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Removal of Methylene Blue Dye from Waste Water By pH Sensitive Hydrogel

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ABSTRACT: Hydrogels have gained importance in many applications like medical, pharmaceutical, environmental remediation, etc. because of its softness, hydrophilic nature and presence of chelation group. In this report, we are exploring the role of a pH sensitive hydrogel as an adsorbent of toxic dyes for environmental remediation specifically for waste water treatment. The biocompatible pH sensitive hydrogel composed of acrylic acid and vinylsulfonic acid was prepared by free radical polymerization reactions. The prepared hydrogel was then characterized by Fourier transform infrared (FTIR) spectroscopy and Field emission scanning electron microscopy (FESEM) techniques. FTIR studies confirmed the formation of Poly (acrylic-covinylsulfonic) acid hydrogel from its monomers. The morphology of the hydrogel corresponding to its pH sensitivity, was explored by FESEM analysis. The prepared hydrogel shows important application in waste water treatment, through significant dye adsorption capacity/performance.

KEYWORDS: Hydrogel, Environmental Remediation, Dye Adsorption

I. INTRODUCTION

Hydrogels have gained importance in a wide variety of applications in medical, pharmaceutical, environmental remediation and related fields.¹ Hydrogels are basically defined as three-dimensional polymeric networks crosslinked by a chemical bond, hydrogen bonding, ionic interaction, hydrophobic interaction which can absorb a large amount of water without dissolving into it. Their hydrophilic nature, softness and presence of chelation groups in the polymeric network make them suitable materials for biomedical devices, tissue engineering, drug delivery, food, pharmaceutical industry, wastewater treatment, etc.²⁻⁵

Stimuli-responsive hydrogels have gained great attention, as these hydrogels show dramatic changes in volume and properties in response to external stimulus such as temperature, pH [the acidity or the alkalinity of any solution can be indicated by the term of pH which stands for the power of the hydrogen ions H^+ , pH is related to the concentration (or more strictly the activity) of hydrogen ions], ionic strength, electric field etc. Their ability to swell and shrink according to the condition makes them interesting for use as intelligent materials (smart gels).⁶⁻⁸ pH is also an important limiting chemical factor for aquatic life. If the water in a stream is too acidic or basic, the H^+ or OH^- ion activity may disrupt aquatic organisms' biochemical reactions by either harming or killing the stream organisms. Wastewater pH has been identified as one of the parameters which influence effective wastewater treatment.⁹ The effective treatment of chemical contaminations of water in the environment has become one of the major issues of public interest due to their toxicity. The presence of dyes is responsible for ecological problems in aquatic environment and toxic to humans if they are introduced into the food chain and ingested beyond prescribed concentration.

There are many kinds of technologies which are used for dye removal from wastewater, such as membrane separation, chemical oxidation, coagulation and flocculation, photocatalytic degradation and adsorption. Adsorption technology is mainly considered to be an effective method for quickly lowering the waste concentration in the effluent. Hydrogel is known as one of the cost effective adsorbents for dye removal.¹⁰⁻¹² pH sensitive polymer/hydrogel contains acidic (carboxylic and sulfonic acid) or basic (ammonium salt) groups that either accept or release protons in response to pH change. Because of the presence of ionic and nonionic groups in these type of hydrogels, they have the property to adsorb ionic dyes and thus, are useful for waste water treatment.¹³⁻¹⁵

Among the various dyes, methylene blue (MB) is a thiazine cationic dye which is applied to leather, wool, silk, paper, plastic as well as for the production of ink, copying paper and cotton mordant with tannin. The color removal process in the textile industries generates effluents polluted with methylene blue dye which is toxic and mixes in the water causing mutation, allergic dermatitis, cancer, skin irritation, eye burns in human and animals, diarrhea and vomiting.¹⁶

In this study, we report the preparation and characterization of a biocompatible poly (acrylic-co-vinylsulfoinc acid) hydrogel whose adsorption capacity of methylene blue dye displays its potential application in waste water treatment.

II. METHODOLOY MATERIALS

The poly (acrylic-co-vinylsulfoinc acid) hydrogel (PAAVSA) were prepared using Acrylic acid (AA) (SigmaAldrich), Vinyl sulfonic (VSA) (Sigma-Aldrich) acid monomers, along with appropriate initiator and crosslinker using free radical polymerization reaction technique⁶. The optimum weight ratio of the AA-to-VSA mixture was determined/adjusted to achieve the better performance of the hydrogel in terms of its dye adsorption capacity. Methylene blue (MB) dye (Sigma-Aldrich) was used to analyse and quantify the dye adsorption capacity of the prepared hydrogel. 0.04 mM methylene blue dye aqueous solution of 50 ml volume were used for dye adsorption measurements at different pH values.

Experimental Techniques

FTIR spectra of dried hydrogel was recorded with Tensor 27, BRUKER Fourier Transform IR (FTIR) spectrometer using KBr disc in the range of 4000-400 cm^{-1} . The morphology of the prepared hydrogel at different pH solution was studied by Field Emission Scanning Electron Microscopy (FE-SEM, Supra55 Zeiss).

The characteristic properties of the hydrogel were explored by quantifying the swelling behavior of the PAAVSA by calculating the swelling ratio.⁶

(1)

Swelling ratio (Q) = $[(W_s - W_d)/W_d] \times 100 \%$

Where, W_s and W_d are the weights of swollen and dried hydrogels, respectively.

The concentration of adsorbed MB dye was determined by using UV-Vis spectrophotometer (Perkin Elmer lamda-35) with spectral range of 200 – 800 nm.

The experiments for dye adsorption by PAAVSA hydrogel were carried out at different pH of the dye solution. The percentage dye adsorption by PAAVSA was calculated by using formula:¹⁷

(2)

Dye Adsorption = $[(A_0 - A_t)/A_0] \times 100 \%$

Where, A_0 and A_t are the UV-Vis absorbance of the dye solution at the initial stage and absorbance of the supernatant liquid collected at different time interval, at different stage of adsorption, respectively.

RESULTS Spectroscopic Analysis

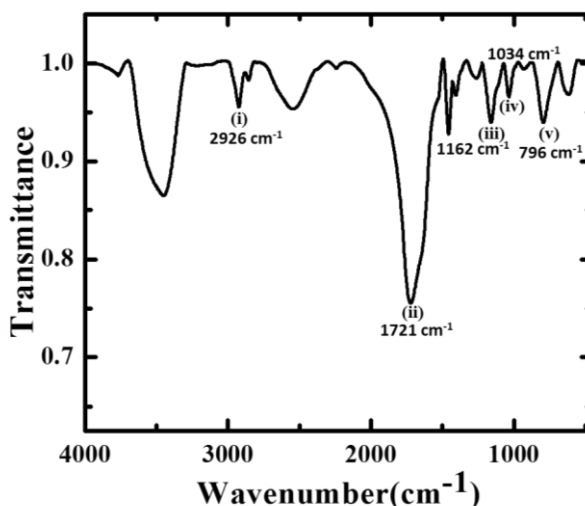


FIGURE 1: FTIR spectra of Poly (acrylic-co-vinylsulfoinc)acid hydrogel (i) CH stretching, AA (ii) CO stretching of COOH, AA (iii) SO_3^- , VSA (iv) S=O, VSA (v) C-S stretching, VSA

The FTIR spectrum shown in Fig.1, displayed absorption peaks at 2926 cm^{-1} (CH stretching of AA), 1721 cm^{-1} (CO stretching COOH, AA), 1162 cm^{-1} (SO_3^- , VSA), 1034 cm^{-1} (S=O, VSA), 796 cm^{-1} (C-S stretching, VSA), which indicate the formation of the desired hydrogel from acrylic acid and vinylsulfoinc acid monomers.

Morphology

Fig.2, shows the SEM morphologies of the poly(acrylic-co-vinylsulfonic) acid (PAAVSA) hydrogel, exposed to different pH solution. SEM images confirm that the PAAVSA hydrogel exhibits large porosity for high pH values, indicating enhanced surface induced activity towards neutral to alkaline dye solution..

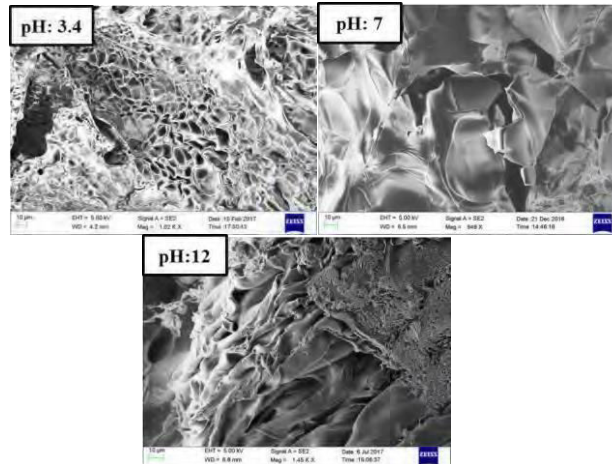


FIGURE 2: Characteristic SEM images of Poly (acrylic-co-vinylsulfonic) acid hydrogel at different pH solutions
Dye Adsorption Properties

The poly(acrylic-co-vinylsulfonic) acid (PAAVSA) shows the distinct swelling behavior of hydrogel at different pH. The results revealed (shown elsewhere¹⁸) that the hydrogel is pH sensitive and with the swelling ratio becoming higher, more than 7000%, at high pH values (neutral to basic range). Dye adsorption studies indicated that the Poly (acrylic-co-vinylsulfonic) acid hydrogel has the ability to adsorb methylene blue dye from the aqueous solution. Fig.3 clearly depicts that the capacity of methylene blue dye adsorption is increased at pH-7 and pH-12, relative to the acidic solution (pH 3). The observed increase in MB uptake at pH-7 and pH-12 is very much consistent with the high porosity of the hydrogel at pH 7 and pH 12 with respect to pH 3.4 (as shown in Fig.2). Generally, the industry generated waste water, which contains dyes, is alkaline in nature (i.e., high pH values)¹⁹, and in that respect the PAAVSA shows its potential application in waste water treatment through its significant dye removal capacity.

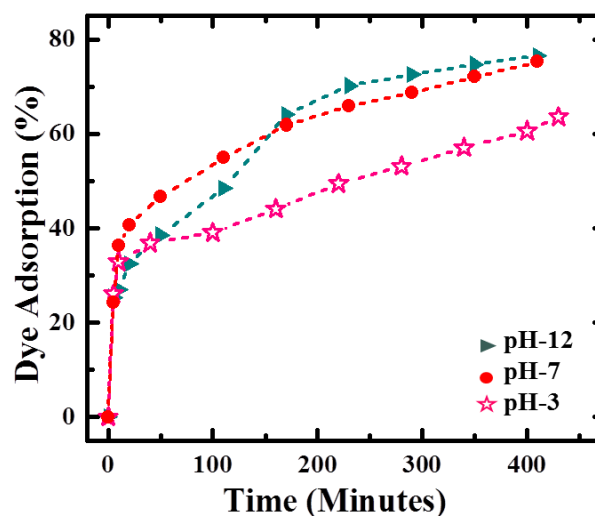


FIGURE 3: Effect of different pH solution on adsorption rate of MB dye with time

Dye adsorption mechanism has been explored by thorough investigation and using the theoretical model to get the quantitative explanation of the dye adsorption rate of the hydrogel²⁰⁻²² to determine the performance of PAAVSA in comparison to other studies, for its potential application in waste water treatment.

III. CONCLUSION

Poly (acrylic-co-vinylsulfonic) acid (PAAVSA) prepared by free radical polymerization method shows its pH sensitive hydrogel properties through its distinct swelling behavior at different pH. The dye adsorption study, along with the FESEM characterization show that the said hydrogel removes the cationic dye MB from aqueous solution very efficiently. The maximum observed dye adsorption occurred at alkaline pH which makes this biocompatible hydrogel a potential adsorbent for the dye containing wastewater treatment.

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