Enhanced photocatalytic degradation of methylene blue and adsorption of metal ions by SDS-TiP nanocomposite

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Abstract

In this paper, a facile and highly efficient nanocomposite sodium dodecyl sulphate-based titanium(IV) phosphate (SDS-TiP) was successfully synthesized by sol-gel method. The surface morphology, crystalline structure, and optical properties were characterized by FTIR, XRD, TGA-DTA, SEM, TEM and UV-Vis diffuse reflectance spectroscopy (DRS). The physiochemical properties such as pH titration, elution behavior and chemical stability of SDS-TiP were studied. The ion exchange capacity of SDS-TP was found to be higher (1.6 meq g^{-1}) for Na^+ ion as compared to their non-SDS material (1.1 meq g^{-1}). For optimal adsorption of metal ions, sorption studies were performed in different solvent systems showing higher distribution coefficient (K_d) values. The SDS-TiP nanocomposite is active as a catalyst under visible light having optical absorption wavelength below 600 nm and the band gap obtained was 3.2 eV indicating that the material is behaving as a semiconductor. The higher photocatalytic activity of SDS-TiP is attributed due to the structure of the catalyst, optimal amount of SDS-TiP (5 g/dm^3) and the initial concentration of methylene blue (MB) was found to be 20 ppm. It was observed that 90% of MB dye was removed after exposure to solar radiation for short duration. SDS-TiP can be effectively used as a highly efficient photocatalyst for the decomposition of MB dye as well for the removal of metal ions.

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Graphic abstract

Keywords Photo-degradation dye · Methylene blue · Adsorption · Nanocomposite · Binary separations

1 Introduction

The rapid growth of the world's industries has created a tremendous increase in pollutants containing toxic metals and dyes (used especially in the textile, leather, pulp, batteries, paper, and cosmetic industries) continuously discharged into water bodies and ultimately enter the human body through various processes viz. inhalation, ingestion of containment food and drinking water [1–6]. The bioaccumulation of dyes and toxic metal ion as waste present in the aquatic system has led to some serious environmental problems. Further, heavy metals are carcinogenic and show ill effects on living beings. In this regard, researchers are trying to develop methodology to prepare highly efficient materials having large surface area and active sites to separate and remove the

contaminants from the environment [7–10]. Various methods have been utilized for the removal of pollutants from aqueous wastewater such as adsorption, membrane filtration, reverse osmosis, solvent extraction, degradation and ion exchange methods. However, ion exchange and degradation of dyes using composites material are most important and widely used due to their potential applications in the removal of heavy metal ions, ease of their preparation, regeneration, environmental and mechanical stability, and low cost [11–14]. The surfactant-based cation exchangers are capable of exchanging and adsorbing toxic metal ions and organic pollutants through the surface sites of surfactant and inorganic constituents [15, 16]. The surfactant molecules in the inorganic matrix plays a crucial role in improving the capacity of ion exchanger as well as enhancing the chemical and thermal properties

of ion exchangers thus making it more stable. The intercalation of an inorganic matrix with surfactant molecules leads to rearrangement in the particles to produce composite material at nanoscale [17]. These nanomaterials were capable of binding a broad range of ions/molecules. They specifically adsorb toxic pollutants including dyes and effective in its removal from the environment [18, 19]. The charged head group of surfactant molecules removes metal ions by binding with oppositely charged ions through complexation effect, electron attraction and charge neutralization [20]. Further the surfactant molecules reduce the interfacial tension between solid and liquid phases, thereby, it helps to wet the surface properly and facilitates the exchange of metal ions easily and readily from the surface of ion exchanger materials because the adsorption of metal ions onto the exchange sites is affected by the charge density of the interface [21, 22]. Ti(IV)-based ion exchangers are known to be chemically and thermally stable under identical conditions of synthesis [23, 24]. The objective of present studies were to (1) synthesize the surfactant based cationic exchange material on nano-scales (2) synthesize material should have higher ion-exchange capacity, better physical and chemical stabilities compared to resin-based or polymer-based ion exchange materials, (3) should be capable of exchanging and removing heavy metal ions and dyes from aqueous solution (3) material thus synthesized must be environment-friendly because it can be decomposed if not required or recycled after it gets exhausted. The following pages describe the synthesis, characterization, and application of nano- sodium dodecyl sulfate-titanium(IV) phosphate (nSDS-TiP) as a new composite material.

2 Experimental

2.1 Materials

Titanium(IV) Chloride (99.5%) (LOBA-Chemie, India), Sodium dodecyl sulphate (90%) (SDFCL, CO. limited-India), Polyoxyethylene (20) Sorbitan monooleate (Tween 80) (lobachemie, India), Cetyltrimethyl ammonium bromide (CTAB) (E. Merck, India), H_3PO_4 (85%) (E. Merck, India), Methylene Blue (E. Merck, India), were used as procured.

2.2 Synthesis of SDS-TiP

SDS-TiP nanocomposite was prepared by drop wise addition of 0.1 M Titanium chloride solution prepared in CCl_4 into mixture of 0.1 phosphoric acid and sodium dodecyl sulphate in different mixing volume ratios at constant temperature ($25 \pm 1^\circ C$) [12]. White precipitate of ion exchanger SDS-TiP was obtained. The rest processes were similar as reported earlier [9, 25].

2.3 Physicochemical parameters

Ion exchange capacity (IEC) of SDS-TiP was estimated by column method [26]. Topp and Pepper [27] procedure was applied for pH studies in LiCl–LiOH, NaCl–NaOH, KCl–KOH, systems. 0.5 g of SDS-TiP was immersed in 50 ml of the concerned solution. The effect of temperature on IEC was studied by heating 1 g of the nanomaterial for 1 h between 100 and 800 $^\circ C$, at 100 $^\circ C$ intervals, in a muffle furnace. For elution behavior, 1.0 g of the SDS-TiP in the H^+ form was eluted by 1 M $NaNO_3$ solution.

Table 1 Conditions for the synthesis of the SD-TiP nanocomposite in different volume ratios

Sample	Mixing ratio			pH	Yield (g)	Na ⁺ I.E.C (meq dry g ⁻¹)
	0.1 M Ti ⁴⁺ in CCl_4	0.1 M H_3PO_4 in DMW	Surfactant 1% in DMW			
S-1	1	1	–	0.5	2.4	0.80
S-2	1	1	1 SDS	0.5	2.9	1.00
S-3	1	2	1 SDS	0.5	3.0	1.15
S-4	2	1	1 SDS	0.5	2.0	0.90
S-5	1	1	–	1.0	2.8	1.10
S-6*	1	1	1 SDS	1.0	3.1	1.60
S-7	1	2	1 SDS	1.0	2.4	0.90
S-8	2	1	1 SDS	1.0	2.6	0.60
S-9	1	1	1 CTAB	1.0	2.0	0.90
S-10	1	1	1 TWEEN	1.0	1.8	1.10

2.4 Characterization of SDS-TiP

A thermogravimetric analysis of SDS-TiP was performed in an automatic thermo-balance in the temperature region 30–800 °C at a constant rate (10 °C/min) in the nitrogen environment using Perkin Elmer instrument. FT-IR analysis was recorded by KBr disc method between 400 and 4000 cm⁻¹ on Perkin Elmer spectronic BX FTIR spectrophotometer. X-ray diffraction analysis was performed using Lab-X, SHIMADZU-XRD-6100 diffractometer employing Cu K α radiation. Scanning electron microscopic studies were performed at 15 kV using JOEL JSM-6510. Transmission electron microscopic analysis was recorded on JOEL-JEM 2100 (Japan) at 20 kV.

2.5 Sorption studies

The distribution coefficient (K_d) of metal ions: Mg²⁺, Ba²⁺, Sr²⁺, Hg²⁺, Ni²⁺, Co²⁺, Cu²⁺, Pb²⁺, Cd²⁺, Zn²⁺, Fe³⁺, La³⁺ and Th⁴⁺ were determined by transferring (0.3 g) of SDS-TiP in H⁺ form into a number of solvents: dimethyl sulfoxide, acetic acid, and mixed systems. SDS-TiP was activated at 100 °C for 6 h and placed into 100-ml conical flasks each containing 30 ml solution of 2×10^{-4} M concentration of metal ions. The mixture was kept at room temperature (25.0 ± 0.5 °C) for 24 h with intermittently shaking to achieve equilibrium [2]. The (K_d) values were calculated using the following relationship:

$$K_d = \frac{I - F}{F} \times \frac{V}{M} \text{ ml g}^{-1} \quad (1)$$

where I is the initial concentration of the metal ion in the solution, F is final concentration of metal ion in the solution phase after treatment with the exchanger, V is the volume of the solution (ml) and M is the amount of ion exchanger (g).

Table 2 Ion-exchange capacity of the exchanger on different exchanging ions on the columns of SDS-TiP

Metal ion taken	pH of metal ion	Ionic radii (Å)	Hydrated ionic radii (Å)	pH	I.E.C (meq/g) in SDS
Li ⁺	6.9	0.68	3.4	1	1.00
Na ⁺	6.2	1.33	2.3	1	1.60
K ⁺	6.7	0.97	2.75	1	1.66
Mg ⁺²	6.0	0.78	7.00	1	1.30
Ca ⁺²	6.5	1.06	6.30	1	1.70
Ba ⁺²	6.2	1.43	5.90	1	1.74
Sr ⁺	6.3	1.27	**	1	1.84

Fig. 1 pH titration curves for different alkali metal systems on SDS-TiP

2.6 Optical properties

The optical properties of SDS-TiP was investigated with a double beam (R Beam Att, S Beam Att, 60 mm sphere) spectrometer (PerkinElmer UV Win Lab 6.0.4.0738/1.61.00 Lambda 850) in the wavelength range 200–800 nm.

2.7 Photocatalytic studies

Methylene blue (MB) is a common organic dye that is very difficult to decompose it in waste streams under sunlight. The photocatalytic activity of SDS-TiP, TiP and Tween-TiP materials was determined by the photodegradation of MB dye in aqueous solution under sunlight [28]. 150 mg of each material was added to initial concentration (C_0) of MB dye (20 mg/L) to form slurry. Then, the slurry was put in dark for 0.5 h with stirring to establish adsorption–desorption equilibrium [29]. 4 ml of aliquots were withdrawn after a certain time of irradiation of the slurry and the catalyst (SDS-TiP) was removed by using a centrifuge (4000 rpm)

Fig. 2 Histogram showing elution behavior of H⁺ on SDS-TiP

Fig. 3 **a** FTIR spectra of (1) TiP, (2) SDS-TiP. **b** FT-IR spectrum of nano SDS-TiP during photocatalysis degradation of methylene blue at different time

Scheme 1 Synthesis of SDS-TiP nanocomposite using sol-gel route

and then the amount of dye degraded (C_t) on the catalyst surface was monitored using (PerkinElmer UV Win Lab 6.0.4.0738/1.61.00 Lambda 850) spectrophotometer in the range 200–800 nm. The percent degradation was calculated using following formula [24]:

$$\% \text{Degradation} = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

where C_0 is the initial concentration of dye and C_t is the concentration of dye at time t .

All of the photocatalyst experiments were carried out in triplicate.

3 Results and discussion

The syntheses of SDS-TiP nanocomposite under varying experimental conditions are listed in Table 1. The reproducibility of SDS-TiP was tested by synthesizing the material three times under identical conditions of concentration, mixing ratio, equilibrium pH and drying temperature. The ion exchange capacities of all the samples were determined and that sample was finally selected which shows highest ion exchange capacity (sample S-6*). The affinity sequence for alkali and alkaline earth metal ions shows a decreasing trend for the ion exchange capacity in the following order: $K^+ > Na^+ > Li^+$ and $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$,

Table 3 Effect of drying temperature on ion exchange capacity of (SDS-TiP) cation exchanger

S. no	Heating temp (°C)	% wt. loss of sample after heating	Color of sample after heating	I.E.C for Na ⁺ ion (meq/dry g)	Retention of exchange capacity (%)
1	50	0	White	1.6	100
2	100	2	White	1.6	100
3	200	6	Brawn white	1.3	95.8
4	300	14	Grayish white	1.09	89.16
5	400	20	Grayish white	1.02	87.5
6	500	22	White	0.91	82.5
7	600	26	White	0.48	40.0
8	700	28	White	0.36	30.0
9	800	28	White	0.22	18.3

Fig. 4 TGA- DTA of SDS-TiP nanocomposite **Table 4** Chemical resistivity of SDS-TiP in various solvents

S. no.	Solvent	Remark
1.	D.M.F	Completely insoluble
2.	Chloroform	Completely insoluble
3.	Acetone	Sparingly soluble
4.	CCl ₄	Insoluble
5.	NH ₄ OH (2 M)	Sparingly soluble
6.	Methanol	Completely insoluble
7.	NaOH (2 M)	Completely insoluble
8.	KOH (2 M)	Completely insoluble
9.	CH ₃ COOH (2.M)	Completely insoluble
10.	HNO ₃ (2 M)	Partially soluble
11.	Perchloric acid (2 M)	Partially soluble
12.	H ₂ SO ₄ (2 M)	Comp. insoluble
13.	HCl (2 M)	Comp. insoluble

respectively (Table 2). The results indicated that the sequence is in accordance with the hydrated radii of the exchanging ions [24].

The pH titration has been investigated for LiOH–LiCl, NaOH–NaCl, KOH–KCl systems (Fig. 1). All curves show one inflection point which indicates a mono-functional weak acid behavior of SDS-TiP [30]. Figure 2 reveals the elution processes of SDS-TiP for H⁺ ions. The exchange steps were quite fast and almost all the H⁺ ions were removed in the first 150 ml of the effluent from a column having 1.0 g of SDS-TiP nanocomposite.

3.1 FTIR analysis

Infrared spectra of TiP (Sample S5) and SDS-TiP (Sample S6), were shown in Fig. 3a(1 and 2). A broad band was

Fig. 5 X-ray diffraction pattern of **a** TiP and **b** SDS-TiP nanomaterial

observed at 3400 cm^{-1} , attributed to stretching symmetric and asymmetric -OH . The band at $1627\text{--}1631\text{ cm}^{-1}$ assigned to H-O-H bond of water and a strong absorption at 1036 cm^{-1} was attributed to $\nu(\text{P=O})/(\text{S=O})$ stretching. The band observed at 1400 cm^{-1} was attributed to δ

(POH) stretching. The peaks at 2927.6 cm^{-1} , 1467.2 cm^{-1} , and 1402.5 cm^{-1} reveal the presence of methyl and/or methylene groups. Bands with values of 516 and 626 cm^{-1} correspond to links O-Ti-O bonds formation. The comparison of IR absorption spectra of the MB before and after photocatalytic degradation on SDS-TiP were shown in Fig. 3a, b. Since the MB molecule consists of several types of bonds, such as C-H , N-CH_3 , C=N , C=S , and Ar-N (has aromatic rings), apparently MB photocatalytic degradation could not undergo complete degradation to produce CO_2 and H_2O , rather many kinds of intermediates compounds were produced during the degradation process. Figure 3b(1–5), indicate the photocatalytic degradation of MB on SDS-TP, a broad peak at 3500 has sharpened and new peaks at 3549, 3472.48, 3415.07, 3237.67 cm^{-1} (representing the stretching vibration of -CH- aromatic and -CH_3 groups of MB) have emerged with the MB bands for the C=N central ring stretching at 1618 cm^{-1} , the C=C side ring stretching at 1466 cm^{-1} (the intensity increases in Fig. 3b(2–5)), the Ar-N stretching at 1337 cm^{-1} (appeared in Fig. 3b (5)). The IR peaks of MB before decomposition

Fig. 6 Scanning electron micrographs at 3000 magnitude **a** before decomposition and **b** after decomposition of MB on SDS-TiP nanocomposite **c** EDAX morphology diagram of TiP

Fig. 7 Transmission electron microphotographs of SDS-TiP nanocomposite

(Fig. 3a(2)) clearly shows the disappearance of IR peaks of MB at 1618 cm^{-1} (for $\text{C}=\text{N}$), decreased intensities at 1459 , 1394 , and 1337 cm^{-1} , as well as the increased intensity at 793 cm^{-1} . Three peaks at 410 , 622.5 , 481.56 (two sharp peaks at 622.5 , 481.56) are seen in Fig. 3a(2). Intensity of these peaks are changing from (1) to (5) (Fig. 3b). The IR results clearly indicate that MB undergoes demethylation and $\text{C}=\text{N}$ bond breaking, which agrees with the reports of Jing et al. [31]. The presence of $\cdot\text{OH}$ radicals on the nSDS-TiP surface oxidizes the MB molecules. The mechanistic details of oxidation of MB by $\cdot\text{OH}$ radicals are described in Scheme 1.

Table 3 shows the effect of variation in of temperature on ion exchange capacity of cation exchanger (SDS-TiP) which reveal that SDS-TiP is thermally stable at $300\text{ }^{\circ}\text{C}$, where 89.36% ion-exchange capacity is retained. At heating range between 300 and $500\text{ }^{\circ}\text{C}$, the ion capacity of the ion exchanger is decreased to about 40.09% , whereas on heating up to $800\text{ }^{\circ}\text{C}$, the material possesses only 18.3% of ion exchange capacity which may be due to calcinations of pores on the surface of material.

Fig. 8 **a** UV-Vis absorption spectra **b** UV-Vis diffuse reflectance of SDS-TiP nanocomposite

3.2 TGA-DTA, XRD, SEM and TEM analysis

The thermo gravimetric analysis (TGA-DTA) curve for SDS-TiP is shown in Fig. 4 that indicates only one region of weight loss which shows that the material is thermally stable. A 23.7% weight loss at 181.5 °C is attributed to the loss of moisture/hydrated water as well as the condensation of structural hydroxyl groups. The weight of the cation exchange material becomes almost constant on heating beyond to 800 °C. A valley at 159 °C in DTA plot shows endothermic nature of the decomposing material.

Table 4 indicates that SDS-TiP is stable in acidic (up to 2 M), basic (up to 2 M) medium as well as in polar solvents. The X-rays pattern of SDS-TiP (Fig. 5) indicates the semicrystalline nature of SDS-TiP nanocomposite.

The SEM images in Fig. 6 show regular spherical and diamond shape surface morphology and the surface composition of material is presented in Fig. 6c. The presence of uniform morphology also indicates the absence of impure phases. Figure 7 shows the TEM images of SDS-TiP

Fig. 9 **a** UV-Vis absorption spectra of methylene blue dye on nano SDS-TiP at different irradiation time. **b** Simultaneous adsorption and photocatalytic degradation of methylene blue dye on TiP, Tween-TiP and SDS-TiP

Fig. 10 Kinetics of MB dye degradation onto SDS-TiP nanocomposite ion exchanger

Fig. 11 **a** Effect surfactant type on catalytic site on the surface of material over a period of 2 h; **b** schematic shows the degradation efficiency after four cycles

having particle size in the range 5–15 nm, thus SDS-TiP is a nanomaterial.

3.3 Optical properties

The conductivity of SDS-TiP was investigated by applying diffuse reflectivity in powder samples. The band gap (E_g) was confirmed at the intersection point between the energy axis and the line extrapolated from the linear portion of the adsorption edge in a plot of Kubelka–Munk function ($K-M$) versus energy (E). $K-M$ function, $(K-M) = (1-R)/2R$, was transformed from the obtained diffuse reflectance result, where R is the diffuse reflectance based on the Kubelka–Munk theory of diffuse reflectance. The E_g value evaluated from the steep absorption edge for SDS-TiP was 3.2 eV which reveals that SDS-TiP is potential semiconductive material as shown in Fig. 8a. Thus, SDS-TiP can be used as catalyst to decompose toxic dyes. Photocatalysis test was performed under sunlight irradiation. But since sunlight contains both UV and visible fraction, it can be concluded that the material is capable to degrade MB in both UV and visible regions of the electromagnetic spectrum. Figure 8b shows the UV–Vis diffuse reflectance of the catalyst which indicates that SDS-TiP can adsorb significantly more light in the wavelength region 350–450 nm suggesting that the catalyst is active in both UV and visible regions of the spectrum.

3.4 Photocatalytic activity

The photo-degradation percentage of methylene blue under sunlight was found to be 90% within 3 h in the

presence of SDS-TiP nanocomposite. Figure 9a shows UV–Vis absorption spectra of degradation methylene blue dye on the surface of SDS-TiP nanocomposite. To ensure experimental control, the solution of MB dye was exposed to sunlight in the absence of any catalyst. The result reveals that no degradation of MB occurred in the absence of SDS-TiP under sunlight. Coupling of sunlight responsive TiP with SDS may suppress the electron–hole recombination rate, hence increment the light assimilation and photocatalytic effectiveness of SDS-TiP [32]. Almost complete adsorption of MB is observed on SDS-TiP within 300 min. Figure 9(b) shows the simultaneous adsorption and photocatalytic degradation of MB as a function of time in presence of different catalysts; TiP (Sample S5), Tween-TiP (Sample S10) and SDS-TiP (Sample S6*) which clearly indicate that SDS-TiP shows promising catalytic properties being the most effective and fastest of the three thus studied. In view of the results obtained under solar irradiation, the main motive of this work is to perform the experiment practically and economically, so full energy spectrum of the sun is utilized to degrade the MB dye in presence of SDS-TiP, hence no filter is used. The borosilicate glass beaker has been used as an experimental vessel which can't transmit UV. So, it can be assumed that practically catalysts are absorbing visible range of rays [33].

The rate of photocatalytic degradation of methylene blue dye was determined using pseudo first order Kinetic model as follow.

$$r = \frac{dC}{dt} = k_{app}t \rightarrow \ln \frac{C_0}{C_t} = K_{app}t$$

Fig. 12 **a** Fluorescence emission of photocatalytic processes for MB in the presence of SDS-TiP. **b** Fluorescence intensity changes in the photocatalytic processes for MB in the presence of SDS-TiP with sunlight irradiation time

where k_{app} is the apparent rate constant, C_0 is the concentrations of dye before illumination and C_t is the concentration of dye at time t .

The plot of $\ln C_0/C_t$ versus irradiation time shows a linear correlation (Fig. 10) which demonstrated that the photo

Table 5 Comparison of the degradation efficiencies of MB dye on SDS-TiP with other catalysts under sunlight

No	Catalysts	Dye (MB) (initial conc.)	Time taken (min)	Degradation efficiency (%)	References
1	ZnO	(7.5 mg/L)	90	91.0	[37]
2	ZnFeAl-LDO	(3.0 mg/L)	180	60.0	[38]
	ZnAl-LDO	(3.0 mg/L)	180	23.0	[38]
3	PAZ/TiO ₂	(50 mg/L)	300	97.0	[39]
4	CdO/GO	(25 mg/L)	90	90.5	[40]
5	MoS ₂ -ZnO	(1.0 mg/L)	120	81.7	[41]
6	SDS-TiP	(20 mg/L)	180	90.0	This study

degradation of MB dye using SDS-TiP nano material cation exchanger followed pseudo first order kinetics [34]. The value of rate constants of TiP (0.00836 min^{-1}), Tween-TiP (0.00947 min^{-1}) and SDS-TiP (0.01321 min^{-1}) were calculated from the slope of the plot and the correlation coefficient values (R^2) were 0.99963, 0.99404 and 0.98565, respectively. Figure 11 indicates the effect of surfactants on the MB dye degradation onto catalytic sites of SDS-TiP, CTAB-TiP and Tween-TiP composites. The SDS-TiP nano composite is found to be the superior compared with the other composites.

The first step in photocatalytic degradation is the absorption of photons from light in the region of a wavelength higher than its band gap ($h\nu \geq E_g = 3.2 \text{ eV}$) by SDS-TiP semiconductor, creating the transmission of an electron (e^-) from the valence level to the conduction level, leaving a hole behind. The importance of the previous reaction is the trapping of hydroxide ions in aqueous solution by holes ($h\nu B^+$) to produce $\cdot\text{OH}$ radicals [32, 34, 35]. As reported earlier, hydroxyl radicals ($\cdot\text{OH}$) have been deemed to be the crucial active species during the photocatalytic process [36]. Therefore, the concentration of ($\cdot\text{OH}$) radicals produced, which can be dictated by fluorescence intensity, highly influencing the photocatalytic decomposition effectiveness of dyes onto SDS-TiP catalyst. The degradation mechanism was as follows:

Fig. 13 **a** Plot of K_d value versus different acetic acid concentration for some metal ions on SDS-TiP. **b** Plot of K_d value versus different DMSO concentrations for some metal ions on SDS-TiP

Fluorescence intensity spectra of MB on SDS-TiP under sunlight irradiation was shown in Fig. 12a. The result indicates that the fluorescence intensity at about 425 nm increases sharply and linearly with the reaction time (Fig. 12b), which indicates that 2-hydroxy terephthalic acid ($\lambda_{\text{max}} = 425$ nm) was formed via the reaction between terephthalic acid and $\cdot\text{OH}$ radical generated during the interaction of SDS-TiP in MB solution. The proposed mechanism of photocatalytic degradation indicates that SDS-TP favors formation of ($\cdot\text{OH}$) radicals under sunlight due to synergistic effect of combination of SDS-TiP and sunlight irradiation. The recycling of SDS-TP for the removal of the

dyes from aqueous solution was studied under sunlight irradiation. It has been observed that SDS-TP continues to maintain excellent photocatalytic activity after four cycles under same condition (Fig. 11b). The decomposition rate of the dye (MB) was 90% in the first cycle in the presence of the SDS-TiP. While after four successive degradation cycles the decline in the catalyst efficiency was not significant (78.7%). Table 5 shows the comparison of the photo-degradation efficiency of SDS-TiP with other catalysts. As it can be seen from Table 5, the photocatalytic activity of SDS-TiP was almost higher as compared with most of the other catalysts except in case of PAZ-TO₂, which indicates the

Table 6 K_d values of metal ions on SDS-TiP column in varied solvent system

Metal ions	AA 0.01	AA 0.05	AA 0.1 M	DMSO 0.01 M	DMSO 0.05 M	DMSO 0.1 M	MDSO-AA 0.01 M
Mg ²⁺	123	98	76	27	35	55	39
Ba ²⁺	141	112	12	48	57	166	77
Sr ²⁺	637	565	530	44	58	134	55
Hg ²⁺	444	387	378	33	39	189	60
Ni ²⁺	322	165	11	123	145	177	88
Co ²⁺	720	630	500	134	180	102	140
Cu ²⁺	430	380	36.8	32	65	123	47
Pb ²⁺	618	432	520	39	64	78	23
Cd ²⁺	207	80	23	24	62	56	48
Zn ²⁺	212	170	145	13	18	–	–
Fe ³⁺	889	779	735	365	401	389	600
La ³⁺	400	347	400	215	256	290	257
Th ⁴⁺	460	430	360	334	377	407	–

superiority of compounds containing Ti particles on the surfaces. Table 6 shows the K_d values for different metal ions in diverse solvents. The uptake preference of the ion exchanger for a particular ion over other depends usually upon the hydrated-size and the charge on the metal ion. Since the hydrated-size of the Fe³⁺ and Co²⁺ is almost same they show similar behavior toward the material. K_d values of the metal ions in DMSO are relatively lower as compared to acetic acid taken as solvent. The increase in concentration of DMSO from 0.01 to 0.1 M results in increased sorption for the metal ions studied. This may be probably due to solvating action of DMSO with metal ions. Further more Fig. 13a, b shows effect the concentration of the solvent systems (acetic acid, DMSO and mixed solvent systems) on K_d values. The K_d value decreases with the increase in the concentration of the acetic acid solvent systems (Fig. 13a). This decrease in K_d values follows linearity (see Table 6). It is apparent from Table 6 that K_d values in DMSO concentrations are relatively lower as compared to acetic acid medium. However, The K_d values increase with the increase in the concentration of the DMSO (Fig. 13b).

4 Conclusion

In the present study, the synthesized nano sodium dodecyl sulfate-Ti(IV) Phosphate (SDS-TiP) is an effective adsorbent for the removal of metal ions. Further it can be considered as an efficient photocatalyst for the degradation of methylene blue under sunlight irradiation. The simultaneous adsorption and photocatalytic processes proved to be highly efficient for the degradation of methylene blue dye. The photocatalytic degradation percentage of MB dye by SDS-TiP nanocomposite was found out to be 90% in 3 h under sunlight irradiation. The kinetic study was best

described by a pseudo-first-order. The mechanism and pathway proposed for the MB degradation in presence of (SDS-TiP) was explained on the basis of fluorescence spectra.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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