

Fabrication and characterization of a nanocomposite hydrogel for combined photocatalytic degradation of a mixture of malachite green and fast green dye

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Received: 22 December 2016 / Accepted: 15 February 2017 / Published online: 22 March 2017
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Abstract In this study, starch/poly(alginic acid-*cl*-acrylamide)/Fe/Zn nanocomposite hydrogel (*ST/PL(AA-cl-AAm)/Fe/Zn NCHG*) was synthesized by polymerization/co-precipitation method. This nanocomposite hydrogel was prepared with the notion to remove the mixture of organic pollutants from the water system. Mixture of malachite green and fast green dye was used to check the photocatalytic degradation ability of the prepared nanocomposite hydrogel. *ST/PL(AA-cl-AAm)/Fe/Zn NCHG* was characterized by X-ray diffraction, transmission electron microscopy, scanning electron microscopy and Fourier transform infrared. The degradation of the two dyes followed the pseudo-first-order kinetics. The results showed that by using the prepared nanocomposite hydrogel, 91% of malachite green and 82% of fast green dye, respectively, were degraded within 5 h of their contact.

Keywords Starch · Nanocomposite hydrogel · Alginic acid · Adsorptional photocatalysis

Introduction

Industrial effluents contribute the most to the addition of various types of dyes into the water system. These dyes not only affect the aquatic life but also disrupt the whole ecosystem. The dyes easily get mixed with the water and reduce the photocatalytic activity of underwater plants, and hence affecting the food chains. In addition, dyes also make the water unfavorable for drinking, irrigation and recreation purposes. Azo dyes are quite toxic and carcinogenic in nature [1]. They easily enter into the body through ingestion and damage the DNA. Workers in textile industries are most prone to respiratory problems caused by the harmful dyes. So, their removal is the major priority. Researchers have tried to remove the dyes from wastewater using different techniques such as osmosis, precipitation, electrokinetic coagulation, microbial degradation, fungal decolorization, electro dialysis, nanofiltration, electrosorption, adsorption and filtration [2–4]. However, adsorption is considered as the best technique for the removal of dyes from the wastewater due to its simple methodology and cost-effectiveness. Different adsorbing materials such as hydrogels, activated carbon and clay minerals have been used for the removal of dyes.

Hydrogels are the three-dimensional network materials having high adsorbing ability. Their water adsorbing ability is due to the hydrophilic groups present in their structure. The organic pollutants get adsorb into hydrogels as the ionic groups of organic pollutants form physical or chemical interaction with hydrophilic groups of hydrogels [5–10]. The addition of reinforcing agents and using crosslinkers during their synthesis helps in increasing the mechanical strength of the hydrogels. Changing the pH, temperature, agitation time, etc. during synthesis of hydrogels helps in tailoring their properties. Their

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application area includes drug delivery in a controlled manner, tissue engineering, micro-irrigation, etc. [11–17].

Nanocomposite hydrogels contain both organic and inorganic counterparts. They bridge the gap between organic and inorganic counterparts and also overcome the nonuniformity at the structural level [18–21]. A major breakthrough occurred when Haraguchi et al. prepared the first ever nanocomposite hydrogel using free radical polymerization. These days, number of materials has been used such as carbon nanotubes, graphene oxide, carbon dots, metal oxides and ceramics, etc. so as to make novel nanocomposite hydrogels having improved mechanical properties [22–25].

The use of nanocomposite hydrogel materials as a photocatalyst is one of the recent inventions which help in the removal of organic pollutants from the wastewater. The photocatalytic ability of these composites helps in monitoring and improving the ecosystem [26–29]. They actually remove the toxic organic pollutants to the maximum extent under different conditions. These are the most preferred materials due to their low cost and almost nil production of harmful by-products [30, 31].

In the present paper, a novel starch/poly(alginic acid-cl-acrylamide)/Fe/Zn nanocomposite hydrogel (ST/PL(AA-cl-AAm)/Fe/Zn NCHG) has been synthesized and the ability of this nanohydrogel composite for the adsorptional photocatalytic degradation of mixture of malachite green and fast green dye has been reported.

Experimental

Chemicals and reagents used

Ferric nitrate, zinc nitrate, starch, ammonium per sulfate and sodium borohydride were obtained from CDH Pvt. Ltd, India. Alginic acid and acryl amide were purchased from Loba Chemie Pvt. Ltd, India. *N,N'*-methylene bis-acryl amide was obtained from S-D Fine Chem. Limited.

Apparatus

Electronic balance (Kerro BLC 3002), centrifuge machine (Instruments, chemical private limited), oven (NSW India) and UV–visible spectrometer (INCO Instrument and Chemical Private Limited). X-ray diffractometer (Philips 1830 diffractometer), transmission electron microscope (Techni G2 20 S-Twin), Fourier transform infrared (FTIR) spectrophotometer (Nicolet 5700 FTIR Spectrophotometer) and scanning electron microscope (JSM 6100) were used for the characterization of the synthesized nanocomposite hydrogel.

Preparation of reagents

2 M solution of acryl amide, 1 M solution of alginic acid, 1% starch solution, 0.1 M ferric nitrate solution, 0.1 M zinc nitrate solution, 0.1 M sodium borohydride solution, 5% ammonium per sulfate (weight of acryl amide, alginic acid and starch) as an initiator and 3% *N,N'*-methylene bis-acryl amide (weight of acryl amide, alginic acid and starch) as a crosslinker were used and prepared in double-distilled water.

Synthesis of ST/PL(AA-cl-AAm)/Fe/Zn NCHG

The ST/PL(AA-cl-AAm)/Fe/Zn NCHG was synthesized by polymerization/co-precipitation method. 1 M alginic acid solution and 1% starch solution were added to the 2 M solution of acryl amide dropwise with constant stirring. Then, 5% ammonium persulfate as an initiator and 3% *N,N'*-methylene bis-acrylamide as a crosslinker were added with constant stirring. The resultant mixture was stirred for 5 h at 65 °C over the magnetic stirrer with hot plate. The obtained precipitates of ST/PL(AA-cl-AAm) NHG were filtered, washed and dried in hot air oven at 50 °C. The precipitates were then added to the mixture of 0.1 M ferric nitrate and 0.1 M zinc nitrate solution and stirred for 4 h. Finally, precipitates were filtered and added to the 0.1 M solution of sodium borohydride, and the solution was made to remain as such for 3 h. The obtained precipitates were filtered, washed and dried in hot air oven at 50 °C. The % yield of the reaction was calculated by using following formula [32]:

$$\% \text{ yield} = \frac{W_R - W_P}{W_R} \times 100 \quad (1)$$

where W_R is the weight of reactants and W_P is the weight of product.

Characterization

Fourier transform infrared (FTIR) spectroscopy

The Fourier transform infrared spectrum of ST/PL(AA-cl-AAm)/Fe/Zn NCHG was recorded using Nicolet 5700 FTIR spectrophotometer. Spectrum was documented in the range of 400–4000 cm^{-1} . The nanocomposite hydrogels were methodically mixed with KBr and were then powdered. A pressure of about 80,000 psi was applied to make a transparent disk and it was then completely characterized to find the type of functional groups present [33].

X-ray diffraction (XRD)

X-ray diffraction data were recorded using X-ray diffractometer (Philips 1830 diffractometer). It helped in

examining the nature of synthesized *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG.

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is the most widely used instrument to characterize the physical properties such as morphology, shape and size distribution of materials at the micro- and nanoscale. SEM helps in the identification and also for the morphological characterization of nanocomposites. SEM uses high-energy electron beam. This electron beam interacts with the sample and helps to appraise the surface and morphological identification of the *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG [34]. The surface and morphological studies of *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG were carried out using scanning electron microscope JSM 6100.

Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) images of the *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG was recorded using Techni G2 20 S-Twin. It is basically an electron-based technique that uses transmitted electrons for the elucidation of the structure, shape and size of the sample. In this technique, ultrasonicated nanocomposite hydrogel was loaded on gold-coated grid and a transmitted electron beam was detected on the other side which helped in the structural explanation.

Adsorptional photocatalysis

The adsorptional photocatalytic activity of *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG was explored for the degradation of mixture of malachite green and fast green dye in the presence of solar light. A double-walled Pyrex glass chamber was jacketed with thermostatic water circulation to carry out the photocatalytic experiments. A constant temperature of $25\text{ }^{\circ}\text{C} \pm 1$ was maintained throughout the experiment. 100 mg of the *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG was added into 2×10^{-6} M solution of malachite and fast green dye to form slurry [35, 36]. The slurry was subjected firstly to adsorption for 1 h kept in dark to attain the adsorption–desorption equilibrium, and after that, it was directly exposed to sunlight for photocatalysis. Nearly around 3 mL of the dye solution was withdrawn at various time intervals and centrifuged to confiscate particles of the *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG. The absorbance was recorded in the range of 300–750 nm, and the kinetics of the adsorptional photocatalytic degradation of mixture of dyes was investigated at 620 nm for MG and 625 nm for FG. The percent degradation of dye was calculated by using following formula [37]:

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

where C_0 and C_t are the concentrations of dye at equilibrium and at time t .

Results and discussion

Synthesis of *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG

The *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG was synthesized using polymerization/co-precipitation method. *ST/PL(AA-cl-AAm)* NHG was prepared by the addition of 1 M alginic acid, 1% starch solution and 2 M acrylamide solution in the presence of crosslinker *N,N'*-methylene bis-acrylamide and initiator ammonium per sulfate. The obtained precipitates of *ST/PL(AA-cl-AAm)* NHG were then made to react with ferric nitrate and zinc nitrate, which resulted in the desired nanocomposite hydrogel, *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG. The reaction yield of *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG was found to be 88%.

Characterization

Fourier transform infrared spectra of *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG are shown in Fig. 1. The peaks between 1078 and 1022 cm^{-1} indicated the characteristic peaks of the crystalline and amorphous structure of starch, respectively [34]. The absorption peaks at 926 and 881 cm^{-1} were assigned to the cyclic ether groups [38]. The projecting peaks at 3333.915 and 1727.489 cm^{-1} were due to –OH and C=O stretching functionalities. The peaks at 459 and 559 cm^{-1} were due to the Fe–O and Zn–O stretching [39, 40]. The XRD pattern of the *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG is shown in Fig. 2. The diffractogram of *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG showed broad peaks at $2\theta = 18.1^{\circ}$, 30.155° , 34.54° , 43.1° , 56.6° and 70.4° for iron and zinc [41–45]. Three diffraction peaks centered at

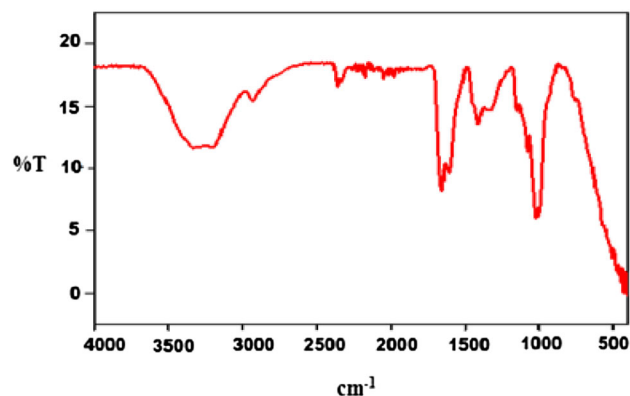


Fig. 1 FTIR spectra of *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG

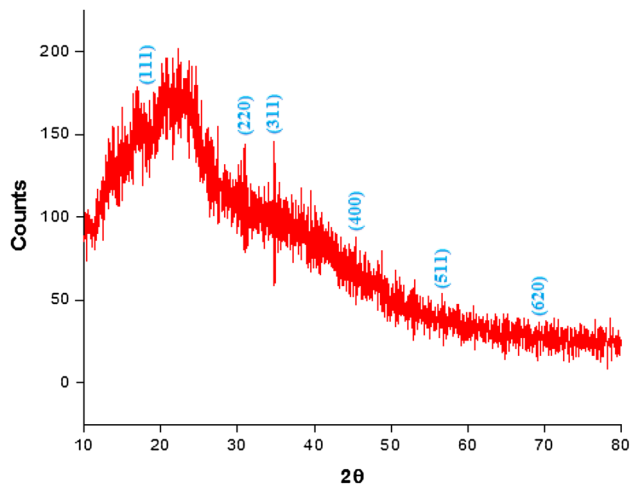


Fig. 2 XRD of *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG

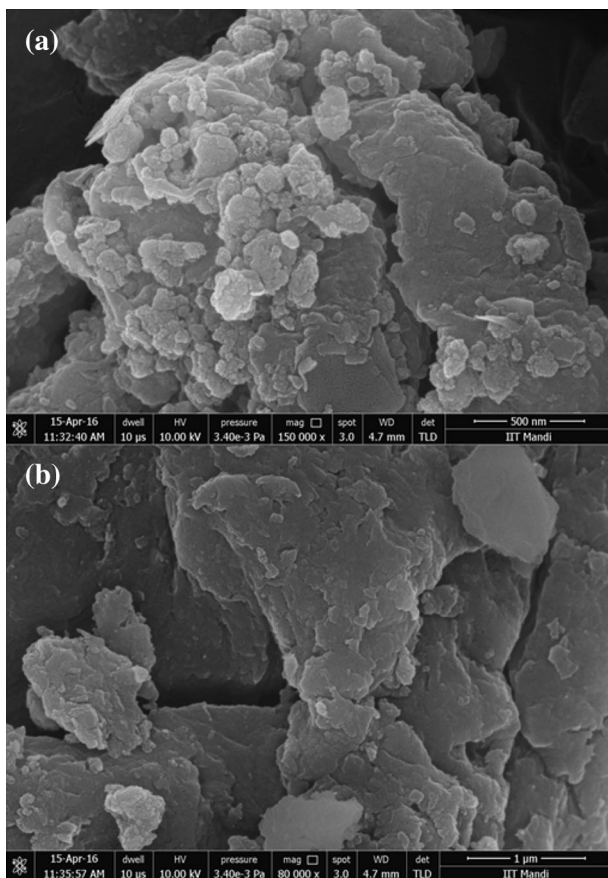


Fig. 3 a, b SEM images of *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG

$2\theta = 30.155^\circ$, 34.54° and 43.1° were observed for iron, which can be assigned to (220), (311) and (400) diffraction planes, respectively. Three diffraction peaks centered at 18.1° , 56.6° and 70.4° are observed for zinc, which can be assigned to (111), (511) and (620) planes, respectively. The

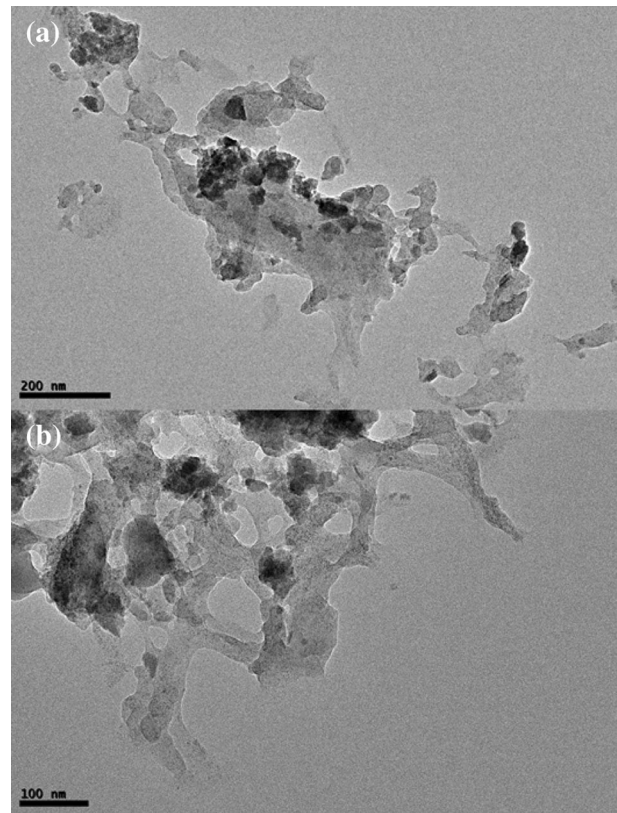


Fig. 4 a, b TEM images of *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG

XRD results confirm the semicrystalline nature of *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG. Figure 3a, b shows the SEM images of *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG at different magnifications. It indicates the irregular and rough nature of the synthesized *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG. TEM images of *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG are shown in Fig. 4a, b at different magnifications. TEM images confirmed the binding between Fe/Zn and *ST/PL(AA-cl-AAm)* NHG. The average size ranges from 40 to 90 nm for *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG.

Applications

Photocatalytic activity

The photocatalytic degradation of mixture of malachite green and fast green dye by *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG is shown in Fig. 5a–c. Figure 5a depicts the changes in absorbance spectrum of malachite green and fast green dye with degradation time. The process of photocatalytic activity occurs in two steps: adsorption and adsorptional photocatalysis [46]. It was observed that maximum 20% of mixture of malachite green and fast green dye get adsorbed after 1 h of contact time and 71 and 62% of malachite green and fast green dye undergoes

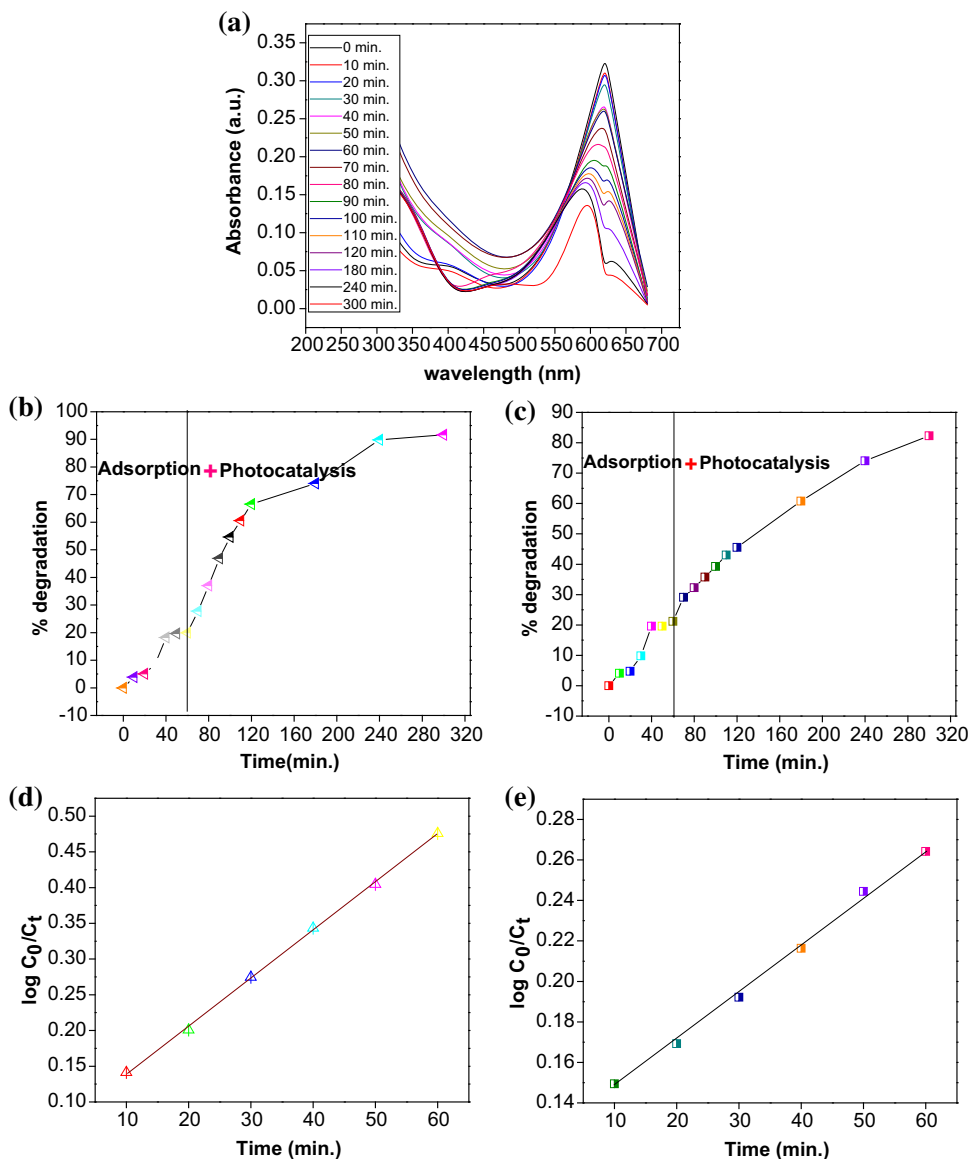


Fig. 5 Degradation and kinetics plots for mixture of malachite green and fast green dye under coupled process in the presence of *ST/PL(AA-cl-AAm)/Fe/Zn* NCHG. **a** Spectrum of malachite green and fast green dye, **b** percent removal of malachite dye, **c** percent removal

of fast green dye, **d** pseudo-first-order kinetics for degradation of malachite dye and **e** pseudo-first-order kinetics for degradation of fast green dye

photocatalysis in 4 h of photoperiod, respectively. About 91% of malachite green and 82% of the fast green dye were degraded within 5 h of combined adsorptional photocatalysis process as shown in Fig. 5b, c. The rate of photocatalytic degradation of different dyes has been reported to follow pseudo-first-order kinetic model [47–51]:

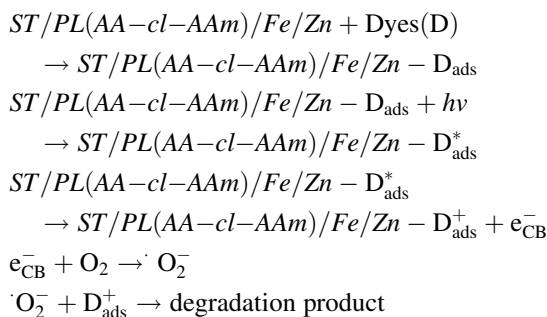
$$r = \frac{dc}{dt} = K_{app}t \tag{3}$$

On integrating the above equation, we get

$$\ln \frac{C_0}{C_t} = K_{app}t \tag{4}$$

where K_{app} is the apparent rate constant, C_0 is the concentration 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 showed a linear correlation with good precision as shown in Fig. 5d, e. Thus, it reveals that the degradation of the two dyes follows pseudo-first-order kinetics [52]. Rate constant of 0.0102 and 0.0019 min^{-1} was observed for malachite green and fast green dye, respectively. The dye degradation under the combined adsorptional photocatalysis process can be schematically represented as:



Conclusion

The synthesis of the starch-based nanocomposite hydrogel (ST/PL(AA-cl-AAm)/Fe/Zn NCHG) has been carried out by simple polymerization/co-precipitation method. It has been used for the photocatalytic degradation of the mixture of two dyes (malachite green and fast green dye), and the results showed that different degradation percentage was observed. The results showed that by using the prepared nanocomposite hydrogel, 91 and 82% of malachite green and fast green dye, respectively, were degraded within 5 h of their contact. The degradation of both the dyes follows pseudo-first-order kinetics. In future, more emphasis will be laid on modifying the prepared nanocomposite hydrogel so as to make it compatible for numerous dyes.

Acknowledgements We would like to thank Shoolini University, Solan for providing the infrastructure and laboratory facilities to carry out the research work.

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