

EFFICIENCY OF BIODEGRADABLE ACRYLIC ACID-CHITOSAN HYDROGEL IN ELIMINATING METHYLENE BLUE FROM WASTEWATER

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ABSTRACT

A novel, regenerative and biodegradable acrylic acid hydrogel having different chitosan composition (w = 0, 0.5, 1.0 and 1.5 %) was constructed using gamma radiation from the Cobalt-60 source. The prepared hydrogel was treated with alkali to enhance its dye adsorption capacity. Uptake capability of the hydrogel at different chitosan percentage, contact time, pH, and methylene blue (MB) concentrations was measured using UV Spectrometer. MB uptake ability obtained was found to escalate proportionately with escalating chitosan percentage and alkali treatment. Kinetics and isotherm of MB adsorption mechanism were analyzed. Pseudo-second-order model and Langmuir isotherm model were followed by the Hydrogel MB uptake capacity. The adsorption efficiency of monolayer saturation of the alkali-treated adsorbent was 322 mg/g as obtained from Langmuir equation. Desorption and reuses of the hydrogel were successfully carried out. The results indicated that acrylic acid-chitosan hydrogel is feasible for elimination of toxic cationic dyes efficiently.

Keywords: Acrylic acid, Chitosan, Hydrogel, Radiation, Methylene blue adsorption.

INTRODUCTION

Polluted wastewater discharged from various industries such as cosmetics, food coloring textile, dying, and printing contributes to enormous production of colored sewages [1]. Over 10,000 dyes are available commercially and about 7×10^5 tons of them are produced every year from various sources [2]. Around 2% dyes are expelled to effluents from mechanized maneuvers, and 10% from textile and related industries each year [3]. Releasing dyes into water bodies in slightest amount can have a massive negative impact on the marine habitats and food chain. Besides, dyes are the cause of allergy and numerous skin diseases. Some of them even cause cancers and mutations in marine life form and human beings [4]. Out of them, methylene blue (MB) is the major matter used for coloring silk and cotton. MB is a cationic thiazine dye, chemically termed as tetramethylthionine chloride and easily recognizable due to its profound blue appearance which shows absorption maxima around two wavelengths 609 and 664 nm [5]. MB can create eye burns and severely damage the eyes of living beings. If inhaled, it causes breathing problems. If ingested, it creates a burning feeling and nausea, mental confusion vomiting tendency, and massive sweating [6]. Therefore, eliminating MB from wastewater is extremely necessary.

Most dyes are neither photodegradable nor biodegradable [7-9]. Thus scientists have been trying their various approaches in order to solve this problem. Until now, various methods like flocculation and coagulation [10], membrane separation [11], oxidation or ozonation [12, 13], electro-coagulation [14] and adsorption have been employed for eliminating dyes. Out of them, adsorption is quite effective, cheap and crucial method for removing dyes [15-17]. Various adsorbents have been constructed for the elimination of color from effluents. Major drawbacks of many adsorbents were low de-colorization rate and secondary pollution of adsorbing materials.

In recent times, elimination of dyes with the help of functional polymers has turned out to be a potential technique. Diverse polymeric sorbents specifically hydrogels consisting functional groups which is capable of forming dye-complex received significant notice and were examined [18-19].

Hydrogel consists of numerous chains of hydrophilic polymer forming a complex network among them. [20]. The potential uses of hydrogel is innumerable. It is extremely hydrophilic, possesses good swelling percentage and biocompatible. All these properties make hydrogels highly usable for various purposes. Hydrogel has been used as water purification material, as an efficient carrier for drug delivery, antibacterial materials, producing self-healing materials, mimicking as muscles in tissue engineering, artificial organ generation, biosensors and sorbents to eliminate of heavy metals and dyes from wastewater. Presently, many researches are ongoing on hydrogel focusing its application in different fields.

In the present study, acrylic acid-chitosan hydrogels were prepared from their aqueous solutions by the application of gamma radiation. The prepared hydrogels were investigated for adsorbing methylene blue. Half of the prepared hydrogels were alkali treated to improve dye uptake capability. Dye uptake capability of alkali treated hydrogel was also studied at different chitosan percentage, different contact times, pH, and concentration of methylene blue solution. Desorption and reuses of the hydrogels were investigated.

EXPERIMENTAL

Reagents and Materials

Chitosan from Aldrich-Chemie, Germany was collected. Acrylic acid supplied by Fluka, Germany was used as received. Methylene blue, NaOH and HCl were purchased from (Merck, Germany). As solvent distilled water was used.

Hydrogel Preparation

At first, 20 % acrylic acid solution in distilled water was prepared. Then to the acrylic acid solution 0, 0.5, 1.0 and 1.5 w/v % of chitosan were added. After that it was then stirred for 1 hr using a magnetic stirrer. The mixture was poured into glass tubes and later subjected to gamma radiation for cross-linking with 25 kGy radiation dosage from Co-60 gamma source. It was a 90 kCi Cobalt-60 Batch Type Panoramic Irradiator (Board of Radiation and Isotope Technology (BRIT), India). Activity was 68.63 kCi and dose rate was 13.7 kGy/h.). After gamma radiation treatment, hydrogel was slashed into small pieces, cleansed with distilled water in order to eliminate un-reacted monomers or homo-polymers and allowed to dry on plastic tray at room temperature (25°C). 50 % of prepared dried hydrogel was treated with KOH for 1hr to increase adsorption capacity.

Methylene blue adsorption by the acrylic acid-chitosan hydrogel

0.05 g of acrylic acid-chitosan hydrogel was kept inside 50 mL aqueous solutions of methylene blue solution at 25°C. The technique was mimicked at different chitosan % (w= 0, 0.5, 1.0 and 1.5 %), pH (2, 3, 5.5, 7.5, and 10.5), contact time (0, 1, 2, 3, 4, 5, 24, 25, 26, 27 and 28 h) and initial MB concentration (50, 110, 160, 200, 250, 350 and 400 ppm). pH of MB solutions were regulated with the help of HCl and NaOH. MB solution concentrations before and after adsorption were assessed using UV Spectrometer (UV-2401PC, Shimadzu, Japan). The MB uptake capacity of acrylic acid-chitosan hydrogel was measured with the help of the following formula:

$$Q = V(C_1 - C_2) / W \dots\dots\dots (1)$$

where,
 Q = Capacity of adsorption (mg/g of adsorbent)
 W = Weight of dried hydrogel (g)
 V = Volume of MB solution (L)
 C₁ = Concentrations (mg/L) of MB before adsorption
 C₂ = Concentrations (mg/L) of MB after adsorption.

Methylene Blue Desorption

MB was desorbed from the swelled hydrogel by treating it with 2M HCl for 24 h. Desorption percentage was estimated as follows:

$$\text{Percent desorption} = (\text{desorbed ions (mg)} / \text{Adsorbed ions (mg)}) \times 100 \dots\dots (2)$$

After that, the hydrogel was regenerated by the treatment with KOH for 1 h.

Reuse of the hydrogel

After desorption of the MB from the adsorbent, the adsorbent was regenerated by alkali treatment and reused for MB adsorption.

RESULTS AND DISCUSSION

MB adsorption by acrylic acid-chitosan hydrogel

Comparison between alkali treated and untreated hydrogel

After preparing the hydrogels, half was treated with alkali (KOH) whereas the other half was left untreated. Both samples were then kept in MB solution for 24 hours. The graphs (Fig. 1) shows the comparison between the dye adsorption capacities of the two samples. Dye uptake capability of the treated and untreated samples after 24 h were 158 mg/g and 31 mg/g respectively as measured using UV Spectrometer. It is evident that the adsorption capacity of treated sample is almost five times more than that of the untreated one. The feat of the hydrogel was enhanced after alkali treatment. The main reason behind this was after alkali treatment, hydrogels went into salt form turning it more anionic which consequently improved its efficiency for adsorption of cationic (MB) from solution.

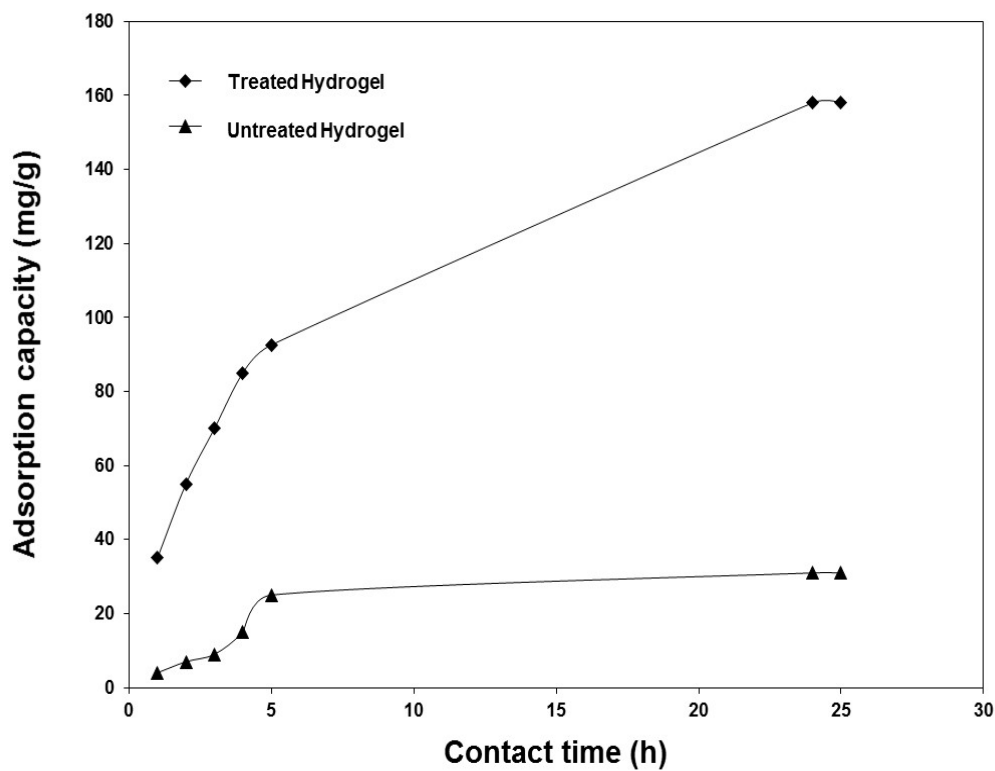


Fig. 1 Comparison between adsorption capacity of treated and untreated hydrogel samples (Chitosan percent: 0.5%, Initial MB concentration: 160 mg/L, pH- 5.5)

Variation of MB adsorption by acrylic acid-chitosan hydrogel with varying chitosan percentage

Chitosan was added to acrylic acid to make the hydrogel biodegradable and eco-friendly. Samples with different chitosan percentage (w = 0, 0.5, 1 and 1.5%) were kept inside solution of MB for around 24 h for studying the effect of chitosan percentage on MB dye adsorption capacity. The result was presented in Fig. 2. It is clear from the graph that, a small amount of chitosan (0.5%) enhances the adsorption capacity, whereas more amount of chitosan (1, 1.5%) slightly decreases adsorption capacity of the hydrogel. This happened because more cross-linking was induced in case of more chitosan percentage, leaving small space inside the adsorbent for cation adsorption. The adsorption capacity of acrylic acid-chitosan hydrogel (w = 0.5, 1, 1.5) was found to be higher than that of pure acrylic acid hydrogel. This is due to the amine and hydroxyl groups present in chitosan that increases the MB adsorption.

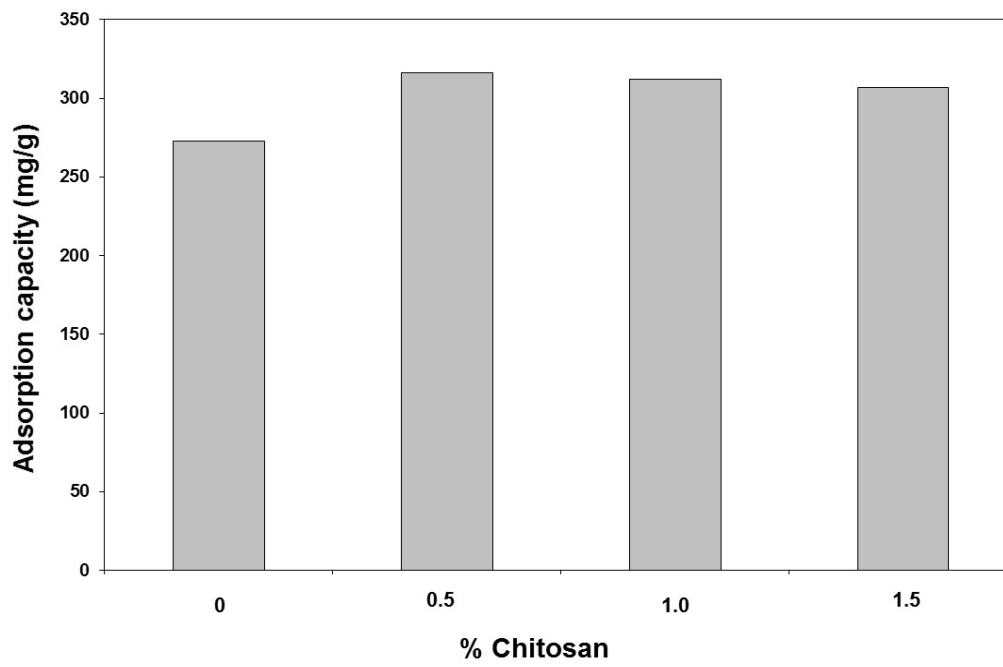


Fig. 2 Variation of MB adsorption by acrylic acid-chitosan hydrogel with varying chitosan percentage (MB concentration at initial stage: 350 mg/L, pH: 5.5, time of contact 24 h)

Contact time impact on capability of MB adsorption by acrylic acid-chitosan hydrogel

To know the impact of contact time on adsorption capability, the prepared hydrogels were kept in the aqueous solution of MB with constant pH (5.50), having initial MB concentration (160 ppm) at room temperature (25°C). The changes in concentration were measured at regular intervals. The impact of contact time was presented in Fig. 3. It is seen that the MB adsorption rate is faster at the beginning and gradually becomes slower near the equilibrium with maximum adsorption of 158 mg/g. Almost 65% of the adsorption occurred within the first 5 hours. The equilibrium adsorption of MB reaches after 24 h contact time.

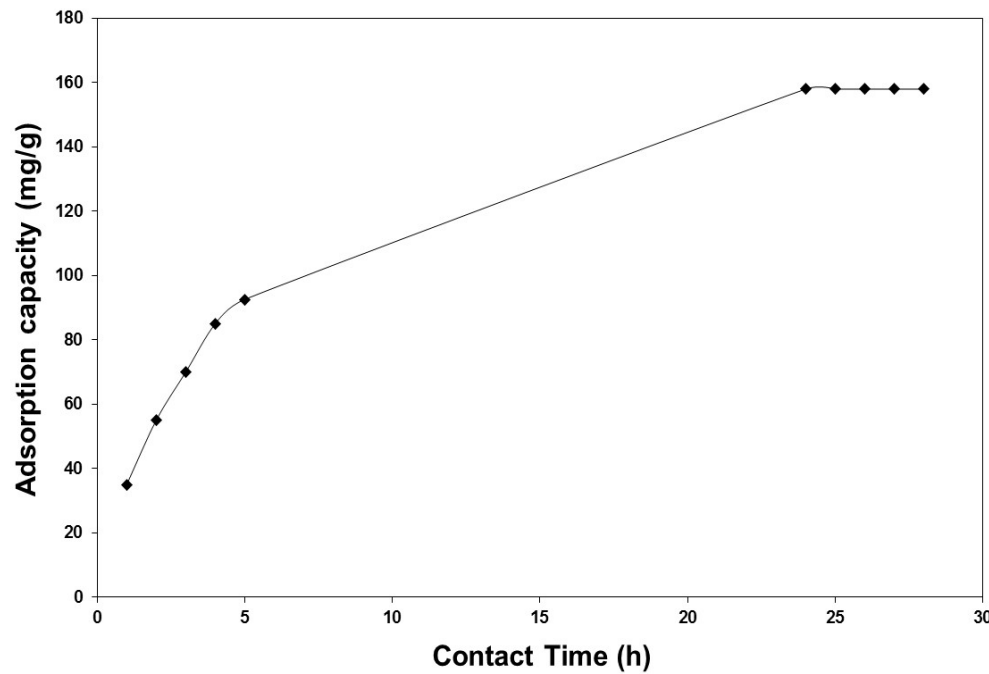


Fig. 3 Impact of contact time on MB adsorption by acrylic acid-chitosan hydrogel (Chitosan percent: 0.5%, Initial MB concentration: 160 mg/L, pH: 5.5)

For fitting MB adsorption by acrylic acid-chitosan hydrogel the models of pseudo 1st and pseudo 2nd order adsorptions were used. The equation used for the models are:

$$\log (Q_e - Q_t) = \log Q_e - (k_1/2.303) t \dots\dots\dots (3)$$

$$t/Q_t = 1/(k_2 Q_e^2) + t/Q_e \dots\dots\dots (4)$$

Where,
 Q_t = Methylene blue adsorbed (mg/g) at any time
 Q_e = Methylene blue adsorbed (mg/g) at equilibrium time
 k_1 = Rate constant (1/h) of first order adsorption
 k_2 = Rate constant (g/h.mg) of second order adsorption.

Fig. 4 shows the graph of $\log (Q_e - Q_t)$ vs t from where the rate constant of pseudo 1st order adsorption is measured. Table 1 represents experimental and theoretical value of Q_e , correlation coefficients (R^2) and rate constant of first order adsorption. From the results it can be concluded that the experimental Q_e and Q_e from kinetic model of 1st order adsorption do not match with each other.

Fig. 5 shows the graph of t/Q_t vs t from where rate constant of pseudo 2nd order adsorption is measured. Table 1 also shows the kinetic parameters of second order MB adsorption. It is evident from the result that the experimental Q_e and Q_e from kinetic model of 2nd order adsorption fit with each other. So, MB adsorption by the hydrogel can be elucidated using the equation of pseudo 2nd order adsorption. The fitting of the experimental kinetic data with pseudo 2nd order model shows that the rate-limiting step of the adsorption was intra-particle diffusion process. Besides, it is also proved that the main reason behind adsorption was chelating interaction.

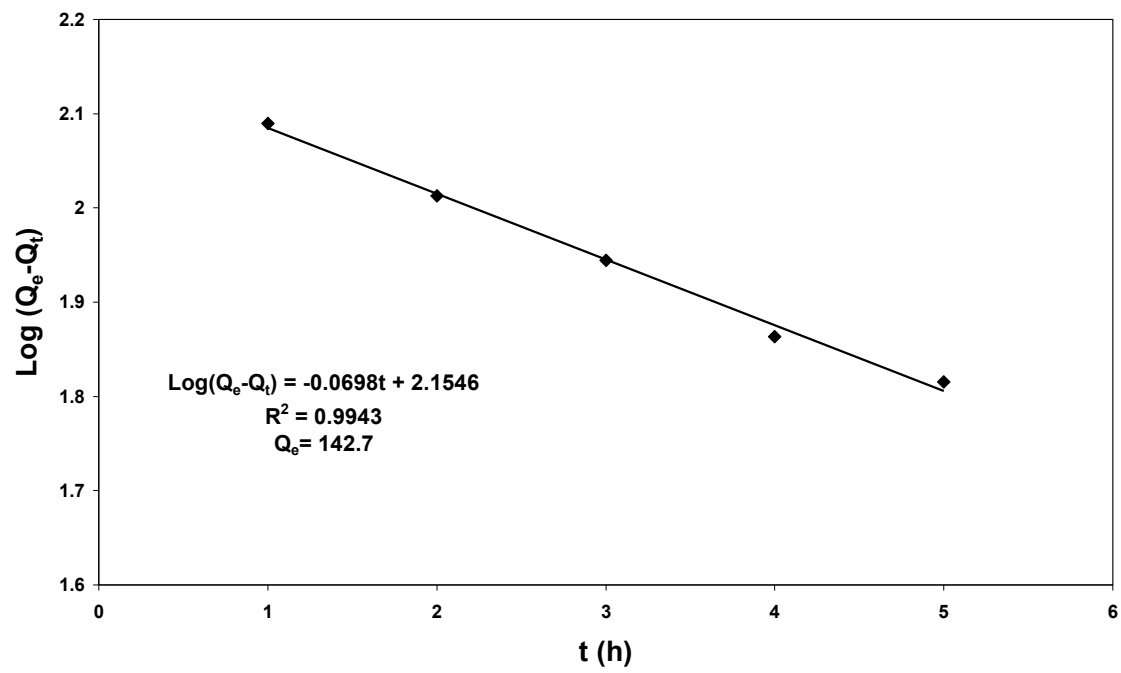


Fig. 4 Pseudo 1st order plot for MB adsorption

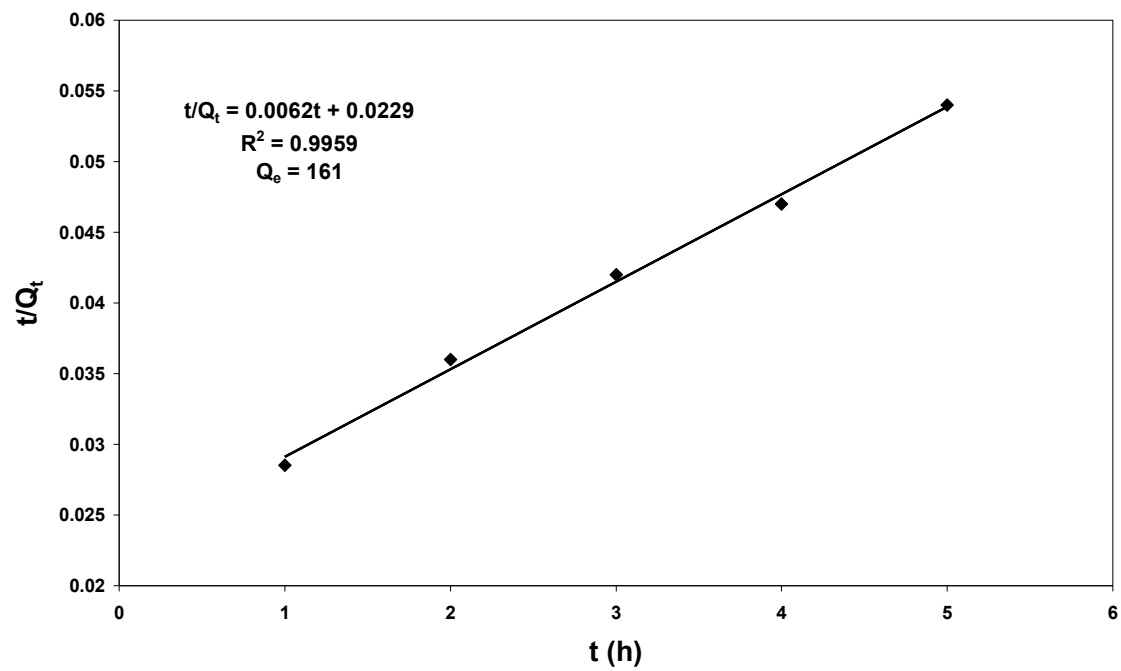


Fig. 5 Pseudo 2nd order plot for MB adsorption

Table 1 Rate constants of pseudo 1st and pseudo 2nd order MB adsorptions by acrylic acid-chitosan hydrogel

Q _e (exp.) (mg/g)	Rate constant of pseudo 1 st order			Rate constant of pseudo 2 nd order		
	Q _e (theor.) (mg/g)	k ₁ (1/h)	R ²	Q _e (theor.) (mg/g)	k ₂ (g/ h. mg)	R ²
158	142.7	0.1607	0.9943	161	0.00168	0.9959

Impact of pH on MB adsorption by acrylic acid-chitosan hydrogel

pH affects the adsorption capacity of adsorbent. Protonation and de-protonation at lower and higher pH respectively changes the surface structure of the adsorbent. The effect of pH as mentioned above is confirmed by Fig. 6 when a variation of adsorption capacity at diverse pH value is observed. From the graph it is evident that the adsorption capacity was highly influenced by pH of the medium with maximum adsorption occurring at pH = 5.5. Comparatively, low adsorption occurred at pH less than 3 due to the presence of protons in solution. Protons are positively charged, therefore it competes with the positively charged MB (cationic dye) for the negatively charged adsorption sites, thus the adsorption of MB decreases. At pH above 5.5, most of the carboxylic groups present in the hydrogel were ionized and strong electrostatic interaction occurred between the dye molecules and hydrogel. Therefore, the adsorption capacity was higher above pH 5.5.

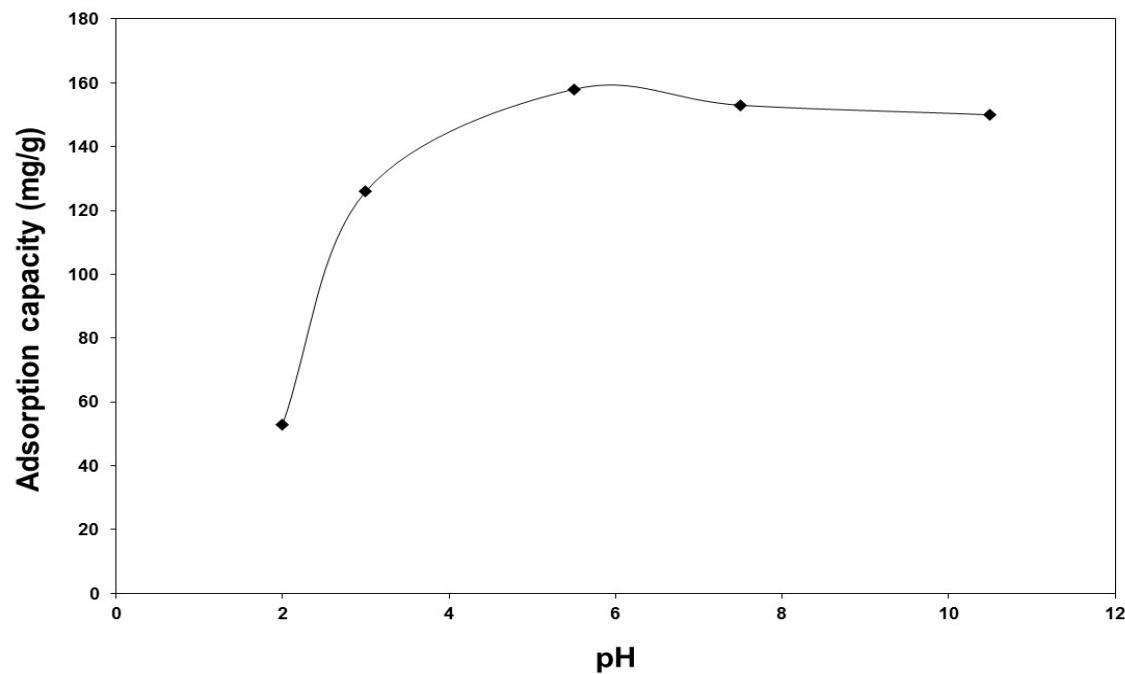


Fig. 6 Impact of pH on MB dye adsorption by acrylic acid-chitosan hydrogel (Chitosan percent: 0.5%, Initial MB concentration: 160 mg/L, time of contact: 24 h)

Effect of initial dye concentration on MB adsorption by acrylic acid-chitosan hydrogel

The dependence of adsorption capacity on different concentration is indicated by Fig. 7. It is seen that with increasing initial concentration adsorption capacity also increases. This trend is followed until reaching the plateau value at a higher concentration. It was due to saturation of chelating sites of the adsorbent at higher dye concentration. However, reaching the equilibrium value, no space was left for further adsorption since each of the holes inside the hydrogel was fully occupied with the cationic dye molecules.

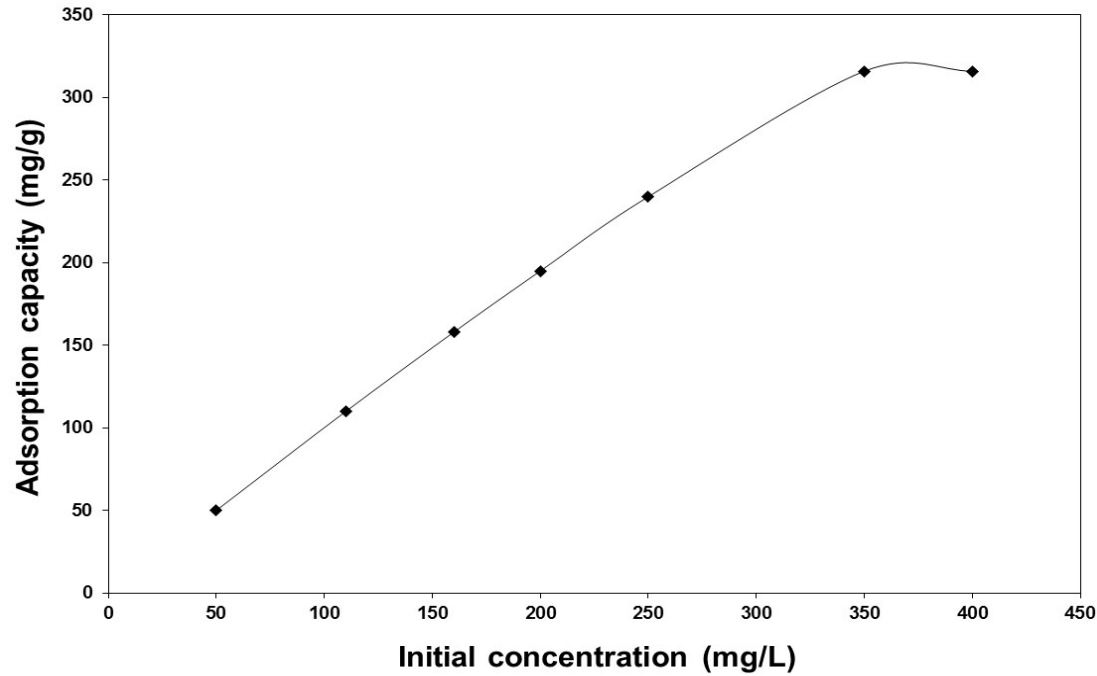


Fig. 7 Effect of initial concentration of MB dye adsorption by acrylic acid-chitosan hydrogel (Chitosan percent: 0.5%, pH: 5.5, contact time: 24 h)

Langmuir isotherm is used to elucidate MB adsorption data. The isotherm in linear form is as follows:

$$C_e/Q_e = C_e/Q_o + 1/(Q_o b) \dots\dots\dots (5)$$

Where,
 C_e = Equilibrium concentration (mg/L),
 Q_o = Adsorption capacity of monolayer saturation of the adsorbent (mg/g),
 Q_e = Equilibrium adsorption capacity (mg/g)
 b = Constant for Langmuir adsorption (L/mg).

Using experimental data from Fig. 7, the graph of C_e/Q_e versus C_e in Fig. 8 was drawn. The linear relationship between C_e/Q_e and C_e proves that the adsorption behavior follows Langmuir adsorption isotherm. Using Langmuir equation monolayer saturation adsorption capacity of the adsorbent found was 322 mg/g of adsorbent.

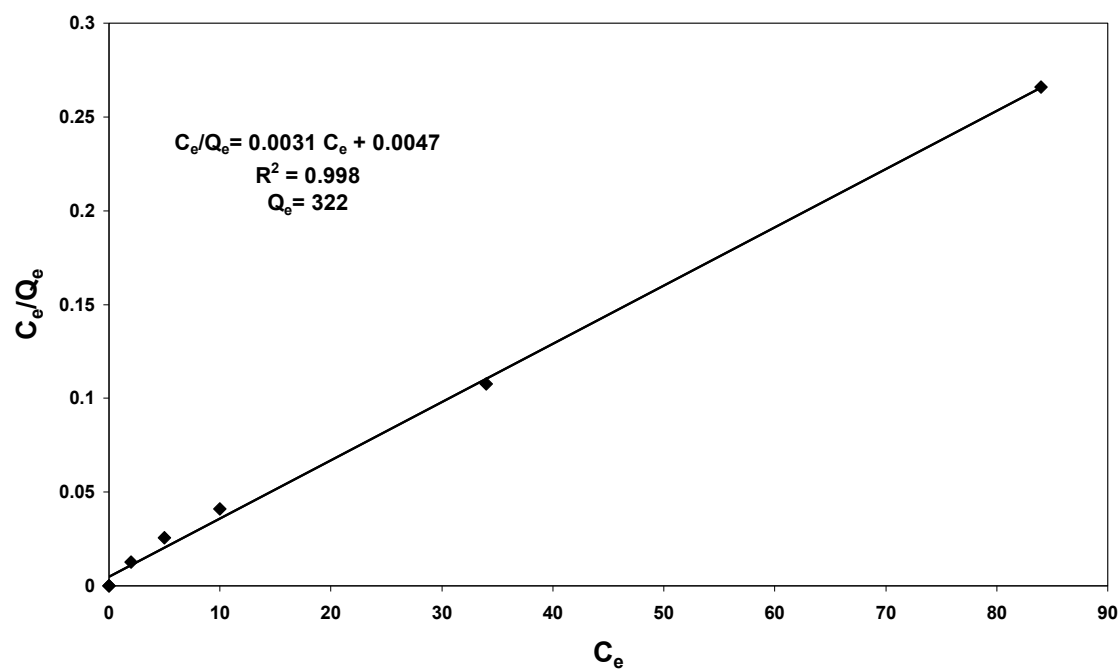


Fig. 8 Graph of Langmuir isotherm for adsorption of MB.

Comparison between MB adsorption capacity of hydrogel prepared in present work and other adsorbents is given by Table 2.

Adsorbent	Adsorption capacity (mg/g)
Acrylic acid-chitosan hydrogel [present study]	322
Carbon monolith [21]	127
Nanocrystalline cellulose [21]	101
Activated carbons from walnut shells [22]	315
Wheat shells [23]	21.50
Gulmohar (<i>Delonix regia</i>) plant leaf [24]	186.22
Tea waste [25]	85.16
Thermally activated coir pith carbon [26]	5.87

Desorption of methylene blue from the hydrogel was done using 2M HCl. The ratio of desorption ratio was 96%. Later the hydrogels were regenerated using alkali treatment and reused for methylene blue adsorption.

CONCLUSION

Acrylic acid-chitosan hydrogels were prepared from their aqueous solution by the application of gamma radiation. The prepared hydrogel was used to remove adsorption methylene blue. The hydrogel was treated with alkali to improve the dye uptake capability. After treating with alkali dye uptake capability increased 5 times than that of normal hydrogel sample. Dye adsorption capacity of the alkali treated hydrogel was also investigated at different chitosan %, different contact time, pH, and concentration of MB solution. Using of small amount of chitosan (0.5%) enhanced the adsorption capacity of the hydrogel, however the use of more chitosan resulted in slight decrease in adsorption capacity of the hydrogel. Dye adsorption of hydrogel reaches equilibrium value after 24 hours standing time. The adsorption capacity was found highest at pH 5.5. The initial concentration at which maximum adsorption occurs was 350 ppm. In case of MB adsorption, the hydrogel follows pseudo 2nd order and Langmuir isotherm. The maximum adsorption capacity of the hydrogel was 322 mg/g of adsorbent.

ACKNOWLEDGEMENT

Authors are pleased to acknowledge IAEA for technical support to carry out the research. Authors would also like to thank the Gamma Source Division of Institute of Food and Radiation Biology, Atomic Energy Research Establishment for providing us the opportunity to use the irradiation facility.

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