



Use of pectin–thorium (IV) tungstomolybdate nanocomposite for photocatalytic degradation of methylene blue

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ABSTRACT

Pectin–thorium (IV) tungstomolybdate (Pc/TWM) nanocomposite was prepared by mixing biopolymer pectin with its inorganic counterpart thorium (IV) tungstomolybdate (TWM) using the sol–gel method. The nanocomposite was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR). Distribution coefficient, thermal stability, pH titrations, elution and concentration behaviour were investigated to explore the ion exchange behaviour of nanocomposite material. Pc/TWM exhibited higher ion exchange capacity (1.10 mequiv/g) than its inorganic counterpart (0.62 mequiv/g). The Pc/TWM nanocomposite ion exchanger was thermally stable as it retained 59% of its ion exchange capacity upto 400 °C. The pH titrations study revealed the bifunctional nature of Pc/TWM. In order to explore the environmental applicability of the Pc/TWM nanocomposite material, its antibacterial and photocatalytic activities was investigated. 76% of methylene blue dye was photocatalytically degraded after five hours exposure. It also totally inhibited *Escherichia coli* at 400 µg/ml concentration of Pc/TWM nanocomposite.

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1. Introduction

The nature has provided us with various inorganic and organic ion exchange materials having their own specificity and selectivity. The inorganic ion exchangers are thermally and chemically stable. Organic ion exchangers have good mechanical strength and can be utilized for treatment of large volume of waste effluents. The composite ion exchangers have been given attention in order to encapsulate the desired properties of both organic and inorganic counter parts into one molecule. The nano domain advanced composite ion exchangers have been used in environmental remediation because of their selectivity, specificity and wide range of applicability (Khan & Alam, 2004; Khan & Khan, 2010; Vatutsina et al., 2007). The efforts have been made to improve the chemical, mechanical and thermal stability as well as their selectivity for certain heavy metal ions (AL-othman, Inamudin, & Naushad, 2011a; AL-othman, Inamudin, & Naushad, 2011b; Bushra, Shahadat, Raeissi, & Nabi, 2012; Islam & Patel, 2008; Khan & Paquiza, 2011;

Nabi & Naushad, 2008; Nabi, Shahadat, Bushra, Shalla, & Azam, 2011).

The biopolymer-based adsorbent materials have been found to be effective and economic for wastewater remediation. A large number of non-conventional bio-adsorbents such as bacterial biomass or biopolymers have been employed to remove toxic metals and dyes from water system (Zhao, Zeng, Hu, Gao, & Zou, 2012a; Zhao et al., 2012b). The bio-adsorbents are biodegradable, harmless and are abundantly available (Constantin et al., 2013; Yang et al., 2012). However, lower stability, difficulty in separation from aqueous phase and lower recovery after desorption are the major limitations for their large-scale applications (Gupta, Pathania, Agarwal, & Singh, 2012).

Combining two different materials possessing entirely different properties and producing materials with unique properties distinct from the constituent's materials produce the hybrid ion exchangers. Besides other advantages, composite ion exchange materials are more stable at high temperature and radiation fields (Siddiqui, Khan, & Inamudin, 2007; Clearfield, 1982). The hybrid ion exchangers display enhanced properties by bridging the property gap between two dissimilar types of materials (Khan, Niwas, & Alam, 2002; Khan, Inamudin, & Alam, 2005). Thus the hybrid ion exchangers have been used for diverse applications such as

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quantitative estimations by ion selective electrodes, antimicrobial activity, catalysis, hydrometallurgy, bimolecular separations, chromatography and environmental science engineering etc. (Arrad & Sasson, 1989; Hassan, Marei, Badr, & Arida, 2001; Khan & Paquiza, 2011; Nabi, Naushad, & Bushra, 2009; Nabi, Shahadat Md Bushra, Shalla, & Ahmed, 2010).

In the present work, a simple sol–gel method has been used for the synthesis of Pc/TWM nanocomposite ion exchanger. Pc/TWM nanocomposite ion exchanger was subjected for different physiochemical analysis. The hybrid material has been exploited for the remediation of difficult methylene blue dye from aqueous medium by photocatalysis and as an antibacterial agent against *Escherichia coli* strain of bacteria present in the aqueous system.

2. Materials and methods

2.1. Reagents

Thorium nitrate, pectin (Loba Chemia Pvt. Ltd., Mumbai, India), sodium tungstate (Qualigens Pvt. Ltd., Mumbai, India) and sodium molybdate (CDH Pvt. Ltd., New Delhi, India) were the main reagents used for the synthesis of nanocomposite ion exchanger. All other reagents used in this study were of analytical grade.

2.2. Instrumentation

A digital pH meter (Elico LI-10, India), a Fourier transform infrared (FTIR) spectrophotometer (Perkin Elmer Spectrum-BX USA), X-ray diffractometer (Perkin Elmer Series ICHNS/O 2400), a UV–visible spectrophotometer (Systeronics, model 2202), scanning electron microscope (Quanta 250, FEI Make Mode No. D9393), transmission electron microscope (FEI Tecnai F 20), muffle furnace (MSW-275, India) and water bath incubator shaker were used.

2.3. Preparation of reagents

Solution of 0.05 M $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ was prepared in 0.1 N HNO_3 . The solutions of 0.05 M $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and 0.05 M $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were prepared in double distilled water. The gel of pectin was prepared in double distilled water.

2.4. Preparation of pectin–thorium (IV) tungstomolybdate (Pc/TWM)

Thorium (IV) tungstomolybdate (TWM) was prepared by adding 0.05 M sodium tungstate and 0.05 M sodium molybdate drop wise with continuous shaking to 0.05 M thorium nitrate solution in equal volume ratio (1:1:1). The pH of resulting mixture was adjusted to 1 by 0.1 N HNO_3 . This mixture was stirred constantly for two hours at 80 °C. The pectin gels of varying concentrations were added to inorganic precipitates of TWM with continuous stirring. The solutions were kept on a magnetic stirrer for four hours at 80 °C. The resultant light yellow colored precipitate was digested for 24 h. The supernatant liquid was decanted and the composite was filtered under suction and washed with double distilled water. The obtained composite material was dried in an oven at 50 °C. The dried product was broken into small granules of uniform size and converted into H^+ form, by treating it with 1 M HNO_3 for 24 h. Finally, the ion exchanger was washed with double distilled water several times to remove excess of acid and dried at 50 °C. On the basis of ion exchange capacity, sample-3 was selected for detailed studies.

2.5. Ion exchange capacity (IEC)

The ion exchange capacity of Pc/TWM was determined by standard column process (Siddiqi & Pathania, 2003). In this process,

1.0 g of Pc/TWM composite in H^+ form was taken in glass column with internal diameter of 1 cm and fitted with glass wool at bottom. 1 M solution of alkali or alkaline earth metal nitrates was used as eluent to elute the H^+ from the composite. The flow rate of eluent was maintained at 0.5 mL/min. The collected eluent was titrated against a standard alkali solution. The hydrogen ions released from the Pc/TWM composite ion exchanger were calculated and ion exchange capacity was determined in mequiv/g.

2.6. Elution behavior and effect of eluent concentration

The optimum concentration of eluent for complete elution of H^+ ions from Pc/TWM was determined by passing a fixed volume of 250 mL of NaNO_3 solution of different concentration through a column containing 1.0 g of Pc/TWM composite exchanger in H^+ form. The flow rate was maintained at the rate of 0.5 mL/min. The collected eluent was titrated against 0.1 M NaOH solution. The efficiency of column was determined by passing 1.0 M solution of NaNO_3 from the column containing 1.0 g of Pc/TWM composite exchanger in H^+ form. The eluent was collected in 10 mL fractions and the amount of H^+ released in each fraction was determined by titrating with 0.1 M NaOH solution.

2.7. pH Titration

The pH titration of Pc/TWM composite ion exchanger was performed as per the method discussed by Topp and Pepper (1949). 0.5 g of Pc/TWM ion exchanger in H^+ form was placed in several 100 mL conical flasks. The equimolar solution of metal chlorides and their hydroxides in different volume ratio were added. The pH of solution was recorded after every 24 h until equilibrium was attained.

2.8. Thermal studies

1.0 g of composite ion exchanger in H^+ form was heated at different temperature (100–700 °C) for 1 h in muffle furnace and cooled to room temperature. The ion exchange capacity was determined by column process as discussed in Section 2.5.

2.9. Fourier transform infrared absorption spectra (FTIR)

FTIR spectra of Pc/TWM composite (Sample-3) was recorded by Fourier transform Infrared absorption spectrophotometer using KBr disc method. The composite in H^+ form was thoroughly mixed with KBr, powdered and a disc was formed by applying the pressure. FTIR absorption spectra were recorded in the region of 400–4000 cm^{-1} .

2.10. X-ray studies

The X-ray diffraction pattern of the composite material (Sample-3) was recorded by X-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$).

2.11. Scanning electron microscopy and energy-dispersive X-ray studies

Scanning electron microphotographs of Pc/TWM composite (Sample-3) were recorded at different magnifications. The elemental composition of the composite material was determined by energy dispersive X-ray coupled to scanning electron microscopy.

2.12. Distribution coefficient studies (K_d)

The distribution coefficient of different metal ions on Pc/TWM composite was determined by batch method. 200 mg of the

nanocomposite exchanger beads (S-3) in H^+ ion form was taken in 20 mL of different metal nitrate solutions and was kept for 24 h with continuous shaking at $25 \pm 2^\circ C$ to attain equilibrium. The metal ions in the solution before and after equilibrium were determined by titrating against standard 0.01 M solution of EDTA and atomic absorption spectrophotometer (AAS). The distribution coefficient (K_d) values were calculated by using the formula (Siddiqi & Pathania, 2003) given below:

$$k_d = \frac{I - F}{F} \times \frac{V}{M} \text{ mL g}^{-1}$$

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

2.13. Photocatalytic activity of Pc/TWM composite ion exchanger

The photocatalytic experiments were carried out in a batch reactor at $25 \pm 0.5^\circ C$ (Gupta, Ali, & Saini, 2007; Gupta, Jain & Varshney, 2007; Gupta, Agarwal & Saleh, 2011; Gupta, Mittal, Malviya & Mittal, 2009; Jain, Gupta, Bhatnagar & Suhas, 2003; Mittal, Mittal, Malviya & Gupta, 2009, 2010; Mittal, Gupta, Malviya & Mittal, 2008; Mittal, Mittal, Malviya, Kaur & Gupta, 2010; Gupta, Gupta, Rastogi, Nayak, & Agarwal, 2011; Gupta, Rastogi, & Nayak, 2010; Gupta, Ali, Saleh, Nayak, & Agarwal, 2012; Liu, Sun, Liu, & Wang, 2013; Oei, Ibrahim, Wang, & Ang, 2009). The batch reactor was surrounded by thermostatic water circulation arrangement. 1.5×10^{-5} M solution of methylene blue (MB) dye was prepared in double distilled water and 100 mg of composite ion exchanger in H^+ form was added to form slurry. In adsorption experiments, slurry composed

of dye solution and Pc/TWM composite ion exchanger suspension was stirred magnetically and was placed in the dark to establish adsorption desorption equilibrium. In the case of photocatalytic studies, suspension composed of dye and catalyst, was stirred for 15 min. The suspension was then exposed to natural solar light with continuous stirring. 3 mL aliquot of the solution was withdrawn, at different time intervals, and centrifuged to remove particles of Pc/TWM composite. The absorption was recorded in the range of 300–750 nm and the kinetics of MB degradation was studied. The percent degradation of dye was calculated using following formula:

$$\% \text{ Degradation} = \frac{C_e - C_t}{C_e}$$

where C_e and C_t are concentration of dye at equilibrium and at time t .

2.14. Antibacterial property of Pc/TWM nanocomposite ion exchanger

Clinical isolates of *E. coli* were obtained from Department of Microbiology, Post Graduate Institute of Research and Development (PGI) Chandigarh. A colony was picked from the overnight Nutrient Agar plate culture of *E. coli* and was inoculated into 10 mL Nutrient Broth (NB) in a universal container and incubated at $37^\circ C$ under shaking condition of 100 rpm for 24 h. The culture was diluted to 10^{-5} CFU/mL (colony forming unit per mL) with NB according to MacFarland standard (Dual, 1963). 5 mL of the diluted culture was aseptically pipetted into 95 mL NB in conical flasks. Four different concentrations (50 $\mu\text{g/mL}$, 100 $\mu\text{g/mL}$, 200 $\mu\text{g/mL}$, and 400 $\mu\text{g/mL}$) of Pc/TWM nanocomposite were added into the

Table 1

Conditions of preparation of various samples of Pc/TWM nanocomposite ion exchanger.

Sample no.	A (mol L ⁻¹)	B (mol L ⁻¹)	C (mol L ⁻¹)	D (%)	Mixing volume ratio (v/v)	Temperature (°C)	Appearance of the sample	Na ⁺ ion exchange capacity (mequiv/g)	Yield (g)
1	0.1	0.1	0.1	0	1:1:1:1	80 ± 2	White	0.62	3.155
2	0.1	0.1	0.1	1	1:1:1:1	80 ± 2	Creamy White	0.84	3.332
3	0.1	0.1	0.1	2	1:1:1:1	80 ± 2	Yellowish White	1.10	3.765
4	0.1	0.1	0.1	3	1:1:1:1	80 ± 2	Yellowish White	0.50	3.660
5	0.1	0.1	0.1	4	1:1:1:1	80 ± 2	Yellowish White	0.68	3.838
6	0.1	0.1	0.1	5	1:1:1:1	80 ± 2	Yellowish White	0.82	3.970

A: thorium nitrate (0.05 M in 0.1 N HNO₃), B: sodium tungstate (0.05 M in DMW), C: sodium molybdate (0.05 M in DMW), D: % of pectin added in DMW.

Table 2

Effect of temperature on the ion exchange capacity of the Pc/TWM nanocomposite ion exchanger for 1 h.

Heating temperature (°C)	Appearance (color)	Weight loss (%)	Na ⁺ ion exchange capacity (mequiv/g)	% Retention of IEC
50	Creamy white	Nil	1.10	100.00
100	Creamy white	4.95	1.10	100.00
200	Yellowish white	8.45	0.96	87.27
300	Brown	16.12	0.72	65.45
400	Gray	22.30	0.65	59.09
500	Black	30.15	0.35	31.81
600	Black	41.32	0.21	19.09
700	Black	59.83	0.12	10.90

Table 3

Ion-exchange capacity of various exchanging ions on the Pc/TWM nanocomposite ion exchanger column.

Exchanging metal ions	pH of the metal solutions	Ionic radii (Å°)	Hydrated ionic radii (Å°)	Ion-exchange capacity (mequiv/gm)
Li ⁺	6.2	0.68	3.40	0.89
Na ⁺	5.7	0.97	2.76	1.10
K ⁺	5.2	1.33	2.32	1.22
Mg ⁺	5.8	0.78	7.00	0.98
Ca ⁺	5.6	1.06	6.30	1.02

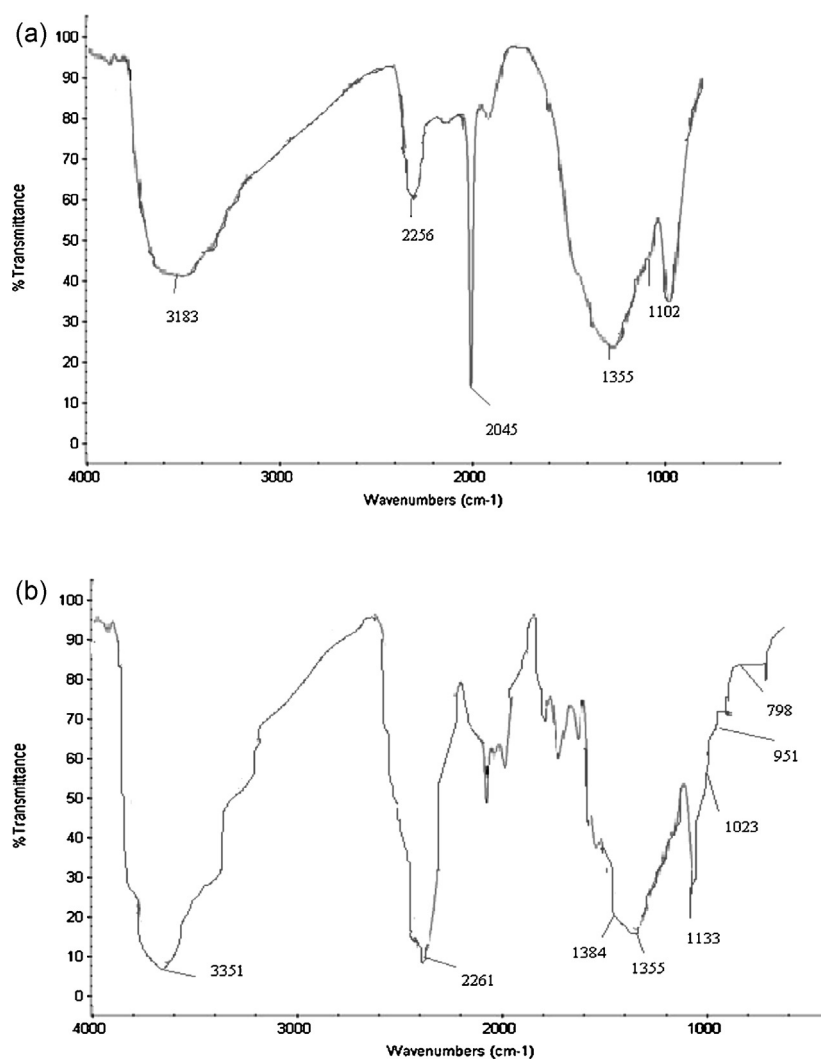


Fig. 1. FTIR spectra of (a) TWM ion exchanger (b) Pc/TWM nanocomposite ion exchanger.

flasks. The flasks were incubated to 100 rpm at 37 °C for 24 h. 3 mL fraction of each sample was analyzed for optical density after every hour spectrophotometrically at 620 nm. A positive control was also analyzed simultaneously.

3. Results and discussion

The various samples of new Pc/TWM composite were synthesized using sol gel method as shown in Table 1. The ion exchange

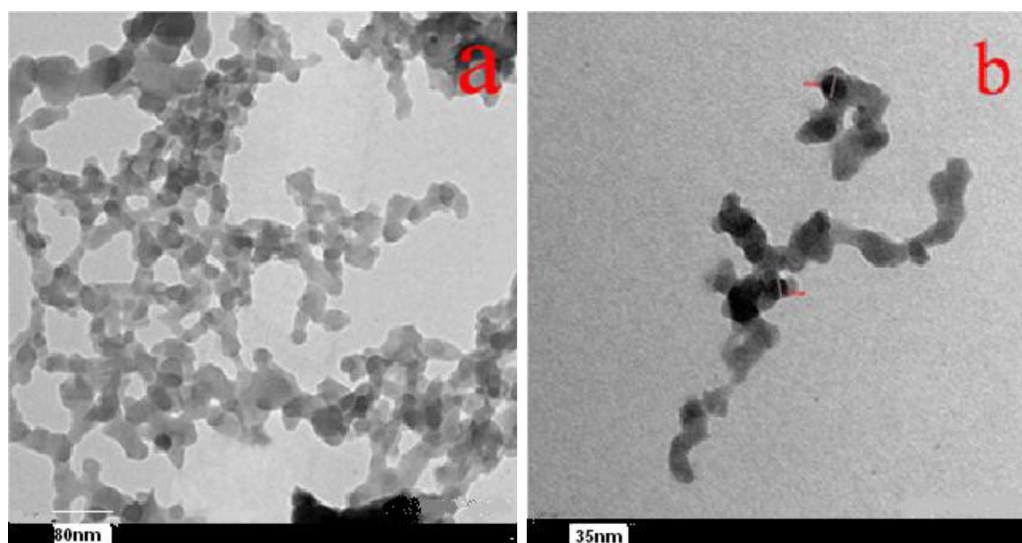


Fig. 2. Transmission electron microphotographs of Pc/TWM nanocomposite ion exchanger.

capacity of different samples was determined by varying the mixing ratio of the different components. The ion exchange capacity of Pc/TWM nanocomposite material (1.10 mequiv/g) was observed to be better as compared to the inorganic counterpart TWM (0.62 mequiv/g). The greater ion exchange capacity of nanocomposite ion exchanger may be due to the incorporation of pectin into the inorganic counterpart. The polymer based ion exchangers have better ion exchange capacity and good thermal stability as polymer backbone provides strength and greater number of sites for attachment of one or more multiple donor atoms (Siddiqui et al., 2007). It was revealed that with increase in the percentage of pectin the ion exchange capacity gradually increased to a certain extent and then decreased abruptly. At higher concentration of pectin, the numbers of sites available for attachment are more and the multiple donor atoms remain constant. Thus the ion exchange capacity of the composite material decreased significantly. The ion exchange capacity of sample-3 was maximum and was hence selected for detailed study.

The effect of temperature on the ion exchange capacity of the Pc/TWM nanocomposite (sample-3) is shown in Table 2. Pc/TWM nanocomposite is thermally stable and retained the ion exchange capacity upto 0.65 mequiv/g at 400 °C. The gradual decrease in ion exchange capacity was due to degradation of organic counterpart i.e., pectin with increase in temperature.

The order of the ion exchange capacity for alkali and alkaline earth metals is related to their hydrated ionic radii onto Pc/TWM nanocomposite ion exchanger as can be seen in Table 3. The affinity order for alkali metal is $K^+ > Na^+ > Li^+$ and for alkaline earth metal ions is $Ca^{2+} > Mg^{2+}$. The affinity trend is parallel to decreased hydrated ionic radii (Nabi, Bushra, Al-Othman, & Naushad, 2011b). Effect of eluent concentration on ion exchange capacity of Pc/TWM nanocomposite revealed that the rate of elution increased with eluent concentration. The highest rate of elution was observed with 1.0 M solution of $NaNO_3$ (Fig not shown).

The elution behaviour of the nanocomposite revealed that its ion exchange capacity was fast as only 60 mL of 1.0 M $NaNO_3$ solution was required for the complete elution of H^+ . The effect of pH of Pc/TWM nanocomposite under equilibrium condition was studied in KOH–KCl and NaOH–NaCl. The results indicated the bifunctional nature of the composite. The Pc/TWM nanocomposite material is a strong cation exchanger as indicated by its low pH value when no OH^- ions were added. At low pH the weak acidic groups remain undissociated. The addition of NaOH neutralized the solution and the weak acidic group dissociates, thus the ion exchange starts toward completion. The pH titration curves showed a gradual rise in pH initially and a steep rise at the end because strong acidic groups were completely exchanged with Na^+ ions at the end. The pH titration curves showed a steep edge at 2.5 mmol g^{-1} at equilibrium. The exchange rate was fast for $H^+ - Na^+$ system than for the $H^+ - K^+$ system.

The FTIR spectrum of TWM and Pc/TWM nanocomposite was shown in Fig. 1(a,b). The broad band at 3183 cm^{-1} was due to interstitial water molecules in TWM (Fig. 1(a)). The Fig. 1 (b) indicates broad band at 3351 cm^{-1} and can be assigned to interstitial water molecules (Inamuddin Khan, Siddiqui, & Khan, 2007). The absorption band at 1102 cm^{-1} was due to M–O–H bending modes (Miller & Wilkins, 1952). The peak at 1023 cm^{-1} may be due to C=O and C=C double bond of pectin. The peaks at 951 cm^{-1} , 798 cm^{-1} and 558 cm^{-1} may be due to molybdate, tungstate and metal-oxide groups respectively (Inamuddin et al., 2007; Miller & Wilkins, 1952). The peaks at 1355 cm^{-1} corresponds to stretching bands of free COO^- group in pectin. The peak at 1384 cm^{-1} was due to the presence of atmospheric CO_2 . The change in intensities of different characteristics peaks clearly indicates the incorporation of biopolymer pectin into inorganic counterpart TWM.

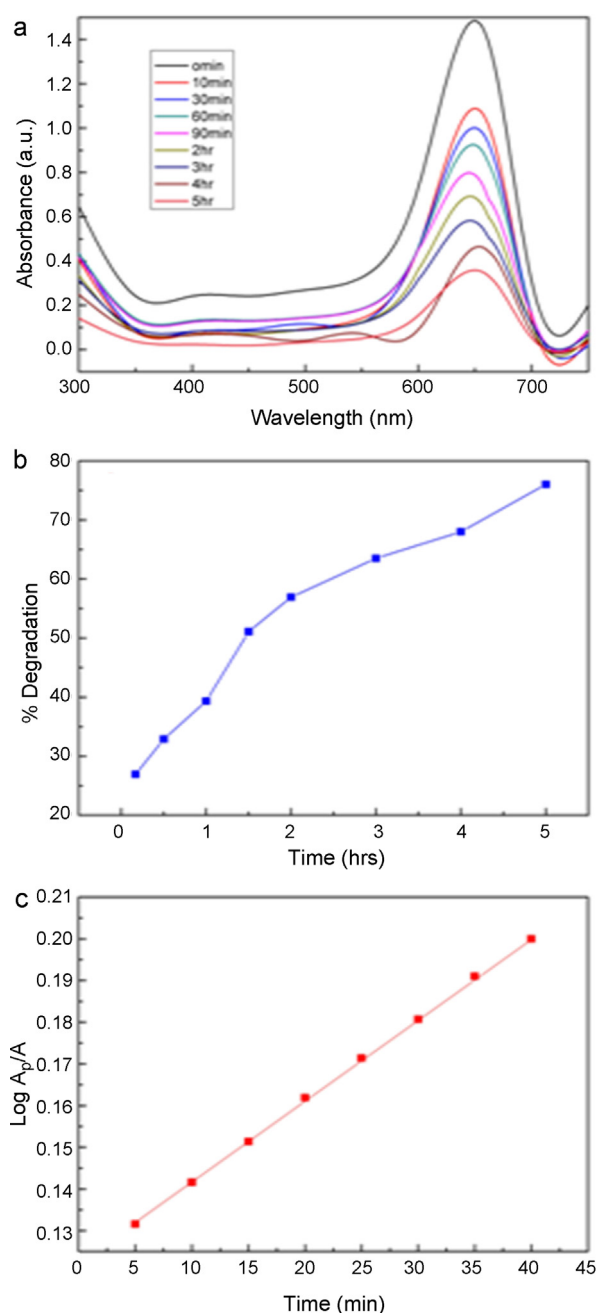


Fig. 3. (a) UV-vis absorption spectra of methylene blue dye for Pc/TWM nanocomposite ion exchanger for different irradiation time (b) percentage degradation of methylene blue dye (c) photocatalytic degradation kinetics of methylene blue dye (initial dye concentration 1.5×10^{-5} , catalyst concentration 0.5 mg/ml).

As evident from TGA analysis of Pc/TWM nanocomposite ion exchanger (Fig not shown), an initial weight loss of 2.94% upto 150°C was recorded. It was due to the removal of external molecules of water from the Pc/TWM nanocomposite (Dual, 1963). A weight loss of 4.6% observed from 150°C to 225°C may be due to the loss of intestinal water molecules by condensation of $-OH$ group. The slow weight loss observed between 225°C and 650°C may be due to the decomposition of organic part of nanocomposite. The weight loss above 650°C may be due formation of metal oxides (Nabi et al., 2011a,b).

The X-ray diffraction pattern of Pc/TWM nanocomposite ion exchanger at room temperature reveals that the nanocomposite material is semi crystalline in nature (Fig not shown).

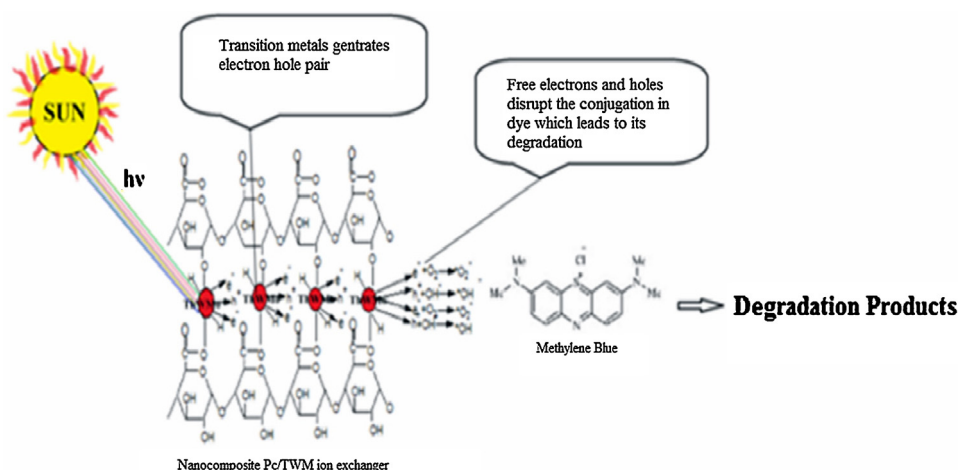


Fig. 4. Proposed mechanism for photocatalysis of methylene blue using Pc/TWM nanocomposite ion exchanger.

Scanning electron micrographs of the TWM and Pc/TWM nanocomposite ion exchanger at different magnification confirmed the rough morphology of Pc/TWM nanocomposite as compared to that of TWM having smooth morphology. SEM images further inferred the incorporation of pectin onto Pc/TWM nanocomposite (Fig not shown).

TEM images of Pc/TWM nanocomposite at different magnification reveals that the particle size in nano range (35–80 nm) (Fig. 2).

The EDX spectrum confirmed that thorium and tungsten were main components present in the nanocomposite.

The distribution coefficients studies for metal ions showed that Pc/TWM nanocomposite material is selective for Cr and Pb.

3.1. Photocatalytic activity

The photo catalytic degradation of methylene blue dye using Pc/TWM nanocomposite is depicted in Fig. 3. It was observed that about 76% of MB dye was degraded with in five hours of photo radiation. The rate of photocatalytic degradation of different dyes has been reported to follow pseudo first order kinetic model (Davis, 1963; Rupa, Manikandan, Divakar, & Sivakumar, 2007; Xu, Ao, Fu, & Yuan, 2008):

$$r = \frac{dC}{dt} = k_{app}t$$

On integrating the above equation, we get

$$\ln \frac{C_0}{C_t} = K_{app}t$$

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 $\ln C_0/C_t$ vs irradiation time showed a linear correlation with good precision as shown in Fig. 3(c). Thus the photo degradation of MB dye using Pc/TWM nanocomposite ion exchanger was fitted in pseudo first order kinetics. The value of rate constant $K=0.00196 \text{ min}^{-1}$ was calculated from the slope of the plot with $R^2=0.9997$.

The photo degradation of methylene blue onto Pc/TWM Nano composite was feasible due to the presence of transition metals such as thorium, tungsten and molybdate present in ion exchanger (Fig. 4). The metal ions generate electron hole pair, which leads to disruption of dye molecules. The proposed mechanism for mineralization of methylene blue dye may be as follows:

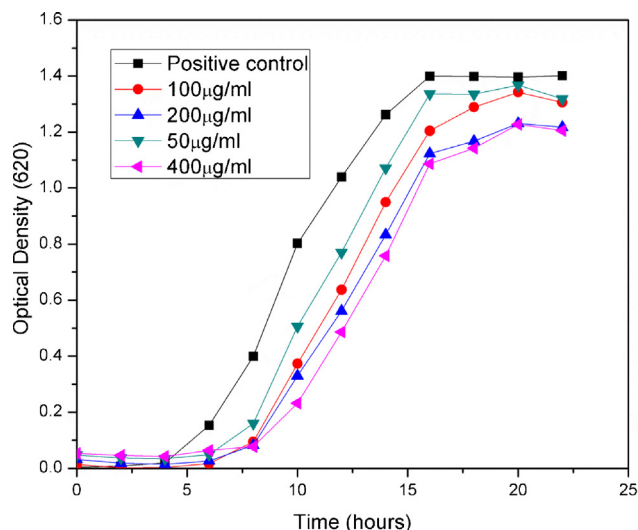
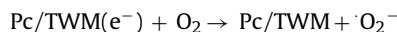


Fig. 5. Growth curve of *E. coli* in presence of Pc/TWM nanocomposite ion exchanger.



3.2. Antibacterial activity

The antibacterial activity of the Pc/TWM nanocomposite was investigated against *E. coli* bacteria as shown in Fig. 5. Pc/TWM exhibited significant antibacterial activity against *E. coli*. The antibacterial activity was optimal at 400 µg/ml of Pc/TWM loading for 24 h.

4. Conclusions

The Pc/TWM nanocomposite demonstrates high ion exchange capacity and thermal stability. The composite was found to be highly selective for Cr and Pb metal ions thereby showing great potential as heavy metal ions removal from aqueous solutions. 76%

of a model methylene blue dye was photocatalytically degraded by the nanocomposite after its exposure to five hours in sunlight that implies its potential as an advanced hybrid photocatalyst for environmental remediation of similar pollutants. Pc/TWM further exhibited significant antibacterial activity against *E. coli* bacteria. The antibacterial activity was optimal at 400 µg/ml of Pc/TWM loading for 24 h; thereby indicating that Pc/TWM may be used as an effective antibacterial material against various microorganisms that can endanger human beings.

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