ERRATUM to "Microwave assisted synthesis of chitosan-*graft*-styrene for efficient Cr(VI) removal": [Adv. Mat. Lett. 2010, 1(1), 59-66]

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ABSTRACT

In this study, we have synthesized chitosan-grafted-styrene (Ch-g-sty) without any radical initiator or catalyst using microwave (MW) irradiation. Ch-g-sty   was synthesized with 187% grafting using 80 % MW power in 40 second at (styrene) 0.13 M, (Chitosan) 0.1 g/25 mL. On the other hand, under similar condition of concentration of styrene and chitosan, 148% grafting was observed with potassium persulphate $(K_2S_2O_8)$/ascorbic acid as redox initiator and atmospheric oxygen as co-catalyst in 1 h using conventional method at 35^oC. Microwave synthesized Ch-g-sty copolymer was characterized by Fourier transform-Infrared (FTIR) spectroscopy, thermo gravimetric analysis (TGA), X-ray diffraction (XRD) measurement and scanning electron microscopy (SEM). Maximum grafting was optimized by varying the microwave power, exposure time and styrene/chitosan concentration. Ch-g-sty copolymer was found to be more efficient for Cr(VI) removal as compare to conventionally and parent chitosan in aqueous solution. Sorption of Cr(VI) was depending upon pH and concentration, with pH=3 being the optimum value. The equilibrium data followed the Langmuir isotherm model with maximum capacities of 526.3 mg/g, 312.5 mg/g and 166.7 mg/g for Ch-g-sty copolymer, conventional (thermostatic water bath) method and parent chitosan respectively. Copyright © 2010 VBRI press.

Keywords: Microwave irradiation; chitosan-*graft*-styrene; ascorbic acid; adsorption

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Introduction

Chitosan is one of natural polymer that attracted great attention [**1**]. Chitosan is a naturally occurring polymer of α-(1-4)-2- amino-2-deoxy-D-glucopyranose, prepared by partial alkaline deacetylation of chitin, a main structural component of the cuticles of insects, mollusks, and crustacean [**2**]. Natural abundant availability, low cost, high biocompatibility, biodegradability, non toxic behaviour and ease of chemical modification are few advantages that compel the researchers to investigate this polymer for various applications such as in wastewater treatment [**3**], drug delivery systems [**4**] cell culture [**5**], antimicrobial agents in textile chemicals [**6**], biomaterials in cartilage tissue [**7**] and superabsorbent materials [**8**]. Many grafted copolymers of chitosan and vinyl monomers have been synthesized and evaluated as flocculants, drug-releaser [**9, 10**] etc. Conventionally, vinyl monomers are grafted onto chitosan using various redox systems [**11-13**]. As microwave (MW) irradiation [**14, 15**] is emerging as an efficient source of thermal energy and constitutes original procedure for the heating of materials different ways from the classical ones. Microwaves can be heat reactants selectively, directly and without thermal inertia and heat exchange with the medium [**16**]. Grafting of butylacrylate [**17**], acrylic acid [**18**] and acrylonitrile [**19**] onto the starch, grafting of acrylamide on to LLDPE (linear low density polyethylene) films [**20**] and grafting of butyl methacrylate on to the wool fibers [**21**] have been studied recently using redox initiators under microwave irradiation. The grafting of methylmethacrylate [**22**] and acrylonitrile [**23**] on to Cassia marginata Seed gum, ethylacrylate on to the guar gum [**24**] and synthesis of acrylamide [**25**] were used without initiators under MW conditions.

The aim of present study is to carry out graft copolymerization of styrene on to the chitosan using microwave irradiation where grafted material has a good yield for short reaction time without any radical initiator/catalyst. This is further compared with potassium persulphate ($K_2S_2O_8$)/ascorbic acid initiated grafting by conventional method. Optimal grafting condition for the microwave method was identified and the properties of the microwave synthesized copolymer were compared with the copolymer synthesized using $K_2S_2O_8$/ascorbic acid initiator on thermostatic water bath at 35 ^{o}C. Chitosan and its derivates are reported to be an efficient heavy metal scavenger due to chelating ability [**26-27**]. The grafted co-polymer thus obtained was therefore investigated for Cr(VI) removal. Main objectives of this paper pertain to the systematic evaluation of the performance of Ch-g-sty by Microwave irradiation for the uptake of Cr(VI) from synthetic solutions. The studies have been conducted on the optimization of various experimental conditions like the pH, equilibrium time and the determination of sorption isotherms.

Experimental

Materials

All the other chemicals used were AR grade. Chitosan flakes (85% deacetylated) and styrene was purchased from Sigma Chemicals, South Africa. Potassium persulfate,

ascorbic acid and potassium chromate were purchased from Merck, South Africa.

Analysis

LG (MS-283 MC; 1200 W) domestic microwave oven having 2450 MHz microwave frequency and a power output from 0 to 800 W with continuous adjustment was used for all the experiments. All the reactions were performed in open glass vessels and each time temperature of the reaction mixture (<100 ºC) was measured by inserting thermometer into reaction vessel just after the exposure. All the reactions were performed in aqueous phase. Dissolved Cr(VI) was determined by the spectrophotometric method at 540 nm using diphenyl carbazide method [**28**] after suitable dilutions. Total chromium concentrations in solution were assessed by Aanalyst 400 Perkin Elmer Atomic Absorption Spectrophotometer at 357.9 nm using a slit width of 0.7 nm. Samples were filtered using Whatman 0.45 mm filter paper and the filtrates after suitable dilutions were analyzed. Control experiments showed that no sorption occurred on either glassware or filtration systems. FTIR spectra were recorded with a Spectrum-100 Perkin Elmer; ATR sampling system. Powder X-ray diffraction data was collected using the Philiphs X'Pert equipped with a primary beam Gobel mirror, a radial Soller slit and TGA was carried out on Perkin–Elmer TGA-4000 in N_2 atmosphere. Scanning electron microscopy (SEM) was carried out on the FEI Nova NanoSEM using an EDAX EDS system. Maximum percent grafting sample was used for the characterization and sorption study. The percentage and efficiency of grafting [**29**] were calculated using following equation **1-2**:

$$\% \text{ Grafting (G)} = \frac{W_1 - W_O}{W_O} \times 100 \qquad (1)$$

$$\% \text{ Efficiency (E)} = \frac{W_1 - W_O}{W_2} \times 100 \qquad (2)$$

where, W_1, W_o and W_2 are the weight of the grafted chitosan, the weight of original chitosan and weight of the styrene used, respectively.

Methods

Conventional thermal grafting using initiator: Homogeneous solution of chitosan (0.1 g) in 25 mL of 2 % aqueous acetic acid, styrene (13 x 10^{-2} M), ascorbic acid (20 x 10^{-2} M), were added and thermostated on water bath at 35ºC. After 30 min $K_2S_2O_8$ (10 x 10^{-3} M) was added and this time of addition of persulphate was taken as zero time. Graft co-polymerization was allowed for 1 h. Grafted chitosan was separated [**30**] from styrene by first raising the pH of the reaction mixture to 6.5–7.0 followed by precipitating it with methanol. Grafted chitosan was repeatedly washed with methanol to remove any of the adhered styrene and dried. Percent grafting and percent efficiency were calculated (%G 148 and %E 43.72) respectively.

Grafting under microwave irradiation: Chitosan (0.1 g) dissolved in 25 mL of 2% aqueous acetic acid and styrene

(13 x 10^{-2} M) was irradiated in a domestic microwave oven in a 100 mL open necked flask. Reaction was repeated with different monomer concentration in the range of 7–15 x 10^{-2} M. Ch-g-sty was separated from styrene as described above. Percentage of grafting and grafting efficiency was calculated (% G 187, % E 55.25). Reaction was studied for optimal grafting at different microwave power and exposure times.

Sorption experiments for Cr(VI) using Ch-g-sty

Ch-g-sty having 187 % G and 55.25 % E was used for the optimization of Cr(VI) removal using batch technique and compare with conventional grafted material and parent chitosan material. For the sorption with time studies, the concentration of the chromium was kept at 100 mg/L in final aqueous volume of 20 mL at 30°C in a shaking incubator for 4 h. To this solution, 0.05 g of Ch-g-sty was added and the pH of the reaction mixture initially adjusted to 3.0 using either hydrochloric acid or sodium hydroxide (1 M). A series of 0.2 mL samples were withdrawn at 30 min time equilibration intervals and analyzed by spectrophotometric method for chromium concentration. For the sorption isotherms, varying Cr(VI) concentrations ranging from 100 to 1600 mg/L were used. The amount of Cr(VI) ions sorbed per gram of the copolymer was calculated by the difference between the initial and the final readings using the following equation (3).

$$q_e \ (mg/g) = \frac{C_O - C_e \ (V/1000) \ L}{W \ (g)} \qquad (3)$$

where q_e is the amount of metal ion adsorbed on the Ch-g-sty, C_O, the initial metal ion concentration (mgL^{-1}), C_e, the equilibrium concentration of metal ion in solution (mgL^{-1}), V, the volume of metal ion solution used (L), and W is the weight of the Ch-g-sty used (g) as adsorbent. All the batch experiments were carried out in triplicate and the values reported are average of three readings.

Results and discussion

Characterization of the Ch-g-sty

FTIR spectra: Ch-g-sty has been synthesized by grafting styrene onto polysaccharide molecule in aqueous medium using microwave irradiation. The grafting and chromium adsorption was confirmed by comparing the IR spectra of chitosan (**Fig. 1A**) with that of the grafted product (**Fig. 1B**) and chromium loaded Ch-g-sty (**Fig. 1C**). The IR spectrum of the chitosan has strong peak around 1027 cm^{-1}, 1060 cm^{-1} due to O–H bending, C–O stretching and 3373 cm^{-1} due to the stretching vibration of O–H, the extension vibration of N–H, and inter hydrogen bonds of the polysaccharide. In graft copolymer the characteristic bands of styrene at 3000–3100 cm^{-1} and the bands of phenyl groups at 1521 cm^{-1}, 1380 cm^{-1}, 700 cm^{-1} were found in the FT-IR spectrum of Ch-g-sty copolymer which confirmed

the formation of Ch-g-sty. The IR spectra of chromium loaded Ch-g-sty showed two new peaks at 777 cm^{-1} and 901 cm^{-1}, suggesting that Cr(VI) was adsorbed on the surface and the nitrogen atoms on the Ch-g-sty was involved in the adsorption. A slight up field trend was observed form $v_{c=o=c}$ at 1215cm^{-1}, after Cr(VI) removal. Based on above observation, the following (**Scheme 1**) has been proposed which show the grafting of chitosan using the microwave irradiation was found to have much better adsorbing power for the Cr(VI) than the graft copolymer synthesized using redox system on thermostatic water bath indicating more grafted chains are incorporated in grafting under microwaves. Adsorption of Cr(VI) is pH dependent at pH = 3, chitosan dissolve in acidic medium so that graft copolymerization also control the solubility.

XRD spectra

X-ray diffraction profiles of chitosan and its graft copolymer are shown in (**Fig. 2**). It was known that the diffraction pattern of original chitosan shows the characteristic peaks at $2\theta = 11^{o}$ and 22° corresponding to crystal forms II (**Fig 2A**). The XRD differences between the Ch-g-sty and the pure chitosan showed that the crystalloids had changed after graft copolymerization of styrene. The X-ray diffraction spectra of the grafted chitosan (**Fig. 2B**) show many crystalline areas between $2\theta = 22–28^{o}$ and $32–45^{o}$ (due to styrene grafts at the chitosan backbone), while no such peaks are visible in the XRD of the chitosan itself. No such peaks were visible (**Fig. 2C**) in the diffractograms of Ch-g-sty after adsorption of chromium indicating that no more binding sites were available for adsorption.

TGA spectra

The thermal stability and degradation behaviour of chitosan and styrene grafted chitosan were evaluated by TGA under nitrogen atmosphere. TGA analysis also confirmed the grafting (**Fig. 3**). TGA of chitosan (**Fig. 3A**) shows a weight loss in two stages. The first stage (**Fig. 3A**) begins at about 50-280 ^{o}C for the chitosan materials with weight loss of 10 % due to loss of residual or physically adsorbed water on membranes surfaces. The second stage of weight loss starts at 350 ^{o}C and that continues up to 528 ^{o}C during which there was 44 % weight loss due to the degradation of chitosan. The TGA of the grafted product (**Fig. 3B**) has three stages of distinct weight loss. The first stage ranges between 50-130 ^{o}C with 6-8 % of the adsorbed and bound water weight loss. The second stage of weight loss starts at 240 ^{o}C and that continues up to 350 ^{o}C during which there is 18 % of weight loss due to the degradation of chitosan at ungrafted part of the Ch-g-sty. There is 5 % weight loss in the third stage from 469 to 677 ^{o}C that contributes to the decomposition of styrene grafted at Ch-g-sty. Only 50 % weight loss up to 758 ^{o}C indicated a high degree of thermal stability of the graft copolymer.
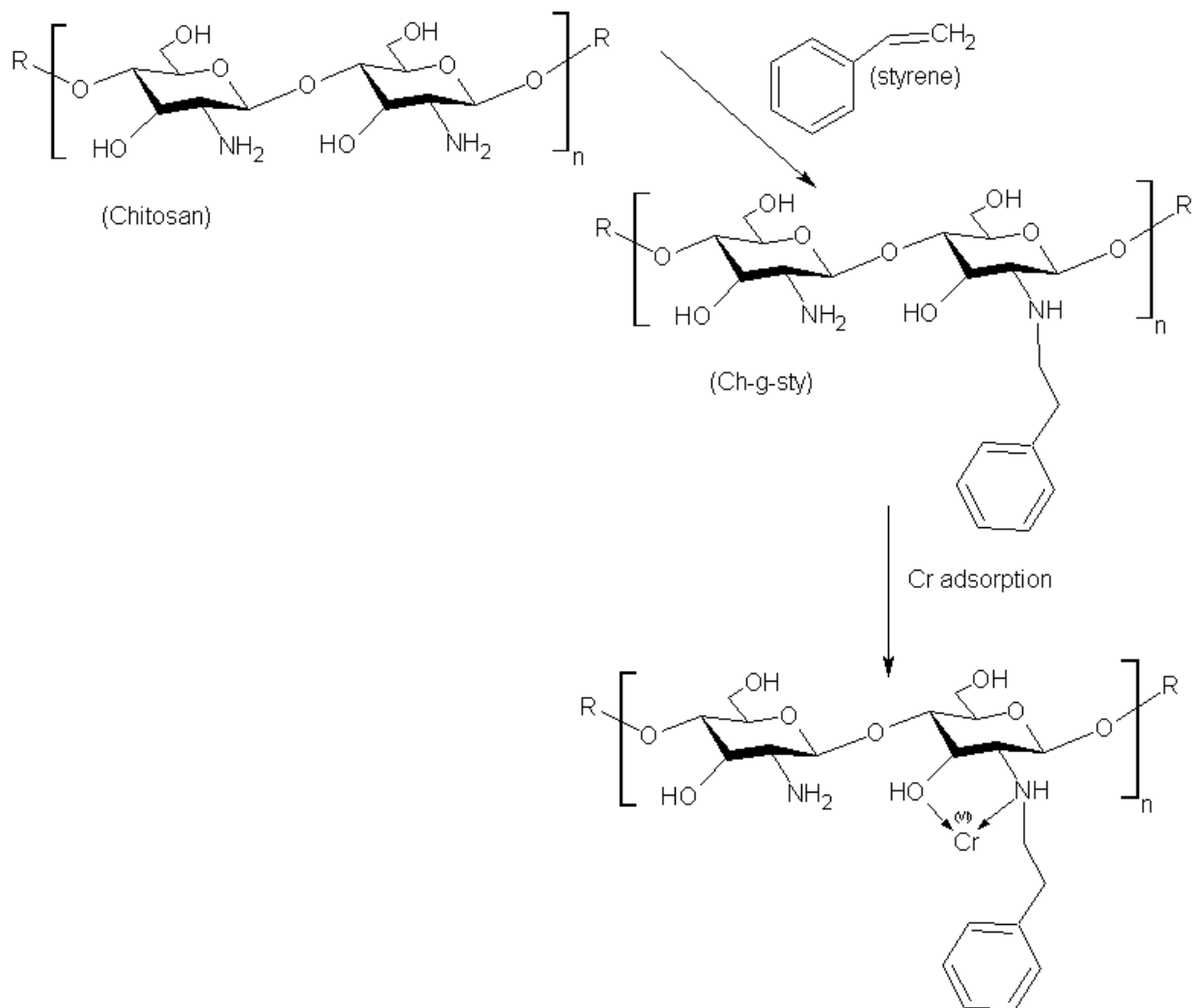
Scheme 1. Proposed scheme for grafting of styrene on to the chitosan followed by Cr(VI) adsorption.

SEM and EDX analysis

The significant change in the surface morphology of the chitosan (**Fig. 4A**) and the modified chitosan (**Fig. 4B**) indicate grafting of styrene onto the chitosan polymer. The SEM micrograph of chitosan matrix show rather a smooth surface as shown in (**Fig. 4A**) when compared to agglomerated surface (**Fig. 4B**) of Ch-g-sty. This can be attributed to the fact that styrene upon grafting formed agglomeration onto the surface of chitosan (**Fig. 4C**) shows granular deposition of Cr(VI) during sorption onto the surface Ch-g-sty. The EDX spectra (**Fig. 4D**) confirm the presence Chromium peak on the surface of the specimen indicating the adsorption capability of the Ch-g-sty.

Optimization of the grafting conditions

Effect of MW power: %G and %E both increases initially with the increasing microwave power up to 1720 GHz (80 %) power, this may be due to more availability microwave energy at high microwave power, causing more monomer and macro radical generation and hence grafting (**Fig. 5**). After 80 % power, decrease in % G and % E both may be attributed to more homopolymer formation at high

microwave powers or to some decomposition of the graft copolymer at high power greater than 80 %.

Effect of microwave exposure time: It was observed that % G and % E initially increase up to 40 seconds when exposed to 80 % microwave power, thereafter both % G and % E decreases with the exposure duration at the fixed concentration of styrene (13 x 10^{-2}) and chitosan (0.1 g/25 mL) (**Fig. 6**). This may be due to decomposition of the graft copolymer at longer duration greater than 80 %.

Effect of styrene concentration: %G and %E both increases with increase in the concentration of styrene in the range of 7-15 x 10^{-2} M. However, both the parameters decreased after 13 x 10^{-2} M styrene concentration (**Fig. 7**). This may be due to the greater availability of the styrene molecules in the proximity of the chitosan increasing the chance of the molecular collision and hence grafting increased.

Effect of chitosan concentration: %G and %E both increases with increase in the concentration of the chitosan in the range of 50–250 mg/25 mL at fixed concentration of the styrene (13 x 10^{-2}M) at 80 % MW power and 40 sec exposure (**Fig. 8**). This may be attributed to more

macromolecular free radical sites available with an increase in the concentration of the chitosan in the studied range.

Adsorption of hexavalant chromium

Effect of initial pH on adsorption: The effect of pH on the removal of Cr(VI) was examined using plain chitosan (CH) and grafted copolymer (Ch-g-sty) at the concentration levels of 100 mg/L (**Fig. 9**) The equilibrium uptake of Cr(VI) was maximum at pH=3.0 for both for CH and Ch-g-sty. Below pHzpc of chitosan [**31**], sorbent was positively charged with the protonated amino group whereas the sorbate was negatively charged, i.e., Cr(VI) existed as $HCrO_4^-$.

Fig. 2. XRD of (A) Chitosan (B) Ch-g-sty (C) styrene grafted chitosan loaded by chromium.

Fig. 1. IR spectra of (A) Chitosan (B) Ch-g-sty (C) styrene grafted chitosan loaded by chromium.

In view of an electrostatic interaction between the sorbent– sorbate systems, it was decided to maintain the pH at 3.0 in further experiments. It was also observed that at the end of the adsorption experiments, pH of the solution increased from 3.0 to 5.5. This might be attributed to the protonation of amine group, $HCrO_4^-$ reduction accompanied by H^+ consumption [**32**] and slow release of alkalinity from the prepared sorbent [**33**].

Effect of Time for sorption of Cr(VI): Effect of Time of Cr(VI) removal by CH and Ch-g-sty indicated rapid binding of Cr(VI) to the sorbent during the first few minutes, followed by a slow increase until a state of equilibrium at 4 h was reached (**Fig. 10**). No change in the uptake capacity was observed with further increase in equilibration time up to 24 h. These observations were in agreement with the work reported earlier with the other metal ion–grafted material systems [**24**].

Adsorption isotherm studies: Adsorption data were fitted to the Langmuir and Freundlich isotherms [**34, 35**]. The Langmuir isotherm is valid for monolayer sorption due to a surface of a finite number of identical sites and expressed in the linear form as below (eq. **4**).

$$Ce/qe = 1/bQo + Ce/Qo \qquad (4)$$

where, Ce is the equilibrium concentration (mg L^{-1}) and qe the amount adsorbed at equilibrium (mg.g^{-1}). The Langmuir constants Q_o (mg.g^{-1}) represent the monolayer adsorption capacity and b (L mg^{-1}) relates the heat of adsorption.
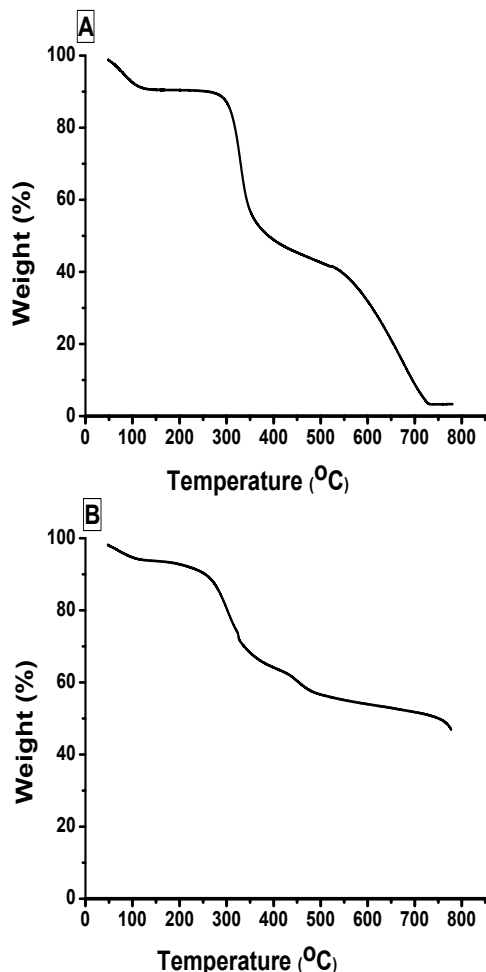

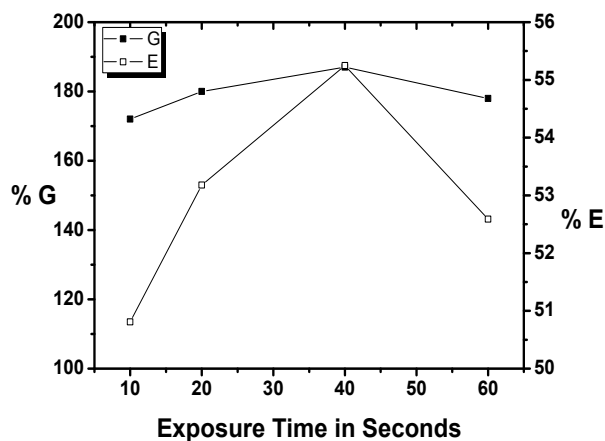**Fig. 5.** % G and % E with changing MW power at fixed concentration of styrene (13 x 10^{-2}), chitosan (0.1 g/25 mL), exposure time, 40 sec.
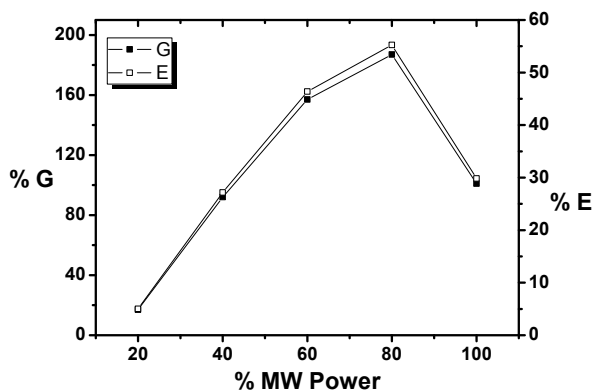

Fig. 6. %G and %E with exposure time at the fixed concentration of styrene (13 x 10^{-2}), chitosan (0.1 g/25 mL) at 80 % MW power.

Fig. 3. TGA analysis of (A) Chitosan (B) Ch-g-sty.

Fig. 4. SEM-EDX analysis of (A) Chitosan (B) Ch-g-sty (C) ch-g-sty loaded by chromium (D) EDX graph of styrene grafted chitosan loaded by chromium.

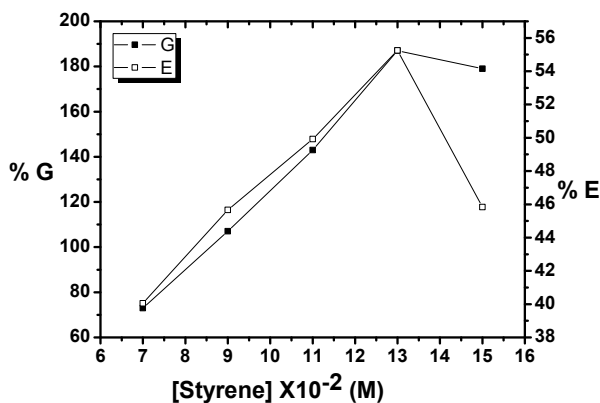**Fig. 7.** % G and % E with changing monomer concentration at fixed concentration of chitosan (0.1 g/25 mL), 80 % MW power, 40 sec exposure time.
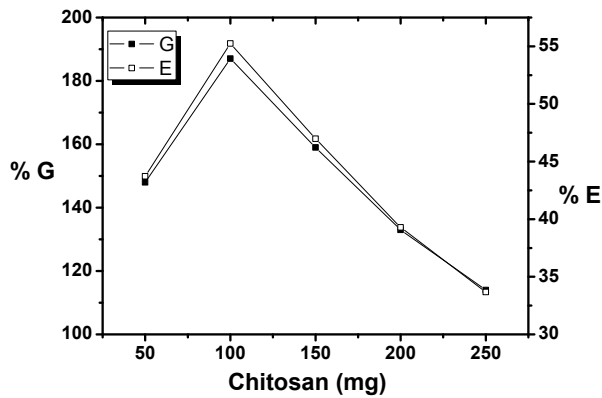
Fig. 8. % G and % E with different chitosan concentration at fixed concentration of styrene (13 x 10^{-2} M) 80 % MW power and 40 sec exposure time.
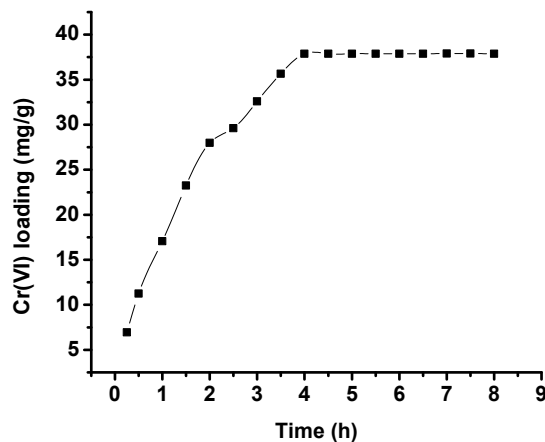

Fig. 9. Effect of pH on equilibirum concentration of Cr(VI) (initial Concentration = 100 mg/L, amount of adsorbent = 0.05 gm, test solution = 20 mL, T = 303 K).
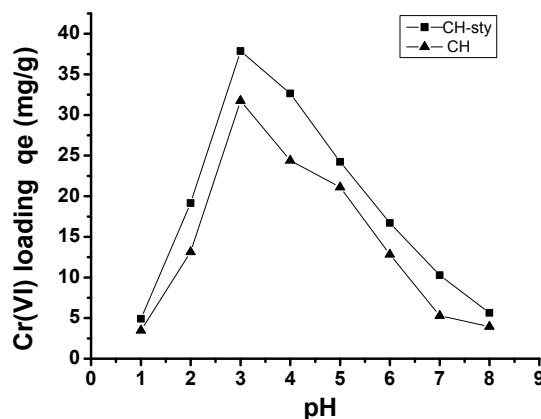

Fig. 10. Effect of Time on equilibirum concentration of Cr(VI) (initial Concentration = 100 mg/L, amount of adsorbent = 0.05 gm, test solution = 20 mL, T = 303 K).

The essential feature of the Langmuir adsorption can be expressed by means of R_L, a dimensionless constant referred to as separation factor or equilibrium parameter
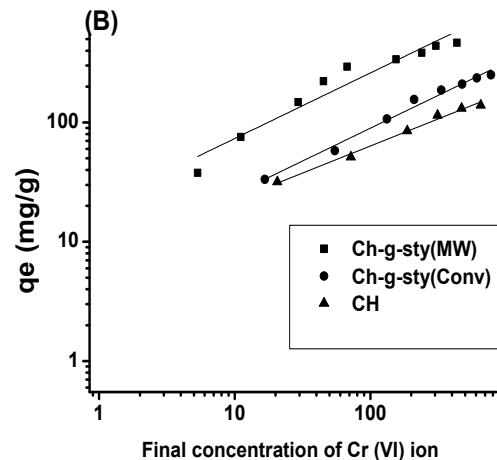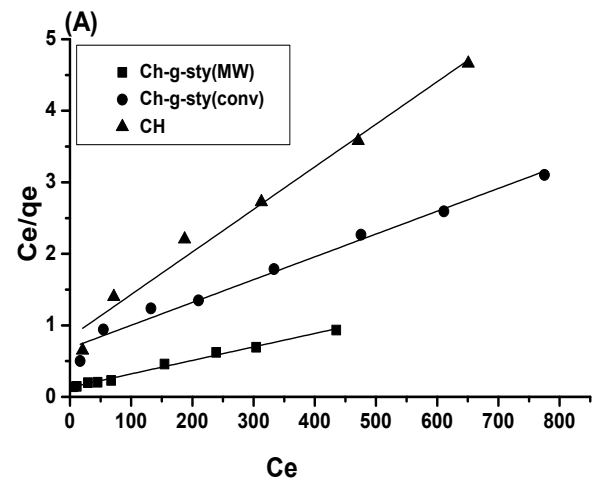

Fig. 11. Adsorption equilibrium (A) langmuir and (B)Frundlich Isotherm on various adsorbents Plain Chitosan (CH), conventional synthesized (Ch-g-sty) and Microwave synthesized (Ch-g-sty).(T = 303 K, pH = 3).

for predicting whether an adsorption system is favorable or unfavorable. R_L is calculated using the following (eq.**5**).

$$R_L = 1/1 + bC_O \qquad (5)$$

where, C_O is the initial Cr(VI) concentration (mg/L). If R_L values lies between 0 and 1, the adsorption is favorable.
The Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form as (eq.**6**):

$$\ln q_e = \ln K_f + 1/n \ln C_e \qquad (6)$$

Where K_f indicates adsorption capacity (mg.g^{-1}) and n an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. The greater the values of the 1/n, better is the favorability of the adsorption. Equilibrium adsorption data of plain CH, microwave as well as conventionally synthesized copolymer could be modelled satisfactorily to both the Langmuir and Freundlich isotherms (**Fig. 11A & B**).

In the studied the sorption equilibrium data, for Ch-g-sty fitted satisfactorily well to both Langmuir and Freundlich models indicating a complex overall sorption

surface as we observed in our previous studies the sorption of Cd(II) by microwave synthesized guar gum-graft poly(ethylacrylate) (GG-g-PEA) [**24**]. However equilibrium adsorption data for Ch-g-sty fitted better to Langmuir model indicating unilayer sorption. As in the previous results in the present study also microwave synthesized copolymer had higher Q_O as compared to the copolymers synthesized conventionally. The Langmuir and Freundlich constants of the plain (CH), conventionally and microwave synthesized graft copolymers have been summarized in **Table 1.**

Table 1. Isotherm constants and correlation coefficients for adsorption of Cr(VI) ions from aqueous solutions.

S. No.	Adsorbents	Langmuir isotherm			Freundlich isotherm		
		Q_{max}	b(ml/mg) x 10^3	R^2	K_f	$1/n$	R^2
1	CH	166.67	7.13	0.9827	7.89	0.453	0.9916
2	Ch-g-sty (conventional)	312.5	4.67	0.9833	7.1	0.5502	0.987
3	Ch-g-sty (Microwave)	526.31	14.15	0.9934	20.7	0.5496	0.9381

Conclusion

Chitosan graft with styrene (Ch-g-sty) was successfully synthesized using microwave irradiation, without any redox initiator or catalyst in much better yield than conventional redox pair, i.e., persulfate/ascorbic acid initiated synthesis. Moreover, the copolymer synthesized using microwaves proved to be a more effective adsorbent for Cr(VI) from synthetic solution as compared to conventionally synthesized copolymer. The sorption was found to be pH dependent and was highest at pH 3.0. It was revealed that more than one adsorption mechanisms are operating in the sorption. Equilibrium adsorption of Cr(VI) in synthetic solution was achieved in about 4 h.

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