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Preparation and Characterization of polysaccharide based superabsorbent nanocomposite and its use in efficient removal of Methylene blue dye

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ABSTRACT

Novel guar gum-g-poly acrylic acid (GG-g-PAA) superabsorbent nanocomposites were prepared in aqueous solution using guar gum (GG), partially neutralized acrylic acid (AA), hydrogen peroxide (HP) as an initiator and N, N-methylene bisacrylamide (MBA) as crosslinkerby free radical graft copolymerization reaction. FTIR spectra confirmed that AA had been grafted onto GG chains. X-ray diffraction (XRD) to study its crystalline nature of the composite. Scanning Electron Microscopy (SEM) results shows that prepared composite have uneven and coarse surface.The present study concerns for the removal of Methylene blue dye using GG-g-PAA superabsorbent nanocomposite. The adsorption behavior of dye was studied using batch techniques at different pH values. The synthesized superabsorbent composite (SAC) was found to be effective in removing methylene blue dye up to 90 % at pH 8.5. The effect of various variables such as dye concentration, contact time, adsorbent dose, pH etc. was analyzed. Study shows that the adsorption kinetics favors pseudo second order reaction kinetics. The process of adsorption of dye follows Langmuir and Freundlich model.

Key words : *Superabsorbent, Nanocomposite, Adsorption, Methylene blue, Dye removal.*

Introduction

Effluent discharge from industries such as textile, paper, rubber, leather, cosmetics, etc. contains harmful residues of dyes. (Rafatullah *et al.* (2010). These dyes are very harmful to environment, they not only disturb the ecosystem but also decrease the aesthetic value of water bodies (Laftah *et al.*, 2011). The colored effluents of industries mixed with the surface water and ground water systems, from where they are transferred to drinking water system creating a threat to human health (Bajpai *et al.*, 2002). Without proper treatment of the effluents and its disposal in water bodies, increase the chemical oxygen demand (COD). As dyes have complex structure and synthetic nature, they are meant for not to be breakdown with time and exposure to sunlight, water, soap, and oxidizing agent, they cannot be easily degraded and removed by conventional wastewater treatment processes. (Mohamadnia *et al.*, 2008).

There are various treatment processes employed for industrial effluent treatment such as coagulation flocculation, chemical oxidation, membrane separation, photocatalysis, adsorption and electrolysis (Jin *et al.*, 2003, Sheng (2009). The most promisingand economic technique among these is found to be adsorption method. Many different types of adsorbents have been reported in research field in removing of color from effluents (Wan Ngah *et al.* 2011,SemaEkici *et al*, (2011) In recent year more em-

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phasis has been given on the absorbents prepared from polysaccharide. The polysaccharide-based adsorbents are effective in treating colored wastewater due to their nontoxic and biodegradability. Superabsorbent polymers (SAP) are 3D cross-linked polymers, which have the ability of swelling and retaining a huge amount of water. SAPs proved to be good enough in removal of dyes using natural polysaccharides hydrogel especially using natural gums. Due to the anionic properties of guar gum composites and its porous structure networks it has the capability of adsorbing cationic dyes such as methylene blue from aqueous solutions via the electrostatic attraction force (Zhao *et al.,* 2010). In this paper, the use of adsorbent prepared by guar gum grafted poly acrylic acid superabsorbent nanocomposite has been investigated as an effective way of removing methylene blue dye from aqueous solution. (Sami *et al.* 2012). Methylene blue is a thiazine cationic dye. (Soni and Sharma (2012). It is a dark green powder that gives a blue solution in aqueous media. MB is not strongly hazardous but have various harmful effects, such as shortness of breath, high BP, headache, vomiting etc. (Li *et al.* 2013). The structure of Methylene blue dye is given in Fig. 1.

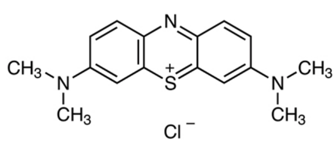


Fig. 1. Chemical Structure of Methylene Blue dye

Materials and Methods

Materials: Guar Gum-g-poly (acrylic acid) superabsorbent hydrogel nanocomposite was prepared in our laboratory using grafting technique. Guar gum (Shri Ram Gum Industries Basni, Jodhpur), Acrylic Acid (AA), N, N-Methylene bisacrylamide, Hydrogen peroxide(AsesChemicals, Jodhpur), Acetone (Fischer Scientific, Qualigens), and Ethanol. Adsorbate Methylene blue ($C_{16}H_{18}N_3SCl._3H2O$) was obtained from E. Merck, India.All of these are used without further purification.

Synthesis of Guar gum-g-PAA Superabsorbent Nanocomposite

GGwas added in distilled water in a round-bottomed flask equipped with stirrer and thermostat water bath. The slurry of GG was made by stirring the solution for one hour. The reaction was initiated by using initiator Hydrogen peroxide (HP) and stirred at 40 ^oC for about 15 minutes to produce radicals. The monomer acrylic acid 6% (v/v) was added in the guar gum slurry and mixture was stirred for half an hour. Further aqueous solution of methylene bisacrylamide (MBA) was added in the mixture. The reaction mixture was continuously stirred and heated at 60 ^oC for about 3 hours. Excess amount of acetone was used to precipitation and kept overnight. Precipitate was wash by mixture of distilled water and ethanol (60:40) to remove homo polymer and unreacted mass. The grafted polymer was dried in oven at 80 ^0C. The dried product was pulverized into powder by using pastel mortar

Absorbency or Swelling Measurement

The equilibrium water absorbency of the superabsorbent was calculated using Eq. (1)

%Swelling = (W2 - W1)/W1 .. (1)

W1 and W2 are the weight of the dry sample and water swollen sample respectively

Characterization of Superabsorbent

FTIR Analysis

In FTIR spectra of guar gum grafted PAA composite a broad peak appears at 3343cm^{-1}, which indicates stretching vibration of the -OH groups of guar gum. A smaller peak at 2922 cm^{-1} is attributed to C-H stretching variations -CH_2 groups. The absorption peak at 1714 cm^{-1} is due to C=Ostretching variations of PAA. The peak at 1011 cm^{-1} is due to the coupling of C-O stretching and O-H'in plane' bending vibrations.There is a distinct absorption band from 1145 cm^{-1} to 1011 cm^{-1} which can be attributed to C-O-C stretching vibration of PAA. The presence of the correct static peaks clearly proves that PAA has been successfully grafted onto the guargum.

XRD Analysis

X-ray diffraction (XRD) pattern was obtained with Philips X'pertpyrosystem Cu Kα radiation (λ=1.54 angstrom and theta = 0-80^o) at room temperature. The grafted composite shows one prominent peak at scattering angle (2theta) at 20.34^o which indicates development of crystallinity in composite.

Fig. 2. FTIR analysis of Guar gum- g- PAA superabsorbent composite

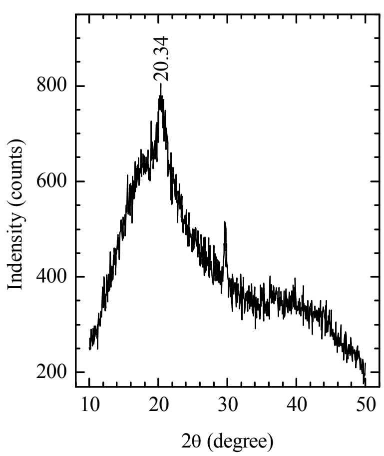


Fig. 3. XRD of superabsorbent composite

SEM Analysis

Scanning electron microscopy (SEM) was used to analyzing surface morphology of composite. SEM composite at different magnification obtained by Zeiss instrument. The prepared superabsorbent composite has uneven and coarse surface. Composite has more rough structure as compared to guar gum and are in good agreement with our water absorbency observations.

Experimental protocols: The batch adsorption experiments were conducted in a set of 250 ml of Erlenmeyer flask containing adsorbent and 50 ml of MB solution with various initial concentrations. Dye solution and adsorbent was taken in flask and magnetically stirred at 120 rpm for a certain time until the equilibrium is reached. The equilibrium concentrations of dye in the solution were measured at 660 nm using UV-visible spectrophotometer. The pH of solution was adjusted with 1N HCl and 1N NaOH solutions. The adsorption capacity at equilibrium Qe (mg/g) calculated using following equation.

$$Qe = \frac{(Co - Ce) \times V}{W} \quad .. (2)$$

Where Qe is amount of dye adsorbed per unit mass of hydrogel (mg/g), Co is initial concentration of dye(mg/L), Ce is concentration of dye at equilibrium (mg/L), V is volume of dye solution, W= weight of super adsorbent nanocomposite used (g).

The percentage removal of methylene blue dye using nanocomposite was calculated using following equation:

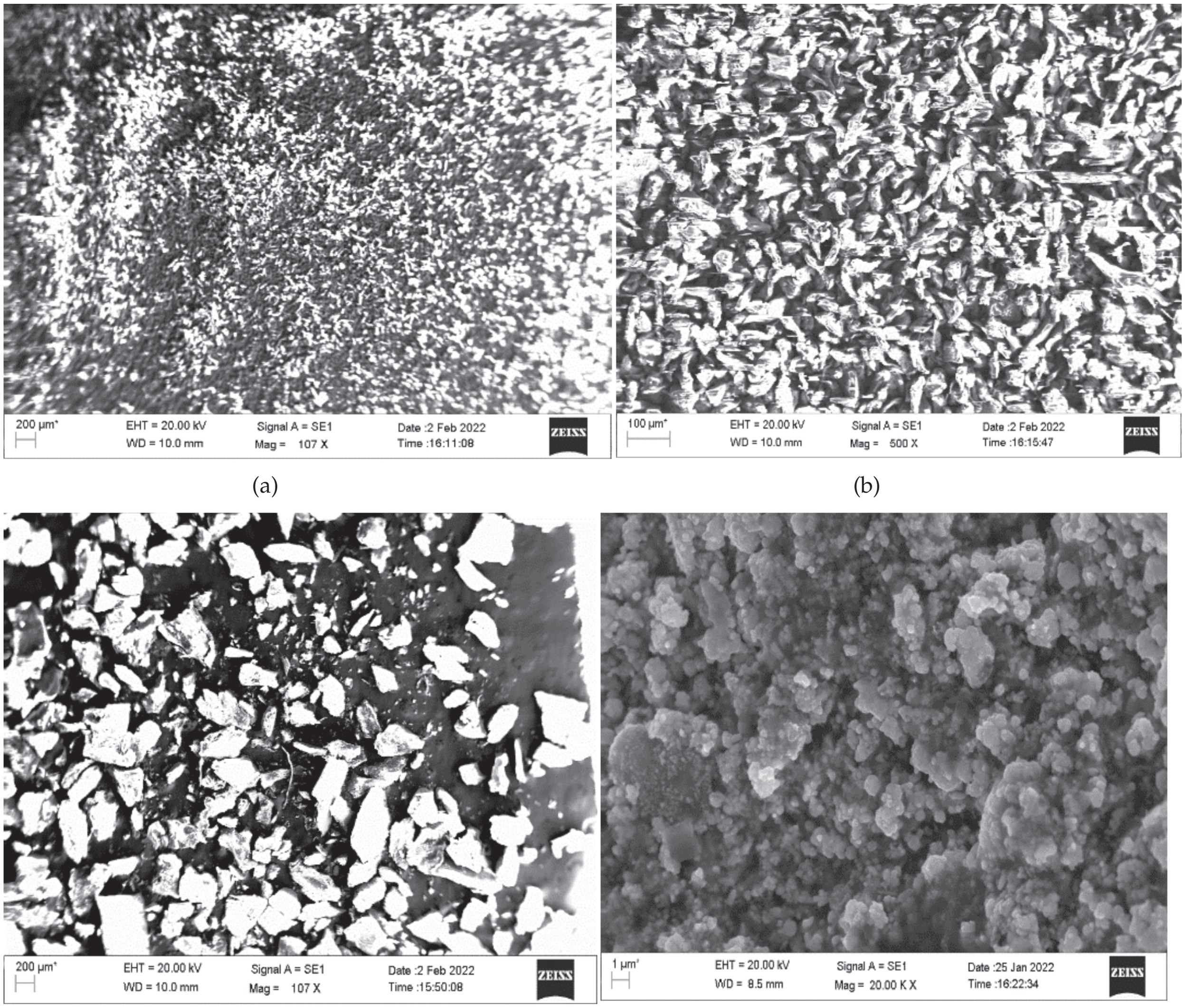
$$\% \text{ Removal} = \frac{Ci - Cf \quad x\ 100}{Ci} \quad .. (3)$$

where Ci is the initial concentration of dye and Cf is the final concentration of dye at the end of adsorption process.

Factors effecting percentage removal of dye

The effects of various parameters like dose of adsorbent, dye concentration, contact time and pH value were studied.

Effect of adsorbent dose: The effect of adsorbent dose on removal of dye was studied by varying the



(c) (d)

Fig. 4. SEM micrographs of (a) Guar gum (Mag = 107 X) (b) Guar gum (Mag = 500 X) (c) GG- g- PAA composite (Mag = 107X) (d)GG -g-PAA composite (Mag = 20 KX)

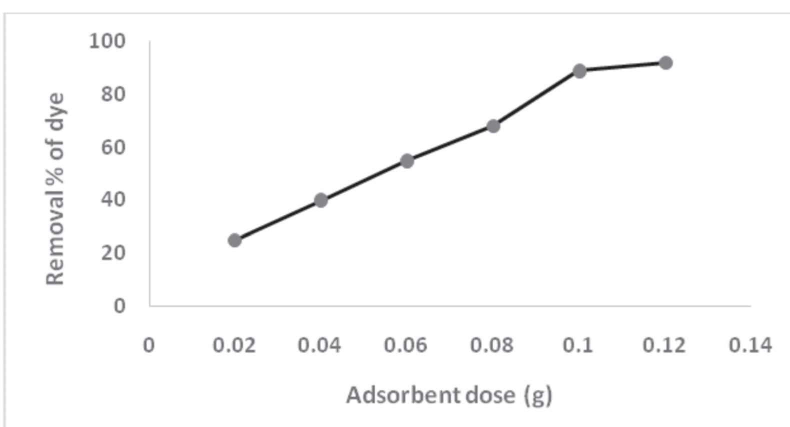


Fig. 5. Effect of adsorbent dose on removal percentage of dye

amount of composite from 0.02 g to 0.12 g. Figure 3: illustrate that the percent removal of dye increases from 20 to 90 % removal. This is due to increase in adsorbent surface area and availability of more adsorption sites (Li and Wang *et al.,* (2013).

Effect of concentration of dye: It is observed from the Figure 6 that the dye removal percentage is inversely proportional to the dye solution concentration. The dye removal percentage decreases from 90 to 20%. This may be due to increase in dye molecules adsorption onto the external surface, increases significantly giving rise to the formation of aggregates of the dye on the polymers particles which consequently reduce the concentration gradient, the driving force for dye adsorption (Tang *et al.,* (2013)

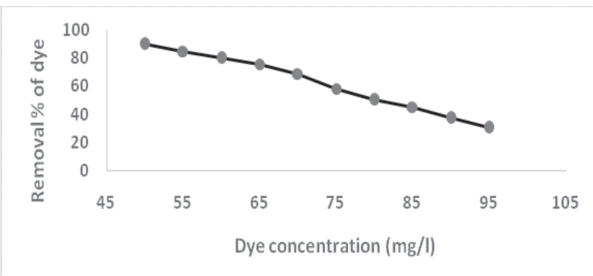


Fig. 6. Effect of concentration of dye on removal percentage of dye

Effect of Contact time: As the contact time was increased from 10 min to 210 minutes the removal percentage of dye increased from 12% to 90%. This behavior may be referred to the reduction of the concentration gradient between the liquid phase and the adsorbent surface (Salleh *et al.,* (2011).

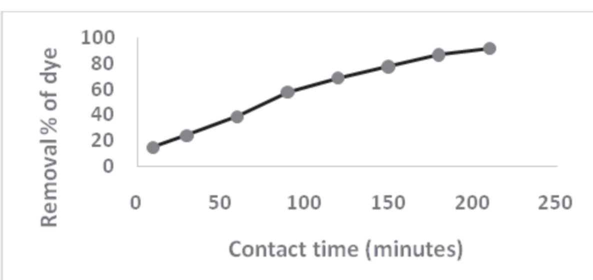


Fig. 7. Effect of contact time on removal percentage of dye

Effect of pH: It was found that percent removal of dye is less in acidic medium because the number of positive charge available sites decreased while the number of the negatively charged sites increases. (Fan *et al.,* (2012). It was analyzed from study that at

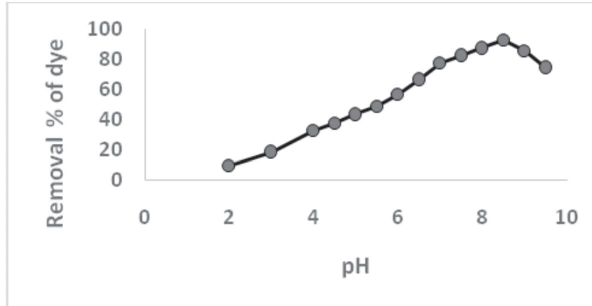


Fig. 8. Effect of contact time on removal percentage of dye

pH 8.5 the percentage removal of dye was 90%.

Study of Adsorption isotherm: Langmuir and Freundlich isotherms were applied to evaluate the adsorption characteristics of adsorbent used. The Langmuir isotherm is applied to equilibrium adsorption assuming monolayer adsorption onto a homogenous surface with a finite number of identical adsorption sites (Liu and Zhang *et al.,* 2015). The linear form of Langmuir equation is written as:

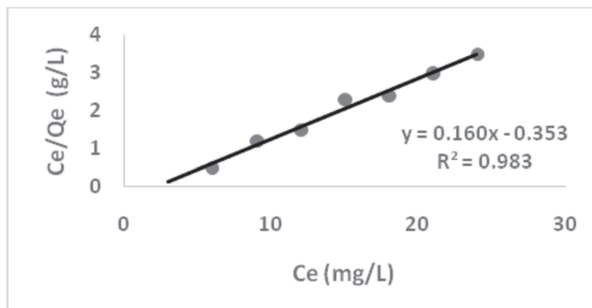


Fig. 9. Langmuir isotherm for adsorption of Methylene blue dye onto superabsorbent nanocomposite

$$Ce/Qe = (1/k\,L) + aL\ /(k\,L.Ce) \qquad ..\ (4)$$

where kL and aL are Langmuir constant (l/g) related to the affinity of binding sites and the free energy of sorption. Qe is dye concentration at equilibrium onto (mg/g), Ce is dye concentration at equilibrium in solution (mg/l). Therefore, the plots of Ce/Qe versus Ce give a straight line with slope of aL /k Land intercept of 1/k L.

The logarithmic form of Freundlich equation for heterogeneous surface energy systems is given by:

$$\log Qe = \log Kf + (1/n) \log Ce \qquad ..\ (5)$$

where Kf and n are Freundlich constants, determined from the plot of ln qe versus ln Ce. The parameters Kf and 1/n are related to sorption capacity and the sorption intensity of the system. The magni-

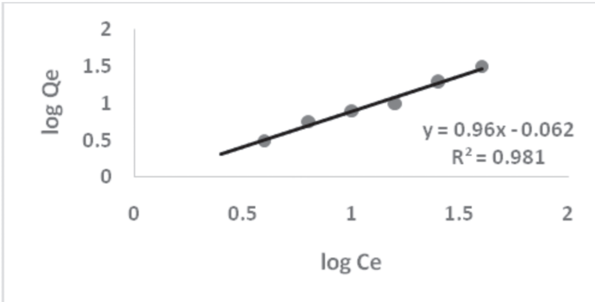


Fig. 10. Freundlich isotherm for adsorption of Methylene blue dye onto superabsorbent nanocomposite

tude of the term (1/n) gives an indication of the favorability of the sorbent/adsorbate system.

Study of dye adsorption kinetics

Adsorption kinetic models apply to the interpretation of adsorption data to gain knowledge into adsorption efficiency, rate, and the rate-controlling step.

Pseudo " first " order model: log (qe " qt) = log qe + K_1 / 2.303 × t (6)

Pseudo " second " order model: t /qt = 1/ $(K_2qe)^2$ + t /qe (7)

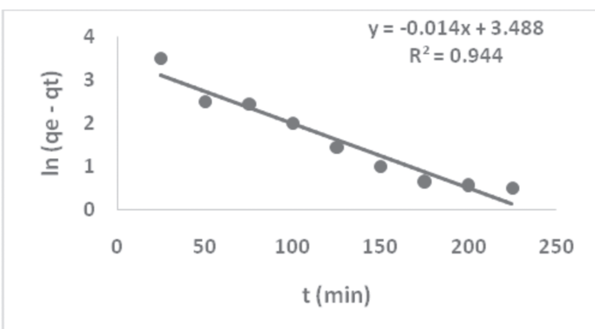


Fig. 11. Pseudo first order kinetic model for adsorption of methylene blue dye onto composite

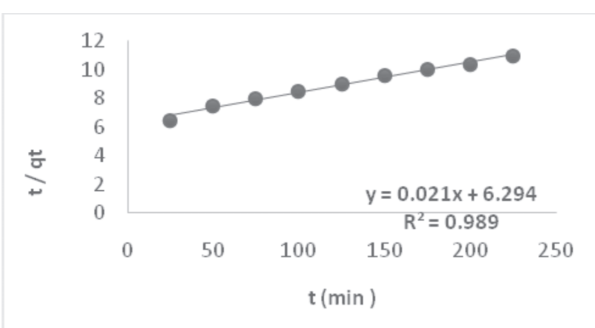


Fig. 12. Pseudo second order kinetic model for adsorption of methylene blue dye onto composite

where, qe (mg/g) is the amount of dye adsorbed at equilibrium, qt (mg/g) is the adsorption capacity at a certain contact time t (min); K_1 and K_2 are the rate constants of pseudo-first order and pseudo-second-order models, respectively. The linear plot of (t/qt) versus t (Figure 12) gives a straight line with linear coefficient $R^2 > 0.95$ which shows that pseudo second order kinetics model fits for kinetics of methylene blue dye adsorption

Conclusion

The aim of above research work was to test the efficacy of guar gum-g-poly (acrylic acid) super absorbent nanocomposite for removal of methylene blue dye. The removal of methylene blue was carried out by process of adsorption from an aqueous solution of superabsorbent nanocomposite at different pH values. Results show that there is highest removal of 90 % at pH 8.5. The effect of various parameters like adsorbent dose, dye concentration, contact time and pH on removal percentage of dye was investigated. The adsorption isotherm study show that it follows Langmuir and Freundlich adsorption model. Adsorption kinetics study shows that it follows pseudo second order reaction. Therefore, guar gum- g-poly (acrylic acid) superabsorbent nanocomposite is potential composite for removal of methylene blue dye from wastewater.

Conflict of interests

The authors have declaredthat there is no competing interest.

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