

A cellulose acetate based nanocomposite for photocatalytic degradation of methylene blue dye under solar light

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Abstract In this work, cellulose acetate–tin (IV) phosphate nanocomposite (CA/TPNC) ion exchanger has been explored for its photocatalytic degradation of methylene blue dye from aqueous solution. The CA/TPNC was characterized using Fourier transform infrared (FTIR) spectroscopy, transmission electron microscopy (TEM) and X-ray diffraction (XRD). The ion exchange capacity of nanocomposite ion exchanger was observed to be high (1.48 meq g^{-1}) for Na^+ ion as compared to their inorganic counterpart (0.56 meq g^{-1}). The CA/TPNC material was the photocatalytic degradation of methylene blue dye onto CA/TPNC was investigated for 140 min of solar irradiation at 662-nm wavelength. The 80 % the dye was removed onto CA/TPNC after 60 min of irradiation. The rate of photodegradation of MB dye onto CA/TPNC followed the pseudo-first-order kinetic model.

Keywords Cellulose acetate · Nanocomposite · Ion exchange property · Photocatalysis

Introduction

Environmental pollution caused by different toxic pollutants from the domestic use and industrial activity has been of significant concern. Organic pollutants have been added into the water system from industrial effluents, agriculture waste and chemical stumple [1–3]. These pollutants due to toxic, mutagenic and carcinogenic nature cause serious effects to human health. Hence, the removal of the organic dyestuff from waste effluents becomes the focus of important concern. The synthetic dyes have adverse impact on the aquatic submerged plants and resulted in slow photosynthesis process [4–6]. Many organic dyes have complex structures and high resistance to biological oxidation; therefore, it was a great challenge for the decolourization and complete removal from the water system [7, 8]. Many methods such as chemical oxidation, biological treatment, coagulation, flocculation, adsorption, electrochemical, precipitation, adsorption and photocatalysis have been used for the removal of dyes from wastewater [9–23]. However, most of these methods are costly and cannot be effectively used for the treatment of a wide range of organic dye [24]. Photocatalysis has been presently considered as the most efficient method for the removal of the organic dyes from wastewater due to its simplicity, financial practicality, technical feasibility and social suitability [25].

Organic–inorganic nanocomposite ion exchanger has been used in environmental remediation due to their good selectivity and specificity [26, 27]. The remediation of metal ions and dyes from polluted water has been carried out by using several biomaterial-based nanocomposite materials [28–30]. A number of bioadsorbents such as bacterial biomass and biopolymers have been explored for the removal of toxic pollutants from water systems [31, 32]. They are biodegradable, cost

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effective, harmless and richly available. Due to low stability, difficulty in separation and low recovery after desorption are the major limitations found in bioadsorbents [33].

Photosensitized degradation of coloured pollutants from wastewater using nanocomposites has been of great significance [34–36]. In recent years, advanced oxidation processes (AOPs) have been suggested as an alternative to conventional methods for the degradation of organic pollutants. AOPs oxidize quickly and non-selectively a broad range of organic pollutants [37, 38]. Heterogeneous photocatalysis via combination of semiconductor and UV light was considered to be one of the promising advanced oxidation processes for the destruction of water-soluble organic pollutants present in wastewater.

In the recent years, our group has been extensively involved for the photocatalytic degradation of dyes using nanocomposite ion exchangers [39, 40]. The outcomes from this research provide great potential of nanocomposite ion exchangers for the treatment of organic pollutant. Until now, no data is available regarding the use of cellulose acetate based tin (IV) phosphate nanocomposite as photocatalyst for the degradation of methylene blue dye from the water system in presence of visible light.

This work deals with the synthesis of cellulose acetate–tin (IV) phosphate nanocomposite (CA/TPNC) ion exchanger by simple sol–gel method. CA/TPNC ion exchanger has been subjected for different spectral analyses. Moreover, the CA/TPNC ion exchanger was investigated for the photocatalytic degradation of methylene blue dye from aqueous medium in presence of sunlight.

Materials and methods

Materials

The reagents tin (IV) chloride and sodium dihydrogen phosphate were procured from Loba Chemia Pvt. Ltd., Mumbai, India. Other chemicals such as formic acid (E. Merck Ltd., India) and cellulose acetate (CDH Pvt. Ltd., New Delhi, India) were used as received. Methylene blue dye was obtained from S. D. Fine Ltd., India. The solutions of desired concentrations were prepared by diluting the stock solution with double-distilled water. The absorbance measurements were recorded on a UV-visible spectrophotometer (Shimadzu UV-1601, Japan).

Synthesis of cellulose acetate–tin (IV) phosphate nanocomposite

Cellulose acetate–tin (IV) phosphate nanocomposite ion exchanger was synthesized using sol–gel method in two steps. In the first step, 0.1 M sodium dihydrogen phosphate solution

and 0.1 M tin (IV) chloride solution were mixed with continuous stirring at pH 0–1 as per method discussed earlier [40]. The mixture was stirred for 60 min to obtain tin (IV) phosphate (TP) precipitates. In next step, 4 % (v/v) cellulose acetate (CA) gel was prepared in concentrated formic acid. The gel was added to tin (IV) phosphate solution with continuous stirring. The resultant mixture was allowed to stand overnight with occasional shaking for digestion. Then, the supernatant liquid was removed and precipitates were washed with demineralized water several times to remove the excess of reagents. The precipitates were converted into H^+ by keeping in 0.1 M HNO_3 solution for 24 h. Then, the precipitates were filtered and washed with demineralized water and finally dried in hot air oven at 50 ± 2 °C.

Ion exchange capacity

The ion exchange capacity of CA/TPNC was determined as per method discussed earlier [40]. In a typical procedure, 1 g of the material in H^+ form was placed in a glass column of 1-cm internal diameter with glass wool support at the bottom. The column was washed with double-distilled water to remove excess of the acid. The H^+ ions from the column of CA/TPNC were eluted with 1.0 M KCl solution. The flow rate was maintained at 0.5 mL min^{-1} . The collected effluent was titrated against a standard alkali solution using phenolphthalein indicator. The hydrogen ions released were calculated using the formula as follows [41, 42]:

$$IEC = \frac{N \times V}{W} \text{mg/g} \quad (1)$$

where IEC is ion exchange capacity, N and V (mL) are the normality and the volume of NaOH, respectively, and W (mg) is the weight of CA/TPNC.

Fourier transformer infrared spectra

Fourier transform infrared (FTIR) absorption spectrum of nanocomposite ion exchanger was recorded in the wave number $400\text{--}4000 \text{ cm}^{-1}$ using a Fourier transform infrared spectrophotometer (Perkin Spectrum-400) using KBr disc method. In this, 10 mg of CA/TPNC in H^+ form was thoroughly mixed with 100 mg of KBr and grounded to very fine powder. The transparent disc was formed by applying the pressure.

Transmission electron microscopy

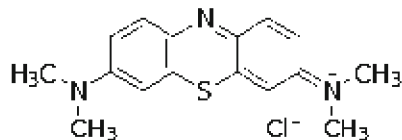
The particles size and morphology of CA/TPNC ion exchanger were analysed with high-resolution transmission electron microscopy (Hitachi, H7500, Germany).

Photocatalytic activity of cellulose acetate–tin (IV) phosphate nanocomposite

The photocatalytic experiment was carried out in a batch reactor at 30 ± 0.5 °C. In this method, 2×10^{-5} M solution of methylene blue (MB) dye was prepared in double-distilled water, and 100 mg of nanocomposite ion exchanger in H^+ form was added with continuous stirring. In adsorption experiments, slurry composed of dye solution and nanocomposite ion exchanger suspension was stirred magnetically and placed in the dark to establish adsorption–desorption equilibrium. In case of photocatalytic studies, the suspension composed of dye and catalyst was stirred for 15 min and exposed to natural solar light radiations. The 5 mL of solution was withdrawn at different intervals of time and centrifuged. The absorbance was recorded in the range of 300 to 750 nm and kinetics of MB degradation was studied. The percentage degradation of methylene blue dye was calculated using the following formula:

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

where C_e and C_t are the concentration of dye at equilibrium and at time t . The structure on MB is shown below:



Results and discussion

FTIR analysis

The observed ion exchange capacity for potassium ions was found to be 1.28 meq/g. FTIR spectra of CA/TPNC and CA are shown in Fig. 1a–c. A broad peak observed at 3434 cm^{-1} may be due to presence of external water molecule [43]. Absorption band at 1741 cm^{-1} corresponds to carbonyl group of cellulose acetate in Fig. 1a. The absorption peak at 1633 cm^{-1} was due to free water molecule and strongly bonded –OH group in the matrix. It is observed that peaks 3434 , 1741 and 1378 cm^{-1} for CA spectra are shifted to 3432 , 1744 and 1376 cm^{-1} spectra of CA/TPNC (Fig. 1b). This shift in the absorption bands confirmed the formation of composite material. The sharp peak at 1039 cm^{-1} may be due to PO_4^{3-} , HPO_4^{2-} and $H_2PO_4^-$ [25]. The absorption peak at 1376 cm^{-1} may be due to vibration of hydroxyl groups. Further, the absorption band at 490 cm^{-1} may be due to superposition of metal–oxygen stretching vibrations confirming the binding

between cellulose acetate and tin (IV) phosphate [44]. The marked shift in peak positions from 3432 to 3433 cm^{-1} , 1744 to 1742 cm^{-1} , 1051 to 1053 cm^{-1} and 1633 to 1647 cm^{-1} in the spectra of CA/TPNC and MB dye adsorbed CA/TPNC (Fig. 1c) suggest the interaction of dye molecules with functional groups of nanocomposite.

Transmission electron microscopy analysis

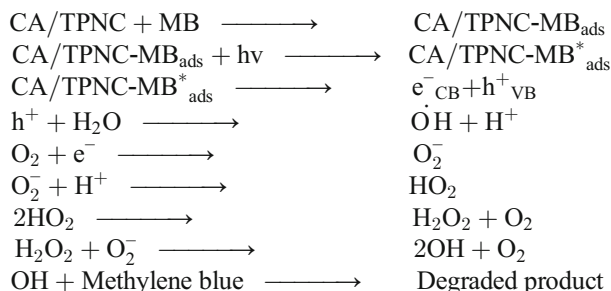
The transmission electron micrographs of CA/TPNC ion exchanger at different magnifications are shown in Fig. 2. The result revealed the wrapping of TP with CA to form the composite material. The TEM images confirmed the formation of particles size in the range of 3–15 nm [45].

Photocatalytic activity of CA/TPNC

The photocatalytic activity of tin (IV) phosphate (TP), cellulose acetate (CA) and cellulose acetate–tin (IV) phosphate nanocomposite (CA/TPNC) were determined for the degradation of methylene blue dye at various parameters as $[MB] = 2 \times 10^{-5}$ M, $pH = 4.2$, catalyst dose = 100 mg, time = 150 min, wavelength = 662 nm. It has been revealed that the decrease in MB absorbance was more in CA/TPNC as compared to TP and CA, which confirmed the more degradation of MB onto composite as shown in Fig. 3.

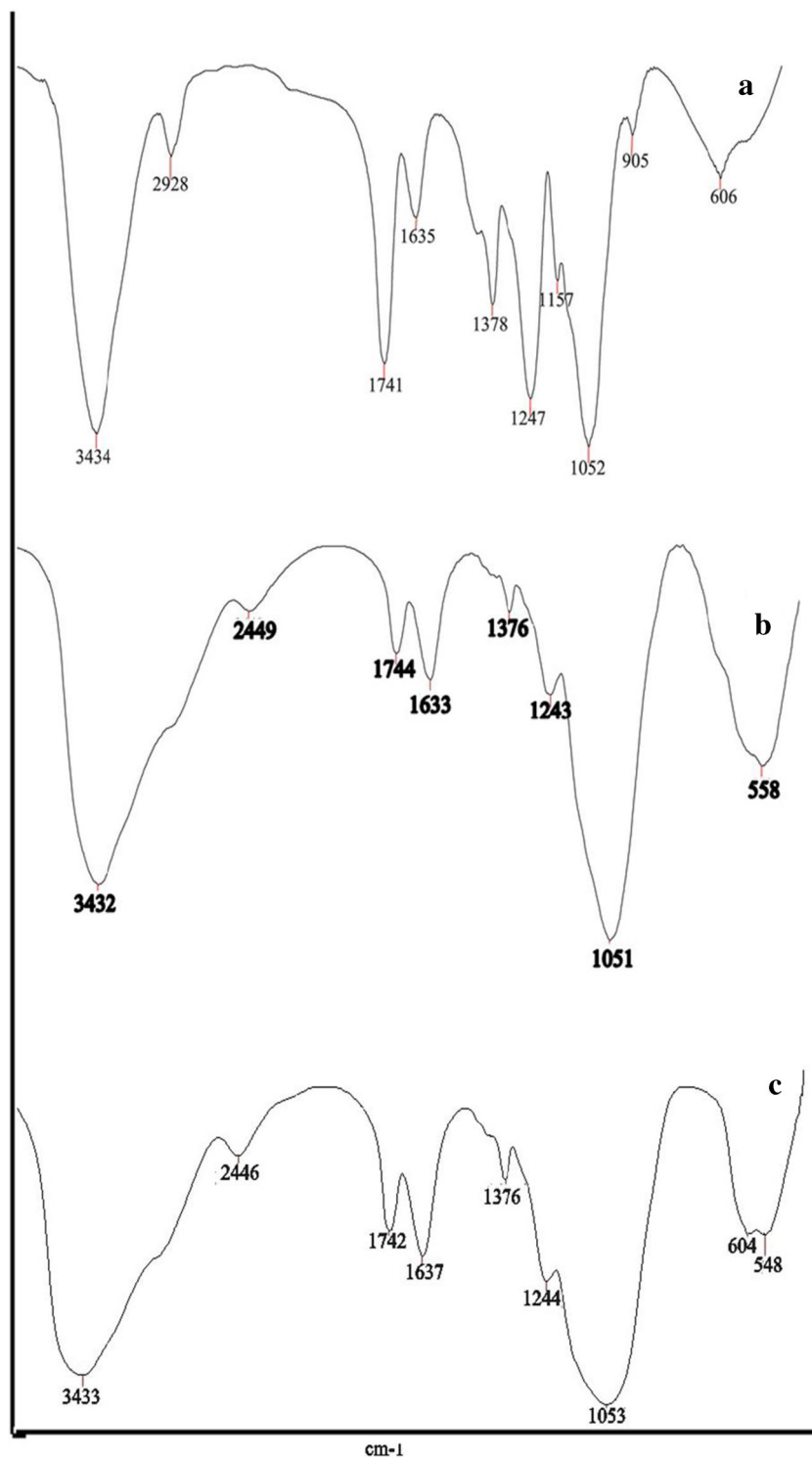
The high degradation percentage of MB onto CA/TPNC was due to the presence of both the CA and TP in a nanocomposite ion exchanger. Moreover, high photocatalytic activity of CA/TPNC ion exchanger may be due to simultaneous adsorption and photocatalytic activity of composite material [46]. The mechanism of photocatalytic degradation of methylene blue (MB) onto CA/TPNC was shown below.

On irradiation, the conduction band electrons were transferred to the surface of catalyst, producing electron–hole pair ($h_{\nu b}^+ / e_{\nu b}^-$). At the conduction band, electrons reduced the O_2 to hydroxyl radicals (OH^\cdot). The valance band holes react with OH^- / H_2O and form OH^\cdot radicals [47]. The highly oxidizing OH^\cdot radicals were responsible for the degradation of MB dye. The probable mechanism is as follows:



As evident from Fig. 5a, about 60 % of the dye was removed in 20 min of radiation time onto CA/TPNC

Fig. 1 FTIR spectra. **a** CA, **b** CA/TPNC and **c** CA/TPNC after adsorption of MB



compared to 18 and 5 % degradation of MB onto TP and CA under the same conditions. The photodegradation of dye was elucidated on the basis of decrease in dye concentration both in bulk solution and catalyst surface [48]. The photocatalytic degradation depends on dye concentration in bulk and on the surface of catalyst. It was observed that about 80 % the MB dye was degraded onto CA/TPNC after 60 min of irradiation.

The photodegradation of MB dye was studied under different conditions—equilibrium adsorption in the dark, simultaneous adsorption and degradation, and equilibrium adsorption followed by photodegradation onto TP, CA and CA/TPNC in presence of solar radiation. For the equilibrium adsorption in the dark, only 8, 3 and 45 % degradation was recorded within 20 min of irradiation for TP, CA and CA/

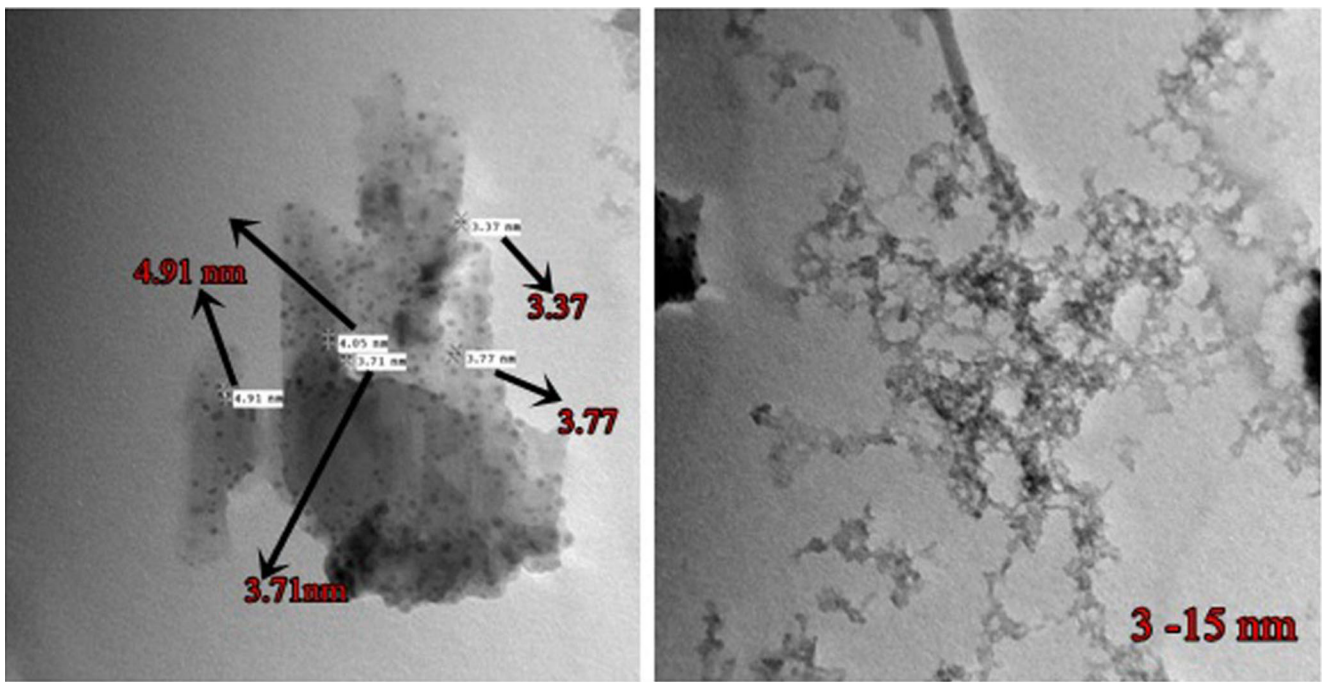


Fig. 2 TEM micrograph of CA/TPNC ion exchanger at different magnifications

TPNC (Fig. 4a). In simultaneous adsorption and degradation (Fig. 3), the MB dye degradation onto different catalysts was 18, 5 and 60 % for TP, CA and CA/TPNC, respectively. In case of simultaneous adsorption followed by photodegradation process (Fig. 5), the instant amount of dye adsorbed onto the surface of catalysts was not very high due to screening effect of sunlight and provided sufficient active sites to generate valance band holes and conduction band electrons [49].

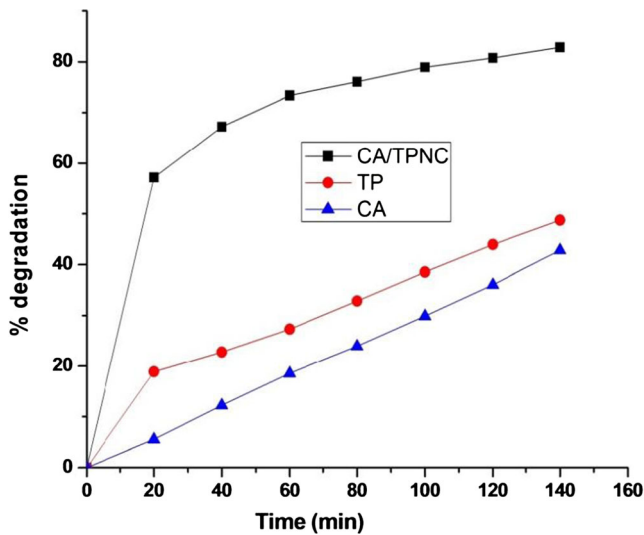


Fig. 3 Photocatalytic degradation of methylene blue dye onto CA, TP and CA/TPNC in presence of solar light at different experimental conditions: initial dye concentration = 2×10^{-5} M, pH=4.2, catalyst dose= 100 mg, time=150 min and wavelength=662 nm

The photocatalytic degradation of dyes obeyed pseudo-first-order kinetic model and the rate of degradation was calculated as follows [50]:

$$r = -\frac{dc}{dt} = k_{app}t \tag{3}$$

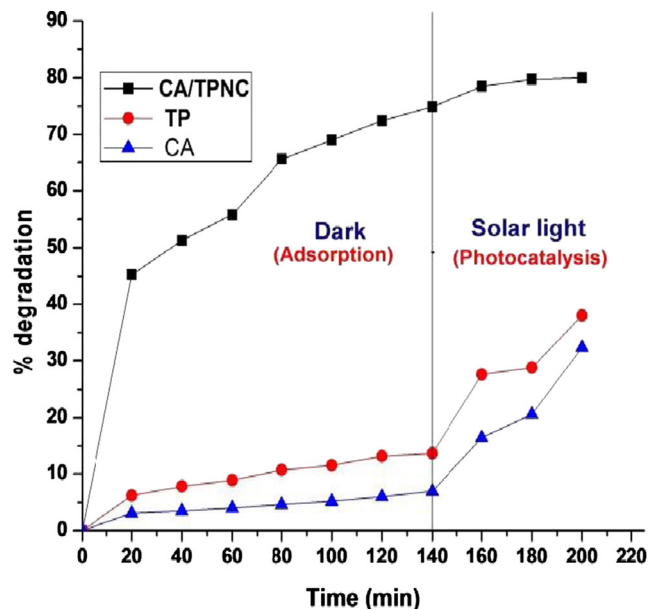


Fig. 4 Equilibrium adsorption followed by photocatalytic degradation onto TP, CA and CA/TPNC in the presence of solar light at different experimental conditions: [MB] = 2×10^{-5} M, pH = 4.2, catalyst dose = 100 mg, time = 150 min and wavelength = 662 nm

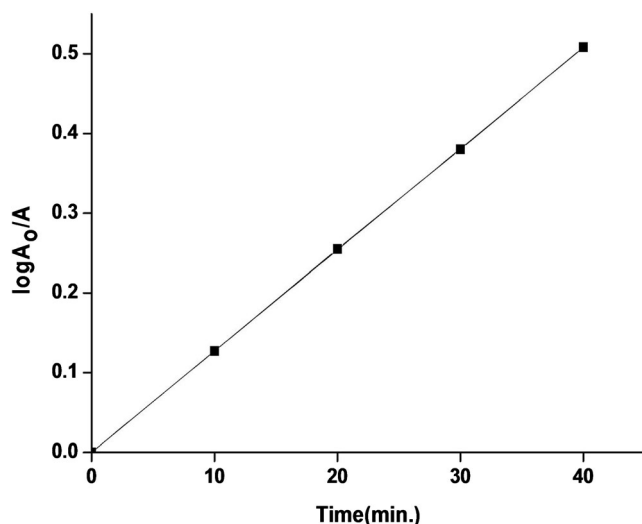


Fig. 5 Kinetics of MB dye degradation onto CA/TPNC ion exchanger

On integrating the above equation, we get

$$\ln C_0/C_t = K_{app}t \quad (4)$$

where K_{app} is the apparent rate constant, C_0 is the concentrations of dye before radiation and C_t is the concentration of dye at time t . The plot of $\ln C_0/C_t$ versus irradiation time resulted in linear correlation with good precision as shown in Fig. 5. Thus, the photodegradation of MB dye using nanocomposite ion exchanger was fitted well in pseudo-first-order kinetics. The value of rate constant $K = 0.0126 \text{ min}^{-1}$ was calculated from the slope of the plot with $R^2 = 0.9998$.

Conclusion

In the present study, the synthesized cellulose acetate–tin (IV) phosphate nanocomposite (CA/TPNC) ion exchanger has been successfully explored for the photocatalytic degradation of methylene blue from wastewater. The different spectral analyses confirmed the formation of nanocomposite material. CA/TPNC exhibited high ion exchange capacity with significant photocatalytic activity compared to their counterparts. The simultaneous adsorption and photocatalytic processes proved to be highly efficient for the degradation of methylene blue dye.

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