 2000; An et al., 1996). However, these traditional methods have some drawbacks, for instance, they just changed the phase of pollutant without its transformation into environmental benign end products, meanwhile, some of them are time consuming while other are costly (Muhd et al., 2014).

Recently, the heterogeneous photocatalytic oxidation is one of the most efficient advanced oxidation processes (AOP), widely applied for industrial wastewater treatment. Thus, various types of metal oxide (WO<sub>3</sub>, ZnO, CeO<sub>2</sub>, Nb<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>) are used as heterogeneous photo-catalyst, in which, TiO<sub>2</sub> attract the attention of scientist because of its exclusive band gap (approx. 3.2 eV) (Fan et al., 2016b), reduction potential to induce many oxidation-reduction reaction and generate reactive species  ${}^{\bullet}OH$  and  ${}^{\bullet}O_{2}^{-}$ . Hence, the generated reactive species attacks on targeted organic pollutant, degrades them into smaller molecules and finally mineralized completely (Abdullah and Chong, 2010). TiO<sub>2</sub> exhibits in 3 crystalline forms with different physiochemical properties (Kim et al., 1994): anatase (four edge sharing partly distorted octahedra), rutile (Two edge sharing nondistorted octahedra), and brookite (Three edges sharing distorted octahedra). The polymorph of TiO<sub>2</sub>, anatase and rutile are extensively used in photocatalytic degradation (Maeda, 2013; Abe et al., 2005). For example, Zubieta et al. studied the adsorption and photodegradation of acridine orange and acriflavine by using anatase and rutile, the results confirmed that the rutile phase adsorption capacity was higher than anatase phase, while anatase showed the highest activity for both dyes in term of photo degradation (Zubieta et al., 2011). However, there is contradiction in literature about the performance of rutile and anatase phase (Carp et al., 2004; Chen and Mao, 2007; Testino et al., 2007), as demonstrated by (Yan et al., 2005) and (Zachariah et al., 2008), the mixed phase  $TiO_2$  exhibited higher photocatalytic activity than any single phase TiO<sub>2</sub> (anatase or rutile) due to the synergistic effects between coexistence rutile and anatase phases. Beside the most reactive nature of TiO<sub>2</sub> (single or mixed phase) against dye degradation, the major disadvantages of  $TiO_2$  in its practical use are aggregates formation and its limited adsorption efficiency toward pollutant, which have a great effect on subsequent degradation, separation and recycling difficulties. To circumvent these limitations, dispersing of TiO<sub>2</sub> particles on mesoporous silicates is an attractive approach for its practical application (Khataee et al., 2009), due to its highly ordered mesoporous structure, thermal and mechanical stability and high surface area (Stevens et al., 2006). Thus, different researchers work on synthesis of mix phase TiO<sub>2</sub> on porous supports. (Jardim et al., 2017) synthesized TiO<sub>2</sub>/SBA-15 composites with controllable crystal phase (anatase or rutile) via direct and post synthesis routs. (El-Gaidoumi et al., 1991) successfully synthesized an efficient photoactive pyrophyllite/TiO<sub>2</sub> hetero-structures using sol-gel route along with calcination at different temperature (450, 550, 650, 750 and 850 °C), however the catalyst PTi750 with mixed phase (52% anatase and 10.7 % rutile) showed highest activity. Recently, our preliminary work (Gul et al., 2021b) reported the preparation of the TiO<sub>2</sub>/BMMs composite using bimodal mesoporous silicas (BMMs) as support by simple impregnation method. The resultant TiO<sub>2</sub>/BMMs composites with highly dispersed anatase-TiO<sub>2</sub> in size of 5.1 nm presented a promising degradation activity (93%) against an anionic dye (Alizarin red). Thus, the results demonstrated that selected support for preparation of the catalysts has key role in its photocatalytic function. Although, numerous literature is available on mix phase (anatase rutile) TiO<sub>2</sub> synthesis but considerably less literature is available on the synthesis of anatase-rutile dispersion on mesoporous support. Furthermore, to the best of our knowledge no literature is available specifically on synthesis of anatase-rutile/BMMs composites for photocatalytic activity of organic pollutant (dyes).

In our group, bimodal mesoporous silicates (BMMs) were used as support to prepare the hybrid nanomaterials for application in drug delivery and organic catalysis. One of the major advantages is that the large mesopores (15–50 nm) allow the big species to active site while small pore (2–3 nm) provide high surface area (Tang et al., 2018). For example, the bi-functional catalysts having imidazolium salt ionic liquid (imi-ILs) and Zn(II) with BMMs used as carrier were successfully synthesized (Shang et al. 2021), in which, Zn(OAc)<sub>2</sub> and 1-(triethoxysilyl)propoy;-3-methylimidazlium chloride were separately grafted into the mesopores of used BMMs, their catalytic performances for CO<sub>2</sub> cycloaddition reaction with epoxides in solvent free condition presented the highest yield (98 %) with highest selectivity (97%). Tang et al. (2018) also synthesized catalyst (Z1-BMMs) by grafting (2S, 2'S)-N,N'-([ 2,2'-bipyridine]-3,3-diyl)bis(pyrrolidine-2-carboxamide) (Z1) onto the BMMs surfaces. Its catalytic activity for aldol reaction showed a good yield (up to 75%) and high stereoselectivity (*ee* up to 82%). Thus, BMMs would be a good support for loaded-TiO<sub>2</sub> with uniformed dispersion due to its high surface area and bimodal mesoporous structure, which would be conductive to reduce aggregation of TiO<sub>2</sub> particles and increase its adsorption property. Hence, BMMs as a support for TiO<sub>2</sub> would be beneficial to enhance the photodegradation of organic pollutant.

Herein, this work mainly focused on dispersion of mixed phase TiO<sub>2</sub> (anatase and rutile) particles on mesoporous BMMs support by hydrothermal plus calcination method. Its physiochemical and structural characteristics were explored in detail via various characterizations, such as X-ray diffractive (XRD) patterns, nitrogen adsorption-desorption isotherm, UV-visible (UV-Vis) and Fourier transform infrared (FT-IR) spectra, inductively coupled plasma atomic emission spectroscopy (ICP-AES), Malvern Zeta-sizer, scanning/transmission electron microscopy (SEM/TEM), energy dispersive X-ray (EDX) and elemental mapping images. Afterward, adsorption and degradation kinetics, as well as thermodynamic parameters (Gibbs free energy change ( $\Delta G_{ads}$ ), enthalpy change  $(\Delta H_{ads})$ , and entropy changes  $(\Delta S_{ads})$ ) were also investigated. Finally, the possible mechanism for adsorption behaviors and degradation efficiency were proposed.

#### 2. Experimental

#### 2.1. Chemicals

Tetraethyl orthosilicate (TEOS, 99 %, molecular weight (M. wt) = 208.33), ammonia solution (25 %), cetyltrimethylammonium bromide (CTAB, 99 %, M.wt = 364.45), titanium chloride (99 %, M.wt = 189.68), CV dye (high purity biological stain, M.wt = 407.97) purchased from J&K Co. Ltd. All the used chemicals were of analytical grade, and the deionized water used in experiments was prepared in lab.

### 2.2. Synthesis of catalysts

The dried BMMs was firstly synthesized on the basis of reported literture (Sun et al., 2003). In detail, CTAB (20.9 g) was mixed with deionized water (832 mL) in 1000 mL beaker, stirred continuously at 40 °C until CTAB was completely dissolved in water and formed transparent solution, then TEOS (64 mL) was added drop by drop. After added ammonia solution 25 % (19.2 mL) at once, the obtained mixtures were allowed to stir at room temperature, until it turned into white gel. Afterward, the gel was filtered by using Buchner funnel to remove any liquid and wash the solid residues with deionized water repeatedly. After washing, dried the white residue in oven at 120 °C overnight, subsequently calcinated at 550 °C for 5 h using heating rate 5 °C/min, the calcinated powder was grinded into fine powder with the help of mortar pestle

and named as BMMs. The molar ratio of the initial reactant composition was  $H_2O$ :  $NH_4OH$ : CTAB: TEOS = 162: 1.73: 0.20: 1.

The different concentration of TiCl<sub>4</sub> solutions (0.1, 0.15, 0.2, 0.25, and 0.3 M) were prepared in ice cold water, then 25 mL of solutions were transferred into different Teflon lined vessel along with 1.0 g of the dried BMMs. The vessels containing these mixtures were subsquently enclosed in stainless steel auto-claves and heated in an oil bath at 150 °C for 3 h under constant stirring. After that, the precipitate was filtered, washed with water repeatedly and dried in an oven at 100 °C for overnight and marked as TBH1, TBH2, TBH3, TBH4 and TBH5 for 0.1, 0.15, 0.2, 0.25 and 0.3 M concentration of TiCl<sub>4</sub> solutions, respectively.

In order to further obtain the mixed phase of  $TiO_2$ , the TBH5 was subjected to calcination at 200, 400, 600, and 800 °C, respectivly, and the second set of catalyts were named as TBH5a, TBH5b, TBH5c and TBH5d with respect to different calcination temperature of 200, 400, 600, and 800 °C, respectively.

### 2.3. CV dye adsorption and degradation experiments

CV dye adsorption tests were performed by immersion of 0.25 g of adsorbent (catalyst) in 100 mL of 15 ppm CV dye solution in 200 mL beakers. Then, the reaction mixture was stirred at 35, 45 and 65 °C in dark, respectively, while the samples were analyzed at different interval of times. At the end of each adsorption period, the supernatant was centrifuged for 8 min at 4000 rpm, and its CV dye concentrations before and after adsorption were subjected to UV–Vis spectrophotometer at 583 nm. The obtained data was used for determination of adsorption isotherm.

The adsorption capacity of CV dye was calculated by following formula (1), in which, standard curve (y = 0.17x - 0.009,  $R^2 = 0.998$ ) was used for determination of dye concentration.

$$q_c = (C_0 - C_t) \times V / m \tag{1}$$

whereas  $C_0$  and  $C_t$  are initial and final concentration of CV dye, respectively,  $q_c$  is the adsorption capacity of catalyst in mg/g, V and m are the volume in liters and mass in grams, respectively (Ullah et al., 2021).

While degradation experiment was carried out at room temperature, after establishment of adsorption desorption equilibrium in 30 min, the reaction mixture was illuminated by UV light for 3 h. At different intervals of time, 3 mL of sample taken out from the reaction mixture and centrifuged, the supernatant was analyzed by UV spectrophotometer. The degradation percentage of CV dye was calculated by following formula (2), in which, the standard curve (y = 0.17x - 0.009,  $R^2 = 0.998$ ) was used for determination of dye concentration.

$$\% Degradation = (C_0 - C)/C_0 \times 100 \tag{2}$$

whereas C and  $C_0$  are the initial and final concentration of CV dye, respectively (Meng et al., 2010).

For degradation experiment, four UV-C light with 20 W each as light source were enclosed in steel box. The spectrum range of UV-C light was from 200 to 280 nm,  $\lambda_{max}$  was 254 nm and fluence rate was 140.2 mW/cm<sup>2</sup>. The reaction

mixture was put straight below the light sources and stirred at 700 rpm. To investigate the effect of pH on degradation process, the pH values of reaction mixture were adjusted by using dilute (0.05 M) solution of HCl or NaOH, which was monitored using digital pH meter (METTLER TOLEDO S220-Bio).

Furthermore, for recycling experiment, the catalyst was centrifuged after every cycle then washed first with deionized water for many times, followed by ethanol and acetone in order to remove the adsorbed dye. After dried in oven at 80  $^{\circ}$ C for 3 h, the obtained catalyst was reused for next cycle.

#### 2.4. Characterizations

Nitrogen adsorption-desorption isotherm achieved by using JWGB JW-BK300 system (Beijing Sci. & Tech. Co. Ltd) at -196 °C was used to explore textural properties of synthesized samples. The synthesized samples were pre-heated at 150 °C (BMMs) or 80 °C (TiO<sub>2</sub>@BMMs) for 5 h in order to remove the moisture. Brunauer-Emment-Teller (BET) method was used for isotherm analysis while Barrett-Joyner-Halenda (BJH) model was used to calculate the pore size distribution on the basis of the desorption branch of the isotherms. Shimadzu UV-2600 spectrophotometer was used to acquire UV-Vis diffused reflectance spectra for band gap measurement. The FT-IR spectrum was obtained in the range of 4000 to 400  $\text{cm}^{-1}$  with 4  $\text{cm}^{-1}$  resolutions to analyze the functional groups on the surface of synthesized samples by using Nicolet 6700 analyzer. The crystalline structure of newly synthesized samples were characterized by using powder XRD

patterns in the  $2\theta$  range of 1.0–10 ° and 5.0–75°, recorded by Persee XD-3 diffractometer (Beijing Purkinje General Instrument Co. Ltd). The CuK $\alpha$  ( $\lambda = 0.154056$  nm) was used as radiation source having 1.0°/ min scanning speed at 20 mA and 36 kV. The crystal size was calculated using Scherer's formula ( $D = K \cdot \lambda / \beta \cdot cos\theta$ ) (Ullah et al., 2020a). The rutile and anatase percentages were calculated by using spurr and Myers's equation (3), as following (Ciara et al., 2016).

$$M_R = 1/(1 + 0.8 (I_A/I_R))$$
(3)

$$M_A = 1 - M_R \tag{4}$$

whereas  $M_R$  and  $M_A$  are the molar percentage of rutile and anatase, respectively.  $I_R$  and  $I_A$  are the peaks intensity of anatase d(101) and rutile d(110), respectively. For percentage calculation, multiplied the obtained molar ratio with 100.

ICP-AES-Perkin Elmer Optima 2000 DV was used to check the elemental composition of synthesized catalysts. Malvern Zeta-sizer (Malvern Instruments Ltd, Malvern, UK) was used to evaluate the surface charge of synthesized material. SEM, TEM, selected area electron diffraction (SAED), and elemental mapping images were taken on (JEOLJEM-220) or (JEOL-2010), respectively.

# 3. Results and discussion

#### 3.1. XRD patterns

Fig. 1 represents the XRD pattern of BMMs and synthesized  $TiO_2$ /BMMs catalysts. As can be seen, Fig. 1A and C exhibited



**Fig. 1** (A) Small and (B) large angle XRD patterns of (a) BMMs, (b) TBH1, (c) TBH2, (d) TBH3, (e) TBH4, and (f) TBH5. While (C) small angle and (D) large angle XRD petterns of (a) TBH5a, (b) TBH5b, (c) TBH5c, (d) TBH5d, and standard TiO<sub>2</sub> (Degussa P25).

the characteristic peak<sub>(100)</sub> at 2 theta of around 2°, similar to reported BMMs (Sun et al., 2003), even after loading TiO<sub>2</sub>. However, the gradual decrease in the peak<sub>(100)</sub> intensity occurred with increasing TiO<sub>2</sub> concentration (Fig. 1A from b to -f), accompanying with little left-shift in 2 theta position of from 2.15 for BMMs to 2.02, 2.0, 1.99, 1.97, 1.95 for TBH1, TBH2, TBH3, TBH4 and TBH5, respectively. These observations indirectly confirmed the incorporation of TiO<sub>2</sub> on/in mesoporous surface of BMMs. Fig. 1B depicts the large angle XRD patterns of TiO<sub>2</sub>@BMMs catalysts, which clearly showed anatase phase at 2 theta positions around 25, 38, 48, 54, 62 and 70 °, indexed as (101), (004), (200), (105), (204) and (216) spatial planes, respectively (Fig. 1B from -b to -f) (Fan et al., 2016a; Yu et al., 2020).

Furthermore, Fig. 1D reveals the XRD patterns of  $TiO_2(a)$ -BMMs calcinated at different temperature, exhibiting the increased crystallinity of TiO<sub>2</sub> phase (Fig. 1D from a to d) with increasing calcination temperature. Additionally, the rutile phase in TBH5c (Fig. 1D-c) appeared at 2 theta of around 27, 36, 41, 56, 64, and 69°, corresponding to (110), (101), (111), (220), (002) and (310) hkl planes. The synthesis method of the supports has a great effect on phase of TiO<sub>2</sub>, the rutile phase in present work appeared via calcination at 600 °C. Comparably, Lachheb et al. synthesized TiO<sub>2</sub> composite supported on SBA-15 by sol-gel method followed by calcination, whereas anatase TiO2 appeared at 700 °C (Lachheb et al., 2011). Additionally, on the basis of their XRD patterns by using Spurr and Myers's equation (3), the percentages of anatase and rutile in TBH5c (Fig. 1D-c) were 76 and 24 %, respectively, similar to that in TBH5d.

While, as can be seen in Fig. 1D-d, the peak intensity of rutile phase in TBH5d became increase than that of anatase phase with 81 % rutile and 19 % anatase, calculated from XRD patterns by using Spurr and Myers's equation (3). On the basis of Scherer' equation the TiO<sub>2</sub> crystallite size in synthesized TiO<sub>2</sub>/BMMs samples are listed in Table 1.

#### 3.2. SEM/TEM micrographs

Figure 2 shows the TEM micrographs of synthesized samples. As can be seen, the loaded  $TiO_2$  particles in TBH5c or TBH5d were well dispersed with little aggregation, in which,  $TiO_2$  par-

ticles presented almost spherical morphologies in TBH5c with a mean size around 19 nm (Figure 2a (inset)), and cubic and spherical shapes in TBH5d with a mean size around 31 nm (Figure 2b (inset)). Obviously, these observations demonstrated that the particle sizes seemed to be increased with increased calcination temperature, similar to report literature (Phromma et al., 2020). The HRTEM micrographs revealed that the TBH5c and TBH5d exhibited the mixtures of anatase and rutile phase. As can be seen in Figure 2c, the d-spacing values of 0.346 and 0.234 nm corresponded to hkl 101 plane of anatase and 101 of rutile, while, the more exposed 101 plane of anatase was observed. However, Figure 2d showed a more prominent rutile phase with d-spacing value of around 0.311, corresponding to 110 hkl plane. Figures 2 g and h revealed the SAED patterns of TBH5c and TBH5d, showing the mixtures of anatase and rutile, in good agreement with the above analysis of XRD results. The Ti mappings in the synthesized samples (as shown in Figures 2e and f) profiled a very well dispersion throughout on/in the mesoporous support surface. However, the Ti dispersion in TBH5c was more even without any aggregation than in TBH5d, which might be due to the large particle size of TiO<sub>2</sub> in TBH5d.

### 3.3. FT-IR spectra

The FTIR spectra of BMMs, TiO<sub>2</sub> and TiO<sub>2</sub>/BMMs composites are shown in Fig. 3. As can be seen, except  $TiO_2$  (Fig. 3b), all of them exhibited the structural features of BMMs, even after TiO<sub>2</sub> incorporation, in which, the peaks at 1065, 802 and 445 cm<sup>-1</sup> were corresponding to Si-O-Si asymmetrical, symmetrical, and Si-OH symmetrical vibration, belonging to the characteristics of BMMs (Mirabedini et al., 2011). Meanwhile, Fig. 3b presented the bands centered on 738 and 428  $\text{cm}^{-1}$  were ascribed to Ti-O-Ti banding vibrations (Rasalingam et al., 2014). As compared with pure BMMs (Fig. 3A-a) and TiO<sub>2</sub> (Fig. 3A-b), TiO<sub>2</sub>/BMMs composites (Fig. 3B from c to g) presented a little shift and broadness in absorption bands centered at 802 and 445 cm<sup>-1</sup> towards lower wavenumber around 793 and 438 cm<sup>-1</sup>. These shifts were also dependent on the concentrations of loaded TiO<sub>2</sub>, the most probable reason is due to overlapping of TiO<sub>2</sub> peak located at 738 and 428  $cm^{-1}$ . The shoulder peak located on

Catalyst	TiO <sub>2</sub> <sup>a</sup> (wt. %)	Particle size (nm) $^{\rm b}$ A/R $^{\rm c}$	A/R <sup>c</sup> (%)	Band gap <sup>d</sup>	
				Indirect	Direct
TBH1	14.76	1.61/unappeared	N/A	N/A	N/A
TBH2	21.50	2.59/unappeared	N/A	N/A	N/A
TBH3	23.07	3.70/unappeared	N/A	N/A	N/A
TBH4	27.71	4.73/unappeared	N/A	N/A	N/A
TBH5	31.15	5.28/unappeared	N/A	3.0	3.14
TBH5c	N/A	18/26.7	76/24	2.86	2.91
TBH5d	N/A	28.35/42.72	19/81	2.85	2.89
TiO <sub>2</sub>	N/A	N/A	N/A	2.66	2.86

 Table 1
 Summaries of varioue parameters of synthesized TiO2@BMMs catalyst

<sup>a</sup> Calculated from ICP data.

<sup>b</sup> Calculation based on the Scherer' equation from XRD patterns.

<sup>c</sup> Anatase and Rutile % calculated from XRD patterns by using Spurr and Myers's equation.

<sup>d</sup> Calculated from UV-DRS spectra in section 3.5 and Figure S1 of the Electronic Supporting Information (ESI) section.



**Fig. 2** . TEM micrographs of TBH5c (a) and TBH5d (b), HRTEM micrographs of TBH5c (c) and TBH5d (d) with insert inverse FFT (Fast Fourier transform) images from image J software, elemental (Ti) mapping of TBH5c (e) and TBH5d (f) with insert HAADF-STEM image, and SAED patterns of TBH5c (g) and TBH5d (h).



**Fig. 3** FT-IR spectra in the region of 400–1000 cm<sup>-1</sup> (A) and 400–4000 cm<sup>-1</sup> (B) of (a) BMMs, (b) TiO<sub>2</sub>, (c) TBH1, (d) TBH2, (e) TBH3, (f) TBH4, and (g) TBH5.



Fig. 4 Zeta potentials of (a) BMMs, (b) TBH5c, and (c) TBH5d.

418 cm<sup>-1</sup> in the TiO<sub>2</sub>/BMMs composite (Figs. 3A-c, -d, -e, -f, and -g) indicated the appearances of the Ti-O bending vibrations deriving from doped-TiO<sub>2</sub> in the composites (Marques et al., 2021), whereas band centered on 2324 cm<sup>-1</sup> (Figs. 3B-c, -d, -e, -f, and -g) may be attributed to the CO<sub>2</sub> adsorptions. The additional peak appeared around 967 cm<sup>-1</sup> could be ascribed to starching vibration of Ti-O-Si (Fig. 3B from c to g), while the peaks around 1532 and 3741 cm<sup>-1</sup> were attributed to the –OH stretching vibration distributed in surface adsorbed water, Ti-OH and Si-OH of mesoporous material (Conceição et al., 2017).

# 3.4. Zeta potential

Fig. 4 shows the zeta potentials of BMMs and synthesized TiO<sub>2</sub>/BMMs samples. As can be seen, the  $pH_{pzc}$  value of BMMs was around 3.6 (Fig. 4a), similar to our previous report (Gul et al., 2021b). However, the  $pH_{pzc}$  values of TBH5c and TBH5d were around 4.0 and 4.1 (Fig. 4b and c), respectively, implying that their surfaces were neutral at pH around 4.0 for THB5c and 4.1 for TBH5d. Otherwise, the surface should be negative charge at pH above  $pH_{pzc}$  (4.0) for THB5c and (4.1) for THB5d, while positive charge below  $pH_{pzc}$  values. Obviously, the TBH5c and TBH5d would show a high catalytic efficiency against cationic CV dye at pH above 4.0 (pH<sub>pzc</sub>).



**Fig. 5** N<sub>2</sub> adsorption/desorption isotherms (A) and corresponding to their pore size distributions (B) of (a) TBH1, (b) TBH2, (c) TBH3, (d) TBH4. (e) TBH5, (f) TBH5a, (g) TBH5b, (h) TBH5c, (i) TBH5d, and (j) BMMs.

#### 3.5. Band gap measurement from UV-Vis reflectance spectra

The data obtained from UV–Vis reflectance spectra were used to assess band gap of bare TiO<sub>2</sub> and TiO<sub>2</sub>/BMMs composites, the related results were collected in Table 1. Tuac relation  $(Ahv)^n = C(hv-E_g)$  was used for calculation, in which  $E_g$ (eV) is band gap, v is light frequency, A is absorption constant, h is Planck's constant, and n value is 2 and  $\emptyset$  for allowed direct and allowed indirect band gap (Wang et al., 2013). As seen in Table 1, the band gap of TiO<sub>2</sub> became increases in



**Fig. 6** % Removal of CV dye by  $TiO_2@BMMs$  catalysts. A: (a) TBH1, (b) TBH2, (c) TBH3, (d) TBH4, (e) TBH5, and (f). TiO\_2. B: (a) TBH5a, (b) TBH5b, (c) TBH5c, and (d) TBH5d. Reaction conditions: degradation time: 180 min, pH: 6.0, conc. of dye: 15 ppm, and catalyst dose: 0.25 g/100 mL.

 $TiO_2/BMMs$  composites as compared to that of bare TiO<sub>2</sub>. According to quantum size effect for semiconductors (Kamil et al. 2006), the increase in band gap of TiO<sub>2</sub> and its decrease in particle size are beneficial to enhance their photocatalytic activity under UV-light irradiation.

#### 3.6. $N_2$ adsorption isotherms

Fig. 5 illustrated the N<sub>2</sub> adsorption-desorption isotherms of pure BMMs and all synthesized TiO<sub>2</sub>/BMMs composites. As can be seen in Fig. 5A, all samples exhibited the characteristic IV type hysteresis loops with two prominent inflections in the  $P/P_0$  range of 0.23–0.43 for small mesopores, corresponding to the small and uniform mesopores with a mean pore size of 2.7-2.8 nm (Fig. 5B). However, the small mesopores size of TiO<sub>2</sub>/BMMs composites, such as 2.76 nm for TBH1 and 2.53 for TBH5d, were slightly smaller than that (2.9 nm) of BMMs. Thus, these results suggest that the smaller  $TiO_2$ particles gradually generated in the early stage of the hydrothermal synthesis, might go inside the small mesopores of the BMMs (Jin et al., 2017), in good agreement with analysis of XRD patterns (as shown in Fig. 1A and C). While, the second inflections at  $P/P_0$  0.6–0.9 were steeper than the first one, indicating the large and broaden mesopores with a mean

![](_page_7_Figure_7.jpeg)

**Fig. 7** pH effects on the CV dye degradation using (A) TBH5c and (B) TBH5d as catalysts. Reaction conditions: catalyst dose: 0.025 g/100 mL, degradation time: 180 min, and dye conc: 15 ppm.

pore size of 16 nm. However, the mean pore sizes of  $TiO_2/$ BMMs composites were around 24.55–33.59 nm, larger than that of BMMs (16 nm). Therefore, the loaded-TiO<sub>2</sub> particles in size of around 19 nm were incorporated onto the larger mesopores of BMMs. Meanwhile, their pore volumes gradually decreased with increased TiO2 loading amount, from 2.41 cm<sup>3</sup>/g for BMMs to 2.27, 2.04 and 1.67 cm<sup>3</sup>/g for TBH5, TBH5c and TBH5d (Fig. 5B-g, -h, and -i), respectively. The declined tendency in surface area also occurred from 1375 m<sup>2</sup>/g for BMMs to 601, 557 and 555 m<sup>2</sup>/g for TBH5, TBH5c and TBH5d, respectively (as shown in Table S1 of the ESI section). Obviously, these phenomena can be correlate with the pores blocking of BMMs due to TiO<sub>2</sub> loading. The surface area of TBH5 with loaded TiO2 (31.15 %) was around 601 m<sup>2</sup>/g, higher than the loaded-TiO<sub>2</sub> (30%) mesoporous silicas (505 m<sup>2</sup>/g) of Zaccariello et al. report (Zaccariello et al., 2014), which can be correlated with the bimodal mesoporous natures of BMMs. Thus, the morphology of the used supports has an important role in TiO<sub>2</sub>-loaded dispersions and surface areas of obtained composites.

#### 3.7. Photocatalytic and adsorption performances

The synthesized TiO<sub>2</sub>/BMMs composites were used catalysts for photocatalytic degradations of CV dye. As can be seen in Figure 6A, the first set of catalysts (TBH1, TBH2, TBH3, TBH4, and TBH5) showed the more efficient photocatalytic activities against CV dye with increasing TiO<sub>2</sub>-loaded amount (Table 1) than that of pure bare TiO<sub>2</sub> (Figure 6A-f), while their adsorption capacities were not very high (less than 8 %). These results may be because the large surface area of BMMs is

![](_page_8_Figure_1.jpeg)

**Fig. 8** Pseudo-2nd order adsorption kinetics using (A) TBH5c and (B) THB5d as the catalysts, (inset) % Adsorption of CV dye using different initial dye concentration (a) 5 ppm, (b) 10 ppm, (c) 15 ppm, and (d) 20 ppm. Pseudo 1st order degradation kinetics using (C) TBH5c and (d) TBH5d as the catalysts. Reaction conditions: catalyst dose: 0.025 g/100 mL, adsorption time: 30 min and degradation time: 50 min, respectively.

conducive to the uniform dispersion of TiO<sub>2</sub> (Kamil et al. 2006), which is useful to prevent the appearances of agglomerated TiO<sub>2</sub> particles, and therefore to increase its catalytic activity. Figure 6B presented the photocatalytic efficiency of the second set of catalysts (TBH5a, TBH5b, TBH5c, TBH5d) against CV dye (15 ppm), As can be seen, the photocatalytic activities were around 75, 94, 97 and 98% for TBH5a, TBH5b, TBH5c, and TBH5d, respectively, showing the enhancement with increasing calcination temperature (200, 400, 600, and 800 °C). Most of main reasons might be due to the phase transformation of loaded TiO<sub>2</sub> in TiO<sub>2</sub>/BMMs catalysts during the calcination from pure anatase phase (TBH5a and TBH5b) to mixed anatase plus rutile (TBH5c and TBH5d) phase, similar results were also obtained by (He et al. 2019). Another probable interpretation is because of the enhanced adsorption behaviors via calcination. Actually, the differences of the photocatalytic activity of removal of CV dye at 180 min among these used catalysts were small. However, their differences were much obvious before 180 min, such as, the % degradation of TBH5a, TBH5b, TBH5c and TBH5d was 12.0, 20.5, 34.0, and 56.5% at 10 min, but 31.0, 54.0, 75.0 and 87.0 % at 60 min, respectively. Therefore, we can conclude that TBH5c and TBH5d were more reactive than TBH5a and TBH5b. As shown in Figure 6B, a prominent improvement in adsorption equilibrium amount occurred gradually with increasing the calcination temperature, such as 10 % for

TBH5a (Fig. 6B-a), 12 % for TBH5b (Fig. 6B-b), 24 % for TBH5c (Fig. 6B-c), and 36 % for TBH5d (Fig. 6B-d). Obviously, we can conclude that the photocatalytic performances of TiO<sub>2</sub>/BMMs catalysts can be greatly affected by loaded amount and nature of TiO<sub>2</sub>, as well as calcination temperatures. Thus, the TBH5c and TBH5d photo-catalysts were selected for further investigation to obtained more information about the effect of nature of TiO<sub>2</sub> on photocatalytic activity.

#### 3.7.1. pH influences

The industrial wastewater contained wide range of pH, the hydroxyl radical generation is also a function of pH value, which subsequently effect on the surface charge of photocatalyst (Kansal et al., 2007; Dubinin and Radushkevich, 1947). Therefore, attempt has been made to explore the influence of pH in the range of 2-10 on photocatalytic efficiency for removal of CV dye. In present study, very little change in color (intensity) of dye was observed at lower pH (pH 2.0), the possible reason is that the appearances of the protonated CV dye at lower pH value tend to block the amine groups and thus decrease the possibility of extending benzene chromophores due to unavailability of the lone pair on nitrogen (Ali et al., 2016; Haik et al., 2010). Obviously, it greatly affects the dye adsorption on positive surface of catalyst (the surface of catalyst is positive charge at lower pH), and subsequently less degradation of dye occurred. However, at extreme high pH

![](_page_9_Figure_1.jpeg)

**Fig. 9** Recycling performances of TBH5c (A) and TBH5d (B) up to 5 cycles.

(pH 11.0) the color of CV dye became almost disappeared due to formation of carbinol base (Haik et al., 2010).

Fig. 7 illustrated that the photocatalytic efficiency of both TBH5c and TBH5d increased with increasing the pH of CV dye solution from 2 to 6 pH and then decreased as further increased pH value. Hence, the optimum pH value for both catalysts (TBH5c and TBH5d) was optimized as pH 6.0, showing the maximum activity, such as 97.0 and 98.5 % by using THB5c (Fig. 7A) and TBH5d (Fig. 7B) as catalysts.

These results can be explained by the fact that their negative charge surface of catalyst (having pHpzc 4.0, as demonstrated in Fig. 4) at higher pH is more favorable to adsorb the cationic CV dyes. Otherwise, the positive charge surface of the used catalysts at lower pH (less than 4.0) caused the occurrences of less adsorption of CV dye, due to the presences of electrostatic repulsion between its positive surface and cationic dye (Youji and Wei, 2011). However, the photocatalytic activity became decrease at high pH of more than 6.0, the probable reason might be that the excessive <sup>•</sup>OH radicals easily react with each other, leading the reduction of <sup>•</sup>OH radicals (Nezamzadeh-Ejhieh and Moeinirad, 2011). Other reason might be due to the electrostatic repulsion between very high negative surface of catalyst and the free electron pairs on CV dye (Gul et al., 2021a). Similar results were obtained by Ullah et al. (Ullah et al., 2020b), the  $pH_{pzc}$  value of the catalysts  $(TiO_2/CP)$  was around 6.0, and thus the maximum degradation was obtained at pH 8.0, due to increase adsorption at pH greater than  $pH_{pzc}$  value.

# 3.7.2. Adsorption performances and degradation kinetics of the $TiO_2/BMMs$

In order to explore the effect of initial concentration (5, 1015 and 20 ppm) of CV dye on the adsorption capacity and degradation kinetics of the synthesized THB5c and THB5ds, the adsorption experiments were performed in dark for 30 min, while degradation was investigated under UV light for 50 min. As shown in Fig. 8A and B, as well as Figure S2 of the ESI section, the adsorption and degradation efficiency became decreased with the increasing initial concentration of CV dye. In details, the adsorption efficiency of TBH5c and TBH5d was around 43 and 79 % for lower initial concentration (5 ppm) of CV dye, but decreased to 22 and 50 % for 20 ppm, respectively. However, the adsorption capacity became increased with increased initial concentration, such as the adsorption capacities of TBH5c and TBH5d were 10, 13, 18 and 20 mg/g, and 17, 25, 26.9 and 33 mg/g at 5, 10, 15 and 20 ppm, respectively. Subsequently, the degradation efficiency of TBH5c and TBH5d exhibited 89 and 79 % for 5 ppm, but decreased to 39 and 21 % for 20 ppm, respectively.

Obviously, the adsorption capacities of TBH5c and TBH5d were not too high. Similar results were also obtained by Alosaimi et al, they synthesized the mesoporous TiO<sub>2</sub>-SBA-15 composites with surface area of around 695 m<sup>2</sup>/g, which showed the highest photocatalytic degradation activity (approximately 100%) for methylene blue dye, however, its adsorption capacity was only 4.1 mg/g (Alosaimi et al., 2021). Da-Silva et al. also synthesized Fe<sub>2</sub>SiO<sub>4</sub>-Fe<sub>7</sub>Co<sub>3</sub>-based nanocomposite using SBA-15 as support with surface area of 435 m<sup>2</sup>/g, which revealed adsorption capacity 7 mg/g for methyl orange, 27 mg/g for Rhodamine B, and 49 mg/g for methylene blue dye, respectively (Da-Silva et al., 2020).

Notably, the degradation efficiency of TBH5c was higher than that of TBH5d although the adsorption efficiency of TBH5c was lower than that of TBH5d, the probable reason may be that anatase phase was higher than rutile phase in TBH5c. As demonstrated by Zubieta et al. (2011), the rutile phase was favorable for dye adsorption, while the anatase phase was favorable for dye degradation. The most probable reason is that the adsorption mainly depends on the presence of exposed oxygen atoms, while the (110) planes of rutile structure exhibit the highest amount of exposed oxygen atoms (Zubieta et al., 2011). As can be seen in Figure 2d, the majority phases in TBH5d was the (110) planes of rutile phase, as compare to that in TBH5c. However, according to computational simulation (Zubieta et al., 2011), the degradation efficiency meanly depends on  $Ti^{4+}/O^{2-}$  ratio in anatase adsorption surface then rutile, hence the metal created more electrons/holes pairs, which might be responsible for higher degradation efficiency of Anatase phase.

Accordingly, the adsorption kinetics of CV dye by TBH5c and TBH5d followed the pseudo second order, represented as following equation (Ho et al., 1996) (5)

$$dq/dt = k_2(q_e - q)^2 \tag{5}$$

whereas,  $k_2$  is pseudo-second-order rate constant and  $q_e$  represents the amount of dye adsorbed (mg g<sup>-1</sup>) at equilibrium, while q is the amount of dye at any time (t). The kinetic

Catalyst	Dye concentration	Adsorption			
	(ppm)	adsorption (%)	$K_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$R^2$	
TBH5c	5	43.22	0.1012	0.999	
	10	30.24	0.0761	0.999	
	15	26.2	0.0659	0.998	
	20	22.5	0.0572	0.999	
TBH5d	5	79.74	0.0548	0.997	
	10	60.05	0.0398	0.999	
	15	45.89	0.0369	0.999	
	20	40.9	0.0301	0.999	

Table 2 % removal of CV dye and corresponding rate constant values of adsorption by using TBH5c and TBH5d.

parameters are listed in Table 2, which revealed that the  $k_2$  values for both catalysts became decreases with increasing of initial concentration of CV dye under high regression co-efficient values. Meanwhile, as can be seen in Fig. 8C and D, the degradation kinetic fitted the pseudo first order modal, showing the decreasing  $k_{app}$  values with increased concentration of CV dye. However, the degradation rate constant  $(k_{app})$  value of TBH5c was higher than that of TBH5d under same reaction conditions. Particularly, the  $k_{app}$  value of TBH5c was also higher, and its % degradation was 46 and 39 (Figure S1-A) for 15 and 20 ppm, higher than that of TBH5d, having % degradation of 40 and 21% (Figure S1-B), respectively. Obviously, these results suggested that the degradation efficiency of more anatase-contained TBH5c was higher than that of TBH5d, while adsorption of more rutile-contained TBH5d is higher than that of TBH5c, similar to the reported literature (Zubieta et al., 2011).

#### 3.7.3. Thermodynamic parameters

In order to explore about the nature of adsorption processes that whether its spontaneous or non, feasible or not, exothermic or endothermic, and the affinity of catalysts for CV dye, the various thermodynamic parameters ( $\Delta G$ ,  $\Delta H$ , and  $\Delta S$ ) were calculated on the basis of the experimental data, as following equations (Miyah et al., 2017):

$$\Delta G = -RT \ln K_d \tag{6}$$

where  $\Delta G$  is change in Gibb's free energy, *R* is gas constant, *T* is absolute temperature and  $K_d$  (dye conc. adsorbed (mg/g) / dye conc. (mg/L) at equilibrium) is distribution coefficient.

$$\Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads} \tag{7}$$

whereas  $\Delta H_{ads}$  and  $\Delta S_{ads}$  is change in enthalpy and entropy, respectively.

The *Ea* (activation energy) values for CV dye adsorption were calculated by investigating the adsorption process at three different temperatures (298, 318 and 338 K) on the basis of Arrhenius equation (Liu et al., 2018) as following:

$$-lnKapp = -lnA + Ea/RT \tag{8}$$

whereas A, R, and T are pre-exponential factor, universal gas constant and absolute temperature. The Ea values are deduced from the slop (slop = Ea/R) of b/w -lnk vs l/T(K) plot, as shown in Figure S3-A and S4-A.

The slops and intercepts obtained from the plot ( $\Delta G$  value vs T(K)) (Figure S3-B and S4-B) were used to determine the  $\Delta S_{ads}$  and  $\Delta H_{ads}$  values for adsorption of CV dye.

Table S2 showed the negative  $\Delta G$  values in case of both TBH5c and TBH5d, indicating the feasibility and spontaneous performances. Furthermore, the  $\Delta G_{ads}$  value revealed physisorption in the range of 0 to 20 kJ/mol, but belonged to chemisorption in the range of -20 to 80 kJ/mol (Ullah et al., 2020b). The obtained very small negative value of  $\Delta G_{ads}$ (as shown in Table S2) indicated the physisorption, thus the CV adsorption on the synthesized catalysts belonged to physical process. While the negative  $\Delta H$  values suggested the exothermic nature of the adsorption process, the  $\Delta H$  values (as shown in Table S2) also suggested that the adsorption process was physisorption (Ullah et al., 2020b). The negative  $\Delta H$ values suggested the exothermic nature of the adsorption process. The positive value of  $\Delta S$  designate good affinity of TBH5c and TBH5d for CV dye, implying the enhanced disorder at solid-solution interface during the adsorption process (Mahmoodi et al., 2011). Furthermore, the  $E_a$  values for adsorption of CV dye were 7.34 and 10.69 kJ/mol for TBH5c and TBH5d, respectively.

## 3.7.4. Adsorption isotherms

The adsorption isotherms were carried out to explore the distribution of adsorption molecules between solid and liquid phase at equilibrium stage (Tan et al., 2008). The fitting of adsorption isotherm data for various model is basic requirement for design of adsorption system (El-Geundi, 1991). Langmuir (9) and Dubinin-Radushkevich (DR) (10) equations were used to validate the adsorption properties, as following:

$$C_e/q_e = 1/k_L \cdot q_m + C_e/q_m \tag{9}$$

$$lnq_e = lnq_m - \beta e^2 \tag{10}$$

whereas,  $C_e$ ,  $q_e$ ,  $q_m$  and  $k_L$  are the equilibrium concentration of CV dye (mg/g), equilibrium adsorption capacity (mg/ g), monolayer maximum coverage capacity (mg/g), and Langmuir isotherm constant (L/mg), respectively (Tan et al. 2008; Zou et al., 2011). While in case of DR isotherm,  $q_m$ ,  $\beta$  and  $e^2$  are theoretical saturation capacity (mg/g), constant related to mean free energy (mol<sup>2</sup>/J<sup>2</sup>) (adsorption/mol of adsorbate), and Polanyi potential ((J/mol)), respectively (El-Geundi, 1991; Langmuir, 1916).

$$e = RT \ln (1 + 1/C_e)$$
 (11)

Catalyst	Temperature (K)	Langmuir isotherm		DR isotherm				
		$q_m \ ({ m mg/g})$	K <sub>L</sub> (L/mg)	$R^2$	$\frac{B}{(\text{mol}^2/\text{J}^2)}$	$q_m \ ({ m mg/g})$	E (J/mol)	$R^2$
TBH5c	298	5.11	-0.13	0.998	3x10 <sup>-5</sup>	4.91	182.5	0.998
	318	4.72	-0.12	0.998	3x10 <sup>-5</sup>	4.39	129.1	0.998
	338	4.85	-0.13	0.975	$2x10^{-5}$	4.85	158.1	0.997
TBH5d	298	10.93	-0.21	0.999	9x10 <sup>-6</sup>	12.65	235.7	0.997
	318	8.86	-0.19	0.998	$1 \times 10^{-5}$	10.01	223.6	0.996
	338	5.83	-0.14	0.982	2x10 <sup>-5</sup>	6.12	158.1	0.997

Table 3 Summaries of Langmuir and DR isotherm constants and regression co-efficient at different temperatures.

$$E = 1/\sqrt{2\beta}$$

(12)

However, Polanyi potential (e) and adsorption energy (E) (J/mol) values could be calculated on the basis of above equations (11) and (12), respectively.

As can be seen in Table 3, the  $k_L$  values are negative for both TBH5c and TBH5d, suggesting that adsorption process of CV dye did not obey Langmuir modal (Nezamzadeh-Ejhieh and Moeinirad, 2011). Figure S5-A and -B showed the fitted Langmuir adsorption for TBH5c and TBH5d, respectively. DR isotherm is invers of Langmuir adsorption isotherm, which is associated to the porous structure of the adsorbent (Helfferich, 1962), because it assumes a heterogeneous surface instead of homogeneous surface. Accordingly, if E value is in the range of 8–16 kJ/mol, the adsorption would be supposed to occur through chemosorption, while, if the E value is less than 8 kJ/mol, the adsorption processes would be considered physical in nature (Ullah et al., 2020b). As can be seen in Table 3, the adsorption isotherms of TBH5c and TBH5d followed DR modal (Figure S5-C and -D) with high regression co-efficient  $(R^2)$  value (as shown in Table 3), whereas the adsorption processes belonged to physo-sorption as the *E* value is less than 8 kJ/mol.

#### 3.7.5. Recycling behaviors

The durability test of synthesized catalyst is an important step for practical implantation. Therefore, the recycling performances of synthesized TBH5c and TBH5d up to 5 cycles were shown in Fig. 9. As can be seen, the gradual decrease occurred in removal efficiency of catalyst with cycle number. The photocatalytic activities of TBH5c and TBH5d were 97.5 and 98% for 1st cycle, while 71.2 and 61% for 5th cycle, respectively. However, the decrease in degradation efficiency of TBH5d was greater than that of TBH5c due to its high adsorption property, in which the major removal of CV dye occurs through adsorption. The overall decrease in the photocatalytic degradation of both catalysts can be correlated with the residues of some adsorbed dye or degraded products on the catalysts surface. The other reason might be the loss of catalyst dosage during recycling process as after every cycle approximately 90% of catalyst was recovered (Ullah et al., 2021).

Figure S6-C and -D showed the large and small angle XRD patterns of TBH5c and TBH5d after 5th cycles, the results demonstrated clear peaks of both phase (anatase and rutile) with little low intensity than fresh sample (Figure S6-A and -B), confirming the structure stability of both catalysts. While, Figure S7 presented the TEM micrographs of TBH5c and TBH5d after 5th cycles, showing that the aggregation occurrences of TiO<sub>2</sub> particles in the reused catalysts.

# 4. Conclusions

The TiO<sub>2</sub>/BMMs composites with mixed phases (anatase and rutile) were synthesized via hydrothermal method followed by calcination. Their structure features and texture parameters were characterized by various techniques, such as XRD patterns, SEM/TEM images, N2 adsorption isotherms, zeta potential, ICP analysis, FT-IR and UV-visible spectra, elemental mapping examinations. The resultant TBH5c and TBH5d (calcinated at 600 and 800 °C) with highly dispersed mixed phases TiO<sub>2</sub> showed maximum dye removal of 97 and 98 %, respectively. The photocatalytic degradation activity of TBH5c (A: R = 76: 24) was higher than that of TBH5d (A: R = 19: 81), while the absorption properties were vice versa. The adsorption and degradation kinetic followed pseudo second and first order model, respectively, however the adsorption equilibrium data fitted to Dubinin-Radushkevich model. The negative  $\Delta G_{ads}$  and  $\Delta H_{ads}$ , values revealed that the adsorption behaviors of CV dye belonged to physisorption, feasible, exothermic and spontaneous in nature, while positive  $\Delta S_{ads}$  verified increased randomness at solid-liquid interface. The structure stabilities and cycling reusability of as-prepared TBH5c (71.2 %) was higher than that of TBH5d (61 %) after 5th cycle, suggesting that TBH5c would be an excellent candidate for practical application in wastewater treatment.

#### CRediT authorship contribution statement

Anadil Gul: Investigation, Writing – original draft. Raza Ullah: Investigation, Writing – original draft. Jihong Sun: Supervision, Conceptualization, Methodology. Tallat Munir: Data curation. Shiyang Bai: Formal analysis, Validation.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.arabjc.2021.103530.

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