

Jute Fiber Reinforced Hydrogel Composite for Removal of Methylene Blue Dye from Water

Ajadur Rahman Shakil¹, Most. Laboni Begum¹, Md. Aftab Ali Shaikh^{1,2}, Shahin Sultana², Md. Shahidur Rahman¹, Md. Mahamudul Hasan Rumon³, Chanchal Kumar Roy³, and Md. Anamul Haque^{1,*}

¹Department of Chemistry, University of Dhaka (DU), Dhaka-1000, Bangladesh

²Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhanmondi, Dhaka-1205, Bangladesh

³Department of Chemistry, Bangladesh University of Engineering and Technology (BUET), Dhaka-1000, Bangladesh

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Abstract

In this study, a hydrogel composite based on natural jute fiber (JF) has been prepared and employed for the removal of methylene blue (MB) dye from aqueous solution. Polyacrylamide (PAAm) hydrogel was synthesized by thermal polymerization in presence of *N,N'*-methylene bisacrylamide (MBAA) as the cross-linker and potassium per sulfate (KPS) as the initiator. JF reinforced hydrogel (JFRH) composite was prepared by incorporating JF into PAAm matrix prior to the polymerization. The prepared JFRH was characterized by FTIR spectroscopy and scanning electron microscope. It was found that, JFRH composite demonstrated strong mechanical properties with a compressive strength of 1.5 MPa at a deformation of above 80%. The prepared JFRH composite can remove more than 90% of MB from an aqueous solution and be separated easily from the solution after the adsorption process. Therefore, the synthesized JF based hydrogel composite could significantly expand the use of our natural golden fiber for reinforcement of composite materials and removal of dyes from water bodies.

Keywords: Jute fiber, Hydrogel, Methylene blue, Composite material

I. Introduction

Over the last couple of decades, environmental pollution has become a very serious problem in the modern world. Industrialization and urbanization are the main catalyst for these pollutions. The major components of environmental pollutants include metal ion, pesticide, organic dye, aromatic compound, and various organic matters¹. Excess and uncontrolled use of organic dyes in textile, paint, rubber, tannery, rubber and plastic industries lead to the release of huge amounts of untreated colored and contaminated water²⁻⁴. These dyes have potential physical, chemical and toxic impacts on living organisms if left untreated before discharge⁵⁻⁷. Removal of dyes from the industrial discharge or surface water is a big challenge for all of us. So far, various treatment methods for removal of dye from effluents have been investigated and reported. These are, chemical oxidation⁸, adsorption⁹⁻¹¹, chemical reduction¹², photo-degradation¹³, electrochemical oxidation^{14,15}, coagulation-flocculation¹⁶, etc. All the above mentioned methods are hardly reusable, recyclable, economical, applicable and operational, environmental friendly and suitable for commercial application. Although the adsorption method is reported as promising, the difficulties in the separation of adsorbent from the medium after the adsorption of targeted species poses a major challenge. Hydrogel, a polymer-based three-dimensional cross-linked network system, is considered as a promising adsorbent due to their unique characteristics and wide range

of applications. They are capable to absorb large amounts of water and dyestuffs in their structure without disintegration, and also able to desorb these species in specific media. Fiber-reinforced hydrogel composite materials have been found as a provocative recycling use. In recent years, environment-friendly and cost-effective composites have been receiving considerable attraction among the researchers. Renewable resource, natural fiber based composite material can be treated as eco-friendly and low-cost alternatives for synthetic fibers such as carbon and glass fibers. Jute fiber collected from jute plant is the cheaper and available source of natural fiber. The jute fiber material provides several advantages among other natural fibers such including good mechanical strength, low cost, and biodegradability. Synthetic fiber replaced by jute fiber can reduce and control environmental pollution. In addition, jute is the golden fiber of Bangladesh which has been grasped attention as a potential reinforcement of polymer composites¹⁷. So far, millimeter-scale jute fiber based hydrogels are rarely reported except few on submicrometer scale such as jute cellulose¹⁸ and carboxymethylated cellulose nanofiber¹⁹ hydrogels.

In this work, jute fiber reinforced hydrogel (JFRH) composite was fabricated by incorporating JF into the polymer matrix of polyacrylamide (PAAm) and the synthesized JFRH was employed for removal of a dye, methylene blue (MB), from aqueous solution. Prior to synthesis JFRH composite, a mixture solution was prepared

* Corresponding author. e-mail: anamul@du.ac.bd

using AAm, MBAA and KPS. Various amount of JF was soaked by the mixture solution in a test tube and kept it in oven at 60°C for polymerization. The prepared JFRH was characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). JFRH composite shows strong mechanical properties with a compressive strength of 1.5 MPa at a deformation of above 80%. The synthesized JFRH composite can successfully remove more than 90% of MB from water. After adsorption, JFRH composite can be separated easily from the aqueous medium after the adsorption process. The JF based hydrogel composite reported in this study could significantly expand the use of the JF as a mechanical reinforcing material and superior adsorbent for effluent treatment plant.

II. Experimental

Materials: JF was collected from Newmarket, Dhaka. Acrylamide (AAm) (Sigma Aldrich, USA), potassium persulfate (KPS) (Merck Germany), *N,N'*-methylenebisacrylamide (MBAA) (Merck Germany), methylene blue (MB) (Merck India) were used without further treatments. Deionized water was used throughout the experiment.

Processing of jute fiber: JF was cut into small pieces and treated by ethanol for 24 h. Treated JF was then dried at 60 °C temperature for 6 h in an oven (Model:JSON-050, JSOF-Series forced convection). The dried JF was sieved using 1mm, 3mm, 5mm pore sized sieve to get the respective size of JF. The JF possesses density, elongation, tensile strength, and Young's modulus of 1.3 g/cm³, ~4, ~500 MPa, and 26.5 GPa, respectively²⁰.

Fabrication of hydrogel composite: Various wt% of treated JF was incorporated into the mixture solution of AAm, KPS and MBAA in a test tube. Then nitrogen gas was purged through the solution to remove O₂ from the mixture and the

test tube was sealed. The mixture was kept for 6 h at 60 °C in an oven. After polymerization, the prepared JFRH composite was removed from test tube, and kept in water for attaining equilibrium swelling state and removing unreacted monomer, initiator, cross linker and unwanted products. Similarly, polyacrylamide (PAAm) hydrogel was prepared by keeping the same concentration of AAm, KPS, MBAA without adding any JF. **Fourier transform infrared spectroscopy (FTIR):** FTIR spectra of JF, PAAm, and JFRH composites were taken by FTIR spectrometer (PerkinElmer, Boston, MA, USA, Model Forntier, serial no. 101393). JF, PAAm, and JFRH composites were freeze-dried and crushed to get fine powder. The fine powdered sample was used to make pellet with potassium bromide for FT-IR measurement. FTIR spectra of these samples were recorded over the frequency range of 4000–700 cm⁻¹.

Scanning electron microscope (SEM): Surface morphology of the JFRH composite was observed using a Scanning electron microscope (SEM) (Model: EVO 18) at high voltage (20 kV) and 1 to 10K magnification. Before observation, the JFRH composite was freeze-dried and fractured. The fractured fresh surface was coated with gold particle using an ion sputter.

Mechanical analysis: The mechanical properties of JFRH composite (compression test) was investigated using Force Transducer (Model SM-250-294) fitted with a 100 N load cell. For compression testing, the gel samples were cut as disk shaped of 1.5 cm diameter and 3.0 mm thick. The disk-shaped samples were gradually compressed above 80% of their original thickness with in a constant crosshead speed of 7.5 mm/min at ambient temperature.

Absorbance measurement: The absorbance of MB solution before and after adsorption was recorded by a double-beam UV-visible spectrophotometer (Shimadzu UV1850 PC, Japan) at 25°C. De-ionized water used as a reference solution.

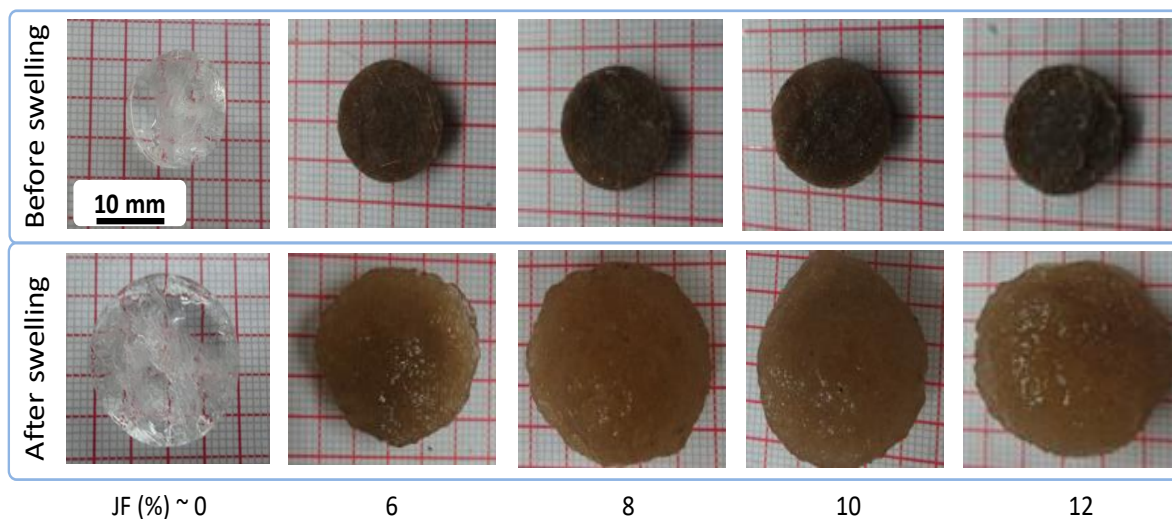


Fig. 1. Photographs of PAAm hydrogels and JFRH composites at various content of JF before (top row) and after swelling (bottom row) in water

III. Results and Discussion

The JFRH and PAAm hydrogels have been synthesized at various compositions and sizes of fibers. The photographs of the JFRH and PAAm hydrogels at various contents of JF were taken from top view before and after swelling in water (Fig. 1). The photographs of JFRH composites after swelling indicates that the gel's diameter increases. The weight swelling ratio of JFRH and PAAm hydrogel were found as 2.3 and 3.1, respectively.

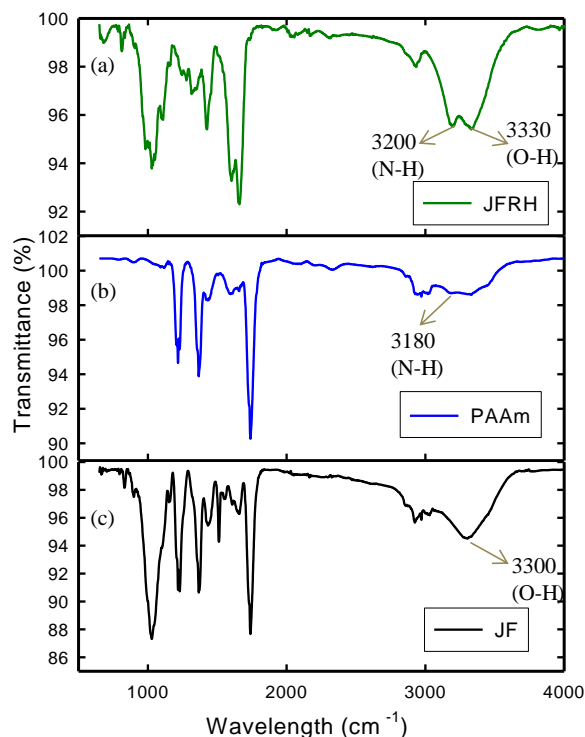


Fig. 2. FTIR spectra of (a) JFRH, (b) PAAm, and (c) JF.

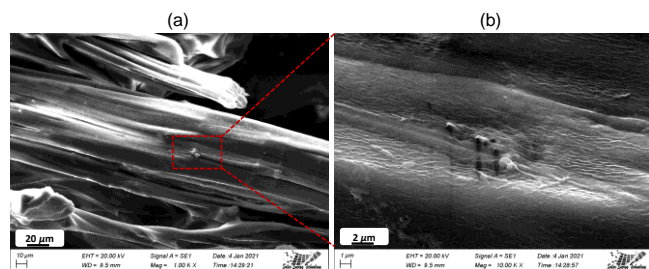


Fig. 3. SEM micrographs of JFRH composite show the elementary fiber (a) and microfibrils (b).

The decrease in swelling ratio with incorporating JF indicates the swelling restriction of PAAm matrix/network in presence of JF. Therefore, it indicates that the polymer chain of PAAm is bonded/linked with the JF in the JFRH composites. To justify this, FTIR of JFRH and PAAm hydrogel were performed and are shown in Fig. 2. The FTIR spectra of JF in Fig. 2 shows several distinctive peaks

at 3300 cm^{-1} (-OH stretching), 2900 cm^{-1} (C-H symmetrical stretching) and 1039 cm^{-1} (C-O stretching) in the cellulose unit. In the FTIR spectra of PAAm, the absorbance band at 3180 cm^{-1} is due to amide N-H stretching. The absorbance peak at 1730 cm^{-1} is associated with the C=O stretching vibrations. The FTIR spectrum of JFRH clearly showed the characteristic absorption band at 3330 , 3200 , 1660 and 1025 cm^{-1} due to -OH, amide-N-H, C=O and C-O stretching vibrations, respectively. Since the JF possesses mostly the cellulose, stable JFRH formed through the H-bond between cellulosic -OH and -CONH₂ of polyacrylamide, which are evident by the peak shifting from 3300 (-OH stretching of JF) to 3330 cm^{-1} (-OH stretching of JFRH) and 3180 (N-H stretching of PAAm) to 3200 cm^{-1} (N-H stretching of JFRH).

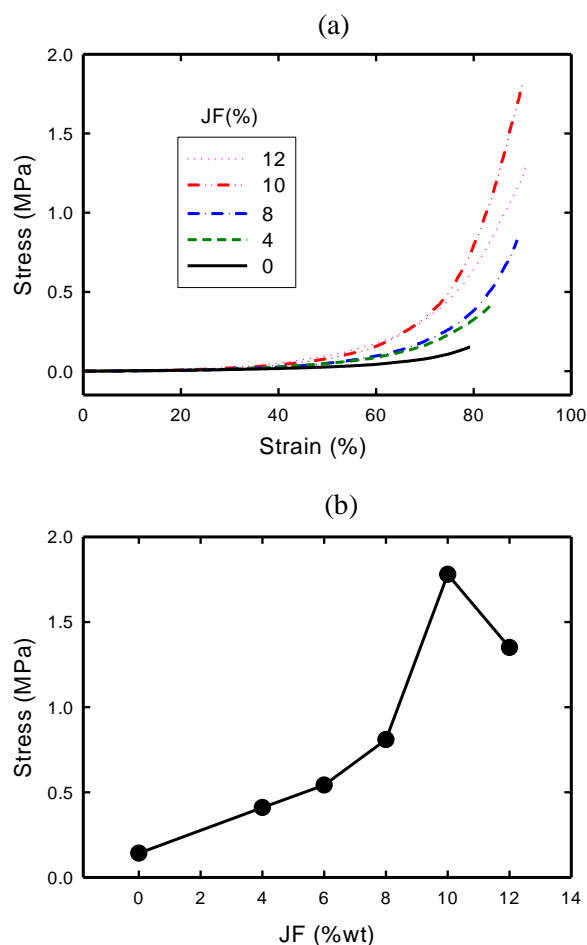


Fig. 4. (a) Stress vs. strain curves of PAAm hydrogels and the JFRH at various contents of JF. (b) The maximum stress at failure strain of JFRH as a function of JF contents.

The SEM images of JFRH (Fig. 3) indicates the characteristic morphological structure of hydrogel composite with jute fiber. The fibrous morphology of the composite is due to the elementary fibers (Fig. 3a) and the microfibrils (Fig. 3b) of JFRH. The size of jute fiber of JFRH in SEM observation is in good agreement with the

size of jute fiber before composite formation. This indicates the formation of composite between PAAm matrix and jute fiber.

The incorporation of JF into PAAm matrix significantly improved the mechanical properties of the PAAm hydrogels. Stress-strain profiles of PAAm hydrogel and JFRH composites at various JF concentrations (fiber length = 1 mm) are shown in Fig. 4a. The PAAm hydrogel shows moderate compressive strength. By the incorporation of JF into the PAAm matrix, the compressive mechanical strength of JFRH improved with the increase of JF content. A very high mechanical strength was noticed for the JFRH at 10 wt% JF of ~1 mm length. The stress at maximum strain before failure was plotted as a function of the JF content (Fig. 4b). It also implies that the increase of JF content of JFRH composite enhances the mechanical strength significantly and the maximum strength of JFRH was achieved at JF of 10 wt%. The higher mechanical stability of JFRH is important to separate it easily from the adsorbent medium.

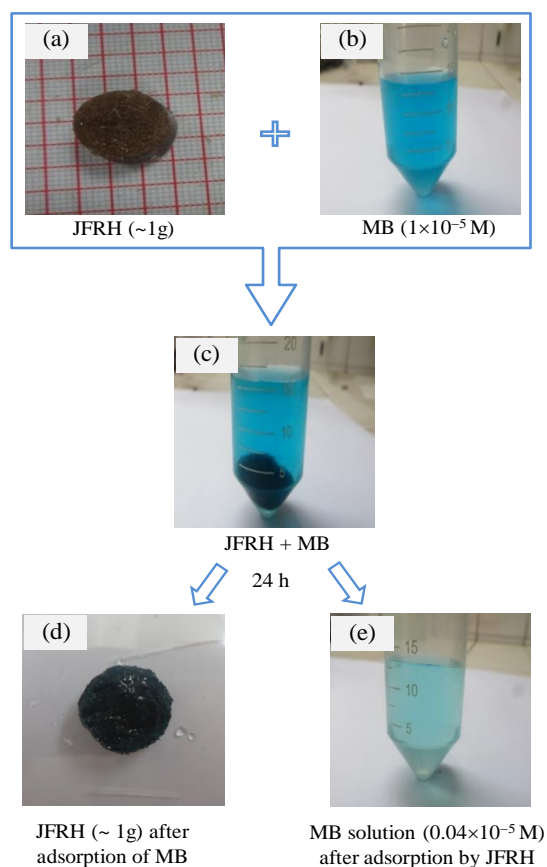


Fig. 5. Photographs of the JFRH composite and MB solution before and after the adsorption process. (a) JFRH composite (JF = 6 wt%) before immersing in (b) MB solution (1×10^{-5} M). (c) Immersed JFRH composite in MB solution during the adsorption process. (d) The JFRH composite and (e) MB solution are separated after the adsorption process (24 h).

The mechanically strong JFRH composite was employed for the adsorption of MB dye from aqueous solution. Prior to adsorption, various concentration of MB solutions (1×10^{-5} to 8×10^{-5} M) was prepared and ~1 g of JFRH composite was immersed in each of the MB solution for adsorption. Photographs of the JFRH composite and MB solution before and after the adsorption are shown in Fig. 5. Fig. 5a and 5b show the JFRH composite (JF = 6 wt%) and MB solution (1×10^{-5} M), respectively before adsorption. Fig. 5c shows the immersed JFRH composite in MB solution during the adsorption process. The darkening of JFRH and fading of MB color indicates the successful adsorption of MB by JFRH. After 24 h of adsorption, JFRH composite (Fig. 5d) was separated from the MB solution (Fig. 5e). The color of JFRH become dark due to adsorption of MB from solution which is also noticed from fading of blue color or reduced concentration (0.04×10^{-4} M) of MB solution compared to the initial color or concentration (1×10^{-5} M) of MB solution. Therefore, it is worth to mention here that JFRH composite can significantly absorb MB dye and easily be separated from the MB solution after adsorption. To check the removal efficiency, MB solutions of various concentration (1×10^{-5} to 8×10^{-5} M) were prepared and their absorbance (A) was measured. The absorbance was plotted as a function of MB concentrations, c (Fig. 6a). Linear fitting of A vs. c plot gives a straight line with $r^2 > 0.99$. The unknown concentration of MB solution after adsorption by JFRH was estimated using the fitted line of A vs. c plot. After adsorption by both JFRH composite and PAAm hydrogel, the absorbance of MB solutions was plotted in the same figure. It is apparent that the absorbance of MB solution after adsorption by both JFRH and PAAm possesses significantly lower value than that before adsorption. However, the absorbance of MB solution after adsorption by JFRH possesses much lower value than that of PAAm hydrogel. The concentration corresponds to the absorbance of MB solution after adsorption was estimated using the calibration plot (Figure 6a) and shown in Fig. 6b. This result primarily indicates the enhanced adsorption of the PAAm hydrogel after incorporating JF. To confirm this, removal efficiency of both JFRH and PAAm were calculated using the equation, % removal = $100 \times (C_i - C_f)/C_i$, where C_i and C_f are the concentration of MB solution before and after adsorption, respectively. The removal percentage for both JFRH and PAAm was plotted in Fig. 6c. A maximum removal efficiency of ~70% was found for the PAAm hydrogel whereas JFRH composite was responsible for over 90% removal of MB from water. The amount of MB dye (mg) adsorbed per gram of adsorbent (JFRH and PAAm) as a function of initial MB concentration are shown in Fig. 6d. It is also indicated that JFRH composite has higher removal efficiency than the PAAm hydrogel. Fig. 6e shows the absorbance of MB solution (6×10^{-5} M) in presence of JFRH and PAAm with time. The maximum adsorption of MB (90% for JFRH and 65% for PAAm) was occurred within 24 h.

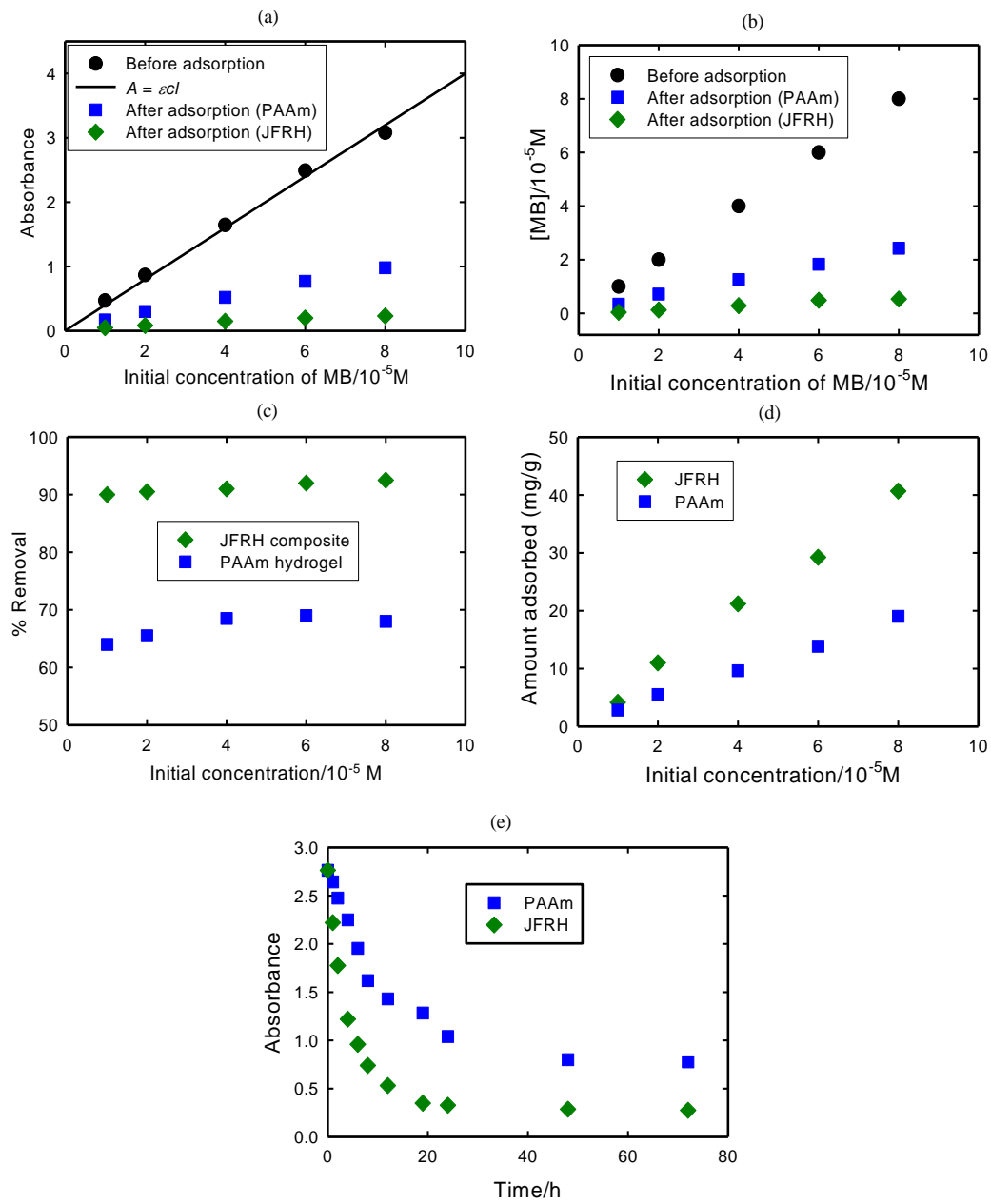


Fig. 6. (a) Absorbance as a function of initial concentration of MB (●). The absorbance of MB solution after adsorption by PAAm hydrogel (■) and JFRH composite (◆). (b) The concentration of MB before adsorption (●) and after adsorption by PAAm hydrogel (■) and JFRH composite (◆). (c) Removal percentage of MB dyes by JFRH composite (◆) and PAAm hydrogel (■). (d) Amount of MB dye adsorbed by per gram of adsorbent JFRH (◆) and PAAm (■). (e) Absorbance of MB solution (6×10^{-5} M) in presence of JFRH (◆) and PAAm (■) as a function of time.

IV. Conclusions

In this study, a hydrogel composite has successfully been fabricated from AAm and JF by thermal polymerization. The obtained JFRH composite is 3-dimensionally stable and self-standing. After incorporation of JF into PAAm matrix, the JFRH composite exhibits enhanced mechanical strength due to significant interaction between JF and PAAm matrix. A significant amount (>90%) of methylene blue (MB) dye was successfully removed from the aqueous solution by the JFRH composite. The JFRH can easily be

separated from the remaining MB solution after significant adsorption. Fabrication of hydrogel composite material based on jute fiber, in this study, is therefore a prominent achievement. Hydrogel composite was produced with expected characteristics under a simple method of fabrication and employed for the removal of dyes. Simple fabrication process of this JFRH composite and its easy utilization in waste removal might add importance in the long run of industrial or scientific purpose compared to conventional adsorbent.

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